CLIMATE CHANGE & SUSTAINABLE DEVELOPMENT: NEW CHALLENGES OF THE CENTURY

MONOGRAPH

supported by
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Mykolaiv – Rzeszow 2021

Petro Mohyla Black Sea National University, Ukraine
Rzeszow University of Technology, Poland

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Olena Mitryasova
Piotr Koszelnik

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The monograph is devoted to problems strategy of sustainable development as a road map of civilization; sustainable development of territories; sustainable use and protection of flora and fauna; environmental biochemistry, physiology and medicine; food technology in the context of sustainable development; monitoring of the atmosphere, hydrosphere and climate management; circular economy; rational use of water resources and wastewater treatment; rational use of land resources and reclamation of disturbed lands; environmental education for sustainable development..
The book is written for scientists, lecturers, postgraduate students, engineers and students who specialize in the field of environmental researches.

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Dedicated to the 25th anniversary of
the Petro Mohyla Black Sea National University

CONTENTS

FOREWORD

Quality of life and sustainable development of society depends on the ability to join forces. Today the sustainable development concept is one of the main documents of development of the world and European countries, in particular the Visegrad countries. Among the great priorities of the movement of Ukraine to Europe, there are directives and regulations concerning sustainable development goals, namely the issue of climate change. Environmental management and climate change issues, environmental security and quality of natural resources, monitoring remain important, and the issue of adapting the national strategy for the future country's development to European policies is extremely relevant.

The problem is that in order to stop the worsening weather conditions by 2050, the increase in global temperature must be limited to about 1.5°C, in line with preindustrial levels. However, the world has already warmed to 1.2°C, thanks to the greenhouse gases that are released into the atmosphere, and the prospects for limiting further temperature increases over the next 30 years look distant. In fact, estimates based on current country pledges to cut emissions suggest that temperatures are likely to rise more than 2°C above pre-industrial levels by mid-century. In such a future, most of the planet is likely to suffer from drought; rainforests are at risk of extinction, and melting ice sheets will cause dangerous sea levels to rise and cause major changes in the behavior of ocean currents such as the Gulf Stream.

Environmental policy is a priority area of cooperation between Ukraine and the Visegrad. The innovative element is that Visegrad–Ukraine partners join efforts of academic and civil societies in the environmental field. Integration in the field may be achieved through the creation of a harmonized legal, regulatory, methodological, and organizational base that should meet the requirements of European and national environmental security. Actual new challenges are in implementing new Visegrad–Ukraine different methodologies into national practices aimed at goals of improving sustainable development. It is extremely important to improve the understanding of the content of European environmental activities in Ukraine. Professionals are gathered to exchange practices and experiences in the field of climate change and sustainable development. The attractive and close collaboration of the partners provides discussion and reflection on Visegrad–Ukraine research partnership and study experience with regard to environmental management, eco-innovations. The content of the monograph has a strong impact on all students, young researchers, and also officials, and publicity through getting knowledge about actual environmental policy in the field of climate change and sustainable development in the EU.

The main thematic topics of the monograph:

- ✓ Strategy of sustainable development as a road map of civilization;
- ✓ Sustainable development of territories;
- ✓ Sustainable use and protection of flora & fauna;
- ✓ Environmental biochemistry, physiology and medicine;
- ✓ Food technology in the context of sustainable development;
- ✓ Monitoring of the atmosphere, hydrosphere and climate management;
- ✓ Circular economy;
- ✓ Rational use of water resources and wastewater treatment;
- ✓ Rational use of land resources and reclamation of disturbed lands;
- ✓ Environmental education for sustainable development.

The book is co-financed by the Governments of Czechia, Hungary, Poland and Slovakia though Visegrad Grant from Inretnational Visegrad Fund. The mission of the fund is to advance ideas for sustainable regional cooperation in Central Europe.

There are chapters of scientists from Visegrad countries and Ukraine on the book's pages. There is especially the wide geography of Ukrainian scientists on the pages of the monograph.

The monograph is the result of the scientific achievements of scientists, leading specialists from universities and organizations:

We express our sincere thanks to all the authors, esteemed colleagues, who in a short time presented the own, original, interesting researches on the problems of climate change and sustainable development, contributing to this book was published.

In the future we hope that the scientific works are on the pages of this edition will find creative affiliate cooperation through successful joint implementation of actual ideas, proposals, scientific and practical developments.

We would like to thank the International Visegrad Fund for supporting the publication of the book within the Grant #22110149.

Prof. Olena Mitryasova & Prof. Piotr Koszelnik

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STRUCTURAL MODEL OF THE SUSTAINABLE DEVELOPMENT STRATEGY IMPLEMENTATION OF UKRAINE

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ABSTRACT

The problem of man-made impact on the state of the environment as a result of human society evolution requires urgent solutions, the success of which is determined by understanding the relationship between environmental and socio-economic systems, understanding the role of which will allow to determine ways of further development of Ukraine. According to the results of the analysis of the environment state, the problems of the relationship between ecological and socio-economic systems are revealed and it is established that one of the most dangerous factors for the realization of ecologically oriented economic interests of the state development is the low level of ecological safety of economic entities, which causes ecological losses, associated with significant pollution of natural components of the environment. The analysis of areas of implementation and actions aimed at achieving sustainable development by minimizing the risks of man-made environmental impact allowed to apply the QFD-methodology (Quality Function Deployment) and build a matrix diagram that visualizes the narrowness of relationships between clearly targeted actions and stages of implementation of sustainable development strategy.

Keywords: sustainable development, ecological safety, environment, structural model, technogenic load.

INTRODUCTION

The problem of the relationship between human society and the environment requires an immediate solution, the success of which is determined by understanding the nature of the relationship between ecological and socio-economic systems, understanding of which will determine the ways of further development of any independent state.

For the first time, the content of the category «balanced development» was recognized at the global level as the main direction of development of each state in the XXI century. Balanced development is declared as a new imperative for the next generation; a new stage of development, which humanity must take in its progress, which requires a rethinking of existing values, a radical change in worldview, priorities, ethical and other norms and forms of rationality [1].

Theoretical foundations of balanced development as a new paradigm of civilization evolution, which provides a harmonious interaction of biological and social factors, can be found in the works of V.I. Vernadsky about the biosphere and noosphere, which focuses on the aware disregard of civilization for the laws of nature and nonunderstanding that person is inseparable from the natural environment, herewith the noosphere is a natural stage of development of the biosphere, the characteristic feature of which is a radical change in human participation on Earth [2]. The ideological successor of the ideas of V.I. Vernadsky about the noosphere was N.N. Moiseev (1917-2000), who in his works gave the scientific basis for Ukraine's transition to balanced development. The main idea of his Concept of Balanced Economic Development is to preserve the quality of life of future generations, through appropriate management of the world economy, which can occur only if society understands that the ecological niche of mankind is the entire biosphere, and therefore balanced development is a common, coordinated biosphere (coevolution). Thus, the balanced development of N.N. Moiseev - is the first step towards the era of the noosphere [3].

Many scientists are differed on the stages of development of human civilization. So, for the first time S.A. Podolinsky combined «physical with economic» [4], E. Leroy defined the noosphere as a «thinking shell» formed by human consciousness [5], the version of P. Teilhard de Chardin is associated with the attempt to combine and synthesize science with religion [6]. In the mid-90's of last century V.O. Koptyug was one of the few who reasoned about the strategy of civilization as a scientist, noting that the search for a balanced development is not one-dimensional and it cannot, as sometimes people try to imagine, lead down to solving environmental problems only. The concept of sustainable development is multidimensional, it connects economic, social, demographic, environmental and political issues into a single whole in order to find and implement a reasonable balance in the interests of people living today and future generations. Only within such an approach it is possible to control the processes that contradict each other - globalization and fragmentation, integration and disorganization [7]. There is also interesting position of A.I. Kuznetsova, who argues that sustainable development should be based on long-term factors, which should include: human capital as the main way of achieving balanced socio-economic development; natural-ecological factor, characterized by climatic conditions, indicators of natural resources security, the state of the environment; scientific, technical and production potential, which determines the possibilities of modernization of production on an innovative technical and technological basis; investments as the main resource, without the involvement of which it is impossible to provide not only expanded but also simple reproduction; institutional environment as a system of state and non-state social, financial, economic and ecologic institutions that ensure sustainable socio-economic development; production and social infrastructure as a basis for ensuring the functioning of enterprises and livelihoods; internal and external economical and political situation [8].

The phenomenon of «sustainable development» has been taking place for a long time, it was comprehended and analyzed by scientists from different countries, but the author of the concept of «sustainable development» in the modern sense is Gru Harlem Brundtland, who first formulated it in 1987 in the report of the International Commission on Environment and Development «Our collective future» [9].

Developed forecasts and future scenarios [10], as well as new data on adverse trends in global biosphere and climate processes [11], led to the belief in the need for radical changes in human development priorities, creating a new model of civilization and a new economic and political strategy. The need to reform the economies of countries to mitigate the effects of the global ecological crisis has already been recognized at the international level and there has been formulated the principles of balanced development, which are recognized by the world community as the dominant ideology of human civilization in the XXI century and were published at the World Conferences on the Environment in Stockholm and Rio de Janeiro (1972, 1992) by almost all participants.

The Organization for Economic Cooperation and Development (OECD) defined the Sustainable Development Strategy (SDS) as a coordinated set of processes of analysis, training, planning, discussions and investments formed by participation and continuous improvement and integrating socio-ecologic and economic goals of society, while looking for compromises where previously this would have seemed impossible [12]. Thus, SDS is not a final constant product, but an interactive process based on the chains of analyzed and made decisions, planning, implementation and revision. The SDS should become a strategic long-term guideline with medium- and short-term objectives that are combined in an action plan with specific goals and time limits.

Despite the recommendations of the UN Commission on Sustainable Development, the SDS of each country is unique due to the economic and legal characteristics of each country, administrative traditions, institutional ability, the distribution of horizontal and vertical responsibilities between authorities. At the same time, certain common characteristics of the existing strategies of sustainable development are revealed: attempts to combine issues of environmental protection and development; application of a fundamental approach to finding ways to solve national problems; application mainly of medium- and short-term planning (but development scenarios for the period of 15 and more years often occur); approach to achieving national interests in the context of international problems and processes; strengthening of the idea of sustainable development as a conceptual basis for the creation of a national SDS. Therefore, to break the ecologic crisis on a global scale, a radical structural rebuild of the entire economic system in accordance with the objective requirements of the ecologic imperative becomes a natural phenomenon, and hence comes up the need to change the paradigm of further development for each state.

National SDSs are best developed in the countries of the European Union (EU) and are characterized by the highest percentage of created and accepted strategies. The explanation for this lies in the existence in EU countries not only of previously developed and tested ecologic policy, but also in the formed supranational initiatives of sustainable development, which stimulate the development of national SDS (Sustainable Development Strategy of the European Union, Sustainable Development Strategy of the Nordic countries).

METHODS AND EXPERIMENTAL PROCEDURES

Most EU member states approved the SDS before the World Summit on Sustainable Development, held in Johannesburg in late 2002. The first EU Sustainable Development Strategy was developed in 2001, which identified priority areas in the socio-ecologic-economic spheres and global governance that had to reinforce each other. And already in 2006 the EU countries officially approved the «Renewed Sustainable Development Strategy of the EU», which defined the general vector of changes at the level of planning both for the EU as a whole and for the member states of the European Union. In 2010, a new European development strategy was approved – «Europe 2020: a strategy for smart, balanced and inclusive growth», which identified areas for change for economic growth (Table 1):

Table 1. The main directions of growth according to the European Development Strategy

№	Growth direction	Path to achievement (growth indicators)
1.	Smart growth	Intellectualization of economic development, research and innovation
2.	Balanced growth	Greening of economic development, rational use of resources
3.	Inclusive growth	Socialization of economic development, increasing the level of employment, achieving social and territorial harmony

To achieve the above table. 1 growth indicators in the «Europe 2020» strategy seven flagship initiatives were identified (1):

$$Ibd = (Iu+Iy+Ii+Ir+Ipg+Ic+Ip), \quad (1)$$

where: *Iu* − «Innovation Union» (providing conditions and opportunities for funding researches and innovations, which will promote economic growth and job creation);

Iy – «Youth on the move» (strengthening the effectiveness of educational systems and promoting the involvement of young people in the labor market);

Ii – «Digital agenda for Europe» (accelerating the development of high-speed internet and providing opportunities for everyone to participate in the global digital space);

Ir – «Europe's efficient resources» (ensuring the transition to a low-carbon economy, increasing electricity production from alternative energy sources; modernizing the transport sector and ensuring the wise use of energy sources);

Ipg – «Industrial policy of the globalization era» (improving the business environment, especially for small and medium-sized businesses, supporting the development of a strong and sustainable industrial base for globalization);

Ic – «Agenda of new competencies and jobs» (modernization of labor markets, giving opportunities for people to gain new knowledge and skills with a further increase in employment opportunities, improving the ratio of supply and demand in labor markets);

Ip – «European platform for poverty reduction» (spreading social and territorial cooperation throughout the EU, reducing poverty in EU countries) [13].

THE RESEARCH RESULTS AND DISCUSSIONS

In practice, the «Europe 2020» strategy has faced many obstacles that have made it impossible to fully implement and achieve its priorities, so a new strategy "Europe 2030" has been formed, which reflects the aspirations of European political elites to overcome the global and regional challenges facing Europe and consists of an optimistic (EU is identified as a key global player contributing to positive changes in climate and energy policy, healthcare, disease prevention and security) and negative (no significant changes and maintaining current trends) scenarios (Table 2).

To calculate the global scenarios of the European strategy, the following criteria were taken into account: the magnitude of economic growth and socio-economic dynamics, which depend on global demographic growth rate in conditions of limited resources, level of people's education, unemployment, pressure from migrants.

Thus, the global priorities for the EU in the negative scenario are preventive measures related to energy, urban, environmental risks and military conflicts. As for the optimistic scenario, it reflects the future of Europe, which is to overcome the challenges associated with the negative scenario [14].

In Ukraine, the implementation of the concept of sustainable development, despite the existing legal and institutional foundations for environmental protection management is quite slow, due to low levels of environmental investments, lack of measures and wasteful use of natural resources, lack of transparent environmental information to ensure ecologic issues control from the informed part of society and stakeholders, the absence of price and market mechanisms necessary for the efficient use of natural resources.

Table 2. Sustainable Development Strategy «Europe-2030»

Positive scenario	Negative scenario
Financing projects with high social impact	The crisis of the legitimacy of capitalism (the emergence of new players in a multipolar political world)
Creating open ecosystems for research, innovation and education	Political events (formation of new political coalitions)
Transition to a low-carbon economy, balanced production and consumption (cyclical economy)	Excessive exploitation of resources
Increasing the amount of funding for research in the field of environmental protection	Financial shocks
Public safety	Security threats
Creation and further development of «smart» cities	Technological changes (in particular, digitalization)
	Speed of technological progress
	Loss of public confidence in government
	The collapse of the EU
Protection of the natural environment	Pandemics
Healthcare	Deterioration of the natural environment

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Along with this, there are positive shifts aimed at addressing the issues of practical achieving of sustainable development, in particular: Resolution of the Verkhovna Rada of Ukraine «On the Concept (foundations of state policy) of national security of Ukraine» [15], Law of Ukraine «On Basic Principles (Strategy) of the state ecologic policy of Ukraine for the period up to 2020» [16], the Law of Ukraine «On Basic Principles (Strategy) of the state ecologic policy of Ukraine for the period up to 2030» [17], which defined a new course of development for the near future (Table 3).

Table 3. Strategic goals of Ukraine for the period up to 2030 according to the Strategy of the state ecologic policy

Area of implementation	Actions to implement the sustainable development strategy
Science	S1. Implementation of the results of modern fundamental ecologic research
	S2. Continuous interaction between scientists and the state system of environmental management
	S3. Taking into account the recommendations of scientific institutions of ecologic orientation in making management decisions and development of regulations projects
	S4. Protection and conservation of typical natural plant groups, biodiversity and landscapes
Education	E1. Ensuring the quality of education from preschool to secondary and vocational education
	E2. Ensuring the quality of higher education
Management	M1. Reducing the negative impact of urbanization processes on the environment
	M2. Stopping the destruction of environment within cities
	M3. Introduction of a green procurement system
	M4. Stimulating the renewal of main funds of industrial and transport infrastructure, and housing and communal services
	M5. Creating a tax, credit and investment climate to attract international donors and private capital to environmental activities
	M6. Stimulating the introduction of eco-friendly, resource-efficient production and ecologic innovations by business entities
	M7. Development of environmental audit
Production	P1. Complete gradual cessation of discharge of untreated and insufficiently treated wastewater into water objects
	P2. Ensuring compliance of the degree of wastewater cleaning with established norms and standards, prevention of groundwater pollution
	P3. Gradual restriction of the use of certain plastic products in the food industry
	P4. Return of resource-valuable materials to economic circulation
	P5. Elimination of the direct dependence of increasing the use of natural resources and energy on economic growth
	P6. Replacement of primary natural resources through the use of industrial waste or by-products, including slag
	P7. Introduction of a balanced management system for waste and hazardous chemicals
	P8. Reducing ecologic risks to ecosystems and public health
Information technology	IT1. Introduction of ecologic risk management based on its real-time modeling
	IT2. Cyber protection of ecologic information resources, systems, databases, implementation of electronic government technologies

Based on the obtained data, it was proposed to visualize the dependence of actions on certain areas of activity for the implementation of the sustainable development strategy at each stage of its implementation (Figure 1).

As a result of the implementation of the updated Strategy, Ukraine by 2030 should introduce modern monitoring systems, market mechanisms for greening the economy, as well as halve the energy capacity of the economy, reduce greenhouse gas emissions by 60% and reduce emissions from stationary sources of pollution by 15% and 30% from mobile sources compared to 2015. A progressive step is that the new version of the Strategy breaks the link between economic growth and increased use of natural resources and environmental pollution, a strategic ecologic rating is conducted for 100% of plans and programs, ecologic priorities are included in all sectoral programs and plans, and the Strategy contains clear completion indicators - 35 indicators by which it will be possible to assess its effectiveness and efficiency.

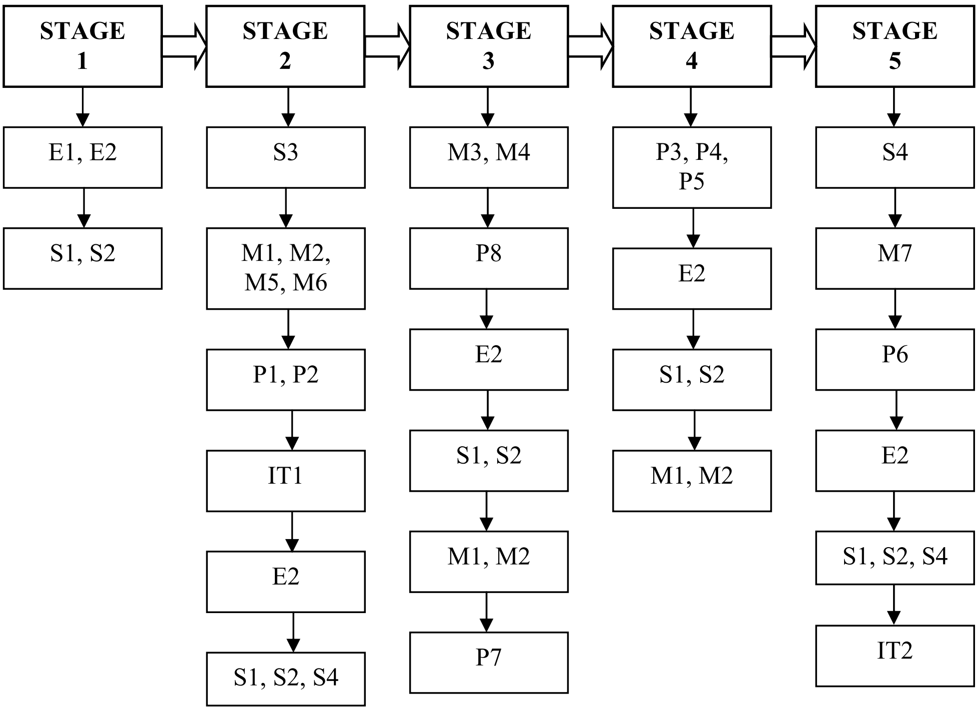

Fig. 1. The scheme of phased implementation of the sustainable development strategy

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The system, which was laid down in the updated Strategy, is successfully operating in the EU and is a doctrine for the formation of new ecologic policy. The document meets European ecologic standards, as well as the medium-term priorities of the Government, because only those economics that have managed to transit to a resource-efficient, cyclical, low-carbon economy will be successful in the future. The strategy provides measures to reduce air pollution, soil cover, water objects and their resources, and general changes in state administration through the introduction of ecologic norms and standards, as in fact two thirds of the population of our country live in areas where air quality does not meet hygienic standards, and the state of land resources and surface water quality according to the degree of pollution are classified as polluted and highly polluted.

The conducted analysis of the activity areas that are the basis for the implementation of the sustainable development strategy of the state and minimization of risks of influence on the environment allowed to apply the QFD-methodology (Quality Function Deployment) and build a matrix diagram [18] to identify links between established areas of activity for implementation of sustainable development strategy and relative stages (Table 4, Figure 2.).

Table 4. Matrix L-shaped diagram

Stage	Areas for the implementation of sustainable development strategy					Ranking
	science	education	production	management	information technologies	
Stage 1	●		◊	●		19
Stage 2		●	○		●	21
Stage 3	●		◊	◊		11
Stage 4	●	●	●	●	◊	37
Stage 5	●	◊	○			13
Sum of ranks	36	19	17	19	10	

Note: Relationship types and valuation: weak – ◊ (1), average – ○ (3), strong – ● (9).

The analysis of this matrix diagram shows that the basic approach in the process of implementing the sustainable development strategy is to ensure the quality of education at all levels, from general education to the training of applicants for the first, second and third qualification levels of higher education. An important addition to these areas of influence on the implementation of sustainable development strategy is management, which requires the application and provision of approaches to managing the processes of both human behavior and the behavior of technical instruments.

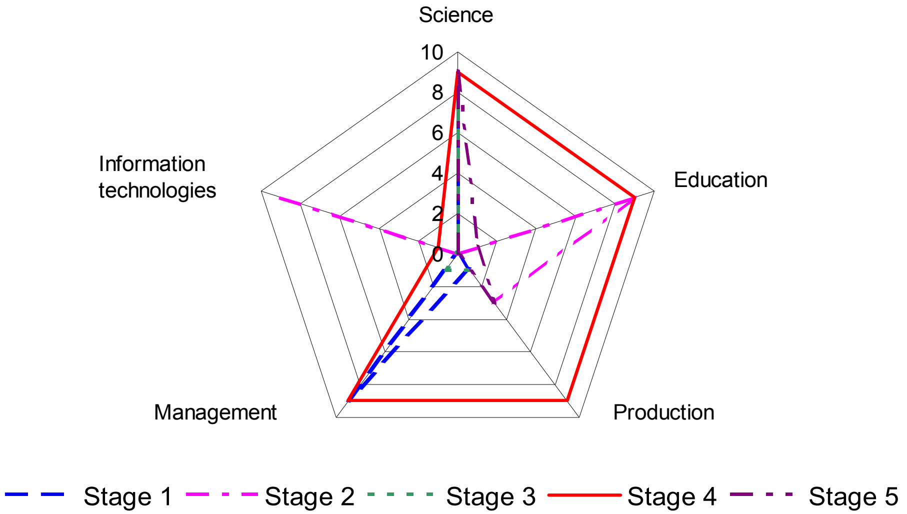

Fig. 2. Vector of the orientation of the sphere of actions for the implementation of the sustainable development strategy

Despite today's conditions, which are in the plane of uncertainty and instability, a major role in the implementation of sustainable development strategy in Ukraine should rely on production and information technology. The importance of these areas of activity is maybe defined as insignificant compared to other areas, but without proper staff motivation and the use of modern IT technologies there will be no increase in the level of ecologic safety of enterprises, which is the foundation of sustainable development.

CONCLUSION

Analysis of the matrix diagram and vector of action areas orientation at each stage shows that the second stage of sustainable development strategy requires the application of the largest number of actions in different areas, which indicates its complexity and significance, because it is the foundation over which should be formed a strong sustainable development structure of Ukraine.

Analysis of the matrix diagram and vector of the orientation of the sphere of actions at each stage shows that the second stage of sustainable development strategy implementation requires the application of the largest number of actions in different areas, which indicates its complexity and significance, because it is the foundation over which a strong structure of sustainable development of Ukraine should be formed.

Thus, the structural model of actions necessary to achieve the goals of sustainable development of Ukraine until 2030 is based on a radical change of priorities for building a new political strategy and a new model of civil society.

REFERENCES:

1. Kuzmina O.S. (2015) Analysis of approaches to the interpretation of the concept of «sustainable development of the enterprise». Bulletin of Khmelnytsky National University. vol. 5. T. 1. pp. 13−21

2. Vernadsky V.I. (1975) A few words about the noosphere. Moscow: 275 c. (in Russian)

3. Moiseev N.N. (1996) Sustainable development or transition period strategy. Moscow: «Energy», pp. 141 (in Russian)

4. Podolinsky S.A. (2000) Human labor and its relation to the distribution of energy. Selected works / order. L.Ya. Korniychuk. Kyiv: KNEU, pp. 203−283.

5. World Encyclopedia: Philosophy / ch. scientific ed. and comp. AA Gritsanov. Moscow: AST, Mn .: Harvest, Sovremennyi literator, 2001. pp. 1312 (in Russian)

6. Teilhard de Chardin P. (2002) As I believe. The human phenomenon: Sat. essays and essays / comp. V. Yu. Kuznetsov. Moscow: «OOO Izdatelstvo AST», pp. 553 (in Russian)

7. Koptyug V.A. (1992) United Nations Conference on Environment and Development (Rio de Janeiro, June 1992). Information Review, RAS, SB. Novosibirsk, pp. 24-28.

8. Kuznetsova A.I. (2010) Infrastructure: questions of theory, methodology and applied aspects of modern infrastructure arrangement. Geoeconomic campaign. Moscow: KomKniga, pp. 456 (in Russian)

9. Brundland G. (1987) Our Collective Future: International Commission on Environment and Development. Oxford: Oxford University Press, pp. 125

10. Mesarovic, M. (1974) Mankind at the Turning Point. The Second Report to the Club of Rome. New-York, pp. 289

11. Our collective future: Report of the International Commission on Environment and Development (ICED). (1989) Moscow: Progress, pp. 376

12. OECD/DAC. Strategies for Sustainable Development: Practical Guidance for Development Cooperation. – OECD: Paris, 2001. 73 p. URL: http://www.oecd.org/dataoecd/34/10/2669958.pdf. (date of application: 18.09.2019)

13. Strategy «Europe-2020» URL: http://ec.europa.eu/eu2020/pdf/COMPLET%20EN%20BARROSO%20%20%20007%20-%20Europe%202020%20-%20EN%20version.pdf (date of application: 15.09.2019)

14. Ibragimova KA Europe 2030: Development of a new EU framework program for research and technological development. The browser. 2017. vol. 11(334). pp. 51−61.

15. On the Concept (foundations of state policy) of national security of Ukraine: Resolution of the Verkhovna Rada of Ukraine of January 16, 1997, no. 3 / 97-BP. URL: http://zakon5.rada.gov./ua/laws/show/3/97-%D0%B2%DI%80. (date of application: 04.08.2019)

16. On the Basic principles (strategy) of the state ecologic policy of Ukraine for the period up to 2020: Law of Ukraine of December 21, 2010, no. 2818-VI. https://zakon.rada.gov.ua/laws/show/2818-17 (date of application: 10.08.2019)

17. Law of Ukraine «On the Basic principles (strategy) of the state ecologic policy of Ukraine for the period up to 2030» (NVR of Ukraine, dated February 28, 2019, no. 2697-VIII). URL: https://zakon.rada.gov.ua/laws/show/2818-17 (date of application: 02.09.2019)

18. Kudryavtsev D.V., Grigoriev L.Yu., Kubelsky M.V., Bobrikov S.A. (2018) Method of strategic alignment of the organization activity on the basis of technology of quality functions deployment. Bulletin of St. Petersburg State University. Management. vol. 17(4): pp. 465-498. https://doi.org/10.21638/11701/spbu08.2018.402.

ALTERATION OF NATURAL ECOSYSTEMS BY PLANTS INVASION: INSIGHTS FROM SOIL CHEMICAL PROPERTIES AND MICROBIAL INDICES

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ABSTRACT

Invasion by alien species is one of the most conspicuous human driven ecological changes, often with undesirable effects on biodiversity and ecosystem functioning. Invasive plants often affect soil conditions, notably through changes in soil chemistry and microbial community composition, potentially leading to altered soil functionality. The success reflects the competitive strength of invasive plants in comparison with the native plant species. When invasive alien plant species dominate in the community, they alter the conditions in the ecosystem in a way that it becomes unsuitable for thriving of native plants. There is a general agreement that soil biochemical, microbiological and biological properties are more suitable than physical and/or chemical properties for estimating alterations in soil quality and hence soil degradation. The aim of this complex study was to report that selected invasive plants species (*Impatiens parviflora*, *Solidago gigantea*, *Fallopia japonica*, *Helianthus tuberosus* and *Heracleum mantegazzianum*) had impact on physico-chemical properties and microbial indices in soil ecosystems. The research was carried out in different localities and ecosystems (forests, grasslands and/or wetland) of South-Eastern Slovakia. Soil reaction, soil moisture, soil organic carbon, soil basal respiration, microbial biomass carbon and soil enzyme activities (urease, FDA, beta-glucosidase, acid and alkaline phosphatases) were determined. Obtained data were compared with uninvaded adjacent sites. Soil physico-chemical properties and activity of microbial population differed between soils under invasive species and those under native plants. Generally, the every single plant invaders altered soil parameters, but those changes varied among localities and there are no general patterns of invasion-induced alteration for these indices. The results also suggested that biology of the invasive plants had the high impact on soil ecosystem and soil enzyme activity played an important role in nutrient cycling in the ecosystems, and thus could be considered as biological indicators of soil health and environmental changes.

Keywords: invasive plants, soil ecosystem, soil enzymes, soil physico-chemical properties, soil indicators

INTRODUCTION

Invasive and non-native plant species

Biological invasions are one of the main threats to natural ecosystems and the impact of invasive plant species on native species, communities, ecosystems and soil biota has been widely recognized over the last decades [1, 2]. One such fundamental, but criticised concept in invasion biology is that of "non-nativeness". Species dispersal is seen by biologists as one of the key driving forces of evolution and indeed, there is no ecological rule or norm that says anything has to stay put, and very few taxa do so [3]. Many species can thus be considered non-native at some point in time. Non-native species of plants (or animals) are those species that do not have a natural area of distribution in natural ecosystems and have been imported into the territory or have spread to natural system in which they similarly do not have a natural area of distribution. Invasive species are non-native species of microorganisms, fungi, plants or animals that have the potential to spread rapidly and adversely affect populations of the native species and native habitats and related ecosystem services [4]. In addition, some invasion biologists define non-nativeness as referring only to those species that are dispersed by humans [5, 6]. Furthermore, species that extend their range by natural means are occasionally also labelled non-native [7]. In particular, the use of synonyms has been widely recognized as an "introduction", "naturalisation" and "invasion". To the further detriment of clarity, invasive and non-native, including their various derivates, such as "exotic" [8], "alien" [9] or "colonial" [10], are also regularly used synonymously [11]. Climate change represents an existential threat to global food security, ecosystems, and public health. The study of Mao et al. [12] shows that the invasion problem is likely to be exacerbated by climate change. The most vulnerable areas are those with high number of endemic species. It is expected that invasive alien species would affect the biodiversity of aquatic ecosystems, especially standing waters, to the greatest extent, while among terrestrial ecosystems the biodiversity of Mediterranean ecosystems is under the greatest pressure [13].

The fact is that the number of invasive plants and their distribution are increasing in many parts of the world. Invasive plants are found to spread even in the ice-free Islands of Antarctica despite the Antarctica treaty [14]. In addition to terrestrial environment, aquatic ecosystems, particularly wetlands are also threatened with invasive species. Many species have been introduced accidentally (e.g., in water ballast, in soil, or as crop seed "contaminants"), but some have been intentionally introduced as ornamentals, food, or fiber products [15]. The study of Lockwood and McKinney [16] state that the introduction of alien species can have many ecological impacts, and contribute to the homogenization of biological systems worldwide. Invasive plants dramatically influence biodiversity in natural areas, often create monocultures where diverse plant communities previously existed [17], and they are now viewed as a significant component of global changes [18]. Invasion of exotic plant species might alter many ecosystem properties, including important soil function and characteristics [19]. Moreover, the same species can have the different impact on soil system, depending on local conditions [20]. Native plants can act as sink for air pollutants and contribute significantly to carbon sequestration [21, 22]. Therefore, loss of native plant diversity through invasive plant pathogens may indirectly affect human health through perturbations in the environmental quality [23]. Invasive species are amongst the most significant drivers of species extinction and ecosystem degradation, causing negative impacts on ecosystem services and human well-being [24]. There are many cases over the world of devastating effects of invasive species on ecosystems and these dramatic invasions emphasize that invaders often parallel environmental changes that are taking place at the regional scale [15]. Therefore, research on the links between invasions and environmental changes is urgent and timely. Biotic invasions are capable of interacting with other anthropogenic changes in the environment to alter biodiversity and ecosystem processes in invaded habitats. For example, there is an evidence from a variety of ecosystems that nitrogen inputs favour alien plant species [25, 26]. Human alteration of the N cycle, however, has increased the rate of N fixation to such an extent that human-derived N now exceeds natural processes [27].

As fossil fuel burning and tropical forest clearing increasingly change the composition of the atmosphere, the Earth's climate is expected to change significantly. Many predictions expect warmer climate and this is already underway [28]. Despite of this unwell trend, many plant and animal species are already responding to changes in temperatures and growing season lengths [29]. The researchers are asking a question if some invasive plant species could be favoured by these climatic changes. Clearly, invasive species whose native ranges are warmer than their introduced ranges would be at an advantage [15]. These species would resist the increasingly hot extreme temperatures better compared to natives. They should also experience less mortality due to extreme weather fluctuations. Species interactions may be as sensitive to changes in precipitation patterns as to warming. The study of Duke and Mooney [30] shows that a wetter climate could cause several invasive plant species become denser, with negative consequences for native plant and animal species. Last decades, land transformation have been very extensive and in most cases irreversible. Inappropriate land use that negatively affects ecological processes and soil quality is generally considered the primary cause of soil degradation in native ecosystems [31]. The ecosystems can change in structure, composition and function. Because plant invasions occur across landscapes, their dispersal and spread depends on landscape structure and dynamics [32]. Understanding land use and land cover changes is useful for detection and management of land-use change to reduce the spread of invasive plant species. There is a general assumption that changes in land use directly increase biological invasions. The study of Wang et al. [33] suggest that conversion of natural habitats need to be controlled and well managed to help mitigate future invasion risk. There are few reasons why changes in land use can influence and favour invasions. First, land use changes are frequently accompanied by disturbances that provide "open window" of better conditions (e.g. more light, space and nutrients) for seedlings establishments and growth [34]. There is an evidence that monitoring of exotic plants are found in higher richness in altered and degraded ecosystems (post-mining sites, ruderal and anthropogenic sites). The other reason is that land use changes include modification in landscape composition and structure, such as fragmentation, which increases the length of edges and the prevalence of corridors that can facilitate invasions. The fragmentations creates more edges, which facilitate the spread of invasive species [15]. Most research on the effects of global environmental changes on biological invasions has examined effects of single environmental factors. Plant invasions transform vegetation structure and, can directly or indirectly affect ecological functioning, and consequently can exacerbate changes in land-use or environmental changes. [35]. The management of biological invasions is necessary, not only to sustain biodiversity and the environment, but also to safeguard productive sectors. Invasive species (weeds, pets, parasites) have significant impact on economical productivity in the agriculture and forestry sectors. Many studies have focused on evaluating the impacts of the introduction and spread of invasive species on biodiversity and ecosystem properties [1, 36]. The invasive plant species have posed several threats to the native biodiversity, ecosystem services, environmental quality and human health. Figure 1 shows relationships within biological invasions and environmental changes to socio-economy and human health.

Interestingly, it has been demonstrated that certain invasive plant species may act as ecological indicators of environmental pollution and other disturbances ([1, 37]. Success of invasive species is not decided by merely a single environmental factor and ecological attribute. The fact is that the plant invasion, anthropogenic disturbances, climate changes, biodiversity and human health may have complex and difficult relationship [38]. Generally, it is well known that highly managed areas (e.g. in natural parks, protected areas) are resistant to plant invasions [39]. Some other studies reveal that the plant invasion is a major threat to forest biodiversity in protected localities and show that these ecosystems are also prone to the invaders [40]. The lack of invasion effects on most soil properties does not necessarily imply the lack of influence of invasive plants, but may suggest that the direction of the changes varies among replicate sites and there are no general patterns of invasion-induced alterations for these parameters [41].

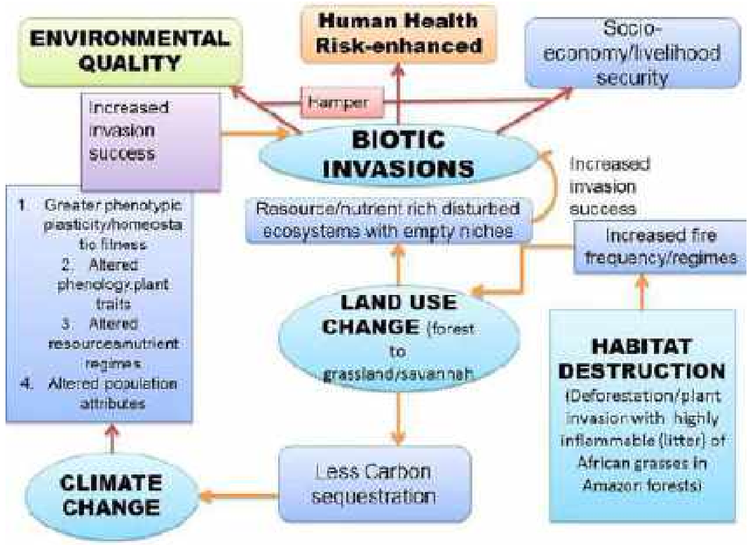

Fig. 1. An interrelation framework, among anthropogenic factors/global environmental changes (biotic invasions, habitat destruction/fragmentation, land-use/ climate change, environmental pollution), impacting socio-economy/livelihood and human health [36]

Soil ecosystem function

Soil perform multiply fraction: a) providing physical support to terrestrial plants, b) supplying fundamental resources (water, nutrients, oxygen required for terrestrial primary production), c) providing habitat to a variety of soil organisms, d) regulating hydrological and nutrient cycling with significant impact on global climate, e) detoxification of organic and inorganic substances, and f) resisting erosion [42]. Soil is a crucial natural resource and at the same time an economic and social potential. It enables the production of food and raw materials, recycles waste, forms a forest landscape, filters and retains water, enables the use and recovery of solar energy, ensures the cycle and balance of substances in nature, maintains the diversity of plant and animal species and primarily shapes the quality of the environment [43]. Land management is the most widespread environmental technology with its positive and negative manifestations. It uses the basic natural resource and at the same time affects another natural environment. Therefore, the biologization of land management is the dominant interest of farmers, but also ecologists [44]. Respect for the principle of soil sustainability, as well as other components of the environment, is a basic precondition for the sustainability of life. Knowledge of soil degradation is important from the point of view of sustainable soil management. Physical degradation of the soil is manifested by clogging of the pores and the formation of soil, loss of soil by erosion and compaction. Manifestations of chemical degradation include, in particular, reduction of the content of soil organic matter (humus), acidification, salinization, loss of nutrients by leaching, pollution by harmful substances. Biological degradation is ultimately associated with a reduction in environmental biodiversity. Soil is itself an environmental filter that gets rid of unwanted solid and gaseous components from water and air [45]. Soil ecosystem services depend on soil properties and their interaction, and are mostly influenced by its use and management. At present, many researches has highlighted the importance of soil and its components in the process of carbon sequestration and its impact on climate change, caused mainly by the release of large amounts of CO_2 and other greenhouse gases into the atmosphere [46, 47]. Soil organism communities have a direct and indirect impact on land productivity, and they are an important element of terrestrial ecosystems, although they represent no more than 0.5% of the total soil volume and 10% of the total organic matter in soil ecosystem. Soil biota play an irreplaceable role in the decomposition of organic matter, in the cycle of carbon, nitrogen, sulphur, phosphorus, the transformation and degradation of various waste and toxic substances, etc. In this context, the impact of soil organisms is becoming a key component of a strategy leading to the sustainability of the soil ecosystem [48]. Invasive plants can affect soil functions in diverse ways. For example, dense invasive thickets could lead to changes in litter fluxes (e.g. high leaf litter input), whereby the presence of the invader leads to the deposition of organic material that differs in chemistry, quantity, and quality from litter inputs prior to invasion. Furthermore, invasion by certain plant functional groups may have distinct impacts on soil organisms. For example, nitrogen-fixing plants can potentially modify soil nitrogen accumulation and cycling rates. [49].

Definition and evaluation of soil quality

Soil, like air and water, is a fundamental natural resource supporting a variety of ecosystem goods and services to the benefit of the mankind. Soil quality is significantly affected by physical, chemical, biological properties and microbial indices that are sensitive to changes in the environment and soil management. The quality of the soil is largely determined by its organic matter, as it combines soil particles, stabilizes the soil, thereby reducing the risk of erosion, increasing the retention water and cation exchange capacity and, last but not least, mitigating the negative effects of pesticides, heavy metals and other pollutants. Ultimately, it directly affects biomass production. The main qualitative feature that distinguishes soil from rock is fertility. At present, soil fertility is evaluated from the ecological or environmental point of view, and therefore the term soil quality dominates in recent literature. It expresses the ability of soil to provide ecological functions in its specific way of use [50]. The study of Doran and Parkin [51] describe soil quality in a broader context. They define soil quality the capacity of soil to function as a vital living system, within ecosystem and land-use boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and promote plant and animal health. Anthropogenic reductions in soil health, and of individual components of soil quality, are a pressing ecological concern. Johnson et al. [52] characterize the term from the environmental context, as a measure of the condition of the soil is its quality associated with the need for one or more biological species or man himself. Harris et al. [53] state that soil quality is a measure of the ability of soil to maintain water and air quality, to support the production and quality of plants and animals, and to promote human health in a given land use and within landscape and climatic conditions. Soil quality is often replaced in the literature by the term soil health. The use of the term soil quality is linked to the good condition of the soil for its specific use and the term soil health is, in a broader sense, the protection and enhancement of biological productivity, environmental quality and health promotion of all living forms, including humans. In this understanding, soil health can be synonymous with the sustainability of the soil ecosystem [54]. Soil health, biodiversity and soil resilience are critically limited in extreme environments and are very sensitive to anthropogenic influences. Only healthy soil is able to retain nutrients, reduce the amount of contaminants and other soluble substances in the soil through sorption and bind them to clay particles and organic material. The quality and health of soil determine agricultural sustainability and environmental quality, which jointly determine plant, animal and human health [42]. There is an increasing need to define thresholds of environmental sustainability that should not be exceeded. In that context, there are thresholds of degradation of soil properties at which irreversible environmental changes occur. However, we lack suitable indicators and threshold values [55]. Decisions and perceptions regarding soil quality are strongly affected by agricultural productivity and are usually based on soil quality indicators such as bulk density, texture, organic matter, fertility (based on plant productivity) and salinity. Effective indicators of soil quality and health should provide an early detection of environmental changes in the ecosystem. They should offer the information about the function, composition structure and activity of the individual components in the soil ecosystems. There is very often problem of interpretation of indicators because there is not always a linear relationship between the indicator value and soil function [56].

Soil quality indicators

The maintenance of the soil quality is critical to environmental sustainability. Soil quality cannot be determined directly, but it should be derived from changes in its parameters or indicators. In practice, the determination of the whole spectrum of suitable indicators is used. As a rule, they should correlate with the processes in the ecosystem and integrate the physical, chemical and biological properties of soils [57]. Selection of key indicators and their critical limits (threshold values), which must be maintained for normal functioning of the soil, are required to monitor changes and determine trends in improvement or deterioration in soil quality for various agro-ecological zones for use at district, national and global levels. Many soil indicators interact with each other, and thus, the value of one is affected by one or more other selected parameters [58]. Opinions on the definition of soil quality assessment and its parameters are different in the literature. The main indicators for assessing of soil quality are physical and chemical, however, soil microbial indices may respond more rapidly to management activities and environment changes [59]. Moreover, the biological component of soil is responsible for many functions of the soil ecosystem, including the decomposition of organic debris, nutrient cycling, synthesis of humic substances, degradation of xenobiotics and nitrogen fixation. Soil biological activity is affected by land management and connected to soil erosion rates [60]. The crucial parameters of soil quality in relation to ensuring the production function are: soil depth over 1 m, slope up to 5%, skeleton content in topsoil up to 10%, grain composition, medium-heavy clay soil with adequate content of clay (20%), dust (50%) and sand (30%) particles, bulk density 1.15 - 1.46 $t.m^{-3}$, total pore volume 40 - 50%, porosity index around 1, water infiltration rate over 30 mm in the first hour, water retention capacity 80 - 90 mm in topsoil and 200 - 300 mm in subsoil, values of sorption capacity in topsoil 15 - 18 $cmol.kg^{-1}$, humus content in topsoil over 2%, pH_{KCl} in the range of 5.6 - 7.2, no occurrence of toxic substances in all soil layers. A number of soil quality and fertility indicators were proposed, none identifies state of soil degradation that affects its functionality [42]. Soil health is worth quantifying because soils and their biota provide ecosystems functions that benefit humans. These ecosystem services can be of considerable value and include soil functions of storing and releasing water, decomposing plant and animal residues, transforming and recycling nutrients, sequestering and detoxifying organic toxicants, and promoting plant health by suppressing plant-pathogenic microbes and phytophagous fauna [51].

Soil organisms as an indicator of soil quality

Soil biodiversity is probably the most important for maintaining ecosystem function in a disturbed environment and can be measured directly (as species richness) or indirectly using standardized procedures (various indices). Soil organisms respond sensitively to land management practice and climate. They are well correlated with beneficial soil and ecosystem function including water storage, decomposition and nutrient cycling, detoxification of toxicants, and suppression of noxious and pathogenic organisms. Soil organisms also illustrate the chain of cause and effect that links land management decisions to ultimate productivity and health of plants and animals. [51]. Bacteria and fungi are key drivers of biogeochemical processes in soil, and microbial enzymes are widely recognized as proximate drivers of organic matter transformation and decomposition. The role of the microbial fraction in mediating soil processes, and their relatively high rate of turnover, logically suggests that microbial fraction could be a sensitive indicator and early predictor of changing soil organic matter processes [61]. Individual soil microbial and biochemical indicators are not useful measures of soil quality, because, not only they vary both seasonally and spatially but also many physical, chemical, and biological properties affect soil quality [43, 58]. The proper approach in defining soil quality indicators must be holistic not reductionistic, thus indicators should describe the major ecological processes in soil, so that a variety of biochemical and microbial analysis should be used when considering the impact of management on soil quality [62]. Biological indicators should be sensitive enough to reflect changes in the soil environment and at the same time be highly informative. From a practical point of view, it is important that they should be simple and economically affordable [51]. When selecting soil quality parameters, their variability over time plays an important role, which is related to the stability of the parameters. Bujnovský and Juráni [50] differentiate between stable soil parameters (e.g. soil depth, soil granularity), relatively stable (e.g. salt content, soil organic matter content, heavy metals contamination), relatively dynamic (e.g. soil pH, nutrient content) and dynamic (e.g. soil moisture and temperature, microbial activity, etc.). Stable and relatively stable soil parameters predominantly affect soil quality, while the relatively dynamic and dynamic properties of soil are more related to its short-term changes. The study of Doran and Parkin [51] present the following soil quality indicators: a) physical parameters - soil granularity, soil depth and depth of soil uprooting, stability of aggregates, bulk density, infiltration, retention water capacity, retention characteristics, water content, temperature; b) chemical parameters - total carbon and nitrogen content, soil pH, electrical conductivity, mineral N ($N\text{-}NO_3$, $N\text{-}NH_4$), P and K content; c) biological parameters – microbial biomass C and N content, potentially mineralizable N, soil respiration, the ratio of microbial biomass C to total organic C, the ratio of respiration to microbial biomass.

The functionality of soil processes can be measured by determining the activity of soil enzymes, nutrient mineralization, potential nitrification, soil respiration, etc. [43, 54]. Representatives of various classes are used as bioindicators of the soil environment and evaluation of its quality. A suitable indicator of soil quality is the use of nematodes, grinders, mites, tail jumps, earthworms, etc. Suitable indicator of an active nematode community, microflora and decomposition activity in grassland soils is the high diversity of nematodes. These communities can also serve as bioindicators of climate change [63]. Based on changes in the occurrence of groups of nematodes, the influence of heavy metals can also be determined. Some species of mites are also considered to be bioindicators of habitats and soil conditions and, together with horsetails, they are among the most numerous groups of soil fauna. Because they accumulate heavy metals, they are suitable for bioindication of metal contaminated soils. The best indicators of soil quality are earthworms due to their easy identification. They can be used as biomarkers to detect the effects of pollutants or to monitor sublethal doses of toxic substances. Some species of earthworms are able to increase the availability of nutrients in the soil (phosphorus and potassium) for plants, increase soil pH and thus immobilize heavy metals in the soil (lead and zinc) probably through the release of substances formed by specific processes within their body. Microbiological characteristics are very often and effectively used as indicators of soil quality, because the large surface area, reactivity, distribution, generation time and diversity of the soil microflora allow a virtually immediate response to any changes [64]. Microbial parameters appear to be useful in monitoring soil contamination by heavy metals, but the determination of only one attribute is of no significance for the soil and its changes in the environment. Therefore, several important microbial activities need to be taken into account, such as soil respiration, carbon and nitrogen mineralization, biological N_2 fixation, soil enzyme activity or soil microbial biomass.

Soil microbial indices

The most commonly used biological indicators of soil quality include soil microbial biomass and its activity, soil enzymatic activities, N mineralization rates, soil respiration, ratios of bacteria to fungi, gram-negative to gram-positive bacteria, and relative proportions of various functional groups of soil fauna [55]. The microbial biomass comprises part of the living component of soil organic matter, being constituted by soil microorganisms and accounting for 2 to 7% of the organic carbon in the soil environment. In addition, soil respiration rate is an important for understanding and modelling the processes related to the transformation of organic matter, as well as the development of management strategies in soil quality and carbon sequestration increase [65]. According to the knowledge of soil biochemistry, high molecular weight organic pollutants are degraded via metabolisms of microorganisms and enzyme activities in the soil.

Soil enzyme activities

Soil enzymes deserve further explanation within the context of this review as they have been used more commonly as soil quality indices. Soil enzyme activities are the direct expression of the soil community to metabolic requirements and available nutrients. While the diversity of soil organisms is important, the capacity of soil microbial communities to maintain functional diversity of those critical soil processes through disturbance, stress or succession could ultimately be more important to ecosystem productivity and stability than taxonomic diversity. One essential microbial function in soils is the processing and recovery of key nutrients from detrital inputs and accumulated soil organic matter. This often requires the activity of extracellular enzymes to process complex organic compounds into assimilable subunits (sugars, amino acids, NH^{4+},PO_4^{-3}) [66]. Activity of soil enzymes is proposed to be an important determinant of soil and water quality improvement in different types of ecosystems (e.g. wetlands) and is affected by many factors, including biological (microbial population, higher taxa and fauna), physico-chemical properties (pH value, organic matter content, nutrient composition, depth, etc.) and climate [67]. The presence and activity of soil enzymes are related to soil physical and chemical properties, composition of microbial population, vegetative cover, management, land use, etc. [31, 43, 55]. Soil microbial community plays a key role in soil processes and soil enzymes catalyse reactions in soil system that have biochemical significance. Soil enzymes participate in nutrient cycles, such as carbon (beta-glucosidase), nitrogen (urease) and phosphorus (phosphatases). These enzymes transfer energy through organic matter decomposition and nutrients are released to be available for plant growth. Enzymes indicate the rate of important microorganism-mediated processes in soil. That makes them suitable indicators of biological activity; energy transfer; detoxification of contaminants; or immobilisation of heavy metals, plant production and the turnover of nutrients. There are over 500 enzymes in soil systems that play the role in soil C, N, P and S cycles. The great diversity of enzymes existing in soil is correlated with the diversity of soil microbial community because the most enzymes originated with microorganisms [68]. Adding soil enzyme functional diversity to the research could significantly increase the understanding of the linkage among resource availability, microbial structure and function, and ecosystem processes [42]. All these referred parameters are more sensitive in assessing changes in soil use and management [31] and such indicators are important for assessing the intensity of soil degradation, as well as extension of plant invasion in soil ecosystems [43]. Recently, a valuation for the impacts of invasive plants on belowground ecosystem processes, such as soil nutrient cycling and soil microbial functioning (as expressed by soil microbial enzyme activities), has emerged [69].

We performed the investigation based on independent study sites to assess the impact of selected invasive and non-native plant species on soil physico-chemical properties and microbial indices. The aim of this complex study was to (i) determine the selected physical and chemical properties, (ii) determine the selected microbial indices and (iii) evaluate the impact of invasive and non-native species on soil properties and enzymatic activity. It was hypothesized that soil microbial activity is altered by invasiveness compared to the native ecosystems. Microbial activity would also differ between the ecosystems where invasion takes place.

METHODS AND EXPERIMENTAL PROCEDURES

Sites and plant materials description

The research of *Impatiens parviflora* was carried out during a vegetation season in July 2015 in three protected areas of North-Eastern Slovakia - National Nature Reserve (NNR) Šarišský hradný vrch, National Nature Reserve (NNR) Kokošovská dubina and Nature Reserve (NR) Fintické svahy (Figure 2). One native site, without *I. parviflora* invasion, was also included for comparative purpose (as a control site). This region is known for its high diversity of animal and plant life, and all these forms are highly responsive to environmental changes. Mostly moderate Cambisols are typical in all researched areas in warm, medium wet climatic regions with the cold winter. NNR Šarišský hradný vrch belongs to *Carpineto-Aceretum*, *Fageto-Quercetum*, *Fageto-Quercetum* versus *Fagetum pauper* habitat with the dominant vegetation of *Acer platanoides*, *Fagus sylvatica* and *Quercus petrea*. NNR Kokošovská dubina and NR Fintické svahy belong to *Fageto-Quercetum* habitat, where *Quercus robur*, *Quercus petraea*, *Acer campestre* and *Acer platanoides* are the predominant species in NNR Kokošovská dubina and *Acer campestre*, *Carpinus betulus*, *Crataegus monogyna*, *Quercus petraea* and invasive species *Robinia pseudoacacia* dominate in NR Fintické svahy [70]. The soil was sampled in three different microhabitats - meadows (a habitat without tree vegetation), a habitat close to the stumps (as the bottom part of a tree left) and a habitat under dense tree vegetation, in each natural reserve.

Impatiens parviflora DC. (small balm), belongs to the Balsaminaceae family, is a native species to Central and Eastern Asia. It was introduced in the 19th century to Central and Western Europe where it could grow on a wide range of mineral soils and in many different plant communities. *I. parviflora* is a non-native species, which, due to its mass occurrence, disturbs the natural vegetation composition in many localities. This alien is often seen dominating herbal layer communities of invaded forests, including sites with relatively low hemeroby, where it potentially could affect rare native species. The character and environmental influence of this species on native biodiversity, through changes in community structure, nutrient cycles, trophic levels, hydrology, competition and others is invasive and may even cause high economic losses by promoting allergic reaction or altering the natural environment [71]. According to Slovak legislation, *I. parviflora* is considered as a dangerous species with the potential to adversely affect natural ecosystems. It is assumed that it was introduced to the Europe by trading as ornamental plant as most of the invasive species and the study of this species revealed the phytotoxic effect on some other native plant species [72].

The study of *Solidago gigantea* was carried out in cadastre of Košice Basin in the lowland of southeast Slovakia (Figure 3) twice, in September 2016 and 2017 from all study sites. Climate in this region is warm and in winter season temperatures range from 1 to 3◦C, in summer season between 18 and 20◦C. Snow covers less 50 days, the number of summer days is 60 to 70 and an annual precipitation is 600 mm. The soil was classified as Halpic Cambisols and both areas are within the same edaphoclimatic conditions. The study sites were located within an area of 20 km×15 km, with mean distance of 3.5 km between each other. Elevation of the study sites ranged from 192 to 380 m a.s.l. The invaded plot was required to have a cover of *S. gigantea* of at least 80%, while the control sites were adjacent uninvaded plots with no invasive species. The mean distance between the invaded and uninvaded sites was 200 m. The uninvaded sites were assumed to represent sites prior to invasion by this species. Pairs of invaded and uninvaded areas did not differ in elevation, inclination, exposition, type and management. The samples were taken from two different habitats: the forest and the grassland ecosystems. *Quercus*, *Fagus*, *Carpinus* and *Betula* tree genus (deciduous forests), dominated the uninvaded forest site. The study sites of uninvaded grassland with indigenous multispecies vegetation was dominated by *Dactylis glomerata*, *Lolium perenne*, *Trifolium pratense*, *Capsella bursa-pastoris* and *Taraxacum officinale* [73].

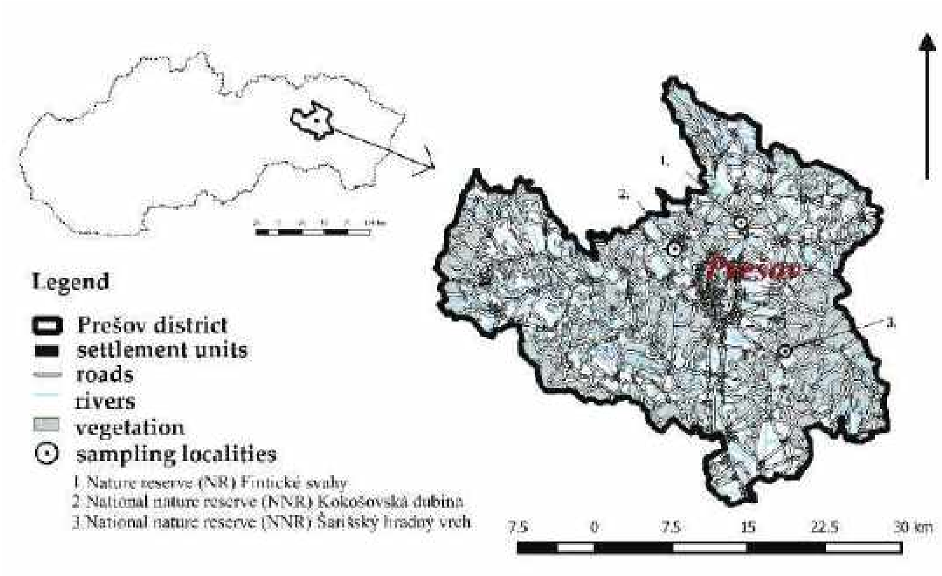

Fig. 2. Study area of *Impatiens parviflora* in the protected areas

Solidago gigantea Aiton (giant goldenrod), belongs to the Asteraceae family, is a North America plant species in the sunflower family that has spread in a number of European and Asian countries after introduction as an ornamental plant in the 18^{th} century. The main period for new rhizome growth relevant to flowering shoots in Slovakia is September (or late August) and is unintentionally spread and commonly found in abandoned farmlands, roadsides, gardens, forests, orchards, and even green spaces of some cities. The species is generally described as having a broad tolerance with respect to soil moisture, lights, nutrient contents, temperature, continentality of pH range. Although, *S. gigantea* prefers rich and rather moist soils, it occurs over a wide range of soil fertility and texture conditions. Its harmful impact to environment has been shown in several studies that focused on soil nutrient cycling and microbial functional diversity, plant diversity and trophic structure of insect-associated communities [41, 74]. To gain insight into the mechanisms of *Solidago* genus, numerous studies have been focused on aboveground communities in non-native areas. These studies have also focused on morphological evaluation of *Solidago* genus in introduced areas, its physiological adaptation to diverse environments and evaluation of its phytoremediation properties in loaded areas in Slovakia [75]. Although these studies shed light on the plant ecological mechanisms of *Solidago* genus invasion in non-native areas, relatively little is known about the effect of *S. gigantea* invasion on activity of soil microbial population.

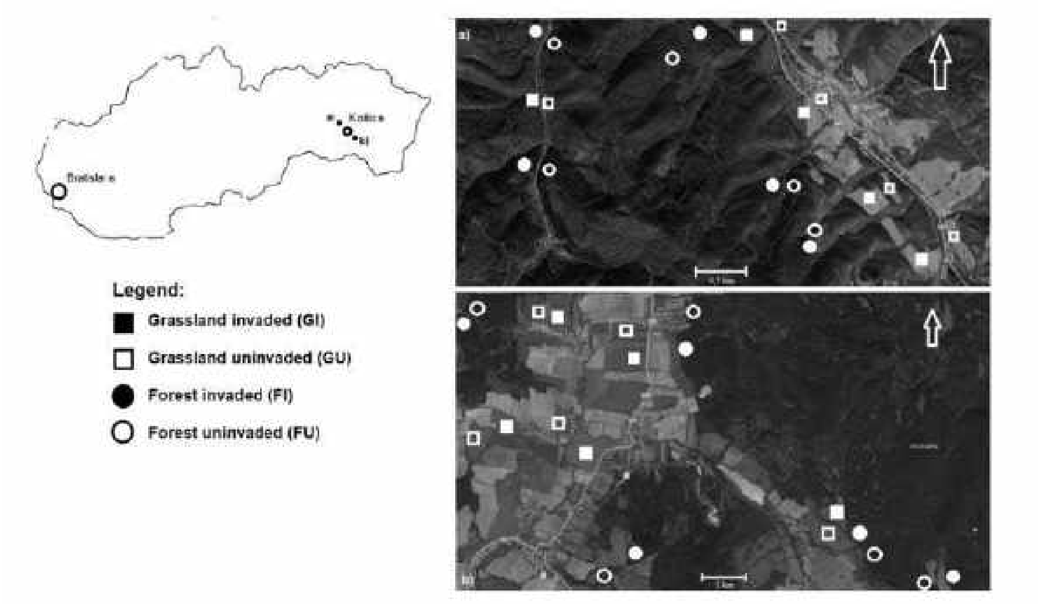

Fig. 3. Study area of *Solidago gigantea* in Košice Basin

The study of *Fallopia japonica* was carried out in a valley close to the Opátka village, which is located in southeast Slovakia (Figure 4) in May 2016. This region has a temperate climate, with an annual average of 40 summer days per year and a warm, moderately dry sub-region with a mild winter. The average daily temperature in January ranges from 1.5 to 4.0°C, the average daily temperature in July ranges from 16.0 to 18.5°C, while the average annual temperature ranges from 5.0 to 7.0°C. The mean annual precipitation is 650 to 700 mm. The soils are characterized as Fluvisols, and the vegetation zone is characterized as Carpathian oak-hornbeam forest. The samples were taken from three different ecosystems: forest, grassland and wetland. The control sites were also selected and represented adjacent areas to invaded sites by *F. japonica*. *Quercus robur*, *Q. cerris*, *Carpinus betulus*, *Acer campestre*, and many shrub species such as mostly *Viburnum sp*. and *Prunus spinosa* mostly dominated in forest uninvaded site. The adjacent forest edge was invaded by *F. japonica* covering an area of 500 m^2, with an estimated time of invasion of 15 years. In the grassland uninvaded site, the species such as *Dactylis glomerata*, *Lolium perenne*, *Trifolium pratense* and *Achillea millefolium* were dominated. The adjacent invaded grassland covers an area about 250 m^2 and the estimated time of invasion is 15 years. Very specific ecosystem wetland that was uninvaded was predominantly covered by *Petasites hybridus*, *Caltha palustris*, *Galium aparine*, *Equisetum sp*., *Ranunculus sp*., and *Urtica sp*. The estimated time of invasion in the adjacent wetland ecosystem is 10 years [76].

Fallopia japonica (Houtt.) Ronse Decr. (Japanese knotweed) belongs to Polygonaceae family, is considered to be one of 100 worst invasive species in the world. It was introduced into North America and Europe in the 19th century as an ornamental plant and cattle fodder. In its native range of Japan, Taiwan and Korea *F. japonica* is found growing in sunny places on hills, high mountains and along road verges and ditches. Considered an aggressive invader in Europe, the United States, and Canada, *F. japonica* spreads by clonal, rhizomatous growth and can quickly form a monoculture. In its introduced range, the plant can be found mainly as a riparian weed as well as an invader of man-made environments such as spoil heaps, derelict land, road and railway verges and gardens and reaches 2 meters in height. *F. japonica* requires high light environments and competes effectively for light in such situations. *F. japonica* can survive very harsh conditions with a pH range of 3.0-8.5, and an ability to survive extreme heavy metal and salt pollution and areas with low available nitrogen [77, 78].

The study of two other invasive species *Heracleum mantegazzianum* and *Helianthus tuberosus* were performed near Lekárovce village along to Uh River in June 2017 (Figure 5). The research locality is represented of Fluvisol soil type that is a genetically young soil in alluvial deposits. Apart from river sediments, they also occur on alluvial plains, river fans, valleys and tidal marshes on all climate zones [79]. Fluvisols belong to a group of high productive arable lands on which cereals, root crops and industrial crops are grown. In some parts, fluvial soils are used as a vegetable land. They are located on the floodplains of rivers, and their development is repeatedly disrupted by floods. Thus, the soil profile is enriched with the sludge sediments [80].

Heracleum mantegazzianum Sommier & Levier (giant hogweed), belongs to the Apiaceae family, is a tall forb from the western Caucasus and is one of the most noxious European invasive plant. It is very tall, typically growing to 3-4 meters in height and may exceed 5 meters. This species occurs in the upper forest belt of the southern slopes, mainly in meadows, clearings and forest margins. It was introduced in the 19th century into European countries and has also spread to other areas in the United States, Canada, Australia and New Zealand. It produces a toxic sap that causes a painful and problematic phototoxic reaction. It is also known to increase erosion of river and steam banks and to be a problematic weed in both agricultural and urban environments [81]. Study of Nielsen et al. [82] showed that winter temperatures are the best explanation factor for the species distribution in Europe and conversely, global warming could help to counteract this trend. It invades nutrient-rich semi-natural grasslands, forest edges, riparian and anthropogenic (disturbed) habitats. However, it is also able to establish in nutrient-poor habitats such as peaty meadows or acidic soils in forest clearings. The weed needs moist conditions for much of the year, but can tolerate moderate summer droughts [83].

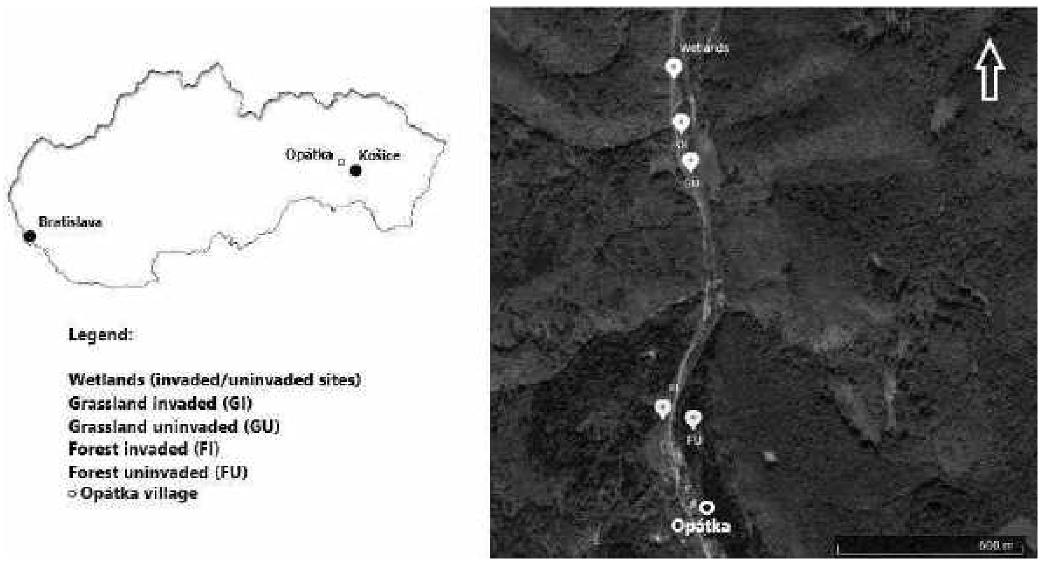

Fig. 4. Study area of *Fallopia japonica* near Opátka village

Helianthus tuberosus L. (Jerusalem artichoke), belongs to the Asteraceae family, is a tall herb that can out-compete invaded natural vegetation and occurs as a sometimes serious agricultural weed. This non-native species behaves invasively and have potential significantly alter native biodiversity. This species is native to eastern North America and were introduced to Western Europe in the 17th century. *H. tuberosus* is only occasionally cultivated in the tropics. This alien plant was cultivated as a vegetable (root vegetable known as topinambur), fodder crop, and a source of inulin for food and industrial purposes, while the sunflower of grown as an oilseed crop [84]. *H. tuberosus* is completely naturalized on moist, nutrient-rich, sandy or loamy soils, especially along rivers. It requires full sunlight and is rarely found in shaded situations. Because of its moderate frost tolerance, its range goes beyond that of most conventional crops and on the other hand, *H. tuberosus* offers nectar for flower visitors. Generally, *H. tuberosus* is salt-tolerant and drought-tolerant species that is easily grown in coastal arid and semi-arid areas. It can grow on poor land and this invasive plant has multiple use values, including resource exploitation and ecological function [85]. *H. tuberosus* is one of the main candidates for use as a raw material for the industrial production of biological fructose and inulin [86], its extracts were found to possess antimicrobial and antifungal activities, it can be considered as a biomass crop for ethanol production) [87], and there and more other benefits from this exotic plants.

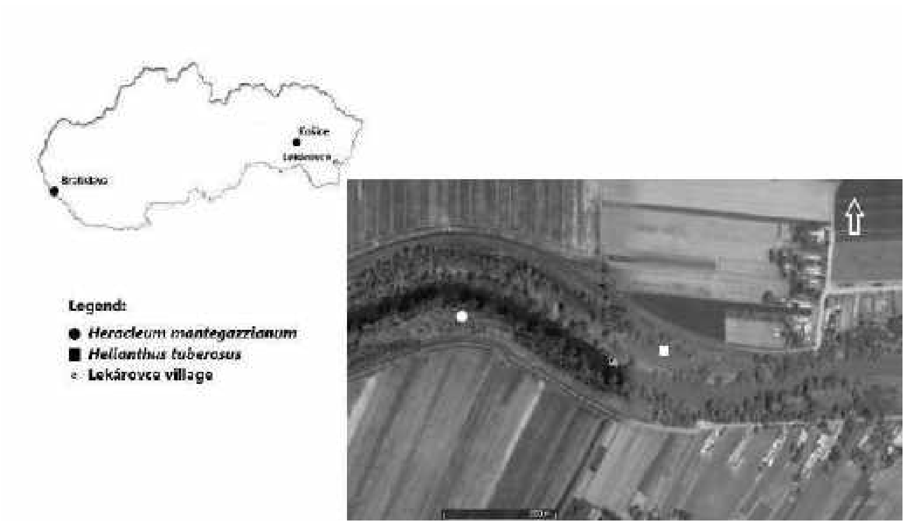

Fig. 5. Study area of *Heracleum mantegazzianum* and *Helianthus tuberosus* near Lekárovce village

Soil sampling

In each invaded area, ten randomly chosen 1m×1m plots were chosen. The invaded plots were required to have a cover of invasive plant species of at least 80%. Similarly, ten 1m×1m plots with an equal spatial distribution were chosen in the corresponding uninvaded areas. The control sites were usually adjacent uninvaded plots with no invasive species observed. The mean distance between the invaded and control sites was approximately 200 m. At each plot, a mixed soil samples consisted of five subsamples in the depth of 0.1-0.2 m. All soil samples were transferred to the laboratory in the plastic bags and homogenized manually prior analysing. In laboratory conditions, the soils were sieved using 2 mm mesh. Sieved soil samples were divided into two parts. Air-dried soil samples were selected to analyse chemical properties and another part stored at 4°C for soil physical properties and microbial indices.

Soil analyses

A portion of soil samples was air-dried for 3 days and completely crushed in a porcelain crucible. These soil samples were used to measure soil reaction and organic carbon content. Soil pH was detected in a 1:3 mixture of soil and 0.01 M $CaCl_2$ solution using a digital pH meter. Soil organic carbon (SOC) was determined by the Turin's method [88]. Gravimetric soil moisture (SM) was calculated on 10 g of fresh subsamples after drying in a 105°C oven for 24 h. Soil basal respiration (SBR) was measured by the CO_2 released from 100 g samples of field moist soil in 500 mL hermetically sealed flasks at 25°C for 48 h. CO_2 was captured by its reaction with NaOH (1mol L^{-1}) and titrated with HCl (0.5 mol L^{-1}) after the addition of $BaCl_2$ (1 mol L^{-1}). The concentration of the released carbon was estimated in µg C-CO_2 g soil $dry^{-1}day^{-1}$ [89]. Microbial biomass carbon (MBC) content was determined using the method of Islam and Weil [90], as oven-dried equivalent (ODE) of field-moist soil adjusted to 80% water-filled porosity was irradiated twice by microwave (MW) energy at 400 J g^{-1} ODE soil to kill the microorganisms. The time settings and MW oven power depended on the total amount of soil in the MW oven. After cooling, soil samples were extracted with 0.5 M K_2SO_4. Carbon content (C*irradiated*) in the extract was quantified by the oxidation with $K_2Cr_2O_7$ dissolved in H_2SO_4 and titrimetrically by $(NH_4)_2Fe(SO_4)_2$. The same procedure was done with a non-irradiated sample (C*non-irradiated*). The microbial biomass carbon was then determined as MBC = (C*irradiated* - C*non-irradiated*)/K_{ME}, whereby extraction efficiency factor K_{ME} = 0.213. The content of MBC was observed only on sites that were invaded by *Fallopia japonica* plant species. Enzymatic activity assays, beta-glucosidase (BGL), urease (URE), fluorescein diacetate (FDA), acid phosphatase ($PHOS_{AC}$) and alkaline phosphatase ($PHOS_{AL}$), were determined using field-moist soil samples using specific substrates of each enzyme. Each enzyme assay was performed as described in Table 1. All determinations were performed in duplicate. The corresponding controls were done for each soil and enzyme activity by the same analytical analysis described, but without the addition of the substrate at the moment of initiating the enzyme reaction. Activity of all enzymes was measured in a spectrophotometer crating a reference curve. The analyses enzymes play key role in soil nutrient cycling. BGL is involved in carbon metabolism through the release of glucose from cellulose, URE is involved in the release of nitrogen by degrading urea to ammonium and phosphatases are involved in the release of phosphate from organic matter by hydrolysing phosphate ester bonds [91]. In this study, we also used the hydrolysis of fluorescein diacetate (FDA) to assess the total microbial activity. FDA is a good general measure of organic carbon turnover in natural ecosystem because most energy flow passes through decomposition of microbial community and several enzyme activities are also involved in this process [92].

Table 1. Incubation conditions of selected enzymes used with biochemical indicators

	Incubation conditions					
Enzyme	**Substrate**	**Buffer (pH)**	**Soil (g)**	**Temperature (°C)**	**Time (h)**	**Reference**
FDA	Fluorescein diacetate	7.6 (PPB)	1	30	1	[93]
$PHOS_{AC}$	p-Nitrophenyl phosphate	5.0 (AB)	5	37	3	[94]
$PHOS_{AL}$	p-Nitrophenyl phosphate	10.0 (BB)	5	37	3	[94]
BGL	4-Nitrophenyl glucopyranoside	6.0 (MUB)	1	37	3	[95]
URE	Urea	6.7 (PB)	5	37	24	[96]

FDA (fluorescein diacetate activity); $PHOS_{AC}$ (acidic phosphatase activity); $PHOS_{AL}$ (alkaline phosphatase activity); BGL (beta-glucosidase activity); URE (urease activity); PPB (potassium phosphate buffer); AB acetate buffer); BB (borate buffer); MUB (modified universal buffer); PB (phosphate buffer).

Statistical analyses

Obtained data were tested by mathematical-statistical methods and performed in R studio program [97]. Normality of the data was verified by the Shapiro–Wilk test. Spearman's correlation coefficient was used to detect relationships between soil properties and microbial indices. The Mann–Whitney non parametrical test was used to determine significant differences in soil properties among different types of ecosystems and between the invasion status (invaded, non-invaded sites) of the evaluated localities.

THE RESEARCH RESULTS AND DISCUSSIONS

Impact of Impatiens parviflora on soil ecosystem

All selected research sites were located in the forest ecosystems that naturally give acidic soil reaction. Table 2 shows the average data of soil physico-chemical properties of three microhabitats in nature protected areas. NR Fintické svahy was represented lower pH and organic carbon content. Soil pH is an important factor of soil health despite of the fact that its value changes under internal and external factors. The study of Chmura [98] confirmed that *I. parviflora* prefers acidic soil reaction, which was also shown in our study. The author also found out the highest influence of chemical features (organic carbon and nitrogen content) of species *I. parviflora* near the stump habitats. Soil physico-chemical properties are indicators of soil ability to absorb and maintain soil water. Soil moisture is considered to be one of the most important factors affecting soil respiration, but our study did not show this significant relation which was also found in the study of Bobuľská et al. [43]. The highest soil moisture was also measured in NR Fintické svahy, especially in the stump habitats. Coombe [99] states that *I. parviflora* grows on non-compacted and structured soils maintained high humidity, except of flooded localities.

Several studies showed that the abundance and biological characteristic of *I. parviflora* depends on soil physico-chemical properties [72, 100], and our study also confirmed that soil microbial activity is one of the main factor affecting the quality and stability of soil ecosystem. Soil microbial activities, soil respiration rate and enzyme activities, are more sensitive compared to physical and chemical properties to changes in soil quality and can be easily quantified. Soil biochemical properties are regarded as relevant indicators of soil quality from an environmental viewpoint and could be useful for monitoring changes in many type of ecosystems [51]. Determination of the intensity of soil basal respiration is very important. It refers not only to the overall biological activity of soil ecosystem, but also to the speed of mineralization processes. In addition to temperature and humidity, soil respiration is influenced by the quality and supply of nutrients in the soil, soil texture, soil aeration, type of ecosystem, and increasingly also by soil managements. In general, invasive species might increase the activity of microbial parameters, as well as the functional diversity of microbial communities with the significant carbohydrate utilization [17] that characterize stress of the bacterial communities due to poor nutrient status. Also in our study, the sites with the invasive species showed higher values of microbial parameters compared to the control sites ($^*p<0.05$). Average values of the selected soil biological (microbial) parameters, such as soil microbial respiration (SMR) and soil enzymatic activities are shown in Table 3. Soil basal respiration was higher under the stamps habitat that was represented by the highest plant individuals. Castillo and Joergensen [101] pointed out that almost all biological properties are significantly influenced by environmental management, of which the soil respiration was the parameter most affected by way of different management and many other factors. Same trend was also observed with the soil urease activity that tends to increase the pH of the environment as it produce ammonia as a basic molecule [102]. There are a number of enzymes in soil, depending on diversity of soil organisms and conditions of organic substances turnover. Soil reaction differs from the pH optimum for phosphatases activity. Soil phosphatase activity is higher in soils with high humidity and because phosphatases have different optimal pH, therefore are divided into acid and alkaline phosphatases [103]. Phosphatases are produced not only by the microorganisms, but also by higher plants. In our study, activity of acid phosphatase was higher compared to alkaline phosphatase activity in all localities (**$p<0.01$), which was closely connected to acidic condition on the research sites. In addition, the activity of acid phosphatase was significantly higher (*$p<0.05$) in the microhabitat under tree vegetation. The high activity of this enzyme may originate from roots of such higher plants [104].

Table 2. Soil physico-chemical properties of three microhabitats in natural protected areas

Natural reserves	Microhabitats	pH/$CaCl_2$	SM	SOC
NNR Šarišský hradný vrch	Meadow	6.7±0.1	26.2±2.5	5.13±0.5
	Habitat under tree vegetation	6.5±0.1	35.8±2.9	5.08±0.4
	Stumps habitat	7.1±0.0	34.9±3.1	4.99±0.5
NNR Kokošovská dubina	Meadow	6.2±0.2	30.7±2.1	5.20±0.7
	Habitat under tree vegetation	7.0±0.1	35.8±2.3	5.12±0.8
	Stumps habitat	6.2±0.2	36.9±2.0	5.08±0.4
NR Fintické svahy	Meadow	5.9±0.1	33.0±2.7	5.15±0.7
	Habitat under tree vegetation	5.8±0.1	40.3±3.1	5.02±0.9
	Stumps habitat	5.4±0.2	54.8±3.5	4,88±0.4
Control site		7.2±0.0	31.5±1.9	5.98±0.4

SM (soil moisture, %); SOC (soil organic carbon, %)

Soil microbial indices, as well as physico-chemical are sensitive to not only under the influence management changes, but under the environmental changes. In the summary, our findings showed that *I. parviflora*, as non-native plant species, shows preferences towards low base soils and significantly alter activity of microbial population in soil ecosystems. It easily penetrates non-ruderal communities and dense ground layers.

Table 3. Soil microbial indices of three microhabitats in natural protected areas

Natural reserves	Microhabitats	SBR	URE	$PHOS_{AC}$	$PHOS_{AL}$
NNR Šarišský hradný vrch	Meadow	103.55±9.7	0.43±0.03	377.81±25.6	266.23±18.3
	Habitat under tree vegetation	127.85±10.1	0.55±0.05	466.60±22.7	305.56±17.9
	Stumps habitat	172.05±10.8	0.74±0.04	394.53±21.3	340.09±18.6
NNR Kokošovská dubina	Meadow	105.67±12.4	0.42±0.01	588.54±36.1	400.75±22.7
	Habitat under tree vegetation	120.41±10.1	0.49±0.01	603.15±36.8	405.83±22.5
	Stumps habitat	135.45±10.5	0.80±0.03	599.11±30.4	389.93±19.6
NR Fintické svahy	Meadow	112.08±9.6	0.52±0.04	467.55±29.7	334.06±16.7
	Habitat under tree vegetation	125.46±10.3	0.63±0.02	527.17±30.2	406.31±20.4
	Stumps habitat	129.89±11.1	0.92±0.04	516.60±29.8	440.18±21.7
Control Site		100.88±8.5	0.41±0.01	237.99±18.3	250.65±15.9

SBR (soil basal respiration, µg $C\text{-}CO_2$ g soil $dry^{-1} day^{-1}$); URE (urease activity, $mgNH_4{}^{+}\text{-}N$ g^{-1} d^{-1}); $PHOS_{AC}$ (acid phosphatase activity, mg P g^{-1} $3h^{-1}$); $PHOS_{AL}$ (alkaline phosphatase activity, mg P g^{-1} $3h^{-1}$)

Impact of Solidago gigantea on soil ecosystem

Figure 6 shows the data of physico-chemical properties of invaded and uninvaded soils from forest and grassland ecosystems. These properties differed across the invasion gradient of *S. gigantea*.

The results represent that soil pH was significantly higher in the grassland ecosystems compared to the forest during the research period (Table 4). The results also revealed that invasive Goldenrod is able to increase the value of pH in both ecosystems, but this relation was statistically observed only in the forest ecosystem (Table 5). The study of some authors showed that the invasion of *S. gigantea* decreased soil pH [105, 106], but the lack of consistent changed in pH were also reported [107]. The exception was only recorded in the grassland ecosystem in 2016, where soil pH slightly decreased. Content of soil moisture was statistically lower in invaded ecosystems compared to the control in both years of our study (Table 5). Lower soil moisture content at the invaded sites during the research period was probably due to more biomass of invasive species that can also strongly influence more physical properties as describe works of some other authors [41, 108]. Organic carbon content was generally higher in uninvaded ecosystems and the higher portion of organic carbon was shown in grassland ecosystems compared to the forest systems (Table 4). However, the content of organic carbon reached very high concentration. Soil physical and chemical properties significantly varied between the years 2016 and 2017, but soil reaction and soil moisture were the only parameters that have not changed in forest ecosystem (Figure 6).

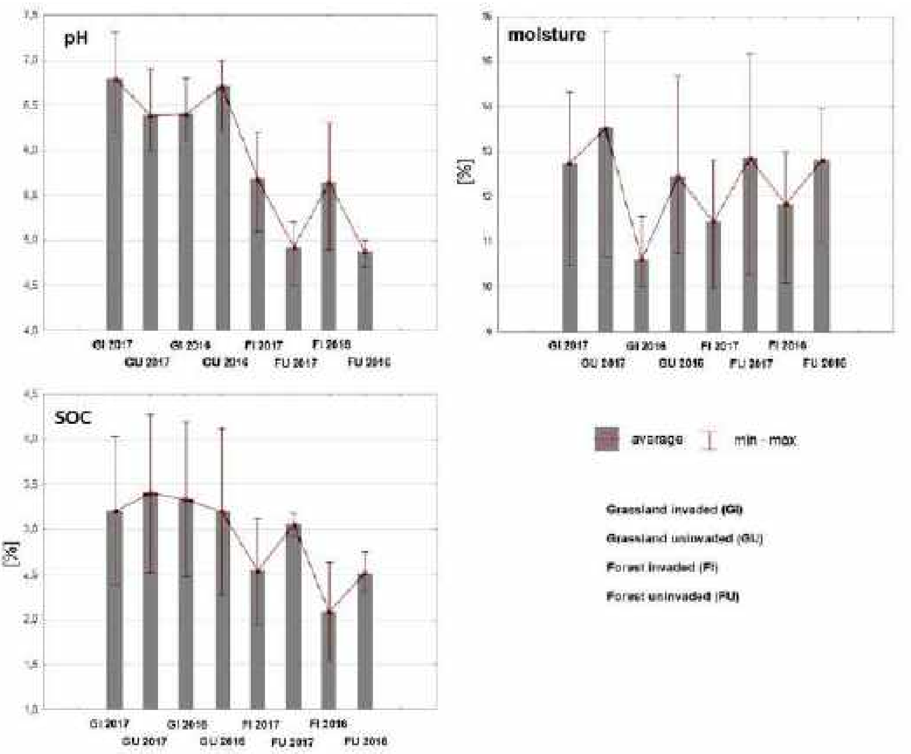

Fig. 6. Soil physicochemical properties in two ecosystems (forest and grassland) under invaded and uninvaded sites

Table 4. The values of Mann–Whitney nonparametrical test for comparison soil characteristics between ecosystems (grassland and forest) regardless of the year and the invasion status (invaded, noninvaded sites).

Parameter		U	z	P value
pH		49.5	−7.2	0.0001 *
MOIS		798	−0.1	0.98
SOC		525	−2.64	0.008 *
BGL		659	1.34	0.17
FDA	**Between ecosystems**	624	1.68	0.05 *
URE		717	0.79	0.42
$PHOS_{AC}$		544	2.45	0.01 *
$PHOS_{AL}$		248	−5.8	0.0001*

MOIS (soil moisture), SOC (soil organic carbon), FDA (fluorescein diacetate activity), BGL (beta-glucosidase activity), URE (urease activity), $PHOS_{AL}$ (alkaline phosphatase activity), $PHOS_{AC}$ (acidic phosphatase activity), * $P < 0.05$

Table 5. The values of Mann–Whitney nonparametrical test for comparison soil characteristics between invaded and uninvaded sites in grassland (G) and forest (F) ecosystem, regardless of the year.

Parameter		F			G		
		U	**z**	**P value**	**U**	**z**	**P value**
pH	**Between invaded and uninvaded sides**	30	4.58	0.0001 *	190	0.25	0.79
MOIS		103	−2.61	0.009 *	102	−2.63	0.008 *
SOC		100	−2.69	0.007 *	175	−0.66	0.50
BGL		68	3.55	0.001 *	96	2.79	0.005 *
FDA		186	−3.6	0.71	64	−3.66	0.0002 *
URE		55	−3.9	0.0001 *	105	−2.54	0.01 *
$PHOS_{AC}$		161	−1.04	0.29	190	−0.25	0.79
$PHOS_{AL}$		90	2.96	0.003 *	95	2.85	0.004 *

MOIS (soil moisture), SOC (soil organic carbon), FDA (fluorescein diacetate activity), BGL (beta-glucosidase activity), URE (urease activity), $PHOS_{AL}$ (alkaline phosphatase activity), $PHOS_{AC}$ (acidic phosphatase activity), * $P < 0.05$

Figure 7 shows the values of soil microbial indices, in which the activity of FDA was the most variable parameter. The results also show that some enzyme activities significantly varied between both researched years (2016 and 2017).

The results also revealed that activity of FDA and acid phosphatase were the parameters more stable in both ecosystems and their values did not significantly changed during both research years. Beta-glucosidase activity was significantly greater in invaded sites compared to uninvaded sites and the same trend was also observed for alkaline phosphatase. The opposite trend was detected for activity of soil urease and activity of FDA, where its value significantly decreased in invaded sites compared to uninvaded (Table 5). In addition, the work of Chacón et al. [109] presented that *S. gigantea* increased the activity of FDA, but the work of Sicardi et al. [110] that corresponded with our study showed that activity of enzymes was decreased by invasion of this exotic species. Activity of acid phosphatase was slightly lower in invaded sites, except in forest ecosystem in 2016 where this trend was opposite, but this relationship was not statistically shown. The effect of *S. gigantea* on soil physico-chemical properties and microbial indices were generally significantly different between invaded and uninvaded sites. Non-significant interaction was only observed for activity of acid phosphatase. The significant correlation was also found between forest and grassland ecosystems for few soil variables regardless of the year of the study and invasion status. Invasion of two different ecosystems in Slovakia by *S. gigantea* is accompanied by the effect of ecosystem functioning and type of ecosystem. This species reduced the content of organic matter and all physico-chemical parameters were significantly changed by invasiveness. In addition, invasion by this species can also generate changes in the activity of soil microbial indices, which may influence the composition of native plants and diversity of soil fauna as was described by some authors [111, 112]. The influence of invasive species on the organic matter cycle has been reported previously, but this influence can be positive or negative. Some authors state that this characteristic of invasive species can increase soil moisture and organic carbon [113, 114], but our study revealed the opposite trend which was also correlated with studies by Feng et al. [115]. The study of Scharfy at al. [107] showed that the effects of *S. gigantea* on abiotic and biotic soil properties between plant communities were not significantly different, but significant interaction was only found for phosphatase activity. Their study also showed that *S. gigantea* reduces bacterial biomass and therefore, alters the activity of many soil enzymes. They revealed that the same invasive plant increased beta-glucosidase activity and organic carbon content that was also shown in our study. Besides microorganisms, plant roots may represent an important source of acid phosphatase in soils. Alkaline phosphatase has been attributed to soil bacteria and fungi, and soil microorganisms have been shown to be a major factor in controlling organic and inorganic P solution concentrations in temperate grassland topsoils [116]. The study of Chapuis-Lardy et al. [117] showed that invasion of *S. gigantea* can modify biogeochemical cycles and soil properties that we also confirmed in our study. Invasion of *Solidago* genus was originally hypothesized to increase the activities of soil extracellular enzymes due to its faster growth and higher productivity leading to increased litter input into the soil [118, 119]. In contrast to their prediction, *S. gigantea* invasion sites showed decreased activity of FDA activity and N-acquisition enzymatic activity. One of the most common enzymes in microbial, animal and plant cells is urease. In many studies, urease activity is correlated to soil organic carbon due to the stimulating effects of soil organic matter on soil microbial biomass and the stabilization of the extracellular urease by humic substances [120]. *S. gigantea* significantly decreased the activity of this enzyme. These conclusions are in line with those of other studies on alien invasive plants, which exhibited that changes in C-, N-, and P-acquisition enzymes were associated with changes in soil available nutrients, indicating that limitations and imbalances of nutrients can partially underlie production of soil enzymes and affect their activity [117]. Changes in soil physical and chemical characteristics caused by plant invasions may be linked to alterations in soil microbial communities, such as microbial biomass, respiration rate, N mineralization, as well as concentration of soil enzymes. Plant invasions influenced activity, biomass and microbial community composition. It seems that microbial soil properties are more responsive to invasion than physical and chemical parameters [41].

Impact of Fallopia japonica on soil ecosystem

Table 6 shows that soil moisture and soil pH differed substantially (Kruskal–Wallis statistics with $p < 0.001$) among the investigated plots. Soil moisture content varied from 9.1% in forest ecosystem to 12.4% in wetlands ecosystem and from 11.7% in invaded forest site to 21.5% in invaded wetland systems. It was statistically confirmed significant ($p < 0.05$) higher soil moisture only in the invaded forest ecosystem than the adjacent uninvaded site. The study of some authors [105, 121] found that invasion of *F. japonica* can reduce soil moisture probably due to its great leaf area promoting high transpiration rate. Our results with significant higher soil moisture in the invaded forest ecosystem than in the adjacent uninvaded plots contradict these findings. This result was probably due to shadow of the tree canopy, as we did not observe different soil moisture between the invaded and the uninvaded plots in grassland and wetland ecosystems. These results are in agreement with those by Stefanowicz et al. [41] who found that *F. japonica* invasion did not affect soil moisture in four river valleys. Soil pH varied from 5.2 in forest ecosystem to 6.8 in wetland ecosystem and from 6.4 in invaded forest ecosystem to 7.2 in wetland ecosystem, but no significant differences were observed between the invaded and the uninvaded plots. The study of Dassonville et al. [122] showed that there was a slight decrease of pH in invaded plots, but our study revealed the opposite trend. Our findings are in agreement with their study, but some other authors reported a high variable pH at sites invaded by *F. japonica*, and this species can survive very harsh condition with a pH range of 3.0 to 8.5 [123, 124]. The results also suggest that the sites that were invaded by *F. japonica* have increased the content of soil organic carbon. Some authors conclude that this invasive plant species produce litter with high decomposition rates than native species and can increase N availability, biomass and net productivity [122, 125]. The opposite trend was observed in the study of Koutika et al. [126] where the authors showed the changes in soil organic matter through a reduction of this parameter (lower particulate organic matter weight and C and N content and lower C mineralization) in the invaded fields compared to the fields under the native vegetation.

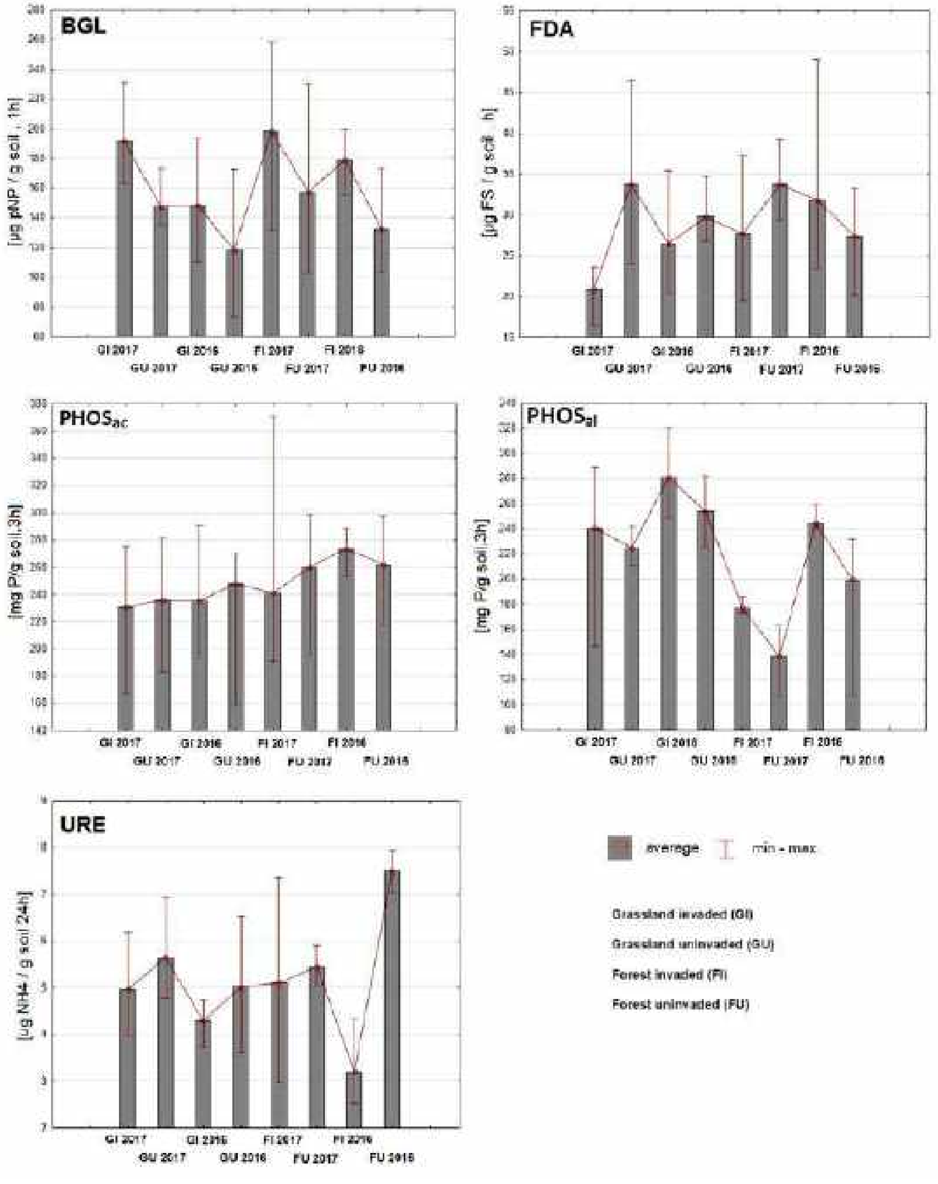

Fig. 7. Soil microbial indices in two ecosystems (forest and grassland) under invaded and uninvaded sites

Table 6. Means and standard errors (±) of the physical properties in different ecosystems invaded by *Fallopia japonica*

Soil indices	H	FU	FI	GU	GI	WU	WI
SM	21.93^{***}	9.1±0.04	14.0±0.55	9.5±0.35	11.7±0.06	12.4±0.94	21.5±0.98
pH/$CaCl_2$	22.30^{***}	5.2±0.06	6.4±0.06	6.1±0.06	6.8±0.06	6.8±0.05	7.2±0.06
SOM	22.16^{***}	2.5±0.3	2.9±0.4	3.4±0.5	3.8±0.7	3.5±0.3	3.9±0.5

SM (soil moisture, %); SOM (soil organic matter, %); H (statistics H (5, N = 24) from Kruskal-Wallis test (For 1N = 42 and for 2N = 30); FU (forest uninvaded ecosystem); FI (forest invaded ecosystem); GU (grassland uninvaded ecosystem); GI (grassland invaded ecosystem); WU (wetland uninvaded ecosystem); WI (wetland invaded ecosystem); Significance level: ***0.001; **0.001 levels, respectively

Figure 8 shows the data representing the selected microbial indices in all research localities. Soil microbial respiration (SBR) and microbial biomass carbon (MBC) content were higher (but not significantly) in all plots invaded by *F. japonica* (forest, grassland and wetlands ecosystem) compare to the uninvaded plots. The study of Stefanowicz et al. [127] showed significant decrease of microbial biomass content, activity of soil urease and soil microbial respiration on sites that were invaded by *F. japonica* under natural conditions. In contrast, the pot experiments showed that *F. japonica* did not reduce activity of microbial population, but the fungal biomass has increased [128]. The study of Koutika et al. [126] showed that invasion of *F. japonica* reduced the soil C respiration and created soil organic matter which decomposed slowly. The opposite trends were found for acid phosphatase; it was lower (but not significantly) in the invaded than the uninvaded plots.

Urease and alkaline phosphatase were affected by *F. japonica* invasion in different ways in the different ecosystems, but no significant differences were found. The analysed microbial characteristics in our study revealed that SBR and MBC content were slightly higher in all ecosystems invaded by F. *japonica* compared to the uninvaded ones, suggesting that invasion did not significantly affect microbial activity in soil ecosystem. This was in line with the measured enzyme activities, which remained unaffected by *F. japonica* invasion probably due the unchanged soil acidity, a factor most affecting activity of soil enzymes [105].

Native flora, as well as actual weather conditions, soil and ecosystem type, date of soil sampling, etc., are probably responsible for the variable impacts of invasion on soil acidity and moisture among studies. *F. japonica* forms dense stands that prevent other species from growing. The study of Kappes et al. [129] and Čerevková et al. [76] evaluated the impact of this plant exotic species on soil fauna and concluded that *F. japonica* significantly affect the faunal community, more that physical and microbial properties, regardless of selected habitat. Their study also concluded that large-scale invasion by *Fallopia* species is therefore likely to seriously affect biodiversity and reduce the quality of riparian ecosystems for amphibians, reptiles, birds and mammals whose diets are largely composed of arthropods.

Impact of Helianthus tuberosus on soil ecosystem

Soil physico-chemical properties and microbial indices from selected locality that present invaded and non-invaded (control) ecosystems are shown in Figures 9 and 10. This study showed, that the status of *H. tuberosus* invasion had significant impact on soil physico-chemical properties and microbial indices on soil ecosystem.

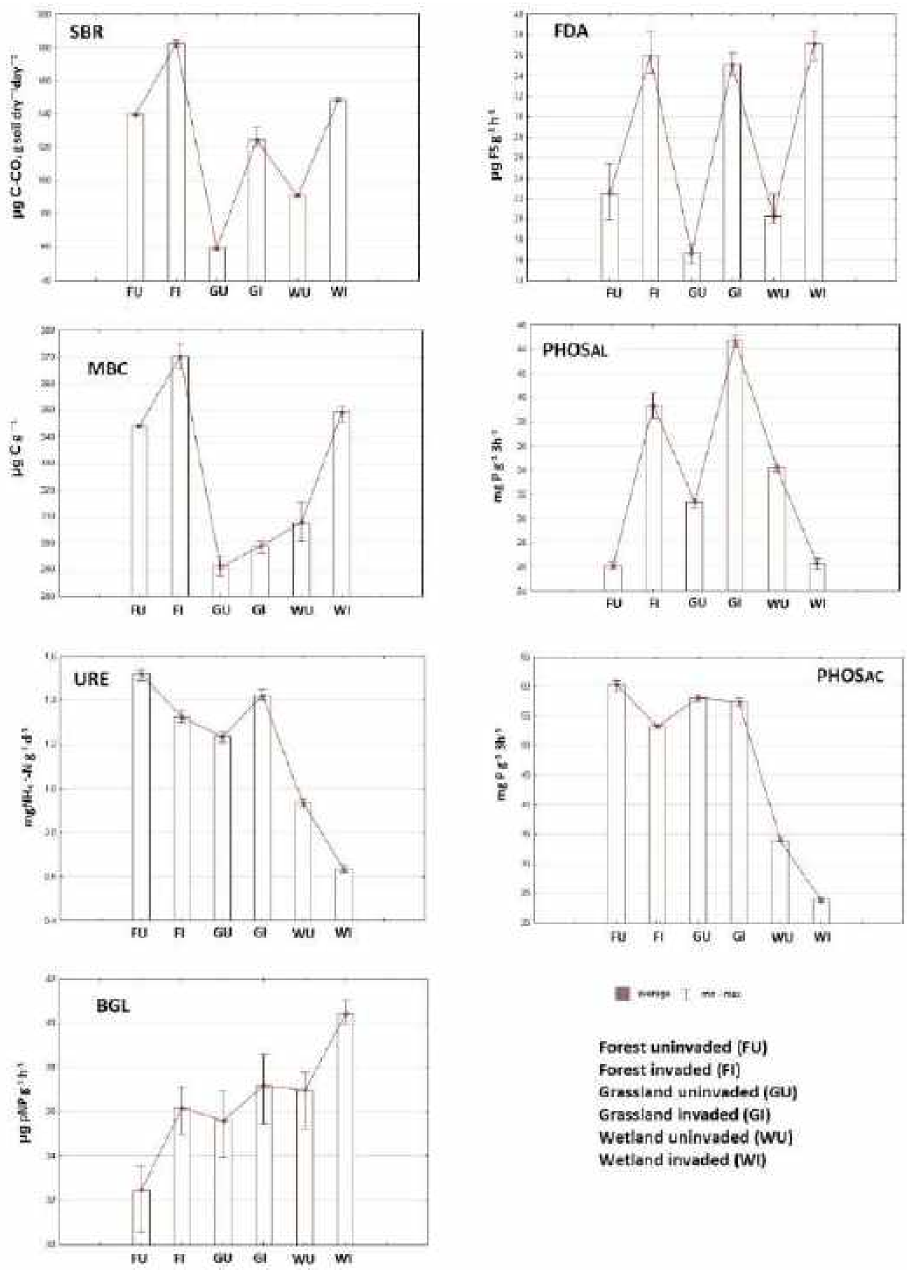

Fig. 8. Soil microbial indices in three ecosystems (forest, grassland and wetland) under invaded and uninvaded sites

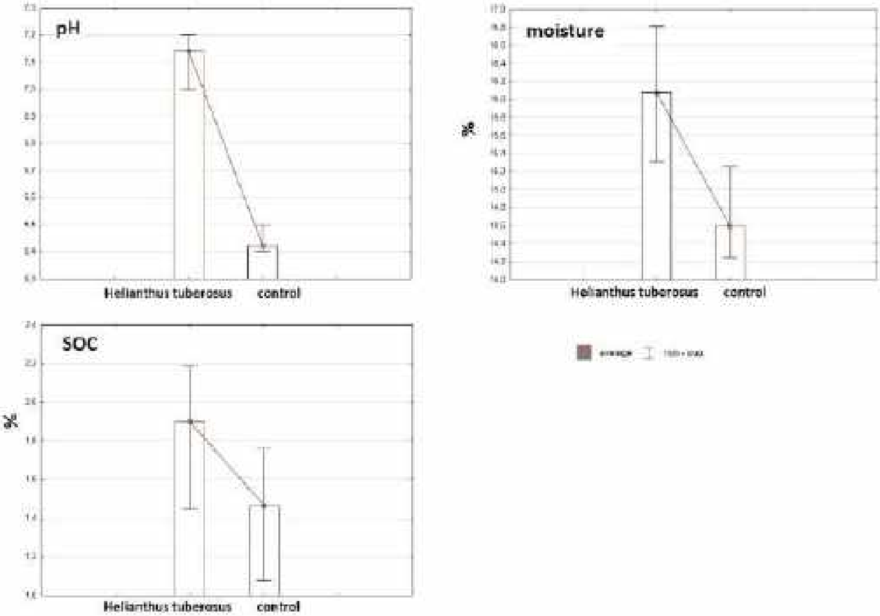

Fig. 9. Soil physico-chemical properties of *Helianthus tuberosus* in Lekárovce locality

The results showed that *H. tuberosus* increased soil moisture compared to the control sites. The study of Ehrenfeld [35] also confirmed that invasive plant species have ability to alter soil moisture content. This might be explained by the fact that invasive plants have shallow root system and lower water supply. The results also revealed that this invasive species is able to increase the value of pH, which was also reported in other studies [75, 76]. *H. tuberosus* is reported to tolerate wide range of pH from 4.5 to 8.2. As a very easily-grown plant, it is a suitable crop that adapts well to a wide range of soil types and pH levels in a sunny position where corn will grow, but the plant production is favoured by slightly alkaline soils [85]. Content of soil organic carbon was slightly higher in invaded sites, but this trend was not statistically observed. Generally, invasive species form dense covers, they are fast growing, produce large amount of litter and therefore are considered to alter nutrient cycling and significantly change soil organic matter [130]. Some studies show that invasive species were able to increase the content of organic carbon [131, 132], but the results of Feng et al. [115] show the opposite trend. Determining of intensity of soil respiration is of great importance for estimation the biological activity in soil ecosystem and the rate of mineralization processes. The soil basal respiration did not statistically vary between invaded and control sites, but had the tendency to be higher in natural habitats. The FDA measures the enzyme activity of a microbial population and can provide an estimate of the total microbial activity in environmental samples. Activity of FDA showed higher values in native ecosystems. Activity of beta-glucosidase was significantly lower in the researched sites that were invaded by *H. tuberosus*. The opposite trend was observed for activity of soil urease, where its value increased in invaded systems. The study of Ying et al. [133] showed that *H. tuberosus* and its residues in soil system decreased the cucumber seedlings growth and the activity of urease activity was increased. Urease activity depends on soil moisture, soil reaction, content and quality of humus, as well as the total content of soil nitrogen [35]. Both phosphatases, acid and alkaline, showed the changes due to the status of ecosystems and study of Ying et al. [133] confirmed that this plant species increased the soil phosphatases and dehydrogenase activities. In soils with low phosphorus content, soil phosphatase activities are very important. The activity of soil phosphatases is a condition for making organic phosphorus available to plants. Phosphatases have different optimal pH values and are divided into acidic and alkaline. The effects of invaded plant species on soil properties were generally significantly different between invaded and non-invaded sites (Table 7).

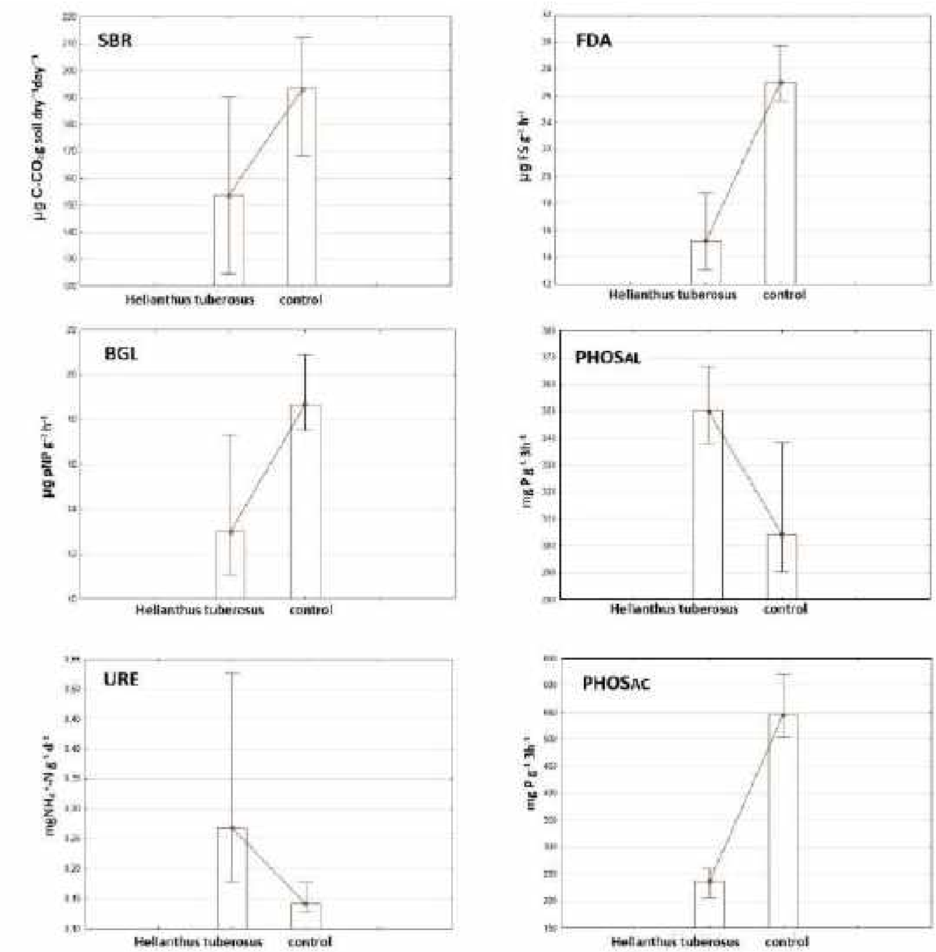

Fig. 10. Soil microbial indices of *Helianthus tuberosus* in Lekárovce locality

Table 7. The values of Mann-Whitney nonparametrical test for comparison soil properties between invasion status by *Helianthus tuberosus* (invaded vs. non-invaded)

Parameter		**U**	**z**	**P value**
pH	**Between invaded and non-invaded sites**	0,00	2,50	0,012 *
SM		0,00	2,51	0,012 *
SOC		4,00	1,67	0,09
SBR		2,00	-2,09	0,03*

BGL	0,00	-2,51	0,012 *
FDA	0,00	-2,5	0,012 *
URE	0,00	2,50	0,012 *
$PHOS_{AC}$	0,00	-2,40	0,011*
$PHOS_{AL}$	1,00	2,29	0,02*

SM (soil moisture), SOC (soil organic carbon), SBR (Soil basal respiration), FDA (fluorescein diacetate activity), BGL (beta-glucosidase activity), URE (urease activity), $PHOS_{AL}$ (alkaline phosphatase activity), $PHOS_{AC}$ (acidic phosphatase activity), * $P < 0.05$.

Even, *H. tuberosus* as a plant has many positive benefits; it alters soil physico-chemical and microbial indices significantly. This exotic plant can greatly reduce the speed of the succession of native communities (especially in the forest ecosystem), since the conditions for germination and growth of the woody species are very poor in such stands [13].

Impact of Heracleum mantegazzianum on soil ecosystem

In this study we demonstrated significant changes in several soil characteristics following the invasion of this exotic plant species. Importantly, there were significant differences between invaded and non-invaded research sites (Table 8). Soil physico-chemical properties and microbial indices from selected locality that present invaded and non-invaded (control) ecosystems by *H. mantegazzianum* are shown in Figures 11 and 12. Soil reaction was significantly higher (Table 8) at invaded sites compared to intacted that was also shown in other studies [126, 134]. Soil moisture and soil organic carbon were parameters not significantly affected by plant invasion, however, the content of organic carbon was slightly increased by invasion status. There are several traits of *H. mantegazzianum* that differentiate this species from native plants, and by being novel to the invaded communities they could contribute to the observed ecosystem changes. The huge biomass of this species on research locality was observed compared to the native grassland species. Hogweed can reach very easily high dominance at invaded sites because of its size (2-5 meters high and almost 3 meters in length) and restricting access to light for native plants [135]. There is the report showing that under the canopy of *H. mantegazzianum*, an increase of concentration of exchangeable essential nutrients was found, mainly for K and Mn, compared to the native species [136]. It was also due to higher primary productivity in exotic invasive plants compared to native vegetation. Contrary, the study of Koutika et al. [126] showed that organic carbon has decreased by *H. mantegazzianum* invasion, as well as particulate organic matter weight and nitrogen content in soil ecosystems.

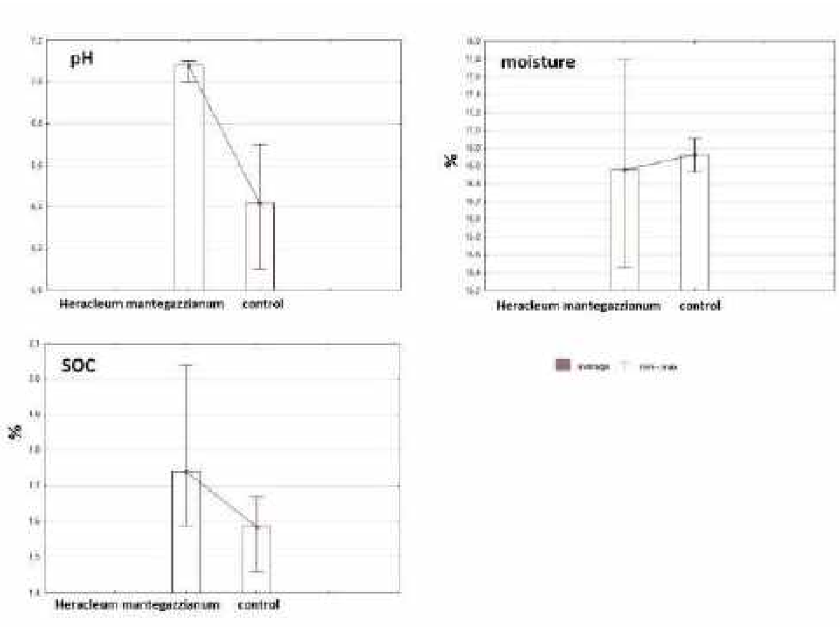

Fig. 11. Soil physico-chemical properties of *Heracleum mantegazzianum* in Lekárovce locality

Their study also showed that *H. mantegazzianum* invasion reduced mineralization of carbon compared to non-invaded sites that was also statistically shown in our study (Table 8). A reduction of carbon mineralization were probably due to the creation of less active soil organic matter that indicate that the invasive plant species litter might decompose slower than the native grassland species. Changes in carbon status might also reduce microbial biomass or alter microbial diversity and activity [137]. Microbial indices, such as soil enzyme activity, are more sensitive than physico-chemical properties to environmental disturbances and can be easily quantified [138]. Changes in enzyme activities are shown in Figure 12. Activity of all selected enzymes appeared to decrease by invasiveness of *H. mantegazzianum*. The activity of soil phosphatases might meet the demand of available P by plants and microbes. The results of activity of soil urease showed that invasive species most affected this parameter among selected enzymes. It can be expected that the substitution by invaders lead to change in composition and activity of microbial communities. There are not many papers describing the effect of this exotic species on soil microbial indices, especially soil enzymes. Therefore, there is a lack of this information and further research is needed.

Some authors [134] state that there is very difficult distinguish whether the modification of ecosystem characteristics was due to the invasion of the exotic species with its novel traits, or rather due to the loss of native species displaced from invaded communities. A particular impact on human health is photodermatitis elicited by furanocoumarins in the sap of *H. mantegazzianum*. Photodermatitis occurs 24-48 h after physical contact of skin when the skin is exposed to sunlight. Impact on humans and reduction of local plant communities are a major problems arising from *H. mantegazzianum* and it is advisable to apply appropriate monitoring and management [139].

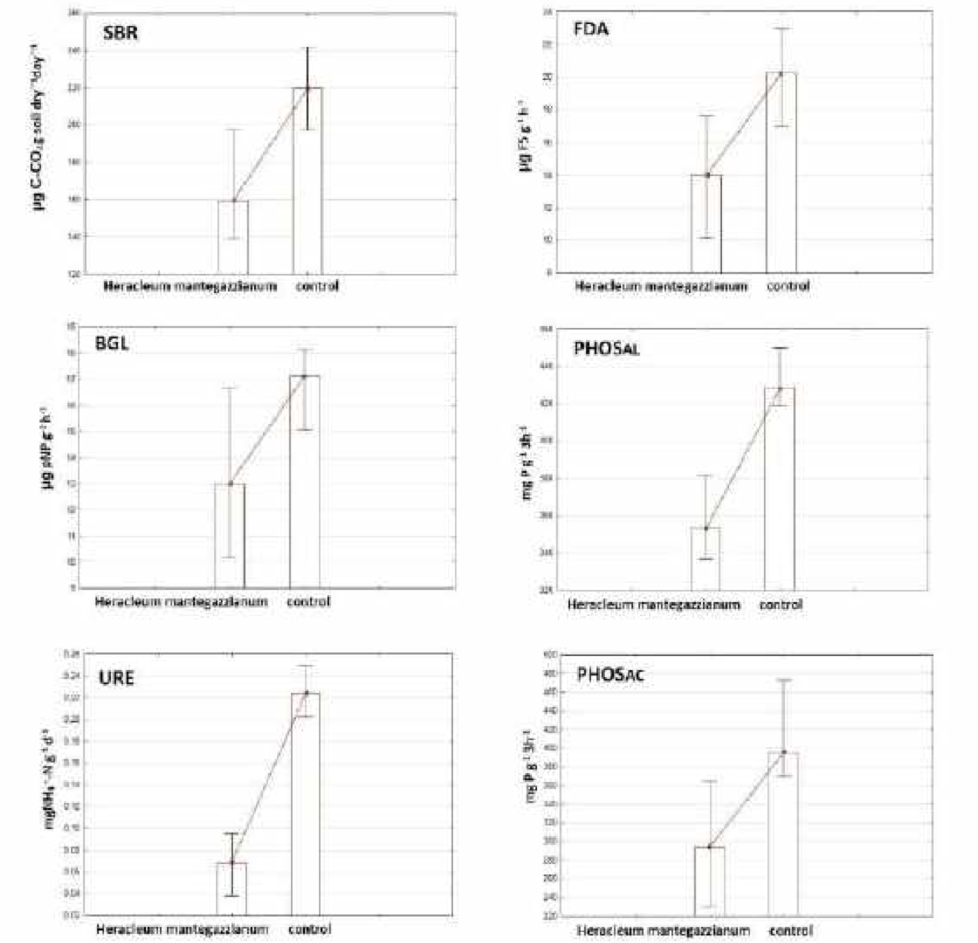

Fig. 12. Soil microbial indices of *Heracleum mantegazzianum* in Lekárovce locality

Table 8. The values of Mann-Whitney nonparametrical test for comparison soil properties between invasion status by *Heracleum mantegazzianum* (invaded vs. non-invaded)

Parameter		U	z	P value
pH		0,00	2,51	0,012 *
SM		10,00	-0,42	0,67
SOC		4,00	1,67	0,09
SBR	**Between invaded and non-invaded sites**	0,50	-2,40	0,016*
BGL		2,00	-2,08	0,03 *
FDA		1,00	-2,30	0,021 *
URE		0,00	-2,51	0,012 *

$PHOS_{AC}$	0,00	-2,50	0,011*
$PHOS_{AL}$	0,00	-2,50	0,011*

SM (soil moisture), SOC (soil organic carbon), SBR (Soil basal respiration), FDA (fluorescein diacetate activity), BGL (beta-glucosidase activity), URE (urease activity), $PHOS_{AL}$ (alkaline phosphatase activity), $PHOS_{AC}$ (acidic phosphatase activity), * $P < 0.05$.

CONCLUSION

The impacts of invasive plants on ecosystem functioning are receiving increasing attention, because these exotic plants can significantly affect the composition of native species, as well as soil properties. Our results suggest that the activity of soil enzymes, as well as physico-chemical properties, respond to soil composition changes represented by invasion of exotic plant species. Therefore, all these parameters might be widely used as an indicator of environmental changes and natural disturbances. Of special note, the activity of soil enzymes has been reported as useful soil quality indicators because enzymes respond very quickly to soil management changes before other indicators changes are detectable. Moreover, soil enzymes are often closely related to physico-chemical properties, microbial activity and biomass in soil systems, and can be an integrative soil biological index of past soil management.

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REFERENCES

1. Bobuľská, L., Demková, L., Effects of invasive species *Impatiens parviflora* on soil microbial indices in the protected areas in Slovakia, VIII International Scientific Agriculture Symposium," Agrosym 2017", Jahorina, Bosnia and Herzegovina, October 2017, Book of Proceedings, pp 1880-1885, 2017.

2. Renčo, M., Baležentiené, L., An analysis of soil free-living and plant-parasitic nematode communities in three habitats invaded by *Heracleum sosnowskyi* in central Lithuania, Biological Invasions, vol. 17/issue 4, pp 1025-1039, 2015.

3. Theodoropoulos, D.I., Invasion Biology. Critique of a Pseudoscience, Avvar Books, Blythe, p 20, 2003.

4. Nentwig, W., Biological Invasions, Ecological Studies, Springer-Verlag, Berlin, 440 p, 2008.

5. Hulme, P.E., Addressing the threat to biodiversity from botanic gardens, Trends in ecology and Evolution, vol. 26, pp 168-174, 2011.

6. McNeely, J.A., The great reshuffling: Human dimensions of invasive alien species, IUCN, Gland, Cambridge, 245 p, 2001.

7. Raymond, B., McInnes, J., Dambacher, J.M., Way, S., Bergstrom, D.M., Qualitative modelling of invasive species eradication on subantarctic Macquarie Island, Journal of Applied Ecology, vol. 48, pp 181-191, 2011.

8. Hladyz, S., Åbjörnsson, K., Giller, P.S., Woodward, G., Impacts of an aggressive riparian invader on community structure and ecosystem functioning in stream food webs, Journal of Applied Ecology, vol. 48, pp 443-452, 2011.

9. Hui, C., Foxcroft, L.C., Richardson, D.M., MacFadyen, S., Defining optimal sampling effort for large-scale monitoring of invasive alien plants: a Bayesian method for estimating abundance and distribution, Journal of Applied Ecology, vol. 48, pp 768-776, 2011.

10. Hopkins, G.A., Forrest, B.M., Jiang, W., Gardner, J.P.A., Successful eradication of a non-indigenous marine bivalve from a subtidal soft-sediment environment, Journal of Applied Ecology, vol. 48, pp. 424-431, 2011.

11. Colautti, R.I., MacIsaac, H.J., Aneutral terminology to define invasive species, Diversity and Distribution, vol. 10, pp. 135-141, 2004.

12. Mao, R., Bajwa, A.A., Adkins, S., A seperweed in the making: adaptation of *Parthenium hysterophorus* to a changing climate. A review, Agronomy for Sustainable Development, vol. 41, 47, 2021.

13. Zelnik, I., The presence of invasive alien plant species in different habitats: case study from Slovenia, Acta Biologica Slovenica, vol. 22/issue 2, pp 25-38, 2012.

14. Hughes, K.A., Convey, P., The protection of Antarctic terrestrial ecosystems from inter- and intra-continental transfer of non-indigenous species by human activities: a review of current systems and practice, Global Environmental Change, vol. 20, pp 96-112, 2010.

15. Vilà, M., Corbin, J.D., Dukes, J.S., Pino, J., Smith, S.D., Linking plant invasion to global environmental change, In: Canadell, J.G., Pataki, D., Pitelka, L. (eds), Terrestrians ecosystems in a changing world, The IGBP Series, Springer-Verlag, Berlin, pp 93-102, 2007.

16. Lockwood, J.L., McKinney, M.L., Biotic homogenization. KluwerAcademic. Plenum Publishers, New York, 283 p, 2001.

17. Zhang, Ch.B., Wang, J., Qian, B.Y., Li, W.H., Effects of the invader *Solidago canadensis* on soil properties, Applied Soil Ecology, vol. 43, pp 163-169, 2009.

18. Vitousek, P.M., D'Antonio, C.M., Loope, L.L., Westbrooks, R., Biological invasions as global environmental change, American Journal of Science, vol. 84, pp 218–228, 1996.

19. Kourtev, P.S., Ehrenfeld, J.G., Huang, W.Z., Enzyme activities during litter decomposition of two exotic and native plant species in hardwood forest of New Jersey, Soil Biology and Biochemistry, vol. 34, pp 1207-1218, 2002.

20. Dassonville, N., Vanderhoeven, S., Vanparys, V., Hayez, M., Gruber, W., Meerts, P., Impacts of alien invasive plant on soil nutrients are correlated with initial site conditions in NW Europe, Oecologia, vol. 157, pp 131-140, 2008.

21. Pejchar, L., Mooney, H.A., Invasive species, ecosystem services and human well-being, Trends in Ecology and Evolution, vol. 24/issue 9, pp 497-504, 2009.

22. Shackleton, R.T., Shackleton, C.M., Kull, C.A., The role of invasive alien species in shaping local livelihoods and human well-being: a review, Journal of Environmental Management, vol. 229, pp 145-157, 2019.

23. Jones, B.A., McDermott, S.M., Health impacts of invasive species through an altered natural environment: assessing air pollution sinks as a causal pathway, Environmental and Resource Economics, vol. 71/issue 1, pp 23-43, 2018.

24. Gallardo, B., Bacher, S., Bradley, B., Comín, F.A., Gallien, L., Jeschké, J.M., Sorte, C.J.B., Vilà, M., InvasiBES: Understanding and managing the impacts of Invasive alien species on Biodiversity and Ecosystem Services, NeoBiota, vol. 50, pp 109-122, 2019.

25. Cui, X., Song, W., Feng, J., Jia, D., Guo, J., Wang, Z., Wu, H., Qi, F., Liang, J., Lin, G., Increased nitrogen input enhances *Kandelia obovata* seedling growth in the presence of invasive *Spartina alterniflora* in subtropical regions of China, Biology Letters, vol. 13, 20160760, 2017.

26. Perry, L.G., Blumenthal, D.M., Monaco, T.A., Paschke, M.W., Redente, E.F., Immobilizing nitrogen to control plant invasion, Oecologia, vol.163, pp 13-24, 2010.

27. Vitousek, P.M., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D., Schlesinger, W.H., Tilman, G.D., Human alteration of the global nitrogen cycle: Causes and consequences. Issues in Ecology, vol. 1, pp 1-17, 1997.

28. Malhi, Y., Franklin, J., Seddon, N., Solan, M., Turner, M.G., Field, Ch.B., Knowlton, N., Climate change and ecosystems: threats, opportunities and solutions, Philosophical Transactions Royean Society B, vol. 375, 20190104, 2020.

29. Root, T.L., Price, J.T., Hall, K.R., Schneider, S.H., Rosenzweig, C., Pounds, J.A., Fingerprints of global warming on wild animals and plants, Nature, vol. 421, pp 57-60, 2003.

30. Dukes, J.S., Mooney, H.A., Does global change increase the success of biological invaders? Trends in Ecology and Evolution, vol. 14, pp 135-139, 1999.

31. Vinhal-Feitas, I.C., Corrêa, G.F., Wendling, B., Bobuľská, L., Ferreira, A.S., Soil textural class plays a major role in evaluation the effects of land use on soil quality indicators, Ecological Indicators, vol. 74, pp 182-190, 2017.

32. With, K.A., The landscape ecology of invasive spread, Conservation Biology, vol. 16, pp 1192-1203, 2002.

33. Wang, W., Zhang, Ch., Allen, J.M., Li, W., Boyer, M.A., Segerson, K., Silander, J.A., Analysis and prediction of land use changes related to invasive species and major driving forces in the state of Connecticut, Land, vol. 5/issue 3, 25, 2016.

34. Hobbs, R.J., Huenneke, L.F., Disturbance, diversity, and invasion: implications for conservation, Conservation Biology, vol. 6, pp 324-337, 1992.

35. Ehrenfeld, J, Effects of exotic plant invasions of ecosystem nutrient cycling processes, Ecosystems, vol. 6, pp 503–523, 2003.

36. Vilà, M., Hulme, P.E., Impact of Biological Invasions on Ecosystem Services. Invading Nature - Springer Series in Invasion Ecology, vol. 12, Springer, Cham, pp 1- 14, 2017.

37. Rai, P.K., Impacts of particulate matter pollution on plants: implications for environmental biomonitoring. Ecotoxicology and Environmental Safety, vol. 129, pp 120-136, 2016.

38. Rai, P.K., Kim, K.H., Invasive alien plants and environmental remediation: A new paradigm in sustainable restoration ecology, Restoration Ecology, vol. 28/issue 1, pp 3-7, 2020.

39. Jarošík, V., Pyšek, P., Foxcroft, L.C., Richardson, D.M., Rouget, M., MacFadyen, S., Predicting incursion of plant invaders into Kruger National Park, South Africa: the interplay of general drivers and species-specific factors, PloS One, vol. 6, e28711, 2011.

40. Randall, L.M., Protected areas, In: Simberloff, D., Rejmánek, M. (eds), Encyclopedia of biological invasions, University of California, Berkley, pp 563-567, 2011.

41. Stefanowicz, A.M., Stanek, M., Nobis, M., Zubek, S., Few effects of invasive plants *Reynoutria japonica*, *Rudbeckia laciniata* and *Solidago gigantea* on soil physical and chemical properties, Science of the Total Environment, vol. 574, pp 938-946, 2017.

42. Laishram, J., Saxena, K.G., Maikhuri, R.K., Rao, K.S., Soil quality and soil health: A review, International Journal of Ecology and Environmental Sciences, vol. 38/issue 1, pp 19-37, 2012.

43. Bobuľská, L., Fazekašová, D., Angelovičová, L., Kotorová, D., Impact of ecological and conventional farming systems on chemical and biological soil quality indices in a cold mountain climate in Slovakia, Biological Agriculture and Horticulture, vol. 31/issue 3, pp 205-218, 2015.

44. Nikitin, A., Kuzicheva, N., Innovative technologies in agriculture, International Journal of Recent Technology and Engineering, vol. 8/issue 4, pp 3802-3807, 2019.

45. Angelovičová, L., Bobuľská, L., Fazekašová, D., Toxicity of heavy metals to soil biological and chemical properties in conditions of environmentally polluted area middle Spiš (Slovakia), Carpathian Journal of Earth and Environmental Sciences, vol. 10/issue 1, pp 193-201, 2015.

46. Benbi, D.K., Brar, J.S., A 25-year record of carbon sequestration and soil properties in intensive agriculture, Agronomy for Sustainable Development, vol. 29, pp 257-265, 2009.

47. Lal, R., Negassa, W., Lorenz, K., Carbon sequestration in soil, Current Opinion in Environmental Sustainability, vol. 15, pp 79-86, 2015.

48. Barrios, E., Soil biota, ecosystem services and land productivity, Ecosystem Economics, vol. 64/issue 2, pp 269-285, 2007.

49. Keet, J.H., Ellis, A.G., Hui, C., Novoa, A., Le Roux, J.J., Impacts of invasive Australian Acacias on soil bacterial community composition, microbial enzymatic activities and nutrient availability in Fynbos soils, Microbial Ecology, https://doi.org/10.1007/s00248-021-01683-1, 2021.

50. Bujnovský, R., Juráni, B., Kvalita pôdy – jej vymedzenie a hodnotenie (in slovak), Soil Science and Conservation Research Institute, Bratislava, 42 p., 1999.

51. Doran, J.W., Parkin, T.B., Defining and Assessing Soil Quality, In: Doran, J.W., Coleman, D. C., Bezdiček, D.F., Stewart, B.A. (eds), Defining Soil Quality for a Sustainable Environment. Soil Science Society of America, Wisconsin, vol. 35, pp 3 – 21, 1994.

52. Johnson, D.L., Ambrose, S.H., Bassett, T.J., Bowen, M.L., Crummey, D.E., Isaacson, J.S., Johnson, D.N., Lamb, P., Saul, M., Winter-Nelson, A.E., Meanings of environmental terms, Journal of Environmental Quality, vol. 26, pp 581 – 589, 1997.

53. Harris, W.G., Rhue, R.D., Kidder, G., Brown, R.B., Littell, R., Phosphorus Retention as Related to Morphology of Sandy Coastal Plain Soil Materials, Soil Science Society of American Journal, vol.60/issue 5, pp 1513 – 1521, 1996.

54. Doran, J.W., Zeiss, M.R., Soil Health and Sustainability: Managing the Biotic Component of Soil Quality, Applied Soil Ecology, vol. 15, pp 3 – 11, 2000.

55. Paz-Ferreiro, J., Fu, S., Biological indices for soil quality evaluation: perspectives and limitations, Land Degradation and Development, vol. 27/issue 1, pp 14-25, 2016.

56. Janzen, H.H., Carbon cycling in earth systems a soil science perspective, Agriculture, Ecosystems and Environment, vol. 104, pp 399– 417, 2004.

57. Javoreková, S. a kol.: Biológia pôdy v agroekosystémoch (in slovak), Slovak Agricultural University, Nitra, 349 p, 2008.

58. Arshad, M.A., Martin, S., Identifying critical limits for soil quality indicators in agro-ecosystems, Agriculture, Ecosystems and Environment, vol. 88/issue 2, pp 153-160, 2002.

59. Paz-Ferreiro, J., Trasar-Cepeda, C., Leirós, M.C., Seoane, S., Gil-Sotres, F., Biochemical properties of acid soils under native grassland in a temperate humid zone, New Zealand Journal of Agricultural Research, vol. 50, pp 537–548, 2007.

60. García-Orenes, F., Roldán, A., Mataix-Solera, J., Cerdà, A., Campoy, M., Arcenegui, V., Caravaca, F., Soil structural stability and erosion rates influenced by agricultural management practices in a semi-arid Mediterranean agro-ecosystem, Soil Use and Management, vol. 28, pp 571–579, 2012.

61. Marinari, S., Mancinelli, R., Campiglia, E., Grego, S., Chemical and biological indicators of soil quality in organic and conventional farming systems in Central Italy, Ecological Indicators, vol. 6/issue 4, pp 701-711, 2006.

62. Bending, G.D., Turner, M.K., Rayns, F., Marx, M.C., Wood, M., Microbial and biochemical soil quality indicators and their potential for differentiating areas under contrasting agricultural management regimes, Soil Biology and Biochemistry, vol. 36, pp. 1785-1792, 2004.

63. Čerevková, A., Renčo, M., Spoločenstvá nematód ako odraz ekologického stavu pôdneho prostredia (in slovak), Životné prostredie, vol. 42/issue 3, pp 145-148, 2008.

64. Kubát, J., Nováková, J., Cerhanová, D., Výskyt a aktivita půdních mikroorganizmů ve dlouhodobých polních pokusech na orné půdě, In: Tesařová, M., Záhora, J. (eds), Biologické indikátory kvality půd (in czech), Mendel University in Brno, pp 18-25, 2002.

65. Wang, W:J., Dalal, R.C., Moody, P.W., Smith, C.J., relationships of soil respiration to microbial biomass, substrate availability and clay content, Soil Biology and Biochemistry, vol. 35/issue 2, pp 273-284, 2003.

66. Caldwell, B.A., Enzyme activities as a component of soil biodiversity: A review, Pedobiologia, vol. 49, pp 637-644, 2005.

67. Bobuľská, L., Demková, L., Čerevková, A., Renčo, M., Impact of wetland restoration on soil microbial activity and nematode communities, Wetlands, vol. 40/issue 4, pp 865-875, 2020.

68. Tabatabai, M.A., Dick, W.A., Enzymes in soil: research and develop-ments in measuring activities. In: Burns, R.G., Dick, R.P. (eds), Enzymes in the environment. Activity, ecology, and applications, Marcel Dekker,Inc., New York, pp 567–595, 2002.

69. Souza-Alonso, P., Guisande-Collazo, A., González, L., Gradualism in *Acacia dealbata* link invasion: impact on soil chemistry and microbial community over a chronological sequence, Soil Biology and Biochemistry, vol. 80, pp 315-323, 2015.

70. Maglocký, Š., Potenciálna prirodzená vegetácia (in slovak), In: Miklós, L. (ed), Atlas krajiny Slovenskej republiky, Ministerstvo životného prostredia SR, Slovenská agentúra životného prostredia, Bratislava, Banská Bystrica, 2002.

71. Medvecká, J., Kliment, J., Májeková, J., Halada, Ľ., Zaliberová, M., Gojdičová, E., Feráková, V., Jarolímek, I., Inventory of the alien flora of Slovakia, Preslia, vol. 84, pp 257–309, 2012.

72. Jurová, J., Matoušková, M., Wajs-Bonikowska, A., Kalemba, D., Renčo, M., Sedlák, V., Gogaľová, Z., Poráčová, J., Šalamún, P., Gruľová, D., Potential phytotoxic effect of essential oil of non-native species *Impatiens parviflora* DC., Plants, vol. 8/issue 7, pp 1-12, 2019.

73. Čerevková, A., Miklisová, D., Bobuľská, L., Renčo, M., Impact of the invasive plant *Solidago gigantea* on soil nematodes in a semi-natural grassland and a temperate broadleaved mixed forest, Journal of Helminthology, vol. 94, article number e51, 2020.

74. Sterzyńska, M., Shrubovycg, J., Nicia, P., Impact of plant invasion (*Solidago gigantea* L.) on soil mesofauna in a riparian wet meadows, Pedobiologia, vol. 64, pp 1-7, 2017.

75. Bobuľská, L., Čekanová, K. Demková, L., Oboňa, J., Sarvaš, J., Evaluation of the phytoremediation properties of the invasive species *Solidago* genus, Annual University of Craiova, vol. 23, pp 314–320, 2018.

76. Čerevková, A., Bobuľská, L., Miklisová, D., Renčo, M., A case study of soil food web components affected by *Fallopia japonica* (Polygonaceae) in three natural habitats in Central Europe, Journal of Nematology, vol. 51/issue 1, pp e2019-42, 2019.

77. Sołtysiak, J., Heavy metals tolerance in an invasive weed (*Fallopia japonica*) under different levels of soils contamination, Journal of Ecological Engineering, vol. 21/issue 7, pp 81-91, 2020.

78. Abgrall, C., Forey, E., Mignot, L., Chauvat, M., Invasion by *Fallopia japonica* alters soil food webs through secondary metabolites, Soil Biology and Biochemistry, vol. 127, pp 100-109, 2018.

79. Jordanova, N., Soil Magnetism: Applications in Pedology, Environmental Science and Agriculture. Academic Press, London, 2017.

80. Vilček, J., Zverková, M., Pedogeografia (in slovak), Prešovská univerzita v Prešove, Prešov, 2015.

81. Pyšek, P., Pyšek, A., Invasion by *Heracleum mantegazzianum* in different habitats in the Czech Republic, Journal of Vegetation Science, vol. 6, pp 711-718. 1995.

82. Nielsen, C., Hartvig, P., Kollmann, J., Predicting the distribution of the invasive alien Heracleum mantegazzianum at two different spatial scales, Diversity and Distributions, vol. 14/issue 2, pp 307-317, 2008.

83. Pyšek, P., Chytrý, M., Pergl, J., Sádlo, J., Wild, J., Plant invasions in the Czech Republic: current state, introduction dynamics, invasive species and invaded habitats, Preslia, vol. 84/issue 3, pp 575-629, 2012.

84. Swanton, C.J., Cavers, P.B., Clements, D.R., Moore, M.J., The biology of Canadian weeds. 101. *Helianthus tuberosus* L., Canadian Journal of Plant Science, vol. 72/issue 4, pp 1367-1382, 1992.

85. Ma, X:Y., Zhang, L.H., Shao, H.B., Xu, G., Zhang, F., Ni, F.T., Brestic, M., Jerusalem artichoke (*Helianthus tuberosus*), a medicinal salt-resistant plant has high adaptability and multiple-use values, Journal of Medicinal Plants Research, vol., 5/issue 8, pp 1272-1279, 2011.

86. Baldini, M., Danuso, F., Turi, M., Vannozzi, P., Evaluation of new clones of Jerusalemartichoke (*Helianthus tuberosus* L.) for inulin and sugar yield from stalks and tubers, Industrial Crops and Products, vol. 19/issue 1, pp 25-40, 2004.

87. Ahmed, M.S., El-Sakhawy, F.S., Soliman, S.N., Abou, H.D.M.R., Phytochemical and biological study of *Helianthus tuberosus* L. Egypt, Journal of Biomedical Science, vol. 18, pp 134-147, 2005.

88. Fiala, K. et al., Partial monitoring system – soil. Binding methods (in slovak), Soil Science and Conservation Research Institute, Bratislava, 139 p, 1999.

89. Alef, K., Nannipieri, P., Methods in applied soil microbiology and biochemistry, Academic Press, London, pp 193-270, 1995.

90. Islam, K.R., Weil, R.R.., Microwave irradiation of soil for routine measurement of microbial biomass carbon, Biology and Fertility of Soils, vol. 27, pp 408–416, 1998.

91. Novoa, A., Rodríguez, R., Richardson, D.M., Gonzáles, L., Soil quality: a key factor in understanding plant invasion? The case of *Carpobrotus edulis* (L.) N.E.Br., Biological Invasions, vol. 16, pp 429-443, 2014.

92. Nannipieri, P.; Ascher, J.; Ceccherini, M.T.; Landi, L.; Pietramellara, G.; Renella, G., Microbial diversity and soil functions, Euopean Journal of Soil Science, vol. 54, pp 655–670, 2003.

93. Green, V.S., Stott, D.E., Diack, M., Assay for fluorescein diacetate hydrolysis activity: optimization for soil samples, Soil Biology and Biochemistry, vol. 38, pp. 693-701, 2006.

94. Grejtovský, A., Influence of soil improvers on enzymatic activity of heavy alluvial soil, Plant, Soil and Environment, vol. 37, pp. 289-295, 1991.

95. Eivazi, F., Tabatabai, M.A., Glucosidases and galactosidases in soils, Soil Biology and Biochemistry, vol. 20, pp. 601-606, 1988.

96. Khaziev, F.K., Soil enzyme activity, Nauka, Moscow, 1979.

97. R Core Team, R: A Language and Environment for Statistical Computing, 1st ed., R. Foundation for Statistical Computing. Vienna, Austria, 2018, available online: https://www.r-project.org/ (accessed on 12 February 2020).

98. Chmura D., Wpływ gatunków inwazyjnych na różnorodnosc fitocenotyczna rezerwatów Wyżyny Krakowsko–Czestochowskiej. Raport koncowy (in polish), Instytut Ochrony Przyrody, Krakow, 2006.

99. Coombe D.E., *Impatiens parviflora* DC., Journal of Ecology, vol. 44, pp. 701-712, 1956.

100. Florianová, A., Münzbergová, Z., The intensity of intraspecific plant-soil feedbacks in alien *Impatiens* species depends on the environment, Perspectives in Plant Ecology, Evolution and Systematics, vol. 32, pp 56-64, 2018.

101. Castillo, X., Joergensen, R.G., Impact of ecological and conventional arable management systems on chemical and biological soil quality indices in Nicaragua, Soil Biology and Biochemistry, vol. 33, pp. 1591-1597, 2001.

102. Monreal, C.M., Bergstrom, D.W., Soil enzymatic factors expressing the influence of land use, tillage system and texture on soil biochemical quality, Canadian Journal of Soil Science, vol. 80, pp. 419-428, 2000.

103. Speir, T.W., Van Schaik, A.P., Lloyd-Jones, A.R., Temporal response of soil biochemical properties in a pastoral soil after cultivation following high application rates of undigested sewage sludge, Biology and Fertility of Soils, vol.38, pp. 377-385, 2003.

104. Senga, Y., Hiroki, M., Nakamura, Y., Watarai, Y., Watanabe, Y., Nohara, S., Vertical profile of DIN, DOC, and microbial activities in the wetland soil of Kushiro Mire, northeastern Japan. Limnology, vol. 12, pp. 17-23, 2011.

105. Dassonville, N., Guillaumaud, N., Piola, F., Meerts, P., Poly, F., Niche construction by the invasive Asian knotweeds (species complex *Fallopia*): impact on activity, abundance and community structure of denitrifiers and nitrifiers, Biological Invasions, vol. 13, pp 1115-1133, 2011.

106. Herr, C, Chapuis-Lardy, L., Dassonville, N., Vanderhoeven, S., Meerts, P., Seasonal effect of the exotic invasive plant *Solidago gigantea* on soil pH and P fractions, Journal of Plant Nutrition and Soil Science, vol. 170, pp 729-738, 2007.

107. Scharfy, D., Güsewell, S., Gessner, M.O., Venterink, H.O., Invasion of *Solidago gigantea* in contrasting experimental plant communities: effects on soil microbes, nutrients and plant–soil feedbacks, Journal of Ecology, vol. 98, pp 1379-1388, 2010.

108. Rusterholz, H.P.; Schneuwly, J.; Baur, B., Invasion of the alien shrub *Prunus laurocerasus* in suburban deciduous forests: Effects on native vegetation and soil properties, Acta Oecologica, vol. 92, pp 44–51, 2018.

109. Chacón, N.; Herrera, I.; Flores, S.; Gonzáles, J.A.; Nassar, J.M., Chemical, physical, and biochemical soil properties and plant roots as affected by native and exotic plants in neotropical arid zones, Biology and Fertility of Soils, vol. 45, pp 321–328, 2009.

110. Sicardi, M.; Garcìa-Prèchac, F.; Frioni, L., Soil microbial indicators sensitive to land use conversion from pastures to commercial *Eucalyptus grandis* (Hill ex Maiden) plantations in Uruguay, Applied Soil Ecology, vol. 27, pp 125–133, 2004

111. Baranová, B.; Manko, P.; Jászay, T., Differences in surface-dwelling beetles of grasslands invaded and non-invaded by goldenrods (*Solidago canadensis*, *S. gigantea*) with special reference to *Carabidae*, Journal of Insect Conservation, vol. 18, pp 623–635, 2014.

112. Richard, M.; Tallamy, D.W.; Mitchell, A.B., Introduced plants reduce species interactions. Biological Invasions, vol. 21, pp 983–992, 2019.

113. Liao, C.Z.; Peng, R.H.; Luo, Y.Q.; Zhou, X.H.; Wu, X.W.; Fang, C.M.; Chen, J.K.; Li, B., Altered ecosystem carbon and nitrogen cycles by plant invasion: A meta-analysis, New Phytologist, vol. 177, pp 706–714, 2008.

114. Yang, W.; Yan, Y.; Jiang, F.; Cheng, X.; An, S., Response of the soil microbial community composition and biomass to a short-term *Spartina alternifolia* invasion in a coastal wetland of eastern China, Plant and Soils, vol. 408, pp 443–456, 2016.

115. Feng, J.; Wang, S.; Wang, S.; Ying, R.; Yin, F.; Jiang, L.; Li, Z., Effects of invasive *Spartina alternifolia* Loisel. and subsequent ecological replacement by *Sonneratia apetala* Buch.-Ham. on soil organic carbon fraction and stock, Forests, vol. 10, pp 171, 2019.

116. Seeling, B, Zasoski, R.J., Microbial effects in maintaining organic and inorganic solution phosphorus concentrations in a grassland topsoil, Plant and Soil, vol. 148, pp 277-284, 1993.

117. Chapuis-Lardy, L., Vanderhoeven, S., Dassonville, N., Koutika, L.S., Meerts, P., Effect of the exotic invasive plant *Solidago gigantea* on soil phosphorus status, Biology and Fertility of Soils, vol. 42, pp 481-489, 2006.

118. Wang, C.; Wu, B.; Jiang, K., Allelopathic effects of Canada goldenrod leaf extracts on the seed germination and seedling growth of lettuce reinforced under salt stress, Ecotoxicology, vol. 28, pp 103–116, 2019.

119. Ren, G.Q.; Zou, C.B.; Wan, L.Y.; Johnson, H.J.; Li, J.; Zhu, L.; Qi, S.S.; Dai, Z.C.; Zhang, H.Y.; Du, D.L., Interactive effect of climate warming and nitrogen deposition may shift the dynamics of native and invasive species, Journal of Plant Ecology, vol. 14/issue 1, pp 84-95, 2020.

120. Corstanaje, R.; Schulin, R.; Lark, R.M., Scale-dependent relationships between soil organic carbon and urease activity, European Journal of Soil Science, vol. 58, pp 1087–1095, 2007.

121. Suseela, V., Alpert, P., Nakatsu, C.H., Armstrong, A., Tharayil N., Plant-soil interactions regulate the identity of soil carbon in invaded ecosystems, implication for legacy effects, Functional Ecology, vol. 30, pp 1227–38, 2016.

122. Dassonville, N., Vanderhoeven, S., Gruber, W., Meerts, P., Invasion by Fallopia japonica increases topsoil mineral nutrient concentration, Ecoscience, vol. 14: pp 230-240, 2007.

123. Rahmonov, O., Czylok, A., Orczewska, A., Majgier, L., Parusel T., Chemical composition of the leaves of *Reynoutria japonica* Houtt. and soil features in polluted areas, Central European Journal of Biology, vol. 9, pp 320–30, 2014.

124. Chmura, D., Tokarska-Guzik, B., Nowak, T., Woźniak, G., Bzdęga, K., Koszela, K., Gancarek M., The influence of invasive Fallopia taxa on resident plant species in two river valleys (southern Poland), Acta Societatis Botanicorum Poloniae, vol. 84, pp 23–33, 2015.

125. Jobbagy, E.G., Jackson, R.B, The uplift of soil nutrients by plants: Biogeochemical consequences across scales, Ecology, vol. 85, pp 2380-2389, 2004.

126. Koutika, L.S., Vanderhoeven, S., Chapuis-Lardy, L., Dassonville, N., Meerts, P., Assessment of changes in soil organic matter following invasion by exotic plant species, Biology and Fertility of Soils, vol. 44, pp 331-341, 2007.

127. Stefanowicz, A.M., Stanek, M., Nobis, M., Zubek, S., Species-specific effects of plant invasions on activity, biomass, and composition of soil microbial communities, Biology and Fertility of Soils, vol. 52, pp 841–52, 2016.

128. Stefanowicz, A.M., Stanek, M., Majewska, M.L., Nobis, M., Zubek S., Invasive plant species identity affects soil microbial communities in a mesocosm experiment, Applied Soil Ecology, vol. 136, pp 168–77, 2019.

129. Kappes, H., Lay, R., Topp, W., Changes in different trophic levels of letter-dwelling. Macrofauna associated with Giant knotweed invasion, Ecosystems, vol. 10, pp 734-744, 2007.

130. Wang, W., Sardans, J., Wang, C., Asensio, D., Bartrons, M., Peñuelas, D., Species-specific impacts of invasive plant success on vertical profiles of soil carbon accumulation and nutrient retention in the Minjiang River Tidal Estuarine wetlands of China, Soil Systems, vol. 2, pp. 5, 2018.

131. Tong, C., Zhang, L., Wang, W., Gauci, V., Marrs, R., Liu, B., Jia, R., Zeng, C., Contrasting nutrient stocks and litter decomposition in stands of native and invasive species in a sub-tropical estuarine marsh, Environmental Research, vol. 111, pp. 909-916, 2011.

132. Metcalfe, D.B., Fisher, R.A., Wardle, D.A., Plant communities as drivers of soil respiration: Pathways, mechanisms, and significance for global change, Biogeosciences, vol. 8, pp. 2047-2061, 2011.

133. Ying, G.Z., Peng, F.X., Gang, Z.X., Zhi, W.F., Wei, L.S., Effects of plant residues on cucumber (*Cucumis sativus* L) growth, soil enzyme activities and microbial communities, Allelopathy Journal, vol. 38/issue 2, pp 147-158, 2016.

134. Jandová, K., Klinerová, T., Müllerová, J., Pyšek, P., Pergl, J., Cajthaml, T., Dostál, P., Long-term impact of *Heracleum mantegazzianum* invasion on soil chemical and biological characteristics, Soil Biology and Biochemistry, vol. 68, pp 270-278, 2014.

135. Dostál, P., Müllerová, J., Pyšek, P., Pergl, J., Klinerová, T., The impact of an invasive plant changes over time, Ecology Letters, vol., 16, pp 1277-1284, 2013.

136. Vanderhoeven, S., Dassonville, N., Meerts, P., Increased topsoil mineral nutrient concentrations under exotic invasive plants in Belgium, Plant and Soil, vol. 275, pp 169-179, 2005.

137. Kourtev, P.S., Ehrenfeld, J.G., Häggblom, M., Experimental analysis of the effect of exotic and native plant species on the structure and function of soil microbial communities, Soil Biology and Biochemistry, vol. 35, pp 895-905, 2003.

138. Pop, O.G., Gruia, R., Marculescu, A., Assessment of the management effectiveness in Romanian protected areas using biological indicators, Environmental Engineering and Management, vol. 9, pp 1593-1599, 2010.

139. Pyšek, P., Cock, M.J.W., Nentwig, W., Ravn, H.P., Ecology and management of Giant Gogweed (*Heracleum mantegazzianum*), CAB International Head Office, Oxfordshire, 324 p., 2007.

THE ROLE OF AUTOMATION IN ENSURING THE INVOLVEMENT OF LOCAL COMMUNITIES IN SUSTAINABLE DEVELOPMENT

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ABSTRACT
This article is devoted to the problem of involvement of local communities in the management of processes that influence climate change at local level and determine the sustainable development of regions. The place of automation in the organization of local government and self-government is revealed. In modern conditions of globalization, digitalization and automation are perceived by the population of many countries as something imposed from above, and strengthening control over the private life of citizens, while removing them from making decisions on vital issues. The article shows the possibilities of using automation and digitalization to enhance the role of local communities and thereby increase the awareness of their behavior in modern conditions, it focuses mainly on ways to solve environmental and public safety issues.
Keywords: sustainable development, automated systems, local communities

INTRODUCTION

The concept of sustainable development was adopted by the World Commission on Environment and Development, and it is generally accepted that sustainable development implies an integrated approach to economic, social and environmental processes. Discussions on sustainable development, however, often focus mainly on the environmental and economic dimensions. The importance of social and cultural factors is not always well recognized.

Climate change is influenced not only by the adopted climate-specific policies (a "climate-first" approach), but also by the set of development options and policies (a "development-first" approach). By building the debate as a development issue rather than an environmental issue, it is possible to move more effectively towards the urgent goals of all countries, including Ukraine.

There are no predictions in which global warming would stop and the world would not get hotter in the coming decades. Perhaps not all of these predictions will become reality, nevertheless, they are made not to scare, but to induce action, thanks to which the darkest scenarios will remain only on paper.

The most widespread example of local government automation is the use of electronic voting and electronic petition systems, but this article focuses on ways to solve environmental and public safety issues. It is important that these actions are carried out not only by eco-activists and formal representatives of the authorities for accountability, but by local communities in general. In the era of digitalization, there is a tendency to automate many processes that determine the life and safety of the population. In our opinion, it is important to organize this process in such a way that it increases the involvement of citizens in the processes of improving society, and does not isolate it from the state with a "barrier" made of machines.

METHODS AND EXPERIMENTAL PROCEDURES

The methods of research are theoretical analysis of scientific literary sources, their synthesis and expedient generalization of information that is being researched. Also, the authors used comparative and systemic methods. In analyzing the collected information, qualitative assessment methods were used. In general, the following main groups of methods were used:

- methods of empirical research (observation, comparison)

- methods of theoretical research (idealization, formalization, logical and historical methods);

- methods that can be applied at the empirical and theoretical levels (abstraction, analysis and synthesis, induction and deduction).

Methods for measuring solar radiation and wind speed for generating green energy will be described in more detail below in the section on alternative energy.

THE RESEARCH RESULTS AND DISCUSSIONS

The main sustainable development goal we will talk about in this article is Goal 11: Sustainable cities and communities [1], but we will focus on environmental and security aspects. According to [2] the strategy of emplementing the Goal 11 is heavily linked to solving the environmental problems and reducing disaster risks**:**

11.4: Strengthen efforts to protect and safeguard the world’s cultural and natural heritage.

11.5: By 2030, significantly reduce the number of deaths and the number of people affected and substantially decrease the direct economic losses relative to global gross domestic product caused by disasters, including water-related disasters.

11.6: By 2030, reduce the adverse per capita environmental impact of cities, including by paying special attention to air quality and municipal and other waste management.

11.7: By 2030, provide universal access to safe, inclusive and accessible, green and public spaces.

11.a: Support positive economic, social and environmental links between urban, per-urban and rural areas.

11.b: By 2020, substantially increase the number of cities and human settlements adopting and implementing integrated policies and plans towards inclusion, resource efficiency, mitigation and adaptation to climate change, resilience to disasters, and develop and implement, in line with the Sendai Framework for Disaster Risk Reduction 2015-2030, holistic disaster risk management at all levels [2].

Below are the results of our analysis of the attitude of local communities to climate change and willingness to actively participate in the implementation of sustainable development, an analysis of world experience in the use of automated systems for environmental safety and recommendations for the implementation of some models in Ukraine. In conclusion, we present the results of the operation of an automated system for measuring parameters necessary for the development of green energy located in the Petro Mohyla Black Sea National University.

The readiness of the population of Ukraine and Russia to take part in solving the problems of climate change and sustainable development

Today, the possibility of including commitments to further reduce greenhouse gas emissions in the European Climate Agreement is being considered. This is facilitated by a public statement by the World Meteorological Organization (WMO) [3]:

1. The increase in CO_2 in 2018 concentration reached new highs in 2018 of 407.8 ppm, or 147% of pre-industrial level in 1750.

2. Methane (CH_4) (the second most important greenhouse gas) reached a new high of about 1869 parts per billion (ppb) in 2018 and is now 259% of the pre-industrial level.

3. Nitrous oxide (N_2O) atmospheric concentration in 2018 was 331.1 parts per billion. This is 123% of pre-industrial levels, etc.

Socis (Center for Public Opinion Research) social surveys [4, 5] show that very often people confuse the concepts of ecology and climate change. These problems are related to some extent and affect each other, but there some nuances. «Pollution» – environmental pollution, these are often local problems such as car exhausts or emissions from metallurgical plants. «Emission» – a term used primarily for "greenhouse gas emissions", in particular CO2.

Do Ukrainians distinguish between environmental and climate issues? Ukraine recently conducted a large-scale study on the environmental awareness of citizens, which was conducted with the support of the Global Environment Facility in the framework of the UN Development Program "Integration of the Rio Convention into Ukraine's national policy." This was the third study, the first two were conducted in 2014 and 2017.

This study was being prepared for the Kyiv International Economic Forum, and it was called «Are Ukrainians Ready for Climate Change?» It showed that

Ukrainians are clearly aware of environmental problems and ways to solve them, but they have a fairly rough idea of the problems of climate change, their causes and options for reducing negative impacts.

According to Oleksandr Stegni, head of the Socis Center for Public Opinion Research [4, 5], it is difficult to determine the level of environmental awareness in Ukraine because there is a correlation: in poor countries or countries in transition, environmental problems are secondary to the population. In the first place is put making a living, even survival of local population.

A survey in Ukraine confirmed this thesis. Landfills and problems with waste recycling were named In the first place - 57.5%.

Ukrainians put the main responsibility for environmental pollution on the government - 51.2%. Our citizens do not want to admit their responsibility: this figure has dropped from 61.4 to 34.2% in five years.

However, more than 90% of Ukrainians are ready to make their own contribution to improving the environment: 41.8% are already doing so, and another 49.1% say they are ready. The vast majority of these measures are related to economic factors - resource-saving practices and modernization of their own homes.

The table. 1 shows the data of a statistical study presented at the Kyiv International Economic Forum, published in [4]. The authors of the article made graphs to facilitate visual analysis of the information given in this table. They are shown in Fig. 1.

Fig. 1 shows a comparative analysis of the readiness of Ukrainian people to take practical action to preserve the environment (dark column) and (according to respondents) their real actions (light column). We see that these figures have changed from year to year, and the subjective practical contribution of the population is gradually increasing. This primarily applies to measures to save water and electricity. The willingness to clean the house by themselseves may also be explained by the reluctance to pay money to the employee.

The decline in the use of environmentally friendly detergents may be due to declining incomes in the last few years, as the promotion of environmentally friendly detergents has not declined and the number of companies trying to sell their detergents as environmentally friendly is increasing every day. While answering this question, many respondents probably did not know that relatively cheap laundry soap without synthetic additives is less harmful to the environment than a number of synthetic washing gels.

It is worth noting the tendency to increase the practical readiness of citizens to cover environmental issues in the media, write complaints and conduct a direct dialogue with violators of environmental regulations. If this trend continues, we can talk about the formation of civil society, which will be able to control the compliance of its members with legal and informal environmental standards.

How do Ukrainians feel about climate change? As for climate change, Ukrainians see it only in terms of "Threats to future generations at the global level." Moreover, the survey was conducted so as to take into account the answers to two questions simultaneously [4, 5]. Thus, in 2019, "environmental pollution" came in first place - 57.9% of Ukrainian respondents, and "depletion of natural resources" in third place - 32.2%.

Analysts [4] consider this a negative phenomenon, because such results demonstrate the lack of global thinking in Ukrainians, the lack of habit to think strategically outside the fate of their own children. The need to work on the development of ecological culture is undeniable, but we will further show that giving priority to climate threats leads to the dangerous disregard of other environmental problems. In fact, for each individual, the environmental problems that harm him or her here and now may not always be considered less significant than global warming 50 years from now.

As for the discrepancies between the willingness to take specific actions and the theoretical understanding that these actions are necessary, the results of the Ukrainian survey coincide with the results of the survey of Russian schoolchildren given in [6].

According to the results of this study, most schoolchildren are ready to take part in environmental actions (78.8% agree in whole or in part), but 51.1% of students are not yet ready to initiate actions and projects. Currently, only 9.2% of schoolchildren participating in the survey are members of public youth organizations, but 37.4% would like to try themselves as a volunteer.

We see that the environmental views of local communities are diverse and contradictory. For effective sustainable development, it is necessary to ensure the diversified participation of communities in solving environmental problems and give them the maximum opportunity to make independent decisions.

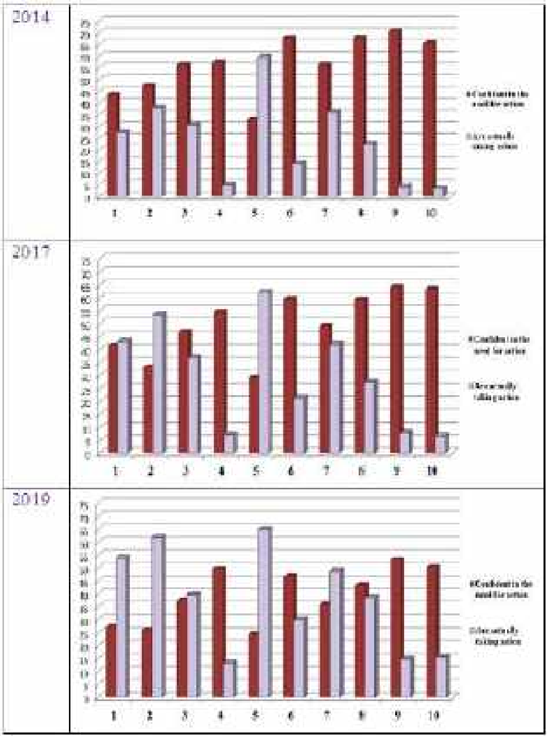

Fig. 1. Hypothetical (respondents are confident in the need for action) and practical (respondents are actually taking action) willingness to act for saving the environment, %

The automatic systems to reduce risks for life safety of population associated with climate change

In modern conditions of a changing climate, the uncertainty of weather conditions increases. Spontaneous manifestation of meteorological phenomena can lead to various negative consequences. This makes the development of risk management plans and action plans an important part of territory and settlement management. Most attention aimed at minimizing the negative impacts of climate change to which city is most vulnerable. Cooperation of units of the Department of Hydrometeorology, organization of the health care system, municipal services of the city, rescue service of the sanitary service, units of the State Water Agency of Ukraine is necessary for coordinated reactions.

For the south of Ukraine, the German experience of combating heat waves can come up. Since 2005 this country has a system of warning about hot weather, which can harm the health (Heat Health Warning System – HHWS). Public alert systems for heat can be on regional or local. The preliminary studies indicate a reduction in the heat related mortality since 2005 [7, 8, 9].

The aim of the German HHWS is the identification of weather situations that adversely affect human health based on human-biometeorological approaches. Thresholds for strong and extreme heat stress based on thermal perception classification are used and build the first approach of the HHWS. The threshold of strong heat stress includes short term adaptation component and the previous thermal stress conditions of the last thirty days. The second step includes nocturnal conditions, based on minimum air temperature and statistical percentages of the specific period or the calculation of indoor temperature simulations for typical houses. Both criteria are important for the decision making about warnings for the present and next days.

Warnings are generated by daily weather forecast and the biometeorology forecaster confirms or adjust.

The warning is valid on regional level including several elevation classes. The heat warning in Germany is available as maps in internet – registered users can receive information by daily newsletter. A specific smartphone app is also available for general use. The main target groups are nursing homes and ministries of the federal states and other authorities. In Ukraine such systems can provide notification to all population categories using various ways of transmitting information: via the internet, SMS, radio and television.

As the summer fires are quite typical for the forest and steppe landscapes of the south of Ukraine, it is important to keep emergency assistance and fire protection in a state of high readiness during periods of intense heat. Additional shaded areas can be provided for the population in parks, squares in periods of high temperatures. For example, France has the so-called "Blue Plan", which involves the organization of cool rooms with air-conditioners in homes for the elderly and health care institutions. At the expense of the budget air conditioners are purchased which should provide the air temperature not higher than 25 ºC in such rooms [10]. It is possible to at least partially introduce it in Ukraine. So far, supermarkets can serve as a public cooling place for those who have to spend a lot of time on their way to their destination.

The systematic insuring of life safety can be implemented by introducing automated monitoring and warning systems into key facilities up to all buildings located on the territory. An example would be Dubai Civil Defence 24x7 Smart Monitoring System, which installation in all public and private buildings is a mandatory requirement according to law No 24 of 2012. With the help of this system Dubai Civil Defence is able to monitor buildings in real-time for life and safety alarms, including fire-, elevator-, emergency alarm, safety equipment malfunction, power interruption, low water level in reservoirs, water pump malfunction and gas leakage alarm. The slogan of this government program is: “By joining hands, you, the people of Dubai and Dubai Civil Defence can make your city a safer place for everyone”. We find this slogan very useful for the formation of a sense of unity and mutual responsibility among the population without negative connotations [11].

Automated systems for monitoring the temperature field

For effective response in periods of high solar activity and heat, as well as frost, monitoring of high quality for the parameters of the external environment is necessary, which is difficult in the cities, because the temperature in the city differs from that given by the official meteorological station located outside it, and it also differs in some cases for different floors, types of buildings, microdistricts.

In the US, the problem was solved by creating the Citizen Weather Observer Program, which involves monitoring not only the temperature, but also some other meteorological characteristics, by private weather stations of various types that citizens install in their own places and serve them themselves [12]. To calibrate such measuring devices, it is proposed to reconcile their data with the data of the official US meteorological service presented on the program website. There after the calibration, the participant uploads his data, which allows creating much more detailed weather maps in the monitored area than can be provided only by official monitoring posts financed from the state budget.

In Chicago for better monitoring in the city, a group of researchers from the Urban Center for Computation and Data developed the project Array of Things. The Array of Things is a collaborative effort among leading scientists, universities, local government, and communities in Chicago to collect real-time data on the city’s environment, infrastructure, and activity for research and public use. The sensors are located on electric poles at a height about two times higher than human height, which solves the problem of vandalism. [13]. These methods are suitable for all countries, and in our study, the measuring instruments were also calibrated according to the data of a local weather station and are regularly checked with it.

The Black Sea National University is in the pilot operation of a set of environmental monitoring tools. This complex consists of a number of microprocessor servers equipped with external sensors, and integrated into a computer network of the University. In particular, this network includes temperature sensors installed indoors, on the pipes of the heating system, and outside the buildings, to monitor the temperature of the external environment. The temperature on these sensors can be tracked on the site http://old.chdu.edu.ua/ [14]. The obtained data are used both for scientific research and for making decisions about optimization of different rooms so that inner environment does no harm the health of people who work and study in them.

Emergency planning as well as climate change modeling is based on available temperature data. In order to achieve the greatest accuracy of models, all available data sources must be used. The density of terrestrial meteorological stations is not high enough for this [15], actinometric data must be supplemented by satellite data, for which various measuring systems are being developed, such as Photovoltaic Geographical Information System (PVGIS) [16]. The PV-GIS technique is an extrapolation of the results of actinometrical measurements based on the results of satellite photographs of real cloud cover.

The focus of PVGIS is research in solar resource assessment, and the dissemination of knowledge and data about solar radiation and PV performance. The largest uncertainty in estimating solar energy system output comes from the solar radiation data. Improving solar radiation data helps to make decisions on green energy; and improving meteorological data - to do planning considering the climate factor by reducing their uncertainty. As a result of comparisons with our local data (Mykolayiv), we were convinced of the high reliability of the PV-GIS technique for estimating illumination and temperature at a specific geographical point.

Another data resource for the south of Ukraine is the Prediction of Worldwide Energy Resource (POWER) project of NASA, which was initiated to improve upon the current renewable energy data set and to create new data sets from new satellite systems. The POWER project targets three user communities: Renewable Energy, Sustainable Buildings, and Agroclimatlogy. Data are available for this region from at least 1996 there [17].

Since in these conditions nuclear power is considered as the most favorable type of alternative energy in Ukraine, special attention should be paid to emergency management in this area. Having many advantages, nuclear energy can cause significant losses to the health of the population and the economy of the country in the event of disasters, which requires a minimum reduction of time for early response to an emergency. The experience of the Chornobyl accident has been used for improving the emergency response system, which should include clear procedures, necessary devices and equipment, pre-defined criteria and decision-making mechanisms.

Timely emergency iodine prophylaxis of the population during an accident at the NPP (nuclear power plant) is one of the important measures of radiation safety of the population. Iodine prophylaxis is to protect human from radioactive iodine by blocking the thyroid gland with stable iodine. The obvious component of iodine prophylaxis in the areas of the NPP is the regular consumption of iodine-containing products (sea kale, etc.), since the accident may occur unexpectedly, and the most affected by radioactive iodine are those who currently have a deficiency of this element in the thyroid gland. At the same time, constant monitoring of the situation in the region’s nuclear facilities is necessary.

In the 90-s of XX century on the territory of the Mykolaiv region functioned the System of quick emergency iodine prevention (SQEIP) of the population in the NPP region developed by Tomilin Yu.A. (Larani Scientific Library) [18]. SQEIP used dosimeters-monitors equipped with sound and visual alarms to react on exceeding the threshold levels located in the regional centers, the central control panel, which was based in the local headquarters for civil protection, and alerting the population by telephone.

Today, the South-Ukrainian NPP uses an automated radiation control system. Radiation control is carried out on the territory of the industrial site of the NPP, in the sanitary protection zone (radius of 2.5 km) and in the observation zone (radius of 30 km). When monitoring the natural environment, the radiation (gamma) level is monitored at 44 stations in the 30-kilometer observation zone and at the control station in the village Ryabokonevo (33.5 km from the South-Ukrainian NPP). In the framework of the reconstruction of the radiation control system of the nuclear power plant a new system of automated control of individual doses of personnel was put into experimental operation [19].

The same way as with monitoring of meteorological parameters, in the future, it would be useful to organize a radiation monitoring system or network in which the population of the region would be involved and which could supplement the measurements organized by the enterprise. Necessary instruments are available on internet: ZIVE, SMTGEG4S, Терра МКС-05, DO-RA etc. Modern devices are often adapted for use with mobile devices, working with networks in automatic mode, which makes them as simple for population as possible. DO-RA, for instance, automatically generates reports on the radioactive background of the territory in real time with GPS-based and GLONASS-based coordinates and passes them to the Radiation Analysis Center. In the world market, radiometric products are represented in a very wide spectrum, but they are usually proposed for individual dosimetry in a working or household environment, without focusing on the systematic use of information accumulated by citizens.

Automated system for measuring solar radiation and wind speed for green energy

Alternative energy sources are today considered as an important component in the transition of states to a carbon-free economy and sustainable development. One of the most suitable VDE for the Mykolaiv region are solar cells and wind power plants. At the local level, many residents are installing private solar panels or solar panel + wind turbine combined systems. The communities also decide on the advisability of placing industrial facilities of these types of energy in the area. The disadvantage of such sources is the high variability of parameters such as incolation and wind speed, which makes it necessary to use automated systems for monitoring and forecasting such parameters.

Petro Mohyla Black Sea National University has many years of experience in the study of solar and wind energy. A set of two polycrystalline silicon solar panels (each has capacity of 25W) was installed on the roof of the university to monitor solar radiation. The design of the stand allows us to explore the impact of batteries' orientation and to perform research on atmospheric transparency. To monitor wind speed there is an anemometer located beside batteries. This anemometer was calibrated using standard tools [20]. Solar panels are connected to the battery, and through an electronic switch to a microprocessor, which at the time of photocurrent measurement switches the battery on the reference load. The duration of a measurement is less than 0.1 seconds, and the interval of surveys is 1 minute, thus measurements do not affect the process of charging the battery. The results of photocurrent and wind speed measurements are processed by a microprocessor and passed on for archiving on a PC.

As expected, the largest wind was in winter, and the biggest insolation in summer. Daily average values of wind speed on the roof of the university changed from 0.5 to 5m/s, with the average value of approximately 1.85m/s. Mean values of the photocurrent in cloudless days changed from 0.43A in summer to 0.26A in winter. Given cloudy conditions (especially in winter) photocurrent decreases several tens of times, so the average of the photocurrent in multiday-interval reaches only 0.25A, which is about 7 times less than maximum photocurrent of the battery pursuant to the passport.

To ensure reliable power supply under conditions of low incoming solar energy or wind power, one should be able to accumulate, storage energy. Naturally, the battery capacity must be the greater, the longer are the "failures" in energy intake. In fact, battery performs averaging ripple of energy at a certain time interval.

The cases of low values for wind energy supply occur much less frequently than for the sun energy. That is the cases of prolonged absence of the sun for a few days (weeks) occur much more frequently than such cases for wind. Windy weather is typical for Mykolaiv region.

Integral probability function which shows how a minimum threshold of security of energy is exceeding relative to the average value was calculated to assess the reliability of energy supply. The corresponding results for several lowest threshold values of energy supply are given in Fig. 2. for 4 averaging intervals: 1, 3, 5, 7 days.

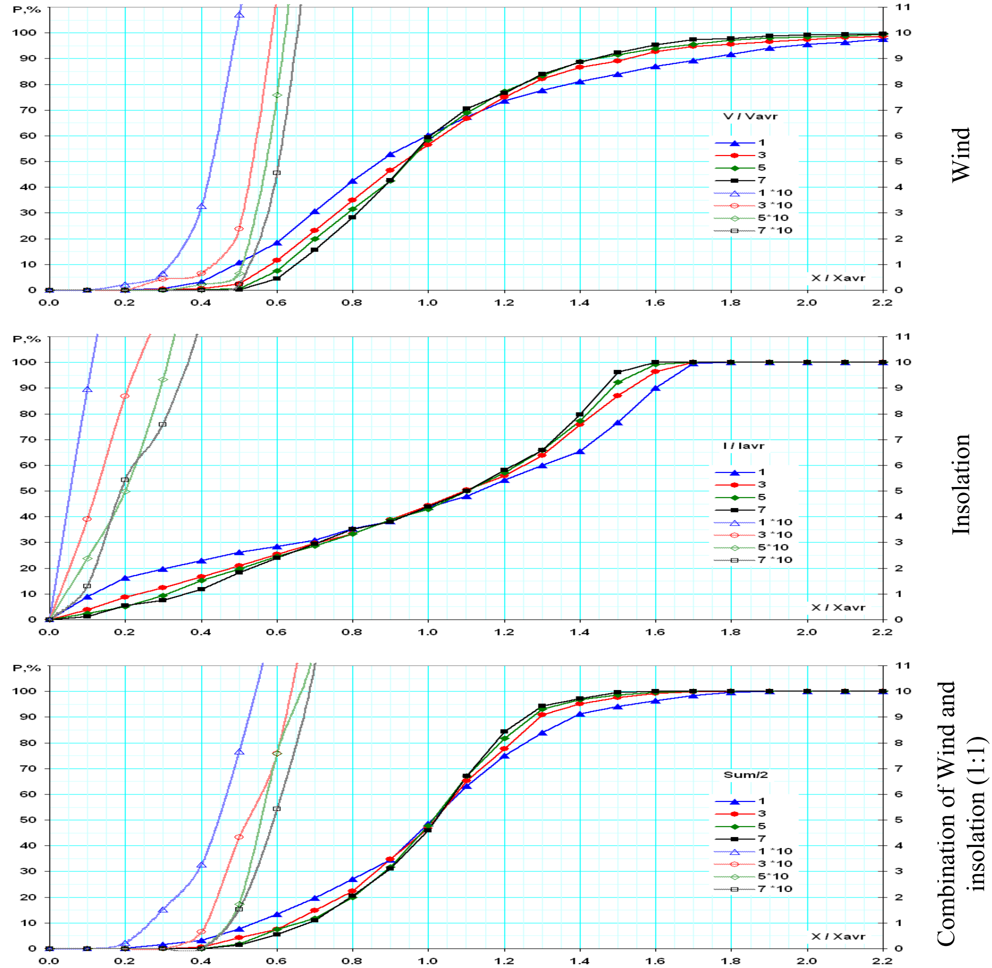

Fig 2. Integrated daily average probability of wind, insolation and their combination for different averaging intervals (accumulation) 1 - 7 days

Pretty optimistic view have the results for combination of wind and solar energy. Having a battery with 2 days capacity is enough to ensure that power does not fall below the threshold 0.3 of annual average. Given the cost of wind and solar power plants and accumulation systems, one could find the economic optimum of profitability ratio to make decisions on needed capacity.

CONCLUSION

1. Climate changes lead to such risks for life and health of the population in the south of Ukraine as heat waves and unexpected frosts. A rise in temperature in the summer months combined with low humidity significantly increases the risk of forest and steppe fires, which also causes the need for reliable information to the public about unfavorable days for picnics in the forest. This requires continuous improvement of meteorological monitoring networks.

2. PV GIS, NASA POWER and other global measurement systems as well as local measurements conducted by citizens help to create a more accurate temperature field, which is necessary to determine the climate characteristics at points where professional actinometrical

observations are not carried out. In the future, this will allow the creation of more accurate models for predicting emergencies and climate change.

3. Various studies show that the conviction of people in adopting environmentally friendly activities and their willingness to participate in these activities themselves do not coincide: people do not realize that many actions cannot be made effective without their own participation. Passivity of local communities is one of major obstacles to sustainable development

4. We believe that popularization of portable electronic devices and systems for monitoring environmental parameters among the population will allow people to feel involved in the processes of monitoring and managing condition of environment and climate change. In addition, it will speed up the response to disasters, as people will be more quickly aware of sudden releases of hazardous substances, and car owners will be able to evacuate themselves. However, this requires further research and development of a response methodology, when implemented, in order to prevent panic among the population.

REFERENCES

1. Sustainable Development Goals by UN.

URL:https://www.un.org/sustainabledevelopment/sustainable-development-goals/.

2. UNEP Environmental programme site. URL:https://www.unep.org/explore-topics/sustainable-development-goals/why-do-sustainable-development-goals-matter/goal-11.

3. WMO Greenhouse Gas Bulletin (GHG Bulletin) – No.15: The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2018. WMO. 2019.

URL:https://public.wmo.int/en/media/press-release/greenhouse-gas-concentrations-atmosphere-reach-yet-another-high.

4. Koval I. Ecology vs climate change: what is the difference and what is more important. How do Ukrainians perceive these risks and are they willing to pay for "security", business portal "mind.ua", 2019. (in Ukrainian). URL:https://mind.ua/publications/20205179-ekologiya-vs-zmina-klimatu-u-chomu-riznicya-ta-shcho-vazhlivishe.

5. Website of the Center for Social and Marketing Research SOCIS (in Ukrainian). URL:http://socis.kiev.ua.

6. Modern environmental problems through the eyes of schoolchildren: results of sociological research. The Bulletin of Pushkin Leningrad State University, Russia, 2018, №4, pp. 265-278. (in Russian). URL:https://cyberleninka.ru/article/n/sovremennye-ekologicheskie-problemy-glazami-shkolnikov-rezultaty-sotsiologicheskogo-issledovaniya.

7. Casanueva A, Burgstall A, Kotlarski S, et al. Overview of Existing Heat-Health Warning Systems in Europe. Int J Environ Res Public Health, Switzerland, 2019, is. 16(15): 2657, pp. 1-22. doi:10.3390/ijerph16152657.

8. Burdelna H., Bozhenko A., Population safety and sustainable development of urban and suburban territories of Ukraine under climate change, Collective monograph «Security management of the XI century: national and geopolitical aspects», Czech Republic, issue 2, pp. 126-133, 2020.

9. Hanna Burdelna, Anna Bozhenko, Apolonia Klepacz. The role of the climate global change mitigation in tactical and strategic planning in the post-Soviet region, Collective monograph «Modern approaches of socio-economic development of regions: theory and practice», Poland, part 1, pp. 128-135, 2020.

10. France's national report for the 18th session of the United Nations Commission on Sustainable Development (CSD-18) URL: https://sustainabledevelopment.un.org/content/documents/dsd/dsd_aofw_ni/ni_pdfs/NationalReports/france/Full_text.pdf .

11.The Official Portal of Dubai Government URL: https://www.dcd.gov.ae/portal/en/item/305.jsp .

12. Citizen Weather Observer Program site. URL: http://www.wxqa.com/index.html.

13. Array of Things project site. URL: http://arrayofthings.github.io/.

14. Bozhenko A. L., Zyulyaev D. D., Kozub S. V., Kubov V. I., Experiment of registering wind parameters in a digital system for measuring environmental parameters, Journal «Naukovi pratsi», series «Technogenna bezpeka», Ukraine, vol. 233, issue 221., pp. 21-32, 2014. (in Russian).

15. Uvarov I. A., Organization of processing meteorological information in remote monitoring information systems, Journal «Modern problems of remote sensing of the earth and space», Russia, v.10., No. 2, pp. 30-45, 2013. (in Russian).

16. The PV GIS project site. URL: https://ec.europa.eu/jrc/en/pvgis.

17. NASA Prediction of Worldwide Energy Resource (POWER) site**.** URL:https://power.larc.nasa.gov/data-access-viewer/

18. Tomilin, Yu. A., Grygorieva, L. I. System of quick emergency iodine prevention (SQEIP) of population in the NPP region, Conference «VI Congress on radiation research (radiobiology, radioecology, radiation safety)», Russia, 2010, vol. 1 (sections I-VII), p. 129. URL:https://inis.iaea.org/search/searchsinglerecord.aspx?recordsFor=SingleRecord&RN=45098664 .

19. Official website of South-Ukraine electric power producing complex.

URL:https://www.sunpp.mk.ua/uk/safety/radiating_safety.

20. Bozhenko A. L., Zyulyaev D. D., Kubov V. I., Pavlenko A. A., Evaluation of the economic efficiency of low-power sources of «green» energy for a summer cottage or backyard economy, Journal «Naukovi pratsi», series «Technogenna bezpeka», Ukraine, vol. 261, issue 249, pp. 22-29, 2015. (in Russian).

GEOINFORMATION SYSTEM OF LAND RESOURCES MANAGEMENT AS A TOOL FOR LAND REFORM IMPLEMENTATION IN TERRITORIAL COMMUNITIES ON THE SUSTAINABLE DEVELOPMENT BASIS

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ABSTRACT

The paper presents a mini-GIS, which was tested in the real sector of the land management system. The presented software is developed on the Windows platform and contains two components of a buz package and the information system developed on its basis. The topography is developed on TechnoCAD Editor's own graphics application. It is possible to use AutoCAD or another graphics editor that will save information in .dxf format. It is indicated that the practical experience of approbation of mini-GIS on the basis of their use in district departments of land resources and in village councils, allows to determine their practical significance and get a high enough positive assessment from the administrative staff of land managers. It is indicated that the Information system for land management can be a center of knowledge and experience in the practical application of map schemes based on GIS technologies for community capacity development. Emphasis is placed on a sufficient level of informativeness and relatively inexpensive, which determines the wide possibilities of its use at the level of territorial communities.

Keywords: geoinformation system, land resources management, topographic basis, decision making, attributive and spatial data

INTRODUCTION

Land relations in Ukraine are realized for ordinary citizens and entrepreneurs under the condition of legal regulation and a simple and convenient tool for its practical implementation. Modern reform of land relations is to implement many aspects, the main of which are:
• reforming in the conditions of decentralization on the basis of the ability of communities to fully dispose of their lands;
• use of cadastral systems to create convenient models of geospatial data;
• elimination of corruption components on the basis of transparent regulation of land relations with the help of the information system of land resources management, protection and rational use of land at the level of united territorial communities.

These are the requirements of modernity. And a decade and a half before that at the Land Resources Management Department, Petro Mohyla Black Sea National University, Professor Gorlachuk V.V. (now deceased), PhD, assoc. prof. Donchenko M.V. and PhD, assoc. prof. Yanchuk V.P. (then head of the Main Department of Land Resources) decided to develop an Information system for land management (ISLM), which was to be implemented at three levels: the Main Department, district offices and village councils.

ISLM has been developed and tested in more than ten village councils in a number of districts of the region. Experts noted the benefits of using the system. In practical terms, it was perceived at a high level due to the informativeness, simplicity and ease of working with it. The development was presented at a seminar in the State Land Committee with the support of the chairman Tretyak Anton Mykolayovych, where it received a positive assessment. The seminar was attended by the heads of the Main Departments of Land Resources of a number of oblasts, who showed interest.

However, at that time this initiative was not widespread in the country, the initiative was not supported by management staff due to the conflicting interests of the stakeholder group. However, the fact remains that the implementation of modern requirements in the reform of land relations is obviously greatly simplified with the help of GIS.

The administrative strategy of formation of territorial communities provides an important basis for the development of economic relations to land, careful treatment of land as a breadwinner, seriously and for a long time. Therefore, the issue of an integrated approach to decision-making on land management based on the use of GIS on the basis of sustainable development is becoming relevant again.

The question arises as to the feasibility of creating your own graphics application TechnoCAD Editor, if you know the basic GIS packages, examples of which are shown in table 1.

Table 1. GIS Software and companies

Manufacturer	Software	Price*
ESRI	ArcView, Arc/INFO	798 840 UAH
Autodesk GmbH	AutoCAD MAP 3D,	$5245
MapInfo	MapInfo Pro	102 000 ₽
Caliper	Maptitude	$995 - $12000
Integraph	GeoMedia	$15000 - 42000
CREDO-dialogue	CREDO	167330 UAH
Shels	GIS6	92680 UAH license for 20 jobs

*Prices are from the official websites of the companies

Packages are known, widely used and determine the sufficient functionality of the respective capabilities. On the basis of these packages it is possible to create GIS of any direction and with any databases. It should also be borne in mind that the creation of an information system based on basic packages is almost two to three times more expensive than the packages themselves, and this in their presence. In addition, the use of GIS requires highly qualified specialists, given the multifunctionality of tasks that can be implemented on the basis of GIS.

The issue of the cost of the basic package, the creation of an information system and its use is relevant, because they are quite expensive. After such arithmetic, it becomes clear that to use the system, it is desirable to create your own ISLM, which is more than ten times cheaper, more convenient and does not require special long training. So we decided to share our achievements and experience.

Theoretical and practical approaches to the creation of geographic information systems for land management as a tool for implementing land reform on the basis of sustainable development are reflected in the works of scientists such as Donchenko M.V.[1,2,3], Babenko OA. [4], Baranenko R. V. [5], Hrebenyk L.A. [6]

METHODS AND EXPERIMENTAL PROCEDURES

The purpose of the article is to analyze the stages of creating sufficiently rich information, simple, convenient, open to correction and addition of data and, at the same time, a cheap information system for land management.

The following task was set to create the ISLM: to develop an information system for the lower level of users, which would be able to operate with spatial and attributive data for decision-making, by monitoring, searching and providing information. The information system must meet the following requirements: accessible interface, ease of use, financially optimal option, does not require long and special training for users.

THE RESEARCH RESULTS AND DISCUSSIONS

In fact, it should be a mini-GIS on the Windows platform. During the development, it was concluded that it is necessary to take into account the possibility of widespread use of the information system on the WEB-platform (in smartphones and tablets) on the basis of open standards by the World Wide Web Consortium.

Since the territorial communities cover an area of several thousand hectares, it was decided to use conditional coordinate systems, building a topographic base at a scale of 1:1.

At the first stage, a topographic base was built, only for the distributed lands. In the future, it was planned to apply all land: water resources, settlements and homesteads, leased fields, as well as agronomic and protective actions in these fields.

Let's consider what ISLM consists of and work with it. The working window of the mini-GIS is presented in Figure 1.

The work window has three zones: a graphic zone, a menu and a zone with work with data.

The menu area consists of a drop-down and a graphical (icon) menu. The drop-down menu is the most complete and includes: opening, storing, setting, queries and navigation (Figure 2).

Fig.1. ISLM working window

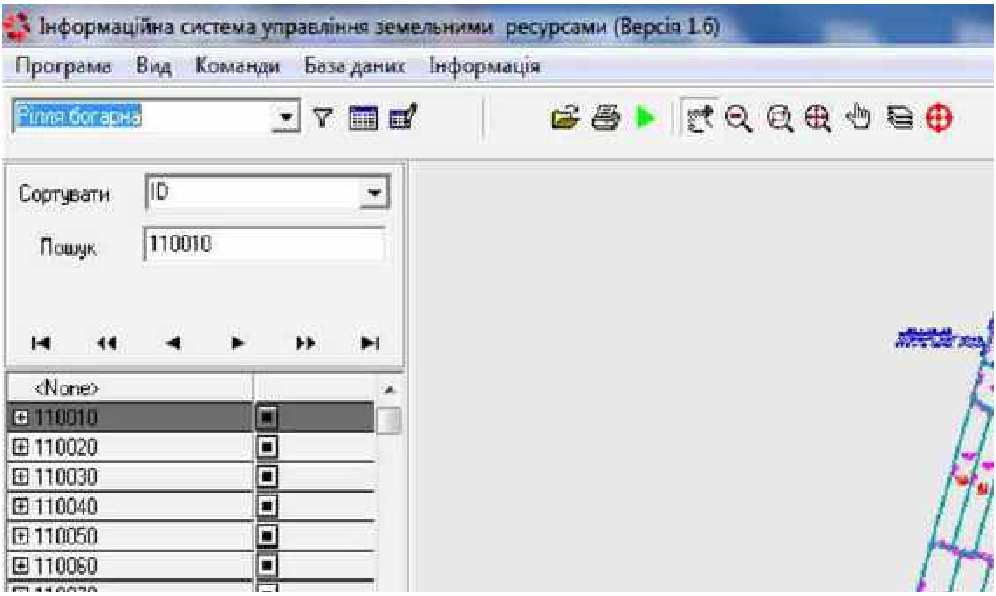

Fig. 2. ISLM menu

Most of these functions are in the graphical menu. Therefore we will consider only the graphic menu on points from left to right.

A list of resources if, for convenience or volume, they were created separately or only databases were created separately. When you select the appropriate section, the window is updated.

Creating queries. Conditions and execution of inquiries are set.

Table. The entire current data table opens.

Form. The current entry form opens.

Open. The required planning basis opens.

Printing. Print screen.

Editing the planning basis. Opens TechnoCAD Editor or AutoCAD (as configured) and loads the current scheduled editing framework.

Navigation. Pan, zoom, shows the selected window, displays the entire planning basis.

Spatial object selection. Displays data for this object.

Balls. Displays a window for working with layers.

Auto zoom. Displays a spatial object (plot) based on selected data with a small area around it.

On the left is **the data window**. You can perform: sort, search, move through the list and open data for the active object.

The list has two zones and two buttons for working with the data of the selected record (see Figure 2).

Working with graphic information. The active (selected in the list) planning basis is displayed in the window (see Figure 1, 2). In this embodiment, only unsoldering. Each plot has the plot number and area, soil types and area for each type, reference points and distances between them. Depending on the resources, there may be plots of arable land, gardens, pastures. If desired, you can put the names of the owner of the site.

You can perform monitoring or manual search by navigating the topoplane. If you activate the selection of a spatial object, the cursor takes the form of a "finger", the selected area is highlighted, and in the data area the corresponding line is highlighted and you can view data for this area in four ways: in the data area, in the table, in the form or all at once. More details on working with the data will be shown below.

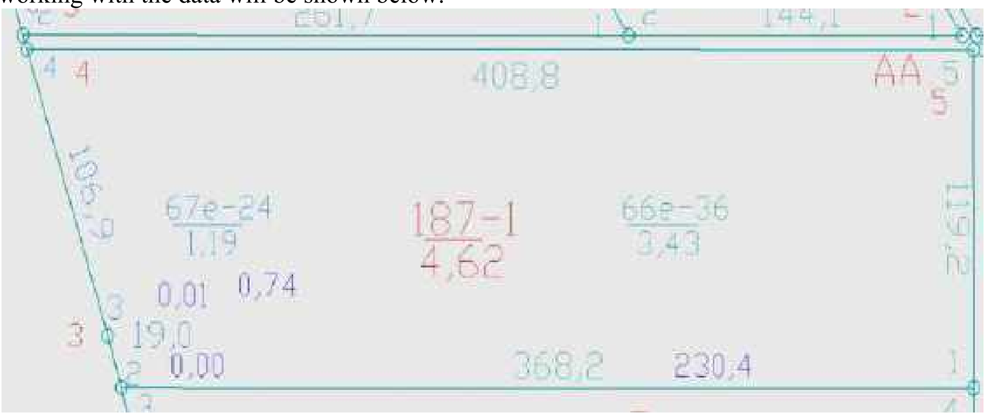

Fig. 3. Soldering section

Working with data. All data are entered into the table (Figure 4). The table can be viewed, edited and supplemented in the window.

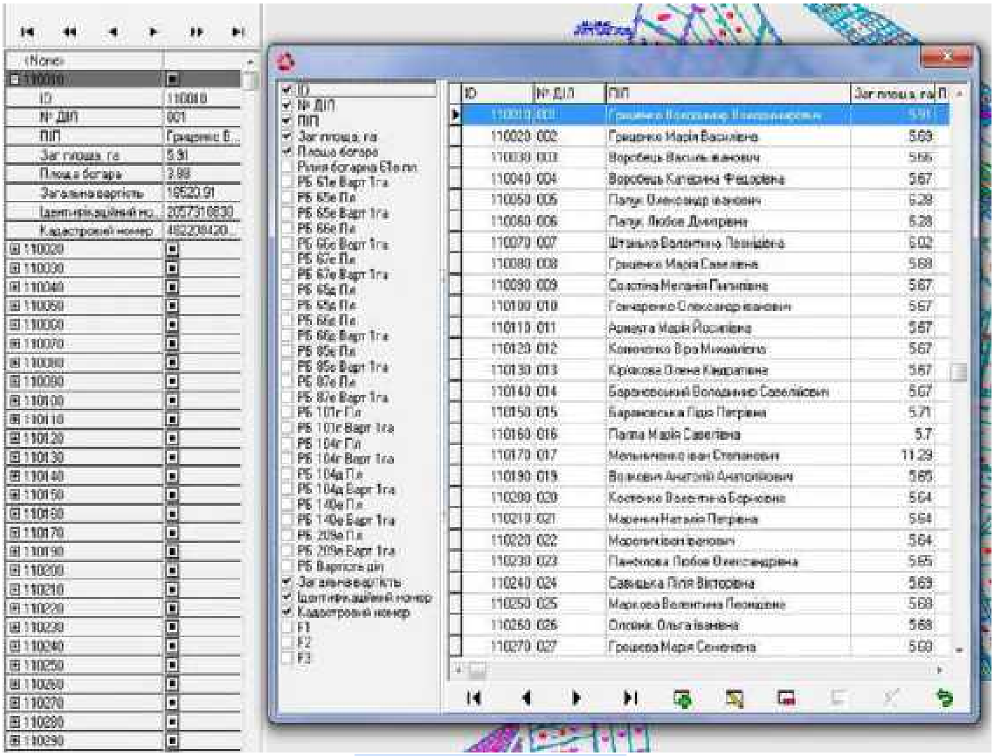

Fig. 4. Worksheet window

The table window has three zones: the table itself, the filter zone, and the control zone. You can use the keyboard to move through the lines using navigation (this can also be done with the arrow keys on the keyboard), and with the other buttons you can add, edit, delete, save or cancel changes, update data.

If you select a row in the table, the corresponding row in the data window is also selected. The same entry is completely displayed in the form window, if it is activated. With the help of filters (left) you can include in the work with data only those categories that are required for operational work and they will be displayed in the data window, in the work window and in the form window. Because the table is bulky, it saves a lot of work on the system desktop.

The data management window has two zones: identification categories and data to these categories. A complete list of large table entries is displayed in the identification area. Each record is identified by one of the categories that are activated in the filter area of the large table. Above the data management window is a list of sort IDs that are activated. Then a list of the corresponding identifier is displayed, for example, Full Name, area, cost. This ID can be used to search for queries (significant letters and numbers plus substitutes * or?). You can search using the navigation buttons.

The data area displays data for the corresponding identifiers.

If you activate the object selection button and click the "finger" on the site, the identification area will open their activated record and data for each of them. A kind of operational data table (Figure 5)

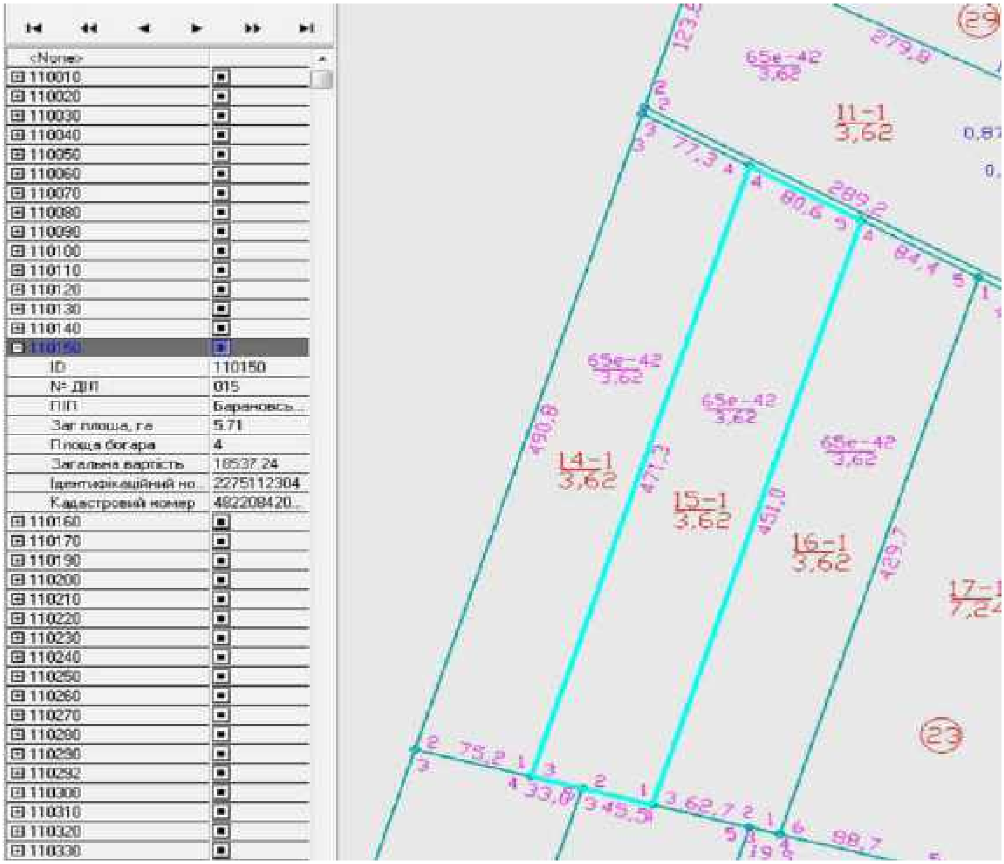

Fig. 5. Site selection and output of data about it

The form window will display the data for the selected area and can be edited. If, at the same time, the table is open, the corresponding record to this site will also be selected (highlighted).

This procedure allows you to obtain information about an object based on spatial data. It is also easy and simple to find (display) a site plan based on attribute data. To do this, activate auto-zoom and press the right button with a black square in the line of the selected ID. An area with some surroundings will be displayed. In this case, the operational plate in the data area will open automatically, and the black square on the button will become a blue triangle. Situational will be as in Figure 5.

If you click on the cross button of the selected record in the area of identifiers, the online data plate will open. Pressing it again will close it.

Using the form (Figure 6) to some extent automates the work with data, reduces the likelihood of error when entering and correcting data, and a floating window allows you to move it so as not to close the desired objects.

A separate query window greatly expands the ability to obtain information to support decision-making for many problems.

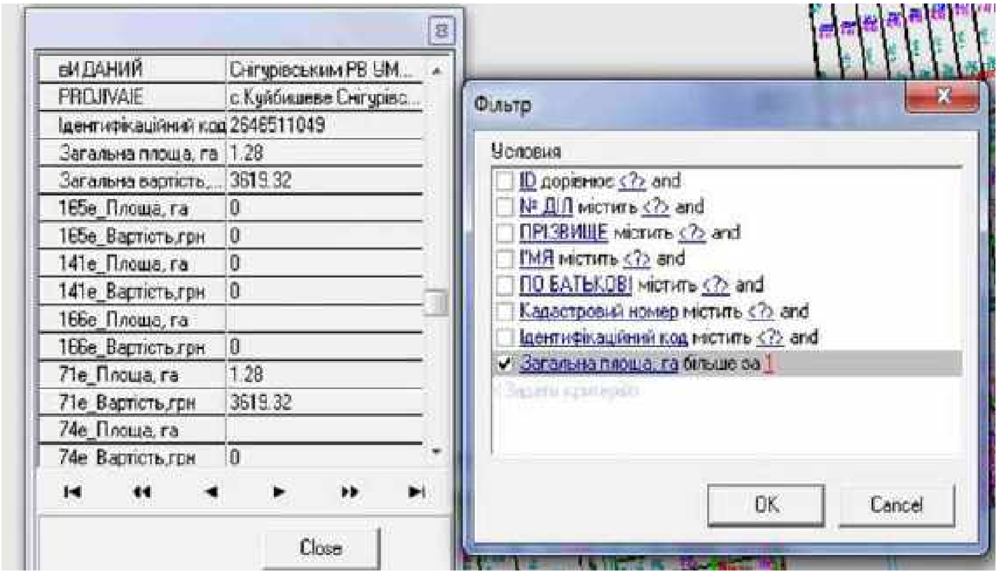

Fig. 6. Form and query windows

As can be seen from the figure, in the query window, you can specify the search condition for the selected category with logical operations and get the necessary information to make a decision.

You can create a topoplane in the created TechnoCAD Editor application, the working window of which is shown in Figure 7.

Fig. 7. TechnoCAD Editor application menu

The set of tools of the graphic editor is sufficient for performance of works on creation of a topographic basis. The menu consists of four groups: working with files, navigation, building primitives and editing objects.

Work with files - open, save, print.

Navigation - pan, zoom, show window, show everything, work with layers.

Construction of primitives - polyline, circle, regular polygon, rectangle, ellipse, text application, raster insertion.

Editing primitives - delete, move, copy, scale, rotate, select, layers, properties.

The graphic editor has its own secure format.

You can use another graphics editor that allows you to build the desired topobase and save it in .dxf format, such as AutoCAD, Corel Draw and others.

Depending on the target, the topoplan may include all land and water resources, settlements, agricultural enterprises, homesteads. It is possible to allocate the leased fields, zones on quality of soils and their condition, zones which need restoration of soils, nature protection zones, etc.

CONCLUSION

Geographic information systems should become a functional basis for the formation of a national informalized system of land resources, as an effective and rational means to obtain an array of spatial and coordinate information of functional purpose and ownership of land resources, monitoring, forecasting, use.

The presented mini-GIS aims to help local communities in the areas of effective land management based on GIS technologies; provide sufficient decision-making opportunities for most land management tasks for relatively small areas; to promote the development of the capacity of territorial communities to attract investments; focused on meeting the needs of local governments and business. The scientific novelty of ISUZR is that the complex problem was solved very simply, conveniently, with sufficient information and relatively inexpensive.

The program demonstrates what a full-fledged electronic system of land resources accounting of territorial communities will look like. The system was well received by experts due to its informativeness, simplicity and convenience of working with it. It can be relatively easy to expand, adjust and replenish. It does not require highly qualified users and is ten times cheaper compared to basic GIS packages.

The approbation of the Information system for land management showed that it is possible not only to organize all services, but also to look for investors. They can analyze all vacant lots in a very short time, seeing their advantages, limitations and opportunities. In fact, according to their model, all communities throughout Ukraine will be able to use such maps.

REFERENCES

1. Donchenko, M.V. & Butri,i A.P. (2004). Development of geoinformation system of the enterprise. Scientific works of NAUKMA. Kyiv: National University of Kyiv-Mohyla Academy, Ukraine. Vol. 35, № 22. pp. 157-162. (in Ukrainian)

2. Donchenko, M. V. & Kazariezov, A. Ya. (2018). Use of geographic information systems for early detection of emergencies. Scientific Journal of Computer Technology. Mykolaiv: Petro Mohyla Black Sea National University.Vol. 308, № 320. pp. 31-37. (in Ukrainian)

3. Donchenko, M.V. & Kovalenko I.I. (2012). Geographic information systems. Mykolaiv: Petro Mohyla Black Sea National University – p. 132. (in Ukrainian)

4. Babenko, O. A. (2018). Application of geographic information systems in land management. Journal of Cartography. Kyiv, Ukraine. Vol. 1(18), pp.17-25. DOI: http://maptimes.inf.ua/CH_18/Ch18_Article2_Using-GIS-in-land-management.html/ (in Ukrainian)

5. Baranenko, R. V. (2008). Models and algorithms of land resources management based on geoinformation technologies: Dissertation of the candidate of sciences. Kherson. p.200. (in Ukrainian)

6. Hrebenyk, L.A. (2018). Determining the optimal software product for monitoring land use by purpose. Journal of Cartography. Kyiv, Ukraine. Vol. 1(18), pp.37-44. DOI: http://maptimes.inf.ua/CH_18/Ch18_Article4_Optimal-soft-for-land-monitoring.html (in Ukrainian)

ACTUAL STATE AND PROSPECTS OF USING THE TERRITORY OF THE ROZDIL MINING AND CHEMICAL ENTERPRISE "SIRKA" FOR THE CONSTRUCTION OF RENEWABLE ENERGY FACILITIES

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ABSTRACT

The aim of the study is to analyze the policy and economics of solar energy sources in Ukraine and, in particular, in western Ukraine. The use of alternative energy sources in Ukraine, especially solar one, is extremely promising. Ukraine must play an important role in the adopted strategy of the state until 2030. The methods of analysis, comparison and synthesis used to assess the level of theoretical research are presented. The advantages and disadvantages of solar energy are given here as well. The directions of fundamental and applied research in Ukraine related to the development of solar energy are highlighted. Investment projects aimed at creating of solar-powered stations are being actively implemented in almost all regions of Ukraine. More than 100 solar energy projects with a total capacity of more than 1380 MW are being implemented at various stages in all regions of the country.

Keywords: solar energy, mining and chemical enterprise, sulfur, basic and applied research, Rozdil MCE *"Sirka"*.

INTRODUCTION

In line with the objectives of the Paris Climate Agreement, a signed and ratified document under the UN Framework Convention on Climate Change (UNFCCC) to regulate measures to reduce carbon dioxide emissions, there is a steady trend in the world to develop renewable energy sources (RES) and gradual replacement of traditional generation. In recent years, Ukraine has seen a gradual increase in installed RES capacity, primarily solar and wind power plants of various installed capacity. This was made possible primarily by the main economic stimulus instrument i.e. the system of "green tariffs", which are approved pegged to the Euro and guaranteed until 2030 (Fig. 1). At least 32% of RES is planned in the EU by 2030 [1-3].

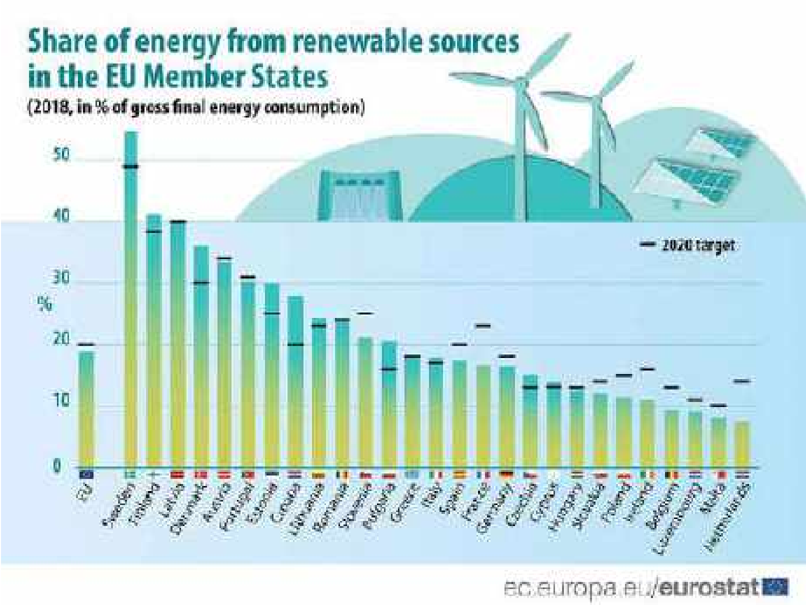

Fig. 1. Ambitions of EU countries for RES.

Currently, in the EU, solar energy creates 1,100 jobs for every TWh of electricity produced. This is several times more than any other energy sector, including nuclear, coal and gas [4–6].

In the world, despite the relatively small share of electricity production, this industry creates more employment than any other energy industry. According to IRENA, in 2017, solar energy created 3.4 million jobs worldwide [7, 8] (fig. 2).

Three out of four jobs in the industry are created locally. Small solar installations in the EU support almost three times more jobs and gross value added than large ones, as two thirds are roof systems that require more installation time.

Operation and maintenance account for about a third of all jobs. As maintenance and monitoring services are provided throughout the life of solar installations, they are a source of long-term jobs that are not affected by market fluctuations.

Solar energy is currently a powerful and fast-growing RES branch of industry.

Accelerated growth of solar PV combined with deep electrification could provide 21% reductions in CO_2 emissions (almost 4.9 gigatons per year) by 2050 [9].

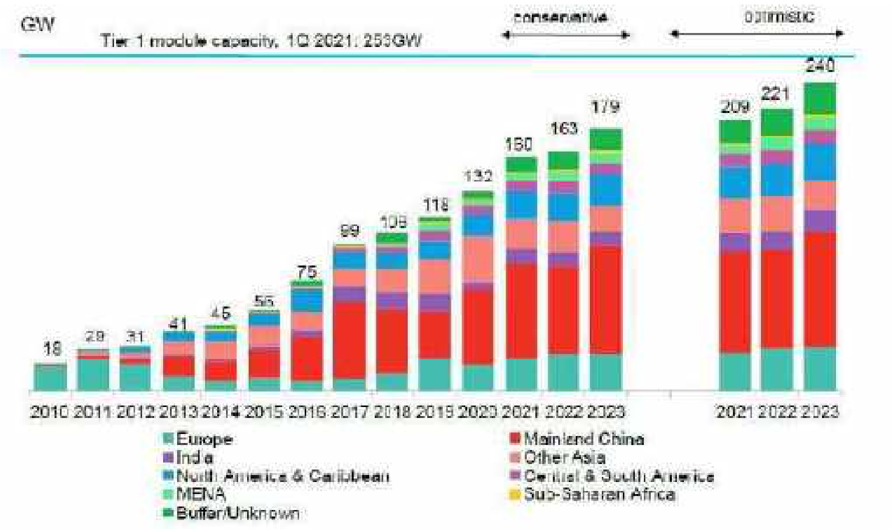

Fig. 2. 132 GW of SES capacity in the world was added in 2020 [10].

Solar electricity could cover a quarter of the world's electricity needs by the middle of the century, becoming the second largest source after wind. Global capacity could exceed 18 times the current capacity by more than 8,000 gigawatts by 2050 [11, 12].

According to official IRENA data from April 4, 2021, the total capacity of solar power plants in the world in 2020 increased by 21.6% – up to 714 GW. In particular, all European countries (including non-EU countries) in 2020 increased the capacity of solar power plants by 14.5% – up to 163.5 GW. In terms of total capacity (7.33 GW), Ukraine ranks 6th in Europe, second only to such industry leaders as Germany (53.8 GW), Italy (21.6 GW), Spain (14 GW), and France (11.7 GW) and the Netherlands (10.2 GW). According to the growth rate of the solar energy sector in 2020, Ukraine is in 4th place with a rate of + 23.5%. As for the American solar energy market, in 2020 the total capacity of solar power plants in the United States amounted to 75.6 GW, which is 24.5% more than in 2019.

According to the IB Center, in 2021 the total investment in solar energy projects may exceed $ 80 billion globally.

The European Union has set itself the goal of obtaining 32% of energy from renewable sources by 2030. As of 2020, the share of renewable energy in the EU is about 20% [13, 14].

In 2017, Ukraine adopted the Energy Strategy of Ukraine, according to which by 2035 Ukraine plans to increase the share of renewable energy in its energy balance to 25%. As of 2020, the share of renewable energy in Ukraine is about 3-4% and it seems that at this level this growth will stop for a long time [15, 16].

As of the end of November 30, 2020, there are more than 27,000 families in Ukraine who have installed home solar power plants. The total capacity of these SES is over 700 MW [17]. More than half a billion euros have been invested by families in their own solar panels. Thanks to SES, all these families become virtually independent in terms of electricity bills. They generate it themselves and use it for their own needs, and the excess of this electricity is sold to the grid, returning their investment.

Maintenance of solar panels is through simple and harmless actions, processes (repair, washing panels with water). The operation of solar panels does not affect the atmosphere in any way, because energy is generated by physical processes without emitting residues, on the contrary, residues - and is the resulting electricity.

The production of solar panels is made of clean materials that do not harm the environment, and their work is entirely to generate solar energy. Technologies have reached such a level that when building or finding a new way of obtaining energy in the first place must be in accordance with environmental standards.

Until 2030, the issue of recycling solar panels is not relevant for Ukraine, and after this period will not be a big threat [18, 19].

The amount of such waste from spent solar stations will be insignificant. The average lifespan of a solar panel is about 30 years. All over the world, electronics manufacturers are already responsible for the full life cycle of their products, including their processing.

The process of disposing of used equipment of solar stations is not complicated. All elements of solar panels - glass, aluminum frame, plastic substrate and thin silicon wafers can potentially be recycled 100%. The vast majority of materials used in solar modules are recyclable and reusable. Today, the volume of waste generation from solar energy is close to zero.

Today, 55 countries, 140 major corporations and hundreds of cities are committed to a full switch to 100% renewable energy. Most countries belong to those where they strictly care about the environment, care about the health and future of their citizens. Even the most meticulous searches find no arguments against the use of "green" energy, which includes solar energy.

Advantages of the technology: do not require fuel; rapid reduction in technology: by almost 90% since 2009. Disadvantages of the technology: require large areas; dependence on weather conditions, time of day and season; impossibility of accurate forecasting of electricity production.

Figure 3 shows the potential of solar energy in different European countries. The use of alternative energy sources in Ukraine, primarily solar one, is very promising. The average solar energy potential in Ukraine (1235 kW h / m) (Fig. 3a) is quite high and much higher than, for example, in Germany - 1000 kW h / m (Fig. 3b) or even in Poland - 1080 kW h / m (Fig. 3c) [20].

Favorable economic conditions for the development of RES contribute to investors' search for areas suitable for the design and construction of solar and wind power plants. Among the requirements for such areas are the purpose of land, among which preference is given to areas outside settlements, non-agricultural land with energy infrastructure - power lines, transformer substations, the presence of electricity consumers, energy facilities that could maintain the energy balance. in case of unstable operation of RES, etc.

6 cities of Ukraine have already officially announced about plans to reach 100% RES by 2050.

The purpose of the work is to assess the prospects of using of the territory of Rozdil MCE "*Sirka*" for the construction of renewable energy facilities. Today, such lands include the territories in the zone of influence of the Rozdil MCE "*Sirka*", which was founded in 1953 in connection with the development of a fairly large Rozdil sulfur field.

METHODS AND EXPERIMENTAL PROCEDURES

Characteristics of the enterprise.

Rozdil MCE "*Sirka*" was developing rapidly in the 50's - 80's of the XXth century, when deposits of sulfur ores were discovered. Then their geological exploration was carried out.

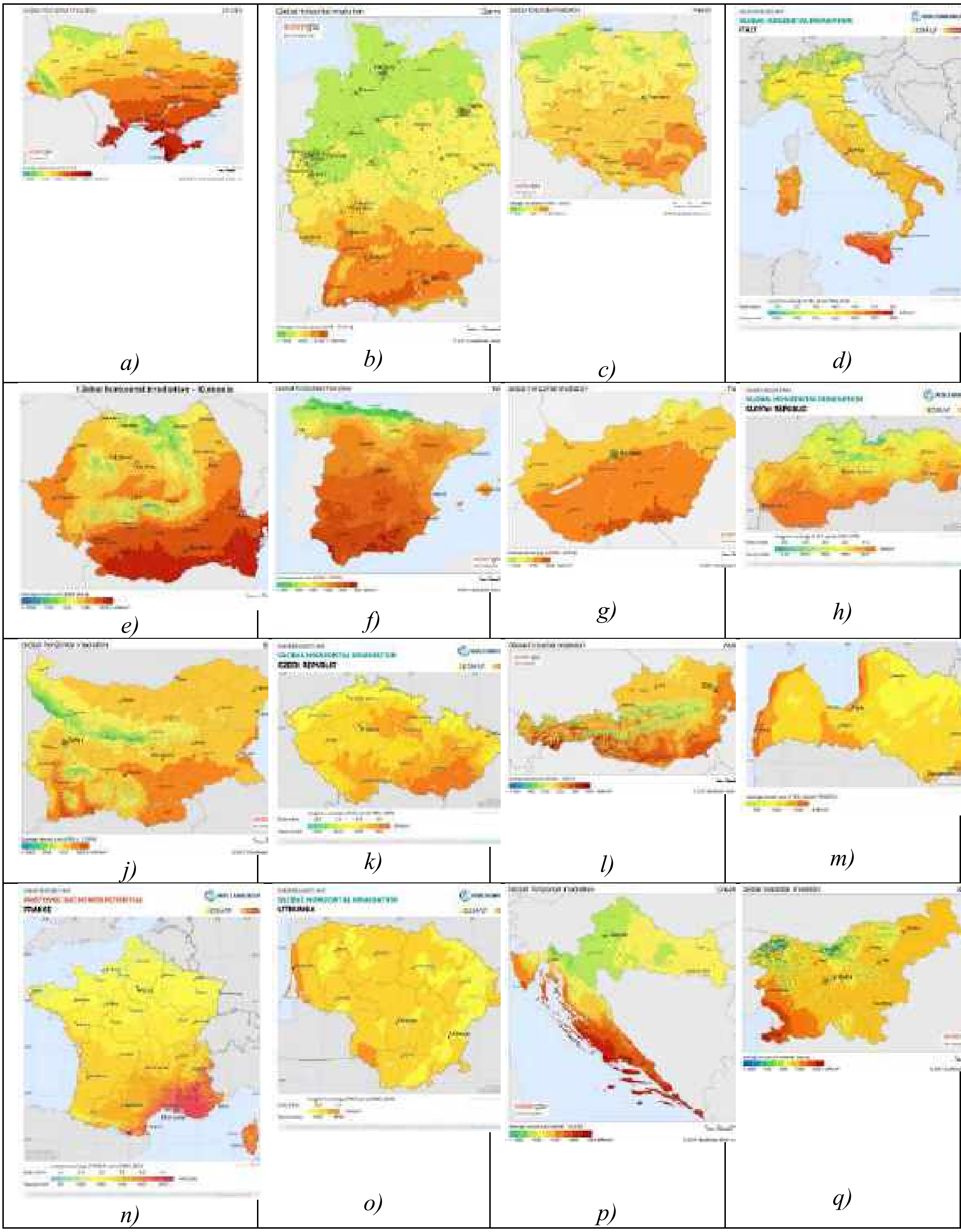

Fig 3. Annual average potential of solar energy in Ukraine – (a), Germany - (b), Poland –(c), Italy – (d), Romania – e), Spain – f), Hangry – g), Slovak Republic – h), Bulgaria – j), Czech Republic – k), Austria – l), Latvia – m), France – n), Lithuania – o), Croatia – p), Slovenia – q)

Three quarries (South, Central and North) were put into operation, a concentrator, a plant of complex mineral fertilizers, and industrial waste storage facilities were built. Sulfur-based mineral fertilizer production was about 800,000 tons per year [21].

SES potential in Ukraine is 68.5 GW by 2040 in order to achieve the goals set by the Paris Climate Agreement, ratified by Ukraine.

The Rozdil plant's facilities cover the floodplain and floodplain terrace of the Dnister River valley within the small rivers of Barvinok and Kolodnytsia. Man-caused objects and formations occupied an area of 2200 ha, including: residual excavation of the quarry – 263 ha, external dumps – 853 ha, tailings pond №1 – 220 ha, tailings pond №2 – 140 ha, settling pond – 130 ha, accumulation pool – 127 ha, sulfur production – 125 ha, hydraulic dump of loams – 125 ha, plant of complex mineral fertilizers – 93 ha, phosphogypsum dump – 58 ha, biostands – 18 ha.

Sulfur deposits near Novyj Rozdil were found in in the middle of the 20th century, where the development of a sulfur deposit was started. Over time, in addition to the quarry, companies specializing in the production of ground sulfur, plant protection products - fungicides and complex fertilizers began to operate. About 12,000 workers were involved in their production.

In the early 1990s, sulfur production ceased, and the process of restructuring of the mining and chemical plant on an area of about 22,000 hectares began. The company has a developed infrastructure, energy and water supply system, railway [22].

As of 2000, the Rozdil sulfur deposit has already been fully developed - all explored deposits have been removed from the subsoil, landscapes disturbed by mining operations within the study area are being rehabilitated and brought to a safe for humans and the environment state in accordance with the developed complex project.

Rozdil MCE "*Sirka*" is located in the floodplain and floodplain terraces of the Dniester river valley, limited by small rivers Barvinok and Kolodnytsia and covers an area of about 22 km^2 (Fig. 4).

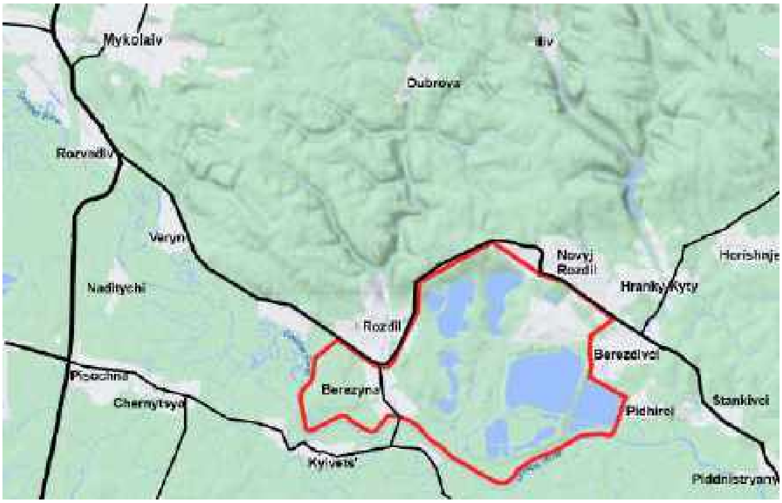

Fig. 4. The location of the zone of influence of Rozdil MCE "*Sirka*" within the Mykolayiv district and neighboring districts of Lviv region.

The location of accumulated waste on the territory of Rozdil MCE "*Sirk*a" is shown in Fig. 5. On the south-eastern shore of Seredne Lake there is a landfill of the town of Novy Rozdil (Fig. 5). Garbage storage area is 8 hectares. The average thickness of the garbage layer is 7 m, the volume can be estimated at 660 thousand m^3. As a result of leaching of easily soluble compounds by atmospheric precipitation, a filtrate is formed, which flows into Seredne Lake. Due to the burning of garbage and the release of biogas, the air is polluted.

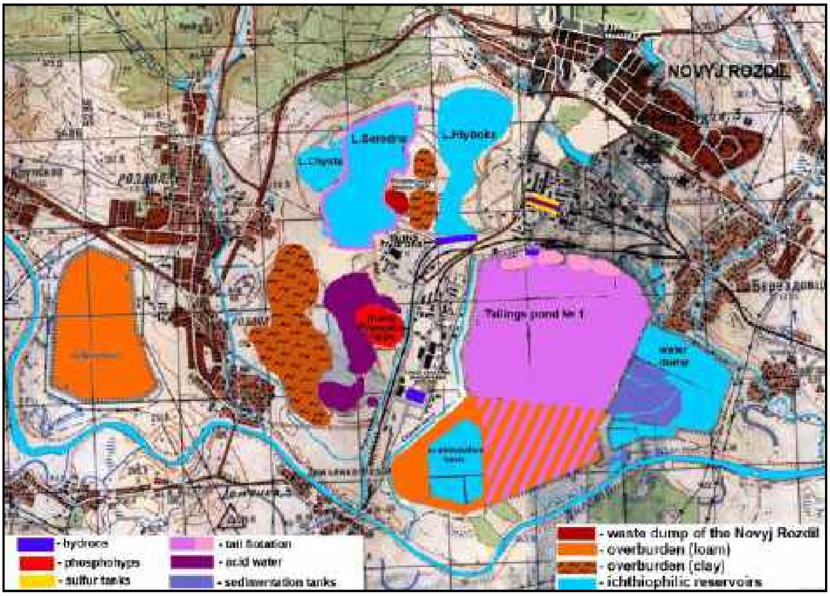

Fig. 5. Spatial location of waste on the territory of Rozdil MCE "*Sirka*"

The eastern part of the Northern quarry was flooded and Lake Hlyboke was formed here with a maximum depth of 45 m. On the southern shore of Hlyboke Lake, at a distance of less than 20 m from the water's edge, there is a tar dump. Two more tar dumps are located in the Cryolite shop of the Novorozdil plant of complex mineral fertilizers and in the northern part of the tailings pond No.1 (Fig. 5). The chemical composition of tar is a residue of oil refining, enriched with heavy hydrocarbons and sulfuric acid. As a result of leaching of toxic compounds: phenols, heavy hydrocarbonsand sulfuric acid the infiltrates are formed, which flow into reservoirs and are a powerful source of pollution of the transboundary Dniester River.

THE RESEARCH RESULTS AND DISCUSSIONS

The Crimean Peninsula and Steppes of Ukraine are the most promising regions of the country for the development of solar energy. Currently, the largest solar power plant is located in Okhotnikiv (Saksky district of the Crimea). At the end of 2012, its capacity reached 80 MW. The size of the solar power plant is equivalent to 207 football fields. Upon completion of construction, the facility is equipped with 360 thousand ground modules. The solar park in the Okhotnikiv district is the fourth PV plant in the world and the third in Europe.

Many studies have been devoted to the efficiency and effectiveness of the use of solar energy in Ukraine [23, 24]. Significant results were obtained at the Institute of Semiconductor Physics and the Institute of Electrodynamics of the National Academy of Sciences of Ukraine, Shevchenko National University of Kyiv, Yuriy Fedkovych National University of Chernivtsi, Kyiv Politechnical Institute National Technical University, Lviv Polytechnic National University, some industrial enterprises ("Pillar", "Kvazar") and other Ukrainian laboratories. Researchers have shown that the cost of solar cells is reduced to 0.5 – 1.1 euros per watt of power. So over the last quarter of a century, it has decreased 20 times (compared to the first model of 1950!). In principle, this is not so far from the characteristics of gas and gasoline engines: 0.1-0.15 euros per watt (Fig. 6).

Fig. 6. Price trend for crystalline silicon panels (ITRP)

So we have good opportunities for efficient use of heat and power equipment in Ukraine. The term "efficient use" means that the solar station can operate with an efficiency of 50% or more, which is 9 months in the southern regions of Ukraine (March to November) and 7 months - in the northern region (April to October). Winter rates are declining, but not disappearing. Thus, in our climate, solar systems operate all year round with some variable efficiency. Therefore, it is necessary to take into account the total annual potential of solar energy in Ukraine.

As for the use of solar radiation for energy production, the technically permissible potential of solar energy on the roof of housing in Ukraine today is 26-37 TW • h / year, which costs (at a current cost of 1 kW • h = 0.05 euros): 1.3 -1.8 billion a year [25].

The use and development of alternative energy sources leads to the creation of a unique new technology. An example is the use of solar energy in domestic aviation. Ukraine has its own aircraft industry (Antonov State Aviation Concern and Ukraine Aviation State Concern) and has inherited the third space potential of the former USSR (the National Space Agency of Ukraine), which in turn is the basis for a pilot project [26, 27].

Advantages of solar energy: solar energy is inexhaustible and available; it is safe for the environment.

Disadvantages: dependence on weather conditions; dependence on the day and night; it must be able to store energy; the construction of power plants of this type is quite expensive; the surface of the panels should be periodically cleaned of dirt and dust; The atmosphere over power source is quite hot.

In developed countries, significant investments are made in new research and development, the main purpose of which is to reduce the cost of solar energy and the formation of new consumption markets. Let us mention the "Million Solar Roofs" program in Germany, Italy. etc. The governments of the United States, Japan and West Europe encourage the use of solar energy by the population, primarily because it is environmentally friendly and in Europe saves limited fossil fuel resources. To do this, interest-free long-term loans to people to purchase solar panels are provided by a free service [28, 29].

*Areas of scientific research of solar cells in Ukraine***.**

Basic research

Due to theoretical limitations in the conversion of useful energy (about 30%) for solar power plants based on solar cells of the first and second generations, it is necessary to have very large plots of land. Therefore, a 1 GW station may require an area of several tens of square kilometers (while in hydropower at the same facilities it is necessary to abandon the use of even much larger land). The construction of solar power plants of the same capacity can cause climate change around the station. Therefore, solar energy is usually built with a capacity of 1-2 MW, which is not too far from direct consumers. Individual or mobile installations are also being built. Panels in large power plants are installed at a height of 1.8-2.5 meters above the ground, so you can use the land under the power plant for agriculture, for example, for grazing. This problem is solved by using a solar station on a balloon. They can be located both on land, in the sea and in the air.

The flow of solar energy, which falls on the photocell installed at the optimal angle, depends on latitude, season and climate and can vary twice depending on the inhabited parts of the land. Atmospheric phenomena (clouds, fog, dust, etc.) not only change the range and intensity of incident solar radiation on the Earth's surface, but also change the relationship between direct and diffuse radiation, which strongly affects certain types of solar power plants, such as concentrators or broad spectrum elements.

Applied research.

Photoelectric cameras operate during the day and with low efficiency in the morning and evening. In this case, the peak of electricity consumption occurs in the evening. In addition, the electricity they produce can change dramatically and change unpredictably depending on the weather. To reduce this dependence, solar power plants use rechargeable batteries (but in this case they are quite expensive). It is possible to convert energy into another form, for example, sometimes a pumping station can be built, which can take up a fairly large area, and it is possible to implement projects based on the concept of hydrogen energy. But now it is not effective. The problem is solved by creating homogeneous networks that redistribute the generated energy and energy consumption. The problem of the dependence of the specific power of solar energy on the time of day and weather conditions is also solved with the help of aerostatic solar systems.

After 30 years of use, the productivity of the elements gradually decreases. Sometimes solar cells contain cadmium, and they can't just be thrown away. There is a problem of their utilization.

On June 3, 2011, the American Journal of Research and Development published the annual list of winners of the prestigious 100 Research and Research Countries Competition, including the Taiwan Institute of Textile Research and Lviv Polytechnic National University. The title of the article was:" Fully flexible fabric capacitor" [30]. The Chicago Tribune called it "The Oscar of Inventions."

Environmental Issues.

The level of pollution in the production of solar cells does not exceed the permitted level for the companies of microelectronic industry. Age of photocells often exceeds 30-50 years.

The use of cadmium compounds in the production of certain types of solar cells raises the question of their disposal, although these items are not very common, except for cadmium compounds in modern production, such solar panels have been replaced. Currently, the increasingly common thin-film solar cells which contain only about 1% of the total mass of silicon. Due to the low cost of materials thin-film silicon solar cells are much cheaper, but they are less efficient and most lose their properties quickly. Now the production of other semiconductor materials, in particular the CIS and KIGS, is developing more and more actively. They can be serious competitors to silicon. So in 2005, company Shell decided to focus on only thin-film cells and got rid of its monocrystalline photovoltaic elements.

Solar Energy Prospects.

According to the International Energy Agency (IEA), energy which is produced with the help of solar energy by 2050, can provide 20-25% of the energy needs of mankind, i.e. in 30 years solar energy can produce about 9000 terawatt-hours. This will reduce carbon emissions by 6 billion tons annually.

In 2001, the price of energy produced by solar panels was 0.09 - 0.12 dollars US per kWh. The US Department of Energy predicts that by 2015-2020 the price of energy produced by solar concentrators will fall to 0.04 - 0.05 dollars. In Ukraine, the established "green" tariff for electricity produced by private households is relatively high. Households that install the installation by January 1, 2015, will be entitled to sell electricity at a price of € 4.67 / kWh (VAT) or approximately 36.2 cents / kWh. This is very attractive compared to Germany, where the "green" tariff is 19.5 cents / kWh.

Production capacity of only such giant industrial associations of microelectronics, as "Kvazar", "IRVA" (Kyiv), "Graviton" (Chernivtsi), "Hartron" (Kharkiv), "Gamma" and "Elektroavtomatika" (Zaporizhzhya), "Dnipro "(Kherson)," Positron "(Ivano-Frankivsk) provide a full technological cycle of solar cells. Ukraine has a highly qualified scientific potential in this field.

There are more than 100 solar energy projects in all regions of Ukraine, the total capacity of which exceeds 1380 MW at different stages of implementation. In Ukraine, solar stations are also being built, in addition to local companies, by companies from Portugal, Germany, France, Austria, the Czech Republic and Israel.

Other applications of solar energy are: telecommunication systems and services (repeaters, telemetry); providing power to navigation lights, buoys, road signs, road lighting at night; corrosion protection of metal structures and pipelines; remote and non-electrified housing for power supply of household appliances; in security alarms; agriculture and arid areas for mining and water supply; creation of a network of automatic stations equipped with various sensors for environmental monitoring, etc. Finally, solar cells play a crucial role in spacecraft and artificial satellites as on-board power systems.

Thus, the use of alternative energy sources in Ukraine, primarily solar energy, will undoubtedly benefit. On the other hand, Ukraine's economy has sufficient capacity to produce the necessary components and create the infrastructure for such capacity.

According to Ukraine's Energy Strategy until 2030, the share of renewable energy should be 11% of total energy produced by Ukraine. This is in line with Ukraine's commitment to the European Energy Community, to which Ukraine is a party. 11% is 12,000 MW, of which 6,800 MW is a large share of hydropower plants (HPPs and PSPs), and 5,200 MW is a share of small hydropower, wind, solar and biomass and biogas. According to the annual commissioning of 500-700 MW of new renewable energy sources, Ukraine will fulfill its obligations by 2030.

Sulfur ore beneficiation wastes as man-made deposits.

In the process of enrichment the sulfur ore was ground and sulfur was extracted by flotation and the tailings were obtained at the outlet which contained several times less sulfur, but higher content of limestone and strontium, compared with the raw materials.

The bulk of the flotation tails (65 million tons) are stored in the tailings pond No. 1, which is located near the southwestern outskirts of the village of Berezdivtsi. It is fenced with a dam on an area of 300 hectares (Fig. 5). After filling this tank, the waste was temporarily accumulated on the territory of the hydraulic dump adjacent to the tailings pond No.1 from the south. It is surrounded by dams from the local soil and filled with sands and loams to the mark of 255 m. The thickness of the washed soil is about 10 m. The thickness of the tail layer is 2 m, the surface mark is about 257 m. gypsum anhydrites lie at the bottom, and limestones and marls near the sides. The bedrock is covered with a poured and compacted layer of dump clays, on which the flotation tails are washed. A total of about 20 million tons of flotation tailings are stored at the hydraulic dump and tailings pond No.2 (Fig. 5).

The mineral composition of the flotation tail is calcite, with impurities of native sulfur, gypsum, celestine, barite, quartz and clay minerals. Physico-mechanical properties of sulfur ore beneficiation waste depend on the particle size distribution. There are sand, dust and clay fractions, their ratio is approximately 25: 35: 40. The sand fraction settled near the place of discharge of waste into the tailings. From there, the sands were excavated and poured into burts - the so-called "Limestone Mountains", where they were drained naturally. Dusty fractions accumulated in the peripheral parts of the tailings. To drain them you need to carry out complex drainage measures. Clay fractions occur in the cores of tailings and remain in a fluid state for decades. Their drainage is associated with significant difficulties.

The technology of sulfur ore beneficiation provided for the reversible use of water. To restore its quality, a settling tank with a pumping station was built by settling. In terms of mineral composition, sediments of circulating waters are similar to flotation tailings and differ from them only by a more fine-grained particle size distribution. Atmospheric precipitation, which infiltrates the thickness of the flotation tails, contributes to microbiological changes in elemental sulfur. This leads to the formation of hydrogen sulfide water, which flows from the drainages in the eastern part of the tailings No.1 in the form of leaks and springs (Fig. 7).

Fig. 7. Leakages of hydrogen sulfide waters from the drainages of the eastern part of the tailings No.1

The increased content of dissolved hydrogen sulfide in the water is recorded at the bottom of Lake Seredne during winter and summer testing. However, the hydrogen sulfide waters at the bottom of Lake Seredne disappear due to mixing with waters containing dissolved oxygen during spring and autumn inversions. Today, the daily surface of tailings No.1 and hydro dump is covered with soil-vegetation layer [31, 32], flotation tailings at tailings № 2 - with a thin layer of silt and lake water.

Prospects for the use of sulfur ore flotation waste are primarily related with their use as raw materials for production of potassium sulphate fertilizers, lime, plaster solutions, putties, spreading screeds for floor bases, bituminous mastics, in the cement industry, for soil liming, neutralization of acid effluents, as a rubber filler, preservative for sugar components, cleaning for baths, which neutralizes the acid reaction, powder for roofing material, flame retardant for extinguishing burnt heaps and mortar material for the elimination of karst cavities and mines.

Strontium present in the tailings of flotation in higher concentrations than in primary sulfur ores is non-radioactive (it does not contain the radioactive isotope Sr-90). Studies have shown that strontium tailings flotation does not have a negative impact on both soils and aquatic ecosystems [33, 34]. Thus, the storage sites of sulfur ore flotation tailings within the Rozdil SMCE "Sulfur" can be considered as promising man-made deposits of ground limestone. Especially valuable are its large factions, stored in burts, the so-called "Limestone mountains". The total residual volume of coarse-grained flotation tailings within the Limestone Mountains is 2.4 million m3. This is a ready-made sulfur-lime fertilizer, which has proven itself effectively during the liming of acidic podzolic soils. Sulfur ore from the Rozdil and Podorozhnensk deposits, which was enriched at the Rozdil MCE "*Sirka*", consisted of approximately 70% limestone, 25% native sulfur and 5% other minerals, including the main carrier of strontium - celestine. In the process of enrichment of sulfur ore, it was ground and sulfur was extracted by flotation the outlet tailings contained several times less sulfur, but higher content of limestone and strontium, compared with the raw materials. In fact, the tailings pond No. 1 (65 million tons) and the hydraulic dump No. 1 (10 million tons) are man-made strontium deposits with a content of 1 to 3.35%, which, under favorable conditions, can be developed on an industrial scale.

In the case when the flotation tailings in the tailings pond NO. 1 will not be developed, *the leakage of hydrogen sulfide waters can be considered as man-made deposits after their capture and conducting research to determine the medicinal properties and calculation of reserves*. In our opinion, there are no strong objections not to use the leaks from the eastern dam of the tailings No.1 as a valuable balneological resource of a promising man-made deposit of hydrogen sulfide waters (Fig. 4).

Lump sulfur is the final product of sulfur ore extraction and enrichment, stored in the open air in the warehouse of Novorozdil sulfur enrichment plant east of Lake Hlyboke and north of the tailings pond No. 1 (Fig. 5). The total volume of stored sulfur is about 700 m^3. After a long time on the day surface, lump sulfur is oxidized and sulfuric acid and acidic waters are formed, with pH values 1-2, which accumulate in the central channel and in the eastern part in the form of spills, and is unloaded in the direction of the Dnister transboundary river. The existing remnants of lump sulfur should first be isolated from the effects of precipitation to prevent the formation of acidic waters. In the presence of consumers, lump sulfur can be used for the production of sulfuric acid, insecticides, etc.

Phosphogypsum ***i**s* an industrial waste from the production of phosphoric acid from apatite concentrates and phosphorites, the main mineral of which is apatite Ca_5 (PO_4) 3F, which is insoluble in water and not absorbed by plants. To obtain a mineral fertilizer, it is converted into a soluble form, for which it is treated with sulfuric acid. As a result, soluble phosphates are formed, and calcium and fluoride go to waste. The production of 1 ton of phosphoric acid, depending on the type of raw material accounts for from 4.3 to 5.8 tons of phosphogypsum. Phosphogypsum is stored in the area between the complex mineral fertilizer plant and the residual excavation of the Central quarry. There are about 3 million tons of phosphogypsum left in the open warehouse (Fig. 5).

In terms of mineral composition, phosphogypsum is a product of chemical reactions between sulfuric acid and apatite concentrate, which mainly contains gypsum (CaSO4 * 2H2O) with an admixture of phosphates and fluorides. In addition to apatite, nepheline and other minerals present in the concentrate also decompose. In terms of dry matter, phosphogypsum contains 94% CaSO4, 1.8% undecomposed apatite, 1.8% phosphoric, 0.22% hydrofluoric acid, 1.92% insoluble residue, up to 1% iron and aluminum oxides. The water content in fresh phosphogypsum is 42%, of which 17-19% is included in the crystal lattice of gypsum, and 22–24% is free.

Stored phosphogypsum quickly coagulates, compacts in proportion to the load and reaches its maximum density at a pressure of 5 - 6 kg / cm^2. At the same time it becomes so dense that dump trucks freely pass a surface of a heap of phosphogypsum. In shear tests, it behaves as a bound ground with an internal friction angle of 31o and a clutch of 21 KPa. But unlike bound soils, phosphogypsum in the load range up to 10 kg / s m2 does not show plastic properties, does not stick to the surface of the excavator bucket or bulldozer shovel. The phosphogypsum filtration coefficient is quite large: 0.46 - 1.4 m / day.

Phosphogypsum is a phytophilous waste for acid-loving woody vegetation, especially sea buckthorn. Embryonic soil is born here. In phosphogypsum mining areas, the embryo soil is disturbed and precipitation gains direct access to unwashed phosphogypsum. As a result, elevated concentrations of toxicants flow into Lake Kysle.

Water leached from phosphogypsum by atmospheric precipitation contains residues of sulfuric, phosphoric, and hydrofluoric acids, resulting in the formation of acidic waters (Fig. 5). The presence of fluorine in apatite causes the formation of hydrofluoric acid HF, which dissolves silicates and turns into hydrofluoric acid H_2SiF_6. In addition to calcium, sulfates, phosphates, fluorine ions, Fe, Na, Al, Mo, Cu, Ba, Cd, Sr ions pass into the solution.

Enriched with these components, acidic waters accumulate in the lake near the phosphogypsum dump. During the operation of the plant complex mineral fertilizers acidic water was neutralized by liming. After the cessation of production, a lake was formed in the excavation of the central quarry, where about 0.5 million m3 of contaminated water accumulated. The water in the lake is acidic with pH values 5-6 on the surface and pH 2-3 at the bottom, contains the above-mentioned pollutants, is ichthyotoxic with a specific greenish-gray color and is a powerful source of pollution of the transboundary Dnister River [35–39].

Phosphogypsum can be used in the cement industry as a raw material for the production of alabaster, plaster solutions, putties, potassium sulfate fertilizers, neutralization of alkaline soils, mortgage material for the elimination of karst cavities and mines. There are significant reserves (3 million tons), and it gives grounds *to consider the phosphogypsum dump as a man-made deposit* [40–42].

Overburden sands, loams, clays and marls. Dump sands and loams, which were extracted from the root deposit by the method of hydromechanization, were accumulated in two hydraulic dumps - near the village of Berezina (hydraulic dump No. 2) and south of the tailings pond No 1 (hydraulic dump No1) – fig. 5. Marl-clay dumps fill the quarries of the Southern and partially Central quarries, they fill the dams separating the excavations of the Northern quarry and internal dumps. Part of the marl-clay heaps is located above the day surface and it can be removed for economic needs (Fig. 5). Both sandy loams and loams, and marly-clay dumps are phytophilous and are overgrown with grass, and sometimes shrubs and trees. They are a valuable raw material for the production of ceramic bricks and cementand and can be considered as a backing material for the elimination of karst cavities and mines. This gives grounds to consider overburden rocks in the places of their occurrence above the day surface as potential man-made deposits [43–45].

Solar power plants on the territory of Rozdil MCE "Sirka".

To date, two solar power plants have been built in the area of influence of Rozdil MCE "*Sirka*" – on hydraulic dumps No. 1 and No. 2 (Fig. 7 and Fig. 8).

Fig. 7. Solar power plant on the hydro dump No. 1

Fig. 8. Solar power plant on the hydro dump No. 2

CONCLUSION

Further development of technologies and growth of installed capacity of electricity storage facilities is expected to ensure the integration of wind and solar electricity in energy systems.

The cost of producing solar electricity, which is already below the marginal cost of producing electricity from fossil fuels in the global dimension, will continue to decline over the coming decades, driven by innovation throughout the value chain. The average annual investment in solar electricity by 2050 will increase by 68%. The global solar-related industry could employ more than 18 million people by 2050. We can expect further growth of solar thermal energy, in particular in district heating and production processes.

The directions of fundamental and applied research in Ukraine related to the development of solar energy are highlighted. The conducted researches give grounds to consider the territory in the zone of influence of Rozdil MCE "*Sirka*" including on sites of storage of waste and products of their natural transformation, as perspective sites for construction of solar and wind power plants. These include tailings of sulfur ore, strontium, hydrogen sulfide, phosphogypsum, dump clay and loam.

REFERENCES

1. For updates see Capacity and Generation tool. BloombergNEF Note. 2020.

2. New Energy Outlook 2021 – Executive Summary. BloombergNEF, 2021, 16 p.

3. https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en

4. EU4USOCIETY. Geletuckha G. Project to promote Ukraine's transition to "green" energy. What is the European Green Course? Advantages of its implementation for Ukraine. 28 s. 2019.

5. EU4USOCIETY. Project to promote Ukraine's transition to "green" energy. Kramar V. The state of development of solar energy in the world and the European Union. 24 s. 2019.

6. EU4USOCIETY. Project to promote Ukraine's transition to "green" energy. Semenyshyn A. Status and prospects of solar energy development in Ukraine in the context of decarbonization. 32 s. 2019.

7. IRENA. Global energy transformation: A roadmap to 2050 (2019 edition), International Renewable Energy Agency, Abu Dhabi. 2019.

8. IRENA, FUTURE OF SOLAR PHOTOVOLTAIC Deployment, investment, technology, grid integration and socio-economic aspects. 73 p. 2019.

9. The main trends in the field of solar energy in 2020 https://solarity.com.ua/blog/pv-trends-2020.

10. Bodis K. et al. Solar photovoltaic electricity generation: A lifeline for the European coal regions in transition, Sustainability, Vol. 11, Issue 13, pp. 3703, 2019. https://doi.org/10.3390/su11133703.

11. Green M.A. Photovoltaic technology and visions for the future, Progress in Energy I, Volume 1, Number 1, 2019, https://doi.org/10.1088/2516-1083/ab0fa8/pdf

12. Kumar N.M., Sudhakar K., Samykano M., Jayaseelan V. On the technologies empowering drones for intelligent monitoring of solar photovoltaic power plants, Procedia Computer Science, Volume 133, pp. 585–593, 2018. https://doi.org/10.1016/j.procs.2018.07.087

13. Thurstom C.,W. Solar carports thrive on dual-use concept. PV Magazine Photovoltaic markets and technology, March 2019.

14. Shravan K., Chunduri K. Advanced solar module technology – The time for a new generation of solar modules has come, Taiyang News, China, 2019.

15. Mysak, Y.S., Vozniak, O.T., Datsko, O.S., Shapoval, S.P. Soniachna enerhetyka: teoriia ta praktyka [Solar energetics: theory and practice], monograph, Lviv, Ukraine, 2014, 340 p.

16. Dziadykevych Yu.V., Buriak M.V., Lubezna I.V. Development of solar energy in Ukraine. Innovative economy 1-2, 2018, pp. 120-125.

17. https://mind.ua/news/20219578-v-ukrayini-27-000-rodin-vstanovili-domashni-sonyachni-elektrostanciyi

18. https://ecodim.net/news/vpliv-sonyachnih-elektrostancij-na-ekologiyu-ta-zdorovya-lyudej

19. https://ecolog-ua.com/news/cisolar-2021-ukrayina-uviyshla-do-top-5-yevropeyskyh-krayin-za-tempamy-rozvytku-sonyachnoyi

20. Global horizontal irradiation (GHI) – SolarGIS. The maps of Global horizontal irradiation for various. http: // solargis.info

21. Zozulya I. I., Gaidin A.M. Green Section. Problems of ecological revival of Novy Rozdil, 30 p., 2002.

22. Pohrebennyk V., Dyakiv V., Dzhumelya E., Kovalchuk M. Assessment of the current state of mining and chemical enterprises at the stage of liquidation. Scientific and pedagogical support of sustainable development: discourse 2019: a collective monograph. Sumy: Vinnichenko M.D., pp. 38–56, 2019.

23. Gibilisco S. Alternative energy without secrets. Moscow, 2010. ISBN 978-5-699-36367-4

24. Vozniak O., Yaniv M. Energy potential of solar energy and prospects of its use in Ukraine. Bulletin of the Lviv Polytechnic National University. Theory and Practice of Construction. Lviv, 2010, 664, pp. 7-10.

25. Petrova A. et al. Energy-saving technologies in industry. Moscow, 2011. ISBN 978-5-91134-458-0

26. Pohrebennyk V., Aleksander M., Karpinski M., Kantor T., Mitryasova O. Prospects of solar energy use in Ukraine. Agricultural Engineering. 2014, № 4 (152). P. 165-173.

27. Pohrebennyk V., Savchyn M. Experience of using solar energy in international and world practice. Unconventional and renewable energy sources as alternatives to primary energy sources in the region. 2013. Lviv, 223-226.

28. Scheer H. The Solar Economy: Renewable Energy for a Sustainable Global Future. Moscow, 2004**.** ISBN 978-1844070756

29. Skryshevsky V.A. What is solar energy and does Ukraine need it today? 2008. http: // aratta-ukraine.com

30. Il’chuk H., Shapoval P. and V. Kusnezh. *Engineering «Energy Engineering» "Solar Cells - Thin-Film Technologies"*, book edited by L. Kosyachenko, ISBN 978-953-307-570-9. Published: Chapter 18 Chemical Surface Deposition of CdS Ultra hin Films from Aqueous Solutions, 2011.

31. Bilonoga V.M. Vegetation succession on dumps of sulfur deposits in the Carpathian region: Author's abstract. dis ... cand. biol. sciences. Dnipropetrovsk, 16 p., 1989.

32. Boyko T.I. Geochemistry of sulfur and strontium in the zone of technogenesis of sulfur mining enterprises of Precarpathia. Author's abstract. Candidate of Dissertation geol. Science. Lviv, 25 p., 1995.

33. Gaidin A.M., Dyakiv V.O., Mazyar L.P. Behavior of strontium in aquatic ecosystems of lakes on the site of sulfur quarries of Precarpathia. Lviv-Shatsk, Abstracts of the scientific conference "Modern problems of the protected area "September 8-9, pp. 3-4, 2006.

34. Halperin A.M., Foerster V.I., Chef H.Yu. Technogenic massifs and environmental protection, Moscow: Publishing house of Moscow State University, 534 p., 1997.

35. Mariskevich O. G, Shpakivska I. M. Peculiarities of soil formation on dumps of Rozdil MCE "Sirka". Scientific notes of the State Natural History Museum of the National Academy of Sciences of Ukraine. Lviv, pp. 147-152, 2001

36. Pohrebennyk V., Dzhumelia E. Environmental assessment of the impact of tars on the territory of the Rozdil state mining and chemical enterprise “Sirka” (Ukraine). In Sustainable Production: Novel Trends in Energy, Environment and Material Systems. Studies in Systems, Decision and Control; Królczyk, G., Wzorek, M., Król, A., Kochan, O., Su, J., Kacprzyk, J., Eds.; Springer: Cham, Switzerland, 2020; V. 198, pp. 201–214, 2020.

37. Pohrebennyk V., Mitryasova O., Dzhumelia E., Kochanek A. Evaluation of surface water quality in mining and chemical industry, 17th International multidisciplinary scientific geoconference SGEM 2017, Bulgaria, pp. 425-432, 2017.

38. Pohrebennyk V., Karpinski M., Dzhumelia E., Klos-Witkowska A., Falat P. Water bodies pollution of the mining and chemical enterprise. In Proceedings of the 18th International Multidisciplinary Scientific GeoConference, SGEM, Albena, Bulgaria, 30th June to 9th July 2018**,** 18 (5.2), pp. 1035-1042.

39. Mitryasova O., Pohrebennyk V. Hydrochemical indicators of water system analysis as factors of the environmental quality state. In Sustainable Production: Novel Trends in Energy, Environment and Material Systems. Studies in Systems, Decision and Control; Królczyk, G., Wzorek, M., Król, A., Kochan, O., Su, J., Kacprzyk, J., Eds.; Springer: Cham, Switzerland, 2020; V. 198, pp 91–104.

40. Pohrebennyk V., Dzhumelia E., Mason A., Cygnar M. X-Ray fluorescent method of heavy metals detection in soils of mining and chemical enterprises. 9th International Conference on Developments in eSystems Engineering (DeSE) : proceedings, 1st August-1st September 2016, Liverpool John Moores university, Al Khawarizimi international college, Leeds Backett University, 2017, pp. 323–328.

41. Ivanov Y., Kovalchuk I., Andreychuk Y. Klyuynyk V. & Tikhanovych Y. Functioning and development of post-mining geosystems of the Western region of Ukraine, Materials of International scientific and technical conference of young scientists “GeoTerrace-2018” - Ukraine, 2018, pp 65-70, (In Ukrainian).

42. Pohrebennyk V., Koszelnik P., Mitryasova O., Dzhumelia E., Zdeb M.: Environmental monitoring of soils of post-industrial mining areas, Journal of Ecological Engineering, 2019, Vol. 20, iss. 9, pp 53–61.

43. Rudko H.I., Bondar O.I., Yakovlev E.A., Mashkov O.A, Plakhotnyi S.A, Ermakov V.N. Ecological safety of coal deposits of Ukraine. Kyiv–Chernivtsi: Bukrek, 2016.

44. Rudko G.I., Ivanov Ye., Kovalchuk I.P. Mining geosystems in the western region of Ukraine, Vol. 1, Kyiv–Chernivtsi: Bukrek, 2019.

45. Rudko G.I., Ivanov Ye., Kovalchuk I.P. Mining geosystems in the western region of Ukraine, Vol. 2, Kyiv–Chernivtsi, Bukrek, 2019.

STUDY OF SUSTAINABLE DEVELOPMENT OF THE TERRITORIES OF MINING INFLUENCE AND CHEMICAL ENTERPRISES BASED ON ENVIRONMENTAL POLLUTANT CONTROL

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ABSTRACT

The development of human society and the satisfaction of its needs takes place with the constant extraction and further use of natural resources. The result is a significant generation and accumulation of industrial waste. Waste management is one of the most painful problems today and is a priority in all developed countries. In Ukraine, because of the generation of large amounts of waste, this problem has become particularly acute. A prerequisite for the transition of society to sustainable development, defined by the "An Agenda for the 21st Century", is the introduction of the principles of sustainable nature management in the economic activities of countries.

Mining activities are one of the main sources of environmental contamination through metals released due to soil erosion. High concentrations of metals in soils and consequently into soil groundwater could have negative effects on terrestrial ecosystems and could pose potential health risks.

This study is based on the principles of a systematic approach to the analysis of the content of pollutants in the elements of the environment in influence of mining and chemical enterprises.

It is concluded that current mining practices need to change and contribute to community development with more equity, and to protect better natural resources and ecosystems to be environmentally acceptable and compliant with sustainable development objectives. As the problem of non-implementation of projects of reclamation and remediation of the territories disturbed by mining and chemical activity still remains acute in Ukraine, it is no less important to ensure sustainable development of the territories of influence of mining and chemical enterprises.

Keywords: sustainable development, environmental monitoring, ecological control, anthropogenic influence on the environment, soil and water pollution.

INTRODUCTION

In its landmark 1987 report, the World Commission on Environment and Development defined sustainable development as "development that meets the needs of today without compromising the ability of future generations to meet their own needs".

Sustainable development is a guiding principle of long-term development that balances economic and social development and environmental sustainability. The universal importance of sustainable development has recently become more firmly recognized than ever, as evidenced by the historic adoption of the 2030 Agenda for Sustainable Development and the 17 Global Sustainable Development Goals (SDGs) by 193 UN member states in 2015.

Studying the current state of achievement of sustainable development goals and effective ways of transition to sustainable development is important for both research and practical needs, as it allows to live in a stable ecosystem. The study of the ecological component of development needs special attention in this issue, because a prerequisite for the transition of society to sustainable development, defined by the "An Agenda for the 21st Century", is the introduction of the principles of sustainable nature management in the economic activity of countries.

Environmental pollution is one of the most serious global challenges. Every year the issue of environmental pollution becomes more acute. Deterioration of the ecological situation is facilitated by the constant release of pollutants into the environment, which cause an increase in the greenhouse effect, acid rain, ozone holes, pollution of the oceans and reduced soil fertility.

As a result of industrial production in areas of location of various enterprises and places of extraction of minerals, and also quite often near settlements there are the centers of industrial desert with insignificant vegetation and even without it. In the ecological aspect, mining facilities form a conditional exclusion zone with indicators of forced man-made impact on the components of the environment. The formed anthropogenic landscape is characterized by significant negative quantitative and qualitative changes in the area of influence of the mining complex. The soil here is contaminated with industrial emissions, construction waste, ash from thermal power plants, rock extracted from mines and quarries as a result of underground work, flooded with petroleum products, household waste, etc. In such areas, the soil is so spoiled that it loses fertility. In 2000, the mass of production waste in the world exceeded 100 billion t; up to 30% of them are solid waste from industry, urban and agriculture.

The industrial load on the environment from emissions of enterprises per 1 km^2 of the country's area is about 6.5 tons, per capita – more than 80 kg / per year. Ukraine has not yet gained serious experience in the field of industrial and household waste disposal: only 5-10% of waste is recycled, and the rest is accumulated in the form of landfills, which become objects of environmental danger. Violation of ecological balance from the impact of the mining and chemical enterprise leads to geochemical and geophysical anomalies of anthropogenic origin. In the area of influence of the mining and chemical enterprise and production wastes, there are zones of the increased concentration of separate chemical elements and their connections [1-7].

The initial idea of creating tailings was the safe storage of industrial waste. But in Ukraine, tailings are often turned into objects of chronic pollution.

Within the Dniester River basin, 32 tailings ponds with 162 million t of waste have been identified. The most dangerous objects in the Dniester basin are the tailings of three enterprises that are in critical condition and need urgent measures to prevent accidents: SE "Rozdil Mining and Chemical Enterprise "Sirka"" (SE "Rozdil MCE "Sirka"") (three tailings ponds, approximately 108.9 million t, distance to the Dniester River is 380 m) LLC "Oriana-Eco" (three tailings, 26 million m^3) PJSC "Stebnyk Mining and Chemical Enterprise "Polimineral"" (one tailing, 12.74 million m^3).

At SE "Rozdil MCE "Sirka"" sulfur production waste generated as a result of former open-pit sulfur production is stored in tailings ponds located in different parts of the field, and waste from the production of mineral fertilizers – in a phosphogypsum dump.

Also, on the industrial site of the enterprise, the modifier of the MG type made of tar residues is stored. 10 years ago, a canal was created from the man-made lake Hlyboke to the cross-border river Dniester without treatment facilities [8, 9].

METHODS AND EXPERIMENTAL PROCEDURES

The purpose of the work is to theoretically and methodologically substantiate a systematic approach to the analysis and control of the content of pollutants in the elements of the environment in the area of influence of mining and chemical enterprises.

The methodological basis of the study is based on the use of methods of analysis, synthesis, comparison, generalization, and formalization to justify the effectiveness of modern and proposed tools for evaluating and ensuring sustainable development.

Structurally, the problem is based on the analysis of the content of modern systems for normalization of anthropogenic pressure on the environment, comparing their advantages and disadvantages, highlighting the problem niche, and the synthesis of potential activities to fill it.

Soil contamination with heavy metals near industrial waste was analyzed by measuring their concentration in the soil at different distances from the landfill.

Soil samplings were analyzed using X-Ray Diffraction (XRD) technique.

The concentration of elements in the sample was determined by X-ray spectrometry using an S2 PICOFOX Bruker X-ray spectrometer – detector type: silicon drift detector, high voltage generator: MNX 50P50 / XCC, X-ray source: metal ceramic air cooled MCB50-0.7G, X-ray optics: multilayer monochromator.

THE RESEARCH RESULTS AND DISCUSSIONS

Territories of mining and chemical enterprises that are in liquidation, in accordance with the law are subject to reclamation, i.e., restoration of valuable properties.

Reclamation work is the responsibility of the industrial enterprises that have destroyed these lands, and the cost of reclamation should be included in the cost of finished products. General requirements for soil reclamation in Ukraine are regulated by GOST 1-7.5.3.04-83.

The "Declaration on Environment and Development" at the UN Conference on Environment and Development, held in Rio de Janeiro from 3 to 14 June 1992, recognizing the integrity and interconnectedness of nature on Earth, proclaimed 27 Principles. Principle 17 states: "One of the instruments of public policy should be the environmental impact assessment carried out in relation to the proposed activities".

To determine the impact of the mining and chemical enterprise on the environment, it is necessary to systematically assess and monitor the state of all elements of the environment both after the completion of the enterprise and during its activities [10].

Carrying out a wide range of environmental monitoring will help to avoid adverse environmental changes in the environment and to model future environmental processes in connection with the activities of mining facilities [11, 12].

Since the ecological system is not in a state of balance, but rather in the process of development, its key feature is sustainability. Internal resilience is the ability of an ecosystem to absorb gradual change [13].

Usually, the ecosystem can absorb and adapt to changes and negative situations. But when massive accidents occur or gradual changes accumulate, the ecosystem cannot cope with it and creates sharp and unexpected signals of change.

Therefore, it is important to control and monitor these changes in order to avoid negative reactions of the ecosystem. Figure 1 shows compartment model of the basic kinds of environment required by man partitioned according to ecosystem development and life-cycle resource criteria. If the volume of one of the types of environment changes, it affects other type.

Concentrated (in settling tanks, reservoirs, and accumulators) waste varies in composition and hazard classes. Organic and inorganic substances, in contact with the atmosphere, the hydrosphere, the lithosphere, with each other, undergo complex physicochemical and biological changes.

As a result, many compounds are formed and released, including toxic, which migrate into the environment, affect the air, soils, surface and groundwater, bottom sediments of nearby reservoirs and streams, vegetation.

To significantly reduce the production waste of mining and chemical enterprises, it is necessary to use a comprehensive approach to addressing this issue.

It should be borne in mind that waste can be a substitute for natural mineral resources and at the same time it is dangerous for the environment. The stored wastes of the enterprises contain not only the mineral components which are applied in the construction industry, but also the precious metals suitable for ferrous and nonferrous metallurgy.

One of the main tools for assessing the quality of the environment in areas affected by mining and chemical enterprises and the process of liquidation and reclamation and prevention of deterioration of environmental safety is environmental monitoring.

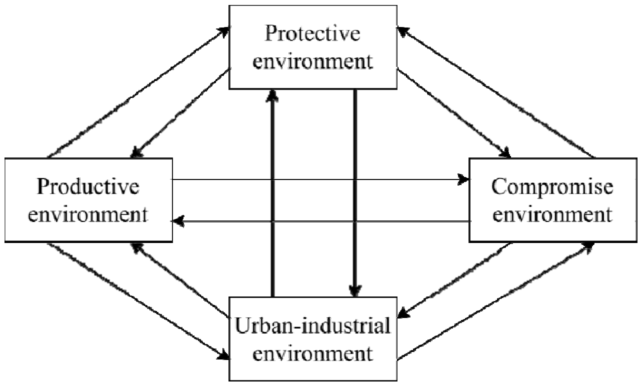

Fig. 1. Compartment model of the basic kinds of environment required by man partitioned according to ecosystem development and life-cycle resource criteria [13]

In order to determine the impact on the environment caused by industrial waste of the enterprise, it is necessary to create a system of control over water bodies on the territory of the enterprise, as well as canals (fig. 2) [14].

The next step is to monitor the ecological status of the aquatic environment outside the enterprise. On the territory of SE "Rozdil MCE "Sirka"" it is possible to allocate 5 points of control over an ecological condition of an aquatic environment. Monitoring of the content of pollutants in these points will allow to quickly prevent pollution outside the enterprise i.e., in the Dniester River, also in the surrounding settlements (fig. 3) [15].

Fig. 2. The part of Hlyboke Lake, which was formed on the site of a sulfur quarry

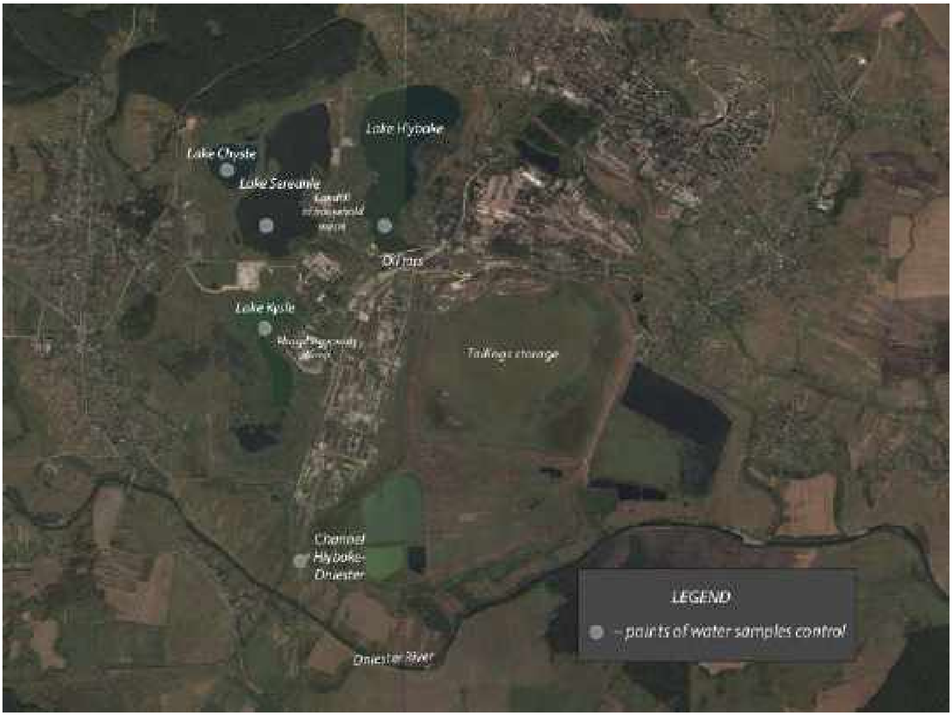

Fig. 3. The points of water sampling for pollutants control of mining and chemical enterprise

Equally important is the control of the content of pollutants in the soil environment (fig. 4). The first step is to analyze the content of contaminants near industrial waste dumps or other sources of pollution. After that, it is necessary to control how the pollution spreads from a distance from the source to the settlements. If the situation is critical, then take the necessary to stop the spread and reduce the amount of pollutants in the study territory [16-20].

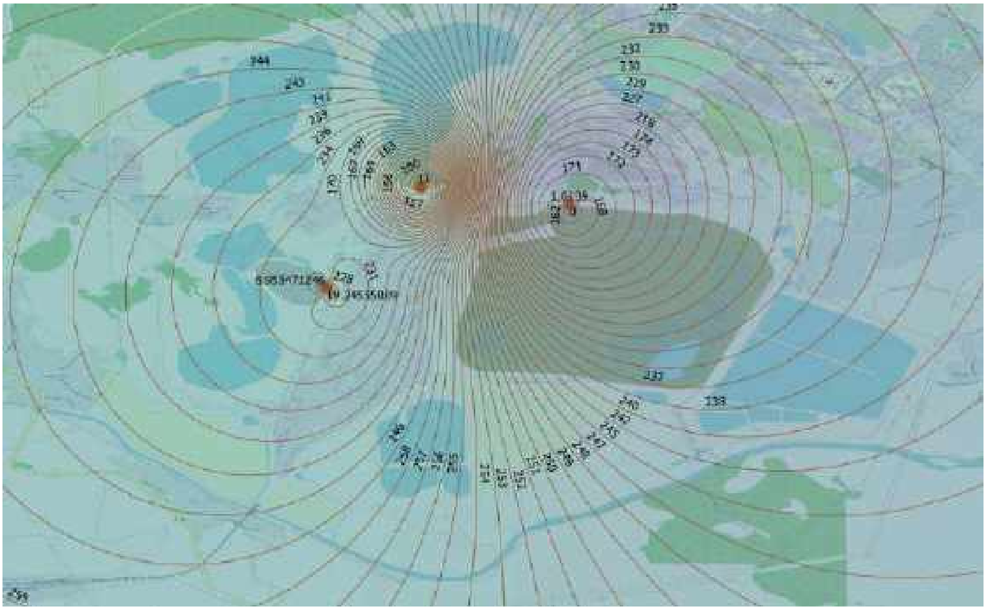

Fig. 4. The proposed control over the content of pollutants in the soil environment on the territory of enterprise

Monitoring the ecological condition of the mining and chemical enterprise's area of influence is one of the key elements of the environmental monitoring system, as it provides information on the level of pollution of important components that do not directly affect the health of a large number of people living in the affected area.

For example, at SE "Rozdil MCE "Sirka"", even now, 20 years after the end of the activity, the zone of negative impact on the environment and human health remains is uncertain. At the same time, the effectiveness and completeness of state environmental monitoring is not always sufficient to address the tasks of environmental inspection, management, response to emergencies, etc. Therefore, there is an obvious need to improve the organizational structure, methods and ways of monitoring the environment [21-25].

Extremely unsatisfactory environmental situation is caused by the consequences of production activities of mining and processing enterprises in Ukraine, due to a few reasons:

– imperfection of the existing legislation in the field of waste management;

– lack of an effective economic mechanism for regulating relations between waste producers and potential consumers of by-products;

– inability to adjust the mechanism of careful attitude of entrepreneurs to the environment through market relations;

– lack of a systematic approach on the part of the authorities in solving this urgent problem [26, 27].

The main reasons for the problems of the state environmental monitoring system are:

– imperfect legal framework;

– low level of coordination of the activities of the subjects of environmental monitoring and information and educational activities;

– insufficient funding, including from extrabudgetary sources;

– the outdated instrument-technical base of subjects of ecological monitoring, etc. [28, 29].

In particular, the control over the content of heavy metals in the soil on the territory of SE "Rozdil MCE "Sirka"" showed that many points at the enterprise are in the range from permissible pollution to hazardous pollution. In our case, the total pollution index at the sampling points was calculated: at a distance of 1 m, 5 m, 10 m, 20 m from the tars; 1 m, 5 m, 10 m, 20 m from the phosphogypsum dump; 1 m, 5 m, 10 m, 20 m from the tailings. Since at each sampling point there are laboratory results and in depth, the average values of each element at a certain point are calculated.

Soils near the phosphogypsum dump belong to the permissible, moderately dangerous and dangerous category of soil pollution (fig. 5). Assessment of the risk of soil contamination by a complex of chemical elements on the indicator Z_c is performed on an evaluation scale, the gradation of which is developed on the basis of studying the health of the population living in areas with different levels of pollution. The total pollution index Z_c is estimated for n taken into account anomalous factors, which determines the polyelement soil contamination and is calculated by the equation of Yu.Ye. Saet [30-38].

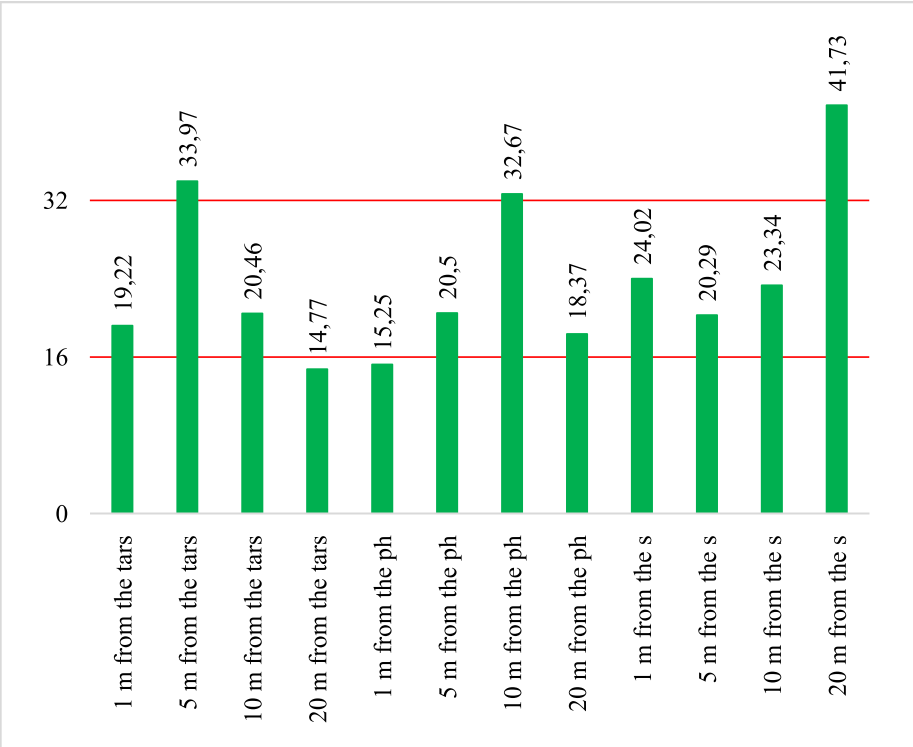

Fig. 5. The total rate of pollution Z_c in the enterprise, where *ph* is soil near the phosphogypsum dump, *s* is soil near the sulfur tailings

Using the total indicator of pollution Z_c in the system of environmental pollutant control it is possible to determine zoning according to the level of danger of soil pollution of the territory of the mining and chemical enterprise at the stage of liquidation.

CONCLUSION

Thus, the environmental situation within the liquidated mining and chemical enterprises is one of the most tense in Ukraine. The problem of closing mining and chemical enterprises and the transformation of man-made landscapes into a natural state in the context of solving priority environmental problems is relevant for Ukraine at the current stage of its development.

It is established that environmental monitoring is an important tool for improving the state of environmental safety and achieving the goals of sustainable development of areas of influence of mining and chemical enterprises.

But still the system of environmental monitoring as an important component of the system of public administration in the field of nature management, ecological safety, formation of the state policy of sustainable development, fulfillment of the international obligations of Ukraine in the field of nature protection needs fundamental improvement.

To ensure the ecological rehabilitation of the territory, it is necessary to have complete, comprehensive information about the state of the region, which is possible only as a result of comprehensive monitoring.

Achieving this goal depends on the ability to correctly determine the priorities of environmental and economic development and successfully select mechanisms for their implementation. To effectively manage the waste management of mining and chemical enterprises, it is necessary to implement certain areas of regulation in this area, namely:

– properly organized system of accounting for the generation, collection, processing, disposal and disposal of waste;

– establishing control over the material balance of production in order to stimulate the introduction of low-waste technologies.

REFERENCES

1. Shkitsa L., Transformation of mining complexes after operation, KSPU Bulletin, № 2 (37), pp. 113-115, 2006. In Ukrainian

2. Aboho S. Y., Anhwange B. A., Onianwa P. C., Ekanem E. O., Assessment of Surface Water Quality around Dumpsites in the City of Ibadan Metropolis, Oyo State, Nigeria, International Journal of Chemistry, Canada, Vol. 4, No. 1, pp. 39-44, 2012.

3. Carvalho F. P., Mining industry and sustainable development: time for change, Food and Energy Security, pp. 61-77, 2017.

4. Miao Y., Kang R., Chen X., Level Evaluation of Ecological Sustainable Development of Chemical Enterprises, 2nd International Symposium on Resource Exploration and Environmental Science, Earth and Environmental Science, China, 170, pp. 1-8, 2018.

5. Lin Z., Research on chemical environmental protection and sustainable development, Chemical Engineering Design Communications, 43 (7): 218, 2017.

6. Lee S., Ji W., Yang H., Reclamation of mine-degraded agricultural soils from metal mining: lessons from 4 years of monitoring activity in Korea, Environ Earth Sci, vol. 76, no. 720, pp. 1-7, 2017.

7. Meng X., Zhang Y., Yu X., Bai J., Chai Y., Li Y., Regional environmental risk assessment for the Nanjing Chemical Industry Park: an analysis based on information-diffusion theory, Stochastic environmental research and risk assessment, Springer-Verlag, vol. 28, is. 8, pp. 2217-2233, 2014.

8. Dzhumelia E., Ecological safety of mining and chemical enterprise at the stage of liquidation, The dissertation for the Degree of PhD in specialty 183 Environmental protection technologies, Ukraine 201 p., 2021. DOI: 10.13140/RG.2.2.22286.89928. In Ukrainian

9. Rhind S. M., Anthropogenic pollutants: a threat to ecosystem sustainability, Phil. Trans. R. Soc. B, 364, pp. 3391-3401, 2009.

10. The Rio Earth Summit: Summary of the United Nations Conference on Environment and Development, 1993. URL: https://sustainabledevelopment.un.org/content/documents/Agenda21.pdf

11. Sherameti I., Varma A., Heavy Metal Contamination of Soils: Monitoring and Remediation, v. 44, Switzerland: Springer, 497 p., 2015.

12. Pohrebennyk V., Dzhumelia E., Evaluation of Impact of Mining and Chemical Enterprise on Ecological State of the Water Environment, Water Security: Monograph, Mykolaiv: PMBSNU – Bristol: UWE, pp. 155-169, 2016.

13. Odum E. P., The Strategy of Ecosystem Development. An understanding of ecological succession provides a basis for resolving man's conflict with nature, Science, vol. 164, No 3877, pp. 262-270, 1969.

14. Pohrebennyk V., Mitryasova O., Dzhumelia E., Kochanek A., Evaluation of surface water quality in mining and chemical industry, 17th International multidisciplinary scientific geoconference SGEM 2017, Bulgaria, pp. 425-432, 2017.

15. Pohrebennyk V., Karpinski M., Dzhumelia E., Kłos-Witkowska A., Falat P., Water bodies pollution of the mining and chemical enterprise," 18th International multidisciplinary scientific geoconference SGEM 2018. Ecology and environmental protection: proceedings, pp. 1035-1042, 2018.

16. Yesilnacar M. I., Cetin, H., Site selection for hazardous wastes: A case study from the GAP area, Turkey, Engineering Geology, 81, pp. 371-388, 2005.

17. Fu L., Wang J., Jin Q., You A., Study of sustainable development in Yongkang city based on environmental capacity and pollutant control, 4th International Workshop on Renewable Energy and Development (IWRED 2020), IOP Conf. Series: Earth and Environmental Science, 510, 2020.

18. UNDP and UN Environment, Managing mining for sustainable development. A sourcebook. Bangkok: United Nations Development Programme, 2018.

19. Przydatek G., Kanownik W., Physicochemical indicators of the influence of a lined municipal landfill on groundwater quality: a case study from Poland, Environmental Earth Sciences, 80:456, pp. 1-14, 2021.

20. Pohrebennyk V., Dzhumelia E., Environmental assessment of the impact of tars on the territory of the Rozdil state mining and chemical enterprise "Sirka" (Ukraine), Studies in Systems, Decision and Control, T. 1, Vol. 198: Sustainable production: novel trends in energy, environment and material systems, Springer, pp. 201-214, 2020.

21. Dartan G., Taspinar F., Toroz I., Analysis of fluoride pollution from fertilizer industry and phosphogypsum piles in agricultural area, Journal of Industrial Pollution Control, 33 (1), pp. 662-669, 2017.

22. Asiedu J.B.K., Technical Report on Reclamation of Small Scale Surface Mined Lands in Ghana: A Landscape Perspective, American Journal of Environmental Protection, 1 (2), pp. 28-33, 2013.

23. Sun J., Geng C. L., Zhang Z. T., Wang X. T., Present situation of comprehensive utilization technology of industrial solid waste, Materials Review, vol. 11, no. 2, pp. 105-109, 2012.

24. Pietrzykowski M., Likus-Cie´slik J., Comprehensive Study of Reclaimed Soil, Plant, and Water Chemistry Relationships in Highly S-Contaminated Post Sulfur Mine Site Jeziórko (Southern Poland), Sustainability, v. 10, № 2442, 2018.

25. Macías F., Pérez-López R., Cánovas C. R., Carrero S., Cruz-Hernandez P., Environmental Assessment and Management of Phosphogypsum According to European and United States of America Regulations, Procedia Earth and Planetary Science, v. 17, pp. 666-669, 2017.

26. Pohrebennyk V., Koszelnik P., Mitryasova O., Dzhumelia E. Zdeb M., Environmental monitoring of soils of post-industrial mining areas, Journal of Ecological Engineering, vol. 20, no. 9, pp. 53-61, 2019.

27. Gorova A., Vysochyn L., Development of methods for assessing and forecasting environmental risks in mining regions, Forum of Mining Engineers. International Scientific and Technical Conference, pp. 200-204, 2014. In Ukrainian

28. Skakalskyi O., Ecological monitoring in the system of environmental protection of regional authorities. Public administration and local self-government, № 4, pp. 152-163, 2015. In Ukrainian

29. Balyuk S., Eterevskaya L., Travleev A., Zverkovsky V., Kobets A., The concept of reclamation of lands disturbed by open pit and underground mining, Ukraine, 51 p., 2012. In Ukrainian

30. Lomnytska F., Vasylechko V., Chykhriy S., Composition and chemical control of environmental objects, Ukraine, 589 p., 2011. In Ukrainian

31. Tetteh E. N., Evaluation of land reclamation practices at Anglogold Ashanti, Iduapriem Mine Ltd, Tarkwa, Kumasi: Kwame Nkruman Univercity of Science and Tecnology, 2010.

32. Spilnik N., Determination of the environmental risk of the use of wastes, Bulletin of the Dnieper State Academy of Civil Engineering and Architecture, № 7-8 (209), pp. 92-97, 2015. In Ukrainian

33. Shulipa Ye., Chernysh Ye., Basis for environmental monitoring of heavy metals content in soil, GeoTerrace–2018 collection of materials International. scientific and technical conf. young scientists (December 13–15, 2018), Lviv, Ukraine, pp. 52-55, 2018. In Ukrainian

34. Štofejová L., Fazekaš J., Fazekašová D., Analysis of Heavy Metal Content in Soil and Plants in the Dumping Ground of Magnesite Mining Factory Jelšava-Lubeník (Slovakia), Sustainability, 13, 4508, 1-13, 2021.

35. Dzhumelia E., Pohrebennyk V., The ecological monitoring system of the territory of the mining and chemical enterprise at the stage of liquidation, VIII International youth science forum "Litteris et Artibus", Lviv, Ukraine, 22-24 November 2018, pp. 288-289, 2018.

36. Chernysh Y., Yakhnenko O. Environmentally safe recycling of technogenic wastes. Environmental security as a basis for sustainable development of society. European experience and prospects: materials III International scientific-practical conf. (Lviv, September 14, 2018). Lviv, Ukraine, 2018. p. 5, 2018. In Ukrainian

37. Dzhumelia E., Pohrebennyk V., Methods of soils pollution spread analysis: Case study of mining and chemical enterprise in Lviv region (Ukraine), Ecological Engineering and Environmental Technology, Poland, 22(4), pp. 39-44, 2021.

38. Bryk M., Kołodziej B., Reclamation problems for the area of a former borehole sulfur mine with particular reference to soil air properties, Land Degrad. Dev., no. 20, pp. 509-521, 2009.

ENVIRONMENTAL AND REGIONAL DIFFERENCES IN MANIFESTATION OF ENDOMETRIOSIS IN WOMEN IN THE KOŠICE AND PREŠOV REGION

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ABSTRACT

Endometriosis is a benign gynecological disease affecting approximately 10 % pre-menopausal women. In the present study we aimed to the occurrence of individual types and stages of endometriosis, clinical signs as well as on the diagnostics methods in Slovak women with endometriosis. We included 48 women from Prešov region and 67 women from Košice region. We found significant differences between Košice and Prešov region in stages of endometriosis ($p = 0.0000$), in clinical symptoms associated with endometriosis ($p = 0.0044$), as well as in methods for disease diagnosis ($p = 0.0000$). No statistically significant differences were recorded between regions in individual types of endometriosis ($p = 0.7699$). Association between the type and stage of endometriosis has not been statistically confirmed ($p = 0.1204$) in Košice region. In contrast, this association was confirmed ($p = 0.0334$) in Prešov region. Based on the results, it can be stated that there exist differences in endometriosis manifestations at regional level.

Keywords: Diagnostics of endometriosis, clinical symptoms, geographical and environmental variation.

INTRODUCTION

Endometriosis is a chronic estrogen-dependent benign inflammatory disease characterized by the presence of implants of abnormally placed tissue similar to endometrium, including glands and stroma, outside the uterine cavity [1, 2, 3]. Endometriotic lesions typically occur in the pelvis and can infiltrate any pelvic structure. The most common sites of endometriosis, in decreasing order, are the ovaries, uterosacral ligaments, uterus, peritoneum, fallopian tubes, sigmoid colon, bladder and appendix [4]. A number of symptoms can occur in women with endometriosis. In addition to infertility, it is commonly associated with symptoms such as dyspareunia, dysmenorrhea, dyschesis, or bladder/bowel symptoms. The chronic pelvic pain is also frequent, it is defined as pain lasting more than 6 months and not just cyclically occurring pain [4]. Endometriosis is very rare in women belonging to the negroid variety. However, women from mongoloid variety were much more likely to have this diagnosis as opposed to women from caucasian variety [5]. Differences in the manifestation of endometriosis and associated characteristics have also been confirmed between different populations, regions, and environments within the Caucasian variety [6]. The fact that endometriosis pathogenesis remains unexplained suggest that multifactorial mechanisms are involved. That includes genetic, epigenetic, hormonal, immunologic, inflammatory, environmental, and geographical influences. Population-based studies have confirmed the genetic heterogeneity of endometriosis [7] but offer little insight into the potential for regional variation. We live in a specific geographical environment. Geographical and regional factors may influence one's ability to access healthcare and treatment of endometriosis through a combination of socioeconomic and genetic influences [8]. The socioeconomic development is difficult in north areas of Prešov region, it´s reflected not only in the unemployment and migration trend associated with younger economically active population leaving the region for work, but also through its facilities, health facilities, the level of social life, the quality of the environment and health care [9, 10]. The main goal of the work was to find regional and environmental differences in clinical manifestations and diagnosis of endometriosis in women in the Košice and Prešov region.

METHODS AND EXPERIMENTAL PROCEDURES

The study population consisted of 115 patients (Fig. 1), i.e., women diagnosed with endometriosis. 48 women were from Prešov region and 67 women from Košice region. This research dealt only with women from the majority population of Slovakia. The women were asked to complete a short questionnaire in collaboration with doctors in the gynecology and obstetrics departments and in private gynecology clinics. The questionnaire provided brief information about disease as well as the nature and significance of the study. The questions aimed to better understand the individual course of the disease in each patient and included the following: age and method of diagnosis, type and degree of endometriosis, related complications and type of treatment related to the disease in the past. All women confirmed their voluntary participation in the research. Statistical analysis was performed in the STATISTICA, ver. 10. For all statistical tests, a significance level of $p < 0.05$ was used.

THE RESEARCH RESULTS AND DISCUSSIONS

The mainly problem at endometriosis field is unexplained etiology of this disease, despite the existence of several theories attempting to explain the mechanism of development of the disease. Theories including retrograde menstruation, altered immunity, coelomic metaplasia, metastatic spread, stem cell or genetic origins of the disease are attractive, but they do not answer several essential questions: How does endometriosis develop only in ~ 10 – 15 % of women (the frequency of this disease in the general population)? The retrograde menstruation (dissemination of endometrial cells during menstruation from the uterus into ectopic location) is a common phenomenon, occurring probably in all women. Why are endometriomas found only in the ovary? Why do some women preferentially develop cystic ovarian and others deep endometriosis [1]? The basic condition is the presence of menstruation. Endometriosis is therefore a gynecological disease affecting women in reproductive age, most often between the age of 20 and 35 [11]. This fact was also confirmed in our research. The age of women from the Košice region ranged from 23 to 47 years (average age 33.17 ± 6.92 years) and the age of women from the Prešov region ranged from 20 to 44 years (average age 32.33 ± 6.53 years). No significant difference in the average age of women from Košice and Prešov region was recorded ($p = 0.5629$).

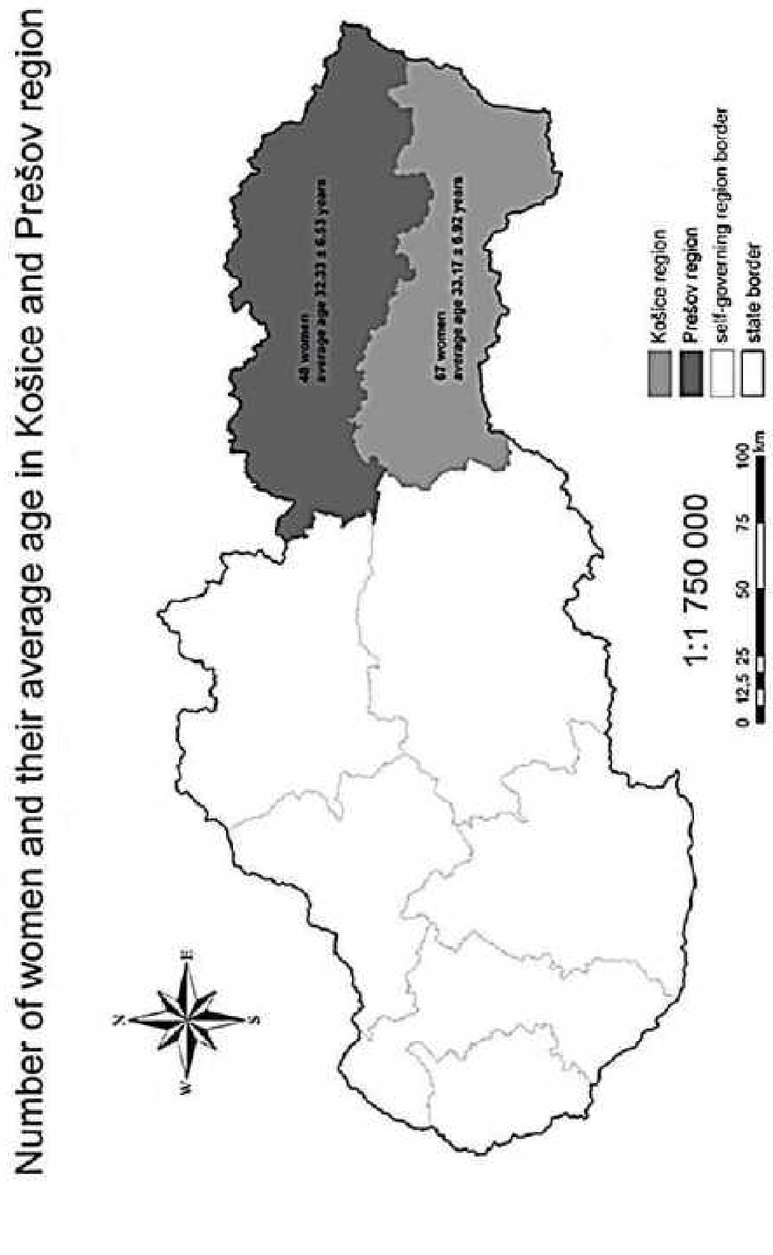

Fig. 1 Number of women and their average age in both regions
Source: own source

The stage of endometriosis of patients was determined by their gynecologist in accordance with data established by the American Fertility Society [12]. Currently, the rASRM (the revised American Society for Reproductive Medicine) score is most commonly used to classify endometriosis. It´s a relatively simple scoring system used worldwide and easy to understand for the patients themselves. Depending on the extend of involvement of the organs, it includes stage I as minimal, stage II as mild, stage III as moderate and stage IV as severe endometriosis. Individual points are assigned based on the size of the lesions on the peritoneum and ovaries, size of the adhesions on the ovaries and Fallopian tubes, and for partial or complete posterior cul-de-sac obliteration (the space between uterus and rectum) [13].

Considering the diagnosed stage of endometriosis, the group of women (Table 1) in Košice region consisted of 34 (50.75 %) women with stage I, 31 (46.27 %) women with stage II and 2 (2.98 %) women with stage III. In Prešov region, the group of women consisted of 5 (10.42 %) women with stage I, 18 (37.50 %) women with stage II, 20 (41.66 %) women with stage III and 5 (10.42 %) women with stage IV. The results show that, in Košice region, women were diagnosed predominantly with a minimal and mild stage of endometriosis, while in Prešov region women were more often diagnosed with mild, moderate to severe stage of endometriosis. The difference in individual stages of endometriosis in women was statistically significant (p = 0.0000) in the comparison between the Košice and Prešov region.

Table 1. Representation of individual stages of endometriosis categorized by rASRM score in Košice and Prešov region

Stages of endometriosis	Košice region n (%)	Prešov region n (%)	p value
Stage I	34 (50.75)	5 (10.42)	**0.0000**
Stage II	31 (46.27)	18 (37.50)	
Stage III	2 (2.98)	20 (41.66)	
Stage IV	0 (0.00)	5 (10.42)	

Source: own source

By the localization, endometriosis is divided into four types, peritoneal endometriosis, ovarian endometriosis, rectovaginal ´deep´ endometriosis and adenomyosis. In the research groups, we found all these types. The representation of individual types of endometriosis (Fig. 2) was similar in both of regions and no significant difference was recorded (p = 0.7699). Yuan stated that the most common form of endometriosis is ovarian endometriosis [14]. This fact was also confirmed in our research. Ovarian endometriosis was the most common, occurring in the Košice region totally in 35 (52.24 %) women. Separately occurred in 30 (44.78 %) women, together with peritoneal endometriosis in 3 (4.48 %) women, together with adenomyosis in 1 (1.49 %) woman and together with peritoneal and rectovaginal endometriosis in 1 (1.49 %) woman. In Prešov region, ovarian endometriosis occurred totally in 31 (70.45 %) women, separately in 25 (56.82 %) women, together with adenomyosis in 3 (6.82 %) women, together with peritoneal endometriosis in 2 (4.55 %) women and together with peritoneal and rectovaginal endometriosis in 1 (2.27 %) woman. Ovarian endometriosis is characterized by the presence of endometrial cysts (endometriomas or "chocolate cysts"). In our research groups the cysts occurred specifically in women with ovarian endometriosis (21 women in Prešov region and 14 women in Košice region). The second most common type of endometriosis was peritoneal endometriosis, which occurred separately in 15 (22.38 %) women in Košice region and in 9 (20.45 %) women in Prešov region. Adenomyosis occurred separately in 11 (16.42 %) women in Košice region and in 3 (6.82 %) women in Prešov region. Rectovaginal endometriosis is the most severe form of endometriosis but has the lowest frequency. It is much less common than ovarian or peritoneal endometriosis and affects approximately 3.8 % women [15]. In our group, rectovaginal endometriosis occurred separately only in 6 (8.96 %) women in Košice region and only in 1 (2.27 %) woman in Prešov Region.

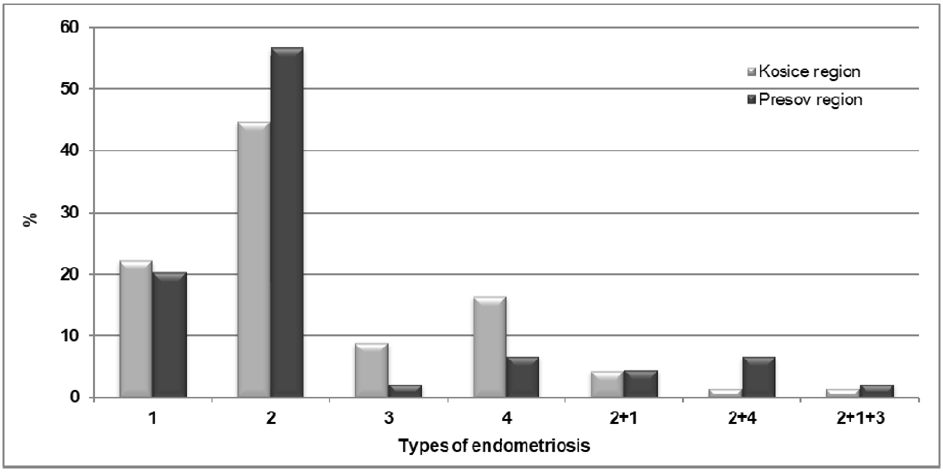

Fig. 2. Representation of individual types of endometriosis in Košice and Prešov region (1 peritoneal, 2 ovarian, 3 rectovaginal, 4 adenomyosis, 2+1 ovarian and peritoneal, 2+4 ovarian and adenomyosis, 2+1+3 ovarian, peritoneal, and rectovaginal)

Source: own source

We examined the association between the type and stage of endometriosis which were diagnosed to women (Tab. 2). In the peritoneal endometriosis was recorded mainly the minimal stage of disease (14.93 %) and in ovarian endometriosis it was mainly the mild stage of disease (23.88 %) in Košice region. Severe stage has not been recorded in any type of endometriosis. Association between the type and stage of the disease was not statistically confirmed (p = 0.1204) in Košice region. In contrast, this association was statistically confirmed (p = 0.0334) in Prešov region. In peritoneal endometriosis was recorded mainly the mild stage of disease (16.67 %) and in ovarian endometriosis it was mainly moderate stage of disease (25.00 %). Only moderate stage of disease was recorded in co-occurrence of ovarian and peritoneal endometriosis; and also, in co-occurrence of ovarian endometriosis and adenomyosis (4.17 %; 6.25 % respectively). Only a severe stage of disease (6.25 %) was recorded in co-occurrence of the three types of endometriosis (peritoneal, ovarian and rectovaginal endometriosis).

The incidence of clinical symptoms associated with endometriosis in research groups is summarized in Table 3. The significant difference in the incidence of clinical symptoms between Košice and Prešov region was recorded (p = 0.0044). The most common symptom in patients was significant pain during menstruation (dysmenorrhea), when the pain is usually the worst around 2nd – 3rd day of the cycle and pain during ovulation. It occurred in up to 59 (88.10 %) women in Košice region and it occurred only in 30 (62.50 %) women in Prešov region. Endometrial cysts ranked second in incidence, occurring in 21 (43.75 %) women, in all cases in connection with ovarian type of endometriosis in Prešov region. Irregular bleeding ranked second in 26 (38.81 %) women in Košice region.

Table 2. Connection between the individual types of endometriosis and diagnosed stages of the disease in Košice and Prešov region

Types of endometriosis	Stages of endometriosis							
	Košice region				Prešov region			
	Stage I	Stage II	Stage III	Stage IV	Stage I	Stage II	Stage III	Stage IV
Peritoneal	**10** (14.9 %)	**5** (7.4 %)	**0** (0.0 %)	**0** (0.0 %)	**1** (2.0 %)	**8** (16.6 %)	**0** (0.0 %)	**0** (0.0 %)
Ovarian	**12** (17.9 %)	**16** (23.8 %)	**2** (2.9 %)	**0** (0.0 %)	**3** (6.2 %)	**8** (16.6 %)	**12** (25.0 %)	**2** (4.1 %)
Rectovaginal	**4** (5.9 %)	**2** (2.9 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**1** (2.0 %)	**1** (2.0 %)	**0** (0.0 %)
Adenomyosis	**6** (8.9 %)	**5** (7.4 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**2** (4.1 %)	**2** (4.1 %)	**0** (0.0 %)
Ovarian and peritoneal	**1** (1.4 %)	**2** (2.9 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**2** (4.1 %)	**0** (0.0 %)
Ovarian and adenomyosis	**1** (1.4 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**3** (6.2 %)	**0** (0.0 %)
Ovarian, peritoneal and rectovaginal	**0** (0.0 %)	**1** (1.4 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**0** (0.0 %)	**3** (6.2 %)
p value	0,1204				**0,0334**			

Source: own source

Table 3. The occurrence of clinical symptoms associated with endometriosis in Košice and Prešov region

Clinical symptoms	Košice region n (%)	Prešov region n (%)	p value
Dysmenorrhea and pain during ovulation	59 (88.1)	30 (62.5)	**0.0044**
Dyspareunia	15 (22.3)	15 (31.2)	
Irregular bleeding	26 (38.8)	17 (35.4)	
Infertility and early abortion	15 (22.3)	12 (25.0)	
Pelvic adhesions	12 (17.9)	13 (27.1)	
Endometrial cysts	14 (20.8)	21 (43.7)	
Asymptomatic	0 (0.0)	3 (6.2)	

Source: own source

Chapron confirmed in their study interesting regional differences, potentially influenced by health care practices specific to the local environment, in the diagnosis, symptomatology, and treatment practices of endometriosis [8]. We also recorded a significant difference (p = 0.0000) in methods (Tab. 4) used to diagnose endometriosis in women between Košice and Prešov region (Fig. 3). Surgery was preferred for diagnosis of the disease in Prešov region, where in up to 70.37 % women just laparoscopy was used. The presence or absence of endometriotic lesions was confirmed by histological findings. At the present, this mini-invasive laparoscopic procedure with tissue biopsy from a suspected lesion is becoming the gold standard for diagnosing the disease. However, surgery poses a potential risk of developing other health problems and complications. The doctors preferred less invasive methods for diagnosis of the disease, especially ultrasound (43.75 %) and gynecological examination (43.75 %) in Košice region. These non-invasive methods are not always successful in diagnosing endometriosis, because even a negative finding does not completely rule out the presence of endometriosis. Ultrasound examination is best suited for the differential diagnosis of ovarian cystic forms of endometriosis, where the examination also allows the evaluation of the volume of preserved ovarian tissue. This is extremely important for the next optimal treatment strategy. Blood tests were the least used and least reliable method of diagnosing the disease. In the remaining women, at least two of these methods were used simultaneously to confirm the presence of the disease.

Table 4. Methods for disease diagnosis in Košice and Prešov region

Diagnosis	**Košice region n (%)**	**Prešov region n (%)**	**p value**
Laparoscopy	3 (6.2)	19 (70.3)	**0.0000**
Ultrasound	21 (43.7)	6 (22.2)	
Blood tests	3 (6.2)	0 (0.0)	
Gynecological examination	21 (43.7)	2 (7.4)	

Source: own source

CONCLUSION

There are many similarities in behaviours, in signs and symptoms, also in types and stages manifested in individual women diagnosed with endometriosis in Košice and Prešov region. This fact supports the universality of the disease process in the development of a disease such as endometriosis. These findings support the current genetic theory, which attempts to explain the origin and development of endometriosis. Geographical, regional, and environmental factors may influence the manifestation of the disease but may also play an important role in the chosen method of diagnosis and treatment of endometriosis. External factors (lifestyle, environment, passing preventive gynecological examination, quality of health care, differences in public or private health facilities) may also affect the correct diagnosis of endometriosis because it normally takes 7 to 10 years before diagnosis occurs. The likelihood of correct and rapid diagnosis is partially influenced by the mode of diagnosis. General consensus is that clinically suspect cases should be confirmed with surgical visualization, others suggest that presenting symptoms, physical examination, and medical history alone provide sufficient criteria for initiating treatment. At the present, laparoscopic surgery is preferred for the diagnosis and treatment of endometriosis, but a combination of several methods is the best choice.

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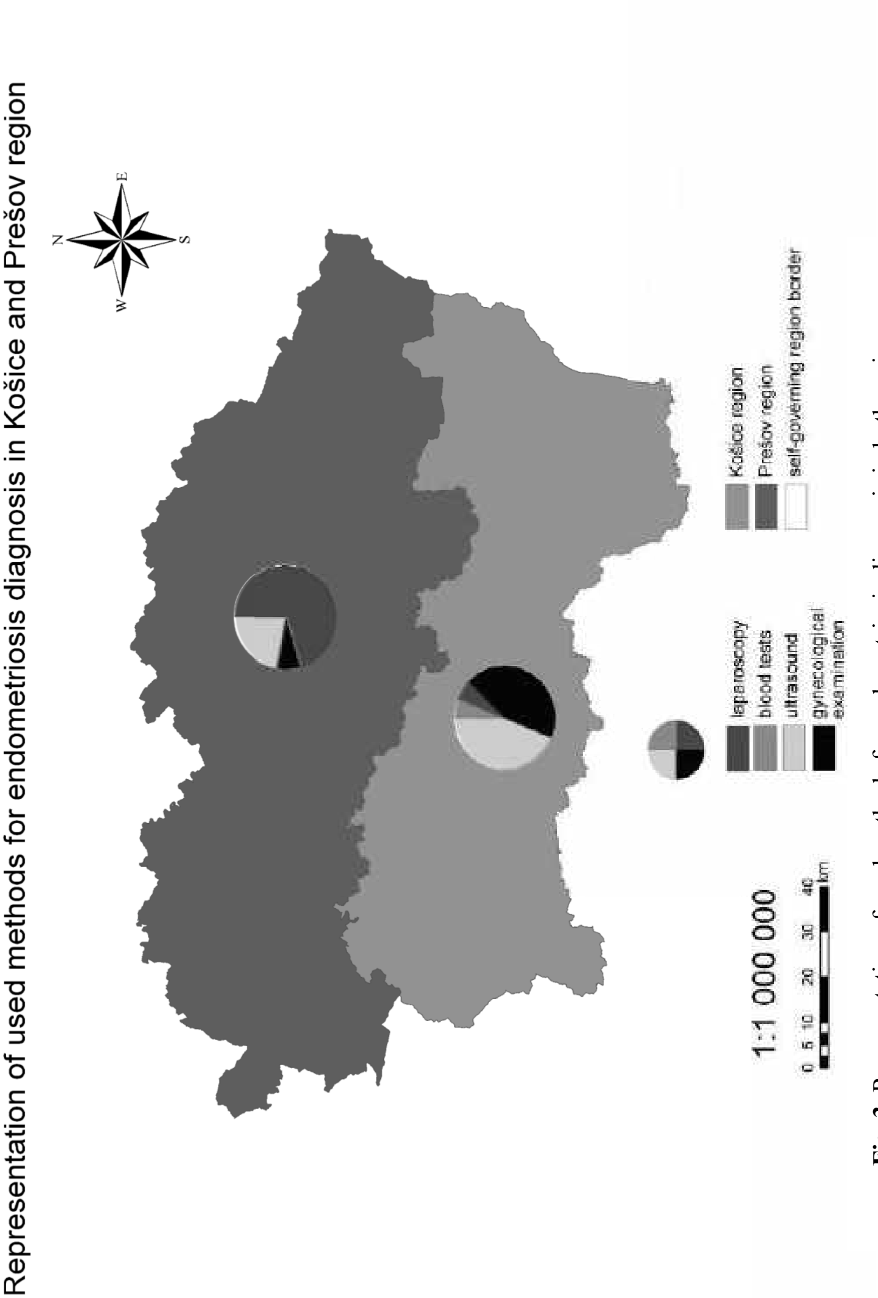

Fig. 3. Representation of used methods for endometriosis diagnosis in both regions
Source: own source

REFERENCES

1. VINATIER, D., ORAZI, G., COSSON, M. and DUFOUR, P., (2001). Theories of endometriosis. *European Journal of Obstetrics & Gynecology and Reproductive Biology*, 96, 1, 21-34.

2. GIUDICE, L. C., KAO, L. C. (2004). Endometriosis. *The Lancet*, 364, 9447, 1789–1799.

3. KENNEDY, S., BERGQVIST, A., CHAPRON, CH., D´HOOGHE, T., DUNSELMAN, G., GREB, R., HUMMELSHOJ, L., PRENTICE, A. and SARIDOGAN, E., (2005). ESHRE guideline for the diagnosis and treatment of endometriosis. *Human Reproduction*, 20, 10, 2698–2704.

4. MACER, M. L., TAYLOR, H. S. (2012). Endometriosis and Infertility. A Review of the Pathogenesis and Treatment of Endometriosis-associated Infertility. *Obstetrics and Gynecology Clinics of North America*, 39, 4, 535–549.

5. KRONEMYER, B. (2019). How race/ethnicity influences endometriosis. *Contemporary OB/GYN Journal*, 64, 5.

6. HADFIELD, R., MARDON, H., BARLOW, D., KENNEDY, S. (1996). Delay in the diagnosis of endometriosis: a survey of women from the USA and the UK. *Human Reproduction*, 11, 4, 878–880.

7. BORGHESE, B., TOST, J., DE SURVILLE, M., BUSATO, F., LETOURNEUR, F., MONDON, F., VAIMAN, D. and CHAPRON, CH., (2015). Identification of susceptibility genes for peritoneal, ovarian, and deep infiltrating endometriosis using a pooled sample-based genome-wide association study. *Biomed Research International,* 1-8.

8. CHAPRON, CH., LANG, J-H., LENG, J-H., ZHOU, Y., ZHANG, X., XUE, M., POPOV, A., ROMANOV, V., MAISONOBE, P. and CABRI, P., (2016). Factors and Regional Differences Associated with Endometriosis: A Multi-Country, Case Control Study. *Advances in therapy*, 33, 8, 1385–1407.

9. ROSIČ, M., MADZIKOVÁ, A., KLAMÁR, R., KROKUSOVÁ, J., PASTERNÁK, T. and KOZOŇ, J., (2018) Unemployment in the context of human resources in the eastern part of the Slovak-Polish border region. *Folia geographica*, 60, 2, 15-48.

10. PETROVIČ, F., MURGAŠ, F. (2020). Holistic and sustainable quality of life. Conceptualization and application. *Folia geographica,* 62, 1, 77-94.

11. OLIVE, D. L., SCHWARTZ, L. B. (1993). Endometriosis. *The New England Journal of Medicine,* 328, 24, 1759-1769.

12. AMERICAN FERTILITY SOCIETY. (1985). Revised American Fertility Society classification of endometriosis. *Fertility and Sterility*, 43, 3, 351–352.

13. HAAS, D., SHEBL, O., SHAMIYEH, A. and OPPELT, P., (2013). The rASRM score and the Enzian classification for endometriosis: their strengths and weaknesses. *Acta Obstetricia et Gynecologica Scandinavica*, 92, 1, 3-7.

14. YUAN, M., WANG, W-W., LI, Y., GAO, L., WANG, T. and WANG, S-X., (2014). Risk factors for recurrence of ovarian endometriomas after surgical excision. *Journal of Huazhong University of Science and Technology Medical Sciences,* 34, 2, 213-219.

15. MOAWAD, N. S., CAPLIN, A. (2013). Diagnosis, management, and long-term outcomes of rectovaginal endometriosis. *International Journal of Women´s Health,* 5, 753-763.

QUALITY OF SURFACE WATER AND FISH RESOURCES IN CLIMATE CHANGE CONTEXT (THE USTYA RIVER BASIN EXAMPLE)

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ABSTRACT

It is established that average increase in the surface water temperature of the Ustya river basin (a tributary of the Horyn River, Pripyat basin) is 1 °C during 2013-2020. Assessment of surface water quality according to the relevant categories (according to I_e index) showed that the waterbodies belong to the III-IV quality classes and characterized as "slightly polluted" – "moderately polluted" – "dirty", by data 2009-2018. There was a significant excess of standards for the content of nutrients in the surface water, in particular phosphates and ammonium nitrogen – up to category 7, the water very dirty. During 2011-2019 annually there were fish kills due to a sharp decrease in dissolved oxygen in conditions of organic pollution and water temperature increase – the loss of fish resources over the years amounted to more than 400,000. Eutrophication and increase in water temperature create favorable conditions for the microflora development, in particular pathogenic. The influence of diseases on fish resources is increasing – pathogens of protozoan, helminthic, mycoses and crustacean diseases in fish have been registered on the most common species – common roach (*Rutilus rutilus*) and silver carp (*Carassius gibelio*) in the river basin. There was also an increase in low-quality fish – from 18 to 21% by the state standard of organoleptic quality.

Keywords: freshwater, eutrophication, climate change, fish kill, crustacean diseases

INTRODUCTION

Freshwater ecosystems of almost all rivers in Ukraine have undergone significant anthropogenic impact, which reflecting some global changes in inland waters – pollution, habitat degradation (including fragmentation), over-exploitation of fish, introduction of non-native species etc; the impacts of climate change will interact with many of these factors [10]. Eutrophication leads algal bloom due to cyanobacterial growth, which toxic substances poison surface waters and could be accumulated in the fish meat, and it becomes dangerous for consumption [9, 17]. Deterioration in the quality of surface waters and fish products due to anthropogenic impact is exacerbated by climate change [5, 11]. An increase in the average water temperature, a change in water content, and a decrease in flow rate cause changes in the hydrochemical and hydrobiological regimes. Society loses freshwater supplies due to pollution and evaporation. In addition, the source of fish resources is also destroying: the diversity of fish fauna decreases and the quality of fish deteriorates [2, 6, 8].

Sustainable development implies the need to protect the interests of future generations, that means the practice of maintaining the productivity by replacing resources used with resources of equal or greater value without degrading or endangering natural biotic systems [16]; therefore, it is necessary to take measures to reduce the pressure on aquatic ecosystems.

The rivers of the Pripyat basin, in particular the Ustya River, are also subject to significant anthropogenic impact. This is reflected in water quality deterioration and decrease in the diversity and quality of aquatic bioresources [6-8, 19, 21]. Indeed, with the existing climate trend, there will be a decrease in fresh water reserves, a reduction in recreational areas, the fish diversity loss, and the quality of the fish will continue to deteriorate, up to a direct threat to the health.

The aim of the study is ecological assessment of the surface water quality and the fish resources state of the Ustya River basin in the current conditions of climate change.

METHODS AND EXPERIMENTAL PROCEDURES

Study area. Investigated waterbodies. The Ustya River is located in north-western part of Ukraine within the 16th European ecoregion by the Water Framework Directive (2000) [25] and Freshwater Ecoregion 425: Dnieper – South Bug by the Freshwater ecoregions of the world [1]. It is a small river (68 km length) in the Pripyat River basin, a left-bank tributary of the Horyn River. On the banks of the river are located the cities of Rivne and Zdolbuniv. Agricultural land is 71.4% of the area of basin. This river has been one of the most polluted by industrial and domestic wastewaters in the Pripyat River basin since the last part of the XX century [23].

Hydrochemical and ichthyoparasitological studies were carried out in 2009-2020 in 7 control sites, which included recreational waterbodies in the cities of Rivne and Zdolbuniv (Fig 1, Tabl.1).

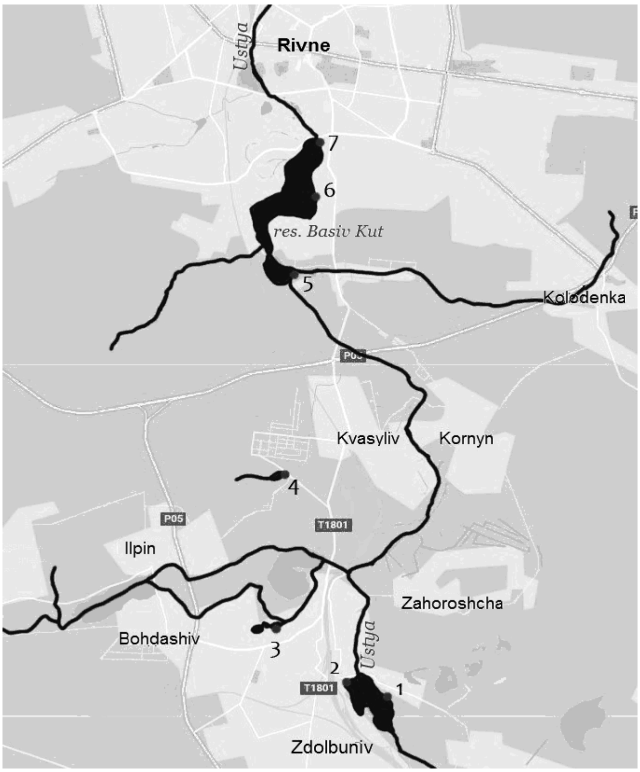

Fig. 1. Control sites in the Ustya River basin

Table 1. Control sites on the water bodies of the Ustya river basin

Site No	Administrative location and site description	The geographic coordinates	
1	Pond (1) in Zdolbuniv on the Ustya River, communal beach	50.516621	26.270268
2	Pond (2) in Zdolbuniv on the Ustya River, communal beach for children	50.518361	26.261134
3	Hydropark, pond (3) in Zdolbuniv	50.527170	26.241168
4	Pond (4) in Zdolbuniv, «the low-flow pond»	50.551816	26.245421
5	The Basiv Kut reservoir, upstream of the Rivne-city	50.584266	26.254708
6	The Basiv Kut reservoir, communal beach, the city of Rivne	50.597828	26.252873
7	The Basiv Kut reservoir outlet, the city of Rivne	50.604701	26.254785

Water quality analysis and assessment. Surface water quality indicators (content of chlorides, sulfates, mineralization, pH, ammonium nitrogen, nitrate and nitrite nitrogen, phosphorus phosphates, dissolved oxygen, COD, iron, copper, zinc, manganese, and petroleum products) were determined in accordance with the current governing normative documents by the department of instrumental laboratory control of the State Environmental Inspection in the Rivne Oblast (2009-2018).

Water quality and the aquatic environment state were evaluated according to the ecological assessment of surface water quality in the relevant categories [24], the quantitative generalization of which is the integral ecological index (Ie), which was set by three blocks indices according to formula (1):

$$I_e = \frac{I_1 + I_2 + I_3}{3}, \tag{1}$$

where I_1 – index of indicators of salt composition; I_2 – index of trophic and saprobic indicators (ecological and sanitary); I_3 – index of indicators of specific toxic substances.

The water quality indices were determined by the mean and worst values.

Collecting and examination of fish and ectoparasites. Amateur fishing gear was used for catching fish, surveys of amateur fishermen were carried out, and floating crafts of the Rivne Fisheries Patrol were involved in the framework of the research. The objects were studied and processed directly in the field, at the sampling sites; part of the ichthyologic material was sent to the laboratory for detailed analysis.

The study of the crustacean diseases in fish was conducted during 2013-2018 on the basis of the Rivne Research Station of Epizootology of the Institute of Veterinary Medicine, and Departments of ecology and water bioresources of the National University of Water and Environmental Engineering. The analysis was conducted according to recommendation of state standards and guidelines. Also we analyzed the reported data of Rivne Regional State Laboratory of Veterinary Medicine – the incidence of fish diseases (2015-2020).

Three main quantitative descriptors of parasite population (or parasitological indices) were used in the research; they are widely used in parasitology [3]:

Prevalence (*P*) – the number of hosts infected with 1 or more individuals of a particular parasite species divided by the number of hosts examined for that parasite, expressed as a percentage, formula (2):

$$P = \frac{N_p}{n} \times 100\% \tag{2}$$

where N_p – number of infected fish, n – total number of examined fish.

Intensity of infection (*II*) – the number of individuals of a particular parasite species in a single infected host, formula (3):

$$II = \frac{m}{n} \qquad (3),$$

where *m* – number of particular parasite species; n – number of infected host species.

Mean abundance (*M*) – the average abundance of a parasite species among all members of a particular host population, formula (4):

$$M = \frac{m}{N} \qquad (4),$$

where *m* – number of particular parasite species; *N* – total number of examined host species (including both infected and uninfected) [4, 20].

The organoleptic quality of fish was determined according to State standard of Ukraine (DSTU 2284: 2010).

THE RESEARCH RESULTS AND DISCUSSIONS

Change in air and water temperature. According to the reported data [22], the years 2018-2019 were abnormal in terms of the amount of heat, and 2 °C warmer than the average values of the base period 1981-2010 – the average air temperature was 10 °C. It is the highest temperature over the entire observation period, that is, a positive temperature anomaly was observed, with an average monthly temperature of 3-5 °C above average values (by 1-2 °C in April, August, and September) [22]. According to our data, the surface water temperature of the Ustya River basin also gradually increases during the summer months – from 18.6-19.1 °C in 2013 to 21-23.2°C in 2020 (Fig. 2). It is established that average increase in the surface water temperature of the basin has been 1 °C during 2013-2020.

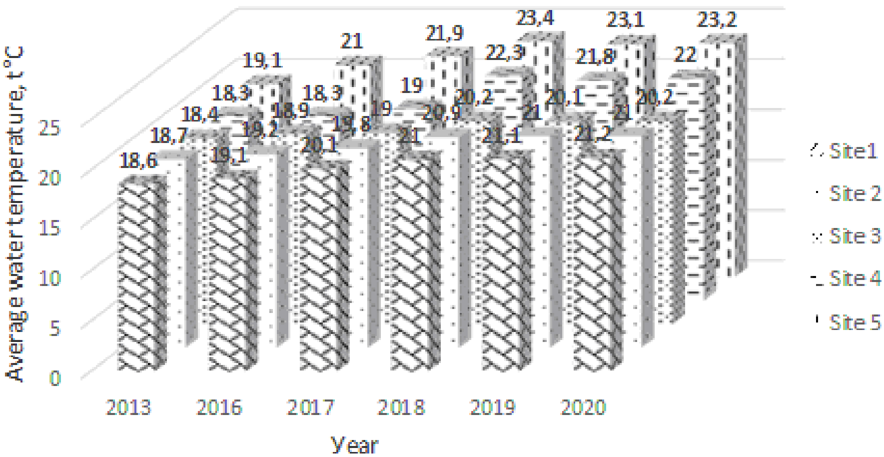

Fig. 2. Dynamics of surface water temperature of the Ustya River basin (averaged over the recreational season)

Water quality. Over the past decades, a steady change in hydrochemical parameters has been observed in the water bodies, as a result, in the class of surface water quality. Artificial flow regulation of rivers leads to a change in the hydrological regime, respectively, a decrease in the water content in the river and reservoirs located in the basin. As a result, small streams and reservoirs are silted up and disappear. In addition, large water bodies are silting up [13].

The ecological assessment of water quality according to the index I_e showed that the surface waters belong to the III quality class in terms of average indicators and are characterized as "polluted" by class and "slightly polluted" by category (Table 2).

Table 2. Assessment of surface water quality by average values (2009-2018)

Site No	I_1	I_2	I_3	I_e	Water quality		Degree of cleanness (pollution)	
					class	category	by class	by category
1	3,3	3,8	4,2	3,8	III	4	polluted	slightly polluted
2	3	4	3,8	3,6	III	4	polluted	slightly polluted
3	3,3	4,8	3,4	3,8	III	4	polluted	slightly polluted
4	3	4,7	5	4,2	III	4	polluted	slightly polluted
5	3	5	5,6	4,5	III	4,5	polluted	slightly polluted - moderately polluted
6	3	4,8	3,8	3,9	III	4	polluted	slightly polluted
7	2,7	4,8	3,5	3,7	III	4	polluted	slightly polluted
Mean value	3,04	4,56	4,19	3,93	III	4,07	polluted	slightly polluted

According to the worst values of indicators, the water belongs to the III-IV quality classes and characterized as "polluted" – "moderately polluted" – "dirty" (Table 3).

Table 3. Assessment of surface water quality by the worst values (2009-2018)

Site No	I_1	The worst indicators	I_2	The worst indicators	I_3	The worst indicators	I_e	Water quality		Degree of cleanness	
								class	category	by class	by category
1	3	total minera-lization, chlo-ride, sulphate	7	nitrate and nitrite nitrogen	5	Fe	5	III	5,0	polluted	moderately polluted
2	4	sulphate	7	nitrate nitrogen	6	petroleum products	5,7	IV	6,0	dirty	moderately polluted
3	5	chloride	7	nitrate nitrogen	6	Cu	6	IV	6,0	dirty	dirty
4	3	total minera-lizaion, chlo-ride, sulphate	7	nitrate and nitrite nitrogen	6	petroleum products	5,3	III	5,0	polluted	moderately polluted
5	4	sulphate	7	phosphorrus phosphates, dissolved oxygen, COD	7	Cu Mn Zn	6	IV	6,0	dirty	dirty
6	3	total minera-lization, chlo-ride, sulphate	7	phosphorus phosphates, nitrate and nitrite nitrogen	6	petroleum products	5,3	III	5,0	polluted	moderately polluted
7	3	total mineraliza-tion, sulphate	7	nitrite nitrogen	6	petroleum products	5,3	III	5,0	polluted	moderately polluted

In all the waterbodies there was a significant excess of the nutrients content standards, in particular, phosphates and ammonium nitrogen – category 7. The water was very dirty and all the studied waterbodies were significantly eutrophied. Eutrophication in combination with climate change, in particular with an annual increase in water temperature, causes the massive development of cyanobacteria long before the onset of maximum temperatures [14]. According to the results of long-term observations, it has been established the algal bloom beginning has shifted by 2-4 weeks in recent years. In particular, in the Basiv Kut reservoir there is a steady algal bloom in 2016-2020, which began even before the maximum temperatures, in the 2-3 decade of June and continued until the 2nd decade of September; in some cases, it was observed in the 3rd decade. The timing of algal bloom also shifted in the recreational waterbodies of the Zdolbuniv (June, 3rd decade). This indicates a high content of nutrients in the water, mainly deposited in bottom sediments during the cold period of the year. New portions constantly enter the reservoir by agricultural runoff and sewage discharges.

Due to the significant eutrophication, favorable conditions are created for the microflora development, in particular, pathogenic. This is evidenced by the study results of the Rivne Regional Laboratory Center during 2013-2019. In eutrophied water bodies, for example the Basiv Kut reservoir, an excess of the titer of *Escherichia coli* was observed up to 48 times (2017-2019). Since 2015, representatives of intestinal infections and pathogenic microflora have been found here every year. In addition, since 2017, cholera-like vibrio has been constantly found in the reservoir. In the recreational reservoirs of the city of Zdolbuniv over the past few years, the hydrochemical regime has significantly deteriorated, and there is also a periodic excess of the titer of lactose-positive *E. coli*.

Fish kill. In addition to chronic pollution, which affects the quality of fish, but does not cause its immediate death, in the waterbodies there are critical consequences of climate change and eutrophication – the death (suffocation) of aquatic organisms due to oxygen depletion. Over a 9-year period on the Ustya River (the Basiv Kut reservoir, the river section within the city of Rivne), fish kills were observed almost annually. A particularly catastrophic suffocation of fish occurred in 2012, caused by a sharp depletion of the dissolved oxygen (Fig. 3).

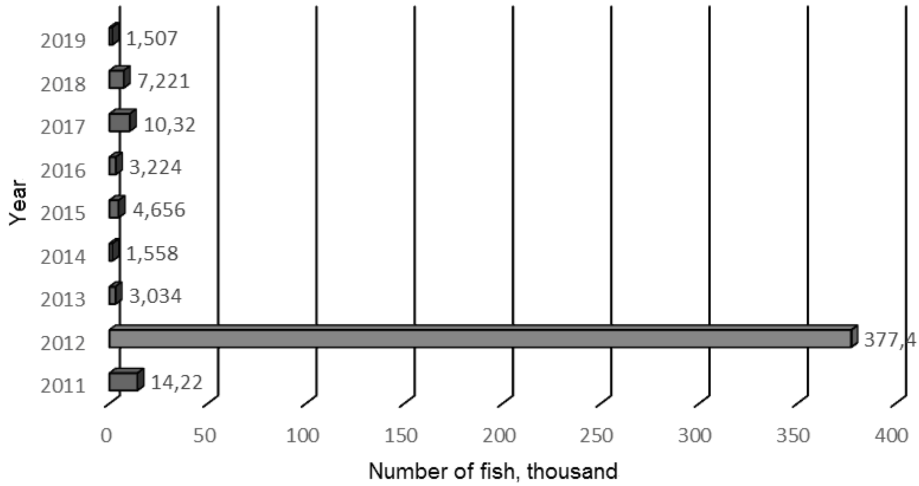

Fig. 3. Number of fish died due to "fish kill", the Ustya River basin (2011-2019)

According to the data of the Rivne Fisheries Patrol, during 2011-2019 the approximate loss of fish resources amounted to 423.14 thousand specimens. This process is a result of the complex action of natural and anthropogenic factors – a decrease in saturation due to an increase in water temperature, the biomass of cyanobacteria growth to the bloom level due to anthropogenic eutrophication [10].

Fish diseases. As mentioned above, climate change influences the hydrochemical, hydrobiological and hydrological characteristics of waterbodies. Their transformation leads to another negative consequence – an increase in the disease incidence of fish fauna. Diseases of various etiologies arise with deterioration of sanitary and ecological conditions and due to the introduction of new species.

If zoohygienic conditions are violated, microorganisms with which the fish are in constant contact become able to penetrate through the skin and gills and cause disease [22]. Favorable factors to the growth of pathogenic microorganisms' colonies are the following: poor-quality feed base of natural waterbodies and feeding fish with low-quality feed in fish farms (leading to a decrease in immunity), a decrease in flow rate, an increase in water temperature, a decrease in the content of oxygen dissolved in water, an increase in the amount of suspended solids, in particular, water pollution by organic substances. Another potential biotic hazard is the spore-forming ability of bacteria, due to which the pathogen in a latent form is able to remain in the aquatic environment for a long time and, under favorable conditions, cause diseases [12].

Specialists of the Rivne Regional State Laboratory of Veterinary Medicine monitor the incidence of fish in the region for diseases of various etiologies. According to the reported data, in the period from 2015 to 2020, no positive results were recorded for viral and bacterial diseases. During the research of 29,504 fish specimens, it was found that the causative agents of protozoan diseases appear in the waterbodies every year. The incidence rate is relatively low – within 1-4%.

The causative agents of mycoses are quite common in natural reservoirs and pond farms. They are dangerous, because the cause of high mortality in different age groups of fish. In case of infection of eggs, they threaten the fish reproduction in general. The situation with the incidence of mycosis of fish fauna in the waterbodies of the Rivne region is relatively favorable. There was high fish morbidity with saprolegniosis – 28.6% in 2011.

Helminthic diseases actually show the sanitary state of waterbodies, because many pathogens of such diseases are carried into the reservoirs and ponds with surface runoff from agricultural land, municipal sewage, as well as violation of veterinary and sanitary standards in fish farming. According to monitoring studies, waterbodies in the Rivne region, in particular in the Ustya river basin, are unfavorable by helminthic diseases. The following agents of helminthic diseases are detected here annually: trematodes (pathogens: *Diplostomum spathaceum, Posthodiplostomum cuticola*), monogenoids (pathogens: *Dactylogyrus vastator, Gyrodactylus cyprini*), cestodes (pathogens belong to several classes – Khalyphylis Pseudophyllidea: *Bothriocephalus gowcongensis, Ligula intestinalis*, nematodes (pathogen – *Philometroides lusiana*) [18]. Although the level of fish morbidity due to helminthiases is currently relatively low (0.3-4%), further deterioration of water quality may lead to an increase in the invasion with parasitic organisms. This will have a negative impact on commercial and recreational fishing, as well as endangering the health of the local population and livestock.

According to the research results, the state of the local ichthyofauna is unfavorable in terms of crustaceosis. In the study region, the most common causative agents of argulosis and lerneosis, and cases of such fish diseases are recorded annually. Assessment the level of infection of the fish fauna, namely the most widespread and numerous of its representatives – silver Prussian carp (*Carassius gibelio* Bloch) and common roach (*Rutilus rutilus* L.), with parasitic crustaceans showed that *Argulus foliaceus* L. (Crustacea: Branchiura: Arguloida) is a common agent of fish disease in the region, which causes argulosis. Fish affected by *Lernaea cyprinacea* L. (Crustacea: Copepoda: Cyclopoida), the causative agent of lerneosis, occurred much less frequently. In recent years (2017-2019), no fish affected by this parasite have been found in reservoirs. It was established that the prevalence of *Argulus foliaceus* on *R. rutilus* ranged from 1.5 to 15.6%, the intensity of invasion was 0.8-2.8, and mean abundance index was 0.02-0.44. The prevalence on *C. gibelio* was from 4.4 to 13.4%, invasion intensity – 0.33-2.56, and the abundance index – 0.07-0.37. On average, the parasite prevalence on *C. gibelio* is higher than on *R. rutilus* – 7.46 vs. 7.04 %. The intensity of invasion and the abundance index, on the contrary, are higher on *R. rutilus* – 1.64 to 1.29 and 0.16 to 0.14, respectively (Table 4) [7].

Parasitic representatives of crustaceans are quite plastic and can be found in different waterbodies. However, due to complex life cycle they need a number of favorable conditions, including a high content of organic matter, water temperature, illumination, etc. In reservoirs with good sanitary and hygienic condition the incidence of crustaceosis is very low. Most often, parasitic crustaceans are found in silted ponds, overgrown with higher aquatic vegetation with weak flow and high temperature; this was also traced in the research results [20].

Table 4. Incidence rates of argulosis in the Ustya River basin (2009-2019)

Site No	Parasitological indices					
	P, %	II	M	P, %	II	M
	Rutilus rutilus			*Carassius gibelio*		
1	15,6	2,8	0,44	13,4	2,56	0,37
2	12,3	2,5	0,31	12	1,85	0,22
3	2,2	0,8	0,06	4,4	1	0,07
4	1,5	0,8	0,02	6,1	0,33	0,07
5	5,5	1,8	0,09	5,5	1,4	0,07
6	7	1,8	0,11	5,6	1,25	0,1
7	5,2	1	0,06	5,2	0,67	0,07
Mean value	7,04	1,64	0,16	7,46	1,29	0,14

In general, scientists in the Rivne region have found 7 types of fish parasites (23 species): ciliates, flatworms (trematodes, monogenea, and cestodes), primary cavities (nematodes), scrapers, leeches, arthropods (crustaceans) and mollusks [8, 21]. Thus, in the region, protozoal, helminthic diseases of fish, crustaceosis, as well as sporadic cases of mycoses are annually recorded. This is indirect evidence of the unsatisfactory ecological and sanitary state of surface waters and ichthyofauna.

The quality of the fish. The waterbodies are used for recreational fishing, therefore, the fish quality is of great importance as food for local population. As we see in previous text, climate changes, combined with anthropogenic impact, have led to deterioration in the ecological state of waterbodies; respectively, we observe a depletion of ichthyofauna and deterioration in the quality of fish resources in water bodies of the basin. Since the second half of the twentieth century, fish fauna underwent a species diversity depletion, as well as a decrease in the size and weight characteristics of individuals in populations. In the catches of amateur fishermen during 2013-2020, low-value common roach and silver carp prevailed; tench, pike perch, pike, and common perch were less common.

In the Basiv Kut reservoir, the poor quality of fish in terms of organoleptic indicators was observed from sampling points located in the lower part of the reservoir (near the dam). However, the fish caught at this site showed no signs of disease, except for a few specimens. In the upper and middle parts of the reservoir, the fish have signs of diseases, in particular, crustaceoses, but their organoleptic and morphological indicators were better. During the study period, common roach (*Rutilus rutilus*) and silver carp (*Carassius gibelio*) from the upper and middle parts of the reservoir met the standard indicators (Fig. 4); and those caught in the lower part of the reservoir had an unusual smell, that is, there was a deviation from DSTU 2284: 2010.

The results of boiling the collected samples showed significant differences between the quality of fish caught at different times and in different areas. In 2013-2014, the broth after boiling was transparent, there were drops of fat on the surface, the smell was pleasant, specifically fishy, and individual muscle fibers easy separated from the muscle tissue. In 2015-2018, the broth from fish caught from the upper and middle parts of the reservoir met the requirements, however, from the lower part it had an unpleasant, muddy, nonspecific smell. This could be a consequence of the algal bloom, as well as pollution, because the presence of oil products and toxic elements was noted in the reservoir.

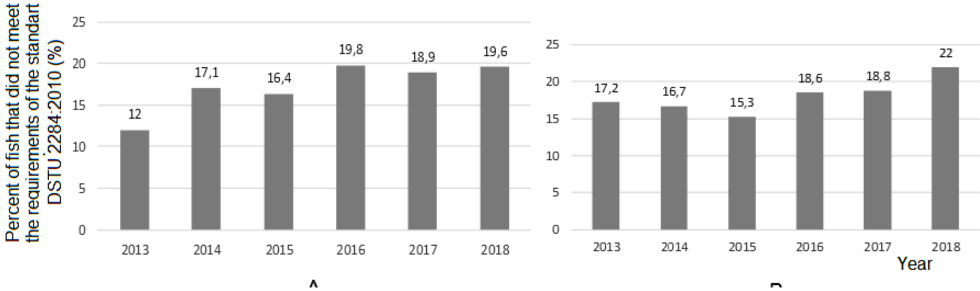

Fig. 4. Amount of *Rutilus rutilus* (A) and *Carassius gibelio* (B) from the Basiv Kut reservoir, which did not meet the requirements of DSTU 2284: 2010 (in %)

Sanitary and microbiological analysis showed that freshwater fish (common roach, silver carp, and bream) did not meet the requirements for such indicators as Mesophilic aerobic and facultative anaerobic microorganisms and the content of Coliform bacteria in the samples. According to the research of the Rivne Regional Laboratory Center of the Ministry of Health of Ukraine, freshwater fish (Rutilus rutilus) did not meet the requirements of state regulations and standarts on the content of bacteria of the Escherichia coli group (coliforms).

Recreational reservoirs in the city of Zdolbuniv are also used for recreational fishing. In contrast to the Basiv Kut reservoir, there is no intensive discharge of domestic and industrial wastewater into these reservoirs. There is only the effect of agricultural pollution from diffuse sources. Therefore, the water quality here is much better and, accordingly, the organoleptic indicators of freshwater fish during the entire study period have met the requirements of DSTU 2284: 2010, except for indicators that related to signs of diseases. When carrying out a test by boiling, the broth was transparent, there were drops of fat on the surface, the smell was pleasant, specifically fishy, and the muscle tissue easy divided into muscle bundles.

CONCLUSION

The study showed that the surface water temperature of the Ustya river basin (a tributary of the Horyn River, Pripyat basin) increased by 1 °C during 2013-2020 by average.

The fish fauna of the basin experiences a significant impact of anthropogenic pollution, the negative consequences of which are exacerbated by climate change, as evidenced by the results of surface water quality assessment according to the ecological classification. On average values, the majority of water bodies belong to the III class (4.0-4.5 categories), that is, they are characterized as “slightly polluted” – “moderately polluted”. According to the worst indicators – to the III-IV classes (5-6 categories), and are characterized as "moderately polluted" – "dirty". The worst indicators (category 7 in terms of phosphate content, nitrate nitrogen, nitrite, COD) predominate in the tropho-saprobiological block. In some reservoirs, the titer of lactose-positive Escherichia coli was 48 times higher than standard and cholera-like vibrio was detected.

Negative anthropogenic impact is manifested in the mass death of fish. Approximate losses of fish resources in the region due to fish kill for the period 2011-2019 amounted to more than 400,000. The reasons for the deaths was a decrease in the content of dissolved oxygen due to a decrease in the flow rate as a result of the construction of dams, as well as climate change and an increase in water temperature, decay of organic compounds due to eutrophication and the discharge of untreated wastewater.

In addition, the unsatisfactory ecological and sanitary state of surface waters has led to the spread of protozoan and helminthic diseases of fish, mycoses and crustaceases. The most common pathogens in the study region are argulosis and lerneosis, such cases are registered annually on the most common species – *Rutilus rutilus* and *Carassius gibelio*. On average, the parasite prevalence on *C. gibelio* is higher than on *R. rutilus* – 7.46 vs. 7.04 %. The intensity of invasion and the abundance index, on the contrary, are higher on R. rutilus – 1.64 to 1.29 and

0.16 to 0.14, respectively. These factors significantly affect the quality of fish; in particular, there was a fairly high percentage of fish that did not meet the requirements of the state standard – 18-21%.

We are losing fresh water supplies due to pollution and mismanagement in the face of climate change, and also losing a source of fish resources. If measures are not taken to reduce anthropogenic pressure on aquatic ecosystems, the diversity of ichthyofauna will decrease to several particularly resistant species (including invasive ones), and the quality of this fish will continue to deteriorate, up to a direct threat to health.

REFERENCES

1. Abell R., Thieme M., Revenga C., Bryer M., Kottelat M., Bogutskaya N., Coad B., Mandrak N., Balderas S.C., Bussing W., Stiassny M., Skelton P., Allen G.R., Unmack P., Naseka A., Ng R., Sindorf N., Robertson J., Armijo E., Higgins J., Heibel T., Wikramanayake E., Olson D., López H., Reis R., Lundberg J., Pérez M., Petry P., Freshwater Ecoregions of the World: A New Map of Biogeographic Units for Freshwater Biodiversity Conservation, BioScience, vol. 58 / issue 5, pp 403-414, 2008.

2. Brander K. M., Global fish production and climate change, Proceedings of the National Academy of Sciences, vol. 104 (50), pp 19709-19714, 2007.

3. Bush A.O., Lafferty K.D., Lotz J.M., Shostac A.W., Parasitology meets ecology on its own terms: Margolis et al. revisited, The Journal of Parasitology, vol. 83, pp 575-583, 1997.

4. Davidov O.N., Temnikhanov Y.D., Diseases of freshwater fish: viral, bacterial, mycotic, parasitic, non-infectious, Kiev, Vetinform, 2004, 544 p.

5. Griffith A.W., Gobler C.J., Harmful algal blooms: A climate change co-stressor in marine and freshwater ecosystems, Harmful Algae, Volume 91, 2020.

6. Grokhovska Y.R., Konontsev S.V., Fish diversity under human impact: A case study of the Pripyat river basin in Ukraine, Actual problems of natural sciences: modern scientific discussions: Collective monograph, Riga: Baltija Publishing, pp 171-187, 2020.

7. Grokhovska Y.R., Parfeniuk I.O., Konontsev S.V., Poltavchenko T.V., Analysis of surface water quality and crustacean diseases in fish (the Ustya River basin, Ukraine), Ukrainian Journal of Ecology, vol. 11(1), pp 94-102, 2020.

8. Grokhovska Y.R., Volovyk H.P., Konontsev S.V., Moshinsky V.S., Mandigra M.S., Mosnitsky V.O., Cadastre of ichthyofauna of Rivne region, Rivne, pp 200, 2012.

9. Hallett C.S., Valesini F.J., Clarke K.R., Hoeksema, S.D., Effects of a harmful algal bloom on the community ecology, movements and spatial distributions of fishes in a microtidal estuary, Hydrobiologia, vol. 763, pp 267-284, 2016.

10. Harrod C., Alejandro Ramírez A., John Valbo-Jørgensen J., Funge-Smith S., How climate change impacts inland fisheries. Chaprer in: Impacts of climate change on fisheries and aquaculture: Synthesis of current knowledge, adaptation and mitigation options, FAO Fisheries and Aquaculture technical paper, Rome, pp 375-387, 2018.

11. Joehnk K.D., Huisman J., Sharples J., Sommeijer B.P, Visser P.M, Stroom J.M., Summer heatwaves promote blooms of harmful cyanobacteria, Global Change Biology, vol. 14(3), pp 495-512, 2008.

12. Katjuha S.M., Voznjuk I.O., Distribution of invasive fish diseases in reservoirs of Rivne region, Veterinary biotechnology, vol. 28, pp 94-101, 2016.

13. Klymenko M.O., Grokhovska Y.R., Hydroecological monitoring and phytoindication of aquatic ecosystems of the Pripyat basin, Bulletin of the National University of Water Management and Environmental Sciences, vol. 2(66), pp 29-38, 2014.

14. Kovalenko Y.O., Shlapak O.O., Potrokhov O.S., Zinkovsky O.G., Influence of anthropogenic pollution on physiological and biochemical parameters of fish and their parasitocenoses, Fisheries science of Ukraine, vol. 49, 3, pp 72-88, 2019.

15. Khudiyash Y.M., Prychepa M.V., Potrokhov O.S., Zinkovsky O.G., Gorbatyuk L.O., Kovalenko Y.O., Medovnyk D.V., Influence of ecological conditions of lakes of Kyiv on the state ichthyofauna, Fisheries science of Ukraine, vol. 51, pp 28-43, 2020.

16. Lynn R. Kahle, Eda Gurel-Atay, eds., Communicating Sustainability for the Green Economy, New York, M. E. Sharpe, pp 320, 2013.

17. Paerl H.W., Paul V.J., Climate change: links to global expansion of harmful cyanobacteria, Water Research, vol. 46 (5), pp 1349-1363, 2012.

18. Parfenyuk I.O., Analysis of the incidence of ichthyofauna of Rivne region, Taurian Scientific Bulletin, issue 97, pp 254-260, 2017.

19. Parfenyuk I.O., Grokhovskaya Yu. R., Mandygra Yu., Analysis of water quality of a reservoir on a small river and the status of ichthyofauna in anthropogenic conditions, Ukrainian Journal of Veterinary and Agricultural Sciences, vol. 2 / N 3, pp 28-31, 2019.

20. Poltavchenko T.V., Bogatko N.M., Parfenyuk I.O., Sanitation and hygiene in fish farming, Laboratory manual, Rivne, 2016, 120 p.

21. Poltavchenko T.V., Parfenyuk I.O., Ecological features of origin and distribution of protozoa in reservoirs and the state of morbidity of pond fish in fish farms of Rivne region, Modern Methodologies, innovations and operational experience in the field of biological sciences, Lublin, pp 160-163, 2017.

22. Report on the state of the region's environment, Department of Ecology and Natural Resources of Rivne Regional State Administration. URL: http://www.ecorivne.gov.ua/report_about_environment/ (20.06.2021).

23. Romanenko V.D., Afanasyev S.A., Vasenko A.G., Osadchiy V.I., Andreichenko Y.I., Nabivanets Y.B., Identification and assessment of sources of pollution of water bodies ("hot spots") in the Dnieper basin on the territory of Ukraine, Kyiv, 2004, 282 p.

24. Romanenko V.D., Zhukinskiy V.M., Oksiiuk O.P., Methodology of ecological assessment of surface water quality according to the relevant categories, Kyiv, pp 28, 1998.

25. Water Framework Directive (Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy), Official Journal of the European Communities, 2000, 72 p.

BOTTOM SEDIMENTS OF RESERVOIRS AS A SOURCE OF GREENHOUSE GASES

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ABSTRACT

This paper describes results of a study of greenhouse gas emissions from selected five reservoirs in southeastern Poland. For this purpose, fluxes of methane (CH_4) and carbon dioxide (CO_2) at the sediment-water interface were analysed for the years 2009-2012. Fluxes of CO_2 and CH_4 at the water-air interface were measured using the "static chamber" method. The results indicate that not only water bodies in the tropical zone, but also objects located in the temperate zone can be a source of significant amounts of greenhouse gases.

Keywords: methane, carbon dioxide, greenhouse gases, reservoir, sediments

INTRODUCTION

Mechanisms of carbon greenhouse gas emissions from reservoirs

Greenhouse gases, produced in bottom sediments or in water during decomposition of organic matter, are consumed in the aquatic system through processes such as photosynthesis or methane oxidation. They can also be emitted to the atmosphere through several processes of a physical, chemical or biochemical nature [1], these are (Figure 1):

- diffusive flux from the water surface,
- release of gas bubbles (ebullition) in shallow parts of reservoirs,
- advection by roots of aquatic plants,
- degassing of the water flow just below the dam and diffusive flow along the river course.

Diffusive flux at the water-air the water-atmosphere interface

Once the gases reach the surface of the water they can diffuse into the atmosphere. Forced diffusion is the driving force from the concentration difference and involves the spontaneous movement of particles from an area of higher concentration to an area of lower concentration. Diffusion of CO_2 and CH_4 into the atmosphere depends on the concentration gradient at the water-atmosphere interface and the gas transfer rate [1,2]. Temporary changes in climatic-atmospheric conditions, such as wind strength and direction or precipitation intensity, can also have an impact [3,4]. Strong winds increase the turbulence of water in the reservoir and thus the flux of gas to the atmosphere [5]. Another important factor affecting gas flux at the water-air across the water-atmosphere interface is temperature. At high temperatures, increased gas fluxes to the atmosphere are usually observed, especially for CH_4 [6, 7, 8].

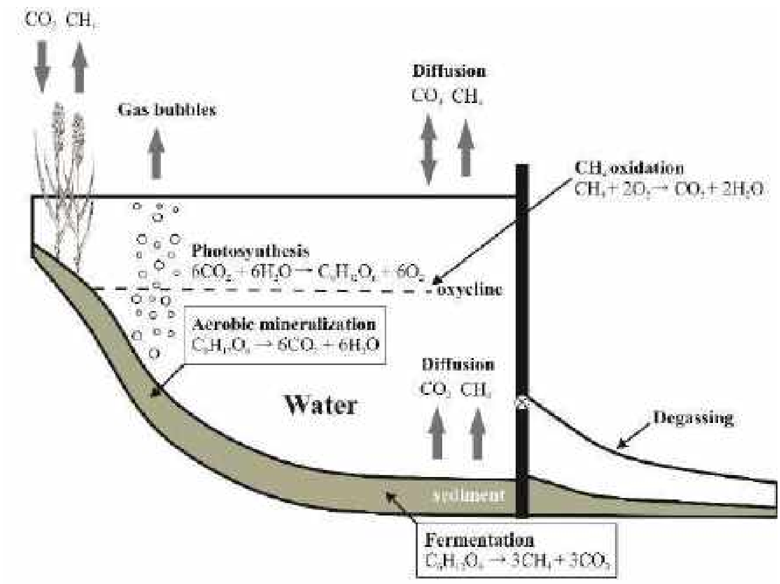

Fig. 1 Production and transport pathways of CH_4 and CO_2 in a reservoir [1]

Gas fluxes are calculated from a linear regression of the change in gas concentration in the chamber as a function of time, taking into account the area and volume of the chamber [1]. Another commonly used technique is to calculate flux from the partial pressure gradient or concentration of the test gas in air and water and the gas flux coefficient, which depend on wind speed, water velocity, precipitation, and temperature [9, 10]. The gas flux (F) across the water-atmosphere interface is calculated from the equation [1]:

$$F = k_x (C_w - C_a) \tag{1}$$

where: C_w i C_a is the gas concentration in water and air, respectively, and k_x is the gas flux coefficient calculated from equation:

$$k_x = k_{600} (Sc/600)^{-x} \tag{2}$$

Sc is the Schmidt number, which is temperature dependent (t). The Schmidt number for CO_2 is:

$$Sc(CO_2) = 1911.1 - 118.11t + 3.4527t^2 - 0.04132t^3 \tag{3}$$

while for CH_4:

$$Sc(CH_4) = 1897.8 - 114.28t + 3.2902t^2 - 0.03906t^3 \tag{4}$$

The k_{600} is the gas flux rate factor, expressed in $cm \cdot h^{-1}$, normalized for CO_2 in freshwater for a Schmidt number of 600:

$$k_{600} = 2.07 + (0.215 \cdot U_{10}^{1,7}) \tag{5}$$

U_{10} is the wind speed at a height of 10 m expressed by the equation:

$U_{10} = 1.22 \cdot U_1$ (6)

where: U_1 is the wind speed at the water surface and is expressed in $m \cdot s^{-1}$.

Ebullition

Gas bubbles formed in bottom sediments are released into the water when the sum of the partial pressures of the dissolved gases is higher than the hydrostatic pressure. The gas bubbles penetrate the water column and are released to the atmosphere. The dominant component of these gas bubbles is CH_4, and the amount of CO_2 is minimal at about 2% by volume [11, 12, 13, 14]. In deep water bodies, gas bubbles dissolve in the water column and the methane produced in the deeper layers of bottom sediments is often oxidized to CO_2 [15]. Many researchers provide that ebullition is the main pathway of CH_4 transport from bottom sediments to the atmosphere only in shallow ecosystems, while in deep ecosystems diffusive flux dominates [16].

Transport through plants

Assimilation and advective transport of greenhouse gases by submerged aquatic plants growing in the littoral zone of ecosystems is a quantitatively significant mechanism for the transport of CH_4 and CO_2 to the atmosphere [17, 18]. The rate of flux of these gases depends on their production and consumption in the rhizosphere. The plant vascular system allows diffusion of CH_4 from bottom sediments to the atmosphere. The same vascular system may contribute to the oxidation of CH_4 by oxygen diffusing there through the roots. The mechanism and efficiency of vascular transport are specific to some plant species [19].

Water degassing below the dam and diffusive flux along the river course

Discharge of water from deep reservoirs is usually through a downstream outlet, through turbines, which causes a sudden change in pressure, temperature, and flow velocity. As a result, large loads of CO_2 and CH_4 are released into the atmosphere below the dams [20]. Because of the sudden change in pressure, methanotrophic bacteria do not have the opportunity to oxidize CH_4 to CO_2 [21]. According to Guérin and Abril [2], about two-thirds of the CH_4 contained in the water is outgassed into the atmosphere after passing through the turbine. In the river below the dam, there is an increase in the turbulence of the water relative to the reservoir water. The turbulent motion makes the water in the river well-mixed, and the gases can diffuse more easily and pass more quickly into the atmosphere. In the case of three tropical Brazilian dam reservoirs: Samuel, Balbina, and Petit Saut, CH_4 emissions from the river below the dam accounted for 23%, 5%, and 9-33% of the total reservoir surface emissions (diffusion + ebullition), respectively, and carbon dioxide emissions via the same path were 20% (Samuel and Petit Saut) and 7% (Balbina) [22].

Using stable isotope analysis to interpret the origin of greenhouse gases in aquatic ecosystems

The uses of isotope ratio mass spectrometry (IRMS) allow, among other things, the documentation of greenhouse gas sources and fluxes. The previously described processes of CH_4 and CO_2 production and transformation in aquatic ecosystems involve carbon isotope fractionation. In methanogenesis, isotopically lighter molecules (containing ^{12}C carbon as opposed to ^{13}C) react faster and are therefore used more frequently than isotopically heavier forms. This results in a significant depletion of biogenic methane in ^{13}C relative to the precursor [23]. During acetate fermentation, the isotopic effect is less pronounced. Consequently, methane produced by acetate fermentation has $\delta^{13}C\text{-}CH_4$ values ranging from -65‰ to -50‰, whereas the $\delta^{13}C$ of methane produced by CO_2 reduction, ranges from -110‰ to -60‰ after [1]. The $\delta^{13}C$ values of coexisting carbon dioxide are also helpful in determining the mechanisms of CH_4

formation. The carbon isotope fractionation between $\delta^{13}C-CO_2$ and $\delta^{13}C-CH_4$ can be expressed as the fractionation factor $\alpha_{CH4-CO2} = (\delta^{13}C-CO_2 + 1000)/(\delta^{13}C-CH_4 + 1000)$. The magnitude of $\alpha_{CH4-CO2}$ associated with methanogenesis in marine environments varies between 1.05 and 1.1 and reaches slightly different values while in marine and freshwater ecosystems [23, 24]. On the basis of knowledge of $\delta^{13}C$ values of coexisting CO_2 and CH_4 it is possible not only to consider different mechanisms of methanogenesis, but also to estimate the intensity of methane consumption. Indeed, methane oxidation causes a significant slowdown in carbon isotope fractionation, resulting in fractionation factor values in the range of 1.005 - 1.025 [23].

The isotopic composition of dissolved inorganic carbon ($\delta^{13}C$-DIC) indicates the primary source of this substance in waters: (i) atmospheric CO_2; (ii) decomposition of organic matter; (iii) dissolution of carbonate minerals; (iv) transformations of the latter associated with photosynthesis and respiration. For photosynthesis, the isotopic effect is about -19‰, which, assuming an atmospheric $\delta^{13}C-CO_2$ of about -7‰, depletes the resulting organic matter into the heavier isotope to -26‰ [25]. The change in $\delta^{13}C$-DIC values along the flow path reflects the relative intensity of photosynthetic assimilation and respiration. Preferential consumption of the lighter carbon isotope ^{12}C by photosynthesis results in higher $\delta^{13}C$-DIC values in waters of the euphotic epilimnion layer, while CO_2 from organic matter mineralization has lower $\delta^{13}C$-DIC values [26]. Mineralization of organic matter or dissolution of $CaCO_3$ in lake sediments releases inorganic carbon that is isotopically similar to sources, i.e., organic carbon in sediments and $CaCO_3$, into the interstitial water. DIC released by methanogenesis occurring in sediments under reducing conditions is enriched in ^{13}C compared to organic carbon in sediments [27, 28].

RESEARCH METHODS

The analysis of CH_4 and CO_2 emissions and the factors influencing them was conducted in 2009-2012 in the ecosystems of five reservoirs of southeastern Poland: Rzeszów, Maziarnia, Nielisz, Besko, Chańcza [1, 8, 29, 30, 31, 32]. The characteristics of the studied reservoirs are given in Table 1.

The studied reservoirs were divided into two groups. In the first one, which consisted of Rzeszów, Nielisz and Maziarnia Rservoirs, high emission of carbon greenhouse gases was observed, while the second one (Besko and Chańcza) was characterized by lower emission of these gases, mainly CH_4).

Table. 1. Characteristics and trophic state of waters of studied reservoirs (E- eutrophy, H- hypertrophy)

Reservoir	Construction year	Coordinates	Capacity	Depth average (max.)	Area	Retention time	Catchment area	TSI – Chla	TSI –TP
			10^3 m^3	M	ha	day	km^2		
Rzeszów	1974	50°00'N 21°59' E	1800	0.6(4.9)	68.2	0.8	2025	H	E
Maziarnia	1988	51°20'N 22°55' E	4.2	2.6(8)	160	36	233	H	E
Nielisz	2008	50°48'N 23°02' E	19.5	2(8)	890	-	-	H	E
Besko	1978	49°33'N 21°55' E	15.4	30(12)	124.5	61	207	E	E
Chańcza	1984	50°38'N 21°03' E	40	11	340	218	475	E	E

RESEARCH RESULTS AND DISCUSSIONS

The measured diffusive fluxes of CH_4 at the water-air interface in the studied reservoirs varied over a very wide range from 0 to 1181.90 $mmol \cdot m^{-2} \cdot d^{-1}$ (0 to 18910.4 $mg \cdot m^{-2} \cdot d^{-1}$). Only reservoirs of the first group showed significant CH_4 emissions to the atmosphere, especially at sites located in the upper part of the reservoirs. Mean values of methane fluxes recorded for sites located near dams were 466.08 $mg \cdot m^{-2} \cdot d^{-1}$, 8.32 $mg \cdot m^{-2} \cdot d^{-1}$ and 243.68 $mg \cdot m^{-2} \cdot d^{-1}$ for Rzeszów, Maziarnia and Nielisz reservoirs, respectively, while mean values for sites located near Tributaries were: 3468.48 $mg \cdot m^{-2} \cdot d^{-1}$, 5958.88 $mg \cdot m^{-2} \cdot d^{-1}$, and 3352.28 $mg \cdot m^{-2} \cdot d^{-1}$. Values of diffusive methane flux to the atmosphere from the surface of temperate zone reservoirs typically vary between 10 and 80 $mg \cdot m^{-2} \cdot d^{-1}$- an average of about 20 $mg \cdot m^{-2} \cdot d^{-1}$, and in the tropics range between 20 and 1500 $mg \cdot m^{-2} \cdot d^{-1}$- an average of about 300 $mg \cdot m^{-2} \cdot d^{-1}$ [33].

In the case of CO_2, the differences between reservoirs were much smaller. Calculated rate of diffusive fluxes of CO_2 at the water-air interface ranged from -1348.16 to 8086.32 $mg \cdot m^{-2} \cdot d^{-1}$. Mean values of fluxes in the studied reservoirs ranged from -154.88 to 3612.84 $mg \cdot m^{-2} \cdot d^{-1}$, with the lowest mean value recorded in Besko Rservoir, and the highest in Maziarnia Rservoir. St. Luis et al. [33] report values of diffusive fluxes of CO_2 to the atmosphere from the surface of reservoirs located in the temperate climate zone to be within the range of 750 to 3100 $mg \cdot m^{-2} \cdot d^{-1}$, while for tropical dam reservoirs within the range of 450 to 10200 $mg \cdot m^{-2} \cdot d^{-1}$. For the reservoirs studied, values of CO_2 flux at the water-air interface were within the range of values characteristic for reservoirs located in the temperate climate zone.

Tables 2 and 3 collect data on carbon greenhouse gas emissions from reservoirs located in different climate zones. As can be seen, the magnitude of CH_4 and CO_2 emissions from the surface of these ecosystems varies significantly between different climate zones. Moreover, CO_2 fluxes at the water-air interface are usually higher than the analogous ones for CH_4, with negative values sometimes observed for CO_2 due to absorption of this gas from atmospheric. It is significant that boreal reservoirs emit much smaller amounts of reenhouse gases than reservoirs from temperate or tropical climate zones. It is also important to note the differences between gas emissions from reservoirs from the same climate zones, confirming that temperature although a major but not decisive factor affecting of these emissions [31, 34].

Table 2. Carbon dioxide and methane emissions from the surface of reservoirs and lakes in the boreal and temperate climate zones; average flux values are in parentheses [1]

Reservoir/lake	CO_2 $mg \cdot m^{-2} \cdot d^{-1}$	CH_4 $mg \cdot m^{-2} \cdot d^{-1}$	Reference
	Boreal zone		
Grand Rapids (Canada)	-347 – 7260 (624)	-0.07 – 27.72 (0.58)	[9]
Jenpeg (Canada)	-926 – 2126 (316)	-0.07 – 10.81 (1.11)	[9]
Kettle (Canada)	-723 – 5646 (514)	-0.19 – 0.97 (-0.01)	[9]
McArthur (Canada)	-1057 – 3556 (367)	-0.03 – 7.15 (0.04)	[9]
EM-1 (Canada)	-4 – 19676 (2426)	-0.04 – 8.18 (0.77)	[9]
RDP (Canada)	-234 – 9380 (665)	-0.05 – 6.38 (0.49)	[9]
LG-2 (Canada)	45 – 6509 (661)	-0.09 – 2.56 (0.14)	[9]
Lokka (Finlandia)	484 – 3212 (1518)	5.28 – 118.4 (22.96)	[12]
Porttipahta (Finland)	880 – 2288 (1540)	2.56 – 4.8 (3.52)	[12]
	Temperate zone		
Wohlen (Switzerland)		(855)	[35]
Gruyere (Switzerland)	(979)	(0.15)	[36]
Lungern (Switzerland)	(242)	(0.13)	[36]
Sihl (Switzerland)	(1100)	(0.21)	[36]
Luzzone (Switzerland)	(1414)	(0.13)	[36]
Solina (Poland)	-914,32 – 648,12	0	[8]
F. D. Roosevelt (USA)	-852 – 251 (-462)	1.6 – 8.2 (3.2)	[37]
Dworshak (USA)	-2278 – -720 (-1195)	0.6 – 14.8 (3.4)	[37]
Wallula (USA)	-1629 – 1060 (-349)	3.5 – 17.0 (9.0)	[37]
Shasta (USA)	351 – 2150 (1247)	-1.5 – 29.2 (9.5)	[37]
Oroville (USA)	266 – 2430 (1026)	1.1 – 10,5 (4.2)	[37]
Eagle Creek (USA)	(2010)	10.49	[37]
5 lakes (Netherlands)	-144 – 2973.6 (1478.4)	33.6 – 434.4 (93.6)	[38]
Three Georges (China)		0 – 15.9 (3.8)	[39]
Three Georges (China)	(2506.32)	(1.2)	[40]
Three Georges (China)	(3919)		[41]
Shuibuya (China)	(3740)	(1.2)	[42]
Reservoirs in the temperate zone	750 – 3100 (1400)	10 – 80 (20)	[33]

Table 3. Carbon dioxide and methane emissions from the surface of reservoirs in subtropical, tropical, climate zones; average flux rates are given in parentheses [1]

Reservoir	CO_2 mg·m^{-2}·d^{-1}	CH_4 mg·m^{-2}·d^{-1}	Reference
Subtropical zone			
Gold Creek (Australia)		6.6 – 4900	[43]
Tropical zone			
Balbina (Brazil)	(1600)	4.96	[44]
Balbina (Brazil)	1258 – 31273 (13845)		[44]
Miranda (Brazil)	16.03 – 61182.5 (4980)	20.002 – 4747.6 (262.4)	[45]
Tres Marias (Brazil)	-10060 – 41.4 (-142)	0.901 – 1446 (382.2)	[45]
Barra Bonita (Brazil)	1614 – 33424 (6434)	3.102 – 50 (19.2)	[45]
Segredo (Brazil)	0.0021 – 46859 (4789)	0.006 – 93 (9.9)	[45]
Xingó (Brazil)	29.004 – 89203.06 (9837)	3.31 – 157 (29.99)	[45]
Samuel (Brazil)	2313.004 – 16348.5 (8087)	4.9001 – 2442 (183.6)	[45]
Tucurui (Brazil)	1314.002 – 142724 (10433)	0.04 – 108.9 (205.4)	[45]
Itaipu (Brazil)	-2646 – 7980.74 (1205)	1.4 – 50.04 (12.9)	[45]
Serra da Messa (Brazil)	-630.87 – 5902.2 (1316)	-3.8 – 1011.3 (121)	[45]
Funil (Brazil)		0.64 – 216 (15.84)	[46]
Santo Antonio (Brazil)		5.28 – 1153.6 (148.8)	[46]
Petit Saut (French Guyana)	580 – 10498 (4460)	4.96 – 3800 (1140)	[47]
Nam Ngum (Laos)	-932.8 – -118.8	1.6 – 9.6	[48]
Nam Leuk (Laos)	-466.4 – 1680.8	12.8 – 190.4	[48]
Reservoirs in tropical zones	450 – 10200 (3500)	20 – 1500 (300)	[33]
Baoshan (Taiwan)	-1224 – 1152	0.72 – 9.6	[49]
Liyutan (Taiwan)	-1200 – -240	0.72 – 28.8	[49]
Tsengwen (Taiwan)	-888 – 864	4.08- 57.6	[49]

CONCLUSION

Analysing the fluxes of CH_4 and CO_2 at the water-air interface, it was found that two groups can be distinguished for the studied reservoirs. Maziarnia, Nielisz and Rzeszów are reservoirs where high CH_4 and CO_2 emissions were observed. In the remaining reservoirs, the emission was small or not observed. Methane fluxes to the atmosphere from the surface for these three active reservoirs were very high and comparable to values characteristic of tropical reservoirs (Table 2). Less differentiation between reservoirs was observed for carbon dioxide emissions than for methane emissions. In most cases, CO_2 fluxes at the water-air interface were comparable to those reported in the literature for reservoirs located in temperate climate zones (Table 3). The obtained data indicate that dam reservoirs located in the temperate climate zone can be a source of large amounts of greenhouse gases, especially during the growing season and at increased trophy. Despite the fact that the rate of CO_2 fluxes into the atmosphere is higher than that of CH_4, it should be assumed that some aquatic ecosystems may large contribute in balance of CH_4 emissions to the atmosphere in the context of the observed greenhouse effect, because Global Warming Potential of CH_4 is 25.

REFERENCES

1. Gruca-Rokosz R., Dynamika węglowych gazów cieplarnianych w zbiornikach zaporowych – mechanizmy produkcji, emisja do atmosfery [Carbon greenhouse gas dynamics in reservoirs - production mechanisms, atmospheric emissions], Monograph, Polnad, 2015.

2. Guérin F. and Abril A., Significance of pelagic aerobic methane oxidation in the methane and carbon budget of a tropical reservoir, Journal of Geophysical Research Atmospheres 112/G3, 2007.

3. Wanninkhof R., Mcgillis W.R., A cubic relationship between air-sea CO_2 exchange and wind speed, Geophysical Research Letters, 26, 1889-1892, 1999.

4. Ho D.T., Veron F., Harrison E., Bliven L.F., Scott N., Mcgillis W.R., The combined effect of rain and wind on air-water gas exchange: A feasibility study, Journal of Maine. Systems, 66, 150-160, 2007.

5. Guérin F., Abril G., Serça D., Delon C., Richard S., Delmas R., Tremblay A., Varfalvy L Gas transfer velocities of CO_2 and CH_4 in a tropical reservoir and its river downstream, Journal of Marine Systems, 66/1-4, 161-172, 2007.

6. Zimov S.A., Voroaev Y.V., Semiletov I.P., Davidov S.P., Prosiannikov S.F., Chapin Iii F.S., Chapin M.C., Trumbore S., Tyler S., North Siberian Lakes: a methane source fueled by Pleistocene carbon, Science, 227, 800-802, 1997.

7. Xing Y., Xie P., Yang H., Ni L., Wang Y., Rong K., Methane and carbon dioxide fluxes from a shallow hypereutrophic subtropical Lake in China, Atmos. Environ., 39, 5532-5540, 2005.

8. Gruca-Rokosz R., Tomaszek J.A., Koszelnik P., Czerwieniec E., Methane and carbon dioxide emission from some reservoirs in SE Poland, Limnological Review, 1, 15-21, 2010.

9. Demarty M., Bastien J., Tremblay A., Hesslein R.H., Gill R., Greenhouse gas emissions from boreal reservoirs in Manitoba and Quebec, Canada, measured with automated systems. Environmental Science and Technology, 43, 8908-8915, 2009.

10. Whitfield C.J., Aherne J., Baulch H.M., Controls on greenhouse gas concentrations in polymictic headwater lakes in Ireland, Science of the Total Environment, 410-411, 217-225, 2011.

11. Huttunen J.T., Lappalainen K.M., Saarijärvi E., Väisänen T., Martikainen P.J., A novel sediment gas sampler and a subsurface gas collector used for measurement of the ebullition of

methane and carbon dioxide from a eutrophied lake, The Science of the Total Environment, 266, 153-158, 2001.

12. Liikanen A. Huttunen J.T., Murtoniemi T., Tanskanen H., Väisänen T., Silvola J., Alm J., Martikainen P.J., Spatial and seasonal variation in greenhouse gas and nutrient dynamics and their interactions in the sediments of a boreal eutrophic lake, Biogeochemistry, 65, 83-103, 2003.

13. Tomaszek, J.A., Czerwieniec, E., Dentrification and oxygen consumption in bottom sediments: factors influencing rates of the processes, Hydrobiologia, 504(1-3), 59-65, 2003.

14. Jędrysek M.O., Hałas S., Pieńkos T., Carbon isotopic composition of early-diagenetic methane: variations with sediments depth, Annales Universitatis Mariae Curie – Skłodowska, LXIX, 29-52, 2014.

15. McGinnis D.F., Greinert J., Artemov Y., Beaubien S.E., Wüest A., Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere?, Journal of Geophysical Research Atmospheres, 111/C9, 2006.

16. Huttunen J.T., Väisänen T.S., Hellsten S.K., Mertikainen P.J., Methane fluxes at the sediment – water interface in some boreal lakes and reservoirs, Boreal Env. Res., 11, 27-34, 2006.

17. Sorrell B.K. and Boon P.I., Biogeochemistry of billabong sediments: II. Seasonal variations in methane production, Freshwater Biology, 27, 435-445, 1992.

18. Hamilton S.K., Sippel S.J., Melack J.M., Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil, Biogeochemistry, 30. 115-141, 1995.

19. Conrad R., Control of methane production in terrestrial ecosystems,[In:] Andrea M.O., Schimel D.S.: Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, J. Wiley & Sons, 39-58, 1989.

20. Fearnside P.M., Greenhouse gas emissions from hydroelectric dams: Controversies provide a springboard for rethinking a supposedly "clean" energy source – An editorial comment, Climatic Change, 66/(1, 2): 1-8, 2004.

21. Kemenes A., Forsberg B.R., Melack J.M., Methane release below a tropical hydroelectric dam, Geophysical Research Letters, 34, L12809, 2007.

22. Guérin F., Abril G., Richard S., Burban B., Reynouard C., Seyler P., Delmas R., Methane and carbon dioxide emissions from tropical reservoirs: Significance of downstream rivers, Geophysical Research Letters, 33/21, 2006.

23. Whiticar M.J., Stable isotope geochemistry of coals, humic kerogens and related natural gases, International Journal of Coal Geology, 32/1-4, 191-215, 1996.

24. Whiticar M.J., Carbon and hydrogen isotope systematic of bacterial formation and oxidation methane, Chemical Geology, 161, 291-314, 1999.

25. Schidlowski M., Isotope fractionations in the terrestrial carbon cycle: a brief overview, Advances in Space Research, 15/3, 441-449, 1995.

26. Myrbo A., Shapley M.D., Seasonal water-column dynamics of dissolved inorganic carbon stable isotopic compositions ($\delta^{13}C_{DIC}$) in small hardwater lakes in Minnesota and Montana, Geochimica et Cosmochimica Acta, 70, 1699-2714, 2006.

27. Ogrinc N., Lojen S., Faganeli J., A mass balance of carbon stable isotopes in an organic-rich methane-producing lacustrine sediment (Lake Bled, Slovenia), Global and Planetary Change, 33, 57-72, 2002.

28. Corbett J.E., Tfaily M.M., Burdige D.J., Cooper W.T., Glaser P.H., Chanton J.P., Partitioning pathways of CO_2 production in peatlands with stable carbon isotopes. Biogeochemistry, 114, 327-340, 2013.

29. Gruca-Rokosz R., Tomaszek J.A., Koszelnik P., Czerwieniec E., Methane and carbon dioxide fluxes at the sediment-water interface in reservoirs, Polish Journal of Environmental Studies, 20/1, 81-86, 2011.

30. Gruca-Rokosz R., Tomaszek J.A., Methane and carbon dioxide in the sediment of a eutrophic reservoir: production pathways and diffusion lluxes at the sediment–water interface. Water, Air and Soil Pollution, 226, 16, 2015.

31. Gruca-Rokosz, R., Bartoszek L., Koszelnik, P., The influence of environmental factors on the carbon dioxide flux across the water–air interface of reservoirs in south-eastern Poland, Journal of Environmental Sciences, 56, 290-299, 2017.

32. Gruca-Rokosz, R., Koszelnik, P., Production pathways for CH_4 and CO_2 in sediments of two freshwater ecosystems in south-eastern Poland. PloS One, 13/6, 2018.

33. St. Louis V.L., Kelly C.A., Duchemin E., Rudd J.W.M., Rosenberg D.M., Reservoir surfaces as sources of greenhouse gases to the atmosphere: a global estimate, BioScience, 50/9, 766-775, 2000.

34. Mander U., Maddison M., Soosaar K., Karabelnik K., The impact of pulsing hydrology and fluctuating water table on greenhouse gas emissions from constructed wetlands, Wetlands, 31, 1023-1032, 2011.

35. Delsontro T., Mcginnis D. F., Sobek S., Ostrovsky I., Wehrli B., Extreme methane emission from Swiss hydropower reservoir: contribution from bubbling sediments, Environmental Science and Technology, 44, 2419 – 2425, 2010.

36. Diem T., Koch S., Schwarzenbach S., Wehrli B., Schubert C.J., Greenhouse gas emissions (CO_2, CH_4, and N_2O) from several perialpine and alpine hydropower reservoirs by diffusion and loss in turbines, Aquatic Sciences, 74/3, 619-635, 2012.

37. Soumis N., Duchemin E., Canuel R., Lucotte M., Greenhouse gas emissions from reservoirs of the western United States, Global Biogeochemical Cycles, 18, GB3022, 2004.

38. Schrier-Uijl A.P., Veraart A.J., Leffelaar P.A., Berendse F., Veenendaal E. M., Release of CO_2 and CH_4 from lakes and drainage ditches in temperate wetlands, Biogeochemistry, 102, 265-279, 2011.

39. Xiao S., Liu D., Wang Y., Yang Z., Chen W., Temporal variation of methane flux from Xiangxi Bay of the Three Gorges Reservoir, Scientific Reports, 3, 2500, 2013.

40. Xiao S., Wang Y., Liu D., Yang Z., Lei D., Zhang C., Diel and seasonal variation of methane and carbon dioxide fluxes at Site Guojiaba, the Three Gorges Reservoir, Journal of Environmental Sciences, 25(10), 2065-2071, 2013.

41. Yang L., Lu F., Wang X., Duan X., Tong L., Ouyang Z., Li H., Spatial and seasonal variability of CO_2 flux at the air-water interface of the Three Gorges Reservoir, J. Environ. Sci., 25, 2229–2238, 2013.

42. Zhao D.Z., Tan D.B., Wang Z.H., Hao C.Y., Measurement and analysis of greenhouse gas fluxes from Shuibuya reservoir in Qingjiang river basin, Journal of Yangtze River Scientific Research Institute, 28(10), 197-204, 2011.

43. Sturm K., Yuan Z., B. Gibbes B., Werner U., Grinham A., Methane and nitrous oxide sources and emissions in a subtropical freshwater reservoir, South East Queensland, Australia. Biogeosciences, 11, 5245-5258, 2014.

44. Kemenes A., Forsberg B.R., Melack J.M., CO_2 emissions from tropical hydroelectric reservoir (Balbina, Brazil), Journal of Geophysical Research, 116, G03004, 2011.

45. dos Santos M.A., Rosa L.P., Sikar B., Sikar E., Dos Santos E.O., Gross greenhouse gas fluxes from hydro-power reservoir compared to thermo-power plants, Energy Policy, 34, 481-488, 2006.

46. Grandin K., Variations of CH_4 emissions within and between hydroelectric reservoirs in Brazil. Master's thesis, Uppsala University, Sweden, 1-61, 2012.

47. Galy-Lacaux C., Delmas R., Jambert C., Dumestre J.-F., Labroue L., Richard S., Gosse P., Gaseous emissions and oxygen consumption in hydroelectric dams: a case study in French Guyana, Global Biogeochemical Cycles, 11, 471-483, 1997.

48. Chanudet V., Descloux S., Harby A. Sundt H, Hansen B. H., Brakstad O., Serca D., Guerin, F., Gross CO2 and CH4 emissions from the Nam Ngum and Nam Leuk sub-tropical reservoirs in Lao PDR, Science of the total Environment, 409/24, 5382-5391, 2011.

49. Wang Y.-H., Huang H.-H., Chu C.-P., Chuag Y.-J., A preliminary survey of greenhouse gas emission from three reservoirs in Taiwan, Sustainable Environment Research, 23/3, 215-225, 2013.

ENVIRONMENTAL SAFETY OF WASTEWATER DISPOSAL - FACTOR OF SUSTAINABLE DEVELOPMENT OF CITIES

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ABSTRACT

The paper examines the environmental safety of wastewater disposal systems – one of the life support systems for a population – as a condition for sustainable urban development. Gaseous emissions from such systems contain a number of highly hazardous substances. The concentrations of hydrogen sulphide and formaldehyde – a hazard category 2 substances – in sewer network emissions and in the underroof space of sewer collectors by direct measurement and a calculation were experimentally investigated. It has been proved that the concentrations of hydrogen sulphide and formaldehyde in the underroof space and in sewer network emissions significantly exceeds the corresponding maximum permissible concentration. The calculation of hydrogen sulfide dispersion, released from the sewerage pipelines, showed, that at some sections of the sewer net the environmentally safe area is at a distance of 225-260 m from the shafts. Cooling and installation of degassers in shafts were suggested as reasonable methods for protecting the city's atmospheric air against the emissions from sewer systems

Keywords: wastewater disposal, gaseous emissions, hydrogen sulfide, formaldehyde, environmental safety

INTRODUCTION

The study of the problems of sustainable development of settlements, especially cities, nowadays is the key area of scientific substantiation of the main paradigm of the 21st century - sustainable economic, social and environmental development. Cities play a special role in achieving sustainable development, since the problems and opportunities of modern civilization are the most significant and noticeable there [1]. What is understood under the term "constant urban development" is a set of socially, economically and ecologically balanced changes in the socio-territorial system of the city, aimed at the fullest possible realization of all its potential's components and preventing the tendencies for the population's quality of life to deteriorate [2], which includes environmental safety as one of its elements. The stability of the city affects the ability to implement the principles of sustainable development of higher-level systems and depends on the sustainability of all the constituent elements included in the socio-economic system of the city.

The concept of sustainable development systematically connected the three main components of the development of society: economic, social and environmental. From an environmental point of view, sustainable development should ensure the integrity of biological and physical natural systems and their viability. Within the city, the viability of natural systems – first and foremost, people (the population of the city) – depends on the environmental safety of the living conditions. It is important, during the practical implementation of the principles of sustainable development of a city, not only to determine its resource provision (resources, their structure, cost, potential), but also to analyze the situation from the perspective of various types of activities, economic areas and their interaction [2, 3].

A big city changes all the environmental components - the atmosphere, the vegetation, the soil, the topography, the hydrographic network, the ground waters and even the climate. This leads to great environmental problems caused by its high population concentration, industrial facilities, and urban infrastructure. The growth of the urban population, especially in recent decades, the rapid concentration and intensification of production and non-production activities have led to the fact that the environment in many cities around the world cannot satisfy all the biological and social requirements of modern man, including ensuring complete environmental safety.

In the context of the foregoing, the reliability and environmental safety of the functioning of city population's life support systems is of particular importance for the sustainable development of cities. One of the links of this system is wastewater disposal, which ensures the environmental safety of water usage and, in general, performs an extremely large-scale environmental function - protecting the natural environment from pollution by liquid anthropogenic wastes.

However, constructions of wastewater disposal are large-scale technical facilities. They exert an intense technogenic load on the environment and often create dangers for urban regions. The sewage disposal by the sewerage pipelines brings a range of risks for environmental safety of air, water and soil environments in settlements. Thus formation and emission of gas compounds from the sewer nets through the sewer shafts and manholes pollute the atmosphere in neighboring urban districts, as in these emissions concentration of series of the compounds mainly sulfur-containing – hydrogen sulfide, sulfur dioxide, mercaptan (alkyl sulphydrate), dimethyl sulphide (DMS), exceeds not only daily average maximum permissible concentration (MPC) for residential areas, but also MPC for working ones (MPC working area – 10, MPC daily average – 0,008 mg/m^3) (table 1, 2).

Table 1. Contents of odour-generating substances in Australian sewers [4, 5]

Substance	Concentration in Australian sewers, µg/m^3
Dimethyl disulphide	8.72
Dimethyl sulphide	65.4
Diethyl sulphide	1.12
Diethyl disulphide	0.15
Ethyl mercaptan	3.81
Hydrogen sulphide	1880
Methyl mercaptan	293
Sulfur dioxide	870–2600

The highest rate of MPC excess in gas release from the sewer nets is marked for hydrogen sulfide – highly toxic and chemically active compound of the second hazard category. Besides, the concentration of hydrogen sulfide, its derivatives and oxidation products in operational environments of the concrete sewerage pipelines (fine water, underroof space, condensate water on the roof) activate biogenic sulfuric corrosion of the roof, that reduces operating life of these pipelines (from planned 50 to 10-15 years). The biogenic corrosion causes 70-75% of reinforced sewerage pipelines breaks, which are followed by failures and landslip seams in the grounds of residential construction and transport systems, destruction of municipal services, pollution of soil and water environments. Frequency of reinforced sewerage pipelines breaks (whose length is 25% of length of the whole sewer net) is 1,8-4,6 km/year, i.e. 2-4 times higher than at the ceramic ones and 20-40 times higher than at the brick ones [6-10].

A number of specialists found not only sulfur-containing compounds of a high hazard category in emissions from sewer networks. Unfortunately, among the carbon-containing gaseous compounds in the emissions from sewer networks there are also many potentially very hazardous substances (Table 2 [11]). When it comes to environmental safety of carbon-containing compounds in emissions from sewer networks, formaldehyde, which was discovered by a number of specialists, attracts great attention [4, 12, 13]. In terms of its effect on the human body, formaldehyde, like hydrogen sulfide, is a highly hazardous substance (substance hazard category 2) [14]. These substances have a pungent and unpleasant odor. Moreover, the MPC of all types of rationing for formaldehyde is significantly lower than the MPC for hydrogen sulfide. Formaldehyde is classified as a probable carcinogen for humans with a minimum single inhalation dose of 1.3 × 10-5 mg/m^3. According to foreign scientists, its concentration in emissions from sewer networks is 0.370 mg/m^3 [10].

Table 2. Chemical compounds in the underroof space atmosphere of sewerage pipelines [11].

Sr. No.	Compound	Arrangement of concentration by volume
1	Carbon dioxide	0,2-1,2 %
2	Hydrocarbons and their chlorinated derivatives	
	a. Hydrocarbons, mainly aliphatic C6-C14, C8-C12 (benzines)	to 500 ppm
	b. Chlorinated derivatives of hydrocarbons, mainly trichloroethene, dichloride of etherin and carbon tetrachloride	10-100 ppm
3	Hydrogen sulfide	0,2-10 ppm
4	Odorous gases and vapors	
	a. Sulfides (mainly mercaptan, DMS, some ethyl mercaptan)	10-50 ppb
	b. Amines (mainly trimethylamine and dimethylamine, some diethylamine)	10-50 ppb
	c. Aldehyds (mainly butyl aldehyd)	10-100 ppb

The presence of this gas in emissions from sewer networks causes such concern because of the steady excess of its concentrations in the cities of Ukraine. [15, 16]. Moreover, such excesses are usually associated with the work of certain industrial enterprises, or vehicles. However, detailed studies in cities with a small number of industrial enterprises also found that the concentration of formaldehyde in atmospheric air was higher than the MPC. Upon conducting detailed studies and calculations, it was found that the contribution of vehicles to formaldehyde emissions was also very small (up to 5%). Potentially, air pollution is the most serious environmental problem for human health in the short and in the long run. It is more difficult to avoid exposure to air pollution than to water pollution [16].

The solution to the problem of protecting the urban environment from pollution by gaseous emissions from sewer networks is carried out in various areas of the project: standardization of industrial enterprises' discharges, operational solutions for the transportation of wastewater, the usage of degassing installations on sewer networks. However, the issue of effective removal of formaldehyde from sewer network emissions to ensure an appropriate level of environmental safety in the urban air hasn't been studied.

FORMATION OF GASEOUS COMPOUNDS IN THE SEWERAGE PIPELINES

The gravity sewerage pipeline can be considered as a technogenic ecosystem, which includes three phases: liquid (sewage disposal), gas (air of the main drainage channel) and solid (concrete of the roof) and their microbiocenosis. Such pipeline is a specific "reactor", where spontaneous chemical and microbiological processes are proceeded. They cause formation of the gas compounds in sewage disposal, which are evolved in the air of the underroof space of the gravity pipelines, are partially dissolved in condensate water on the roof of the buildings and interact with concrete either directly or after microbiological transformations (Fig. 1) [4, 6, 11-13].

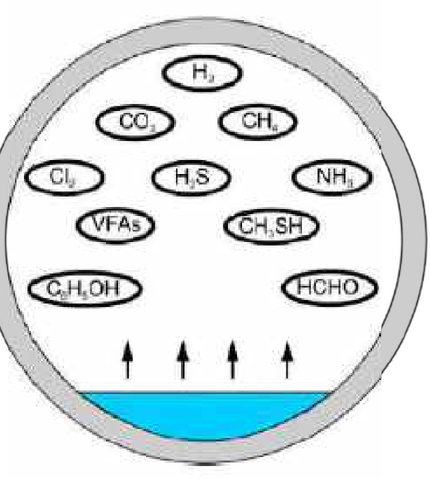

Fig. 1. Odor emission in the sewage system [4]

Formation of hydrogen sulfide in the sewage disposal results from microbiological processes of disassimilation sulfate reduction (reduction of sulfates with the hydrogen sulfide emission), which obligate anaerobic sulfate-reducing bacteria perform. The activity level of hydrogen sulfide formation and its emissions in the air of the pipeline depends on many factors: COD of sewage water, concentration ratio of sulfates and COD, temperature, pH and Eh of sewage water, flow turbulence and others. [6-8]. Thus the hydrogen sulfide concentration in the underroof space of different sections fluctuates very significantly even within 24 hours [17]. Regulation of the hydrogen sulfide concentration in the underroof space air of the sewer nets, carried out at regular times as a rule, does not allow to estimate reasonably the condition. The processes of hydrogen sulfide emission through the sewer shafts into the urban environment and its dispersion are studied rather partially. The particular calculations and measurements testify high ecological hazard of the process for the urban environment [18, 19].

The methods of operating monitoring of these objects corrosion damage and concentration activity of hydrogen sulfide in them are necessary for reliability control of concrete sewerage pipelines running and increasing of their operating life. Permanent control (monitoring) of this compound concentration on the sections of the net, information storage and rendering to the maintenance departments of the sewer nets in the modern form are necessary for provision of ecological safety and operation reliability of the sewage disposal by the concrete pipelines (development and implementation of gas emission cleaning methods, squelching methods of processes, producing hydrogen sulfide).

Providing ecological safety of sewerage pipelines running and protection of urban atmosphere from pollution of toxic gas compounds, released from sewerage pipelines, various engineering solutions are developed: suppression of hydrogen sulfide formation in sewage disposal, suppression of hydrogen sulfide elutriation from sewage disposal in the underroof space, clearing of gas releases. In Ukraine there is some experience of usage of gas-cleaning plants - utility company (UC) “Kharkovvodokanal”. On its basis such protective measure of urban atmosphere is recommended by regulatory documents of Ukraine - Ukrainian national construction regulation [20].

The object of this research is to assess the level of health hazard posed by the presence of gaseous compounds of the 2nd hazard class – hydrogen sulfide and formaldehyde – in sewer network emissions and some environmentally friendly means of solving this problem.

METHODS AND EXPERIMENTAL PROCEDURES

The studies were carried out in real conditions together with the employees of the operational service of UC “Kharkovvodokanal”. The measurements of the concentrations of H_2S, SO_2, CO, CO_2 and CH_4 were performed with universal portable gas analyzer UG-2, “Dozor” and mine interferometer ShI-11 in the underroof space of the collector, where the device for sampling the air-gas mixture was lowered through the entire height of the shaft. The concentration of these substances is periodically measured by the analytical laboratory of UC “Kharkovvodokanal”. The average annual concentration of hydrate sulfide in the gaseous fluid at the different height of the sewer shafts was established by the method, developed in [17]. It is based on the nondestructive evaluation of the depth of biogeneous corrosion concrete with a concrete corrosimeter – a device, authorized in Ukraine. The concentrations of formaldehyde and volatile organic compounds were determined at the outlet of the sewer shaft by using a digital formaldehyde detector, the WP6910 air quality analyzer.

The obtained data was applied for the calculation of the hydrogen sulfide concentration in the gaseous emission and for calculation of its dispersion in the environment of the particular districts in Kharkiv. The calculation of hydrogen sulfide dispersion was performed with the program “EOL +”. OND-86 (National statutory document) “Calculation procedure of repugnant substances concentration in open air, contained in emissions of enterprises” is basically applied to the calculation.

The visualization of the monitoring system of the ecological safety and operating reliability of the sewerage pipelines in Kharkiv was carried out with the help of the specialized software, based on the ecological charting procedure and the geoinformational technologies.

METHODS AND EXPERIMENTAL PROCEDURES

The chemical composition of the underroof space atmosphere of the sewerage pipelines (regular monitoring data), identified in different shafts in Kharkov, is presented in Table 3. As it is seen from the table data, hydrogen sulfide has the highest excess of MPC of working area/daily average, in gas environment of the underroof space of sewerage pipelines (in tens/hundreds times). Shafts No.11 and 12, in gas environment of the underroof space, whose hydrogen sulfide concentration accesses 31350 MPC daily average, are extremely close to residential development (from 35 to 50 m). At the whole explored section of the collector, these mines are represented as the most ecologically hazardous for urban atmosphere and safety life-sustaining ability of population, living in the area of their location.

Sewerage pipeline laying depth in Kharkov is 40 meters at some sections. Gas hydrogen sulfide is heavier than air and thus its concentration at the output from the mine is less than the concentration, determined under the surveying of the pipelines. Degradation of the concentration depends on aerodynamic environment, that determines draft at the given section, temperature inside the mine and ambient temperature, height of the mine and others. These factors are required to be averaged for longer period taking into account the sizable fluctuations of the hydrogen sulfide concentration in the environment of the underroof space, the broad range of aerodynamic environment changes and temperatures. The measurement of corrosion rate of the concrete heightwise of some sewer shafts at different sections of sewage environment were applied for such averaging. With the help of the obtained data the averaging dependence, represented in Fig. 2., was formed. As it is seen from the represented data, degradation of the hydrogen sulfide concentration is approximately 7,4% for every meter of the mine height.

Table 3. The ecologically hazardous concentration of gas compounds in the underroof atmosphere of the sewerage pipelines at collector section in Kharkov

Shaft No.	Concentration of gas compounds							
	SO_2, mg/m^3	Rate of MPC excess working area/ daily average, quantity of MPC	H_2S, mg/m^3	Rate of MPC excess working area/ daily average, quantity of MPC	CO, mg/m^3	Rate of MPC excess working area/ daily average, quantity of MPC	CO_2, volume %	CH_4, volume %
4	35	3,5/70	24,6	2,46/3075	0	-	0,75	0
	35	3,5/70	42,7	4,27/5337	0	-	0,57	
	35	3,5/70	137	13,7/17125	0	-	0,63	
	35	3,5/70	126,6	12,6/15825	0	-	0,63	
	35	3,5/70	188,1	18,8/23512	4,2	-	0,84	
6	35	3,5/70	9,5	-/1187	0	-	0,57	0,57
	0	-	7,6	-/950	0	-	0,38	0,19
	0	-	12,6	1,26/1575	0	-	0,42	0,21
	0	-	11,6	1,16/1450	0	-	0,42	0,21
	35	3,5/70	17,8	1,78/2225	0	-	0,63	0,42
8	0	-	4	-/500	0	-	0,2	0,2
	0	-	6	-/750	0	-	0,2	0,4
	0	-	6	-/750	0	-	0,2	0,4
	0	-	12	1,2/1500	0	-	0,2	0,6
	0	-	12	1,2/1500	0	-	0,4	0,4
10	35	3,5/70	10,4	0,4/1300	0	-	0,19	0
	0	-	9,5	-/1188	0	-	0,57	0,38
	0	-	8,4	-/1050	0	-	0,21	0,21
	0	-	12,5	1,25/1563	0	-	0,62	0,42
	35	3,5/70	20,9	2,9/2613	0	-	0,63	0,84
11	0	-	12	1,2/1500	0	-	0,2	0,2
	0	-	18	1,8/2250	0	-	0,4	0,4
	0	-	23	2,3/2875	0	-	0,4	0,4
	0	-	24	2,4/3000	0	-	0,4	0,6
	0	-	28	2,8/3500	0	-	0,4	0,6
12	35	3,5/70	52,1	5,21/6513	0	-	0,76	0,76
	35	3,5/70	113,7	11,37/14213	3,9	-	0,76	0,57
	35	3,5/70	36,9	3,69/4612,5	0	-	0,42	0,42
	35	3,5/70	38	3,8/4750	0	-	0,63	0,21
	35	3,5/70	250,8	25,08/31350	0	-	1,25	1,25

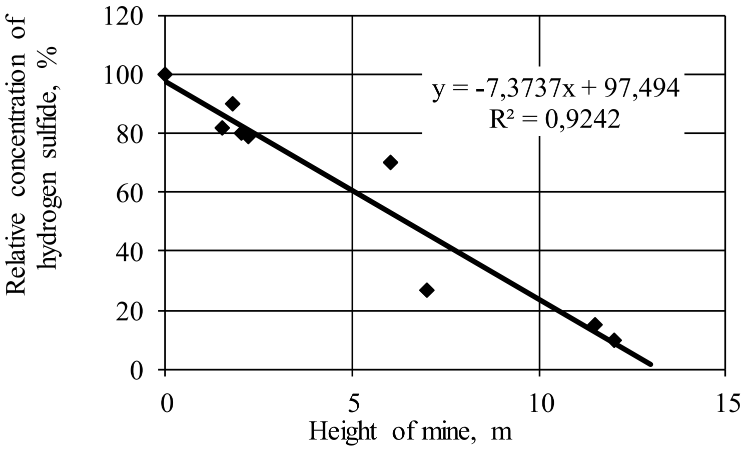

Fig. 2. Dependence of degradation of relative hydrogen sulfide concentration in the air-gas environment on the mine depth

In this way using the data on the concentration of gaseous substances (H_2S) in the underroof space, we can calculate the concentration of these contaminants in the emissions from the shaft (at the outlet of the shaft). For this calculation, an empirically established dependence (Fig. 2) of the concentration of H_2S in sewer shafts and the height of the shaft was used.

$$N = 7{,}37\ H + 97{,}49 \tag{1}$$

where N - relative concentration of H_2S at the output from the shaft with respect to the concentration in the underroof space, %;
H – height of shaft, m.

$$N = \frac{C\ output \cdot 100}{C\ underroof\ space}\ , \tag{2}$$

where Coutput - concentration of H_2S at the output from the shaft, mg/m³;
C underroof space - concentrations of H_2S in the underroof space, mg/m³;
100 – conversion factor, %.
Hence:

$$Coutput = \frac{(7{,}37\ H + 97{,}49)\ C\ underroof\ space}{100} \tag{3}$$

The calculation of gas emissions dispersion in the districts, where the sewer shafts No.51 and No. 52 are located, was performed. Daily average MPC (0,008 mg/m^3) was taken as a standard indicator. The depth of the surveyed shafts was 12 and 10 m. The height of the emission sources above ground was taken equal to 0,05 m. The baseline data for the calculation of dispersion is represented in Table 4, the data of the dispersion is represented in Table 5. The dispersal map of hydrogen sulfide, released from the mine No.51 into the atmosphere of the particular urban district, is represented in Fig.3.

Table 4. Parameters of the emission sources of polluting substances into the urban atmosphere from the sewer shafts

Emission source	Parameters of the emission source		Characteristic of the gas-air mixture at the output		Concentration H_2S, mg/m^3		Emission rate, g/s
	height, m	diameter, m	velocity, m/s	temperature, ^oC	in the pipeline	at the output from the Shaft	
Shaft No.51	0,05	0,7	1	18	40,1	4,01	0,004
Shaft No.52	0,05	0,7	1	18	20,4	5,1	0,005

Table 5. Calculation data of hydrogen sulfide dispersion

Emission source	Distance to the residential construction, m	Concentration of H_2S in the residential area, MPC part	Distance to the safe area, m
Shaft No.51	35	3,19	225
Shaft No.52	30	4,58	260

The calculation of gas emissions dispersion in the district, where the shaft No.51 is located, was performed. Daily average MPC was taken as a standard indicator. The map of hydrogen sulfide dispersion, released from the shaft No.51 in the atmosphere of the particular city district, is represented in Fig. 3.

Calculation of hydrogen sulfide dispersion in the explored area has shown, that in the nearest point, located in residential construction (35 m), hydrogen sulfide concentration is equal to 0,025 mg/m^3, that in 3,19 times excesses daily average MPC. As it is seen from the represented data, the residential construction on the surveyed section is located in the environmentally fragile area: the hydrogen sulfide concentration in the open air exceeds MPC. The performed calculations of hydrogen sulfide dispersion, released from the sewerage pipelines, show, that at some sections of the sewer net the environmentally safe area is at a distance of 225 m from the shafts.

This dependence (Formula 1) could be used for an approximate calculation of concentrations of gases that have a molecular weight close to the molecular weight of hydrogen sulfide (34), for example formaldehyde (the molecular weight 30). Taking into account that the concentration of SO_2, CO and CH_4 is proportional to the dynamic of H_2S in sewer networks [6-8], it can be used for a rough estimate of the concentration of these gases as well. Concentrations of polluting substances at the output from the surveyed shaft No.52 represented in table 3.

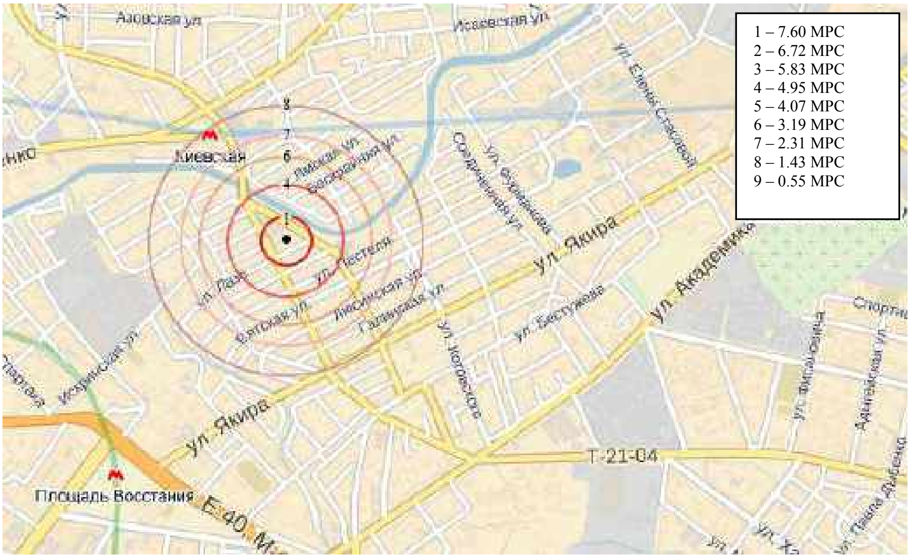

Fig. 3. Calculated dispersion of hydrogen sulfide, released from the water disposal pipeline in the section of the sewer shaft No.51

Table 6. Concentrations of polluting substances at the output from the surveyed shaft

Polluting substance	Concentrations of polluting substances in release from the shaft, mg/m³	MPC$_{daily\ average}$, mg/m³	Rate of MPC excess
Hydrogen sulfide, H_2S	1,5**	0,008	188
Sulphur dioxide, SO_2	3,5**	0,05	70
Carbon oxide, CO	0**	3	
Carbon dioxide, CO_2	0,083**	-	
Methane, CH_4	458**	-	
Formaldehyde, CH_2O	1,99*	0,003	663
Volatile organic compounds	4,88*	-	

* - concentration values obtained using direct measurement at the shaft;
** - the concentration value calculated in accordance with the dependence determined by the authors

As it is seen from table 3, formaldehyde – a hazardous gas – poses the biggest threat as its concentration in the gaseous emissions from the observed sewer shaft 663 times is much higher than the MPC. The concentrations of H_2S and SO_2 also significantly exceed the MPC $_{daily\ average}$. This creates a special danger for citizens living in areas adjacent to sewer shafts, since all these gases belong to hazard class 2. Given that formaldehyde is close in its molecular weight to hydrogen sulfide, the concentration of formaldehyde at the outlet of the shaft (in the emission) can be used to calculate its approximate concentration in the underroof space of the sewer collector using the determined dependence (1). The concentration of formaldehyde in the underroof space (C underroof space) could be calculated using the equation:

$$\text{C underroof space} = \frac{\text{C output} \cdot 100}{(7{,}37\ \text{H} + 97{,}49)} \tag{4}$$

where, 100 – conversion factor, %.

According to the calculation, this concentration is 19.9 mg/m³, while the MPC of formaldehyde in the atmospheric air of the working area is 0.5 mg/m³.
The obtained data indicates a consistently high concentration of formaldehyde in the underroof space of the sewer networks. So, while carrying out repairs in sewer network collectors, employees of the maintenance and repair services of drainage networks are exposed to environmentally hazardous concentrations of formaldehyde and other hazardous gaseous substances, which negatively affects their performance and general physical condition. Measures must be taken to prevent maintenance workers from getting poisoned by sewer gases that can vary in composition.

Based on the established positive correlation between the concentration of hydrogen sulfide in sewer networks and the concentration of formaldehyde [13], it is safe to assume that the concentration of formaldehyde is very high in the emissions from the shafts with the concentration of hydrogen sulfide that is substantially higher than 1.5 mg/m^3 [12, 21]. This should be taken into account when calculating the dispersion of gaseous substances in emissions from sewer shafts in the atmospheric air of cities. Such calculations were performed almost exclusively for H_2S, as a hazardous component of such emissions [21]. It is worth noting that the $MPC_{daily\ average}$ for formaldehyde is 2.7 times lower than the $MPC_{daily\ average}$ for hydrogen sulfide.

Among the methods for protecting the urban atmospheric air against the emissions of H_2S and formaldehyde (two gaseous compounds, which are hazard category 2 substances) from water disposal systems, the most promising are cooling and the installation of degasifiers on the shafts [6]. These methods [19, 21] have shown their effectiveness in protecting atmospheric air in Kharkov against the H_2S pollution and safety for the urban environment. The prospects of using wastewater cooling transported by networks to reduce formaldehyde emissions are quite good, since it is a product of microbiological metabolism and microbial destruction of wastewater pollution under anaerobic conditions. It is known that the rates of microbiological reactions follow the temperature dependence of Vant-Hoff: with an increase in temperature by 10 °C, the speed increases by a factor of 2–3. Therefore, just like in the case with H_2S, this effect halves the concentration of gaseous matter in the atmosphere of the underroof space, and, consequently, in the emissions from the shafts into the urban atmospheric air. The usage of a degasifier to remove formaldehyde from gaseous emissions from water disposal systems also has positive prospects, since the tests of biochemical treatment of emissions of a similar composition were able to demonstrate a high cleaning effect [22]. Moreover, the videoecological problems of such installations for cleaning gaseous emissions from sewer networks (degasifier) – visual discomfort when located among residential and historical buildings, parks, and recreational areas – have been successfully resolved as well [23]. Various design solutions can help to harmoniously blend in these technogenic elements (small architectural forms) with the urban environment.

In addition to this, not only do the suggested technical solutions (cooling of wastewater transported by sewage networks and degasifiers on sewer networks) effectively remove H_2S, but they also remove an even more environmentally hazardous gas – formaldehyde, which significantly increases their environmental and economic attractiveness.

Gathering of objective information on quantitative characteristics of formation and emission of hydrogen sulfide, depth and velocity of biogeneous corrosion of concrete at different sewer shafts of the net in Kharkiv, allowed to form a data base, that is necessary for creation of the page, that is compatible with the geoinformational system of the sewer nets, existing at the enterprise. The developed methodology of visualization of the ecological safety and operating reliability parameters at the separate sections of the sewerage pipelines includes recording of the hydrogen sulfide concentration in the sewage disposal and the hydrogen sulfide concentration in the air-gas environment, recording of calculating velocity of concrete corrosion, rate of MPC excess as per hydrogen sulfide in gas release, availability of protection tools of atmosphere (degasifiers) and others. For visualization of ecological and operational parameters the interface of the page is designed with the ecological safety and operating reliability parameters of the separate sections of the sewerage pipelines for the geoinformational system of the urban sewer nets (Fig.4).

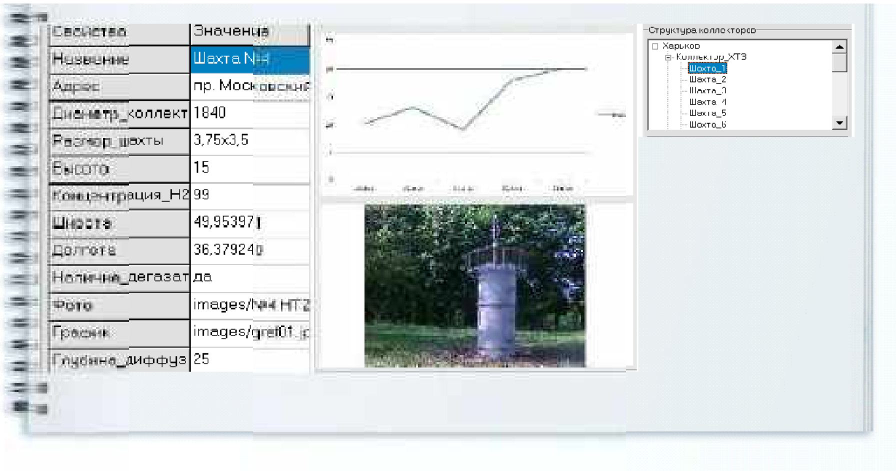

Fig. 4. The interface of the page with the monitoring parameters of operating reliability of the separate sections of sewer

CONCLUSION

One of the most important factors in ensuring sustainable development of cities is the security of the living environment of its inhabitants, which includes atmospheric air. One of the sources of urban air pollution by environmentally hazardous substances are wastewater disposal constructions.

Hydrogen sulfide and formaldehyde are among the most environmentally hazardous gases (hazard class 2) emitted from sewerage networks. On the explored shafts it was shown that the concentrations of H_2S and formaldehyde in emissions from sewer shafts are many times greater than the $MPC_{daily\ average}$ for this compound: 663 times for formaldehyde and 188 times for H_2S.

The performed calculations of hydrogen sulfide dispersion, released from the shafts, have shown, that the residential development is located in the section of above-level hydrogen sulfide content (daily average MPC). Ecologically safe section is located in the distance of 225-260 m from the shafts.

Two technical solutions that have proven to be effective in the removal of H_2S were deemed promising for the effective extraction of this compound from emissions from sewer shafts: cooling of wastewater transported by water disposal networks and degasifiers on sewer networks. Such technical solutions could significantly reduce the level of danger that such gaseous emissions from sewage networks pose for the urban atmosphere. They are environmentally friendly and safe in terms of their visual perception.

The interface of the page is designed with the monitoring parameters of the ecological safety and operating reliability at separate sections of the sewerage pipelines for the geoinformational system of the urban sewer nets.

REFERENCES

1. Goptsiy, D.O. Scientific approaches to understanding the concept of sustainable development and directions of its use in urban development planning. Bulletin of Sumy National Agrarian University. Series Economics and Management, 5 (64), Ukraine, 2015, pp. 25-29.

2. Mozgovoi, A.A. Sustainable urban development: preconditions and contradictions. Sustainable socio-economic and environmental development: from theory to practice: materials intern. scientific-practical conf., Ukraine, 2014, pp. 58 - 61.

3. Kovalevskaya, A.V., Zelensky, S.V, Petrova, R.V. Sustainable city development: the essence of the concept and prerequisites of implementation**,** Social economics, 2017, 53 (1), pp. 69-75.

4. Pochwat K., Kida M., Ziembowicz S., Koszelnik P. Odours in sewerage-a description of emissions and of technical abatement measures environments, Environments, 6, 89, 2019, pp. 1 - 14.

5. Shammay, A.; Sivret E.C., Le-Minh N., Fernandez R.L., Evanson, I., Stuetz, R.M. Review of odour abatement in sewer networks. Environ. Chem. Eng., 4, 2016, pp. 3866–3881.

6. Drozd I.E., Zotov N.I., Maslak V.N. Sewer pipelines: reliability, diagnostics, sanitation. IEP NAS of Ukraine, Ukraine, 2003, 260 p.

7 Stein, D. Rehabilition and Maintenance of Drains and Sewers. Univ.-Prof. Dr.-lng. habil. Ruhc-University Bochum (RUB), Faculty of Civil Engineering, Germany, 2001, 804 p.

8 Iurchenko, V., Brigada, E. Kinetic characteristics of microbial corrosion of concrete drainage networks. Water and ecology. Problems and solutions, 1, Russia, 2014, pp. 51-61.

9. Yurchenko, V.A., Brigada, E.V., Arkhipov, O.V. Kinetics of biogenic corrosion in concrete sewer networks (chemistry, microbiology and control of the process). Lambert Academic Publishing, Saarbrücken, Germany, 2016, 69 p.

10. Vasilyev, V.M., Pankova, G.A., Stolbikhin, Y.V. Destruction of sewer tunnels and structures on them by microbiological corrosion. Water supply and sanitation, 9, 2013, pp. 67-76.

11. Simon, G., Alix, C., Arrebola, V. Odor control – solutions for managing emissions from wastewater treatment facilities. Florida Water Resources Journal,7 (2), 2010, **7**, pp. 32-34.

12. Hvitved-Jacobsen, T., Vollertsen, J., Haaning Nielsen A. Odor from sewer networks - processes and prediction. 9th NORDIWA Conference, Stockholm, Sweden, 2005, pp. 1-15.

13 Yan-li Zhu, Guo-di Zheng, Ding Gao and el. Odor composition analysis and odor indicator selection during sewage sludge composting. Journal of the Air & Waste Management Association, 2016, pp. 930-940.

14. Dorogova, V.B., Taranenko, N.A., Rychagova, O.A. Formaldehyde in the environment and its effect on the body (review). Bulletin of the VSSC SB RAMS, 1(71), 2010, pp. 32 – 35.

15. Zerkalov, D.V. Ecological safety: management, monitoring, control. CST, Dakor, Osnova, 2007, 412 p.

16. Survey of Formaldehyde. A LOUS review project. The Danish Environmental Protection Agency, 2014, 73 p.

17. Brigada, E.V. Monitoring of operation indices of reinforced concrete river outlets. Thesis, PhD, Kharkov, Ukraine, 2013, 168 p.

18. Zhang, L., De Schryver P., De Gusseme B. et.al. Chemical and biological technologies for hydrogen sulphide emission control in sewer systems. A review. Water Research, 42, 2008, pp. 1-12.

19. Lebedeva, E.S. Protection of atmospheric air from pollution by hydrogen sulfide emissions from sewerage networks. Thesis, PhD, Sumy, Ukraine, 2017, 159 p.

20. Sewage. External networks and constructions. Basic principles designings: SBC V.2.5 - 75:2013, Kyiv: Ministry of Regional Development, Construction and Housing of Ukraine, 2012.

21. Iurchenko, V., Lebedeva, E., Brigada, E. Environmental Safety of the Sewage Disposal by the Sewerage Pipelines. Procedia Engineering, 134, 2016, pp. 181-186.

22. Kulikov, N.I., Annan, A.A., Kostik, V.V., Beldiy M.G. Installation for researching the processes of biochemical purification of industrial gas emissions. Chemistry and Water Technology, 17 (60), 1995, pp. 621-624.

23. Iurchenko, V., Lebedeva, E. Reduction of environmental hazard of hydrogen sulfide emission from sewerage pipelines and visual pollution, formed by degassing units. Environmental problems, 1 (2), Ukraine, 2016, pp. 155 – 158.

FIELD PRACTICE AS A TOOL FOR SUSTAINABLE ENVIRONMENTAL EDUCATION A CASE STUDY IN ALSÓ-HEGY

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ABSTRACT

The aim of environmental engineering B.Sc. study is to give high level theoretical knowledges, practical skills, and ecological attitudes to the students. The field practices are crucial to gain appropriate skills among real conditions. Such a field training helps also to develop teamwork abilities and program solving attitudes. There are several karstic landscapes in Hungary, therefore it is important to show to environmental engineering students a karstic region during their summer practice.

The National Parks are excellent to study a closely natural landscape. The Aggteleki National Park shows several karstic phenomena including vertical caves, mostly in Alsó-hegy. The Alsó-hegy was chosen, for a one-day trip, because it has a well design loop observation path: Vertical Caves Observation Trail (Zsombolyos tanösvény).

This observation path presents well the surface karstic formations (karen fields, limestone queries, dolines, sinkholes, springs). The subsurface formations were also studied during the field practice: vertical as well as horizontal caves, dripstone formations (stalagmites, stalactites, helictites and popcorns). Different strata and their characteristic features were recognized along the trip. During the field practice the vegetations were also studied, water chemistry and water flow volumetric measurements were also done. The anthropogenic effects were evaluated on the Alsó-hegy emphasizing the sustainability.

Keywords: field trip, karstic phenomena, caves, education for sustainability

INTRODUCTION

The studying topics of the environmental engineers (B.Sc.) contain a theoretical knowledge, practical routines and ecological attitudes. The appropriate routines can get during field trainings [1]. The field practices are also good to use the theoretical classroom knowledge of different courses in real conditions [2]. The field practices also improve the right research methodology of students: observation evaluations and conclusions [3, 4]. The conditions of national parks offer a good field practice. Their protected flora and fauna, show a good example for the sustainability.

This paper presents a one-day trip on Alsó-hegy following the stages of Zsombolyos Tanösvény loop trip. Our field trip however was tuned up comparing the original excursion plan. Extra background knowledge was added, and some experiments were also done which suit better to our education level of environmental engineer B.Sc. students.

Aggteleki National Park (Aggteleki Nemzeti Park, ANP) which was established in 1985 was chosen for our summer field practices of environmental engineering students (B.Sc.). This area shows almost total spectra of karstic phenomenon with its surface formations and very high density of vertical and horizontal caves [5]. The natural and cultural treasures of ANP were the reason, why it has sort out for UNESCO Word Heritage network in 1995 [6].

Alsó-hegy was chosen for one of our study trips in our summer practice. Alsó-hegy is an excellent terrain to learn the karstic phenomena for our students. Several big vertical caves locate here. An observation pass has been marked out with 14 stations and its guidebook has been published with the title: Observation pass of vertical caves of Alsó-hegy (Alsó-hegyi Zsombolyos Tanösvény) [7]. The booklet directs along the pass and contains explaining texts, pictures, and surface and cave maps. On the other hand, the text of the booklet was expanded higher level knowledge, and some experiments were also done.

This observation trip includes not only several vertical caves, but it also presents karren fields phenomena: dints, dolines, sink holes, canyons and springheads in surface. The path touches the entrances of vertical and horizontal caves. The guidebook of observation pass presents maps of several caves. It also contains explanations of the cave genesis, emphasising the local specialities (e.g., the role of volcanic ash from Mátra mountains). The booklet deals with not only the karstic aspects, but it presents other natural phenomena (e.g., tuff scatterings, meteorological phenomena, and rare species of vegetation) and cultural heritages (e.g., churches, cemeteries).

Dedicated, high level explanations were added to text of booklet to reach of B.Sc. level studies, emphasising the sustainability aspects of this field trip. This paper contains this extra knowledge and some field experiments too.

Aggtelek National Park (Aggteleki Nemzeti Park, ANP)

ANP is most famous karstic regions of Hungary, because it has unique natural beauties (e.g., Baradla, Rákoczi, Vass Imre, Vecsembükk caves). Several books and monograph deal with these caves and report of their explorations [8, 9 and 10].

Geological and geographical description of Alsó-hegy and its close surrounding

The overwhelming part of 200 km^2 karstic region of Northern Hungary originates from shallow see Wetterstein formation (Limestone). The rocks of this area are deposited approximately 220 million years ago in Mesozoic, Triassic period [10]. The recent formations are results of five million years genesis. This famous karstic region is separated by Hungarian-Slovakian border. The Northern part of Gömör-Tornai karst region (Fig 1) belongs to Slovakia, which is also a protected area called Slovak Karst Nature Conservation Area.

The micro-region of Alsó-hegy belongs to the North Hungarian Mountain (Északi-középhegység) according to Marosi and Somogyi's landscape classification [11].

Alsó-hegy is bordered: south, Bódva river and Ménes creek; north, Torna creek; west, Szilice plateau. Its expansion is 50 km^2 with 400-500 m average elevation [10]. The most part of the landscape is practically unsettled. Only one settlement (Szögliget) situates in the edge of this mountains. The climate of the area is moderatly cool and humid. The amount of precipitation is about 680mm yearly [11].

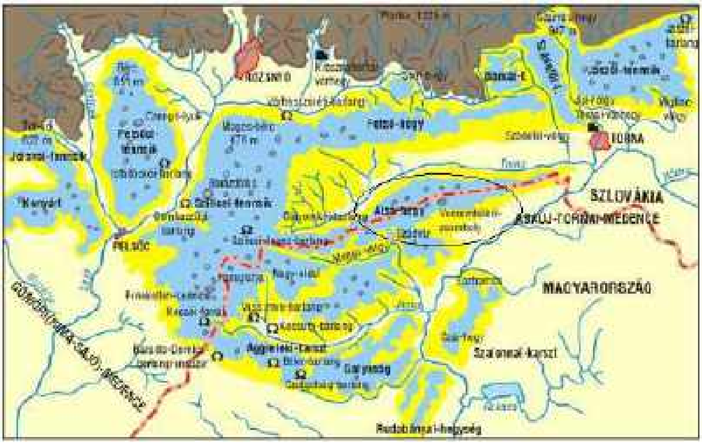

Fig. 1. Map of Gömör-Tornai karst [12]. The Alsó-hegy is circled. The red dash and dot line show the border between Hungary and Slovakia.

The vegetation of this area shows high diversity. The hornbeam and oak are the dominant tree species, but several other species occur. The glades among the woods have forest steppe characters [7]. The typical trees of southern slops are oaks and junipers. The meadows are evidence of human influences in the dry plateau. The largest species of vertebrates are the birds with 127 species. The most famous species of birds is the highly protected imperial eagles [13] The most valuable species are the Panonn gyík (Ablepharus Kitaibelii Fitzingeri) from the lizards, and the heraldic animal of the ANP the spotted salamander (Salamandra Salamandra) from amphibians (Fig 2). The student made determination of species flora and fauna.

Fig. 2. The spotted salamander (Salamandra Salamandra) the heraldic animal of ANP [7]

The most characteristic karst formations of Alsó-hegy are the 112 vertical caves, from which 64 are situated in Hungary [14]. Vertical caves (shaft, pot hole) are special types of the caves, which have Hungarian name: zsomboly. The Alsó-hegy is extremely rich in vertical caves [15 and 16]. Several karst springs characterize this region breaks up from slope of the Alsó-hegy (examples: springs of Csemetekert, Medvekert, Szarvastetői) [11].

The Vertical Cave Observation Path

The observation pass is 8.5 km long and rises 355 meter having 14 stations (Fig 3.). The trailhead of the pass is situated in the middle of Bódvaszilas village. A reference map is exhibited in the trailhead, for the sake of easy orientation.

Fig. 3. The map of stations of „Zsombolyos tanösvény" vertical cave observation pass [7]

Kavacsos

The trip passes by a classical manorial granary from 18th century toward to Kavacsos. This building has been transformed to art camp. It is good example the sustainable reuse the old buildings, for recent use. The rock of Kavacsos consists of Late Permian red sandstone and a well-cemented rock (conglomerate). The students observed the gravels of Kavacsos. They sorted the rocks according to the following: color, hardness, stratification, measure of particles and their dispersion. They also studied the erosion channels on the bedrock.

The trail crosses hornbeam forest and later a planted spruce forest. The traces of lime kilns can be easily recognizing. The student could recognize the differences between the dents of lime kilns and the cones of sinkholes. The sinkholes have no cupping rim, but the dents have definite emerged circle contour rims.

Cat Church (Macskatemplom), Pályi well (Pályi kút)

The route follow its direction to Macskatemplom a big grey pink-foliated limestone slab (Hallstatt formation) (Fig 4) and the Pályi-kút.

Fig. 4. Macskatemplom (cat church) Hallstat limestone [7]

Macskatemplom is excelent for the recognition of erosion phenomena. The cracks are created by water and vegetation. The water erosion make broader and shallower cracks than vegetation created. The dried-up spring of Páyi-kút ilustrates well that new springs are born from time to time. The deepening of the caves result in new springs in a lower level of the mountains than previous ones. The old, flood springs can be reactivated after a heavy rain or in snowmelt times. Relatively fresh debris deposition show the temporary activity of Pályi kút.

Marble mine (" Márvány"-bánya)

There are several limestone mines for decorative purposes in the Gömör-Tornai karst region. Two mossy hewn rock cubes indicate an old rock mine quarry (Fig 5). The remaining rock slabs offer a good opportunity to show the structure of the hard limestone. The fresh fracture on the rock show gray calcite veins observable with a magnifying glass. Grey veins of calcite-crystals can be observed crossing each other and filling out the basically grey or pink angular patches on the rock (1-2 cm). The explanation of this texture is the following: The original limestone had broken for gravels (breccia), and the spaces among the gravels were filled by the precipitating calcite. These calcite veins make hard the rock. Such a small-scale sustainable mining activity gives a big contrast with the landscape destroying rock mining in North corner of Alsó-hegy and in the opposite mountain (Extramos).

Fig. 5. A carved stone in an abandoned limestone mine (árvány bánya) [7]

The trail crosses a young oak-hornbeam forest and a shrubby meadow, then a field with dints (ördögszántás, devil plowing). The dints are the consequences of clearances and viticulture activity. Namely these activities have resulted in intensified soil and rock erosions. This point is excellent to study the steps of karstic erosion. The niches and spherical holes were made corrosion of the humic acids from the roots, which were strengthened by human activities.

Bak Antal's doline (Bak Antal töbre), Tektonik vertical cave (Tektonik-zsomboly)

The next station of this observation pass is Bak Antal töbre, a typical doline. The dolines are the most characteristic formations of karstic surfaces. Generally, the dolines are circular, caldron shape depressions. The characteristic shapes of the dolines have 50-200meter diameters and 10–20-meter depths in Alsó-hegy. The infiltrating water of rains and snowmelts solves the limestone intensively. The acidic carbon dioxide strengthens the solving effect of water shifting the chemical equilibrium toward to hydro carbonate state.

The microclimatic differences can be observed in this doline. The rims of dolines produce less dense vegetation, than the bottom of doline. Namely the soil is thicker in the bottom of doline offering richer nutrients. The lower parts of dolines catch more humidity and runoff water too. The slopes of the doline differ from each other in their vegetation according to their orientation. The differently orientated slops catch non-uniform quantity of sunshine.

The Tektonik-zsomboly (Fig 6) is the first vertical cave of the trail [29]. Its entrance is a narrow fissure. The cave is 80 meter deep (the fourth deepest cave in Alsó-hegy) and 350 long (Fig 7).

The developments of the pits of caves start independently from each other's. The infiltrating water leaches the limestone along the vertical cracks. Further dissolutions of limestone result in bigger and bigger pitches and interconnections of caverns. During the enlargement processes, the remaining clay deposits at the bottom of pitches. The clay layer clogs the water flow; therefore, the water flows down in the neighboring pits. The roofs of caverns, nearest to the surface, collapse, because the rocks erode most intensively close to the surface [23]. Every vertical cave shows significant tectonic activity, with vertical rifts as starting point of cave genesis. The vertical caves of Aggtelek karstic region were born in Pliocene age [16].

The entrance and the segment maps of the Tektonik represent well the vertical caves forms for students. The cave starts with a vertical pitch. The diameters of pitches become broader and broader downward. The cave does not start with a sinkholes. Their entrances are in the upper third parts of dolines, because the bottoms of dolines are clogged by debris and clay.

Fig. 6.
Entrance fissure of Tektonik vertical cave [29].

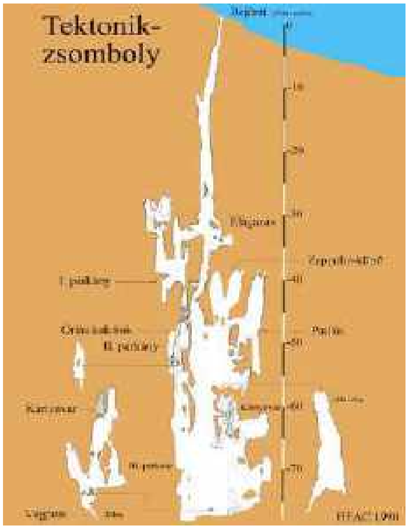

Fig. 7.
Map of the Tektonik vertical cave [29].

Vecsembükk vertical cave (Vecsembükki-zsomboly)

After the Tektonik cave the trail leads above 500 meter elevation to Vecsembükk. This is the densest zone of vertical caves of Alsó-hegy. 21 vertical caves are located in half square kilometer area. The Vecsembükki zsomboly is the one of the deepest (3rd) cave in Hungary (Fig 8 and 9). This cave has 236 m depth recently, but further explorations are in progress to reach the level of karstic water. On the other hand, Vecsembükki zsomboly it has a deepest pit (90 m) in Hungary. The exploration of Vecsembükki zsomboly shows well the improvement of caving exploration technology. The discovery of this vertical caves started in 1911 [17]. The first successful attempt to reach the bottom of first pit was done by H. Kessler in 1927 [18] building temporarily belay in 40 depths. The intensive research of these cave happened between 1965-1978 [19]. Two big cave explorations (1969, 1971) were organized by I. Szenthe aiming to reach the karst water level [19]. They mapped the several new pits reaching 236 m recent depth. The liquid clay mixtures and cool temperature, however, hindered the expedition members to get at the karst water level, which is expected approximately 300-meter depth. These expeditions used ropes and windlasses. The pull-ups were made by human puling from the top pit. The path of the pulling groups can be recognizable in the dolina even recently.

Their genesis [20-23], meteorological features [24] and hydrological properties [25-28] were detailed studied. These expeditions made several scientific observations. The increased radioactivity showed the partly volcanic origin of the debris in the bottom of pits. Probably the volcanic ash of Mátra covered the surface of limestone. This layer played important role in the formation of these vertical caves. The water of the Vecsembükki zsomboly appears in Zsámánykút and Kör-kút springs in Slovakia in north. 1 tons salt was thrown into the cave and the conductivity of the spring water of surrounding springs were measured. The water of the nearest spring, the Vecsem-forrás did not show any change in its conductivity to the south.

The mouth of the Vecsembükki zsomboly is rather broad comparing Tektonik zsomboly (Fig. 6 and 7) The pits of Vecsembükki zsomboly are rather close to each other (Fig y).

Only narrow walls separate the parallel caverns. Flowstone layers cover the walls of the cave. Stalagmite and stalactite formations are in the upper part of the cave. The palm tree formations are frequent in lover parts of the cave. The drops of the water fall down from big elevation, and they create aerosol which crystalize in palm tree formations [30].

Honey-moon cave (Nászút-barlang)

Characteristic forms of plateau are the depressions. The ceilings of the caverns weakened by leaching and fall down later. The debris consists of big pile of rock slabs, which leave holes among them. Small animals occupy these holes 7]. The students can recognize the small soil piles here, which were scraped out by the resident animals. From this point the trail lost its elevations toward the foot of the mountain.

Fig. 8. The entrance of Vecsembükk vertical cave

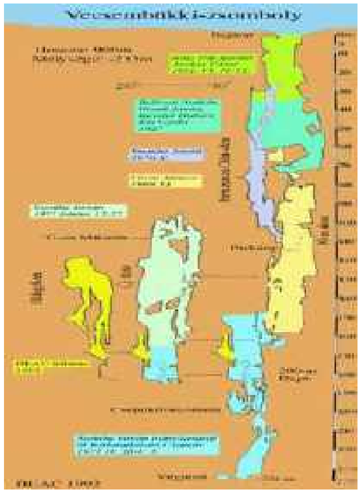

Fig. 9. The map of Vecsembükk vertical cave [32]

Szabó-pallag and nearby vertical caves

Szabó-pallag is a rather big meadow (Fig 10). The vegetation of this area is a typical middle dry mountain meadow. The booklet of the trip and our plant adverb helped the students to determine the typical species. The anthropogenic effects can easily recognize in Szabó-pallag.

Fig. 10. Szabó-pallag with a wild feeder [7]

The forests were cleaned, and the area was used for hay production for animal feeding. Later this activity stopped, and the forest has been started gaining back its territory. Recently there are several juniper groves, oaks and elm in these meadows. A moderate size invasive pine forest was planted, after a total cut deforestration in the corner of Szabó-pallag.

Close to the trail is located the 100 meter deep and 358 meter long Almási-zsomboly and 120 m further the Széky-zsomboly. The later cave is 50 meter deep having a stepped structure. The most interesting phenomena of this cave are the helicities the bent stalactites. The nearby Baglyok szakadéka (Owl canyon) is 151 meter deep and has 850 horizontal dimensions. Its name was gain after the owls nest in its first big pit.

Small and Big Watery doline (Kis és a Nagy vizes töbör)

The path follow the bottom of a small valley to the doline called Kis-Vizes töbör. The rocks of the Kis-Vizes-töbör belong to Hallstat formations (Hangandrotkalk). The pink-red rocks of this doline differ from the pervious seen grey rock formations.

Here is the entrance of Meteor horizontal cave, which was discovered in 1961. The Meteor cave is not a vertical cave, but it belongs to the typical karstic formations of Alsó-hegy. Its more than 120 long cavern, Titánok csarnoka (Hall of Titans) is the largest cavern of Hungarian caves. There are huge colorful stalagmites and stalactites. A lot of colorful straws, stalactite curtains, sinter pools and helicities are visible in very diverse forms.

Next station is a sinkhole, a typical formation of carstic surfaces in Nagy-Vizes-töbör (Big Watery Doline), the Pócsakői viznyelő (Pócsakői sinkhole, Figure 11 and 12) It has a steep cone shaped depression with thick soil deposition and pile of big rocks. A big hole, the entrance of Pócsakői viznyelőbarlang (Pócsakői sinkhole cave) is at the bottom of the cone. This cave is a typical example the sinkhole originated caves. It is 87 meter long and 51 meter deep [14]. The water of these sinkholes and several caves comes to the surface in the Vecsem spring [8].

Fig. 11. Entrance of Pócsakői sinkhole cave

Fig. 12. Map of Pócsakői sinkhole cave [14]

The sinkholes are created by the dissolving of the carbonate rocks by water. They have conical depressions with steep funnel type convex slopes. They have definite catchment area. The sinkholes swallow up the solved rocks and soil, and their growing processes transform the sinkholes to doline. The sinkholes frequently solve out caves at their bottom.

3.9. *Vineyard or Caver spring (Szőlősfej-kerti-Barlangkutató forrás)*

The last station of observation trail is the spring of Szilas creek, which is called Szöllös-kerti or Barlangkutató spring (Fig 13). It has 151 l/min average discharge.

The vicinity of spring is covered by sandstone flakes. The spring is situated on the border of water permeable carbonate rock and watertight sandstone rocks. The student measured the discharge of the spring. The filling period of the known volume bucket was measured.

At the end of the trip a new flush flood reservoir was built in a big gully. The dam of reservoir prevents the village from floods after big storms in a sustainable way.

Fig. 13. Vineyard or Caver spring

Chemical and biological testing of spring of Alsó-hegy

The summer practice includes some chemical analysis of springs and creeks. The 2-3 member groups of students looked up the spring of Hungarian part of Alsó-hegy. The springs were fund by GPS and they were sampled. The measurements were done in-site (pH, conductivity, temperature) and off-site (NO_3-N, p-alkalinity, m-alkalinity, COD, Ca, Mg) in the camp. The BISEL method was applied to test the ecological states of creeks of Alsó-hegy.

CONCLUSINS

This trip is appropriate to join together the theoretical knowledge and the real-life conditions in the nature. This education method is convenient for students to recognize complexity of environment and recognize their relations each other. The Alsó-hegy also show the practical evaluation of sustainability with national parks.

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REFERENCES

1. Kárász I., Környezetvizsgáló módszerek (terepgyakorlatok), Oktatási segédanyag a Környezettan B.Sc szak részére Eszterházy Károly Főiskola Környezettudományi Tanszék, Eger, Hungary, 2009, pp. 8.

2. Némethné Katona J., A környezet- és természetvédelmi oktatás terepi lehetőségeinek alkalmazása és módszereinek továbbfejlesztése a Máriaremetei-szurdokvölgy példáján Ph. D. thesis NYME Környezettudományi Intézet, Sopron, Hungary, 2004, pp. 47.

3. Kováts-Németh M., Az erdőpedagógiától a környezetpedagógiáig Comenius Kft., Pécs, Hungary, 2010, pp .231-246.

4. Takács B., A gyakorlati oktatás jelentősége a BSc képzésben, különös tekintettel a terepgyakorlat megvalósítására Tudományos Diákköri Dolgozat Budapesti Műszaki Főiskola Rejtő Sándor Könnyűipari és Környezetmérnöki Kar konzulens: Bodáné Kendrovics Rita, Hungary 2009, pp. 25-26.

5. Székely K. (ed.), Az Aggteleki karszt barlangjai Világörökség a Föld mélyén Aggteleki Nemzeti Park Jósvafő, Hungary, 2003, pp.12-36.

6. Caves of Aggtelek Karst and Slovak Karst, http://whc.unesco.org/en/list/725.

7. Koleszár K., Alsó-hegyi Zsombolyos Tanösvény Kirándulásvezető füzet HOLOCÉN Természetvédelmi Egyesület, Bódvaszilasért Baráti Kör, 2004-2005, Hungary, ISBN 963 219 995.

8. Kiss Cs., 1998: Caves of Hungary. http://www.fsz.bme.hu/mtsz/barlang/english/0_angol.htm

9. Székely K. (ed), Magyarország fokozottan védett barlangjai. Mezőgazda Kiadó, Budapest, Hungary, (2003). ISBN 963 935 896 7

10. Dénes Gy, Jakucs L., Aggteleki-karsztvidék - Gondolat Könyvkiadó. Budapest, Hungary (1975).

11. Dövényi Z. (ed) Magyarország kistájainak katasztere, MTA Földrajztudományi Kutatóintézet, Budapest, Hungary, 2010. pp. 766-768

12. Pannon Enciklopédia. Magyarország földje. Hungary, 1997, Cd-rom. Arcanum Adatbázis Kft.

13. Horváth et al.: Population Dynamics of the Eastern Imperial Eagle (Aquila heliaca) in Hungary between 2001 and 2009. Acta Zoologica Bulgarica, Suppl. 3, 2011, pp. 61-70.

14. Nyerges A., Aggteleki-karszt Zsombolyai Karsztfejlődés VI. Szombathely, Hungary, 2001,. pp. 265-279.

15. Kósa A., Nyolcvan év az Alsó-hegyen (Még egy szó a zsombolyokról) in: Magyar Karszt és Barlangkutató Társulat Karszt és barlang című folyóirata I.-II., Hungary 1992, pp. 9-14.

16. Nyerges A., A zsombolyok megismerése in: Nyerges A. and Nyerges M., A Tornai -Alsó-hegy magyarországi barlangjainak bejárási útmutatója Magyar Természetbarát Szövetség Barlang Bizottsága, Hungary 2000, http:/www.fsz.bme.hu/mtsz/barlang/4TINFO/MO/alsh/alt.htm

17. Stömpl G., Előzetes jelentés az 1911 év nyarán az Abaúj-Gömöri barlangvidéken végzett barlangkutatásokról. Földtani Közlöny, Hungary (1912) pp. 3.

18. Kessler H., A Vecsembükki és az Almási zsombolyok első bemászása. Turistaság és Alpinizmus, XVII. Hungary 1927, pp. 123-127.

19. Szenthe I., Sikeres feltáró eredmények a Vecsembükki-zsombolyban. Karszt és Barlang, Hungary,1970, pp. 15-16.

20. Kessler H., A zsombolyok keletkezéséről – Barlangvilág, Hungary 1932/3-4, pp. 20-22.

21. Kósa A., A zsombolyképződés kérdéseiről – Tájékoztató, Hungary, 1964/5-6, pp. 88.

22. Szenthe I., Újabb adatok az Alsó-hegy ősföldtani képéhez különös tekintettel a zsombolyokra. - Karszt- és Barlangkutatási Tájékoztató, Hungary, 1971/3, pp. 3-4.

23. Müller P., Sárváry I., Pure Corrosive Model of the Development of Vertical Karst Shafts - Symposium on Karst Morphogenesis Budapest, Hungary 1973, pp. 233-245.

24. Walkowsky A., Mikroklímamérések a Vecsem-bükki-zsombolyban - Karszt és Barlang, Hungary 1970/I, pp. 17.

25. Dénes Gy., Az Alsó-hegy karsztjának hidrográfiai viszonyairól – Karszt és Barlankutatási Tájékoztató, Hungary 1963/9, pp. 163.

26. Dénes Gy., Karszthidrográfiai összefüggések kutatása az észak-borsodi Alsóhegyen – Karszt és Barlankutatási Tájékoztató, Hungary 1964/2-3, pp. 30-33.

27. Hazslinszky T., Az Alsó-hegy vázlatos vízháztartási mérlege - Karszt és Barlang, Hungary 1974/I, pp. 11.

28. Sárváry I., Víznyomjelzés az Alsó-hegy zsombolyaiban.-Karszt és Barlang, Hungary 1971/I, pp. 25-32.

29. http://www.termeszetvedelem.hu/index.php?pg=cave_5452-45.

30. Kordos L., Jakucs L., Gádoros M., Tardy J., Magyarország barlangjai. pp.108-111, Gondolat, Budapest, Hungary 1984, ISBN 963 -281 -351 -0.

31. http://www.barlang.hu/pages/alsohegy/vecsem.htm.

32. http://www.termeszetvedelem.hu/_user/cave_images/5452-4_1415704316.jpg.

THE RELATIVE RISK OF THYROID CANCER INCIDENCE: OVERVIEW AND STATISTICS IN UKRAINE

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ABSTRACT

The primary purpose of this study was to present detailed information on the thyroid cancer incidence among the male and female in Ukraine and to calculate the relative risk of this thyroid pathology during 2000-2016. To study the thyroid cancer incidence among the male and female, the database of the National Cancer Register of Ukraine within 2000-2016 was analyzed (Cancer in Ukraine: Bulletin of the National Cancer Register of Ukraine, No. 3-19). A permanent number of the Ukrainian population was taken into account by Demographic Yearbook "The Population of Ukraine for 2015", State Statistics Service of Ukraine, 2015. The calculation of relative risk (RR), confidence intervals (CI), as well as the significant level (p) and χ^2 calculated by Cochran–Mantel–Haenszel test, was performed using the EpiInfo program recommended by WHO (Woodward, 1999), using the absolute values of the disease incidence. According to the National Cancer Register of Ukraine, the increase in the thyroid cancer incidence (per 100,000 population) among the population of Ukraine, male and female as well, within 2000-2016 was noted. The peak of thyroid cancer incidence among the total population of Ukraine in this period was in 2015 (8.7 per 100,000 population). The relative risk of thyroid cancer incidence among the Ukrainian population in each subsequent year, relative to the previous one, was higher from 2001 to 2008, from 2010 to 2013, and in 2015. Thus, the tendency to an annual increase of thyroid cancer in the total Ukrainian population was confirmed. The relative risk of thyroid cancer incidence in 2016 compared to 2000 was noted. The highest incidence rate among the male population was detected in 2014 (3.6 per 100,000 population). In general, from 2000 to 2016, the thyroid cancer incidence among the male population was increased by 2-fold (from 1.5 to 3.0 per 100,000 population). The thyroid cancer relative risk was higher each year than in the previous year except for 2005 compared to 2004, 2013 compared to 2012, 2015 compared to 2014, and 2016 compared to 2015 in this population group. The highest relative risk was established in 2007 compared to 2006 (RR = 1.11, p = 0.135). The relative risk of thyroid cancer among the male population of Ukraine in 2016 compared to 2000 was 1.69 (p<0.001). There was a tendency to increased thyroid cancer incidence among the female population. The study revealed that thyroid cancer incidence among the female population was increased from 6.3 in 2000 to 13.2 per 100,000 population in 2016, i.e. by 2.1-times (p<0.05). The peak incidence rate was 13.4 per 100,000 population in 2015. An increase in the thyroid cancer incidence from 2001 to 2006, in 2008, from 2010 to 2013, and in 2015 compared to previous years was observed. The highest relative risk was recorded in 2011 compared to 2010 (RR = 1.18, p<0.001). The thyroid cancer relative risk among the female population in Ukraine has increased from 2000 to 2016. These results suggest the need for primary prevention of cancer, taking into account regional peculiarities incidence and prevalence of cancer pathology, providing programs to environmental protection against carcinogens-induced pollution, the implementation of measures and training of the population to healthy lifestyle issues (rationale and optimal nutrition, rest, personal hygiene, smoking cessation, alcohol abuse, etc.). To include preventive measures and various forms of health education work designed to detect preclinical forms of cancer.

Keywords: thyroid cancer, relative risk, crude incidence rate, Ukraine

INTRODUCTION

The thyroid cancer incidence and mortality can simultaneously be considered as indicators of the socio-economic development of the state in general and public health systems in particular. It has been proved that in the occurrence of oncological pathology, in general, an essential role is played by such risk factors as stress, unhealthy lifestyle, unsatisfactory social conditions, poverty of the population, anthropogenic-induced environmental pollution, harmful working conditions, smoking, drinking alcohol, unhealthy food, etc. [9]. The etiopathogenetic thyroid cancer factors include the chronic hyperplastic processes in the gland, heredity, thyroid-induced hormonal disorders, and hormonal imbalance associated with other endocrine organs, an inadequate intake of trace elements, primarily iodine, as well as iron, copper, selenium, cobalt, zinc, etc. [5].

The worldwide incidence of thyroid cancer is increasing substantially, almost exclusively attributable to small papillary thyroid cancers. Increased use of diagnostic imaging is considered the most likely explanation for this reported rise, but other factors may also be contributing i.e. the status of iodine sufficiency and access to the healthcare system [12, 23]. The thorough evaluation of a thyroid nodule includes a review of the patient's medical and family history, followed by thyroid ultrasound and fine-needle aspiration biopsy [2, 12, 23].

Cancer of the thyroid gland in pediatric patients is rare and if left untreated spreads and becomes lethal [20]. Thyroid nodules in pediatric patients are four times more likely to be malignant than adult nodules. The incidence of thyroid cancer in children increases with age, sex, race, and nodule size. Exposures to the low level of head and neck irradiation at a young age, cancer survivors, family history of thyroid cancer, and iodine deficiency are specific risk factors to develop thyroid cancer [20]. Similar to adults, the majority of nodules in children are benign; however, there is a 3- to 5-fold higher risk that a nodule found in a pediatric patient (less than 18 years) will be malignant when compared to an adult. Differentiated thyroid carcinoma is the most common malignancy with approximately 90-95% being papillary thyroid carcinoma and the remainder follicular thyroid carcinoma. With proper evaluation and management, the prognosis for pediatric patients with differentiated thyroid carcinoma is excellent; however, the risk of treatment complications and recurrence is relatively high [2].

Thirty-five years have passed since radioactive releases from the Chernobyl nuclear accident led to the exposure of millions of people in Europe. Studies of affected populations have provided important new data on the links between radiation and cancer-particularly the risk of thyroid tumors from exposure to iodine isotopes-that are important not only for a fuller scientific understanding of radiation effects but also for radiation protection [8]. In the decade after the accident, a substantial increase in thyroid cancer incidence was observed among exposed children in the affected countries, and compelling evidence of an association between pediatric thyroid cancer incidence and radiation exposure to the thyroid gland accumulated. The data currently available suggest that both the magnitude and patterns of thyroid cancer risk are generally consistent with those reported following external exposure [21]. The incidence of thyroid cancer in Ukraine in 1990 was 0.23, in 1991 – 0.19, and in 1992 – 0.35 per 100,000 children under 14-aged years. In Ukraine, the incidence of thyroid cancer in 1981-1985 did not exceed 0.04-0.06 cases per 100,000 children [16].

This study is a continuous line of our previous analysis of thyroid cancer incidence and mortality among different gender groups in Ukraine [13-15]. Our study suggested that the mortality rate of thyroid cancer in the last decade is occurred mainly due to the female population of Ukraine. High mortality rates during 2004-2014 among females were observed in Zhytomyr (1.9-1.3 per 100,000 population), Zaporizhia (1.5-1.0 per 100,000 population), and Poltava regions (1.1-1.4 per 100,000 population). Even though the overall mortality among females in 13 regions of Ukraine during 2004-2014 did not change, this index in this group was increased. Among the male population, high mortality during 2004-2014 was noted in Cherkasy and Chernihiv regions (0.8-0.9 per 100,000 population). The increase in mortality among males over the past decade is demonstrated in 8 regions of Ukraine, although the national average index remains unchanged [13]. Over the past 10 years, the incidence and prevalence of thyroid cancer in Ukraine were increased by 1.61 and 1.97-fold, respectively. Statistics show that these indicators have regional characteristics. The highest thyroid cancer incidence and prevalence in 2004-2014 were observed in Kyiv city and Kyiv region among both female and male populations. High rates of thyroid cancer incidence over the past 10 years were also found in some northeastern and southern regions, and the lowest - in the western regions of Ukraine. It was found that the increase in thyroid cancer incidence has occurred mainly among the female population. The thyroid cancer incidence among females over the past 10 years was higher by 3.63-3.58-fold, while the prevalence – by 5.01-5.04-fold than the same index among males [14].

In the continuation of our previous study, the primary purpose of this analysis was to present detailed information on the thyroid cancer incidence among the male and female in Ukraine and to calculate the relative risk of this thyroid pathology within 2000-2016.

MATERIALS AND METHODS

To study the thyroid cancer incidence among the male and female, the database of the National Cancer Register of Ukraine for 2000-2016 was analyzed [7]. A permanent number of the Ukrainian population was taken into account by Demographic Yearbook "The Population of Ukraine for 2015", State Statistics Service of Ukraine, 2015 [10].

The calculation of relative risk (RR), confidence intervals (CI), as well as the significant level (p) and χ^2 calculated by Cochran–Mantel–Haenszel test, was performed using the EpiInfo program recommended by WHO [25], using the absolute values of the disease incidence.

Statistical analysis of the obtained results was carried out using the standard statistical package STATISTICA 8.0 (StatSoft, Krakow, Poland) [26].

THE RESEARCH RESULTS AND DISCUSSIONS

The National Program for Combating Cancer Diseases was implemented in Ukraine (http://zakon5.rada.gov.ua/laws/show/ 1794-17), as well as an Order of the Ministry of Health of Ukraine dated October 1, 2013, No. 845 "On the System of Cancer Assistance to the Population of Ukraine" was adopted (http://zakon2.rada.gov.ua/laws/show/z0077-14) [17, 18].

These documents are designed to develop and implement cancer prevention programs among various age and gender groups in Ukraine at the national and regional levels.

According to the National Cancer Register of Ukraine, the increase in the thyroid cancer incidence (per 100,000 population) among the population of Ukraine, male and female as well, during 2000-2016 was recorded (Fig. 1). The peak of thyroid cancer incidence among the total population of the country in this period was in 2015 (8.7 per 100,000 population).

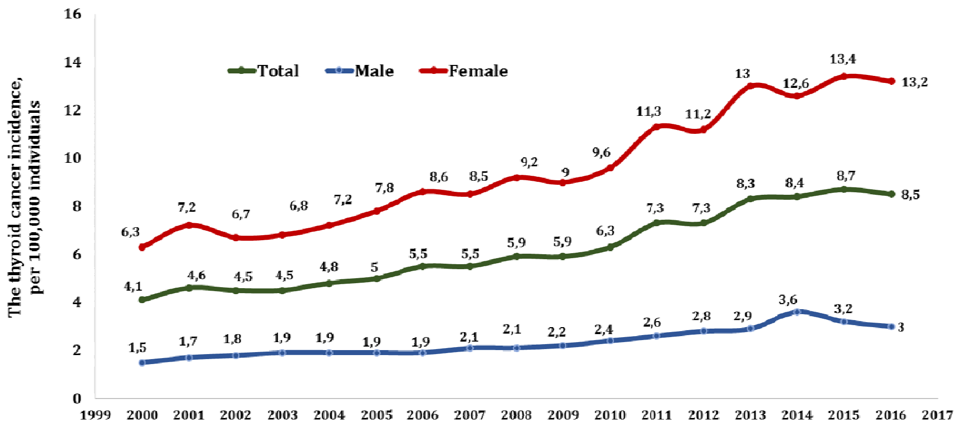

Fig. 1. The thyroid cancer incidence (per 100,000 population) among the total population of Ukraine, male and female as well, during 2000-2016

The thyroid cancer crude incidence rate per 100,000 population in different regions of Ukraine in 2000 (A), 2005 (B), 2010 (C), and 2016 is presented in Fig. 2. In 2000 and 2005, the highest value of the crude incidence rate per 100,000 population was noted in the Kyiv region (Fig. 2A, 2B), while in 2010, the increase of the crude incidence rate was observed in Kyiv, Kherson, Sumy regions (Fig. 2C). In 2016, the increase of thyroid cancer incidence was noted in Kirovohrad (15.4 per 100,000 population), Kyiv (14.5), Sumy (12.9), Kherson (12.0), and Vinnytsia regions (12.7) (Fig. 2D).

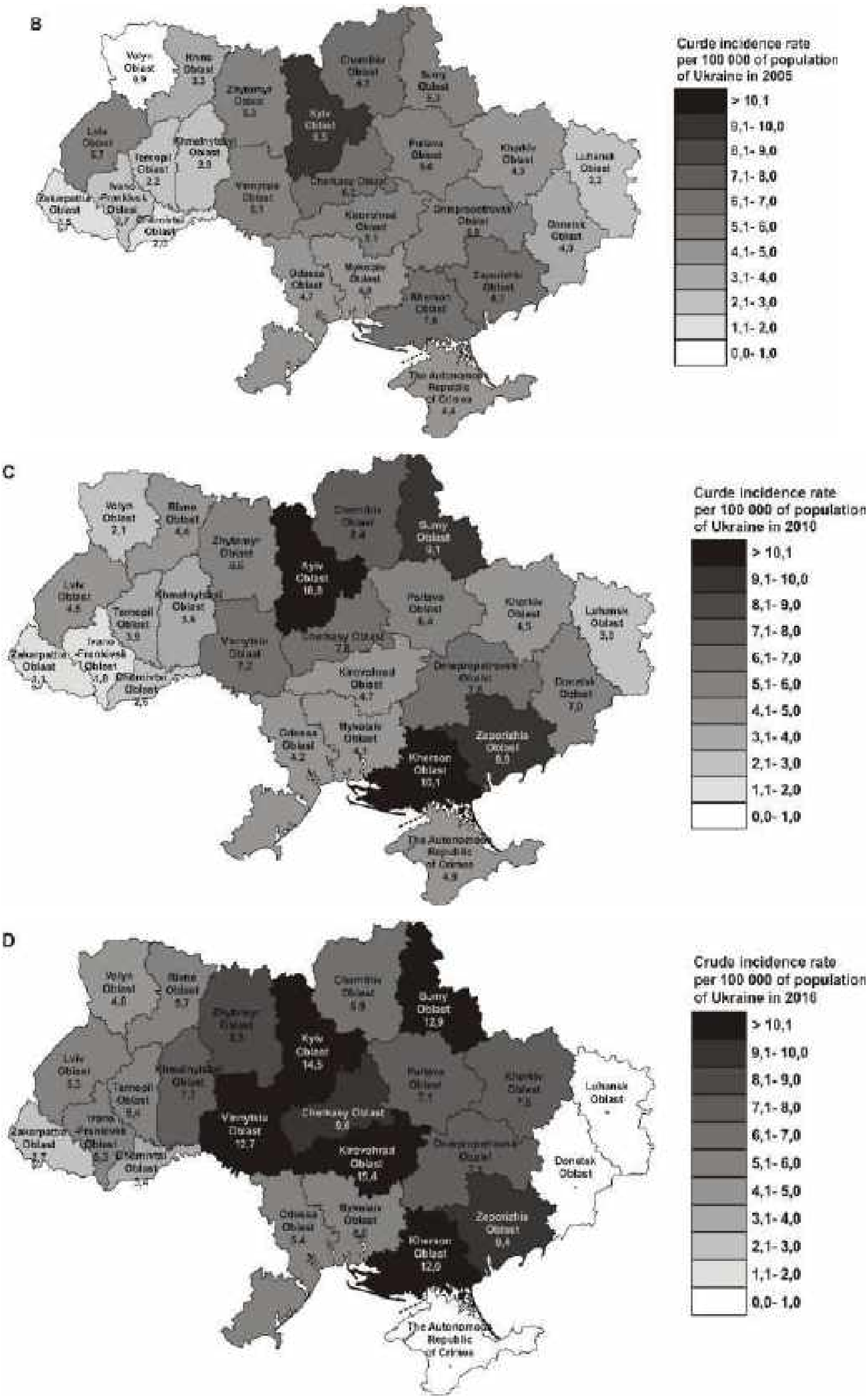

Fig. 2. The thyroid cancer crude incidence rate per 100,000 population in different regions of Ukraine in 2000 (A), 2005 (B), 2010 (C), and 2016 (D).

The relative risk of thyroid cancer incidence among the Ukrainian population in each subsequent year, relative to the previous one, was higher from 2001 to 2008, from 2010 to 2013, and in 2015 (Table 1). Thus, the tendency to an annual increase of thyroid cancer in the total Ukrainian population was confirmed. The relative risk of the thyroid cancer incidence in 2016 compared to 2000 was calculated (RR = 1.75; CI = 1.66-1.85; χ^2 = 391.58; p <0.001).

Table 1. The relative risk of thyroid cancer incidence among the population of Ukraine within 2000-2016

Years	Thyroid cancer incidence (per 100,000 population)	Number of resident population	Relative risk (RR)	Confidence interval (CI)	Cochran–Mantel–Haenszel test, χ^2	Significance, p
2000	4.1	49114950	-	-	-	-
2001	4.6	48663609	**1.05**	0.99-1.12	2.34	0.126
2002	4.5	48240.902	**1.03**	0.97-1.10	1.21	0.272
2003	4.5	47823108	**1.02**	0.96-1.08	0.44	0.505
2004	4.8	47442079	**1.05**	0.99-1.12	2.92	0.087
2005	5.0	47100462	**1.05**	0.99-1.12	3.09	0.079
2006	5.5	46749170	**1.10**	1.04-1.16	10.92	<0.001
2007	5.5	46465691	**1.0**	0.95-1.06	0.01	0.937
2008	5.9	46192309	**1.07**	1.01-1.13	6.08	<0.05
2009	5.9	45963359	**0.99**	0.94-1.04	0.13	0.719
2010	6.3	45782592	**1.07**	1.01-1.13	5.95	<0.05
2011	7.3	45598179	**1.16**	1.11-1.22	34.71	<0.001
2012	7.3	45453282	**1.0**	0.96-1.05	0.04	0.848
2013	8.3	45372692	**1.07**	1.02-1.12	8.31	<0.01
2014	8.4	45245894	**0.86**	0.82-0.90	36.71	<0.001
2015	8.7	42759661	**1.09**	1.04-1.14	11.26	<0.001
2016	8.5	42590879	**0.98**	0.93-1.03	0.88	0.349

For a detailed analysis of the thyroid cancer incidence among different gender groups, an estimation of the incidence rates and the relative risk of thyroid cancer incidence among the male and female population of Ukraine during the years 2000-2016 has been evaluated according to the data of the National Cancer Register of Ukraine (Tables 2 and 3). The highest incidence rate among the male population was detected in 2014 (3.6 per 100,000 population) (Table 2). In general, from 2000 to 2016, the thyroid cancer incidence among males was increased by 2-fold (from 1.5 to 3.0 per 100,000 population). The thyroid cancer relative risk was higher each year than in the previous year except for 2005 compared to 2004, 2013 compared to 2012, 2015 compared to 2014, and 2016 compared to 2015 in this population group. The highest relative risk was established in 2007 compared to 2006 (RR = 1.11, p = 0.135) (Table 2).

Table 2. Indices of the relative risk of thyroid cancer incidence among the male population of Ukraine within 2000-2016

Years	Thyroid cancer incidence (per 100,000 population)	Number of resident population	Relative risk (RR)	Confidence interval (CI)	Cochran–Mantel–Haenszel test, χ^2	Significance, p
2000	1.5	22754.662	-	-	-	-
2001	1.7	22530.402	**1.07**	0.92-1.24	0.72	0.396
2002	1.8	22316.317	**1.13**	0.98-1.31	2.97	0.085
2003	1.9	22112.534	**1.04**	0.91-1.12	0.34	0.558
2004	1.9	21926.809	**1.02**	0.89-1.16	0.05	0.821
2005	1.9	21753.993	**0.97**	0.84-1.11	0.23	0.632
2006	1.9	21574.667	**1.02**	0.89-1.17	0.09	0.769
2007	2.1	21434.680	**1.11**	0.97-1.27	2.24	0.135
2008	2.1	21297.678	**1.01**	0.89-1.15	0.03	0.871
2009	2.2	21184.932	**1.06**	0.93-1.21	0.81	0.367
2010	2.4	21107.067	**1.07**	0.95-1.21	1.16	0.281
2011	2.6	21032.616	**1.08**	0.96-1.22	1.58	0.208
2012	2.8	20976.712	**1.08**	0.96-1.21	1.67	0.197
2013	2.9	20962.744	**0.97**	0.86-1.09	0.27	0.605
2014	3.6	20918.288	**1.06**	0.95-1.19	1.06	0.304
2015	3.2	19787.826	**0.95**	0.84-1.06	0.90	0.342
2016	3.0	19717.881	**0.93**	0.82-1.05	1.55	0.213

Relative risk of the thyroid cancer among the male population of Ukraine in 2016 compared to 2000 was RR = 1.69; CI = 1.47-1.94; χ^2 = 56.90; $p<0.001$. There is a tendency to increased thyroid cancer incidence among the female population (data according to the National Cancer Registry of Ukraine during 2000-2016). The study revealed that thyroid cancer incidence among females was increased from 6.3 per 100,000 population in 2000 to 13.2 per 100,000 population in 2016, i.e. by 2.1-times ($p<0.05$). The peak incidence rate was 13.4 per 100,000 population in 2015 (Table 3).

Table 3. Indices of the relative risk of thyroid cancer incidence among the female population of Ukraine in 2000-2016

Years	Thyroid cancer incidence (per 100,000 population)	Number of resident population	Relative risk (RR)	Confidence interval (CI)	Cochran–Mantel–Haenszel test, χ^2	Significance, p
2000	6.3	26360.288	-	-	-	-
2001	7.2	26133.207	**1.04**	0.98-1.12	1.64	0.200
2002	6.7	25924.585	**1.01**	0.95-1.08	0.15	0.697
2003	6.8	25710.574	**1.02**	0.95-1.08	0.20	0.654
2004	7.2	25515.270	**1.06**	0.99-1.13	3.16	0.075
2005	7.8	25346.469	**1.07**	1.01-1.14	4.61	<0.05

2006	8.6	25174.503	**1.11**	1.05-1.18	12.01	<0.001
2007	8.5	25031.011	**0.98**	0.93-1.04	0.35	0.555
2008	9.2	24894.631	**1.08**	1.02-1.15	6.87	<0.01
2009	9.0	24778.427	**0.98**	0.92-1.03	0.66	0.417
2010	9.6	24675.525	**1.07**	1.01-1.13	4.81	<0.05
2011	11.3	24565.563	**1.18**	1.12-1.25	34.92	<0.001
2012	11.2	24476.570	**0.99**	0.94-1.04	0.13	0.716
2013	13.0	24409.948	**1.09**	1.04-1.15	11.70	<0.001
2014	12.6	24327.606	**0.82**	0.78-0.87	51.03	<0.001
2015	13.4	22971.835	**1.13**	1.06-1.19	17.57	<0.001
2016	13.2	22872.998	**0.99**	0.93-1.04	0.21	0.647

The estimated relative risk of thyroid cancer incidence among the female population of Ukraine during 2000-2016 was represented in Table 3. An increase in the thyroid cancer incidence from 2001 to 2006, in 2008, from 2010 to 2013, and in 2015 compared to previous years was observed. The highest relative risk was recorded in 2011 compared to 2010 (RR = 1.18, $p < 0.001$). The thyroid cancer relative risk among female population in Ukraine has increased since 2000 to 2016 (RR = 1.76; CI = 1.66-1.88; $\chi^2 = 334.41$; $p<0.001$).

A substantial increase in thyroid cancer incidence has been observed after the Chernobyl accident in the whole of Belarus and Ukraine, and the four most affected oblasts of the Russian Federation among those exposed as children or adolescents [24]. It is now well documented that children and adolescents exposed to radioiodines from Chernobyl fallout have a sizeable dose-related increase in thyroid cancer, with the risk greatest in those youngest at exposure and with a suggestion that deficiency in stable iodine may increase the risk [8]. Data on thyroid cancer risks to other age groups are somewhat less definitive. In addition, there have been reported increases in incidence and mortality from non-thyroid cancers and non-cancer endpoints. Although some studies are difficult to interpret because of methodological limitations, recent investigations of Chernobyl clean-up workers ('liquidators') have provided evidence of increased risks of leukemia and other hematological malignancies and cataracts, and suggestions of an increase in the risk of cardiovascular diseases, following low doses and low dose rates of radiation [8]. The dominant risk factor was thyroid exposure by ^{131}I resulting from the ingestion of milk. A minimum latency period for the identification of thyroid cancer incidence of 4-5 years has been observed. The cancer incidence among males who were 10 years old at the time of the accident was more than a factor of 4 lower than among females. The incidence data in this age group registered during the period 1991-2015 continuously increased with time to approach several 20,000 thyroid cancer cases at the end of this period [24].

The growing evidence of increased thyroid cancer rates among Chornobyl liquidators has occurred. Although this could be partially attributed to increased medical surveillance, the observed pattern of standardized incidence ratio (SIR) increase warrants further investigation of a potential contribution of radiation exposure to the elevated thyroid cancer rates in this large population. Ostroumova and co-workers (2014) have studied thyroid cancer incidence in a cohort of 150,813 male Chornobyl clean-up workers ("liquidators") from Ukraine by calculating SIR using national cancer statistics [19]. Follow-up began on the liquidator's registration date with the Chornobyl State Registry of Ukraine (the earliest date was 05.05.1986) and continued through December 31, 2010, date of thyroid cancer diagnosis, date of death, or date of last known vital status, whichever came first. There were 196 incident thyroid cancers in the study cohort with an overall SIR of 3.50 [95% confidence interval (CI) 3.04-4.03]. A significantly elevated SIR estimate of 3.86 (95% CI, 3.26-4.57) was observed for liquidators who had their first clean-up mission in the Chornobyl zone in 1986 when levels of external and internal exposure to radiation were highest; the SIR estimates for later calendar years of first clean-up mission, while significantly elevated, were lower. The SIR estimates were elevated throughout the entire follow-up period but were especially high 10-18 years after the accident: 4.62 (95% CI, 3.47-6.15) and 4.80 (95% CI, 3.78-6.10) for the period 1995-1999 and 2000-2004, respectively [19].

According to data of epidemiological cohort studies outlined in the annual report of the State Institution "National Research Center for Radiation Medicine of the National Academy of Medical Sciences of Ukraine" (NRCRM) concerning medical problems of the Chornobyl disaster, radiation medicine, radiobiology, radiation hygiene and epidemiology in collaboration with the WHO network of medical preparedness and assistance in radiation accidents, increased incidence (1990-2012) of thyroid cancer in victims of Chernobyl accident (liquidators – in 4.6 times, evacuated – in 4.0 times, residents of contaminated areas – in 1.3 times) and increased incidence of breast cancer in female workers of 1986-1987 (in the 1994-2012 biennium. SIR = 160.0%, 95% CI: 142.4-177.6) was found [3]. Retrospective studies of thyroid cancer ("case-control") in cohorts and 152 thousand liquidators were continued together with the US National Cancer Institute. Radiation risks of multiple myeloma and chronic lymphocytic leukemia were found. Molecular effects of the remote period after radiation exposure include changes in gene expression, telomere length, the protein expressions. An association of molecular changes with cognitive deficits was defined. The possibility of persistence of radiation-modified hidden chromosomal instability in consecutive generations of human somatic cells was proven. The status of reproductive function and peculiarities of baby nutrition in a population of contaminated areas were studied. In the framework of National social programs for improving safety, occupational health, and working environment in 2014. For the first time in Ukraine developed and completed inter-calibration of 18 laboratories for individual monitoring. Studying of medical effects of radiation in interventional cardiologists was started. Experimental studies concerned the impact of radio-induced modifications on cell systems. The report also shows the results of scientific organizations and healthcare work, staff training [3].

Also, Tronko and co-workers (2010) have described the epidemiology and pathology of thyroid cancer in Ukraine and performed the molecular analysis of genetic alterations more frequently found to be associated with papillary carcinomas in a selected group [22]. Relationship between the thyroid cancer incidence and gender, age, and place of residence of subjects aged 0-18 years at the time of the Chernobyl accident (5427 subjects of thyroid cancer, among which 3996 (73.6%) were children aged 0 to 14 years at the time of the accident, and 1431 (26.3%) were adolescents aged 15 to 18 years were studied. Pathologically analyzed thyroid carcinomas were obtained from 640 patients (20-40 years old at the time of surgery and born before the Chernobyl accident), and from 90 patients (11-22 years old at the time of surgery and born after the accident). All patients were operated on during 2006-2008. A comparison between the thyroid cancer incidence rates in the 6 highest contaminated regions of Ukraine and the other 21 regions shows the most significant difference between the rates for the last three years of follow-up, which confirms that a direct relationship is still present between the rise in thyroid cancer incidence and the post-Chernobyl radiation exposure. The much lower incidence of thyroid cancer in subjects, who were born after the accident, additionally confirmed a direct relationship between the Chernobyl accident and thyroid cancer development at least in those who were aged up to 18 years at the time of the nuclear accident. After 22 years after the Chernobyl nuclear accident, the number and incidence of thyroid cancer cases in Ukraine were steadily increased in the cohort of those who were children and adolescents at the time of the accident [22].

Moreover, Fuzik and co-workers (2013) have investigated the thyroid cancer incidence in the whole territory of Ukraine and to clear up its age and gender patterns depending on average regional (oblast) thyroid doses from radioactive iodine due to the Chornobyl accident [11].

Based on average accumulated thyroid doses from radioactive iodine, the geographical regions of Ukraine with low and high average thyroid doses were identified for a comparative analysis performance. Results of their study confirmed the radiation excess of thyroid cancer in individuals who were children and adolescents in 1986. Some excess was observed in elder age groups too. The special situation was observed in the female age group 40-49 at the moment of the Chornobyl accident i.e. the age-specific thyroid cancer incidence rates were significantly higher in "high exposure" regions comparing with "low exposure" ones during all years of observation within 1989-2009. A probable radiation excess of thyroid cancer was suggested not only in children and adolescents but also in adult age groups. In elder age groups this excess was less expressed and manifested after a longer period [11]. Some excess is observed in population groups exposed as adults. In the female age group of 40-49 at the moment of the accident, the age-specific thyroid cancer incidence rates were significantly higher in 'high exposure' regions versus 'low exposure' ones for all the years of follow-up from 1989 until 2012 [4].

Bogdanova and co-workers (2018) have compared structural characteristics and invasive features of papillary thyroid carcinoma in two age-matched groups: patients who were children (less than 4 years old) at the time of the Chernobyl accident and who lived in three regions of Ukraine most contaminated by radioactive iodine ^{131}I ("radiogenic" cancer), and those who lived in the same regions but who were born after 1987 and were not exposed to ^{131}I ("sporadic" cancer) [6]. Further, the histopathologic features of papillary thyroid carcinoma were analyzed about age and individual ^{131}I thyroid dose. The study included 301 radiogenic and 194 sporadic papillary thyroid carcinomas. According to age at surgery, patients were subdivided into children (less than 14 years old), adolescents (15-18 years old), and adults (19-28 years old). Analyses of morphological features related to ^{131}I doses were conducted among exposed patients on categorical and continuous scales controlling for sex and age. Among children, radiogenic papillary thyroid carcinoma displayed a significantly higher frequency of tumors with a dominant solid growth pattern, intrathyroidal spread, extrathyroidal extension, lymphatic/vascular invasion, and distant metastases. Exposed adolescents more frequently displayed extrathyroidal extension, lymphatic/vascular invasion, and distant metastases. Exposed adults more frequently had intrathyroidal spread and extrathyroidal extension. The frequency of papillary thyroid carcinoma with dominant papillary pattern and oxyphilic cell metaplasia was significantly lower in radiogenic compared to sporadic tumors for all age groups. Manifestations of tumor aggressiveness were most frequent in children compared to adolescents and adults regardless of etiology. Radiogenic papillary thyroid carcinoma is less likely to demonstrate a dominant papillary growth pattern and more likely to display more aggressive tumor behavior than sporadic papillary thyroid carcinoma [6].

Based on data from case-control studies, iodine deficiency appeared to enhance the risk of developing thyroid cancer following exposure from Chernobyl. Results from a recent large cohort study, however, did not support these findings. Data on adult exposure are limited and not entirely consistent. Similarly, information on thyroid cancer risks associated with in utero exposure is insufficient to conclude. The lack of information on these two population groups indicates an important gap that needs to be filled. Thirty years after the accident, excess thyroid cancers are still occurring among persons exposed as children or adolescents, and, if external radiation can be used as a guide, we can expect an excess of radiation-associated thyroid cancers for several more decades [21].

It is also proved that some groups of fungicides and herbicides are capable of affecting the thyroid gland, provoking its growth, leading to a compensatory change in the activity of the synthesis of the hormones. Therefore, the presence of their residual amounts in the plant may affect the level of thyroid gland pathology. Antonenko and co-workers (2018) have analyzed the influence of pesticide application on the Ukrainian adult population morbidity with thyroid diseases in the period from 2001 to 2014 [1]. The maximum level of thyroid pathology was found in the northern, western, and northwestern regions, where the diffuse goiter dominates in the morbidity and prevalence of thyroid diseases; minimal – in the southern, eastern, and south-eastern regions. It was established that the highest volumes of application of chemical plant protection products in the period 2001-2013 took place in the southern and central regions of Ukraine, namely in Poltava, Vinnytsia, Kharkiv, Dnipropetrovsk, Khmelnytsky, Odesa, and Mykolaiv regions. Sufficiently high levels of pesticide application were in the Kyiv, Kherson regions, Crimea, Zaporizhia, Kirovograd, and Cherkasy regions [1].

In our previous study, we also have assessed the regional features of incidence and prevalence of thyroid cancer among the adult and children populations in Ukraine in 2000 and 2015 [15]. The thyroid cancer incidence (per 100,000 population) among the total and children population of Ukraine was analyzed. The current level of thyroid cancer prevalence and incidence in Ukraine has significant regional differences. When analyzing the dynamics of the thyroid cancer prevalence among the total population of Ukraine, a stable trend towards the increase of intensive indicators for the period 2000 and 2015 was established. In 2000, the thyroid cancer prevalence among the population of the country was 35.3, while in 2015 – 90.1 per 100,000 population (increased by 2.55-fold). The highest thyroid cancer prevalence among the total population of Ukraine in 2000 was established in Kyiv city and the Kyiv region (81.9 and 77.0 per 100,000 population, respectively). High rates of thyroid cancer prevalence were noted in this year also in Kherson, Vinnytsia, Kharkiv, Dnipropetrovsk, Chernihiv, Donetsk, and Zaporizhia regions (72.2, 44.6, 43.2, 38.9, 38.9, 37.3, and 36.1 per 100,000 population, respectively). The low level of prevalence in 2000 was found in Ternopil (7.6 per 100,000 population), Ivano-Frankivsk (13.2), Volyn (14.1), and Zakarpattia (16.0) regions. In 2015, the thyroid cancer prevalence was increased in most regions of Ukraine. The highest prevalence among the total population of the country was observed in Kyiv city and the Kyiv region (220.1 and 216.0 per 100,000 population). High indices of thyroid cancer in 2015 were also noted in Kherson, Vinnytsia, Rivne, Cherkasy, Zaporizhia, Zhytomyr, Dnipropetrovsk, and Odesa regions, and amounted to 156.5; 125.9; 122.4; 114.2; 101.9; 100.1; 99.5; and 95.5 per 100,000 population, respectively. In other areas of Ukraine, the thyroid cancer incidence was lower than the mean level for Ukraine, which was 90.1 per 100,000 population. The lowest rates of thyroid cancer incidence were demonstrated in 2015 in Kharkiv, Chernihiv, Luhansk, Zakarpattia, and Ivano-Frankivsk regions (3.0, 14.2, 16.9, 24.5, and 29.4 per 100,000 population, respectively) [15].

Thus, over the past 15 years, the thyroid cancer prevalence in Ukraine was increased among the total population, including among children 0 to 14-aged years. However, statistics showed that these indices had their regional characteristics. The highest thyroid cancer incidence and prevalence among the Ukrainian population for the period 2000-2015 was observed in Kyiv city and the Kyiv region. High indices of thyroid cancer incidence and prevalence during this period were also found in some northeastern and southern regions and the lowest - mainly in the western regions of Ukraine. In 2000, the thyroid cancer incidence among the Ukrainian population was 3.9 per 100,000 population, and this indicator was already 6.9 per 100,000 population in 15 years (1.8-fold increasing rate). The highest incidence rates were studied in 2000 among the total population of Ukraine in comparison with the all-Ukrainian indices was recorded in Kyiv city and Kyiv region, as well as in Vinnytsia, Dnipropetrovsk, Zhytomyr, Lviv, Odesa, Kherson, and Chernihiv regions and amounted to 12.8; 9.8; 4.8; 4.7; 4.9; 3.9; 4.1; 5.4 and 5.4 per 100,000 population, respectively. Low incidence rates were found in Volyn (1.7 per 100,000 population), Zakarpattia (1.1 per 100,000 population), Ivano-Frankivsk (1.6 per 100,000 population), Ternopil (1.6 per 100 population), and Chernivtsi regions (1.3 per 100,000 population). According to statistical data in 2015, the highest incidence rates were registered in the following regions of Ukraine: in the Kirovohrad region and Kyiv, as well as in Vinnytsia, Sumy, Kyiv, Kherson, Cherkasy, Zhytomyr, and Zaporizhia regions (15.8; 15.5; 14.3; 14.2; 11.7; 10.6; 10.5; 8.0 and 7.9 per 100,000 population, respectively). In other regions of Ukraine, the thyroid cancer incidence per 100,000 population in 2015 was below the total mean rate in the Ukrainian population. Low incidence in this year was identified among the population of the

Zakarpattia (1.1 per 100,000 population) and Lugansk regions (1.6 per 100,000 population). The increased rate of these indices among the population over 15 years is 1.77-fold. The incidence rate of thyroid cancer for the investigated period was decreased only in the Donetsk and Luhansk regions, the highest increase rate of this indices was found in the Cherkasy region (5.83-fold). Among children from 0 to 14 years, the mean level of thyroid cancer prevalence in 2000 was 0.58 per 100,000 population. The highest rates were observed among residents of Kyiv, Zhytomyr, Kherson, Cherkasy, and Dnipropetrovsk regions (1.83; 1.81; 1.27; 1.16 and 1.15 per 100,000 population, respectively). In Zaporizhia, Luhansk, Rivne, and Sumy regions, the thyroid cancer prevalence among children population in 2000 was not found [15].

In 2015, the thyroid cancer prevalence among the children population was 0.70 per 100,000 population. The increase of these indices for the period 2000-2015 was 1.21-fold. Higher thyroid cancer prevalence compared to national mean value was recorded in Rivne, Khmelnytskyi, Ivano-Frankivsk, Poltava, Kirovohrad, Chernihiv, Chernivtsi, Cherkasy, Kyiv, Volyn, and Zhytomyr regions (2.6, 2.0, 1.7, 1, 5, 1,4; 1,4; 1,3; 1,2; 1,1; 1,0, and 1,0 per 100,000 population, respectively), while thyroid cancer prevalence among children population in Donetsk, Luhansk, Mykolaiv, Ternopil and Kherson regions was not recorded. The highest thyroid cancer prevalence was recorded in the Ivano-Frankivsk region and was 5.15-fold. Increased prevalence among children in 2000-2015 also was established in Volyn, Kirovohrad, Lviv, Odesa, Poltava, Rivne, Kharkiv, Khmelnytskyi, Cherkasy, Chernivtsi, and Chernihiv regions. In other regions of the country, thyroid cancer prevalence among children tended to decrease. The thyroid cancer incidence in 2000 among the children population was 0.16 per 100,000 population. The incidence in this year was revealed in Vinnytsia, Dnipropetrovsk, Zhytomyr, Zakarpattia, Ivano-Frinkivsk, Kirovohrad, Luhansk, Mykolaiv, Odesa, Kherson, Khmelnytskyi, Cherkasy, Chernivtsi regions, and Kyiv city. In other regions of Ukraine, thyroid cancer incidence among children has not been established. The all-Ukrainian indices of the thyroid cancer incidence in 2015 among the children population were 0.28 per 100,000 population; the increasing degree over 15 years was 1.75-fold. The highest incidence of thyroid cancer among children in this period was found in Poltava and Chernivtsi regions (1.52 and 1.30 per 100,000 population, respectively). The increased level in the thyroid cancer incidence was highest in the Ivano-Frankivsk region (2.87-fold). An increase in thyroid cancer incidence was also observed in the Odesa, Poltava, Khmelnytskyi, Cherkasy, and Chernivtsi regions, while in other regions the incidence rate in the period 2000-2015 was decreased. Thus, over the past 15 years, the thyroid cancer prevalence and incidence in Ukraine was increased among the total population, including children 0 to 14-aged years. The highest thyroid cancer incidence and prevalence among the total population for the period of 2000-2015 was observed in Kyiv city and the Kyiv region. The thyroid cancer prevalence and incidence among children in the country were noted at a rather low level. In many regions, the rates of thyroid cancer didn't register, or during the studied period, significantly decreased. However, the increase of total indices of thyroid cancer prevalence and incidence among the children was due to the high intensive indices in some regions [15].

CONCLUSIONS

According to the National Cancer Register of Ukraine, the increase in the thyroid cancer incidence (per 100,000 population) among the population of Ukraine, male and female as well, during 2000-2016 was noted. The peak of thyroid cancer incidence among the total population of Ukraine in this period was in 2015 (8.7 per 100,000 population). The relative risk of thyroid cancer incidence among the Ukrainian population in each subsequent year, relative to the previous one, was higher from 2001 to 2008, from 2010 to 2013, and in 2015. Thus, the tendency to an annual increase of thyroid cancer in the total Ukrainian population was confirmed. The relative risk of thyroid cancer incidence in 2016 compared to 2000 was noted. The highest incidence rate among the male population was detected in 2014 (3.6 per 100,000 population). In general, from 2000 to 2016, the thyroid cancer incidence among the male population was increased by 2-fold (from 1.5 to 3.0 per

100,000 population). The thyroid cancer relative risk was higher each year than in the previous year except for 2005 compared to 2004, 2013 compared to 2012, 2015 compared to 2014, and 2016 compared to 2015 in this population group. The highest relative risk was established in 2007 compared to 2006 (RR = 1.11, p = 0.135). The relative risk of thyroid cancer among the male population of Ukraine in 2016 compared to 2000 was 1.69 ($p<0.001$). There was a tendency to increased thyroid cancer incidence among the female population. The study revealed that thyroid cancer incidence among the female population was increased from 6.3 in 2000 to 13.2 per 100,000 population in 2016, i.e. by 2.1-times ($p<0.05$). The peak incidence rate was 13.4 per 100,000 population in 2015. An increase in the thyroid cancer incidence from 2001 to 2006, in 2008, from 2010 to 2013, and in 2015 compared to previous years was observed. The highest relative risk was recorded in 2011 compared to 2010 (RR = 1.18, $p<0.001$). The thyroid cancer relative risk among the female population in Ukraine has increased from 2000 to 2016. These results suggest the need for primary prevention of cancer, taking into account regional peculiarities incidence and prevalence of cancer pathology, providing programs to environmental protection against carcinogens-induced pollution, the implementation of measures and training of the population to healthy lifestyle issues (rationale and optimal nutrition, rest, personal hygiene, smoking cessation, alcohol abuse, etc.). To include preventive measures and various forms of health education work designed to detect preclinical forms of cancer. It is also necessary to conduct secondary prevention involved organizing preventive examinations of the population, especially women of all ages, involving endocrinologists and other doctors using modern diagnostic methods.

REFERENCES

1. Antonenko A.M., Vavrinevych O.P., Korshun M.M., Omelchuk S.T., Hygienic assessment of the effects of pesticides application on adult population morbidity with thyroid gland diseases, Wiad. Lek., vol. 71/issue 2, pt. 2, pp 353-357, 2018.

2. Bauer A.J., Thyroid nodules and differentiated thyroid cancer, Endocr. Dev., vol. 26, pp 183-201, 2014.

3. Bazyka D., Sushko V., Chumak A., Buzunov V., Talko V., Yanovich L., State Institution "National Research Center for Radiation Medicine of the National Academy of Medical Sciences of Ukraine" - research activities and scientific advance in 2014, Probl. Radiac. Med. Radiobiol., vol. 20, pp 12-24, 2015. [Article in English, Ukrainian]

4. Bazyka D.A., Prysyazhnyuk A.Y., Fuzik M.M., Fedorenko Z.P., Thyroid Cancer and the Chornobyl Accident in Ukraine: Experience With the Implementation of a Follow-Up Programme, Radiat. Prot. Dosimetry, vol. 171/issue 1, pp 32-40, 2016.

5. Berstein L.M., Thyroid cancer: epidemiology, endocrinology, factors and mechanisms of carcinogenesis, Practical Oncology, vol. 8/issue 1, pp 1-8, 2007.

6. Bogdanova T.I., Saenko V.A., Brenner A.V., Zurnadzhy L.Y., Rogounovitch T.I., Likhtarov I.A., Masiuk S.V., Kovgan L.M., Shpak V.M., Thomas G.A., Chanock S.J., Mabuchi K., Tronko M.D., Yamashita S., Comparative Histopathologic Analysis of "Radiogenic" and "Sporadic" Papillary Thyroid Carcinoma: Patients Born Before and After the Chernobyl Accident, Thyroid, vol. 28/issue 7, pp 880-890, 2018.

7. Cancer in Ukraine: Bulletin of the National Chancery Register of Ukraine No. 3-19 [Electronic resource]. Access: http://www.ncru.inf.ua/publications/index.htm.

8. Cardis E., Hatch M., The Chernobyl accident - an epidemiological perspective, Clin. Oncol. (R. Coll. Radiol.), vol. 23/issue 4, pp 251-260, 2011.

9. Decyk O.Z., Rudko I.V., Analysis of morbidity and mortality from malignant neoplasms of the lips and oral cavity in Ukraine and Ivano-Frankivsk region for 2007-2016. Ukraine, The Health of Nation, issue 3, pp 95-100, 2017.

10. Demographic Yearbook "The Population of Ukraine for 2015" State Statistics Service of Ukraine. Kyiv, 2015. 120 pp.

11. Fuzik M.M., Prysyazhnyuk A.Y., Shibata Y., Romanenko A.Y., Fedorenko Z.P., Gudzenko N.A., Gulak L.O., Trotsyuk N.K., Goroh Y.L., Khukhrianska O.M., Sumkina O.V., Saenko V.A., Yamashita S., Age and gender patterns of thyroid cancer incidence in Ukraine depending on thyroid radiation doses from radioactive iodine exposure after the Chornobyl NPP accident, Probl. Radiac. Med. Radiobiol., issue 18, pp 144-155, 2013.

12. Global Cancer Facts & Figures [Electronic resource]. 2nd Edition WHO, American Cancer Society, 2011.

13. Kasiyan O., Tkachenko H., Łukaszewicz J., Mortality from thyroid cancer among a population of Ukraine over the past ten years. In: Globalisation and regional environmental protection. The technique, technology, ecology. T. Noch, W. Mikołajczewska, A. Wesołowska (Eds), Publishing House of the Gdańsk Higher School, pp 31-51, 2016.

14. Kasiyan O., Tkachenko H., Łukaszewicz J., The dynamic of thyroid cancer incidence and prevalence among the population of Ukraine over the past ten years, Słupskie Prace Biologiczne, vol. 13, pp 77-96, 2016.

15. Kasiyan O., Tkachenko H., Łukaszewicz J., Thyroid cancer incidence and prevalence among adult and children population of Ukraine in 2000 and 2015, Słupskie Prace Biologiczne, vol. 14, pp 149-168, 2017.

16. Kuchuk A.A. 1994. Health problems of the population in different regions of Ukraine. Toxicol. Lett., 72(1-3): 213-217.

17. On Approval of the National Program for Combating Cancer Diseases for the Period until 2016: Law of Ukraine dated December 23, 2009. No. 1794-VI. - Access: http://zakon5.rada.gov.ua/laws/show/ 1794-17.

18. On the system of cancer care to the population of Ukraine: the order of the Ministry of Health of Ukraine dated October 1, 2013, No. 845. - Access: http://zakon2.rada.gov.ua/laws/show/z0077-14.

19. Ostroumova E., Gudzenko N., Brenner A., Gorokh Y., Hatch M., Prysyazhnyuk A., Mabuchi K., Bazyka D., Thyroid cancer incidence in Chornobyl liquidators in Ukraine: SIR analysis, 1986-2010, Eur. J. Epidemiol., vol. 29/issue 5, pp 337-342, 2014.

20. Rivera G., Lugo-Vicente H., Thyroid cancer in children, Bol. Assoc. Med. P.R., vol. 106/issue3, pp 48-54, 2014.

21. Ron E., Thyroid cancer incidence among people living in areas contaminated by radiation from the Chernobyl accident, Health Phys., vol. 93/issue 5, pp 502-511, 2007.

22. Tronko M., Bogdanova T., Voskoboynyk L., Zurnadzhy L., Shpak V., Gulak L., Radiation-induced thyroid cancer: fundamental and applied aspects, Exp. Oncol., vol. 32/issue 3, pp 200-204, 2010.

23. Tufano R.P., Noureldine S.I., Angelos P., Incidental thyroid nodules and thyroid cancer: considerations before determining management, JAMA Otolaryngol. Head Neck Surg., vol. 141/issue 6, pp 566-572, 2015.

24. Weiss W., Chernobyl thyroid cancer: 30 years of follow-up overview. Radiat. Prot. Dosimetry, vol. 182/issue 1, pp 58-61, 2018.

25. Woodward M., Epidemiology: study design and data analysis, New York: Chapman and Hall, CRC, 1999.

26. Zar J.H., Biostatistical Analysis, 4th ed., Prentice Hall Inc., New Jersey, 1999.

REGIONAL CHARACTERISTICS OF THE THYROID PATHOLOGY AMONG THE CHILDREN POPULATION IN THE ENDEMIC REGIONS OF WESTERN UKRAINE

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ABSTRACT

Regional peculiarities of prevalence, morbidity, and relative risk in the incidence of thyroid pathology among children of 20 regions and 8 large industrial towns of the Lviv region through 2010-2016 were revealed. Reduction in the rates of prevalence and morbidity of thyroid pathology among children (781.9 in 2016 versus 985.5 per 10,000 population in 2010 and 80.4 versus 104.8 per 10,000 population, respectively) in 14 districts and 6 towns were established. The risk rates were higher in 2016 than in 2010 in five districts (RR = 1.15, p <0.001, RR = 1.06, p = 0.102, RR = 1.95, p <0.001, RR = 1.05, p = 0.161 and RR = 1.06, p = 0.211) and two industrial towns in the region (RR = 1.12, p = 0.06, and RR = 1.04, p = 0.411). Based on the quantitative assessment of iodine concentration in the water of districts and cities in the region, regions with different degrees of iodine deficiency have been determined. The relative risk in the incidence of thyroid pathology among the children of the Lviv region was higher in regions with high and moderate degrees of iodine deficiency compared to the average rate in the region and lower in regions with mild iodine deficiency. To reduce the risk of diseases caused by iodine deficiency in the endemic region, a differentiated approach to iodine prophylaxis has been suggested, taking into account the regional degree of iodine level and individual iodine intake.

Keywords: iodine, thyroid gland, prevention, endemic region, relative risk.

INTRODUCTION

Iodine is an essential trace mineral, required for the production of thyroid hormone [47]. The thyroid gland is an effective collector of iodine and has several protective mechanisms resulting in the maintenance of normal thyroid function despite wide fluctuations of the daily iodine intake. Ingestion of several commonly used drugs and food conservatives results in acute or chronic excessive iodine intake. Failure to escape from the iodine-induced organification inhibition can cause hypothyroidism, which is temporary and subsides after iodine exposure ceases. Iodine excess may also establish a status of excessive thyroid hormone synthesis and release, thus inducing autonomic thyroid function in iodopenic areas or can contribute to the development of iodine-induced hyperthyroidism in iodine abundant areas. In the presence of defective auto-protective mechanisms, excessive iodine ingestion can divert the normal thyroid function [34]. Normal thyroid function and adequate thyroid hormone are a prerequisite for neurocognitive development and growth in children, as well as are critically important for normal growth and neurodevelopment in fetal life, infancy, and childhood [12, 47]. Iodine deficiency may result in goiter, hypothyroidism, miscarriage, stillbirth, congenital anomalies, infant and neonatal mortality, and impaired growth [47]. Hypothyroidism or hyperthyroidism as a result of supraphysiologic iodine exposure might be either subclinical or overt, and the source of the excess iodine might not be readily apparent [39].

The primary source of iodine in the diet is *via* consumption of foods that have been fortified with iodine, including salt, dairy products, and bread, or that are naturally abundant in the micronutrient, such as seafood. For adults who are not lactating or pregnant, the US Institute of Medicine, and jointly by the WHO, United Nations Children's Fund (UNICEF), and the International Council for the Control of Iodine Deficiency Disorders (ICCIDD), recommend a daily iodine intake of 150 µg and stated a tolerable upper level (the approximate threshold below which notable adverse effects are unlikely to occur in the healthy population) of 1,100 µg per day in adults [13, 39,55]. The recommended iodine intake during pregnancy is 250 µg/day. A daily iodine intake below this threshold poses risks of various degrees of thyroid insufficiency for both the mother and the fetus [43]. However, in certain susceptible individuals, including those with pre-existing thyroid disease, the elderly, fetuses, and neonates, or patients with other risk factors, the risk of developing iodine-induced thyroid dysfunction might be increased [39].

At least one-third of the world's population is estimated to be iodine-deficient predominantly in developing countries [57]. Although international public health efforts over the past several decades have been highly effective, nearly one-third of children worldwide remain at risk for iodine deficiency, and iodine deficiency is considered the leading preventable cause of preventable intellectual deficits [47]. Iodine deficiency causes significant health problems and so, the term iodine deficiency disorders (IDD) has been introduced. The earliest sign of IDD is a goiter, but these disorders also include cretinism, neonatal hypothyroidism, and congenital defects, as well as retardation of mental and physical development, etc. IDD is a worldwide problem. WHO estimates that substantially more than 800 million people are at risk and more than 190 million suffer from IDD; over 3 million people have cretinism and in the largest and worst affected areas many millions suffer from mental and physical developmental defects [36]. Iodine deficiency affects an estimated 241 million school-aged children in the world [41]. IDD can be eliminated by prophylaxis using iodine administered in salt, oil, or some other vehicle [36].

The population iodine status is most commonly assessed using median urinary iodine concentration values, but goiter prevalence (determined by palpation or by ultrasound), serum thyroglobulin levels, and neonatal thyroid-stimulating hormone values can also be used [47]. In some countries, assessing iodine nutrition at the population level is usually done by estimating household coverage of adequately iodized salt (HHIS) [62].

Iodine supplementation may be required in areas where dietary fortification is not feasible or where it is not sufficient for vulnerable groups such as pregnant women [47]. Globally, iodine supplementation has been the primary method over the past century to decrease iodine deficiency, which is the leading cause of preventable mental retardation [13]. In nearly all countries, the best strategy to control iodine deficiency is the iodization of salt, which is one of the most cost-effective ways to contribute to economic and social development [63]. When iodization of salt is not possible, iodine supplements can be given to susceptible groups. Iodine has been administrated as iodized oil orally, introduced into the water supply, used in crop irrigation, incorporated into animal fodder, and introduced into food through salt iodization, bread iodophors, and other products [39, 63].

Universal salt iodization programs have been the mainstay of public health efforts to eliminate iodine deficiency worldwide [47]. There has been substantial recent progress in the global effort to control iodine deficiency [62]. Over the past decade, the number of countries that are iodine deficient has fallen from 54 to 30. The number of iodine-sufficient countries has increased from 67 to 112, while the number with excessive iodine intake has increased from 5 to 10. In most countries with excess intake, this is due to the overiodization of salt and/or poor monitoring of salt iodization. Out of 128 countries with HHIS data, at least 90% of households in 37 countries consume adequately iodized salt, but in 39 countries, coverage rates are below 50%. Overall, about 70% of households worldwide have access to iodized salt [62]. However, in some regions targeted fortification of foods such as bread has been used to combat iodine deficiency. Thirty-two European countries were still affected by mild to severe iodine deficiency in the late 1990s. The most severely affected countries were in Eastern Europe, including Central Asia, but Western Europe was also still affected [5]. However, iodized salt programs need to be carefully monitored to ensure adequate iodine intake while avoiding iodine excess [62].

According to studies conducted, about 70% of the population in Ukraine is suffering from an iodine deficiency in the diet. Children are the most sensitive to iodine deficiency, therefore, the generally accepted criteria for iodine deficiency assessment are based on data from the examinations of the children's population in the endemic region [3, 33, 35, 44, 45]. In recent years, the tendency to increase the incidence of thyroid pathology among the Ukrainian population has been observed. According to official statistics, almost every tenth school-aged child in the country has a goiter, and in some regions, its frequency exceeds these indices [40].

The occurrence of thyroid diseases is determined by the interplay between genetic and environmental factors. The major environmental factor that determines goiter prevalence is iodine status, but other environmental factors influencing entire populations have been identified such as goitrogens in food and drinking water [32]. Endemic goiter occurs when the prevalence of thyroid enlargement in the population of an area exceeds 10%. With few exceptions, its cause is iodine deficiency superimposed on other goitrogenic factors normally present and responsible for sporadic goiter [36]. The goiter prevalence is higher in certain groups in the population. The variation in goiter prevalence between the genders is well known with a higher occurrence among women. The association with age is probably dependent on iodine status because it seems that the zenith of goiter prevalence appears earlier in life the more severe iodine deficiency the population is exposed to [32]. The difference in age maximum in goiter prevalence suggests that monitoring of iodine deficiency disorders should ideally include a spectrum of age groups [32].

The deterioration of the environmental situation increases iodine deficiency creating conditions for increasing the incidence of thyroid pathology [11, 33]. Iodine deficiency is a widespread natural phenomenon associated with the lack of iodine in water and soil in a particular region, and, consequently, in food products in the area [40]. According to the iodine level in the water, different degrees of iodine deficiency in the endemic regions are distinguished: its content to 2 $\mu g/dm^3$ indicates a high degree of endemic deficiency, 2-3 $\mu g/dm^3$ – moderate deficiency, and 3-4 $\mu g/dm^3$ – mild deficiency [3, 44]. Since the iodine content in the biosphere is practically unchanged [44, 45], the study on the concentration of this trace element in drinking water makes it possible to correctly plan and improve effective methods and ways of eliminating iodine deficiency, to carry out iodine prophylaxis and treatment of iodine-dependent diseases more differentiated concerning iodine deficiency among residents of each region.

Lviv region in Ukraine, along with Volyn, Rivne, Ternopil, Ivano-Frankivsk, Zakarpattia, Chernivtsi regions, is one of the regions with a high degree of endemic iodine deficiency. In Ukraine, areas with partially expressed iodine deficiency, with moderate and mild iodine deficiency, as well as regions with sufficient iodine availability have been identified [35]. The unequal degree of iodine deficiency within the Lviv endemic region based on the iodine content in the drinking water of settlements was also revealed [26-28]. Since the whole territory of Ukraine is not iodine deficient, and even in the same region the unequal degree of iodine deficiency is recorded, the approach to the prevention of iodine-dependent diseases in different regions should be differentiated.

The aim of our study was the assessment in the incidence of thyroid pathology among the children population of Lviv region during 2010-2016, as well as to demonstrate the relative risk in the incidence of thyroid pathology among this age group in the Lviv region and other regions of Ukraine possessing different degrees of iodine deficiency.

MATERIAL AND METHODS

The incidence of thyroid diseases among different age groups of the Lviv region in the studied period was analyzed according to the Statistical Directory of Population Health Indicies and Activities of the Health Care Institutions in the Lviv region for 2010 and 2016 [50, 51].

A quantitative determination of iodine concentration in drinking water was carried out by inversion voltammetry method using a voltammetric AVA-2 analyzer with a measurements range of iodine content in water from 0.002 to 0.500 mg/dm^3 (Method for measurements of the iodine concentration in drinking and mineral water, salt, bakery products, dairy products by the method of inversion voltammetry on a solid rotating electrode, 2002) [42]. Water samples were taken from sources of centralized and decentralized water supply in all districts of the region (total 336 samples).

The relative risk (RR) in the incidence of thyroid pathology among the children was calculated using the results of epidemiological studies and the computer program EpiInfo, recommended by the WHO, with an estimated of a probable 95% interval and a probability determination [58].

The study was covered the children population of 20 districts and 6 towns of the Lviv region. To assess RR of thyroid pathology in regions with different degrees of iodine deficiency, all districts and towns of the Lviv region were divided into groups according to iodine deficiency: the first group included iodized districts where the mean of iodine concentration in drinking water was more than 4 μg/dm^3, the second group – regions with a low iodine deficiency with iodine concentration 3-4 μg/dm^3, the third group included districts with moderate iodine deficiency with iodine concentration in the water 2-3 μg/dm^3 and the fourth group – a region with high iodine deficiency with a concentration of iodine <2 μg/dm^3 [44].

The statistical analysis of the results obtained was done by Zar (1999) using STATISTICA 13.3 software (StatSoft, Krakow, Poland) [59].

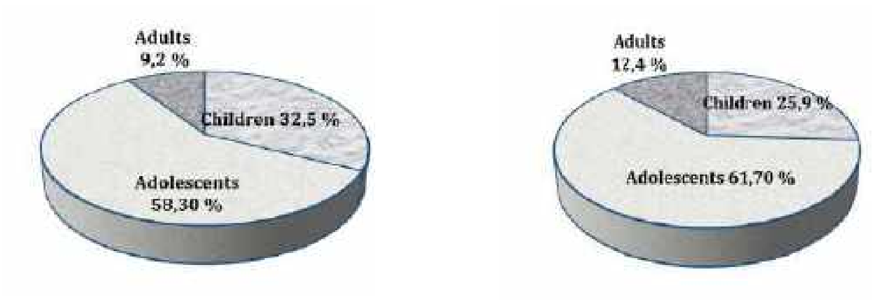
THE RESEARCH RESULTS AND DISCUSSIONS

Incidence rates of thyroid pathology among different age groups in the population of the Lviv region were presented in Table 1.

Table 1. Incidence rates of the thyroid pathology among different age groups in the population of Lviv region

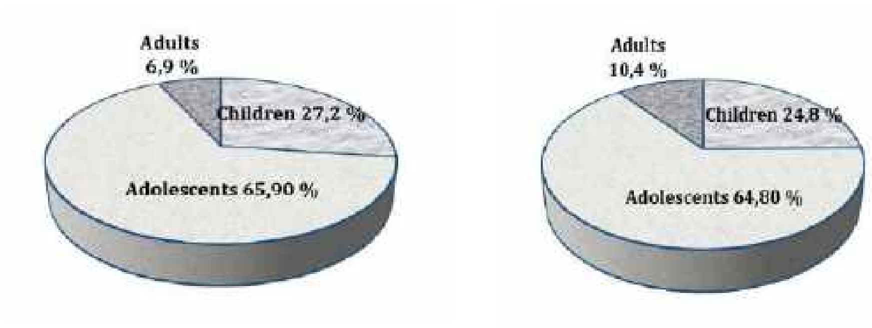
Years	Prevalence of thyroid pathology, per 10,000 individuals			Incidence of thyroid pathology, per 10,000 individuals		
	Children	Adolescents	Adults	Children	Adolescents	Adults
2010	985.5	1766.7	279.3	104.8	254.6	26.8
2016	781.9	1861.9	372.5	80.4	210.3	33.9

Our results demonstrated that the average incidence rate of thyroid pathology among the children population of the Lviv region through 2010 to 2016 was decreased from 985.5 to 781.9 per 10,000 population, while among adults and adolescents, the incidence of this pathology in the studied population was increased from 1766.7 to 1861.9 and from 279.3 to 372.5 per 10,000 population, respectively. The incidence of thyroid pathology among children and adolescents through 2010 to 2016 was decreased from 104.8 to 80.4 and from 254.6 to 210.3 per 10,000 population, respectively, while among adults it was increased from 26.8 to 33, 9 per 10,000 population ($p<0.001$) (Table 1). The highest average incidence rate of thyroid pathology was recorded through the study period among the adolescent population (15 do17-years old), while the lowest rates were observed among adults (Figs 1 and 2).



A B

Fig. 1. Percentage in the prevalence of thyroid pathology between different age groups in the Lviv region in 2010 (A) and 2016 (B)



A B

Fig. 2. Percentage in the incidence of thyroid pathology among different age groups of the Lviv region in 2010 (A) and 2016 (B)

Among the children population of the Lviv region, the average incidence rate of thyroid pathology through the studied period was higher in Brody, Zhovkivskyi, Zolochivskyi, Kamianka-Buzka, Mykolaiv, Mostyska, Skole, Sokal, and Turkivskyi districts, as well as in the

Boryslav, Drohobych, Morshyn, Novy Rozdil and Stryi than the mean value in Lviv region (Table 2). High rates in morbidity of thyroid pathology among this age group of the population were established in Zhydachivskyi, Zhovkivskyi, Zolochivskyi, Kamianka-Buzka, Mykolaiv, and Mostyska districts, as well as in the Lviv and Drohobych towns (Table 2).

Table 2. Prevalence and morbidity of the thyroid pathology among children (up to 14 years old) in the Lviv region

Districts and towns	The prevalence of thyroid pathology, per 10,000 population		The morbidity of thyroid pathology, per 10,000 population	
	2010	2016	2010	2016
		Districts		
Brody	1311.3	1537.6	62.4	58.2
Busk	460.7	190.0	34.6	32.5
Horodok	987.6	784.7	88.0	96.7
Drohobych	799.5	791.3	12.2	23.0
Zhydachivskyi	862.4	1131.5	134.3	176.4
Zhovkivskyi	1199.2	839.4	142.9	14.1
Zolochivskyi	1206.2	1189.6	104.4	93.8
Kamianka-Buzka	1556.1	1051.7	207.4	110.1
Mykolaiv	1244.7	1336.0	117.0	117.1
Mostyska	1007.8	811.4	134.7	108.4
Peremyshliany	560.8	339.9	41.3	40.9
Pustomyty	149.8	297.5	30.6	103.0
Radekhiv	937.7	870.3	5.9	6.1
Sambir	1444.8	569.9	364.5	191.3
Skole	1414.7	1492.2	60.1	142.0
Sokal	1076.3	989.1	46.2	11.1
Starosambirskyi	879.7	805.6	180.9	166.0
Stryiskyi	933.8	993.0	53.9	5.9
Turkivskyi	2132.6	1514.5	39.5	11.5
Yavorivskyi	1584.7	515.2	47.3	39.9
Sum in Districts	**1098.0**	**862.2**	**101.6**	**77.6**
		Towns		
Lviv	603.0	532.7	115.0	99.8
Boryslav	1116.0	1100.3	46.9	42.3
Drohobych	1273.1	1130.4	131.6	97.1
Morshyn	2455.7	822.9	559.3	13.9
Novy Rozdil	1035.9	1173.9	16.7	20.5
Stryi	1023.8	1072.5	182.8	12.6
Truskavets	789.9	276.8	45.4	46.1
Chervonograd	1469.4	593.5	48.5	47.9
Sum in Towns	**804.4**	**655.2**	**110.1**	**84.8**
Total in districts and towns	**985.5**	**781.9**	**104.8**	**80.4**

The decrease in the average incidence rate of thyroid pathology through the studied period among the children population was established in 14 districts and 6 towns of the region. In some regions (Zhydachivskyi, Mykolaiv, Pustomyty, Skole districts, and the Novyi Razdil city), the increase in both the incidence and morbidity of thyroid pathology were detected (Table 2). In particular, in 6 districts and 2 cities of the Lviv region, an increase in the average incidence rate of thyroid pathology in 2016 compared to 2010 was noted. In Brody district, this index was increased by 1.17-fold, in Zhydachivskyi – by 1.31-fold, in Mykolaiv – by 1.07-fold, in Skole – by 1.05-fold, in Stryiskyi – by 1.06-fold, in Pustomyty – by 1.98-fold, in the Novy Rozdil city – by 1.13-fold, and in Stryi – by 1.05-fold. The incidence of thyroid dysfunction among children has also increased in 6 districts and 2 cities: in Horodok – by 1.10-fold, in Drohobych – by 1.89-fold, in Zhydachivskyi – by 1.31-fold, in Pustomyty – by 3.37-fold, in Skole – by 2.36-fold, and in Mykolaiv – did not change; in the Novy Rozdil city – by 1.23-fold, in Truskavets – by 1.02-fold.

Statistically significant differences between the prevalence and incidence rates of thyroid pathology among the children population of the Lviv region in 2010 and 2016 were not established ($p = 0.052$ and $p = 0.145$). Furthermore, there are no statistical differences between the same indices among children living in large industrial cities of the Lviv region ($p = 0.093$ and $p = 0.069$).

The results according to the estimation of relative risk of the thyroid pathology among the children group in the Lviv region by absolute numbers (number of patients and population) were presented in Table 3. The relative risk was higher in 2016 than in 2010 among the children of five districts (Brody: RR = 1.0, $p<0.001$; Mykolaiv: RR = 1.06; $p = 0.102$; Pustomyty: RR = 1.95; $p = <0.001$; Skole: RR = 1.05; $p = 0.161$; Stryiskyi: RR = 1.06; $p = 0.211$) and two towns (Novy Rozdil: RR = 1.12, $p = 0.06$; Stryi: RR = 1.04; $p = 0.411$) (Table 3). In other districts and towns of the Lviv region, the relative risk of thyroid pathology in 2016 was lower than in 2010. The lowest relative risk ratios were recorded in the Busk, Sambir, and Yavorivskyi districts, as well as in the Morshyn and Truskavets towns.

Table 3. The relative risk in the incidence of the thyroid pathology among children population (up to 14 years) of the Lviv region in 2016 compared to 2010

Districts and towns	Relative risk	Confidence limits	p
	Regions		
Brody	**1.15**	1.07-1.23	<0.001
Busk	**0.42**	0.35-0.51	<0.001
Horodok	**0.81**	0.74-0.88	<0.001
Drohobych	**0.99**	0.91-1.08	0.882
Zhydachivskyi	**0.80**	0.74-0.85	<0.001
Zhovkivskyi	**0.73**	0.68-0.78	<0.001
Zolochivskyi	**0.99**	0.93-1.07	0.885
Kamianka-Buzka	**0.71**	0.66-0.76	<0.001
Mykolaiv	**1.06**	0.99-1.14	0.102
Mostyska	**0.82**	0.75-0.89	<0.001
Peremyshliany	**0.62**	0.53-0.73	<0.001
Pustomyty	**1.95**	1.69-2.25	<0.001
Radekhiv	**0.93**	0.85-1.03	0.153
Sambir	**0.43**	0.40-0.46	<0.001
Skole	**1.05**	0.98-1.13	0.161
Sokal	**0.93**	0.87-0.99	<0.05
Starosambirskyi	**0.92**	0.85-1.00	0.054
Stryiskyi	**1.06**	0.97-1.15	0.211
Turkivskyi	**0.75**	0.70-0.79	<0.001
Yavorivskyi	**0.36**	0.34-0.38	<0.001

Towns			
Lviv	**0.89**	0.86-0.92	<0.001
Boryslav	**1.0**	0.90-1.10	0.961
Drohobych	**0.90**	0.84-0.96	<0.001
Morshyn	**0.38**	0.29-0.50	<0.001
Novy Rozdil	**1.12**	1.0-1.26	0.06
Stryi	**1.04**	0.95-1.13	0.411
Truskavets	**0.36**	0.28-0.47	<0.001
Chervonograd	**0.44**	0.40-0.48	<0.001
Total	**0.81**	0.80-0.82	<0.001

In our previous studies [26-28], the unequal degree of iodine deficiency in the endemic Lviv region was revealed. The iodine concentration in drinking water in different regions of the Lviv region was ranged from 0.02 μg/dm^3 to 6.63 μg/dm^3. Among the 336 samples of drinking water, the iodine level in drinking water in 72 samples was lower than 2 μg/dm^3, which was 21.4% of the total number of samples; in 96 samples, the iodine content in drinking water ranged from 2 to 3 μg/dm^3 (28.6%); while in 76 samples the iodine content in drinking water ranged from 3 to 4 μg/dm^3 (22.6%); in 92 samples, the iodine level in drinking water was higher than 4 μg/dm^3 (27.4%).

In summary, in the 27.4% of drinking water samples, analyzed from sources of centralized and decentralized water supply, the mean iodine concentration was higher than 4 μg/dm3, indicating the adequate condition of this area with iodine supply. Instead, in 72.6% of samples, the iodine content in drinking water was recorded at a level below 4 μg/dm^3, which indicates the presence of high, moderate, and mild iodine deficiency in most districts of the Lviv region. At the same time, even within the same area, there are fluctuations in the iodine concentration at different degrees of iodine deficiency. Thus, iodine content in the drinking water indicates that most of the Lviv region territory is iodine deficient. Measurement error was less than 30%, which indicated the representativeness of the results of the measurements in all cases.

The results of our research revealed that to regions with a high degree of iodine deficiency according to the mean of iodine concentration in drinking water (iodine content in drinking water was up to 2 μg/dm^3) were included Brody, Busk, Zhovkivskyi, Peremyshliany districts, and Drohobych town; regions with a moderate degree of iodine deficiency (iodine content in drinking water ranges from 2 to 3 μg/dm^3) were included Zhydachivskyi, Kamianka-Buzka, Radekhiv, Sambir, Sokal districts, and Borislav and Chervonograd towns; to regions with a mild degree of iodine deficiency (iodine content in drinking water ranged from 3 to 4 μm/dm3) were included to Drohobych, Zolochivskyi, Mykolaiv, Stryiskyi, Turkivskyi, Yavorivskyi districts and Lviv and Stryi towns; to regions with an adequate iodine supply (iodine content in drinking water is more than 4 μg/dm^3) were included Horodok, Mostyska, Pustomyty, Skole, Starosambirskyi districts and Truskavets.

The RR estimation in regions with different iodine concentrations in drinking water to assess the relative risk in the incidence of thyroid pathology in the regions with different concentrations of iodine in drinking water compared to the mean value in the Lviv region among the children population with high, moderate and low levels of iodine deficiency, as well as regions with sufficient concentrations of this trace element has been calculated (Table 4).

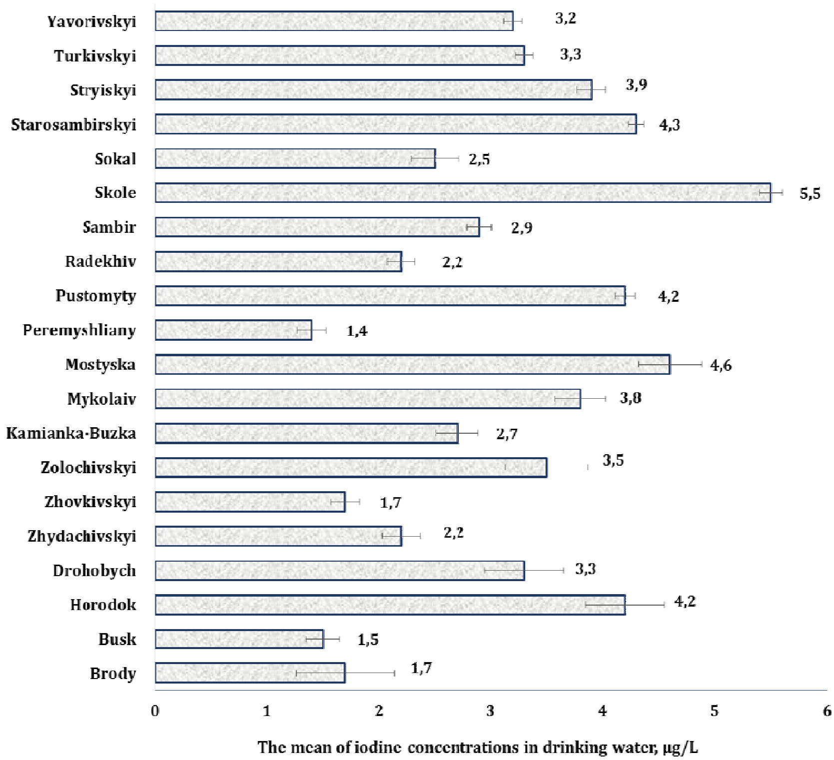


Fig. 3. The mean iodine concentrations in drinking water (µg/L) in the districts of the Lviv region

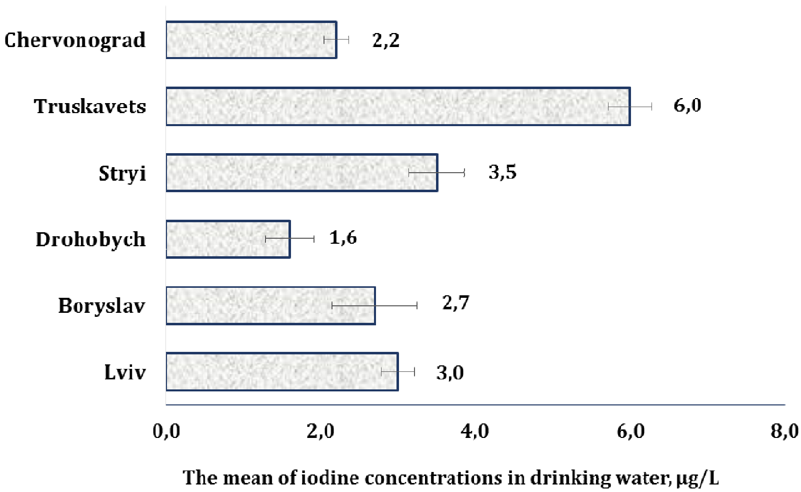


Fig. 4. The mean iodine concentrations in drinking water (µg/L) in the towns of the Lviv region

Table 4. The relative risk in the incidence of thyroid pathology among children population (up to 14-years old) in districts of Lviv region with varying degrees of iodine deficiency in comparison with the mean regional value

The degree of iodine deficiency	Relative risk	Confidence limits	p
High	1.12	1.09-1.15	<0.001
Moderate	1.10	1.07-1.12	<0.001
Mild	0.94	0.92-0.95	<0.001
Adequate iodine level	0.94	0.91-0.96	<0.001

It was determined that the relative risk in the incidence of thyroid pathology among the children population of the Lviv region was higher in districts with high and moderate degrees of iodine deficiency compared to the mean regional value and it was lower in districts with a mild degree of iodine deficiency and the adequate iodine level.

Thus, in the endemic region, there are regional peculiarities of the prevalence and morbidity of thyroid diseases among the children's population. These indicators were recorded at a high level in some regions from year to year. Regions with the increased values of relative risk of thyroid pathology during the studied period, despite the general tendency to reduce the relative risk of thyroid pathology among the children, were also established.

Our previous study [18-20] revealed a decrease in the average incidence rate of diffuse goiter (DG) I degree from 307.5 to 197.2 per 10,000 population among the adult population during 2000-2010. A significant reduction in the average incidence rate of DG I degree among adults from the towns of the Lviv region was noted. It was 133.1 per 10,000 population in 2000 and 99.6 per 10,000 population in 2010. There was a decline in the average incidence rate of DG I degree from 231.8 to 155.3 per 10,000 population among adults in the Lviv region during 2000-2010. In 2010, the incidence of thyroid diseases among adults from districts was higher compared to the adults from towns (197.2 compared to 99.6 per 10,000 population, respectively). The highest average incidence rate of DG among adults was noted in Busk, Starosambirskyi, Pustomyty, Sokal, Turkivskyi districts (489.1-1448.5; 359.6-776.2, 282.4-766.0, 166.3-625.1, 443.4-518.3 per 10,000 population, respectively), and in Truskavets, Drohobych, and Boryslav (14.1-340.2, 61.2-218.2, 96.3-160.7 per 10,000 population, respectively). The increase in the average incidence rate of DG I degree in 7 districts among 20 districts (Brody, Zhydachivskyi, Mykolaiv, Peremyshliany, Radekhiv, Sambir, Skole) and 1 town among 6 towns (Chervonograd) of Lviv region during 2000-2010 was observed. The decrease in the average incidence rate of DG II and III degrees from 31.4 to 29.6 per 10,000 population during 2000-2010 was noted. A significant increase in the average incidence rate of DG II and III degrees among adults from the districts of the Lviv region was demonstrated. It was 29.9 per 10,000 population in 2000 and 37.3 per 10,000 population in 2010. There was a decline in the average incidence rate of DG II and III degrees from 33.3 to 19.4 per 10,000 population among adults living in towns of the Lviv region during 2000-2010. In 2010, the average incidence rate of thyroid diseases among adults from districts was higher compared to the adults living in towns (37.3 compared to 19.4 per 10,000 population, respectively). The increased average incidence rate of DG II and III degrees among adults of Lviv region was observed in Radekhiv, Peremyshliany, Skole, Turkivskyi, and Busk districts in 2000 (80.9, 73.7, 63.7, 62.5, 51.5 per 10,000 population, respectively), in Busk, Radekhiv, Sokal, Peremyshliany, Skole, and Turkivskyi districts in 2004 (130.2, 110.6, 86.9, 86.4, 67.5, 62.7 per 10,000 population, respectively), in Sokal, Radekhiv, Peremyshliany, Skole, and Turkivskyi districts in 2010 (105.7, 97.8, 90.5, 79.4, 71.0 per 10,000 population, respectively). The decrease in the average incidence rate of DG among adults in the 15 districts (Busk, Horodok, Drohobych, Zhydachivskyi, Zolochivskyi, Sokal, Starosambirskyi, Stryiskyi) and all towns (except

Drohobych and Chervonograd) in the Lviv region was noted. Our results indicate the need to clarify the relevant influencing factors of DG incidence among the population of the Lviv region, the definition of the risk of thyroid pathology in each district of the region among the different age groups, which will propose measures to prevent further increase of DG incidence.

Compared to the adult population [18], the DG incidence among the adolescent population was higher by 7.5-9.7 fold ($p<0.05$) compared to adults. During 2000-2014, a decrease in the average incidence rate of DG I degree among the adolescent population of the Lviv region was observed (1747.72 per 10,000 population in 2000 and 1571.29 per 10,000 population in 2014). However, an increase in the average incidence rate of DG I degree among adolescents living in districts during 2000-2014 years was found (1591.92 per 10,000 population in 2000 and 1785.56 per 10,000 population in 2014). The peak of incidence was noted in 2014. Among adolescents living in towns, a decrease in the average incidence rate of DG I degree from 2000 to 2014 was found; it was 1971.74 and 1185.52 per 10,000 population, respectively. A decrease in the average incidence rate of DG II and III degrees from 115.54 to 82.46 per 10,000 population during 2000-2014 years was observed. A significant decrease in the average incidence rate of DG II and III degrees among adolescents from the districts of the Lviv region was noted. It was 140.82 per 10,000 population in 2000 and 124.08 per 10,000 population in 2014. There was a decline in the average incidence rate of DG II and III degrees from 79.03 to 21.81 per 10,000 population among adolescents from towns in the Lviv region during 2000-2014. In 2014, the incidence of diseases among adolescents living in districts was higher compared to the adults from towns (124.08 compared to 21.81 per 10,000 population, respectively) [19, 20]. We also observed that DG incidence among adolescents in altitude regions was higher compared to the plateau regions, a finding similar to trends in previous surveys that may be explained by deficiencies in natural iodine at high altitudes and limited educational and economic support for the people who reside there. According to the present information, the average incidence rate of DG also was differed in districts and towns. DG is more common in districts than in the towns, which may be explained by lifestyle choices. Furthermore, females were at greater risk for DGs and this difference was not changed when females were further divided into rural, mixed, and urban groups. Our results indicate the need to clarify the relevant influencing factors of DG incidence among the population of the Lviv region, the definition of the risk of thyroid pathology in each district of the region among the different age groups, which will propose measures to prevent further increase of DG incidence [19, 20].

Although iodine supplementation has decreased the number of people at risk of iodine deficiency and its associated sequelae, particularly in the past few decades, the use of iodine has also led to concerns of excessive iodine exposure in some individuals [39]. A study published in 2012 reported that the median urinary iodine concentrations (UIC) (730 μg/l) of the populations of two Somali refugee camps in Kenya who were receiving iodine supplementation was in the range consistent with excessive iodine intake [30]. About 20% of the study subjects had 'more than adequate' urinary iodine, while over 71% had excessive UIC. Salt iodine content varied between 5.1 and 80.1 ppm in the five market salt samples analyzed. The excessive iodine intake was evident in the Dadaab refugee camps in the North Eastern Province of Kenya in 2002 [30].

In a study of above 200 Chinese adults, subclinical hypothyroidism was more common in those supplemented with a 400 μg iodine tablet than in those given a placebo [49]. The mean iodine intake from the diets and salt intake of the participants were (105 ± 25) and (258 ± 101) μg/d, respectively. In comparison with the placebo group, all iodide-supplemented groups responded with significant increases in median urinary iodine concentrations ($P < 0.05$) and in thyroid-stimulating hormone concentration ($P < 0.05$). Thyroid volume decreased after 4 wk in the high-iodine intervention groups (1500-2000 μg). Subclinical hypothyroidism appeared in the groups that received 400 μg/L (5%) and 500-2000 μg/L (15-47%) [49].

These findings are similar to the results of other studies in Denmark and New Zealand, which also showed an increased prevalence of transient hyperthyroidism. The study of Laurberg and co-workers (2006) showed profound effects of even small differences in iodine intake level on the prevalence of goiter, nodules, and thyroid dysfunction in Denmark [38]. Mild and moderate iodine deficiency was associated with a decrease in serum thyroid-stimulating hormone (TSH) with age. Other environmental factors were also important for goiter development (increase in risk, smoking, and pregnancy; decrease in risk, oral contraception, and alcohol consumption), and the individual risk depended on the genetic background. Environmental factors had only a minor influence on the prevalence of thyroid autoantibodies in the population. There were more cases of overt hypothyroidism in mild than in moderate iodine deficiency caused by a 53% higher incidence of spontaneous (presumably autoimmune) hypothyroidism. On the other hand, there were 49% more cases of overt hyperthyroidism in the area with moderate iodine deficiency. The cautious iodine fortification program, aiming at an average increase in iodine intake of 50 μg/day has been associated with a 50% increase in the incidence of hyperthyroidism in the area with the most severe iodine deficiency. The incidence is expected to decrease in the future, but there may be more cases of Graves' hyperthyroidism in young people [38]. Thomson and co-workers (2011) have investigated the effects of excess iodine intake as iodate on thyroid and selenium status in New Zealand. Excess iodate induced hypothyroidism in some participants and hyperthyroidism in others. Most abnormalities disappeared after 4 weeks. Excess iodate reduced whole blood glutathione peroxidase activity and resulted in smaller increases in whole blood glutathione peroxidase after selenium supplementation [52].

The incidence of thyrotoxicosis was increased following periods of mandatory salt iodization, compared with when supplementation was not required, i.e. Spain [7] and Zimbabwe [54]. The study of Galofré and co-workers (1994) determined the incidence rate of thyrotoxicosis before and during dietary-iodine supplementation in an iodine-sufficient area [7]. The study was carried out in Vigo, South Galicia (northwest of Spain), from January 1977 to December 1989. The mean population throughout the study period was 267,330 inhabitants (47% males and 53% females). From January 1985, mandatory consumption of iodized salt on the whole population started in Galicia. This region was considered as an iodine-deficient area but Vigo is an iodine-sufficient area. All newly diagnosed thyrotoxicosis cases in Vigo city within the study period were included in this study. Diagnosis of thyrotoxicosis was based on the clinical manifestations, an elevated level of T4, and suppressed TSH values. The difference between diffuse and nodular forms of goiter was assessed by scintigraphy. The average incidence rate was determined in two periods, before (1977-1984) and during (1985-1989) iodine supplementation. The average incidence rate throughout the whole study period was 4.89 new cases per 100,000 population, 95% confidence limits 4.16 to 5.63; average incidence rate was 1.34 for males and 8.03 for females. The average incidence rate in the period 1985-1989 was significantly higher concerning 1977-1984, 7.68 and 3.10 per 100,000 respectively. The confidence interval for the difference was from -20.4 to 30.1, $p < 0.05$. The increase in the incidence of thyrotoxicosis was comprised of both nodular and diffuse goiters. Dietary iodine supplementation in iodine-sufficient areas may induce an increase in the incidence of thyrotoxicosis. This could be explained by the fact that individuals and populations differ widely in terms of optimal daily requirements as well as adverse responses to both deficiency and excess of iodine [7].

Another iodine supplementation program in Bangladesh has shown no increased risk of thyroid dysfunction [46]. The effect of iodized and non-iodized table salt in goiter hyper-endemic area on the thyroid gland and its hormones T3, T4, and Thyroid Stimulating Hormone (TSH) were studied in two hundred subjects from the Center for Nuclear Medicine and Ultrasound, Mymensingh, Bangladesh. There was no significant change in the occurrence of (hypo and hyperthyroidism or iodinated salt-induced thyrotoxicosis) adverse effect, following iodine supplementation. The study shows that mandatory mass iodination of table salt consumption in a hyper-endemic iodine-deficient area is safe and does not cause any side effects. Parveen and co-workers (2007) suggest close regular monitoring of T3, T4, and TSH and further evaluation by specifically designed studies for any probable link between iodine-induced hypo or hyperthyroidism and mass iodination of table salt consumption [46].

Iodine supplementation also affects other aspects of thyroid health [39]. Partly reversible iodine-induced thyroid dysfunction and autoimmunity were observed among patients with endemic goiter [14]. For example, high iodine intake seems to increase the prevalence of autoimmune thyroiditis in the Bio-Breeding/Worcester rat model and humans. It has been suggested that the incidence of Hashimoto's thyroiditis is increased in the presence of high iodine intake. The iodine intake significantly affects the incidence of spontaneous lymphocytic thyroiditis in young, genetically predisposed rats [1].

The number of reported cases of thyroid cancer, particularly papillary thyroid cancer, has also increased following iodine supplementation in some studies, including a nearly 20-year study in northeastern China [6] and an above 50-year study in Denmark [2]. An increase in the prevalence of thyroid disease has been found with increasing iodine intake since universal salt iodization was instituted throughout China in 1996. Dong and co-workers (2013) have analyzed the incidence of thyroid carcinoma before and after universal salt iodization in Shenyang, a city in northeastern China. The detection rate of thyroid carcinoma, papillary thyroid carcinoma, and medullary thyroid carcinoma increased; that of follicular thyroid carcinoma decreased, and that of undifferentiated thyroid carcinoma showed, no change after universal salt iodization. The constituent ratio of papillary thyroid carcinoma increased, that of follicular thyroid carcinoma and undifferentiated thyroid carcinoma decreased, and that of medullary thyroid carcinoma showed no change after universal salt iodization. The mean age of female patients with thyroid carcinoma decreased after universal salt iodization. The incidences of papillary thyroid carcinoma complicated with either nodular goiter or chronic lymphocytic thyroiditis increased after universal salt iodization. The detection rate of thyroid carcinoma increased significantly, papillary thyroid carcinoma predominated in the histological types of thyroid carcinoma, and the mean age of female patients with thyroid carcinoma decreased after universal salt iodization. Therefore, the patients with either nodular goiter or chronic lymphocytic thyroiditis under high iodine intake should be followed up [6].

In a nationwide study, Blomberg and co-workers (2012) have aimed to identify the overall incidence of thyroid cancer in Denmark during 66 years (1943-2008) and incidences of the four main histological types of thyroid cancer from 1978 to 2008. Data were obtained from the nationwide Danish Cancer Registry, and authors have focused especially on the period after implementation of compulsory iodine supplementation, which was established on a national level in 2000. They have calculated age-standardized incidence rates per 100,000 person-years, and age-period-cohort models were fitted to describe trends in incidence. From 1943 to 2008, 1,947 men (29%) and 4,682 women (71%) were diagnosed with thyroid cancer. The age-standardized incidence increased in both sexes; in men from 0.41 to 1.57 per 100,000 and from 0.90 to 4.11 per 100,000 in women, corresponding to a significant average annual percentage change of 1.7 and 1.8%, respectively. The incidence increased with younger birth cohorts. The rise was almost exclusively caused by papillary carcinomas, and it was particularly present during the last decades of the study period. It cannot be ruled out that iodine supplementation may play a role in the risk of thyroid cancer, but as the strongest increase in incidence began in the years before the implementation, it is likely that improvement in diagnostic modalities increased diagnostic activity, and/or new unknown risk factors are also important contributors to the increase [2].

In our previous study, the assessment of the average incidence rate of Hashimoto's thyroiditis (HT), as well as relative risk (RR) of HT among children (0-14 years old), adolescents (14-18 years old), and adults (above 18 years old) in Lviv region (western Ukraine) through years 2000-2010 was done [15-17, 21-25, 29, 53]. Assessment of air quality, water, and soil quality, and food quality according to the hygienic indicators (the number of samples that do not match to standards, %) in districts of Lviv region in 2000, 2004, and 2010 years was also performed. The decrease of the average incidence rate of HT from 4.7 to 2.7 per 10,000 children through 2000-2010 years was observed. A significant reduction in the average incidence rate of HT among children from cities was noted. It was 7.1 per 10,000 population in 2000 and 2.1 per 10,000 population in 2010. There was a decline in the average incidence rate of HT from 3.2 to 2.4 per 10,000 population among children from districts during 2000-2004, and its increase to 3.1 per 10,000 population from 2004 to 2010 years. The increase of the average incidence rate of HT in 8 of the 20 districts and 2 of the 6 towns of the Lviv region during 2000-2010 was observed. The increase of the average incidence rate of HT in the Lviv region during 2000-2010 was mainly in the Brody, Peremyshliany, and Turkivskyi districts. In these districts, a high level of samples that did not match to standards according to the air and food quality was observed. Moreover, the high relative risk of HT incidence among children population in Lviv region was also noted in Brody and Turkivskyi districts in 2000-2010 years, and Peremyshliany district during 2000-2004 years compared to Kamianka-Buzka as control district. Our study confirmed that mainly nutritive factors and environmental pollution by metals and chemicals are the main factors in the present-day HT incidence. The increased average incidence rate of HT among adolescents from towns during 2000-2004 years was found. The peak of disease prevalence was noted in 2000 and 2004. Among adolescents both in districts and towns, a decrease in HT incidence from 2004 to 2010 was found. The decrease of HT incidence among adolescents from rural areas during 2000-2004 years was observed, while its increase from 2004 to 2010 was noted. In our study, the average incidence rate of HT among adolescents was the highest in Brody, Turkivskyi, Sambir, Sokal, and Horodok districts during 2000-2010. In these districts, high numbers of air and food samples that did not match standards were noted. The increase of HT incidence in the Lviv region during the 2000-2010 years was mainly due to the adult population from urban areas, and less – by inhabitants of rural areas. Increased HT incidence among adults was found in 16 districts and 3 towns in the Lviv region; among adolescents – in 5 districts; among children – in 8 districts and 2 towns. The relative risk of HT incidence among adults living in more polluted areas is higher compared with the inhabitants from relatively clean areas of the Lviv region. The risk of HT incidence among inhabitants of agricultural districts has a significant impact of chemical pollution of water and soil, among inhabitants of towns – air pollution. The observed pattern is to determine the differentiated nature of preventive and therapeutic measures for the decrease of HT incidence in regions with varying degrees of environmental chemical pollution. Our results indicate the need to clarify the reasons for the increased HT incidence among the population of Lviv region, the definition of the risk of thyroid pathology in each district of the region among the different age groups, which will propose measures to prevent further increase of HT incidence [15-17, 21-25, 29, 53].

The diet is the main way of achieving adequate iodine nutrition [39]. The amount of iodine that can be obtained from plant-based food is minimal and is dependent on the local environment (that is, iodine levels in the soil, groundwater used for irrigation, crop fertilizers, and livestock feed) [61]. Dairy products (due to the use of iodophor cleaners for milk cans and teats), some bread (due to the use of iodate bread conditioners), seaweed, and other seafood and iodized salt are the most common iodine-containing foods [39]. In children from the USA aged 6-12 years, dairy intake is a particularly good source of adequate iodine, probably due to the abundance of dairy content in the diet of children in this age range. The iodine intake among many U.S. children may be above the requirements. Perrine and co-workers (2013) have described the association of iodine sources with iodine status among children [48]. They analyzed 2007-2010 NHANES data of urine iodine concentration spot tests for children aged 6-12 y (n = 1553) and used WHO criteria for iodine status. In adjusted regression analyses, recent dairy intake and recent supplement use were significantly positively associated with urine iodine concentration levels, whereas recent grain intake was negatively associated. Adding salt to food at the table was not associated with urine iodine concentration. Iodine-containing supplements are likely not needed by most schoolchildren in the U.S. because dietary iodine intake is adequate in this age group [48]. Australia introduced the iodization of bread in 2009, which resulted in a modest increase in the median urinary iodine concentrations of a small group of pregnant women. Women ($n = 196$) were recruited prospectively at the beginning of pregnancy and urine was collected at 12, 18, 30, 36 weeks gestation, and 6 months postpartum. The use of a multivitamin supplement was recorded at each visit. Spot urinary iodine concentrations were assessed. Median UICs were within the mildly deficient range in women not taking supplements (<90 μg/L). Among the women taking iodine-containing multivitamins, urinary iodine concentrations were within WHO recommendations (150-249 μg/L) for sufficiency and showed an increasing trend through gestation. The fortification of bread with iodized salt increased the median urinary iodine concentrations from 68 μg/L to 84 μg/L ($p = 0.011$) which was still in the deficient range [4].

The many varieties of seaweed are a unique potential source of excess ingestion of iodine. Seaweed is a popular food item in many parts of the world, particularly in Japan and other Asian countries, where the ingestion of seaweed soup is common in the everyday diet and is a frequent practice during the postpartum period [39]. By combining information from dietary records, food surveys, urine iodine analysis (both spot and 24-hour samples), and seaweed iodine content, Zava and Zava (2011) have estimated that the Japanese iodine intake - largely from seaweeds – averages 1,000-3,000 μg/day (1-3 mg/day) [60].

Salt iodization is viewed as one of the safest and most effective methods of achieving iodine sufficiency across a population [13]. The dissolution of the Soviet Union in 1991 resulted in the absence of a legislative framework to support the regulatory monitoring of iodized salt production. Most post-Soviet countries have since adopted national universal salt iodization strategies [9], however, despite clear evidence of widespread deficiency in populations, the governments in Ukraine have been reluctant to re-introduce mandatory universal salt iodization, interpreting it as an alleged potential violation of "consumers' right for choice" and "industry's freedom of enterprise" [8, 9]. The Government of Ukraine adopted a decree in 1997 titled "On measures to prevent iodine deficiency disorders". However, the associated regulations in decree stipulated a voluntary model of prevention, with no specific enforcement mechanism in place, and resulted in low levels of production and supply of iodized salt in the country [31, 56].

From 2008 to 2015, the Global Alliance for Improved Nutrition (GAIN) and UNICEF worked in a partnership with a grant from the Bill & Melinda Gates Foundation to intensify business-oriented efforts towards the global elimination of iodine deficiency through USI ("the Partnership Project"). The goal of the Partnership Project was to sustainably improve population-wide iodine intakes, primarily by increasing the supply of, and access to, adequately iodized food-grade salt in 13 countries with: a very high population numbers unprotected from iodine deficiency through lack of access to adequately iodized (≥15 mg/kg) household salt; the lowest percentage of household iodized salt coverage; and/or the greatest potential for sustainably scaling-up efforts through innovative business approaches (Knowles et al., 2017). The GAIN-UNICEF USI Partnership Project initially engaged in high-level advocacy with key policymakers in Ukraine aiming for mandatory legislation on the use of iodized salt in bread bakeries. Specific activities included support for the preparation of draft legislation put before the Council of Ministers in Ukraine, and hosting of a high-level regional forum in 2011 in Belgrade, Serbia, which brought policymakers, academics, consumer interest groups, and the food and salt industries from Russian Federation and Ukraine together with regional champions for USI from Belarus, Kazakhstan, and Serbia (United Nations Children's Fund (UNICEF) GAIN Belgrade Forum, 2011) [31].

In Ukraine, the Partnership Project focused primarily on building consumer demand and bread industry approval for iodized salt use in bread products through an awareness campaign and evidence of the success of this approach in other countries. The Partnership Project liaised with the Bread Association to disseminate the Russian research and brought technical experts from the Russian and Belarussian bread industry to conduct interactive workshops with Ukrainian bakers. Also, a national public health communication campaign on iodine was conducted, and an official iodized salt logo was made available for bakeries and other food processors for use on their products. The campaign promoted the logo on billboards, at urban and rural food fairs, and on city light displays, posters, booklets, and leaflets attracting over 6 million views over 2012-2013 [10]. Finally, the Partnership Project consulted with individual bread companies to understand and overcome their perceived barriers to using iodized salt in bread products, through the provision of technical and advocacy support, including providing testing equipment to measure iodine levels in salt in their factories [31].

The communication and awareness-raising activities of UNICEF and GAIN in Ukraine resulted in two registered medium- to large-scale bakeries located in Lviv and Kyiv changing their production processes to use iodized salt in bread baking in 2012. The volume of bread production reported by these bakeries had an estimated reach of 19,000 people (about 0.04% of the population), based on an average per capita consumption of 240 g of bread/day [31, 37].

Thus, the process of compensation for iodine deficiency should begin with some special studies: a) the determination of the iodine concentration in the objects of the environment, b) the determination of the relative risk of thyroid disease developing in each endemic region, which will enable iodine prophylaxis to be more differentiated. For iodine prophylaxis, it is necessary to use a salt iodized by potassium iodide, but not potassium iodate, in physiologically safe doses. However, salt iodization and other foods should be preceded by a thorough analysis of the situation regarding iodine-dependent diseases in the region. Total salt iodization can lead to unforeseen consequences. To solve this problem, it is necessary to implement an integrated approach using food products with organic iodine compounds, e.g. plant origin. In this case, iodine preparations should be used individually, in each case by the physician's control and the assessment of laboratory indicators and instrumental studies of the morphofunctional state of the thyroid gland by ultrasound assessment, as well as the urine iodine concentration. To reduce thyroid pathology among children, large-scale preventive measures should be carried out under the constant supervision of doctors.

CONCLUSIONS

The average prevalence and morbidity rates of thyroid pathology among the children population of the Lviv region from 2010 to 2016 was decreased from 985.5 to 781.9 and from 104.8 to 80.4 per 10,000 population, respectively. The decrease in prevalence and morbidity rates of thyroid pathology through the studied period among the children population was established in 14 districts and 6 large industrial towns of the Lviv region. However, in 6 districts and 2 cities, an increase in the prevalence and morbidity rates was observed in 2016 compared to 2010.

The relative risk in the incidence of thyroid pathology among the children population was higher in 2016 than in 2010 in five districts and two towns of the Lviv region.

Our study revealed regions with high, moderate, and mild iodine deficiency and regions with sufficient iodine levels according to the mean iodine concentrations in drinking water in the settlements of the Lviv region.

In regions with high and moderate levels of iodine deficiency, the relative risk in the incidence of thyroid disease in the children population of the Lviv region was higher compared to the mean regional value and lower in regions with mild iodine deficiency and adequate iodine support.

To reduce the risk in the incidence of thyroid pathology in the endemic region, a differentiated approach to prophylaxis measures with the endemic regional approach of the iodine level evaluation and the individual iodine availability to the organism is proposed.

REFERENCES

1. Allen E.M., Appel M.C., Braverman L.E., The effect of iodide ingestion on the development of spontaneous lymphocytic thyroiditis in the diabetes-prone BB/W rat, Endocrinology, vol. 118/issue 5, pp 1977-1981, 1986.

2. Blomberg M., Feldt-Rasmussen U., Andersen K.K., Kjaer S.K., Thyroid cancer in Denmark 1943-2008, before and after iodine supplementation, Int. J. Cancer, vol. 131/issue 10, pp 2360-1366, 2012.

3. Bodnar P.M., Endocrinology. Vinnytsia, The New Book, 2007.

4. Clifton V.L., Hodyl N.A., Fogarty P.A., Torpy D.J., Roberts R., Nettelbeck T., Ma G., Hetzel B., The impact of iodine supplementation and bread fortification on urinary iodine concentrations in a mildly iodine deficient population of pregnant women in South Australia, Nutr. J., vol. 12, pp 32, 2013.

5. Delange F., Iodine deficiency in Europe and its consequences: an update, Eur. J. Nucl. Med. Mol. Imaging, vol. 29/Suppl. 2, pp S404-416, 2002.

6. Dong W., Zhang H., Zhang P., Li X., He L., Wang Z., Liu Y., The changing incidence of thyroid carcinoma in Shenyang, China before and after universal salt iodization, Med. Sci. Monit., vol. 19, pp 49-53, 2013.

7. Galofré J.C., Fernández-Calvet L., Ríos M., García-Mayor R.V., Increased incidence of thyrotoxicosis after iodine supplementation in an iodine-sufficient area, J. Endocrinol. Invest., vol. 17/issue 1, pp 23-27, 1994.

8. Gerasimov G., Increasing iodine intakes in populations through the use of iodized salt in baking, IDD Newsl., vol. 33, pp 9-12, 2009.

9. Gerasimov G., Sustaining USI Achievements in Central and Eastern Europe, IDD Newsl., vol. 2, pp 6, 2015.

10. Gerasimov G., van der Haar F., Selling iodized salt: How a public health campaign fell short in Ukraine, IDD Newsl., vol. 43, pp 9-10, 2015.

11. Horlenko O.M., Aleksandrov O.Yu., Ecological-induced deficiency states among children from the endemic zone and ways of its correction, Modern Pediatrics, vol. 5, pp 85-89, 2008.

12. Ikomi C., Cole C.R., Vale E., Golekoh M., Khoury J.C., Jones N.Y., Hypothyroidism and Iodine Deficiency in Children on Chronic Parenteral Nutrition, Pediatrics, vol. 141/issue 4, pp e20173046, 2018.

13. International Council for the Control of Iodine Deficiency Disorders, 2013, http://www.iccidd.org.

14. Kahaly G.J., Dienes H.P., Beyer J., Hommel G., Iodide induces thyroid autoimmunity in patients with endemic goitre: a randomised, double-blind, placebo-controlled trial, Eur. J. Endocrinol., vol. 139/issue 3, pp 290-297, 1998.

15. Kasian O., Manenko A., Tkachenko H., Kurhalyuk N., Retrospective analysis of morbidity for autoimmune thyroid disease in the Lviv region of Ukraine during 1999-2006. XLIII Symposium of the Polish Society for Histochemistry and Cytochemistry, Bydgoszcz, September 21-23, 2009. In: Medical and Biological Sciences, vol. V. XXIII, Suppl. 2, pp 49, 2009.

16. Kasiyan O., Łukaszewicz J., Tkachenko H., Hashimoto's thyroiditis prevalence among adults in the Lviv region in the 2010 year. Abstracts of the International Scientific Conference "Medical science and practice of XXI century", 7-8 February 2014, Kyiv, pp 101-104, 2014.

17. Kasiyan O., Manenko A., Kurhalyuk N., Tkachenko H., Kamiński P., Retrospective analysis of morbidity for autoimmune thyroid diseases in the Lviv region during 1999-2006. In:

Globalization and the issues of environmental protection, T. Noch, A. Wesołowska (Eds), Gdańsk: Publishing House of the Gdańsk Higher School of Administration, pp 359-371, 2010.

18. Kasiyan O., Tkachenko H., Łukaszewicz J., Assessment of diffuse goiter prevalence among adults in endemic Lviv region (western Ukraine), Słupskie Prace Biologiczne, vol. 12, pp 93-110, 2015.

19. Kasiyan O., Tkachenko H., Łukaszewicz J., Fifteen-year follow-up of diffuse goiter prevalence among adolescents in endemic Lviv region (western Ukraine), Słupskie Prace Biologiczne, vol. 13, pp 55-76, 2016.

20. Kasiyan O., Tkachenko H., Łukaszewicz J., The diffuse goiter prevalence among children in endemic Lviv region (western Ukraine) during 2000-2014, In: Globalisation and regional environment protection. Technique, technology, ecology. T. Noch, W. Mikołajczewska, A. Wesołowska (Eds). Gdańsk, Publishing House of the Gdańsk Higher School, pp 53-72, 2016.

21. Kasiyan O., Tkachenko H., Łukaszewicz J., Kurhaluk N., Assessment of autoimmune thyroiditis prevalence among Adults in Lviv Region during 2000-2010 years, Słupskie Prace Biologiczne, vol. 10, pp 93-105, 2013.

22. Kasiyan O., Tkachenko H., Łukaszewicz J., Kurhaluk N., Hashimoto's thyroiditis prevalence in Lviv region in the 2010 year, International Student’s Journal of Medicine (ISJM), Special issue, pp 607-611, 2014.

23. Kasiyan O., Tkachenko H., Łukaszewicz J., Kurhaluk N., Prevalence of nontoxic goiter among adults in Lviv region during years 2000-2010. In: Globalization and the issues of environmental protection, T. Noch, J. Saczuk, A. Wesołowska (Eds). Gdańsk, Publishing House of the Gdańsk Higher School of Administration, pp 91-121, 2014.

24. Kasiyan O., Tkachenko H., Łukaszewicz J., Zub S., Kurhaluk N., Prevalence of Hashimoto’s thyroiditis among children population in Lviv region during 2000-2010 years. Proceedings of V All-Ukrainian scientific conference of young scientists and students "Biological research – 2014", March 4-5, 2014, Ivan Franko Zhitomir State University, Zhitomir, pp 381-384, 2014.

25. Kasiyan O.P., The risk of thyroid cancer development in regions with a different prevalence of autoimmune thyroiditis and thyrotoxicosis, Hygiene of settlements, vol. 65, pp 119-123, 2015.

26. Kasiyan O.P., Manenko A.K., Tkachenko H.M., Pavliv R.M., Halay O.A., Application of inversion voltamperometry method for determination of iodine content in drinking water of the endemic region, Hygiene of settlements, vol. 53, pp 86-88, 2009.

27. Kasiyan O.P., Pavliv R.M., Halay O.A., Khabarova O.V., Manenko A.K., Determination of iodine content in drinking water of the endemic region of Ukraine, on the example of Lviv region, Practical Medicine, vol. XIII/issue 1, pp 110-116, 2007.

28. Kasiyan O.P., Pavliv R.M., Halay O.A., Khabarova O.V., Manenko A.K., Quantitative determination of iodine concentration in drinking water of the endemic region of Ukraine (Lviv region), Practical Medicine, vol. XIV/issue 1, pp 71-74, 2008.

29. Kasiyan O.P., Yurchenko S.T., Tkachenko H.M., Kurhaluk N.M., Risk assessment of autoimmune thyroiditis among a population living in regions with various iodine supplies. Young scientists for medicine: Proceedings of the XIX Scientific Conference of Young Scientists and Specialists of the Federal State Budgetary Educational Institution of Higher Education "North-Ossetian State Medical Academy" (FSBEI HE NOSMA) of the Russian Ministry of Health with international participation. – Vladikavkaz: FSBEI HE NOSMA of the Ministry of Health of Russia: CPI IP Tsopanova A.Yu., pp 151-155, 2020.

30. Kassim I.A., Ruth L.J., Creeke P.I., Gnat D., Abdalla F., Seal A.J., Excessive iodine intake during pregnancy in Somali refugees, Matern. Child Nutr., vol. 8/issue 1, pp 49-56, 2012.

31. Knowles J., van der Haar F., Shehata M., Gerasimov G., Bimo B., Cavenagh B., Maramag C.C., Otico E., Izwardy D., Spohrer R., Garrett G.S., Iodine Intake through Processed Food: Case Studies from Egypt, Indonesia, the Philippines, the Russian Federation and Ukraine, 2010-2015, Nutrients, vol. 9/issue 8, pp 797, 2017.

32. Knudsen N., Laurberg P., Perrild H., Bülow I., Ovesen L., Jørgensen T., Risk factors for goiter and thyroid nodules, Thyroid, vol. 12/issue 10, pp 879-888, 2002.

33. Kosminina N.S., Gnateyko O.Z., Lukyanenko N.S., Kech N.R., Estimation of the functional state of the pituitary-thyroid system at iodine-deficient conditions in children living in an environmentally polluted region, Bukovinsky medical bulletin, vol. 17/issue 1, pp 52-55, 2013.

34. Koukkou E.G., Roupas N.D., Markou K.B., Effect of excess iodine intake on thyroid on human health, Minerva Med., vol. 108/issue 2, pp 136-146, 2017.

35. Kozyarin I.P., Korzun V.N., Medico-social problems of prevention of iodine deficiency diseases, The Art of Treatment, vol. 4, pp 39-43, 2009.

36. Lamberg B.A., Endemic goitre - iodine deficiency disorders, Ann. Med., vol. 23/issue 4, pp 367-372, 1991.

37. Larive Ukraine, Bakery Chain in Ukraine, Ministry of Economic Affairs, Agriculture, and Innovation; The Hague, The Netherlands, 2011.

38. Laurberg P., Jørgensen T., Perrild H., Ovesen L., Knudsen N., Pedersen I.B., Rasmussen L.B., Carlé A., Vejbjerg P., The Danish investigation on iodine intake and thyroid disease, DanThyr: status and perspectives, Eur. J. Endocrinol., vol. 155/issue 2, pp 219-228, 2006.

39. Leung A.M., Braverman L.E., Consequences of excess iodine, Nat. Rev. Endocrinol., vol. 10/issue 3, pp 136-142, 2014.

40. Mamenko M.Ye., Prevention of iodine deficiency: what should a pediatrician and general practitioner know and do? (Clinical Recommendations), Modern Pediatrics, vol. 2, pp 8-16, 2017.

41. Melse-Boonstra A., Mackenzie I., Iodine deficiency, thyroid function, and hearing deficit: a review, Nutr. Res. Rev., vol. 26/issue 2, pp 110-117, 2013.

42. Method for measurements of the iodine concentration in drinking and mineral water, salt, bakery products, dairy products by the method of inversion voltammetry on a solid rotating electrode No. 081 / 12-0092-03; St. Petersburg, 30 p., 2002.

43. Moleti M., Trimarchi F., Vermiglio F., Thyroid physiology in pregnancy, Endocr. Pract., vol. 20/issue 6, pp 589-596, 2014.

44. Oliynyk V.A., Endemic Goiter, Treatment and diagnosis, vol. 1, pp 38-40, 1997.

45. Pankiv V.I., Iodine deficiency diseases: diagnostics, prevention, treatment, Problems of Endocrine Pathology, vol. 2, pp 75-86, 2002.

46. Parveen S., Latif S.A., Kamal M.M., Uddin M.M., 2007. Effects of long-term iodized table salt consumption on serum T3, T4, and TSH in an iodine deficient area of Bangladesh, Mymensingh Med. J., vol. 16/issue 1, pp 57-60.

47. Pearce E.N., Iodine deficiency in children, Endocr. Dev., vol. 26, pp 130-138, 2014.

48. Perrine C.G., Sullivan K.M., Flores R., Caldwell K.L., Grummer-Strawn L.M., Intakes of dairy products and dietary supplements are positively associated with iodine status among U.S. children, J. Nutr., vol. 143/issue 7, pp 1155-1160, 2013.

49. Sang Z., Wang P.P., Yao Z., Shen J., Halfyard B., Tan L., Zhao N., Wu Y., Gao S., Tan J., Liu J., Chen Z., Zhang W., Exploration of the safe upper level of iodine intake in euthyroid Chinese adults: a randomized double-blind trial, Am. J. Clin. Nutr., vol. 95/issue 2, pp 367-373, 2012.

50. Statistical Directory of Population Health Indicators and Activities of the Health Care Institutions in the Lviv Oblast for 2016, Lviv, 2017.

51. Statistical Directory of Population Health Indicators and Activities of the Health Care Institutions in the Lviv Oblast for 2010, Lviv, 2011.

52. Thomson C.D., Campbell J.M., Miller J., Skeaff S.A., Minimal impact of excess iodate intake on thyroid hormones and selenium status in older New Zealanders, Eur. J. Endocrinol., vol. 165/issue 5, pp 745-752, 2011.

53. Tkachenko H.M., Kasiyan O.P., Łukaszewicz J., Kurhaluk N.M., Zub S.T., Prevalence of autoimmune Hashimoto’s thyroiditis among the adolescent population in Lviv region during 2000-2010 years. International scientific conference of students and youthful scientists “Topical issues of modern medicine”, April 17-18, 2014, Kharkiv, Ukraine. Abstracts book of the conference, pp 205-206, 2014.

54. Todd C.H., Allain T., Gomo Z.A., Hasler J.A., Ndiweni M., Oken E., Increase in thyrotoxicosis associated with iodine supplements in Zimbabwe, Lancet, vol. 346/issue 8989, pp 1563-1564, 1995.

55. United Nations Children’s Fund (UNICEF) GAIN Belgrade Forum accelerates national efforts in the Russian Federation and Ukraine to ensure optimum iodine nutrition, IDD Newsl., vol. 39, pp 8-9, 2011.

56. van der Haar F., Gerasimov G., Tyler V.Q., Timmer A., Universal salt iodization in the Central and Eastern Europe, Commonwealth of Independent States (CEE/CIS) Region during the decade 2000-09: experiences, achievements, and lessons learned, Food Nutr. Bull., vol. 32/Suppl. 4, pp S175-294, 2011.

57. Vanderpump M., Thyroid and iodine nutritional status: a UK perspective, Clin. Med. (Lond.)., 14 Suppl., pp s7-s11, 2014.

58. Woodward M., Epidemiology: study design and data analysis. New York: Chapman and Hall, CRC, 1999.

59. Zar J.H., Biostatistical Analysis, 4th ed., Prentice Hall Inc., New Jersey, 1999.

60. Zava T.T., Zava D.T., Assessment of Japanese iodine intake based on seaweed consumption in Japan: A literature-based analysis, Thyroid Res., vol. 4, pp 14, 2011.

61. Zimmermann M.B., Iodine deficiency, Endocr. Rev., vol. 30/issue 4, pp 376-408, 2009.

62. Zimmermann M.B., Iodine deficiency and excess in children: worldwide status in 2013, Endocr. Pract., vol. 19/issue 5, pp 839-846, 2013.

63. Zimmermann M.B., Jooste P.L., Pandav C.S., Iodine-deficiency disorders, Lancet, vol. 372/issue 9645, pp 1251-1262, 2008.

A NEW METHOD FOR THE DETERMINATION OF PHOSPHATE IONS IN NATURAL AND TREATED WASTEWATERS

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ABSTRACT

A new indirect method for the determination of phosphate ions in natural and waste waters after purification is proposed. The method is based on the formation of a molybdophosphate complex (MPhC), its separation from the excess of unbound molybdate by extraction with isoamyl acetate, reextraction of MPhC into a weakly alkaline aqueous phase, and determination of the amount of molybdenum after the destruction of MPhC by the sulfonitrazo DAP reagent. The method has been tested on model solutions, natural and treated waste waters. The method allows to determine from 0.02 to 0.43 mg/dm^3 of phosphate ion (in terms of phosphorus), regression equation A = 0,032±0,035 + (1,15±0,05)C(P), correlation coefficient r = 0,995, C_{min} = 0,01 mg/dm^3.

Key words: orthophosphate ions, molybdophosphate complex, spectrophotometry, sulfonitrazo DAPH reagent, natural and waste waters.

INTRODUCTION

Determination of small amounts of phosphate ions in low-concentration solutions is of great importance for various industries, environmental, agrochemical and biological research. This applies primarily to natural and treated wastewater, because the determination of the phosphate content allows to control the process of pollution of water bodies with nutrients.

The concentration of phosphorus in waters varies from 0.02 to 5.4 mg/dm^3 (in terms of phosphorus), that is, the upper limit significantly exceeds the maximum allowable concentrations that do not cause eutrophication. There are many catchment areas in Ukraine, the economic activity of which has entered the zone of ecological risk. These are, first of all, the main rivers of Ukraine − Dnieper, Danube, Dniester, Southern Bug, which make the main contribution to the inflow of water with high content of phosphorus compounds in the Ukrainian coastal waters of the Black Sea − 0.57 km^3/year (70.5%) at an average phosphate concentration of 0.15 mg/dm^3 [1,2]. The accumulation of phosphorus compounds in the waters of small rivers of the Crimea, Odessa and Mykolayiv regions and the Ingul River is 0.086 thousand tons/year. Analysis of the average annual concentrations of phosphates for 2010 − 2020 shows an increase in their content in the water of the Dnieper in 2… 2.5 times [3,4]. As a result of eutrophication, the oxygen content decreases, fish die, and large amounts of biomass make water treatment much more difficult.

It is known, that eutrophication is limited only, when the phosphorus concentration in reservoirs decreases below 0.5 mg/dm^3, and at a concentration below 0.05 mg /dm^3 it almost completely stops [1−3]. Given the importance of quantifying orthophosphates in natural objects, this problem is highlighted in a separate section of analytical chemistry [5].

The main source of phosphate ion in urban wastewater is synthetic detergents. A large number of detergents contain as an alkaline agent with a large buffer capacity of trisodium phosphate Na_3PO_4. A characteristic property of the phosphate ion is the ability to form condensed systems − polyphosphate, metaphosphate ions and so on. These compounds are formed during the polymerization of the orthophosphate ion and consist of two or more PO_4^{3-} groups. Some of them are also used in industry and everyday life as emollients and may be present in wastewater. These include, for example, sodium pyrophosphate ($Na_4P_2O_7$), sodium tripolyphosphate ($Na_5P_3O_{10}$), sodium hexametaphosphate ($Na_6P_6O_{12}$), and others. Polyphosphate ions in water undergo stepwise hydrolysis, turning into orthophosphate ions. The rate of hydrolysis is strongly influenced by pH, temperature and salt composition of water. Organophosphorus compounds are widely used in the national economy as active insecticides, acaricides, defoliants, herbicides and others. These include carbophos, chlorophos, phosphamide, trichlorometaphos. By their chemical structure, they are derivatives of phosphorus, phosphonic, and others phosphoric acids, esters of thio- and dithiophosphoric acids. All these compounds are unstable in the environment, but their time in the water may be sufficient for a significant deterioration in the quality of natural waters, often undecomposed drugs fall into water treatment plants.

The main conversion reactions of almost all of these compounds are hydrolysis and oxidation. The vast majority of phosphorus-containing compounds in water are almost completely hydrolyzed and the end product of these processes are acidic phosphates. The rate of hydrolysis is influenced by pH, temperature and salt composition of water. The presence of bacteria accelerates the hydrolysis process [6]. The total (gross) phosphorus content in the water sample is determined after the conversion of all phosphorus-containing compounds into orthophosphate ions [5,7].

The content of phosphorus-containing compounds is regulated depending on the nature and purpose of the waters. Thus, the maximum permissible concentration of phosphate ions in water, water for domestic needs and fisheries in Ukraine is 3.5 mg PO_4^{3-}/dm^3 (1.14 mg P/dm^3).

Constant monitoring of the phosphate content in water bodies and drinking water by different methods makes it possible to assess the degree of risk for aquatic ecosystems, especially for organisms living in the aquatic environment, and a person who uses water resources [8,9].

Among the large number of proposed methods for the determination of phosphorus in these objects, spectrophotometric methods with extraction or sorption concentration are most often used. In many methods, the main form of phosphorus (V) determination is heteropoly acids − molybdophosphate complex (MPhC). The color, intensity and color stability of these compounds depend on the quantitative and qualitative composition, their structure, as well as on the use of reducing agents with a certain redox potential in the system [5,7].

To determine the phosphorus content, the reaction of formation of a yellow (unreduced) heteropoly acid − $H_3[P(Mo_3O_{10})_4]$, (λ_{max} = 310 nm, $\varepsilon_{310} = 1.2 \cdot 10^4$) is often used in the interaction of phosphate ions and sodium or ammonium molybdate [9]. In the studied solutions, according to the experimental conditions, there is always an excess of molybdate ions, the maximum light absorption of which is also in the UV region of the spectrum; therefore, phosphate ions can be determined only at wavelengths greater than 345 nm, at which the sensitivity is much lowerMethods using reduced forms of blue MPhC are more common. The molar absorption coefficients of the reduced and mixed complexes are much higher and allow a greater sensitivity to be achieved than using the yellow MPhC. For example, for molybdophosphate blue, $\varepsilon_{665} = 2.2 \cdot 10^4$ [8]. The process of MPhC formation occurs when an excess of ammonium or sodium molybdate solution is added to an acidic solution containing orthophosphate ions. As reducing agents are used ascorbic acid, stanum(II) chloride, hydrazine sulfate, etc. [10, 11]. Ascorbic acid is a mild oxidizing agent and does not reduce the excess of molybdate ions; the use of the reducing agent stanum(II) chloride increases the rate of reduction.

Methods for determining phosphorus based on the formation of MPhC have a number of disadvantages. For the yellow complex, this is work in the UV region, low sensitivity and selectivity − a number of cations and anions interfere with the determination of phosphorus − arsenate, tungstate, dichromate, nitrite and thiosulfate anions, cations Al^{3+}, Cu^{2+}, Fe^{3+}.

Methods for the determination of orthophosphate ions with the formation of a blue heteropoly acid after the reduction of MPhC in the aqueous or organic phase are more sensitive. However, they all have low reproducibility, which is due to the unstable ratio of valence forms of molybdenum Mo(V) /Mo(VI), which depends on the acidity of the solution and the nature of the reducing agent. The intensity of the color changes with time and influence of temperature, therefore, it is necessary to strictly observe the conditions of the experiments, which complicates the analysis as a whole [13].

For the purpose of concentrating the phosphate ion, separating it from interfering ions and excess molybdate ion and increasing the sensitivity of determination, the extraction of MPhC with organic reagents in the form of a yellow or blue complex is used. Usually, the yellow complex is extracted and the reduction is carried out in the organic phase, but techniques are known using the reduction in the aqueous phase. Extracts of reduced and unreduced MPhC retain the color inherent in their aqueous solutions. The general view of the spectra is identical, but the absorption maxima of this compounds in organic solvents, as a rule, are slightly shifted to the short-wavelength region. Reduced MPhC are extracted better than unreduced ones.

Alcohols, ketones, ethers, petroleum ether, carbon tetrachloride, chloroform and some others were studied as extractants. Among aliphatic alcohols, alcohols with 4-8 carbon atoms have the best extraction properties; alcohols with a smaller number of carbon atoms extract MPhC from solutions non-quantitatively, while those with a larger amount form stable emulsions at the phase boundary. During extraction with octanol, the excess molybdic acid practically does not pass into the organic layer.

The most suitable extractants were found to be a 20% solution of butan-1-ol in chloroform (extract 98.9% of MPhC), butyl acetate (99.9%), cyclohexanone (99.9%), and quinoline (95.7%). For complete extraction, it is necessary that the ratio of Mo : P in an aqueous solution be greater than 42 [14,15].

In the case of butanol, the determination of less than 50 mg P is not interfered with by 4 mg of As, Si, and up to 1 mg of Ge. In addition, the extraction removes a significant part of the excess molybdate ion, which also absorbs in the ultraviolet region of the spectrum. Butanol is used for the extraction of trace amounts of phosphate ion in the form of MPhC from wastewater.

In [16], a sequential selective extraction of heteropoly complexes of arsenic (MAC), silicon (MSC), and phosphorus (MPhC) using various extractants was proposed. At pH 1.8, MPhC is extracted with diethyl ether, then, by changing the acidity, MSC and methyl isobutyl ketone MAC are extracted with butanol.

It was found that during extraction with butyl acetate, molybdic acid is practically not recovered. The acidity of the medium and the concentration of the molybdate ion have little effect on the extraction, but it is better to carry out it from 0.5 N HCl in the presence of 0.5 % sodium or ammonium molybdate solution. The composition of the complex, extracted with butylacetate, corresponds to the ratio P: Mo = 1: 12. For other extractants, this ratio may be different [9]. The extract is characterized by an absorption maximum at 320 nm, $\varepsilon = 2.3 \cdot 10^3$. It has been shown that the presence of salts (NaCl, $NaNO_3$, Na_2SO_4 etc.) in a solution in small concentrations (1−3 %) does not have a noticeable effect on the extraction, which is important for determining the phosphate-ion in waters [10].

In addition to the methods for determining the phosphate ion in the form of MPhC, methods with the formation of ternary complexes are often used. The quality of the third component in these complexes are present ions V (V), Bi (III) or Sb (III). Molar absorption coefficients these compounds allowing to reach greater sensitivity, then MPhC. . So, for the yellow ternary complex of molybdovanadophosphate acid $\varepsilon = 1.7 \cdot 10^4$ [10, 11], for molybdobismuthphosphate blue $\varepsilon_{720} = 1.66 \cdot 10^4$ [10,14].

The most sensitive group of methods for determining the phosphate ion are methods with the formation of ionic associates of MPhC with basic dyes. These methods were developed by Babko and Pilipenko and their staffes [10]. They are also convenient in that silicon does not form such compounds and does not interfere with the determination. The molar extinction coefficients of the dyes themselves are high and often reach 10^5, and 1 molecule of the MPhC can attach 3 or more molecules of the main dye, which leads to a sharp increase in the detection sensitivity. The following basic dyes were used: crystal violet, malachite green, iodine green, brilliant green, safranin, etc.

Intensely colored associates are found in solutions in the form of colloids or suspensions. In practice, the determination of the phosphate ion in the form of MPhC associates with basic dyes is carried out in three versions: with the extraction separation of colored compounds and photometry of extracts, with separation of the solid phase by centrifugation, its subsequent dissolution in suitable solvents and photometry of the solution, and with the stabilization of the solid phase in aqueous solutions. Various surfactants are used as stabilizers, in particular, nonionic ones, for example, OP-10. The use of associates and surfactants makes it possible to determine 1–200 mcg/dm^3 of phosphate ion. However, these methods require careful observance of the analytical conditions, especially the acidity of the medium, removal or destruction of excess dyes, since the latter often absorb in the same spectral region as the associate. The methods are characterized by low reproducibility and analysis duration due to the need to separate, stabilize, and dissolve the formed colored compounds [17−19].

Some sources propose the determination of phosphate ions by an indirect method using the multiplication reaction. The principle of this method is that the formed MPhC with a strict stoichiometric ratio of the amounts of molybdenum and phosphorus is destroyed and the content of molybdenum is determined, and then recalculated to the content of phosphorus. For example, in [13, 17], the reduced blue MPhC was separated from the excess of molybdate ions by extraction, the complex was reextracted into a weakly alkaline aqueous phase, decomposed, and the content of molybdenum with the reagent 2,3,7-trioxyfluorone was determined in the presence of neonol.

In [20, 21], the yellow MPhC was separated from the excess of molybdate ions by extraction, its aqueous phase was transferred, the complex was destroyed, and the amount of molybdenum in the final solution was photometrically determined, which is equivalent to the amount of phosphorus in the MPhC, by the sulfonitrazo E reagent. The advantage of using unreduced heteropolyoxoacid $H_3[P(Mo_3O_{10})_4]$ is the preparation of a compound with a strictly stoichiometric composition, in which the ratio P: Mo = 1:12, therefore the multiplication factor in this reaction is 12, and the detection sensitivity depends on the sensitivity of the reaction to molybdenum.

The aim of this work was to improve the method for the indirect determination of phosphate ions using a sensitive and selective reagent for molybdenum − sulfonitrazo DAPh (SN DAPh) and to develop a new sensitive and selective method for the determination of small amounts of phosphate ions in natural and purified wastewaters.

MATERIALS AND METHODS OF RESEARCH

The following reagents were used: potassium dihydrogen phosphate KH_2PO_4; sodium molybdate dihydrate $Na_2MoO_4{\cdot}2H_2O$; hydrochloric acid HCl, saturated, 38%; ammonium hydroxide NH_4OH, 25%, ρ = 0.91 g/dm^3; reagent sulfonitrazo DAPh; isoamyl acetate $CH_3{-}CH(CH_3){-}CH_2{-}CH_2{-}OCO{-}CH_3$; potassium hydrogen phthalate $HOOC{-}C_6H_4{-}COOK$, c.

To register the optical density, we used a photoelectric photometer KFK-3-01- "ZOMZ".

A pH meter/MV/ISE/Temp ADWA AD1200 PBX was used to control the pH.

The following solutions were used for the studies.

1. Standard solutions of phosphate ion [10]:

1.1. Phosphate ion standard solution № 1. A portion of potassium dihydrogen phosphate weighing 0.4394 g was dissolved in distilled water and diluted in a 1 dm^3 volumetric flask with water to the mark. C(P) = 0.1 g P/dm^3 (100 mg P/dm^3).

1.2. Phosphate ion standard solution № 2. A solution of № 1 with a volume of 10 cm^3 was transferred to a volumetric flask with a capacity of 100 cm^3 and made up to the mark with water. C(P) = 0.01 g P/dm^3 (10mg P/dm^3).

1.3. Phosphate ion standard solution № 3. A solution of № 2 with a volume of 10 cm^3 was transferred to a volumetric flask with a capacity of 100 cm^3 and made up to the mark with water. C(P) = 0.001 g P/dm^3 (1 mg P/dm^3).

2. Standard solutions of molybdate ion [22]:

2.1. Molybdate ion standard solution № 1. A portion of sodium molybdate dihydrate weighing 2.5219 g was dissolved in a small amount of hot distilled water, 1 cm^3 of saturated HCl was added, cooled, quantitatively transferred to a 1 dm^3 volumetric flask and diluted with water to reflux. C(Mo) = 1 g Mo/dm^3.

2.2. Molybdate ion standard solution № 2. A solution of № 1 with a volume of 10 cm^3 was transferred to a volumetric flask with a capacity of 100 cm^3 and made up to the mark with water. C(Mo) = 0.1 g Mo/dm^3.

3. Sodium molybdate solution, 10%.

4. Hydrochloric acid solutions: saturated, 5% and 0.1 N.

5. A solution of ammonium hydroxide, 0.1%.

6. Isoamyl acetate.

7. Phthalate buffer solution. To a 200 cm^3 volumetric flask was added 15.7 cm^3 of 0.1 N hydrochloric acid solution, 50 cm^3 of 0.2 M potassium hydrogen phthalate solution and made up to the mark with water; pH = 3.5 [23].

8. Aqueous solution of SN DAPh, 0.05%.

RESULTS AND DISCUSSION

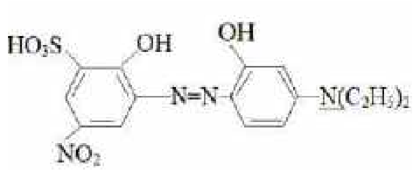
STUDY OF EXTRACTION AND REEXTRACTION OF MPhC

After receiving the yellow complex of MPhC, it was extracted to separate from the excess of molybdate ions. The best extractants for MPhC are ethers (the separation coefficient of molybdenum heteropoly- and isopolycomplexes, equal to the ratio of their distribution coefficients > 1000). After twice washing the extract with acidic solutions, the minimum value of the light absorption of the blank experiment is reached [13].

Investigated the extraction of MPhC with butyl acetate, amyl acetate, and isoamyl acetate in an acidic medium. In the case of using amyl and isoamyl acetate, there is no foaming and fast phase separation is achieved. Under these conditions, practically all of the unbound molybdate ion remains in the aqueous phase together with the ions that interfere, which significantly increases the selectivity of the method. It was found that the complex is more fully reextracted if the volumes of the organic and aqueous phases are approximately the same.

The process of interaction of molybdate ions with SN DAPh after reextraction of the molybdophosphate complex into the aqueous phase was studied separately. In this case, in a weakly alkaline medium, there is a course of competing complexation reactions between the MPhC and the SN DAPh complex. The alkaline environment causes the destruction of MPhC. But at pH 9.5 ... 10 this process slows down and the complex begins to break down, so it is necessary to strictly observe the pH value of the solution in the range of 8 ... 9. To do this, it is advisable to use a dilute 0.1% solution of ammonium hydroxide.

INVESTIGATION OF THE INTERACTION OF MOLYBDATE IONS WITH SULFONITRASO DAPH



Among the o,o’-dioxyazocompounds, the sensitive and contrast reagent for the molybdate ion is SN DAPh − 3-sulfo-5-nitro-4’-diethylamino-2,2’-dioxyazobenzene [24].

The study of the use of the reaction of molybdate ion with SN DAPh for indirect determination of phosphate ions was not performed.

The MoO_4^{2-} ion reacts with SN DAPh at pH = 3.5 in phthalate buffer medium.

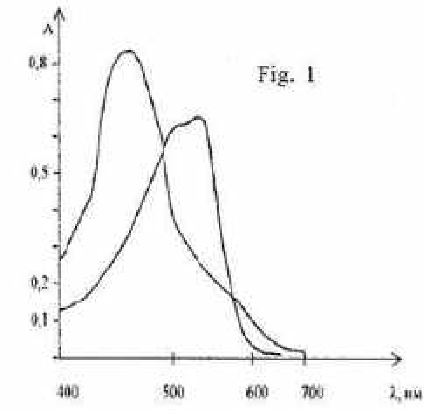
The formation of the complex occurs immediately after the addition of the reagent. The color intensity of the newly formed complex with the reagent SN DAPh is stable over time and does not change during the day. The molar ratio of the components in the complex with an excess of reagent is 1:1, λ_{max}(reagent) = 460 nm, λ_{max}(complex) = 560 nm. The color of the reagent solution is orange, and the color of the complex with molybdate ions is intensely crimson. The difference between the light absorption λ_{max} is 100 nm, i.e., the reagent is sufficiently contrast and almost does not absorb at 560 nm, which distinguishes it from the reagent sulfonitrazo E. The molar light absorption coefficient of this complex with SN DAPh is $\varepsilon = 1.3 \cdot 10^4$.

To clarify the interval of concentrations, reproduction and testing of the method of determining the amount of molybdate ion, a graph № 1 of the dependence of the optical density on the concentration of molybdate ions − $A = f(C_{Mo})$ was constructed.

To do this, in eight volumetric flasks of 25 cm^3 consistently made, respectively, 0; 0.2; 0.5; 1.0; 1.5; 2.0; 3.0 and 4.0 cm^3 of a standard solution of molybdate ion № 2, then to each was added 3 cm^3 of phthalate buffer and 2 cm^3 of 0.05% solution of SN DAPh reagent, the contents of each flask were adjusted to the mark with water. After 5 min, the optical density was determined at λ = 560 nm in a cuvette 2 cm thick.

The regression equation of the graduated graph $A = 0.029 \pm 0{,}03 + (1.05 \pm 0{,}05)C(\mathrm{Mo})$, correlation coefficient $r = 0{,}990$.

The experiment showed that the range of concentrations that can be determined is from 0.75 to 16 mg Mo /dm^3 ($0.84 \cdot 10^{-5} \ldots 16.8 \cdot 10^{-5}$ mol Mo/m^3).



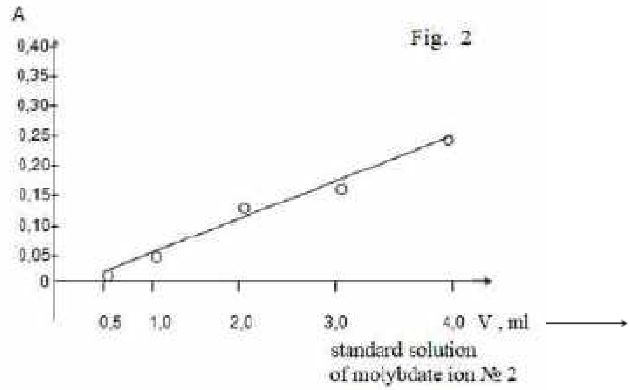


Fig. 1. Spectra of the reagent SN DAPh (1) and its complex with modibdate (2) ($C_R = C_{comp} = 3{,}6 \cdot 10{-}6$ mol/25 ml solution)

Fig. 2. Calibration graph for determining the range of optimal concentrations of molybdate ion when determining it with sulfonitrazo DAF reagent ($\lambda = 560$ nm)

DEVELOPMENT OF METHODS FOR INDIRECT DETERMINATION OF PHOSPHATE IONS WITH SULFONITRAZO DAPH REAGENT

1. Construction of a graduated graph № 2 to determine the concentrations of molybdate ion after reextraction and destruction of the MPhC complex.

Based on the analysis of the composition of the MPhC complex $H_3[P(Mo_3O_{10})_4]$, the calculated range of concentrations of phosphate ions, which can be determined by the developed method, is from $C(P)_{min} = 0.02$ mg P /dm^3 to $C(P)_{max} = 0.43$ mg P/dm^3.

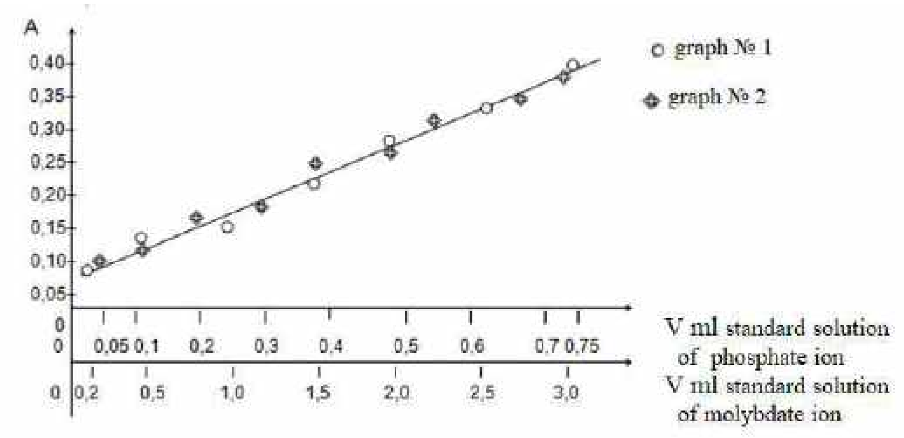
Based on these data, the volumes of standard solutions of phosphate ions were determined to build a graduated graph for determining the content of these ions in the studied objects.

1.1. To the separating funnel per 100 cm^3 was made separately for each experiment, respectively, 0; 0.5; 1.0; 2.0; 3.5; 5.0; 7.5; 10.0 and 12.5 cm^3 of a standard solution of phosphate ion № 3, then 0.5 cm^3 of a 10% solution of sodium molybdate, 1 cm^3 of HCl saturated and 30 cm^3 of distilled water. Within 1 min, MPhC is formed in the solutions, so the solution becomes yellowish.

1.2. Isoamyl acetate, 10 cm^3, is added to the separating funnel with the MPhC solution and shaken for one minute. The formed MPhC passes into an organic phase. The aqueous phase is poured into the second funnel, to which is added 5 cm^3 of isoamyl acetate. Shake for one minute. The organic phase after the second extraction turns yellow. Both extracts (~15 cm^3) are poured into one separatory funnel and washed twice with portions of 5% HCl of 10 cm^3 each, the washings are discarded.

1.3. The organic phase, 15 cm^3 of water and 0.5 cm^3 of 0.1% ammonium hydroxide solution (pH of the solution 8… 9), shake for 1… 2 min. The complex in the slightly alkaline medium is reextracted to the aqueous phase. After stratification, the aqueous phase containing MPhC is placed into a 25 cm^3 volumetric flask, 3 cm^3 of phthalate buffer solution, 2 cm^3 of SN DAPh reagent solution are added, heated in a water bath and boiled for 3 minutes. The last operation is performed for the complete destruction of the MPhC complex. After cooling, the solution is made up to the mark with water, stirred and photometered at 560 nm in a cuvette with l = 2 cm relative to the comparison solution (3 cm^3 of phthalate buffer, 2 cm^3 of SN DAPh reagent solution, water to the mark in a 25 cm^3 flask).

Construct a graduated graph of the dependence A = f (m (P) based on the recalculation of $m(P) = \dfrac{m(Mo)\cdot 30{,}97}{95{,}94\cdot 12}$ mg.



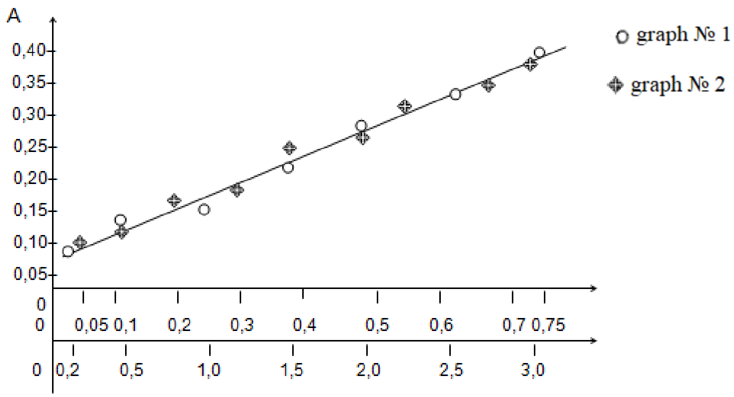


Fig. 3. Calibration graphs for determining the content of phosphate ion in a solution by the amount of molybdate ion.

Regression equation of the obtained graduated graph A = 0,032±0,035 + (1,15±0,05)*C*(P), correlation coefficient *r* = 0,995. So, that is, the slope and range of the determined concentrations of phosphate ions by the definition of these ions through the molybdophosphate complex and the direct determination of molybdate ions are almost the same. This means that the processes of extraction and reextraction allow to almost completely separate the MPhC from the excess molybdate ions, quantitatively translate it first into the organic, then into the inorganic phase, and then − quantitatively translate it into a complex with SN DAPh.

The range of phosphate ion concentrations to be determined is 0.02… 0.43 mg P /dm^3.

DETERMINATION OF PHOSPHATE ION CONCENTRATION IN MODEL SOLUTIONS AND IN INVESTIGATED WATERS

The method was tested on model solutions by the method of "taken-found" and on samples of tap, wastewater and natural water.

The test water up to 20 cm^3 was added to a 25 cm^3 volumetric flask, 0.5 cm^3 of 10 % sodium molybdate solution, 0.5 cm^3 of HCl saturated and water were added to the mark. MPhC is formed in the solution within 1 min. Further analysis was performed according to items 1.2 and 1.3.

Model solutions were prepared from distilled water by adding the calculated volumes of standard phosphate ion solution.

Sampling was performed in the summer according to GOST R 51593-2000 on the day of determination. Samples of test waters, based on the results of previous studies, were pre-diluted four times: to 5 cm^3 of water was added 15 cm^3 of distilled water.

The content of phosphate ions in terms of phosphorus was determined by the formula:

$$C(\mathrm{P}) = \frac{m(\mathrm{P})\cdot 1000}{V_{\mathrm{samp}}} \text{ mg P/dm}^3,$$

where m(P) is the mass of phosphorus, determined on the sample, V_{samp} is the volume of water under study.

The research results are presented in the tables.

The results of the analysis of the given types of waters presented in the table show satisfactory reproducibility and correctness of the offered technique.

Table 1. The results of determination of phosphate ions in in model aqueous solutions (n = 5, P = 0.95))

Sample	Taken P, mg /dm^3	Found P, mg /dm^3	RSD (%)
1	0,025	0,024±0,0008	0,1
2	0,05	0,05±0,002	0,4
3	0,10	0,11±0,004	0,9
4	0,20	0,21±0,006	0,8
5	0,40	0,40±0,014	1,6

Table 2. Results of determination of phosphate ion (in terms of phosphorus) in tap, river and waste waters (n = 5, P = 0.95)

Sample	Found P, mg /dm^3	RSD (%)
Tap water	0,08 ± 0,0025	2,5
Wastewater is treated after the machine-building plant PTZ	0,38 ± 0,015	1,8
Annual water (Yzh. Bug river)	0,31 ± 0,012	1,4
Artesian water (gardening well "Southern Bug")	<0,02	

CONCLUSIONS

An indirect method for the determination of phosphate ions in natural and treated wastewater is proposed, which is based on the formation of molybdophosphate heteropoly acid, its extraction with isoamyl acetate in order to separate from the excess molybdate ion and other ions in the water, determining the equivalent amount of molybdate ions with the reagent sulfonitrazo DAF. The range of determined concentrations of phosphate ion (in terms of phosphorus) is 0.02… 0.43 mg/dm^3, regression equation A = 0,032±0,035 + (1,15±0,05)C(P), correlation coefficient r = 0,995, C_{min} = 0,01 mg/dm^3. This method allows assessing the contamination of water with phosphates at the level necessary to control eutrophication processes in lowconcentrated natural and treated wastewater.

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REFERENCES

1. Pro fosfaty, fosfonaty ta problemy zabrudnennia vodoyim v Ukraine. / Derzhavne agenstvo vodnyikh resyrsiv Ukrainy. Ofiziyinyi sait. Opublikovano 13.12.2019 r.

2. Kresin V.S., Eremenko E.V., Zaharchenko V.A., Yurchenko A.I. Dynamika postupleniia soedineniyi fosfora v ukrainskie pribrezhnye vody Chornogo moria i complex vodo-okhannyh meropriiatiyi. *Ekologiya dovkillya ta bezpeka zhittediial'nosti*. 2008, №5. 28-33.

3. Dolina L. F. Ochistka stochnyh vod ot biogennyh elementov: Monografiya. Dnepropetrovsk : Kontinent. 211, 198 s.

4. Polishchuk A. A., Ialovsky G.V., Mozolevska T.M., Goltsov V.I. Vmist fosfativ v r. Dnister ta stichnykh vodakh m. Odesa. *Ukrainskiy gidrometeorologichny zhurnal*. 2012, №11, 195-201.

5. Basova E. M., Ivanov V.M. Spektrofotometricheskoye opredeleniye ortofosfat-ionov v plastovyh vodakh dlia provedeniya indikatornykh issledovaniyi. *Vest. Mosk. Un-ta. Ser.2. Khimiya*. 2012. (53), № 3, 165-180.

6. Litvinenko A., Stepova N., Kushka O. EU and Ukrainian regulations concerning phosphorous compounds in water and detergents // Proceedings International Conference "BuildMaster-Class-2018", Kyiv, 2018. P. 272-273.

7. Zaporozhetc O.A., Zin'ko L.S., Sumarokova. G.S. Trends in phosphorus determination in biological and environment objects (Review). *Method and object Chemical Analysis*. 2019, 14 (4), 175-191.

8. Yakist vody. Vyznachennia fosforu. Spektrometrchnyi metod iz zastosuvanniam amoniyi molibdatu: DSTU ISO 6878:2008.−[Chynnyi vid 01-01-2010] −K. Derzhspozhyv-standart Ukrainy, 2011.

9. DSanPiN 2.2.4−171−10. Derzhavni sanitarni normy ta pravila "Hihiienichni vymohy do vody pytnoi, pryznachenoi dlia spozhyvannia liudinoiu .−[Chynnyi vid 12-05-2010]. MOZ Ukrainy, 2010.

10.Babko A.K., Pilipenko A.T. Fotometricheskiyi analiz. Metody opredeleniia nemetalov. M. Khimiia. 1974, 360 s.

11.Kolorimetricheskie (fotometricheskie) metody opredeleniia nemetalov. Pod red. A.I. Buseva. M. Inostrannaia literatura. 1963, 467 s.

12.Fedorov A.A. Analiticheskaia khimiia elementov. Analiticheskaia khimiia fosfora. M. Nauka. 1974, 220 s.

13.Vishnikina E.V., Vishnikin A.B., Chmilenko F.A. Extraction-photometric determination of phosphate by means of 12-molybdophosphate. *J. Water Chem. Technol*. 2003, 25(6), 541-548.

14.Trokhimenko O.M., Sukhan V.V., Nabivanets B.I. Optimizatsiia metodiki fotometricheskogo opredeleniia polifosfatov v vodakh posredstvom molibdata i olova (II). *Khimiya i tehnologia vody*. 2000, 22(2), 145-150.

15.Trokhimenko O.M. Contsentrirovanue i opredelenie microkolichestv fosfora (V) I Tl(I) v vodakh s ispol'zovaniem geteropolikompleksov fosfora. Avtoref. Dis…kan. Chim. Nauk. KNU im. Shevchenko.,Kiev,2000.7 p.

16.Dubovik D.B., Tikhomirova T.I., Ivanov A.V.- Determination of silicon, phosphorus, arsenic and germanium as heteropoli acids. *J. Analyt. Chem*. 2003, 58(9), 802−819.

17.Vishinkina E.V., Vishinkin A.B., Chmilenko F.A. Extractsionno-fotometricheskoe opredelenie ortofosphate-iona s ispol'zovaniem metalzameshchenyh geteropolikompleksov $PMeMo_{11}O_{40}^{6-}$ (Me = Bi^{3+}, Sb^{3+}). *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2008, (1), 13-16.

18.Motomizu S., Oshima M. Spektrofotometric determination of phosphorus as ortophosphate based on solvent extraction of the ion associate of molybdophosphate with malachite green. *Analist*. 1987.112(3). 295−300.

19.Trokhimenko O.M. Fotometrichne viznachennia fosforu (V) u vigliagi ionnogo asotsiatu molybdofosfatu z diamantovim zelenym. Ukr. Chim. Zhur. 2002, 68(6), 88−91.

20.Dedkov Yu. M., Kel'ina S.Yu., Konichev M.A. Fotometricheskoe opredelenie fosfat-ionov v prirodnyh i stochnyh vodah. *Khimiya i tehnologia vody*. 2001, 23(4), 395-399.

21.Dedkov Yu. M., Kel'ina S.Yu., Konichev M.A. Opredelenie fosfatov v vodah na urovne PDK. *Zavodskaia laboratoriia*. 2001, 67(7), 8-13.

22.Lur'e Ju. Ju. Analiticheskaia khimiia promyshlennyh stochnyh vod. M.: Himiia. 1984. 448 s.

23.Lur'e Ju. Ju. Spravochnik po analiticheskoy khimii. M.: Himiia. 1989. 448 s.

24.Av. Sv. *№ 1330139 SU*, MPK *A*1. 3-Sul'fo-5-nitro-4′-diamino-2,2′-dioksiazobenzol v kachestve reagenta dlia fotometricheskogo opredeleniia galliia, indiia, molybdena i vanadiia. / Dedkov Yu. M., Ermolenko L. V., № 3927920; zayavl. 05.07.85; opub. 15.08.1987.

CONTAMINATED BOTTOM SEDIMENTS - METHODS OF REDUCING THE ENVIRONMENTAL IMPACT

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ABSTRACT

Accumulation of excessive amounts of bottom sediment in rivers and water reservoirs reduces their capacity and depth and adversely affects the usability of the reservoirs. Accumulated sediments cause turbidity of water, are a place of deposition of pollutants and have a negative impact on water quality. Therefore, it is necessary to periodically remove sediments, i.e. dredging. The bottom sediments obtained after this treatment must be properly managed or neutralized so that they do not pose a threat to the environment and living organisms. Among the techniques of bottom sediment treatment, there are in-situ and ex-situ methods, both physical, chemical, thermal, biological and combined. The paper presents the characteristics of bottom sediments in terms of the presence of pollutants and methods of their removal from excavated bottom sediments, as well as discusses the methods of management of excavated bottom sediments.

Keywords: bottom sediments, pollution, management of bottom sediments, in-situ and ex-situ methods

INTRODUCTION

Bottom sediments are one of the most important elements of any aquatic ecosystem, they are an integral part of the surface water environment. They are formed at the bottom of lakes, rivers, river channels and dam reservoirs as a result of the accumulation of allochthonous and indigenous substances. The basic composition of the sediments usually includes: SiO_2 (6.83-79.94%), Al_2O_3 (1.24-17.08%), Fe_2O_3 (2.07-13.08%), MnO (0.03-0.75%), MgO (0.33-13.30%), CaO (0.43-30.69%), Na_2O (0.05-1.13%), K_2O (0.16-2.49%), TiO_2 (0,06-1,02%), P_2O_5 (0.06-5.28%), S (0.0-4.97%), with ignition losses of 4.71-47.71% [1], [2], [3], [4], [5], [6]. Usually, the dominant mineral in river sediments is most often quartz, carbonates and feldspars are present in smaller amounts, which occur in grain fractions larger than 0.06 mm, which most often constitute 90% of the sediment. In the fine-grained fraction below 0.06 mm, the predominant minerals are compounds from the mica/illite group, quartz, kaolinite and chlorites [7].

The quality of bottom sediments is conditioned by a number of natural and anthropogenic factors. Among the natural ones, the lithological structure of the catchment, the type of soil cover, the topography and climatic conditions play a major role. These factors determine the course of weathering processes, the activation of elements as well as their migration and accumulation in the environment. In particular, the content of trace elements and organic impurities in the surface layer of sediments is constantly changing. The chemical composition of bottom sediments is also greatly influenced by changes in the degree of water oxygenation, water balance, primary production and the intensity of photosynthesis processes, especially the persistence of the periodic advantage of evaporation over supply and changes in the intensity of denudation in the catchment area. The method of the catchment management also determines the quality of bottom sediments. In non-industrialized areas, the composition of sediments depends primarily on the geological structure of the catchment area or climatic conditions, which determine the weathering processes and the form of transport as well as the migration of elements and their accumulation in the environment. In urbanized areas, the composition of bottom sediments depends primarily on human economic activity conducted in the water reservoir catchment area. Discharges of both industrial and municipal wastewater, leaks from landfills and gas and dust pollution of the atmosphere are the source of information on the degree of anthropogenic pressure in the water ecosystem [3], [4], [8].

An important problem is also the excessive accumulation of bottom sediments, which causes a number of adverse effects in water reservoirs, hindering their proper functioning. The increase in the thickness of bottom sediments primarily contributes to the reduction of the volume and depth, limiting the usability of water reservoirs. In the inlet part to the water reservoir, there is a shallowing and intensive overgrowing with vegetation, which contributes to flooding of the adjacent areas. The retention capacity also decreases - it is especially important for reservoirs whose primary function is flood protection. On the other hand, at low water levels, contaminated bottom sediments have a negative impact on its quality. Recreational functions are also limited [9], [10], [11].

Small retention reservoirs are characterized by more intense silting compared to large dam reservoirs. For small reservoirs, these values are in the range of 1.87-5.08%. For comparison, the average annual silting rate of reservoirs, which belong to the global average category, is in the range of 0.02-0.58% [12], [13]. According to Hartung (1959) [14], if the capacity of the reservoir is reduced by 80%, it does not fulfill its function. On the other hand, Michalec (2012) [15] states that the limitation of the functions of small water reservoirs occurs already when the capacity is reduced in the range of 40-60%. Studies aimed at determining the thickness increment of bottom sediments were carried out by Madeyski et al. (2008) [13], according to which the silting degree for the Rzeszów reservoir was 66% after 13 years of operation (average annual - 5.07%). The Brzóza Stadnicka reservoir is also characterized by a high degree of silting, for which this value after 7 years of operation was 44.66% (average annual - 6.38%), while after 16 years it was over 80%.

CONTAMINANTS IN BOTTOM SEDIMENTS

Bottom sediments are one of the elements of the environment into which the most pollutants are introduced, and unfortunately their number continues to increase in the environment (Table 1). The knowledge of the chemical composition of sediments is in many cases a better indicator of water pollution than the knowledge of the chemical composition of water, which is more variable over time. Due to the many times higher concentrations of harmful substances in the sediments as compared to their content in water, the chemical analysis of the sediments enables the detection and observation of changes in their content even with a relatively low degree of contamination [1], [2], [3], [15], [16], [17].

The greatest threat is posed by organic substances such as phthalic acid esters (PAEs), polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), organic halogen compounds, nonylphenols, nonylphenol ethoxylates. Inorganic impurities include selected heavy metals, including cadmium, lead, nickel and mercury. They are chemical substances that are usually characterized by relative resistance to degradation, translocation in the environment, toxicity to organisms and the possibility of entering the trophic chain and bioaccumulation. Additionally, they are not easily removable by conventional processes. In recent years, many times increased content of metals such as: cadmium, chromium, copper, nickel, lead or zinc has been observed - elements that are widely used in industry and economy [18], [19], [20], [21].

Table 1. Number of known chemical compounds [22]

Year	2014	2015	2016
Number of known substances	65 844 568	66 324 359	66 664 872
Number of chemicals available for sale	86 820 549	104 517 210	110 378 650
Number of regulated chemicals	312 274	344 630	345 575

Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 (Water Framework Directive) [23] was developed in order to systematize the type and harmfulness of chemical compounds introduced into the aquatic ecosystem and measures aimed at counteracting the pollution of waters and bottom sediments. This document obliges the EU Member States, inter alia, to monitor surface and groundwater, especially bearing in mind the developed list of 33 basic pollutants that significantly affect the quality of the aquatic environment. Among these chemical compounds, a group of hazardous priority substances has been distinguished. Some assumptions of Directive 2000/60/EC were changed by Directive 2008/105/EC of 16 December 2008 [24]. Introduced, among others Environmental Quality Standards (EQS) for priority substances and other pollutants. If the EQS value is exceeded, it is impossible to achieve good status for selected rivers and lakes and related artificial or heavily modified water bodies. Directive 2013/39/EU of 12 August 2013 [25] also extends the monitoring list of priority substances to another 12 substances or groups of substances and tightens the environmental quality standards for the seven existing pollutants. At the same time, it introduces the obligation to monitor chemical compounds that may pose a risk to the aquatic environment. The presence of heavy metals and other elements in bottom sediments at their natural level does not pose a threat to aquatic ecosystems. Currently, the natural content of heavy metals in the environment is modified as a result of anthropogenic pressure. The toxicity of metals depends on the concentration and solubility of their compounds in water and on their chemical reactivity, i.e. the ability to form complexes with fractions of organic matter and with inorganic compounds, as well as binding with living organisms. The most toxic are inorganic metal connections. Organic metal connections are much less harmful, but the possibility of their biochemical release poses a great risk to all organisms [17], [26], [27], [28].

The course of the process of sorption of pollutants in the sediments is influenced by the sediment structure. Heavy metals in water sediments are partially bound in the structure of minerals relatively resistant to weathering, partially they are present in newly formed chemical compounds (sulphides, carbonates, oxides) or in forms absorbed by clay minerals, organic substances and hydrated iron oxides. The main role in retaining heavy metals in sediments is played by Fe and Mn oxides and hydroxides, organic substances and clay minerals [7]. An important factor when examining the content of heavy metals in bottom sediments is the selection of an appropriate grain fraction. It has been found that the heavy metal content increases with decreasing grain size. However, other studies have shown that the heavy metal content is lower in the finer fraction than 0.2 μm. It may be related to the decreasing sorption capacity of the weakly crystalline, partially amorphous components of this sediment fraction [29].

A significant part of the inorganic and organic pollutants entering the aquatic environment is retained in bottom sediments. However, some of them can be re-activated to the water phase as a result of chemical and biochemical processes in the sediments. The process of releasing the ingredients into the water column can be triggered, among others, by as a result of resuspension resulting from the mechanical disturbance of the sediment structure, due to natural processes. Moreover, during a flood, contaminated sediments can be transported and deposited in other places, also not included in the water ecosystem (apart from the river bed in flood plains) [2], [30], [31].

METHODS OF REMOVING PERSISTENT ORGANIC POLLUTANTS FROM BOTTOM SEDIMENTS

The problem of safe treatment and management of bottom sediments is still not very popular and underestimated. Bottom sediments are excavated only in cases of excessive shallowing of reservoirs, lakes or when it is necessary to open up rivers, therefore research on the removal of organic pollutants from bottom sediments is sparse [32]. Currently, excavated bottom sediments that do not meet the requirements of the current legal regulations are subject to the appropriate procedure. The extracted material can be neutralized by depositing in properly secured landfills or by using pyrolytic disposal of bottom sediments.

However, during the storage of spoil containing hazardous substances, various biological, physical and chemical processes take place, which lead to changes in the properties of bottom sediments. These processes can lead to leaching of pollutants, posing a serious threat to environmental quality. Moreover, the extracted spoil has a tendency to putrefy and generate large amounts of leachate, which may adversely affect, in particular, soil and groundwater. Moreover, the problem is to find a suitable land for storage and the high costs of maintaining it in the required conditions [33], [34]. Taking into account all aspects, including financial ones, it would be beneficial to clean and properly manage the bottom sediments. Most of the bottom sediment treatment methods (Figure 1) have been developed based on the techniques used for soil remediation. Among the methods of treating the excavated sediments (ex-situ methods), there are physical, chemical, thermal, biological and combined methods. They are carried out on a specially prepared technological stand, which allows easy control and a relatively short time of the process. There are also in-situ methods for removing contaminants from bottom sediments. They differ from those used in soil remediation because the processes for transporting pollutants are more complex in the aquatic environment as compared to the soil environment. In-situ methods are considered less effective compared to ex-situ methods. Remediation of bottom sediments based on in-situ methods is much more difficult to implement and sometimes more expensive. This is due to, inter alia, from the need to use non-invasive environmental methods of cleaning and setting up and maintaining a base near the reservoir [35], [36], [37], [38], [39], [40], [41], [42].

Thermal methods are highly effective in removing pollutants, in particular of petroleum products. These technologies are judged to be fast, effective and easy to implement [39], [43], [44], [45], [46], [47]. However, the challenge in designing these methods is to protect against air pollution, in particular the production of hazardous by-products. Scrubbers are required to treat the air before the resulting gases are released into the atmosphere, which generates additional costs. The disadvantage of incineration of bottom sediments or soil is also the presence of water, which significantly reduces the efficiency of the process, as well as excessive consumption of energy necessary to heat the soil to the required temperature [35], [43], [45]. According to Acharya and Ives (1994) [48], in order for the process of removing contaminants such as PAHs to be effective, the process temperature should be in the range of 870-1200 °C. The problem is also the change in soil quality - the absorption of nutrients for plants decreases. Thermal desorption, on the other hand, is limited to removing volatile contaminants only. However, in the case of using microwave radiation, the reservations result primarily from health aspects and energy consumption. This method can also pose a safety risk, especially for the remediation of organic rich soil/bottom sediments. Falciglia and Vagliasindi (2014) [47] conducted research on the removal of diesel fuel from soil by means of microwave radiation with a power greater than 600 W. After 30 minutes of the process, almost 95% efficiency of removing these pollutants was achieved. Compared to the thermal desorption carried out in the rotary kiln, the energy consumption was 25% lower. This shows that the microwave method of bottom sediment/soil remediation can be a suitable alternative to conventional thermal methods. However, more research is still required, especially towards heat recovery, to minimize energy consumption. There are also some promising methods to remove a specific pollutant or group of substances in the literature, but these are ongoing studies that require additional analyzes. An example is the remediation of bottom sediments by resuspension [49], [50], in-situ removal of pesticides with the use of activated carbon and carbon nanotubes [40], and in-situ removal of petroleum substances with the use of zeolites in combination with microbial decomposition [51].

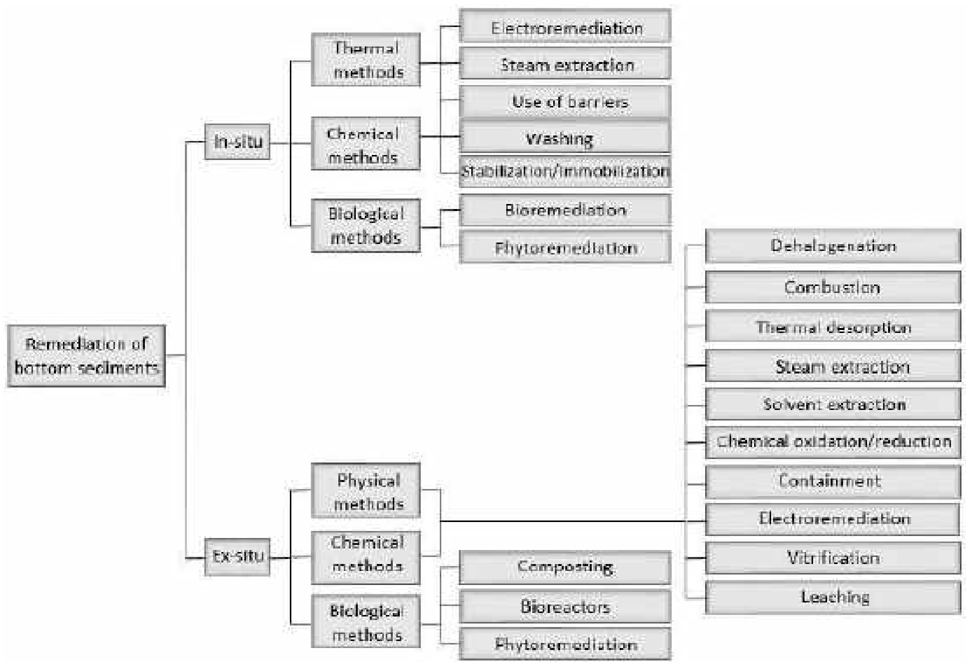

Fig. 1. Methods of remediation of bottom sediments [based on [41], [42]]

Nevertheless, biological methods are most often used to remove contaminants from bottom sediments. However, in many cases such solutions are impossible to apply because too high a content of hazardous organic substances and heavy metals is toxic to organisms. These substances prevent their development and, as a result, limit the possibility of removing pollutants from sediments [35], [52]. According to the studies by Gao and Chen (2008) [53], the content of phthalates in the soil at the level of about 100 mg/kg inhibits the growth of microorganisms and the activity of the catalase enzyme. In turn, Margesin et al. (2007) [54] showed that in soil samples, the increase in the diesel oil content from 2500 mg/kg to 20,000 mg/kg resulted in a 60% decrease in the efficiency of bioremediation. A similar result was obtained by Silva-Castro et al. (2015) [55]. The physical and chemical parameters of the analyzed soil also have a significant impact on the process of removing both diesel oil and other pollutants. Rahman et al. (2002) [56] showed that the optimal pH is 7.5 for the effective course of soil bioremediation from petroleum products (about 78%). Extreme pH values resulted in a reduction in the activity of soil microorganisms towards the degradation of these products. On the other hand, the optimum humidity should be about 80% of the water capacity, and the relative humidity should not be less than 15%. The limited availability of contaminants for cells also very often inhibits the bioremediation process. The best way to increase bioavailability is to use surfactants. Synthetic surfactants are commercially available, but many of them are of limited use, mainly due to their toxic effects and rapid degradation by bacteria, therefore microorganisms producing biosurfactants are increasingly used [57]. Among the tested compounds, the best results were obtained with the rinsing solutions containing rhamnolipids or cyclodextrins (a group of glycolipids). Dahrazma and Mulligan (2007) [58], using rhamnolipids to remove selected metals from bottom sediments, achieved 37% reduction in copper content, 13% zinc and 27% nickel. Similar results of 18% zinc removal in contaminated marine sediments were obtained by Mulligan et al. (2001) [59], while the copper removal efficiency was 65%.

Despite many advantages, biological methods require a long process time (even several years) to obtain satisfactory results in the removal of contaminants. In this case, physical, chemical or physicochemical methods can be used first for the treatment of bottom sediments, followed by biological methods. Research in this direction was carried out by, among others Wu et al. (2015) [60], who tested the suitability of solvent extraction and biodegradation to remove petroleum products from soil. About 90% of the impurities were removed after 15 minutes of extraction with a mixture of hexane and pentane (4:1, v/v%). The use of bioremediation as the next step lowered the content of petroleum substances to 97% after 132 days of the process duration. On the other hand, by combining electroremediation with biodegradation (electrobioremediation), after 14 days of the process, a 30% efficiency in the removal of petroleum products was achieved [61]. Ramirez et al. (2015) [62] removed 27% of these pollutants from a soil sample (initial oil content - 10 g/kg) using electrobioremediation. The authors conducted their research in the presence of a surfactant.

The use of chemical methods not only increases the bioavailability of hazardous and hardly biodegradable chemical compounds by reducing their toxicity, but also very often causes complete decomposition of pollutants into carbon dioxide and water. Advanced oxidation processes (AOPs) are especially recommended in this case. They are safe for the environment, which is a decisive advantage over other methods used. Unlike most methods, they do not transfer pollutants to another environment, but contribute to their degradation [37].

Their common feature is the production of highly reactive hydroxyl radicals ($HO^{\bullet}$), which have one of the highest oxidizing potentials (2.80 V). The effectiveness of this process depends mainly on the type and concentration of the substance to be removed and the presence of other organic and mineral compounds. Hydroxyl radicals react quickly and non-selectively with almost all organic compounds, leading to their mineralization. Therefore, other substances present in the bottom sediments will compete with each other for the possibility of reacting with them, acting as the scavenger of highly active HO radicals [19]. Various oxidation systems are used in advanced oxidation methods. Generally, they can be divided into three groups. The first includes chemical processes, which include oxidation with ozone, hydrogen peroxide or the simultaneous use of both of these reagents, the Fenton reaction with the use of iron (II) ions and hydrogen peroxide, supercritical water oxidation (SCWO), wet air oxidation (WAO) and ultrasound assisted Fenton's reagent. The second group includes processes using electromagnetic radiation using electrodes with high oxygen evolution overvoltage and electric-assisted Fenton's reagent. On the other hand, the third group includes photochemical processes, including photocatalytic degradation in aqueous semiconductor suspensions, Fenton's reagent assisted with UV light, processes such as UV/H_2O_2, UV/O_3, $UV/H_2O_2/O_3$ [63].

Currently, there are several patents on the international market that are designed to remove contaminants from bottom sediments. In 2007, the technology of soil and bottom sediment treatment from heavy metals was developed for ex-situ application using advanced oxidation methods (code: SI22156) [64].

The available literature data indicate that this technology has also been used, among others, in for removing PCBs, pesticides, dioxins and hydrocarbons. Research on the removal of phthalates by this method is sparse and incomplete, especially in bottom sediments. Besides, like every method, also this one has its limitations, which is why new and better solutions are constantly searched for. In order to obtain satisfactory final results, in many cases it is necessary to use several methods together [65].

Management of bottom sediments can be an effective method of obtaining profits greater than the costs incurred for their removal from water reservoirs, especially since the storage of excavated sediments generates huge costs and poses a risk of secondary environmental pollution. The deposition of bottom sediments on land in atmospheric conditions leaches many hazardous substances into the natural environment, consequently leading to the pollution of surface and ground waters. On the other hand, the use of excavated bottom sediments allows to save natural land, which is of great importance from the point of environmental protection [16], [32].

MANAGEMENT METHODS OF EXCAVATED BOTTOM SEDIMENTS

Agricultural management of bottom sediments

Bottom sediments are perceived as a valuable soil fertilizing material, because they are characterized by high sorption capacity, compact grain size, and a significant content of both organic matter and micro- and macronutrients [1]. The natural use of bottom sediments uncontrolled in terms of chemical composition, however, is associated with the risk of increasing the content of hazardous substances in the soil environment. Research on the possibility of agricultural management of bottom sediments was carried out, among others by [1], [12], [13], [33], [66], [67], [68], [69].

According to Madeyski and Tarnawski (2006) [66], the agricultural use of bottom sediments is influenced not only by the content of heavy metals and persistent organic pollutants, but also by the appropriate content of available forms of Mg, K and P, which prove the fertility of these sediments. Gałka and Wiatkowski (2010) [67] analyzed the quality of bottom sediments in the Młyny reservoir. The sediments were characterized by the properties typical for soils of high agricultural value (appropriate grain size and content of organic matter and macronutrients, pH in the range 6.9-7.4). Bottom sediments, characterized by an alkaline or neutral reaction, with a high content of loam and silty fractions, may improve the physical and chemical properties of light and acidic soils. Baran et al. (2009) [68] conducted a study in which they used bottom sediments from the reservoir located in Zesławice, characterized by a low content of heavy metals and alkaline reaction. In the two-year research period, an increase in the pH value was observed for the soils that contained the addition of bottom sediments in the amount of 5 and 10% in relation to the dry weight of the soil. Research was also conducted on the possibility of agricultural use of bottom sediment as an additive to light soil, based on its impact on the content of heavy metals in plants, based on the example of maize. The addition of bottom sediments in the amount of 5% reduced the content of heavy metals (Cu, Ni, Cd) in the above-ground biomass, which met the requirements for the content of heavy metals for good quality feed. According to the authors, this is due to the use of alkaline bottom sediments, which acted as a trap for heavy metals.

Based on the research conducted by Madeyski and Tarnawski (2006) [67], bottom sediments from the reservoirs in Krempna, Zesławice and Majdan Sopocki also met the requirements for agricultural and even horticultural management. The excavated sediments from the reservoir in

Wilcza Wola also did not pose a threat to the soil and water environment and could be used to improve the quality of soil in green areas and agricultural lands [12]. In turn, bottom sediments extracted from the Bydgoszcz Canal were characterized by the quality of land located in industrial and communication areas, excluding their use in agriculture without treatment [70]. Also bottom sediments from the dam reservoir in Rzeszow, the quality of which was analyzed in the studies by Baran and Tarnawski (2012) [34] and Bartoszek et al. (2015) [20], should be stored under controlled conditions due to the risk of leaching of pollutants during the storage of previously untreated sludge. The most threatened by pollution are bottom sediments in reservoirs located in highly industrialized areas. In the bottom sediments of the Rybnik reservoir, the presence of cadmium was recorded, the share of which in the total pollution amounted to over 70%, disqualifying the possibility of using the bottom material before prior treatment. Bottom sediments can also be used as a material for the reclamation of industrially degraded areas or constitute the foundation of a new layer of soil formed on coal and slag heaps, and a layer covering unexploited landfills that have undergone rehabilitation [13].

Management of bottom sediments in construction

The excavated bottom sediments are also a valuable geotechnical material that could be used for various types of earth structures, in particular for the construction of road embankments, mineral screens in landfills and hydrotechnical structures such as flood embankments, dykes, earth dams. However, bottom sediments must not contain harmful substances or should be properly cleaned beforehand [71], [72], [73].

Bottom sediments to be used in construction must primarily meet the geotechnical criteria. When selecting materials for the construction of embankments, parameters such as grain size, resistance to crushing, plasticity, cohesion, content of organic parts, presence of water-soluble substances, resistance to weathering and susceptibility to volumetric changes are important. For the construction of insulation screens in landfills, an important criterion is also a suitably low water permeability (filtration coefficient), because they are designed to prevent the migration of leachates to the natural environment, as well as groundwater to the interior of the landfill [71], [72]. For this purpose, the bottom sediments of the Rożnów Reservoir were analyzed and the results showed that they can be used to form the lower part of the mineral barrier [74]. Based on the research of geotechnical properties carried out by Koś and Zawisza (2012) [73], also sediments from the Rzeszow Reservoir can be used to form sealing screens in municipal landfills. However, in terms of their usefulness in road construction, they were stabilized with lime and cement in order to improve geotechnical properties. Positive results were obtained when lime was used as a stabilizing material. In the absence of an appropriate material, methods are often used to improve the properties of the soil by adding, inter alia, lime, cement, bentonite, fly ash, as well as through moisture control, geotextile reinforcement and supplementing the graining characteristics with additives of other soils [71]. An economical solution is also to use soil material closest to the construction site, as it allows to reduce investment costs [71], [73].

Other methods of bottom sediment management

Bottom sediments were also successfully used as a binding material in biocomponents, such as sawdust or bagasse, which made it possible to obtain material with high energy parameters. It is also possible to obtain energy from the combustion of bottom sediments or from the production of biogas. The production of biogas from bottom sediments is possible due to the high calorific value. Additionally, the research results confirm that bottom sediments are a natural source of gases: methane, carbon dioxide and nitrogen [16].

In recent years, there has been a growing interest in the use of natural materials such as bottom sediments, natural silicates or sand as effective catalysts in the oxidation of organic compounds or their use in the production of heterogeneous catalysts. For example, Rahman et al. (2007) [75] used marine sediments as supports for the TiO_2 catalyst. These sediments included SiO_2 (51.09%), Al_2O_3 (16.54%), CaO (13.41%), Fe_2O_3 (5.63%), K_2O (3.52%), MgO (2.35%), Na_2O

(1.58%) and TiO_2 (0.57%). This material was selected due to the high content of SiO_2 and Al_2O_3. The obtained catalysts were used in the photocatalytic process of humic acid degradation, obtaining a high degree of mineralization. In recent years, there has been an increase in the number of literature reports on the method of producing heterogeneous catalysts from natural clay materials whose chemical (oxide) composition is similar to that of bottom sediments.

Idrissi et al. (2014) [76] modified natural clay with the following chemical composition: SiO_2 (37.86%), Al_2O_3 (10.43%), Fe_2O_3 (4.65%), MnO (0.06%), MgO (2.52%), CaO (18.72%), Na_2O (0.26%), K_2O (2.34%) by impregnation with $Cu(NO_3)_2$ salt. The obtained catalysts, rich in Cu (II) ions, were used to effectively decolorize the solution containing methyl orange in a modified Fenton process. The same material was also impregnated with $FeCl_3{\cdot}6H_2O$, thanks to which heterogeneous iron-rich catalysts were obtained, which were used in the degradation of the dye (crystal violet), also in the Fenton process. Complete mineralization of the dye was achieved after 10 minutes of reaction, using the catalyst containing 5% Fe.

The composition of bottom sediments is very similar to the naturally occurring materials used as heterogeneous Fenton catalysts. An obstacle to the direct use of bottom sediments, e.g. for agricultural or natural purposes, may be high pollution, including heavy metals. Metals deposited in sediments, including heavy metals, which are treated as impurities, can be used in chemical reactions. The ions of many of these metals exhibit catalytic activity, i.e. they can be used in catalytic reactions. An example is the Fenton reaction in which transition metal ions are used as a catalyst. Therefore, bottom sediments containing these metals (e.g. Fe, Mn, Cu) are their natural source. In the case of bottom sediments, it is possible to use them directly or as a substrate for the immobilization of metal ions. The advantage of bottom sediments is that it is an easily available and cheap material [42]. The approach of using natural materials in catalytic processes is not only in line with sustainable chemistry. The technology using natural material can be successfully used for environmental remediation, without creating additional risks resulting from the dosing of unnecessary chemicals into the environment. The use of naturally occurring material makes it possible to apply it in-situ [42].

CONCLUSION

Monitoring the pollution of bottom sediments allows for early identification of undesirable changes in the aquatic ecosystem and for taking measures to reduce and eliminate pressures and negative environmental impacts. In addition, determining the chemical composition of the sediment is important not only in assessing the degradation of the aquatic ecosystem, but also in determining the management options of the excavated sediment. It is especially important for small water reservoirs due to the quick silting process and the necessity to periodically remove them. Due to the contamination of the extracted matter with organic compounds and heavy metals, its management is a significant problem.

The choice of the bottom sediment management method depends on their physicochemical properties. It is possible to use uncontaminated bottom sediments for agriculture, construction, thermal energy production and chemical processes. The use of bottom sediments in chemical processes is an alternative way of managing excavated bottom sediments containing high concentrations of heavy metals. The composition of bottom sediments also allows them to be used to immobilize heavy metals and obtain heterogeneous sediments/catalysts of different composition.

Most anthropogenic chemicals, such as pesticides, phthalic acid esters, polycyclic aromatic hydrocarbons and many others, are poorly disposed of by conventional processes. As a result, new technologies are implemented, based in particular on the concept of green technology. The introduction of the principles of green chemistry results in the search for ways to widely implement safe oxidants, minimizing the use of non-renewable catalysts and auxiliary substances. The pillar of green chemistry are the processes of advanced oxidation, which are also one of the effective methods of removing micropollutants.

REFERENCES

1. Gałka B., Assessment of the degree of pollution and the possibility of managing bottom sediments from small water objects in the park in Wrocław-Pawłowice. Protection of the environment and natural resources, vol. 42, pp. 233-239, 2010.

2. Bojakowska I., The geochemistry of surface sediments in the Baltic Sea. Chapter 2.4. Polish Geological Institute - National Research Institute, edited by S. Uścinowicz, Warsaw, 2011.

3. Tarnawski M., Baran A., Jasiewicz C., Assessment of the physical and chemical properties of bottom sediments of the Chańcza reservoir. Proceedings of ECOpole, vol. 6(1), pp 305-311, 2012.

4. Fonti V., Dell'Anno A., Beolchini F., Does bioleaching represent a biotechnological strategy for remediation of contaminated sediments? Science of the Total Environment, vol. 563, pp 302-319, 2016.

5. Szydłowski K., Podlasińska J., Characteristics of bottom sediments of ponds. Ecological Engineering, vol. 47, pp 40–46, 2016.

6. Rzętała M.A., Selected geomorphological changes in the basins of water reservoirs and the assessment of pollution of reservoir sediments under conditions of differentiated anthropopressure (on the example of the Upper Silesia and Zagłębie region), Katowice, pp 76-80, 2014.

7. Bojakowska I., Sokołowska G., Geochemical purity classes of water sediments. Geological Review, vol. 46(1), pp 49-54, 1998.

8. Malina G., Elimination of the threat to the soil and water environment in polluted areas. Polish Association of Sanitary Engineers and Technicians, Branch in Wielkopolska, Poznań, 2011.

9. Koś K., Zawisza E., Stabilization of bottom sediments from Rzeszowski Reservoir, Annals of Warsaw University of Life Sciences – SGGW Land Reclamation, vol. 47(2), pp 127-137, 2015.

10. Gorączko M., Woziwodzki Z., Zawalski A., Dzieweczyński P., Assessment of the possibility of cleaning the bottom of the water reservoir by means of a pipe drain in the body of the dyke. Journal of Civil Engineering, Environment and Architecture JCEEA, vol. 63 (1/II/16), pp 9-16, 2016.

11. Zawadzki P., Błażejewski R., Pawlak M. Review of desludging methods of water reservoirs.Acta Scientiarum Polonorum. Formatio Circumiectus, vol. 16(2), pp 217-228, 2017.

12. Tarnawski M., Michalec B., Quantitative and qualitative characteristics of bottom sediments of the water reservoir in Wilcza Wola. Infrastructure and Ecology of Rural Areas, vol. 3(1), pp 31-43, 2006.

13. Madeyski M., Michalec B., Tarnawski M., Silting of small water reservoirs and the quality of bottom sediments. Infrastructure and Ecology of Rural Areas, vol. 11, 2008.

14. Hartung F., Cause and prevention of silting up of reservoirs in dams. Water management, vol. 1, pp. 3-13, 1959.

15. Gajewska M., Kopeć Ł., Obarska-Pempkowiak H., Operation of small wastewater treatment facilities in a scattered settlement. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), vol. 13(1), pp 207-225, 2011.

16. Maj K., Koszelnik P., Methods of managing bottom sediments.Journal of Civil Engineering, Environment and Architecture JCEEA, vol. 63 (2/I/16), pp 157-169, 2016.

17. Mielczarek M., Szydłowski K., The role, division and quality classification of bottom sediments of water reservoirs. Ecological Engineering, vol. 18(3), pp 194-201, 2017.

18. Piekarski J., Dąbrowski T., Numerical method of assessing the sorption of pollutants from wastewater. Mineral Resource Management, vol. 25, pp 101-117, 2009.

19. Włodarczyk–Makuła M., Selected organic micropollutants in waters and soils. Publishing House of the Częstochowa University of Technology, Częstochowa, 2013.

20. Bartoszek L., Koszelnik P., Gruca–Rokosz R., Kida M., Assessment of agricultural use of the bottom sediments from eutrophic Rzeszów reservoir. Rocznik Ochrony Środowiska, vol. 17, pp 396-409, 2015.

21. Kida M., Koszelnik P., Occurrence of phthalates and surfactants in the environment. Journal of Civil Engineering, Environment and Architecture, vol. 62(1), pp 279-298, 2015.

22. Chemical Abstract System (CAS). Website: http://www.cas.org/index, dostęp: marzec 2021.

23. Directive 2000/60 / EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy (Water Framework Directive).

24. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC , 84/491/EEC and 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.

25. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2008/105/EC and 2000/60/EC as regards priority substances in the field of water policy.

26. Pawłowski J., Rozental M., Drzewińska A., Neffe, S., Speciation analysis of bottom sediments collected in the Kampinos National Park. Bulletin of the Military University of Technology, vol. 63(4), pp 113-134, 2014.

27. Kida, M., Ziembowicz, S., Koszelnik, P., Bottom sediments - their role and importance in the environment. Gospodarka Wodna, vol. 10, pp 13-20, 2019.

28. Podlasińska J., Szydłowski K., Characterization of concentrations of selected heavy metals in the bottom sediments of Lake Byszyno and determination of their potential environmental threat. Water-Environment-Rural Areas, vol. 17, 2017.

29. Aleksander-Kwaterczak U., Distribution of trace metals in sediment cores of selected Polish rivers. AGH University of Science and Technology Publications, 2007.

30. Kasperek R., Rosik–Dulewska C., Wiatkowski M., Studies of bottom sediments in the area of the border meanders of the Upper Odra. Rocznik Ochrona Środowiska, vol. 9, pp 293-302, 2007.

31. Bełdowski J., European Arctic - Marine Use Guide. Chemical exchange between water and sediments, Institute of Oceanology of the Polish Academy of Sciences, Sopot, 2012.

32. Siebielec S., Siebielec G., Smreczak B., River bottom sediment pollution and reservoirs. Studies and Reports of IUNG-PIB, vol. 46(20), pp 163-181, 2015.

33. Ciesielczuk T., Kusza G., Karwaczyńska U., Natural use of bottom sediments in the light of applicable regulations. Rocznik Ochrona Środowiska, vol. 13, pp 1327-1337, 2011.

34. Baran A., Tarnawski M., The content of heavy metals in water extracts prepared from bottom sediments of the Rzeszów reservoir. Proceedings of ECOpole, vol. 6(2), pp 671-675, 2012.

35. Agarwal A., Liu Y., Remediation technologies for oil-contaminated sediments. Marine pollution bulletin, vol. 101(2), pp 483–490, 2015.

36. Akcil A., Erust C., Ozdemiroglu S., Fonti V., Beolchini F., A review of approaches and techniques used in aquatic contaminated sediments: metal removal and stabilization by chemical and biotechnological processes. Journal of Cleaner Production, vol. 86, pp 24–36, 2015.

37. Lim M. W., Von Lau E., Poh P. E., A comprehensive guide of remediation technologies for oil contaminated soil—present works and future directions. Marine pollution bulletin, vol. 109(1), pp 14–45, 2016.

38. Trellu C., Mousset E., Pechaud Y., Huguenot D., Van Hullebusch E. D., Esposito G., Oturan M. A., Removal of hydrophobic organic pollutants from soil washing/flushing solutions: a critical review. Journal of hazardous materials, vol. 306, pp 149–174, 2016.

39. Falciglia P. P., Malarbì D., Maddalena R., Greco V., Vagliasindi F. G., Remediation of Hg – contaminated marine sediments by simultaneous application of enhancing agents and microwave heating (MWH). Chemical Engineering Journal, vol. 321, pp 1–10, 2017.

40. Morillo E., Villaverde J., Advanced technologies for the remediation of pesticide-contaminated soils. Science of the Total Environment, vol. 586, pp 576–597, 2017.

41. Wang M., Zhu Y., Cheng L., Andserson B., Zhao X., Wang D., Ding A., Review on utilization of biochar for metal–contaminated soil and sediment remediation. Journal of Environmental Sciences, vol. 63, pp 156–173, 2018.

42. Kida, M., Ziembowicz, S., Koszelnik, P., Methods of removing persistent organic pollutants from bottom sediments. Instal, vol. 6, pp 49-55, 2019.

43. Anthony E. J., Wang J., Pilot plant investigations of thermal remediation of tar–contaminated soil and oil–contaminated gravel. Fuel, vol. 85(4), pp 443–450, 2006.

44. Li D., Zhang Y., Quan X., Zhao Y., Microwave thermal remediation of crude oil contaminated soil enhanced by carbon fiber. Journal of Environmental Sciences, vol. 21(9), pp 1290–1295, 2009.

45. Chang H. J., Jou C. J. G., Lee C. L., Treatment of heavy oil contaminated sand by microwave energy. Environmental Engineering Science, vol. 28(12), pp 869–873, 2011.

46. Tatàno F., Felici F., Mangani F., Lab–scale treatability tests for the thermal desorption of hydrocarbon-contaminated soils. Soil and Sediment Contamination: An International Journal, vol. 22(4), pp 433–456, 2013.

47. Falciglia P. P., Vagliasindi F. G. A., Remediation of hydrocarbon-contaminated soils by ex situ microwave treatment: technical, energy and economic considerations. Environmental technology, vol. 35(18), pp 2280–2288, 2014.

48. Acharya P., Ives P., Incineration at Bayou Bounfouca remediation project. Waste Management, vol. 14(1), pp 13–26, 1994.

49. Pourabadehei M., Mulligan C. N., Resuspension of sediment, a new approach for remediation of contaminated sediment. Environmental pollution, vol. 213, pp 63–75, 2016.

50. McGoldrick D. J., Pelletier M., de Solla S. R., Marvin C. H., Martin P. A., Legacy of legacies: Chlorinated naphthalenes in Lake Trout, Walleye, Herring Gull eggs and sediments from the Laurentian Great Lakes indicate possible resuspension during contaminated sediment remediation. Science of The Total Environment, vol. 634, pp 1424–1434, 2018.

51. Zhao G., Sheng Y., Wang C., Yang J., Wang Q., Chen L., In situ microbial remediation of crude oil-soaked marine sediments using zeolite carrier with a polymer coating. Marine pollution bulletin, vol. 129(1), pp 172–178, 2018.

52. Płaza G., Nałęcz–Jawecki, G., Ulfig K., Brigmon R.L., The application of bioassays as indicators of petroleum-contaminated soil remediation. Chemosphere, vol. 59, pp 289–296, 2005.

53. Gao J., Chen B. Q., Effects of PAEs on soil microbial activity and catalase activity. Journal of Soil and Water Conservation, vol. 22, pp 166–169, 2008.

54. Margesin R., Hämmerle M., Tscherko D., Microbial activity and community composition during bioremediation of diesel-oil-contaminated soil: effects of hydrocarbon concentration, fertilizers, and incubation time. Microbial Ecology, vol. 53(2), pp 259-269, 2007.

55. Silva–Castro G. A., Uad I., Rodríguez–Calvo A., González–López J., Calvo C., Response of autochthonous microbiota of diesel polluted soils to land–farming treatments. Environmental research, vol. 137, pp 49–58, 2015.

56. Rahman K. S. M., Thahira–Rahman J., Lakshmanaperumalsamy P., Banat I. M., Towards efficient crude oil degradation by a mixed bacterial consortium. Bioresource technology, vol. 85(3), pp 257–261, 2002.

57. Podsiadło Ł., Krzyśko–Łupicka T., Techniques of bioremediation of petroleum substances and methods of assessing their effectiveness. Environmental Engineering and Protection, vol. 16, 2013.

58. Dahrazma B., Mulligan C. N., Investigation of the removal of heavy metals from sediments using rhamnolipid in a continuous flow configuration. Chemosphere, vol. 69(5), pp 705–711, 2007

59. Mulligan C. N., Yong R. N., Gibbs B. F., Heavy metal removal from sediments by biosurfactants. Journal of hazardous materials, vol. 85(1–2), pp 111–125, 2001.

60. Wu G., Zhu X., Ji H., Chen D., Molecular modeling of interactions between heavy crude oil and the soil organic matter coated quartz surface. Chemosphere, vol. 119, pp 242–249, 2015.

61. Mena E., Villaseñor J., Cañizares P., Rodrigo M. A., Effect of a direct electric current on the activity of a hydrocarbon-degrading microorganism culture used as the flushing liquid in soil remediation processes. Separation and Purification Technology, vol. 124, pp 217–223, 2014.

62. Ramírez E. M., Jiménez C. S., Camacho J. V., Rodrigo M. A. R., Cañizares P., Feasibility of coupling permeable bio-barriers and electrokinetics for the treatment of diesel hydrocarbons polluted soils. Electrochimica Acta, vol. 181, pp 192–199, 2015.

63. Barbusiński K., Intensification of the wastewater treatment process and stabilization of excess sludge with the use of Fenton's reagent. Science notebooks. Environmental Engineering/Silesian University of Technology, vol. 50, pp 7–169, 2004.

64. European Patent Office, ep.espacenet.com. 2014.

65. Reis E., Lodolo A., Miertus S., Survey of sediment remediation technologies: International Centre for Science and High Technology (ICS). Google Scholar, 2007.

66. Madeyski M., Tarnawski M., Assessment of the ecological state of bottom sediments of selected small water reservoirs. Infrastructure and Ecology of Rural Areas, vol. 4(3), pp 107-116, 2006.

67. Gałka B., Wiatkowski M., Characteristics of bottom sediments of the Młyny dam reservoir and the possibility of agricultural use. Water-Environment-Rural Areas, vol. 4(32), pp 53-63, 2010.

68. Baran A., Jasiewicz C., Tarnawski M., Influence of reservoir bottom sediment on changes in physical and chemical properties of light soil. Proceedings of ECOpole, vol. 3(2), pp 403-408, 2009.

69. Baran A., Jasiewicz C., Tarnawski M., Effect of bottom sediments collected from the Besko reservoir on the yield and macronutrient content in maize biomass. Proceedings of ECOpole, vol. 7(1), pp 194-198, 2013.

70. Bojakowska, I., Dobek, P., Wołkowicz, S., Trace elements in the Bydgoszcz Canal sediments. Mining and Geology, vol. 5(4), pp 41-50, 2010.

71. Gwóźdź R., Properties of the cohesive sediments of Lake Rożnów in terms of their geotechnical use. PhD thesis. Cracow University of Technology, 2007.

72. Kozielska–Sroka E., Chęć M., Properties of bottom sediments of Lake Czorsztyn in terms of their use in earth construction. Mining and Geoengineering, vol. 33(1), pp 369-376, 2009.

73. Koś K., Zawisza E., Assessment of the suitability of bottom sediments of the Rzeszów reservoir for the construction of seals in municipal landfills. Acta Sci. Pol., Formatio Circumiectus, vol. 11(4), pp 49-60, 2012.

74. Gwóźdź R., Geotechnical properties of sediments deposited in Lake Rożnowskie and the possibility of their use for the construction of mineral screens in municipal landfills. Technical Journal, vol. 1, pp 13-23, 2008.

75. Rahman M.A., Kaneco S., Suzuki T., Katsumata H., Ohta K., Alam A.S., Development of sintering materials by sea sediments and TiO_2 for the cleaning technology. Pakistan Journal of Analytical and Environmental Chemistry, vol. 8(1-2), pp 26-35, 2007.

76. Idrissi M., Miyah Y., Lahrichi A., Chaouch M., Zerrouq F., Preparation and Characterisation A Catalytic System Cu-Clay for Catalytic Oxidation of Methyl Orange with H_2O_2. International Journal of Innovative Research in Science, Engineering and Technology, vol. 3, pp 17359-17369, 2014.

TRENDS IN THE FORMATION OF SNOW COVER AGAINST THE BACKGROUND OF GLOBAL CLIMATE CHANGES (ACCORDING TO OBSERVATIONS AT THE UKRAINIAN ANTARCTIC STATION "ACADEMIC VERNADSKY")

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ABSTRACT

In order to obtain the characteristics of the snow cover, and to identify its changes and their main trends, in this work, using mathematical and statistical methods, we analyzed snow observation data at the meteorological site of the Ukrainian Antarctic station "Academic Vernadsky" for the period 1997-2020. The obtained results indicate a significant shift in the time boundaries of the period of occurrence of the snow cover, as well as the structure of its deposition, which may be evidence of changes in the nature of atmospheric processes. Attention should be paid to the fact that after 2005 there have been changes in the structure of formation of the snow cover at the area of Academic Vernadsky polar research base: this process has become slower, especially in the first half of winter. At the same time, the total amount of precipitation to the end of the snow accumulation season remains relatively stable. As a result of the study, it was possible to identify the long-term component of the snow cover height, the period of which is 11.03 years with overtones of 5 and 2.5 years, the analysis of which indicates a possible effect on formation of the snow mass in the studied area of the El Niño phenomenon. The results should be used in developing weather forecast models.

Keywords: snow cover height, snow mass growth, harmonics, amplitudes, phases.

INTRODUCTION

Snow is a product of atmospheric processes, therefore, the characteristics of the snow cover have a significant amount of information about the processes themselves: their power, nature, spatial and temporal scales, etc. Unlike other weather parameters, which are instantaneous or discrete, the snow cover remains for a certain time on the underlying surface, thereby opening up wider prospects to its researchers. Based on regional characteristics, as well as modern climate changes, it can be assumed that its characteristics undergo changes and require constant updating, especially in the Polar Regions.

Snow cover in the area of the Ukrainian Antarctic Station (UAS) “Academic Vernadsky” persists for most part of the year, and in some cases − the whole year. Therefore, its influence on the weather conditions of the region and their formation is extremely significant, which, accordingly, increases interest in the study of snow cover [4, 7-9, 11, 13]. Being a product of atmospheric precipitation, snow cover, in turn, significantly affects them, primarily as a component of the water and radiation balance of certain territories [1, 2, 17, 18].

Snow is the main component the glacial mass gains. According to the estimates by many scientists (Velicogna 2009; Mouginot et al. 2019; Rignot et al. 2019) [19, 20, 22] the ice sheets today are significantly reduced due to thawing. Thus, the study of snow is important for explaining the mass balance of glaciers.

Quantifying snow precipitation in Antarctica faces many unique challenges such as wind and other technical difficulties due to the harsh environment. In view of the logistic difficulty in obtaining reliable snow measurements, researchers have resorted to using other means, like satellite observations, reanalysis data sets and climate models [15]. But direct measurement of snow precipitation in Antarctic using ground-based instruments is important to validate the results from climate models, reanalyses and satellite observations. This study analysed snow measurements and these data of measurement can be used as a standard for validating snow observations from satellites and the long-term results obtained from climate models and reanalysis data sets.

METHODS AND EXPERIMENTAL PROCEDURES

The study of the characteristics and conditions of formation of the snow cover in the above-mentioned area was began from the beginning of the operation of British station Faraday − from the middle of the twentieth century [3, 21]. In the work, using by physical and statistical methods, analyzed the data of daily observations of the snow cover height obtained at the meteorological playground of the Ukrainian “Academic Vernadsky” polar research base (65°14′44″S, 64°15′28″W) from 1997 to 2020, which made with 2 stationary snow depth gauges.

The available series of instrumental observation data for precipitation at Antarctica are extremely limited, which is associated, first of all, with the late discovery of the continent, as well as with the limited logistics operations in the region even today. In the course of the work, well-known methods of mathematical and statistical analysis were used, implemented through the built-in functions of the software Microsoft Excel, Statistica from StatSoft Inc., Surfer from Golden Software LLC.

To analyze the observational data in order to identify the components of the precipitation variability, a harmonic analysis technique was used, i.e. there were obtained trigonometric functions (harmonics) that were multiples of the series length. In this case, the harmonic equation has the following form:

$$G_k = A_k \cdot \cos(\omega_k \cdot t - \varphi_k), \qquad \omega_k = 2 \cdot \pi / T_k \qquad (1),$$

where k is the harmonic number, A_k – k^{th} harmonic amplitude, ω_k – k^{th} harmonic frequency, T_k – k^{th} harmonic period, φ_k – k^{th} harmonic phase, t – time (Brooks 1953).

Full expansion in a Fourier series involves the determination of harmonics, in the amount of *N/2*, where *N* is the series length. Harmonic characteristics are determined by finding the Fourier coefficients a_k and b_k are given as:

$$a_k = 2 \div N * \sum_{i=1}^{N} [x_i * \sin(\omega_k * t_i)],\ b_k = 2 \div N * \sum_{i=1}^{N} [x_i * \cos(\omega_k * t_i)] \qquad (2)$$

With the aim of the Fourier coefficients calculation by the linear regression method in Microsoft Excel, the sines and cosines of harmonics for a certain date were calculated as used by (Blattner et al.1999):

$$\sin_i = \sin(i \cdot \Omega \cdot date),\ \cos_i = \cos(i \cdot \Omega \cdot date) \qquad (3),$$

where $\Omega = \frac{2 \quad \pi}{T}$; *date* – date corresponding to the source series value.

The linear regression equations were estimated using the coefficient of determination (Kd) R^2, which is the proportion of the variance in the dependent variable that is predictable from the independent variable(s). The significance of the coefficients was checked by using t-Student's criterion. The F-statistic was used to determine whether the observed relationship between the dependent and independent variables was random.

THE RESEARCH RESULTS AND DISCUSSIONS

Snow cover is one of important elements of the environment. The research area is characterized by unstable weather conditions, which are formed under the influence of marine air mass (Averyanov 1990; Sedunov 1991; Bogdanova et al. 2007; Klok 2010, 2013). With unstable weather, often in winter there is precipitation both in the liquid and in the solid phase, which affects the quality of precipitation measurement. In this work, we analyzed the data of daily snow precipitation amounts as well as about daily snow depth.

It has been established that the formation of a snow mass of 2-3 m high in the region occurs under relatively warm conditions (average January temperature of 0.7 °C, the sum of the temperatures of the winter months is -23.7 °C) and during long (6-7 months) winter. Therefore the snow cover has distinctive features. In particular, snow falls wet, its temperature is close to 0 °C, the dynamic factor increases its density to 0.5 g/cm^3 and higher. It is formed by the compaction type, which indicates the predominance of the destructive metamorphism processes − especially at the initial stage. In the subsequently, there is an intensification of the constructive metamorphism processes, although, due to an increase in wind load during snowfalls and a fairly loyal temperature regime, they are somewhat limited.

The greatest practical interest, taking into account the planning of economic activities, is the analysis of main dates of the snow mass formation during the year: the dates of the beginning and the end of period of the snow deposition, the dates of the snow cover maximum thickness, the dates of the period of maximum increments of the snow mass, as well as the dates of formation of its main layers [1-2]. At the UAS “Academic Vernadsky” meteorological site, daily observations of the snow height have been constantly recorded since 1997 [7-15]. The accumulated material makes it possible to analyze the dynamics of dates of the beginning and the end of existence of the snow cover and make conclusions about the duration of the existence of the snow cover (Fig. 1).

As can be seen from fig. 1, during the 24-year (1997-2020) observation period, there is a clear tendency to shift the timing of beginning of the permanent snow cover formation to later, and its complete destruction − to earlier dates. If at the beginning of the studied period the formation of snow cover was observed in March, today it is stable in April.

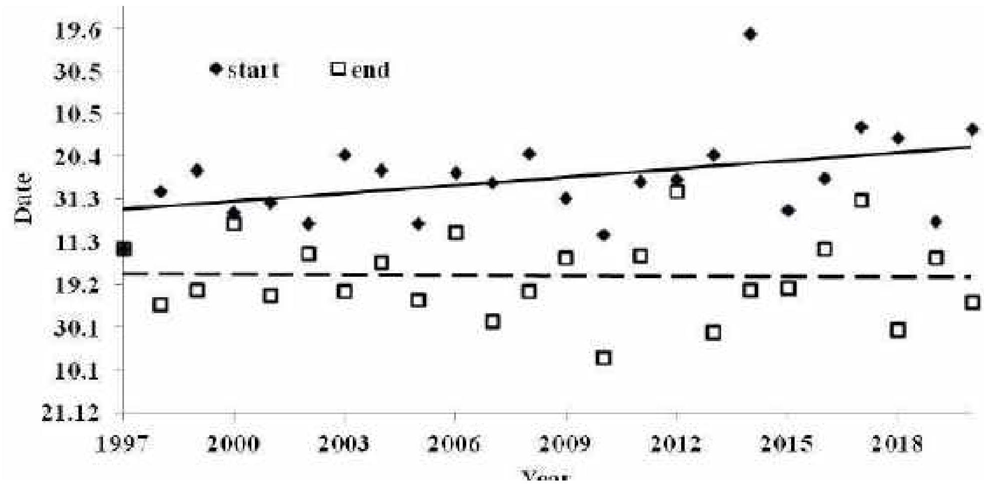

Fig. 1. Dynamics of dates of the beginning and the end of snow cover period at the meteorological site of the UAS "Academic Vernadsky"

The average dates for the destruction of snow cover also shifted, although somewhat less − from the third decade of February to mid-February. As a result, we have a stable tendency to decrease of snow cover occurrence period in the study area. More details of formation of the snow cover and its statistical characteristics are reflected in Table 1. It should be noted that the coefficient of determination (R^2) is the most effective estimate of the regression model and shows how the obtained result describes the observational data. At the same time, the F-statistic (Fisher's criterion) demonstrates how much the result obtained can be trusted − a confidence interval of 95% corresponds to a value of F-statistic more than 2.0 [5].

Table 1. Characteristics of stages of the snow cover formation at the meteorological site of the UAS "Academic Vernadsky" for 1997-2020

Phases' characteristics	Period, days	Average date		Trend, days per 10 years	Coefficient of determination	F-statistic	Uncertainty, days
		1997	2020				
the beginning of snow cover period	366.52	25.III	25.IV	12.70	18.10	4.860	0.6
the end of snow cover period	356.16	24.02	21.II	-0.80	0.09	0.019	0.6
the maximum of snow cover depth	365.55	24.X	1.XI	0.46	0.46	0.100	0.9

As already noted, the dates of the beginning of formation of the snow cover shifted most significantly. With a linear trend of 12.7 days over 10 years, a shift of 1 month occurred over a 24-year observation period (Fig. 2). An analysis of dates of the maximum snow cover for the period under study also showed their shift to later dates. However, the dates of maximum snow depth as well as the dates snow thawing have shifted less significantly.

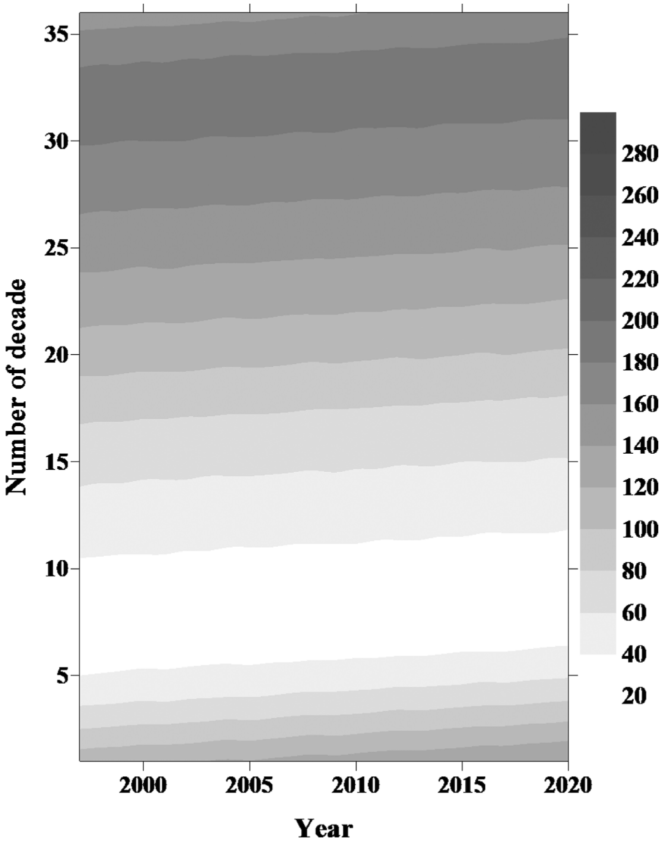

Fig. 2. Diagram of dates of the establishment of the maximum height of snow cover at the meteorological site of the UAS "Academic Vernadsky" for the period 1997-2020

Some statistical characteristics of dynamics of the shift in the date of the maximum height of snow cover, which were calculated in the course of this work, are reflected graphically in Table 2.

Table 2. Characteristics of dynamics of the intra-annual component of snow cover depth according to the observations at UAS "Academic Vernadsky" (1997-2020)

Duration of observation	Period, days	Uncertainty, days	Trend, cm per 10 years	R^2	F
1997-2020	365.8	0.6	2.7	0.66	1693.5

With the help of mathematical and statistical methods, we obtained the amplitudes and phases of harmonics of the intra-annual component of the snow depth, among which the next three were statistically significant − 57, 103 and 240 days (Fig. 3). The first two harmonics are characterize the initial period of formation of the snow cover, and the third − the period of maximum increments of the snow mass (late July − early August), which will be discussed below.

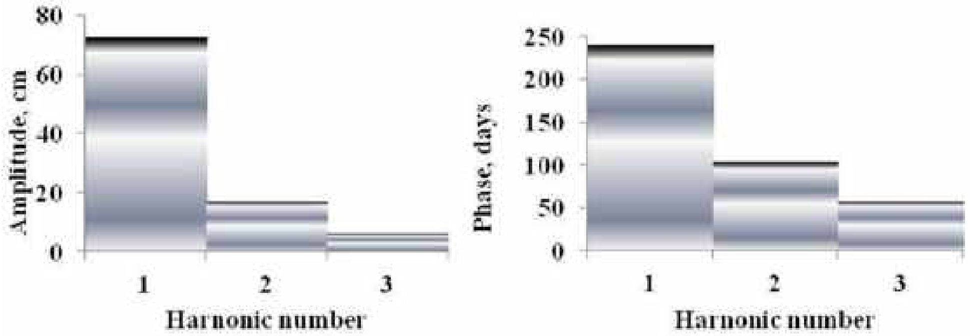

Fig. 3. Amplitudes and phases of seasonal component of the snow cover height according to the data of observations at UAS "Academic Vernadsky" for the period of observations 1997-2020

Accordingly, during 1997-2020 at area of UAS "Academician Vernadsky" there is a Fig. 4. Today, the maximum depth of the snow cover at UAS is fixed in early November.

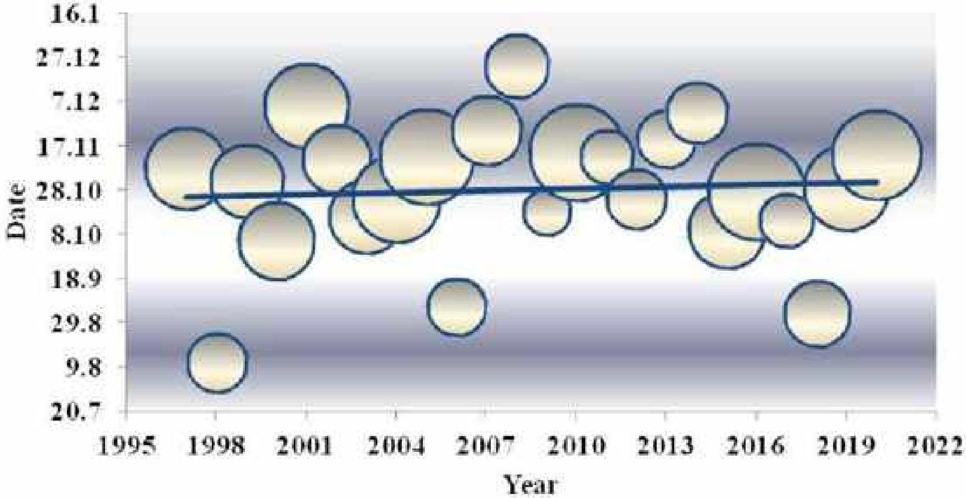

Fig. 4. Dates of maximum of the snow cover depth at the meteorological site of UAS "Academic Vernadsky" for the period 1997-2020

The long-term intra-annual distribution of the snow cover height and its increments is shown in Fig. 5.

It should be noted that the statistical analysis of increments of the snow cover height (in this case, the daily increments) makes it possible to identify the main periods of snow accumulation, during which the formation of various snow layers are occurs. Since snow is a type of atmospheric processes, these periods are especially clearly visible when comparing data on the amount of snowfall with the snow pits (vertical sections) of snow mass, the analysis of which is extremely informative [11, 12].

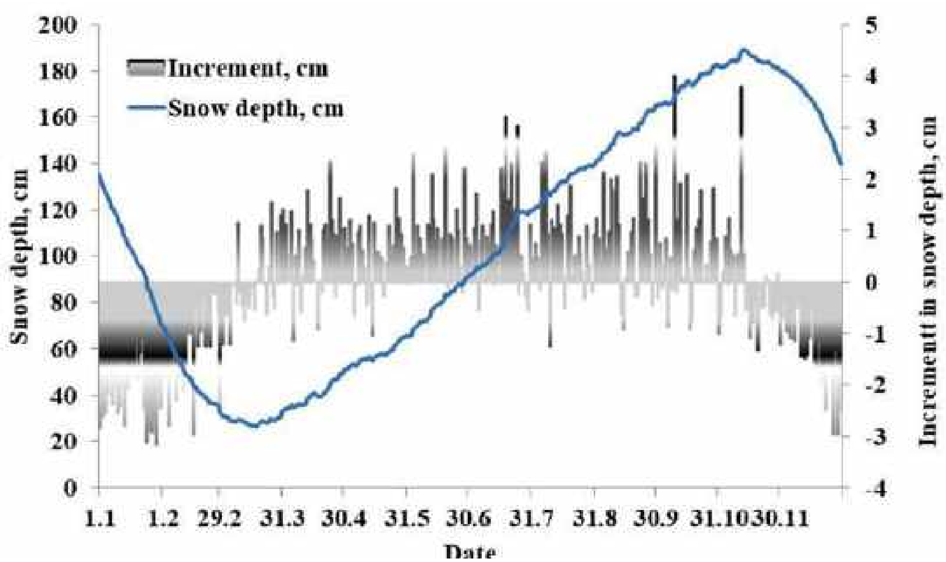

Fig. 5. Long-term seasonal distributions of the snow cover height and its daily increments at the UAS "Academic Vernadsky" meteorological site for the period 1997-2020

Analysis of the snow accumulation curve showed, that during the period from April to August are formed 6-8 stable layers (although in some unstable winters their number may be greater), the total height of which is about 250-260 cm. Because the layers are built by certain atmospheric processes, the dates of their formation from year to year are quite close. During the period of maximum snow growth (July-August) an avalanche-hazardous layer of insignificant vertical thickness is formed. The snow thawing time is characterized by 3-4 stable periods.

All of the above mentioned us to make an assumption about the presence of significant changes in the very process of formation of the snow mass at area of "Academic Vernadsky" polar research base, which is manifested in changes in the height of the snow cover at the UAS during 1997-2020, the dynamics of which is shown in Fig. 6.

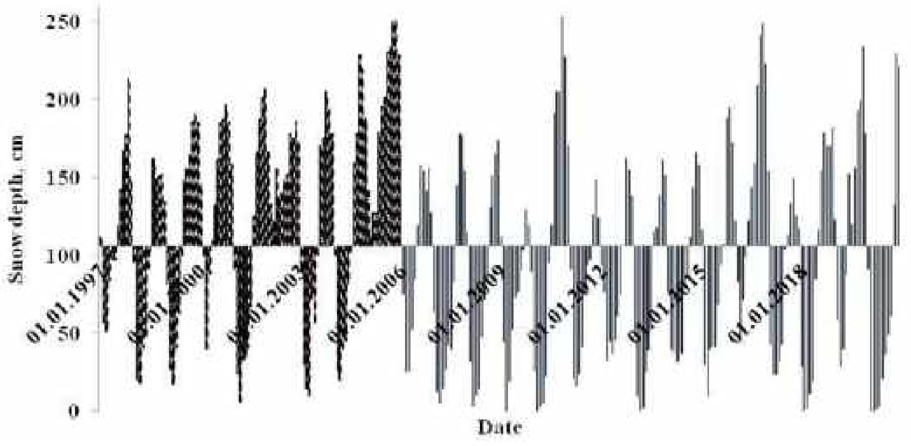

Fig. 6. Dynamics of height of the snow cover at the meteorological site of the UAS "Academician Vernadsky" for the observation period 1997-2020

On the background of variability of the intra-annual component of height of the snow cover, of interest is, first of all, the abrupt decrease in the values of this indicator and the duration of the period with snow after 2005; secondly, the presence of quasiperiodic components, which are clearly seen on given earlier Fig. 4.

The process of snow cover formation at the UAS "Academician Vernadsky" is shown in more detail in the following diagram (Fig. 7), which reflects the full distribution of the snow cover depth by months during all observation years. Changes in the structure of snow deposition since 2006 are obvious. The snow cover formation process in the first half of the winter season became slower and its height was less, although the amount of precipitation during the winter season remained practically unchanged. In this case, it may be logical to assume certain changes in the general atmospheric circulation system, in particular, the trajectories and power of cyclones that form the snow cover of the region. Also important are the role of other factors that cause snow compaction and a change of aggregate state of the precipitation.

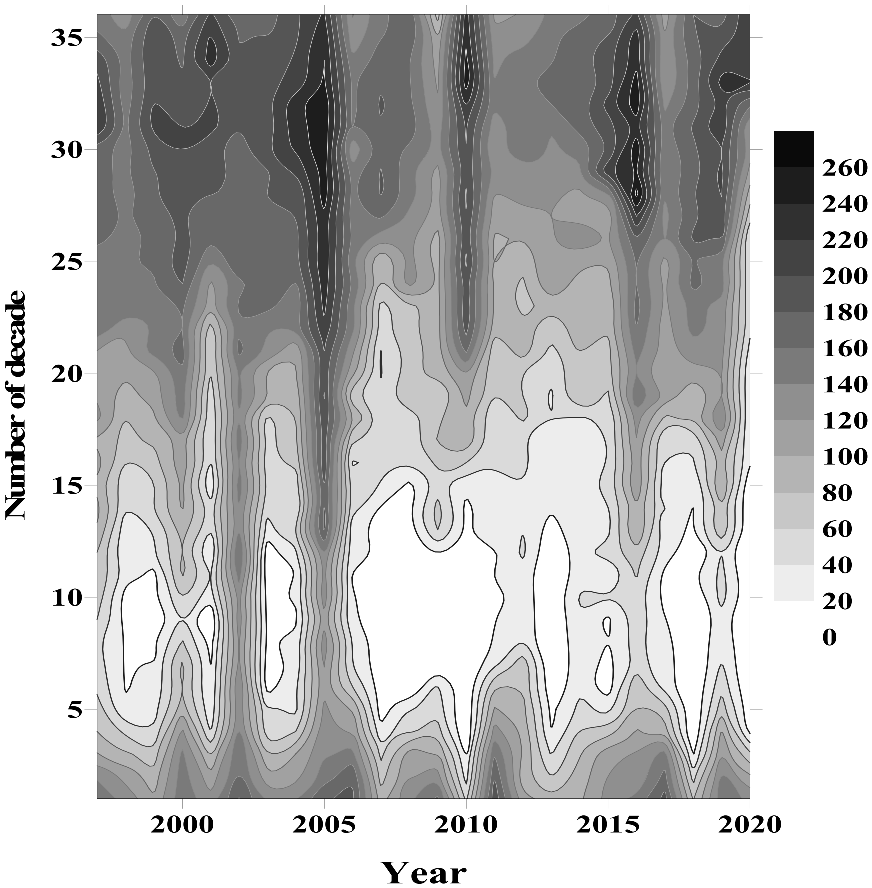

Fig. 7. Full distribution of the snow cover depth at the area of UAS "Academic Vernadsky" for the observation period 1997-2020

In addition to the intra-annual component, during the study the long-period component of dynamics of the snow cover height was identified (Fig. 8), the period of which is 11.03 years. More detailed information about the obtained component of slow fluctuations of the snow cover height is shown on Fig. 8, in particular, here can be seen the limits of the main periods in 2005 and 2015.

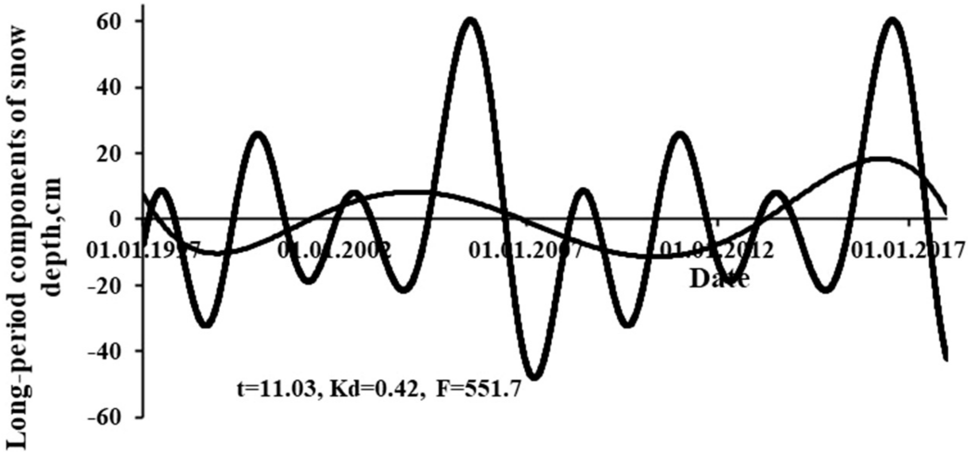

Fig. 8. Long-period component of the snow cover height with a period of 11.03 years according to observations at the UAS "Academic Vernadsky" for the period 1997-2020

The overtones of the fundamental harmonic, at the level of periods of 5 and 2.5 years, are of particular interest, since they are identical to the El Niño harmonics, which may indicate the influence of this phenomenon on the formation of the snow mass on the UAS "Academic Vernadsky" (Fig. 9).

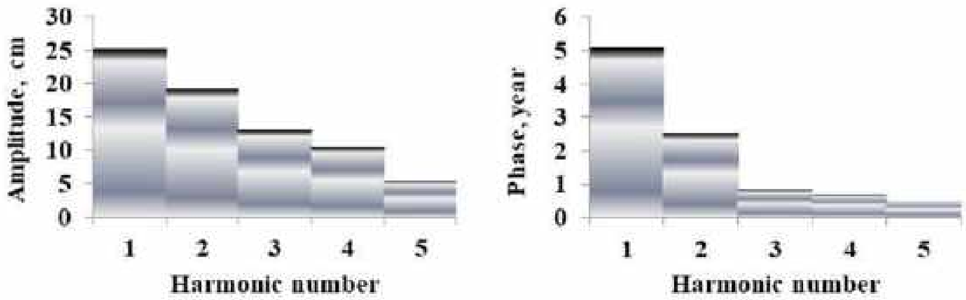

Fig. 9. Amplitudes and phases of harmonics of the snow cover height according to observations at the UAS "Academic Vernadsky" for the period 1997-2020

Obviously, the spectrum of harmonics of the snow cover depth is so much wider, but today its more detailed studies are limited by the duration of a number of instrumental measurements.

CONCLUSION

During the study period, significant changes in the process of snow cover formation in the area of the UAS "Academic Vernadsky" have been observed. First of all, there is a shift in the main dates characterizing the snow cover: the dates of the beginning and the end of the snow cover period, as well as the maximum of snow accumulation, to later dates.

The formation of layers of the snow cover, differing in the type of compaction (the number of which ranges from 6 to 8), occurs at the same time from year to year. Obviously, this indicates that the stratification of the snow mass arises under the influence of the same synoptic processes. The maximum increase of the snow mass is observed in July, as a result of which the most unstable layers of snow are formed at this time, which can be potentially avalanche-prone layers.

Attention should be paid to the fact that after 2005 there have been changes in the structure of formation of the snow cover at the area of UAS "Academic Vernadsky": this process has become slower, especially in the first half of winter. At the same time, the total amount of precipitation to the end of the snow accumulation season remains relatively stable. As a result of the study, it was possible to identify the long-term component of the snow cover height, the period of which is 11.03 years with overtones of 5 and 2.5 years, the analysis of which indicates a possible effect on formation of the snow mass in the studied area of the El Niño phenomenon. The seasonal component (annual cycle) with a period of 366.04 days (which explains the shift of main data of the snow cover) describes 58% of the total variability, and the long-period (period of 11.03 years) − 17.6%.

The obtained results give a broad understanding of the properties of snow and the very process of snow accumulation in the study area. It should be noted the importance, relevance and prospects of conducting glaciological studies in the future, since the amount of snowfall to a large extent forms the water balance of the territory, and the conditions and duration of its occurrence − the radiation balance of the Polar regions. The stratigraphy of the snow mass reflects its seasonal dynamics, the processes occurring within it under the influence of various factors. It also makes it possible to assess the real amount of precipitation. The results should be used in developing weather forecast models.

REFERENCES

1. Atmosphere: Reference book, USSR, 1991, 512 p. (in Russian).

2. Averyanov V.G., Glacio-climatology of Antarctica, USSR, 1990, 198 p. (in Russian).

3. Barnett T.P. et al., The effect of Eurasian snow cover on regional and global climate variations / J. of Atm. Sci., Vol. 46, №5, USA, pp. 661-685, 1989.

4. Belokrinitskaya L.M., Grishchenko V.F., Ivchenko V.N., Klok S.V., Kruchenitsky G.M. Seasonal and long-term variability of snow cover thickness on the Galindez glacier / Ukrainian Antarctic Journal, Ukraine, № 4-5, pp. 295-299, 2006 (in Russian).

5. Blattner P., Cook K., Ulrich L., Dyck T. Special Edition Using Microsoft Excel 2000, USA, 1999, 1088 p.

6. Bogdanova E.G., Il'in, B.M. & Gavrilova, S.Y., Advanced methods for correcting measured precipitation and results of their application in Polar Regions of Russia and North America / Russian Meteorology and Hydrology, №32(4), pp. 229–244. 2007, doi: https://doi.org/10.3103/S1068373907040036 (in Russian).

7. Govorukha L.S., Brief geographical and glaciological characteristics of Argentine Islands archipelago / Bulletin of Ukrainian Antarctic Center, Ukraine, Issue 1, pp. 17-19, 1997 (in Russian).

8. Govorukha L.S., Glaciological research on Galindez Island / Bulletin of Ukrainian Antarctic Center, Ukraine, Issue 1, pp. 67-76, 1997 (in Russian).

9. Grishchenko V.F., Klok S.V., Timofeev V.E., Features of the regime and characteristics of the snow cover of Galindez Island / Proceedings of X Scientific Conference "Scientific research in Antarctica", Ukraine, pp. 84-92, 2006 (in Russian).

10. Klok S. V., Kornus A. O., Kornus O. H. The Components of Seasonal Variability of the Snow Depth in the Area of the Ukrainian Antarctic Akademik Vernadsky Station / Book of abstracts X International Antarctic conference dedicated to the 25th anniversary of raising of the national flag of Ukraine at the Ukrainian Antarctic Akademik Vernadsky station, Ukraine, pp. 89-90, 2021.

11. Klok S., Kornus A., Danylchenko O. Current state of snow cover in the area of Ukrainian Antarctic research base "Academician Vernadsky" / Book of abstracts submitted to the Scientific Committee Antarctic Research Open Science Conference in Hobart, Australia, p. 128. 2020.

12. Klok S.V., Aftenyuk A.A., The results of snow mass drilling in the area of Ukrainian Antarctic station "Academic Vernadsky" / Scientific Bulletin of Chernivtsi University, Issue 803, Geography, Ukraine, pp. 141-149, 2018 (in Russian).

13. Klok S.V., Analysis of the main dates and individual characteristics of the snow cover in the area of the Ukrainian Antarctic Station "Academic Vernadsky" / Ukrainian Antarctic Journal, № 15, Ukraine, pp. 35-40, 2016 (in Russian).

14. Klok S.V., Features of measurement of the precipitation at the Ukrainian Antarctic station Academician Vernadsky / Ukrainian Antarctic Journal, №9, pp. 222–230, 2010 (in Ukrainian).

15. Klok S.V., The distribution of precipitation on the observations on Ukrainian Antarctic station "Academician Vernadsky" / Hydrology, hydrochemistry and hydroecology, №3(30), Ukraine, pp. 98–104, 2013 (in Ukrainian).

16. Malcolm S.Y., Tang S.N., Chenoli S., Colwell R., Grant M.S., Law J., Samah A.A., Precipitation instruments at Rothera Station, Antarctic Peninsula: a comparative study / Polar Research, №37, Norway, pp. 1-13, 2018, doi: https://doi.org/10.1080/17518369.2018.1503906

17. Martazinova V.F., Klok S.V., Anomaly of the weather conditions of Antarctic Peninsula near the location of Ukrainian Antarctic station "Academic Vernadsky" / Scientific works of UkrHMI, Issue 262, Ukraine, pp. 91-101, 2012 (in Ukrainian).

18. Martazinova V.F., Timofeev V.E., Ivanova E.K., Atmospheric circulation of the southern polar region and the climate of Antarctic Peninsula, Ukraine, 2010, 92 p. (in Russian).

19. Mouginot J., Rignot E., Bjørk A. A., van den Broeke M., Millan R., Morlighem M., Noël B., Scheuchl B., Wood M., Forty-six years of Greenland Ice Sheet mass balance from 1972 to 2018 / Proceedings of the National Academy of Sciences, №116 (19), USA, pp. 9239–9244, 2019, doi: https://doi.org/10.1073/pnas.1904242116

20. Rignot E., Mouginot J., Scheuchl B., van den Broeke M., Millan R., Morlighem M., Noël B., Scheuchl B., Wood M., Four decades of Antarctic Ice Sheet mass balance from 1979–2017 / Proceedings of the National Academy of Sciences, №116 (4), USA, pp. 1095–1103, 2019, doi: https://doi.org/10.1073/pnas.1812883116

21. Thomas R.H. Studies on the ice cap of Galindez Island, Argentine Islands / British Antarctic Survey Bulletin, Vol. 6, United Kingdom, pp. 27-43, 1963.

22. Velicogna I., Increasing rates of ice mass loss from the Greenland and Antarctic ice sheets revealed by GRACE / Geophysical Research Letters, №36, USA, L19503, 2009, doi: https://doi.org/10.1029/2009GL040222.

MARKETING AND ECOLOGICAL ASPECTS OF MANAGEMENT OF HYDROCARBON FUELS REPLACEMENT WITH FUEL OF BIOLOGICAL ORIGIN AT THE MINING ENTERPRISES

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ABSTRACT

The problem of replacing hydrocarbon fuels for fuels of biological origin, especially derived from waste, in the mining industry remains very relevant. Active use of hydrocarbon fuels, in particular diesel fuel, to power the engines of vehicles and special equipment in the mining industry creates significant pressure on the environment. This leads to the irrational use of natural resources, creates dangerous working conditions, raises up significant pollution of air, soil, surface waters and groundwater. One of the most effective ways to reduce the toxicity of diesel exhausts is the replacement of hydrocarbon fuel with fuel of biological origin. So, in this chapter the situation on the fuel market was studied; the perspectives of the biofuel use during special equipment operation on mining enterprises were analyzed; the unique 'green' startup-project, aimed at using as a motor fuel for special vehicles of the mining industry and heavy trucks mixed biofuels, was substantiated; marketing aspects of the innovative 'green' startup project were provided. The experiment was shown that the main characteristics of the obtained mixed biofuels (with biodiesel content up to 30 %vol.) meet the current standards. Positive changes in some ecological parameters of diesel engine have been observed (for example, decrease of smoke content, CO in exhaust gases). The content of nitrogen oxides (in terms of NO_2) was ambiguous. When adding biodiesel in a concentration of up to (16±1) %vol. this indicator decreases by 5.5…11.3 %, but with a further increase of the biodiesel content it increased by an average of 5.3 %. So, the developed 'green' startup-project allows to significantly reduce the use of high-carbon fossil fuel by partially replacing it with mixed biodiesel, as well as reduce emissions of harmful substances, including greenhouse gases, aerosols, etc. from exhausts of diesel engines of heavy trucks and special equipment on mining enterprises. Penetrating soils and surface waters, biodiesel does not cause adverse effects on ecosystems.

Keywords: biofuel, biodiesel, motor fuel, innovative development, special equipment, mining enterprise, air pollution, marketing, 'green' startup project.

INTRODUCTION

Dependence of Ukraine on foreign energy resources and current conditions of economic and political instability on its borders cause not only the state's revision of its own energy strategies, development of new legislation, financial mechanisms, etc., but also ensuring the transition of the country's economy to non-traditional, renewable energy sources, including energy of biological origin. According to the [1], in Ukraine more than 62 % of domestic gasoline consumption and up to 90 % of diesel fuel is imported fuel, although, according to experts' point of view, up to 35 % of diesel fuel import could be replaced by national biodiesel (BD) production.

According to [2], the trends of recent years have a very positive impact on the development of various branches of bioenergy in the country and even on the prospects for the sale of various types of biofuels (BF) and energy raw materials on the international market.

The adoption of the Law 'On Alternative Fuels' with changes from 20 September 2019 by the Government of Ukraine was a serious step towards the replacement of fossil fuels with fuels of biological origin. The main task of the law is to increase the production and use of bio- and mixed fuels in the country [3]. That is, the use of fuels from organic raw materials, and even better – fuels produced from production and consumption waste, is recognized as an innovative direction of development of the energy sector of Ukraine, a promising way to make it 'greener' [4, 5].

Many papers of well-known scientists, including B. Barton, V. Barannik, I. Binko, U. Bihun, D. Bohi, O. Vlasyuk, M. Zemlianyi, N. Mironov, P. Nemish, O. Okhrimenko, A. Petersen, B. Piriashvili, D. Preiger, J. Romm, A. Shevtsov and others, have been devoted to the study of ways to overcome the country's energy dependence. Issues of efficient use of fuel and energy resources have been covered in the works of V. Geets, V. Besedin, V. Kaviertsiev, V. Diahiliev, V. Melnik, I. Diak, I. Shlonchak, A. Shidlovsky.

The theoretical basis of ecological marketing was developed by O. Balatsky, S. Ilyashenko, L. Melnyk, Yu. Tunitsa, V. Shevchuk. At the same time O. Gavrish, N. Ilyashenko, S. Ilyashenko, O. Shafalyuk, Yu. Shipulina, S. Solntsev, O. Teletov, S. Voitko, O. Zozul`ov and others have made a significant contribution to the development of theoretical and methodological issues of marketing and management of innovations. Theoretical and practical issues of innovative projects realization have been developed in the works of national specialists S. Legenchuk, N. Sytnyk, as well as foreign ones – S. Blank, B. Dorf, E. Ries, A. Romans, P. Thiel. In turn, K. Beigul, S. Nikiforova, N. Joglekar, E. Vanicheva paid attention to the research of issues related to innovative projects marketing.

Issues regarding the ecological pressure on the environment from pollutant emissions from the combustion of fossil fuels and the prospects for the development of the bioenergy industry in the country and the world in general have been considered in the works of O. Adamenko, M. Dyvak, O. Yevtushenko, V. Gavrish, G. Geletukha & T. Zhelezna, G. Kaletnik, M. Korchemny, O. Kushnir, A. Panteleymonenko, M. Roik, V. Samotuha, I. Fedotov and other scientists. However, at this time the problem of replacing hydrocarbon fuels with non-traditional fuels of biological origin, especially derived from waste, in the mining industry remains relevant, and therefore requires additional research.

This is due to the fact that today the carbon intensity of Ukraine's gross domestic product (GDP) (in absolute terms) is still at a very high level. In particular, greenhouse gas emissions per unit of GDP are almost 4 times higher than the same indicators for the EU countries, and the absolute energy intensity of GDP is 3.5 times higher than the EU average [6].

Thus, high levels of energy intensity of the mining industry of Ukraine leads to the conclusion that its innovative development through the use of fuels of biological origin, as well as balanced marketing tools are necessary for ‘green’ growth of national economy and the undoubted future of our country. So, the main objectives of the research are: to study the situation on the fuel market of Ukraine, to analyze the prospects of the biofuel usage in the activities of mining enterprises; to develop marketing principles for the fossil fuels replacement with mixed fuels and biofuels in order to improve the environmental situation and ensure energy saving measures, ‘greening’ the country's energy sector.

METHODS AND EXPERIMENTAL PROCEDURES

The methodological basis of the study are experimental methods in combination with methods of comparative analysis, synthesis and generalization, statistical analysis, marketing research, etc., taking into account both national interests and globalization processes in the world.

It is well known that today marketing provides one of the most important functions in managing the activities of any enterprise. Thanks to the use of marketing research methods it becomes possible to analyze the internal and external environment and the movement of goods, develop pricing, product, sales and communication policy of the enterprise; organize strategic and tactical planning. If an enterprise is going to succeed in the market, it has to develop and coordinate innovative, environmental and marketing activities [7, 8].

According to the leading national economist and marketing professional S. Ilyashenko [9], such coordination will be effective due to the implementation of the concept of innovative marketing (including environmental and ‘green’ marketing), which aims to create an improved product or even fundamentally new products – innovation, innovative product. Innovation in this study means not only updated (or improved) products, but also new or improved technologies, services and even non-standard management solutions, especially in the field of resource conservation and environmental protection. Thus, in this context, we believe that ensuring the competitiveness of mining enterprises through the use of ‘green’ innovations is one of the main goals of the national economy.

The main principles of improving the efficiency of any industrial enterprise, including mining enterprises, are the unity of purposes and consistency of the use of management tools at both the corporate and functional levels. We believe that the innovative activities of mining enterprises for partial or complete fossil fuels replacement with fuels of biological origin, combined with the concept of innovative ‘green’ marketing will not only improve the management of such enterprises, but also ensure resource conservation, energy security and as a consequence, sustainable development of the country's mining industry.

THE RESEARCH RESULTS AND DISCUSSIONS

The current stage of development of the countries of the world, including Ukraine, is characterized by the active use of innovative resource-conservation measures and technologies in all spheres of the national economy. For mining enterprises, this area is extremely important and promising because of their significant pressure on the environment, active use of natural resources, etc. According to the results obtained by many authors, the introduction of ecological and economic mechanisms of balanced management of innovative resource conservation in the mining industry will give them, taking into account the harsh market relations, additional competitive advantages – technological, financial, economic, environmental, social, organizational, etc. At the same time, according to the content of the processes taking place at the enterprise, innovative resource conservation can be considered in two main aspects – as savings of valuable natural resources, and as their rational, balanced use [10, 11].

In this aspect, improving the efficiency of the mining industry should, firstly, be achieved through the introduction of innovative technologies for mining, rational organization of the production process. And, secondly, from the point of view of sustainable development of the mining industry, the policy of enterprise management should provide special resource-saving measures, including, for example, such as the use of biofuels. At the same time, serious attention should be paid to reducing the negative impact on all components of the environment and especially – on air quality.

Thus, the strategy of increasing the competitiveness of mining enterprises through innovative resource conservation involves the search and development of competitive advantages, ensuring their relative stability, prospects, etc. by replacing hydrocarbon fuels with fuel of biological origin. In this case, as noted, an important condition is a comprehensive assessment and consideration of environmental factors, not only the economic ones (Fig. 1). At the present stage of development of society the environmental component is becoming more and more important, shaping the strategic future of the world's economies. Therefore, mining enterprises, implementing resource-saving innovations, have to take into account environmental factors in their activities.

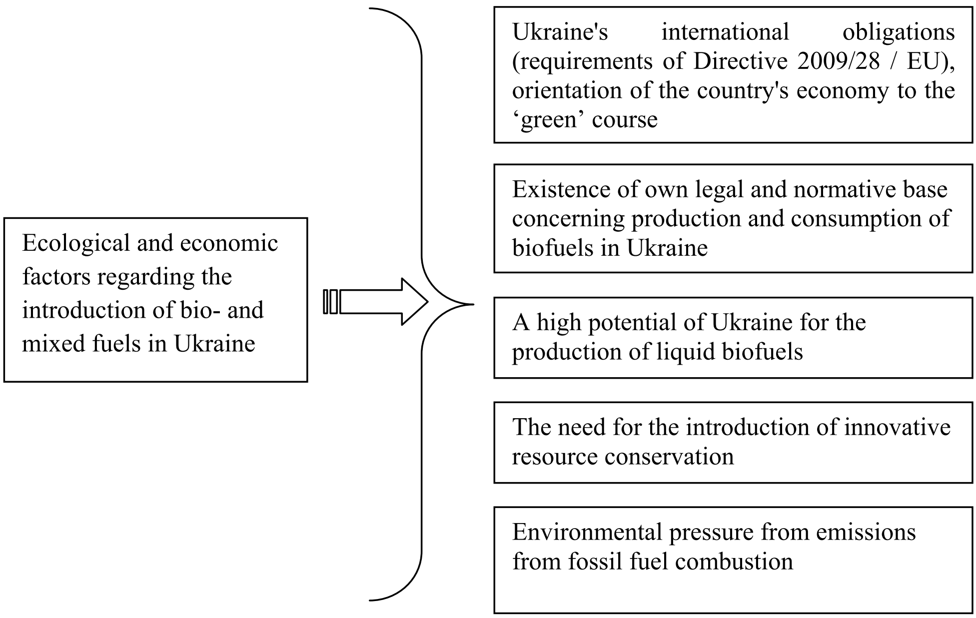


Fig. 1. Ecological and economic factors of expediency of introduction of bio- and mixed fuels at the enterprises of the mining industry.

It is well known that the active use of hydrocarbon fuels to power the engines of vehicles, especially heavy trucks and special equipment, other mechanisms, etc. creates significant pressure on the environment. This causes not only irrationally usage of valuable natural resources – crude oil and petroleum products (the volume of oil production with gas condensate in Ukraine is shown on Fig. 2), but is also dangerous for workers’ health and raises up pollution of air, soil, surface waters and groundwater. Harmful emissions of diesel engines are mostly dangerous and also cause negative impact on climate change on the planet.

Therefore, reducing emissions from engine exhausts will also reduce their toxic effects on the environment and human health. And one of the most effective ways to reduce the toxicity of emissions of diesel vehicles, engines of special equipment and other mechanisms is the partial (or complete) hydrocarbon fuel replacement with fuel of biological (organic) origin. This becomes especially relevant because of the constant rise of prices for petroleum fuels (Fig. 3), limited reserves of crude oil and other problems.

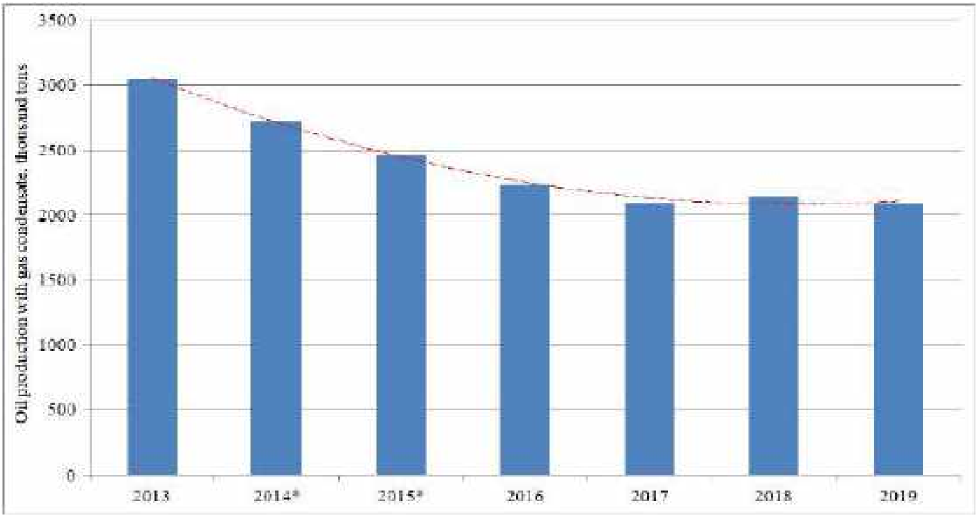


Fig. 2. Oil production with gas condensate in Ukraine, thousand tons [12]

Note. *excluding data from JSC 'NJSC 'Chornomornaftogaz'.

Modern technologies allow to use alcohol and/or ester biofuels − biomethanol, bioethanol, biobutanol, biodiesel, etc. without any modifications to power engines of special equipment (tractors, bulldozers, excavators, graders, etc.) and heavy trucks. Usage of mixed biofuels with different fossil fuel content has significant potential. Fig. 4 shows the production volumes of gasoline and diesel fuel from traditional crude oil in Ukraine, as well as forecast approximation equations for the prospects of their production in scenarios based on statistical data processing, starting from 2015 [12].

It is known that modern innovative solutions, including environmentally friendly ones, are developed and implemented, as a rule, either by specialized departments of large enterprises or by independent teams of 2−10 innovators (startups, startup-projects). Analysis of scientific and professional literature sources shows that Ukraine has significant scientific and technical potential to create 'green' startups. Good opportunities for the development of innovative entrepreneurship are provided by the gradual transformation of production processes under the influence of the concepts of 'Industry 4.0' and the knowledge economy.

So, let's consider our 'green' startup-project both from environmental and economic aspects. The concept of our startup is to use mixed biofuels (with a BD content $\varphi_{BD} \leq 20-25$ %vol.) as a motor fuel for special vehicles of the mining enterprises and heavy trucks. Biodiesel fuel – the basis for mixed BF was obtained by an improved method using a new surface-active catalyst for the transesterification process of vegetable oils (or animal fats) from production waste or from pure oil products [14].

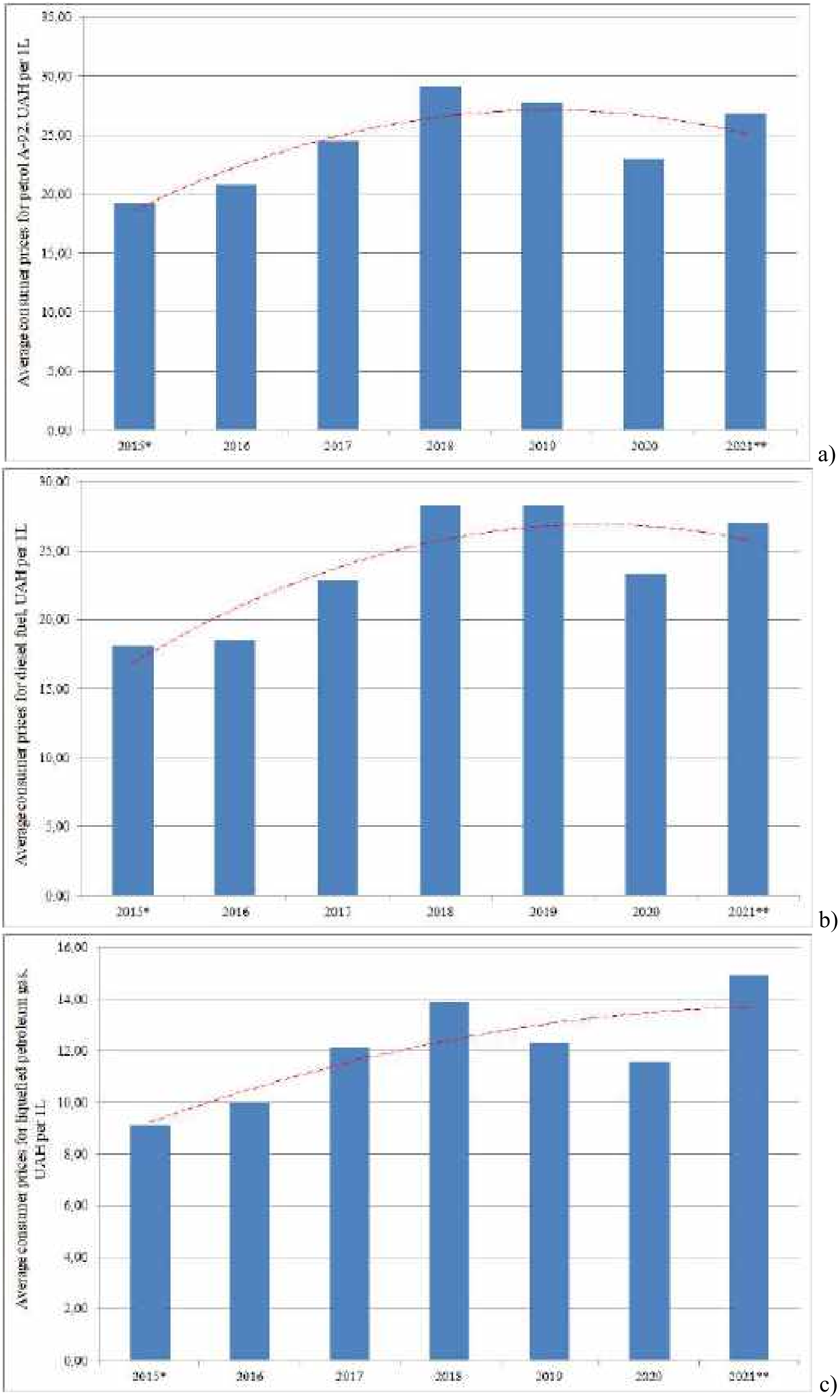
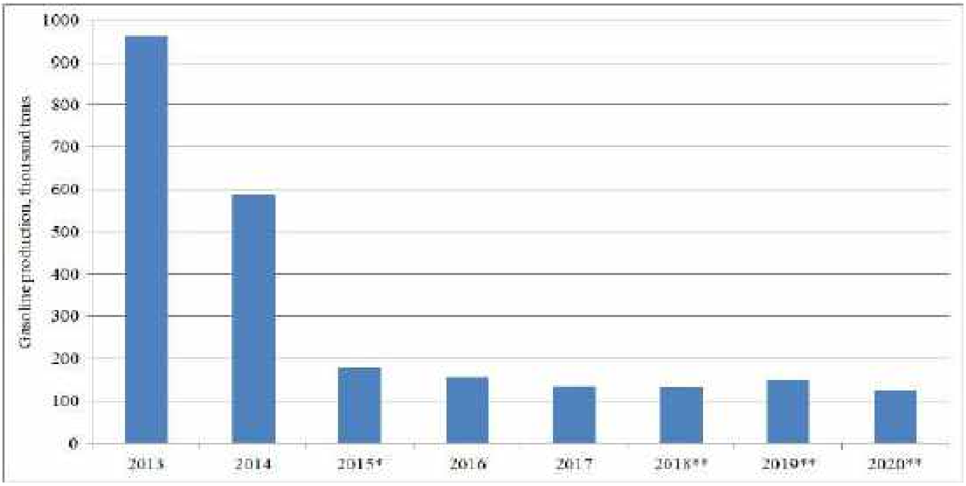
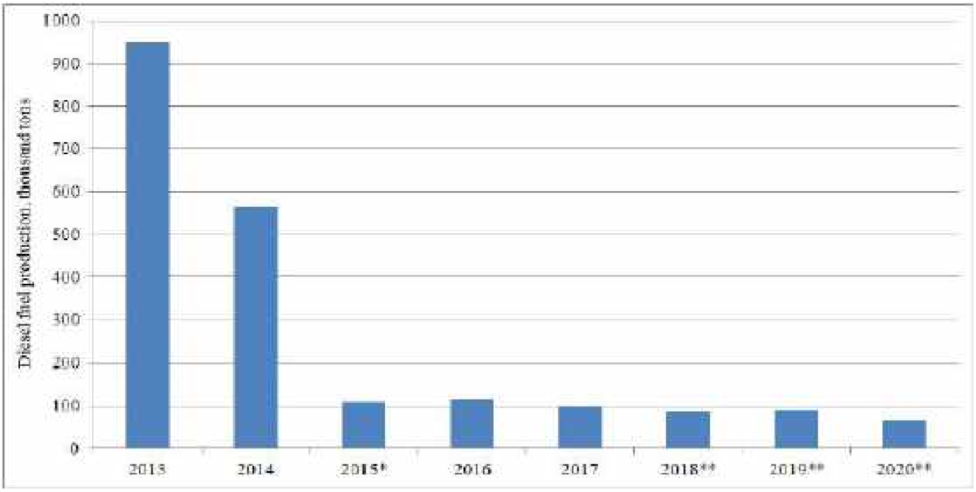


Fig. 3. Average consumer prices for fuel in Ukraine: a) A-92 gasoline; b) diesel fuel; c) gas [13].



a)



b)

Fig. 4. Production of: a) gasoline ($y = -7.78x + 173.05$, coefficient of determination $R^2 = 0.58$); b) diesel fuel ($y = -8.7657x + 124.55$, $R^2 = 0.84$), thousand tons (2020 – for 11 months).
Notes. *excluding Kremenchug Refinery; **information on Shebelinsky Refinery.

Analysis of the quality of the obtained biodiesel (ethyl esters of fatty acids of rapeseed and other oils in the case of food waste usage) was carried out immediately after its obtaining. The main characteristics of the obtained biodiesel and mixed biofuels based on it are presented in the Table. So, these indicators meet the current standards DSTU 8695:2016, DSTU 7688:2015 and European EN 14214:2008+A1:2009.

There were a certain variations in the physico-chemical and operational characteristics of BF obtained from food industry waste, due to the wide variation of raw material properties. But all parameters are still within acceptable limits for use as motor fuel and correspond to the European standard EN 14214 (one of the advantages of using diesel engines is the possibility of wide variation of physical and chemical properties of motor fuel [15]). Higher value of the cetane number of the obtained biofuel and hence a better flammability, which corresponds to the data of [16], have been observed.

Table 1. Comparison of quality characteristics of the obtained biodiesel and mixed biofuels

Fuel quality characteristics	100 % summer diesel fuel, $C_{16.2}H_{28.5}$, M = 222.9 g/mol	100 % BD, $C_{21,2}H_{39,6}O_2$, M = 326,0 g/mol	BD − 10 %vol.	BD − 15 %vol.	BD − 30 %vol.	Standards for EN 14214: 2008+A1: 2009 on fatty acid methyl esters for diesel engines
Density at 20°C, kg/m^3	847.6	885.4	851.3	854.3	860.1	860−900 (15 °C)
Kinematic viscosity, mm^2/s at: − 20°C − 40°C − 50°C − 100°C	 6.53 4.01 3.89 1.02	 8.12 4.85 5.01 1.49	 6.62 − − −	 6.76 − − −	 6.92 − − −	 − 3.5−5.0 − −
Coefficient of surface tension (20 °C), mN/m	27.31	32.00	28.2	28.9	29.7	−
Cetane number	51.3	65.1	51.4	51.5	53.6	≥51
The amount of air required for the combustion of 1 kg of substance (stoichiometric coefficient), kg	14.50	12.68	14.28	14.16	13.99	−
Lower heat of combustion, Q_l, MJ/kg	42.93	38.29	42.80	42.70	41.00	42.70
Flash point in a closed crucible, °C	62	197	78	85	89	≥120
Turbidity temperature, °C	-12.3	-9.0	-11.2	-10.9	-10.4	-12.0
Freezing point, °C	-22.4	-14.5	-19.6	-18.3	-16.1	-24.0
Sulfur content, mg/kg	−	<10	−	−	−	≤10

						Table continuation
Content, wt% − Carbon C − Hydrogen H − Oxygen O	 87.21 12.78 0.01	 78.04 12.15 9.81	 84.31 12.44 3.25	 83.46 12.38 4.16	 81.14 12.07 6.79	
Coking 10 % residue, %, not more than	0.20	0.29	0.23	0.25	0.29	≤0.3
Ash content, %	0.01	0.01	0.01	0.01	0.005	≤0.02
Water content, mg/kg, %vol.	56 –	167 traces	– traces	– traces	– traces	≤500 –
The content of mechanical impurities, mg/kg	traces					≤24
Corrosion resistance (copper plate test, 3 h at 50 °C), evaluation	class 1 withstands					class 1
Acid number, mg KOH/g	0.14	0.17	0.13	0.13	0.14	≤0.50
Iodine number, g I_2/100 g of the product	6.3	81.78	–	–	–	≤120
Flash delay, (ITQ), ms	3.87	3.12	–	–	–	3.60
Oxidative stability, 110 °C, h	–	more than 20.0				not less than 6.0

Note. '–' – property was not determined or not specified.

A four-stroke two-cylinder water-cooled diesel engine – a Kipor KM2V80 tractor diesel has been selected for road tests in the startup-project. This tractor engine can be used not only in mining industry, but also in road construction and other special equipment. The research program included determination of engine effective indicators at operating on loading characteristics from idling to the power close to nominal, with frequencies of rotation of a crankshaft n = 3000 min^{-1}, 3200 min^{-1} and 3500 min^{-1} with diesel, biodiesel and mixed biofuels ($\varphi_{BD} \leq 30$ %vol.) usage.

The tests were performed at temperatures of +10…+18 °C and atmospheric pressure of 740…760 mm Hg; the coefficient of air excess α varied in the range of 1.53…2.24 and increased with increasing crankshaft rotational speed; the set angle of advance of fuel injection during investigations did not change. Biofuel compositions were prepared immediately before testing by prolonged mixing of the components to achieve a homogeneous mixture. The results of motor tests of the engine on different types of fuels at the frequency n = 3500 min^{-1} (close to the nominal) are shown on Fig. 5−7 (data was obtained with the participation of the researchers of GNDL ‘Reactor’ OKB ‘Storm’ of Igor Sikorsky Kyiv Polytechnic Institute).

So, the decrease of smoke content indicator in exhaust gases of diesel using mixed biofuels to power the engine (Fig. 7) is due to the increased oxygen content in the molecules of biodiesel (~10 %) and mixed biofuels (3…7 %). This causes more complete oxidation of the fuel and, consequently, a reduction of products of its incomplete combustion in exhaust gases.

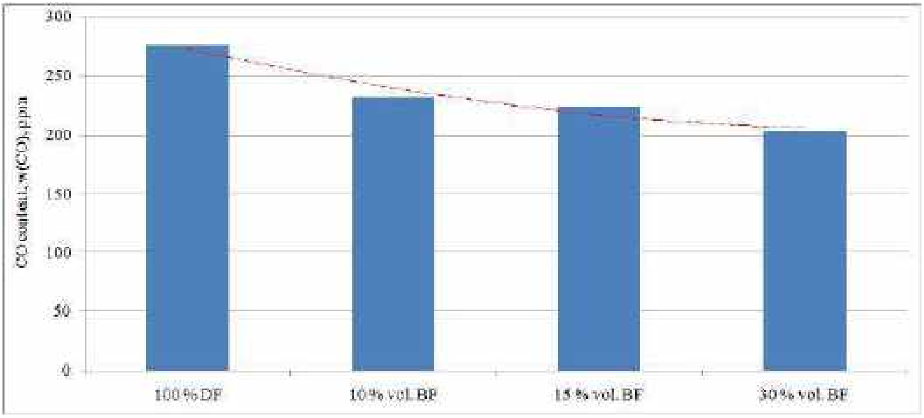


Fig. 5. The content of CO in the exhaust gases of the diesel engine operating on diesel fuel and mixed biofuels (n = 3500 min^{-1}).

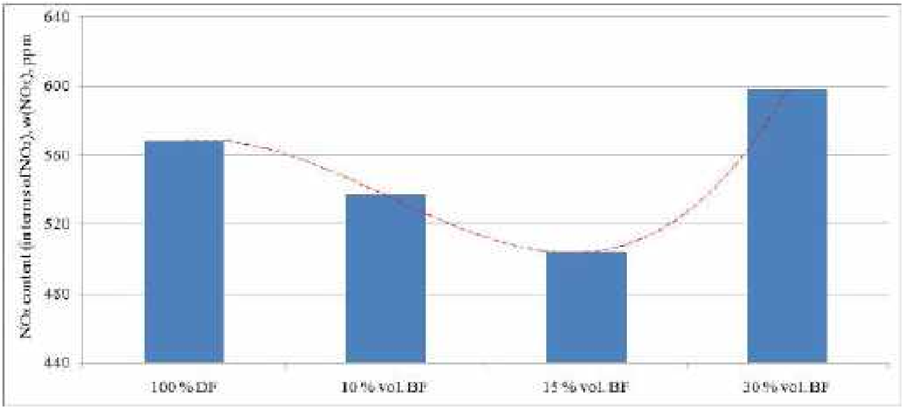


Fig. 6. NO_x content in the exhaust gases of the diesel engine during its operation on diesel fuel and mixed biofuels (n = 3500 min^{-1}).

However, the increased content of Oxygen in the BF, in turn, causes the temperature increasing in the engine combustion chamber and, as a consequence, the intensification of the interaction of oxygen and nitrogen (from the air) and of free radical chemical transformations. This slightly increases NO_x emissions when the engine operates on mixtures with a BF content of more than 20−25 %vol. On the other hand, increasing the combustion temperature of fuel has a positive effect on the rate of its oxidation [17] and reduces the content of incomplete oxidation products of fuel combustion, in particular, carbon monoxide, smoke, unburned hydrocarbons, etc.

Thus, the content of additional oxygen in the BF leads to a significant reduction in the toxicity of diesel exhaust gases. On average, specific emissions of CO using mixed biofuels ($\varphi_{BD} \leq 30$ %vol.) were reduced by 15.9…26.4 %, while emissions of smoke – by 7.6…34.3 % depending on the test mode. At the same time the content of nitrogen oxides (in terms of NO_2) was ambiguous. Adding biodiesel in a concentration up to (16±1) %vol. this indicator decreased by 5.5…11.3 %, but with a further increasing of BD content it increased by an average of 5.3 % that can be explained by the temperature of BF oxidation increase due to the presence of additional oxygen, as well as by different mechanisms of nitrogen oxides formation.

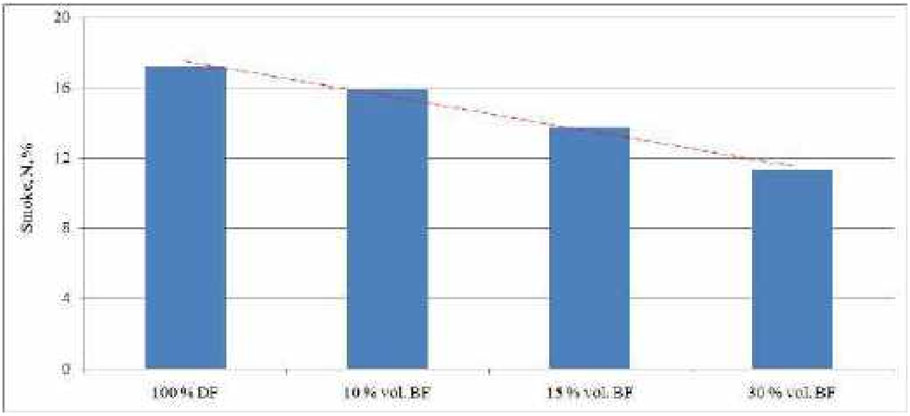


Fig. 7. Smoke index (luminous flux attenuation coefficient) of the exhaust gases of the diesel engine operating on diesel fuel and mixed biofuels (n = 3500 min^{-1}).

A slight increase in the specific fuel consumption (by 5…12 %) during the road tests was observed, which is due to the smaller value of the lower heat of combustion of biodiesel compared to traditional diesel fuel (Table). Usage of mixed biofuels makes it possible to reduce the emission of CO_2 (by reducing the carbon number C:H) and sulfur oxides (due to the absence of its active compounds in biodiesel) from diesel engine exhausts. The results of road tests also showed that there is an almost linear dependence between the smoke index of exhaust gases and the mass fraction of oxygen in the molecules of the investigated mixed biofuels in all test modes of the diesel engine. The approximation equation of the studied dependence has the form:

$$N, \% = -69{,}226w(O) + 17{,}164, \quad R^2 = 0{,}89.$$

Thus, the introduction of our ‘green’ startup-project for the partial replacement of fossil fuel with biofuels ($\varphi_{BD} \leq 20-25$ %vol.) in the special equipment of mining enterprises allows to improve the environmental indicators of diesel engines without worsening their operational characteristics. So, usage of mixed biofuels helps to increase the level of environmental safety in the operation of diesel engines of heavy trucks and special mining equipment by reducing emissions of soot, carbon monoxide and carbon dioxide, sulfur oxides, polycyclic hydrocarbons, etc [18].

Other indicators of the diesel engine operating on different types of fuel did not differ significantly, although the specific consumption of biofuel was slightly higher than the consumption of fossil fuel, and engine power was sometimes slightly reduced due to lower calorific value of biofuel. However, biodiesel has better lubricating properties compared to low-sulfur diesel fuels, which is most often used to power engines, so even minor BF additives to traditional diesel fuel will have a positive effect on reducing wear of fuel equipment parts.

It is well known that most startups have quite high risks at all stages of their market realization. Specialists of Forbes [19] and Fortune [20] journals note that only 10 % of all startup-projects are successful. This is mostly due to the fact that today the marketing principles for the implementation of such projects are still insufficiently formed. According to the results of a comprehensive analysis conducted by the agency 'CB Insights' [21], the products of almost 42 % of startups do not have market demand. Thus, the development of marketing principles for the environmentally friendly startup-projects implementation, especially in the mining industry, will give their founders the opportunity to increase the probability of projects success in both domestic and international markets.

The realization of startup-projects is a complex and multitasking process that requires consideration of a large number of different factors and implementation of relevant marketing tools. The traditional marketing apparatus for the startup-projects realization, including environmentally oriented ones, is usually ineffective due to the objective disregard of their unique features. Therefore, we have proposed a new approach to marketing basis for the implementation of 'green' startup-projects in the mining industry, based on a conceptual combination of the theory of innovation marketing, industrial marketing, small businesses marketing and venture projects marketing (Fig. 8) [22].

In addition, in order to make projects more productive and rational it is proposed to implement the ideas of E. Ries and his colleagues [23–25] in our innovative approach of the startups realization. This idea is based on lean-methodology and provides cyclical and continuous testing of hypotheses throughout the project realization. Proposed approach for startup success achievement on a marketing basis involves assessing the feasibility of the project realization at different stages of its growth based on the T. Saaty's analytic hierarchy process, as well as the need for prognostic assessments of general startup success based on probabilistic-graphical modeling.

So, we will consider in detail the proposed method of assessing the feasibility of a startup successful realization at different stages of market production based on the T. Saaty's method [26], implemented in RStudio. The methodology takes into account the market, investment and marketing attractiveness of developed projects. The corresponding hierarchy is created on the basis of the selected set of criteria on each of components of attractiveness of a startup. For example, we considered:

– the level of formation of market demand;

– the degree of actualization of needs by the target audience;

– availability of production facilities;

– content support of product category, etc.

The final conclusion will be made on the basis of providing appropriate degrees of advantage by different groups of experts using classical fundamental scale of absolute values, as a result of which we choose one of two alternatives – to continue or terminate the realization of the startup. Thus, as a result of a comprehensive analysis of the potential success of proposed 'green' startup-project, it was found that it is quite promising for further realization by our team and for financing by investors too. Thus, the expediency of our project further realization is 81.6 %; 29.4 % are determined by marketing attractiveness, 26.2 % – by investment attractiveness and 26.0 % – by market attractiveness.

Quite often, it is necessary for investors to assess the overall attractiveness of the startup industry in a country, in a particular branch of industry or even in the whole world. In this case, according to the proposed approach, the formation of prognostic estimates of the success of startups using Bayesian networks (probability-graphical models) in the RStudio software environment have to be developed [27]. With the help of mathematical models we will evaluate the internal and external environment, as well as the activities of startups.

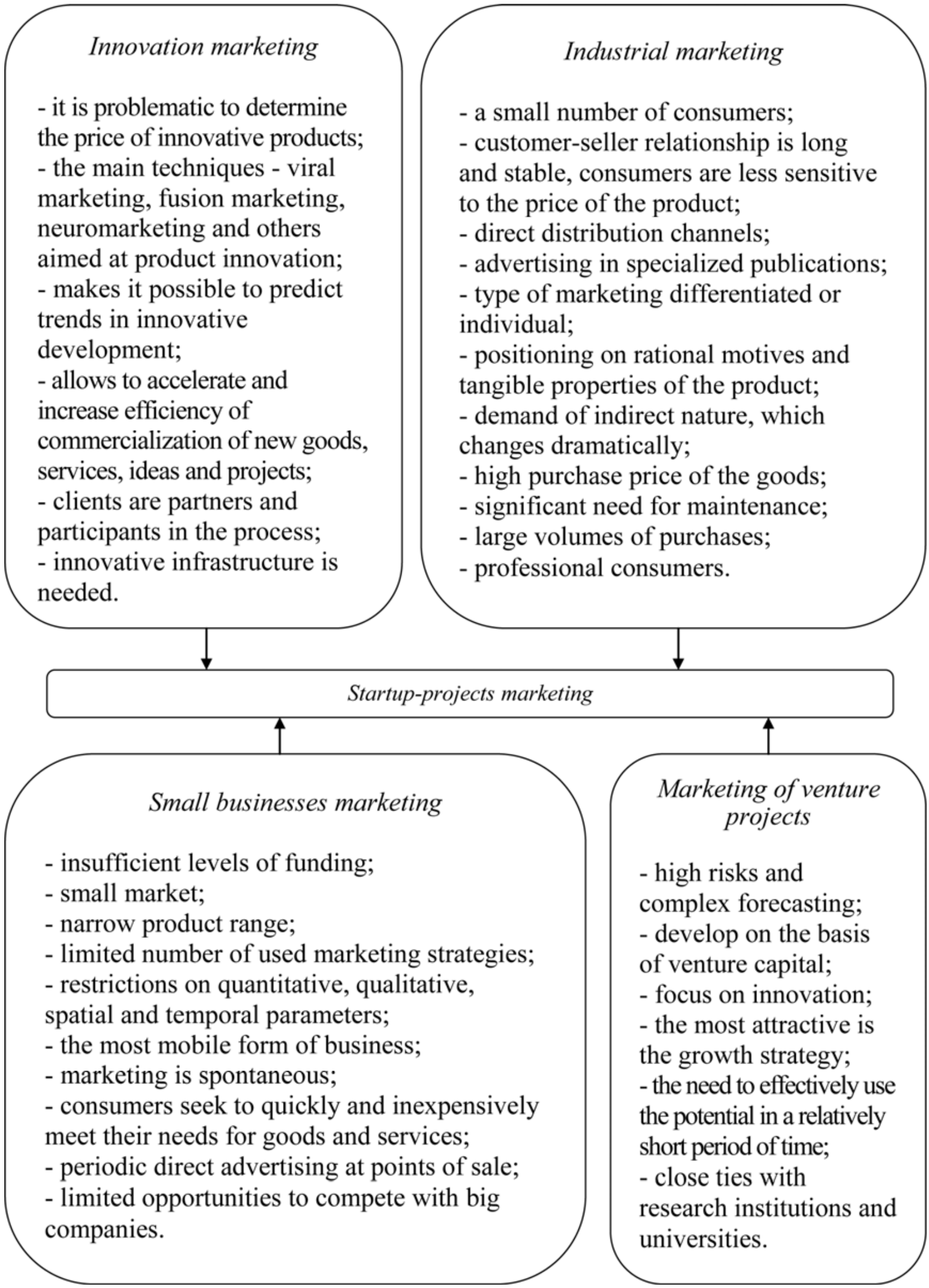


Fig. 8. Marketing conceptual basis for startup-projects realization.

As a result of the analysis of criteria for each of the three groups (internal and external environment, activities of startups), we will determine the forecast levels of success of the startup industry at the particular time period. For example on the Fig. 9 the fragment of the Bayesian network for successful startups realization is shown. The detailed description of the scheme and interpretation of the symbols are given at the previous work of the authors [27]. Thus, by the complex assessment of the startup industry we found that the probability of success of startups in the world is mainly at low and medium levels – 43.9 % and 41.4 %, respectively, while the probability of a high level of startups success does not exceed 14.7 % [27]. These data can be offered to potential investors for decision about funding level for the ‘green’ startup-project.

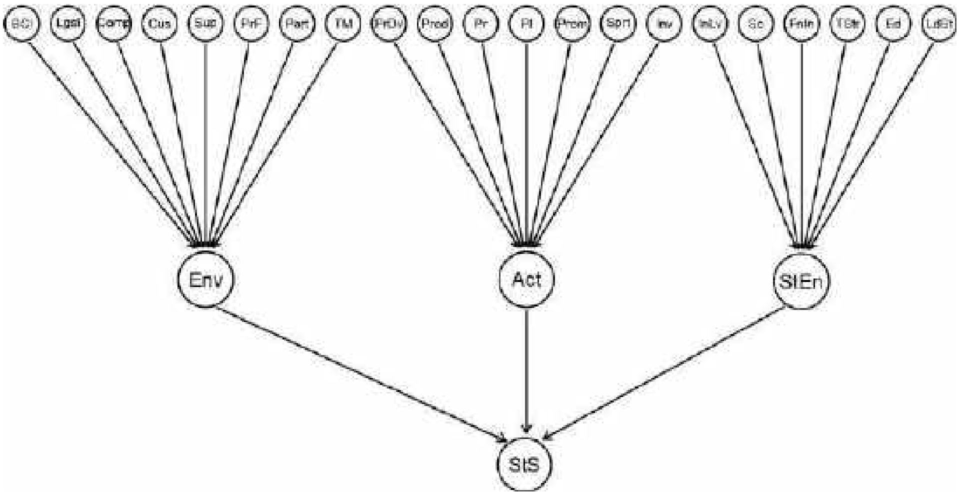


Fig. 9. The fragment of the Bayesian network for success assessment of the startups (in RStudio software environment).

CONCLUSION

So, the global trends of recent years for the ‘green’ orientation of various sectors of the national economy and social life have become very relevant for Ukraine. Taking into account the use of outdated production technologies, as well as the high level of energy intensity of enterprises, especially in the mining industry, the country's resource and energy dependence on imports, the issue of transition to ‘green’ growth should be considered as a priority.

In addition to the high energy intensity of Ukraine's GDP, mining companies face many other problems, including significant import dependence on the foreign vehicles, special equipment and other machinery powered by fossil fuels, as well as inefficient market infrastructure.

The scientific novelty of the study is, in particular, the following: assess the prospects of replacing (partial or complete) fossil fuel with fuel of biological origin in the mining industry to power heavy trucks and special equipment and the development of marketing principles of ‘green’ startup realization. The multilateral analysis allows us to prove both the ecological and economic significance and expediency of such replacement.

Thus, we developed a ‘green’ startup-project that can significantly reduce the usage of high-carbon fossil fuel by partially replacing it with biodiesel, as well as reduce emissions of harmful substances, including greenhouse gases, aerosols, etc. from exhausts of diesel engines of heavy trucks and special equipment of the mining enterprises. The energy potential of biofuel is close to the energy potential of diesel fuel, but biodiesel is non-toxic, does not contain any active compounds of sulfur, toxic benzene and other aromatic compounds. Penetrating soils and surface waters, biodiesel does not cause adverse effects on ecosystems, decomposing naturally.

The startup provides for the use of production and consumption waste to produce biofuel compositions and does not compete with food sources or deplete the country's land resources. The experiment was shown that startup implementation will have positive changes in ecological parameters of diesel engine (for example, decrease of smoke content, CO in exhaust gases). The content of nitrogen oxides (in terms of NO_2) was ambiguous. When adding biodiesel in a concentration of up to (16±1) %vol. this indicator decreases by 5.5…11.3 %, but with a further increase of the biodiesel content it increased by an average of 5.3 %.

So, in modern conditions mining enterprises need innovative development, attraction of investment resources to modernize and restructure the production and make national economy stronger. Thus, on the example of our project it was shown that the realization of 'green' startup-projects will be able to raise the mining industry to a new level, increase the efficiency of operational processes, contribute to resource saving in the industry.

REFERENCES

1. Better Regulation Delivery Office [within the FORBIZ project and the EU4Business Initiative] / Biofuel Production will allow Ukraine to replace up to 35 % of imported diesel and up to 10 % of gasoline, URL: https://brdo.com.ua/top/vyrobnytstvo-biopalyv-dozvolyt-ukrayini-zamistyty-35-importnogo-dyzelyu-10-benzynu (in Ukrainian);

2. Sinchenko V. M., Gumentyk M. Ya., Balikina V. V., State and development of bioenergy in the current legislation of Ukraine and the EU, Scientific works of the Institute of Bioenergy Crops and Sugar Beets: Scientific Bulletin, 2013, № 19, pp. 239−245 (in Ukrainian);

3. Law of Ukraine 'On Alternative Fuels', URL: https://zakon.rada.gov.ua/laws/show/1391-14#Text (in Ukrainian);

4. Skrypnychenko V. A., Innovative aspects of biofuel production in Ukraine: state, problems, prospects, Scientific Bulletin of the National University of Life and Environmental Sciences of Ukraine, 2009, pp. 175−180 (in Ukrainian);

5. Adamenko O., Vysochansky V., Letko V., Mykhailiv M., Alternative fuels and other non-traditional energy sources, ed. V. Letko, Ukraine, 2000, 270 p. (in Ukrainian);

6. Andrusevych A., Andrusevych N., Kozak Z., Khomyakova O., Towards green growth: monitoring progress in Ukraine, Ukraine, 2014, 76 p. (in Ukrainian);

7. Zaylyk M. F., Vivchar O. I., Peculiarities of innovative marketing in Ukraine, Bulletin of Dnipropetrovsk University, series: Economics, 2011, № 5/2, pp. 185–190 (in Ukrainian);

8. Sumets A., Innovations in the activities of the enterprise, Marketing and advertising, 2006, № 11 (123), pp. 28–33 (in Russian);

9. Ilyashenko S. M., Marketing. Management. Innovations: monograph, Ukraine, 2010, 624 p. (in Ukrainian);

10. Shvidanenko G., Tepliuk M., Budiaiev M., Developing an innovative model of resource efficiency for industry. Scientific Journal of Polonia University, 2017, № 25(6), pp. 19–27, DOI: 10.23856/2502 (in English);

11. Shabunina T. V., Shchelkina S. P., Rodionov D. G., An innovative approach to the transformation of eco-economic space of a region based on the green economy principles, Academy of Strategic Management Journal, 2017, № 16, pp. 176–185 (in English);

12. Ministry of Energy of Ukraine. Statistical information, URL: http://mpe.kmu.gov.ua/minugol/control/uk/publish/archive?cat_id=35081&page=1 (in Ukrainian);

13. Minfin. Prices for gasoline, diesel fuel, gas in Ukraine, URL: https://index.minfin.com.ua/ua/markets/fuel (in Ukrainian);

14. Kofanova Ye. V.,Vasylkevich A. I., Kofanov A. Ye., Stepanov D. N., Resource-saving and low-waste biodiesel production technology, Scientific and Technical Journal Mine Mechanical Engineeringand Machine-Building, 2015, № 2, pp. 96–102 (in Russian);

15. Korpach A. A., Levkivsky O. O., Possibilities and prospects of using biofuels in diesels, Motorway of Ukraine, 2009, № 12, pp. 156−158 (in Ukrainian);

16. Gorokhov D. G., Baburina M. I., Ivankin A. N., Proshina O. P., Liquid biofuel from plant and animal raw materials. Technical and economic aspects, Forest Bulletin, 2010, № 4, pp. 74−78 (in Russian);

17. Wcisło G., Determination of the impact of FAME biocomponent on the fraction composition of diesel engine fuels, Combustion Engines, 2013, № 154(3), pp. 1098–1103 (in English);

18. Kofanov O., Kofanova O., Vasylkevych O., Zozul’ov O., Kholkovsky Yu, Khrutba V., Borysov O., Bobryshov O., Mitigation of the environmental risks resulting from diesel vehicle operation at the mining industry enterprises, Mining of Mineral Deposits, 2020, № 14(2), pp. 110–118, DOI: 10.33271/mining14.02.110 (in English);

19. Patel N., 90 % of startups fail : Here's what you need to know about the 10 %, Forbes, 2015, URL : https://www.forbes.com/sites/neilpatel/2015/01/16/90-of-startups-will-fail-heres-what-you-need-to-know-about-the-10 (in English);

20. Griffith E., Why startups fail, according to their founders, Fortune, 2014, URL : http://fortune.com/2014/09/25/why-startups-fail-according-to-their-founders (in English);

21. Research Briefs. The top 20 reasons startups fail, CBInsights, URL : https://www.cbinsights.com/research/startup-failure-reasons-top (in English);

22. Kofanov O., Zozul`ov O., Scientific and methodological principles of the marketing strategy development of startups in the industrial market, Economic space, 2016, № 115, pp. 202−211 (in Ukrainian);

23. Blank S., B. Dorf., The startup owner’s manual : The step-by-step guide for building a great company, USA, 2012, 571 p. (in English);

24. Graham P., Startup and growth. Graham PaulGraham, URL : http://www.paulgraham.com/growth.html (in English);

25. Ries E., The lean startup : How today’s entrepreneurs use continuous innovation to create radically successful businesses, USA, 2011, 296 p. (in English);

26. Saaty T. L., Vargas L. G., Decision making with the analytic network process. Economic, political, social and technological applications with benefits, opportunities, costs and risks. USA, 2013, 363 p., DOI: 10.1007/978-1-4614-7279-7 (in English);

27. Kofanov O., Zozul’ov O., Successful development of startups as a global trend of innovative socio-economic transformations, International and Multidisciplinary Journal of Social Sciences, 2018, № 7 (2), pp. 191−217, DOI: 10.17583/rimcis.2018.3576 (in English).

TABACCO AND EFFECT OF MALE FERTILITY

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ABSTRACT

This study aimed to sperm parameters in male smokers and non-smokers and observe the impact of smoking on sperm count, motility and morphology in a selected male population of Prešov and Košice region in East Slovakia. Study was conducted from January 2019 to January 2020 in Slovakia. The subjects were recruited from the Clinic of Assisted Reproduction in Košice based on defined inclusion criteria and were categorized into infertile non-smokers (n = 70) and infertile smokers (n = 75). Semen analysis included determination of semen volume, sperm concentration, percent sperm motility and morphology according to methods recommended by WHO (1999) guidelines. A total of 158 semen evaluations were performed. Semen volume was significant greater ($p < 0.01$) by non-smokers than by smokers. Sperm concentration determined using heamacytometer chambers was consistently higher by non-smokers ($p < 0.001$) than by smokers. The percentage of motile sperm was assessed by a counting technique on the basis of progression, but was not statistically different between smokers and non smokers ($p > 0.05$). This study has shown that the semen parameters (total count, motility, and morphology) are decreased in fertile smokers as compared to infertile non-smokers. Analysis showed that smoking causes a significant decrease in sperm count and morphology but it did not have any significant effect on motility.

Keywords: infertility, smokers, semen parameters, motility.

INTRODUCTION

Infertility and problems of impaired fecundity have been a concern through ages, which affects 15 % of couples worldwide. Of all infertility cases, approximately 40 % is due to male factor infertility and as many as 7 % of all men will exhibit suboptimal sperm parameters. It may be one or a combination of low sperm concentration, poor sperm motility, or abnormal morphology [1,29]. The rates of infertility in industrialized nations are markedly higher and environmental are responsible for a greater proportion of infertility [1,2]. Research studies dating over the last half-century consistently demonstrate a decline in male fertility that is incompletely explained by obesity, known genetic causes, or diet and lifestyle changes alone. Human exposures have changed dramatically over the same time course as this fertility decline. Synthetic chemicals surround us, many are known to cause disruption of the hypothalamic-pituitary-gonadal axis and impair spermatogenesis. Establishing causality and the proportion of idiopathic infertility attributable to environmental toxin exposures remains elusive, however, continued investigation, avoidance of exposure, and mitigation of risk is essential to our reproductive health. Males with sperm parameters below the WHO normal values are considered to have male factor infertility [3]. The most significant of these are low sperm concentration (oligospermia), poor sperm motility (asthenospermia), and abnormal sperm morphology (teratospermia). Other factors less well associated with infertility include semen volume and other seminal markers of epididymal, prostatic, and seminal vesicle function [4,9]. As high as 90% of male infertility problems are related to count and there is a positive association between the abnormal semen parameters and sperm count. The problem with sperm count, motility, and morphology stems from disarray in control mechanism, including pre-testicular, testicular, and post-testicular factors [5]. Smoking is amongst the modifiable risk factors of reproductive health and approximately 35 % of men of reproductive age smoke cigarettes. Consumption of tobacco is increasing globally, particularly in developing countries. Smoking causes six million deaths each year directly, and 600,000 deaths indirectly per year from second-hand smoke exposure. Toxins from tobacco smoking have adverse effects on semen quality, including semen volume, sperm density, motility, viability, and normal morphology, thus causing male infertility. In addition to its link with male fertility impairment, tobacco smoking is also accountable for an upsurge in DNA injury, aneuploidies, and sperm mutations and increased apoptosis of spermatogenic cells [6]. Tobacco is considered a known cause of male factor infertility, with cigarette smoking linked to decreases in semen volume, sperm count, and sperm motility in a dose-dependent and reversible manner. A recent meta-analysis evaluated data from 16 studies of men with male factor infertility and determined that sperm count and morphology were reduced; while motility and semen pH were preserved. Cigarette smoking was associated with reduced count and motility [10,17]. Polycyclic aromatic hydrocarbons, well-recognized endocrine disrupting chemicals and reproductive toxicants in cigarette smoke, can induce endocrine-disrupting effects in males through dysregulation of testicular gap junction intercellular communication and subsequent degradation of testicular gap junction protein connexin 43 in Leydig cells. In addition to toxins found in cigarette smoke, nicotine is also thought to independently have a negative impact on semen parameters [9,11]. Cigarette smoke is composed of gases, vaporized liquid, and particles. Nearly 4,000 compounds are released through the chemical processes of hydrogenation, pyrolysis, oxidation, decarboxylation, and dehydration. The smoke release is biphasic, in the first gaseous phase, carbon monoxide is released, and in the second particulate phase, nicotine and tar are released. Cigarette smoke contains several toxic chemicals, mutagenic substances, and carcinogens, including nicotine and its metabolites, cotinine, radioactive polonium, benzopyrene, dimethylbenzanthracene, naphthalene, methylnaphthalene, polycyclic aromatic hydrocarbons and cadmium [7]. The major active components of smoke that influence semen parameters are the heavy metals cadmium and lead. The negative effect of cadmium on sperm parameters has been previously shown in animal studies. Elevated seminal cadmium in smokers has been observed if >20 cigarettes/day are consumed, and cadmium levels in the blood have been found show a statistically significant positive correlation with cigarette-years and a statistically significant negative correlation with sperm density. Additionally, lead levels in seminal plasma have been shown to be higher in infertile smokers than in fertile men and infertile non-smokers. Moreover, negative associations between seminal lead and cadmium concentrations and sperm concentration, motility, and morphological abnormalities in abnormal spermatozoa have been observed [8]. Another important biological activity is sperm motility. Creatine kinase is an enzyme expressed by cells, such as spermatozoa, that require large amounts of energy. It plays a major role in adenosine triphosphate (ATP) and adenosine diphosphate metabolism, and also provides an ATP buffering system. Ghaffari and Rostami [11,12] reported that creatine kinase activity in sperm was reduced in smokers, affecting sperm motility and overall fertility.

METHODS AND EXPERIMENTAL PROCEDURES

The study was conducted between January 2019 and January 2020 in the Clinic of Assisted Reproduction and of the Department of Biology, University of Prešov. Men with a history of infertility for at least 1 year, were consecutively evaluated. Medical history was assessed using a questionnaire including the number of cigarettes per day and the duration of smoking. Men who had stopped smoking ≥6 months prior to the examination for infertility were classified as ex-smokers and men who had never smoked as non-smokers. Every man who had smoked cigarettes for >6 months and was still smoking was classified as a smoker. Smokers were categorized as mild (≤10 cigarettes per day), moderate (>10 and ≤20 cigarettes per day) and heavy smokers (>20 cigarettes per day).

Semen samples were collected by masturbation in a clean specimen container after a sexual abstinence for 3 days, allowed to liquefy and evaluated immediately thereafter according to WHO guidelines. Ejaculate volume and time to liquefaction were measured. Sperm concentration and the concentration of round cells were determined using a haemocytometer twice per sample (Thoma, Germany). In the presence of $>10^6$ round cells/ml these cells were further differentiated using histo-chemical staining to detect peroxidase positive cells. The percentage of peroxidase positive round cells staining brown was determined by counting ≥100 round cells under the microscope (Axiolab, Germany) at 10×40 magnification. Thereafter the concentration of peroxidase positive cells was calculated by multiplying the percentage of peroxidase positive cells by the total concentration of round cells.

For evaluation of sperm morphology, prestained slides, which are used for blood cell differentiation, were smeared with a small volume of semen and allowed to air dry (Testsimplets®,Germany). Sperm morphology was determined using the WHO criteria [30]. Besides the percentage of morphologically abnormal sperm, the sperm head, neck and mid-piece, tail defects, as well as the presence of cytoplasmic droplets were assessed. Multiple defects per spermatozoon were noted, if present, by means of a laboratory cell counter (Clay Adams, USA) The total number of defects was counted and the teratozoospermic index was calculated (total number of defects/number of sperm with defects).

Motility was determined by evaluating 300 sperm per sample, 90 min after semen collection. Motility was graded according to the WHO criteria [30]. Normozoospermia was diagnosed when sperm concentration, motility and morphology were within the reference values. The reference value for sperm concentration was $\geq 20\times10^6$ sperm/ml, for motility ≥ 50 % sperm with forward progression or ≥ 25 % sperm with category movement, and for morphology ≥ 30 % sperm with normal morphology respectively. Oligozoospermia was determined when sperm concentration was less than the reference value. Severe oligozoospermia was diagnosed when the sperm concentration was $< 5\times10^6$/ml and included men who had oligozoospermia alone or in combination with asthenozoospermia or teratozoospermia. Likewise, asthenozoospermia was diagnosed when motility, and teratozoospermia when morphology, were below the reference values. An oligoasthenoteratozoospermia was diagnosed when all three variables (concentration, motility, morphology) were disturbed. Combinations (oligoasthenozoospermia, oligoteratozoospermia and asthenoteratozoospermia) were used when two variables were disturbed. Azoospermia was diagnosed when, even in the sediment after centrifugation at >3000 g for 15 min, no sperm were detected.

A descriptive analysis of the data was performed and the variables were further analysed with a t-test and analysis of variance ANOVA, Wilcoxon–Mann–Whitney test and the Kruskal–Wallis test depending on the normality assumption. Statistical analysis was performed by a bio-statistician using statistical software Statistics ver.13.

THE RESEARCH RESULTS AND DISCUSSIONS

Smoking causes reproductive hormone disorders, impairment in spermatogenesis and maturation of sperm, and compromised functioning of spermatozoa. It is an eminent risk factor for reproductive health [13,29]. Some meta-analysis addressing the association between cigarette smoking and semen quality, it was noted that most of the studies report a significant difference in semen quality were performed in normal, non-infertility clinic men. Seven out of nine studies in fertile and only six out of 19 studies in infertile men reported a statistically significant difference in semen quality. In our study on 145 infertile men, including 75 smokers, differences with respect to conventional semen parameters (sperm concentration and morphology) between non-smokers and smokers were observed. For infertility were evaluated in all 145 men. Of these, 70 were non-smokers and 75 smokers. Smokers were categorized as mild (≤10 cigarettes per day, n = 11), moderate (>10 and ≤20 cigarettes per day, n = 48) and heavy smokers (>20 cigarettes per day, n= 16). The results of categorization of infertile men are given in Figure 1.

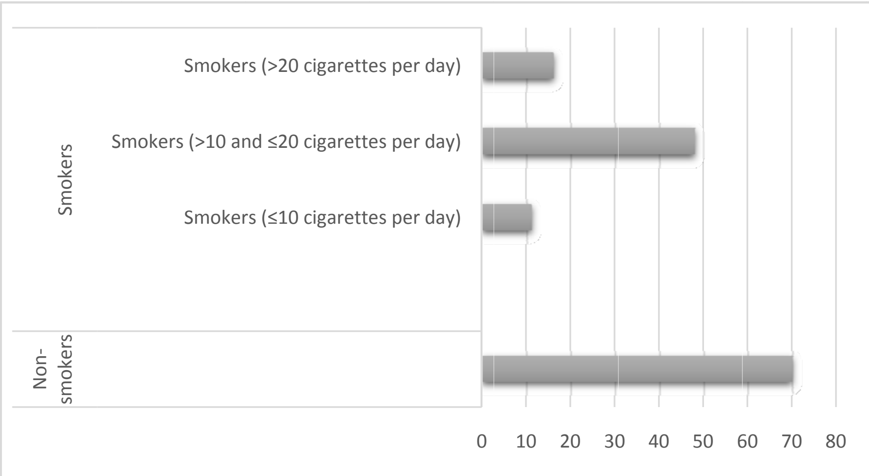

Fig. 1. The distribution of infertile men into smoking and non-smoking

Significant differences in the results of seed analyzes were seen between non-smokers and smokers, where with smokers azoospermia was observed significantly often ($p = 0.00014$). Significant differences in the results of seed analyzes were seen between non-smokers and smokers, where with smokers teratozoospermia was observed significantly often ($p = 0.00016$) and oligozoospermia ($p = 0.0011$). The results of seed analyzes are given in Table 1.

Severe oligozoospermia (sperm concentration $<5 \times 10^6$ / ml) was diagnosed in 19 men (13.10 %) and were found in 7 (10.00 %) non-smokers and 12 (16.00 %) smokers. Azoospermia was diagnosed in 14 men (9.65 %) and were found in 2 (2.85 %) non-smokers, 12 (85.72 %) smokers respectively. Teratozoospermia was diagnosed in 29 men (20.00 %) and were found in 2 (2.82 %) non-smokers and 27 (36.00 %) smokers. The difference between smokers and non-smokers was statistically significant (***$p < 0.001$ and **$p < 0.01$).

Advancing age is associated with decreased semen volume and motility and increase in abnormal morphology but with no consistent effect on sperm concentration. Sperm morphology is an indicator of the state of the seminal epithelium; degenerative changes due to ageing may affect spermatogenesis and thus alter sperm morphology [14]. We found that cigarette smoking was associated with reduced sperm quality (lower total sperm count combined with increased abnormal morphology). The mechanisms by which cigarette smoking affect semen quality are not fully understood. The fact that nicotine and its water-soluble metabolite cotinine are detectable in the seminal plasma of smokers suggests that other harmful components of tobacco smoke would pass through the blood–testis barrier [15,28]. Zavos et al. (1998) investigated the effect of smoking on the ability of seminal plasma to maintain sperm viability and found that seminal plasma from smokers had a strong detrimental effect on motility of spermatozoa from nonsmokers. Washing of sperm from smokers and exposure to seminal plasma from nonsmokers restored motility [16]. In our study differences of sperm motility between non-smokers and smokers were not observed ($p = 0.114$).

Table 1. Results of semen analyses

	Non-smokers (%) (n = 70)	**Smokers (%) (n = 75)**
Normozoospermia	44 (62.85 %)***	7 (9.33 %)
Asthenozoospermia	2 (2.85 %)	4 (5.33 %)
Oligozoospermia	7 (10.00 %)	12 (16.00 %)**
Teratozoospermia	2 (2.85 %)	27 (36.00 %)***
Asthenoteratozoospermia	7 (10.00 %)	6 (8.00 %)
Oligoasthenozoospermia	1 (1.42 %)	3 (4.00 %)
Oligoteratozoospermia	2 (2.85%)	3 (4.00 %)
Oligoasthenoteratozoospermia	3 (4.28%)	1 (1.33 %)
Azoospermia	2 (2.85 %)	12 (16.00 %)***
Values in parentheses are percentages		
*****p < 0.001; **p < 0.01, n- total**		

Mean age, body mass index, as well as semen parameters for non-smokers and smokers shown in Table 2. Compared with non-smokers, smokers were significantly younger ($p < 0.05$), had significantly more round cells in their ejaculates ($p < 0.05$). The percentage of ejaculates with > 1×10^6 / ml peroxidase positive round cells was also significantly higher in smokers than non-smokers ($p < 0.01$). Non-smokers had a significantly higher BMI ($p = 0.043$) compared with smokers. We reviewed several studies [18, 19, 20, 21] to determine the mechanism by which BMI influenced semen quality and male fertility. This mechanism comprises dysfunction of the hypothalamus pituitarygonadal axis, abnormal levels of reproductive and related hormones (INH-B, FSH, LH, E2 , PRL, leptin, T, SHBG, and AMH), dysfunction of male sexual accessory glands (neutral alpha-glucoside enzyme and seminal plasma fructose), and living and dietary habits (coffee intake volume) in overweight or obese patients. An increase in weight or BMI might have no apparent impact or damage on the sperm output from the testes while it influences sperm maturity, motility, or DNA damage. Indeed, BMI, abstinence period, and coffee intake might improve semen quality and enhance male fertility. There is disagreement as to whether or not BMI has an influence on semen parameters and semen quality [27]. Our research demonstrated that the most adversely affected susceptible factor among the semen parameters was not sperm motility. Indeed, statistical differences not existed in sperm motility among the different groups. Teratozoospermic index was significantly higher in smokers than non-smokers ($p < 0.01$). Sperm concentration was significantly higher in non-smokers than smokers ($p < 0.001$).

Out of 75 smokers, 21 were classified as mild, 48 as moderate and 16 has heavy smokers. Classifying smokers as mild, moderate and heavy, only BMI (25.6, 26.5, 24.3 kg / m^2, $p = 0.05$), the mean number of cigarettes per day (5.1, 14.7, 33.4, $p < 0.001$) and the duration of smoking (8.1, 14.5, 16.9 years, $p < 0.001$) were significantly different between mild, moderate and heavy smokers Table 3.

Table 2. Mean age, body mass index and the results of the semen analyses of non-smokers and smokers

	Non-smokers ± SD (n = 70)	**Smokers ± SD (n = 75)**	**p**
Age	36.74 ± 0.87	33.47 ±0.14	0.036*
Body mass index (kg/m^2)	27.03 ± 0.65	26.41 ± 0.11	0.043*
Volume (ml)	3.45 ± 0.97	3.57 ± 0.86	0.603
Liquefaction time (min)	36.12 ± 1.45	37.11 ± 1.74	0.759
Morphologically abnormal (%)	56.7 ± 4.23	57.27 ± 5.11	0.235
Head defects (%)	38.54 ± 2.14	39.74 ± 4.12	0.137
Tail defects (%)	13.12 ± 1.23	14.77 ± 2.31	0.065
Teratozoospermic index[c]	1.16 ± 0.13	1.48 ± 0.65	0.002**
Sperm concentration (×10^6/ml)	59.16 ± 1.29	56.84 ± 2.71	0.000***
Sperm motility (%)	22.45 ± 2.40	19.13 ± 1,73	0.114
Round cells (×10^6/ml)	2.69 ± 0.42	3.45 ± 1.05	0.017*
Values are means, (SD), n - total			
[a]Significantly different from non-smokers			
[b]Significantly different from smokers			
[c]Teratozoospermic index = total number of defects/number of sperm with defects			

Table 3. Classifying smokers as mild, moderate and heavy

	Smokers (n = 75) ± SD			**p**
	Mild (n = 11)	Moderate (n = 48)	Heavy (n = 16)	
BMI [kg/m^2]	25.6 ± 0.25	26.5 ± 1.3	24.3 ± 1.31	0.05*
cigarettes per day	5.1 ± 0.17	14.7 ± 1.23	33.4 ± 0.93	0.001***
duration of smoking	8.1 ± 2.41	14.5 ± 1.74	16.9± 1.43	0.001***
Values are means, (SD), n – total, ***p < 0.001; **p < 0.01; * p < 0.05 significantly				

In our study, 44 non-smokers had normozoospermia with their semen parameters falling within the normal ranges. In contrast, samples from only 7 smokers qualifi ed as normozoospermia. This fi nding underscores the fact that smoking certainly has an adverse infl uence on the semen quality, as concluded in several other studies [22, 23]. A was dominant semen variable contributing to the semen quality of smokers (n = 32) as well as non-smokers (n = 13), individually as well as in combination with other variables like teratozoospermia (A+T), oligozoospermia, (A+O) and (A+O+T) (Table 4-5). A appears to be a premier factor contributing to the infertile status of a male. But T was the most dominant semen variable contributing to the semen quality of smokers (n = 36) as well as non-smokers (n = 14), individually as well as in combination with other variables. Viable and morphologically normal spermatozoa, if they are not actively motile, showing linear forward motion in the seminal fl uid, they will fail to fulfi l their prime function of traversing the complex route through the female genital tract to seek and fertilise an ovum. In assessing the semen quality of an individual, emphasis has always been on the sperm count and sperm morphology. In comparison, less number of cases showed contribution of O among smokers but their numbers were still higher than in non-smokers (Table 5). This again shows that smoking contributes to the deterioration of the semen quality of smokers when compared with non-smokers. Isolated A was seen in 1 of light smokers and 3 of moderate smokers, while no such case was detected among heavy smokers (Table 4).

Table 4. Semen variables among different groups of smokers in comparison to non-smokers

Diagnosis	Non-smokers (n = 70)	Smokres (n = 75)			p
		Mild (n = 11)	Moderate (n = 48)	Heavy (n =16)	
Normozoospermia	44	4	3	0	<0.001
Asthenozoospermia	2	1	3	0	NS
Oligozoospermia	7	1	8	3	<0.01
Teratozoospermia	2	1	19	7	<0.001
Asthenoteratozoospermia	7	1	4	1	NS
Oligoasthenozoospermia	1	1	1	1	NS
Oligoteratozoospermia	2	1	1	1	NS
Oligoasthenoteratozoospermia	3	0	1	0	NS
Azoospermia	2	1	8	3	<0.001
*****p < 0.001; **p < 0.01, n- total, NS – not significantly**					

Researchers have variously concluded that toxins in cigarette smoke reach the male reproductive system, and their effects, though still under research, are mainly due to their direct interaction with seminal fl uid components and the accessory glands, which contribute their secretions to the seminal fl uid, leading to its increased viscosity, reduced seminal volume and delayed liquefaction time, thus reducing forward linear progression of spermatozoa, manifesting as teratozoospermia and asthenozoospermia [26,27,28]. In studies conducted on fertile men, it was observed that those who were smokers showed a reduction in semen volume in comparison to non-smokers and this reduction in semen volume was in proportion to the number of cigarettes smoked per day. Direct exposure of spermatozoa to the toxins in cigarettes smoke probably tilts the delicate balance of reactive oxygen species (ROS) that are produced by spermatozoa for their special functions like decapitation. Increased quantities of ROS have been shown to be detrimental to the DNA of spermatozoa, thus producing a negative effect on the viability and morphology of spermatozoa [24,25]. Thus, smoking plays a role in producing teratozoospermia and asthenozoospermia in otherwise normal and viable spermatozoa, and can be a very subtle “early indicator” of deterioration in semen quality. Since 14 % of non-smokers too showed T (Table 5), many of these non-smokers may be innocent “passive smokers” or may be affected by environmental pollutants, chemicals and other unknown factors awaiting discovery. A higher level of research in non-smokers cases may unmask the infl uence of these additional factors.

In conclusion, teratozoospermia is the most common anomaly of semen, whether present individually or in combination with asthenozoospermia and/or oligozoospermia. The presence of asthenozoospermia can be a very subtle “early indicator” of reduction in the semen quality of an individual, which frequently gets ignored, if the semen sample shows adequate sperm count and normal morphology. Smoking does affect semen quality. Deterioration in semen quality appears in direct proportion to the number of cigarettes smoked. There is no “safe” quantity of cigarette smoking as refl ected by predominance of asthenozoospermia in moderate smokers. Heavy and moderate smoking reduce semen quality further by also producing teratozoospermia. Oligozoospermia may be a result of other aetiological factors besides smoking, and this needs further exploration.

Table 5. Semen variables in smokers and non-smokers

Semen variable	**Smokers (n = 75)**				**Non-smokers (n=70)**	**p-value***
	Mild (n=11)	**Moderate (n=48)**	**Heavy (n=16)**	**Total (n=75)**		
Asthenozoospermia (A)+(A+T)+(A+O) + (A+O+T)	3	21	8	32	13	<0.001
Teratozoospermia (T)+(A+T)+(O+T) + (A+O+T)	2	25	9	36	14	<0.01
Oligozoospermia (O)+(A+O)+(O+T) + (A+O+T)	4	11	5	20	13	<0.05
A: Asthenozoospermia; O: Oligozoospermia; T: Teratozoospermia; *p-value						

CONCLUSION

Smoking has a significant effect on fertility, specifically sperm count and normal morphology of sperm. This might be due to OS produced by smoking, which has devastating effects on semen parameters, thus reducing male fertility. Smoking has measurable effect on semen quality and function in men. This may be attributed to impaired semen parameters and spermatozoa function at the primary level in the infertile population. Epigenetic changes that result from smoking may correlate directly with reduced sperm function and reduced fertility, thereby providing a possible mechanism for the effect of smoking on male fertility. This correlation should be further investigated. Healthcare providers should facilitate smoking cessation by education, monitoring, and constant support. The data on smoking and male fertility reinforce the preferred preventive approach of discouraging smoking and eliminating exposure to tobacco smoke among both males and females in general, and in particular, while trying to conceive.

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REFERENCES

1. Molina R.I., Martini A.C., Tissera A., Olmedo J., Senestrari D., de Cuneo M.F., Semen quality and aging: Analysis of 9.168 samples in Cordoba, Argentina Arch Esp Urol., vol. 63, pp 214–222, 2010;

2. Mascarenhas M.N., Cheung H., Mathers C.D., Stevens G.A., Measuring infertility in populations: Constructing a standard definition for use with demographic and reproductive health surveys, Popul Health Metr., 2012, pp 10-17;

3. Plachot M., Belaisch-Allart J., Mayenga J.M., Chouraqui A., Tesquier L., Serkine A.M. Outcome of conventional IVF and ICSI on sibling oocytes in mild male factor infertility. Hum Reprod., vol. 17, pp 362–9, 2002;

4. Harris I.D., Fronczak C., Roth L., Meacham R.B., Fertility and the aging male, Rev Urol., vol. 13, pp 184–90, 2011;

5. Sabra S.M., Al-Harbi M.S., An influential relationship of seminal fluid microbial infections and infertility, Taif Region, KSA., World J Med Sci., vol. 10, pp 32–37, 2014;

6. Alsaed Laith W., Barkhudarov A., The effect of smoking on the male factor of infertility, Biomed. Sociology, vol. 3, pp 23–25, 2018;

7. Richthoff J., Elzanaty S., Rylander L., Hagmar L., Giwercman A., Association between tobacco exposure and reproductive parameters in adolescent males., Int J Androl., vol. 31, pp 31–39, 2008;

8. Pant N., Kumar G., Upadhyay A.D., Gupta Y.K., Chaturvedi P.K., Correlation between lead and cadmium concentration and semen quality, Andrologia, vol. 47, pp 887–891, 2015;

9. Kubincová P., Sychrová E., Raška J., Polycyclic Aromatic Hydrocarbons and Endocrine Disruption: Role of Testicular Gap Junctional Intercellular Communication and Connexins, Toxicol Sci, vol. 169, pp 70-83, 2019;

10. Kovac J.R., Khanna A., Lipshultz L.I., The effects of cigarette smoking on male fertility, Postgrad Med, vol. 127, pp 338-341, 2015;

11. Bundhun P.K., Janoo G., Bhurtu A., Tobacco smoking and semen quality in infertile males: a systematic review and meta-analysis, BMC Public Health, 2019, pp 19-36;

12. Miyaji K., Kaneko S., Ishikawa H., Aoyagi T., Hayakawa K., Hata M., Creatine kinase isoforms in the seminal plasma and the purified human sperm, Arch Androl., vol. 46, pp 127–134, 2001;

13. Ghaffari M.A., Rostami M., The effect of cigarette smoking on human sperm creatine kinase activity: as an ATP buffering system in sperm, Int J Fertil Steril., vol. 6, pp 258–265, 2013;

14. Kumar, S., Murarka, S., Mishra, V., Gautam, A., Environmental & lifestyle factors in deterioration of male reproductive health, Indian J. Med. Res., vol. 140(Suppl. 1), pp S29–S35, 2014;

15. Kidd S.A., Eskenazi B., Wyrobek A.J., Effect of male age on semen quality and fertility: a review of the literature, Fertil Steril, vol. 75, pp. 237-248, 2001;

16. Vine M.F., Hulka B.S., Margolin B.H., , Truong Y.K., Hu P.H., Schramm M.M., Cotinine concentrations in semen, urine, and blood of smokers and nonsmokers, Am J Public Health, vol. 83, pp. 1335-1338, 1993;

17. Zavos P.M., Correa J.R., Antypas S., Zarmakoupis P.N., Zarmakoupis C.N., Effects of seminal plasma from cigarette smokers on sperm viability and longevity, Fertil Steril, vol. 69, pp. 425-429, 1998;

18. Bundhun P.K., Girish J., Bhurtu A., Teeluck A.R., Soogund M.Z.S., Pursun M.,Huang F., Tobacco smoking and semen quality in infertile males: a systematic review and meta-analysis BMC, Public Health, 2019, pp 19 - 36;

19. Håkonsen L.B., Thulstrup A.M., Aggerholm A.S., Olsen J., Bonde J.P., Andersen C.Y., Bungum M., Ernst E.H., Hansen M.L., Ernst E.H., Does weight loss improve semen quality and reproductive hormones? Results from a cohort of severely obese men, Reprod Health, 2011, pp 8 – 24;

20. Wogatzky J., Wirleitner B., Stecher A., Vanderzwalmen P., Neyer A., Spitzer D., Schuff M., Schechinger B., Zech N.H., The combination matters—distinct impact of lifestyle factors on sperm quality: a study on semen analysis of 1683 patients according to MSOME criteria, Reprod Biol Endocrin, 2012 pp 10 -115;

21. Hofny E.R., Ali M.E., Abdel-Hafez H.Z., Kamal Eel D., Mohamed E.E., Abd El-Azeem H.G., Mostafa T., Semen parameters and hormonal profile in obese fertile and infertile males, Fertil Steril, vol. 94, pp 581–584, 2010;

22. Martini A.C., Tissera A., Estofán D., Molina R.I., Mangeaud A., de Cuneo M.F., Ruiz R.D., Overweight and seminal quality: a study of 794 patients, Fertil Steril, vol. 94, pp 1739–1743, 2010;

23. Kunzle R., Mueller M.D., Hanggi W., Semen quality of male smokers and nonsmokers in infertile couples, Fertil Steril, vol. 79, pp 287-91, 2003;

24. Zhang J.P., Meng Q.Y., Wang Q., Effect of smoking on semen quality of infertile men in Shandong, China. Asian J Androl, vol. 2, pp143-6, 2003;

25. Pasqualotto F.F., Sobreiro B.O., Hallak J., Pasqualotto E.B., Lucon A.M., Cigarette smoking is related to a decrease in semen volume in a population of fertile men, BJU Int, vol. 97, pp 324-6, 2006;

26. Harlev A., Agarwal A., Gunes S.O., Shetty A., du Plessis, S.S., Smoking and Male Infertility: An Evidence-Based Review, World J Mens Health, vol. 33, no. 3, pp 143–160, 2015;

27. Trummer H., Habermann H., Haas J., Pummer K., The impact of cigarette smoking on human semen parameters and hormones, Human Reproduction, vol. 17, no. 6, pp 1554–1559,2002;

28. Wen-Hao T., Xin-jie Z.,Lu-Lin M., Qiao J., Hong K., Lian-Ming Z., De-Feng L., Jia-Ming M., Hong-Liang Z., Shan-Jie Z., Hui J., Correlation between body mass index and semen quality in male infertility patients, Turk J Med Sci, vol. 45, no. 6, pp 1300-1305, 2015;

29. Kumar N., Singh A.K., Trends of male factor infertility, an important cause of infertility: A review of literature, J Hum Reprod Sci., vol. 8, no. 4, pp 191–196, 2015;.

30. Organization World Health, WHO Laboratory Manual for the Examination of Human Semen and Semen—Cervical Mucus Interaction, 4th ed. Cambridge, United Kingdom: Cambridge University Press, 1999;

RATIONAL LAND USE IN THE LAND MANAGEMENT SYSTEM

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ABSTRACT

The purpose of the article is to substantiate the role of rational land use in the land management system. The paper defines that the effectiveness of managerial influence on land use should be assessed through the prism of land use rationalization. It was found that the main condition for the rational use and protection of land is the organization of land management on a landscape basis. It is determined that the content of rational land use is to apply a set of investment and non-investment factors aimed at increasing soil fertility, their protection, increasing the number of products needed by society, improving its quality, increasing productivity. It was found that the rational use of land is to achieve the maximum effect in the implementation of strategic goals of land use, taking into account its full interaction with other natural and environmental factors. It is believed that an important role in achieving the condition of rationalization of land use belongs to land management, through which the condition of rational organization of the territory and location of production is achieved. It is noted that the development of land use development strategy should be based on such successive steps as establishing the types, species and number of crop rotations; placement of crop rotations; placement of crop rotation fields and working areas; placement of field protection strips; placement of field roads; location of field camps and water sources; placement of irrigation network. The goals and objectives of rational land use are defined. The main components that will affect the rational use of land are indicated.

Keywords: rational land use, land management, land management, land organization, soil fertility, land use optimization.

INTRODUCTION

Exit from the crisis of the agricultural sector of the economy is not possible without the dominance of innovation and the formation of innovative development of enterprises. This will increase the competitiveness and competitive position of the latter in both domestic and foreign markets. Achieving innovation is directly related to achieving rational use of land resources.

Rational land use today should be actively designed to increase the efficiency of agricultural land use, which will improve the level and quality of life of the population, ensuring the formation and development of sustainable land use.

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Many economists, each trying to understand the problems of land use in their own way, have made significant scientific and practical contributions to elucidating the development of economic views on land use and protection.

Well-known scientists have devoted a number of works to the problems of rational land use as S. Volkov, V. Viyun, D. Gnatkovich, V. Horlachuk, B. Danilishin, D. Dobryak, A. Martin, V. Mesel-Veselyak, L. Novakovsky, P. Sabluk, A. Sohnich, A. Tretyak, M. Fedorov and others.

Their works formulate methodological aspects of management, some ways of practical implementation of measures aimed at improving land use.

Analyzing the processes of land use, outlining the prospects for their development, it is necessary to have a clear vision of why at all stages of the evolution of land society was given special importance. Historical experience has shown that the concept of "fatherland", its sacred value, still remains in people's minds, and a mentality has been formed, formed due to respect for the agricultural work of our ancestors. The point is that the whole course of society's development was based on the struggle for land ownership as the main priority of the economy.

The intensification of economic activity on land in a market economy has become the basis for the accelerated transformation of traditional mechanisms of land use into new, democratic, market. This process is due to the fact that traditional mechanisms have long remained quite imperfect, did not provide effective land use management, as a result of which in Ukraine the use and protection of land resources were destructive, economically costly and carried out mainly without clearly defined environmental, economic and social justification.

But even today the implementation of the market model of agricultural land development is accompanied by significant difficulties, complicated by the practice of land management. A wide range of issues related to ensuring the rational use and protection of land remains unresolved, namely: problems related to ensuring the rational use and protection of land, namely: no comprehensive inventory of the state land fund; no preconditions have been created for scientifically substantiated distribution of land by purpose, taking into account the interests of landowners and land users; unresolved issues of organization of agricultural land use; a rational system of land tenure and land use has not been formed to create ecologically balanced landscapes.

In a market economy, when there is a need for the development of competitive land use, there is a lack of existing research, which would reveal the theoretical, methodological and methodological foundations of the strategy for the development of rational land use. Moreover, the multifaceted nature of this problem requires the formation of an effective organizational and economic mechanism of strategy for the development of rational land use, improving management efficiency based on the laws and principles of strategic management, which determines the relevance of research.

METHODS AND EXPERIMENTAL PROCEDURES

The theoretical and methodological basis of scientific research are the fundamental provisions of the economics of land use, general theoretical provisions of rational land use, domestic and foreign research on land management in the system of rational land use.

To solve the tasks set in the work, the following methods were used: abstract-logical (for theoretical generalizations of scientific research results and formation of conclusions); analysis and synthesis (with a comprehensive assessment and clarification of the current state of land use); graphic (to illustrate the results of the study); analogies and generalizations (to develop a system of measures to justify the role of rational land use in the land management system).

THE RESEARCH RESULTS AND DISCUSSIONS

The works of the above researchers are a basis for the development of various aspects of the problem of rational land use. However, at all stages of development of society this problem was considered differently.

Thus, the famous Ukrainian scientist P. Vedenichev wrote that the term "rational use" of land resources should be understood as the feasibility, completeness and degree of efficiency of land use. These scientists made an attempt to look at the problem of rational land use from these positions and to propose the ideology of land policy. This concept has led to the negative trends we currently have in land use: the spread of erosion processes, low land productivity, catastrophic losses of humus in the soil and others. Therefore, the formation of an effective land use policy taking into account the environmental component and led to the choice of the topic of this article, because the current environmental and economic situation suggests that the relevance of research in the field of land relations is not decreasing.

Examining this problem, the authors concluded that the rational use of land should be considered through the prism of the maximum possible at this level of scientific and technological progress of socially necessary products per unit area with minimal socially necessary costs for its production with constant improvement of productive land properties. This idea is decisive because it initiates the harmony of society and nature as a primary component of rational land use. On the other hand, the concept of "rationality" is very abstract and does not reflect the essence of the problem of land use. That is why it is logical, in our opinion, to use the term "optimal" land use. Therefore, in each case regarding land use, it is necessary to proceed from the position of "optimal land use", which in a narrow and broad sense reflects the process of land use and preservation of its useful properties.

A. Radchenko in his work [1] notes that the rational use of land is their targeted and comprehensive use, which achieves a balance (optimal, harmonious relationship) between the efficiency of land use and environmental requirements. As we can see, the author emphasizes that rational use is the optimal use of land, which does not contradict our opinion on the use of the term "optimal land use" or "optimal land use". In this sense, modern science relies on ecology to perceive new requirements for land use optimization.

Yes, Professor M. Fedorov noted that the rational use of land is "… such land use, which provides a scientifically sound economic effect of management and at the same time improves soil fertility and ecological condition of the environment" [2, p. 200]. However, we believe that this definition is limited because it does not take into account the impact of social factors on land use results.

Other scientists [3] noted that the rational use of land means the use that meets its intended purpose, provides high efficiency of land use and protection, aimed at preventing unjustified withdrawal of agricultural land, protection from anthropogenic impact, reproduction and increase soil fertility.

Researcher L. Fomenko considers the concept of "rational land use" as "… socio-economic category that expresses the relationship between people in the process of technological production cycles" in order to meet the needs of the population in food, while ensuring the restoration and increase of productive potential land resources… " [4, p. 6]. The proposed concept of rational land use is based on the social component, although it does not take into account the conditions that ensure the formation of efficient land use.

Considering the issue of land use rationalization, we can agree with the opinion of M. Stupen, who argued that the rational use of land is "a complex problem that affects all aspects of the organization of agricultural production and requires appropriate investment" [5, p. 58]. However, in our opinion, the researcher somewhat narrows the understanding of the essence of rational land use, affecting mainly agricultural land, ignoring the land of other categories by purpose.

Today the government representatives have not authorized the adoption of social, economic, environmental and other development programs territories. Therefore, to address these and other problems there is a need to create conditions for optimal economic independence of undertakings on the ground. Considering that the financial and economic basis at the local level are such natural resources as land, it has to ensure socio-economic development of the region. That region is characterized not as a subsystem of the country, but as an independent entity with an internal mechanism of reproduction, that includes an independent production and realization of elaborated product on the land.

Each individual entity on the land has to link the results of production activities of its financial achievements. In Ukraine, solving environmental and economic problems associated with the introduction of the modern achievements of science and technology that can ensure intensive development of social production and increase its competitiveness.

Generally, it can be ascertain that further development of ecologically safe land use should be considered in the light of adaptation of land legislation with international standards as modern system of land use in Ukraine, which is the result of structural deformation of the economy, does not provide safe conditions of the formation and management of land.

Considering that each region has individual characteristics in a territorial system, the nature of its economic development has to be formed taking into account the specific characteristics of the territory.

After a theoretical analysis of the analyzed concept, we came to the conclusion that "rational land use" should be understood as the process of maximum satisfaction of socio-economic needs with minimal costs within the relevant categories of land for its intended purpose.

Note that the rational use of land resources should provide a qualitative transformation of accumulated knowledge in the field of land use. Achieving this condition is ensured by a clear conceptual and categorical apparatus that meets the needs of society.

In this regard, it should be noted that the effectiveness of management influence on land use should be assessed through the prism of land use rationalization.

The main condition for the rational use and protection of land is the organization of land management on a landscape basis, the essence of which is not only to take into account a set of natural - economic factors, but also to learn the laws of landscape structure, processes that take place in them, for a certain period of time, which arise under the influence of anthropogenic action, etc. Only under this condition will the optimal land relations be formed, which will allow to resolve the existing contradictions of the relationship between man and the natural environment, will be solved socio-economic, economic and other problems of rational land use. Actually, the organization of rational land use should be focused on overcoming problematic situations in nature use in general and in land use in particular.

Previously, a significant obstacle to management decisions was the lack of ecological and economic zoning of the territory based on the assessment of the ecological condition of land resources, their ability to recover. Without this kind of information, it is impossible to substantiate any territorially differentiated measures of rational land use.

The content of rational land use is to apply a set of investment and non-investment factors aimed at increasing soil fertility, their protection, increasing the number of products needed by society, improving its quality, increasing productivity. In other words, these factors should be focused on improving the quality characteristics of the main means of production. As a result, an objective possibility of dynamic development of rational land use is formed.

Algorithm of formation of the mechanism of rational use and protection of lands, acceptance of the correct administrative decisions concerning their use cause necessity of methodological and methodical substantiation of essence of rational land use which would be adequate to a modern situation in the state and region. In general, the complexity of the problem of rational use of agricultural land is the absence or ambiguity of a formalized assessment of a standard set of indicators that would allow to draw an appropriate conclusion. In addition, back in 1992, the United Nations Conference on Environment and Development in Rio de Janeiro stressed the need to develop indicators that would take into account the many relationships and patterns between the development of society and the state of the environment. This issue was then considered at the sessions of the UN International Commission on Environment and Development as one of the priorities.

The Millennium Summit in 2000 adopted the Millennium Declaration, which formulated a number of goals, targets and quantitative indicators, known as the Development Goals.

In general, an indicator is a tool that simplifies the characterization of a situation that is part of a complex or system [6].

Thus, indicators serve as criteria for determining indicators of further development.

As for the legal provision of rational use and protection of land, today there is a need to adopt and adopt the Law of Ukraine "On Rational Land Use", which would define both political, legal, environmental, economic and innovative aspects of rational use of land resources, would take into account the conditions use of land resources on the basis of sustainability of land use. Such a law would revive competitive advantages due to the regulatory role of the state by supporting domestic producers, initiating the development of the land market, development of market infrastructure, the introduction of economic methods of regulating land relations. The implementation of this Law will outline the strategy of rational development of land use in the state and the region.

In addition, it can be stated that an important role in achieving the condition of rationalization of land use belongs to land management, through which the condition of rational organization of the territory and location of production is achieved.

Understanding the uniqueness of the role of land as the main means of production in agriculture and forestry, the spatial basis of economic activity by economic entities, in general, objectively there is a need to develop forecasting, planning and design documentation for land management, which would reflect the model of land use, focused on meeting the socio-economic, cultural, environmental and other needs of society and the state without losing the useful consumer properties of the land.

The purpose of land management at the local level is to organize the territory of agricultural enterprises in order to organize agricultural land, providing environmental and economic optimization of land use, location of industrial buildings and structures, determining the types and types of crop rotations, crop rotation schemes, organization of haymaking and , development of a system of measures on specific land plots for the preservation and improvement of natural landscapes, allotment of land plots in case of their provision, transfer, withdrawal or alienation for other needs, landscaping of settlements.

In order to dynamize the developed land management measures at this level, working land management projects are developed in order to implement measures "provided for in land use and protection schemes, schemes and land management projects" [7, Art. 54].

But although management activities are aimed at implementing appropriate transformations in agricultural land use through appropriate Programs and Schemes, the set of goals and means to achieve them is functionally inconsistent and not interdependent, so they will not be able to ensure predetermined results.

This indicates the mobilization of efforts to develop regional land management Schemes, which are the driving force behind the process of rational use and protection of land. The development of such Schemes should be part of the Program for the development of land relations in the region with the allocation of funds for its development.

But in practical terms, regional land management Schemes should be developed on the basis of land management schemes of administrative-territorial entities, although in general the regional Scheme should be developed on the principle of general to partial, however, the regional Scheme should be the result of district. This is the main requirement, because not always in the region will be the right solution to all issues of rational land use on the basis of arithmetic sums of district studies, as not all issues at the level of administrative-territorial formation can be properly solved without studies in the region.

Regarding the methodological provisions for the development of Schemes of administrative-territorial entities, their content should include:

- general characteristics of the district in the context of the territories of the respective councils;

- analysis of the current state of land use, their distribution by forms of ownership and management of land;

- justification of the limited land use regime;

- development of project proposals.

From the above it is clear that the decisions taken by the authorities on the development of land management Schemes are practical steps towards the implementation of comprehensive systemic measures for the rational use and protection of land. Therefore, given the positive experience in developing such schemes, we believe that the National Program of Land Use and Protection is less important than the development of regional targeted programs, because it is the territorial authorities who have the main responsibility for the results of social and economic development.

On the other hand, land use planning and protection is better adapted to the development of a more specific area development strategy than considering national land use planning.

Today it is necessary to form clear methodological positions on the organization of agricultural land use, which would prevent the development of degradation processes, ensure the preservation and reproduction of soil fertility, biodiversity and landscapes, production of quality agricultural products in domestic and foreign markets. In this regard, the purpose of land management is, first of all, to form a general theoretical and methodological basis for constructing a model of development of the territory, which ensures its long-term development. Land management is a unifying force in the implementation of a set of measures to ensure and uniform development of strategic plans of land management, improves the patterns of land use, which derives the principles, methods and techniques of land use, outlines the methodological foundations of land management. It is an important link in the implementation of a set of all measures for the organization of use, accounting, assessment, protection and reproduction of soil fertility, conservation of diversity and landscapes.

With the help of land management, land relations are strengthened, state and local interests are harmoniously reconciled, and as an element of the development of productive forces, it is an integral part of the social mode of production.

In summary, we can say that the land management project is a business plan for land use development, which initiates the efficient use of natural resources and human potential, enhances domestic and foreign investment, expanding economic integration, determines the totality and interaction of legal, social, economic, environmental, organizational, cultural, technological and other relations between people in the process of land use and protection.

Following these approaches to running a business, we can conclude that business is primarily a creative activity on the opportunities of the external environment to create the potential for entrepreneurial success and methods of its implementation in practice.

We believe that in agricultural land use the business model is a way to create value (running business) in economic activities in rural areas, which opens new opportunities to involve the rural people in production and provides access to all people to economic benefits from increased profitability and diversification of economic activity.

Based on the all mentioned above, it is proposed to focus on the development of land use schemes of local councils territories, which will develop projects of contour and reclamation organization of the territory for each land entity. Moreover, it will positively affect the quality and efficiency of agricultural production.

The peculiarity of such schemes should be its tracing of the integrity of the land use strategy in local councils territories, the identification of the uncertainties and risks of predictable and unpredictable events in land use.

At the same time, the primary purpose of the business model of agricultural land use development is to represent a holistic picture both of a specific land use and agricultural enterprise, to agree on different points of view on the functioning of agrarian business. Therefore, the critical elements of the business model of land use that determine its content are:

- the value of services offered by the agricultural enterprise for external users;

- possible suppliers of raw materials and materials necessary for running a business in the countryside (insufficient planting material, fertilizers, etc.);

- assets produced by the agricultural enterprise for the creation of valuable services and livelihood of both its community and external users;

- financial model of the village community, which determines both the structure of its costs and ways to make a profit.

So the main tasks of the business model of agricultural land use are the following:

- obtaining a holistic picture of the economic cycle, the coordination of different points of view on the changing and continuously evolving business;

- mobilization of capital through investors and creditors, accumulation of sales revenues and their use in the daily activity of the enterprise;

- ensuring the reduction of production costs and increase the level of quality and service;

- development of a business plan package for each of the market segments of rural areas, which will practically implement a comprehensive environmental, economic and social strategy for land use development, which will address the organization of land use on a profitable basis;

- coordination of efforts of local authorities, land management entities, small and medium businesses, investors, scientific and technical centers for the production of competitive goods, and access to domestic and world markets.

So in the agricultural land use sphere, the business model reflects all the objects, principles, processes, rules of operations, the existing development strategy, as well as criteria for assessing the effectiveness of land use.

Accordingly, land management as part of the social mode of production, based on the relevant forms of land ownership is a source of land capital growth based on the planned and scientifically sound use of land and other means of production.

Today, when there is mainly a redistribution of agricultural land between all participants in land relations, the main focus of land management is on the internal organization of land use.

Modern features of economic activity on the land, the latest vision of the process of organizing the territory of agricultural land use gives grounds for the development and implementation of land management projects according to the following scheme:

- analysis of land use;

- functional zoning of lands (types and subtypes of land use, restrictions and encumbrances on land use, land easements, engineering arrangements, etc.);

- landscaping of arable land;

- landscaping of perennial plantations;

- landscaping of forage lands;

- determining the effectiveness of the project;

- transfer in kind of elements of the designed actions;

- state and self-government control over land management.

Thus, the importance of the problem of rational use and protection of land requires an in-depth analysis of the land fund, the study of objective indicators of this phenomenon.

Rational use of land is the achievement of the maximum effect in the implementation of strategic goals of land use, taking into account its full interaction with other natural and environmental factors.

It should be noted that the analytical work should be carried out according to the scheme of two stages:

- preparatory work, taking into account the development of the main directions of land use and the development of land use production in the future;

- field land surveys.

The analysis will identify problem points and identify priority strategies for land use development, taking into account its strengths and weaknesses.

Functional zoning is the division of land into zones according to their categories and types of land use, economic suitability for growing certain crops.

The concept of zoning should take into account the types and subtypes of land use:

- agricultural, which includes subtypes: field, soil protection, garden, hay-pasture, special mixed;

- residential, which includes subtypes: manor, cottage, etc .;

- production, which includes subsidiary farmyards, field mills, livestock complexes, etc .;

- protected, which includes subtypes: protected, protected and recreational and environmental;

- recreational, which includes subtypes: country, for the organization of recreation, tourism and sporting events;

- historical and cultural;

- forestry, which includes subtypes: production, protective, special;

- water management, which includes subtypes: production, protective, special;

- selection of areas not suitable for growing major crops according to the level of cost recovery;

- allocation of zones of ecological restrictions, which include subtypes: sanitary protection zones, protection zones, sanitary protection zones, zones of special land use regime, zones of technogenic-contaminated lands (radiation-dangerous and radioactively contaminated, lands contaminated with heavy metals, other chemical elements, etc.);

- areas subject to conservation of degraded and unproductive lands;

- engineering and transport infrastructure, etc.

The development of land use development strategy should be based on the following methodology:

- establishment of types, types and quantity of crop rotations;

- placement of crop rotations;

- placement of crop rotation fields and working areas;

- placement of field protection strips;

- location of field roads;

- location of field mills and water sources;

- placement of an irrigation network.

To ensure greater efficiency of perennial plantations, the maximum use of mechanization of production processes, a detailed arrangement of each array of plantations.

In this regard, the work is performed in the following sequence:

- breeds and grades are placed;

- quarters and brigade sites are located;

- protective forest plantations are located;

- the road network and water sources are located;

- in case of need the irrigation network is placed.

In the context of landscaping pastures, the following elements are distinguished:

- establishment of pasture changes;

- placement of wholesale and flock areas;

- placement of detachments for grazing;

- location of summer camps;

- location of water sources;

- placement of cattle runs.

In addition, for conditions with insufficient soil moisture, pasture irrigation is provided.

Landscaping of hayfields provides:

- placement of hayfields;

- location of the road network;

- location of water sources and other elements, based on specific conditions.

One of the key points in the management of agricultural land is to identify the effectiveness of the planned measures. This determines the economic and social efficiency and environmental efficiency by preventing (preventing) destructive processes in land use.

One of the final stages of land management projects is the transfer of the project in kind, the essence of which is that the projected boundaries and turning angles of different areas were shown and fixed by boundary markers in kind.

It should be noted that land management as an effective tool for land management at the regional and local levels requires strict adherence to all its regulatory positions.

Ukraine's orientation to join the European Union indicates the need to create enterprises focused on the market model of agricultural development as a strategic direction for the transformation of land resources. Meanwhile, it is important to provide a reliable source of financial resources for measures to improve and protect land, which will better ensure the efficient use of land resources, encourage businesses to improve the quality of land.

In this context, we believe that the rational use of land resources should be based on the following guidelines:

- taking into account intra-industry and inter-industry relations;

- taking into account the land and resource dynamics of resettlement and the peculiarities of the development of productive forces;

- budget support for agricultural producers;

- compliance with the condition of priority of environmental protection and reproduction of soil fertility;

- observance of balance of economically expedient and ecologically safe level of return of land resources;

- improving the regional approach to land use rationalization based on land use, taking into account specific local conditions that are specific to a particular area;

- creation of a single information base and introduction of modern information technologies;

- information support of the principles of land use rationalization;

- ensuring the implementation of land development programs;

- creation of a reliable and effective system for the development of regulations in the field of land use rationalization;

- optimization of the structure of agricultural landscapes;

- taking into account soil and climatic features;

- innovative level of business organization.

Thus, this indicates that success in the implementation of issues of rational use of agricultural land can be ensured through an adequate mechanism for managing the process of land use and protection and the effectiveness of administrative and economic levers of direct influence of the authorities. Taking into account the above prerequisites for the formation and key aspects of the mechanism of rational land use are presented in Fig. 1.

However, today the requirements of rational land use are not met. The areas of eroded arable lands, saline and acidified soils increase every year, there is a decrease in humus on arable lands.

It should be noted that the effectiveness of rational land use can be determined by comparing individual data on agricultural development, forest cover, level of urbanization and industrial technologies with the relevant science-based standards. These standards should be based on the norms of loading on the components of the landscape, so as not to lead to a violation of their structure. Such standards should be the basis for the rationalization of land use and serve as a regulatory framework for the regulation of land relations.

One of the possible ways to optimize land use is the organization of territorial conditions for the introduction of industrial technologies in agriculture and the withdrawal from active circulation of degraded and unproductive arable land, where crop production is costly.

At the same time, the strategy of land use development should be focused on the use of both highly productive and degraded and unproductive lands. The first case involves the formation of a system of crop rotations, which will grow crops on intensive technologies, in the second case - anthropogenic pressure will be minimized by providing for the use of disturbed lands for permanent irrigation or afforestation. Under such circumstances, the process of further degradation of these lands as one of the conditions for rationalization of land use will be stopped at insignificant costs.

Prerequisites for the formation of rational land use - compliance with the requirements and principles of rational land use, compliance with the functions of rational land use

The purpose of rational land use - the maximum satisfaction of socio-economic needs at minimum cost

Objectives of rational land use - increase production, production of environmentally friendly food, ensuring a deficit-free balance of humus in the soil, increase

Tasks of rational land use - efficient use of available production and resource potential, provision of a system of environmental and land protection measures, determination of the optimal system of land and crop rotations, minimization of costs based on the use of resource-saving technologies

Fig. 1. Key aspects of the rational land use formation

Given the acquired domestic and foreign experience, to prevent degradation processes it is necessary to apply a fundamentally new approach to the organization of land use. Management decisions to optimize land use and protection necessitate a comprehensive analysis and systematic updating of data on their quantitative and qualitative composition based on systematic observations, ie land monitoring, which provides objective information on the quality of land. To do this, at the regional level it is necessary to identify crisis areas and provide feasibility studies for land management projects. It is necessary for the oblast council to consider the information on the state of the oblast's soils in no more than five years in order to include the financing of specific projects in the budget. Each region must have several reference samples of protected areas. These will be a kind of demonstration fields for studying and disseminating the experience of land use rationalization. At the same time, the main task of local governments is to concentrate efforts focused on land inventory based on GIS technologies.

We believe that the main components that will affect the rational use of land are:

- a comprehensive description of the entire ecosystem "land", including soil, climatic, hydrogeological and other characteristics;
- reliability and stability over time of basic factors, characteristics of soil and ecological situation.

The methodological basis of rational land use is the concept of economic growth while maintaining the optimal possible growth of products with minimal losses.

We believe that the basic principles of land use rationalization should be:

- environmentally friendly economic activity;
- minimal impact on land, abandonment of unfounded landscape transformation projects in order to "develop new or improve existing land";
- limited withdrawal of valuable agricultural land is allowed;
- preservation of natural agro-landscapes disturbed by man in the process of previous unreasonable activity;
- land monitoring and control over land use and protection;
- forecast of any consequences of economic activity;
- decision-making on environmentally safe and rational land use;
- compliance with environmental, social and economic standards.

In determining the parameters of land use rationalization should be guided by the principle of system-diagnostic analysis, through which the strategy of rational land use development should be developed in accordance with the established priority objectives only after a detailed analysis of land use. The implementation of this principle will allow the use of land, based on its qualitative assessment and economic feasibility, will create optimal conditions for a significant increase in land resource potential, will turn it into an independent factor of economic growth.

To address the issue of improving the environmental safety of land use at the state level, an appropriate mechanism should be created to prevent the spread of degradation processes occurring in the soil, as well as based on such organizational levers as standardization and regulation in land use and protection, environmental examination of land management projects, monitoring of soil quality and control over the quality and environmental safety of products, etc.

The scientific basis for determining the normative assessment of land, land tax, rent should be the natural-agricultural zoning of land, which needs to be improved in order to create the necessary information base.

Natural and agricultural zoning will also serve as a basis for addressing land use and protection issues. In order to scientifically substantiate the system of environmental measures for specific regional conditions, it is important to develop a Scheme of soil erosion zoning, which would serve as a scientific basis for developing a system of environmental measures taking into account specific climatic conditions.

In the course of the research it was determined that the amount of land tax should be differentiated. Yes, some businesses do not use the land for their intended purpose, they do not want to work on it efficiently. In such cases, the lever of influence on the land owner or land user is to increase the amount of land tax in order to compensate for the loss of production and protect the interests of the state in the rational use and protection of land. It is necessary to increase the amount of land tax on lands located within the coastal protection zones, districts and zones of sanitary protection, health resorts and resorts, within the lands of historical and cultural purpose.

The main for the rationalization of land use are rational for the region their size, organization of rational composition of land and sown areas (structure of agricultural landscapes), rational organization of the territory taking into account ecologically safe land management, ensuring soil fertility, restoring productivity of eroded lands, obtaining containers of agricultural products without damaging the fertile soil layer. Rational use of land, in our opinion, will contribute to the organization of the production process, in which land should be used safely, and its productive properties should provide an environmentally sustainable effect while maintaining soil fertility.

When addressing the organization of land use from an ecological standpoint, there is a need to use an ecosystem approach. The organized territory should be considered as a complex ecosystem of different levels of landscape organization.

CONCLUSION

Land management is the methodological basis of socio-economic development of regions, individual land entities, improving the formation of the ecological network, creating conditions for the use of areas aimed at maintaining economic, social and environmental balance between environmental opportunities and economic development needs.

In the course of the research it was established that the key point in the technology of rational use and protection of lands is the organization of the territory of agricultural land use. Today, the methodological and methodological support for the implementation of such works has not been finalized, although we have the following plan for the development of land management projects: analysis of land use; functional zoning of lands (determination of types and subtypes of land use, establishment of restrictions and encumbrances and use of land, land easements, engineering arrangement, etc.); landscaping of arable land; landscaping of perennial plantations; landscaping of forage lands; determining the effectiveness of the project; transfer to nature of the elements of the designed measures; state and self-government control over the implementation of land management projects.

It is determined that the process of rational use of land resources requires focusing on the systematization of terminological vocabulary in the field of land use. However, in the economic literature there is no single point of view on the definition of "rational land use". The search for the best version of this concept allowed us to conclude that the rational use of land should be understood as the process of maximum satisfaction of socio-economic needs with minimal costs within the relevant categories of land for its intended purpose.

Therefore, the key aspects of the formation of rational use of land resources should be aimed at identifying priority areas for action aimed at ensuring the environment for greening the environment and creating the conditions for the development of competitive market land use.

The implementation of the developed scientific provisions, conclusions and recommendations will contribute to the harmonious development of nature and society, increase competitiveness, efficient use of available resources and natural resource potential.

REFERENCES

1. Radchenko, A. Rational use of the land: concept and maintenance. Personnel (2005). Vol. 8. pp. 92-96. (in Ukrainian).

2. Fedorov, M. Economic incentives for businesses for the rational use and protection of land. Collection of scientific works of Luhansk National Agrarian Universityю. Lugansk. Vid-vo LANY (2002). Vol. 19 (31), pp. 200-203. (in Ukrainian).

3. Horlachuk, V., Pechanska, I., Skorohodov, V. Land management: a textbook. (2006). К. : Publishing house "Professional", 192 p. (in Ukrainian).

4. Fomenko, L. Rational use of agricultural land Abstract of the dissertation for the degree of Candidate of Economic Sciences: specialty 08.07.02 "Economics of Agriculture and AIC". State Agroecological University. Zhytomyr. (2006). 20 p. (in Ukrainian).

5. Stupen, M., Gulko, R., Stupen, N. Improving the rational use of land resources on a mortgage basis. Bulletin of Agricultural Science. (2006). Vol. 8, pp. 58-60. (in Ukrainian).

6. America and sustainable development. New concept of environmental protection. ZKOS. Vol. 4, 95 p. (in Ukrainian).

7. About land management. Law of Ukraine from 22.05.2003 № 858-IV. Information of the Verkhovna Rada of Ukraine. (2003). № 36. Art. 282. (in Ukrainian).

ECO-FRIENDLY SYNTHESIS OF GOLD NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

Nanomaterials have become the object of extensive studies in recent decades due to their unique chemical, physical and physico-chemical properties. Unusual electronic, magnetic, thermal, and optical properties can find the application in various areas. Optical properties of gold nanoparticles are size- and shape-dependent, whereby they exhibit the light absorbance in a wide range of optical spectrum spanning the visible and near infrared-spectral regions. The response in the range of 650-1350 nm, also known as the biological transparency window or therapeutic window, open new possibilities to diagnostics, therapeutics, and drug delivery systems.

Recent studies have developed the various physical, chemical, and biological methods for the synthesis of gold nanoparticles. The group of methods that involves the application of non-toxic natural reactants received the name of “green chemistry methods”. These methods are based on the use of actinomycetes, bacteria, fungi, plants, viruses, and yeasts.

In this report, we present the recent results in the field of the development of green synthesis protocols for the synthesis of gold nanoparticles using extracts of selected plants. It was observed that the utilization of the different ratios of the aqueous *Mentha × piperita* plant extract can be successfully used for the preparation of the prismatic-shaped gold nanoparticles with absorbance in the near-infrared region.

Keywords: phytosynthesis, green chemistry, surface plasmon resonance, plasmonics, transmission electron microscopy

INTRODUCTION

“Green Chemistry” for “Sustainable development” has been commonly studied for less than decades. Chemistry has received the reputation of a hazardous science, and often, the public associates the word “chemistry” with hazard and toxicity. Sustainable development is the development which considers the needs of the present and future generations to meet their individual needs. Sustainable development has high significance for chemistry-based industries, including nanotechnology, due to the evidence of enormous pollutions and the huge use of natural resources.

Nanomaterials have become an important field of modern materials science due to the unique physical and chemical properties. The application of their unusual catalytic, electric, magnetic, and optical properties was recognised as a new and efficient way in the creation of novel advanced materials.

The bulk gold is a well-known noble metal which has been in human use for a long time due to the chemical stability and numerous physical qualities. For example, the characteristic brightness and stability even after exposure in very harsh conditions, making it a perfect material for the fabrication of jewellery, coins, as well as printed circuit boards, and electric bonding wires. Despite the common opinion that nanomaterials belong to a very recent generation of materials, gold nanoparticles containing glass was manufactured in ancient Egypt in the 2nd millennium BC and in ancient Rome from the 1st century AD (for example, the Lycurgus cup) [1]. High chemical stability makes the gold a perfect material for preparation of nanomaterials.

Optical properties (surface plasmon resonance), biocompatibility and possibility of functionalization by biomolecules of gold nanoparticles open the possibility of its modern applications is in nanomedicine, which is currently being actively developed. Nanoparticles of gold are utilized to deliver therapeutics and mediate heat and light to specific types of tissues [2]. The electronic and optical properties of gold nanoparticles can be defined by adjustment of size and shape. Therefore, there are prospective to utilisation for advanced photothermal therapy [3], bioimaging [4] and the controlled drug delivery and release systems [5].

Various methods for the synthesis of metal nanoparticles were developed in recent decades. Such as coprecipitation, hydrothermal synthesis, microemulsion, inert gas condensation, ion sputtering scattering, microwave, pulse laser ablation, sol-gel, spark discharge, sonochemical, and biological synthesis. Physical methods usually require the involvement of highly expensive equipment and often do not provide the control over parameters of final nanoparticles (size and shape). However, the traditional wet chemistry methods were recognised as preferable. The main disadvantage of these protocols is the need to use toxic reducing and capping agents which stay in resulting nanocolloids and limits their coexistence with biomolecules. As result, such nanoparticles show high cytotoxicity towards living organisms and are unsuitable for application in biomedicine. The reasonably efficient way to solve this problem is the application of the green approach which consists in the application of ecologically friendly compounds for the fabrication of nanoparticles [6]. Biological methods of the nanoparticle's synthesis also belong to green methods. They are based on the application of biological materials (plants, fungi, bacteria) and widely accepted as a possible alternative. Such methods are also time- and cost-effective and environmentally friendly. This is the reason why they are often called "green chemistry methods". One of the routes for obtaining biocompatible gold nanoparticles in the greenest manner is phytosynthesis - the using of extracts of plant or their parts [7]. From one hand, the plant material is cheap and easily available almost everywhere on the Earth, and the preparation of plant extracts is a simple process. From other hand, the plant extract is a complicated mixture of numerous chemical compounds with different chemical properties. Despite the extensive studies, the wide application of photosynthetic protocols is restricted due to the limited knowledge on the nanoparticle's formation mechanism [8].

In this study we consider the recent progress in the development of the phytosynthesis protocols for preparation of gold nanoparticles with optical activity in the near infrared region.

METHODS AND EXPERIMENTAL PROCEDURES

Chemicals

Acetic acid (CH_3COOH, 99% p.a., Centralchem, Slovak republic) and sodium hydroxide ($NaOH$) 0.1 mol/L standard solution (Normanal, Lach-Ner, s.r.o., Czech Republic) were used for adjustment of pH of solutions. Chloroauric acid hydrate ($HAuCl_4 \cdot H_2O$, Sigma-Aldrich, St. Louis, MO, USA) was used for gold nanoparticle synthesis. Double-distilled water and ethanol (C_2H_5OH, 96% p.a., ITES Vranov, Slovak Republic (Slovak republic)) were used for the preparation of extract, reagents and synthesis of nanoparticles.

Synthesis of nanoparticles

Aqueous leaves extract of the peppermint (*Mentha × piperita*) was prepared by the 1-hour maceration in double distilled water (ratio was 1g of dry leaves in 10ml of water) at 60°C, filtered, centrifugated and used for the synthesis of gold nanoparticles. Syntheses were performed at an ambient room temperature (25 °C) by the direct interaction of the plant extracts diluted to various concentrations by double distilled water with 1 mM $HAuCl_4$ aqueous solution under continuous stirring. Amounts of extract were normalized to dry matter content, with the estimation of 0.25-1.5 mg/ml of the dry matter in the final solution. In a typical synthesis, the estimated volume of plant extract was diluted by double distilled water followed by addition of 1 mM $HAuCl_4$ solution under continuous stirring. Aqueous extract of elderberry fruits (*Sambucus nigra*) prepared according to previously published protocol [9] was used for preparation of gold nanoparticles by direct interaction of extract with 1 mM $HAuCl_4$ at 55°C for 24 hours. The pH of the reaction mixture was adjusted with NaOH solution.

Characterization of nanoparticles

Shimadzu UV-1800 spectrophotometer was used for collection of UV-Vis spectra in the range of 180-1100 nm. Transmission electron microscopy images were received with a JEOL JEM-2100F microscope equipped with attachments for electron-dispersive X-ray analysis and a GIF TRIDIEM post-column energy filter for the acquisition of energy-filtered images and selected area electron diffraction. TEM specimens were prepared by dropping a sonicated aqueous suspension of gold nanoparticles on a carbon-coated copper grid and followed with drying it under the infrared lamp. Transmission electron images of different magnifications were captured at a maximum acceleration voltage of 200 kV.

THE RESEARCH RESULTS AND DISCUSSIONS

Green synthesis of gold nanoparticles

The green approach for the fabrication of gold nanoparticles consists in the use of the bioactive agents as the reducing agent which convert metal ions into metal atoms and capping agent which stabilize the nanoparticles. Different sources of biological materials have been used: actinomycetes [10], algae [11, 12], fungi [13], lichens [14], bacteria [15, 16], plant extracts [17, 18, 19]. Each source presents the unique composition of natural compounds. Plant based green synthesis (phytosynthesis) is very popular because it is faster compared to microorganisms (bacteria or fungi), cheap due to availability of plants, simple (single step), non-pathogenic and environmentally friendly. Another advantage of phytosynthesized nanoparticles is their biocompatibility. If we consider the chemistry of plant extracts, the different parts of the plants, barks, flowers [20], essential oils [21], fruits [22], leaves, roots, seeds, shoots, stems, delivers different profiles of chemicals in the formation of nanoparticles. Alkaloids, carotenoids, flavonoids, phenolic acids, sugars, proteins, tannins, terpenoids and other plant metabolites interplays critical roles for the reduction of metal ions to yield nanoparticles and for their stabilisation.

The concentration of the extract, extract to metal salt ratio, temperature, metal salt, reaction time and pH are the key influencing parameters after the plant extract has been chosen.

Properties of phytosynthesized gold nanoparticles

Here we consider the optical properties of gold nanoparticles prepared using extracts of selected plants. UV-Vis spectroscopy was applied to monitor the formation of gold nanoparticles through the observation of the position and shape of surface plasmon resonance peaks (Fig. 1). The spectrum of gold nanoparticles prepared with elderberry extract contains the single surface plasmon resonance peaks at 535 nm, which evidence about the formation of spherical nanopar-

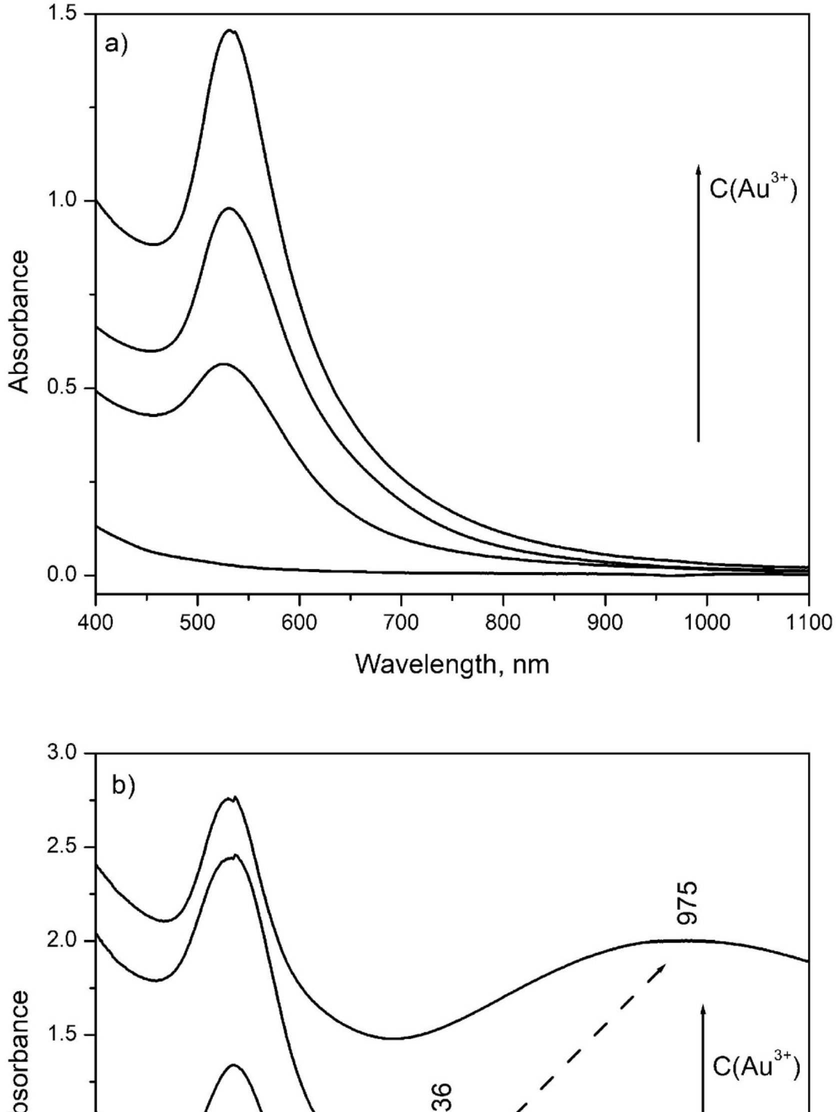

Fig. 1. UV-Vis spectra of gold nanoparticles prepared using extracts of a) elderberry fruits (*Sambucus nigra*) and b) peppermint (*Mentha pipperita*).

ticles (Fig. 1a). The absorbance of gold nanoparticles solutions increases with increase of the concentration of nanoparticles. However, the spectra of gold nanoparticles prepared using other extracts are different. The UV-Vis spectra of gold nanoparticles prepared from the extract of peppermint show the presence of two absorption maximums (Fig. 1a). First maximum at 535 nm indicates the formation of spherical nanoparticles and second with maximum in the near infrared range evidence about the formation of irregularly shaped nanoparticles. The absorbance maximum in the near infrared range depends on the extract to Au^{3+} ions ratio. The higher the concentration of Au^{3+} ions in the reaction mixture, the stronger is the shift of surface plasmon resonance maximum to near infrared range.

A simultaneous presence of highly monodisperse spherical gold (Fig. 2a) nanoparticles with diameter of 10 nm in nanocolloid solution prepared using elderberry fruits extracts confirmed by transmission electron microscopy. However, using the peppermint extract, the shape of gold nanoparticles depends on the initial concentration of Au^{3+} ions. At lower concentrations, the typical transmission electron microscopy image (Fig. 2b) shows the presence of triangular and pseudospherical particles in the nano-dimensions. At higher concentrations, the dominant shape of nanoparticles is hexagonal (Fig. 2c).

Above-mentioned studies confirm that the choice of plant or its part influence the morphology of resulted nanoparticles. In some cases, the composition of extract supports the formation of regular (spherical) nanoparticles [23, 24]. In other, the product is characterized by the high polydispersity of nanoparticles [25, 26, 27]. However, such nanocolloids contains nanoparticles with different sizes regardless of the intensity of stirring during the preparation. This might be solved by fractionalization of extract before the synthesis of nanoparticles. Therefore, additional studies are needed to learn the role of different components of extract.

Capability of gold nanoparticles for biomedicine

Anisotropic gold nanoparticles can have very important and unique applications in a wide range of fields, including optical sensing and biomedicine. Especially, for the applications based on the hypothermia effect. The development of new synthetic methodologies has become a recent trend in nanotechnology, in which the morphology design of fabricated gold nanoparticles (e.g., nanoplates, nanorods, nanotriangles, nanohexagons and nanostars) is the highest priority.

The biomedical applications of gold nanoparticles are also defined by their optical properties. The effective utilisation of nanoparticles for photothermal therapy or drug delivery and release systems requires nanoparticles with response in the second near infrared range because of the deeper penetration of long-wave radiation [28]. By this reason, the interest of scientists is dedicated to the development of the synthesis protocols of gold nanoparticles with regular (spherical) and irregular shapes (non-spherical) – nanospheres [23, 24], nanoprisms [4], nanotriangles [25, 26], nanohexagons [27]. nanorods [29], nanoshells [30] and nanostars [31].

Particles of gold with a size of several to a few hundred nanometres absorb the light radiation due to the surface plasmon resonance in the wavelength range of 510-560 nm (Fig. 3, curve 1). The wavelength of surface plasmon resonance can be adjusted by variation of size and shape of nanoparticles. While the increase of the nanoparticle's size leads to a moderate shift of surface plasmon resonance, the change of the shape leads to shifts of hundred nanometres. Therefore, the synthesis research is focused on the preparation of gold nanoparticles with surface plasmon resonance absorbance maximum within the biological transparency window of 650-1350 nm. This region is divided into two optical near-infrared ranges, at λ = 650-850 nm and 950-1350 nm, respectively (Fig. 3).

These requirements are fulfilled by gold nanoparticles synthesised using the extract of peppermint. Thus, the position of absorption maximum depends on the size and shape of nanoparticles. Triangular and hexagonal nanoparticles are characterized by high aspect ratio. Therefore, by control of the reaction conditions, there is a possibility of preparing gold nanopar-

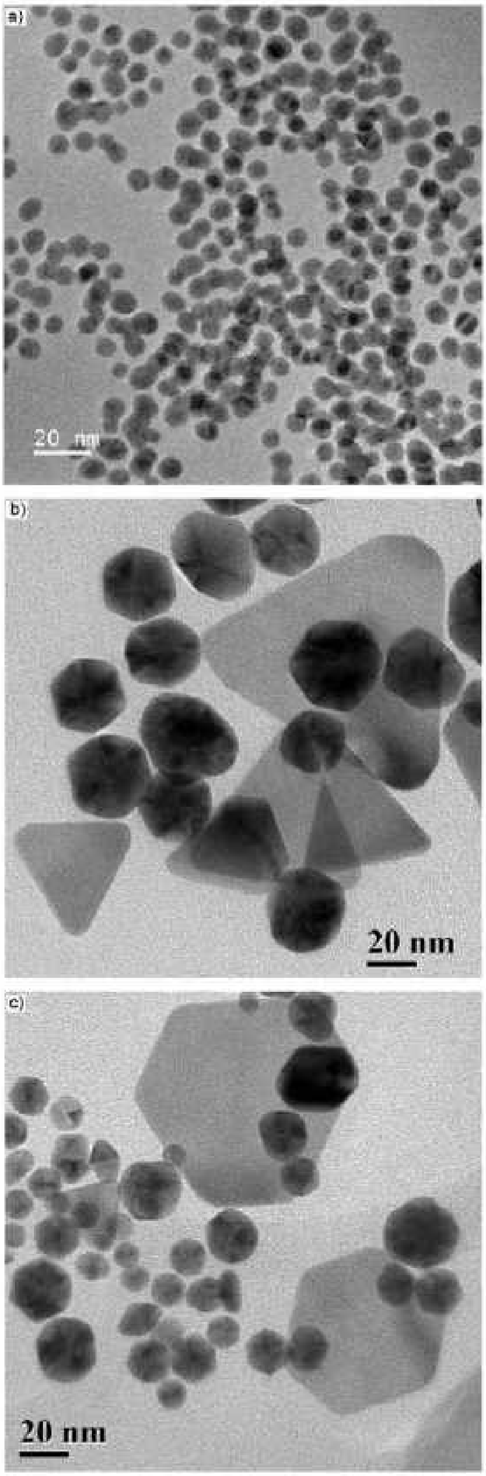

Fig. 2. Transmission electron images of gold nanoparticles prepared using extracts of a) elderberry fruits (*Sambucus nigra*), b) and c) peppermint leaves (*Mentha piperita*).

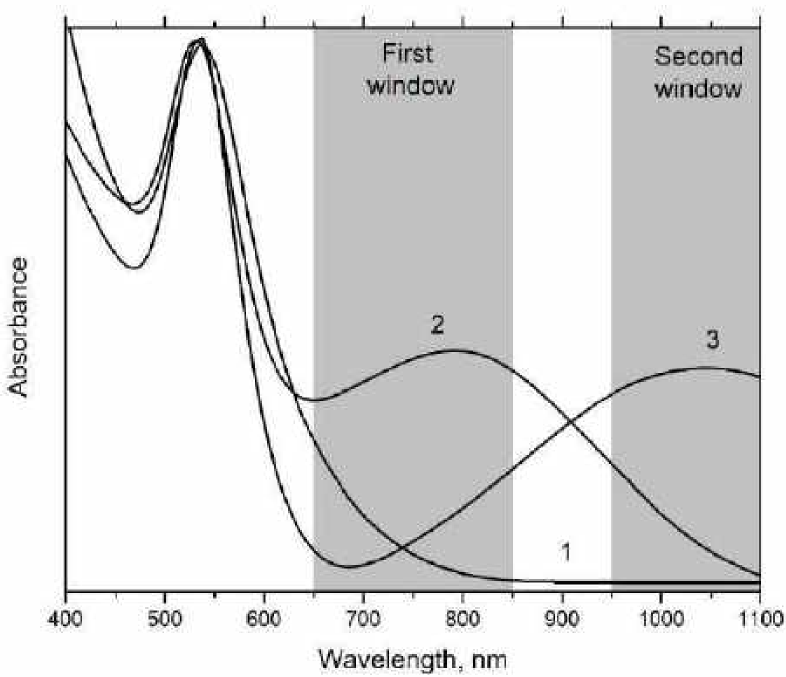

Fig. 3. Optical windows in biological tissues and UV-Vis spectra of phytosynthesized gold nanoparticles: spherical (1), triangular (2) and hexagonal (3).

ticles with response in near infrared range (Fig. 3, curves 2 and 3). Unfortunately, the resulting nanocolloid solutions contain the mixture of gold nanoparticles with different morphologies. Predominantly, there are pseudo-spherical and triangular-hexagonal nanoplates. However, these results look promising because they show the possibility of obtaining the nanoparticles with response even in the second biological transparency window. The more attention must be paid to the identification of natural compounds which support the formation of irregular shapes and to the understanding of the processes of nanoparticles formation [32]. Other alternative for preparation of monodisperse irregular shape gold nanoparticles is further separation by centrifugation or electrophoresis.

CONCLUSION

Nanomaterials have become the object of extensive studies in recent decades due to their unique chemical, physical and physico-chemical properties. Unusual electronic, magnetic, thermal, and optical properties can find the application in various areas. Optical properties of gold nanoparticles are size- and shape-dependent, whereby they exhibit the light absorbance in a wide range of optical spectrum spanning the visible and near infrared-spectral regions. The response in the range of 650-1350 nm, also known as the biological transparency window or therapeutic window, open new possibilities to diagnostics, therapeutics, and drug delivery systems.

Recent studies have developed the various physical, chemical, and biological methods for the synthesis of gold nanoparticles. The group of methods that involves the application of non-toxic natural reactants received the name of “green chemistry methods”. These methods are based on the use of actinomycetes, bacteria, fungi, plants, viruses, and yeasts.

In this report, we compare the recent results in the field of the development of green syntheses protocols for the fabrication of gold nanoparticles using extracts of selected plants. It was observed that the utilization of the different ratios of the aqueous *Mentha × piperita* plant extract can be successfully used for the preparation of the prismatic-shaped gold nanoparticles with absorbance in the near-infrared region. The synthesis of nanoparticles is a prospective route for green preparation of biocompatible nanoparticles for biomedical applications, but there are still many questions which need to be answered.

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REFERENCES

1. Liz-Marzán L.M., Nanometals: Formation and color, Materials Today, vol. 7/ issue 2, pp 26-31, 2004.

2. Quintana C., Cifuentes M.P., Humphrey M.G., Transition metal complex/gold nanoparticle hybrid materials, Chemical Society Reviews, vol. 49, pp 2316-2341, 2020.

3. Yang W., Liang H., Ma S., Wang D., Huang J., Gold nanoparticle based photothermal therapy: development and application for effective cancer treatment. Sustainable Materials and Technologies, vol. 22, AN e00109, 2019.

4. Bao C., Beziere N., del Pino P., Pelaz B., Estrada G., Tian F., Ntziachristos V., de la Fuente J.M., Cui D., Gold nanoprisms as optoacoustic signal nanoamplifiers for in vivo bioimaging of gastrointestinal cancers, Small, vol. 9, pp 68-74, 2013.

5. Rejinold N.S., Choi G., Choy J.H., Recent trends in nano photochemotherapy approaches and future scopes, Coordination Chemistry Reviews, vol. 411, AN 213252, 2020.

6. Duan H., Wang D., Li Y., Green chemistry for nanoparticle synthesis, Chemical Society Reviews, vol. 44, pp 5778-5792, 2015.

7. Alavi M., Varma R.S., Phytosynthesis and modification of metal and metal oxide nanoparticles/nanocomposites for antibacterial and anticancer activities: Recent advances, Sustainable Chemistry and Pharmacy, vol. 21, AN 100412, 2021.

8. Lucena-Serrano C., Contreras-Cáceres R., Sánchez-Molina M., Casado-Rodríguez M.A., Cloarec J.M., Mainetti E., López-Romero M., Preparation and application of non-spherical metal nanoparticles: reality and perspectives, Current Organic Chemistry, vol. 21, pp 1-22, 2017.

9. Mariychuk R., Eliasova A., Porubska J., Poracova J., Simko V., Isolation and lyophilisation of anthocyanins from fruits of blackcurrant, Acta Horticulturae, vol. 1133, pp 329-333, 2016.

10. Kumari S., Tehri N., Gahlaut A., Hooda V., Actinomycetes mediated synthesis, characterization, and applications of metallic nanoparticles, Inorganic and Nano-Metal Chemistry, In press DOI: 10.1080/24701556.2020.1835978, 2020.

11. Taghizadeh S.-M., Morowvat M.H., Negahdaripour M., Ebrahiminezhad A., Ghasemi Y., Biosynthesis of metals and metal oxide nanoparticles through microalgal nanobiotechnology: Quality control aspects, BioNanoScience, vol. 11, pp 209–226, 2021.

12. Uzair B., Liaqat A., Iqbal H., Menaa B., Razzaq A., Thiripuranathar G., Rana N.F., Menaa F., Green and cost-effective synthesis of metallic nanoparticles by algae: Safe methods for translational medicine, Bioengineering, vol. 7/issue 4, AN 129, pp 1-22, 2020.

13. Kitching M., Ramani M., Marsili E., Fungal biosynthesis of gold nanoparticles: mechanism and scale up, Microbial Biotechnology, vol. 8, pp 904–917, 2015.

14. Hamida R.S., Ali M.A., Abdelmeguid N.E., Al-Zaban M.I., Baz L., Bin-Meferij M.M., Lichens - a potential source for nanoparticles fabrication: A review on nanoparticles biosynthesis and their prospective applications, Journal of Fungi, vol. 7/issue 4, AN 291, 2021.

15. Bahrulolum H., Nooraei S., Javanshir N., Tarrahimofrad H., Mirbagheri V.S., Easton A.J., Ahmadian G., Green synthesis of metal nanoparticles using microorganisms and their application in the agrifood sector, Journal of Nanobiotechnology, vol. 19/ issue 1, AN 86, 2021.

16. Sachin K., Karn S.K., Microbial Fabricated Nanosystems: Applications in Drug Delivery and Targeting, Frontiers in Chemistry, vol. 9, AN 617353, 2021.

17. Behzad F., Naghib S.M., Kouhbanani M.A.J., Tabatabaei S.N., Zare Y., Rhee K.Y., An overview of the plant-mediated green synthesis of noble metal nanoparticles for antibacterial applications, Journal of Industrial and Engineering Chemistry, vol. 94, pp 92-104, 2021.

18. Hashmi S.S., Shah M., Muhammad W., Ahmad A., Ullah M.A., Nadeem M., Abbasi B.H., Potentials of phyto-fabricated nanoparticles as ecofriendly agents for photocatalytic degradation of toxic dyes and wastewater treatment, risk assessment and probable mechanism, Journal of the Indian Chemical Society, vol. 98 /issue 4, AN 100019, 2021.

19. Bao Z., Lan C.Q., Advances in biosynthesis of noble metal nanoparticles mediated by photosynthetic organisms - a review, Colloids and Surfaces B: Biointerfaces, vol. 184, AN 110519, 2019.

20. Kumar H., Bhardwaj K., Kuča K., Kalia A., Nepovimova E., Verma R., Kumar D., Flower-based green synthesis of metallic nanoparticles: Applications beyond fragrance, Nanomaterials, vol. 10/issue 4, AN 766, 2020.

21. Sana S.S., Li H., Zhang Z., Sharma M., Usmani Z., Hou T., Netala V.R., Wang X., Gupta V.K., Recent advances in essential oils-based metal nanoparticles: A review on recent developments and biopharmaceutical applications, Journal of Molecular Liquids, vol. 333, AN 115951, 2021.

22. Ali S., Chen X., Ajmal Shah M., Ali M., Zareef M., Arslan M., Ahmad S., Jiao T., Li H., Chen, Q., The avenue of fruit wastes to worth for synthesis of silver and gold nanoparticles and their antimicrobial application against foodborne pathogens: A review, Food Chemistry, vol. 359, AN 129912, 2021.

23. Fizer M.M., Mariychuk R.T., Fizer O.I., Gold nanoparticles green synthesis with clove oil: spectroscopic and theoretical study, Applied Nanoscience, In press DOI: 10.1007/s13204-021-01726-6, 2021.

24. Mariychuk R., Porubská J., Ostafin M., Čaplovičová M., Eliašová A., Green synthesis of stable nanocolloids of monodisperse silver and gold nanoparticles using natural polyphenols from fruits of Sambucus nigra L. Applied Nanoscience, vol. 10/issue 12, pp 4545-4558, 2020.

25. Mariychuk R., Fejér J., Porubská J., Grishchenko L.M., Lisnyak V., Green synthesis and characterization of gold triangular nanoprisms using extract of *Juniperus communis* L., Applied Nanoscience, vol. 10/ issue 8, pp 2835-2841, 2020.

26. Mariychuk R., Smolková R., Bartošová V., Eliašová A., Grishchenko L.M., Diyuk V.E., Lisnyak V.V., The regularities of the *Mentha piperita* L. extract mediated synthesis of gold nanoparticles with a response in the infrared range, Applied Nanoscience, In press DOI: 10.1007/s13204-021-01740-8, 2021.

27. Mariychuk R., Gruľová D., Grishchenko L.M., Linnik R.P., Lisnyak V., Green synthesis of non-spherical gold nanoparticles using *Solidago canadensis* L. extract, Applied Nanoscience, vol. 10/issue 12, pp 4817-4826, 2020.

28. Smith A., Mancini M., Nie S., Second window for in vivo imaging, Nature Nanotechnology, vol. 4, pp 710-711, 2009.

29. Lohse S.E., Murphy C.J., The quest for shape control: a history of gold nanorod synthesis. Journal of Materials Chemistry, vol. 25, pp 1250-1261, 2013.

30. Lopatynskyi A.M., Malymon Y.O., Lytvyn V.K., Mogylny I.V., Rachkov A.E., Soldatkin A.P., Chegel V.I., Solid and hollow gold nanostructures for nanomedicine: comparison of photothermal properties, Plasmonics, vol. 13, pp 1659-1669, 2019.

31. Ortiz-Castillo J.E., Gallo-Villanueva R.C., Madou M.J., Perez-Gonzalez V.H., Anisotropic gold nanoparticles: A survey of recent synthetic methodologies, Coordination Chemistry Reviews, vol. 425, AN 213489, 2020.

32. Sayadi K., Akbarzadeh F., Pourmardan V., Saravani-Aval M., Sayadi J., Chauhan N.P.S., Sargazi, G., Methods of green synthesis of Au NCs with emphasis on their morphology: A mini-review, Heliyon, vol. 7/issue 6, AN e07250, 2021.

ENVIRONMENTAL RISK AND STATE OF SURFACE WATER RESOURCES

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ABSTRACT

Almost all over the world there is a growing negative impact on the quantitative and qualitative state of water resources such factors as land use, population growth, water pollution and climate change.

Objective is to carry out a qualitative and quantitative assessment of the ecological status and to determine the level of environmental risk of surface water resources in the Mykolaiv region on the basis of the appropriate methods.

Ecological quality classification of surface waters and estuaries of Ukraine is built on ecosystem principle. The necessary completeness and objectivity of the characteristics of surface water quality are achieved a fairly wide set of indicators that reflect the characteristics of abiotic and biotic components of aquatic ecosystems.

The base of the study is selected organoleptic and sanitary-toxicological indices of water quality, because its most fully reflect the ecological condition of water resources. Assessment of ecological status according to the organoleptic properties of water provides for evaluation in terms of color, pH index and suspended solids. Based on sanitary-toxicology data includes the assessment of COD and, nitrates (NO_3^-), total hardness, chlorides, sulphates, phosphates, total ferrum and manganese. The assessment of the status of water in terms of ecological risk coincides with the assessment of environmental quality. Individual points are class II quality "good". Quite often water is "unsatisfactory", class 4 quality. 5 class of water quality is "bad", separately found almost for each item of observations, due to excessive concentrations as a result of an anthropogenic impact on water objects. This situation indicates that water bodies in the study area have somewhat disturbed the ecological parameters of their ecological status is estimated as "ecological regression". The research presented that water objects of the area are unsuitable for drinking water supply. The ecological condition is characterized by ecological imbalance due to excess concentrations of pH, suspended solids, color, COD, BOD_5, total hardness, sulfates, chlorides, total iron and manganese.

Key words: surface water pollution, the maximum permissible concentration, environmental risk.

INTRODUCTION

Ecological problems of today create a danger to human existence at all levels - from local to global. Particularly acute, these problems are acquired in areas that are experiencing significant anthropogenic pressures. Currently, the problems of environmental assessment of water resources are particularly relevant.

Almost all over the world there is a growing negative impact on the quantitative and qualitative state of water resources such factors as land use, population growth, water pollution and climate change.

Water is a natural resource and an integral part of the existence of all living things on the planet. The problem of human supplying beings with drinking water is extremely important nowadays, since the available water resources in many areas are not sufficient to provide all consumers not only in the future but also today.

In addition, it is necessary to take into account also the fact that Ukraine is one of the least secured in Europe for fresh water supplies. So, for one inhabitant, there are only 1 thousand m^3 of water, while in Sweden and Germany - 2,5 thousand m^3, France - 3,5 m^3, in the UK - 5 m^3. Almost 1,300 settlements in Ukraine live on imported water, which are almost 1 million inhabitants. The greatest shortage of water is on the steppe areas of Donbass, Polissia, Podillia and Crimea. Meanwhile, the volume of water consumption in Ukraine over the past 20 years has doubled. All these sources, according to official data, are polluted. Virtually no water surfaces that meet to the first class of hygienic requirements and this means that there is no qualitative drinking water in Ukraine [8].

Scientists have analyzed how rivers will change under two different climate change scenarios: "mild", which involves reducing greenhouse gas emissions under the Paris Agreement, and "hard", in which no measures will be taken to combat the climate crisis.

The results show that by the end of the century in most basins of Ukraine river runoff will decrease in both scenarios:

In the Dnieper basin, water runoff is expected to decrease by an average of - 20% (and up to 24% in summer), from January to March a slight increase is possible.

In the Western Bug basin, runoff can decrease by an average of 28% to 30% in all months except February; the largest decrease is expected in autumn (up to 32%).

In the Dniester basin, according to the "hard" scenario, a catastrophic decrease in runoff is expected at the end of the century - up to 36-38% in some months.

The reduction of water runoff in the Pripyat River basin will be in the range from - 12 to - 23%, but the reduction of runoff during the summer season can reach 37%.

No significant changes are forecast in the Desna basin, but in January-March the river runoff may increase from 28% to 45%; in other months a slight decrease in runoff is expected.

In the basin of the Southern Bug at the end of the century is expected to significantly reduce the average annual runoff - up to 30%, and in some months up to 45%.

"Different sectors of the economy will suffer from water shortages. First of all, it will be felt by agriculture, which is already suffering from drought. Vulnerable industries also include energy and metallurgy, which are already the largest consumers of water. Utilities will also suffer - up to the restriction of water supply for the population, which will affect large cities [2].

The part of water that suitable for use by the population and industry is very limited. Quantitative and qualitative composition of water have experienced by anthropogenic impact. Indicators of the qualitative composition of water are one of the determining factors during assessing of environmental situation.

The most promising method for identifying areas of high environmental hazard is the assessment of the environmental status. This allows determining the permissible anthropogenic pressure in order to save equilibrium in the natural environment.

Environmental assessment of surface water quality is the basis for establishing ecological standards for water quality, both for individual water bodies and their parts, groups of water bodies and river basins. It is also the basis for environmental risk management of anthropogenic pressure on environmental objects.

For the Mykolaiv region of Ukraine the problem of water resources pollution due to wastewater discharges is significant, which is greatly hampered by the lack of centralized drainage networks and qualitative cleaning of domestic and industrial discharges [9].

It is important to do the monitoring the water status in the direction of the state national policy in the field of improving the quality and efficiency of water resources management. The scientific substantiation of carrying out water protection measures, development of the further strategy of using water resources for the purpose of improvement of the management of the Southern Buh river basin are urgent [18].

Objective: to carry out a qualitative and quantitative assessment of the ecological status and to determine the level of environmental risk of surface water resources in the Mykolaiv region on the basis of the appropriate methods.

The formulated purpose is realized in the research by solving of the following **tasks**:

• assessment and characterization of the water resources state in Mykolaiv region on the basis of literary sources;

• study of legislative normative acts about water resources management;

• determination and assessment of the water resources quality on the basis of hydrochemical information;

• on the basis of environmental assessment of the water resources status justification the relevant conclusions and proposals.

MATERIALS AND METHODS

The total area occupied by surface water objects of the Mykolaiv region is 150,5 thousand hectares, which is 6,1 % of its territory. In the area, there are 121 rivers, channels and 26 lakes, 45 reservoirs, 1153 streams, 7 swamps and estuaries. Water resources of the region are very limited and depend mainly on inflows from other regions.

Governance has registered 47 water users that discharge wastewater into surface water bodies. In the course of 2015, the total wastewater discharge amounted to 105,2 million m^3, of which 24,3% (25,55 million m^3) – contaminated wastewater [14].

Since 2010, on the territory of the Mykolaiv region not recorded discharges of wastewater without treatment (emergency wastewater discharges). Large wastewater discharges without any treatment were observed from 1995 to 2003, discharges of insufficiently treated wastewater are annually decreasing in comparison with 1991 when discharge was equal to 69,4 million m^3 [5].

The discharge of industrial waters into surface water objects is carried out by the energy companies and the engineering industry. In these discharges include heat exchangers waters that the composition is classified as normatively clean without treatment. The discharge of normatively clean without treatment of wastewater from said water user in 2016 amounted to 22,20 million m^3, which in comparison with the corresponding volume of water discharged in 2015, more to 1,2 million or 1,05 % [5].

The greatest discharge of normatively clean without treatment of wastewater in the Mykolaiv region is made by South Ukraine Nuclear Power Plant which includes Alexandrivka hydroelectric power station and Tashlyk pumped storage power plant. The volume of discharge specified enterprise is located 47, 4 % of the total volume of wastewater discharges in the region, and is 39, 76 million m^3. Exceeding the established norms of wastewater discharges is undertaken by enterprises and public utilities.

After analyzing the data of the Mykolaiv Regional Department of Water Resources, there is a gradual decrease in water intake by 76.2% (from 1125.5 million m^3 to 267.6 million m^3). The volume of surface water discharges to the surface also decreased by 43% [12–14]. The dynamics of water use and sewerage indicate the irrational use of resources, the deterioration of the environmental condition of water bodies and the inefficiency of treatment facilities (Fig. 1). In water abstraction and resource use decreased due to reduced water use for production and irrigation.

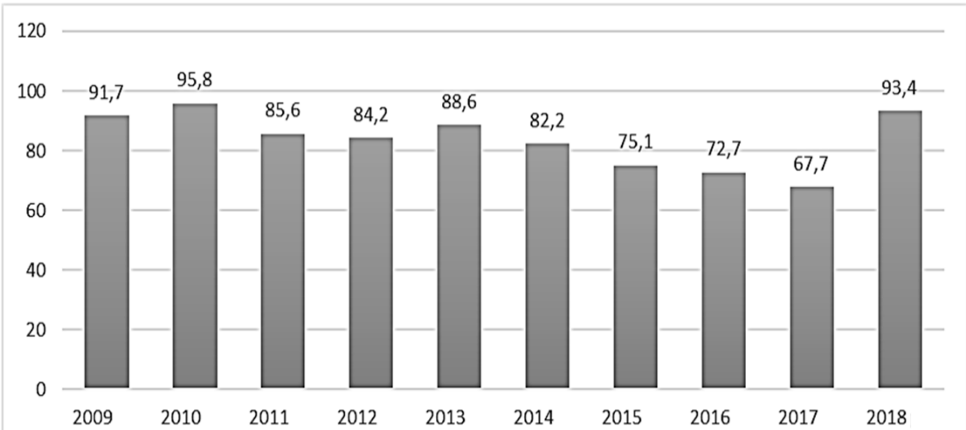


Fig. 1. Volumes of discharges of return waters to surface water bodies of the region, million m^3

Analyzing the use of water in Ukraine, it is necessary to pay attention to the reversible and repeated use of water. Reversible and re-sequential water use is the amount of savings in fresh water intake through the use of reverse and re-water supply systems, including the use of wastewater and collector-drainage water. The volume of circulating and re-sequential use of water also decreased, compared to 2019 - by 2743 million cubic meters. m or 6.3%, and compared to 2010 - by 5.7%.

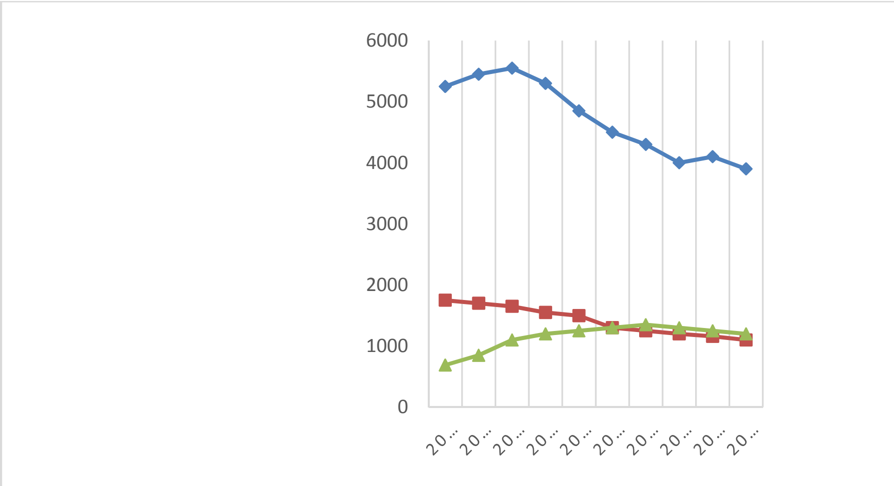
Volumes of water intake and water use are graphically presented in fig. 2.

In 2019, the water bodies in the Mykolaiv region dropped 64.90 mln. m^3 wastewater (32% contaminated, 66% pure without purification regulatory, legislative 2% purified) [12–14]. The Mykolaiv area is considered a zone of risky agriculture therefore there is a need for irrigation.

A marked decrease of the water amount discharge is connected with its reduction of enterprises and population. Water has become a very expensive resource. Businesses and people become more frugal with water.

For inefficient cleaning of sewer drains of Mykolaiv, for the past eight years "Mykolaivvodokanal" is the main polluter of water resources in the region. Over the past year to the water bodies dropped 26, 23 million m^3 of wastewater, of which insufficiently treated –

23,83 million m^3. 91% of the total number of reset mentioned utilities are contaminated with sewage, which in its own turn, affects the state of water resources [5; 15].



Use of fresh water for production needs, million cubic meters. m;
Use of fresh water for drinking and sanitary needs, million cubic meters. m;
Use of fresh water for irrigation, million cubic meters. m

Fig. 2. Dynamics of water use by types of needs

The principle of quality management of the environment is currently expected the requirement to ensure hygienic standards of maximum permissible concentrations (MPC) of polluting substances in natural components (air, water, soil) and physical factors (noise, vibration and the like). Therefore, according to conservation methodology, the assessment degree of pollution of the environment is performed by comparing the concentration of the contaminant with the MPC. However, the hygienic standards are inherent in the anthropocentric approach to the assessment of the environmental state, i.e., under safe conditions of living are not taken into account peculiarities of functioning in the actual ecosystems [18].

Actual is the need to develop more comprehensive criteria for assessing the quality of the environment.

According to the Water code of Ukraine [18] assessment of water quality is based on regulations of environmental safety of water use and environmental standards of water quality of water bodies.

It is established that now the total number of methods of evaluation and water quality classifications is sufficiently large, but none of them is widely used in water protection practice, because it does not take into account the integral display quality of water, that is, the total effect of hydrophysical, hydrochemical and other data [3; 4; 7; 17; 19].

The system of environmental quality classification of surface water and estuaries of Ukraine has two subordinate classifications, namely: on biological parameters and physical and chemical and chemical indicators. The complex of indicators of environmental quality classification of surface water includes general and specific indicators. The general indicators characterize salt composition and trophic and saprobic of waters (ecological and sanitary), that are inherent to water ecosystems ingredients, whose concentration can vary under the influence of economic activity [7]. Specific indicators characterize the content in water pollutants and toxic radiation exposure (fig. 2) [15].

But analysis of biomonitoring of surface waters of Ukraine shows that this component of the state monitoring system of the environment is in poor condition. This is reflected in the limited number of points observations, the practical absence of the expedition survey of water bodies of the country, low use of results of biological monitoring of water quality in water protection practices.

The specified demonstrates the need for a complex of works on improvement of biomonitoring of the country, above all to improve its efficiency and harmonization with similar systems in developed countries [17].

On the basis of "Methods of environmental quality assessment of surface waters by corresponding categories" [1; 16]), we developed a more complete and more accessible methodology that includes the definition of environmental assessment of surface water quality and ecological risk for the water bodies.

Ecological quality classification of surface waters and estuaries of Ukraine is built on ecosystem principle. The necessary completeness and objectivity of the characteristics of surface water quality are achieved a fairly wide set of indicators that reflect the characteristics of abortion and biotic components of aquatic ecosystems [15].

A complex of indicators of ecological quality classification of surface waters includes the General and specific indicators. The overall performance, which includes indices of the salt composition, trophy-saprobes waters (ecological and health), which characterize usual water ecosystems, the ingredients, the concentration of which can vary under the influence of economic activity. Specific indicators characterize the content in water of polluting substances of toxic and radiation action.

RESULTS AND DISCUSSION

The assessment of the water quality and the ecological state of Mykolaiv region surface waters (namely, Southen Buh, Inhul, Mertvovid and Synyukha) was performed in the period from 1990 to present for 13 sections, in which the specialists of the Southen Buh Basin Water Resources Department perform monitoring.

The base of the study is selected organoleptic and sanitary-toxicological indices of water quality, because its most fully reflect the ecological condition of water resources. Assessment of ecological status according to the organoleptic properties of water provides for evaluation in terms of color, pH index and suspended solids. Based on sanitary-toxicology data includes the assessment of COD and, nitrates (NO_3^-), total hardness, chlorides, sulphates, phosphates, total ferrum and manganese [17].

Environmental indices and categories of water quality are calculated using the functions of the software package MS Excel and are the average values at each point of the selection in fig. 3.

Risk for water body was determined by the formulas 1-3 [1; 6; 11] and represented on fig. 4.

$$R = -\ln(P), \tag{1}$$

– where $$P = \frac{\sum n_i}{N}, \tag{2}$$

– where $$\sum n_i = \sum \frac{C_i}{MPS}, \tag{3}$$

– where C_i is the concentration of the pollutant substances (PS),
MPC (PS that do not exceed the MPC in the formula (3) is substituted);
N – is the total number of analyzed PS.

The total environmental risk of deterioration in status of water bodies is determined by the rule of multiplication of probabilities, where the multipliers are not the values of the risk, and values characterizing the probability of its absence:

$$ER = 1 - (1 - R_1) \times (1 - R_2) \times \ldots \times (1 - R_n), \qquad (4)$$

where *ER* is the total environmental risk of deterioration of water objects;

$R_1, \ldots Rn$ – environmental risk of each pollutant.

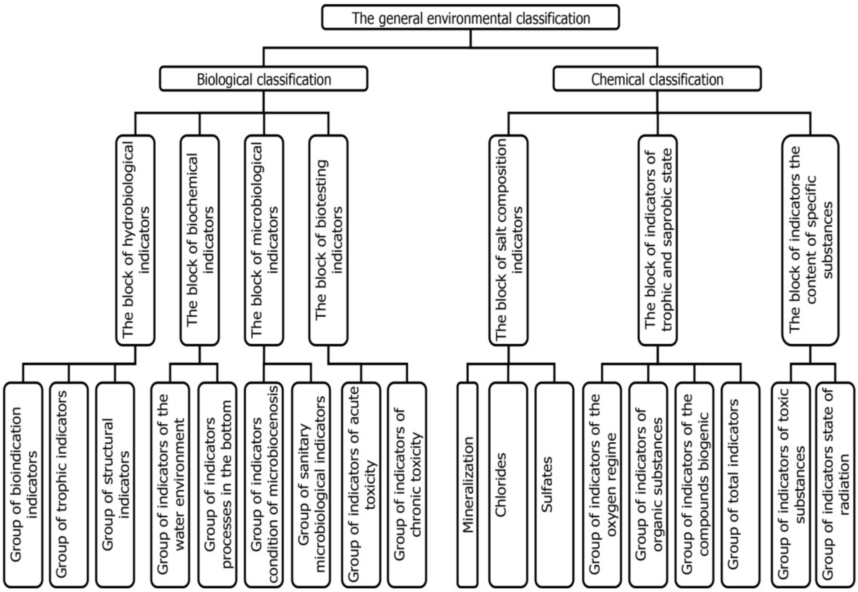


Fig. 2. Structure of the general environmental classification of surface waters

The data indicate that the predominant class of water quality is 3 quality categories with 4 and 5, that is, water in most rivers and reservoirs of the Mykolaiv region are "satisfactory" and "satisfactory mediocre", that is, weakly and moderately contaminated.

In general, the assessment of the status of water in terms of ecological risk coincides with the assessment of environmental quality. Individual points are class II quality "good". Quite often water is "unsatisfactory", class 4 quality (r. Southern Buh in the city of Pervomaisk, and within Mykolaiv). 5 class of water quality is "bad", separately found almost for each item of observations, due to excessive concentrations as a result of an anthropogenic impact on water objects. This situation indicates that water bodies in the study area have somewhat disturbed the ecological parameters of their ecological status is estimated as "ecological regression".

The state of the region water resources is the most degraded by the substances that included in the chemical trophus-saprobiological criterion of pollution, namely: pH, suspended solids, color, COD, BOD_5, total hardness and also by the salt composition criterion: sulfates and chlorides. Pollution of water by components of toxic and radiation action (total iron and manganese) is moderate.

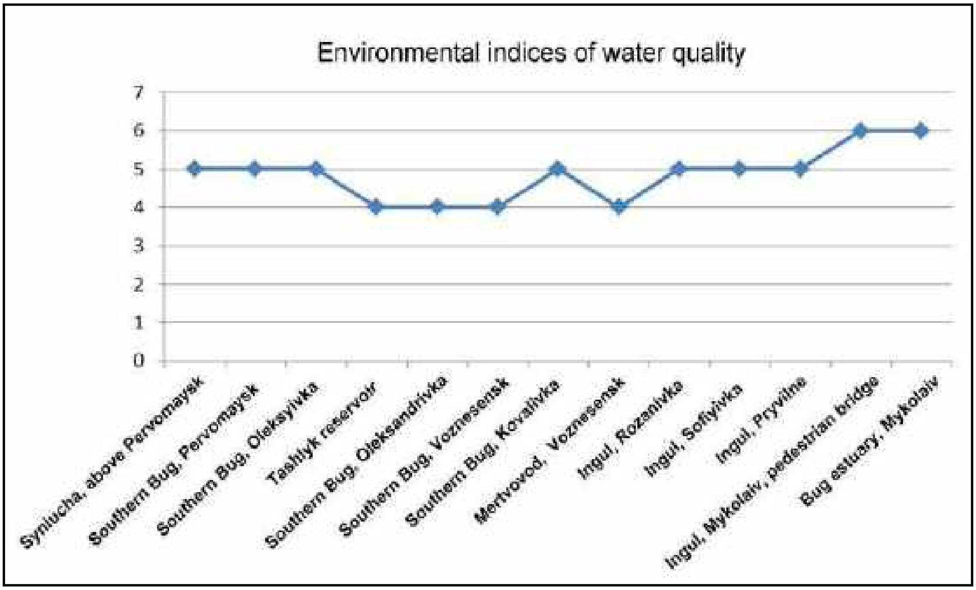


Fig. 3. Water quality environmental indices.

CONCLUSIONS

The upgraded method has represented the correct and reliable results of environmental risk calculations.

The research presented that water objects of the area are unsuitable for drinking water supply. The ecological condition is characterized by ecological imbalance due to excess concentrations of pH, suspended solids, color, COD, BOD_5, total hardness, sulfates, chlorides, total iron and manganese.

The main problem of Mykolaiv region is the question of polluted water resources due to unsatisfactory condition, namely, the deterioration of sewage treatment plants. This issue can be solved by expanding and reconstructing wastewater treatment facilities in Mykolaiv, Pervomaysk and Voznesensk; expand and reconstruct sewerage network in these cities; to implement a system of local treatment facilities and disinfection stations, to expand and reconstruct rainwater drainage in the city; to introduce the system of alternative drinking water supply of high-quality purified water with the use of modern technologies; create a system of filtering forest plantations for the treatment of wastewater from the territories of settlements, industrial objects, farms, landfills and fields of filtration.

All of this requires from environmental protection institutions and production organizations that are involved in the field of drinking water supply, to take appropriate measures to improve the situation. The main objective of these measures should be the desire to reduce concentrations of priority pollutants, the list of which was established during the calculations, namely, suspended solids, total iron, manganese, sulphates and chlorides. Of course, these measures will not be able to solve fully the problem of the lack of quality drinking water in the region, but it will be a decisive step forward to improving the environmental situation in the region.

In order to ensure balanced use and protection of water, it is expedient to develop integrated programs of protection and use of water supply sources and drinking water quality in the region; to introduce low-water and water-saving technologies, new modern means of treatment and decontamination of water at water supply facilities; to strengthen the managerial support of the efforts of entrepreneurs to create domestic water treatment equipment.

Due to the limited inventory of fresh groundwater, the presence of load on the ecosystem of water facilities as a result of discharges of poorly treated return water from enterprises and utilities, the decision of the issue of quality drinking water supply of the population is a priority for the oblast.

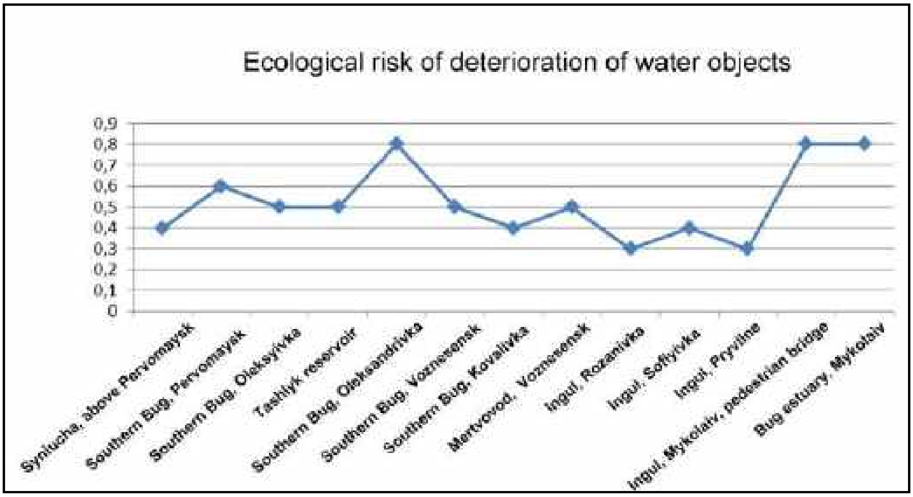


Fig. 4. Ecological risk of water objects deterioration.

ACKNOWLEDGMENTS

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REFERENCES

1. Alymov, V. T., Tarasov, N. P. (2005). Technological risk: analysis and evaluation,. IKTS Akademkniga, Moscow, 2005. (in Russian)

2. Analysis of The Influence of Climate Change on The Water Resources of Ukraine (study summary) (2021). Snizhko S., Shevchenko O., Didovets Y., Ed. Sadogurska SS Center for Environmental Initiatives "Ecodia", 2021, 32 p. (in Ukrainian)

3. Bharti, N., Katyal, D. (2011). Water quality indices used for surface water vulnerability assessment. *Inter. J Environ. Sciences*, 2 (1), 154-173.

4. Cordoba E. B., Martinez A. C., Ferrer E. V. (2010). Water quality indicators: Comparison of a probabilistic index and a general quality index. *The case of the Confederacion Hidrogaafica del Jucar (Spain). Ecological Indicators*, 10 (5), 1049-1054, Spain.

5. The dynamics of discharge of sewage in Mykolaiv region for 1990–2016, The Southen Buh Basin Water Resources Department in Mykolaiv region, Mykolaiv, (2016). (in Ukrainian)

6. Gritsenko, A.V., Vasenko, O.G., Vernichenko, G.A. & others. (2012). *The methodology of ecological assessment of surface water quality in Ukraine,* UkrNDIEP, Charkiv, Ukraine, 37, 2012. (in Ukrainian)

7. Holodenko, V.S., Kosyak, D.S. (2014). Ecological assessment of Stavy river water quality of Rivne region, *Geopolitics and ekogeodinamics*, vol. 10, issue. 1, 923-926, Simferopol, 2014. (in Ukrainian)

8. Klymenko, M. O., Pryshhepa, A.M., Voznyuk, N.M. (2006). *Monitoring of the Environment),* «Alma mater», Kyiv, 2006. (in Ukrainian)

9. Mitryasova O., Mats A. (2016). Environmental Status of Surface Water Resources in Mykolaiv Region. *Water Security : Monograph*., Mykolaiv: PMBSNU – Bristol: UWE, 2016, 121–130.

10. Pohrebennyk V., Mitryasova O., Dzhumelia E., Kochanek A. (2017). Evaluation of surface water quality using water quality indices in mining and chemical industry. *Conference Proceeding. 17th International Multidisciplinary Scientific Geoconference SGEM 2017* (29 June – 5 July, 2017). Bulgaria, Albena, V. 17. Ecologe, Economics, Education and Legislation. Issue 51, 425-432.

11. Mitryasova, O. Pohrebennyk, V., Selivanova, A. (2018). Environmental Risk of Surface Water Resources Degradation, Water Supply and Wastewater Removal, Monografie, Politechnika Lubelska, 2018, 152–162.

12. Regionalnyj ofis vodnyh resursiv u Mikolaïvs'kij oblasti (Regional office of water resources in the Mykolaiv area). URL: http://mk-vodres.davr.gov.ua/water_resources . (in Ukrainian).

13. Regional'na dopovid' pro stan navkolishn'ogo prirodnogo seredovishcha v Mykolaïvskij oblasti (Regional report on a condition of environment in the Mykolaiv area). URL: - http://www.niklib.com/eco/dop.pdf

14. Regional'na dopovid' pro stan navkolishn'ogo prirodnogo seredovishcha v Dnipropetrivskij oblasti (Regional report on a condition of environment in the Dnipropetrivk area). URL: https://adm.dp.gov.ua/pro-oblast/rozvitok-regionu/ekologiya

15. Ridey, N.M., Zaharkevich, I.V. *Екологічний контроль за якістю поверхневих водних джерел озер навчально-дослідного господарства «Великоснітинське» ім. Музиченка* (Environmental quality control of surface water sources lakes educational and research farms "Velikosnìtinske" by Muzychenka), *Bulletin of Zaporizhzhya National University*, №2, 172-176, Zaporizhzhya, 2008. (in Ukrainian)

16. Rybalova, O.V. Комплексний підхід до визначення екологічного стану басейнів малих річок (A comprehensive approach to the determination of the ecological state of pools of small rivers). *The problems of environmental protection and technological safety,* XXXIII, 88-97, Kharkov, 2011 (in Ukrainian)

17. Selivanova, A.M., Mitryasova, O.P. Моніторинг стану поверхневих вод Миколаївської області (Monitoring of surface water status of Mykolaiv region). *The collection of materials of Ukrainian scientific-practical conference «The applied aspects of urban ecological security».* NUCZU, 122-123, Kharkov, Харків, 2013. (in Ukrainian)

18. *The Water Code of Ukraine*: Law of Ukraine on June 6, 1995, № 213/95-VR Electronic resource / Verkhovna Rada of Ukraine. http://zakon4.rada.gov.ua/laws/show/213/95-%D0%B2%D1%80. (in Ukrainian)

19. Yidana S.M., Yidana A. Assessing water quality using water quality index and multivariate analysis *Environ Earth Sciences*, 1461-1473, USA, 2010.

WEATHER'S COMFORT OF MYKOLAIV AND ADAPTATION TO CLIMATE CHANGE

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ABSTRACT

The article presents the results of search and statistical analysis of the dynamics of environmental quality indicators. The ratio of days with comfortable weather conditions to the maximum possible number of them is calculated. Graphical representation of individual indicators allowed us to draw conclusions about climate change at the local level. The only right way for humanity is a strategy of sustainable development.

Keywords: anthropocentrism, neoanthropocentrism, sustainable development, comfortable weather, quality of environment, adaptation.

INTRODUCTION

Scientists' predictions about the consequences of climate change are beginning to come true today, and it is clear that this is just the beginning of irreversible changes on the planet. Man's consumer way of life, his selfishness and greed, launched a destructive scenario of human existence. Anthropocentrism of the nineteenth and twentieth centuries has been the cause of many environmental problems that still remain unresolved.

The environment has almost lost the ability to self-healing, so only the future actions of mankind depends on the future of the biosphere. The transition from anthropocentrism to neoanthropocentrism, from a consumerist way of life to sustainable development, from greedy expansion to rational use of nature is the only sure way to salvation [3].

The UN Framework Convention and the "Agenda for the XXI Century" identify the main cause of climate change as an increase in air emissions [1,2,3]. In particular - greenhouse gases, the main representatives of which are carbon dioxide and methane. The scientific and technical standard of living does not allow to stop emissions completely, because the needs of mankind are too high. We try to reduce them by all means, but is that enough? So far there are no results. The average temperature on the planet continues to rise.

The zone of tolerance (comfort) for living organisms is narrowing, so environmental factors force them to adapt to survival. Man is no exception. Global climate change at the local level in the form of adverse weather conditions and phenomena has become a significant problem today in all areas of socio-ecosystems.

Mykolaiv region is characterized by a temperate continental climate with mild snowless winters and hot dry summers. As geolocation is decisive in the formation of weather and climatic conditions, the area has four seasons. Residents of Mykolaiv, as well as other representatives of live organisms, are historically acclimatized to the given conditions of environment and adapted to the corresponding actions of its factors. Therefore, any critical deviations from the norm pose a potential threat to their health or even life. Environmental quality assessment and risk calculation are important indicators of the actual ecological characteristics of the socio-ecosystem and allow to respond effectively to dangerous challenges [4].

METHODS AND EXPERIMENTAL PROCEDURES

The most favorable weather conditions for inhabitants of Mykolaiv are indicators of a summer season as this period as much as possible covers optimum limits of comfort. To assess it, two main factors were used - the average daily temperature (n_1) and the average relative humidity (n_2). For the first the optimal range is 20 - 25 ° C, for the second - 65 - 75%. Optimal limits of comfort were defined according to biological needs of Mykolaiv as living organisms.

On the basis of statistical data of the Mykolaiv hydrometeorological station the sample was formed: 2440 days of potentially comfortable weather for 20 years. The distribution of the number of calculated ranges of each factor is presented in Tables 1 and Table 2.

Sampling period: 1998 - 2017. This choice is explained by the need to assess the ratio of the number of "comfortable" days to "uncomfortable" for a period of exactly 20 years, excluding the last three (2018, 2019, 2020). Then the calculated probability index (B) can be taken as a standard and then compared with the current time.

Table 1. Quantitative indicators of the factor n_1

№	**Moon**	**t° C**		
		to 20	**20 - 25**	**above 25**
1	June	212	348	40
2	July	56	389	175
3	August	86	373	161
4	September	455	141	4
Total		**809**	**1251**	**380**
%		**33**	**51**	**16**

Table 2. Quantitative indicators of the factor n_2

№	**Moon**	**w, %**		
		to 65	**65 - 75**	**above 75**
1	June	347	155	98
2	July	425	134	61
3	August	478	101	41
4	September	299	132	169
Total		**1549**	**522**	**369**
%		**64**	**21**	**15**

The formula for calculating the probability of action of the factor [4]:

$$B = \frac{n_i}{N} \quad , \tag{1}$$

where n_i is a quantitative indicator of the factor;

N is the maximum possible period of optimal interaction of factors (2440 days).

Because the factors are independent of each other, their effect on the object is summed. The formula for calculating the ratio of comfortable weather (K) to uncomfortable [4]:

$$К = \frac{В_1 + В_2}{2} \quad , \tag{2}$$

where B is the probability of action of the factor.

The visual analysis of the statistics of the first and last frosts in the transition seasons between summer and winter weather conditions deserves special attention. Estimating the period 1998-

2017, it is possible to clearly identify trends and understand the forecasts for future years. This information can be useful for the agricultural sector in the context of adaptation to climate change. Actual data of Table 3 are statistics of observations of the Mykolaiv hydrometeorological station.

Table 3. Frosts in the air at a height of 2 m

Years	Date of last frost in spring	Date of first frost in autumn
1998	31.03	08.10
1999	06.04	19.10
2000	12.04	24.10
2001	02.04	17.10
2002	08.04	01.11
2003	11.04	25.10
2004	04.04	13.10
2005	09.04	21.10
2006	27.03	19.10
2007	18.04	05.11
2008	27.03	07.11
2009	23.04	31.10
2010	24.04	29.10
2011	12.04	24.10
2012	02.04	13.11
2013	31.03	20.10
2014	07.04	19.10
2015	05.04	08.10
2016	22.03	18.10
2017	31.03	16.11

After an assessment of quality of the environment of inhabitants of Mykolaiv (on comfort of weather conditions), it is necessary to check the tendency of changes of volumes of emissions in atmospheric air for the similar period of years. The dynamics in graphical form will allow us to conclude about the effectiveness of measures to combat climate change at the local level. Emission indicators are presented in Table 4, which is formed on the basis of statistical data of annual national and regional reports of management of ecology of the city of Mykolaiv. Statistics of emissions from mobile sources from 2016 ceased to be recorded by the relevant decision of the Cabinet of Ministers, so the real complex figure of emissions is unknown. Stationary sources are well monitored, so you can analyze their performance. Also, from regional reports it became known that in 1998 emissions from mobile sources accounted for 66% of the total, in 2003 - 78%, and in 2005 - 92%.

Table 4. Dynamics of emissions from stationary sources, thousand tons:

Years	Total emissions	Including CO_2
1992	55,93	-
1993	40,37	-
1994	43,30	-
1995	36,60	-
1996	27,72	-
1997	19,86	-
1998	19,60	7,40
1999	14,00	-
2000	11,43	-
2001	13,27	-
2002	15,38	-

Years	Total emissions	Including CO_2
2003	15,36	-
2004	22,17	2,63
2005	24,29	2,86
2006	21,19	2,10
2007	22,66	1,81
2008	25,78	1,67
2009	24,43	1,56
2010	21,45	1,57
2011	25,69	1,93
2012	25,14	2,22
2013	20,37	1,60
2014	15,91	1,44
2015	15,79	1,74
2016	13,89	1,69
2017	14,18	1,89
2018	13,10	1,95
2019	12,07	1,67

THE RESEARCH RESULTS AND DISCUSSIONS

According to formula 1, the probability of optimal action of factors is:

$B_1 = 0{,}512$

$B_2 = 0{,}213$

Because the factors are independent, their effect is summed. Therefore, according to formula 2, it becomes known the percentage of "comfortable" days from their potentially the maximum possible number per year:

$$К = \frac{0{,}512 + 0{,}213}{2} = 0{,}362$$

Figure 1 shows the nature of the distribution of the action of the two factors and the allocation of the tolerance zone - the range (2.5 - 3.5), under the conditions of simultaneous action on the object. The ranges (1 - 2.4) and (3.6 - 5) have unfavorable weather conditions, so they are uncomfortable.

The percentage of days with comfortable weather to uncomfortable is presented in Figure 1.

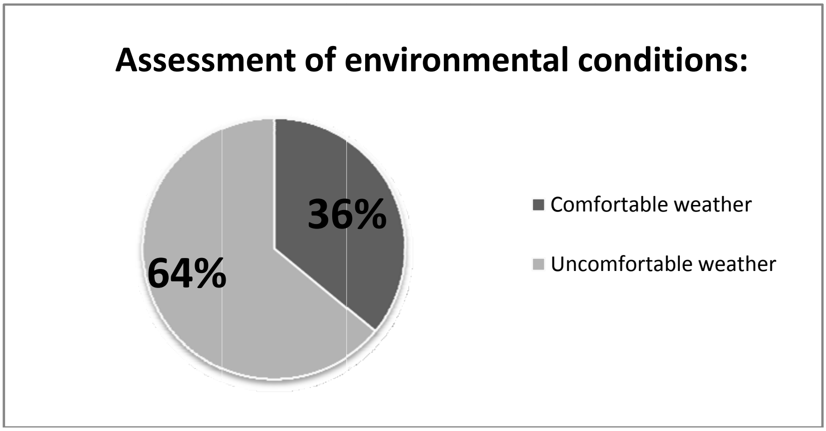

Fig. 1. The indicator of weather`s comfort in the Mykolaiv

For living organisms living in areas characterized by the presence of four seasons (winter, spring, summer, autumn), the most difficult are the transitional adaptation periods of spring and autumn. Biological systems work cyclically and have biorhythms that synchronize with seasonal weather changes and depend on them.

As a result of global climate change at the local level there is an increase in the number of adverse weather events - floods, downpours, droughts, tornadoes, tsunamis, fires, landslides and more. Weather anomalies are also felt in the Mykolaiv region.

If we look at the statistics of the first and last frosts for the period 1998 - 2017, we can trace the tendency to increase the amplitude of fluctuations in the occurrence and termination of frosts. In addition to the sharp differences in amplitude, Figure 2 visually confirms the phenomenon of global warming, as in recent years frosts appeared later and disappeared earlier. The winter season gradually loses its historical characteristics and acquires signs of transitional seasons (spring and autumn).

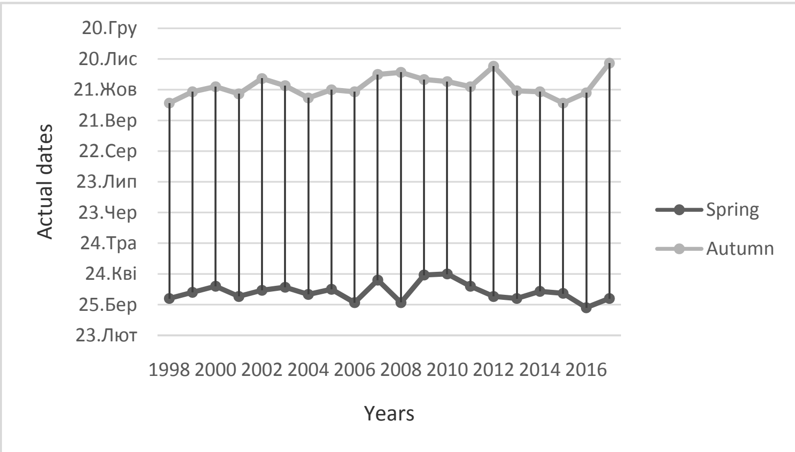

Fig. 2. Frosts in the air at a height of 2 m

The adoption of a sustainable development strategy has set a course to reduce emissions into the atmosphere. For years, monitoring has been collecting factual information on quantitative emissions, with a special focus on greenhouse gases. According to the Department of Ecology of Mykolaiv, the record holders of air pollution are mobile sources, as their number has grown sharply every year and continues to increase. Unfortunately, up-to-date data on their emissions statistics are no longer published. As the territory of Mykolaiv region has an exit to the sea, freight transport from all Ukraine uses logistics of our area for journey to ports. Harmful emissions into the air have reached enormous volumes and continue unabated.

As for stationary sources of pollution, the situation is improving. In Fig. 3 and Fig. 4, the diagrams show a positive reduction in emissions for the period 1992 - 2019.

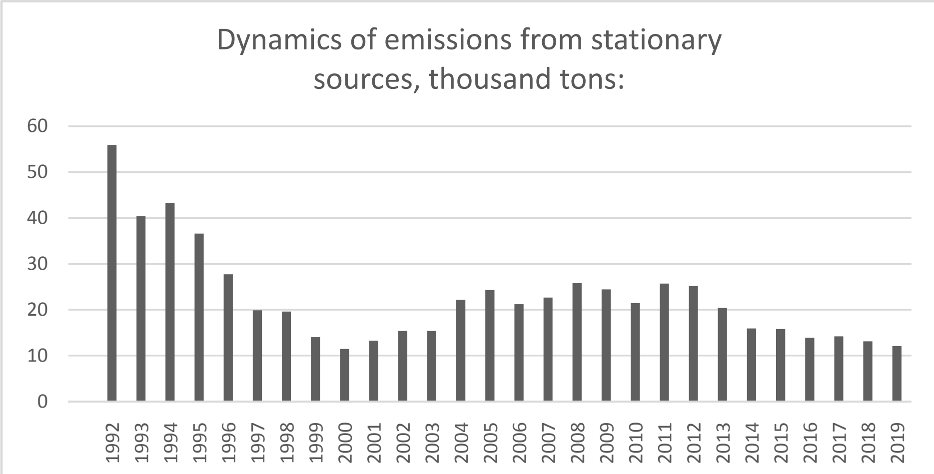

Fig. 3. Diagram of positive changes

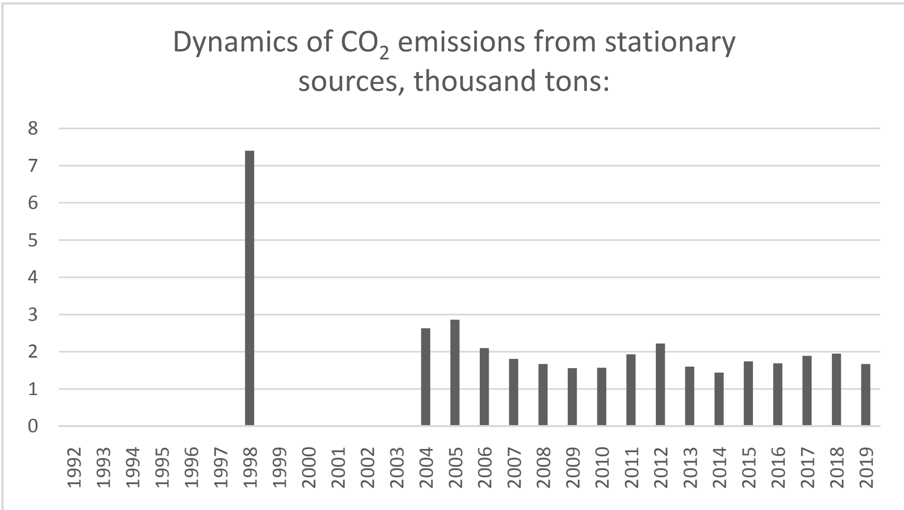

Fig. 4. Trend in greenhouse gas emissions

Optimal environmental conditions allow for full development, and stressful conditions mobilize internal reserves and encourage survival. Living matter exists on the principle of "adaptation or death", so the reaction to a stress stimulus (factor) may be different. Under constant stress, everyone equally goes through three stages of reactions - resistance, opposition, exhaustion [5,6]. Man, as a biosystem, also has its own spectrum of reflections - ignoring (conscious or unconscious), patience, escape, struggle, adaptation, suicide [6]. Even people react accordingly to the problem of climate change. Obviously, this issue at this stage of scientific and technological progress is still impossible to solve by struggle. So, the only thing left for humanity is to adapt to change.

For a clear understanding and selection of the necessary types of measures to adapt to climate change, Table 5 presents their comprehensive classification. The table is functional and provides for adjustments and additions in accordance with current ideas.

Table 5. Classification of adaptive measures:

№	Classes	Types	Examples
1	on the scale of	global	studies of ozone "holes", remote sensing of the Earth
		regional	rescue of wild animals from forest fires, closure of landfills
		local	bird feeders in the garden, planting trees
2	at the level of	international	conferences, treaties
		national	development programs
		local	work plans
3	by the number of people involved are	mass	recycling products
		collective group	collective protests
		individual	vegetarianism, reusable clothing
4	by value	required	compliance with the law
		recommended	abandonment of fossil fuels
		prohibited	ban on CFCs in refrigerators
5	by duration of action	one-time	action "day without electricity"
		causal (phased)	transition to renewable energy sources
		cyclic	cleaning the effects of floods
6	by field of activity	production and industrial	reduction of harmful emissions
		agricultural	rational use of fertilizers and pesticides
		utilities (maintenance)	restrictions on the use of plastic
		cultural and educational	conducting trainings, ecological agitation
7	by type	technical	filters, replacement of parts
		technological	energy saving technologies
		ecological	tree planting, protection of nature reserves
		psychological	eco-consciousness
8	by mode of action	material	physical work on the site - digging a drainage channel
		intangible	information education
9	by money value	financially dependent	construction, demolition
		free	go on foot where possible
		mixed	volunteers collect and sort garbage
10	in reverse	inevitable	shooting wild wolves
		variables	dam, land reclamation
11	by expiration date	temporary	seasonal reclamation
		permanent	rejection of plastic
12	by response speed	urgent priority	evacuation, medical care
		planned	fencing the boundaries of the reserve

Gone are the days when it was necessary to draw attention to environmental issues because they became obvious. Economic giants no longer need to manipulate the minds of scientists for their own selfish purposes, because the truth can no longer be hidden. The world is changing, environmental information is available and open. It is time for decisive action in the strategy of sustainable development. People are ready to work on their mistakes.

CONCLUSION

1. Comfort of weather conditions in Mykolaiv is low as makes only 36% of their maximum possible quantity.

2. The dynamics of the first and last frosts confirms the phenomenon of global warming.

3. The dynamics of harmful emissions from stationary sources indicates a positive reduction in air pollution. But the situation with mobile sources is critical and requires prompt response.

4. Adaptation measures should be improved and implemented as soon as possible.

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REFERENCES

1. UN Framework Convention on Climate Change

2. Action program "Agenda for the XXI century". - К.: Інтелсфера, 2000. - 360 с.

3. Dobrovolsky V.V. Methodological support of sustainable development: the use of the method of contradictions / V.V. Dobrovolsky // Scientific works: scientific and methodical magazine. - Mykolaiv: BSU Publishing House named after Petra Mogili, 2012. - Vol. 179, Vip. 167. - P. 119 - 123

4. Dobrovolsky VV Basic principles of the theory of environmental quality assessment / V.V. Dobrovolsky // Scientific works: scientific and methodical magazine. - Mykolaiv: BSU Publishing House named after Petra Mogili, 2015. - Vol. 256, Vip. 244. - P. 10 – 14

5. Ishcheikina YO, Filatova VL, Nechepaeva LV, Burya LV, Sargosh OD, Bychko MV Fundamentals of human safety. Tutorial. - Poltava: Publishing House PO "Fast Print", 2013. - 113 p.

6. Ionov IA Physiology of higher nervous activity (GNI): textbook / I.A. Ionov, TE Komisova, A.V. Мамотенко, С.О. Шаповалов, O.M. Sukach, N.F. Teremetska, ОО Катеринич. - Н.: FOP Petrov V.V., 2017. - 143 p.

7. Statistical data of the Mykolaiv hydrometeorological station

8. Statistical data of management of ecology of Mykolaiv

SEARCHING FOR SUSTAINABLE DEVELOPMENT

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ABSTRACT

Civilizations, just like individual people and whole species, emerge, grow, age, and disintegrate. The failure of creative power often follows after a period of major accomplishments. Because our Western civilization has enjoyed enormous technological progress and accumulation of wealth in the past two centuries, we should take care to keep our eyes open at this point.

The article consists of three development scenarios: sustainable development, sustainable retreat, and collapse of society. Sustainable development was formulated in 1987 by the United Nations. It is a development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

In 2006, British physicist James Lovelock came with the idea that it is too late for sustainable development, we should strive for sustainable retreat instead. For Lovelock, the deadliest issue is the ongoing climate change, as it is irreversible and can only be mitigated.

Why some societies perish while others survive? Whether a society collapses or not depends largely on its environment. The absolute key is nevertheless the society´s response to its problems and its capacity to solve them. A major societies, empires, and civilizations, in a similar way to humans, go through the stages of youth, adulthood, and old age. The duration of the stages varies. Unlike in humans, they need not "die" but can instead transform into a new form.

A crisis is usually followed by hope, rebirth, and flourishing. Regardless how big a crisis is, it always presents an opportunity for catharsis and hope for a new beginning. However, there is no physical law stating that a crisis must be followed by restoration and prosperity.

Keywords: sustainable development, sustainable retreat, Gaia, collapse of societies, restoration of civilizations

INTRODUCTION

One of the most renowned historians studying the development of civilizations, Arnold Toynbee, was aware that civilizations, just like individual people and whole species, emerge, grow, age, and disintegrate. He also noticed that civilizations begin to fall apart once they lose their ability to respond creatively to great challenges. The failure of creative power often follows after a period of major accomplishments made by the civilizations.

Given the scientific and technological progress and accumulation of wealth that our Western Euro-American civilization has enjoyed for the past two centuries, we should take special care to keep our eyes open at this point.

It is not humanly possible to forecast which direction humankind will head in the 21st century. We can, however, try to describe the major threats and risks as well as opportunities that await us on our journey through the 21st century. The elementary "map of the future" could, I believe, consist of three basic scenarios: sustainable development, sustainable retreat, or chaos and anarchy.

SUSTAINABLE DEVELOPMENT

Politics and economics have a rich glossary for one´s triumph over another but limited vocabulary for love and victory of both parties. We assume that if one is to win, the other must inevitably lose. One of the principles of sustainable development, however, is a positive approach, i.e. everyone can win. (Dennis Meadows)

Sustainable development was formulated by the UN World Commission on Environment and Development in the report "Our Common Future" in 1987. It is a development that meets the needs of the present without compromising the ability of future generations to meet their own needs. In its broadest sense, the strategy for sustainable development aims to promote harmony among human beings and between humanity and nature. This definition is quite vague though, and its biggest deficiency is the fact that it fails to even attempt to define human needs.

Headed by the then Prime Minister of Norway, Gro Harlem Brundtland, the Commission had big plans for sustainable development: *We need to successfully carry out the most important global transformation since the agricultural and the industrial revolution – the transition to sustainable development.* (United Nations World Commission on Environment and Development, 1987). It is one thing to formulate sustainable development but quite another to have the will to promote it. Sustainable development, nevertheless, remains perhaps the most serious attempt at finding an answer to the question of how to allow all people and nations to develop and improve their quality of life, while preserving functional ecosystems and a healthy environment for humankind.

Six years later, in 1993, Czech environmentalist, Josef Vavroušek, came up with a more relevant definition of sustainable development: *Sustainable development, and more specifically a sustainable lifestyle, aims at the ideals of humanism and harmonious relationships between man and nature. It is a way of life that searches for a balance between the freedoms and rights of each individual and his or her responsibility to other people and nature as a whole, including responsibility to future generations.*

Based on the above definitions we can now formulate four specific requirements that need to be gradually fulfilled in order for us to head toward long-term sustainable development:

1. the requirement that all the people on Earth are able to meet their (basic, at minimum) needs;
2. the requirement to respect the right of future generations to be able to meet their needs;
3. the requirement to respect an adequate level of rights for other living beings;[2]
4. the requirement to learn from the future (learning based on forecasting the potential consequences of our current activities) and respect the precautionary principle.[3]

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[2] Peter Singer (1975) says: *We are equal, but equal does not mean the same.* Erazim Kohák (1998) adds: *We may have different needs but we have the same right to satisfy them.*

[3] The precautionary principle is defined in Principle 15 of the Rio Declaration on Environment and Development: *Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation.* (Moldan, 1993)

Following 34 years of striving to promote sustainable development, and three major UN conferences on these issues (Rio de Janeiro in 1992, Johannesburg in 2002, and again in Rio in 2012), it is now easy to see that moving towards sustainable development is probably beyond our strength, especially on the international and global level.

The United Nations is today (unfortunately) an organization of 193 member states that promote above all their own individual or group interests, and not the interests of the planet as a whole. This all does not, however, mean that we should not strive for sustainable development.

Sustainable development may be feasible if:

- We gradually change our values to make them comply with the principles of sustainable development. The value sphere is quite permanent, and only changes very slowly, over decades and centuries. A change in value orientation is taking place inconspicuously, although it is crucial for the promotion of sustainable development. The question is then whether we have enough time for the necessary change in value orientation.
- We manage to create and enforce economic tools directing us towards sustainable development. Or more generally, we manage to implement new, eco-friendly priorities for economics and the world economies that will respect the ecosystem´s sustainable capacity. A key economic instrument to implement sustainable development is ecological tax reform. The essence of the ecological tax reform is to shift the tax burden from what we want to have in sufficient amounts (e.g. labour) onto what we want to have in minimal amounts (e.g. the depletion of natural resources). It therefore means gradual (long-term) significant taxation and also an increase in the prices of energy and raw material resources which would, however, be balanced by the lower or even zero taxation of labour.
- We manage to create and enforce economical and more effective technologies. The aim is to imitate to the maximum possible extent the functioning of ecosystems that produce no waste, or ecosystems in which the waste from one process is the initial raw material of another process. Similarly to nature´s economy, human economy should also head towards the termination of material flows and use of energy from renewable energy sources that build on the energy of the sun´s rays.
- We manage to build functional and effective states and self-governing municipalities and regions, while becoming able to agree on the basic principles of international or global governance. We need an effective tool to solve global problems, namely global governance – which does not mean a "global government", but a set of jointly adopted, respected, and enforceable rules. These rules are similar to traffic regulations: all around the world drivers need to stop at red at traffic lights and not overtake another vehicle when there is a solid line. This is not understood as a threat to our personal freedom but as a precondition for all road users to stay alive and safe.

SUSTAINABLE RETREAT

Inside I am truly scared, but I am not sure whether my feelings are reflecting the atmosphere in society or the actual condition of the planet. (Václav Cílek)

If we admit that we will never make sustainable development a reality, that there is not enough will or time for its implementation, then it is wise to explore other options. In 2006, in his book *The Revenge of Gaia*[4], the British physicist James Lovelock was probably the first to articulate

[4] In 1979, Lovelock came up with the „Gaia" hypothesis, based on which the Earth behaves as a unified self-regulatory system composed of physical, chemical, biological, and human elements. Interactions and feedback between individual components are complex, exhibiting time and space variability on multiple levels. It is a dynamic physiologic system that has been preserving conditions for life for more than three billion years. The „Gaia" hypothesis views the biosphere as an active adaptive system capable of keeping the Earth in homeostasis.

the idea that it is too late for sustainable development and that we should strive for sustainable retreat instead:

It is much too late for sustainable development; what we need is a sustainable retreat. The error the supporters of sustainable development and laissez faire of business share is the belief that further development is possible, and the Earth will continue, more or less as now, for at least the first half of this century. Expecting that sustainable development or a conventional method are viable approaches is to think that lung cancer can be cured by giving up smoking. (Lovelock, 2006)

For Lovelock, the deadliest issue is the ongoing climate change, as it is irreversible and can only be mitigated. He compares the growing global temperatures to a growing temperature (fever) in the human body. In humans, fever always indicates there is something wrong in the body, even if it is not yet certain precisely what.

James Lovelock is aware that so far we have not been able to adopt effective preventive measures, and with respect to his age he can see it is not the first time this has happened in his lifetime: *I am old enough to notice a marked similarity between attitudes over sixty years ago towards the threat of war and those now towards the threat of global warming. Most of us think that something unpleasant may soon happen, but we are as confused as we were in 1938 over what form it will take and what to do about it. ... The Kyoto Protocol* (which was adopted in 1997 and dealt with limits on greenhouse gas emissions – author´s note) *was uncannily like that of Munich, with politicians out to show that they do respond but in reality playing for time.* (Lovelock, 2006)

Lovelock believes that we will not be able to avoid the painful consequences of our universal dependency on fossil fuels, the burning of which produces the greenhouse gas carbon dioxide. Today human society depends on fossil fuel energy like addicts depend on drugs. While treatment is possible, it is painful and requires determination on the addict´s side, not resignation: *We as a civilization are all too much like someone addicted to a drug that will kill if continued and kill if suddenly withdrawn.* (Lovelock, 2006)

Since the first report to the Club of Rome, *The Limits to Growth*, was published in 1972, we have been warned that the exponential growth of population, energy, raw materials, and population is not viable in the long run in our space-limited biosphere. For 34 years, since 1987, we could and should have been promoting and cultivating the concept of sustainable development, but instead we have failed to take any affective action, at least on the international and global level.

Although there is still some time left to strive for sustainable development, it is also time to brace ourselves for the fact that these efforts may fail and that we will have to give up our high demands on materials and energy. Now is the time to admit this is possible and begin devising how to minimize the damage and pain this will bring.

Sustainable retreat is hard to enforce politically and difficult to absorb mentally. We may thus trifle away our most precious, finite, and non-renewable source – time. We will continue to exponentially increase our consumption of resources and production of waste until we exceed the bearing capacity of ecosystems to such a degree that the ecosystems collapse. Acting in line with the precautionary principle will turn out to have been too difficult a task for humans.

COLLAPSE – PERIOD OF ANARCHY AND CHAOS

A crisis is not a disaster; rather it is a turning point, the outcome of which depends entirely on us. (Lubor Kysučan)

Whole civilizations (for instance the ancient Egyptian and Minoan civilizations) and empires (including the Persian and Roman empires) have collapsed in the past. Such a decline may take place over dozens or even hundreds of years.

Why some societies perish while others survive is the theme of the book *Collapse* (2004) by the biologist and cultural anthropologist Jared Diamond. He defines collapse of a civilization as a decrease in population size or political, economic, and social complexity over a large area for a long time.

The collapse of ancient societies was caused at least partly by environmental problems that Diamond places into eight categories:

- deforestation and habitat destruction;
- soil problems (erosion, salinization, and fertility losses);
- water management problems;
- overhunting;
- overfishing;
- effects of introduced species on native species;
- human population growth;
- increased per-capita impact of people.

Nowadays, in addition to the old dangers, we are facing four more environmental factors that pose a threat to societies:

- anthropogenic climate change;
- the accumulation of toxic chemicals in the environment;
- energy shortages;
- a near-full use of the Earth´s photosynthetic capacity for human needs.

Whether a society collapses or not depends largely on its environment, including such factors as friendly or hostile neighbours and the existence or absence of trade partners. The absolute key is nevertheless the society´s response to its problems and its capacity to solve them.

RISE AND FALL OF CIVILIZATIONS

The ascent of man will go on. But do not assume that it will go on being carried by Western civilization as we know it. We are being weighed in the balance at this moment. If we give up, the next step will be taken – but not by us. We have not been given any guarantee that Assyria and Egypt and Rome were not given. (Jacob Bronowski)

All major societies, empires, and civilizations, in a similar way to humans, go through the stages of youth, adulthood, and old age. The duration of the stages varies. Unlike in humans, they need not decline („die“) but can instead transform into a new form. Western civilization, for example, has been built on, and simultaneously has continued, the legacy of Hellenic civilization and the Roman Empire.

According to Samuel Huntington (1996), who continued in the tradition of the great historian Arnold Toynbee (1985), there are eight civilizations on the Earth today: Western, Orthodox, Hispanic, Islamic, Sinic, Hindu, Buddhist, and Japanese. A possible ninth major civilization is Sub-Saharan Africa, deemed „possible“ because it includes fragmented tribal communities.

For two hundred years, the world has been dominated by the Western civilization due to its technological superiority. Today, though, the Islamic and Sinic civilizations are also competing for the privileged position, the former thanks to its demographic growth and determination to spread Islam and the latter on the grounds of its economic growth.

As the American futurologist Alvin Toffler (1980) says, Western civilization has already started to gradually transform: *We are the final generation of an old civilization and the first generation* *of a new one. If we identify key change patterns as they emerge, we can influence them. The more basic political question, as we shall see, is not who controls the last days of industrial society but who shapes the new civilization rapidly rising to replace it. Some generations are born to create, others to maintain a civilization.*

In Toffler´s view, the decay of Western civilization as we know it is not necessarily a tragedy or a negative development overall. The old makes room for the new. The generations that maintained the Western civilization will be replaced by generations that will create a new civilization. The most important thing is our attitude to the crisis, how we deal with it.

Humans will tolerate a great deal of suffering as long as it is meaningful to them. Without a sense of common purpose, feelings of futility and despair will begin to control our lives. The fundamental challenge then is to find a new „common purpose“: *We cannot be purposely building a future that we are unable to envision. The first requirement is to create a realistic, convincing, and arresting vision of a future that is easy to communicate. We need to find a story to describe the next chapter of our evolution and to catalyze our energy and enthusiasm.* (Elgin, 1993)

Along similar lines, the founder of logotherapy, Viktor Frankl, says: *Man´s primary motivational force is his will to meaning. True efforts to find meaning form a substantial aspect of human nature and self-transcendence. We live in a century of a spreading feeling of meaninglessness. In reality, though, a man can only survive if he has something to live for. It seems this is true not only about the survival of an individual but also about the survival of humanity. Mere survival cannot constitute the supreme value. To be human means not the place oneself in the centre.* (Frankl, 2006)

If the will to meaning is suppressed, it is replaced by a „will to power“ and/or a „will to pleasure“. The more a man or woman desires pleasure, however, the more it escapes them. Viktor Frankl postulates that we need to overcome the preconception that humans principally strive to be happy. What they really want is to have a reason for happiness. Frankl sees meaning in doing or creating. Secondly, he sees meaning in gaining experience and loving another.

RESTORATION FOLLOWING MAJOR CRISES

Nobody made a greater mistake than he who did nothing because he could do only a little. (Edmund Burke)

A crisis is followed by hope, rebirth, and flourishing. This is a pattern in nature. Since the Paleozoic Era, the Earth has experienced at least five major global catastrophes (caused by events such as asteriod impacts, or climate change). For reasons still unknown to us, these were never followed by permanent reductions in the diversity of life or periods of stagnation but, on the contrary, evolution toward higher life forms.

Human society has followed a similar trend. For example, after the Second World War, European countries enjoyed a baby boom with an extraordinarily increased birth rate. Likewise, the 1950s and 1960s were a time of blossoming and prosperity for European economies.

The Thirty Years War between Catholics and Protestants ended in Europe with the signing of the Peace of Westphalia in 1648. Among other benefits, the treaty brought about a giant shift in relations between individual countries. The principle of national sovereignty, the cornerstone of international relations for nearly 400 years now, was adopted.

The Civil War that broke out in North America eventually claimed 970,000 lives. On the other hand, it led to the abolishment of slavery in 1865, when the 13th Amendment to the U.S. Constitution was adopted.

Clearly, regardless how big a crisis is, it always presents an opportunity for catharsis and hope for a new beginning. However, there is no physical law stating that a crisis must be followed by restoration and prosperity; we need to make an effort, and furthermore there is no guarantee of the results.

CONCLUSION

On 14 April 1912, twenty minutes to midnight, the „unsinkable" Titanic collided with an iceberg while on her maiden voyage from Europe to New York. The ice mass tore a 90 m gap in the starboard side, below the waterline but above the double bottom level. Five minutes to midnight the captain ordered the crew to launch lifeboats. At half past midnight the boats began filling with women and children. Some boats remained nearly empty as men were not allowed to board and some families wished to stay together. Others were reluctant to board the boat and set off in the dark, leaving behind the only well-lit place in sight. Only the very last boat was crowded.

On 15 April 1912 at two twenty in the morning the Titanic sank. Of the 1,316 passengers and 855 members of the crew, only 706 people survived. More than two thirds of the people onboard died, most from hypothermia and drowning.

The Titanic story can be inspiring in the 21st century, in which we still either manage to act with foresight, or we will not, which will have painful consequences.

It has been over a hundred years since the disaster, and now more that ever before, the tragic fate of the Titanic should serve as a lesson and warning. Escalating global problems of humankind could exceed the ecosystem´s limits, and it would take entire biosphere to buffer and absorb these problems. We can ignore hazards and warning signs but that does not mean that the problems will go away.

The future ahead of us is open, and thanks to our free will, also susceptible to human influence. Even now we have the capacity to destroy ourselves (through, for example, a global nuclear war or by initiating climate change of such scope and intensity that there will be no way back). We still have two roads before us: evolution or revolution, transformation or a series of disasters of possible apocalyptic dimensions.

REFERENCES

1. Diamond, J. Collapse: *How Societies Choose to Fail or Succeed.* Penguin Books Ltd., London, 2004
2. Elgin, D. *Voluntary Simplicity: Toward a Way of Life That is Outwardly Simple, Inwardly Rich.* Quill, New York, 1993
3. Frankl, V. *Vůle ke smyslu. Vybrané přednášky o logoterapii.* Cesta, Praha (in Czech), 2006
4. Huntington, S. *The Clash of Civilizations and the Remaking of World Order.* Simon&Schuster, New York, 1996
5. Kohák, E. *Zelená svatozář.* Sociologické nakladatelství, Praha (in Czech), 1998
6. Lovelock, J. *Gaia: A New Look at Life on Earth.* Oxford University Press, Oxford, 1979
7. Lovelock, J. *The Revenge of Gaia.* Basic Books, New York, 2006
8. Meadows, D., Meadows, D., Randers, J. *The Limits to Growth.* Universe Books, New York, 1972

9. Moldan, B. *Konference OSN o životním prostředí a rozvoji. Dokumenty a komentáře.* Management Press, Praha (in Czech), 1993
10. Singer, P. *Animal Liberation.* Avon Books, New York, 1975
11. Toffler, A. *The Third Wave.* Bantam Books, New York, 1980
12. Toynbee, A. *A Study of History. (Abridgement of Volumes I-X.)* Oxford University Press, Oxford, 1985
13. United Nations World Commission on Environment and Development. *Our Common Future.* Oxford University Press, Oxford, 1987
14. Vavroušek, J. *Perspektivy lidských hodnot slučitelných s trvale udržitelným způsobem života.* In: Nováček, P., Vavroušek, J., eds. Lidské hodnoty a trvale udržitelný způsob života. Sborník přednášek. Vydavatelství Univerzity Palackého, Olomouc, str. 91 – 100 (in Czech), 1993

ANTIBACTERIAL FUNCTIONALITY OF LEAF EXTRACT OF *FICUS BENJAMINA* L. (MORACEAE) AND ITS CULTIVARS AGAINST *AEROMONAS* STRAINS AS AN ALTERNATIVE APPROACH FOR SUSTAINABLE AQUACULTURE

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ABSTRACT

The present study is an *in vitro* study to evaluate the antimicrobial activity of the ethanolic extracts derived from leaves of *Ficus benjamina* and its cultivars, i.e. *F. benjamina* 'Safari', 'Baroque', 'Amstel Gold', 'Reginald' against three *Aeromonas* strains, i.e. *Aeromonas sobria* (K825) and *Aeromonas hydrophila* (K886), as well as *Aeromonas salmonicida* subsp. *salmonicida* (St30) to assess the possible use of this plant in preventing infections caused by these fish pathogens in aquaculture. Antimicrobial susceptibility of the tested *Aeromonas* strains was performed by the Kirby-Bauer disc diffusion method according to the recommendations of the Clinical and Laboratory Standards Institute (CLSI). Our results revealed, that *F. benjamina* and its cultivars possessed antibacterial properties against *Aeromonas sobria* strains. The ethanolic extract obtained from leaves of *F. benjamina* 'Safari' exhibited the maximum antimicrobial activity against *Aeromonas sobria* (the mean of inhibition zone diameter was

26.19±1.32 mm). *Aeromonas sobria* strain was susceptible to the *F. benjamina* 'Amstel Gold' (15.25±1.25 mm) and 'Reginald' (16.25±1.10 mm). On the contrary, *Aeromonas sobria* strain was the most resistant to *F. benjamina* (12.5±0.80 mm) and *F. benjamina* 'Baroque' (13.63±0.75 mm) leaf extracts. The ethanolic extract obtained from leaves of *F. benjamina* 'Safari' exhibited the maximum antimicrobial activity against *Aeromonas hydrophila* (the mean of inhibition zone diameters was 12.38±0.78 mm). *Aeromonas hydrophila* strain was susceptible to the *F. benjamina* 'Amstel Gold' (12.13±0.77 mm) and 'Reginald' (9.56±0.65 mm). *Aeromonas hydrophila* strain was the most resistant to *F. benjamina* (9.31±0.73 mm) and *F. benjamina* 'Baroque' (9.25±0.56 mm) leaf extracts. The ethanolic extract obtained from leaves of *F. benjamina* 'Reginald' exhibited the maximum antimicrobial activity against *Aeromonas salmonicida* subsp. *salmonicida* (the mean of inhibition zone diameters was 15.25±1.05 mm). *Aeromonas salmonicida* subsp. *salmonicida* strain was susceptible to the *F. benjamina* ‘Safari' (10.63±0.38 mm) and 'Baroque' (9.63±0.46 mm). *Aeromonas salmonicida* subsp. *salmonicida* strain was the most resistant to *F. benjamina* (9.13±0.35 mm) and *F. benjamina* 'Amstel Gold' (9.25±0.59 mm) leaf extracts. The results of this study provide a new perspective for the use of various *Ficus* species as medicinal plants to improve the antibacterial responses in aquaculture. Scanning electron microscopy has been employed to observe micromorphological leaf structures which can be used to assure the correct identification of plant raw materials. Further studies including the use of other medicinal plants as food additives in aquaculture, the assessment of their antioxidant effects on various tissues of salmonids are in progress.

Keywords*:* *Ficus benjamina* L., *Aeromonas* strains*,* antimicrobial activity, disc diffusion technique, ethanolic extracts

INTRODUCTION

Intensification of consumer demand and the annual growth of rapidly expanding aquaculture needs a higher amount of feed supply, water treatment and reuse, and high stocking density resulting in aquatic environmental degradation [27]. On the other hand, quality deterioration of the living environment and increased stress in fish result in magnification of the activity and virulence of infectious and opportunistic microbial pathogens [47]. Moreover, the overuse of antibiotics for the treatment of diseases has increased the chemical concentrations in culture systems and weakened the natural immunity of aquatic organisms [26].

To eliminate parasitic diseases in the aquaculture industry, different chemotherapeutics, i.e. synthetic antibiotics, chemical drugs, vaccines, etc. are being used at high rates year after year [28, 69, 90]. Vaccination to prevent disease is used routinely in finfish aquaculture, especially for Atlantic salmon (*Salmo salar*), while in a limited capacity (or not at all) in many other fish species due to lack of vaccines, poor performance, or cost [1]. The selective pressure exerted by these drugs, which are usually present at sub-therapeutic levels for prolonged periods in the water and the sediments, provides ideal conditions for the emergence and selection of resistant bacterial strains and stimulates horizontal gene transfer [62]. The potential bridging of aquatic and human pathogen resistors leads to the emergence of new antimicrobial-resistant bacteria and global dissemination of them and their antimicrobial resistance genes into animal and human populations [13]. The treatment of infectious diseases and parasitic infestation in aquaculture by natural substances and compounds is the demanding sustainable aquaculture feature [27, 55, 82].

The use of medicinal plants and their derivatives in aquaculture is increasing day by day all over the world because of having biodegradable properties, availability, and ease of cultivation, and do not accumulate in animal tissues as a residue [27, 32, 35, 49, 51, 54, 70]. Reports have also described that plant-derived compounds act as a better antibacterial, antiviral, immunostimulant, and antistress effect in fish and shellfish aquaculture [32, 83]. For that reason, there has been considerable interest in the use of medicinal plants in aquaculture to provide safe and eco-friendly compounds for replacing antibiotics and chemical compounds as well as to enhance immune status and control fish diseases [4]. In addition to the immunostimulant properties, it has also been demonstrated that many medicinal plants are also able to have other positive effects on fish, such as the stimulation of fish growth, weight gain, and early maturation of cultured species [10, 32, 52, 83].

In this study, attention focused on the genus *Ficus* L., a genus with diverse ethnobotanical uses in its geographical distribution range, which has occupied an important place among plant genera applied for the treatment of a broad spectrum of diseases and disorders. Along with being an object of extreme interest for researchers during the last two centuries, *Ficus* has a long history of use by humans as a food source, in medicine, planting, and other industries and fields of human activity, partly owing to its great diversity and wide distribution range. Among popular ethnomedicinal uses of *Ficus* are treatments of skin damages, disorders of the digestive system and related organs, and parasitic infections. Besides these, the range of healing targets for particular *Ficus* species compiled from local medicines can be competitive with that of broad-spectrum traditional remedies [8, 9, 18]. Among the pharmacological properties evidenced for the compounds present in the genus *Ficus* are anticonvulsant, anti-inflammatory, analgesic, antimicrobial, antiviral, hypolipidemic, antioxidant, immunomodulatory, antiasthmatic, parasympathetic modulatory, estrogenic, antitumor, antiulcer, antianxiety, antihelmintic, analgesic, tonic, anti-diabetic, antipyretic, anti-inflammatory, antitussive, hepatoprotective activities, etc. [2, 5, 11, 25, 43, 67, 89]. For all these reasons, plants belonging to the genus *Ficus* could be considered a priori as a good source of new natural compounds to treat, prevent, and control fish diseases in aquaculture.

Ficus benjamina L. also referred to as a weeping fig tree, is a multipurpose tree found in a large area including India, southern China, Southeast Asia, Malaysia, the Philippines, northern Australia, and the islands of the South Pacific [59]. It grows as a large evergreen shrub, up to 8 m tall, with nearly 10 m wide-spreading crown and drooping shoots with young slender twigs [38]. It is one of the most popular indoor ornamental plants worldwide. The plant is well known due to its medicinal potential. Its latex and some fruit extracts are used by indigenous communities to treat skin disorders, inflammation, piles, vomiting, leprosy, malaria, nose diseases, and cancer besides the use as a general tonic. The plant is also used as an antimicrobial, antinociceptive, antipyretic, hypotensive, and anti-dysentery remedy. The leaves and twigs are used as insect repellants [38]. The leaves, bark, and fruits of *F. benjamina* contain various bioactive constituents like cinnamic acid, lactose, naringenin, quercetin, caffeic acid, and stigmasterol [68]. *F. benjamina* wood uses in aerobic biofiltration as a support medium for the treatment of Tequila vinasses [33].

In this study, we evaluated the antimicrobial activity of the ethanolic extracts of *F. benjamina* and its cultivars, i.e. *F. benjamina* 'Safari', 'Baroque', 'Amstel Gold', 'Reginald' against three *Aeromonas* strains, i.e. *Aeromonas sobria* (K825) and *Aeromonas hydrophila* (K886), as well as *Aeromonas salmonicida* subsp. *salmonicida* (St30) to evaluate the possible use of this plant in preventing infections caused by this fish pathogen in aquaculture. The current study was conducted as a part of an ongoing project between the Institute of Biology and Earth Sciences (Pomeranian University in Słupsk, Poland), National Veterinary Research Institute (Puławy, Poland), M.M. Gryshko National Botanic Gardens of National Academy of Sciences of Ukraine (Kyiv, Ukraine), and Ivan Franko National University in Lviv (Lviv, Ukraine) undertaken in the frame of cooperation program aimed at assessment of medicinal properties of tropical and subtropical plants, cultivated under *ex-situ* conditions.

MATERIALS AND METHODS

Collection of plant material and preparing plant extract. The leaves of *F. benjamina* and its cultivars ('Safari', 'Baroque', 'Amstel Gold', 'Reginald') plants were sampled at National Botanic Garden, National Academy of Sciences of Ukraine (Kyiv, Ukraine), and Botanic Garden of Ivan Franko National University in Lviv (Lviv, Ukraine). The sampled leaves were brought into the laboratory for antimicrobial studies. Freshly sampled leaves were washed, weighed, crushed, homogenized in 96 % ethanol (in proportion 1:10) at room temperature, and centrifuged at 3,000 g for 5 minutes. Supernatants were stored at -20°C in bottles protected with laminated paper until required.

Bacterial strains for antimicrobial activity assay. Three *Aeromonas* strains: *Aeromonas sobria* (K825) and *Aeromonas hydrophila* (K886), as well as *Aeromonas salmonicida* subsp. *salmonicida* (St30), originated from freshwater fish species such as common carp (*Cyprinus carpio* L.) and rainbow trout (*Oncorhynchus mykiss* Walbaum), respectively, were isolated in the Department of Fish Diseases, The National Veterinary Research Institute in Puławy (Poland). Bacteria were collected from fish exhibiting clinical disorders. Each isolate was inoculated onto trypticase soy agar (TSA) (BioMérieux Polska Sp. z o.o.) and incubated at 27°C ± 2°C for 24 h. Pure colonies were used for biochemical identifications, according to the manufacturer´s instructions, except for the temperature of incubation, which was at 27ºC ± 1ºC. The following identification systems were used in the study: API 20E, API 20NE, API 50CH (BioMérieux Polska Sp. z o.o.). Presumptive *Aeromonas* isolates were further identified to the species level by restriction analysis of 16S rDNA genes amplified by polymerase chain reactions (PCR) [40, 41].

Susceptibility to antimicrobial agents. The antimicrobial sensitivity of each selected *Aeromonas* isolate was investigated with the Kirby–Bauer technique [7]. The disc-diffusion method was carried out on Mueller–Hinton agar (Oxoid, UK) according to the recommendations of the Clinical and Laboratory Standards Institute [17]. The following chemotherapeutics (Oxoid, UK) from different groups of drugs were used: the sulfonamides consisted of compound sulfonamides (S3) and sulfamethoxazole with trimethoprim (SXT); the quinolones were oxolinic acid (OA), flumequine (UB), and enrofloxacin (ENR); the tetracyclines comprised only oxytetracycline (OT); florfenicol (FFC) was the single selection from the amphenicols. After media plate inoculation and placing of appropriate antimicrobial discs (five discs per plate) on them, the plates were incubated at 28 ± 2°C for 24 h. After that, the diameters of the growth inhibition zones were measured to estimate the zone diameter breakpoints (mm) of tested isolates. Because very few internationally harmonized interpretive criteria were available for bacteria isolated from aquatic animals, we generated our own to establish the meaning of the obtained results, adapting those available for *Aeromonas salmonicida* [16].

Bacterial growth inhibition test of plant extracts by the disk diffusion method. The sensitivity of *Aeromonas* strains to selected *Ficus* extracts was determined by the Kirby–Bauer technique [7], by the guidelines of the Clinical and Laboratory Standards Institute [17], with our modifications. A suspension of each bacterial species was inoculated on Mueller–Hinton agar. Five wells per Petri dish with a diameter of 6 mm were made in the medium, and plant extracts were added to them. Ethanol at 96% strength (POCH, Poland) as used to prepare the extracts was used as the negative control. Plates were incubated at 28 ± 2°C for 24 h and the growth inhibition zones for each well were measured. The interpretation criteria for the phytochemicals tested were that a zone ≥15 mm was termed susceptible (S), one of 10–15 mm intermediate (I), and a ≤10 mm zone was indicative of a resistant microorganism (R) [53].

SEM investigation of leaf surface micromorphology. Leaf samples for examination by scanning electron microscopy were kept in 100% *tert*-butyl alcohol for 1 h at a temperature of – 10 ^{0}C. Metal boxes with frozen samples were placed on a table cooled to - 60 ^{0}C in the working volume of the vacuum universal post (VUP-5M). When vacuuming the working volume, the samples were dried due to the sublimation of frozen *tert*-butyl alcohol. The dried leaf samples were sputter-coated with carbon in a vacuum universal post (VUP-5M) and platinum in a JEOL JFC-1600 Auto Fine Coater. Visualization of leaf surfaces micromorphology of *F. benjamina* was undertaken with JEOL JSM-6700F scanning electron microscope at 15 kV acceleration voltage in the high vacuum mode.

Statistical analysis. Statistical analysis of the data obtained was performed by employing the mean ± standard error of the mean (S.E.M.). All variables were tested for normal distribution using the Kolmogorov-Smirnov test ($p>0.05$). To find significant differences (significance level, $p<0.05$) between groups, the Kruskal-Wallis test by ranks was applied to the data [92]. All statistical analyses were performed using STATISTICA 8.0 software (StatSoft, Poland).

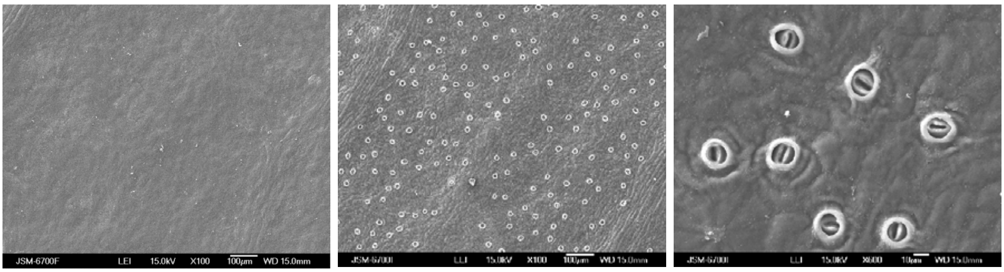
THE RESEARCH RESULTS AND DISCUSSIONS

The genus *Aeromonas* (family *Aeromonadaceae*) is ubiquitous in aquatic ecosystems that include chlorinated drinking water, raw sewage, and natural waters (i.e., fresh and brackish water) and free-living fish in such habitats [29]. *Aeromonas* is a significant cause of infections associated with natural disasters (hurricanes, tsunamis, and earthquakes) and has been linked to emerging or new illnesses, including near-drowning events, prostatitis, and hemolytic-uremic syndrome [39]. It is a major etiologic agent of motile aeromonads septicemia in a variety of aquatic animals [31].

Aeromonas sobria is a Gram-negative, rod-shaped, mesophilic motile aeromonad, and ubiquitous bacterium. *A. sobria* is currently depicted as an opportunistic pathogen of freshwater fish, amphibians, and reptiles [39, 86, 91]. *A. sobria* isolated from the farmed perch had a hemolytic effect on sheep and trout erythrocytes, autoaggregated, was cytotoxic for cultured fish cells and possessed genes involved in type III protein secretion [86].

Given that standardization and quality control are essential analytical steps to assure the correct identification of plant raw materials to be used as plant-derived medicines [64], the micromorphological investigation of *F. benjamina* leaf has been undertaken using scanning electron microscopy as a part of this research.

As can be seen from Fig. 1, *F. benjamina* leaves are hypostomatic. Leaves possess paracytic stomata with a random distribution throughout the leaf surface, predominantly between veins (Figure 1B). They are surrounded by a cuticular thickening that formed a rim (Figure 1C). The adaxial leaf surface is moderately undulate and pavement cells in the adaxial surface are difficult to recognize due to the well-developed cuticle. The epicuticular wax structures on the adaxial surface have not been observed. While the abaxial leaf surface has exhibited the deposition of small epicuticular wax plates.



A B C

Fig. 1. SEM micrographs of adaxial (A) and abaxial (B, C) leaf surfaces of *Ficus benjamina* L.

Results on *in vitro* antimicrobial activity assessment of ethanolic extracts derived from leaves of *F. benjamina* and its cultivars ('Safari', 'Baroque', 'Amstel Gold', 'Reginald') against *Aeromonas sobria* strain expressed as a mean of diameters of inhibition zone are presented in Figure 2.

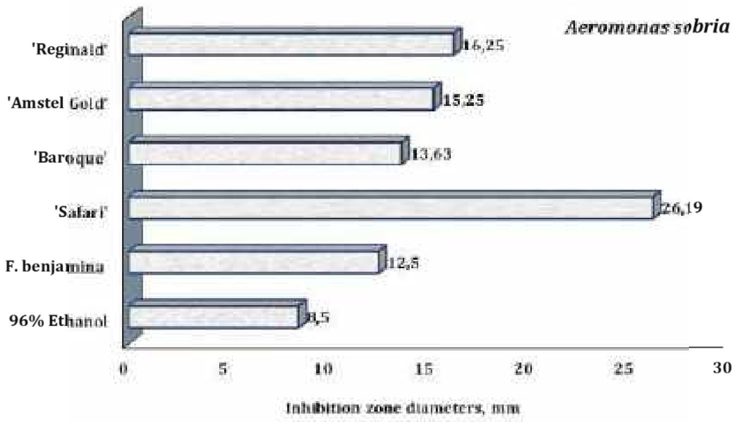


Fig. 2. The mean inhibition zone diameters induced by ethanolic extracts derived from leaves of *F. benjamina* and its cultivars ('Safari', 'Baroque', 'Amstel Gold', 'Reginald') against *Aeromonas sobria* strain (1000 µL inoculum) (M ± m, n = 8)

Our results of the antimicrobial screening revealed, that *F. benjamina* and its cultivars possessed antibacterial properties against the *Aeromonas sobria* strain. The ethanolic extract obtained from leaves of *F. benjamina* 'Safari' exhibited the maximum antimicrobial activity against *Aeromonas sobria* (the mean of inhibition zone diameters was 26.19±1.32 mm). *Aeromonas sobria* strain was susceptible to the *F. benjamina* 'Amstel Gold' (15.25±1.25 mm) and 'Reginald' (16.25±1.10 mm). *Aeromonas sobria* strain was the most resistant to *F. benjamina* (12.5±0.80 mm) and *F. benjamina* 'Baroque' (13.63±0.75 mm) leaf extracts (Fig. 2).

A. hydrophila is an opportunistic pathogen and often causes severe infections in different types of animals and humans [48]. *A. hydrophila* is also a well-established fish pathogen involved in a range of diseases, including motile aeromonad septicemia in carp, tilapia, perch, catfish, and salmon; red sore disease in bass and carp; and ulcerative infections like epizootic ulcerative syndrome in catfish, cod, carp, and goby [15, 36]. It can cause disease outbreaks in aquatic animals and lead to high mortality [56, 93].

Results on *in vitro* antimicrobial activity assessment of ethanolic extracts derived from leaves of *F. benjamina* and its cultivars against *Aeromonas hydrophila* strain expressed as a mean of diameters of inhibition zone are presented in Figure 3.

Similar to the *Aeromonas sobria* strain, *F. benjamina* and its cultivars possessed antibacterial properties against *Aeromonas hydrophila* strain. The ethanolic extract obtained from leaves of *F. benjamina* 'Safari' exhibited the maximum antimicrobial activity against *Aeromonas hydrophila* (the mean of inhibition zone diameters was 12.38±0.78 mm). *Aeromonas hydrophila* strain was susceptible to the *F. benjamina* 'Amstel Gold' (12.13±0.77 mm) and 'Reginald' (9.56±0.65 mm). *Aeromonas hydrophila* strain was the most resistant to *F. benjamina* (9.31±0.73 mm) and *F. benjamina* 'Baroque' (9.25±0.56 mm) leaf extracts (Fig. 3).

Non-motile *Aeromonas salmonicida* subsp. *salmonicida* is a ubiquitous gram-negative bacterium that is the causative agent of furunculosis in salmonid fish. This pathogen causes hemorrhagic sepsis, ulcerative lesions, pointed bleeding, and death [24, 44].

Results on *in vitro* antimicrobial activity assessment of ethanolic extracts derived from leaves of *F. benjamina* and its cultivars against *Aeromonas salmonicida* subsp. *salmonicida* strain expressed as a mean of diameters of inhibition zone is presented in Figure 4.

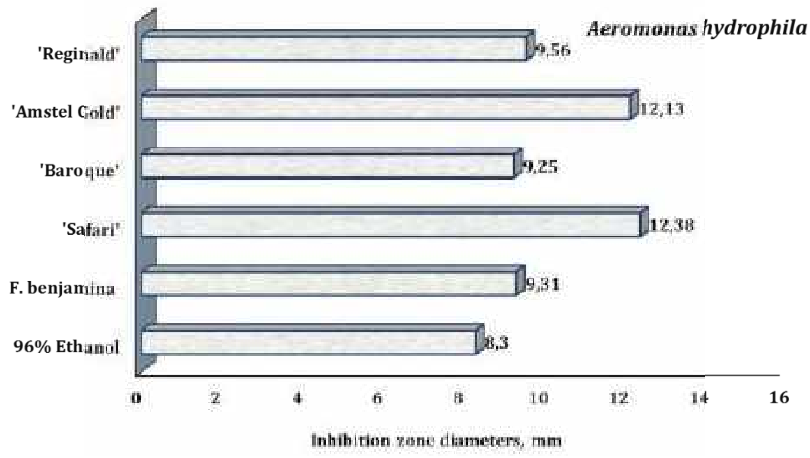


Fig. 3. The mean inhibition zone diameters induced by ethanolic extracts derived from leaves of *F. benjamina* and its cultivars ('Safari', 'Baroque', 'Amstel Gold', 'Reginald') against *Aeromonas hydrophila* strain (1000 µL inoculum) (M ± m, n = 8)

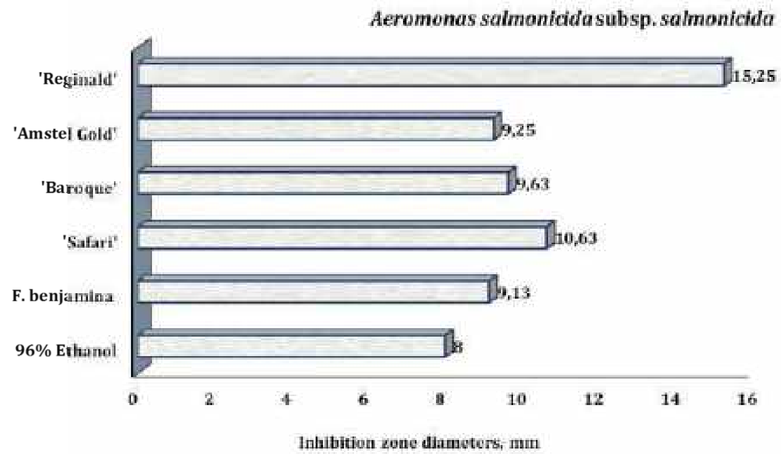


Fig. 4. The mean inhibition zone diameters induced by ethanolic extracts derived from leaves of *F. benjamina* and its cultivars ('Safari', 'Baroque', 'Amstel Gold', 'Reginald') against *Aeromonas salmonicida* subsp. *salmonicida* strain (1000 µL inoculum) (M ± m, n = 8)

F. benjamina and its cultivars possessed antibacterial properties against *Aeromonas salmonicida* subsp. *salmonicida* strain. The ethanolic extract obtained from leaves of *F. benjamina* ' Reginald ' exhibited the maximum antimicrobial activity against *Aeromonas salmonicida* subsp. *salmonicida* (the mean of inhibition zone diameters was 15.25±1.05 mm). *Aeromonas salmonicida* subsp. *salmonicida* strain was susceptible to the *F. benjamina* 'Safari' (10.63±0.38 mm) and 'Baroque' (9.63±0.46 mm). *Aeromonas salmonicida* subsp. *salmonicida* strain was the most resistant to *F. benjamina* (9.13±0.35 mm) and *F. benjamina* 'Amstel Gold' (9.25±0.59 mm) leaf extracts (Fig. 4).

In our previous studies, the therapeutic potential for the use of various plants of the *Ficus* genus in the control of bacterial diseases was evaluated against fish pathogens in *in vitro* study with promising results [12, 72-80]. Most ethanolic extracts obtained from *Ficus* spp. leaves in our previous studies proved effective against the bacterial strain of Gram-negative *A. hydrophila* tested, with 10-12 mm zones of inhibition were observed. *A. hydrophila* demonstrated the highest susceptibility to *F. pumila* leaf extract. Likewise, the highest antibacterial activity against *A. hydrophila* (200 μL of standardized inoculum) was displayed by *F. benghalensis, F. benjamina, F. deltoidea, F. hispida, F. lyrata* leaf extracts [78]. Additionally, among various species of the *Ficus* genus exhibiting moderate activity against *A. hydrophila* (400 μL of standardized inoculum), the highest antibacterial activity was displayed by *F. benghalensis, F. benjamina, F. deltoidea, F. hispida, F. lyrata* leaf extracts [80]. Antibacterial properties of plant extracts have been by far the most studied bioactivity with potential applications in aquaculture systems [58].

Moreover, in our previous study [12], we have evaluated the *in vitro* effect of extracts obtained from leaves of *F. benjamina* and its cultivars on the oxidative stress biomarkers (carbonyl content of the oxidatively modified proteins, total antioxidant capacity) in the muscle tissue of the rainbow trout. Our results have shown that extracts derived from leaves of *F. benjamina* 'Safari' and 'Reginald' cultivars decreased the lipid peroxidation biomarker and the ketonic derivatives of oxidatively modified proteins levels in the muscle tissue. However, this trend did not reach statistical significance. Furthermore, our results showed that extracts obtained from leaves of *F. benjamina* and its cultivars increased substantially the total antioxidant capacity in muscle tissue by 76.9 % (*F. benjamina*), 66.9 % (*F. benjamina* 'Safari'), 70.5 % (*F. benjamina* 'Baroque'), 49.4 % (*F. benjamina* 'Amstel Gold'), and 42.8 % (*F. benjamina* 'Reginald') ($p<0.05$). The results of this study provide a new perspective on the use of various *Ficus* species as a medicinal plant to improve the antioxidant response of rainbow trout [12].

It would be reasonable to suggest that these antimicrobial effects are determined by plant by-products, i.e. flavonoids. Indeed, the results of Imran and co-workers (2014) indicated that *F. benjamina* is a good source of components with high antibacterial activity. It was evidenced that the extracts and fractions of stem, root, and leaves exhibited considerable antimicrobial activity against four bacterial and two fungal strains. The range of antimicrobial activity expressed as diameters of inhibition zone for stem was 10.5 mm (n-hexane) – 22.83 mm (n-butanol). All the butanol fractions exhibited strong activity. The methanol extract (22.63 mm against *Pseudomonas aeruginosa*) and an n-butanolic fraction (22.83 against *Bacillus subtilis)* of the stem showed substantial activity. The n-hexane, chloroform, and ethyl acetate sprouted a moderate value of diameters of inhibition zone, with maximum value disclosed by ethyl acetate (16.88 mm). The stem extract and fractions revealed the following order of antimicrobial potential against *Bacillus cereus*: methanolic > n-butanolic > ethyl acetate > chloroform > n-hexane [38].

F. benjamina also is used in the treatment of malaria which may be attributed to ursolic acid and lupeol. The study of Singh and co-workers (2020) emphasized the investigation of antiplasmodial activity of triterpenoids isolated from *F. benjamina* leaves [66]. An unsaponified fraction of petroleum ether extract of plant leaves was subjected to silica gel column chromatography which led to the isolation of two known triterpenoids; namely ursolic acid and lupeol. These compounds were evaluated for antiplasmodial activity by schizont maturation inhibition assay using 3D7 *Plasmodium* strains. Both, ursolic acid and lupeol were found to exhibit significant antiplasmodial effects with an IC_{50} value of 18 μg/ml and 3.8 μg/ml, respectively [66].

Wanderley and co-workers (2018) have evaluated the anthelmintic potential of a protease purified from the latex of *F. benjamina* against *Haemonchus contortus*, a gastrointestinal nematode that is responsible for high mortality rates in ruminant herds. A cysteine protease (FbP) inhibited both the development and escheatment of *H. contortus* larvae, with 50% effective concentrations of 0.26 and 0.79 mg/mL, respectively. Thus, this cysteine protease from

F. benjamina latex with anthelmintic activity against *H. contortus* could be a promising alternative for the development of products for use in parasite control programs [87].

Imran and co-workers (2014) showed that the HPLC analysis for the presence of phenolic acids permitted the identification of 5 phenolic acids, three in the stem, four in the root, and one in leaves [38]. The total phenolic content (Folin-Ciocalteu) of the leaves of *F. benjamina* and *F. luschnathiana* were evaluated and screened by HPLC-DAD by da Cruz and co-workers (2012) [22]. *F. luschnathiana* crude extract (CE) presented phenolic content higher than that of *F. benjamina* (149.92 ± 3.65 versus 122.63 ± 2.79 mg of GAE). Kaempferol (1.63 ± 0.16 $mg \cdot g^{-1}$ dry weight of CE) and chlorogenic acid (17.77 ± 0.57 $mg \cdot g^{-1}$ of butanolic fraction) were identified and quantified in *F. benjamina*. Additionally, rutin (15.55 ± 1.92 $mg \cdot g^{-1}$) and quercetin (3.53 ± 0.12 $mg \cdot g^{-1}$) were quantified in ethyl acetate and butanolic fractions, respectively. Sirisha and co-workers (2010) reported the presence of ursolic, α-hydroxy ursolic, protocatechuic, and maslinic acids in *Ficus* species [68], while cinnamic and caffeic acids and quercetin have been reported in leaves, bark, and fruits of *F. benjamina* [3]. All the detected phenolic acids are known to have antioxidant properties [38]. So these phenolic acids may be responsible for the antibacterial activities of *F. benjamina* and its cultivars.

In addition to their antioxidant activity, flavonoids also show good antibacterial activity against both Gram-positive and Gram-negative isolates [6, 19, 23]. Flavonoids can be divided into six subfamilies based on differences in their molecular backbone structure: flavonols, flavones, flavanols, flavanones, anthocyanidins, and isoflavonoids [6]. They can inhibit DNA gyrase, cell membrane function, and bacterial energy metabolism [21, 61]. In recent years, flavonoids have been studied for their ability to interact with DNA helicases, proteins essential for DNA replication, repair, and recombination [45], and to prevent dNTPs binding. In particular, Chen and Huang (2011), studied 4 flavonoids (galangin, kaempferol, quercetin, and myricetin at 10 μM) revealed that they are capable of inhibiting the interaction of *Klebsiella pneumoniae* DnaB helicase with dNTPs [14]. Similarly, Huang and co-workers (2015) have demonstrated that some flavonoids (kaempferol and myricetin, at 35 μM) inhibit the PriA helicase activity of *Staphylococcus aureus* [6, 37].

In our study, the antibacterial activity of ethanolic extracts of *Ficus* leaves is presumably linked to the presence of flavonoids, steroids, saponins, and/or tannins. The antibacterial activity of tannins and saponins isolated from plant species are well documented [34, 81]. The presence of flavonoids and polyphenols is the basis for the analgesic and anti-inflammatory activities of various parts of *Ficus* including the fruit, latex, bark, roots, and leaves [30, 50]. Fever may be a result of infection or a result of one of the sequels of tissue damage, inflammation, graft rejection, or other disease states [85]. The antimicrobial activity of purified flavonoids may result in susceptibility differences against species with different origins and backgrounds [71]. This could explain the difference in sensitivity to *Ficus* extracts used in this work and a previously tested other species of *Ficus* [12, 72-80]. The highest antibacterial potential of *Ficus* could be explained by the amount of flavonoids present. However, the activity showed by ethanolic extracts of *Ficus* species may result from the interactions of different polyphenols. Most studies on the antimicrobial potential of polyphenols have been focused on the inhibitory activity of individual components. The inhibitory effect of phenolics could be explained by absorption to cell membranes, interactions with enzymes, substrate, and metal ion deprivation [63]. Direct interaction between the two compounds may result in changes of the structural conformation thus reducing the inhibitory activity. The antagonistic interaction observed with all combinations against *Listeria monocytogenes* may be the result of several mechanisms such as competition for target sites or inhibition of uptake by the cells [46]. On the other hand, synergism was observed between flavanone and phenolic acid against *Staphylococcus. aureus* and *S. enterica*, between flavanone and epicatechin against *S. enterica* and *S. aureus,* and between phenolic acid and epicatechin against *S. aureus* could be because of their combined reaction with the cell membrane as a possible primary target site [65].

Antibacterial flavonoids might be having multiple cellular targets, rather than one specific site of action [42]. One of their molecular actions is to form a complex with proteins through nonspecific forces such as hydrogen bonding and hydrophobic effects, as well as by covalent bond formation. Thus, their mode of antimicrobial action may be related to their ability to inactivate microbial adhesins, enzymes, cell envelope transport proteins, and so forth. Lipophilic flavonoids may also disrupt microbial membranes [20, 42]. Moreover, many flavonoids are shown to have antioxidative activity, free radical scavenging capacity, coronary heart disease prevention, hepatoprotective, anti-inflammatory, and anticancer activities, while some flavonoids exhibit potential antiviral activities [42].

Coumarin itself has a very low antibacterial activity, but compounds having long-chain hydrocarbon substitutions such as ammoresinol and ostruthin show activity against a wide spectrum of Gram-positive bacteria such as *Bacillus megaterium, Micrococcus luteus, Micrococcus lysodeikticus*, and *S. aureus* [84]. Another coumarin compound anthogenol from green fruits of *Aegle marmelos* shows activity against *Enterococcus*. Imperatorin, a furanocoumarin isolated from *Angelica dahurica* and *Angelica archangelica* (Umbelliferae), shows activity against *Shigella dysenteriae* [57]. Aegelinol and agasyllin isolated from the roots of *Ferulago campestris* (Apiaceae) showed significant antibacterial activity against clinically isolated Gram-positive and Gram-negative bacterial strains such as *Staphylococcus aureus, Salmonella typhi, Enterobacter cloacae*, and *Enterobacter aerogenes* [60]. Antibacterial activity was also found against *Helicobacter pylori* where a dose-dependent inhibition was shown between 5 and 25 mg/mL [84]. Several coumarins have been tested for antifungal activity, and the three most effective ones are psoralen, imperatorin, and ostruthin [84]. Osthole exhibited a wide spectrum of antifungal activity against important plant pathogens such as *Rhizoctonia solani, Phytophtora capsici, Botrytis cinerea, Sclerotinia sclerotiorum*, and *Fusarium graminearum* [88].

Qualitative and quantitative microscopic features may help establish a standardized quality control profile of herbal medicine.

CONCLUSIONS

The present study was carried out to provide evidence of the antibacterial potency of the extracts obtained from leaves of *F. benjamina* and its cultivars as a potential source of natural antimicrobial agents. *F. benjamina* disclosed substantial bioactivity, and this plant can be regarded as a potential source of antibacterial agents. In conclusion, the results of this study provide a new perspective for the use of various *Ficus* species as medicinal plants to improve the antibacterial responses in aquaculture. Further studies including the use of other medicinal plants as food additives in aquaculture, the assessment of their antioxidant effects on various tissues of salmonids are in progress. Additionally, our results suggest that a micromorphological leaf study should be incorporated in pharmacological investigations for application in the quality control of herbal medicines.

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REFERENCES

1. Adams A., Progress, challenges and opportunities in fish vaccine development, Fish Shellfish Immunol., vol. 90, pp 210-214, 2019.

2. Ahmed F., Urooj A., Traditional uses, medicinal properties, and phytopharmacology of *Ficus racemosa*: a review, Pharm. Biol., vol. 48/issue 6, pp 672-681, 2010.

3. Almahyl H.A., Rahmani M., Sukarp M.A., Ali A.A., Investigation on the chemical constituents of the leaves of *Ficus elastica* Roxb. and their antimicrobial activity, Pertanika J. Sci. Tech., vol. 11, pp 57-63, 2003.

4. Awad E., Awaad A., Role of medicinal plants on growth performance and immune status in fish, Fish Shellfish Immunol., vol. 67, pp 40-54, 2017.

5. Badgujar S.B., Patel V.V., Bandivdekar A.H., Mahajan R.T., Traditional uses, phytochemistry and pharmacology of *Ficus carica*: a review, Pharm. Biol., vol. 52/issue 11, pp 1487-1503, 2014.

6. Barbieri R., Coppo E., Marchese A., Daglia M., Sobarzo-Sánchez E., Nabavi S.F., Nabavi S.M., Phytochemicals for human disease: An update on plant-derived compounds antibacterial activity, Microbiol. Res., vol. 196, pp 44-68, 2017.

7. Bauer A.W., Kirby W.M., Sherris J.C., Turck M., Antibiotic susceptibility testing by a standardized single disk method, Am. J. Clin. Pathol., vol. 45/issue 4, pp 493-496, 1966.

8. Berg C.C., Corner E.J.H. 2005. *Moraceae* (*Ficus*). In *Noteboom H.P. (ed.) Flora Malesiana*, Ser. 1, vol. 17, Part 2. National Herbarium Nederland, Leiden, p. 1–730.

9. Berg C.C., Wiebes J.T., *African fig trees and fig wasps*. Koninklijke Nederlandse Akademie van Wetenschappen, Verhandelingen Afdeling Natuurkunde, 2[de] reeks, deel 89. North-Holland, Amsterdam, p. 298, 1992.

10. Biller-Takahashi J.D., Urbinati E.C., Fish Immunology. The modification and manipulation of the innate immune system: Brazilian studies, An. Acad. Bras. Cienc., vol. 86/issue 3, pp 1484-1506, 2014.

11. Bunawan H., Amin N.M., Bunawan S.N., Baharum S.N., Mohd Noor N., *Ficus deltoidea* Jack: A Review on Its Phytochemical and Pharmacological Importance, Evid. Based Complement. Alternat. Med., vol. 2014, pp 902734, 2014.

12. Buyun L., Tkachenko H., Maryniuk M., Kharchenko I., Osadowski Z., Honcharenko V., Prokopiv A., *In vitro* evaluation of oxidative stress biomarkers in the muscle tissue of rainbow trout (*Oncorhynchus mykiss* Walbaum) exposed to leaf extract of *Ficus benjamina* L. and its cultivars, Agrobiodiversity for Improving Nutrition, Health and Life Quality, issue 2, pp 159-169, 2018.

13. Cabello F.C., Godfrey H.P., Buschmann A.H., Dölz H.J., Aquaculture as yet another environmental gateway to the development and globalisation of antimicrobial resistance, Lancet Infect. Dis., vol. 16/issue 7, pp e127-e133, 2016.

14. Chen C.C., Huang C.Y., Inhibition of *Klebsiella pneumoniae* DnaB helicase by the flavonol galangin, Protein J., vol. 30/issue 1, pp 59-65, 2011.

15. Citterio B., Francesca B., *Aeromonas hydrophila* virulence, Virulence, vol. 6/issue 5, pp 417-418, 2015.

16. *Clinical and Laboratory Standards Institute*: VET03-/VET04-S2 Performance standards for antimicrobial susceptibility testing of bacteria isolated from aquatic animals. Second Informational Supplement, Vol. 34/No. 15, CLSI, Wayne, 2014.

17. *Clinical and Laboratory Standards Institute*: VET03-A: Methods for antimicrobial disk susceptibility testing of bacteria isolated from aquatic animals. Approved Guideline, Vol. 26/No. 23, CLSI, Wayne, 2006.

18. Cook J.M., Rasplus J.-Y. 2003. Mutualists with attitude: coevolving fig wasps and figs. Trends in Ecology & Evolution, 18(5): 241-248.

19. Coppo E., Marchese A., Antibacterial activity of polyphenols, Curr. Pharm. Biotechnol., vol. 15/issue4, pp 380-390, 2014.

20. Cowan M.M., Plant products as antimicrobial agents, Clin. Microbiol. Rev., vol. 12/issue 4, pp 564-582, 1999.

21. Cushnie T.P., Lamb A.J., Antimicrobial activity of flavonoids, Int. J. Antimicrob. Agents, vol. 26/issue 5, pp 343-356, 2005.

22. da Cruz R.C., Agertt V., Boligon A.A., Janovik V., Anraku de Campos M.M., Guillaume D., Athayde M.L., *In vitro* antimycobacterial activity and HPLC-DAD screening of phenolics from *Ficus benjamina* L. and *Ficus luschnathiana* (Miq.) Miq. leaves, Nat. Prod. Res., vol. 26/issue 23, pp 2251-2254, 2012.

23. Daglia M., Polyphenols as antimicrobial agents, Curr. Opin. Biotechnol., vol. 23/issue 2, pp 174-181, 2012.

24. Dallaire-Dufresne S., Tanaka K.H., Trudel M.V., Lafaille A., Charette S.J., Virulence, genomic features, and plasticity of *Aeromonas salmonicida* subsp. *salmonicida*, the causative agent of fish furunculosis, Veterinary Microbiology, vol. 169, pp 1-7, 2014.

25.Dangarembizi R., Erlwanger K.H., Moyo D., Chivandi E., Phytochemistry, pharmacology and ethnomedicinal uses of *Ficus thonningii* (Blume Moraceae): a review, Afr. J. Tradit. Complement. Altern. Med., vol. 10/issue 2, pp 203-212, 2012.

26. Dawood M.A.O., Abo-Al-Ela H.G., Hasan M.T., Modulation of transcriptomic profile in aquatic animals: Probiotics, prebiotics and synbiotics scenarios, Fish Shellfish Immunol., vol. 97, pp 268-282, 2020.

27. Dawood M.A.O., El Basuini M.F., Zaineldin A.I., Yilmaz S., Hasan M.T., Ahmadifar E., El Asely A.M., Abdel-Latif H.M.R., Alagawany M., Abu-Elala N.M., Van Doan H., Sewilam H., Antiparasitic and Antibacterial Functionality of Essential Oils: An Alternative Approach for Sustainable Aquaculture. Pathogens, vol. 10/issue 2, pp 185, 2021.

28. Embregts C.W., Forlenza M., Oral vaccination of fish: Lessons from humans and veterinary species, Dev. Comp. Immunol., vol. 64, pp 118-137, 2016.

29. Esteve C., Alcaide E., Blasco M.D., *Aeromonas hydrophila* subsp. *dhakensis* isolated from feces, water and fish in Mediterranean Spain, Microbes Environ., vol. 27/issue 4, pp 367-373, 2012.

30. Eteraf-Oskouei T., Allahyari S., Akbarzadeh-Atashkhosrow A., Delazar A., Pashaii M., Gan S.H., Najafi M., Methanolic Extract of *Ficus carica* Linn. Leaves Exerts Antiangiogenesis Effects Based on the Rat Air Pouch Model of Inflammation, Evid. Based Complement. Alternat. Med., vol. 2015, pp 760405, 2015.

31. Furmanek-Blaszk B., Phenotypic and molecular characteristics of an *Aeromonas hydrophila* strain isolated from the River Nile, Microbiol. Res., vol. 169/issue 7-8, pp 547-552, 2014.

32. Galina J., Yin G., Ardó L., Jeney Z., The use of immunostimulating herbs in fish. An overview of research, Fish Physiol. Biochem., vol. 35/issue 4, pp 669-676, 2009.

33.Garzón-Zúñiga M.A., Alvillo-Rivera A.J., Ramírez C.E., Buelna G., Díaz-Godínez G., Estrada-Arriaga E.B., Evaluation of *Ficus benjamina* wood chip-based fungal biofiltration for the treatment of Tequila vinasses, Water Sci. Technol., vol. 77/issue 5-6, pp 1449-1459, 2018.

34. Gayathri M., Kannabiran K., Antimicrobial activity of *Hemidesmus indicus*, *Ficus bengalensis* and *Pterocarpus marsupium* Roxb., Indian J. Pharm. Sci., vol. 71/issue 5, pp 578-581, 2009.

35. Harikrishnan R., Balasundaram C., *In vitro* and *in vivo* studies of the use of some medicinal herbals against the pathogen *Aeromonas hydrophila* in goldfish, J. Aquat. Anim. Health, vol. 20/issue 3, pp 165-176, 2008.

36. Holmes P., Niccolls L.M., Sartory D.P., The ecology of mesophilic *Aeromonas* in the aquatic environment. In: The genus *Aeromonas*. Austin B., Altwegg M., Gosling P.J., Joseph S. (ed.), West Sussex, England: John Wiley & Sons Ltd., pp 127-150, 1996.

37. Huang Y.H., Huang C.C., Chen C.C., Yang K.J., Huang C.Y., Inhibition of *Staphylococcus aureus* PriA Helicase by Flavonol Kaempferol. Protein J., vol. 34/issue 3, pp 169-172, 2015.

38.Imran M., Rasool N., Rizwan K., Zubair M., Riaz M., Zia-Ul-Haq M., Rana U.A., Nafady A., Jaafar H.Z., Chemical composition and Biological studies of *Ficus benjamina*, Chem. Cent. J., vol. 8/issue 1, pp 12, 2014.

39. Janda J.M., Abbott S.L., The genus *Aeromonas*: taxonomy, pathogenicity, and infection, Clin. Microbiol. Rev., vol. 23/issue 1, pp 35-73, 2010.

40. Jorgensen J.H., Ferraro M.J., Antimicrobial susceptibility testing: a review of general principles and contemporary practices, Clin. Infect. Dis., vol. 49/issue 11, pp 1749-1755, 2009.

41.Kozińska A., Dominant pathogenic species of mesophilic aeromonads isolated from diseased and healthy fish cultured in Poland, J. Fish Dis., vol. 30/issue 5, pp 293-301, 2007.

42. Kumar S., Pandey A.K., Chemistry and biological activities of flavonoids: an overview, ScientificWorldJournal, vol. 2013, pp 162750, 2013.

43.Lansky E.P., Paavilainen H.M., Figs: the genus *Ficus*. In: Hardman R. (ed.) Traditional herbal medicines for modern times, vol. 9. CRC Press, Boca Raton, pp 1-357, 2011.

44. Lim J., Hong S., Characterization of *Aeromonas salmonicida* and *A. sobria* isolated from cultured salmonid fish in Korea and development of a vaccine against furunculosis, J. Fish Dis., vol. 43/issue 5, pp 609-620, 2020.

45. Lohman T.M., Tomko E.J., Wu C.G., Non-hexameric DNA helicases and translocases: mechanisms and regulation, Nat. Rev. Mol. Cell Biol., vol. 9/issue 5, pp 391-401, 2008.

46. Mandalari G., Bisignano C., D'Arrigo M., Ginestra G., Arena A., Tomaino A., Wickham M.S., Antimicrobial potential of polyphenols extracted from almond skins, Lett. Appl. Microbiol., vol. 51/issue 1, pp 83-89, 2010.

47. Martos-Sitcha J.A., Mancera J.M., Prunet P., Magnoni L.J., Editorial: Welfare and Stressors in Fish: Challenges Facing Aquaculture, Front Physiol., vol. 11, pp 162, 2020.

48. McCoy A.J., Koizumi Y., Toma C., Higa N., Dixit V., Taniguchi S., Tschopp J., Suzuki T., Cytotoxins of the human pathogen *Aeromonas hydrophila* trigger, *via* the NLRP3 inflammasome, caspase-1 activation in macrophages, Eur. J. Immunol., vol. 40/issue 10, pp 2797-2803, 2010.

49. Mishra P.M., Sree A. Chemical investigation of *Finlaysonia obovata*: part I – a rare triterpene acid showing antibacterial activity against fish pathogens, Nat. Prod. Res., vol. 22/issue 9, pp 801-807, 2008.

50. Modi R.K., Kawadkar M., Sheikh S., Kastwar R., Tiwari G., A review on: comparative studies on ethanolic extract of root and stem bark of *Ficus carica* for analgesic and antiinflammatory activities. International Journal of Pharmacy and Life Sciences, vol. 3/issue 8, pp 1930-1934, 2012.

51. Mostafa A.A., Al-Askar A.A., Almaary K.S., Dawoud T.M., Sholkamy E.N., Bakri M.M., Antimicrobial activity of some plant extracts against bacterial strains causing food poisoning diseases, Saudi J. Biol. Sci., vol. 25/issue 2, pp 361-366, 2018.

52. Newaj-Fyzul A., Austin B., Probiotics, immunostimulants, plant products and oral vaccines, and their role as feed supplements in the control of bacterial fish diseases, J. Fish Dis., vol. 38/issue 11, pp 937-955, 2015.

53.Okoth D.A., Chenia H.Y., Koorbanally N.A., Antibacterial and antioxidant activities of flavonoids from *Lannea alata* (Engl.) Engl. (Anacardiaceae), Phytochem. Lett., vol. 6, pp 476-481, 2013.

54. Pękala-Safińska A., Tkachenko H., Kurhaluk N., Buyun L., Osadowski Z., Honcharenko V., Prokopiv A., Studies on The Inhibitory Properties of Leaf Ethanolic Extracts Obtained from *Ficus* (Moraceae) Species Against *Aeromonas* Spp. Strains, J. Vet. Res., vol. 65/issue 1, pp 59-66, 2021.

55. Perry W.B., Lindsay E., Payne C.J., Brodie C., Kazlauskaite R., The role of the gut microbiome in sustainable teleost aquaculture, Proc. Biol. Sci., vol. 287/issue 1926, pp 20200184, 2020.

56. Qin Y., Lin G., Chen W., Xu X., Yan Q., Flagellar motility is necessary for *Aeromonas hydrophila* adhesion, Microb. Pathog., vol. 98, pp 160-166, 2016.

57. Raja S.B., Murali M.R., Roopa K., Devaraj S.N., Imperatorin a furocoumarin inhibits periplasmic Cu-Zn SOD of *Shigella dysenteriae* there by modulates its resistance towards phagocytosis during host pathogen interaction, Biomed. Pharmacother., vol. 65/issue 8, pp 560-568, 2011.

58. Reverter M., Bontemps N., Lecchini D., Banaigs B., Sasal P., Use of plant extracts in fish aquaculture as an alternative to chemotherapy: Current status and future perspectives, Aquaculture, vol. 433, pp 50-61, 2014.

59.Riffle R.L., The Tropical Look. Portland, Oregon: Timber Press, Inc., 1998.

60. Rosselli S., Maggio A.M., Faraone N., Spadaro V., Morris-Natschke S.L., Bastow K.F., Lee K.H., Bruno M., The cytotoxic properties of natural coumarins isolated from roots of *Ferulago campestris* (Apiaceae) and of synthetic ester derivatives of aegelinol, Nat. Prod. Commun., vol. 4/issue 12, pp 1701-1706, 2009.

61. Safavi M., Shams-Ardakani M., Foroumadi A., Medicinal plants in the treatment of *Helicobacter pylori* infections, Pharm. Biol., vol. 53/issue 7, pp 939-960, 2015.

62. Santos L., Ramos F., Antimicrobial resistance in aquaculture: Current knowledge and alternatives to tackle the problem, Int. J. Antimicrob. Agents, vol. 52/issue 2, pp 135-143, 2018.

63. Scalbert A., Antimicrobial properties of tannins, Phytochemistry, vol. 12, pp 3875-3883, 1991.

64. Serrano R., da Silva G., Silva O., *Application of light and scanning electron microscopy in the identification of herbal medicines*. In: Microscopy: Science, Technology, Applications and Education (Microscopy Book Series, Number 4), A. Méndez-Vilas & J. Díaz, editors, Vol. 1. Badajoz, Formatex Research Center, pp 182-190, 2010.

65. Sikkema J., de Bont J.A., Poolman B., Interactions of cyclic hydrocarbons with biological membranes, J. Biol. Chem., vol. 269/issue 11, pp 8022-8028, 1994.

66. Singh A., Mukhtar H.M., Kaur H., Kaur L., Investigation of antiplasmodial efficacy of lupeol and ursolic acid isolated from *Ficus benjamina* leaves extract, Nat. Prod. Res., vol. 34/issue 17, pp 2514-2517, 2020.

67.Singh D., Singh B., Goel R.K., Traditional uses, phytochemistry and pharmacology of *Ficus religiosa*: a review, J. Ethnopharmacol., vol. 134/issue 3, pp 565-583, 2011.

68.Sirisha N., Sreenivasulu M., Sangeet A K., Chetty C.M., Antioxidant properties of *Ficus* species, a review, Int. J. Pharma Techn. Res., vol. 4, pp 2174-2182, 2010.

69. Sommerset I., Krossøy B., Biering E., Frost P., Vaccines for fish in aquaculture, Expert Rev. Vaccines, vol. 4/issue 1, pp 89-101, 2005.

70. Sutili F.J., Silva Lde L., Gressler L.T., Gressler L.T., Battisti E.K., Heinzmann B.M., de Vargas A.C., Baldisserotto B., Plant essential oils against *Aeromonas hydrophila*: *in vitro* activity and their use in experimentally infected fish, J. Appl. Microbiol., vol. 119/issue 1, pp 47-54, 2015.

71. Taguri T., Tanaka T., Kouno I., Antimicrobial activity of 10 different plant polyphenols against bacteria causing food-borne disease, Biol. Pharm. Bull., vol. 27/issue 12, pp 1965-1969, 2004.

72. Tkachenko H., Buyun L., Kasiyan O., Terech-Majewska E., Honcharenko V., Prokopiv A., Osadowski Z., Preliminary *in vitro* screening of antibacterial activity of leaf extract from *Ficus natalensis* subsp. *natalensis* Hochst. (Moraceae) against fish pathogens, Agrobiodiversity for Improving Nutrition, Health and Life Quality, issue 2, pp 170-183, 2018.

73. Tkachenko H., Buyun L., Osadowski Z., Honcharenko V., Prokopiv A., The antimicrobial efficacy of ethanolic extract obtained from *Ficus benghalensis* L. (Moraceae) leaves, Agrobiodiversity for improving nutrition, health, and life quality, issue 1, pp 438-445, 2017a.

74. Tkachenko H., Buyun L., Osadowski Z., Terech-Majewska E., Honcharenko V., Prokopiv A., Comparative study of the antimicrobial efficacy of the ethanolic leaf extract of *Ficus benghalensis* L. (Moraceae) against bacterial fish pathogens, Słupskie Prace Biologiczne, vol. 14, pp 209-228, 2017b.

75. Tkachenko H., Buyun L., Terech-Majewska E., Honcharenko V., Prokopiv A., Osadowski Z., Preliminary *in vitro* screening of the antibacterial activity of leaf extracts from various *Ficus* species (Moraceae) against *Yersinia ruckeri*, Fish. Aquat. Life, vol. 27, pp 15-26, 2019.

76. Tkachenko H., Buyun L., Terech-Majewska E., Osadowski Z., Antibacterial activity of ethanolic leaf extracts obtained from various *Ficus* species (Moraceae) against the fish pathogen, *Citrobacter freundii*, Baltic Coastal Zone – Journal of Ecology and Protection of the Coastline, vol. 20, pp 117-136, 2016a.

77. Tkachenko H., Buyun L., Terech-Majewska E., Osadowski Z., Antibacterial screening of ethanolic extracts obtained from leaves of various *Ficus* species (Moraceae) against *Citrobacter freundii*, Trudy VNIRO, vol. 167, pp 138-149, 2017c.

78. Tkachenko H., Buyun L., Terech-Majewska E., Osadowski Z., *In vitro* antimicrobial activity of ethanolic extracts obtained from *Ficus* spp. leaves against the fish pathogen *Aeromonas hydrophila*, Arch. Pol. Fish., vol. 24, pp 219-230, 2016b.

79. Tkachenko H., Buyun L., Terech-Majewska E., Osadowski Z., Sosnovskyi Y., Honcharenko V., Prokopiv A., *In vitro* antibacterial efficacy of various ethanolic extracts obtained from *Ficus* spp. leaves against the fish pathogen, *Pseudomonas fluorescens*. In: *Globalisation and regional environment protection. Technique, technology, ecology*. Eds T. Noch, W. Mikołajczewska, A. Wesołowska. Gdańsk, Gdańsk High School Publ., pp 265-286, 2016d.

80. Tkachenko H., Buyun L., Terech-Majewska E., Osadowski Z., Sosnovskyi Y., Honcharenko V., Prokopiv A., The antimicrobial activity of some ethanolic extracts obtained from *Ficus* spp. leaves against *Aeromonas hydrophila*, Trudy VNIRO, vol. 162, pp 172-183, 2016c.

81. Usman H., Abdulrahman F., Usman A., Qualitative phytochemical screening and *in vitro* antimicrobial effects of methanol stem bark extract of *Ficus thonningii* (Moraceae), Afr. J. Tradit. Complement. Altern. Med., vol. 6/issue 3, pp 289-295, 2009.

82. Valentim D.S.S., Duarte J.L., Oliveira A.E.M.F.M., Cruz R.A.S., Carvalho J.C.T., Conceição E.C., Fernandes C.P., Tavares-Dias M., Nanoemulsion from essential oil of *Pterodon emarginatus* (Fabaceae) shows *in vitro* efficacy against monogeneans of *Colossoma macropomum* (Pisces: Serrasalmidae), J. Fish Dis., vol. 41/issue 3, pp 443-449, 2018.

83. Vallejos-Vidal E., Reyes-López F., Teles M., MacKenzie S., The response of fish to immunostimulant diets, Fish Shellfish Immunol., vol. 56, pp 34-69, 2016.

84. Venugopala K.N., Rashmi V., Odhav B., Review on natural coumarin lead compounds for their pharmacological activity, Biomed. Res. Int., vol. 2013, pp 963248, 2013.

85. Vikas V.P., Bhangale S.C., Patil V.R., Evaluation of anti-pyretic potential of *Ficus carica* leaves, International Journal of Pharmaceutical Sciences Review and Research, vol. 2/issue 2, article 010, 2010.

86. Wahli T., Burr S.E., Pugovkin D., Mueller O., Frey J., *Aeromonas sobria*, a causative agent of disease in farmed perch, *Perca fluviatilis* L., J. Fish Dis., vol. 28/issue 3, pp 141-150, 2005.

87. Wanderley L.F., Soares A.M.D.S., Silva C.R.E., Figueiredo I.M., Ferreira A.T.D.S., Perales J., Mota H.R.O., Oliveira J.T.A., Costa Junior L.M., A cysteine protease from the latex of *Ficus benjamina* has *in vitro* anthelmintic activity against *Haemonchus contortus*, Rev. Bras. Parasitol. Vet., vol. 27/issue 4, pp 473-480, 2018.

88. Wang C.M., Zhou W., Li C.X., Chen H., Shi Z.Q., Fan Y.J., Efficacy of osthol, a potent coumarin compound, in controlling powdery mildew caused by *Sphaerotheca fuliginea*, J. Asian Nat. Prod. Res., vol. 11/issue 9, pp 783-791, 2009.

89. Yadav R.K., Nandy B.C., Maity S., Sarkar S., Saha S., Phytochemistry, pharmacology, toxicology, and clinical trial of *Ficus racemose*, Pharmacogn. Rev., vol. 9/issue 17, pp 73-80, 2015.

90. Yang C., Song G., Lim W., A review of the toxicity in fish exposed to antibiotics, Comp. Biochem. Physiol. C Toxicol. Pharmacol., vol. 237, pp 108840, 2020.

91. Yang Q.H., Zhou C., Lin Q., Lu Z., He L.B., Guo S.L., Draft Genome Sequence of *Aeromonas sobria* Strain 08005, Isolated from Sick *Rana catesbeiana*, Genome Announc., vol. 5/issue 2, pp e01352-16, 2017.

92. Zar J.H., Biostatistical Analysis. 4th ed., Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1999.

93. Zhang M., Kang J., Wu B., Qin Y., Huang L., Zhao L., Mao L., Wang S., Yan Q., Comparative transcriptome and phenotype analysis revealed the role and mechanism of ompR in the virulence of fish pathogenic *Aeromonas hydrophila*, Microbiologyopen, vol. 9/issue 7, pp e1041, 2020.

ASSESSMENT OF THE ENVIRONMENTAL CONDITION OF THE DNISTER RIVER BASIN UNDER CLIMATE CHANGE

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ABSTRACT

A comprehensive study of the problems of nature management is especially relevant for regions with a high degree of economic development of natural resources, long duration (several centuries) of their intensive exploitation. The Dniester basin belongs to such areas. Intense anthropogenic pressure on the environment has caused a violation of the natural balance in basin systems. Increasing and preserving the water level of the Dniester in the conditions of climate change and maintaining the quality of the water basin are important tasks today. The purpose of this study is to assess the environmental status of the Dniester River in the context of climate change. The value of hydrochemical parameters along the river, from the town of Sambir, Lviv region, to the Kuchurgany village, Odesa region. Exceedances in the content of nitrite ions, sulfate ions, chloride ions, ammonium ions, and the indicator of biochemical oxygen consumption at individual observation posts were established. The change of ammonium content and the value of biochemical oxygen consumption (BOD) according to the results of surface water monitoring from observation posts in the period from 2014 to 2020 in the Dniester river basin was studied. According to the average annual concentrations of pollutants in the control areas of water bodies of the region for the reporting year, the index of water pollution was calculated and the class of water quality in the areas of the village. Rozvadiv, Lviv region and Mayaki Odesa region A comparative characterization of water quality according to the calculated WPI of these water bodies in 2016, 2018, and 2020. The upper reaches of the Dniester River (the village of Rozvadiv, Lviv region) are characterized by significantly higher values of the water pollution index compared to the Dniester valley (the village of Mayaki, Odesa region). According to certain values of the water pollution index, it can be assumed that the water of the Dniester River has not yet reached the critical level of pollution and has the potential for self-purification.

Keywords: Dniester river, climate change, water pollution, hydrochemical indicators of water quality.

INTRODUCTION

The basis for achieving sustainable development of any territory is not only the availability of a certain amount of water resources but also their appropriate quality.

A comprehensive study of the problems of nature management is especially relevant for regions with a high degree of economic development of natural resources, long duration (several centuries) of their intensive exploitation. The Dniester basin belongs to such areas.

The Dniester is one of the largest rivers in Ukraine and the largest river in Moldova, which together with the Danube, Dnieper, and Southern Bug belongs to the Black Sea basin. The total length of the river is 1350 kilometers, the area of the basin is over 72 thousand km^2. The Dniester originates in the Carpathians at an altitude of 911 meters above sea level and flows into the Dniester estuary - a bay of the Black Sea, separated from it by a narrow spit. In the northwest the Dniester basin borders the Vistula basin, in the north - the Dnieper, in the southeast - the Southern Bug, in the west and southwest - the Danube with the Tisza, Prut, and small straits, in the south - with the basins of small rivers flowing into the Black Sea. (Fig. 1).

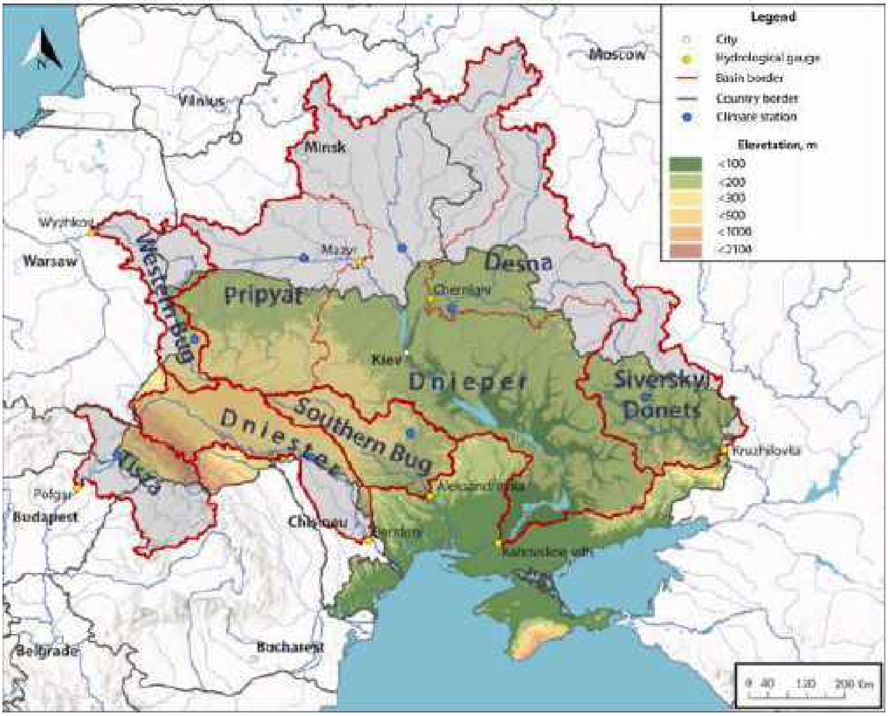


Fig. 1. The main river basins of Ukraine

The basis for achieving sustainable development of any territory is not only the availability of a certain amount of water resources but also their appropriate quality.
A comprehensive study of the problems of nature management is especially relevant for regions with a high degree of economic development of natural resources, long duration (several centuries) of their intensive exploitation. The Dniester basin belongs to such areas.

Continental and global hydrological models have been used in studies to assess the impact of climate change on water resources in the world [1−4] and in Europe in particular [5−7]. There are many regional studies based on hydrological models of watersheds [8−12]. They focus on specific watersheds or parts of the country and do not take into account changes in water resources at the national level. The assessment of the impact of climate change on the availability of water in the main Ukrainian river basins using global hydrological models was carried out to improve the understanding of expected changes and adaptation options at the national level.

As part of adapting to climate change at the basin level, the issues of greatest interest are related to the aquatic environment, changes in water regime and the state of water resources. For the Dniester basin, the likely change in the volume and seasonal distribution of runoff is one of the critical consequences of climate change. The expected changes in runoff are associated with a possible deterioration in the quality of the Dniester water. Some other problems of climate change in the Dniester basin are also largely determined by changes in the regime and state of water resources, although, except for water supply, there is a significant impact of other climatic factors [13].

Compared with 1981–2010, by the middle of the century we can expect an increase in the average annual, maximum and minimum air temperatures by 1.0–1.2 ° C (Table 1). At the same time, the increase in the minimum temperature will probably be greater than the maximum, as a result of which the monthly and annual temperature amplitudes will decrease. The greatest warming should be expected in the cold season, especially in the winter months.

By the middle of the XXI century in the Dniester basin it is possible to change the humidification regime. Although the total amount of precipitation per year will not change significantly (in the chosen scenario, their increase and decrease are equally likely), their significant redistribution between seasons and months is possible. Probably, the period without rains will be extended, but at the same time intensity and frequency of heavy precipitations (especially heavy rains) and their uneven distribution on the territory of the pool will increase. In general, the pool can be expected in milder and wetter winters, hotter and drier summers, warm and humid September and drier and warmer autumns.

Analysis of expected changes by the middle of the century compared to the period 1971–2000 shows the same trends, although the quantitative parameters of these changes differ slightly due to differences in climatic characteristics of the two base periods [14].

Table 1. Expected change in average air temperature and precipitation in the Dniester basin in 2021–2050 compared to 1981–2010.

	The pool as a whole	Upstream	Middle current	Downstream
The year as a whole	+1.1°C +9%	+1.0°C +1.0…1.8%	+1.1°C -0.9%	+1.2°C -2.8…-1.7%
Winter	+1.2°C +9%	+1.1°C +10%	+1.2°C +6…+7%	+1.2°C +8…+11%
Spring	+0.7°C -0.6%	+0.7°C +0…1.5%	+0.7°C -1%	+0.8°C -3%
Summer	+1.0°C -1.0%	+1.0°C -1.0%	+1.0°C -1…-0.2%	+1.2°C -7…-4%
Autumn	+1.3°C -5.0%	+1.3°C -2.8…-1.5%	+1.3°C -10…-7%	+1.4°C -11…-6%

Among all the problems of climate change in the Dniester basin, the problems with the highest probability and the most serious consequences include changes in water regime, degradation of soils and agricultural lands, as well as the effects of climate on human health. According to the general notions of risk analysis, such problems require urgent solutions.

In recent years, some special studies and reviews of possible consequences have been performed. The main ideas about the impact of climate change on natural resources and industries within the basin are given below [15–20].

The most vulnerable to climate change in the Dniester basin resources and industries are:
– water resources - increasing variability of the regime and volume of runoff, especially in the middle and lower parts of the Dniester. Deterioration of surface water quality due to rising air temperature, reduced runoff and anthropogenic pollution. Continued decline in groundwater levels. Further deterioration of small rivers;
– forest resources - a probable change in species composition and change in the height boundaries of tree species (Carpathians). Disappearance of some moisture-loving plant species in the middle and lower parts of the Dniester. Probable emergence of new diseases and pests that may pose a threat to the environment;
– ecosystems and wetlands − reduction of biodiversity, reduction of the range of indigenous species due to drying of habitats, deterioration of water quality and the introduction of alien species;
– ichthyofauna − reduction of species composition, extinction or decrease in the number of spawning grounds, increasing influence of alien species;
– agriculture - increasing the frequency and intensity of droughts and other extreme events. Lack of water for irrigation. Deterioration of fertility due to soil salinization, erosion and landslides. Decreased productivity and degradation of pastures. The emergence of new plant pests and animal diseases;
– water supply − lowering the level of groundwater, drying of wells and springs - the main suppliers of water in rural areas. Possible shortage of available water resources in the lower part of the basin and deterioration of water quality;
– infrastructure − possible deterioration due to the direct effects of climate change (eg, high summer temperatures, heavy rainfall, floods);
– population − risk to life associated with extreme weather and hydrological phenomena. General vulnerability due to low incomes, social stratification, deteriorating demographic situation, declining quality of education [21].

Problems with serious consequences, but less likely to occur (in the Dniester basin, these include deteriorating water quality and changes in groundwater levels) require, above all, constant monitoring and supervision to identify signs and causes of deterioration. Problems with a high probability of occurrence, but less serious consequences (damage to ecosystems, irrigation, erosion of riverbeds) must be addressed step by step in the framework of multi-purpose tasks that reduce the negative impact of various factors, including climate.

Increasing and maintaining the water level of the Dniester in the conditions of climate change and maintaining the quality of the water basin are now important tasks.

The purpose of this study is to assess the environmental status of the Dniester River under climate change.

METHODS AND EXPERIMENTAL PROCEDURES

The method of assessing water quality by a complex indicator - the index of water pollution (WPI) is recommended for use by units of the State Committee for Hydromet. This is one of the simplest methods of comprehensive water quality assessment. Estimation of the WPI indicator makes it possible to compare the water quality of different water bodies with each other, regardless of the presence of different pollutants, to identify the trend of changes in water quality over time.

WPI is calculated by formula (1)

$$WPI = \frac{1}{n}\sum_{i=1}^{n}\frac{C_i}{MPC_i} \ , \tag{1}$$

where C_i – is the average concentration of one of the n water quality indicators;; MPC_i – maximum permissible concentration of each of *n* water quality indicators

Usually WPI is calculated for six − seven hydrochemical indicators, mandatory are: the composition of dissolved oxygen, hydrogen index, biochemical oxygen consumption and others.

The initial data for the work were the materials of laboratory analysis of water of control areas, conducted by specialists of the Department of Ecology and Natural Resources of Lviv and Odesa regions.

Table 2. Criteria for assessing water quality by WPI

Water quality class	The value of WPI	Text description
I	<0.3	Very clean
II	>0.3 – 1	Clean
III	>1 – 2.5	Moderately polluted
IV	>2.5 – 4	Contaminated
V	>4 – 6	Dirty
VI	>6 – 10	Very dirty
VII	>10	Extremely dirty

To compare the quality of water in different areas, to determine their dynamics are used as criteria for water quality classes:
1. Class I includes waters that are least affected by anthropogenic load. The values of their hydrochemical and hydrobiological indicators are close to the natural values for this region.
2. Class II waters are characterized by certain changes compared to natural ones, but these changes do not disturb the ecological balance.
3. Class III includes waters that are under significant anthropogenic influence, the level of which is close to the limit of ecosystem resilience.
4. Waters of IV−VII classes are waters with the broken ecological parameters, their ecological condition is estimated as ecological regress.

THE RESEARCH RESULTS AND DISCUSSIONS

The extensive nature of nature management in the Dniester basin in recent years has led to significant depletion of its water resources and deterioration of the ecological status of surface waters. The extremely deformed structure of industry, which was dominated by fuel and energy, chemical, oil refining, forestry and woodworking basic industries, led to the hypertrophied development of large industrial hubs.

Today, the environmental tasks for the Dniester basin that need to be addressed are: protection of water resources and soils from degradation, elimination or minimization of the negative consequences of water use and industrial construction, monitoring the state of the environment in areas of possible impact of water management and reclamation facilities on natural complexes of adjacent territories [22].

Water pollution in the Dniester basin has disrupted natural self-treatment processes and made it difficult to obtain quality drinking water at water supply stations. Water treatment plants can no longer prevent a significant amount of inorganic and organic pollutants from entering drinking water.

The problem is exacerbated by the fact that existing drinking water treatment technologies involve the widespread use of chlorine, in particular to neutralize the decomposition products of phytoplankton, resulting in the formation of a large number of toxic carcinogenic organochlorine compounds in drinking water. Poor quality water is one of the reasons that in recent years in Ivano-Frankivsk region there has been an increase in the level of diseases such as gastric ulcer, gallstone disease, respiratory diseases, etc. [23].

The waters of the Dniester and its basin satisfy the needs for technical water supply of such large industrial units as the Ivano-Frankivsk concern Barva, CJSC Lukor, Burshtyn TPS, and others.

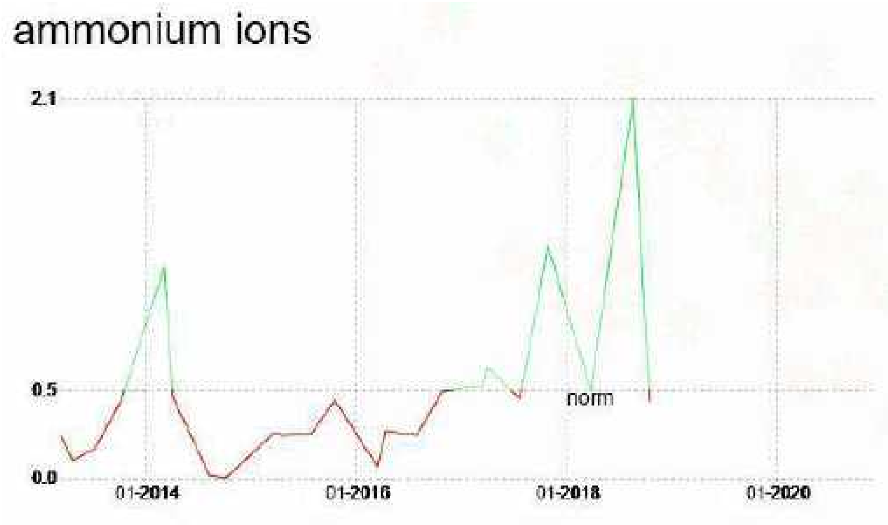
Areas with the most difficult environmental situation include: Halytskyi district, where the energy giant Burshtyn TPS operates, Kalush - with the chemical company CJSC "Lukor", Nadvirnyansky − with the refinery OJSC "Petrochemical Prykarpattia, no less difficult environmental situation in the area. OJSC “Barva” firm and concentrated industrial units of the regional center function.

But the most important in terms of water resources of the Dniester is that it is a "receiver" of return waters of a huge territory with a population of almost one and a half million and a developed industry and agriculture. The river directly or through tributaries of the first and second orders receives runoff from many large and several hundred less water-intensive water users. Thus, the Dniester is a direct recipient of wastewater from cities, villages, factories and factories, starting from the town of Stary Sambir in the Lviv region.

The main source of surface water pollution, which directly affects its color is wastewater (untreated or insufficiently treated), which is formed due to the use of water in the home, industrial enterprises, poultry and livestock complexes, etc. [24]. Partial pollution of water resources occurs by surface runoff: rain, storm water, as well as water formed during snowmelt. Sewage and surface runoff "pour" into the reservoir a significant amount of suspended solids and organic compounds, resulting in increased color, reduced transparency, increased biochemical oxygen demand (BOD), reduced dissolved oxygen, increased concentration of nitrogenous substances and chlorides [25].

The change of ammonium content and the value of biochemical oxygen consumption (BOD5) during the last six years was studied according to the results of surface water monitoring from observation posts in the period from 2014 to 2020 from such regions as:
- Rozvadiv, Lviv region Sampling point - sewage discharge of Drohobych industrial hub, left bank, 200 m above the bridge on the road Lviv − Stryi;
- Mohyliv-Podilskyi, Vinnytsia region. Place of sampling - customs crossing with the Republic of Moldova;
- Mayaki Odesa region Sampling place - GNS of the Lower Dniester Armed Forces.

As a result of the analysis of changes in the ammonium content from the water intake of the village of Rozvadiv, we can conclude that the exceedance occurred in the period from 2017 to 2019. The maximum value of ammonium concentration is 2.1 mg/dm^3 at a maximum concentration limit of 0.5 mg / dm. Regarding BOD, the excess in this period was insignificant and amounted to 3.3 mg / dm^3 in July 2015 and October 2017 at a maximum concentration limit of 3 mg/dm^3 (Fig. 2).



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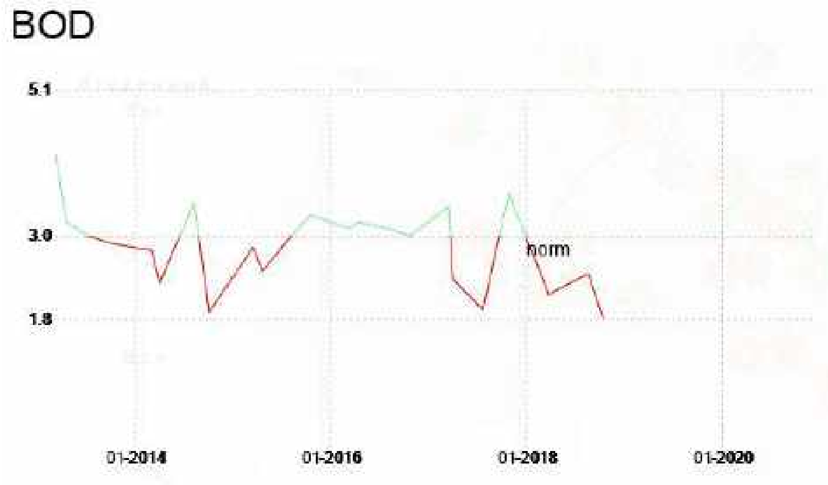
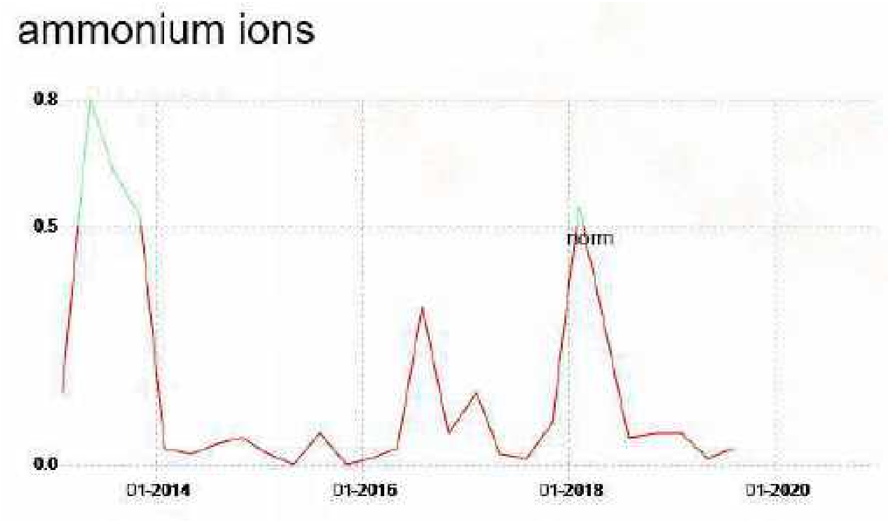


b)

Fig. 2. Change in the content of ammonium ions (*a*) and biochemical oxygen demand (BOD) (*b*) in the period from January 2014 to January 2020 from the water intake in Rozvadiv

According to the change in the ammonium content from the water intake in Mohyliv-Podilskyi, we see that during the time, a partial excess of 0.55 mg/dm^3 was observed in March 2018. Most of the period, the ammonium content was not more than 0.3 mg/dm^3. According to BOD, for six years there were no exceedances of the maximum concentration limit of 2.9 mg/dm^3 (Fig. 3).



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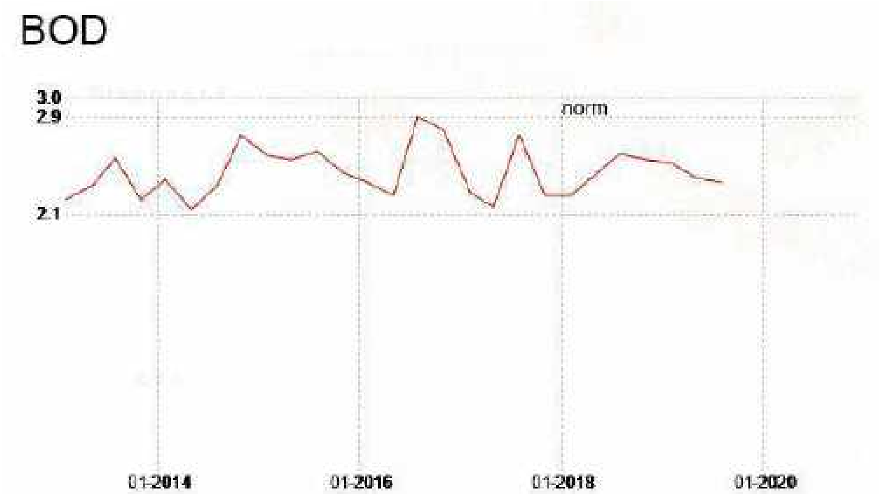
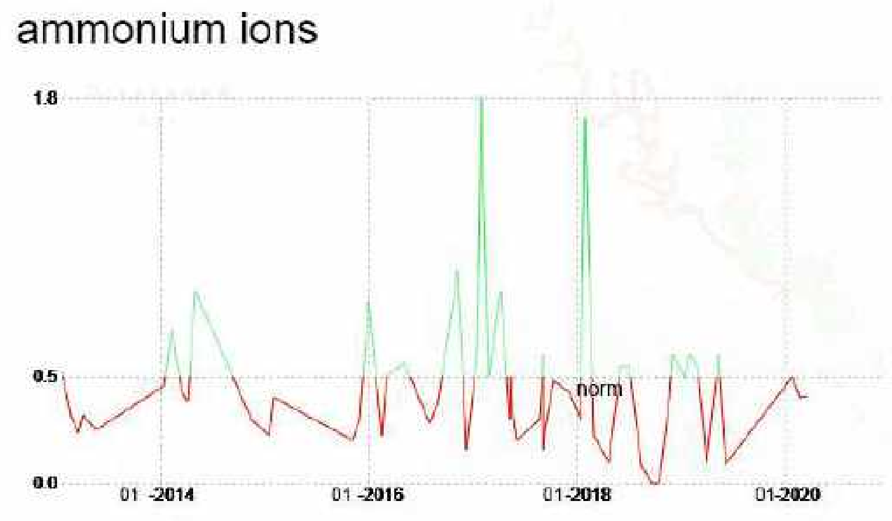


b)

Fig. 3. Change in the content of ammonium ions (*a*) and biochemical oxygen demand (BOD) (*b*) in the period from January 2014 to January 2020 from the water intake of Mogilev−Podolsky

The content of ammonium ions within Mayaki twice exceeded the norm − in January 2017 and in February 2018. At a maximum concentration limit of 0.5 mg/dm^3, the highest values were 1.8 mg / dm^3 and 1.7 mg/dm^3, respectively. The graph shows that the seasonal fluctuations of ammonium are characterized by a reduced content in summer and autumn and the highest values - in winter. Biochemical oxygen consumption, on the other hand, is most pronounced in winter (at a rate of 3 mg / dm^3 is up to 9 mg/dm^3), and least in summer (not more than 0.3 mg/dm^3) (Fig. 4).



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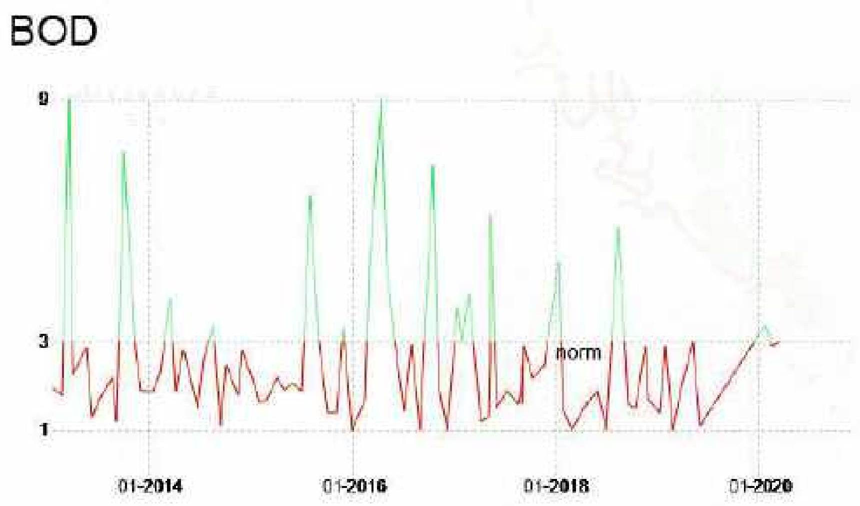

b)

Fig. 4. Change in the content of ammonium ions (*a*) and biochemical oxygen demand (BOD) (*b*) in the period from January 2014 to January 2020 from the water intake.

<u>*Assessment of water quality by hydrochemical parameters*</u>

The chemical composition of water determines the path taken by water in the process of its circulation. The amount of solutes in such water depends, on the one hand, on the composition of the substances with which it came into contact, on the other - on the conditions where all these interactions took place. The chemical composition of water can be affected by various factors: rocks, soils, climate, relief, living organisms, human activities, water regime, vegetation, natural and anthropogenic factors [26–28].

Water quality primarily depends on natural factors and the level of anthropogenic pressure on the river basin, in the lower part of which are water intakes. In this regard, assessing the quality of the main source of drinking water − the Dniester River, is perhaps the most important scientific and practical importance.

Taking into account the scale of the basin and the number of inflows given to it, it is possible to trace the dynamics of changes in the actual value of chemicals. For example, the latest observational data in cities and villages adjacent to the Dniester basin were taken. The indicators will reflect the change in the content of chemicals and the excess of the maximum permissible concentration along the river, starting from the town of Sambir, Lviv region, ending with the village Kuchurgany, Odesa region [29–30].

1. Full name of the observation point: Dniester River, 1278 km, Sambir, upper reaches of the Dniester River, under the bridge on the road to Drohobych; date of observation − October 9, 2018; The monitoring was carried out by the Western Bug and Xiang Water and Soil Monitoring Laboratory.

Table 3. Data from the observation post in Sambir

Indicator	Actual value	MPC	Exceeding the standard, times
Total nitrogen, mg / dm^3			None
Biochemical oxygen consumption for 5 days, mg O_2 / dm^3	1.18	3	None
Suspended (suspended) substances, mg / dm^3	3	15	None
Dissolved oxygen, mg O_2 / dm^3	8.03	>4	None
Sulfate ions, mg / dm^3	34.61	100	None
Chloride ions, mg / dm^3	24.32	300	None
Ammonium ions, mg / dm^3	0.22	0.5	None
Nitrate ions, mg / dm^3	3.45	40	None
Nitrite ions, mg / dm^3	0.36	0.08	**4.5**
Phosphate ions (polyphosphates), mg / dm^3	0		None

Data from the observation post in Sambir (Table 3) indicate an excess of nitrite ions in 4.5 times (according to data from 09.10.2018). Other indicators are within the norm.

2. Full name of the observation point: Tysmenytsia River, 21 km, Drohobych, the impact of sewage from the Drohobych industrial hub, under the bridge on the Lviv-Drohobych road; river basin district: Dniester; date of observation - October 9, 2018; The monitoring was carried out by the Western Bug and Xiang Water and Soil Monitoring Laboratory.

Table 4. Data from the observation post in Drohobych

Indicator	Actual value	MPC	Exceeding the standard, times
Total nitrogen, mg / dm^3			None
Biochemical oxygen consumption for 5 days, mg O_2 / dm^3	5.2	3	**1.73**
Suspended (suspended) substances, mg / dm^3	3	15	None
Dissolved oxygen, mg O_2 / dm^3	5.87	>4	None
Sulfate ions, mg / dm^3	89.82	100	None
Chloride ions, mg / dm^3	210.18	300	None
Ammonium ions, mg / dm^3	2.6	0.5	**5.2**
Nitrate ions, mg / dm^3	22.95	40	None
Nitrite ions, mg / dm^3	1.34	0.08	**16.75**
Phosphate ions (polyphosphates), mg / dm^3	0.87		None

Data from the observation post in Drohobych (Table 4) indicate that for two indicators - BOD and ammonium ions, there is an excess of 1.73 and 5.2 times, respectively. An extraordinary excess is observed in the indicator of nitrite ions - 16.75 times.

3. Full name of the observation point: Sivka River, 2 km, Sivka-Voynylivska village, mouth, impact of sewage of the Kalush industrial hub, 40 m below the bridge on the Halych-Zalukva-Voynyliv road; river basin district: Dniester; date of observation - 19.11.2018; monitoring was carried out by the laboratory of water and soil monitoring of the Dniester.

Table 5. Data from the observation post in village Sivka-Voynylivska

Indicator	Actual value	MPC	Exceeding the standard, times
Total nitrogen, mg / dm^3			None
Biochemical oxygen consumption for 5 days, mg O_2 / dm^3	3.8	3	**1.27**
Suspended (suspended) substances, mg / dm^3	69	15	**4.6**
Dissolved oxygen, mg O_2 / dm^3	12.5	>4	None
Sulfate ions, mg / dm^3	184	100	**1.84**
Chloride ions, mg / dm^3	210.18	300	None
Ammonium ions, mg / dm^3	0.58	0.5	**1.16**
Nitrate ions, mg / dm^3	6.2	40	None
Nitrite ions, mg / dm^3	0.041	0.08	None
Phosphate ions (polyphosphates), mg / dm^3	0.078		

Data from the observation post in Sivka−Voinylivska (Table 5) indicate a slight excess of the standard indicators of BOD, sulfate ions, chloride ions and ammonium ions. But the number of suspended (suspended) substances exceeds the norm by 4.6 times.

4. Full name of the observation point: Dniester, 826 km, Khotyn, left bank, 600 m above the bridge on the road Chernivtsi − Kamyanets-Podilsky; river basin district: Dniester; date of observation − 04.12.2019; monitoring was carried out by the basin laboratory of water and soil monitoring of basin management of water resources Prut and Siret.

Monitoring data from the observation post in Khotyn (Table 6) show that there are no exceedances of any indicator.

Table 6. Data from the observation post in Khotyn

Indicator	Actual value	MPC	Exceeding the standard, times
Total nitrogen, mg / dm^3	2.53		None
Biochemical oxygen consumption for 5 days, mg O_2 / dm^3	1.96	3	None
Suspended (suspended) substances, mg / dm^3	14	15	None
Dissolved oxygen, mg O_2 / dm^3	11.4	>4	None
Sulfate ions, mg / dm^3	83.2	100	None
Chloride ions, mg / dm^3	37.2	300	None
Ammonium ions, mg / dm^3	0.04	0.5	None
Nitrate ions, mg / dm^3	10.8	40	None
Nitrite ions, mg / dm^3	0.06	0.08	None
Phosphate ions (polyphosphates), mg / dm^3	0.21		

5. Full name of the observation point: Dniester, 631 km, Mohyliv-Podilskyi, Vinnytsia region, bridge, customs crossing with Moldova; river basin district: Dniester; date of observation - November 5, 2019; monitoring was carried out by the laboratory of water and soil monitoring of basin management of water resources Prut and Siret.

Monitoring data from the observation post in Mohyliv-Podilskyi (Table 7) show that, as in the case of the observation post in Khotyn, there are no significant exceedances of chemical indicators.

Table 7. Data from the observation post in Mohyliv-Podilskyi

Indicator	Actual value	MPC	Exceeding the standard, times
Total nitrogen, mg / dm^3			
Biochemical oxygen consumption for 5 days, mg O_2 / dm^3	2.3	3	None
Suspended (suspended) substances, mg / dm^3	12	15	None
Dissolved oxygen, mg O_2 / dm^3	8.23	>4	None
Sulfate ions, mg / dm^3	55.8	100	None
Chloride ions, mg / dm^3	22.1	300	None
Ammonium ions, mg / dm^3	0.08	0.5	None
Nitrate ions, mg / dm^3	5.42	40	None
Nitrite ions, mg / dm^3	0.05	0.08	None
Phosphate ions (polyphosphates), mg / dm^3	0.23		

6. Full name of the observation point: Biloch river, 15 km, village Shershentsi, border with Moldova; river basin district: Dniester; date of observation - 27.01.2020; monitoring was carried out by the laboratory of monitoring of waters and soils of basin management of water resources of the Black Sea and lower Danube rivers.

Data from the observation post village Shershentsi (Table 8) indicate a fairly significant excess of dissolved oxygen 13.33 times. The indicator of suspended solids exceeds the norms by 2.33 times.

Table 8. Data from the observation post village Shershentsi

Indicator	Actual value	MPC	Exceeding the standard, times
Total nitrogen, mg / dm^3			
Biochemical oxygen consumption for 5 days, mg O_2 / dm^3	1	3	None
Suspended (suspended) substances, mg / dm^3	35	15	**2.33**
Dissolved oxygen, mg O_2 / dm^3	0.3	>4	**13.33**
Sulfate ions, mg / dm^3	97.92	100	None
Chloride ions, mg / dm^3	26.59	300	None
Ammonium ions, mg / dm^3	0.1	0.5	None
Nitrate ions, mg / dm^3	24.8	40	None
Nitrite ions, mg / dm^3	0.028	0.08	None
Phosphate ions (polyphosphates), mg / dm^3	0.1		

7. Full name of the observation point: Kuchurgany, Kuchurgan Reservoir, on the east bank of the reservoir, 2 km below the bridge over the river; river basin district: Dniester; date of observation − 27.01.2020; monitoring was carried out by the laboratory of monitoring of waters and soils of basin management of water resources of the rivers of the Black Sea coast and the lower Danube.

Data from the observation post village Kuchurgany (Table 9) indicate a significant excess of sulfate ions, chloride ions and ammonium ions. The excess is 8.76, 1.95 and 4.2 times, respectively.

Table 9. Data from the observation post village Kuchurgany

Indicator	Actual value	MPC	Exceeding the standard, times
Total nitrogen, mg / dm^3			
Biochemical oxygen consumption for 5 days, mg O_2 / dm^3	2.2	3	None
Suspended (suspended) substances, mg / dm^3	12.6	15	None
Dissolved oxygen, mg O_2 / dm^3	11.5	>4	None
Sulfate ions, mg / dm^3	876.48	100	**8.76**
Chloride ions, mg / dm^3	584.93	300	**1.95**
Ammonium ions, mg / dm^3	2.1	0.5	**4.2**
Nitrate ions, mg / dm^3	0.8	40	None
Nitrite ions, mg / dm^3	0.019	0.08	None
Phosphate ions (polyphosphates), mg / dm^3	0.05		None

Determination of water quality class based on the results of surface water monitoring from observation posts in the village of Rozvadiv, Lviv region and Mayaki in Odesa region.

According to the average annual concentrations of pollutants in the control areas of water bodies of the region for the reporting year, the WPI was calculated and the water quality class in the areas of the village was established. Rozvadiv, Lviv region and Mayaki Odesa region (Tables 10, 11). A comparative characterization of water quality according to the calculated WPI of these water bodies in 2016, 2018 and 2020.

Table 10. WPI and water quality class (according to the observation post in the village of Rozvadiv, Lviv region)

Year	Value WPI	Water quality class	Water characteristics
2016	1.9	III	Moderately polluted
2018	3.9	IV	Contaminated
2020	1.3	III	Moderately polluted

Control target, located in the village. Rozvadiv, Lviv region, is characterized in 2018 by an increase in the water pollution index compared to 2016, the water quality class changes from III − moderately polluted to IV - polluted water. In 2020, there is a decrease in the index of water pollution compared to 2018, the water quality class changes from IV - polluted water to III - moderately polluted.

Table 11. WPI and water quality class (according to the observation post in village Mayaki Odesa region)

Year	Value WPI	Water quality class	Water characteristics
2016	1.1	III	Moderately polluted
2018	0.9	II	Clean
2020	1.2	III	Moderately polluted

Control target, located in the village Mayaki Odesa region in 2018 is characterized by a decrease in the index of water pollution compared to 2016 (water quality class changes from III − moderately polluted to II - clean water) and a slight increase in the index of water pollution in 2020 compared to 2018 (water quality class varies from II - clean water to III - moderately polluted).

According to the determined values of the water pollution index, it can be assumed that the water of the Dniester River has not yet reached the critical limit of pollution and has the potential for self-purification. Water users only need to maintain and improve this potential.

This requires preventing the possibility of leakage from production areas and forming a biological barrier to protect water bodies, to retain and neutralize excess nutrients and toxic compounds. The upper reaches of the Dniester River (the village of Rozvadiv, Lviv region) are characterized by significantly higher values of the water pollution index compared to the Dniester valley (the village of Mayaki, Odesa region).

CONCLUSIONS

Thus, the analysis of the environmental status of the Dniester basin and its trends leads to the conclusion that mainly extensive water consumption in almost all sectors of the economy, growth of total unproductive water consumption, significant reduction of water resources due to pollution and depletion of water sources necessitate large-scale environmental economic measures for the use of water.

The value of hydrochemical parameters along the river, starting from the town of Sambir, Lviv region, ending with the village of Kuchurgany, Odesa region. The content of nitrite ions was exceeded 4.5 times at the observation post in Sambir and 16.75 times at the observation post in Drohobych. Data from the observation post Sivka-Voynilivska indicate a slight excess of the standard indicators of BOD, sulfate ions, chloride ions and ammonium ions. But the number of suspended (suspended) substances exceeds the norm by 4.6 times. Monitoring data from the observation post in Mohyliv-Podilskyi show that, as in the case of the observation post in Khotyn, there are no significant exceedances of chemicals. Data from the observation post in Shershentsi indicate a fairly significant excess of dissolved oxygen 13.33 times. The indicator of suspended solids exceeds the norms by 2.33 times. Data from the observation post Kuchurgany indicate a significant excess of sulfate ions, chloride ions and ammonium ions. The excess is 8.76, 1.95 and 4.2 times, respectively.

According to the average annual concentrations of pollutants in the control areas of water bodies of the region for the reporting year, the index of water pollution was calculated and the class of water quality in the areas of the village. Rozvadiv, Lviv region and Odesa region. A comparative characterization of water quality according to the calculated WPI of these water bodies in 2016, 2018 and 2020. The upper reaches of the Dniester River (the village of Rozvadiv, Lviv region) are characterized by significantly higher values of the water pollution index compared to the Dniester valley (the village of Mayaki, Odesa region).

According to the determined values of the water pollution index, it can be assumed that the water of the Dniester River has not yet reached the critical limit of pollution and has the potential for self-purification.

Although the quality of water in the Dniester has improved over the last two or three years, this should not be reassuring, as the expected economic recovery could change dramatically for the worse and with the modern independence of industrial enterprises could pose a threat of new environmental catastrophes.

REFERENCES

1. Xu H., Liu L., Wang Y., Wang S., Hao Y., Ma J., and Jiang T. Assessment of climate change impact and difference on the river runoff in four basins in China under 1.5 and 2.0 °C global warming, Hydrol. Earth Syst. Sci., 23, 4219–4231, https://doi.org/10.5194/hess-23-4219-2019, 2019.

2. Chen J., Xia J., Zhao, C., Zhang S., Fu G., and Ning L.: The mechanism and scenarios of how mean annual runoff varies with climate change in Asian monsoon areas, J. Hydrol., 517, 595–606, https://doi.org/10.1016/j.jhydrol.2014.05.075, 2014.

3. Müller Schmied H., Adam L., Eisner S., Fink G., Flörke M., Kim H., Oki T., Portmann F. T., Reinecke R., Riedel C., Song Q., Zhang J., and Döll P. Variations of global and continental

water balance components as impacted by climate forcing uncertainty and human water use, Hydrol. Earth Syst. Sci., 20, 2877–2898, https://doi.org/10.5194/hess-20-2877-2016, 2016.

4. Todd M. C., Taylor R. G., Osborn T. J., Kingston D. G., Arnell N. W., and Gosling S. N. Uncertainty in climate change impacts on basin-scale freshwater resources – preface to the special issue: the QUEST-GSI methodology and synthesis of results, Hydrol. Earth Syst. Sci., 15, 1035–1046, https://doi.org/10.5194/hess-15-1035-2011, 2011.

5. Donnelly C., Greuell W., Andersson J., Gerten D., Pisacane G., Roudier P., Ludwig F. Impacts of climate change on European hydrology at 1.5, 2 and 3 degrees mean global warming above preindustrial level. Clim. Change. 2017.h, ttps://doi.org/10.1007/s10584-017-1971-7.

6. Mentaschi L., Alfieri L., Dottori F., Cammalleri C., Bisselink B., Roo A.D., Feyen L. Independence of Future Changes of River Runoff in Europe From the Pathway to Global Warming[v1] | Preprints. 2019. https://doi.org/10.20944/preprints201912.0092.v1.

7. Van Vliet M.T.H., Donnelly C., Stromback L., Capell R., Ludwig F. European scale climate information services for water use sectors. J. Hydrol., 2015, https://doi.org/10.1016/j.jhydrol.2015.06.060.

8. Didovets I., Lobanova A., Bronstert A., Snizhko S., Maule C.F.C.F., Krysanova V. Assessment of climate change impacts on water resources in three representative ukrainian catchments using eco-hydrological modelling. Water (Switzerland), 2017, 9, 204. https://doi.org/10.3390/w9030204.

9. Fischer S., Pluntke T., Pavlik D., Bernhofer C. Hydrologic effects of climate change in a sub-basin of the Western Bug River, Western Ukraine. Environ. Earth Sci., 2014, 72, 4727–4744. https://doi.org/10.1007/s12665-014-3256-z.

10. Didovets I., Krysanova V., Bürger G., Snizhko S., Balabukh V., Bronstert A. Climate change impact on regional floods in the Carpathian region. J. Hydrol. Reg. Stud., 2019, 22. https://doi.org/10.1016/j.ejrh.2019.01.002.

11. Piniewski M., Szczes'niak M., Huang S., Kundzewicz Z.W. Projections of runoff in the Vistula and the Odra river basins with the help of the SWAT model. Hydrol. Res., 2018, https://doi.org/10.2166/nh.2017.280.

12. Hesse C., Stefanova A., Krysanova V. Comparison of water flows in four European lagoon catchments under a set of future climate scenarios, Water, 2015, 7, 716–746. https://doi.org/10.3390/w7020716.

13. Alekseevsky NI, Melnik OV The structure and features of the development of the relief of gravel-pebble and boulder channels, Geomorphology, 1991, No. 3, pp. 59-65 (In Russian).

14. Zakrevskiy D. V. About the development of anthropogenic storage of chemical components in river runoff, Gidrotekhnika and Melioratsia, 1995, Vip. 4, pp. 85-90. (In Ukr.)

15. UNECE and OSCE 2005. Transboundary Diagnostic Study of the River Basin Dniester. United Nations Economic Commission for Europe, Organization for Security and Cooperation in Europe, Kiev-Vienna-Geneva.

16. ENVSEC, UNECE, OBS. Strategic direct adaptation to change the climate in the Dnistra basin, 72 p., 2015.

17. Mitryasova Olena, Smirnov Victor, Bezsonov Eugene. Ecological integrated water resources

management in European countries, textbook. manual, ed. prof. Elena Mitryasova, Nikolaev, ChNU of them. Petra Mogili, 288 pp., 2020.

18. Water Security, monograph, issue 2, Mykolaiv, PMBSNU – Bristol, UWE, Editor: prof. Olena Mitryasova and prof. Chad Staddon, 444 p., 2021.

19. Mitryasova O. P., Pohrebennyk V. D., Petrov O. S., Bezsonov Ye. M., Smyrnov V. M. Environmental water security policy in the EU, Ukraine and other developing countries, Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 2021, 2, 125-130.

20. Mitryasova O., Pohrebennyk V., Salamon I., Oleksiuk A., Mats A. Temporal Patterns of Quality Surface Water Changes, Journal of Ecological Engineering, 2021, Vol. 22, nr 4, 283–295.

21. Shvets OI Modeling the impact of economic activity on the environment of the Berezhnytsia river basin (right bank of the Dniester): dissertation for the degree of Candidate of Geographical Sciences, 11.00.11, Lviv. nat. Univ. Ivan Franko, 200 pp., 2013.

22. Cream R.O. Geomorphology of the Watershed-Verkhovyna Carpathians. Lviv, LNU Publishing Center named after I. Franko, 149 pp., 2001.

23. Report on research work. Conducting a spatial analysis of changes in the water regime of basins of surface water bodies on the territory of Ukraine due to climate change. Kyiv, 104 pp., 2013.

24. Topolny F., Gelevera O., Mospan S. and others. Ecological problems of agriculture in the Carpathians. Works of NTSh: ecological collection. Volume XI: Environmental problems of the Carpathian region. Lviv, 2003. S. 351-360.

25. Obodovsky O. Hydrological and ecological assessment of channel processes (on the example of rivers of Ukraine) Kyiv, Nika-Center, 274 p., 2001.

26. Prikhodko MM Ecological safety of natural and anthropogenically modified geosystems: monograph, Kyiv, Center for Environmental Education and Information, Ukraine, 201 p., 2013.

26. Dniester river basin. Ecological Atlas, Chisinau, 59 p., 2012.

28. Kilimnik O. M. ta in. Hydroecosystem of the girlovo region, r. Dnister, Odessa: Poligraph, 319 p., 2013.

29. Pohrebennyk Volodymyr. Assessment of the quality of the water of the Dnister River, Applied Science and Technology, Ivano-Frankivsk, Ukraine, 5-7 April 2021, Academy of Technical Sciences of Ukraine, Ivano-20 Frankivsk: M. Vidiavets, 2021, 18-20.

30. Melnyk M.O., Pohrebennyk V.D. Directions of adaptation to change the climate in the Dniester basin, Eco Forum - 2020: collection of abstracts of the IV Specialized International Zaporizhzhya Ecological Forum, 15-17 June 2020, Zaporizhzhia, 2020, p. 86-88.

ECOLOGICAL AND ECONOMIC ASPECTS OF WASTEWATER TREATMENT OF GALVANIC PRODUCTION

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ABSTRACT

Ukraine has an urgent need for copper, which is used in various industries. Electroplating and PCB manufacturing are sources of environmental hazard. The purpose of the work is environmental and economic justification for the removal of copper from wastewater and its further use for metallization and for remelting as secondary raw materials.
The main factors of the negative impact of waste of boards and galvanics` production on the environment are revealed. In order to avoid the accumulation of sludge on the territory of the enterprises it is proposed to use the regeneration technology of waste digestion solutions, in which the recovered metal is used as secondary raw material for copper production, and the recovered solution is reused for etching of printed circuit boards.
The scientific novelty of the work lies in the fact that the proposed approach and the mechanism of obtaining additional raw materials from the sewage of PCB production has been discovered.
The practical significance is that the obtained results can be applied in the production of printed circuit boards to reduce the environmental impact of production wastes, as well as to obtain cheap raw materials from industrial wastewater. It is also important to reduce the environmental impact of production waste. The total sludge hazard index for the existing state of sludge storage in the territory of enterprises (0.045) and after the implementation of wastewater recovery (100) is determined. The economic indicators of the equipment created on the basis of this research are estimated. Implementation of new wastewater treatment technology with only one plant can bring more than 2.8 million UAH of economic effect.

Key words: copper, galvanic production, sewages, printing boards, regeneration

INTRODUCTION

There is an urgent need for copper in Ukraine, which is used in various industries. Meanwhile, there is insufficient exploration of copper ores in Ukraine. Prospective and predictive resources of copper ores are estimated: in the Volyn region, in Donbass and in the Dnieper-Donetsk basin within the Ukrainian Shield in the Mid-Dnieper and Volyn regions. Total resources of ores of

Volyn region with an average copper content of 1.0% are estimated at 28 million tons of metal. All the above points to the lack of copper ore deposits in Ukraine. The annual needs of Ukraine for this metal are about 120-140 thousand tons, twenty percent of which provide their own copper scrap, and the rest in the form of rough copper has to be imported from neighboring Russia and Poland [1].

Galvanic production is one of the most dangerous sources of environmental pollution, mainly surface and groundwater reservoirs, due to the formation of large volumes of wastewater, as well as a large amount of solid waste, especially from the reagent method of wastewater disposal. The compounds of metals transported by the sewage of galvanic production have quite a detrimental effect on the soil-plant-animal-human-ecosystem [2-8].

The use of galvanic processes in modern production creates a risk associated with emergencies, which can be considered as a risk of waste storage and the direct carrying out of technological processes. It is safe to identify technical, technological, organizational and other causes of adverse situations. Waste storage and technological processes are hazardous to the environment in which humans, wildlife and fauna are located. Therefore, this risk can be called environmental.

Modern enterprises, producing up to about $4 \cdot 10^3$ m^2 of boards, have accumulated around 1500-3000 tons of waste per year in their territory in the form of salts stored in tanks, plastic bags and subject to atmospheric precipitation. In the course of atmospheric precipitation, salts are washed away and transferred to soils, surface waters, polluting the environment.

The production of printed circuit boards in Ukraine is represented by the following enterprises: JSC NPO “ETAL”, Kirovograd, which produces about 4-5 thousand m^2 of boards, with capacity for production of up to 50000 m^2 of boards, SE “Galvanotechnika”, PJSC “Kyiv Radar Plant”, PJSC Novator (Khmelnitsky) with output within 0.9 thousand m^2, PJSC Concern-Electron - 0.8 thousand m^2. This means that only one enterprise can dump wastewater or accumulate sludge up to 5-6 tons of copper per year, which clearly does not contribute to improving the environmental situation around the enterprises engaged in the production of boards. Until 1992, nearly 20 tonnes of copper were dumped annually in Kyiv. The Electronmash plant annually etches ≈15000 m^2 of boards (which leads to the allocation of 7500 kg of copper) [8].

To avoid the accumulation of sludge on the territory of enterprises it is proposed to use the technology of regeneration of waste digestion solutions, in which the isolated metal is used as a secondary raw material for copper production, and the recovered solvent is reused for etching of printed circuit boards [9-12].

To open the ore in an open manner, it is necessary to carry out the excavation work with the movement of a large number of soils and other rocks. Thus, if 20-25 years ago the marginal coefficient of overburden was taken in the size of 2-4 m^3 / t, now during the development of deposits with rock formations it reaches values of 5-10 m^3 / t, and during the development of sloping fields with soft cover rocks - 20-25 m^3 / t. Now open development of mineral deposits can be performed at depths up to 250 m. These are the large masses that need to be moved, encumbered, which indicates significant work and material costs [13-15].

Environmental protection activities in the field of subsoil use are regulated, among others, by the Mining Law of Ukraine, which defines the following basic requirements for mining operations: ensuring the safe conduct of mining operations and rational extraction, use of minerals and protection of subsoil [5].

The complexity and severity of the problem is due to the fact that Ukrainian consumers, who are in need of copper, are forced to buy a large part of it outside Ukraine and because of the lack of foreign currency to reduce the production of goods. At the same time, the existing capacities for the production of rolled copper and its alloys in Ukraine are not loaded because there is no copper raw material, and a large part of copper-containing scrap and waste is exported for various reasons, even though the export of rolled copper and its alloys is much more efficient than export of copper scrap. For each tonne of exported rental, in addition to saving jobs, you can receive up to $ 1.000 in foreign exchange earnings, that is 30-40$ million per year [1, 8, 16]. But analysis of the patent and technical literature has shown that in the absence of raw materials for the smelting of non-ferrous metals, the issue of copper extraction from wastewater is given insufficient attention.

Formulating the goals of the article (setting the task). Non-ferrous metal production technology has its own peculiarities. This is due to the low concentration of non-ferrous metals in the ore compared to iron (only a few percent in non-ferrous ores) and the presence of several metals in the ore. In particular, ore with a base metal content of on average 2-3% is used to produce copper. Transporting them is not great. Therefore, copper smelting is carried out near the mining sites. Initially, copper ores are enriched and receive a copper concentrate with a metal content of 35%. Then the melting and purging in the converter to produce rough copper takes place, the last step is the removal of impurities (refining). With the use of special technology of copper ore can be obtained and some other non-ferrous metals [1, 8]. The specific energy consumption during the smelting reaches 230 - 350 kWh per 1 ton of copper. This requires a considerable amount of energy input. And the production of scrap metal is cheaper by 25 times, the cost of transportation of raw materials is reduced by 5-6 times. This reduces the period of metal production and reduces electricity consumption; there is a nature conservation effect [1, 8].

In Ukraine, the non-ferrous base of non-ferrous metallurgy is insufficient, and many enterprises operate on imported raw materials or process non-ferrous metal scrap. The location of these businesses also take into account consumer, transport and environmental factors. Non-ferrous metallurgy is a pollutant of the environment and the main source of heavy metals [8, 14-15, 17].

At the same time, the source of replenishment of non-ferrous metal scrap may be partly the production of boards and electroplating, where copper is used as a conductive material and is etched in the process of surface preparation for use.

The purpose of the work is environmental and economic justification for the removal of copper from wastewater and further use for industrial purposes.

METHODS AND EXPERIMENTAL PROCEDURES

Surveys have shown that companies engaged in the manufacture of printed circuit boards dumped a whole range of metals - copper, iron, nickel, chromium, etc. In particular, during the annual one-line operation of the etching line of printed circuit boards with a productivity of 14 m^2 / h, nearly 28000 m^2 of blanks will be produced, and the amount of extracted (etched) metal (copper) will be about 14 tons, which at prices of UAH 85 / kg will be 14000 kg · 85 UAH / kg = 1190000 UAH. This metal can be reused. The amount of metal that will be etched during the resumption of industrial production of boards can be (at one-shift work and the number of lines in the work of 350 pieces) 14000 kg · 350 = 4900000 kg = 4900 tons.

The most common method of extraction of metal ores (including copper) is open-cast mining, through which more than 2/3 of all minerals are extracted from the bowels. This is a relatively inexpensive way of developing powerful and high-performance equipment. However, when conducting open works for many decades, huge tracts of farmland and forestland are removed from economic circulation. To access the deposit from the surface it is necessary to remove, move and put in the waste heaps of rock, the volume of which is several times bigger than the volume of extracted minerals [1, 8].

The second most important method of field development is underground, which accounts for about 20% of iron production, up to 45% of copper production, up to 70% of zinc, up to 75% of tin and lead, 100% of tungsten. Ore mining costs during underground mining are noticeably higher than open pit. However, it is conducted in fields that are not economically feasible or technically impossible to develop in an open manner. Due to the primary depletion of readily available metal ore reserves, the depth of development is gradually increasing, increasing the cost of underground mining. The trend of increasing depth of development is being observed all over the world. In Canada, ores containing gold, copper, nickel are mined at depths of 1800–2600 m, in the USA, copper and gold, at depths of 1700–3000 m, in India, gold is extracted from a depth of 3500 m. The world's deepest deposit is being developed in the Republic of South Africa, with work at more than 4,000m depth. Underground development in some cases allows to completely save the earth's surface, which provides a significant advantage over opencast mining [1, 8].

At the same time, some of the required copper raw materials can be obtained not from the bowels, but by sewage treatment for the production of boards and electroplating.

Studies have shown that the existing options for the organization of galvanic wastewater treatment systems do not provide the required quality of treatment not only for the main components of heavy metals, but also for salt and organic impurities, and such insufficiently treated effluents are discharged into the city sewer network or nearby rivers and water bodies. which complicates the operation of the sewerage system, pollutes rivers and reservoirs.

For the proposed scheme of regeneration of the spent pickling solution in the pickling module used only solid electrodes. For such purposes, use platinum and graphite, which in this work were taken as a basis. The possibility of replacing expensive platinum with a titanium electrode has been investigated. The corrosion behavior of titanium in the etching solution was previously investigated. The weight of the sample of titanium wire with a length of 100 mm and a diameter of 0.7 mm (0.2104 g) after 115 hours in the etching solution did not change when weighed on analytical balances. This allowed the use of a titanium electrode in the pickling solution as a working one.

The authors proposed and investigated the scheme of wastewater regeneration from etching, washing, with the release of copper-metal in sheet form for possible remelting at the metallurgical enterprise.

The sludge hazard index for copper compounds is calculated by the formula:

$$K_i = \frac{\mathrm{MPC}_i}{(S + C_w)_i}, \tag{1}$$

where

K_i – hazard index;

i – is the serial number of the substance,

MPC_i – maximum permissible concentration in the soil of a dangerous chemical substance contained in waste, mg / kg of soil;

S – is the coefficient of solubility of a chemical in water;

C_w – the content of the chemical in the total mass of waste, mg / kg;

The total hazard index, determines everything by the formula:

$$K = \frac{1}{n^2} \sum_{i=1}^{n} K_i, \tag{2}$$

where, n – is the amount of hazardous chemicals contained in the sludge production boards and electroplating.

Determination of waste hazard class: based on the actual content in the waste, water solubility, active reaction, the lowest toxicity index have sodium compounds, hydroxide in particular.

The toxicity index of an individual chemical waste ingredient is determined by:

$$K_c = \frac{\lg(LD_{50})i}{(S + 0{,}1F + C_w)i}, \quad (3)$$

where, LD_{50} – the average lethal dose of a chemical ingredient when ingested, S – a coefficient that reflects the solubility of a chemical ingredient in water, F – the coefficient of volatility of the chemical ingredient, C_w – the amount of this ingredient in the total weight of the waste, or part of t/t; i – serial number of a specific ingredient.

To assess the carcinogenic risk of heavy metal, we calculate the average daily dose of LADD, moderated with considering the average life expectancy (70 years) according to the formula [25]:

$$LADD = \frac{C \cdot CR \cdot ED \cdot EF}{BW \cdot AT \cdot 365}, \quad (4)$$

where: $LADD$ – average daily dose, mg/(kg×date);
C – the concentration of the substance in the contaminated environment, mg/kg;
CR – the rate of quantitative flow of the active medium, kg/day;
ED – duration of action, years; EF – frequency of action, days/year; BW – human body weight, kg;
AT – exposure averaging period (for carcinogens AT = 70 years; 365 – number of days in the year.

The value of the risk of non-carcinogenic effects for certain substances is determined on the basis of calculations of the hazard factor according to the formula:

$$HQ = AD/RfD, \quad (5)$$

where: HQ – danger factor; AD – average dose, mg/kg; RfD – reference (safe) dose, mg/kg.
The hazard index under the conditions of simultaneous action of several substances is calculated by the formula:

$$HI = \sum_{i}^{n} HQ_i, \quad (6)$$

where: HQ_i – hazard factors for the individual components of the mixture of substances.

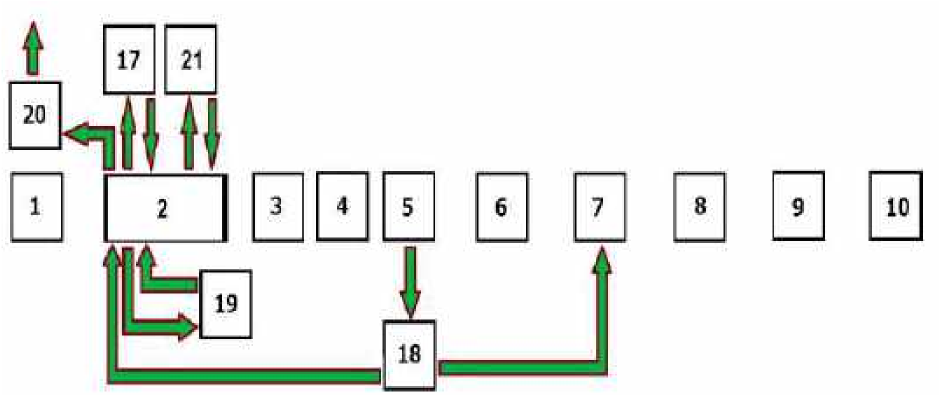
THE RESEARCH RESULTS AND DISCUSSIONS

Currently, the most common reagent technologies for removing metals from water do not provide the necessary efficiency of water purification for its re-use, leading to the formation and accumulation of toxic sludges that continue to accumulate in the territories of both existing enterprises of the former USSR and newly formed. The question of the utilization of regenerative solutions formed during the use of ion-exchange technologies, which make it possible to create closed systems of water use in galvanic industries, remains unsolved [14-15, 17-18]. The drawing shows the scheme of the line of digestion with wastewater for regeneration [8].

In the existing scheme, after the operation of etching and saturation of the solution with copper compounds in the etching module, the etching rate decreases and the etching solution must be replaced with a fresh one capable of etching at a sufficient rate. The spent solution is sent to the factory treatment facilities for pre-treatment, in which the residue can be discharged into the municipal sewer system after reaching the content of the components of the indicators set by the municipal water utility. The authors proffer a scheme for wastewater regeneration from etching operations, washing with the release of copper in sheet form for possible remelting at a metallurgical enterprise.

To implement the proposed scheme, a series of studies and tests were conducted, among which the following steps can be noted.

The analysis of existing problems of galvanic production, control systems, accumulation of waste in the territories of the enterprises is executed. Ways to reduce the harmful environmental impact on the environment and human life have been identified.



Drawing. Diagram of a line of etching of printed circuit boards with a lead for regeneration: 1 – module load; 2 – etching module; 3 – lighting module; 4 – overview module; 5 – the third module of cascading washing; 6 – is a second module of cascade washing; 7 – the first module of cascading washing; 8 – module of hot drying; 9 – module of cold drying; 10 – module unloading; 17 – regenerator etching solution; 18 – regenerator of wash water; 19 – filtration unit; 20 – treatment plants of the enterprise; 21 – installation of coating (if necessary).

Based on the analytical decision of Carslou-Eger, the impact of soil contamination in the storage area of galvanic waste and printed circuit boards was established, and it is shown that in one year the top layer of soil (0,5 m thickness) will pass into the category of slightly saline, and in 10 years the salt profile will reach depth of 1,5 m, which will lead to the destruction of living soil organisms for many years and after the elimination of sludge storage facilities.
The composition of the components of the pickling solution is optimized by the methods of factorial experiment, which according to its characteristics allows to provide balanced indicators of the process speed and simultaneous recovery of the spent solution without emissions into the environment.

The possibility of using ecologically safe technology of copper extracted from wastewater for metallization of printed circuit board substrates is theoretically substantiated and experimentally proved, which made it possible to offer specific technical solutions for environmental safety management, to stabilize and improve the environment.

To purify flushing wastewater with low concentrations of harmful substances at a final concentration of metal in the flushing water in the range of 0,002-0,005 g/l a fluidized bed installation of non-conductive parts is used, which prevents the formation of highly toxic substances and contributes to environmental safety.

The possibility of using electrochemical methods to determine the thickness of tin coatings on a copper basis is examined, which allows to automate the process of manufacturing boards and ensures its integration into the overall system of environmental safety.

The possibilities of using I2XI8HT stainless steel electrodes during the removal of heavy metals have been experimentally tested, which makes it possible to offer specific technical solutions for environmental safety management.

Namely, the creation of a new scheme is determined by a number of studies aimed at reducing environmental damage from the operation of pickling lines and storage of sludge in the enterprise.

The developed scheme allows to carry out regeneration of solutions in the course of etching and constant maintenance of concentration of elements, that means, providing constant speed of etching of boards. At the same time the scheme of such line allows to use the extracted copper in metallization processes without sewage discharges, allowing no pollution of environment.

Assembling of installations is simple: they are established near the etching module and are connected to it by two pipelines. If necessary, the line of etching and installation of reproduction of water solutions can be placed in various rooms and even floors. In this case, the last ones are additionally equipped with a storage tank with a pumping station.
The introduction of electrochemical reduction of water solutions allows:
– to avoid volley discharges of concentrated waste water solutions to treatment facilities;
– to reduce water consumption in flushing operations after etching of printed circuit boards and electroplating due to its reusability;
– to return to production of precious metals, thereby increasing the efficiency of basic technological processes;
– reduce the cost of chemicals to neutralize spent water solutions;
– water is 0,8 m^3 per hour and used only for cooling.

Assembling of installations does not demand a long stop and readjustment of production, and the modular principle of construction allows to increase productivity on metal removal, concerning the sizes needed for the customer.

As shown by the results of research, copper removed from wastewater meets the requirements that allows it to be used for further melting or for metallization of substrates in the corresponding technological processes [8].

Considering the fact that the creation of equipment that is environmentally safe and energy-efficient, it is possible to evaluate the economic indicators created on the basis of this research equipment. It is necessary to take into account the specific prices for the basic materials used in the technological process and the parameters of the plants, which make it possible to reuse aqueous solutions without discharging the treatment plants of both enterprises and cities. When determining the economic feasibility it should be based on the criterion of harm to the environment [19-24].

During the calculations, we take into account the fact that the existing line connects the sewage recovery (regeneration) installation without making structural changes to the PCB etching line and does not require any changes in the manufacturing process of the circuit board.The necessary data for the calculations are presented below:
– the price of water and sewerage in Kyiv as of 2019 – 21.756 UAH / m^3;
– the price of electricity in Kiev as of 2019 - 2.47 UAH / kWh;
– the cost of installing wastewater recovery (regeneration) for the PCB digestion line - UAH 450000;
– the cost of copper scrap is 140 UAH / kg.

The cost-effectiveness of new equipment implementation will be performed for the annual workpiece production and work program. In this case, we take into account that the annual fund of working time will be 247 days, which in one-shift work will give $247 \cdot 8 = 1976$ hours.
During this time 1976 will be produced $\cdot$ 12 m^2 / h = 23712 m^2 of blanks. The amount of extracted metal (copper) will be 23712 $m^2 \cdot 0.5 = 11856$ kg.

The results of the cost-effectiveness calculations are summarized in Table 1.

Cost estimate for the billing period (year):
The basic variant: Z_{Tv} = 1200000 + 206351 + 63000 + 2100000 = 3569351 UAH.

New version: Z_{Tb} = 1200000 + 450000 + 55000 + 34391 + 7500 + 35141- 1659840 +600000 = 722 192 UAH.

Table 1. Results of cost-effectiveness calculations

The name of the article costs	Basicversion	A new variant is proposed
Cost of materials (basic and auxiliary for connection to the line), UAH	–	55000
Water consumption for process support , m^3 / h	4.8	0.8
Price for water and sewerage, UAH / m^3	21.756	21.756
Water cost program per year (1976 year) , UAH / m^3	21.756·4,8 1976=206351	21.756·0.8·1976=34391
Number of sludge formed , t	2.1·12 =25.2	0.25·12 =3
The cost of removal of sludge (2500UAH / t) , UAH	25.2·2500= 63000	3·2500=7500
Increasing the amount of electricity used to provide wastewater recovery, kWh	–	14227.2
Price for electricity, UAH / kWh	2.47	2.47
Increase in the cost of electricity to support the process , UAH	–	14227.2·2.47= 35141
The amount of extracted metal (copper) , kg	–	11856
The cost of the selected metal (copper) , UAH	–	11856·140= 1659840
Solutioncosts , UAH	2100000	600000
Total, UAH	3569351	722192

The economic effect will be $E = With_{TB} - W_{tn}$ = 3569351-722192 = 2 847 159 UAH.

The results of the calculation of the total sludge hazard index for the removal of copper compounds at one of the enterprises of Ukraine are presented in Table 2.

Table 2. The results of the calculation of the total sludge hazard index

A group of substances	MPC_i, mg / kg	$(S + C_в)_i$, mg / kg	K_i	K
Copper compounds	3	73.98	0.0405	0.7575
		21.15	0.141	

After removal of copper compounds from wastewater (not converted to sludge), the total hazard index becomes practically non-hazardous (Table 3).

Table 3. Results of the calculation of the total sludge hazard index for the production of boards and electroplating after the introduction of copper removal activities

A group of substances	MPC_i, mg / kg	$(S + C_в)_i$, mg / kg	K_i	K
Copper compounds	3	0.01	300.0	100
		0.03	100.0	

The calculation data (Table 2) shows that after removal of copper compounds from wastewater (not converted to sludge), the overall hazard index has improved. In addition, the raw material for smelting copper is received.

The calculation`s results of the total sludge hazard index of the board`s production and electroplating for one of the existing enterprises showed an increase (the value of the total sludge hazard index instead of the existing values of 0.7575 was respectively 100).
As the amount of sludge and copper in them sharply decreases, and this leads to an improvement of indicators of the hazard index, that is, to increase of ecological safety.

When setting a task to predict the environmental risk from a source that contains toxic substances, the main object of care and responsibility is the person. Therefore, all types of risks, including environmental, social and individual, must be focused on the saving of human life and health. Therefore, the most correct principle should be the application of an integrated risk indicator, as all areas of human activity are inseparably linked and have a corresponding interaction.

As a rule, for quantitative analysis and measurements the basic indicators-risks to human life and life – quality and longevity are used.

Quantitative assessment of the scope and severity of adverse effects that may occur as a result of the actual or intended exposure to the substance should be the entry of pollutants into the human body.

To determine the quantitative inflow of pollutants into the human body, which may be in the area of negative impact of galvanic production sludge, it is necessary to assess these hazards, which can be performed in the following stages:
– characteristic of the environment with the analysis of the main physical standarts of the study area;
– determination of ways of influence of pollution sources and their distribution;
– determination and evaluation of the level, frequency and duration of action of each pollutant identified in the second stage.

Consider the situation with the preservation of sludge in the enterprise and the possible consequences of such a decision for the environment and human health. For example, we`ll take a separate Ukrainian enterprise that has been accumulating waste for several years (table 4).

Waste is galvanic sludge with a precipitator: alkali, soda. Appearance and consistency: dry porous lumps of yellow-green color, odorless. General information about waste: waste is generated by repeated treatment of pipe blanks in baths with alkaline solution. After solidification has a firm consistency. Qualitative composition of waste and the content of hazardous substances in them: sodium hydroxide - 38-65 wt. %; sodium nitrate - 24-35 wt. %; sodium chloride - 5-6 wt. %; insoluble impurities (cinder, glass mass) - up to 100%; the active reaction of the water extract from the waste pH is 11.68.

Given the toxicity index of waste, calculated through the LD50 for laboratory animals, one of the most dangerous components - sodium hydroxide ($1.3 < Kc < 3.3$), galvanic sludge with a precipitator (alkali, soda) are highly hazardous waste (toxicity class II). Taking into account the sharply alkaline reaction of water extract from waste, their utilization should be carried out in compliance with safety rules while working with aggressive substances. The hazard class of waste can be reduced after neutralization.
According to the results of the study of the composition of galvanic sludge, the mass content of priority pollutants at the levels is defined: chromium – 1.25 kg/t, nickel – 0.01 kg/t.
We obtain:

$$Kc=\lg(150)/(1.0+0.0+0.56)=1.39. \quad (7)$$

Using the necessary initial data for the calculation, some of which are specified in the annexes [25], we obtain the following value of the average daily dose of nickel:

$$LADD = \frac{C \cdot CR \cdot ED \cdot EF}{BW \cdot AT \cdot 365} = \frac{10 \cdot 0.2 \cdot 5 \cdot 365}{70 \cdot 70 \cdot 365} = 2 \cdot 10^{-3}\,\textit{мг}/(\textit{кg} \cdot 24h). \qquad (8)$$

Table 4. Concentration and toxicity class of the substance

Form	Concentration, mg/kg (X), substance toxicity class						
	Pb(1)	Cd(I)	Zn(1)	Mn	Cu(2)	Cr(2)	Ni(2)
Gross	26.88	1.87	3.68	626.73	86.25	12497	8.79
Mobile for *t* =25°C	<0.5	<0.25	1.64	<0.5	73.24	200.4	<1.0
Hydrosoluble for за *t*=25°C	<0.5	<0.25	2.08	<0.5	0.53	201.8	<1.0
Solubility in the experiment,	insoluble	insoluble	56,5	insoluble	insoluble	16.0	insoluble
Average amount in waste, (kg/t)	0.027	0.002	0.004	0.63	0.086	1.25	0.01
MPC in the soil, (mg/kg) – gross form	32.0	1.5	–	1500.0	–	80.0	–
MPC in the soil, (mg/kg)	–	–	23.0	–	3.0	6.0	4.0

The carcinogenic risk of nickel as an additional probability of cancer in an individual during the life of CR is determined by the formula:

$$CR = LADD \cdot SF = 2 \cdot 10^{-3} \cdot 0.84 = 1{,}68 \cdot 10^{-3}. \qquad (9)$$

where, *SF* – tilt factor, $(mg/(kg \times date))^{-1}$.

Determine the hazard index according to the formula for priority pollutants of galvanic plant waste, in particular, for cadmium, nickel, lead, chromium:

$$HI = \sum_{1}^{4} HQ_i = \frac{0.002}{0.0005} + \frac{0.01}{0.02} + \frac{0.027}{0.0035} + \frac{0.005}{0.005} = 82.5. \qquad (10)$$

As the hazard index HI>1, this level of risk is unacceptable, and pollutants, which are contained in galvanic sludge and entered the environment as a result of an emergency situation will adversely affect human health.
The novelty of the work is that the mechanism of obtaining additional raw materials from wastewater from the production of printed circuit boards is detected. The significance lies in the fact that the obtained results can be applied in the production of printed circuit boards to reduce the impact of industrial waste on the environment, as well as to obtain cheap raw materials from industrial wastewater.

The novelty of the work lies in the fact that the mechanism of additional raw materials from the wastewater of PCB production is obtained. Significance is shown in that the obtained results can be applied in the production of printed circuit boards to reduce the environmental impact of production wastes, as well as to obtain cheap raw materials from industrial wastewater.

CONCLUSIONS

Therefore, the economic effect of the introduction of new wastewater treatment technology and the reduction of the amount of sludge over the billing period (1 year) will be UAH 2847159. That is, the introduction of a new wastewater treatment technology with only one installation can bring more than 2.8 million UAH of economic effect, improve the environment and will make it possible to implement an ecologically safe process of electroplating copper sewage. The increase in electricity costs for the process of wastewater regeneration (recovery) is offset by a sharp increase in the level of environmental safety (the total sludge hazard index instead of the existing values of 0.7575 became 100 respectively) of the environment around the production plants and in general in the region of industry.

REFERENCES

1. Chervonyy I.F., Bredikhin V.M., Gritsay V.P., Ignatev V.S., Ivaschenko V.I., Manyak M.O., Smirnov V.O. Non-ferrous metallurgy of Ukraine. T.1, ch.1: monografiya. Zaporizhzha : ZDIA, 2014. 380 p.

2. National report on the state of the environment in Ukraine. http://old.menr.gov.ua/index.php/dopovidi.

3. Grizzetti B., Pistocchi A., Liquete C., Udias A., Bouraoui F., van de Bund W. Human pressures and ecological status of European rivers. Scientific Reports. 2017. Vol. 7, https://www.umwelt-bundesamt/sites/2018_indikatoren-bedeutung-wasser.pdf.

4. Mitryasova O., Pohrebennyk V., Selivanova A. Environmental Risk of Surface Water Resources Degradation. Water Supply and Wastewater Removal, Politechnika Lubelska, 152–162, 2018.

5. Makisha N., Yunchina M. Methods and solutions for galvanic waste water treatment. Moscow state University of civil engineering, Russia International science conference on smart city, spbwosce. Saint-Petersburg, 2016.

6. Oliveira A.D., Bocio A., Beltramini Trevilato T.M, Magosso Takayanagui A.M., Domingo J.L., Segura-Muñoz S.I. Heavy metals in untreated/treated urban effluent and sludge from a biological wastewater treatment plant. Environ Sci Pollut Res 2007; 14: 483-489.

7. Petryk A., Chop M., Pohrebennyk V. The assessment of the degree of pollution of fallow vegetation with heavy metals in rural administrative units of Psary and Płoki in Poland // 18th International multidisciplinary scientific geoconference SGEM 2018. Ecology and environmental protection: proceedings, 2–8 July, 2018, Albena, Bulgaria, 2018, 921–928.

8. Nester A.A. Wastewater treatment for PCB production. Khmelnitsky National University: monograph. 2016. 219 p.

9. Cui J., Zhang L., Mater J.H. Metallurgical recovery of metals from electronic waste: review. 2008,158:228–256. https://www.sciencedirect.com/science/article/pii/S0304389408002161?via%3Dihub

10. Nester A.A., Drapak G.M. Microstructure research and recovery copper technology, released from restored water solutions. Polish Journal of Environmental Studies. Vol.17, No. 3A, Olsztyn, 2008, 423-426.

11. Nester A.A., Evgrashkina G.P. Forecast of pollution of machine-building enterprise by sludges at manufacture of boards and electroplating. News of the TulState University. Technical science. Release 6, 2017, 193-200.

12. Liu Y., Lam M.C., Fang H.H.P. Adsorption of heavy metals by EPS of activated sludge. Water Sci Technol. 2001; 43: 59-66.

13. Girnychyy Zakon Ukraine vid 6.10.1999 №1127-XIV. Vidomosti Verkhovnoy Rady Ukraine (VVR), 1999, № 50, 433 http://zakon5.rada.gov.ua/laws/show/1127-14

14. Pashayan A.A. Karmanov D.A. Disposal of galvanic effluents without formation of galvanic slums, Volume 22, № 12, 2018, 19-21. https://doi.org/10.18412/1816-0395-2018-12-19-21.

15. Proleutchik A.Y. Gaponenkov I.A., Fedorov O.A. Extraction of heavy metal ions from inorganic waste water. Volume 22, No. 3, 2018, 35-39. https://doi.org/10.18412/1816-0395-2018-3-35-39.

16. Bloomberg M., Paulson H., Steyer T. Risky Business: The Economic Risks of Climate Change in the United States. Available online: http://riskybusiness.org/ (accessed on 26 June 2014).

17. Klachkin V.N., Shirkunova K.S., Bart A.D. Analysis of Stability of Chemical Composition of Waste Water in the Production of Printed Circuit Boards. Vol. 23, No. 5, 2019. 47-51. https://doi.org/10.18412/1816-0395-2019-5-47-51.

18. Vershinina I.A., Martynenko T.S. Waste management problems and socio-ecological inequality, Vol. 23, № 5, 2019, 52-55. https://doi.org/10.18412/1816-0395-2019-5-52-55

19. Dorokhina E.Y., Harchenko S.G. Economics of closed cycles: problems and ways of development. Vol. 21, № 3, 2017, 50-55. https://doi.org/10.18412/1816-0395-2017-3-50-55

20. Alekhya M., Divya N., Jyothirmai G., Rajashekhar K. Reddy Secured landfills for disposal of municipal solid waste. International Journal of Engineering Research and General Science. Vol. 1, Issue 1. 2021, 368–373.

21. Bates B.C.; Kundzewicz Z.W.; Wu S.; Palutikof J.P. Climate Change and Water; Intergovernmental Panel on Climate Change: Geneva, Switzerland, 2008, 210 p.

22. Ishchenko V., Pohrebennyk V., Borowik B., Falat P., Shaikhanova A. Toxic substances in hazardous household waste, International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, 18 (4.2), 2018, 223-230.

23. Magalhaes J.M., Silva J.E., Castro F.P. Labrincha J.A., 2005. Kinetic study of inmobilization of galvanic sludge in clay based matrix. J. Hazard. Mater. B121, 69-78.

24. Mymrin V., Borgo S. C., Alekseev K., Avanci M. A., Rolim P. H., Argenda M. A., Klitzke W., Gonçalves A. J., Catai R. E. Galvanic Cr-Zn and spent foundry sand waste application as valuable components of sustainable ceramics to prevent environment pollution. The International Journal of Advanced Manufacturing Technology. Feb 24 2020, 12 p.

25. Rukovodstvo P2.1.10.1920-04. 2004. Rukovodstvo po otsenke riska dlya zdorovya naseleniya pri vozdeystvii khimicheskikh veschestv, zagryaznyayuschikh okruzhayuschuyu sredu. M. Federalnyy tsentr gossanepidnadzora Minzdrava Rossii. (In Russ.), 144 p.

STUDY OF CHANGES IN THE ECOLOGICAL CONDITION OF THE PSEL RIVER

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ABSTRACT

The article analyzes the changes in the ecological status of the water of the Psel river and identifies possible causes of its pollution. The change in the ecological status of the surface water body was carried out by analyzing the data of monitoring and ecological assessment of water resources of Ukraine of the State Agency of Water Resources of Ukraine for the period 2010-2020. The change in the content of the main normative indicators that determine the ecological status of the surface water body is analyzed: polyphosphates, chlorides, nitrates and nitrites, ammonium and sulfates. The analysis was carried out according to the control of water intake from 6 posts along the entire length of the watercourse of the river Psel in Ukraine. As a result of the analysis, it was found that further change in the ecological status of the surface water body in the direction of its improvement requires the development and implementation of a reliable and effective model for forecasting its ecological status. In the future, the results of the study can be used in the development and implementation of a reliable and effective model for forecasting the ecological status of surface water bodies, including the river Psel.

Keywords: surface water bodies, pollutants, water intake posts, concentration of normative indicators, Psel river

INTRODUCTION

Ukraine is one of the countries with insufficient water resources. Water natural resources of Ukraine are, first of all, local and transit runoff of rivers, water reserves of lakes, artificial reservoirs and underground horizons.

Due to the constant development of industry, pollutants are released into the atmosphere, into surface water bodies and the disposal of hazardous waste. Thus, the objects of the natural environment are continuously polluted. Mankind makes a lot of efforts to regulate emissions into the environment: install treatment plants, dispose of waste, introduce new processes in the enterprise, which are environmentally friendly, etc. [1, 4]

Water resources are an important component of human life. Every year, the man-made load is constantly growing and issues related to water quality are becoming increasingly important. Continuous human activity constantly leads to deterioration of water quality and ecological regime of river runoff. Man-made activities can lead to regional and global environmental changes. Changes in the quality of water with a tendency to constant deterioration are observed in almost all surface sources of water supply in the country. Today, quite acute and vital environmental problems associated with the hydrosphere of the planet are the conditions for providing the population with quality drinking water and the ability to improve its quality, including by improving the ecological status of surface water bodies.

The problem of assessing water quality at the present stage of development of society is important and of paramount importance and occupies a central place in water protection activities [2]. The ecological problem of hydrosphere protection at the economic and technogenic level has a significant impact on the ecological state of surface water bodies, which requires monitoring studies using modern interactive online cartographic resources.

To obtain a holistic picture of the current environmental situation, large enough administrative-territorial units of the industrialized countries of the world, in particular Ukraine, even with the gradual reduction of industrial potential, use environmental monitoring. The main component of such monitoring is the process of obtaining the necessary initial data (for example, the results of analysis of surface water samples).

In Ukraine, the main thing is the monitoring of surface water bodies within the river basin. Following the approval in 2018 by the Cabinet of Ministers of Ukraine of the Procedure for State Water Monitoring, surface water monitoring is carried out to ensure the collection, processing, storage, synthesis and analysis of information on the status of surface water bodies, forecasting its changes and developing scientifically sound recommendations for decision-making in the field of use, protection of water and reproduction of water resources.

Objects of state water monitoring are: massifs of surface waters (surface water bodies or their parts), including coastal waters and zones (territories), which are subject to protection; massifs of groundwater (groundwater bodies or parts thereof), including areas (territories) that are subject to protection; sea waters within the territorial sea and the exclusive maritime economic zone of Ukraine, including zones (territories) subject to protection.

State monitoring of waters is carried out by the Ministry of Environmental Protection and Natural Resources of Ukraine, the State Agency of Water Resources of Ukraine, the State Service of Geology and Subsoil of Ukraine, the State Emergency Service, and the State Agency of Ukraine for Exclusion Zone Management (in the exclusion zone and the zone of unconditional (compulsory) resettlement of the territory that was exposed to radioactive contamination as a result of the Chornobyl catastrophe).

According to the Procedure [1], state water monitoring is divided into several types: diagnostic monitoring, operational monitoring, research monitoring and seawater monitoring.

Diagnostic monitoring is performed to assess the impact of man-made loads on surface and groundwater bodies. For surface water bodies, diagnostic monitoring is carried out only in the first year of state monitoring, and for groundwater - the first two years.

Operational monitoring is carried out annually to assess changes in the ecological and chemical status of surface water bodies and in the quantitative status and chemical composition of groundwater. They also study the trends of increasing concentrations of pollutants in water bodies, which are caused, inter alia, by man-made impacts on the environment.

Research monitoring is carried out only for surface water bodies in order to establish the reasons that lead to the impossibility of achieving environmental standards for these objects. In order to conduct research monitoring, the subjects of state monitoring independently determine the sampling points for its conduct.

Seawater monitoring is carried out for the territorial sea and the exclusive maritime economic zone of Ukraine. The purpose of this monitoring is to study the ecological status of seawater and assess the impact of natural and anthropogenic factors on the status of seawater.

Subjects of monitoring conduct monitoring on certain indicators and enter the obtained data into the relevant documents with further analysis, summarizing and indicating recommendations, if necessary.

METHODS AND EXPERIMENTAL PROCEDURES

In Ukraine, almost 80% of the population is supplied with drinking water from surface water bodies. Within Ukraine, the Psel river flows through the territory of Sumy and Poltava regions. The river Psel is part of the Dnieper river basin (it is its left tributary). The length of the Psel river, which flows through the territory of Ukraine is 502 km, and in total – 717 km. The catchment area of the Psel river in Ukraine is 16.27 thousand km^2. The sources are located in the Russian Federation, within the Belgorod region. About 10 small reservoirs have been created on the Psel river. Most of them are located at HPPs (Nizivska, Malovorozhbyanska, Mykhailivska, Bobrivska, Shyshatska, Ostap'evska, Sukhorabivska). The right tributaries of the Psel river are Oleshnya, Sumka, Vorozhba, Mezhyrichka, Grun, Vuzka, Vovnyanka, Balakliyka, Khorol, and the left - Udava, Syrovatka, Vilshanka, Budylka, Borovenka, Vepryk, Bobryk, Lyutenka.

In the water of the main waterway of the country - the Dnieper river, environmentalists have identified more than 160 pollutants, namely: acids, alkalis, mineral salts, petroleum products and pesticides and others. It is known that pollutants have been found in the river, to which water treatment systems are not adapted.

The main problems of surface water bodies today are:

– large littering of shores;

– construction of coastal protection strips;

– deterioration of hydraulic structures, which threatens accidents and pollution of water bodies; excessive overgrowing of water area with aquatic vegetation;

– drainage of rain sewerage practically without cleaning;

– discharge of untreated municipal wastewater from apartments that are not connected to the centralized sewerage system;

– weakening of state control over environmental offenses;

– inefficient water monitoring system;

– imperfection of the existing system of public administration in the field of use, protection and restoration of water resources, lack of clear delineation of functions;

– non-full use of domestic scientific innovations in the field of biochemistry.

The main sources of man-made load on surface water bodies in Ukraine are:

– industrial wastewater;

– outdated systems, drainage and wastewater treatment;

– domestic wastewater, which is dominated by feces, surfactants, fats, microorganisms, including pathogenic;

– precipitation, which contains chemicals of air of industrial origin;

– precipitation and meltwater from agricultural lands with residues of mineral fertilizers and plant protection products, organic matter;

– sewage from city streets - they contain petroleum products, phenols, oxides of heavy metals;

– Lack in some regions of Ukraine of the basin principle of management, control and responsibility for the state of surface sources of drinking water supply [6].

In wastewater containing large amounts of organic matter, blue-green and brown algae, phytoplankton multiply rapidly, and biological oxygen consumption increases. As a result, anaerobic processes that determine eutrophication (increase of biological productivity during the accumulation of nutrients under the influence of anthropogenic or natural factors) begin to predominate in the reservoir.

Analysis of changes in the ecological status of surface water bodies is carried out on the basis of comparative analysis of their hydrophysical, hydrochemical, hydrobiological, bacteriological, toxicological and other indicators that reflect the characteristics of abiotic and biotic components of aquatic ecosystems.

Standardized indicators, which are most often used to determine the quality of surface water bodies, are divided into:

1) oxygen - includes dissolved oxygen in water, biochemical oxygen demand, chemical oxygen demand;

2) toxicological - combines ammonium nitrogen, nitrites and heavy metals;

3) sanitary-toxicological - determines the content of nitrates, heavy metals and mineralization with all its components;

4) fishery - combines petroleum products, phenols and pesticides.

Assessment of the quality of surface water bodies is necessary in cases where it is necessary to trace the trend of spatio-temporal changes in water status under the influence of natural and man-made processes.

The State Agency of Water Resources has launched an interactive map «Monitoring and environmental assessment of water resources of Ukraine» [3]. On the map it is possible to track the data of monitoring of surface water bodies for a certain period of time on indicators such as: nitrates, nitrites, phosphates, ammonium ions, sulfates.

Based on the monitoring data of the State Agency of Water Resources, an analysis of changes in the ecological status was carried out, according to the main indicators of the Psel river for 2010-2020.

The analysis was carried out on the basis of data from 6 water sampling posts in the Psel river (Figure 1): 1) Psel river, 528 km, Krasnopil district, administrative road of the city; 2) Psel river, 480 km, the village of Velyka Chernetchyna, the administrative road of the city above the technical water intake of Sumy; 3) Psel river, 444 km, Chervone village, below Sumy, administrative road of the city; 4) Psel river, 405 km, Bishkin village, administrative road of the city; 5) Psel river, 350 km, Kaminne village, administrative road of the city, border of Sumy and Poltava regions; 6) Psel river, 172 km, Velyka Bagachka urban-type settlement, technical water intake of the settlement [3, 5].

THE RESEARCH RESULTS AND DISCUSSIONS

To date, the assessment of qualitative changes in surface water bodies is performed by comparing the chemical composition of water at sampling points upstream and downstream. The reliability of the obtained results should be carried out taking into account the error of determination and averaging of concentrations of substances, due to the expediency of taking into account the condition of seasonal recurrence of the chemical composition of water in the annual cycle each year. In this regard, a comparative analysis was conducted on an average annual basis [7].

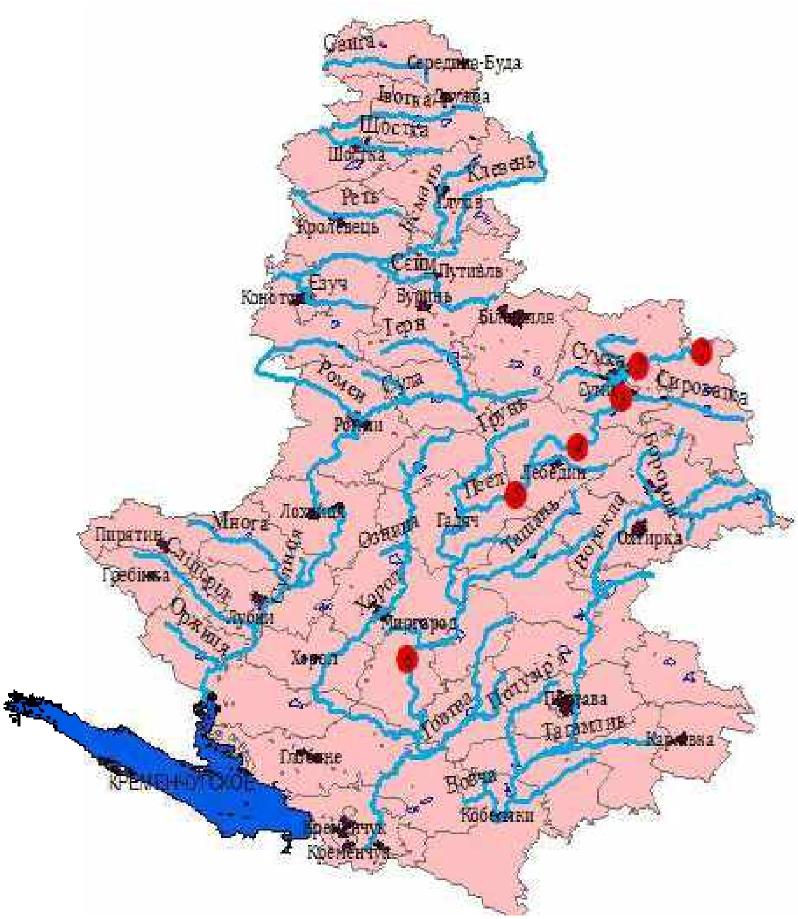

Fig. 1. Schematic placement of the existing 6 checkpoints of water intake, according to which the study was conducted (names are given in the original language)

Nitrogen and its compounds get into surface water bodies with domestic and industrial effluents from waste of livestock complexes and farms, mineral fertilizers. The increased content of ammonium indicates the deterioration of the sanitary condition of the water. The increase in concentration is due to the inflow into domestic waters of domestic wastewater, nitrogen and organic fertilizers. The content of ammonium in high concentrations in drinking water has a negative effect on the human body. Blood pressure may rise, there are various disorders of the liver and kidneys. The main source of nitrates and nitrites in the environment is nitrogen fertilizers. The source of nitrogen in natural waters is decomposed protein residues.

The content of chloride ions in surface water bodies is due to its widespread use in public utilities, such as water disinfection and the destruction of bacteria. Lack of chlorine in the human body leads to general weakness, decreased blood pressure, loss of appetite, etc. When chlorine is added to water, trihalomethane compounds can be formed. Getting into the human body cause asthma, skin diseases, diseases of the cardiovascular system, disorders of the gastrointestinal tract. Also, these compounds are carcinogenic, provoking the development of cancer.

Phosphorus is a necessary chemical element necessary for living organisms. When it hits surface water, it causes algae, especially blue-green ones, to grow rapidly, disrupting the natural biosystem. Phosphates have a negative effect on human health. If there is a large amount of water used for bathing and washing dishes, dermatitis and irritation may occur.

The content of nitrates and nitrites is an indicator of the chemical composition of natural water used in environmental assessment. This information is also needed when deciding on the balance of nutrients, the relationship between the life processes of aquatic organisms and the chemical composition of water. Nitrates enter water bodies during the decomposition of animal and plant proteins by microorganisms, when ammonium compounds are released, which are oxidized to nitrites and nitrates upon contact with air. The consequence of nitrate consumption is the formation of methemoglobin. The transport of oxygen to human tissues is disturbed, in the future there is a violation of the nervous system. Excess nitrate content also leads to disorders of the pancreas and thyroid glands, cancer, heart failure, kidney disease, cardiovascular disease.

The content of sulfates in natural waters varies widely and is due to the leaching of salt-containing rocks or discharge into reservoirs of industrial and domestic wastewater. The main source of sulfates in surface waters are the processes of chemical weathering and dissolution of sulfur-containing minerals, mainly gypsum, as well as oxidation of sulfides and sulfur. Significant amounts of sulfates enter the reservoirs in the process of extinction of organisms, oxidation of terrestrial and aquatic substances of plant and animal origin and with underground runoff.

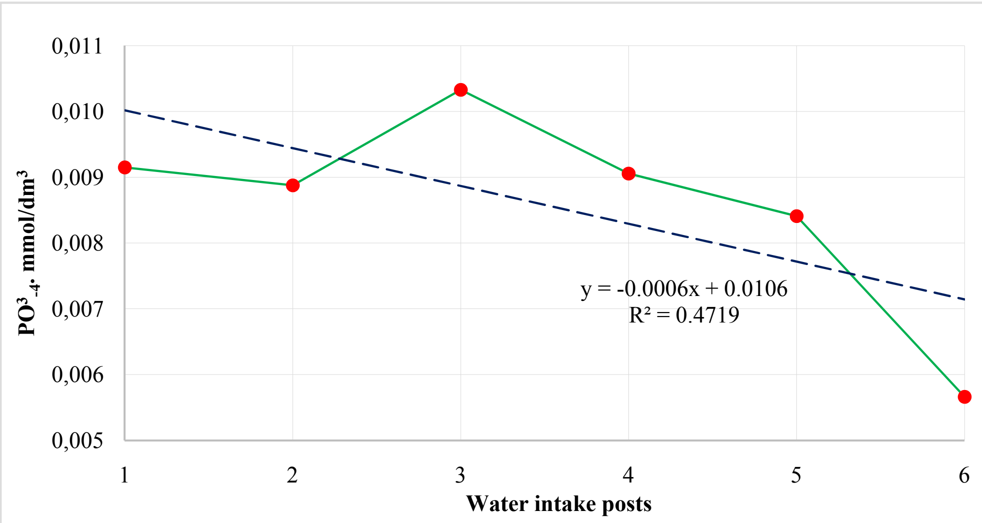

Fig. 2. Average annual concentrations of phosphate ions (polyphosphates) at the posts of water intakes of the river Psel for the period from 2010 to 2020

After analyzing Figure 2, we can conclude that in the river Psel there is a decrease in the total phosphate content from post 1 to post 6. Regression equation of the detected dependence: $y = -0.0006x + 0.0106$ reliability of approximation $R^2 = 0.471$.

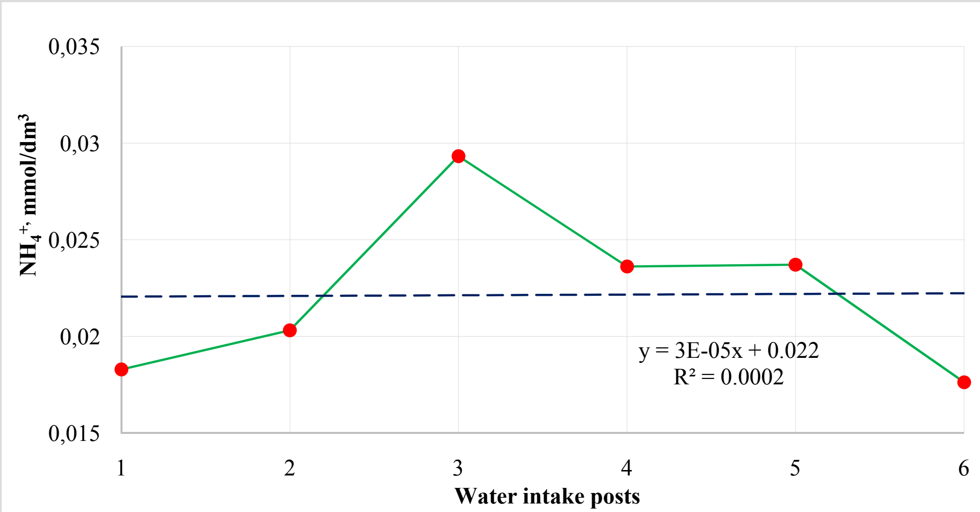

Fig. 3. Average annual concentrations of ammonium ions at water intake posts of the Psel river for the period from 2010 to 2020

At the same time there is a significant increase in post 3. Figure 3 shows that in the river Psel there is no change in the total ammonium content from post 1 to post 6. Regression equation of the detected dependence: $y = 3E + 05x + 0.022$ reliability of approximation $R^2 = 0.0002$. The ammonium content increases in post 3.

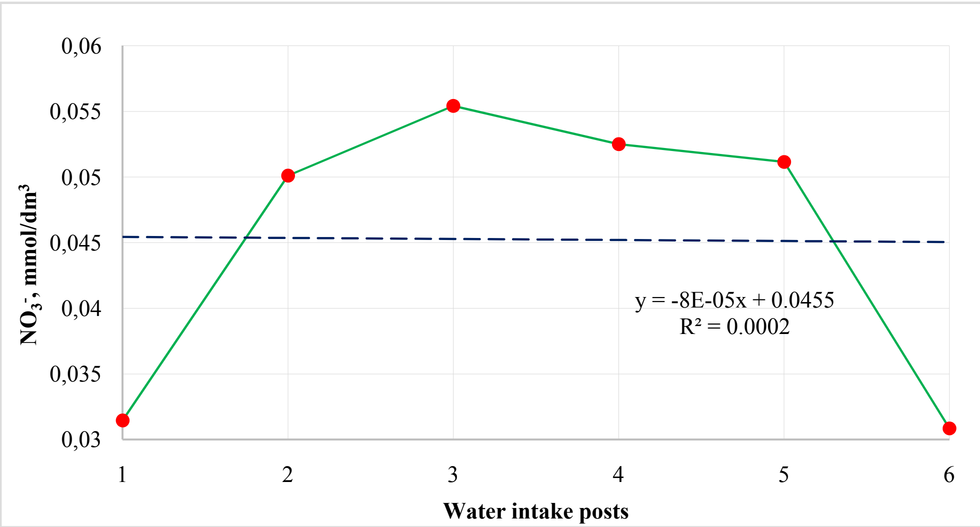

Fig. 4. Average annual concentrations of nitrate ions at the posts of water intakes of the river Psel for the period from 2010 to 2020

Considering Figure 4, we can say that in the river Psel decreases the content of nitrates from post 1 to post 6. Regression equation of the detected dependence: $y = -8E - 05x + 0.0455$ reliability of approximation $R^2 = 0.0002$.

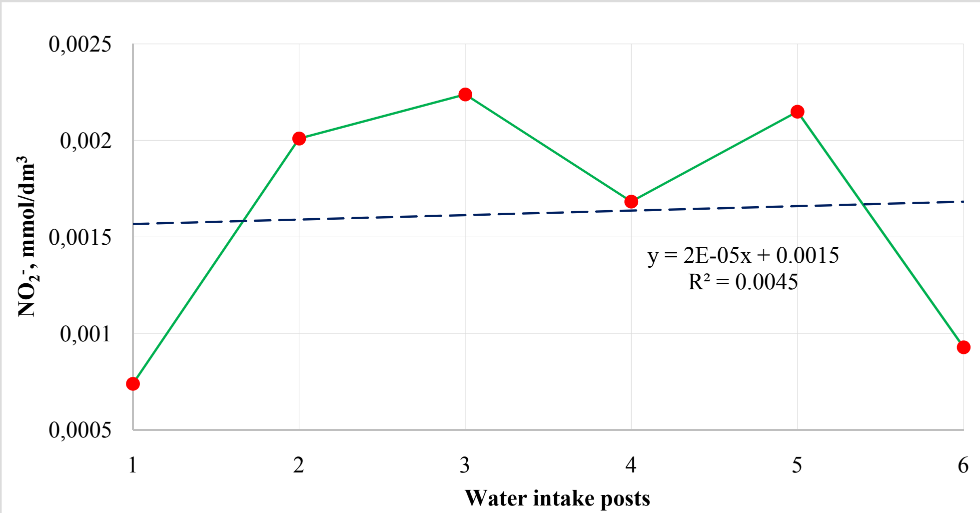

Fig. 5. Average annual concentrations of nitrite ions at the posts of water intakes of the river Psel for the period from 2010 to 2020

Analyzing Figure 5 revealed a slight increase in the total nitrite content from post 1 to post 6. There is a significant increase in post 3. Regression equation of the detected dependence: $y = 2E - 05x + 0.0015$ reliability of approximation $R^2 = 0.0045$.

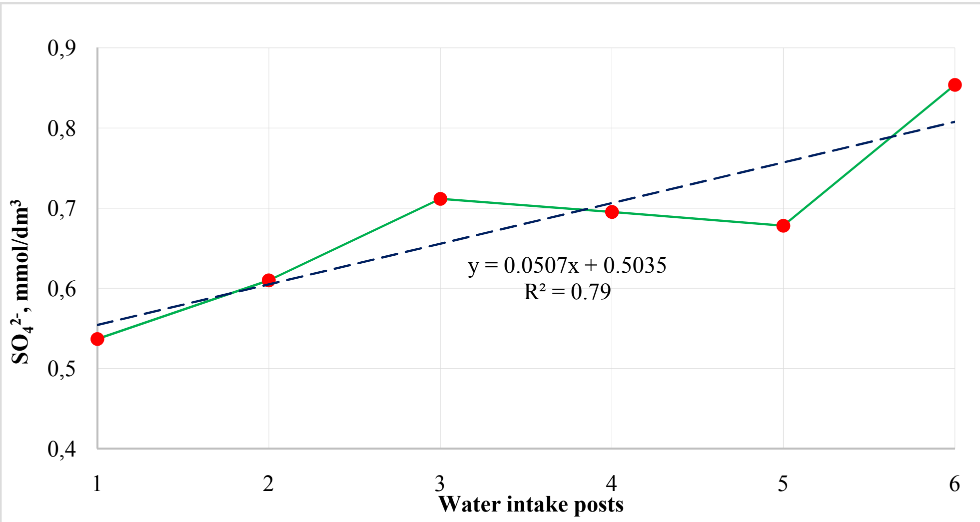

Fig. 6. Average annual concentrations of sulfate ions at the posts of water intakes of the river Psel for the period from 2010 to 2020

Figure 6 shows an increase in the content of sulfates Regression equation of the detected dependence: $y = 0.0507x + 0.5035$ reliability of approximation $R^2 = 0.79$.

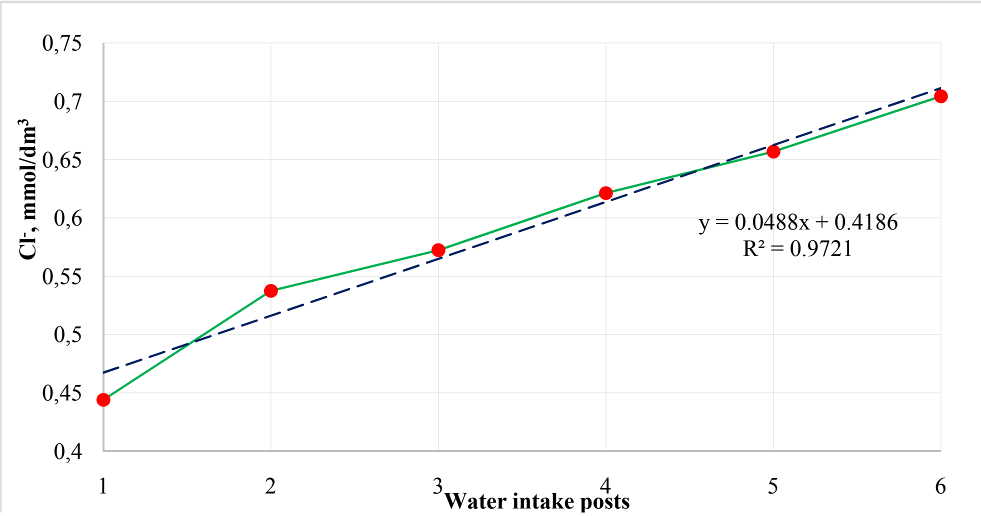

Fig. 7. Average annual concentrations of chloride ions at the posts of water intakes of the river Psel for the period from 2010 to 2020

Figure 7 shows an increase in chloride content. Regression equation of the detected dependence: $y = 0.0488x + 0.4186$ reliability of approximation $R^2 = 0.9721$.

Table 1 shows the average annual data on the content of pollutants (polyphosphates, ammonium ions, nitrate ions, nitrite ions, sulfate ions, chloride ions) in total at posts 1 – 6 of the river Psel.

Table 1. Average annual data on the content of pollutants in total for posts 1 – 6

Years	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Average annual values (PO^{3-}_4), mmol/dm^3	0.008	0.014	0.008	0.006	0.007	0.005	0.009	0.006	0.012	0.007	0.011
Average annual values (NH_4^+), mmol/dm^3	0.017	0.019	0.027	0.022	0.022	0.023	0.025	0.020	0.025	0.022	0.020
Average annual values (NO_3^-), mmol/dm^3	0.0013	0.0021	0.0016	0.0016	0.0034	0.0005	0.0009	0.0010	0.0021	0.0008	0.0010
Average annual values (NO_2^-), mmol/dm^3	0.031	0.064	0.047	0.042	0.051	0.069	0.026	0.040	0.042	0.018	0.022
Average annual values (SO_4^{2-}), mmol/dm^3	0.633	0.907	0.810	0.752	0.795	0.721	0.581	0.450	0.457	0.735	0.495
Average annual values (Cl^-), mmol/dm^3	0.674	0.715	0.647	0.461	0.607	0.490	0.459	0.532	0.656	0.561	0.504

Based on the data obtained, the following conclusions can be drawn. In the Psel river there is a significant increase in the content of pollutants at post 3 (Psel river, 444 km, the village of Chervone, below Sumy, administrative roads of the city). The reason for such a point increase may be the location of the fence post in the village (village of Chervone), where there are no treatment facilities. The population can discharge domestic wastewater, which contains harmful pollutants, into surface water bodies. For example, phosphates are part of washing powders, detergents, etc. At present, there are no standards for the content of phosphates in household detergents in Ukraine. Elevated levels of nitrates indicate that the technology of water treatment is violated. Nitrates and nitrites enter the water from the effluents of industrial and agricultural enterprises. Developed agriculture also pollutes the environment, including surface water bodies, with mineral fertilizers that contain pollutants. An additional source of pollutants in the waters of the Psel river may be industrial wastewater from enterprises, in particular PJSC «Sumykhimprom».

The results of the research allow us to state a significant deterioration of the ecological condition of the river Psel, which today, due to man-made impact, leads to a deterioration of water quality and the regime of its river runoff.

CONCLUSION

Based on the data of the «Monitoring and Environmental Assessment of Water Resources of Ukraine» of the State Agency of Water Resources for 2010-2020, an analysis of changes in the ecological status of the Psel river on the average annual content of pollutants in total at posts 1 – 6. The tendencies to deterioration of the ecological condition of the surface water body have been revealed. This can be explained by the increase in man-made load on the surface water body.

This approach allows its use to analyze changes in the ecological status of such surface water bodies.

REFERENCES

1. On approval of the Procedure for state water monitoring: Post of the Cabinet of Ministers of Ukraine of September 19, 2018 № 758 Kyiv: website. URL: https://zakon.rada.gov.ua/laws/show/758-2018-%D0%BF#Text.

2. Ponomarenko R.V. Scientific and theoretical bases of reduction of technogenic loading on systems of water supply of region taking into account the basic principles of basin management of water resources: monograph / R.V. Ponomarenko, Ukraine, 2020, p. 112.

3. State Agency of Water Resources of Ukraine. State Water Agency official website: website. URL: https://www.davr.gov.ua/.

4. Kovalenko S.A., Ponomarenko R.V., Assessment of the impact of anthropogenic load on the ecological condition of the Dnieper basin / S.A. Kovalenko, R.V. Ponomarenko // Proceedings of the III All-Ukrainian scientific-practical conference «Prospective technologies for ensuring the safety of life and longevity», Ukraine, 2021, pp. 113 – 115.

5. Kovalenko S.A., Ponomarenko R.V., Interactive map of river pollution in Ukraine / S.A. Kovalenko, R.V. Ponomarenko // Collection of abstracts of the XXIV International scientific-practical online conference «Ecology, environmental protection and sustainable use of nature: education - science – production, Ukraine, 2021» pp. 41 – 42.

6. Ponomarenko R.V, Pliatsuk L.D., Kovalov P.A., Investigation of changes in the quality of the surface water body under man-caused load / R.V. Ponomarenko, L.D. Pliatsuk, P.A. Kovalov, Й. Затько // Technogenic and Ecological Safety, Ukraine, №. 8(2/2020). pp. 48 – 54. – DOI: 10.5281/zenodo.4300769, 2020

7. Ponomarenko R.V, Pliatsuk L.D., Tretiakov O.V. Kovalov P.A., Determining the ecological status of the main source of water supply in Ukraine R.V. Ponomarenko, L.D. Pliatsuk, O.V. Tretiakov. P.A. Kovalov // Technogenic and Ecological Safety, Ukraine, № 6(2/2019), pp. 69 – 77. – DOI: 10.5281/zenodo.3559035, 2019.

TECHNOLOGICAL ASPECTS OF ANAEROBIC WHEY FERMENTATION

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ABSTRACT

Whey is an important by-product of milk processing, a source of wastewater pollution and, at the same time, has significant potential for biogas production. The main technological aspects of methane fermentation of whey were investigated in laboratory conditions with the help of original methods. The study results can be applied to a continuous industrial method of whey anaerobic fermentation. The chemical composition of whey and fermentation products was determined by standard modern methods of chemical and physicochemical analysis. Fermentation was performed at a temperature of 50 ^{0}C. The dynamics of biogas accumulation and its composition were studied. It is established that there is a possibility of complete fermentation of the secondary product within 10 days with 5% replacement of the substrate content. The amount of gaseous products formed in each cycle was stable and ranged from 14.9 to 17.0 liters per liter of serum. Variation of whey flow rate through the fermentation apparatus is an important factor influencing the quality of biogas composition and completeness of whey fermentation. The best results were achieved with 10% daily substrate replacement. The destruction of lactose in this case was complete. The optimal flow rate in production conditions is a value that corresponds to 20% of the replacement (0.0083 h^{-1}). With the growth of this indicator, an increase in the concentration of lactic acid was studied, which indicates a violation of the methane fermentation process.

Keywords: dairy food waste, anaerobic digestion, methane, whey

INTRODUCTION

Dairy enterprises are potential sources of large amounts of whey and important factors in the hydrosphere pollution. Whey accumulation is increasing from year to year due to the growth of dairy protein production and the widespread introduction of membrane methods of milk concentration. Despite its high nutritional value, whey is rarely used for the production of feed and food products and additives. Almost half of it enters the sewer, which is a serious problem in wastewater treatment. That is why the problem of whey processing does not lose its relevance and is closely related to environmental protection [1, 2, 3, 6].

Under industrial conditions, the problem of whey processing has never been solved by biotransformation using methane fermentation. Products of aerobic fermentation or incomplete anaerobic decomposition of carbohydrates (organic acids, alcohol, lactase enzyme, etc.) were obtained by microbiological processing [1, 2].

The issue of whey processing using methane fermentation was not raised for various reasons. First, the importance of new sources of fuel gas became relevant for Ukraine only after the country switched to an independent path of development. Second, the application of methane fermentation to raw materials containing high concentrations of carbohydrates encounters biochemical barriers (lactose effect, critical concentrations of methane precursors, etc.)[1, 4].

Scientists offer dozens of options for whey processing, among which the undisputed leader is biotechnology. It uses microorganisms, immobilized enzymes, a combination of enzymes and microorganisms. Anaerobic fermentation makes it possible to obtain ethyl alcohol, propionic and acetic acids, riboflavin, etc. from whey. Aerobic fermentation is usually accompanied by the accumulation of large amounts of biomass. Therefore, on the basis of yeast concentrates it is possible to produce a number of feed and food protein products [1, 4].

A special place in biotechnology is occupied by the production of vitamin B_{12}, which is synthesized exclusively by microorganisms, such as the propionic acid bacteria *P.shermanii*. Vitamin B_{12} is also produced by microorganisms of eclectic cultures of methane fermentation [3].

Most studies that have been investigating methane fermentation of whey considered this problem mostly in the periodic version, which to some extent inhibited interest in this unique process due to a number of limitations [6, 8, 9]. A feature of methane fermentation, as is known, is its associative nature that is it occurs under the influence of the microorganisms' association. In monocultures, almost no one was able to do it. The reasons for this have not been fully studied, although much in this regard has become clear thanks to the work of Professor G. Nikitin [11]. The same reasons lead to another, very important feature: methane fermentation, unlike all other types of fermentation, cannot be carried out with a small amount of inoculums, as is customary in other cases. Alcohol or milk fermentation can be carried out with a very small amount of inoculums and even with a single cell of yeast or lactic acid bacteria, although this takes a long time. Methane fermentation in this way is not possible. If a small amount of active culture of methane-forming bacteria is added to the medium, fermentation will take place, but it stops at the stage of acid formation and does not turn into methane fermentation. The explanation of the reasons of such phenomenon is given in the specified works of G. Nikitin. The point is that it is very difficult to carry out the periodic process of methane fermentation for the above reasons. In practice, it is carried out only in a continuous manner, when the ratio of inoculums and the medium being fermented is the opposite of what occurs in all other microbiological processes. The concept of inoculums does not exist here, because it is all the culture fluid in the fermentation tank, and the medium (substrate), which is fermented, is fed into the apparatus in small portions.

However, to determine the approximate parameters of methane fermentation (the rate of medium supply to the apparatus, the amount of formed product, and other indicators by which to judge the course of normal methane fermentation) it is necessary to investigate periodic fermentation.

These parameters can be studied by bypassing the periodic process. You need to find the right amount of active culture fluid, start a continuous process immediately, adding small portions of the fermentation medium. However, this approach does not allow getting any idea about the dynamics of organic matter consumption and the formation of fermentation products. The study of any fermentation or aerobic fermentation begins with a batch process. In the case of methane fermentation, the above difficulties of the batch process can be solved by applying a relatively large number of inoculums.

The purpose of the presented work is to study the main technological aspects of the continuous method of methane fermentation of whey.

METHODS AND EXPERIMENTAL PROCEDURES

The object of research is the quark whey of the enterprise. 15% of activated sludge from methane tanks of urban treatment plants was added to the whey. The mixture was placed in a flask with a water seal and equipment, which is shown in Fig.1.

The fermentation vessel was placed in a thermostat. Acidity was monitored daily (pH 6.5… 7.0). Mass concentrations of lactic and volatile fatty acids, lactose were periodically determined according to the methods [10]. The biogas composition was determined using a Chromatec Crystal 5000 gas chromatograph.

The laboratory installation (Fig. 1) allows determining the amount of biogas released.

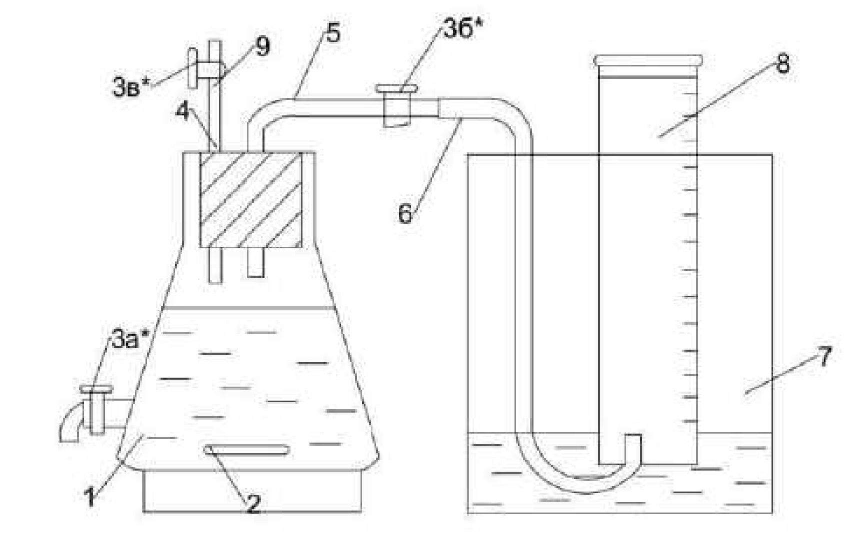


Fig. 1. Scheme of laboratory installation:

1. Flask; 2. Magnetic mixer; 3 a, b, c - taps; 4. Rubber stopper; 5. Glass elbow; 6. Rubber tube 7. Glass cup; 8. Measuring cylinder; 9. Glass tube with tap.

The glass flask 1 contains a magnetic mixer 2. The rubber stopper 4 seals the internal volume and has a hole for the exit of biogas through the elbow 5, the tap 3, and the rubber tube 6 into the measuring cylinder, which is immersed in the water of the glass cylinder 7. The measuring cylinder is filled with water, which when entering the measuring cylinder of biogas is displaced into the cylinder 7. The difference in the height of the columns of liquid in the cylinders is the volume of biogas. The tap 3a is used for sampling the substrate. Tube 9 with tap 3b is designed to supply reagents and whey.

To organize continuous fermentation in the laboratory, we used the original technique. An approach was used to determine the maximum yield of methane without long-term adjustment of the continuous process by the amount of released methane relative to the amount of processed whey. To do this, in the fermentation tank filled with active culture fluid, a minimum whey amount was added, which guarantees complete processing or maximum methane formation. The end of gas emissions indicates this fact. The methane volume relation to the amount of added whey determined its maximum yield. This technique uses a modified periodic process, in which the ratio of the amount of substrate and inoculums is inverse, because it is used in the traditional periodic process. This makes it possible to completely prevent the imbalance between the rate of progenitors' accumulation and the rate of their transformation into methane. In essence, this technique is semi-continuous.

Previous experiments have shown that the minimum amount of whey should be 5% of the volume of culture fluid contained in the fermenter. After each replacement of the contents of the fermentation apparatus with whey, the fermentation at 50 °C lasted 6-8 hours, as indicated by the cessation of gas formation. During the research, the primary amount of sludge was completely removed, that is, methane fermentation occurred due to activated sludge, which was fully formed from the beginning of the experiment. This proves that the implementation of normal methane fermentation of whey is possible in a continuous manner.

THE RESEARCH RESULTS AND DISCUSSIONS

To find out the oriented technological indicators of any fermentation, it is known that a periodic process is carried out. In the same way, research on the technology of total wastewater treatment is carried out.

The obtained results are not given, because effective methane fermentation of whey in a periodic way could not be obtained. The design of these results in the form of tables and figures did not make sense, because the results (parameters) of fermentation were not typical for methane fermentation. We present these data as a brief description. It is known that the intensity of methane fermentation depends on the amount of microbial biomass used as inoculums. For different types of fermentation, this pattern is different, and to start fermentation requires a different amount of inoculums. Methane fermentation in this case is different from all types of fermentation. According to previous experiments and many years of research, periodic methane fermentation on food waste can be carried out using activated sludge as inoculums in an amount of 30% by volume of the substrate. We mean biomass of 75% moisture or sediment after prolonged settling of the culture fluid. According to the modern theory of the mechanism of methane fermentation, this is explained by the fact that at high substrate content relative to the number of methane producers, the balance between the rate of accumulation of precursors and the rate of their transformation into methane is disturbed. In the presence of carbohydrates as a source of nutrition, the intensity of fermentation increases sharply compared to what happens on mixed substrates that contain protein, amino acids, organic acids and more. Ignorance of the mechanism of methane fermentation led early researchers to erroneous views on the physiology of these microorganisms. It is natural that the presence of large amounts of lactose in the whey (in the absence of other carbohydrates) creates problems with periodic methane fermentation. At low concentrations of lactose (in previous experiments) we were able to carry out the process of methane fermentation, although with a long duration of culture. In experiments with natural whey, this was not possible for obvious reasons: the intensity of the accumulation of methane precursors did not compare with the rate of methane formation. However, from experiments on periodic fermentation of natural whey we can conclude that it is of great interest to know the mechanism of biotransformation of various substrates under anaerobic conditions and the physiology of microorganisms that make up the microbial association used in industry. In the fermented culture fluid accumulates mainly lactic acid and VFA, and to the same extent. The accumulation of VFA is the result of incomplete methane fermentation, the deviation of the process towards the formation of acids. However, lactic acid does not belong to the final product of incomplete oxidation, it is only an intermediate metabolite, which is a nutrient substrate for many microorganisms, including methanogens.

Table 1 and Figure 2 show data for a 10-day period of methane fermentation of whey. The whey lactose content was 3.8% (38 g/l). None of the many types of wastewater or secondary raw materials contain so many carbohydrates, which is why anaerobic and aerobic fermentation is much easier to carry out. The high concentration of lactose in the whey was not an obstacle only because the introduction of 5% whey in the fermenter was diluted 20 times, that is the initial concentration of lactose was only 0.19% (1.9 g/l). The specified amount of carbohydrates in the waste does not interfere with methane fermentation or aerobic fermentation in wastewater treatment.

The amount of gaseous products formed in each cycle was relatively stable and ranged from 14.9 to 17.0 liters per liter of whey, averaging 15.8 l/l. The relative stability of gas formation can be seen in Fig. 1, where the curve of gas formation is almost parallel to the coordinate axis. A slight upward trend of the curve indicates that over time, the activated sludge adapts to the substrate, and the transformation of substances into biogas becomes the most complete. Biogas consisted almost entirely of methane, with about 13% carbon dioxide. Experiments show that the combustion of biogas occurs in the same way as pure methane, which is used in everyday life that is purification of biogas for practical use is not required.

Table 1. Dynamics of biogas formation in the process of methane fermentation of whey (initial concentration of lactose in whey is 3.8%, volume of daily replacement of culture fluid is 5%)

Indexes	The number of replacements of culture fluid with whey									
	1	2	3	4	5	6	7	8	9	10
Volume of the allocated gases, l/l	15.2	14.9	15.0	15.5	17.0	15.8	15.5	16	16.5	17.0
The ratio of CO_2: CH_4, %:%	16:84	15:85	15:85	10:90	12:88	10:90	16:84	15:85	12:88	12:88
The amount of methane, l/l	12.8	12.7	12.8	14.0	15.0	13.5	13.0	13.6	14.5	14.0

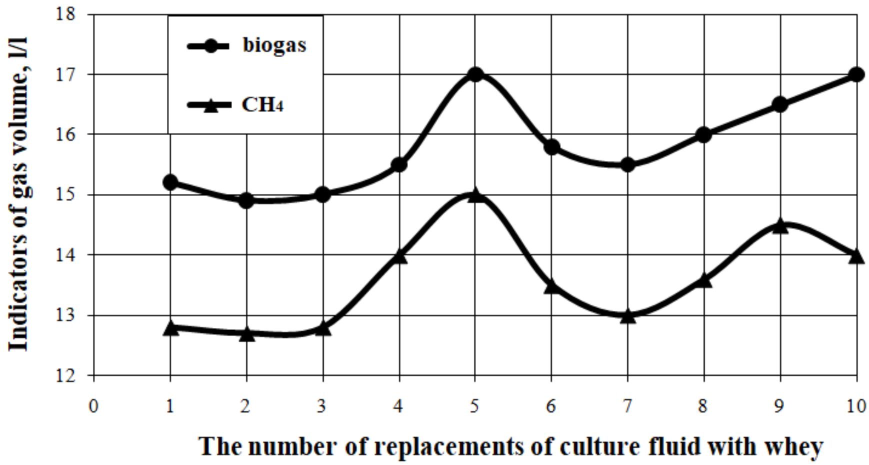


Fig. 2. Dynamics of biogas formation in the process of methane fermentation of whey at minimum flow (D = 0,0021 h^{-1})

Based on the curve in Fig.1, the formation of methane occurs with slight fluctuations. This is due to the instability of the experiments' conditions in the laboratory. This should not be the case in a continuous process in production conditions. Thus, we can assume that methane fermentation of whey produces a significant amount of biogas. This significantly exceeds the biogas yield in the processing of wastewater and various food wastes. On the other hand, the amount of whey is small compared to the amount of wastewater of any enterprise, including dairy. However, the volume of fuel gas obtained only from whey for a plant processing 100 m^3 of milk in dairy production, including cheese, is more than 1500 m^3 per day, that is 1.5 tons of conventional fuel per day or about 45 tons per month . If the plant discharges up to 80 m^3 of wastewater per day, from which up to 4-5 thousand m^3 of biogas can be obtained, then, processing them together (or separately) with whey, it can have up to 180 tons of conventional fuel per month due to biogas production.

The question of how to ferment wastewater and whey, together or separately, is decided for each production differently. In some cases, there may be a situation where it is not economically feasible to build large treatment plants to treat all total runoff. In this case, it is necessary to take measures to separately collect the most contaminated wastewater (for example, from washing technical equipment), mix them with whey and subject to methane fermentation in relatively small devices. Discharge the main amount of total effluent with reduced contamination into the sewage system or treatment plant of a neighboring plant (together with wastewater obtained after methane fermentation of whey). In that case, if the issue of wastewater and whey treatment is solved at one plant, two options are possible: joint methane fermentation, and subsequent aerobic treatment, or separate methane fermentation followed by joint aerobic treatment [8,9].

Given the possible options for processing wastewater and whey, we considered it appropriate to use the basic parameters of methane fermentation of whey to develop a hardware-technological scheme of its biotransformation into methane. The main parameters were the maximum (optimal) flow rate, the concentration of the final products – volatile fatty acids (VFA), lactic acid, biogas, as well as the completeness of lactose fermentation. All parameters, of course, are set at the optimum flow rate. Its excess is accompanied by an increase in the concentration of dissolved end products that is incomplete decomposition of organic matter.

However, the flow below the optimum does not change anything; on the contrary, the parameters obtained at low flow, to a greater extent characterize methane fermentation. It was decided to investigate the parameters at the minimum flow used to determine the yield of methane, after which experiments were performed to determine the optimal flow.

Table 2 and Figure 3 show the studies' data of the parameters of the whey methane fermentation.

Table 2. Change in the main indicators of methane fermentation of natural whey

($D = 0.0021\ h^{-1}$)

Lactose, g/l		VFA, g/l		Lactic acid, g/l		Biogas, l/l			
initial	final	initial	final	initial	final	the total number	the ratio of $CH_4 : CO_2$, %	CH_4	CO_2
38.0	–	0.6	3.8	10.9	0.8	15.8	88 : 12	13.9	1.9

The content of dissolved end products is typical for methane fermentation in general, regardless of the substances nature: the concentration of VFA is 3.8 g/l, the one of lactic acid is 0.8 g/l. In works on methane fermentation, in most cases, there are data on the concentration of VFA (or acetic acid) within these limits. Lactic acid in our experiments was less than is known from the literature. This indicates the completeness of the transformation of all whey substances into methane, which is likely with a minimum flow in the fermenter per unit time. The complete transformation of lactose at its high initial content is very important. It should be noted that the traditional notion of the initial concentration of the substrate in wastewater or other fermentable medium is contradictory.

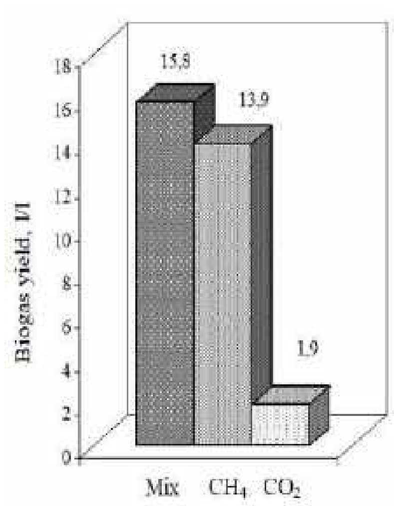
On the one hand, the initial concentration of substances is that which is contained in the fermentation medium before fermentation, the final concentration is that which remains after processing. On the other hand, this does not correspond to what happens in the methane tank: the concentration of substances there is never equal to what we call the initial [3, 9].

Only at periodic process the initial concentration of lactose, for example, in our experiments made 38 g/l (taking into account the certain cultivation according to volume of inoculums). In a continuous process, the initial concentration of the substrate that enters the apparatus, that is the culture fluid, depends on the flow rate. In our case, at 5% daily replacement that is at introduction of only 5% of whey to volume of liquid in the fermenter only a part of lactose from its initial content in whey is brought in culture liquid. In a real continuous process, when the substrate enters the fermentation vessel without a break, it is generally problematic to talk about the initial concentration of the substrate in the culture fluid. Substances that arrive at the optimal flow are immediately converted into the final product that is in the fermentation apparatus a constant balance is maintained between the amount of substances entering and those that are converted into products.

Under optimal conditions, this balance is zero, because in the culture fluid should be neither the initial nor the final concentration of the substrate (lactose or other substances). When conditions change (increase in flow above optimal), this balance shifts toward increasing the concentration of substrate in the culture fluid. It is impossible to consider it initial or final concentration. The theory of continuous processes is far from fully understood.

The average amount of emitted gases in these experiments was the same as in previous ones, with a slightly different ratio of CH_4:CO_2. Figure 3 shows that the amount of methane is close to the total amount of gases.

Thus, the obtained results give a general idea of the indicators of methane fermentation in relation to the concentration of dissolved end products and biogas. The main criterion for the development of proposals for the hardware-technological scheme is the optimal flow rate.
Since the simulation of continuous fermentation in the laboratory was carried out by the method of addition with simultaneous selection of the substrate, different variants of the flow rate were determined by the daily amount of whey fed to the fermenter as a percentage of the culture fluid volume in the apparatus. It was accepted 10, 20 and 30% (given that 5% replacement has already been carried out in previous experiments). In terms of the parameters of the continuous process, the flow rate was respectively 0.0042; 0.0083 and 0.0125 h^{-1}. It should be recognized that the common technique to reflect the flow rate in such units in laboratory studies, where the actual flow is not possible, is not entirely true.



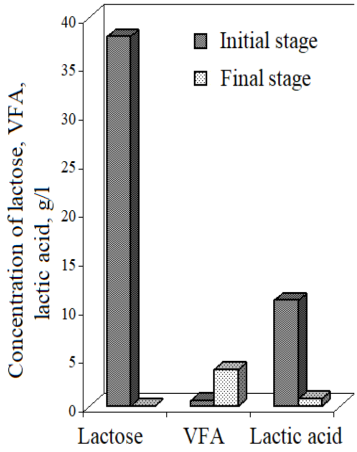


Fig.3. Change in the main indicators of methane fermentation of natural whey

Table 3 and Figure 4 represent the results of experiments showing an increase in the concentration of the fermentation final products with increasing flow rate.

The experiments were not performed simultaneously, the composition of the whey differed slightly in the initial content of organic matter. It didn't matter much. It is well known that the concentration of the final products in stable methane fermentation does not depend on the initial concentration of organic matter, but on the conditions that ensure the most intensive fermentation.

From Table 3 and Figure 4 it is seen that with increasing flow rate in the culture fluid the residual amount of lactose appears, and then increases. In relation to VFA the table and columns of the diagram show sharp increase in their concentration in increase process in flow rate. It should be noted that the VFA concentration at 6.0 g/l is close to the typical characteristics of methane fermentation of various substrates (in the case of 20% replacement), but the value of 11.0 g/l indicates that this mode (30% replacement) is unfavorable for practical use.

Table 3. Change in methane fermentation at different flow rates, D

Flow rate, D, h^{-1}	Change of indicators								
	Lactose, %		VFA, g/l		Lactic acid, g/l		Biogas, l/l		
	initial	final	initial	final	initial	final	total	CO_2 : CH_4	CH_4
0.0042	3.5	-	1.5	4.5	6.0	1.0	15.8	15 : 85	13.43
0.0083	3.8	0.1	1.8	6.0	5.5	4.8	15.0	15 : 85	12.8
0.0125	3.0	0.5	1.2	11.0	5.8	6.2	14.6	60 : 40	5.84

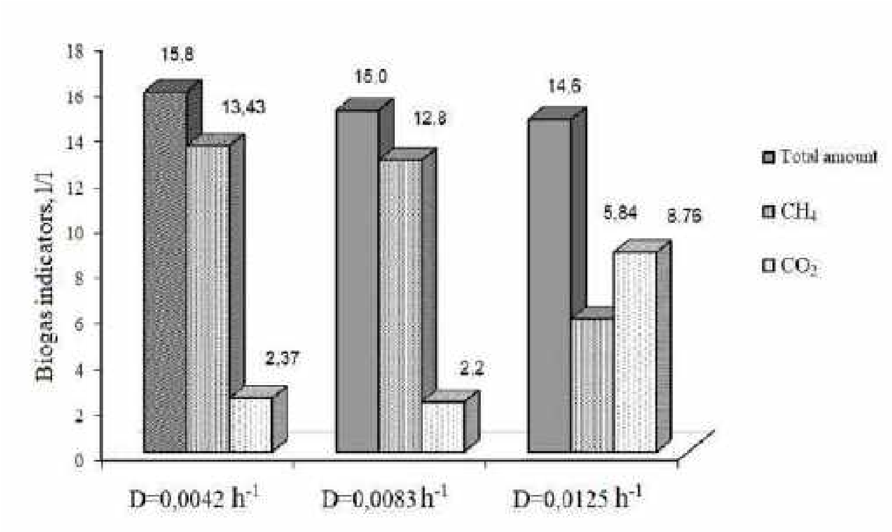


Fig. 4. Formation of gases in the process of methane fermentation of whey at different flow rates, D

With flow rate increasing, significant changes occur in relation to lactic acid. This is especially clear in the diagram. At 10% replacement its destruction is almost complete, at 20% replacement the final concentration of lactic acid is acceptable for typical methane fermentation, at 30% replacement the increase in lactic acid concentration, even compared to its initial content, indicates a clear violation of methane fermentation that leads to resynthesis of lactic acid.

Summarizing the data from the main parameters, we can conclude that the most likely optimal flow rate in production conditions is the value corresponding to 20% of the replacement (0.0083 h^{-1}).

The most pronounced characteristic of methane fermentation at different flow rates is the amount of formed gases and the content of methane in them (table 3). Methane fermentation at a flow rate of 0.0042 and 0.0083 h^{-1} occurs with very close indicators of the amount and composition of gases. The diagrams constructed from these data differ little from each other. A further increase in the flow rate dramatically changes this picture. The total amount of gases is almost the same as in other versions of the experiments, but the ratio is significantly different: the concentration levels of methane and carbon dioxide change places. The amount of CO_2 is close to the methane amount in the previous versions, and the amount of methane, on the contrary, decreases in the same proportion.

The study of any aerobic fermentation begins with a batch process. In the case of methane fermentation, the above difficulties of the periodic process can be solved by using a relatively large number of inuculums, which is 30% of the volume of the fermentation medium.

It should be noted that this technique does not always lead to a positive result that is the probability of methane fermentation in this case is small. Methane fermentation that has begun is easy to determine by the methane release or more simply by the pH value, which should not be below 7.0. This means that fermentation does not deviate in the direction of acid formation, but occurs with the formation of neutral or alkaline products characteristic of true methane fermentation.

Table 4.1 represents the results that show the change in the main indicators of periodic methane fermentation of wastewater from the dairy plant. Samples were taken during the washing of the equipment, when wastewater pollution was high and amounted to 3100 mg/l by COD. Importantly, the wastewater contained up to 6.0 g/l of lactose.

In this regard, repeated attempts to carry out periodic methane fermentation failed. In this case, its presence indicated that lactose is a constant component of dairy industry wastewater, regardless of the plant profile. Therefore, the study of methane fermentation (as well as aerobic fermentation) should be carried out in wastewater that contains a certain amount of lactose.

Table 1. The main indicators of the process of methane fermentation of dairy wastewater in the periodic mode

Indexes		COD, mg/l	Lactose, g/l	VFA, g/l	Lactic acid, g/l	pH	Gas volume, l/l	The ratio of CH_4:CO_2
Initial		3100	6.0	0.3	2.0	7.2	-	-
After sowing		2900	4.5	0.3	1.5	7.3	-	-
Duration of fermentation, days	1	2100	3.6	0.3	1.4	7.3	0.6	-
	2	-	-	-	-	7.2	2.0	-
	4	1900	3.0	2.6	2.9	7.3	3.2	80:20
	6	-	-	-	-	7.1	3.0	78:22
	8	1500	1.2	4.5	6.5	7.2	1.9	81:19
	10	-	-	-	-	7.4	1.0	-
	12	1100	0.3	5.0	5.4	7.4	0.34	70:30
	14	-	-	-	-	7.4	0.2	-
	16	900	0.0	4.5	3.5	7.4	0.2	50:50

The studied wastewater contained a small amount of volatile fatty acids (0.3 g/l, table. 4.1). Their sources may be different. They are present in natural milk and are partially formed in the process of its processing as a result of the microorganisms' development in wastewater. Lactic acid is always present in the wastewater of dairies, in this case its concentration is 2.0 g/l. The presence of lactic acid in wastewater of any origin is favorable for methane fermentation, because it is easily converted into pyruvic acid, which is one of the precursors of methane.

Methane fermentation did not begin immediately, based on the slight release of methane on the first day of fermentation (table 4.1). However, the reduction of COD in the initial period was very significant – from 2900 to 2100 mg/liter. Probably, this was due to the consumption of lactose, as well as other substances that were not taken into account in these experiments (amino acids, proteins, higher fatty acids). The decrease in COD occurred within 16 days, after which methane fermentation almost stopped, based on the small amount of gases emitted (0.2 l/l). The final COD was 900 mg/l that is wastewater treatment as a result of methane fermentation occurred by approximately 70%. In a continuous process, the degree of purification changes to a greater extent.

In this case, the results of the process of periodic methane fermentation give an idea of how effective it is in relation to the elimination of wastewater pollution in this category.

The final level of COD, based on the data of Table1, due to the presence of volatile fatty acids (VFA), residual lactic acid, as well as unfermented substances not included in these experiments. The main purpose of these experiments was to determine the values of the main parameters that control the process of methane fermentation – COD, the concentration of VFA, lactic acid. The data on the amount of gaseous products and the amount of methane are very useful. In this case, the total volume of gases formed was more than 11 l/l. This is a significant value that has important practical significance.

Based on the data obtained from this series of experiments, it is possible to recommend for practice the flow rate during methane fermentation of whey, which corresponds to 20% replacement that is 0.0083 h^{-1}. In the laboratory, this is the maximum rate, as exceeding it can lead to disruption of the process. Under production conditions, the flow rate guarantees the implementation of continuous methane fermentation without disturbance for an indefinite period of time.

CONCLUSION

Research shows that methane fermentation of whey, which contains a large amount of lactose, can be carried out. Fermentation time does not significantly exceed this indicator for methane fermentation of many wastes from food and other industries. Methane fermentation at a flow rate of 0.0042 and 0.0083 h^{-1} occurs with very close indicators of the amount and composition of gases. Under production conditions, you can expect to reduce the fermentation time and, accordingly, increase the flow rate. This is close to the characteristics of methane fermentation of wastewater in most food industries.

Methane fermentation of whey can be a significant source of fuel gas. According to the calculations of each m^3 of whey, you can get about 15 m^3 of methane. Given that the main number of ways of processing whey are laboratory developments (except for the production of lactose and galactose-glucose syrups), it can be considered that the creation of biotechnological processing of whey as a secondary raw material for biogas is appropriate.

In conditions of fuel gas shortage, complex processing of whey into methane, with simultaneous wastewater treatment, should take one of the leading places in the direction of food raw materials recycling.

Further prospects for research in this area can have a significant effect on the use of membrane bioreactors for the concentration of biomass and removal of fermentation products and their purification.

REFERENCES

1. Demirel, B., O. Yenigun. Anaerobic treatment of dairy wastewaters: A review. Process Biochem.,2005, pp 2583–2595.

2. Martin J.N. A comparison of dairy manure management with and without anaerobic digestion and biogas utilization , 2003,pp 35-58.

3. Desai, M., and D. Madamwar. Anaerobic digestion of a mixture of cheese whey, poultry waste and cattle dung: A study of the use of adsorbents to improve digester performance/Environ. Pollut.№ 86,1994, pp 337–340.

4. Omill F., Carrido J., Arrojo B., Mendez R. Anaerobic filter perfomance for the treatment of complex dairy wastewater at industrial scale / Water res., №17, 2003, pp 4099-4108.

5. Youn J.-H., Shin H.-S. Comparative performance between temperature-phased and conventional mesophilic two-phased processes in terms of anaerobically produced bioenergy from food waste/*Waste Management and Research.,* 23(1),2005,pp 32–38.

6. Brone I., Allen E., Murphy J. Evaluation of the BMP from multiple waste streams for a proposed community scall anaerobic digestion / Fuel. – Kidlington: Elsevier Sci Ltd., 2011. – Vol. 90. – No. 7, pp. 2404 – 2412.

7. Nadais H., Capela I., Arroja L., Duarte A. Optimum cycle time for intermittent UASB reactors treating dairy wastewater / Water research. Vol. 39, №8,2005, pp 1511-1526.

8. Cai J. Effects and optimization of the use of biochar in anaerobic digestion of food waste / J. Cai, P. He, Y. Wang, L. Shao, F. Lu / Waste Manag. Res. , No. 5, 2015 , pp 409 – 416.

9. Nasir I. M., Ghazi T. I. M., Omar R. Production of biogas from solid organic wastes through anaerobic digestion / *Applied Microbiology and Biotechnology.* 95(2), 2012, pp321–329;

10. Inikhov G.S., Brio N.P. Methods for the analysis of milk and dairy products. Moscow: Food Industry, 1971, 422 p.

11. Nikitin G.A. Methane fermentation in biotechnology. Kiev: High School, 1990, 207 p.

THE OPTIMAL SOLUTION FOR SUSTAINABLE ENVIRONMENTAL DEVELOPMENT

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ABSTRACT

In this section describes a possible classification of modelling the state of the environment with an emphasis on nature-centrism. A new problem studied. The optimal solution for sustainable environmental development is its digital modelling, model verification and forecasting. The main idea is to highlight to the reader possible real solutions for sustainable development and the optimal solution as a cause-and-effect conclusion. Special attention paid to the optimal solution for modelling the state of the environment implements a program of sustainable development, in general, through a balanced combination of green economy, techno-ecology, and responsible society. The corrosive properties section describes the types of environmental modelling: digital; economic, environmental, social; educational and scientific; informational. Examples and implementations given for each type. A new way of purification recommended as digital environmental modelling determined by the quality of computer software and computer technology, industry experts. It is possible to train a specialist in digital modelling of the environment, if the Framework of digital competencies of citizens and the corresponding special competence tasks for their formation introduced into the educational process. A general conclusion made concerning as with a highly qualified master's degree specialist, you can implement the strategy of sustainable development of the state through computer technology, new remote platforms, experimental skills of digitalization of society and the environment in it.

Keywords: Nature-Centrism, Environmental Modelling, Environmental Forecasting, Optimal Solution, Sustainable Development.

INTRODUCTION

In the modern World, the issues of environmental friendliness of the economy and comfortable coexistence of man and nature are relevant. Environmental friendliness of the economy implemented in the Green Economy in general. Comfortable coexistence of man and nature realized through the formation of ecological consciousness. We believe that it is worth implementing modern innovative ways of integration. These are viral marketing on social networks, social advertising about the environment, environmental promotion, educational activities of the environment, economy, society, active motivation of environmental trends in the world, the habit of living without waste and more.

Interesting and new ways to implement sustainable development are managerial influences. This is a psychological attitude to environmental friendliness, the suggestion of attitudes to the excellence of nature, involvement in active environmental lifestyles.

Psychological attitude to environmental friendliness introduced through active advertising in the media. Suggestion of attitudes to the superiority of nature introduced through the purpose of education in a natural direction. Involvement in the active activity of ecological lifestyle introduced through one's own example as imitation, through the provision of special tasks for the implementation and formation of environmental friendliness.

These managerial influences on human consciousness used to accelerate the improvement of the environment and minimal impact. Managerial influences are universal ways of manually controlling the minds of young people for the formation of integrated thinking.

The current state of affairs requires innovative solutions for Sustainable Environmental Development. Trend solutions are the processes of modelling and forecasting the state of the environment. Digital modelling and forecasting of the state of the environment occupy a prominent place among innovative ecological technologies of impact on the environment.

Fashion trends around the World are the use of innovative technologies to digitize the environment. Currently, the trends are digital environmental modelling, digital environmental forecasting, digitalization of environmental management, digitalization of the environment in which people live. New Green Technologies allow increasing the number of green jobs and introducing new equipment, facilities, and production technologies in general.

The World dominated by the Kovid-19 Pandemic, which has forced Humanity to accelerate the formation of Digital Competencies and the introduction of Digital Technologies. Humanity has talked about the Digital Economy, the Digital Environment, and the Digital Society. In general, we are talking about the balance between the Economies, Ecology, and Society in digital format. Sustainable development assessed against the criteria of modelling environmental systems and further forecasting of environmental conditions. This is the Optimal Solution for Sustainable Environmental Development.

There are many solutions for Sustainable Environmental Development. There are 17 sustainable development goals. The realisation of these goals guarantees the Sustainable Development of the Environment. These are the goals. Identified 17 Sustainable Development Goals [1]:

1. End poverty in all its forms everywhere

2. End hunger, achieve food security and improved nutrition and promote sustainable agriculture

3. Ensure healthy lives and promote well-being for all at all ages

4. Ensure inclusive and equitable quality education and promote lifelong learning opportunities for all

5. Achieve gender equality and empower all women and girls

6. Ensure availability and sustainable management of water and sanitation for all

7. Ensure access to affordable, reliable, sustainable and modern energy for all

8. Promote sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all

9. Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation

10. Reduce inequality within and among countries

11. Make cities and human settlements inclusive, safe, resilient and sustainable

12. Ensure sustainable consumption and production patterns

13. Take urgent action to combat climate change and its impacts

14. Conserve and sustainably use the oceans, seas and marine resources for sustainable development

15. Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss

16. Promote peaceful and inclusive societies for sustainable development, provide access to justice for all and build effective, accountable and inclusive institutions at all levels

17. Strengthen the means of implementation and revitalize the Global Partnership for Sustainable Development

However, the best solution for the implementation of Sustainable Environmental Development, we see a balance between the Economy, Ecology, Society.

Of course, the integration of the natural sciences best seen in the study of nature. The natural sciences focused on the study of the laws and regularity of nature. Next, humanity must use the laws and regularity of nature to live comfortably in the World. Ecology is a multifaceted natural science that is able to realize the comfortable coexistence of man and nature. Economics as a science shows the patterns of capital growth from natural and human factors. Sociology as a science studies the lives of people in various spheres of residence.

METHODS AND EXPERIMENTAL PROCEDURES

In this section of the monograph, we used theoretical and empirical research methods. Theoretical research methods are the analysis and synthesis of materials, literature, sources. We also used the induction and deduction of literary and Internet resources. The cause-and-effect relationship helped us to choose the Optimal Solution for this study. Modelling and forecasting as research methodology methods implemented 17 solutions in achieving sustainable environmental development.

Empirical methods of this study used for observation, measurement, evaluation, correction, control, and data experiments. These data are both environmental, economic and social bases.

Experimental research methods in this essay focused on the active involvement of students in the observation of natural phenomena, measurement and processing of experimental samples and data, research of natural phenomena, modelling and forecasting of the environment.

Students introduce active experimental research of nature in the performance of laboratory-practical block of studying disciplines of ecological and economic character. Also various practices such as production, field, laboratory, computing. It is also a collection of experimental materials, preparation and public demonstration of results of term papers and qualifying theses.

Natural science, such as physics, chemistry, ecology, biology, economics, requires the superiority of experimental research methods over theoretical research methods. For this reason, we encourage students to be as active as possible in the practical and laboratory workload of hours for the study of nature. Various practices allow you to immerse yourself in the research process, to obtain scientific results. These results presented in the form of term paper, scientific thesis, abstract, articles, and abstracts, materials for conferences, forums, webinars, and symposia. These scientific experimental results publicly demonstrated and discussed. They evaluated by experts. Moreover, form the natural professional competencies of the future specialist.

THE RESEARCH RESULTS AND DISCUSSIONS

In general, the Optimal Solution for modelling the state of the environment implements the program of sustainable development, through balanced combination of green economy, techno-ecology, and responsible society. Integration into each other with the trio as economy-ecology-society will form the optimal system of the environment for a comfortable life of man and nature. Sustainable Development of the country is directly proportional to the sum of development of both the Green Economy, and Techno-Ecology, and a Responsible Society. This is the ideal formula for the formation of any state in the World. Word, that seeks harmonious development.

The Green Economy in the Sustainable Development of the state is a new direction of the economy, which can replace the Capital Economy. Techno-Ecology in the Sustainable Development of the state acts as a catalyst between old and new equipment, equipment of enterprises, big business, and agriculture. A responsible society in Sustainable Development will bring global development to future generations in an innovative World, a World dominated by Nature is in cooperation, not competition with the Man of the Future.

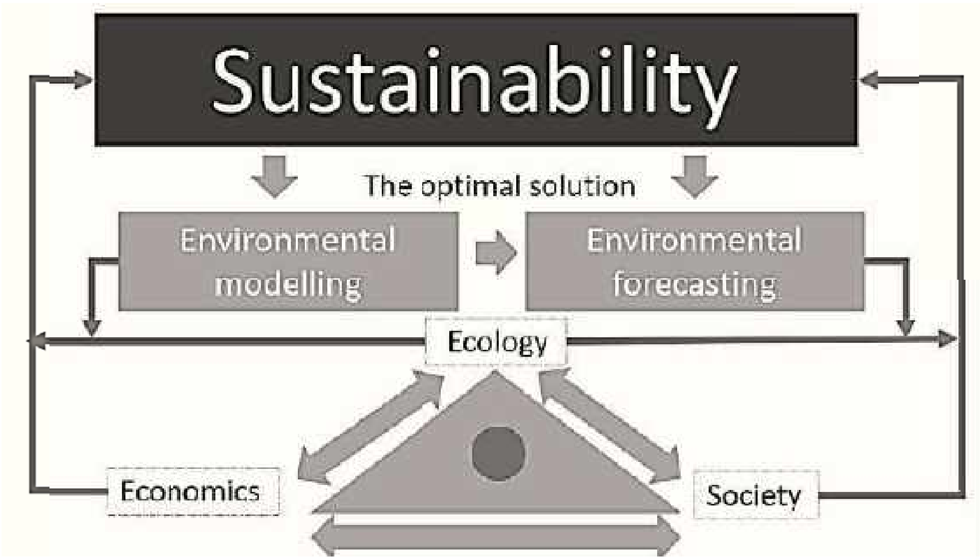

Fig.1. Optimal Solution for Sustainable Development

In general, the Sustainable Development of the World is the Optimal Solution to global economic and environmental problems of civilization. Consider Figure 1.

Modelling the state of the environment is becoming an increasingly normal process of manual control of anthropogenic pressure on Nature. Then, forecasting the state of the environment allows us to anticipate the human factor of influence on Nature and make constructive and optimal decisions of balancing and integration between the Economies, Ecology, and Society to achieve a common goal: Sustainable Development of the World.

Consider the modelling and forecasting of the environment.

In the modern World, all processes first modelled, and then the models are modified, idealized standardized originals and templates introduced into the real life of society. Based on correct models and modelling of process the problem of forecasting of further activity and processes realized. Thus, we have a cause-and-effect type of system construction, which guaranteed to work efficiently in manual mode, taking into account the laws and patterns of animate and inanimate nature. At present, the World is talking about the digitalization of processes. Thus, this idea and its implementation for modelling and forecasting the environment is reliable, effective, and efficient. Computer technology performs the technical work of environmental modelling calculations better than humans do. The main task of a person is to become a competent user of a computer program for modelling and forecasting the environment or its developer.

If you manually influence the environment as atmosphere, water, soil, biota, etc., you can achieve balanced and sustainable development of the economy, ecology, society.

Consider Figure 2 on modelling and forecasting the environment with species relationships.

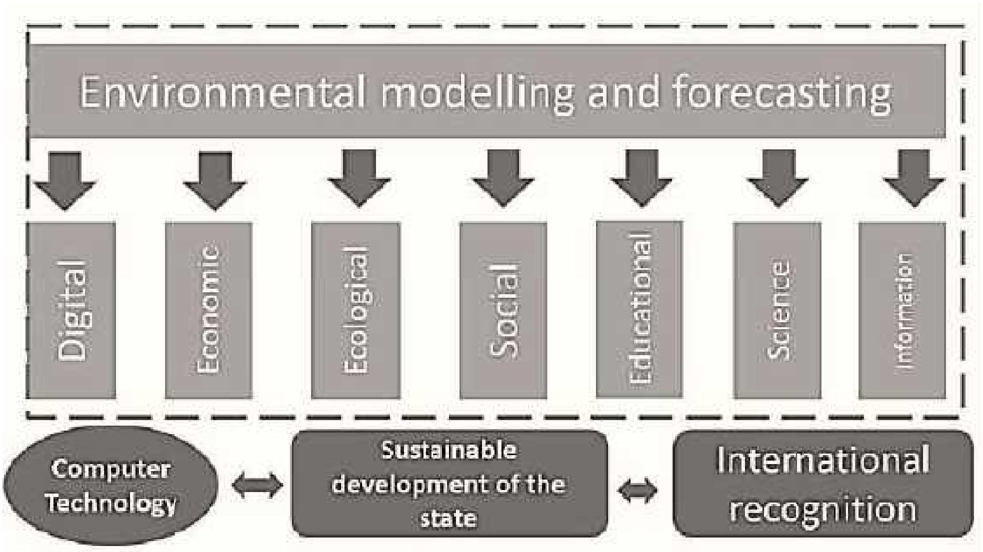

Fig. 2. Environmental modelling and forecasting as species relationships

From the figure 2, we can see that the types of environmental modelling, it`s can be different in function and purpose. These are the following types as digital; economic, environmental, social; educational and scientific; informational. Of course, there are many other types of environmental simulations. However, these types of environmental modelling are hierarchically a priority throughout the World and in Ukraine in particular.

Digital Environmental Modelling determined by the quality of computer software and computer technology, experts in this field. It is possible to train a specialist in Digital Modelling of the environment under the condition of introduction in the educational process of the Framework of digital competences of citizens and corresponding, special, competence tasks for their formation. With a highly qualified master's degree specialist, you can implement the strategy of sustainable development of the state through computer technology, new remote platforms, experimental skills of digitalization of society and the environment in it.

Economic Modelling of the environment determined by the quantity and quality of the introduction of the Green Economy in the modern World, by experts in this field. It is possible to train specialists in this field under the condition of large-scale use of techno-ecologies. Techno ecology has different areas of implementation. We distinguish the following areas of technological ecology's scientific and technological revolution. Its environmental and social consequences. In addition, technological and production processes; techno sphere; industrial production; innovative processes in technologies; greening of production. In addition, material and energy resources of industry; raw. Moreover, Water, air and energy in industry. In addition, techno ecology of production of ferrous and non-ferrous metals; techno ecology of the fuel industry. And techno ecology of the mining industry; techno ecology of mechanical engineering; techno ecology of the chemical industry; techno ecology of energy; technology of construction; techno-ecology of forest, woodworking and pulp and paper industries; techno-ecology of transport; techno ecology of agricultural production; techno ecology of military activity.

As we can see, techno-ecology covers virtually all spheres of human life, and thus, we can influence the modernization of economic change in society.

Ecological Modelling of the environment determined by the integration of techno-ecologies into various elements of the environment, training of specialists in this field. Environmentalists are able to interpret knowledge about the environment, to be carriers and repeaters of ideas for global climate improvement, drinking water quality, waste management, a planet without plastic, veganism and more. The modern ecologist is dynamic to changes in the environment and his knowledge is strong and modern, because this is what the modern World requires. An ecologist balanced between the current state of the environment and the future of an improved environment. The profession of ecologist is relevant in time. An ecologist acts as an organizer of a popular ecological lifestyle, teaches how to handle waste, water, soil, atmosphere, the price of biota, and so on. This profession is trendy and has an innovative meaning of renewing the planet within the framework of natural expediency, combined with the modern economy and modern people.

Social Modelling of the environment is revealed in the social intellect and understanding that Nature and Man are one. Raising the public environmental awareness of people in general is the main task of the sociality of the team of people. Specialists who know how to convey such information are teachers and lecturers. The teaching profession implements the problem of education, upbringing and development of the younger generation, focusing on the new foundations of ecological lifestyle. From the school years, the child writes down truths about nature, about being, about the universe. Then, in high school, teachers deepen and expand the boundaries of knowledge about nature, life, the universe. Thus, a generation of people responsible for nature is being prepared. This is the basis of social modelling of the environment.

Educational Modelling of the environment revealed through environmental education and upbringing in the society of citizens. The younger generation will be fully aware of the importance of ecology in its life, provided the promotion of such a way of life. Educational modelling of the environment forms environmental competencies in the younger generation, in the learning process. Ecological disciplines develop and constitute the worldview of a specialist with elements of ecological provisions. Moreover, such a worldview forms the consciousness of the citizen on the balanced use of the economy, ecology and society for sustainable development. Teachers and educators, responsible parents, can do this.

Scientific modelling of the environment involves cause-and-effect construction of work and study of environmental elements for further forecasting. Scientific style of thinking with ecological accents allows treating the environment responsibly. Optimal scientific decisions have a strategic and tactical character in the national security of Ukraine. That is why true scientific statements with emphasis on ecology can carry into society the stereotypes of nature-centrism.

Information Modelling of the environment provides a large database of environmental data from around the world and its free use for the accuracy of processing experimental data on ecology, building a clear model of the environment, forecasting the state. Digital informatisation of the environment is trending in terms of content around the world due to the accessory flow of information from various sources during the Pavid-19 pandemic. Digitalization of the environment is possible by manual control of anthropogenic load and natural opportunities. This correlation leads to a cause-and-effect relationship between information technology and nature-centrism in general.

Consider Figure 3. We have provided a correlation analysis of the relationship between environmental modelling and the guaranteed result: stable balanced sustainable environmental development.

The trinity of components of sustainable environmental development: economy-ecology-society is the optimal solution for modern innovation trends in these industries.

For the economy-ecology duo, the optimal solution for Sustainable Development will be a Green Economy with the use of new techno-ecologies. For the duo ecology-society, the optimal solution is the formation and formation of ecological consciousness of the population. In addition, here it is important to lay in the standards of education and science environmental provisions for the psychological attitude and suggestion of attitudes. For the economy-society duo, the optimal solution is the Digital Economy of Humanity. Here it is important to master, form and develop digital competencies of the individual to involve him in professional activities.

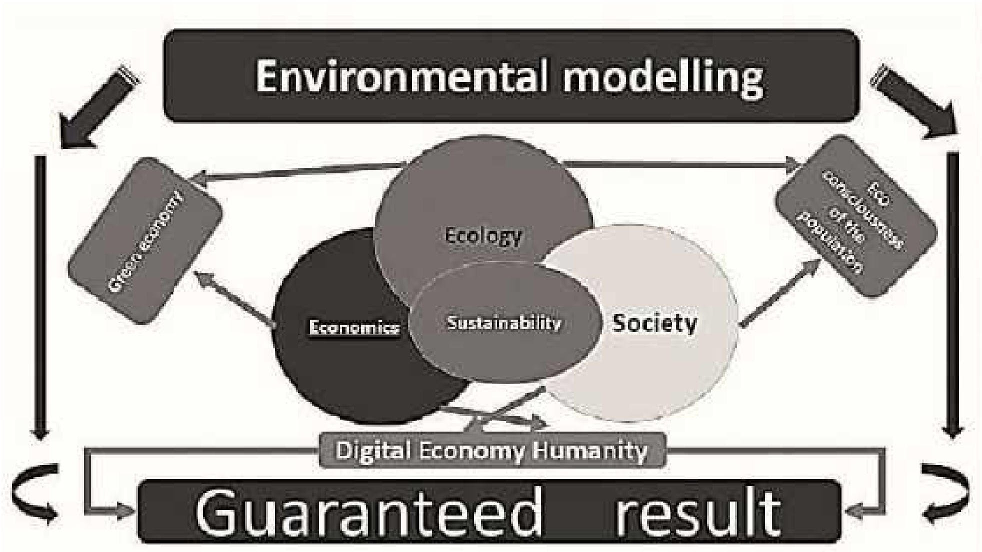

Fig. 3. Modelling of the state of the environment in correlation with the guaranteed result

Consider Figure 4. As you can see, schematically presented a variant of the optimal solution for modelling the state of the environment. This decision will lead to the formation and formation of digitalization of the environment, 100% of the result of a quality and clean environment.

It is obvious that the pollution of water, atmosphere, and soil is directly proportional to the pollution of the entire ecosystem, which leads to environmental pollution in general. The optimal solution will be manual control of anthropogenic load: balancing between economy-ecology-society. This optimal solution guaranteed to meet the needs of society in the digitization of the environment in general.

Digital Modelling of the state of the environment - the future of our coexistence with nature and the rational use of its resources, resources, minerals. For now, a lot of mental work is able to perform robotic machines under the control of a professional in the field of digitization. It is worth thinking about future developments of digital environmental models that will be able to service robotic machines under the guidance of a specialist. Universities with specializations: economics, ecology, social sciences with accents of the teaching sphere are able to form such a digitalized specialist. Both engineers and teachers of the digitalized new society are useful in the introduction of professional competencies in the minds of people: the younger generation, youth, and the elderly, ordinary citizens.

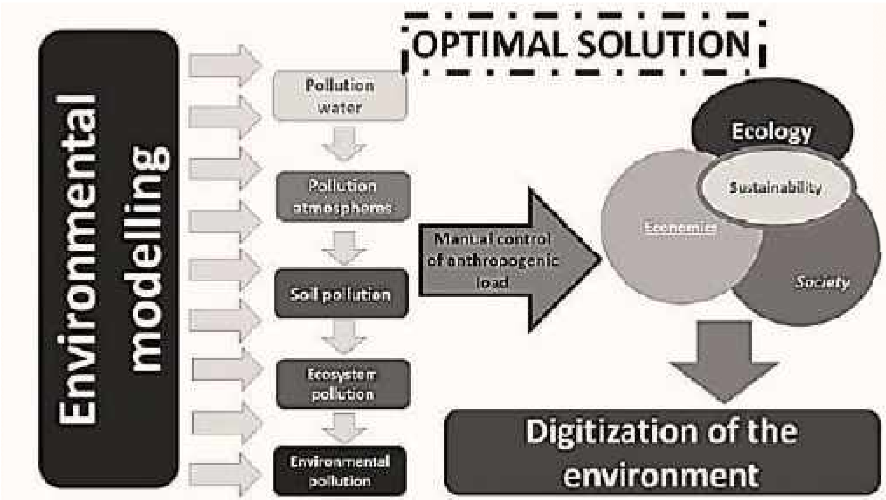

Fig. 4. A variant of the optimal solution for modelling the state of the environment

In order to educate, form and become an engineer or teacher of digital economics, digital ecology, digital social science, it is necessary to rely on managerial influences that fully guarantee the quality of education. These are modern methods of managerial influences: psychological attitude, suggestion of attitudes, and involvement in activities.

Psychological attitude, as a modern method of knowledge management, targets those who want to learn on specific and clear guidelines, determines the route of educational activities. Here, students reveal the main motives for learning and activate the brain to perform further actions.

Suggesting attitudes to the subject as a method of managerial influence helps to promote, actively motivate those who want to learn, imitate successful professional activities, copy the winners, stereotype the leaders of their business, template constructive decisions, inspire self. These are success stories, stories about inventions, explanations of legends, paradoxes, sophisms, explanations of legends, examples of biographies of famous scientists, etc.

Involving those who want to learn as a method of managerial influence focuses on the reflected actions of the mentor, such as "Do as I do… Do better than me ...". It is the active imitation of a mentor, tutor, coach, teacher, teacher, consultant, etc., brings a guaranteed result that the subject of learning will acquire knowledge in the course of practical and experimental activities. And the acquired knowledge will be applied, the individual will be able to apply them in professional activities.

Thus, managerial influences on those who want to learn, allow the optimal solution of the invention of the model of the state of the environment in general, and quality education in particular.

Consider Figure 5.

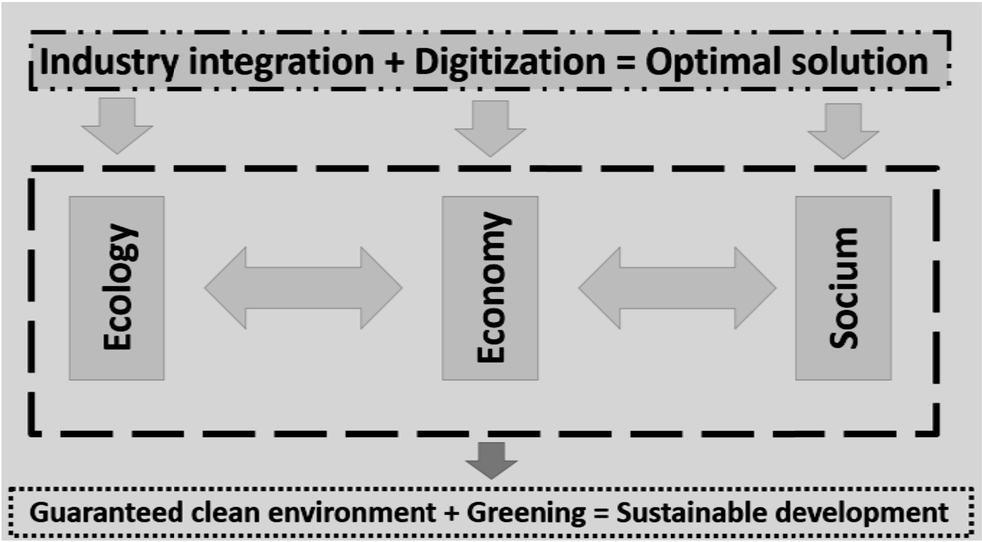

Fig. 5. Guaranteed clean environment + Greening = Sustainable development

As can be seen from Figure 5, the Optimal Solution for Sustainable Environmental Development is the integration of industries such as Ecology, Economics, Society and Digitalization of the environment. At present, the rapid development of society, the environmental friendliness of the economy is a panacea for comfortable living in society. These are new jobs for people. These are new ecological technologies of production, business. This is the formation of the natural consciousness of young people to protect nature. It guaranteed to implement the strategy of sustainable development by implementing the environmental friendliness of the capital economy. Guaranteed result and environmental friendliness reveals the stable development of the state, the world as a whole.

Ecology is an integrated natural science that has only one way to study nature as experimental. There are many methods of implementing an experimental method of studying nature, such as observation, measurement, experiments, and so on. Both ecology and science reveal the limits of nature research in modelling and programming the state of the environment.

Economics is an applied science that also has the method of research experiment priority. The modern economy focuses on the digitalization of capital. This area of the economy is environmentally friendly and new to jobs.

Sociology is the humanities, which has a basic method of research such as observation, followed by measurement and sociological experiment. That is, the method of studying society is experimental as well.

So, combining these three branches of science through an experimental method of research we will get at the break, a new direction of development of the scientific field, for example, stable development of the environment. In addition, this direction combines natural, applied and humanitarian components of the object and subject of research. The common goal is the sustainable development of the environment. Tasks in each field of these sciences are interdisciplinary and the main ones are as follows.

Task 1. Analyse the state of the environment.

Task 2. Identify the global environmental problem.

Task 3. Describe the theoretical concept of the environment.

Task 4. Develop a model of the environment in three areas such as ecology, economics, and society.

Task 5. Verify the obtained model of the environment.

Task 6. To specify the received model on experiments.

Task 7. Make a large-scale experiment of the environmental model.

Task 8. Introduce a model of the environment in society and predict conditions.

Task 9. Make timely conclusions to adjust the model, continuous environmental monitoring on this model.

Task 10. Conclusions and suggestions for further activities in environmental development.

Based on these integrated tasks it is possible to solve the problem of integration of three directions, such as ecology, economy, and society. These common tasks will help to build an integrated ideal model of the environment through the balance of ecology, economy, and society.

Considering the five figures, it is obvious that a triune model of the environment can be theoretically describe in concept. Digitization of the environment helps to implement a theoretical model into a practical, human-driven, original ideal standard of the environment in which we want to live. When there is a theoretical standard of the environment, then comparing the existing environment with the standard, we can adjust; verify the model to the ideal state of the environment.

Drawings help us to see obvious objects focused on a specific task, such as the idealization of the environmental model through ecology, economy and society. The standard of the environmental model reveals the manual management of the environment and its correction, control, verification. Constantly monitor the reference model for changes in environmental, economic and social factors. Among the environmental factors are climate change, sustainable development. Among the economic factors are the green economy and the economy of capitalism. Among the social factors is a personality-oriented approach and collectivism.

CONCLUSION

Sustainable development serves as the optimal solution for modelling the state of the environment. The subsequent model of the environment varied to the minimum error and received original model of the concrete environment guaranteed effectively predicted and qualitatively used under the condition of nature-centrism.

We see that the integration of scientific natural branches has a clear development. The greening of the environment guaranteed to contribute to the introduction of new economic directions of capital and the development of the society in which we live. Balance and integration of economy, ecology in a society of people has the optimum decision for constant development of environment.

The Optimal Solution for Sustainable Development of the environment is the integrated application of Ecology and Economy among people. Of course, there are 17 goals for achieving sustainable environmental development. In addition, this is a universally recognized goal of the constant development of the World. However, a simple solution is a balance between new technologies in the economy and the optimal impact on Nature. People are defenders of Nature. People respect the laws of Nature. People explore them. Nevertheless, for useful purposes use natural resources for social welfare.

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REFERENCES

1. Sustainable Development Goals and Ukraine, 2015. [Electronic resource] : https://www.kmu.gov.ua/en/cili-stalogo-rozvitku-ta-ukrayina-eu

2. The Best European Practices for the «Water Security» Platform to Achieve the Goals of Sustainable Development, 2018-2021. [Electronic resource] : https://watersecurityproject.chmnu.edu.ua

3. Kamianets-Podilskyi National Ivan Ohiienko University, 2021. [Electronic resource] : http://kpnu.edu.ua

4. Water Security: Monograph. Issue 2. – Mykolaiv: PMBSNU – Bristol: UWE, 2021. Editors: prof. Olena Mitryasova & prof. Chad Staddon. – 444 p.

RECULTIVATION OF DISTURBED LANDS DURING THE LIQUIDATION OF SLUDGE STORAGE LIMITED LIABILITY COMPANY "OCEAN SHIPBUILDING PLANT"

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ABSTRACT

The article highlights the requirements of the legislative and regulatory framework for land recultivation. A brief description of galvanic production and projected sludge storage activities is presented. The purpose of the sludge storage is determined: temporary storage of liquid industrial waste of galvanic, electrode and acetylene production. The further inexpediency of operation of sludge storage in connection with reorganization of technological processes is substantiated. Attention is focused on the scientific and organizational principles of development of the project of recultivation of disturbed lands. The volume of waste in the sludge storage was estimated; chemical composition and hazard class of waste stored in the sludge storage. The hazard class of waste according to the content of exchange forms of heavy metals is determined. The choice of recultivation methods is substantiated. The organizational component of the work is determined. Work planning has been adjusted. The stages of sludge recultivation measures are analyzed.

Keywords: rational use of lands, recultivation of disturbed lands, land management, galvanic production, sludge storage

INTRODUCTION

The industrialization of society, the intensification of the agricultural sector of the economy, the development of new technologies, the creation of new materials leads to increasing human intervention in the life of nature. This is manifested in the consumption of natural resources, on the one hand, and on the other - in the generation of waste that enters the natural environment. Galvanic production is no exception to this pattern.

In general, galvanic production is developing in accordance with technical progress, is used in many traditional and new industries, one of which is shipbuilding.

The advantages of electrochemical technologies for processing metallic and non-metallic materials are the ability to fine-tune the structure and thickness of the resulting surface films, electrodeposition of such alloys and composite coatings, which can not be obtained by other methods, uniform surface treatment on protrusions, holes and depressions.

At the same time, an important aspect of the application of galvanic production is its environmental hazard. The use of various chemicals, including heavy metals, raises the issue of waste disinfection, reducing their amount or their complete exclusion, which should be addressed in the development and implementation of technological processes.

Recultivation of disturbed lands at machine-building enterprises is part of the problem of rational use of natural resources and environmental protection. There is a constant increase in the area of disturbed land plots within the industrial sites of enterprises. Therefore, the issue of restoration of disturbed lands in Ukraine is quite relevant and requires state regulation.

The choice of the method of recultivation and implementation of its stages requires a comprehensive comparison taking into account economic, environmental, social and technological factors.

Recultivation is considered as a set of two successive stages: technical and biological. At the end of the XX century, the concept of the technical stage of recultivation was formulated as a preliminary stage in the preparation of areas after the development of minerals, the end of the life of sludge storage for various types of further development of the territory.

Experts say that the scientific basis of recultivation should be a complex of such geographical sciences as landscape science, biogeocenology, geobotany, plant ecology, soil science, agrochemistry, forestry, phytomelioration and more. Scientists reduce the problem of recultivation of disturbed lands to the solution of two interrelated main tasks - the technical solution to the problem of reclamation of disturbed lands and the formation of a new natural landscape.

Technical recultivation is defined as a cycle of works on forming the surface of landscapes and covering their surface with a fertile layer, forming terraces, stable slopes of quarries, sludge storages, their terracing, strengthening the surface of dumps from water and wind erosion, etc.

The purpose of biological recultivation is to restore the fertility and biological productivity of disturbed lands. This can be achieved in several ways: continuous application of the soil layer on the disturbed lands; cultivation of soils by planting and fertilizing; stimulation - cultivation of soils by introducing bioactive reagents and structuring polymers; cultivation of soils by applying a small amount of soil and planting perennials; cultivation of soils by introducing bioactive reagents and microorganisms.

METHODS AND EXPERIMENTAL PROCEDURES

The purpose of the article is to highlight the scientific and organizational aspects of recultivation of disturbed lands of sludge storage LLC "OCEAN SHIPBUILDING PLANT".

The following tasks were set during the study:

1. Analyze the scientific and organizational principles of recultivation of disturbed lands;

2. General characteristics of the sludge storage of LLC "OCEAN SHIPBUILDING PLANT" to give;

3. Analysis of project activities for the recultivation of sludge storage LLC "OCEAN SHIPBUILDING PLANT".

During the study, the following research methods were used: analysis and synthesis, which allows to determine the scientific and organizational aspects of recultivation of disturbed lands; statistical method used during the processing of statistical materials to assess the volume and dynamics of waste accumulation in the sludge storage; the graphic method was used for the purpose of formation of graphic material concerning project measures of recultivation of LLC "OCEAN SHIPBUILDING PLANT".

REQUIREMENTS OF THE LEGISLATIVE AND LEGAL FRAMEWORK FOR LAND RECULTIVATION

During the construction of the sludge storage, the management of LLC "OCEAN SHIPBUILDING PLANT" used the State Construction Standards B.2.4-2-2005 "Landfills for solid waste" [1]. It was planned that waste from galvanic production of hazard class IV should be stored on the territory of the sludge storage, which corresponds to the hazard class of solid household waste.

The operation of the sludge storage of LLC "OCEAN SHIPBUILDING PLANT" was implemented on the basis of the management of the following regulatory and legislative requirements: the Law of Ukraine "On regulation of urban planning activities" [2]; Law of Ukraine "On Strategic Environmental Assessment" [3]; State Construction Standards B.2.2-12: 2018 "Planning and development of territories" [4]; State Construction Standards-173 "State sanitary rules of planning and development of settlements" [5]; State Construction Standards B.2.3-5-2001 "Streets and roads of settlements" [6]; State Construction Standards B.1.1-14: 2012 "Composition and content of the detailed plan of the territory" [7], GOST 17.5.3.04-83. Conservation. Earth. General requirements for land recultivation [8].

Now, when the main activity of LLC "OCEAN SHIPBUILDING PLANT" has changed and the need for sludge storage has disappeared, there is a need to implement recultivation measures for disturbed lands of sludge storage.

Land legislation stipulates that lands are subject to recultivation, which have undergone changes in the structure of the terrain, the ecological condition of soils and parent rocks and in the hydrological regime due to mining, exploration, construction and other works. In this case, before the start of these works, the working project is developed and approved in the prescribed manner with the mandatory involvement of government agencies.

According to Article 166 of the Land Code of Ukraine [9]:

1. Recultivation of disturbed lands is a set of organizational, technical and biotechnological measures aimed at restoring soil cover, improving the condition and productivity of disturbed lands.

2. For recultivation of disturbed lands, restoration of degraded lands, soil is used by applying it to unproductive areas or areas without soil cover, which is removed during mining, exploration, construction and other works.

According to Article 52 of the Law of Ukraine "On Land Protection" [10]:

1. Lands that have undergone changes in the structure of the terrain, the ecological condition of soils and parent rocks and in the hydrological regime due to mining, exploration, construction and other works are subject to recultivation;

2. Recultivation of land plots is carried out by layer-by-layer application on low-yielding land plots or plots without soil cover of the removed soil mass, and if necessary - of the parent rock in the order that ensures the highest productivity of reclaimed lands;

3. Works on removal, storage, preservation and application of soil mass on the disturbed land plots shall be carried out at the expense of natural and legal persons, on whose initiative or fault the soil cover is disturbed. Works on application of the removed soil mass on unproductive lands are carried out at the request of owners or land users, including tenants, of these land plots at their expense.

At the enterprise level, the procedure for waste management is regulated by departmental regulations, including general guidance documents. But a significant breakthrough in the regulatory framework was approved by the state sanitary norms DSanPiN 2.2.7.029-99 "Hygienic requirements for the management of industrial waste and determining their class of danger to public health" from 01.07.1999 № 29 [11].

Also, the Ministry of Regional Development, Construction and Housing of Ukraine plans to revise state building codes for the design of industrial waste landfills. The new normative document plans to introduce a number of modern solutions and technologies for industrial waste management, which are used throughout the civilized world and are aimed at improving the environmental situation on the planet.

Therefore, the new normative document plans to prescribe the requirements for mandatory recultivation of landfills after the end of their service life or in the absence of the need for their further operation in order to create a safe and pleasant environment in places where landfills were previously located.

THE RESEARCH RESULTS AND DISCUSSIONS

Brief description of galvanic production and projected sludge storage activity.

Galvanic production is an electrochemical method of applying metal and chemical coatings on a material to give it certain properties: protective anti-corrosion, protective-decorative, decorative, special: antifriction, to give hardness, wear resistance.

The technological process is implemented in galvanic baths, where the process of coating metal products takes place (Figure 1).

Pollution from the technological process is divided into phases: liquid, solid and gaseous.

Liquid contaminants are wastewater that is formed as a result of washing parts and equipment, as well as processing and replacement of spent electrolytes.

Solid waste is generated mainly in the processes of wastewater treatment or concentrated electrolytes.

Gaseous gases are toxic gases, vapors, aerosols and air-gas mixtures released in technological processes both in galvanic shops and in sewage treatment plants.

Gaseous waste is generated during machining of parts, during operation of electrolytes, during wastewater treatment, processing of spent electrolytes. But gaseous emissions are not the cause of major environmental problems. However, they are quite dangerous and require disposal.

There are different types of harmful gaseous substances in galvanic waste. Thus, in the process of degreasing parts, vapors of organic solvents, aerosols, alkalis are formed; during digestion - aerosols of acids, various gases (nitrogen oxides). Ammonia, hydrogen cyanide, and aerosols of all electrolyte salts can also enter the atmosphere.

A particularly large amount of gaseous waste is generated in the following cases:

a) the use of highly light components (carbohydrate degreasing compounds, ammonia electrolytes);

b) operation of hot solutions;

c) implementation of chemical and electrochemical reactions with the release of gases; even if the gas itself is not harmful, it carries out droplets of electrolytes, forming toxic aerosols (eg, chromium plating).

Fig. 1. Galvanic bath for coating

When using chlorinated tin, titanium tetrachloride and silicon, keep in mind that they easily absorb water from the air, forming thick fogs. Toxic dust occurs in the processes of polishing, grinding, trimming, sandblasting, as well as stripping of anodes and rods. In the process of preparation of electrolytes, the emergence of dust of organic origin from glue, gelatin is also possible. Solid wastes are mainly insoluble metal compounds, such as sludges after liquid waste treatment, solution filtration products. It is as a result of cleaning that solid waste is formed, which is often buried in a special sludge storage. This also includes anode residues, metal dendrites, dust or powders, insoluble polymer compounds and the like.

Liquid waste. Electroplating uses 30-80% of metals, only 5-20% of acids and 2-3% of water. Everything else goes into wastewater, which becomes the main source of environmental pollution by toxic substances. In the case of insufficient wastewater treatment, the entire ecosystem is polluted: water bodies > soil > flora and fauna > man.

Sludge storage of LLC "OCEAN SHIPBUILDING PLANT" is intended for storage and temporary storage of liquid industrial waste of galvanic, electrode and acetylene production.

According to the project documentation (Figure 2), the site is located in the south-eastern part of the territory of LLC "OCEAN SHIPBUILDING PLANT", which is surrounded by a concrete fence, behind the open site of shop № 11, at a distance of 200 m west of the Bug estuary, 60 m south of concrete fence of the plant, 120 m to the east of the fire and rescue unit №7.

The site has a natural depth of 2 m from the surface of the terrain, which was used during the works. A layer of soil with vegetation was cut along the bottom of the site and the bottom and slopes were planned. The soil surface is rolled: the density of the base should provide a deformation modulus of 50 kg/cm. The planned and rolled surfaces were treated with an aqueous solution of the herbicide of continuous action. The bottom of the site is covered with 0.2 mm polyethylene film in 2 layers and covered with a layer of sand 500 mm thick. Slopes are covered at an angle of 40o, covered with polyethylene film in 2 layers, filled with moist soil at an angle of 60o and reinforced with concrete panels PG 60.12-2-L.

The site measures 210 × 51 m. It is surrounded by a barbed wire fence. There are 2 pits for storage and temporary storage of industrial waste measuring 36 × 42 m (S=1512 m^2) and 60 × 42 m (S=2520 m^2).

Trapezoidal embankment from the soil with bases of 3000 mm and 500 mm, height 1000 mm was made along the perimeter of the pits. The separation of industrial waste storage sites is based on the annual volumes of waste and their chemical composition: galvanic sludge (neutral medium), carbide sludge (alkaline medium), electrode production sludge (alkaline medium).

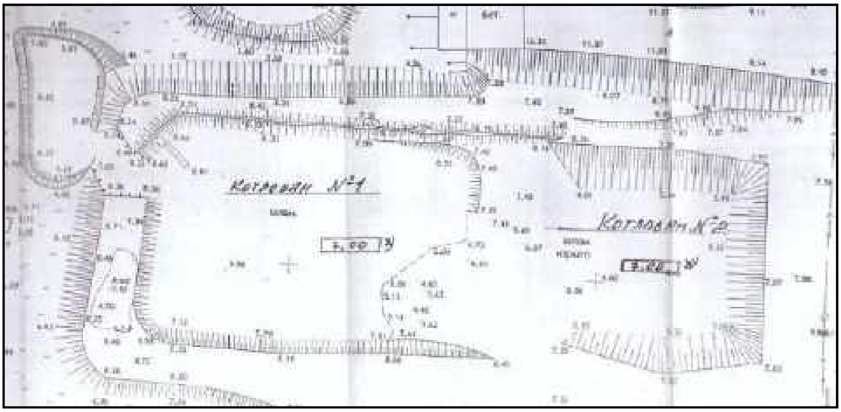


Fig. 2. Map-scheme of the sludge storage LLC "OCEAN SHIPBUILDING PLANT"

At the neutralization station of LLC "OCEAN SHIPBUILDING PLANT", galvanic sludge is formed, which has the following qualities: pasty, fireproof, explosion-proof, unstable, hazard class 4. Wastes of galvanic productions include neutral or alkaline solutions containing metal hydroxides, neutralized waste which are formed during degreasing of metal surfaces, waste containing liquid glass.

The mass fraction of chemical elements in terms of hydroxide from dry matter is:

- iron hydroxide - 22.6%;

- zinc hydroxide - 3.8%;

- calcium hydroxide - 52.9%.

The galvanic wash water enters the neutralization station, where it is mixed with lime milk in the reactor and thus neutralized. Next, the neutralized solutions enter the carbide-type clarifier, where the deposition of sludge is performed. Illuminated industrial effluents, free from harmful impurities of heavy metals (pH 7.5-8.5), enter the sewer network of the plant, and then enter the municipal sewer system.

The formed precipitate (neutral sludge) enters the sludge storage of the neutralization station with a water content of 96-98%. Then the sludge is taken to the sludge storage by sewage machines.

In the sludge storage water evaporates, galvanic sludge settles to the bottom and should be removed by truck as it accumulates.

Estimation of volume and dynamics of waste accumulation in sludge storage.

Sludge storage of LLC "OCEAN SHIPBUILDING PLANT" is two hollows designed and constructed in accordance with the design documentation (Figure 3).

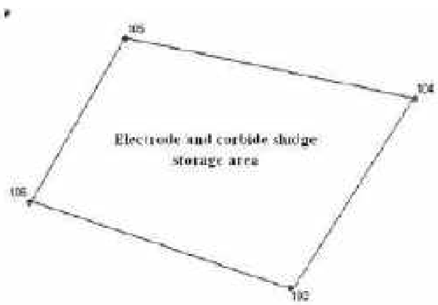
- Site for storage of electrode sludge and carbide sludge

The surface area of the filling area for storage of electrode sludge and carbide sludge is 870 m^2, the perimeter along the upper edge of the filling - 119 m. The absolute height varies within 1 m above sea level. The design filling volume of the Hollow № 1 is 3000 m^3.

Estimated fill volume is:

$$870\ m^2 \times 2{,}0\ m = 1740\ m^3 \qquad (1)$$

According to the test data, the density of the filling material of the hollow for storage of electrode sludge and carbide sludge in the air-dry state is 350 kg/m^3. The volume of the dry residue of the pit filling is about 610 t. The hygroscopicity of the sludge is 38%, respectively the filling volume is about 850 t. The design volume of the pit filling № 2 is 5000 m^3.



Hollow №1

Hollow №2

Fig. 3. Natural and design sites of waste storage

- *Site for storage of galvanic sludge*

The area of the Hollow №2 for storage of galvanic sludge is 1524 m^2, perimeter 166 m. The absolute height of the basin varies within 1 m above sea level. The estimated amount of waste is stored at the site for storage of galvanic sludge:

$$1524\ m^2 \times 1{,}5\ m = 2286\ m^3 \qquad (2)$$

The filling density of the air-dry sludge residue is 708.5 kg/m^3. The volume of dry residue filling the pit is about 1620 tons, hygroscopicity is 24.4%. Taking into account the hygroscopicity, the volume of filling is about 2025 tons.

The material composition of the sludge is determined by the place of formation at certain stages of production (table 1):

- electrode production sludge;

- sludge from phosphating baths (galvanic production);
- sediments of heavy metals (galvanic production);
- sludge from the degreasing process (galvanic production).

Table 1. The composition of the waste sludge

Name of waste	Phase composition	Code	Danger class	Substance composition		Number
				Substance	%	
Electrode production sludge	Liquid	1.48.00	3	Not specified		4500 tons
Sludge from phosphating baths (galvanic production)	Pasty	1.04.00	2	Fe Zn Mn Na P Cl^- NO_3^- pH	26,4 2,6 1,1 0,1 19 0,9 0,9 1,5-2	64.2 tons/year
Sediments of heavy metals (galvanic production)	Solid	1.04.00	2	$Fe(OH)_3$ $Ni(OH)_2$ $Zn(OH)_2$ $Ca(OH)_2$ $Cu(OH)_2$ H_3CrO_3 pH	17 0,2 4 35 0,6 0,5 12.7	108,4 tons/year
Sediments of the degreasing process (galvanic production)	Solid	1.04.00	2	Al Fe Cu Mn Zn Cr Ni PO_4^{3-} CO_3^{2-} pH	19,1 0,7 0,1 0,45 0,6 0,04 0,02 15,3 10,3 12,0	17,2 tons/year

According to the test data in the waste stored and stored in the sludge storage, the mass fraction of chemical elements in terms of dry matter is: iron hydroxide - 22.6%; zinc hydroxide - 3.8%; calcium hydroxide - 52.9% (table 2).

Table 2. Waste toxicity index

Chemical substance	Ingredient weight, t/t	Saturated vapor pressure, mm Hg	Solubility in water, g/100 g	MPC in soil, mg/kg on metal	Danger class	Toxicity index
$Fe(OH)_3$	0.226	0	$2{,}03 \cdot 10^{-8}$	Not regulated	III	605,3
$Zn(OH)_2$	0.038	0	Not regulated	23,0	II	
$Ca(OH)_2$	0.529	0	0,148	Not regulated		

According to calculations of laboratory of the Nikolaev Center "Regional State Fertility" the total toxicity index made 1606,3. Therefore, in accordance with DSanPiN 2.2.7. 029-99 waste is classified as hazard class 3. This conclusion was made on the basis of detection in the filling material of iron sludge (classified as hazard class 3 with organoleptic limited trait), for which the maximum concentration limit in the soil is not regulated, at a concentration of 1501.6 mg/kg.

Project measures for recultivation of sludge storage of LLC "OCEAN SHIPBUILDING PLANT" For the purpose of ecological safety and on the basis of sustainable development of territories, the project envisages recultivation of disturbed lands during liquidation of sludge storage.

When developing measures for the restoration of land are taken into account: the type of further use of recultivated land, the natural conditions of the area of work, location and area of the affected area, the actual condition of the disturbed land.

Before starting work, the engineer-technologist with the master must inspect the areas to be recultivated, to clarify their boundaries, places of arrival of equipment, to understand the location of communications.

Execution of the necessary permits for work, safety briefing, acquaintance of foremen and workers with the location of the areas of communications, delivery of personnel, equipment of the economic unit and delivery of equipment.

- *Technical recultivation*

The purpose of technical recultivation is to bring the land into a condition suitable for further biological stage of recultivation.

The technical stage is aimed at restoring natural conditions close to natural, localization and elimination of damage and unwanted processes, as well as includes preparatory work for biological recultivation.

The duration of the technical stage depends on the production of major works on the elimination of sludge on the basis of relevant design materials and schedules.

Technical recultivation of the sludge storage of LLC "OCEAN SHIPBUILDING PLANT" included the following measures:

- planning of territories;

- cleaning of garbage, materials, as well as all pollutants

- import and storage of soil and vegetation layer;

- planning of soil and vegetation layer.

The main stages of technical recultivation included the following works:

1. Formation of a technological (clay) screen 0.5-1 m thick at the bottom of the hollow, made of polymerized bentonite clay (Figure 4) (experimental batches are produced at the Institute of Environmental Geochemistry of the National Academy of Sciences and the Ministry of Emergencies of Ukraine).

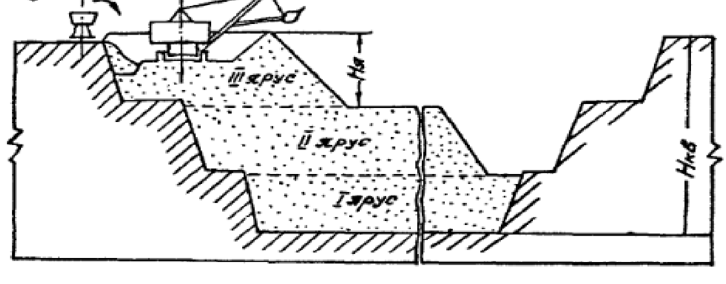


Fig. 4. Technological scheme of recultivation of hollow storage basins

The imported clay was leveled on the bottom of the hollow and compacted with a roller. The volume of clay for the screen was:

- for hollow № 1 V= L*B*h = 60*42*0,5=1260 m^3 (3)
- for hollow № 2 V= L*B*h = 36*42*0,5=756 m^3 (4)

2. Formation of a protective screen. The protective screen was arranged on top of the technological screen. It consists of the following layers (Figure 5):

- recultivation layer not less than 1 m thick, having a layer of fertile soil 30 ... 50 cm thick;

- drainage layer at least 30 cm thick;

- protective fine sand layer at least 20 cm thick;

- a layer of synthetic waterproofing with a thickness of at least 3 mm, resistant to chemical and biological aggression and rodent damage;

- mineral waterproofing layer consists of two layers of compacted clay, with a total thickness of about 1 m. The total filtration coefficient of waterproofing layers (synthetic and mineral) is about 9 m/s.

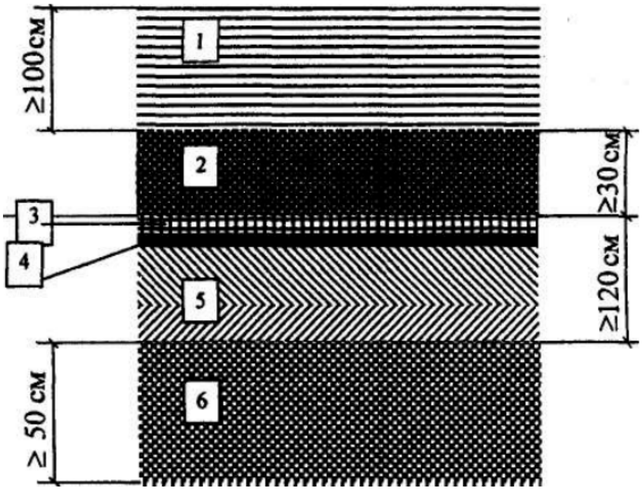


Fig. 5. Scheme of the layered structure of the technological stage of recultivation
Note: 1 - recultivation layer; 2 - drainage layer; 3 - protective layer; 4 - synthetic waterproofing; 5 - mineral waterproofing layer; 6 - leveling layer

The general protective screen was:

- for hollow № 1 V= L*B*h = 60*42*2 = 2630 m^3 (5)
- for hollow № 2 V= L*B*h = 36*42*2 = 1640 m^3 (6)

The hollows were filled in tiers from bottom to top. Tiers were poured sequentially taking into account the period of active shrinkage of rocks. Delivery of material for backfilling took place by road. Use roads on the territory of the enterprise to deliver clay and soil. The soil was leveled with a bulldozer. Layer-by-layer soil compaction was performed with rollers. Recultivation works were carried out in the warm season.

3. *Laying of slopes* during the technical stage of recultivation works was carried out on the principle of "top to bottom" (Figure 6).

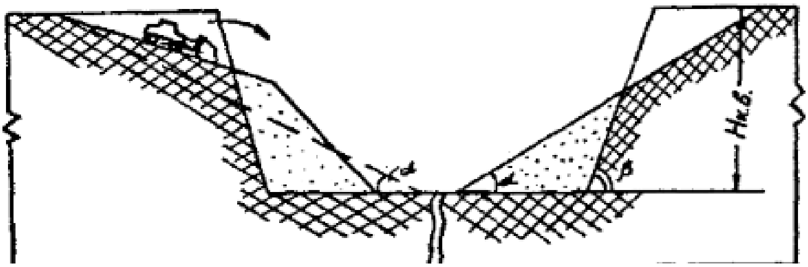


Fig. 6. Technological scheme of laying the slopes of the sludge basins

4. Wrapping the remains of the embankment and its compaction by a bulldozer required an additional volume of soil:

- for hollow № 1 volume amounted to: V= 700 m^3 (7)

- for hollow № 2 volume amounted to: V= 400 m^3 (8)

5. Formation of a leveling layer and gas drainage with a total thickness of about 0.5 m. Soil compaction works were carried out in layers.

Fertile lands were imported by road from places of temporary soil storage. Planning of a surface to a standard slope and its consolidation is carried out by the bulldozer.

Planning work was carried out with machines with low specific pressure on the ground to reduce the compaction of the surface of the recultivated layer. The formed relief has a calm plain character, without potholes and hollows. The surface of the sludge storage sites was leveled to the absolute mark of 7.0. Thus, the goal of technical reclamation has been achieved in full, the land has been brought to a condition suitable for the further biological stage of recultivation.

- Biological recultivation

The main purpose of biological recultivation is to create a secondary ecosystem. The biological stage of recultivation is soil preparation, fertilizer application, selection of grasses and grass mixtures, sowing of grasses, care of crops. The project provides for the creation of a full-fledged soil cover by applying mineral fertilizers and sowing a mixture of grasses after work on the territory. These works were carried out only in the warm season after the snow cover melted.

The biological stage of recultivation includes measures to restore the sludge storage area for further use and is at least 5 years.

At the biological stage of recultivation in order to prepare the soil surface, the project provided for the following measures:

1) small plowing to a depth of 20 cm with a tractor Belarus KO-705. Plowing reduces the number of weeds, loosens and makes the soil softer and more pliable, facilitates further sowing;

2) disking - the use of disk tools (including harrows and trowels) to loosen the top layer of soil.

The applied fertile layer is disposable, this operation is necessary for grinding and loosening the soil.

Disking was performed with a T-4A.01 tracked tractor with a BDT-3 disc harrow.

3) application of mineral fertilizers - was carried out in a previously created recultivation layer superficially, followed by sealing with a rake. The application of mineral fertilizers provided for the provision of recultivation grasses with mineral nutrients in the first period of plant life.

Doses, terms and methods of pre-sowing fertilization were determined taking into account soil and climatic conditions and biological characteristics of grasses.

Surface application technologies were used for pre-sowing fertilization. Fertilizers were evenly distributed on the soil surface and laid in the soil.

When making preference was given to convenient fertilizers in complex application, containing nitrogen, phosphorus, potassium in a form accessible for rapid assimilation by plants.

According to research, the soil imported to the sludge storage is a medium soil. The following fertilizer application rates were used to create grass stands: nitrogen - 30 kg/ha, phosphorus - 60 kg/ha, potassium - 60 kg/ha.

Mineral fertilizers were applied by a T-4A.01 tracked tractor equipped with an NRU-0.5 sprayer. Fertilizers applied to the soil were laid with disc harrows to a depth of 0.06 m. The uniform distribution of chemicals and the recommended application rate were maintained.

4) surface harrowing is loosening of the surface layer of soil with harrows and rotating hoes. Protects the soil from drying out, levels its surface, destroys the soil crust.

A T-4A.01 tracked tractor with a BZTS-1.0 harrow was used for harrowing. The working body of the harrow is rotating disks. The harrow is intended for work on all soils, with soil humidity no more than 35%. Harrow width 3.5 m, cultivation depth up to 12 cm, productivity 0.9 ha/h.

• sowing a mixture of grass seeds in a pre-formed reclamation layer of soil;

• rolling the soil after sowing.

5) selection of the range of perennial herbs (Table 4);

Sowing herbs is necessary for the following purposes:

• rapid consolidation of soils from water and wind erosion,

• restoration of their fertility,

• increasing biodiversity.

Table 4. Arrangement of the upper recultivation layer

Type of recultivation	Height of the reclamation layer	
	Underlying layer, cm	The height of the bulk layer fertile soil, cm
Sowing of perennial grasses	70	30

6) sowing and care of crops. All areas of the sludge storage should be covered with vegetation soil 0.3 m thick with leveling of the surface without compaction. The volume of vegetative soil for the whole area is V = 1760 m^3.

Herbal mixtures of grass species adapted to local conditions were used, which were created by combining species of different life forms: long-rhizome, loose- or dense-bush and plants with a universal root system. The grass mixture simulates the accumulation of plants in natural groups.

Accepted composition of the grass mixture: meadow forest tail (12-14 kg/ha) + meadow fire (6-8 kg/ha) + meadow thyme (4-6 kg/ha). It is to accelerate the processes of turf formation, to restore and form the root layer and its enrichment with organic matter, it was advisable to sow a selected mixture of herbs from several types of herbs.

To increase the germination of seeds before sowing was treated with peat-humic biological product "Flora-C" according to the manufacturer's instructions.

The sowing of the grass mixture on the total area of the hollows №1 and № 2 is S = 5865 m^3. Sowing of grass seeds was carried out in windless weather with a caterpillar tractor T-4A.01, equipped with a spreader NRU-0.5. The main condition is to ensure uniform scattering of seeds.

To preserve soil moisture, ensure friendly grass seedlings, reduce erosion processes after sowing, rolling was used as an effective agronomic technique that provided crushing of soil depths, lumps and crusts, leveling and compaction of the soil surface layer. To do this, used a mounted tool, as a field roller KTR 30.

Measures to care for crops were aimed at forming a stable grassland. That is why over the next five years, the sowing of grasses on bare areas and watering on drying soils is planned.

CONCLUSION

Scientific and organizational principles of recultivation of disturbed lands are aimed at shaping the landscape in accordance with the purpose of the land and socio-economic feasibility. Restoration of disturbed lands and their subsequent use in the economy is focused on the observance of ecological balance, ensuring harmlessness to the natural environment and preservation of local aesthetic values.

Sludge storage of LLC "OCEAN SHIPBUILDING PLANT" is designed for storage and temporary storage of industrial waste of galvanic, electrode and acetylene production. The waste disposal site is located in the south-eastern part of the territory of LLC "OCEAN SHIPBUILDING PLANT". The 210 × 51 m site is surrounded by a barbed wire fence. There are 2 hollows for storage and temporary storage of industrial waste measuring 36 × 42 m (1512 m^2) and 60 × 42 m (2520 m^2). A trapezoidal embankment made of soil with bases of 3000 mm and 500 mm and a height of 1000 mm was made along the perimeter of the pits. The separation of industrial waste storage pits is based on the annual volume of waste and its chemical composition.

The analysis of the factors of the impact of the waste disposal site on the natural environment is assessed as acceptable. The negative impact of local soil contamination was determined within the industrial site. To reduce the negative impact on the geological environment, flora and fauna, it is advisable to implement protective, protective, compensatory, restorative and other design solutions.

Project measures for recultivation of disturbed lands of sludge storage LLC "OCEAN SHIPBUILDING PLANT" are developed in accordance with the norms and rules of environmental protection and environmental safety requirements at all stages of its implementation. The mining stage involves planning the surface of the hollows with a volume of 1260 and 756 m^3, laying the slopes, wrapping the remnants of the embankment. The biological stage includes a set of agrotechnical and phytomeliorative measures aimed at improving agrophysical, agrochemical, biochemical and other soil properties for 5 years. Sow the surface of the cover with lawn grass.

The scientific novelty of the obtained results of the research is as follows: for the first time proposals have been put forward for the development of scientific and organizational measures for the recultivation of disturbed lands of the sludge storage of LLC "OCEAN SHIPBUILDING PLANT". The practical significance of the obtained results is the implementation of the use of recultivation lands of the sludge storage of LLC "OCEAN SHIPBUILDING PLANT".

REFERENCES

1. State Construction Standards B.2.4-2-2005 "Landfills for solid waste" June 17, 2005, № 101, *STATE BUILDING STANDARDS OF UKRAINE*. URL: https://www.minregion.gov.ua/wp-content/uploads/2017/02/Zmina-1-DBN-V.2.4-2-2005-Poligoni-tverdih-pobutovih-vidhodiv.pdf (in Ukrainian)

2. Law of Ukraine "On regulation of urban planning activities" of April 28, 2021, № 31423-IX, *Information from the Verkhovna Rada of Ukraine,* URL: https://zakon.rada.gov.ua/laws/show/3038-17#Text (in Ukrainian)

3. Law of Ukraine "On Strategic Environmental Assessment" of January, 2018, № 2354-VIII, *Information from the Verkhovna Rada of Ukraine*. URL: https://zakon.rada.gov.ua/laws/show/2354-19#Text (in Ukrainian)

4. State Construction Standards B.2.2-12: 2018 "Planning and development of territories" of April 23, 2018, № 100, *STATE BUILDING STANDARDS OF UKRAINE*. URL: http://kbu.org.ua/assets/app/documents/ (in Ukrainian)

5. State Construction Standards-173 "State sanitary rules of planning and development of settlements" of June 19, 1996, № z0379-96, *Information from the Verkhovna Rada of Ukraine*. URL: https://zakon.rada.gov.ua/laws/show/z0379-96#Text (in Ukrainian)

6. State Construction Standards B.2.3-5-2001 "Streets and roads of settlements" of April 11, 2001, № 89, *STATE BUILDING STANDARDS OF UKRAINE*. URL: http://kbu.org.ua/assets/app/documents/dbn2/75.1.% (in Ukrainian)

7. State Construction Standards B.1.1-14: 2012 "Composition and content of the detailed plan of the territory" of October 01, 2012, *STATE BUILDING STANDARDS OF UKRAINE*. URL: https://dbn.co.ua/load/normativy/dbn/1-1-0-1027 (in Ukrainian)

8. GOST 17.5.3.04-83. Conservation. Earth. General requirements for land recultivation of April 30, 1983, № v1521400-83, *Information from the Verkhovna Rada of Ukraine*. URL: https://zakon.rada.gov.ua/laws/show/v1521400-83#Text (in Ukrainian)

9. Land Code of Ukraine of July 24, 2002, № 2768-III, *Information from the Verkhovna Rada of Ukraine*. URL: https://zakon.rada.gov.ua/laws/show/2768-14#Text (in Ukrainian)

10. Law of Ukraine "On Land Protection" of May 27, 2003, № 962-IV, *Information from the Verkhovna Rada of Ukraine*. URL: https://zakon.rada.gov.ua/laws/show/962-15#Text

11. DSanPiN 2.2.7.029-99 "Hygienic requirements for the management of industrial waste and determining their class of danger to public health" of July 01, 1999 № 29. URL: https://zakon.rada.gov.ua/rada/show/v0029588-99#Text (in Ukrainian)

ADAPTATION OF THE TERRITORIAL COMMUNITIES TO THE GLOBAL CLIMATE CHANGES

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ABSTRACT

Climate change is one of the modern challenges to humanity. Only a coordinated global macroeconomic and financial policy can halt the process of its changes. The research of climate changes in a wide range of meteorological values, including the study of the current state and forecasting change trends in thermal and humidification regimes of the surface air layer for the future is important in scientific and practical aspects. Not only air temperature, but also other characteristics: atmospheric circulation, humidification regime, duration of seasons, aridity, etc. against the background of global and regional climate warming is changing. Changes in air temperature determine the dynamics of landscapes, which cannot be characterized as optimal now. Moderate continental climate of Ukraine is gradually changing because of global warming, which will probably lead to the establishment of subtropical one.

It is especially important to solve the regional ecological and social-and-economic consequences of climate change, which are manifested on the territory of Ukraine.

Keywords: global climate changes, thermal regime, humidification regime, territorial communities, natural assets management, land use, agroclimatic resources.

INTRODUCTION

It is clear to scientists that the climate change has taken place and it will continue to do so. Discussions last over how much the climate can change and how to prevent it. Climate change is one of the modern challenges to humanity, because it concerns everyone. This challenge required the cooperation of all governments and countries, as well as significant resources. The markets themselves, of course, were not able to respond adequately. Only a coordinated global macroeconomic and financial policy can halt the process of climate change. The year of 2020 was to be decisive. That is, the scenario, which envisages keeping the planet's temperature at 2 °C (as in the Paris Agreement of 2015), says that there should be a peak of all greenhouse gas emissions in the year of 2020. If we manage to see a decrease after 2020, we will be able to hold the situation.

Over the past decades, the scientific literature and the media have widely discussed the issues of regional ecological and social-and-economic consequences on the territory of Ukraine from the global climate changes. Research of the age course of air temperature anomalies on the territory of Ukraine during the XX - beginning of the XXI centuries found similarities with the age course of the global temperature.

RESEARCH METHODS

The research of climate changes in a wide range of meteorological values, including the study of the current state and forecasting change trends in thermal and humidification regimes of the surface air layer for the future is important in scientific and practical aspects.

RESEARCH AND DISCUSSION RESULTS

One of the most relevant scientific problems of the modern world is the global changes in the long-term weather regime, initiated by human economic activity. Solving the regional ecological and social-and-economic consequences of the climate change, which are manifested on the territory of Ukraine is especially important. If the intensity of global warming in the XX century was about 0.5ºC and it was expected its increase, then the growth rate of annual temperature on average in Ukraine was 1.5 times faster than in global level over the past decade. This factor gives special importance to the problem of climate change in Ukraine over the last 10 years and requires detailed study. The research of climate changes in a wide range of meteorological values, including the study of the current state and forecasting change trends in thermal and humidification regimes of the surface air layer for the future is important in scientific and practical aspects. In this regard, attention is paid to the spatio-temporal features of changes in air temperature and amount of precipitation on the territory of Ukraine over the last 5 years to identify tendencies in heat supply of the territory.

The first three decades and forties of the XX century were the coldest ones. The highest increase in temperature was observed in the north and central regions of Ukraine, it was slightly less in the western and southern regions and it was not almost observed on the Crimean peninsula. The difference between the initial and final value of the temperature according to the trend in the period of 1901-2005 increased from 0.5°C to 1.2°C. The change in temperature indicators during 2010-2020 is a matter of concern. The increase in temperature is also characteristic for certain months of the year. This is especially true for winter and spring months, and for summer months – in the last decade of the XX and at the beginning of the XXI centuries. This can be compared with the generalized results of meteorological observations published by the Copernicus Climate Change Service, which confirmed the warming tendency in Europe.

Not only air temperature, but also other characteristics: atmospheric circulation, humidification regime, duration of seasons, aridity, etc. against the background of global and regional climate warming is changed. Changes in air temperature determine the dynamics of landscapes, which cannot be characterized as optimal now.

Moderate continental climate of Ukraine is gradually changing because of global warming. According to environmental specialists, climate zones have shifted by 1^{o} – about 112 km in recent decades. According to the forecasts of the Finnish Meteorological Institute, Ukraine will have a subtropical climate by the year of 2100. This will naturally affect the flora and fauna, as well as the Ukrainian chernozems and crops that can be grown.

V. M. Babichenko, M. B. Barabash, S. Boichenko, O. A. Donich, O. K. Ivanova, O. O. Kosovets, V. A. Martazynova, O. Ye. Pakholiuk, O. H. Tatarchuk, V. M. Voloshchuk, V. Yeriemieiev, V. Yefimov and others considered the problems of climate change and its individual characteristics on the territory of Ukraine in their works.

The authors noted that climate changes were indisputable facts in the context of global warming and these changes had a negative impact on the general environmental condition at the global and regional levels while examining current climate changes and their manifestations. In particular, M. B. Barabash, O. H. Tatarchuk, studying the spatio-temporal dynamics, found the main patterns of temperature regime on the territory of Ukraine in the context of global warming and noted a significant increase in temperature throughout the country. Analysis of changes in the sum of active temperature during the first decades of the XXI century proves the specified tendency to warming within the vegetative period in the future in the conditions of the forecasted warming of the global climate.

V. M. Babichenko, N. V. Nikolaieva, L. M. Hushchyna, considering the course of air temperature on the territory of Ukraine at the end of the XX and the beginning of the XXI century, mentioned that the average monthly air temperature over the past 15 years suffered significant changes compared to the climatic standard (1961-1990) because of the global climate change, which affected the transformation of the regional climate and certain meteorological values. The air temperature rose in most months and, in general, for the year it became slightly lower only in September, November and December.

V. F. Martazinova, O. K. Ivanova pointed out that in accordance with global warming, changes in annual temperature were observed almost throughout Ukraine except the southern regions and this increase was 1.5-2.3°C in winter months. According to generalized theoretical researches, the authors considered the current manifestations of climate change, their possible consequences both at the global level and on the example of the territory of Ukraine and stated that climate change was an indisputable fact in the conditions of global warming, these changes negatively affected the general ecological state of environment and population. All this determines the need for further development of adaptive measures through appropriate comprehensive scientific researches by relevant sectoral, governmental and interstate programs.

A significant amount of work on the calculation and generalization of the climatic standards is performed by the specialists of Borys Sreznevsky Central Geophysical Observatory. In particular, since 2007, O. A. Donich, O. O. Kosovets, O. Ye. Pokhaliuk have conducted an annual analysis of the climatic features of the territory of Ukraine, which makes it possible to determine the manifestation of global warming within our country.

Sustainable development requires a clear approach to resource use. Each of us needs to learn constantly – to live by the principles of "life-long learning".

One of the main results of decentralization in Ukraine became the transfer of responsibility for the local development to the level of territorial communities, which requires a comprehensive approach to asset management in communities and is characterized by significant differences in views and opinions of experts and scientists. This issue became especially relevant in the context of systemic reforms, which stimulated the strengthening of the role and expansion of local government functions. At the same time, it has received increased attention for a long period of time in the developed countries and in the international arena.

Environmental issues – new requirements for a low-carbon economy, restrictions on access to drinking water, movement of dry areas to the north, which will disrupt traditional agricultural production, become great problems.

In these conditions, the winner will be the one who will start adapting communities to such challenges earlier, who will stimulate the development of local industries aimed primarily at the community market, who will have areas to accommodate residents from other cities and regions where the situation can be significantly worse.

For a long time, the issue of centralized management of natural assets, i.e. natural resources involved in economic turnover or used in the production of goods or providing services was raised at the international and state levels, and the introduction of the concept of participation, the main idea of which was taking into account the interests of all interested parts, was offered.

The idea of natural resources management with the participation of local communities which, despite various areas of implementation in practice based on clearly defined principles (subsidiarity, sustainability, fairness, answerability, efficiency, activity, adaptability, environmental responsibility, inclusiveness) has become widespread. Qualitative management of natural assets at the level of territorial communities is connected with the powers of governing bodies in the sphere of provision of qualitative public services, including water supply and sewerage, land resources management, environment preservation, tourism development, etc. [12].

In Ukraine, communities uniting is still creating the preconditions for such further economic development, and the development of infrastructure which is not possible without land, territories, population is this basis. In addition to the legislative process, climatic conditions significantly influence the mechanism of land use.

According to NASA, on a global scale, the average air temperature in the year of 2016 was 0.99°C higher than in general in the XX century, and it increased by 1.1°C since the end of the XIX century. Experts' forecast is disappointing – if the increase in global temperature rises above 2°C, it will lead to catastrophic warming, which will have devastating consequences on the entire Earth [14].

Directly in Ukraine the air temperature has arisen by 0.8°C during the last two decades and Ukraine has already crossed the limit of 1.5°C. The system broke down which led to an increase in the number of dangerous weather events. According to the Ukrainian Hydrometeorological Institute, over the past 30 years, the number of cases of meteorological disasters in Ukraine has doubled, and their destructive power is constantly growing. Ukraine was included in the infamous list of countries that are leaders in the number of human victims of natural disasters. Unfortunately, not everyone understands the realities in which Ukraine finds itself. Recently, calculated new climatic standards which will allow assessing climatic conditions of the territory of Ukraine in a different way have been adopted. The climate is still moderate continental one. According to scientists, high temperatures will come to Ukraine after the year of 2030 [14].

Two thirds of Ukraine's lands have changed into a risky farming zone in recent years because of the climate changes. A shift of soil-and-climatic zones is observed; particularly critical periods – July-August are noticed. In particular, there was no precipitation at all in some regions of Ukraine during 4 months last year. Accordingly, this led to a reduction in the use of various biological products, as there was an understanding that the use of classical chemical plant protection products in conditions of insufficient moisture was more harmful to plants than beneficial. Today, farmers are forced to change approaches to land use, move away from the classic plowing technology, move to energy-saving technologies that provide minimal passing through the field, preserving of plant residues in the fields, reducing fuel and chemicals by 30-40%. Farmers are currently adapting to precision farming, to modern tillage technologies, without which they are uncompetitive.

Accordingly, the change in climatic conditions and non-observance of agricultural technology leads to the fact that the lands degradation is extremely rapid in Ukraine and this negative process is only accelerating. The Ministry of Agrarian Policy and Food estimates that today more than 6 million hectares of agricultural land need conservation. If, under the current conditions, the conservation mechanism is not introduced, the country will lose huge areas of fertile land every year.

The leadership of the Ministry of Agrarian Policy and Food of Ukraine has a very simple vision of the development of the agricultural sector in a ten-year cycle – minimizing the use of heavy plant protection products, reducing fuel use through the introduction of modern tillage technologies, expanding the volume of organic lands in Ukraine.

Ukraine is the number one country in terms of organic products export to Europe and wants to remain a leader and increase its production. Ukraine's agricultural sector is responsible for 98 million tons of CO_2 emissions, which is 24% of the country's total emissions, and "this is a very global figure".

Global climate change should stimulate re-equipment, modernization of the industry, introduction of new technologies, decarbonization of production, directly the issue of introduction of precision farming, rational use of water resources and interaction with sustainable environmental policies. The way out is very simple – either Ukraine re-equips the agro-industrial complex or agriculture will lose its leader positions. Agriculture is in full symbiosis with environmental policy [11].

As noted, the year of 2016 was recognized as the warmest on Earth since 1880 in the Southern and Northern Hemispheres. Its anomaly was +0.94°C, the year of 2015 took the second place with a deviation of +0.90°C, the year of 2014 took the third place with an anomaly of +0.74°C.

However, in Ukraine, the year of 2016 was only among the twenty warmest years since 1891, its average temperature was +9.5°C, which was 1.7°C higher than the climatic standard. The warmest weather was in Odesa and Kherson regions, where annual temperatures reached almost +12°C, the coldest weather was in Ivano-Frankivsk region, where the annual temperature at Pozhezhevska meteorological station was only +3.9 °C, and in Sumy region the annual temperature reached +7.2°C at Druzhba meteorological station. In Kyiv, the year of 2015 became the sixth among the warmest years since 1881 by the average annual air temperature of +9.5°C which exceeded the climatic standard by almost 2°C (1961-1990). In 2016, 33 temperature records were registered, which in 1.5 times less than in the record year of 2015. The "most productive" months in records were February (10 records) and April (7 records), which exceeded previous maxima, which is convincing evidence of global warming [7].

In general, winter in Ukraine was warmer by 3.4 °C as in recent years (Table 1). The deviation of the indicators from the climatic standard was 3.7 °C and 6.4 °C, respectively (Table 2). February was the only month of the year that had the largest positive deviation from the climatic standard; the absolute maximum temperature reached +22.7 °C in Izmail (Odesa region) on February 23. The absolute minimum air temperature of -25.6 °C was recorded in Chernivtsi region at Seliatyn meteorological station on February 20.

Table 1. Deviations from the standard of average monthly air temperature (°C) and monthly precipitation (mm) in Ukraine by seasons (2016) [7]

Parameters		Winter*	Spring	Summer	Autumn
Temperature	Seasons	-0.3	10.4	21.0	8.1
	Standard (1961-1990)	-3.7	8.0	18.7	8.3
	Deviation	3.4	2.4	2.3	-0.2
Precipitation	Seasons	136	178	169	181
	Standard (1961-1990)	129	137	219	129
	Deviation	7	41	-50	52

*years of 2015-2016.

Table 2. Deviations from the standard of average monthly air temperature (°C) and monthly precipitation (mm) in Ukraine (2016) [7]

Months	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
2016	-5.1	2.6	4.4	11.7	15.0	20.1	21.8	21.1	15.5	6.9	1.9	-2.3	9.5
Standard	-5.2	-3.8	0.8	8.5	14.7	18.0	19.4	18.7	14.2	8.1	2.5	-2.0	7.8
Deviation	0.1	6.4	3.6	3.2	0.3	2.1	2.4	2.4	1.3	-1.2	-0.6	-0.3	1.7
2016	67	46	38	51	89	72	48	49	25	90	66	42	683
Standard	42	37	36	44	57	78	81	60	47	36	46	50	614
Deviation	25	9	2	7	32	-6	-33	-11	-22	54	20	-8	69

The amount of precipitation for winter exceeded the standard – 105% (136 mm) on the territory of Ukraine.

April was singled out against the background of high air temperature in most months of the year, when the temperature significantly exceeded the climatic standard in Ukraine by 3.2°C (Fig. 1) and took the 3rd place among the warmest months. The highest values of +30.7°C were recorded on April 18 by Sarata meteorological station (Odesa region).

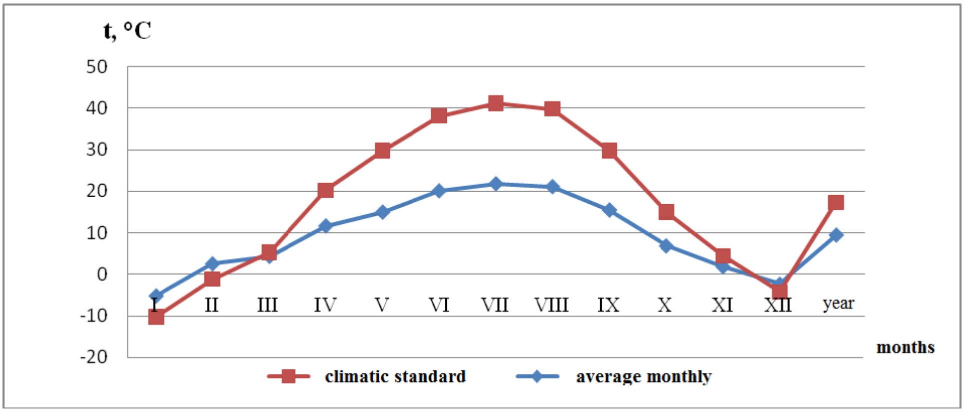

Fig. 1. Annual cycle of air temperature (Ukraine, 2016) [7]

Spring 2016 in the capital city was in the top ten warmest in the climate chronicle due to anomalous April. This spring was 2.4°C warmer than the standard in Ukraine and Kyiv, where it began on January 28, when the average daily temperature exceeded 0 °C in the direction of positive temperature indicators.

The peculiarities of spring 2016 included extremely humid May, when precipitation was 270% of the climatic standard. However, there was its deficit of 77% in the summer season. In addition, the highest daily precipitation in Ukraine was recorded on June 22 in Sumy region at Konotop meteorological station – 99.3 mm (Fig. 2)

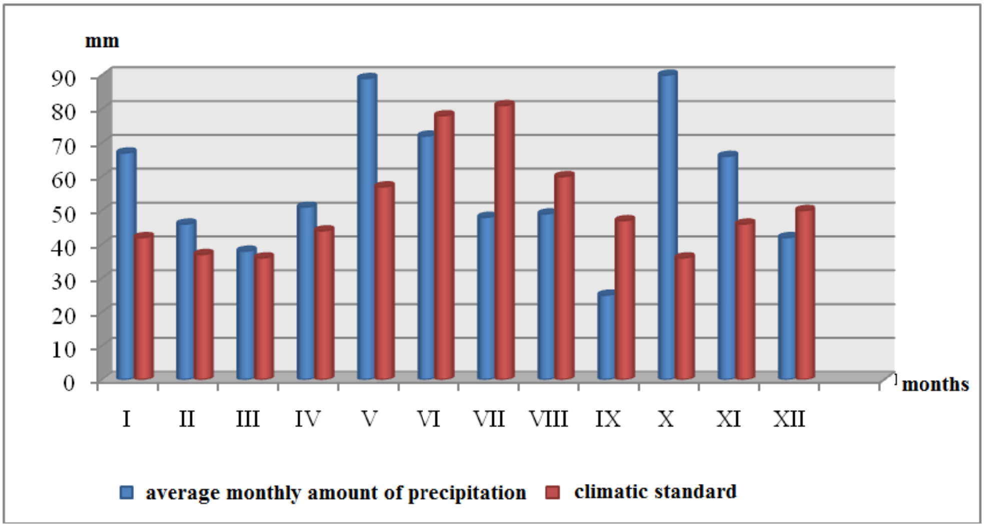

Fig. 2. Monthly amount of precipitation (Ukraine, 2016) [7]

All summer months turned out to be warmer than standard, especially July, which had an anomaly of +2.4°C. The absolute maximum temperature of +40.0°C was recorded on July 17 at Kupiansk meteorological station (Kharkiv region).

The warmest weather in autumn months in Ukraine was September 9 at Sarata station of Odesa region, where the absolute maximum air temperature reached +34.1°C. October had the largest negative deviation from the climatic standard: -1.2 °C among all the months of the year in Ukraine. The average temperature for the autumn season was slightly lower than standard – by 0.1-0.2°C because of cool October and November [7].

During the autumn months in Ukraine, precipitation was higher than standard – 140%. Its excess occurred at the expense of October, when almost 3 monthly precipitation standards were recorded.

December, as the first winter month in Kyiv, turned out to be almost 1.0°C warmer than standard. In general, the deviation from standard in Ukraine was -0.3°C. The lowest temperature was observed on December 17 that was -26.8°C at Troitske station (Luhansk region), the highest temperature – on December 11 that was +14.8°C at Izmail station of Odesa region. Precipitation in December as on the territory of Ukraine was slightly less than standard – 84%, respectively [7].

According to the American service NOAA, the year of 2017 was the third warmest on Earth since 1880. Its anomaly was +0.84 °C, the first place remained in 2016 with a deviation of +0.94°C, and second place was taken in 2015 with an anomaly of +0.90°C.

In Ukraine, the year of 2017 shared the third place with the year of 2013 among the warmest years since 1891; its average temperature was +9.6°C, which was 1.8°C higher than climatic standard. The warmest weather was in Mykolaiv region, the annual temperature in Mykolaiv city reached almost +13°C, and the coldest one, as always, was in Ivano-Frankivsk region, where the annual temperature at Pozhezhevska meteorological station was only +3.9°C, and in Zakarpattia – the annual temperature reached +4.1 °C at Plai meteorological station. In 2017, 24 temperature records were recorded, which was slightly less than in 2016. The largest number of temperature records was recorded in September (7) and April (6), all of them exceeded previous maxima, which was convincing evidence of continuing global warming. [8].

In general, winter in Ukraine, as in recent years, was warmer by 0.4°C. In February, the deviation from the climatic standard was 1.4°C, the absolute maximum temperature was observed on February 28 in Chernivtsi city and reached +19.3°C. The absolute minimum air temperature, which was -26.8°C, was recorded on February 9 at Lebedyn meteorological station (Sumy region), but the lowest winter temperature (-29.0°C) was recorded on January 8 at Slavske meteorological station (Lviv region). The amount of precipitation during winter was below standard – 111 mm (86%) (Tables 3, 4).

Table 3. Deviations from the standard of average monthly air temperature (°C) and monthly amount of precipitation (mm) in Ukraine by seasons (in 2017) [8]

Parameters		Winter*	Spring	Summer	Autumn
Temperature	Seasons	-3.3	9.8	20.8	9.7
	Standard (1961-1990)	8.0	18.7	8.3	8.0
	Deviation	1.8	2.1	1.4	1.8
Precipitation	Seasons	111	134	206	127
	Standard (1961-1990)	129	137	219	129
	Deviation	-18	-3	-13	-2

*years of 2016-2017

Table 4. Deviations from the standard of average monthly air temperature (°C) and monthly amount of precipitation (mm) in Ukraine (2017) [8]

Months	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
2017	-5,4	-2,3	5,8	9,0	14,6	19,6	20,5	22,2	16,4	9,0	3,6	2,6	9,6
Standard	-5,2	-3,8	0,8	8,5	14,7	18,0	19,4	18,7	14,2	8,1	2,5	-2,0	7,8
Deviation	-0,2	1,5	5,0	1,5	-0,1	1,6	1,1	3,5	2,2	0,9	1,1	4,6	1,8
2017	35	34	28	47	45	49	68	34	58	60	45	81	584
Standard	42	37	36	44	57	78	81	60	47	36	46	50	614
Deviation	-7	-3	-8	3	-12	-29	-13	-26	11	24	-1	31	-30

March was singled out against the background of high air temperature in most months of the year, when the temperature significantly exceeded the climatic standard in Ukraine by 5.0°C. The highest temperature (+24.0°C) was observed on March 22 at Khust meteorological station (Zakarpattia region). In general, spring in Ukraine was 1.8°C warmer than standard [8].

The characteristic feature of the year of 2017 was the deficit of precipitation throughout the year, but the least of its fell in June – only 63% of the climatic standard. June was among the twenty driest months since 1891 according to observations. However, at the same time, the greatest monthly amount of precipitation in June in Ukraine was recorded at Mizhhiria meteorological station (Zakarpattia region) – 183 mm, and the least – only 5 mm was recorded at the meteorological stations of Nyzhni Sirohozy and Strilkove (Kherson region) and Loshkarivka (Dnipropetrovsk region).

Thus, in Ukraine the amount of precipitation was slightly less than standard – 95%, but its distribution by seasons was uneven [8].

All summer months in Ukraine turned out to be warmer than standard, especially August, which had an anomaly of +3.5°C. August was on the 7th position among the warmest months for 137 years of observations. The absolute maximum air temperature (+40.6°C) was recorded on August 7 at Melitopol meteorological station (Zaporizhzhia region).

In autumn months, the absolute maximum air temperature (+35.5°C) was recorded on September 18 at Huliaipole meteorological station (Zaporizhzhia region) and repeated on September 21 at Komisarivka meteorological station (Dnipropetrovsk region) [8].

The average temperature for the autumn season in Ukraine exceeded the standard by 1.4°C due to the fact that all autumn months turned out to be warmer than climatic standard. In autumn, the area was humidified by 98%.

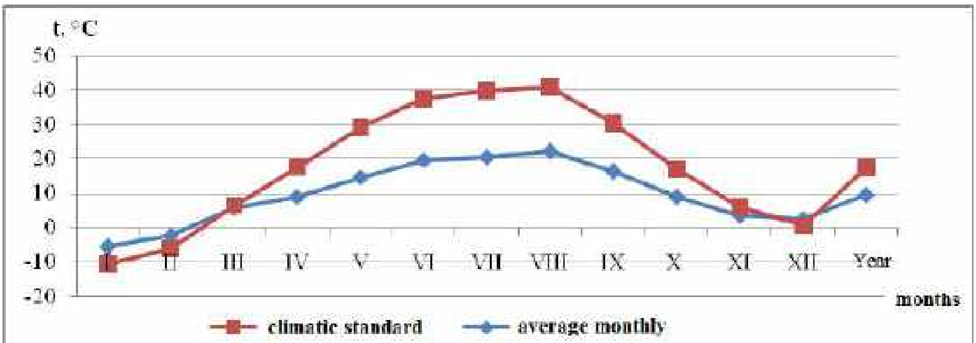

Fig. 3. Annual cycle of air temperature (Ukraine, 2017) [8]

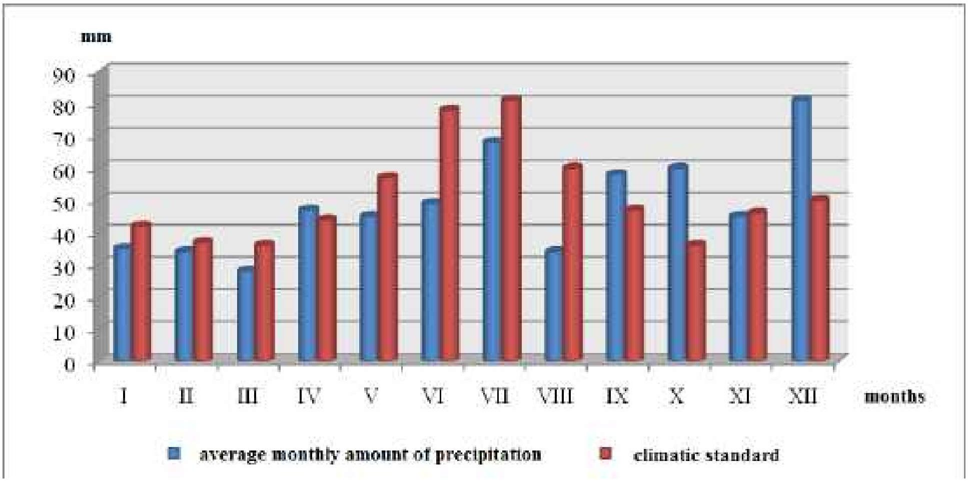

Fig. 4. Monthly amount of precipitation (Ukraine, 2017) [8]

December, as the first winter month, turned out to be 4.6°C warmer than standard. It took the second place among the warmest months according to all observations in Ukraine after 1960. The lowest temperature in Ukraine, -12.2°C, was observed on December 20 at Pozhezhevska meteorological station (Ivano-Frankivsk region), and the highest one, +17.3°C, – on December 2 at the meteorological stations of Vylkove (Odesa region) and Kolomyia (Ivano-Frankivsk region). The amount of precipitation in December on the territory of Ukraine was much higher than standard – 1.5 climatic standards. By the way, only in December, precipitation was measured the most in Ukraine among all the months of the year. Most of them were recorded at Pozhezhevska meteorological station (Ivano-Frankivsk region) – 266 mm, and the least – at Khorly meteorological station (Kherson region) – only 14 mm (Fig. 3, 4) [8].

According to the American service NOAA, the year of 2018 became the fourth warmest on Earth since 1880 in the Southern and Northern Hemispheres. Its anomaly was +0.79°C, the year of 2016 remains in the first place with a deviation of +0.95°C.

In Ukraine, the year of 2018 took the third place among the warmest years, starting with 1891; its average temperature was +9.7°C, which was 1.9°C higher than climatic standard. The warmest weather was in Odesa region, where the annual temperature reached 12.7°C at Vylkove meteorological station, and the coldest, as always, was in Ivano-Frankivsk region, where the annual temperature was only +4.7°C at Pozhezhevska meteorological station, and in Zakarpattia where the annual temperature reached + 5.1°C at Plai meteorological station [9].

In general, winter in Ukraine, as in recent years, was warmer by 2.9°C (Table 5). The absolute maximum temperature of +14.3°C was reached at Yaremcha meteorological station (Ivano-Frankivsk region) on January 6. The absolute minimum air temperature of -27.0°C in winter was recorded at Hlukhiv meteorological station (Sumy region) on February 27.

The amount of precipitation during winter significantly exceeded standard and it was 172 mm (133%) (Table 6) [9].

Only March and November were colder than standard by 1.9°C and 1.0°C, respectively, against the background of high air temperature in most months of the year in Ukraine. The lowest temperatures of -26.9°C were observed at Drohobych meteorological station (Lviv region) on March 2. April had a significant deviation from the climatic standard towards warming – by 4.3°C. April became the warmest in Ukraine and in the capital during the whole observation period. The warmest weather in Ukraine, +30.0°C, was at Khust meteorological station

(Zakarpattia region) on April 29. The hottest day with the temperature of +33.9°C was on May 31 (Voznesensk meteorological station (Mykolaiv region). May took the third position in Ukraine in the ranking among the warmest months since 1881 [9].

Table 5. Deviations from the standard of average monthly air temperature (°C) and monthly amount of precipitation (mm) in Ukraine by seasons (2018) [9]

Parameters		Winter*	Spring	Summer	Autumn
Temperature	Seasons	-0.8	9.9	21.2	9.6
	Standard (1961-1990)	-3.7	8.0	18.7	8.3
	Deviation	2.9	1.9	2.5	1.3
Precipitation	Seasons	172	127	196	110
	Standard (1961-1990)	129	137	219	129
	Deviation	43	-10	-23	-19

Table 6. Deviations from the standard of average monthly air temperature (°C) and monthly amount of precipitation (mm) in Ukraine (2018) [9]

Months	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
2018	-1,9	-3,1	-1,1	12,8	18,0	20,1	21,4	22,1	16,6	10,8	1,5	-1,4	9,7
Standard	-5,2	-3,8	0,8	8,5	14,7	18,0	19,4	18,7	14,2	8,1	2,5	-2,0	7,8
Deviation	3,3	0,7	-1,9	4,3	3,3	2,1	2,0	2,4	2,4	2,7	-1,0	0,6	1,9
2018	46	45	74	17	36	80	95	21	54	28	28	69	593
Standard	42	37	36	44	57	78	81	60	47	36	46	50	614
Deviation	4	8	38	-27	-21	2	14	-39	7	-8	-18	19	-21

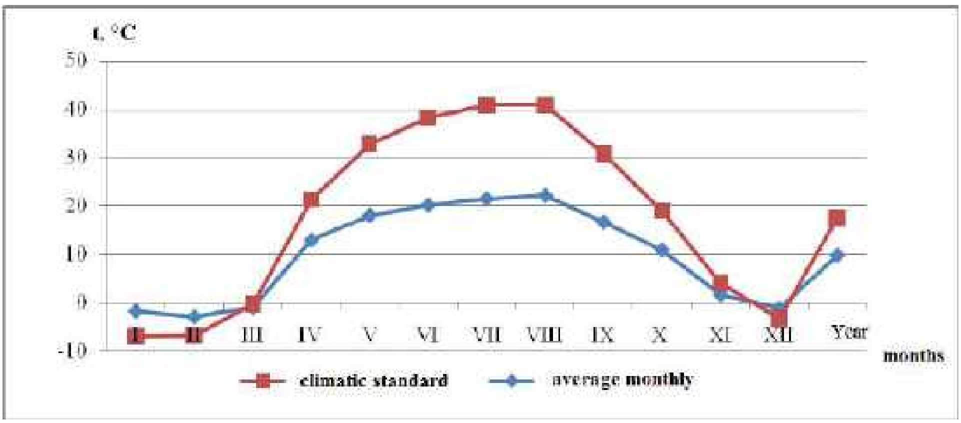

Fig. 5. Annual cycle of air temperature (Ukraine, 2018) [9]

Spring was almost a month shorter than climatic standard. The humidification regime in spring conformed to normal due to wet March.

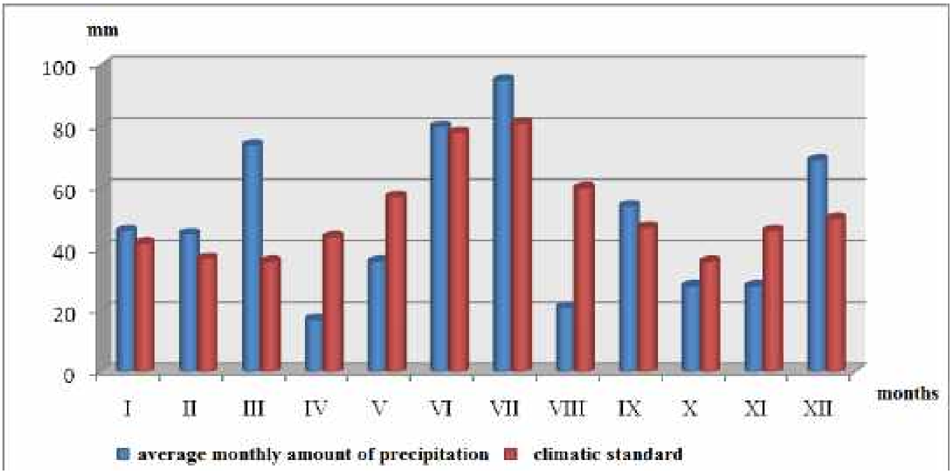

Fig. 6. Monthly amount of precipitation (Ukraine, 2018) [9]

The characteristic feature of the year of 2018 was the deficit of precipitation in April and August – 39 and 35%, April became the 7th among the driest months since 1891, and August took the second place in this ranking of years in Ukraine. August 2018 was extremely dry in Zaporizhzhia, Dnipropetrovsk, Donetsk, Mykolaiv, Kherson, Odesa regions, there was no precipitation at all; at the same time the highest monthly amount of precipitation in August in Ukraine was recorded at Seliatyn meteorological station (Chernivtsi region) – 98 mm.

In general, Ukraine received precipitation close to the standard – 97%, but their distribution by seasons was uneven [9].

All summer months turned out to be warmer than standard, especially August, which had an anomaly of +3.4°C and got into the top ten warmest in Ukraine. Thus, hot maxima of air temperature of +38.2°C were recorded at the meteorological stations of Kherson (Kherson region) and Rozdilna (Odesa region) on August 16 and 17.

The highest temperatures in autumn months were observed at Smila meteorological station (Cherkasy region) on October 18, where the absolute maximum air temperature reached +27.3°C.

Despite the fact that September and October were much warmer than climatic standard, the average temperature during the autumn season in Ukraine was only 1.3°C higher than standard [9].

Generally, the territory of Ukraine was moistened by 85%.

Meteorological winter came two weeks earlier in relation to the climatic standard. On the territory of Ukraine, the lowest temperatures were observed at Seliatyn meteorological station (Chernivtsi region) on November 30. It should be noted that a stable snow cover was formed in Kyiv as early as November 15 which lasted for 3 months.

December, as the first winter month, in Ukraine was 0.6°C warmer than standard. The highest temperatures in Ukraine of +12.0°C were observed at Yaremcha meteorological station (Ivano-Frankivsk region) on December 4. Precipitation in December in Ukraine was much higher than standard – 138% of the average indicators. The largest number of them was recorded at Pozhezhevska meteorological station (Ivano-Frankivsk region) – 152 mm, and the smallest one – at Sarata meteorological station (Odesa region) – only 16 mm [9].

According to the American service NOAA, the year of 2019 became the second one after the year of 2016 among the warmest ones on Earth since 1880 in the Southern and Northern Hemispheres. Its anomaly was + 0.95 °C.

In Ukraine, the year of 2019 took the first place among the warmest ones since 1891, its average temperature was +10.5°C, which was 2.7°C higher than climatic standard. The warmest weather was in Odesa region, where the annual temperature at Vylkove meteorological station reached +13.8°C, and the coldest weather, as always, was in Ivano-Frankivsk region, where the annual temperature was only +5.0°C at Pozhezhevska meteorological station and in Zakarpattia, where the annual temperature at Plai meteorological station was + 5.1°C. 34 temperature records were recorded, the great number of which was registered in June and December: 10th and 9th, respectively. These records exceeded previous maxima, which is convincing evidence of continuing global warming [10].

Standard during previous winter was exceeded by 2.2°C (Table 7). Winter in Kyiv was also mild, especially due to warm February, the deviation from the climatic standard of temperature in which was 4.8°C (Table 8).

In Ukraine, the positive temperature deviation in February was 4.4°C. Last winter in the capital lasted 111 days, which was 6 days less than the climatic standard. It was the fourth in duration among all the winters of the XXI century, despite its mildness. In Ukraine, the absolute maximum air temperature of +13.6°C in January was registered in Odesa region at Izmail station (January 29). On February 28, the maximum was +17.0°C at Chernivtsi station. The absolute temperature minimum of -25.8°C in winter was recorded in Cherkasy on January 22 [10].

The amount of precipitation during winter was higher than standard because of wet December, when in Kyiv, for example, there were almost 1.5 monthly precipitation standards: 110% (142 mm) on the territory of the country and 105% (154 mm) in the capital.

Table 7. Deviations from the standard of average monthly air temperature (°C) and monthly amount of precipitation (mm) in Ukraine by seasons of 2019 [10]

Parameters		Winter*	Spring	Summer	Autumn
Temperature	Seasons	-1.5	10.3	21.2	10.7
	Standard (1961-1990)	-3.7	8.0	18.7	8.3
	Deviation	2.2	2.3	2.5	2.4
Precipitation	Seasons	142	157	150	87
	Standard (1961-1990)	129	137	219	129
	Deviation	13	20	-69	-42

* years of 2018-2019.

Table 8. Deviations from the standard of average monthly air temperature (°C) and monthly amount of precipitation (mm) in Ukraine (2019) [10]

Months	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
2019	-3.7	0.6	4.7	10.0	16.2	22.7	20.1	20.8	15.7	10.7	5.6	2.5	10.5
Standard	-5.2	-3.8	0.8	8.5	14.7	18.0	19.4	18.7	14.2	8.1	2.5	-2.0	7.8
Deviation	1.5	4.4	3.9	1.5	1.5	4.7	0.7	2.1	1.5	2.6	3.1	4.5	2.7
2019	56	17	23	41	92	53	53	44	24	29	34	37	503
Standard	42	37	36	44	57	78	81	60	47	36	46	50	614
Deviation	14	-20	-13	-3	35	-28	-28	-16	-23	-7	-12	-13	-111

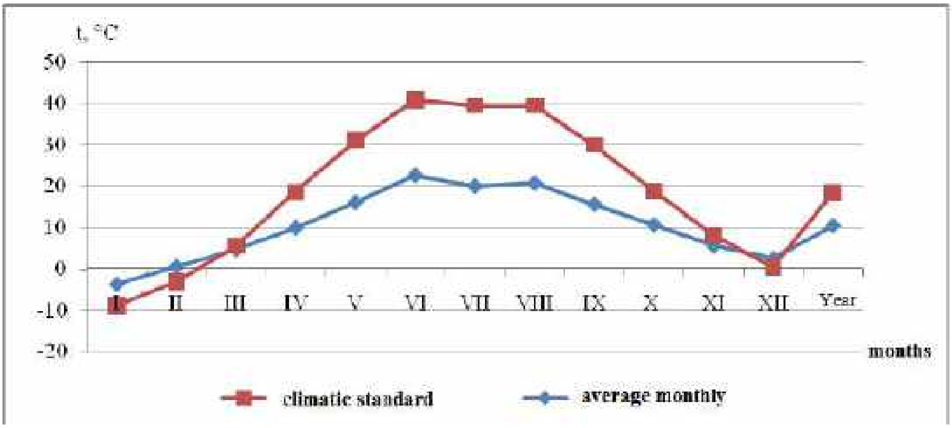

Fig. 7. Annual cycle of air temperature (Ukraine, 2019) [10]

The characteristic feature of the year of 2019 was the fact that all the months turned out to be warmer than climatic standard.

Analysis of spring temperature regime showed that the highest temperature of +23.0°C was observed at Mohyliv-Podilskyi meteorological station (Vinnytsia region) on March 18. March indicators had a significant deviation from the climatic standard towards positive values by 3.9°C (Fig. 7). In general, the month entered the top ten warmest months in Ukraine and in the capital for the entire period of observations. In Kyiv, the temperature record of the maximum air temperature of +17.7°C was recorded on March 8. In April, the highest indicator of +29.0°C was observed at Berehove meteorological station (Zakarpattia region) on April 26. The hottest day of May was its last day at the meteorological stations of Voznesensk (Mykolaiv region) and Pavlohrad (Dnipropetrovsk region) when it was +33.6°C. Spring 2019 in Kyiv took the fourth place in the ranking of the warmest ones since 1881 [10].

The amount of precipitation during the spring season was slightly higher than standard. This became possible due to wet May, when there was 1.5 monthly standard of precipitation in the capital. In general, May took the sixth position among the wettest ones since 1891.

The characteristic feature of the year of 2019 was the deficit of precipitation, except for mentioned May (Fig. 8). In May 2019, 305 mm of precipitation fell at Yaremcha meteorological station in Ivano-Frankivsk region. At the same time, the least monthly amount of precipitation was recorded in Odesa region at Zatyshshia meteorological station – only 9 mm.

Thus, there was recorded 82% of the precipitation standard in spring in Ukraine.

All summer months turned out to be warmer than standard, especially June with an anomaly of +4.7°C and it became the warmest one in the history of Ukraine. In Ukraine, hot maxima air temperatures of +36.9 °C were recorded at the meteorological stations of Voznesensk (Mykolaiv region), Kherson (Kherson region) and Izium (Kharkiv region) on June 22 and 23 [10].

In autumn, 9 temperature records were observed, which allowed it to take the eighth position in Ukraine. The warmest weather was at Strilkove meteorological station (Kherson region) on October 3, where the absolute maximum air temperature reached +28.6°C.

The average temperature for the season in Ukraine was 2.5°C higher than standard due to the fact that the autumn months were much warmer than climatic standard [10].

In autumn, the territory of Ukraine was moistened by an average of 70% of the average long-term values.

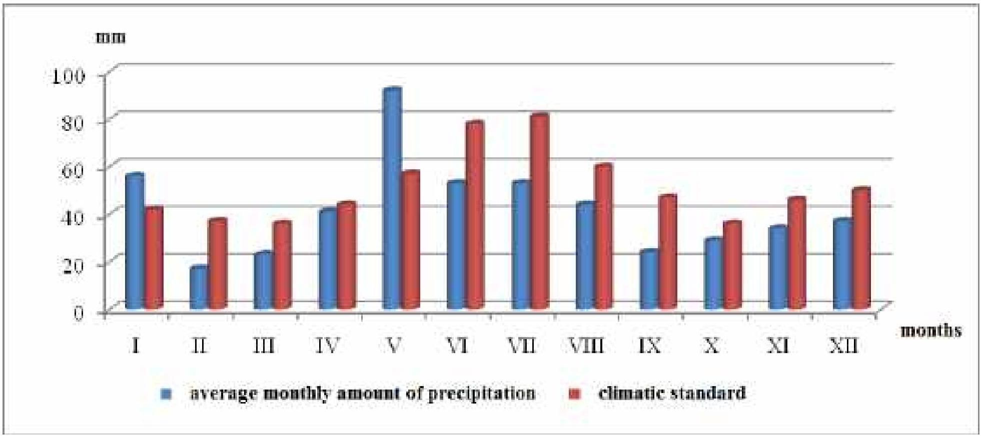

Fig. 8. Monthly amount of precipitation (Ukraine, 2019) [10]

Taking into account abnormally warm December, there was no meteorological winter on the territory of Ukraine, which happened for the first time in the history of all observations. In Ukraine, the maximum value of air temperature of +19.2°C was recorded at Izmail meteorological station (Odesa region) on December 22.

Precipitation on the territory of Ukraine fell on average 37 mm, i.e. 74% of standard. Most of it was recorded in December at Plai meteorological station (Zakarpattia region) – 170 mm, and the least – at Mohyliv-Podilskyi meteorological station (Vinnytsia region) – only 12 mm [10].

According to the American service NOAA, the year of 2020 became the second warmest one on Earth since 1880. Its positive anomaly was 0.98°C.

In Ukraine, the year of 2020 took the first place among the warmest ones since 1891; its average temperature was +10.6°C, which was 2.8°C higher than climatic standard (1961-1990). The warmest weather was in Odesa region, where the average annual temperature at Vylkove meteorological station reached 13.6°C, and the coldest one, as always, was in Zakarpattia region –annual temperature was only +4.7°C at Play meteorological station, and annual temperature reached + 4.8°C at Pozhezhevska meteorological station (Ivano-Frankivsk region). The year of 2020 in Kyiv by an average annual air temperature of + 10.9°C, which exceeded the climatic standard by 3.2°C (1961-1990), became the warmest one since 1881 [11].

In general, winter in Ukraine turned out to be the warmest for the whole period of observations. Its temperature was 5.3°C higher than climatic standard (Tables 9, 10).

There was no stable transition of the average daily air temperature over 0°C towards negative values during calendar winter of 2019-2020. All winter months had positive average monthly temperatures, and in general it was +2.0°C in December-February. Climatologists of the CGO noted that meteorological winter in Kyiv did not come for the very first time for 140 years, and the air temperature below -10°C was not observed. This fact is explained by the global warming, the pace of which, unfortunately, is accelerating.

The amount of precipitation was 100 mm (Table 10), which was 70% of seasonal standard. Stable snow cover was not formed [11].

Table 9. Deviations from the standard of average monthly air temperature (°C) and monthly amount of precipitation (mm) in Ukraine by seasons (2020) [11]

Parameters		Winter*	Spring	Summer	Autumn
Temperature	Seasons	1.6	9.2	21.1	11.4
	Standard (1961-1990)	-3.7	8.0	18.7	8.3
	Deviation	5.3	1.2	2.4	3.1
Precipitation	Seasons	120	138	172	124
	Standard (1961-1990)	129	137	219	129
	Deviation	-9	1	-47	-5

* years of 2019-2020.

Table 10. Deviations from the standard of average monthly air temperature (°C) and monthly amount of precipitation (mm) in Ukraine (2020) [11]

Months	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
2020	0.4	1.8	5.9	8.9	12.8	20.8	21.4	21.0	17.6	12.7	3.9	-0.1	10.6
Standard	-5.2	-3.8	0.8	8.5	14.7	18.0	19.4	18.7	14.2	8.1	2.5	-2.0	7.8
Deviation	5.6	5.6	5.1	0.4	-1.9	2.8	2.0	2.3	3.4	4.6	1.4	1.9	2.8
2020	23	60	24	15	99	88	58	26	48	52	24	39	555
Standard	42	37	36	44	57	78	81	60	47	36	46	50	614
Deviation	-19	23	-12	-29	42	10	-23	-34	1	16	-22	-11	-59

Absolute maximum air temperature of +19.1°C was observed on February 27 at Bilhorod-Dnistrovskyi meteorological station (Odesa region). The absolute minimum air temperature of –23.2°C in winter was recorded at Kyrylivka meteorological station (Zaporizhzhia region) on February 9.

The amount of precipitation in winter in Ukraine was close to standard – 93% (120 mm) [11].

The characteristic feature of the year of 2020 was the fact that all months of the year were warmer than climatic standard, except for May, which turned out to be unusually cool with air temperature below the standard by 1.9°C.

In March, the warmest weather with +24.7°C was at Guliaipole meteorological station (Zaporizhzhia region) on the 9th. The first month of calendar spring had a significant positive deviation from the climatic standard by 5.1°C and took the third place in the ranking of the warmest months in Ukraine since the beginning of observations (Fig. 9).

In April, the highest temperature in Ukraine of +26.3°C was observed at Shepetivka meteorological station (Khmelnytskyi region) on the 29th [11].

Thus, Ukraine received below-standard precipitation – 90%, because its deficit was observed for almost the entire year.

Summer months turned out to be warmer than standard, especially June, which had an anomaly of +2.8°C. It became the 11th in the ranking of the warmest months in the history of observations in Ukraine. The hot maximum air temperature of +37.2°C was recorded at Troitske meteorological station (Luhansk region) on June 13.

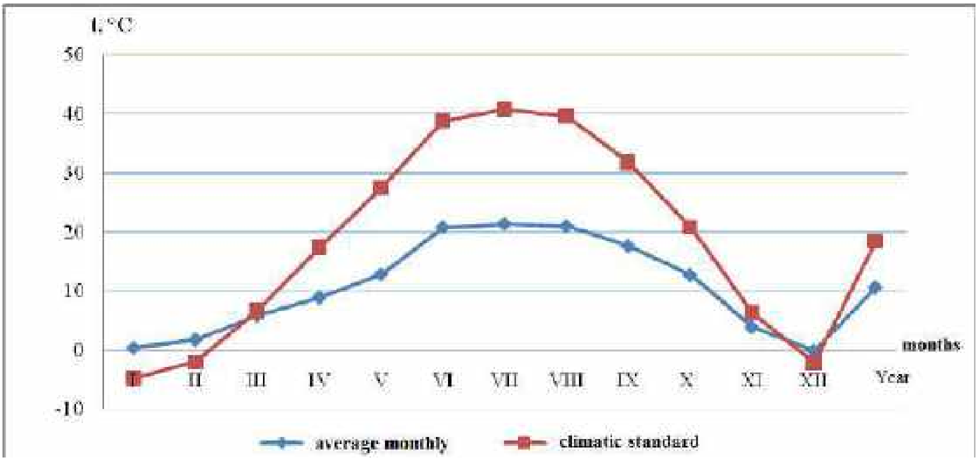

Fig. 9. Annual cycle of air temperature (Ukraine, 2020) [11]

6 temperature records were set in autumn, which turned out to be the warmest season with the fourth position in the ranking of the warmest seasons in Ukraine. The warmest day was at Vylkove meteorological station (Odesa region) on October 7, where the absolute maximum air temperature reached +27.9°C.

Autumn months were much warmer than climatic standard, so the average temperature during the season in Ukraine was 3.1°C higher than usual. In autumn, the amount of precipitation was close to the average annual values – 98% [11].

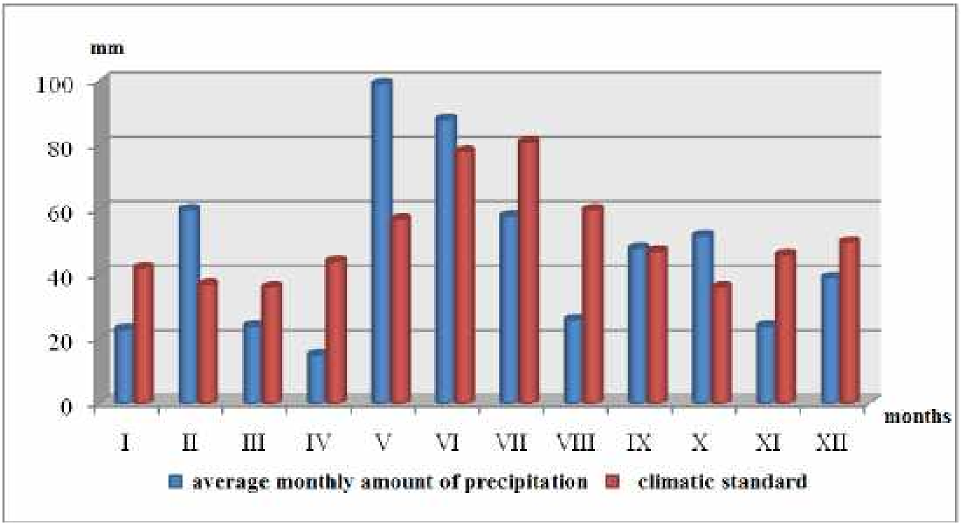

Fig. 10. Monthly amount of precipitation (Ukraine, 2020) [11]

December 2020 began with real winter and ended as a warm autumn. On December 5 and 29, the maximum values of air temperature of +15.9°C were recorded at the meteorological stations of Berehove (Zakarpattia region) and Izmail (Odesa region).

Precipitation in Ukraine for a month was 39 mm or 78% of standard. Its largest number was recorded at Mizhgiria meteorological station (Zakarpattia region) – 113 mm, and the smallest one – at Askania-Nova meteorological station (Kherson region) – only 14 mm [11].

CONCLUSIONS

Thus, forecasted changes in climatic conditions by the middle of the XXI century, namely – changes in the thermal regime (rise in summer temperature and increase in the duration of the warm and growing season, increase in the number of hot days, corresponding decrease in the duration of the cold period); change of the humidification regime (redistribution of precipitation between periods and months, change of the precipitation structure – decrease in number of rainy days and increase in daily amount of precipitation, increase in pounding rains; general tendency of temperature rise cannot be compensated by increase in the number of precipitation for separate periods; causing the development of soil water erosion by pounding rains, the cold period will be wetter and warm period will be arid, possible increase in the number of days with rain in winter, a significant change in agro-climatic resources (sums of active air temperatures and growing season, change in humidity and hydrothermal coefficient; coverage of the southern regions by aridization processes; further change in the boundaries of soil-and-climatic zones; increase in water shortages for the needs of plants causes concern and requires responsible action by the leadership of the united territorial communities, the agricultural sector). Expansion of the rights of local government requires qualitative management of natural assets. Managing in conditions of insufficient moisture means to be prudent, thinking over own actions in advance with the understanding that moisture is one of the most valuable resources, which is becoming more and more expensive from year to year.

REFERENCES

1. In Ukraine, more than 6 million hectares of agricultural land need conservation. URL: https://www.ukrinform.ua/rubric-economy/3260458-v-ukraini-ponad-6-mln-ga-silgospzemel-potrebuut-konservacii-minagro.html
2. Global warming. URL: https://www.google.com/url?sa=i&url=https%3A%2F%2Fuk.wikipedia.org.
3. Two thirds of the land becomes a zone of risky agriculture. URL: https://www.ukrinform.ua/rubric-economy/3260441-dvi-tretini-zemel-staut-zonou-rizikovanogo-zemlerobstva-lesenko.html.
4. Donich O. A. Climatic features of the year of 2020. *Proceedings of the Central Geophysical Observatory.* Kyiv, 2021. Issue. 17(31). p. 4-10.
5. The task for 10 years is to expand the area of organic land. URL: https://www.ukrinform.ua/rubric-economy/3260478-lesenko-zavdanna-na-10-rokiv-rozsiruvati-plosi-organicnih-zemel.html.
6. Climate changes in Ukraine: prospects for becoming an "agrarian supercountry" are postponed. URL: https://www.google.com/url?sa=i&url=https%3A%2F%2Fklymenko-time.com%2Fuk%2Fekonomika%2Fklimaticheskie-izmeneniya-v-ukraine-perspektivy-stat-agrarnoj.
7. Kosovets O. O., Donich O. A. Climatic features of the year of 2016 in Ukraine. *Proceedings of the Central Geophysical Observatory.* Kyiv, 2017. Issue 13(27). p. 4-10.
8. Kosovets O. O., Donich O. A. Climatic features of the year of 2017 in Ukraine. *Proceedings of the Central Geophysical Observatory.* Kyiv, 2018. Issue 14(28). p. 10-16.
9. Kosovets O. O., Donich O. A. Climatic features of the year of 2018 in Ukraine. *Proceedings of the Central Geophysical Observatory.* Kyiv, 2019. Issue 15(29). p. 4-10.
10. Kosovets O. O., Donich O. A. Climatic features of the year of 2019 in Ukraine. *Proceedings of the Central Geophysical Observatory.* Kyiv, 2020. Issue 16(30). p. 19-25.

11. Vulnerability assessment to climate change. URL: http://necu.org.ua › ukraine_cc_vulnerability.
12. Patytska Kh. O. Management of natural assets of territorial communities in terms of decentralization: theoretical principles. *Management and rational use of land resources in the newly created territorial communities: problems and ways to solve them:* materials of the V All-Ukrainian sci-and-prac. conf. (Kherson, March 4-05, 2021). Kherson: KhDAEU, 2021. p. 62-65.
13. Threshold of irreversible changes: temperature in Ukraine has increased by 2 degrees in 100 years. URL: https://www.volynnews.com/news/all/-porih-nezvorotnykh-zmin-temperatura-v-ukrayini-za-100-rokiv-zbilshyla/.
14. Svitlana Krakovska: The weather is dictated by the ocean. URL: https://zn.ua/eng/ECOLOGY/svitlana-krakovska-pogodu-nam-diktuye-okean-311637_.html.
15. Khvesyk M. A., Bystriakov I. K., Klynovyi D. V. Financial-and-economic mechanism of reconstructive development of Ukraine on the basis of decentralized management of natural resources. Ukraine economy. 2018, 3 (676). p. 3-20.
16. What challenges await the territorial communities of Ukraine in the next 10 years? URL: https://www.prostir.ua.

ANTIBACTERIAL PROPERTIES OF ROOT AND STALK EXTRACTS OF *CHELIDONIUM MAJUS* L. (*PAPAVERACEAE*) AGAINST *ENTEROCOCCUS FAECALIS* STRAIN

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ABSTRACT

The present study is an *in vitro* study evaluating the antimicrobial activity of the ethanolic extracts derived from roots and stalks of *Chelidonium majus* L. against *Enterococcus faecalis* strain to assess the possible use of this plant in preventing infections caused by this pathogen. Antimicrobial susceptibility of the tested *E. faecalis* strain was performed by the Kirby-Bauer disc diffusion method. Our results revealed, that *C. majus* and possessed antibacterial properties against *E. faecalis* strain. The ethanolic extract obtained from roots of *C. majus* exhibited the maximum antimicrobial activity against *E. faecalis* (the mean of inhibition zone diameters was 8.77 mm) compared to the control samples (7.48 mm). Stalk extracts of *C. majus* collected from urban areas also exhibited antibacterial ability (7.9 mm) against *E. faecalis* strain compared to the control samples (7.48 mm). Stalk extracts also showed antibacterial properties against the *E. faecalis* strain, but a larger diameter of the zone of inhibition was observed in stalk extracts from rural areas (7.97 mm) compared to the control samples (7.48 mm). *E. faecalis* strain was also susceptible to the stalk extracts from urban agglomerations (7.9 mm). The results of this study provide a new perspective for the use of various species belonging to the *Papaveraceae* family as medicinal plants to improve the antibacterial responses. Further studies including the use of other medicinal plants and the assessment of their antioxidant effects are in progress.

Keywords*:* *Enterococcus faecalis* strain*, Chelidonium majus* L.*,* antimicrobial activity, disc diffusion technique, ethanolic extracts

INTRODUCTION

Since earliest times, many plants have been known to exert healing properties against animal and human infections due to their content of secondary metabolites, which in more recent times have been found to act as antimicrobial agents against pathogens [14-16, 63, 73]. Over the past decade, much attention has been placed on the study of plant-derived compounds for their antibacterial activity, especially against multidrug-resistant Gram-negative and Gram-positive bacteria [1, 5, 18, 38].

In this study, attention focused on the *Papaveraceae* family, with diverse ethnobotanical uses in its global distribution range, has occupied an important place among plant genera applied for the treatment of a broad spectrum of diseases and disorders [6, 23, 27, 67, 71]. The Papaveraceous plants are very well-known for their extensive economic use as well as medicinal ones, which are directly associated with their rich production of alkaloids with novel structures and significant bioactivities [17, 52, 70, 81, 85]. A variety of alkaloids, such as morphine, codeine, protopine, sanguinarine, and tetrahydropalmatine, were discovered in this family, and they have irreplaceable therapeutic value in the treatment of many diseases [21, 22, 28, 44, 52, 58, 79, 84]. Among the pharmacological properties demonstrated for the compounds present in the plants of the *Papaveraceae* family are anti-inflammatory [66], antimicrobial [50, 89], antiviral [35, 61], antioxidant [46], immunomodulatory [68], parasympathetic modulatory [12], antitumor [83], hepatoprotective activities [76], etc. For all these reasons, plants belonging to the family *Papaveraceae* could be considered a good source of new natural compounds to treat and control many diseases.

Chelidonium majus L. (*Papaveraceae*), or greater celandine, is a short-lived hemicryptophyte. It has up to 1 m high stem, branched and sparsely pubescent. The alternately placed leaves are light bluish at the bottom and green at the top. The basal leaves are long-petioled, with the obovate in contour, pinnatisect leaflets with 5–7 lobed segments (Fig. 1). The plant produces umbellate inflorescences from April to October with 2–6 flowers with 4 bright yellow petals, and two whitish, early dropping sepals. The whole plant contains yellow to orange latex. *C. majus* grows in the lowlands and foothills in leafy forests, in brushwood, parks, gardens, roadsides, and buildings. This plant is native in Europe, the western and central part of Asia, and northern Africa. It occurs from Portugal in the West, to Central, Eastern to Northern Europe. The Asian range covers Turkey, Iran, Kazakhstan, Mongolia, Caucasus, and Siberia. In North America, it is an introduced plant [87].

Fig. 1. *Chelidonium majus* L. in natural habitat. The photo was taken during collecting research material in the Pomeranian region of the northern part of Poland (Pomeranian Voivodeship, 54°20′06″N 18°12′05″E)

C. majus is a plant highly praised for its therapeutic potential in western phytotherapy and traditional Chinese medicine [23]. *C. majus* has been known as medicinal species since very Antiquity. Medicinal properties of *C. majus* were described by Dioscorides and Pliny the Elder in the first century AD [87]. The plant contains, as major constituents, isoquinoline alkaloids (such as sanguinarine, chelidonine, chelerythrine, berberine, protopine, and coptisine), phenolic acids, and flavonoids [12, 77, 87]. Both crude extracts of greater celandine and purified compounds derived from it exhibit a wide variety of biological activities (anti-inflammatory, antimicrobial, immunomodulatory, antitumoral, choleretic, hepatoprotective, analgesic, etc.) which are in concordance with the traditional uses of *C. majus* [41, 42]. Moreover, the herb was shown to exert cytostatic and cytotoxic effects [13, 29, 69, 72, 74]. The milky juice of the greater celandine herb has been used in folk medicine and homeopathy to treat viral warts and bacterial infections for years [56, 57].

It has been shown that *C. majus* exhibits antimicrobial properties [88, 89], so we attempted to investigate this activity. In this study, we evaluated the antimicrobial activity of the ethanolic extracts derived from roots and stalks of *C. majus* collected from rural and urban agglomerations against the *Enterococcus faecalis* strain to evaluate the possible use of this plant in preventing infections caused by this strain. *E. faecalis* is one of the most frequently isolated bacterial species across all types of wounds, including diabetic foot ulcers, burns, and surgical sites [4, 34, 65]. In surgical site infections, *E faecalis* is the third most commonly isolated organism [11, 24]. *E faecalis* infections are increasingly difficult to treat due to their intrinsic and acquired resistance to a range of antibiotics [8, 33].

MATERIALS AND METHODS

Collection of plant material and preparing plant extract. Plants materials were harvested from natural habitats on the territory of the Kartuzy district (54°20′06″N 18°12′05″E) in the Pomeranian Voivodship (northern part of Poland) (Fig. 1). Raw materials were sourced from urban and rural agglomeration. The plant's samples were brought into the laboratory for antimicrobial studies. Plant samples (roots and stalks) were thoroughly washed to remove all the attached materials and used to prepare extracts. All extracts were stored at -20°C until use. Freshly sampled roots and stalks were washed, weighed, crushed, homogenized in 96 % ethanol (in proportion 1:19, w/w) at room temperature. The extracts were then filtered and used for analysis. The current study was conducted at the Institute of Biology and Earth Sciences (Pomeranian University in Słupsk, Poland) to evaluate the medicinal properties of plants belonging to the *Papaveraceae* family *in vitro* cultures.

Bacterial strains for antimicrobial activity assay. The *Enterococcus faecalis* (Andrewes and Horder) Schleifer and Kilpper-Balz (ATCC® 51299™) strain was used in the current study. Strain tested was plated on Muller-Hinton agar and incubated for 24 h at 37°C. Then the suspension of microorganisms was suspended in sterile PBS and the turbidity adjusted equivalent to that of a 0.5 McFarland standard.

Bacterial growth inhibition test of plant extracts by the disk diffusion method. The antimicrobial susceptibility testing was done on Muller-Hinton agar by the disc diffusion method (Kirby-Bauer disk diffusion susceptibility test protocol) [2]. Muller-Hinton agar plates were inoculated with 200 µl of standardized inoculum (10^8 CFU/mL) of the bacterium and spread with sterile swabs. Sterile filter paper discs impregnated by extracts were applied over each of the culture plates, 15 min after bacteria suspension was placed. A negative control disc impregnated by sterile 96 % ethanol was used in each experiment. After culturing bacteria on Mueller-Hinton agar, the disks were placed on the same plates and incubated for 24 hr at 37°C. The assessment of antimicrobial activity was based on the measurement of the diameter of the inhibition zone formed around the disks. The diameters of the inhibition zones were measured in millimeters and compared with those of the control and standard susceptibility disks. The activity was evidenced by the presence of a zone of inhibition surrounding the well. The results of the disk diffusion test are “qualitative,” in that a category of susceptibility (i.e., susceptible, intermediate, or resistant) is derived from the test rather than a MIC [39].

Statistical analysis. Zone diameters were determined and averaged. Statistical analysis of the data obtained was performed by employing the mean. All variables were randomized according to the antibacterial activity of tested extracts. All statistical calculation was performed on separate data from each extract. The data were analyzed using one-way analysis of variance (ANOVA) using Statistica software, version 8.0 (StatSoft, Poland) [82]. The following zone diameter criteria were used to assign susceptibility or resistance of bacteria to the phytochemicals tested: Susceptible (S) ≥15 mm, Intermediate (I) = 10–15 mm, and Resistant (R) ≤10 mm [59].

THE RESEARCH RESULTS AND DISCUSSIONS

E. faecalis is a Gram-positive commensal member of the gut microbiota of a wide range of organisms. With the advent of antibiotic therapy, it has emerged as a multidrug-resistant, hospital-acquired pathogen. Highly virulent strains of *E. faecalis* express a pore-forming exotoxin, called cytolysin, which lyses both bacterial and eukaryotic cells in response to quorum signals. *E. faecalis* is an opportunistic pathogen that causes diseases in plants, animals, and humans [19, 37].

Results on *in vitro* antimicrobial activity assessment of ethanolic extracts derived from roots and stalks of *C. majus* against *Enterococcus faecalis* (Andrewes and Horder) Schleifer and Kilpper-Balz (ATCC® 51299™) strain expressed as a mean of diameters of inhibition zone is presented in Figs 2 and 3.

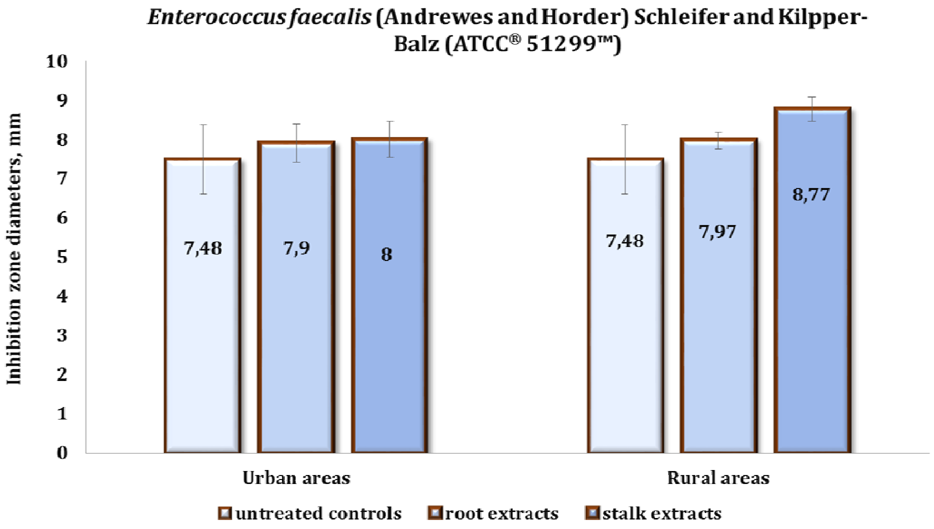
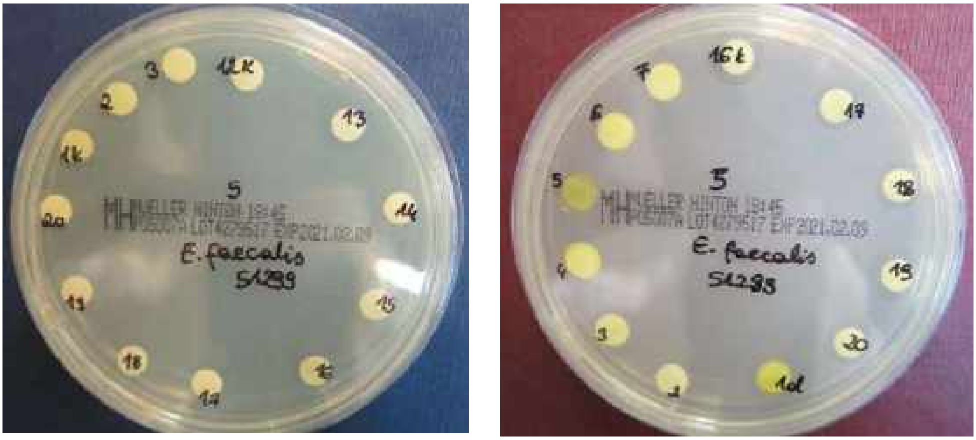


Fig. 2. Zones of growth inhibitions of *Enterococcus faecalis* (Andrewes and Horder) Schleifer and Kilpper-Balz (ATCC® 51299™) strain induced by the extracts derived from stalks and roots of *C. majus* collected from the rural and urban agglomerations (M ± m, n = 8)

The extracts derived from stalks and roots of *C. majus* collected from the rural and urban agglomerations have shown weak antibacterial activity against the tested strain. The results of antibacterial activity screening are given in Fig. 3, which indicates that the extracts have shown weak antibacterial activity against *E. faecalis* strain.



A B

Fig. 3. Example of plates in a disc diffusion assay showing the halos in the bacterial growth resulting from the antibacterial activity of extracts derived from roots and stalks of *Chelidonium majus* L. collected from rural and urban agglomerations

Our results of the antimicrobial screening revealed, that *C. majus* possessed mild antibacterial properties against *E. faecalis* strain. The ethanolic root extracts of *C. majus* collected from rural agglomerations exhibited the maximum antimicrobial activity against *E. faecalis* (the mean of inhibition zone diameters was 8.77 ± 1.21 mm) compared to the control samples (7.48 ± 0.99 mm). There was a 17% increase in the zone of inhibition compared to the control samples. Stalk extracts of *C. majus* collected from urban areas also exhibited antibacterial ability against *E. faecalis* strain (7.9 ± 1.08 mm) compared to the control samples. There was a non-significant increase in the zone of inhibition by 5,6% compared to the control samples. Stalk extracts also showed antibacterial properties against the *E. faecalis* strain, but a larger diameter of the zone of inhibition was observed in stalk extracts of *C. majus* collected from rural areas (7.97 ± 0.85 mm) compared to the control samples. *E. faecalis* strain was also susceptible to the stalk extracts of *C. majus* collected from urban agglomerations (7.9 ± 1.08 mm) (Fig. 2).

Similar results in context for antibacterial activity of *C. majus* were obtained by other researchers. Plant material of *C. majus* derived from different natural habitats and *in vitro* cultures was used for the phytochemical analysis and antimicrobial tests in the study of Zielińska and co-workers (2019). The composition of alkaloids was analyzed using chromatographic techniques (HPLC with DAD detection). The results have shown that roots contained higher numbers and amounts of alkaloids in comparison to aerial parts. All tested plant extracts manifested antimicrobial activity, related to different chemical structures of the alkaloids. Root extract used at 31.25-62.5 mg/L strongly reduced bacterial biomass. From the seven individually tested alkaloids, chelerythrine was the most effective against *Pseudomonas aeruginosa* (MIC at 1.9 mg/L), while sanguinarine against *Staphylococcus aureus* (MIC at 1.9 mg/L). Strong antifungal activity was observed against *Candida albicans* when chelerythrine, chelidonine, and aerial parts extract were used [87].

Also, Cheng and co-workers (2006) have studied the inhibitory effects of *C. majus* extractive on the growth of *Streptococcus mutans in vitro*, and explore its mechanism in caries prevention. *Streptococcus mutans* 25175 was chosen as the experimental bacterium. The *C. majus* extractives chelidonine and chelerythrine were double diluted to different concentrations by two-fold dilution. The inhibitory effect of *S. mutans* was measured by the slip diffusion method. The minimal inhibitory concentration (MIC) was also determined. Inhibition zone of *S. mutans* appeared in some concentrations of chelerythrine, but no inhibition zone in each concentration of chelidonine. The MIC of chelerythrine was 0.78 mg/ml which was determined by liquid culture medium. The concentration of chelerythrine was highly related to the inhibitory zone of *S. mutans* (r=0.99, P<0.01). The antibacterial activity of *C. majus* extractive chelerythrine on *S. mutans* was significant, and the antibacterial activity of the concentration 100 mg/ml was higher than that of 0.16% liquor hibitane as a control (19.4 mm), indicating that chelerythrine can be used as an agent for prevention of dental caries [9].

Using high-performance liquid chromatography (HPLC), infrared radiation (IR) spectroscopy and nuclear magnetic resonance (NMR), Wei and co-workers (2020) proved that the extract of *C. majus* consists of chelerythrine (CHE) [78]. The antifungal activity of CHE against five fungal pathogens of rice was researched *in vitro*, revealing that CHE inhibited *Ustilaginoidea virens* (*U. virens*) and *Cochliobolus miyabeanus* (*C. miyabeanus*) with 50% effective concentrations (EC_{50}) of 6.53 × 10^{-3} mg/ml and 5.62 × 10^{-3} mg/ml, respectively. When the concentration of CHE was 7.5 × 10^{-3} mg/ml, the inhibition rate of *U. virens* reached 56.1%. Moreover, CHE (4 × 10^{-3} mg/ml) exhibited the greatest efficacy in inhibiting spores of *U. virens* growth with an inhibition rate as high as 86.7%. CHE displayed the best inhibitory activity against *U. virens* at the concentration of 7.5 × 10^{-3} mg/ml, compared with the other two isoquinoline alkaloids and commercial fungicide validamycin. After treating *U. virens* mycelia with CHE, twisted and atrophied mycelia were observed by optical microscopy. SEM results demonstrated narrow and locally fractured mycelium. TEM observations showed that the cell wall had become thin and broken, and most organelles were difficult to recognize. Furthermore, the membrane of mycelia was destroyed and reactive oxygen species (ROS) of spores was accumulated, which induced apoptosis of pathogenic fungi. From these results, understanding of the mechanisms of antifungal activity of CHE against *U. virens* was enriched and the research of Wei and co-workers (2020) is relevant for developing novel pesticides.

Moreover, alkaloids from *C. majus* engage the well-documented antimicrobial potential. The selective antibacterial activity for 8-hydroxylated benzo[c]phenanthridine-type alkaloids isolated from *C. majus* opens the possibility that they could be helpful for the developing of new antibacterial agents for treating the infection of clinical strains of methicillin-resistant *Staphylococcus aureus* (MRSA) which has created nosocomial problems worldwide. Zuo and co-workers (2008) have described the antibacterial effect of extracts and compounds isolated from the aerial part of *C. majus* acting against MRSA. The activities were evaluated by using the macrobroth dilution method. Bioassay-guided fractionation of the most active extract from the aerial parts (EtOAc) led to the isolation of benzo[c]phenanthridine-type alkaloids 8-hydroxydihydrosanguinarine (hhS), 8-hydroxydihydrochelerythrine (hhC), which were potently active against MRSA strains [89].

An alkaloid that exhibits antibacterial activity is sanguinarine. It has long been known that sanguinarine, a benzophenanthridine alkaloid derived from the rhizomes of *Sanguinaria canadensis* L., has broad antimicrobial activity and anti-inflammatory properties. In fact, *in vitro* studies have shown that sanguinarine can inhibit bacterial adherence to the surface of teeth, exerting an anti-plaque action [25, 32]. Sanguinarine has broad antimicrobial activity as well as anti-inflammatory properties. *In vitro* studies indicate that the anti-plaque action of sanguinaria is due to its ability to inhibit bacterial adherence to the newly formed pellicle, its retention in plaque being 10-100 times its saliva concentration, and its antimicrobic properties. The MIC of sanguinarine ranges from 1 to 32 µg/mL for most species of plaque bacteria. Long-term use of sanguinaria-containing toothpaste and oral rinse products does not predispose users to detrimental shifts in oral flora. Electron microscopic studies of bacteria exposed to sanguinarine demonstrate that bacteria aggregate and become morphologically irregular [25]. Long-term clinical evaluation of toothpaste and oral rinse containing sanguinaria extract in controlling plaque, gingival inflammation, and sulcular bleeding during orthodontic treatment was done by Hannah and co-workers (1989). The sanguinaria regimen reduced plaque by 57%, gingival inflammation by 60%, and sulcular bleeding by 45% from baseline compared with placebo group reductions of 27% (plaque) and 21% (gingival inflammation), and an increase of 30% in bleeding index [32].

This alkaloid exerts its antibacterial activity by perturbing bacterial FtsZ Z-ring formation and inhibiting bacterial cytokinesis [3, 43]. Sanguinarine did not perturb the membrane structure in *Escherichia coli*. However, it perturbed the cytokinetic Z-ring formation in *E. coli*. In addition, sanguinarine strongly reduced the frequency of the occurrence of Z rings/micrometer of *Bacillus subtilis* length but did not alter the number of nucleoids/micrometer of cell length. The results of Beuria and co-workers (2005) suggested that sanguinarine inhibited cytokinesis in *B. subtilis* by inhibiting Z-ring formation without affecting nucleoid segregation. Sanguinarine inhibited the assembly of purified FtsZ and reduced the bundling of FtsZ protofilaments *in vitro*. Sanguinarine was found to bind to FtsZ with a dissociation constant of 18-30 microM. The results together show that sanguinarine inhibits bacterial division by perturbing FtsZ assembly dynamics in the Z ring and provide evidence in support of the hypothesis that the assembly and bundling of FtsZ play a critical role in bacterial cytokinesis [3]. The presence of a hydrophobic functionality at either the 1-position of 5-methylbenzo[c]phenanthridinium derivatives or the 2-position of dibenzo[a,g]quinolizin-7-ium derivatives is associated with significantly enhanced antibacterial activity (Kelley et al., 2012). 3-Phenylisoquinoline represents a subunit within the ring-systems of both of these alkaloids. Several 3-phenylisoquinolines and 3-phenylisoquinolinium derivatives have been synthesized and evaluated for antibacterial activity against *Staphylococcus aureus* and *Enterococcus faecalis*, including multidrug-resistant strains of methicillin-resistant *S. aureus* (MRSA) and vancomycin-resistant *E. faecalis* (VRE). Toxicological assessment of select compounds revealed minimal cross-reaction mammalian β-tubulin as well as little or no human cytotoxicity [43].

The authors of two studies [30, 31] tested a combination of sanguinarine, EDTA, and vancomycin and a combination of sanguinarine, EDTA, and streptomycin against Gram-positive and Gram-negative bacteria, including Multi-Drug Resistant (MDR) bacteria. The results of these studies showed that sanguinarine has strong activity against all the strains tested (Minimum Inhibitory Concentration (MIC): 0.5-128 μg/ml); additive and synergistic effects were recorded for all sanguinarine + EDTA and sanguinarine + EDTA + vancomycin associations against Gram-negative bacteria. The combination of sanguinarine + EDTA + streptomycin also showed synergistic activity against almost all the strains except Methicillin-Resistant *Staphylococcus aureus* (MRSA). The combination of drugs, which interfere with different molecular targets, can be an important strategy to combat multidrug-resistant bacteria [30].

Berberine, an isoquinoline-type alkaloid, contributes to oral health benefits. Several studies have demonstrated the efficacy of berberine against oral streptococcal growth and selected endodontic pathogens using a multispecies biofilm tooth model [20, 80]. Dziedzic and co-workers (2015) have assessed the antibacterial activity of berberine chloride (BECl) in light of the effect exerted by common antibiotics on selected reference strains of oral streptococci (OST), and to evaluate the magnitude of interactions [20]. Three representative oral microorganisms were investigated: *Streptococcus mutans* ATCC 25175 (SM), *S. sanguinis* ATCC 10556 (SS), *S. oralis* ATCC 9811 (SO), and microdilution tests, along with disc diffusion assays were applied. Researchers reported that the growth (viability) of all oral streptococci was reduced by exposure to BECl and was dependent primarily on exposure/ incubation time. MIC of BECl against OST ranged from 512 μg/mL (SS) to 1024 μg/mL (SM, SO). The most noticeable antibacterial effects were observed for *S. sanguinis* (MIC 512 μg/mL) and the most significant synergistic action was found for the combinations BECl-penicillin, BECl-clindamycin, and BECl-erythromycin. The synergy between berberine and common antibiotics demonstrates its potential use as a novel antibacterial tool for opportunistic infections and also provides a rational basis for the use of berberine as an oral hygiene measure [20]. Xie and co-workers (2012) have evaluated the antimicrobial efficacy of berberine solution against selected endodontic pathogens using a multispecies biofilm tooth model. The bacterial species used were *Fusobacterium nucleatum*, *Enterococcus faecalis*, and *Prevotella intermedia*. The minimal inhibitory concentration of berberine against *F. nucleatum*, *P. intermedia*, and *E. faecalis* was 31.25 µg/mL, 3.8 µg/mL, and 500 µg/mL, respectively. Instrumentation and irrigation resulted in 99% bacterial reduction in all groups. All tested solutions resulted in a statistically significant reduction in bacteria when compared with the saline control. When used alone, berberine (2 mg/mL) was less effective than the other test irrigants. However, when combined with 1% CHX, berberine (2 mg/mL) was comparable in bactericidal activity with 5.25% NaOCl, 2% CHX, and 1% CHX. Moreover, Xie and co-workers (2012), demonstrated that berberine is more effective than saline as an endodontic irrigant against selected endodontic pathogens *in vitro* and, when combined with chlorhexidine 1%, is comparable with NaOCl in its bactericidal efficacy [80]. Kang and co-workers (2015), showed that berberine has an inhibitory effect on the growth of *Actinobacillus pleuropneumoniae* with a MIC value of 0.3125 mg/ml. Berberine inhibited the synthesis of proteins associated with the growth and cleavage of bacteria and then blocked the division and development of bacteria. The compound ultimately induced cytoplasm pyknosis and bacterial death [40].

One of the therapeutic agents based on *C. majus* is the anticancer drug Ukrain™ known as a semi-synthetic *C. majus* alkaloid derivative. Although there are no doubts about the antitumor properties of the drug, there is still controversy about its composition. In the study of Jesionek and co-workers (2016), Ukrain™ was subjected to TLC and LC-MS/MS analyses to compare it with *C. majus* alkaloid root extract and to determine its composition [36]. Moreover, the microbiological activity of both Ukrain™ and the alkaloid extract was tested against *Bacillus subtilis* strains using TLC-direct bioautography. Sanguinarine, chelidonine, α-homochelidonie, and chelerythrine were found to have antibacterial properties. Besides chelidonine, sanguinarine, chelerythrine, protopine, allocryptopine, homochelidonie, berberine, and coptisine reported earlier in literature, the presence of stylopine, norchelidonine, dihydrochelidonine, and hydroberberine in Ukrain™ was detected, and they have been reported in the study of Jesionek and co-workers (2016) for the first time [36].

Also, Paczkowska and co-workers (2020) have aimed to prepare mucoadhesive vaginal drug delivery systems composed of *Chelidonii* herba lyophilized extract and chitosan as an effective way to treat vaginitis [62]. The pharmacological safety of usage of isoquinoline alkaloids, based on MTT test, were evaluated for the maximum doses 36.34 ± 0.29 µg/mL and 0.89 ± 1.16 µg/mL for chelidonine and sanguinarine, respectively. Dissolution rate profiles and permeability through artificial membranes for chelidonine and sanguinarine after their introduction into the chitosan system were studied. The low permeability for used save doses of isoquinoline alkaloids and results of microbiological studies allow confirmation that system *Chelidonii* herba lyophilized extract chitosan 80/500 1:1 (w/w) is a promising strategy for vaginal use. *Ex vivo* studies of mucoadhesive properties and evaluation of tableting features demonstrated that the formulation containing *Chelidonii* herba lyophilized extract (120.0 mg) with chitosan (80/500-100.0 mg) and polymer content (HPMC-100.0 mg, microcrystalline cellulose-50.0 mg, lactose monohydrate-30.0 mg, and magnesium stearate-4.0 mg) is a vaginal dosage form with prolonging dissolution profile and high mucoadhesion properties (up to 4 h) [62].

The overall results of Meng and co-workers (2009) have provided important information for the potential application of the 8-hydroxylated alkaloids from *C. majus* in the therapy of serious infection caused by drug-resistant fungi [51]. These authors have evaluated the *in vitro* antifungal activity of the active components from *C. majus* against clinical drug-resistant yeast isolates. Of the six compounds determined, 8-hydroxydihydrosanguinarine (1) and 8-hydroxydihydrochelerythrine (2) demonstrated potent activity with the MIC ranges of 2-80 and 4-100 µg/mL, respectively. Dihydrosanguinarine (3), dihydrochelerythrine (4), sanguinarine (5), and chelerythrine (6) had some degree of antifungal activity [51].

Also, other plants belonging to the *Papaveraceae* family, as well as their alkaloids exhibited antimicrobial activity. For example, the species of Glaucium genus have been used in Iranian herbal medicine as laxative, hypnotic, narcotic, and antidiabetic agents and also in the treatment of dermatitis [53]. The extracts obtained from root, stem, leaf, and fruit pericarps of *Glaucium flavum* showed antibacterial activity in an *in vitro* assay. The root extract was the most active against the Gram-positive bacteria [7]. Belonging to the *Papaveraceae* family, *Glaucium vitellinum* is one of the Persian endemic plants which has not been investigated biologically. Mehrara and co-workers (2015) have assessed the antibacterial and antifungal activities of the total methanol extract and alkaloid sub-fraction of the flowering aerial parts of *G. vitellinum* [50]. The antibacterial and antifungal activities were investigated using the cup plate method and disc diffusion assay, respectively. The MIC values of the active samples were determined using the microplate dilution method. The crude extract and alkaloid sub-fraction of *G. vitellinum* had significant inhibition activity on the growth of *S. aureus* and *S. typhi*. From the antifungal assay, it is concluded that only the yeast *C. albicans*, showed high sensitivity to the extract and especially to the related alkaloid sub-fraction. Regarding the results of Mehrara and co-workers (2015), *G. vitellinum* could be employed as a natural antibacterial and antifungal agent against *S. aureus*, *S. typhi*, and *C. albicans*, respectively [50].

The analgesic activity of the aerial parts of *Glaucium* Freyn (*Papaveraceae*), a native plant of Iran, was studied by Morteza-Semnani and co-workers (2006) using formalin, hot plate, and writhing tests in rodents [53, 54]. The methanolic extract and total alkaloids of *Glaucium paucilobum* caused graded inhibition of both phases of formalin-induced pain. In the hot plate test, i.p. administration of *G. paucilobum* extract at the doses of 50-90 mg/kg and total alkaloids at the dose of 10-60 mg/kg significantly raised the pain threshold at an observation time of 30 min in comparison with control ($p < 0.001$). In the writhing test, the extract at the doses of 30-90 mg/kg and total alkaloids at the doses of 10-60 mg/kg produced a significant decrease in the number of writhings in comparison with the control group ($p < 0.001$). The methanolic extract and total alkaloids of *G. paucilobum*, at antinociceptive doses, did not affect the motor coordination of animals when assessed in the rotarod model. The results of Morteza-Semnani and co-workers (2006) showed that the analgesic activity of this plant may be related partly to the alkaloids. Also, topical preparation containing *G. grandiflorum* methanolic extract showed an analgesic effect in concentrations of more than 4% w/w in the early phase in the formalin test. This activity was observed in concentrations of more than 3% w/w in the late phase. The topical analgesic activity of the extract was less than the analgesic activity of methyl salicylate ointment [53].

The antibacterial activity of other species belonging to the *Papaveraceae* family – *Hylomecon hylomeconoides* was investigated in the study of Choi and co-workers (2010). The ethanolic extract and its fraction (n-hexane, CH_2Cl_2, EtOAc, and H_2O) were investigated against methicillin-resistant *Staphylococcus aureus* (MRSA). The most active extract (CH_2Cl_2) led to the isolation of 6-methoxydihydrosanguinarine (6-MS), 6-acetonylhydrosanguinarine, and dihydrosanguinarine. These compounds were very active against MRSA strains with minimum inhibitory concentrations (MICs) ranging from 1.95 to 250 μg/ml [10].

Two alkaloid constituents of *Bocconia arborea* (dihydrochelerythrine and dihydrosanguinarine) showed considerable antimicrobial activity against Gram-positive and Gram-negative bacteria and *Candida albicans* [55].

In the genus *Macleaya* (*Papaveraceae*), *Macleaya cordata* and *Macleaya microcarpa* have been recognized as traditional herbs that are primarily distributed in China, North America, and Europe and have a long history of medicinal usage [47]. These herbs have been long valued and studied for detumescence, detoxification, and insecticidal effect. Plants from the genus of *Macleaya* provide a source of bioactive compounds, primarily alkaloids, with remarkable diversity and complex architectures, thereby having attracted attention from researchers. These purified compounds and/or crude extract possess antitumor, anti-inflammatory, insecticidal, and antibacterial activities in addition to certain potential toxicities [47].

Macleaya cordata (plume poppy) is a source of bioactive compounds, mainly isoquinoline alkaloids which are used in phytopreparations with anti-inflammatory and antimicrobial activities [45]. In the study of Kosina and co-workers (2010), the alkaloids sanguinarine, chelerythrine, their dihydro derivatives, protopine, and allocryptopine and phenolics, gallic, protocatechuic, p-hydroxybenzoic, m-hydroxybenzoic, gentisic, p-coumaric, caffeic, ferulic, and sinapic acids were determined in extracts prepared from M. cordata aerial part, seeds, and seed capsules using HPLC with UV detection and/or LC/MS with electrospray ionization. The highest content of sanguinarine and chelerythrine was found in capsules. Protopine and allocryptopine were major alkaloids in leaves including footstalks. The seed oil contained dihydrosanguinarine, dihydrochelerythrine, and twelve fatty acids of which linoleic, oleic, palmitic and stearic acids predominated. In addition, sanguinarine reductase, a key enzyme in sanguinarine/dihydrosanguinarine equilibrium in plants, was found for the first time, in the soluble proteins of leaves. Finally, extracts were tested for antimicrobial activity using the microdilution method on standard reference bacterial strains [45].

Wang and co-workers (2016) have identified an endophytic fungus BLH34 isolated from the leaf of *Macleaya cordata* with antibacterial activity, and to optimize its fermentation medium. The results showed that the strain BLH34 had antimicrobial activity to the test strains, especially it showed a significant inhibitory effect on *Staphylococcus aureus*. The strain BLH34 was identified as *Penicillium turbatum*. The antimicrobial activity of the crude extract was significantly increased after optimization, which could provide a basis for further separation and purification of the antibacterial substances extracted from strain BLH34 [75].

The activity of the alkaloids from *M. cordata* against economically important phytopathogenic fungi and bacteria has been reported by Liu and co-workers (2009). Bioassay-guided fractionation of the crude extract of the whole plant of *Macleaya cordata* R. Br. led to the isolation of four alkaloids, which were identified as sanguinarine (1), chelerythrine (2), protopine (3), and alpha-allocryptopine (4) based on their physicochemical and spectrometric data. Compounds 1 and 2 demonstrated significant antifungal activity against the six test fungi with median inhibitory concentrations (IC_{50}) ranging from 0.47 to 6.13 μg/mL. Compound 1 was the most effective with an IC_{50} of 0.47 μg/mL on *Rhizoctonia solani*. Furthermore, compounds 1 and 2 also demonstrated strong antibacterial activity, with IC_{50} values ranging from 5.01 to 11.3 μg/mL, and minimum inhibitory concentrations (MIC) ranging from 8.0 to 32.0 μg/mL [48].

The antimicrobial activity of extracts and isoquinoline alkaloids of selected *Papaveraceae* plants was studied by Opletal and co-workers (2014). Alkaloidal extracts of seven selected plants of the family *Papaveraceae* were studied concerning their activity against six strains of pathogenic bacteria and their alkaloidal fingerprint. Twenty-four alkaloids were determined by GC/MS, and twenty of them were identified from their mass spectra, retention times, and retention indexes. In the antibacterial assay, three Gram-positive (*Enterococcus faecalis*, *Staphylococcus aureus*, and *S. hyicus*), and three Gram-negative (*Escherichia coli*, *Proteus mirabilis*, and *Pseudomonas aeruginosa*) strains were used. The most promising antimicrobial activity was shown by the alkaloidal extract of *Macleaya cordata* with MIC values of 16 μg/mL for *Staphylococcus aureus*, 32 μg/mL for *Enterococcus faecalis*, and 64 μg/mL for *Staphylococcus hyicus* and *Escherichia coli*. All the tested pure isoquinoline alkaloids were considered inactive within the tested concentrations [60].

Methanol extracts of the rhizomes of *Sanguinaria canadensis*, and the roots and rhizomes of *Hydrastis canadensis*, two plants used traditionally for the treatment of gastrointestinal ailments, were screened by Mahady and co-workers (2003) for *in vitro* antibacterial activity against 15 strains of *Helicobacter pylori*. The rhizome extracts, as well as a methanol extract of

S. canadensis suspension-cell cultures, inhibited the growth of *H. pylori in vitro*, with a MIC_{50} range of 12.5-50.0 µg/ml. Three isoquinoline alkaloids were identified in the active fraction. Sanguinarine and chelerythrine, two benzophenanthridine alkaloids, inhibited the growth of the bacterium, with an MIC_{50} of 50.0 and 100.0 µg/ml, respectively. Protopine, a protopine alkaloid, also inhibited the growth of the bacterium, with a MIC_{50} of 100 µg/ml. The crude methanol extract of *H. canadensis* rhizomes was very active, with an MIC_{50} of 12.5 µg/ml. Two isoquinoline alkaloids, berberine, and beta-hydrastine were identified as the active constituents, and having an MIC_{50} of 12.5 and 100.0 µg/ml, respectively [49].

Sanguinarine and chelerythrine constitute alkaloids that have exhibited antifungal activities. However, the effects of a 1:1 mixture of these agents against *Candida albicans* and *Cryptococcus neoformans* have remained largely unexplored. Qian and co-workers (2020) have assessed the anti-fungal and anti-biofilm efficacy of combined chelerythrine-sanguinarine against *C. albicans* and *C. neoformans in vitro*. Combined chelerythrine-sanguinarine inhibited *C. albicans* and *C. neoformans* growth with minimum inhibitory concentrations (MICs) of 2 and 16 µg/mL, respectively, and effectively inhibited adhesion and biofilm formation of these pathogens at minimum biofilm inhibitory concentrations of 1 and 8 µg/mL. Notably, the mixture significantly eradicated mature *C. albicans* and *C. neoformans* biofilms at 8 and 128 µg/mL, respectively. In particular, the mixture was found to disrupt cell membrane integrity and enhance penetration of antibiotics into fungal cells, suggesting its antifungal mode of action. Hence, combined chelerythrine-sanguinarine shows promise as a potential antifungal and anti-biofilm agent for the management of serious infections caused by *C. albicans* and *C. neoformans* [64].

Gong and co-workers (2019) have evaluated whether chelerythrine (CHT) exhibited antifungal activity against *Candida albicans in vitro* and *in vivo* and explore the underlying mechanisms. Broth microdilution assay and *Galleria mellonella* model were used to evaluate the antifungal effect *in vitro* and *in vivo*, respectively. Mechanism studies were investigated by morphogenesis observation, Fluo-3/AM, DCFH-DA, and rhodamine6G assay, respectively. CHT exhibited antifungal activity against *C. albicans* and performed biofilms with minimum inhibitory concentrations ranging from 2 to 16 µg/ml. Besides, CHT protected *G. mellonella* larvae infected by *C. albicans*. Mechanisms studies revealed that CHT inhibited hyphal growth, increased intracellular calcium concentration, induced accumulation of reactive oxygen species, and inhibited drug transporter activity [26].

On the other hand, Zhong and co-workers (2017) have evaluated sanguinarine (SAN) for its activity against *Candida albicans* biofilms and explore the underlying mechanism. The MIC_{50} of SAN was 3.2 µg/ml, while ≥0.8 µg/ml of SAN could suppress *C. albicans* biofilms. Further study revealed that ≥0.8 µg/ml of SAN could decrease cellular surface hydrophobicity (CSH) and inhibited hypha formation. Real-time reverse transcription-PCR (RT-PCR) results indicated that the exposure of *C. albicans* to SAN suppressed the expression of some adhesion- and hypha-specific/essential genes related to the cyclic AMP (cAMP) pathway, including ALS3, HWP1, ECE1, HGC1, and CYR1 Consistently, the endogenous cAMP level of *C. albicans* was downregulated after SAN treatment, and the addition of cAMP rescued the SAN-induced filamentation defect. In addition, SAN showed relatively low toxicity to human umbilical vein endothelial cells, the 50% inhibitory concentration (IC_{50}) being 7.8 µg/ml. Collectively, the results show that SAN exhibits strong activity against *C. albicans* biofilms, and the activity was associated with its inhibitory effect on adhesion and hypha formation due to cAMP pathway suppression [86].

CONCLUSIONS

In this study, we have evaluated the antimicrobial activity of the ethanolic extracts derived from roots and stalks of *Chelidonium majus* collected from rural and urban agglomerations against the *Enterococcus faecalis* (Andrewes and Horder) Schleifer and Kilpper-Balz (ATCC® 51299™) strain to evaluate the possible use of this plant in preventing infections caused by this strain. Our results revealed, that *C. majus* possessed mild antibacterial properties against *E. faecalis* strain. The ethanolic extract of *C. majus* derived from roots collected from rural agglomerations exhibited the maximum antimicrobial activity against *E. faecalis* (the mean of inhibition zone diameters was 8.77 mm) compared to the control samples (7.48 mm). There was a 17% increase in the zone of inhibition compared to the control sample. Stalk extracts of *C. majus* collected from urban areas also exhibited antibacterial ability against *E. faecalis* strain (7.9 mm) compared to the control samples (7.48 mm). There was a non-significant increase in the zone of inhibition by 5,6% compared to the control samples. Stalk extracts also showed antibacterial properties against the *E. faecalis* strain, but a larger diameter of the zone of inhibition was observed in stalk extracts of *C. majus* collected from rural areas (7.97 mm) compared to the control samples (7.48 mm). *E. faecalis* strain was also susceptible to the stalk extracts of *C. majus* collected from urban agglomerations (7.9 mm). Based on these results, investigated plant extracts can be recommended for further investigations of antibacterial and antioxidant activity.

REFERENCES

1. Barbieri R., Coppo E., Marchese A., Daglia M., Sobarzo-Sánchez E., Nabavi S.F., Nabavi S.M., Phytochemicals for human disease: An update on plant-derived compounds antibacterial activity, Microbiol. Res., vol. 196, pp 44-68, 2017.

2. Bauer A.W., Kirby W.M., Sherris J.C., Turck M., Antibiotic susceptibility testing by a standardized single disk method, Am. J. Clin. Pathol., vol. 45/issue 4, pp 493-496, 1966.

3. Beuria T.K., Santra M.K., Panda D., Sanguinarine blocks cytokinesis in bacteria by inhibiting FtsZ assembly and bundling, Biochemistry, vol. 44/issue 50, pp 16584-16593, 2005.

4. Bjarnsholt T., Kirketerp-Møller K., Jensen P.Ø., Madsen K.G., Phipps R., Krogfelt K., Høiby N., Givskov M., Why chronic wounds will not heal: a novel hypothesis, Wound Repair Regen., vol. 16/issue 1, pp 2-10, 2008.

5. Borges A., Saavedra M.J., Simões M., Insights on antimicrobial resistance, biofilms and the use of phytochemicals as new antimicrobial agents, Curr. Med. Chem., vol. 22/issue 21, pp 2590-2614, 2015.

6. Bournine L., Bensalem S., Peixoto P., Gonzalez A., Maiza-Benabdesselam F., Bedjou F., Wauters J.N., Tits M., Frédérich M., Castronovo V., Bellahcène A., Revealing the anti-tumoral effect of Algerian *Glaucium flavum* roots against human cancer cells, Phytomedicine, vol. 20/issue 13, pp 1211-1218, 2013.

7. Cabo J., Cabo M.M., Cabo M.P., Cruz T., Ruiz C., *Glaucium flavum* Crantz. IV. Antimicrobial activity, Microbios, vol. 56/issue 228-229, pp 177-180, 1988.

8. Chen L., Li X., Zhou X., Zeng J., Ren Z., Lei L., Kang D., Zhang K., Zou J., Li Y., Inhibition of *Enterococcus faecalis* Growth and Biofilm Formation by Molecule Targeting Cyclic di-AMP Synthetase Activity, J. Endod., vol. 44/issue 9, pp 1381-1388, 2018.

9. Cheng R.B., Chen X., Liu S.J., Zhang X.F., Zhang G.H., [Experimental study of the inhibitory effects of *Chelidonium majus* L. extractive on *Streptococcus mutans in vitro*], Shanghai Kou Qiang Yi Xue, vol. 15/issue 3, pp 318-320, 2006.

10. Choi J.G., Kang O.H., Chae H.S., Obiang-Obounou B., Lee Y.S., Oh Y.C., Kim M.S., Shin D.W., Kim J.A., Kim Y.H., Kwon D.Y., Antibacterial activity of *Hylomecon hylomeconoides* against methicillin-resistant *Staphylococcus aureus*, Appl. Biochem. Biotechnol., vol. 160/issue 8, pp 2467-2474, 2010.

11. Chong K.K.L., Tay W.H., Janela B., Yong A.M.H., Liew T.H., Madden L., Keogh D., Barkham T.M.S., Ginhoux F., Becker D.L., Kline K.A., *Enterococcus faecalis* Modulates

Immune Activation and Slows Healing During Wound Infection, J. Infect. Dis., vol. 216/issue 12, 1644-1654, 2017.

12. Colombo M.L., Bosisio E., Pharmacological activities of *Chelidonium majus* L. (Papaveraceae), Pharmacol. Res., vol. 33/issue 2, pp 127-134, 1996.

13. Cordes N., Plasswilm L., Bamberg M., Rodemann H.P., Ukrain, an alkaloid thiophosphoric acid derivative of *Chelidonium majus* L. protects human fibroblasts but not human tumour cells *in vitro* against ionizing radiation, Int. J. Radiat. Biol., vol. 78/issue 1, pp 17-27, 2002.

14. Cruz Martínez C., Diaz Gómez M., Oh M.S., Use of traditional herbal medicine as an alternative in dental treatment in Mexican dentistry: a review, Pharm. Biol., vol. 55/issue 1, pp 1992-1998, 2017.

15. Das S., Natural therapeutics for urinary tract infections – a review, Futur. J. Pharm. Sci., vol. 6/issue 1, pp 64, 2020.

16. Diaz-Sanchez S., D'Souza D., Biswas D., Hanning I., Botanical alternatives to antibiotics for use in organic poultry production, Poult. Sci., vol. 94/issue 6, pp 1419-1430, 2015.

17. Doncheva T., Staniloval M., Vutov V., Philipov S., Alkaloids of Seeds, *in vitro* Cultivated, and *ex vitro* Adapted Plants of the Bulgarian Endemic Species *Papaver degenii* (*Papaveraceae*), Nat. Prod. Commun., vol. 12/issue 3, pp 359-361, 2017.

18. Doyle A.A., Stephens J.C., A review of cinnamaldehyde and its derivatives as antibacterial agents, Fitoterapia, vol. 139, pp 104405, 2019.

19. Dunny G.M., Leonard B.A., Hedberg P.J., Pheromone-inducible conjugation in *Enterococcus faecalis*: Interbacterial and host-parasite chemical communication, J. Bacteriol., vol. 177, pp 871-876, 1995.

20. Dziedzic A., Wojtyczka R.D., Kubina R., Inhibition of Oral *Streptococci* Growth Induced by the Complementary Action of Berberine Chloride and Antibacterial Compounds, Molecules, vol. 20/issue 8, pp 13705-13724, 2015.

21. Ellingsrud C., Agewall S., Morphine in the treatment of acute pulmonary oedema – Why? Int. J. Cardiol., vol. 202, pp 870-873, 2016.

22. Gardiner S.J., Chang A.B., Marchant J.M., Petsky H.L., Codeine versus placebo for chronic cough in children, Cochrane Database Syst. Rev., vol. 7/issue 7, pp CD011914, 2016.

23. Gilca M., Gaman L., Panait E., Stoian I., Atanasiu V., *Chelidonium majus* – an integrative review: traditional knowledge versus modern findings, Forsch. Komplementmed, vol. 17/issue 5, pp 241-248, 2010.

24. Gjødsbøl K., Christensen J.J., Karlsmark T., Jørgensen B., Klein B.M., Krogfelt K.A., Multiple bacterial species reside in chronic wounds: a longitudinal study, Int. Wound J., vol. 3/issue 3, pp 225-231, 2006.

25. Godowski K.C., Antimicrobial action of sanguinarine, J. Clin. Dent., vol. 1/issue 4, pp 96-101, 1989.

26. Gong Y., Li S., Wang W., Li Y., Ma W., Sun S., *In vitro* and *in vivo* activity of chelerythrine against *Candida albicans* and underlying mechanisms, Future Microbiol., vol. 14, pp 1545-1557, 2019.

27. Guo Q., Bai R., Zhao B., Feng X., Zhao Y., Tu P., Chai X., An Ethnopharmacological, Phytochemical and Pharmacological Review of the Genus *Meconopsis*, Am. J. Chin. Med., vol. 44/issue 3, pp 439-462, 2016.

28. Gupta M., Msambichaka L., Ballas S.K., Gupta K., Morphine for the treatment of pain in sickle cell disease, ScientificWorldJournal, vol. 2015, pp: 540154, 2015.

29. Habermehl D., Kammerer B., Handrick R., Eldh T., Gruber C., Cordes N., Daniel P.T., Plasswilm L., Bamberg M., Belka C., Jendrossek V., Proapoptotic activity of Ukrain is based on

Chelidonium majus L. alkaloids and mediated *via* a mitochondrial death pathway, BMC Cancer, vol. 6, pp 14, 2006.

30. Hamoud R., Reichling J., Wink M., Synergistic antibacterial activity of the combination of the alkaloid sanguinarine with EDTA and the antibiotic streptomycin against multidrug resistant bacteria, J. Pharm. Pharmacol., vol. 67/issue 2, pp 264-273, 2015.

31. Hamoud R., Reichling J., Wink M., Synergistic antimicrobial activity of combinations of sanguinarine and EDTA with vancomycin against multidrug resistant bacteria, Drug Metab. Lett., vol. 8/issue 2, pp 119-128, 2014.

32. Hannah J.J., Johnson J.D., Kuftinec M.M., Long-term clinical evaluation of toothpaste and oral rinse containing sanguinaria extract in controlling plaque, gingival inflammation, and sulcular bleeding during orthodontic treatment, Am. J. Orthod. Dentofacial. Orthop., vol. 96/issue 3, pp 199-207, 1989.

33. Hollenbeck B.L., Rice L.B., Intrinsic and acquired resistance mechanisms in enterococcus, Virulence, vol. 3/issue 5, pp 421-433, 2012.

34. Hurlow J., Bowler P.G., Potential implications of biofilm in chronic wounds: a case series, J. Wound Care, vol. 21/issue 3, pp 109-110, 112, 114, 2012.

35. Istatkova R., Nikolaeva-Glomb L., Galabov A., Yadamsuren G.O., Samdan J., Dangaa S., Philipov S., Chemical and antiviral study on alkaloids from *Papaver pseudocanescens* M. Pop. Z Naturforsch C J. Biosci., vol. 67/issue 1-2, pp 22-28, 2012.

36. Jesionek W., Fornal E., Majer-Dziedzic B., Móricz Á.M., Nowicky W., Choma I.M., Investigation of the composition and antibacterial activity of Ukrain™ drug using liquid chromatography techniques, J. Chromatogr. A, vol. 1429, pp 340-347, 2016.

37. Jha A.K., Bais H.P., Vivanco J.M., *Enterococcus faecalis* mammalian virulence-related factors exhibit potent pathogenicity in the *Arabidopsis thaliana* plant model, Infect. Immun., vol. 73, pp 464-475, 2005.

38. Joray M.B., González M.L., Palacios S.M., Carpinella M.C., Antibacterial activity of the plant-derived compounds 23-methyl-6-O-desmethylauricepyrone and (Z,Z)-5-(trideca-4,7-dienyl)resorcinol and their synergy with antibiotics against methicillin-susceptible and resistant *Staphylococcus aureus*, J. Agric. Food Chem., vol. 59/issue 21, pp 11534-11542, 2011.

39. Jorgensen J.H., Ferraro M.J., Antimicrobial susceptibility testing: a review of general principles and contemporary practices, Clin. Infect. Dis., vol. 49/issue 11, pp 1749-1755, 2009.

40. Kang S., Li Z., Yin Z., Jia R., Song X., Li L., Chen Z., Peng L., Qu J., Hu Z., Lai X., Wang G., Liang X., He C., Yin L., The antibacterial mechanism of berberine against *Actinobacillus pleuropneumoniae*, Nat. Prod. Res., vol. 29/issue 23, pp 2203-2206, 2015.

41. Kedzia B., Hołderna-Kedzia E., The effect of alkaloids and other groups of plant compounds on bacteria and fungi, Post. Fitoter., vol. 1, pp 8-16, 2013.

42. Kedzia B., Łozykowska K., Gryszczynska A., Chemical composition and contents of biological active substances in *Chelidonium majus* L., Post. Fitoter., vol. 3, pp 174-181, 2013.

43. Kelley C., Zhang Y., Parhi A., Kaul M., Pilch D.S., LaVoie E.J., 3-Phenyl substituted 6,7-dimethoxyisoquinoline derivatives as FtsZ-targeting antibacterial agents, Bioorg. Med. Chem., vol. 20/issue 24, pp 7012-7029, 2012.

44. Kim S.R., Hwang S.Y., Jang Y.P., Park M.J., Markelonis G.J., Oh T.H., Kim Y.C., Protopine from *Corydalis ternata* has anticholinesterase and antiamnesic activities, Planta Med., vol. 65/issue 3, pp 218-221, 1999.

45. Kosina P., Gregorova J., Gruz J., Vacek J., Kolar M., Vogel M., Roos W., Naumann K., Simanek V., Ulrichova J., Phytochemical and antimicrobial characterization of *Macleaya cordata* herb, Fitoterapia, vol. 81/issue 8, pp 1006-1012, 2010.

46. Krošlák E., Maliar T., Nemeček P., Viskupičová J., Maliarová M., Havrlentová M., Kraic J., Antioxidant and Proteinase Inhibitory Activities of Selected Poppy (*Papaver somniferum* L.) Genotypes, Chem. Biodivers., vol. 14/issue 9, 2017.

47. Lin L., Liu Y.C., Huang J.L., Liu X.B., Qing Z.X., Zeng J.G., Liu Z.Y., Medicinal plants of the genus *Macleaya* (*Macleaya cordata, Macleaya microcarpa*): A review of their phytochemistry, pharmacology, and toxicology, Phytother. Res., vol. 32/issue 1, pp 19-48, 2018.

48. Liu H., Wang J., Zhao J., Lu S., Wang J., Jiang W., Ma Z., Zhou L., Isoquinoline alkaloids from *Macleaya cordata* active against plant microbial pathogens, Nat. Prod. Commun., vol. 4/issue 11, pp 1557-1560, 2009.

49. Mahady G.B., Pendland S.L., Stoia A., Chadwick L.R., *In vitro* susceptibility of *Helicobacter pylori* to isoquinoline alkaloids from *Sanguinaria canadensis* and *Hydrastis Canadensis*, Phytother. Res., vol. 17/issue 3, pp 217-221, 2003.

50. Mehrara M., Halakoo M., Hakemi-Vala M., Hashemi S.J., Asgarpanah J., Antibacterial and antifungal activities of the endemic species *Glaucium vitellinum* Boiss. and Buhse, Avicenna J. Phytomed., vol. 5/issue 1, pp 56-61, 2015.

51. Meng F., Zuo G., Hao X., Wang G., Xiao H., Zhang J., Xu G., Antifungal activity of the benzo[c]phenanthridine alkaloids from *Chelidonium majus* Linn against resistant clinical yeast isolates, J. Ethnopharmacol., vol. 125/issue 3, pp 494-496, 2009.

52. Meyer A., Imming P., Benzylisoquinoline alkaloids from the *Papaveraceae*: the heritage of Johannes Gadamer (1867-1928), J. Nat. Prod., vol. 74/issue 11, pp 2482-2487, 2011.

53. Morteza-Semnani K., Mahmoudi M., Heidar M.R., Analgesic activity of the methanolic extract and total alkaloids of *Glaucium paucilobum*, Methods Find Exp. Clin. Pharmacol., vol. 28/issue 3, pp 151-155, 2006.

54. Morteza-Semnani K., Saeedi M., Hamidian M., Anti-inflammatory and analgesic activity of the topical preparation of *Glaucium grandiflorum*, Fitoterapia, vol. 75/issue 2, pp 123-129, 2004.

55. Navarro V., Delgado G., Two antimicrobial alkaloids from *Bocconia arborea*, J. Ethnopharmacol., vol. 66/issue 2, pp 223-226, 1999.

56. Nawrot J., Wilk-Jędrusik M., Nawrot S., Nawrot K., Wilk B., Dawid-Pać R., Urbańska M., Micek I., Nowak G., Gornowicz-Porowska J., Milky Sap of Greater Celandine (*Chelidonium majus* L.) and Anti-Viral Properties, Int. J. Environ. Res. Public Health, vol. 17/issue 5, pp 1540, 2020.

57. Nawrot R., Lippmann R., Matros A., Musidlak O., Nowicki G., Mock H.P., Proteomic comparison of *Chelidonium majus* L. latex in different phases of plant development, Plant Physiol. Biochem., vol. 112, pp 312-325, 2017.

58. Niu X., Fan T., Li W., Xing W., Huang H., The anti-inflammatory effects of sanguinarine and its modulation of inflammatory mediators from peritoneal macrophages, Eur. J. Pharmacol., vol. 689/issue 1-3, pp 262-269, 2012.

59.Okoth D.A., Chenia H.Y., Koorbanally N.A., Antibacterial and antioxidant activities of flavonoids from *Lannea alata* (Engl.) Engl. (Anacardiaceae), Phytochem. Lett., vol. 6, pp 476-481, 2013.

60. Opletal L., Ločárek M., Fraňková A., Chlebek J., Smíd J., Hošt'álková A., Safratová M., Hulcová D., Klouček P., Rozkot M., Cahlíková L., Antimicrobial activity of extracts and isoquinoline alkaloids of selected *Papaveraceae* plants, Nat. Prod. Commun., vol. 9/issue 12, pp 1709-1712, 2014.

61. Orhana I., Ozçelik B., Karaoğlu T., Sener B., Antiviral and antimicrobial profiles of selected isoquinoline alkaloids from *Fumaria* and *Corydalis* species, Z. Naturforsch. C J. Biosci., vol. 62/issue 1-2, pp 19-26, 2007.

62. Paczkowska M., Chanaj-Kaczmarek J., Romaniuk-Drapała A., Rubiś B., Szymanowska D., Kobus-Cisowska J., Szymańska E., Winnicka K., Cielecka-Piontek J., Mucoadhesive Chitosan Delivery System with *Chelidonii* Herba Lyophilized Extract as a Promising Strategy for Vaginitis Treatment, J. Clin. Med., vol. 9/issue 4, pp 1208, 2020.

63. Poulios E., Vasios G.K., Psara E., Giaginis C., Medicinal plants consumption against urinary tract infections: a narrative review of the current evidence, Expert. Rev. Anti Infect. Ther., vol. 19/issue 4, pp 519-528, 2021.

64. Qian W., Yang M., Li X., Sun Z., Li Y., Wang X., Wang T., Anti-microbial and anti-biofilm activities of combined chelerythrine-sanguinarine and mode of action against *Candida albicans* and *Cryptococcus neoformans in vitro*, Colloids Surf. B Biointerfaces, vol. 191, pp 111003, 2020.

65. Rahim K., Saleha S., Zhu X., Huo L., Basit A., Franco O.L., Bacterial Contribution in Chronicity of Wounds, Microb. Ecol., vol. 73/issue 3, pp 710-721, 2017.

66. Rao C.V., Verma A.R., Gupta P.K., Vijayakumar M., Anti-inflammatory and anti-nociceptive activities of *Fumaria indica* whole plant extract in experimental animals, Acta Pharm., vol. 57/issue 4, pp 491-498, 2007.

67. Shang X., Wang D., Miao X., Wang Y., Zhang J., Wang X., Zhang Y., Pan H., Antinociceptive and anti-tussive activities of the ethanol extract of the flowers of *Meconopsis punicea* Maxim., BMC Complement Altern. Med., vol. 15, pp 154, 2015.

68. Song J.Y., Yang H.O., Pyo S.N., Jung I.S., Yi S.Y., Yun Y.S., Immunomodulatory activity of protein-bound polysaccharide extracted from *Chelidonium majus*, Arch. Pharm. Res., vol. 25/issue 2, pp 158-164, 2002.

69. Susak Y.M., Skivka L.M., Rudik M.P., Pozur V.V., Liubunya A.V., Comparative investigation of the effect of Ukrain on growth of ascites and solid forms of Ehrlich's carcinoma, Exp. Oncol., vol. 32/issue 2, pp 107-110, 2010.

70. Tani C., Nagakura N., Saeki S., Kao M.T., Alkaloids of papaveraceous plants, Planta Med., vol. 41/issue 4, pp 403-405, 1981.

71. Teschke R., Frenzel C., Glass X., Schulze J., Eickhoff A., Greater Celandine hepatotoxicity: a clinical review, Ann. Hepatol., vol. 11/issue 6, pp 838-848, 2012.

72. Uglyanitsa K.N., Nefyodov L.I., Doroshenko Y.M., Nowicky J.W., Volchek I.V., Brzosko W.J., Hodysh Y.J., Ukrain: a novel antitumor drug, Drugs Exp. Clin. Res., vol, 26/issue 5-6, pp 341-356, 2000.

73. Vale F.F., Oleastro M., Overview of the phytomedicine approaches against *Helicobacter pylori*, World J. Gastroenterol., vol. 20/issue 19, pp 5594-5609, 2014.

74. Voltchek I., Kamyshentsev M., Lavinsky Y., Nowicky J., Medvedev Y., Litvinchuk L., Comparative study of the cytostatic effects of Oliphen and Ukrain, J. Chemother., vol. 8/issue 2, pp 144-146, 1996.

75. Wang X.J., Min C.L., Han P.L., Qian J., [Identification and Fermentation Optimization of an Endophytic Fungus BLH34 with Antibacterial Activity from *Macleaya cordata*], Zhong Yao Cai, vol. 39/issue 8, pp 1728-1733, 2016.

76. Wang Y., Wang D., Zhang J., Liu D., Wang Z., Meng D., Isoquinolines from *Corydalis tomentella* from Tibet, China, possess hepatoprotective activities, Phytochemistry, vol. 155, pp 93-99, 2018.

77. Warowicka A., Popenda Ł., Bartkowiak G., Musidlak O., Litowczenko-Cybulska J., Kuźma D., Nawrot R., Jurga S., Goździcka-Józefiak A., Protoberberine compounds extracted from *Chelidonium majus* L. as novel natural photosensitizers for cancer therapy, Phytomedicine, vol. 64, pp 152919, 2019.

78. Wei Q.H., Cui D.Z., Liu X.F., Chai Y.Y., Zhao N., Wang J.Y., Zhao M., *In vitro* antifungal activity and possible mechanisms of action of chelerythrine, Pestic. Biochem. Physiol., vol. 164, pp 140-148, 2020.

79. Xia X., He J., Liu B., Shao Z., Xu Q., Hu T., Yu C., Liu X., Liao Y., Liu N., Huang H., Targeting ERα degradation by L-Tetrahydropalmatine provides a novel strategy for breast cancer treatment, Int. J. Biol. Sci., vol. 16/issue 12, pp 2192-2204, 2020.

80. Xie Q., Johnson B.R., Wenckus C.S., Fayad M.I., Wu C.D., Efficacy of berberine, an antimicrobial plant alkaloid, as an endodontic irrigant against a mixed-culture biofilm in an *in vitro* tooth model, J. Endod., vol. 38/issue 8, pp 1114-1117, 2012.

81. Yu X., Gao X., Zhu Z., Cao Y., Zhang Q., Tu P., Chai X., Alkaloids from the tribe *Bocconieae* (*Papaveraceae*): a chemical and biological review, Molecules, vol. 19/issue 9, pp 13042-13060, 2014.

82.Zar J.H., Biostatistical Analysis, 4th ed., Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1999.

83. Zhang B., Huang R., Hua J., Liang H., Pan Y., Dai L., Liang D., Wang H., Antitumor lignanamides from the aerial parts of *Corydalis saxicola*, Phytomedicine, vol. 23/issue 13, pp 1599-1609, 2016.

84. Zhang B., Zeng M., Li M., Kan Y., Li B., Xu R., Wu Y., Wang S., Zheng X., Feng W., Protopine Protects Mice against LPS-Induced Acute Kidney Injury by Inhibiting Apoptosis and Inflammation via the TLR4 Signaling Pathway, Molecules, vol. 25/issue 1, pp 15, 2019.

85. Zhang R., Guo Q., Kennelly E.J., Long C., Chai X., Diverse alkaloids and biological activities of *Fumaria* (*Papaveraceae*): An ethnomedicinal group, Fitoterapia, vol. 146, pp 104697, 2020.

86. Zhong H., Hu D.D., Hu G.H., Su J., Bi S., Zhang Z.E., Wang Z., Zhang R.L., Xu Z., Jiang Y.Y., Wang Y., Activity of Sanguinarine against *Candida albicans* Biofilms, Antimicrob. Agents Chemother., vol. 61/issue 5, pp e02259-16, 2017.

87. Zielińska S., Jezierska-Domaradzka A., Wójciak-Kosior M., Sowa I., Junka A., Matkowski A.M., Greater Celandine's Ups and Downs-21 Centuries of Medicinal Uses of *Chelidonium majus* From the Viewpoint of Today's Pharmacology, Front. Pharmacol., vol. 9, pp 299, 2018.

88. Zielińska S., Wójciak-Kosior M., Dziągwa-Becker M., Gleńsk M., Sowa I., Fijałkowski K., Rurańska-Smutnicka D., Matkowski A., Junka A., The Activity of Isoquinoline Alkaloids and Extracts from *Chelidonium majus* against Pathogenic Bacteria and *Candida* sp., Toxins (Basel), vol. 11/issue 7, pp 406, 2019.

89. Zuo G.Y., Meng F.Y., Hao X.Y., Zhang Y.L., Wang G.C., Xu G.L., Antibacterial alkaloids from *Chelidonium majus* Linn (*Papaveraceae*) against clinical isolates of methicillin-resistant *Staphylococcus aureus*, J. Pharm. Pharm. Sci., vol. 11/issue 4, pp 90-94, 2008.

TRANSFORMATION OF THE WATER AND MASS EXCHANGE ON THE SHATSK NATIONAL NATURAL PARK TERRITORY UNDER THE INFLUENCE OF CLIMATIC AND ANTROPOGENIC FACTORS

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ABSTRACT

The article is devoted to the estimation of the influence of climatic and anthropogenic factors on the hydro-ecological state of the Shatsk National Natural Park territory.The analysis of surface and ground water regimes during the last years is provided. Some aspects of the ecological state of Shatsk National Natural Park lakes are considered. The new complex mathematical model of the water-and massexchange is developed for forecasting of these processes on long period of time.It is shown that ecological situation on the considered territory has become worse substantially in whole. The environmental damage on the water resources in giving territory owing to anthropogenic activity is discussed.

Key words: Shatsk reserve, quarry, environment, filtration, ground water pollution, forecast, numerical calculations, modeling, recommendations

INTRODUCTION

The stable development of any territory presupposes first of all an effective system of vital activity of the population including the corresponding list of necessary requirements and needs and also a problem of environmental protection. One of such territoriy is Shatsk National Nature Park (Fig.1,4).It was established in 1983 and is the Ukrainian part of the Trilateral Poland-Belarusian-Ukrainian Biosphere Reserve "Western Polissya" with a total area of 75075 ha within which there are four functional zones: protected, regulated, stationary recreation and economic. At the same time the Shatsk Lakes are recognized by UNESCO as the most valuable freshwater ecosystem in Eastern Europe. Therefore the preservation of the park from harmful factors that can disrupt the ecological balance and stability here is one of the priorities in the environmental activities of our state.In modern conditions as evidenced by the monitoring of the main indicators of the natural environment there is a significant impact of climatic and anthropogenic factors on the hydro-ecological condition of the study area [1,2,5,9,11,12].The aim of the research is to assess the impact of climatic and anthropogenic factors on the ecological condition here including the possible impact on the hydrodynamics of groundwater the Khotyslav quarry of building materials development(Republic of Belarus).

THE RESEARCH RESULTS AND DISCUSSIONS

As known the hydrogeological conditions of this region are quite complex and insufficiently studied. From the west to the east the territory is crossed by the valley of the river Pripyat with main tributaries of the rivers Tenetyska and Vyzhivka and others and from the west it is limited by the main river the Western Bug (Fig.1). The conventional watershed between the Baltic and Black Seas runs through the study area[1,5,11,20,22,23]. Global climate changes and increasing of the water consumption by the population in the region worsen the hydro-ecological conditions of this territory. According to observations of ground water levels (GWL) for 2015-2019 there is decreasing in comparison to previous years despite the relative stability of the value of infiltration inflow to groundwater. One of the factors of such influence is global warming and increasing of the evaporation from a surface of the earth which prevails on the infiltration in the given territory causing the processes of increasing of the aeration zone capacity and decreasing of the GWL. So from 2010 to 2018 years the value of precipitation was changed from 660.0 to 477.0 mm/ year in average where as the value of evaporation was changed from 794.0 to 822.0 mm/ year indicating on the climate warming in this region [3,12,16,22,23]. The analysis of the dynamics of changes in water levels of Shatsk lakes allowed to estimate the its fluctuations and showed the downward trend in general (Table 1). Comparison of water levels in reservoir Turske and Dovge from 1991 to 2016 years showed that in reservoir Turske the levels decreased from 0.77 to 0.41 m and in lake Dovge- from 1.33 to 0.62 m. As can saw the amplitude of level fluctuations is significant in 2016 both in the lakes and in the reservoir Turske. The long-term level fluctuations for the year 2014 were 0.12 m and then in 2015 and 2016 - 0.85 m. The maximum changing of levels in the lakes were observed in April 2015 with precipitation in March 124% of normal and in April 108% of normal. But with precipitation of 280.7% of the norm in March and 210.5% of the norm in April no increasing in the levels was observed. In reservoir Turske the water level in 2015 was 0.97 m, in 2016 - 0.41 m and in lake Dovge the water level regime has not changed [2,16,23].

Table 1. Water level regime of Shatsk lakes during 1991-2016 years

Lake	Abs.mark of check point near water plane (2013 y.), m	critical (on 25.09.1991 y.)		natural (on 23.10. 1992 y.)	Modern average in month water levels					
					2014 year		2015 year		2016 year	
		Abs.mark of water level,m	Water level, m		Abs.mark of water level ,m	Water level, m	Abs. mark of water level, m	Water level	Abs.mark of water level,m	Water level , m
Reservoir Turske	156,17	155,4	0,77	156,02	156,38	0,20	157,14	0,97	156,58	0,41
Dovge	156,22	154,89	1,33		156,89	0,67	156,84	0,62	156,84	0,62
Svjate	158,15	157,33	0,82	158,55	158,70	0,55	158,82	0,67		

The highest levels in lake Svityaz were observed in 2007-2010 and the lowest - in 1973 - 1974 after drainage works and active use of drained lands until the mid-90s of the last century were provided. However in the future despite the increase in evaporation the water levels in general increased and fluctuations occurred according to the seasons and cyclically in the "dry - wet" years depending on the weather conditions. Most likely that the stabilization and increase of the water levels during the above period was due to the decrease in the intensity of drainage.

Despite this starting from 2010-2011 there has been a slight decrease in water levels especially the minimum which cannot be explained only by the changes in climatic conditions. It is obvious that there is a man-made impact on the hydrological regime of the lakes [3,16,19]..

Although fluctuations occur seasonally there is a dependence of fluctuations in artesian water levels on precipitation and air temperature with some delay of up to six months. Fluctuations in groundwater levels respond more quickly to rainfall as their area of supply coincides with the area of distribution. The reaction of artesian water levels is closer in nature to changes in the levels in lake Svityaz which may be explained by the predominance of artesian waters in its supply.As the all lakes of Shatsk National Park have a close hydraulic connection the same situation is observed in other lakes [4,5,7,23]. According to this we may to consider that the all water system in this region attained the relative balance during last 29-25 years.In the some other state is the problem of water media polution [4,5,14,18]..Studying of the hydro-chemical conditions of the surface and ground waters have shown that for all water-bearing system the exceeding of the limiting concentrations of the nitrogen compounds, phosphates, ferrous and BOD_5 is characterized. This situation is caused by the presence of the numerous sources of the ground waters pollutions, namely: domestic, industrial waste waters, agricultural works, drainage systems exploitation, transport ones and etc [14,22,23].. So during the agricultural works in the periods of the fertilizers using and with the precipitation increasing and at the high levels of surface and ground waters the significant ground water pollution is observed. In summer the increasing of the pollutants concentrations is due with the precipitation deficit, high air temperature and the relative low moisture. As a result the decreasing of the water levels in the channels and in the exploit wells and increasing of the anaerobic processes intensity are observed. At this the values of the BOD_5 and COD are increasing and the water chemical properties have become worse but during of cleaning of the some land-reclamation systems the concentrations of the nitrogen ammonium , phosphates and ferrous decreasing was observed owing to increasing of the flow velocity and the oxygen in its [4,5,11,14,18].

The main role in the ground waters contamination play the concentrated sources of the pollution. They are the earth storage ponds of the industrial, domestic and agricultural wastes. To the potential sources of the pollution belong the storages of the rubbish with the solid domestic wastes. The bottom most of them has not isolation, some of ones have isolate screens or the clay bottom that decrease of the penetration of the pollutants to ground waters but the drainage ditch gutters with the isolation are absent. The seasonal or constant fluctuations of the ground waters levels on 0.3-1.5 m in the some rubbish storages in the region are an additional factors of pollution ones. Besides that the monitoring of the ground waters quality is not carried out. All cleaning plants in the settlements and numerous depositories of the mineral fertilizers and pesticides are the sources of the ground water pollution too. They are situated in Shatsk, Ratno, Starovyzivka, Kamin-Kashyrsk , Zabolottya and in other places. The surface waters are not protected and not use for municipal water-supply. They are used in villages for individual supply of the population in the draw-wells. The main aquifer in the region is in the Upper cretaceous sediments which are separated from aquifer in Quaternary ones by the impenetrable layer of the soft formation chalk with thickness 7-10m [22,23]. This layer is absent on the watersheds and in the overdeepening river valleys where the aquifer pollution by the infiltration waters have a place. For water supply the individual wells and water uptakes are used (Ratno water uptake). This aquifer is perspective for water supply expansion on West Polyssya territory in future. The main rivers of the region are contaminated by the municipal and industrial sewage and transport systems [14,18,23]. An additional pollution of the river ecosystem is connected with uncontrolled activity of the guests and tourists especially on the territory of the Park [5,14]. One of the sources of the rivers and lakes pollution are the surface runoff from the territories of the settlements and the washing off the chemicals from the agricultural fields. Discharge of the not clean completely sewage from municipal treatment plants and milk factories goes to all rivers of the regions and contaminate theirs. So the total wash off of the waste waters that goes to ground waters, rivers and ponds during the year contains in average 20-50 kg /ha of the phosphorous and 100-180 kg/ha of nitrogen. Only the discharge of the not cleaned completely water in Prypyat river reached more than 420 t/year. Analysis of the state of the ground waters pollution problem in the given region allows to conclude that without special protective measures the water system will be received in later on only from the fields almost to 25% of nitrogen and 5% of phosphorous from common volume of the introduced fertilizers [5,14,18,20,23]. Beside of the problems of protection of the water resources on observed territory from contamination of different origin there are several main anthropogenic factors that significantly impact on the ecological conditions of the Park, namely: drainage reclamation systems, development of the Khotyslavske building material deposit, increase in water consumption, the Zhyrychi ore deposit development near district Ratno on the against the global climate changes in[3,4,19]. The main and serious source of the ground waters pollution in region is the Khotislav chalk quarry situated in Belarus near the border with Ukraine. The results of the monitoring, hydrodynamical calculations and modeling have shown that the influence of quarry exploitation on ground water drawdowns reaches Prypyat river now and will be spread in radius 30 km and more on 2040 year [2,16,19]. Obviously that it influences and will be influences later on the all ecological situation of the Western Volyn territory in whole. Many scientific papers, journalistic materials and discussions are devoted to this problem [3,5,7,8,11,19,22]. In 2009 the Belarusian side assessed the impact of the development of this field on the environment using mathematical modeling methods. Based on the data of forecast modeling for the period up to 2040 the authors claimed that a significant impact on the hydrodynamics of groundwater in Ukraine including the territory of Shatsk Park is not expected [8,13].

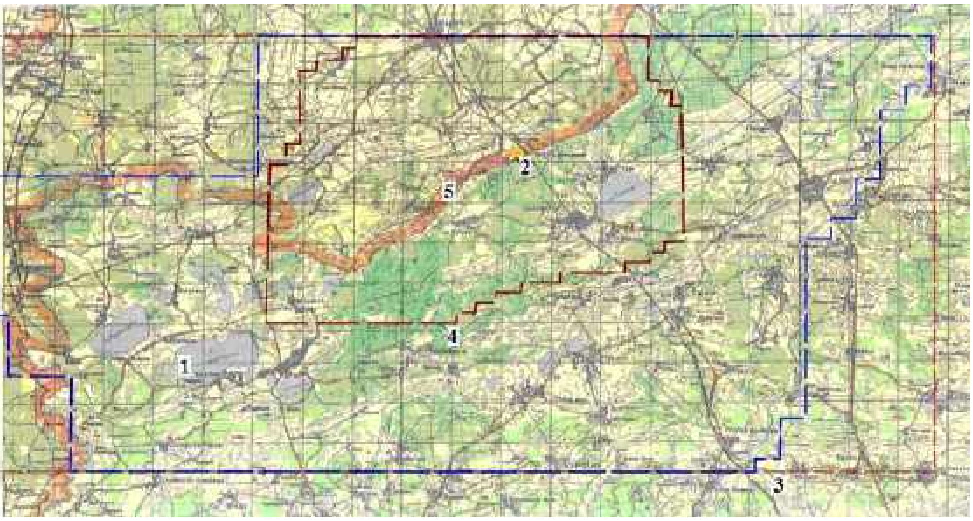

Fig. 1. Fragment of the Volyn region topographical map scale 1:200 000 with the boundares of created geofiltration model including of the territory of Shatsk National Natural Park.Within the model domain the Belarusian side model is highlighted [21]:
1- territory of Shatsk National Natural Park; 2- Khotislav quarry location; 3- boundary of created geofiltration model; 4- geofiltration model of Belarus side; 5- border Ukraine-Belarus

Analysis of this model results showed that one is limited and not includes the territory of the park and therefore the conclusions concerning the area of possible influence are rather doubtful (Fig.1). It is obvious that the development of a quarry to a depth of 40-50 m poses a serious threat to the existence of the Shatsk Lakes as some of them represent a single water system with the Rita River which begins from lake Krymno in Ukraine that in turn it is connected with other lakes of the park by natural watercourses and canals [5,22,23]. According to the simulation data of the Belarusian side at the end of the forecast period quarry development (2040) the water discharge from the quarry will completely take up the flow of this river which will lead to unpredictable consequences on the hydrological regime of Shatsky lakes and aquifers of the active water exchange zone. In addition the territory of the park is heavily karstified and the karst is confined with a depth more than 60 m. As the main direction of ground water flow is directed towards quarry the lakes of karst origin may disappear[23]. In connection with the above and that to account of the main factors of formation the hydroecological situation in this region in details the new permanently working mathematical model was created. The model covers the area about 3200 km^2. That to takes into account outflow from quarry more precisely the choosed discrete mesh is uneven with minimal step 0.5 km and maximum 2.0 km. The total number of model mesh nodes is 1176 including of the all ones (fictive and active). The ground water filtration is considered as a system with two aquifers in Quaternary sediments and in the fractured chalk ones which interact hydraucally with each other throug a weakly permable clay layer [2,5,13,16,20,22].The aim of this model realization is in the comparison the results of the forecasts on the created model with the modeling data of the Belarus side. At this the data on the filtration characteristics of aquifers and all water system of the Belarus side were partially used during the forecast calculations [8,13]. On the first stage of model creation the schematization of the filtration domain was carried out both in plane and in section. Waterbearing thickness was schematized in section as two-layer aquifer with a single weekpermable separative layer. Discharge on the model was taken into account as a difference between the average values of infiltration and evaporation and the inflow to aquifer from bulow was assumed to be zero. The evaporation data on period 2019-2018 years were calculated with using a famous equation of Penman-Monteith [15]. In plane the external boundaries were choosed on river South Bug (west boundary of model) and on river Vyzhivka (east boundary of model). The south boundary of model was given along to line of regional watershed between basins of Black and Baltic seas and the north boundary coinside with part of Belarus model, with the border line Ukraine-Belarus and is propagated on Ukrainian territory on 11 km to east (Fig.1). On the west and east boundaries were given the third kind boundary conditions and on the others the first one as a constant values of ground water levels. The mesh of reclamation canals, reservoir and lakes were given on model as boundary conditions of second kind (Q=const) or third kind (Q= f(z)) in dependence of conditions of interaction the surface and ground water. The filtration losses on water cources were determined in dependence on filtration resistances of understream sediments, transmissivity of aquifers and the river width. Mathematical model of transient filtration in this domain taking into account on the adopted schematization is described in many corresponding works dealing with the problems of the water resources valuation and protection from its contamination [17]. That to increase the reliability of the forecast problem solutions the model calibration was performed which consisted in the solutions the inverse problems for refining and determining of its main parameters using of the modern methods of identification and corresponding program software. The preliminary analytic and numerical calculations shows that under influence of Khotyslav quarry exploitation in a short time this waterbearing system may be considered as one aquifer with integrated filtration parameters of all watersaturated thickness [16]. To proceed from this fact the transient radial filtration problem for scheme of infinite filtration with integrated flow parameters was realized firstly [2,16]. On the Fig.2-4 and in Table 2 the results of numerical-analytic modeling are presented. On the section on Fig.2

the graphs of drawdowns of ground water in direction to reservoir Turske on 2040 year at drawdowns on the contour of quarry S_0 = 12.0 and 45.0 are showed. Reserve is located on distance 7.6 km from quarry in south-east directions on territory of Ukraine and the posible drawdown in it will be 7.96 m at S_0= 45.0 m in quarry (Table 2). In such drawdown and present depth in it (about 2.0 m) reserve will turn into marsh that will influence substantially on all reclamation system in this region. The spreading of the drawdowns on the west in direction to lake Krymno will reach 29.0 km to village Khripsk and will spread all over the territory of Shatsk park (Fig.3,4; Table 2).

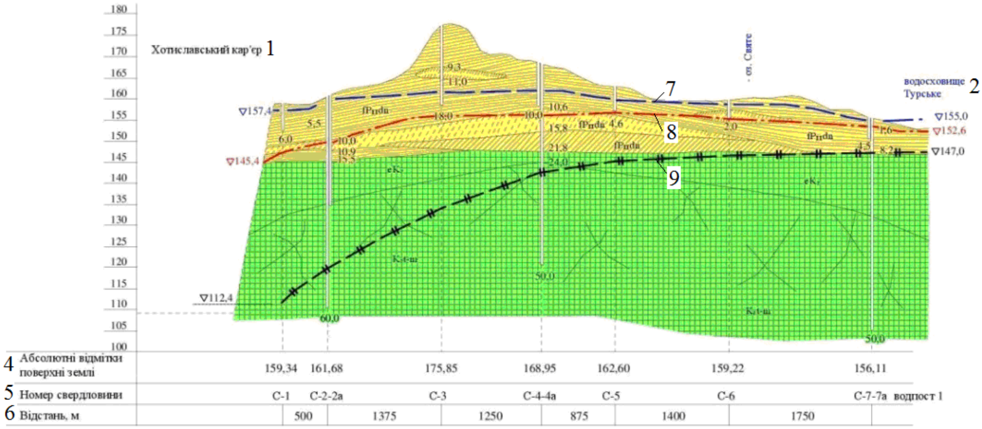

Fig.2. Longitudinal geologic-hydrogeologic section along the range reservoir Turske-Khotislav quarry

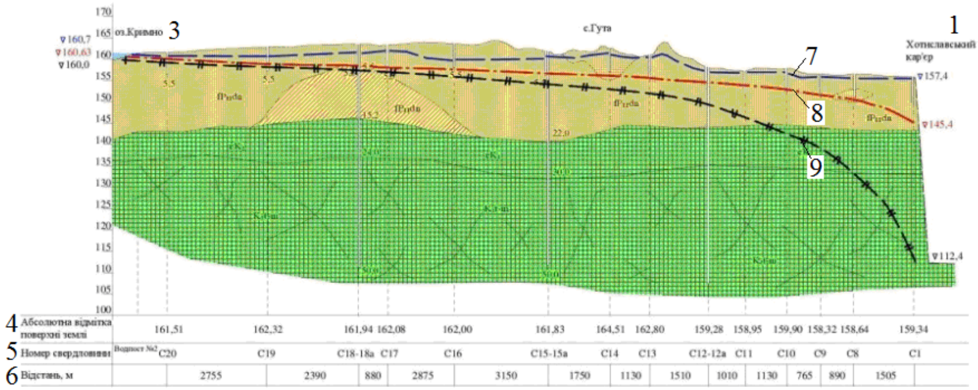

Fig.3. Longitudinal geologic-hydrogeologic section along the range lake Krymno-Khotislav quarry: 1-Khotislav quarry; 2- reservoir Turske; 3- lake Krymno; 4- absolute mark of earth surface,m; 5- number of well; 6- distance between the wells; 7-phone ground water levels; 8- ground water levels at the drawdown S_0 =12.0 m on the quarry contour on 2040 year; 9- ground water levels at the drawdown S_0 =45.0 m on the quarry contour on 2040 year;

Table 2. Data on groundwater level drawdowns obtained by numerical simulation results at S_0 = 45.0 m

№ n/a	Distance from the career, km	S_0 = 45,0 m, t = 2040 year
1.	lake Svyate, 6,0	10,37 m
2.	village of Guta, 7,0	8,86 m
3.	settlement of urban type Zabolotya, 7,0	8,86 m
4.	lake Velikhov, 7,2	8,46 m
5.	reservoir Turske, 7,6	7,96 m
6.	village Zalisy, 10,0	2,97 m
7.	village Yarevishche, 14,4	2,48 m
8.	Pripyat River, 16,4	1,5 m
9.	lake Krymno, 17,2	1,43 m
10.	settlement of urban type Ratne, 23,4	0,39 m
11.	lake Liutsymer, 25,6	0,2 m
12.	lake Svityaz, 25,8	0,19 m
13.	village Khripsk, 29,0	0,10 m

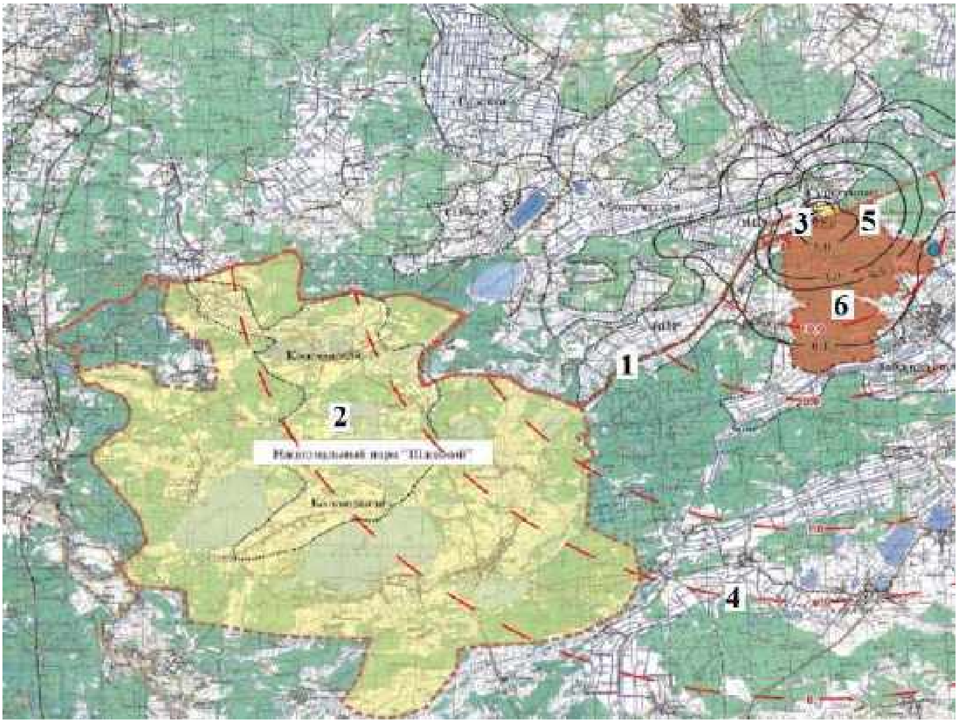

Fig.4. Fragment of the Volyn region map scale 1:200000 with selected territory of Shatsk National Natural Park and with data of isolines of drawdowns on 2040 year at S_0 =45.0 m on the Khotislav quarry contour obtained by numerical modeling on the creative alternative model: 1-Ukraine-Belarus border; 2- territory of Shatsk Park; 3- Khotislav quarry location; 4- drawdown isolines of ground water, m; 5- contours of depression cone calculated by numerical modeling on the Belarus model; 6- reserve “Lipinky“ on the Ukrainian territory.

As one can see from the Table 2 and Fig 4 the possible quarry influence on the Shatsk park territory will show itself in the drawdowns on 0.1-0.2 m in average. If to compare the calculated drawdowns values with the depths of the some lakes so it can see that depth of lake Svjate will decrease on 10.0 m at today's depth 15.0 m; lake Liutsymer on 0.2 at today's 11.2 m; lake Svityaz on 0.19 m at today's 58.4 m and etc. Identical picture will wait for river mesh. If takes into account on the fact that almost all rivers and canals are characterized by the small depths, for example, the depth of Prypjat river near village Rechytsja is 2.73 m and above the stream is smaller yet, the depth of Vyzhivka is 0.97 m then may be full dry up all rivers and drain canals.

As the Khotyslav quarry is located on the conditional watershed between the water basins of Baltic and Black Seas we make proposal that in future will begin the redistibution of water resources from south to north in quarry direction and its depletion.The approximate calculations of environmental damage due to the redistribution of water resources showed that the damage will be above 10 000 000 UAN per year only at the expence of Black Sea basin resources decreasing [10,19]. The depletion of water resourses river Prypjat basin will lead to unpredictable negative consequences for territory Shatsk park and West Volyn in whole.

The system environmental problems of the transboundary impact of quarry will lead to that some types of hydrophilic flora and fauna may disappear when groundwater levels fall by even one meter [22,23]. Another no less important anthropogenic factor in the studied area is the exploration of the Zhyrychy copper ore deposit. At the beginning of its exploration many large-diameter productive wells were drilled which due to many factors led to mixing of waters of different underground horizons, their pollution and deterioration of drinking water quality in general. Lack of the valid data on the work of this quarry not allows to takes into account its exploitation regime now but it will be realized during solutions of new forecast problems on the created model. Global climate change and increasing water consumption by the population of the border area also have a negative impact on the hydro-ecological condition of the territory of Western Polissya. According to project decisions relative increasing of the water-supply in the given region to 70 000 m^3 /day the load on the water resources will increase substantially and decrease the ground water levels in addition. At this the cone of depression will spread to Western Bug valley [11,14,16,22]. A previous calculation of the water balance in this area showed that the replenishment of lakes occurs both at the expense of aquifer water and from the inflow of precipitation. Despite the fact that in 2016 the annual rainfall exceeded the norm by almost 100 mm the water levels in the lakes decreased that indicates about the impact on the levels the anthropogenic factors and Khotislav quarry in the first place [2,3,16].

CONCLUSIONS

The analysis of anthropogenic and climatic conditions of the studied territory of Shatsk park shows that the hydro-ecological condition of the territory is actually influenced by both climatic and man-made factors main of which is the exploitation of the Khotyslav quarry that began in 2009. According to the forecast calculations the impact will increase due to further development of the quarry violating the overall ecological condition of the areas that fall into the zone of its possible impact. In whole the anthropogenic influence have changed the geochemical situation in region and the chemical content of the surface and ground waters. That to improve the quality of water resources we propose the some methods and measures, namely: to stop the discharge of the not cleaned completely effluent sewage. For that it is necessary to reconstruct the treatment plants and increase the productivities ones in such case that theirs capacity would be more than the volume of effluent sewage; to provide the additional effluent sewage cleaning before discharging waste waters in the rivers in dependence of pollution type; implementation of the water supply return systems that allows to use the cleaned sewage repeatedly for technical aims; live-stock complexes and farms must have the separate cleaning of the live-stock and domestic sewage; matter must to store in special depositories with impenetrable bottom and the sloping ditch gutters; rain waters from the places where the live-stocks are situated must to be cleaned obligatory; drainage systems must to be cleaned regularly that to improve theirs run-off and dissolution of the different pollutants; creation along the rivers and reservoirs shores the protective zones in 200m width where using of any pesticides and fertilizers will be interdicted ; to develop effective technical and management measures for reducing of the negative influence on the ecology of the territory the Khotislav quarry exploitation [6,14,16,18]. On our opinion the measures and recommendations proposed by Belarus side relative decreasing of the negative impact of the quarry exploitation on the territory Park and West Polissja are not real and justify, namely: the “wall in the soil” above 60 m depth that is technologically very hard to realize; building of compensations canals around of quarry perimeter for decreasing of ground water flow to quarry that is not efficient taking into account on the depth quarry development; creation of the hydraulic screens and ets [8,13]. It should be noticed that the numerical scientific-practical meetings and conferences on the situation around the quarry come to discussion on improving of the water levels monitoring. The quarry development is projected on 30 years and according to obtained forecast calculations inflow to one will be the millions cubic metres of water that is equal the third part of West Polyssja territory water resources. It means that will be unpredictable negative consequences relative ecological state of water system here. That to avoid the forecast catastrophe on the West Polyssja territory most effective and to our opinion only one of proposition is carrying over the quarry deep down in Belarus territory on 30-40 km that allows to preserve the stable water-ecological state of all West Volyn region as the proposed measures and recommendations of Belarus side relative ecological protection of Shatsk park are not real and substantiate as was said above. In addition that to improve the arise situation it is necessary to our mind to provide the complex of the scientific and researches investigations on the given territory aimed on the evaluation of natural conditions , the impact of agricultural activity, intensity of water resources exploitation for water supply purposes, reconstruction of meliorate and water treatment systems, valuation of the main filtration parameters of the geo- hydrogeological media; valuation of the biochemical processes in soils and content of the organic matter and carbon/nitrogen balance, investigations of the influence of the climate, precipitation and temperature, selection of suitable cultures and determination of the rotation systems, using of suitable fertilizers and chemical inhibitors, determination of the quantity, times and ways of fertilizer application with the aim of minimizing of the fertilizer losses from plant-soil systems, determination of the schemes of drainage systems cleaning, monitoring of water quality and pollution sources in saturated- unsaturated zone, study wash-out and leaching of salts from the soils and transformation processes into unsaturated-saturated zones, selection of suitable methods for modeling transport and transformation processes in flow systems, control of the agricultural activities and recommendations for changes in its. evaluation of the economic and social consequences of proposed changes in given region, creation and improving of the permanently working mathematical models geofiltration and masstransfer of the region for solution the problems of management and control.

REFERENCES

1. Alexeevskyi V.V. Ecological accompaniment of the canal regeneration works on Prypiat river upper reaches on Volyn. IWPiM, Kyiv-Kovel, 2001.-34p.

2.Diatel O.O.,Telyma S.V.Calculations and prognosis of the influence of the “Hotyslavskyi” open quarry on the hydrodynamic of the ground and underground waters of the Volyn Polissya. Land reclamation and Water management, IWPiM, Kyiv, iss.1(107), 2018.-P.73-79.

3. Diatel O.O.,Tsvetova O.V.,Turaeva O.V.,Telyma S.V. Valuation of the influence of the building materials quarry “Khotyslavskyi” development on the ground and underground water levels of the Western Polissya. Materials of International scientific-practical conference “Nature for Water”.IWPiM,Kyiv, 2018.-P.122-123.

4. Iatsyk A.V., Pashenyuk I.A, Gopchak I.V.,Basyuk T.O. Ecological state of the small river basins of the Ukrainian Polissya. Materials of International scientific-practical conference “Nature for Water”.IWPiM, Kyiv, 2018.-P.73-74.

5. KhomikN.V. Water resources of Shatsk National Nature Park: modern state, protection, mmanagement.Kyiv, Agrarian Science, 2013.-240p.

6. Marivoet J.L.,De Smedt F.,Van der Beken A.,Dirickx J., Van Granenbroeck W. Application to rivers and underground waters.Water Science Technology,vol.14, 1982.-P.1073-1094.

7. Martyniuk V.O.,Zaleskyi I.I.,Zubkovych I.V.The geoecological monitoring of lakes of the zone of potential tekhnogenic impact of the “Khotyslavskyi” quarry (on the example of Sviate Lake ,Volyn Polissya).Colloqium-journal,series Geografical Sciences,Warzawa,Poland,2020.-P.5-13.

8. Muzykin V.P., Antipirovich Yu.F., Budko S.A. Comprehensive solution of environmental protection issues under the transboundary impact of the development of the field of building materials "Khotislavskoe" in the Brest region. Institute of Nature Management of the National Academy of Sciences of Byelarussia,2017.- P.299–302.

9. National Report “Aimes of the stability development: Ukraine”. Ministry of economical development and trade of Ukraine. Kyiv, 2017.-176p.

10. Romaschenko M.I. Methodology of forming the cost of services for water supply for irrigation, industrial and communal needs. IWpiM,Kyiv,2012.-33 p.

11. Romaschenko M.I. Present situation of the ecologic and reclamation state of the Prypiat River upper reaches IWPiM,Kyiv, 2014.- 210p.

12. Romaschenko M.I. Influence of climate changes on the state of the available water supply of Ukraine by the water resources. Materials of International scientific-practical conference “Water for All”.IWPiM,Kyiv,2019.-P.11-12.

13. Report on the results of the environmental impact assessment of chalk mining at the Khotislavskoye field in the Maloritsky district of the Brest region. RUE "TSNIIKIVR", Minsk, 2009. -142 p.

14. Report “About ecological- reclamation state of the land drainage in 2015-2016 years in Ratno district”.Wolyn regional water resources office,vol.1,Lutsk,2016.-52p.

15. Stannard D.J., Comparison of Penman-Monteith, Shuttleworth-Wallace and modified Priestley-Taylor evapotranspiration models for Wildland Vegetation in semiarid rangeland.Water Resour.Res., vol.29, no.5,1993.-P.1379-1392.

16. Telyma S.V. Influence valuation on the hydrodynamic of ground and underground waters in the West Volyn the Khotislav deposit of chalk and sand development on territory Republic Belarus.Report,IWPiM, Kyiv, 2017.- 105p.

17. Telyma S.V.,Kremez V.S. The methodic of calculations of the contamination of the ground waters on irrigated and the ajoined territories.Environmental safety and natural resources,iss.4(28),KNUBA,Kyiv,2018.-P.82-93.

18. Telyma S.V. Analysis and perspectives on improvement of the surface and ground water quality in West Polissya territory. Collection of Materials of 1 All-Ukrainian scientific-practical conference with international participation “Ecology. Surrounding Media. Energy Saving”, National Univercity “Poltava Politekhnika”, Poltava, 2020.-P.61-65.

19. Telyma S.V.Diatel O.O.,Ulitsky O.A.,Boyko K.V. Assesment of the changes in hydroecological state of Western Polissya under influence of climatic and technogenic factors.

International scientific-practical conference “Geologic, hydrologic and biologic variety of Polissya.NUWN, Rivne, 2020.-P.179-183.

20. Tsvetova O.V., Riabtseva G.P., Nacedkin I.Yu. Hydroecological conditions of the Upper Reaches Prypiat River Valley. Kovel, 2013.- 210p.

21.Volyn region map scale 1:200 000. Political-administrative map, Kyiv, Kartographia, 2015.

22.Zuzuk F.V.,Sukhomlin K.V.,Illin L.V. Nature of the Western Polissya adjacent to Khotyslavskyi quarry in Belorussia.Lutsk, 2014.-246p.

23. Zuzuk F.V.,Melnychuk V.G.,Mateyuk V.V.,Brovko G.I. Shatsk Overlake.Geological structure and hydroecological conditions,v.1, VNU, Lutsk,2014.-198p.

PROTECTIVE FOREST PLANTATIONS AS A SYSTEM OF PROTECTION BIOCENOSES AND TECHNOCENOSES FROM THE NEGATIVE EXTERNAL FACTORS IMPACTS

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ABSTRACT

Technocenoses, as a structural unit of biocenoses, are constantly changing and expanding. Forests are an important component of the safe development of natural systems and the human environment, because they are one of the most important ways of ensuring the sustainability of the natural environment by preserving the gene pool of flora and fauna and the sustainability of ecosystems. Protecting ecosystems from negative anthropogenic man-made impacts is a global, universal problem. Ensuring the restoration and preservation of land fertility is impossible without a full range of organizational, economic, agricultural and technical, hydro-ameliorative, forest reclamation and anti-erosion measures.

Studies have shown [1] that Protective Forest Landscapes (PFL) have an important functional role in the operation of anthropogenic landscapes (AL).

Different types forest plantations are creating an autotrophic block of natural and anthropogenic systems and have an integral effect on the biosphere for a number of factors: they form primary bioproducts and produce oxygen; absorb carbon dioxide; trap dust and soot, toxic substances and having an important role in biochemical cycles of substances and energy circulation. In addition, they are an important component of the soil restoration processes.

Protective forest strips are forest areas that perform the function of environmental protecting and engineering objects from the negative impact of natural and anthropogenic factors, including forest plantations of the linear type (protective forest strips belonging to agroforestry, state protective forests and forest strips along built-up areas of settlements) [1].

Agroforestry plantations and natural forests, in combination with agricultural lands, form forest-agricultural landscapes, which create favourable conditions for increasing a productivity of agricultural lands and environmental protection.

Forest plantations as one of the most important components of natural complexes are contributes to the intensification of soils formation, increases crop yields, affects the formation

of microclimate, have an impact on heat and moisture balance, reduces water and wind erosion, prevents shallowing, pollution and siltation of rivers [3].

The current state of agroforestry, their sustainable functioning and reclamation efficiency, environmental and ecological potential, depends on the compliance of species composition with forest vegetation conditions, types and schemes of trees mixing that are applying in the different landscapes, age of stands, background of anthropogenic activity and climatic conditions.

There are three main types of agroforestry systems:

a) *Agrisilvicultural* systems are a combination of crops and trees, such as protective forests, alley cropping, homegardens.

b) *Silvopastoral* systems combine forestry and grazing of domesticated animals on pastures, rangelands or on-farm.

c) The three elements, namely trees, animals and crops, can be integrated in what are called *agrosylvopastoral* systems and are illustrated by homegardens involving animals as well as scattered trees on croplands used for grazing after harvests.

Today, there is no accurate information on the state of field protective forest belts (PFB) in the country, and during the land reform, this important component of Ukrainian agricultural landscapes was left out of consideration. Due to the long-term uncertainty of the legal status of PFP, most of them were left without care and protection, which led to their deterioration and partial destruction.

A significant proportion of these plantations under the influence of anthropogenic, abiotic and biotic factors, lose or have lost their protective properties by condition, construction, breed composition, with age.

In this work, we had observed forest reclamation protective plantations, which belong to the anti-erosion nature protection with permanent action and have a long payback period and, in their properties, are multifunctional. They perform climate regulation, soil protection, water protection, filtering, barrier functions. Such complexes, of different types of plantations, have certain special constructions and interact with each other, create reclamation and eco-regulatory effects in a certain area to protect bio- and technocenoses from the harmful natural effects.

Studied area belongs to the protective forest plantations of Boguslav agroforestry. The object of the study was the section of the road, near to the complex of Protective Forest Plantations and field, in which was a significant anthropogenic impact and no reclamation and restoration measures were carried out.

We analysed the protective forest plantations along the areas that are located near the roads. Was found, that on the experimental areas, pollutants from roads, are washed away to fields and there are no agroforestry engineering solutions of this ecological problem. All this is an extremely important and topical issue that needs immediate solution.

Keywords: natural landscape, forest reclamation protective plantations, assimilation potential, protective forest plantations, natural and anthropogenic impact.

INTRODUCTION

Forest ecosystems are one of the most important components of the natural systems safe development and an integral part of ensuring the sustainability of socio-economic systems. That is why, if we want to ensure an ecological security of the state at different levels (regional, local), it requires expanded information about forest ecosystems and preservation of their ecological and stabilizing role in nature, about their assimilation potential.

The system of plantations reclamation is a complex of different types of plantations, which have appropriate structures and are interacting with each other. They are creating reclamation effects in a certain area and protect soils and crops from harmful natural impacts, contributing to high and sustainable yields.

Forest reclamation plantations, which are effective in selected areas, belong to the anti-erosion measures of permanent action with a long payback period, they are multifunctional in own properties.

The most important properties are basing on the environmental protection function (according to the Agroforestry Research Trust):

- They can control runoff and soil erosion, thereby reducing losses of water, soil material, organic matter and nutrients.

- They can maintain soil organic matter and biological activity at levels satisfactory for soil fertility. This depends on an adequate proportion of trees in the system- normally at least 20% crown cover of trees to maintain organic matter over systems as a whole.

- They can maintain more favourable soil physical properties than agriculture, through organic matter maintenance and the effects of tree roots.

- They can lead to more closed nutrient cycling than agriculture and hence to more efficient use of nutrients. This is true to an impressive degree for forest garden/farming systems.

- They can check the development of soil toxicities, or reduce exiting toxicities-both soil acidification and salinization can be checked and trees can be employed in the reclamation of polluted soils.

- They utilize solar energy more efficiently than monocultural systems different height plants, leaf shapes and alignments all contribute.

- They can lead to reduced insect pests and associated diseases.

- They can be employed to reclaim eroded and degraded land.

- Agroforestry can augment soil water availability to land use systems. In dry regions, though, competition between trees and crops is a major problem.

- Nitrogen-fixing trees and shrubs can substantially increase nitrogen inputs to agroforestry systems.

- Trees can probably increase nutrient inputs to agroforestry systems by retrieval from lower soil horizons and weathering rock.

- The decomposition of tree and pruning can substantially contribute to maintenance of soil fertility. The addition of high-quality tree prunings leads to large increase in crop yields.

- The release of nutrients from the decomposition of tree residues can be synchronized with the requirements for nutrient uptake of associated crops. While different trees and crops will all have different requirement, and there will always be some imbalance, the addition of high quality prunings to the soil at the time of crop planting usually leads to a good degree of synchrony between nutrient release and demand.

- In the maintenance of soil fertility under agroforestry, the role of roots is at least as important as that of above-ground biomass.

- Agroforestry can provide a more diverse farm economy and stimulate the whole rural economy, leading to more stable farms and communities. Economics risks are reduced when systems produce multiple products.

As well as building on practices used in forestry and agriculture, agroforestry also works towards land protection and conservation through more effective protection of stock, control of soil erosion, salinity and water tables and a higher quality control of timber.

The formation of landscapes, which are resistant to anthropogenic pressures, requires the determination of the optimal ratio of natural and economically altered areas. This is the main criterion for assessing ecological status of such landscapes (FLP) [4].

Studies of all processes in the system "Protective Forest Plantations – Anthropogenic Landscapes" were conducted on the territory of Boguslav State Agricultural Forestry of Kyiv region, Ukraine. Forestry primary task is to ensure functioning of Protective Forest Plantations on the territory of Anthropogenic Landscapes in accordance with the conditions of the concept of sustainable environmental development.

The forests of Boguslav district belongs to the I forest group - forests that perform mainly protective functions; anti-erosion forests [5].

Forests of the first group perform soil protection and water protection, health and sanitary and aesthetic functions. They occupy the entire area of the agroforestry fund, which is 4065.0 hectares.

Each economic section, and there are 3 of them on the territory of agroforestry (coniferous, hardwood and softwood) (Figure 1), is aimed at growing certain root or target species, according to forest types. To this end, are taken some measures which are aimed to ensure the most effective implementation of protective functions, water protection, sanitation and other natural functions of forest.

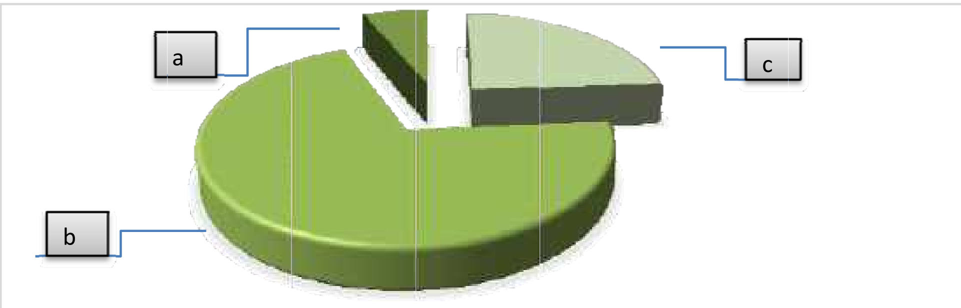

Fig. 1. Forest lands allocation, covered with vegetation, by groups of trees species: a) Softwood forests – 233,1 (6 %), b) Hardwood forests -2698,3 (70%), c) Coniferous – 915,4 (24%)

METHODS AND EXPERIMENTAL PROCEDURES

To develop measures for practical and theoretical improvement of the existing system of protective forest use, it was decided to develop a complex of forest reclamation measures for the reproduction and preservation selected area.

The main task of research is to preservation ensuring assimilation potential and dynamic adaptation of the ecosystem to ecological changes to provide restoration on disturbed and polluted areas along highways.

Analytical tools, such research, is to conduct environmental monitoring system by using environmental potential assessment of Protective Forest Plantations on the current territory and defining the main types of pollutants. The monitoring was carried out on the basis of the assessment of the forestry activity of Boguslav agroforestry according to [6, 7] regarding afforestation and methods of reforestation and afforestation.

According to [8], the roads that pass through the territory of the research area belong to the territorial roads of local significance of the V category with traffic intensity up to 150 transport units per day (on average per year) [9].

According to the levels of environmental impact [10], roads on the territory of agroforestry belong to the roads of III ecological class - roads of II and III categories with estimated traffic intensity up to 2000 traffic units per day and structures located on such roads belong to technically simple roads objects.

In designing of Protective Forest Plantations on a given section near the highway, was taken an indicator of the maximum allowable concentration of harmful substances for tree plantations into account (Table 1).

Table 1. The value of the trees MPC for a particular type of pollution, mg/m^3

Pollutant	Maximum permissible concentrations, mg/m^3	
	average value per year	average value per day
F	0.020	0.003
HCHO	0.020	0.003
SO_2	0.300	0.015
Cl_2	0.025	0.015
NO_2	0.040	0.040
NH_3	0.100	0.040
H	0.080	0.080
H_2SO_4	0.100	0.030
C_6H_6	0.100	0.050
O_3	-	-
CH_4O	0.200	0.100
C_6H_{12}	0.200	0.200
CO	3.000	1.000

Applying techniques, based on theoretical and empirical Gauss model [11], we calculated the main environmental pollutants along the roads.

To calculate them, the street and road network was divided into sections (Rmn) of a certain length (LRmn, m) with homogeneous traffic conditions. According to initial data, was taken that the line emission of pollutants is centred in planar source. The approximate estimating of the maximum single concentration of NO2, Pb, CxHy or CO at low altitudes in the area of the road network influence [3] was calculated by the formula (1):

$$C_i = \frac{800 \text{ x } P_i^r}{\sigma(R_{cp}) \text{ x } U_\text{в} \text{ x } \text{K}(\vartheta_w)} + C_i^{back}, \quad (1)$$

C_i is the concentration of the i-th pollutant, mg/m^3; C_i^{back} - maximum single background concentration of pollutant, mg/m^3, P_i^r - running power of emission of the i-th substance by the source Rmn, g/s×m; σ (Rcp) is the standard deviation of Gaussian vertical scattering, m; R_{cp} - distance from the calculating point CP to the edge of the roadway, m; Uв - wind speed prevailing in the calculation month of the warm period with the highest traffic intensity, m/sec; K (ʋw) is a function of the angle ʋw between the wind direction and the route.

Frequently, in the main area, air pollution with nitrogen dioxide NO_2 and soils with lead compounds Pb need to be calculated. The depth of penetration of these pollutants into the main area is calculated by the formula (2, 3):

$$L_{MPC}NO_2 = 47{,}62\ln(2{,}5\text{x}10^{-2}\text{x}N_P\text{x}N_{BA}\text{xexp-}0{,}148\text{HxДж} \quad (2)$$

$$L_{MPC}Pb = 47{,}62\ln(0{,}124N_p - N_{BA})\exp\cdot 0{,}1, \quad (3)$$

where $L_{MPC}NO_2$ - the maximum possible depth of penetration of NO_2 into the main area to the level of 1.0MPC.ma, m; $L_{MPC}Pb$ - the maximum possible distribution of Pb in the soils of the main territory (up to the level of 1.0 MPC.gr), m.

Lead compounds are accumulated in the soil along the highway. Depending on the concentration of compounds, the level of lead in the air is (4):

$$CPb_{\lim} = 2.57(1 - \exp(-1.75\ C_{air}.Pb)), \quad (4)$$

where CPb_{lim} - concentration in the soil relative to the MPC.soil.Pb .; C_{air}.Pb - concentration in the air, MPC.mr.Pb.

All data are listed in table. 2.

Table 2. Values of pollutant levels at the studied site, mg/m^3

Pollutant name	*Concentration, C_i, mg/m^3*
NO_2	0.42
Pb	0.003
CO	3.09

Found, that 1 ha of protective plantations, reduce overall air pollution at 10-35% and provides a reduction in temperature and humidity in the roadway adjacent to the area of 10-15%; strip of trees and shrub plantings of 25-30 m width reduces the level of carbon dioxide by 70% and absorbs 75–80 kg of fluorine, 200 kg of sulfuric dioxide, 30–70 tons of dust [14].

On the basis of the research, was offered a new approach to store contaminated areas. The optimal distance from the road surface to the protective Forest Plantations was calculated to provide their optimal environmental, air and water treatment functions and would have a positive restorative effect on the soil cover of the territory.

In order to ensure soil restoration processes, protective plantations must meet certain requirements and criteria and perform hydrological functions, which are divided into [15]:

• retention - the impact on rainwater retention;

• accumulation - the impact on water accumulation;

• retarding - the effect on deceleration of runoff;

• regulatory - the impact on the balance of water flow;

• water protection - impact on water quality and hygiene, including turbidity of watercourses and subsequent siltation of reservoirs;

• leveling - impact on the quality, quantity, distribution and movement of snow.

Agroforestry reclamation plantations should provide improving physical properties of soils, improve surface air moisture and create a favourable temperature condition for heat-loving plants. The yield of grain crops increases by an average of 2-3 kg/ha.

Using protective plantations water features is closely related to the water balance of forest ecosystems, which reflects the relationships between water supply components (precipitation) and water flow components (total evaporation, surface and groundwater runoff) thereby affecting the infiltration properties of soils.

In the case if precipitation (Z) is the only source of water for forest plantations (in this case, water washed away from the roadway and meltwater), we can write the equation of the total water balance (5):

$$Z = \Delta W + ET + O, \tag{5}$$

In this equation the average rainfall is equal to the total evaporation (ET) and runoff (infiltration) of water (O), ΔW is the change in water reserves in the soil and phytomass [16].

This amount of water should provide the necessary amount of moisture for normal growth and development of Protective Forests. All of this, provide the balance in the system "Protective Forest Plantations – Agricultural Landscapes".

Due to the increase of infiltration properties of soils, there are processes of slowing down the flow of water with a large amount of precipitation and the accumulation function of forests.

Providing a balance of physical and chemical properties of soils, make them able to purify water from surface runoff of road surface, thereby providing remediation of contaminated groundwater.

As shown by monitoring data and experimental studies [15] on the distribution of pollutants in the roadside area, their maximum concentrations are observed just above the road.

It has been proven, that Protective Forest Plantations will prevent the dispersion of pollutants and dilute them with streams of unpolluted air. All this clearly proves, that the concentration of pollution within Protective Forest Plantations is much higher than in more remote areas, which in turn has a negative impact on the ecosystem of such Plantations.

In according all the results of monitoring studies, was proposed a scheme for the placement of Protective Forest Plantations on the roadside area, which would satisfy environmental requirements and reduce the negative effects of impacts from vehicles.

THE RESEARCH RESULTS AND DISCUSSIONS

As we know, different types of stands react differently to environmental pollutants and have different ecological and ameliorative regenerative properties. Selection of plant species and the scheme of their location in the selected area of the study, was carried out depending on the following physical and morphological properties.

The main indicators, taken according woody crops selection were: assimilation potential, ability to develop in potentially contaminated areas, ability to provide environmental regulatory functions, natural potential for self-renewal, impact on soil cover.

Protective Forest plantations was designed according to their ecological properties and meet the following requirements: on the distance from the axis of the road could be observed the minimum concentrations of pollutants, and their height and width must to be equal to the maximum amplitude of the wave movement of pollutant particles.

Based on the monitoring data and reclamation calculations and typical types of Protective Forest Plantations structure, was proposed a three-row openwork-purge structure with two rows of shrubs.

The optimal distance from the roadway was 11.25 m, depending on the intensity of traffic. The width of Protective Forest Plantations was taken approximately 15 m, which is the optimal width to ensure the physical-ecological and sanitary-recreational parameters of the selected area. As a main tree species was chosen white acacia, the related - small linden, and shrubs - sea buckthorn and dog rose (all trees types was chosen from the range of species that are most appropriate to grow on ordinary chernozems, which are presented of the selected area). All tree species are confirmed their efficiency for the selected area. They are presented in Table 3.

Table 3. The main range of wood and shrubs for protective afforestation in the study area

Soil and geographical conditions	*Species recommended for growing*		
	main	related	shrubs
Ordinary chernozems	Pine (ordinary, black), acacia white, birch, sycamore, oak, willow, poplar, walnut	Forest pear, hornbeam, maple, linden	Elderberry, hazel, sea buckthorn, currant, thorn, dog rose, alder

As can be seen in Fig. 2, at the selected site was proposed a drain pipe installation, which aims to ensure the drainage of rain and melt water, thereby preventing destruction of the roadway and embankment erosion.

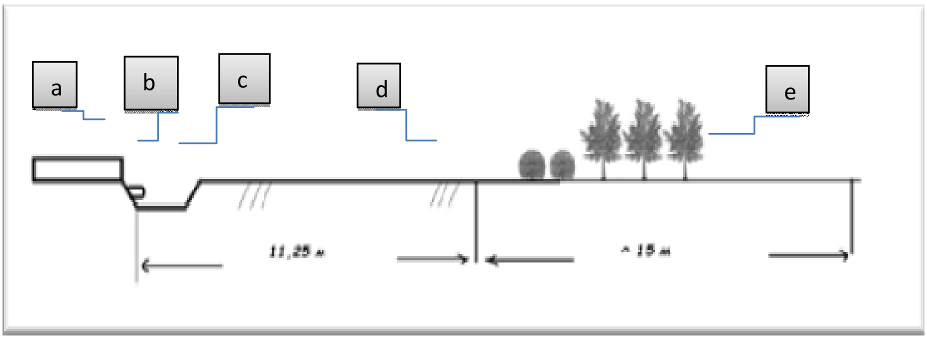

Fig. 2. Scheme of Protective Forest Plantations along the experimental section of the road. a - road surface, b - drain pipe, c - side ditch, d - section of the roadside from the road to Protective Forest Plantations, e - Protective Forest Plantations

Fig. 3. Drain pipe on the selected territory

Drain pipe diameter was calculated including amounts of rain and melt water, which are flowing during the calculation period. Drain pipe selection (Fig.3) must to ensure drainage from the territory on both sides of the road, to the area, where the Protective Forests is planted, with its subsequent absorption by soils.

CONCLUSION

Based on the research in the system " Protective Forest Plantations – Anthropogenic Landscapes" was established:

- agroforestry reclamation measures on the selected area, have a significant environmental effect: soil and air protection by landscaping the roadside area should be provided as combined measures. Was proved, only green strips using for acoustic and chemical pollution protection (on the not too busy roads parts) is appropriate for environmental criteria, because a vegetation significantly reduce an acoustic and chemical pollution of the selected width and type of green strips;
- conducted ecological and agroameliorative measures contribute to the process of ecological balance restoring in the selected area of Protective Forest Plantations;
- changes in physical and chemical properties of soils, their growing efficiency to self-cleaning drainage water, that coming from the curb and roadway, are caused by Protective Forest Plantations;

- research results are showing an importance of Protective Forest Plantations development ensuring in the territory of anthropogenically altered landscapes, as those, that support an assimilation capacity of the environment and causing development of these areas;
- it has been proven role of proposed decisions on an agroforestry and technical measures and means combination to ensuring sustainability of ecological systems on anthropogenically modified landscapes;
- was confirmed a positive impact on the Protective Forest Plantations biocenoses and technocenoses on the selected area of study.

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REFERENCES

1. Udod V.M., Trofimovich V.V., Voloshkina O.S., Trofimchuk O.M. Technoecol. (2007) 195:102.

2. Resolution of the Cabinet of Ministers of Ukraine. May 16, 2007 № 733.

3. Y.F. Gutarevich. Ecology of road transport: textbook. (2002) 296:125

4. S.Schnell, C.Kleinn, G.Ståhl. Monitoring trees outside forests: a review. Environ. Monit. Assess (2015) 187.

5. Recommendations for condition improving and reclamation efficiency increasing of protective forest plantations for various purposes. (2010) 120:74.

6. On approv. the proc. of forests divi. into groups, assigning them to a prot. cat. and det. of prot. forest areas: Resol. of the Cabinet of Ministers of Ukraine (2007). Kyiv. Nat. Book Project.

7. The Forest Code of Ukraine: Code of Ukraine. (2011). Kyiv: National Book Project.

8. Instr. of design, techn. acc. and accept.of quality assessm. Silvic. sites: Manual State Forestry Com. of Ukraine. (1997). Kyiv. National Book Project.

9. The Law of Ukraine "On highways" № 2862-IV (2005).

10. State build. codes of Ukraine. Transp. fac. Highways. SBC. 2.3-4: 2007. (2007) 87.

11. Law of Ukraine "On Air Protection". - № 2556-14. (2001).

12. Dietrich, C. R., and G. N. Newsam. "A Fast and Exact Meth. for Multidimens. Gaussian Stochastic Simul.." Wat. Res. Research 29 (8). (2002) 2861–2869.

13. The Law of Ukraine "On Environmental Protection". - № 1268-XII (1268-12) (1991).

14. Pavlishyna O.M. Prot. Forest plant. of the south-western railway of sciences. Scient. Jorn. (2009). 19.15.: 98:102.

15. Sushkov A.S. Meth. Bas. of est. of infl. of forest transp. Proc. on env. XIII Int. Youth Scientific Conference SEV. (2012).

16. Čaboun, V. 2009a: Nový prístup k funkc. lesov a ich integrovanému využívaniu v krajine ako persp. Lesn. In: Lesy pre spoločnosť: 1. Medz. konf. vlastníkov lesa a obhospodarovateľov lesov na Slovensku: Zborník príspevkov, Košická Belá 10. – 11. (2009) 9–11.

17. Čaboun, V. Vplyv lesných ekosyst. na odtokové pomery z povodia. Výskum vplyvu antropogénnych faktorov na vodné systémy. VÚVH Bratislava. (2003) 17.

EFFECTS OF THERAPEUTIC FORMALIN-INDUCED TREATMENT ON OXIDATIVE STRESS BIOMARKERS IN THE GILLS OF RAINBOW TROUT (*ONCORHYNCHUS MYKISS* WALBAUM)

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ABSTRACT

The present study aims to explore the potential contributions of formalin-induced disinfection to the development of oxidative stress and antioxidant defenses in the gills of rainbow trout (*Oncorhynchus mykiss* Walbaum). In this study, we sought to determine whether the profile of 2-thiobarbituric-acid-reacting substances (TBARS), aldehydic and ketonic derivatives of oxidatively modified proteins, as well as activities of superoxide dismutase (SOD), catalase (CAT), glutathione reductase (GR), glutathione peroxidase (GPx), and total antioxidant capacity (TAC) in gills of juvenile rainbow trout, changed following exposure to formalin. Assays for oxidative stress and antioxidant defenses were used to identify potential biomarkers in the assessment of formalin disinfection of rainbow trout. The test group was exposed to formalin in a final concentration of 200 mL per m^3. Fish were bathed for 20 min, three times, every 3 days. Two days after the last bathing fish were sampled. 2-Thiobarbituric acid reactive substances (TBARS) and carbonyl derivatives of protein oxidative destruction, as well as antioxidant defense biomarkers, were determined. The formaldehyde-exposed animals showed a decrease in lipid peroxidation biomarker (TBARS), aldehydic and ketonic derivatives of oxidatively modified proteins, and decreased glutathione peroxidase activity. Recognizing the role of biochemical changes in the tissues of formalin-exposed trout has important implications for understanding the complexity of the physiological changes that occur during disinfection but also for improving aquaculture practices to maximize tissues growth and health of treated trout. For the present study, the prophylactic treatments in rainbow trout should be performed at the abovementioned and lower concentrations of formalin.

Keywords: rainbow trout *Oncorhynchus mykiss*, formalin, oxidative stress, antioxidant defense, gills.

INTRODUCTION

Formalin is a generic term that describes a solution of 37% formaldehyde gas dissolved in water [15]. It has long been used as a traditional treatment for fish ectoparasites. It is extremely effective against most protozoans as well as some monogenetic trematodes using a bath, flush, or flowing treatment methods [25]. Formalin solutions for use on fish should contain 10 to 15% methanol, which inhibits the formation of par formaldehyde, a highly toxic compound [63]. In aquaculture, formalin (in a 1-h static bath at 200 mg per L repeated twice weekly) can be used as a disease prophylaxis regime with no negative effects on the growth of juvenile rainbow trout [51]. According to Abessa (2006), biological factors such as physiological conditions, nutritional status, and stage in the life cycle may interfere with chemical absorption rate, then fish larvae tend to be more sensitive to xenobiotic action than juvenile or adult animals [1]. However, each species responds differently to the action of a substance, therefore the importance of conducting toxicity tests with different organisms [47].

Formaldehyde inactivates microorganisms by alkylating the amino and sulfhydryl groups of proteins and ring nitrogen atoms of purine bases [14]. It is one of the most commonly used chemical treatments for fungal control in fish hatcheries. It's effective in the control of fungus on eggs without adverse effects on hatchability and post-hatch survival as reported by many researchers [2, 3, 38, 48, 51, 60]. Speare and MacNair (1996) assessed the effects of twice-weekly exposure to formalin (200 mg per L in a 1-h static bath) on juvenile rainbow trout (57.4 g initial weight) in a completely random, matched-pairs, 12-week growth trial [51]. Growth rates, appetite, feed conversion, and body condition index of the fish were not significantly affected by formalin treatment after 6 and 12 weeks. There was no evidence of a cumulative effect of formalin treatments over time because the similarities between treated and untreated groups of fish persisted over the 12-week trial [51].

Formaldehyde is used in aquaculture to control bacterial diseases, fungal and parasitic diseases, demonstrating efficacy in short-term baths [13, 47]. Formalin treatments are used to control fungal infections in eggs of rainbow trout *Oncorhynchus mykiss* [2]. Waterstrat and Marking (1995) evaluated the effectiveness of formalin, hydrogen peroxide, and salt (NaCI) in controlling fungal infections in eggs of fall chinook salmon (*Oncorhynchus tshawytscha*) under hatchery conditions [60]. The clinical trial involved the treatment of eggs exposed to *Saprolegnia parasitica* with daily 15-min treatments of either 500 ppm or 1,000 ppm formalin. Both agents at concentrations of either 500 ppm and 1,000 ppm appeared effective in controlling infections. Hydrogen peroxide and formalin at concentrations of 500 ppm and 1,000 ppm appear to be effective alternatives to the standard hatchery practice of treating eggs with formalin at a concentration of 1,667 ppm [60]. Rach and co-workers (2005) suggested that both therapeutics were effective in increasing lake trout egg survival up to the eyed egg stage; however, formalin was the most efficient [38].

Formalin-treated juvenile rainbow trout (in a 1-h static bath at 200 mg/L repeated twice weekly) had significantly better fin condition and a lower incidence of corneal opacity than untreated fish [51]. Small and Chatakondi (2005) examined the efficacy of formalin (50 ppm (mg/L), 100 ppm, 200 ppm) for disinfecting hybrid catfish (channel catfish *Ictalurus punctatus* and blue catfish *I. furcatus*) eggs and compared it with that of three other potential chemotherapeutics (125 ppm, 250 and 500 ppm hydrogen peroxide; 50 ppm, 100 ppm, and 200 ppm povidone-iodine; 2.5 ppm, 5 ppm, and 10 ppm copper sulfate) [48]. Hatching success was the highest among eggs treated three times daily in a 15 min bath with 100 ppm formalin (87.7%). This method was recommended to maximize hatching efficiency. Barnes and co-workers (2003) compared the effects of daily hydrogen peroxide treatments (700 mg/L for 15 min) from the eyed stage of egg development to fry hatch with those of formalin treatments (1,667 mg/L for 15 min) and the physical removal of dead eggs from vertical-flow incubator trays containing eggs of landlocked fall chinook salmon *Oncorhynchus tshawytscha*. Both the hydrogen peroxide and formalin treatments significantly increased embryo survival to hatch, relative to that resulting from the removal of dead eggs alone. No fungal or bacterial growth was observed in any of the incubator trays throughout the experiment [3].

Formalin is a recommended treatment for ichthyophthiriosis in the Australian fish silver perch (*Bidyanus bidyanus* Mitchell), but the disease is difficult to control in ponds, particularly at low water temperatures [43]. This study has developed a new formalin-treatment regime for the control of ichthyophthiriosis and demonstrated that copper sulfate is a potential therapeutant for this serious disease of silver perch. Both formalin and copper controlled ichthyophthiriosis in silver perch, but success was dependent on the maintenance of efficacious concentrations of each chemical in both aquaria and ponds. A concentration of 30 $mg{\cdot}L^{-1}$ formalin prevented re-infestation of silver perch by theronts, but fish treated with 20 $mg{\cdot}L^{-1}$ remained infested with both theronts and trophonts, and those treated with 10 $mg{\cdot}L^{-1}$ died as a result of the infestation [43].

However, formaldehyde is a mutagen and carcinogen even at low concentrations and presented toxicity in a variety of organisms. In aquatic organisms, deleterious effects were observed on the concentration of 1 $mg{\cdot}L^{-1}$ for fish and 5 $mg{\cdot}L^{-1}$ for microcrustaceans and algae. [47]. The effects of these products in fish can be manifested at various levels of biological organization, including physiological dysfunction, structural changes in organs and tissues, and behavioral changes that lead to impaired growth and reproduction [47].

Although formalin may continue to be useful in the aquaculture industry it causes potentially harmful alterations to fish skin [45] and induces bronchial lesions [50]. Among the morphological changes observed in organs of fishes exposed to xenobiotics are gill hyperplasia [21], disarrangement and vacuolization of hepatocytes, and focal necrosis in the liver [42, 47]. These biological responses to stress caused by xenobiotics can be used to identify early signs of damage to fish [47, 61]. It was reported that rainbow trout exposure to various concentrations of formalin affected the mucous cells resulting in increased release of mucus [6]. Blebbing of epithelial cell membranes was the first sign of the injury. Highly irregular organization of the cells followed, with regional differences occurring in different parts of fins [6]. Moreover, significant pathological changes and cell damage violence in the different formaldehyde concentrations were detected [10]. Hyperplasia, epithelial disruption, and necrosis cloudy swelling, hemorrhage and the accumulation of pigments in gill, necrosis in the liver parenchyma and renal tubules, and degeneration as the histological effect of applying different formaldehyde concentrations ranging between 50 to 500 ppm to the fry (with 6 g average weight) of *Chanos chanos* were observed [10]. Degeneration in the epithelial cells and pilar in the gill lamellae, lymphoid infiltration, interlamellar necrosis and degeneration of the muscle tissue, dilatation in the liver, congestion in veins, degeneration in hepatocytes, damage in the blood vessels of rainbow trout treated with formaldehyde were determined by Bulut and co-workers (2015) [7].

Santos and co-workers (2012) have evaluated the acute toxicity of formalin and histopathological effects on the Amazon ornamental fish, blue-spotted coridora (*Corydoras melanistius*). A randomized design was used, with ten concentrations of formalin (40%) (0, 3, 6, 12, 25, 50, 100, 150, 200, and 250 $mg{\cdot}L^{-1}$) with four replicates and five fish per container (3L) in the static system for 96 hours. At the end of their experiment, the following mortality rates (%) were obtained in increasing order of exposure: 0, 0, 0, 0, 0, 65, 85, 100, 100, and 100%. The lethal concentration 50% (LC_{50}-96h (I)) estimated was 50.76 $mg{\cdot}L^{-1}$ with regression of y = 0.51x, and $r^2 = 0.80$. Further, in higher concentrations, morphological changes as gill hyperplasia, with a filling of interlamellar spaces, disorganization of liver arrangement, and necrosis in the kidney were observed. In this study, the formalin can be considered slightly toxic to blue-spotted corydora, and cause morphological changes when exposed to high concentrations [47].

The toxicity of formaldehyde has been attributed to its ability to form adducts with DNA and proteins [55]. Formaldehyde enters the single-carbon cycle and is incorporated as a methyl group into nucleic acids and proteins. formaldehyde reacts chemically with organic compounds (e.g., deoxyribonucleic acid, nucleosides, nucleotides, proteins, amino acids) by addition and condensation reactions, thus forming adducts and deoxyribonucleic acid-protein crosslinks [56]. It causes oxidative DNA damage in cells by increasing the production of reactive oxygen species (ROS) [9]. On the other hand, formaldehyde covalently binds with proteins to form formaldehyde-protein conjugates, which may lead to the formation of formaldehyde-specific antibodies [30].

Reactive oxygen species (ROS), including singlet oxygen $^1O_2$, the hydrogen peroxide (H_2O_2) and hydroxyl radicals, superoxides, peroxynitrites (HOONO), hypochloric acid (HOCl), lipid peroxyl radicals (ROO), and alkoxyl radicals (RO), are naturally produced during several cellular pathways of aerobic metabolism including oxidative phosphorylation, electron transport chains in mitochondria and microsomes, the activity of oxidoreductase enzymes producing ROS as intermediates or final products, or even immunological reactions such as active phagocytosis [20, 33, 39]. They greatly differ in terms of cellular reactivity and potential to cause toxic insults to lipids, proteins, and DNA [39, 40].

Under basal conditions, the adverse effects of oxyradicals are prevented by the antioxidant system, consisting of a wide array of low molecular weight scavengers and antioxidant enzymes which interact in a sophisticated network with both direct and indirect effects [39]. Scavengers neutralize ROS by direct reaction with them, thus being temporarily oxidized before being reconverted by specific reductases to the active form. Scavengers can act as antioxidants in the cytoplasm or are intended to arrest the propagation of lipid peroxidation reactions on the membranes. The most abundant cytosolic scavenger is reduced glutathione (GSH), a tripeptide (γ-glutamyl–cysteinyl glycine), which directly neutralizes several reactive species through its oxidation to GSSG; in addition, GSH acts as a cofactor of several antioxidant glutathione-dependent enzymes [39]. The balance between ROS production and their removal by antioxidant systems is the "redox state". Oxidative stress is defined as excess production of ROS relative to the levels of antioxidants. When the production of ROS exceeds the capacity of antioxidant defense, oxidative stress harms the functional and structural integrity of biological tissue [59].

The present study aims to explore the potential contributions of formalin-induced disinfection to the development of oxidative stress and antioxidant defenses in the gills of rainbow trout. In this study, we sought to determine the profile of 2-thiobarbituric-acid-reacting substances (TBARS), aldehydic and ketonic derivatives of oxidatively modified proteins, as well as activities of superoxide dismutase (SOD), catalase (CAT), glutathione reductase (GR), glutathione peroxidase (GPx), and total antioxidant capacity (TAC) in gills of juvenile rainbow trout following exposure to formalin. Assays for oxidative stress and antioxidant defenses were used to identify potential biomarkers in the assessment of formalin disinfection of rainbow trout.

MATERIALS AND METHODS

Experimental Fish. Twenty-one clinically healthy rainbow trout specimens with a body mass of 45.0 ± 2.2 g were used in the experiment. The study was carried out in a Department of Salmonid Research, Stanisław Sakowicz Inland Fisheries Institute in Olsztyn, Poland. The experiment was performed at a water temperature of 16 ± 2°C and a pH of 7.5. The dissolved oxygen level was about 12 ppm with an additional oxygen supply with a water flow of 25 L/min and a photoperiod of 7 hours per day. Fish were fed with a commercial pelleted diet. All enzymatic assays were carried out at the Department of Zoology and Animal Physiology, Institute of Biology and Earth Sciences, Pomeranian University in Słupsk (Poland).

Experimental groups. The fish were divided into two groups and held in 250-L square tanks (70 fish per tank) supplied. Fish were disinfected using formalin in a final concentration of 200 mL per m^3 (Group II, n = 10). The control group (Group I, n = 11) was handled in the same way as a formalin-exposed group. Fish were bathed with formalin (Group II) for 20 min and the procedure was repeated three times every 3 days. Two days after the last bathing fish were killed and decapitated. No anesthetic agent was used before the killing, decapitation, and tissue sampling of specimens.

Tissue isolation. Gills were excised from trout after decapitation. One specimen of rainbow trout was used for each homogenate preparation containing gill samples (10% w/v). Gills were excised, weighed, and washed in the ice-cold buffer. The organ was rinsed clear of blood with cold isolation buffer and homogenized using a glass homogenizer H500 with a motor-driven pestle immersed in an ice water bath to yield a homogenate in proportion 1:9 (weight/volume). The isolation buffer contained 100 mM tris-HCl; a pH of 7.2 was adjusted with HCl. Homogenates were centrifuged at 3,000 rpm for 15 min at 4°C. After centrifugation, the supernatant was collected and frozen at −25°C until analyzed. Protein contents were determined using the Bradford method (1976) with bovine serum albumin as a standard. Absorbance was recorded at 595 nm [5]. All enzymatic assays were carried out at 22±0.5°C using a Specol 11 spectrophotometer (Carl Zeiss Jena, Germany) in duplicate. The enzymatic reactions were started by the addition of the tissue supernatant. The specific assay conditions were as follows.

Oxidative stress biomarkers assay. ***Assay of 2-thiobarbituric acid reactive substances (TBARS).*** An aliquot of the homogenate was used to determine the lipid peroxidation status of the sample by measuring the concentration of 2-thiobarbituric-acid-reacting substances (TBARS), according to the method of Kamyshnikov (2004). TBARS values were reported as nmoles malonic dialdehyde (MDA) per mg protein [26].

Assay of carbonyl groups of oxidatively modified proteins. Carbonyl groups were measured as an indication of oxidative damage to proteins according to the method of Levine and co-workers (1990) [29] in the modification of Dubinina and co-workers (1995) [11]. The carbonyl content was measured spectrophotometrically at 370 nm (aldehydic derivatives, OMP_{370}) and 430 nm (ketonic derivatives, OMP_{430}) (molar extinction coefficient 22,000 $M^{-1}\cdot cm^{-1}$) and expressed as nmol per mg protein.

Assay of superoxide dismutase activity. Superoxide dismutase (SOD, E.C. 1.15.1.1) activity in the supernatant was determined according to Kostiuk and co-workers (1990) [28]. SOD activity was assessed by its ability to dismutate superoxide produced during quercetin auto-oxidation in an alkaline medium (pH 10.0). Activity is expressed in units of SOD per mg of tissue protein.

Assay of catalase activity. Catalase (CAT; EC 1.11.1.6) activity was determined by measuring the decrease of H_2O_2 concentration at 410 nm according to Koroliuk and co-workers (1988) [27]. The rate of decrease in H_2O_2 content is directly proportional to the CAT activity in the sample. One unit of CAT activity was defined as the decrease of 1 μmol of H_2O_2 per minute per mg of tissue protein.

Assay of glutathione reductase activity. Glutathione reductase (GR, EC 1.6.4.2) activity was assayed as described by Glatzle and co-workers (1974) with some modifications [17]. The enzymatic activity was assayed spectrophotometrically by measuring NADPH consumption. In the presence of GSSG and $NADPH_2$, GR reduces GSSG and oxidizes NADPH, resulting in a decrease of absorbance at 340 nm. Quantification was based on the molar extinction coefficient of 6.22 $mM^{-1}\cdot cm^{-1}$ of $NADPH_2$. One unit of GR was defined as the amount of enzyme that reduced 1 μmol of $NADPH_2$ with GSSG per minute per mg of tissue protein.

Assay of glutathione peroxidase activity. Glutathione peroxidase (GPx, EC 1.11.1.9) activity was determined by the detection of nonenzymatic utilization of GSH as the reacting substrate at an absorbance of 412 nm after incubation with 5,5-dithiobis-2-nitrobenzoic acid (DTNB) according to by Moin method (1986) [34]. A unit of enzyme activity is defined as the amount of enzyme catalyzing the formation of 1 μmol of GSH per min, and the activity of GPx was calculated based on tissue protein concentration.

Assay of total antioxidant capacity (TAC). The TAC level was estimated spectrophotometrically at 532 nm following the method with Tween 80 oxidation by Galaktionova and co-workers (1998) [16]. TAC level was expressed in %.

Statistical analysis. Results are expressed as mean ± S.E.M. All variables were tested for normal distribution using the Kolmogorov-Smirnov test (P>0.05). The significance of differences in the oxidative stress biomarkers in the gill tissue of rainbow trout between control and formalin-exposed groups (significance level at p<0.05) was examined using the Mann-Whitney *U* test according to Zar (1999) [64]. In addition, the relationships between oxidative stress biomarkers of all individuals were evaluated using Spearman's correlation analysis. All statistical calculations were performed on separate data from each individual with STATISTICA 8.0 software (StatSoft, Krakow, Poland).

THE RESEARCH RESULTS AND DISCUSSIONS

Fig. 1 shows the TBARS level and level of aldehydic and ketonic derivatives of oxidatively modified proteins in the gills of formalin-exposed trout. The results in Fig. 1 indicate that the trout exposed to formalin expressed a significantly lower TBARS level in the gills by 29.7% (p=0.009) compared to the control group.

Levels of aldehydic and ketonic derivatives of oxidatively modified proteins were significantly lower (by 32.4%, p=0.0060 and by 37.6%, p=0.001, respectively) in the gills of formalin-exposed trout compared to the control group (Fig. 1).

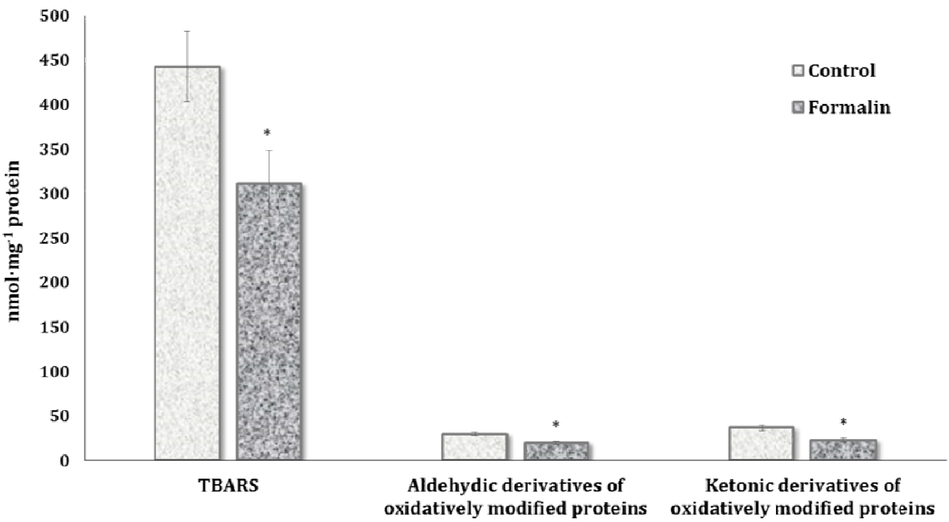

Fig. 1. Lipid peroxidation level measuring by the quantity of TBARS level (nmol MDA·mg^{-1} protein), levels of the aldehydic and ketonic derivatives (nmol·mg^{-1} protein) in the gills of rainbow trout treated by formalin

Values expressed as mean ± S.E.M.

* the significant change was shown as p<0.05 when compared to untreated group values.

Diverse specific and nonspecific antioxidant defense systems exist to scavenge and degrade ROS to nontoxic molecules. Under physiological conditions, their toxic effects can be prevented by scavenging enzymes such as superoxide dismutase, glutathione peroxidase, and catalase, as well as by other nonenzymatic antioxidants [59]. Despite being an antioxidant, SOD represents a source of hydrogen peroxide, being thus necessary that its activity is coordinated with that of H_2O_2 reducing enzymes, like catalase, CAT, or glutathione peroxidases, GPx [39]. Mostly present within peroxisomes, catalase is an extremely active catalyst for the reduction of H_2O_2 to H_2O [20]. At high levels of H_2O_2, the reaction involves two H_2O_2 molecules, serving both as acceptors and as a donor of hydrogen molecules, and leading to the production of H_2O and O_2 ($2H_2O_2 \rightarrow 2H_2O + O_2$). At low H_2O_2 concentrations, catalase modulates the detoxification of other substrates, as phenols and alcohols, through reactions coupled with H_2O_2 reduction. In the presence of reduced iron (Fe^{2+}), the Fenton reaction efficiently converts H_2O_2 to hydroxyl radicals, highly reactive initiators of membrane lipid peroxidation which are poorly neutralized by cellular antioxidants; in this respect, the antioxidant role of catalase is essential in preventing the formation of these ROS, and removal of the main precursor is thus considered the key antioxidant strategy adopted in marine organisms against ·OH [39]. Hydrogen peroxide is a substrate also for glutathione peroxidases (GPx), using reduced glutathione (GSH) as an electron donor to catalyze the reduction of H_2O_2 to H_2O. GPx and some isoforms of glutathione S-transferases (GST) reduce lipid hydroperoxides to alcohol, with the concomitant oxidation of GSH to GSSG. The oxidized glutathione is reconverted to GSH by glutathione reductase (GR) which, despite not being a real antioxidant enzyme, is nonetheless essential to maintain the correct GSH/GSSG ratio and the intracellular redox status in marine organisms [39].

Activities of antioxidant enzymes and total antioxidant capacity (TAC) in the gills of rainbow trout treated by formalin are presented in Table 1.

Table 1. Activities of antioxidant enzymes and total antioxidant capacity (TAC) in the gills of rainbow trout treated by formalin

Antioxidant enzyme activity	The unhandled group	The formalin-treated group
SOD, $U \cdot mg^{-1}$ protein	485.74±13.80	449.79±28.85
Catalase, $\mu mol\ H_2O_2 \cdot min^{-1} \cdot mg^{-1}$ protein	12.18±1.26	10.57±1.13
GR, $\mu mol\ H_2O_2 \cdot min^{-1} \cdot mg^{-1}$ protein	6.11±0.64	16.91±1.39*
GPx, $\mu mol\ H_2O_2 \cdot min^{-1} \cdot mg^{-1}$ protein	231.32±10.85	113.84±18.14*
TAC, %	47.70±4.23	60.32±3.75

Values expressed as mean ± S.E.M.; * see Fig. 1.

The GR activity in the gills of formalin-exposed trout according to Table 1 was significantly increased by 177% ($p=0.000$), while GPx activity was decreased by 50.8% ($p=0.000$) as compared with the unhandled group. SOD activity in the formalin-exposed trout was non-changed. Catalase activity was decreased non-significantly compared to the unhandled group. No significant alterations in TAC activity between formalin-exposed trout and control trout were observed (Table 1).

Data of correlative analysis between lipid peroxidation and oxidatively modified proteins in the gills of trout disinfected by formalin is shown in Fig. 2.

The ketonic derivatives of oxidatively modified proteins correlated positively with TBARS level ($r=0.661$, $p=0.038$) and aldehydic derivatives of oxidatively modified proteins ($r=0.745$, $p=0.013$) (Fig. 2). We can, therefore, summarize that the decreased level of oxidatively modified proteins resulted in a decrease of lipid peroxidation (TBARS level) in the gills of formalin-disinfected trout.

Results of this study showed that disinfection by formalin decreased the level of oxidative stress markers given as decreased lipid peroxidation and oxidatively modification of proteins, as well as alteration of GR and GPx activity in the gills (Fig. 1). Spearman's correlation analysis indicated that oxidatively modified proteins were influenced by lipid peroxidation (Fig. 2). Direct relationships between lipid peroxidation (TBARS level), ketonic and aldehydic derivatives of protein damage in the gills of formalin-exposed trout were noted (Fig. 2). We conclude that the content of oxidatively modified proteins, lipid peroxidation marker, the activity of glutathione-related enzymes may function as useful biomarkers for formalin-induced oxidative stress in gills.

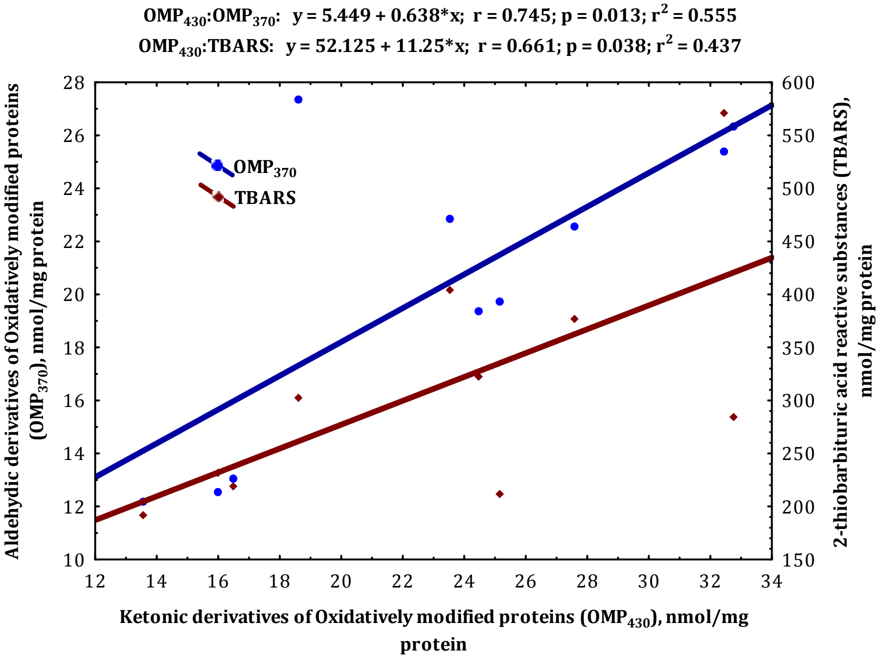

Fig. 2. Correlations between levels of TBARS, aldehydic derivatives of oxidatively modified proteins in the gills of trout disinfected by formalin

Other research suggested that suggest that formaldehyde can induce oxidative stress by increasing ROS formation [4, 19, 44, 53, 65]. Formaldehyde generates ROS that induces DNA base modifications and DNA strand breakage contributes to mutagenesis and other pathological processes [65]. Moreover, excessive ROS production can cause developmental toxicity through oxidative damage to key cellular components such as DNA, proteins, and lipids [12]. Saito and co-workers (2005) using Jurkat cells, assessed oxidative stress markers such as cellular glutathione (GSH) content and cellular ROS and DNA-protein cross-links, which formed as the result of formaldehyde treatment. Cellular ROS were synergistically increased before cell death. The formation of DNA-protein cross-links was observed in the presence of formaldehyde. Co-incubation with semicarbazide, which inactivates formaldehyde, prevented this cell death induced by a combination of formaldehyde and water-soluble radical initiator, 2,2'-azobis-[2-(2-imidazoline-2-yl)propane] dihydrochloride. Semicarbazide also exhibited an inhibitory effect on the synergistic increment of cellular ROS and the formation of DNA-protein cross-links [44].

The biological action of formaldehyde is dose-dependent [53]. In vitro studies on a tumor cell and endothelial cell cultures showed that formaldehyde in the concentration of 10.0 mM caused necrotic cell death, 1.0 mM resulted in enhanced apoptosis and reduced mitotic activity while 0.5 and 0.1 mM enhanced cell proliferation and reduced apoptotic activity [53]. Among formaldehyde organic compounds N-hydroxymethyl-L-arginine, 1'-methyl ascorbigen, and the formaldehyde donor resveratrol may be considered as potential inhibitors of cell proliferation. The genotoxic and carcinogenic effects of formaldehyde are due to the production of DNA-protein cross-links. Low doses of formaldehyde by reducing apoptotic activity may also accumulate cells with such cross-links [53]. Ozen and co-workers (2008) investigated formaldehyde-induced oxidative damage and apoptosis in rat tests [36]. The activities of SOD and GPx decreased significantly, whereas the level of malondialdehyde (MDA), a lipid peroxidation product commonly used as a biomarker of oxidative damage, significantly increased in testes of male Wistar rats treated with formaldehyde. Apoptosis of spermatogenetic and Leydig cells of testicular tissues was observed [36]. MDA was significantly increased in the testicular tissues of male mice treated with formaldehyde at 20 mg per kg [54].

TBARS, a lipid peroxidation biomarker commonly used as a biomarker of oxidative damage, were significantly increased in the cardiac tissues of male rats exposed to formaldehyde in subacute and subchronic studies of Güleç and co-workers (2006). These researchers evaluated the oxidant and antioxidant status as well as lipid peroxidation in the heart of rats exposed to formaldehyde inhalation for four weeks (subacute) or 13 weeks (subchronic) continuously. They revealed that subacute and subchronic formaldehyde inhalation may stimulate oxidative stress and thus, some secondary toxic effects in cardiac cells and tissue [19]. A marked formation of ROS in isolated rat hepatocytes incubating with low concentrations of formaldehyde was observed by Teng and co-workers (2001). A marked decrease in mitochondrial membrane potential and inhibition of mitochondrial respiration that was accompanied by ROS formation occurred when isolated rat hepatocytes were incubated with low concentrations of formaldehyde in a dose-dependent manner [55]. Hepatocytic's GSH level was also depleted by formaldehyde in a dose-dependent manner. At higher formaldehyde concentrations, lipid peroxidation ensued followed by cell death. Cytotoxicity was also prevented when cyclosporine or carnitine was added to prevent the opening of the mitochondrial permeability transition pore which further suggests that formaldehyde targets the mitochondria [55].

Formaldehyde may also exert these oxidative stress effects in tissues indirectly, mediated by an inflammatory response [37, 44]. The reaction of formaldehyde with amino groups of proteins is critical in inducing an immune response *in vivo* [30]. Li and co-workers (2007) studied the formation of antibodies against formaldehyde-protein conjugates in Sprague-Dawley rats for their possible use as biological markers of formaldehyde exposure. A greater response of highly specific antibodies on formaldehyde with an exposure period (for up to 6 months) was observed [30]. Lino dos Santos Franco and co-workers (2006) have used a pharmacological approach to study the mechanisms underlying the rat lung injury and the airway reactivity changes induced by inhalation of formaldehyde (1% formalin solution, 90 min once a day, 4 days). Formaldehyde exposure may affect lung resident cells, including macrophages and mast cells that could mediate the lung inflammatory response and the systemic release of inflammatory mediators. The inflammatory mediators may trigger systemic immune responses [31].

Yildiz and co-workers (2009) also found that non-specific immune parameters of rainbow trout after exposure to formalin have undergone alterations in general. The increase in hematocrit, leucocrit, and serum glucose levels in fish exposed to formalin was noted [62]. Im and co-workers (2006) investigated the effects of formaldehyde on rat plasma proteins. Rats were exposed to three different concentrations of formaldehyde (0, 5, 10 ppm) for 2 weeks at 6 hours per day and 5 days per week in an inhalation chamber. Levels of MDA, carbonyl insertion, and DNA damage in plasma, livers, and in the lymphocytes of rats exposed to formaldehyde were found to be increasingly dependent on the dose. Proteins involved in apoptosis, transportation, signaling, energy metabolism, cell structure, and motility were found to be up- or down-regulated associated with formaldehyde exposure [23]. Cytotoxic effects of formaldehyde in rat lung tissues exposed to ambient air and two different concentrations of formaldehyde (0, 5, 10 ppm) for 2 weeks at 6 h per day and 5 days per week in an inhalation chamber were confirmed by Sul and co-workers (2007) [52].

Formalin at even sublethal concentrations caused genotoxic effects in peripheral blood erythrocytes of *Danio rerio*. Resendes and co-workers (2018) have verified the toxic and genotoxic effects of formalin and determined the lethal concentrations of this chemical to support its safe use in disinfection processes [41]. The genotoxic effect of formalin was evaluated with the micronucleus test using blood samples, which were collected at 96 and 192 h of exposure. The LC_{50}-96h of formalin in *D. rerio* was 45.73 mg·L^{-1}, demonstrating its high resistance compared to other species. Regarding the genotoxic effect, the sublethal concentrations of formalin showed a positive correlation with micronuclei according to the increase in its concentration independent of the time of exposure. The incidence of micronuclei increased with concentration, and the addition of 1 mg·L^{-1} formalin corresponded to an increase of 2.9% in the average number of micronuclei [41]. Also, Santana and co-workers (2015) concluded that formaldehyde is genotoxic to tadpoles of bullfrogs, and the choice of this chemical should be contemplated before its use in animals in captivity [46]. The study of these researchers aimed to determine the median lethal concentration (LC_{50}-96h) of formaldehyde in bullfrog tadpoles and to evaluate the possible genotoxic effects in acute exposition. Accordingly, the animals were exposed to formaldehyde in the concentrations of 6, 9, 12, 15, and 18 mg·L^{-1}, and after 96 h blood samples were drawn for the micronucleus (MN) test. The LC_{50}-96h was 10.53 mg·L^{-1}, and the MN frequency increased in proportion to the formaldehyde concentrations, with an estimated frequency in the negative control being 1.35 MN/individual [46].

Chmelova and co-workers (2016) have assessed the effects of a treatment bath in a formalin solution on fish, focusing on hematological, biochemical, and histopathological profiles [8]. A total of 96 common carps (*Cyprinus carpio*) were randomly assigned to eight groups. Four experimental groups were placed in the test solution for 60 minutes. The concentration of the formalin bath was 0.17 ml/l (38% formaldehyde), with a water temperature of 20°C. The effects of the bath were monitored immediately (E0) and 24 hours (E24h), 48 hours (E48h), and 10 days (E10d) after the bath. There was a control group (C0, C24h, C48h, C10d) for each of the experimental groups. Histopathological indices were strongly affected. Extensive changes were found on the gill and skin immediately and also after 24 h, 48 h, and 10 d of the formalin treatment bath. A plurality of mucinous elements was observed on the skin. Moreover, structural devastation of lamellas and numerous mucinous cells were observed on the gill. Changes were also found in hematological and biochemical indices. It can be concluded that after applying the treatment bath in the formalin solution, the monitored profiles were affected immediately after the bath and also after 10 days (histopathological changes of skin and gill). Such significant impact of therapeutic formalin bath should be considered in the treatment of fish [8].

The results of Neves and co-workers (2020) showed that the developmental stage influenced the sensitivity of animals to formalin [35]. These researchers have evaluated the acute toxicity of formalin and its level of therapeutic safety in the early stages of *Lophiosilurus alexandri*. Experiment 1, larvae 7 days after hatching (DAH) were exposed to 43.2, 86.4, 172.8, 345.6, 691.2, 1404.0 mg·L^{-1} of formalin. Experiment 2, juveniles with 22 DAH exposed to 54, 108, 216, 432, 648 mg·L^{-1}. Experiment 3, 45 DAH exposed to 86.4, 172.8, 345.6, 691.2, 1036.8 mg·L^{-1}. The experiments had control without the addition of formalin and all were carried out in duplicate. The LC_{50}-12 h were: Experiment 1 = 108.86 mg·L^{-1}; 2: 152.74 mg·L^{-1}; 3: 244.38 mg·L^{-1} of formalin. The respective safety levels were: Experiment 1 = 66.22 mg·L^{-1} (1 h), 10.89 mg·L^{-1} (12 h); 2 = 49.17 mg·L^{-1} (2 h), 15.27 mg·L^{-1} (12 h); 3 = 68.89 mg·L^{-1} (2 h), 24.44 mg·L^{-1} (12 h).

Formalin used in the bath is probably safe as an antiparasitic treatment of fish. The study of Hodkovicova and co-workers (2019) have revealed the most effects 10 days after the treatment of a formalin bath in the concentration of 185.3 mg·L^{-1} (0.17 mL·L^{-1}) at a temperature of 20°C when these researchers observed the decrease of lysozyme in skin mucus, the decrease of anti-inflammatory cytokine transforming growth factor-beta in gill tissue of common carp, and increase of interleukin 10 in cranial kidney tissue. The pro-inflammatory cytokine interleukin 1b showed an increase in gill tissue immediately after the bath and the increase in glutathione peroxidase in gill tissue was also observed 24 h and 10 days after bath treatment. The other investigated parameters did not show any significant changes [22].

Both the induction and suppression of antioxidant enzymes by formaldehyde have been also demonstrated. These enzymes including GPx, SOD, CAT, and glutathione (GSH) protect cells against oxidative damage and a change in their activity levels may indicate the level of oxidative damage in target tissues and/or cells [12]. Lino-dos-Santos-Franco and co-workers (2011) investigated the effects of formaldehyde (inhalation of 1% formaldehyde, 90 min daily for 3 consecutive days) on the activities and gene expression of GPx, GR, glutathione S-transferase (GST), SOD1 and 2, CAT, nitric oxide synthase (iNOS and cNOS) and cyclooxygenase (COX) 1 and 2 in the lung of male Wistar rats. Formaldehyde inhalation did not modify the activities of GPx, GR, GST, and CAT but reduced the activity of SOD. Significant increases in SOD-1 and SOD-2, CAT, iNOS, cNOS, and COX-1 expression were observed in the formaldehyde group. The authors proposed that formaldehyde disrupts the physiological balance between oxidant and antioxidant enzymes, most likely favoring the oxidant pathways and thus positively modulating inflammation [32]. Songur and co-workers (2008) examined the effects of formaldehyde inhalation during the early postnatal period on some oxidant and antioxidant systems of the rat cerebellum in the developmental process. The activity of GPx and levels of MDA and NO were increased; the activity of total SOD was decreased significantly in the rats treated with formaldehyde [49]. Significantly reduced levels of SOD and GPx and higher amounts of MDA in the testicular tissue of male Wistar rats were found [36]. Formaldehyde induces the antioxidant defense mechanism in rodent testicular tissue and may impair its effects. Reduced amounts of the trace metals, copper, and zinc, cofactors of SOD, in the testicles of male mice could contribute to the reduced SOD activity [54].

Response of antioxidant system to formalin in the whole body of rainbow trout, *Oncorhynchus mykiss*, was assessed by İspir and co-workers (2017). Fish were exposed to formalin at doses of 50, 100, and 200 ppm for 1 h. Fish were then left to depurate for 24 h in formalin-free water. At the end of the test, whole bodies were isolated and homogenized to measured malonic dialdehyde (MDA) and reduced glutathione (GSH) levels and catalase (CAT) and glutathione peroxidase (GPx) activities. Results obtained showed that formalin significantly ($p < 0.05$) increased the MDA level. There was a statistically significant decrease in the CAT activity of the experimental groups when compared to the control group. After the recovery period, the CAT activity was still found to be lower than the control level. The GPx activity and GSH level decreased by formalin exposures and did not return to the control values during recovery periods. From the findings of the study of İspir and co-workers (2017), it can be interpreted that acute formalin treatment may cause oxidative stress and thus, some secondary toxic effects in the whole body [24].

In our previous study, inverse alterations in the hepatic tissue of formalin-disinfected trout were observed [57, 58]. Our analyses for oxidative stress biomarkers in the liver of rainbow trout showed that exposure to formalin caused the decrease of aldehydic and ketonic derivatives of oxidatively modified proteins and an increase of SOD activity. These findings suggest that formalin disinfection of trout has a reverse effect on the cardiac and hepatic tissue, causing oxidative stress in the cardiac tissue and a decrease in protein damage in the hepatic tissue. There were inverse correlations between SOD activity and derivatives of oxidatively modified proteins. Increased SOD activity resulted in a decreased protein damage level in the hepatic tissue. A high level of oxidative stress biomarkers (TBARS and oxidatively modified proteins) were observed in the cardiac tissue, therefore SOD is highly vulnerable to inhibition by free radicals. CAT activity was increased in the formalin-disinfected group, which might be related to the free radical-induced lipid peroxidation and consequently might reduce the SOD activity. SOD controls the level of superoxide in the extracellular space by catalyzing the dismutation of superoxide into hydrogen peroxide and molecular oxygen. In addition, the enzyme reacts with hydrogen peroxide in a peroxidase reaction, which is known to disrupt enzymatic activity [18].

The inactivation of SOD by peroxidase activity plays a role in regulating SOD activity *in vivo*, as even low levels of superoxide allow for the peroxidase reaction to occur [18]. In our study, we speculate that increased CAT activity and a high level of hydrogen peroxide can inhibit SOD activity in cardiac tissue of formalin-exposed trout [57, 58].

Our results about gill antioxidant defense showed a significant reduction of GPx activity in the formalin-exposed trout (Table 1). Decreased levels of oxidative stress biomarkers (TBARS and oxidatively modified proteins) were observed in the gill tissue, therefore GPx is highly vulnerable to inhibition by free radicals. GPx activity was decreased in the formalin-disinfected group, which might be related to the inhibition of free radical-induced lipid peroxidation after formalin-induced disinfection. GPx and some isoforms of glutathione S-transferases (GST) reduce lipid hydroperoxides to alcohol, with the concomitant oxidation of GSH to GSSG [39]. Future biochemical-based studies using oxidative stress biomarkers are needed to expand our knowledge on molecular processes involved in salmonids' response to formalin bath treatment.

CONCLUSIONS

In the present study, we demonstrated that the oxidative stress biomarkers were significantly decreased in the gills of the formalin-disinfected group. Thus, it might be concluded that the antioxidant defenses can decrease oxidative stress in the gills of formalin-disinfected rainbow trout. The decrease of lipid peroxidation and oxidatively modified proteins caused the decrease of glutathione peroxidase activity in the gills after formalin-induced disinfection. Recognizing the role of biochemical changes in the tissues of formalin-exposed trout has important implications for understanding the complexity of the physiological changes that occur during disinfection but also for improving aquaculture practices to maximize tissues growth and health of treated trout. For the present study, the prophylactic treatments in rainbow trout should be performed at the abovementioned and lower concentrations of formalin.

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REFERENCES

1. Abessa D.M.S., Ecotoxicologia marinha, In: Sanidade de organismos aquáticos no Brasil, Souza-Silva A.T. (Ed.), Abrapoa, pp 19-41, 2006.

2. Arndt R.E., Wagner E.J., Routledge M.D., Reducing or withholding hydrogen peroxide treatment during a critical stage of rainbow trout development: effects on eyed eggs, hatch, deformities, and fungal control, North American Journal of Aquaculture, vol. 63, pp 161-166, 2001.

3. Barnes M.E., Stephenson H., Gabel M., Use of hydrogen peroxide and formalin treatments during incubation of landlocked fall chinook salmon, North American Journal of Aquaculture, 65, pp 151-154, 2003.

4. Bono R., Romanazzi V., Munnia A., Piro S., Allione A., Ricceri F., Guarrera S., Pignata C., Matullo G., Wang P., Giese R.W., Peluso M., Malondialdehyde-deoxyguanosine adduct formation in workers of pathology wards: the role of air formaldehyde exposure, Chem. Res. Toxicol., vol. 23, pp 1342-1348, 2010.

5. Bradford M.M., A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding, Anal. Biochem., vol. 72, pp 248-254, 1976.

6. Buchmann K., Bresciani J., Jappe C., Effects of formalin treatment on epithelial structure and mucous cell densities in rainbow trout, *Oncorhynchus mykiss* (Walbaum), skin, J. Fish Dis., vol. 27, pp 99-104, 2004.

7. Bulut C., Kubilay A., Hanol Bektaş Z., Birden B., Histopathological Effects of Formaldehyde (CH_2O) on Rainbow Trout (*Oncorhynchus mykiss* Walbaum, 1792), Journal of Limnology and Freshwater Fisheries Research, vol. 1, pp 43-48, 2015.

8. Chmelova L., Sehonova P., Doubkova V., Plhalova L., Blahova J., Tichy F., Modra H., Svobodova Z., Effects of therapeutic formalin bath on selected indices in fish, Neuro Endocrinol. Lett., vol. 37/Suppl. 1, pp 67-77, 2016.

9. Ciftci G., Aksoy A., Cenesiz S., Sogut M.U., Yarim G.F., Nisbet C., Guvenc D., Ertekin A., Therapeutic role of curcumin in oxidative DNA damage caused by formaldehyde, Microsc. Res. Tech., vol. 78, pp 391-395, 2015.

10. Cruz E.R., Pitogo C.L., Tolerance level and histopathological response of milkfish (*Chanos chanos*) fingerlings to formalin, Aquaculture, vol. 78, pp 135-145, 1989.

11. Dubinina E.E., Burmistrov S.O., Khodov D.A., Porotov I.G., Oxidative modification of human serum proteins. A method of determining it, Vopr. Med. Khim., vol. 41, pp 24-26, 1995.

12. Duong A., Steinmaus C., McHale C.M., Vaughan C.P., Zhang L., Reproductive and developmental toxicity of formaldehyde: a systematic review, Mutat. Res., vol. 728, pp 118-138, 2011.

13. Fajer-Ávila E.J., Parra I.A., Zarate G.A., Arce R.C., Ramírez J.Z., Lozano M.B., Toxicity of formalin to bullseye puffer fish (*Sphoeroides annulatus* - Jenyns, 1843) and its effectiveness to control ectoparasites, Aquaculture, vol. 223, pp 41-50, 2003.

14. Favero M.S., Bond W.W., Chemical disinfection of medical and surgical materials. In: Block S.S., ed. Disinfection, sterilization, and preservation. Philadelphia: Lea & Febiger, pp 617-641, 1991.

15. Francis-Floyd R., Use of Formalin to Control Fish Parasites. Document Nr VM-77 of a series of the College of Veterinary Medicine, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida, 1996.

16. Galaktionova L.P., Molchanov A.V., El'chaninova S.A., Varshavskiĭ Bla., Lipid peroxidation in patients with gastric and duodenal ulcers, Klinicheskaia Labaratornaia Diagnostika, vol. 6, pp 10-14, 1998.

17. Glatzle D., Vuilleumier J.P., Weber F., Decker K., Glutathione reductase test with whole blood, a convenient procedure for the assessment of the riboflavin status in human, Experientia, vol. 30, pp 665-667, 1974.

18. Gottfredsen R.H., Larsen U.G., Enghild J.J., Petersen S.V., Hydrogen peroxide induces modifications of human extracellular superoxide dismutase that results in enzyme inhibition, Redox Biol., vol. 1, pp 24-31, 2013.

19. Güleç M., Songur A., Sahir S., Ozen O.A., Sarsilmaz M., Akyol O., Antioxidant enzyme activities and lipid peroxidation products in heart tissue of subacute and subchronic formaldehyde-exposed rats: a preliminary study, Toxicol. Ind. Health, vol. 22, pp 117-124, 2006.

20. Halliwell B., Gutteridge J.M.C., Free Radicals in Biology and Medicine (fourth ed.), Oxford University Press, New York, 2007.

21. Henares M.N.P., Cruz C., Gomes G.R., Pitelli R.A., Machado M.R.F., Toxicidade Aguda e Histopatologia do Herbicida Reward® na Brânquia e no Fígado do Pacu (*Piaractus mesopotamicus*), Maringá, vol. 30/issue 1, pp 77-82, 2008.

22. Hodkovicova N., Chmelova L., Sehonova P., Blahova J., Doubkova V., Plhalova L., Fiorino E., Vojtek L., Vicenova M., Siroka Z., Enevova V., Dobsikova R., Faldyna M.,

Svobodova Z., Faggio C. The effects of a therapeutic formalin bath on selected immunological and oxidative stress parameters in common carp (*Cyprinus carpio*), Sci. Total Environ., vol. 653, pp 1120-1127, 2019.

23. Im H., Oh E., Mun J., Khim J.Y., Lee E., Kang H.S., Kim E., Kim H., Won N.H., Kim Y.H., Jung W.W., Sul D., Evaluation of toxicological monitoring markers using proteomic analysis in rats exposed to formaldehyde, J. Proteome Res., vol. 5, pp 1354-1366, 2006.

24. İspir U., Kirici M., Yonar M.E., Mişe Yonar S., Response of antioxidant system to formalin in the whole body of rainbow trout, *Oncorhynchus mykiss*, Cell Mol. Biol. (Noisy-le-grand), vol. 63/issue 1, pp 13-16, 2017.

25. Jung C., Formaldehyde residues in formalin treated olive flounder *Paralichthys olivaceus*, black rockfish *Sebastes schlegeli*, Aquaculture, vol. 194, pp 251-262, 2004.

26. Kamyshnikov V.S., A reference book on the clinic and biochemical researches and laboratory diagnostics, MEDpress-inform, Moscow, 2004.

27. Koroliuk M.A., Ivanova L.I., Maĭorova I.G., Tokarev V.E., A method of determining catalase activity, Laborotornoe Delo, vol. 1, pp 16-19, 1988.

28. Kostiuk V.A., Potapovich A.I., Kovaleva Zh.V., A simple and sensitive method of determination of superoxide dismutase activity based on the reaction of quercetin oxidation, Voprosy Meditsinskoĭ Khimii, vol. 36, pp 88-91, 1990.

29. Levine R.L., Garland D., Oliver C.N., Amici A., Climent I., Lenz A.-G., Ahn B.-W., Shaltiel S., Stadtman E.R., Determination of carbonyl content in oxidatively modified proteins, Methods Enzymol., vol. 186, pp 465-478, 1990.

30. Li H., Wang J., König R., Ansari G.A., Khan M.F., Formaldehyde-protein conjugate-specific antibodies in rats exposed to formaldehyde, J. Toxicol. Environ. Health A, vol. 70, pp 1071-1075, 2007.

31. Lino dos Santos Franco A., Damazo A.S., Beraldo de Souza H.R., Domingos H.V., Oliveira-Filho R.M., Oliani S.M., Costa S.K., Tavares de Lima W., Pulmonary neutrophil recruitment and bronchial reactivity in formaldehyde-exposed rats are modulated by mast cells and differentially by neuropeptides and nitric oxide, Toxicol. Appl. Pharmacol., vol. 214, pp 35-42, 2006.

32. Lino-dos-Santos-Franco A., Correa-Costa M., Durão A.C., de Oliveira A.P., Breithaupt-Faloppa A.C., Bertoni Jde A., Oliveira-Filho R.M., Câmara N.O., Marcourakis T., Tavares-de-Lima W., Formaldehyde induces lung inflammation by an oxidant and antioxidant enzymes mediated mechanism in the lung tissue, Toxicol. Lett., vol. 207, pp 278-285, 2011.

33. Lu J.M., Gong N., Wang Y.C., Wang Y.X., D-Amino acid oxidase-mediated increase in spinal hydrogen peroxide is mainly responsible for formalin-induced tonic pain, Br. J. Pharmacol., vol. 165, pp 1941-1955, 2012.

34. Moin V.M., A simple and specific method for determining glutathione peroxidase activity in erythrocytes, Labaratornoe Delo, vol. 12, pp 724-727, 1986.

35. Neves L.D.C., Miranda Filho K.C., Lorenzini J.P.S., Nakayama C.L., Luz R.K., Effect of formalin in early stages of the freshwater neotropical catfish, *Lophiosilurus alexandri*, Environ. Toxicol. Pharmacol., vol. 73, pp 103277, 2020.

36. Ozen O.A., Kus M.A., Kus I., Alkoc O.A., Songur A., Protective effects of melatonin against formaldehyde-induced oxidative damage and apoptosis in rat testes: an immunohistochemical and biochemical study, Syst. Biol. Reprod. Med., vol. 54, pp 169-176, 2008.

37. Persoz C., Achard S., Leleu C., Momas I., Seta N., An *in vitro* model to evaluate the inflammatory response after gaseous formaldehyde exposure of lung epithelial cells, Toxicol. Lett., vol. 195, pp 99-105, 2010.

38. Rach J.J., Redman S., Bast D., Gaikowski M.P., Efficacy of hydrogen peroxide versus formalin treatments to control mortality associated with saprolegniasis on lake trout eggs. North American Journal of Aquaculture*,* vol. 67, pp 148-154, 2005.

39. Regoli F., Giuliani M.E., Oxidative pathways of chemical toxicity and oxidative stress biomarkers in marine organisms, Mar. Environ. Res., vol. 93, pp 106-117, 2014.

40. Regoli F., Winston G.W., Quantification of total oxidant scavenging capacity of antioxidants for peroxynitrite, peroxyl radicals, and hydroxyl radicals, Toxicol. Appl. Pharmacol., vol. 156/issue 2, pp 96-105, 1999.

41. Resendes A.S., Dos Santos D.S., França F.M., Petesse M.L., Badaró-Pedroso C., Ferreira C.M., Acute toxic and genotoxic effects of formalin in *Danio rerio* (zebrafish), Ecotoxicology, vol. 27/issue 10, pp 1379-1386, 2018.

42. Rodrigues E.L., Fanta E., Liver histopathology of the fish *Brachydanio rerio* Hamilton-Buchman after acute exposure to sublethal levels of the organophosphate dimethoate 500, Rev. Bras. Zool., vol. 15/issue 2, pp 441-450, 1998.

43. Rowland S.J., Mifsud C., Nixon M., Read P., Landos M., Use of formalin and copper to control ichthyophthiriosis in the Australian freshwater fish silver perch (*Bidyanus bidyanus* mitchell), Aquaculture Research, vol. 40, pp 44-54, 2009.

44. Saito Y., Nishio K., Yoshida Y., Niki E., Cytotoxic effect of formaldehyde with free radicals *via* increment of cellular reactive oxygen species, Toxicology, vol. 210, pp 235-245, 2005.

45. Sanchez J.G., Speare D.J., Sims D.E., Johnson G.J., Morphometric assessment of epidermal and mucous-biofilm changes caused by exposure of trout to chloramine-T or formalin treatment, J. Comp. Pathol., vol. 118, pp 81-87, 1998.

46. Santana J.M., Dos Reis A., Teixeira P.C., Ferreira F.C., Ferreira C.M., Median lethal concentration of formaldehyde and its genotoxic potential in bullfrog tadpoles (*Lithobates catesbeianus*), J. Environ. Sci. Health B, vol. 50(12), pp 896-900, 2015.

47. Santos R.F., Dias H.M., Fujimoto R.Y., Acute toxicity and histopathology in ornamental fish amazon blue-spotted corydora (*Corydoras melanistius*) exposed to formalin, An. Acad. Bras. Cienc., vol. 84/issue 4, pp 1001-1007, 2012.

48. Small B.C., Chatakondi N., Efficacy of formalin as an egg disinfectant for improving hybrid catfish (channel catfish × blue catfish) hatching success, North American Journal of Aquaculture, vol. 68, pp 9-13, 2006.

49. Songur A., Sarsilmaz M., Ozen O., Sahin S., Koken R., Zararsiz I., Ilhan N., The effects of inhaled formaldehyde on oxidant and antioxidant systems of rat cerebellum during the postnatal development process, Toxicol. Mech. Methods, vol. 18, pp 569-574, 2008.

50. Speare D.J., Arsenault G., MacNair N., Powell M.D., Branchial lesions associated with intermittent formalin bath treatment of Atlantic salmon, *Salmo salar* L., and rainbow trout, *Oncorhynchus mykiss* (Walbaum), J. Fish Dis., vol. 20, pp 27-33, 1997.

51. Speare D.J., MacNair N., Effects of intermittent exposure to therapeutic levels of formalin on growth characteristics and body condition of juvenile rainbow trout, Journal of Aquatic Animal Health*,* vol. 8, pp 58-63, 1996.

52. Sul D., Kim H., Oh E., Phark S., Cho E., Choi S., Kang H.S., Kim E.M., Hwang K.W., Jung W.W., Gene expression profiling in lung tissues from rats exposed to formaldehyde. Arch. Toxicol., vol. 81, pp 589-597, 2007.

53. Szende B., Tyihák E., Effect of formaldehyde on cell proliferation and death, Cell Biol. Int., vol. 34, pp 1273-1282, 2010.

54. Tang M., Xie Y., Yi Y., Wang W., Effects of formaldehyde on germ cells of male mice, Wei Sheng Yan Jiu*,* vol. 32, pp 544-548, 2003 (Article in Chinese, Abstract in English).

55. Teng S., Beard K., Pourahmad J., Moridani M., Easson E., Poon R., O'Brien P.J., The formaldehyde metabolic detoxification enzyme systems and molecular cytotoxic mechanism in isolated rat hepatocytes, Chem. Biol. Interact., vol. 130-132, pp 285-296, 2001.

56. Thrasher J.D., Kilburn K.H., Embryo toxicity and teratogenicity of formaldehyde, Arch. Environ. Health, vol. 56, pp 300-311, 2001.

57. Tkachenko H., Grudniewska J., Evaluation of oxidative stress markers in the heart and liver of rainbow trout (*Oncorhynchus mykiss* Walbaum) exposed to the formalin, Fish Physiol. Biochem., vol. 42, pp 1819-1832, 2016.

58. Tkachenko H., Grudniewska J., Oxidative stress biomarkers in the heart and liver of rainbow trout (*Oncorhynchus mykiss* Walbaum) upon disinfection by formalin, Baltic Coastal Zone – Journal of Ecology and Protection of the Coastline, vol. 21, pp 177-196, 2017.

59. Tsutsui H., Kinugawa S., Matsushima S., Oxidative stress and heart failure, Am. J. Physiol. Heart Circ. Physiol., vol. 301/issue 6, pp H2181-2190, 2011.

60. Waterstrat P.R., Marking L.L., Clinical evaluation of formalin, hydrogen peroxide, and sodium chloride for the treatment of *Saprolegnia parasitica* on fall chinook salmon eggs, The Progressive Fish-Culturist*,* vol. 57, pp 287-291, 1995.

61. Winkaler E.U., Silva A.G., Galindo H.C., Martinez C.B.R., Biomarcadores histológicos e fisiológicos para o monitoramento da saúde de peixes de ribeirões de Londrina, Estado do Paraná. Acta Sci. Maringá, vol. 23, pp 507-514, 2001.

62. Yildiz H.Y., Guzey I.M., Ergonul M.B., Changes of non-specific immune parameters in rainbow trout, *Oncorhynchus mykiss*, after exposure to antimicrobial agents used in aquaculture, J. Appl. Aquaculture*,* vol. 21, pp 139-150, 2009.

63. Yisa T.A., Tsadu S.M., Aidoo T., Ibrahim A., Gana E.S., Adama B.S., Effect of chemical disinfectant (formalin) on hatching of eggs of African catfish (*Clarias gariepinus*), survival and growth performance of Fry, Int. J. Curr. Microbiol. App. Sci., vol. 3, pp 1133-1138, 2014.

64. Zar J.H., Biostatistical Analysis, 4^{th} ed. Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1999.

65. Zhang R., Kang K.A., Piao M.J., Kim K.C., Lee N.H., You H.J., Hyun J.W., Triphlorethol-a improves the non-homologous end joining and base-excision repair capacity impaired by formaldehyde, J. Toxicol. Environ. Health A, vol. 74, pp 811-821, 2011.

THE STATE OF THE FAUNA OF BATS IN THE UKRAINIAN AZOV REGION IN MODERN ENVIRONMENTAL CONDITIONS

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ABSTRACT

The article presents the results of regional surveys of bats in 2010-2020 in places planned for the construction of wind farms. The almost complete transformation of the steppe into agrocenoses bordered by forest belts and irrigation canals undoubtedly affected bats against the background of global warming. With the use of modern ultrasonic detectors, licensed computer programs and an electronic library of voices, 15 species were found in the Ukrainian Pryazovia. Their greatest diversity (11–13 species) is recorded between the Dnieper valley and the Crimean Peninsula, where intensive migration flows take place. Probably, in this bottleneck, bats migrating from the northern and northeastern continental regions cross the land and join those moving along the Azov coast. During the winter, with limited research in this period, 8 species were identified, during spring and autumn migrations – 13 and in summer – 11 species.

In recent years in the Ukrainian Pryazovia there has been a decrease in the number of *Pipistrellus pygmaeus* and *Eptesicus serotinus*, as well as an increase in groups of *Nyctalus noctula, Pipistrellus kuhlii, Pipistrellus nathusii* and *Vespertilio murinus*. In all seasons the least common and not numerous were *Plecotus auritus, Myotis daubentonii, Nyctalus lasiopterus, Nyctalus leisleri, Hypsugo savii* and *Barbastella barbastellus*.

Key words: Ukrainian Pryazovia, global warming, detector, bat, wind power plant, research

INTRODUCTION

The fauna, distribution and number of bats on the territory of our state can still be considered insufficiently studied. Despite the appearance of a large number of articles and 4 monographs

[1, 23, 24, 25], in most regions of Ukraine bats remain the least known mammals. These animals were particularly affected by significant global warming, which helped to reduce the duration of hibernation, changed the rhythm of this process, as well as the cyclical development of insects, which are their main food. The lack of long-term regional research hinders not only the writing of reviews, but also the dissemination of knowledge about these unique animals, as well as the implementation of measures aimed at protecting and preserving their diversity.

The aim of the work is to acquaint the scientific community with the results of the study of bats in the Ukrainian Pryazovia during the significant global warming, which we have been carrying out in 2010-2020.

METHODS AND EXPERIMENTAL PROCEDURES

The research was conducted in a narrow strip (up to 100 km wide) of the Sea of Azov coast from Mariupol to the Sivash Lake exclusively in places planned for the construction of wind farms (WPPs): Manhush (Donetsk region); Berdiansk, Prymorsk, Prymorsk-II, Botiieve, Zaporizhzhia (Zaporizhzhia region); Novotroitske, Overianivka, Myrne and Chaplynka (Kherson region); Armiansk and Dzhankoi (Crimea). Part of the research was conducted on the protected territories (the Azov-Sivaskyi National Nature Park (NNP), the Pryazovskyi NNP, the Meotyda NNP). The length of this area was about 600 km (Fig. 1).

Fig. 1. Research Areas: 1 – Chaplynka; 2 – Armiansk; 3 – Askaniia-Nova; 4 – Solone Lake; 5 – Overianivka; 6 – Sadky (Biriuchyi Island); 7 – Mordvynivka; 8 – Melitopol; 9 – Stepanivka-I; 10 – Botiieve; 11 – Orlivka; 12 – Naberezhne (Obytichna spit); 13 – Prymorsk; 14 – Novopetrivka; 15 – Manhush.

The research methodology was developed according to the recommendations of the "Surveillance and Monitoring Methods for European Bats Guidelines produced by the Agreement on the Conservation of Populations of European Bats (EUROBATS)" [26] taking into account the experience of European researchers [5]. Given the applied significance of research [9], it was carried out under the supervision of international expert groups: Mott MacDonald (the UK), Ramboll Environ (Poland), CDM Smith (the USA) and ERM (Romania).

Ultrasound detection throughout the night was carried out by certified ultrasonic detectors (Table 1) mostly during the spring and summer-autumn seasons: at stationary vantage points with the installation of devices at a height of 2.5 m; in separate vantage points; on transects with a length of 500 m to 11 km, the number of which corresponded to the approximate standard of 1 km / 500 ha of the project area of the wind farm.

Table 1. Features of the use of ultrasonic detectors

Research methodology	Ultrasonic detectors (quantity), years of application		
	Pettersson D240x (n = 2)	Pettersson D500x (n = 3)	LunaBat DFR-1 PRO (n = 1)
Manual detection at vantage points for 10 minutes	2010-2020	2013-2014	–
Automatical detection throughout the night at a stationary vantage point	–	2013-2020	2019-2020
Research on transects (on foot)	2011-2020	2013	2019-2020
Research on transects (by car)	–	2018-2019	2019-2020

On all transects, 3-5 evenly spaced places were selected, on each of which an ultrasound examination of the vocal activity of bats was carried out for 5 min. Therefore, the duration of observations within 1 transect was 37-50 minutes taking into account the 3-5 minute walking transitions between them. Besides, additional research sites which seemed sufficiently representative to estimate the distribution and number of bats were selected around each stationary vantage point (Table 2). The distance between them was 2.5–3.0 km that to some extent corresponds to the distances of daily forage movements of bats.

Table 2. Locations and characteristics of research

№	Nearest settlement	Location		Term of research: years (months)	Number of signals	Duration, min
		Latitude	Longitude			
1.	Armiansk	46º06'55.40"	33º41'17.27"	2010, 2012, 2013 (IV-IX)	400	3019
2.	Chaplynka	46º21'51.56"	33º32'07.06"	2012, 2013, 2017, 2018, 2020 (III-XI)	3206	21080
3.	Askaniia-Nova	46º27'27.13"	33º52'21.22"	2010-2020 (I-XII)	9609	59760
4.	Overianivka	46º13'22.74"	34º22'31.31"	2017, 2018, 2020 (III-XI)	958	5912
5.	Solone Lake	45º53'03.18"	34º27'08.12"	2010, 2011, 2012 (IV-X)	278	3698
6.	Sadky	46°06'16.93"	35°03'56.59"	2011, 2014, 2017 (VIII-IX)	650	?
7.	Melitopol	46°50'38.78"	35°21'46.56"	2012-2020 (I-XII)	34630	217490
8.	Mordvynivka	46°44'19.52"	35°22'07.42"	2011, 2012, 2014, 2016 (III-XI)	7034	56413
9.	Stepanivka-I	46°27'31.25"	35°30'32.13"	2012, 2015, 2017, 2018, 2019 (V-VIII)	2274	?
10.	Botiieve	46°41'00.04"	35°50'25.68"	2010-2020 (III-X)	4116	36073
11.	Orlivka	46°42'26.58"	36°01'54.31"	2018, 2019, 2020 (III-X)	1225	16462
12.	Naberezhne	46°30'30.61"	36°09'03.93"	2011, 2016, 2018 (IV-V, VIII-IX)	622	?
13.	Prymorsk	46°44'03.62"	36°21'06.27"	2013, 2018, 2019, 2020 (III-X)	2145	28805
14.	Novopetrivka	46°49'39.41"	36°53'43.94"	2020 (III-VII)	197	2758
15.	Manhush	47°03'03.85"	37°18'00.81"	2019, 2020 (V-X)	1554	15176
Total:					68898	>466646

No animal capture was performed during the studies. Exceptions were the accidental detection of bats in some hiding places (for example, in a flower pot on the balcony, in a broken tree) during migration and wintering.

Identification

In the process of interaction with each other, bats emit social acoustic signals, which are similar in physical and technical characteristics to the sounds of other mammals. However, in flight, they use signals that have maximum amplitude in the ultrasonic range of 20–120 kHz [12]. On the one hand, echo analysis allows bats to distinguish obstacles as well as small objects, which is important for orientation in space and when searching for food. On the other hand, the constant production of ultrasonic signals by these animals allows researchers to determine the presence, number of bats and their spatial movements with the help of detectors.

Previously, we used the licensed computer programs BatSound 4.1 and BatExplorer 2.1 [28] to determine the species composition. Despite their apparent perfection, they did not make a clear distinction between species whose signal frequencies overlapped, for example, the *Pipistrellus kuhlii – Pipistrellus nathusii* and *Plecotus auritus – Plecotus austriacus*, and so on. The situation has been significantly improved with the use of the European Bat guideline [2] and the electronic library of voices of European bat species BatLib Application [27].

Ultrasonic detectors (Pettersson D500x or LunaBat DFR-1 PRO) are able not respond to extraneous sounds that do not belong to bats. However, this ability is not absolute and during their operation, especially in automatic mode, a lot of extraneous noise is recorded on the memory card. That's why before analyzing the vocal activity of bats, the selection of sounds belonging only to these animals was performed using the BatSound computer program (Fig. 2). However, despite the latest equipment and modern software, the species of all bats could not be determined at each research site. Some of them were identified to the genus, for example: *Plecotus sp.* or *Myotis sp.*

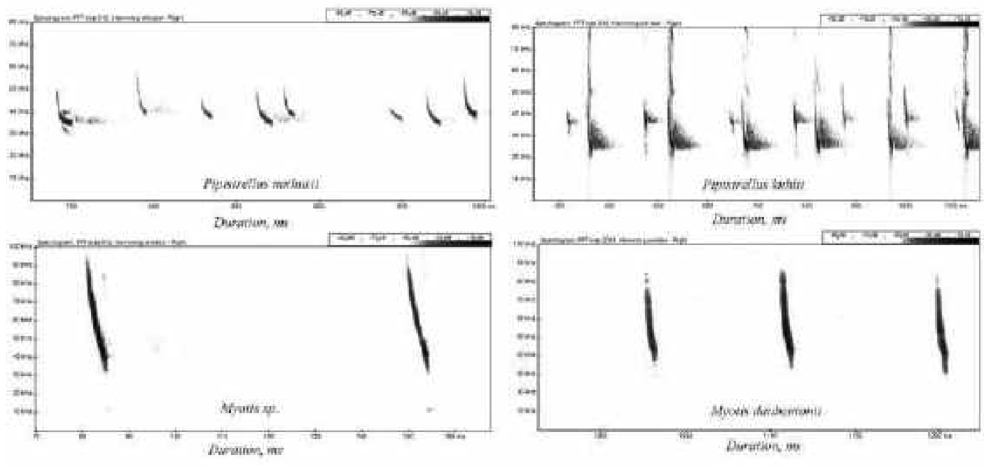

Fig. 2. Spectrograms of the *Nathusius pipistrelle, Kuhl's pipistrelle, Myotis sp*. and *Daubenton's Bat*

Of the almost 69,000 tracks, we were unable to accurately identify 983 tracks, which amounted to 1.44%. In particular, we have never come across *Myotis aurascens*, found on June 27, 1908 in the Provalskyi steppe in the modern Luhansk region [11]. In July 2008, the *Myotis aurascens* was registered with the help of an ultrasonic detector west of the village of Bezimenne in the Novoazovsk district of the Donetsk region on the coast of the Sea of Azov [8]. In 2013, several individuals of this species were found in the same administrative district during the winter [3].

In August 2010, one adult male of the *Myotis aurascens* was caught with a mist net in the Vasylivka district of the Zaporizhzhia region on the Velyki Kuchugury islands (the Dnipro River) in the Velykyi Luh National Nature Park [18].

RESEARCH RESULTS AND DISCUSSIONS

There were detected 15 species of bats in a large area of the Ukrainian Pryazovia in different seasons of the year. Their greatest diversity (11–13 species) is characteristic of places where intensive migration flows take place (Table 3). First of all, these are the points: 1 (Armiansk), 2 (Chaplynka) and 3 (Askaniia-Nova), which are located between the Dnieper valley and the Crimea Peninsula. It is possible that in this bottleneck, bats migrating from the northern and northeastern regions cross the land and join those moving along the coast of the Sea of Azov, and vice versa. To these points should be added Melitopol (7), which is located on the banks of the Molochna River, along the floodplain of which is also noticeable the movement of a large number of animals. A relatively large variety of bats occurs at points 10 (Botiieve), 11 (Orlivka) and 13 (Prymorsk), located directly on the northern shore of the Sea of Azov, along which autumn and spring migration flows are particularly strong [9, 20].

Table 3. Variety of bats and places of their detection

Species	Research sites in accordance with Table 2														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Plecotus auritus	+	+	+	+	–	–	+	–	–	+	–	–	–	–	
Plecotus austriacus	–	+	+	+	–	–	+	+	+	+	+	+	–	–	+
Myotis mystacinus	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
M. daubentonii	–	–	–	–	–	–	–	–	–	+	–	–	–	–	–
Nyctalus lasiopterus	+	–	+	–	–	–	+	–	–	–	–	–	+	–	–
Nyctalus noctula	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Nyctalus leisleri	+	–	–	–	–	–	+	–	–	+	–	–	–	–	+
Pipistrellus kuhlii	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Pipistrellus nathusii	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Pipistrellus pipistrellus	+	+	+	+	+	–	+	+	+	+	+	+	+	+	+
Pipistrellus pygmaeus	–	+	+	+	–	+	+	+	+	+	+	–	–	–	+
Hypsugo savii	–	+	–	–	–	–	+?	–	–	+	–	–	–	+	–
Vespertilio murinus	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Eptesicus serotinus	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Barbastella barbastellus	+	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Total:	11	11	11	10	7	7	13	9	9	13	9	8	8	8	10

According to zoologists who worked in Askaniia-Nova in the first third of the twentieth century, it is known that *Nyctalus noctula, Nyctalus lasiopterus, Nyctalus leisleri, Vespertilio murinus,*

Pipistrellus pipistrellus, Pipistrellus nathusii were exclusively migratory species in the steppe zone of Ukraine [13]. In the following years, with a significant change in the ecological situation and global warming, the fauna of bats has changed greatly. After 1979, in Askaniia-Nova, the party has been registered all year round, and its winter colonies appeared in the village. Later, with the help of an ultrasonic detector, extremely rare species were detected: *Nyctalus leisleri, Pipistrellus pipistrellus, Pipistrellus nathusii* [14].

The most numerous species in all research sites was the *Pipistrellus kuhlii*, the expansion of which from the Caucasus began in the 80s of the twentieth century [17]. For unknown reasons, some of the animals began to settle in the northeastern direction [16] and some – in the west, along the coast of the Sea of Azov. In 1975, this bat was found in Rostov [22], in 1985 – in Melitopol [14]; by 1990, the *Pipistrellus kuhlii* occupied all the Pryazovia region and became a numerous species in many settlements [19].

Distribution of this bat on the territory of Ukraine continues today [25]. So it is not surprising that in all places of our research the share of the *Pipistrellus kuhlii* was: 41.9 % – Askaniia-Nova; 58.1 % – Armiansk, Chaplynka and 74.9 % – Mordvynivka. Everywhere this figure was close to 50% or even exceeded this value. The second species in number was the *Vespertilio murinus*: 5.3 % – Solone Lake; 5.8 – 11.4 % – Overianivka; 16.2 % – Askaniia-Nova and 8.0 % – Prymorsk.

In the 50s of the twentieth century the *Vespertilio murinus* occurred sporadically throughout Ukraine, and it was most numerous near the Sivash Lake. In the 80s of the twentieth century, the *Vespertilio murinus* was a rare species (3 finds) in Rostov located in the lower reaches of the Don River [22] and in the Rostov region in general [7]. Until recently, it was considered rare and settled in the Black Sea Biosphere Reserve [15], and in the Crimea – a rare and migratory species [6]. In 2011-2012, this species, despite our intensive and regular research, was not detected on the east coast of the Molochnyi Estuary [20]. Given that the *Vespertilio murinus* was subsequently found in all places of our research and, moreover, its number became significant, we can state the increase of its groups in the Ukrainian Pryazovia.

In recent years, in all places of Pryazovia, against the background of a decrease in the number of *Pipistrellus pipistrellus* and *Eptesicus serotinus*, there has been an increase in the number of groups of *Nyctalus noctula*, the share of which was: 2.6 % – Solone Lake; 4.9 % – Overianivka; 12.3 % – Mordvynovka; 5.8 % – Prymorsk and 21.5 % – Askaniia-Nova. In some places the share of the *Pipistrellus nathusii* was quite significant: 5.3 % – Askaniia-Nova; 22.4 % – Overianivka; 4.0 – 15.0 % – Solone Lake, which is connected with migrations of this dendrophilous species and their stops in settlements in the absence of forest. In several places of the research region (Krasnoperekopsk: 12–14.04.13; Askaniia-Nova: 16–29.07.13, 12–20.04.15 and 19–21.05.15) the *Nyctalus lasiopterus* was recorded, 1 specimen of which from Melitopol (November 7, 1898) was kept in the Natural History Museum of Simferopol [10]. In 2020, in the warm winter weather, the ultrasonic signals of the *Nyctalus lasiopterus* were recorded by P. Horlov in Melitopol, as well as near Prymorsk [21]. Due to the rarity of the species, its identification passed an additional expert verification, which confirmed the accuracy of species identification.

The biological cycle of bats in the Ukrainian Pryazovia can be divided into 4 unequal periods, the duration of which varies greatly over the years (Table 4). It should be noted that to a large extent, our knowledge of the presence of certain species of bats in different places during the biological cycle is related to the depth and abundance of regional research. But in some places we have not been able to fully cover all its phases.

Table 4. The maximum number of bat species at the sites of detection and by phases of the biological cycle

Phases of the biological cycle	Research sites in accordance with Table 2														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Wintering (XI-III)	–	6	7	4	–	–	5	4	–	4	3	–	2	–	5
Spring migration (IV-V)	8	8	9	8	6	–	11	7	5	10	7	6	7	5	8
The emergence and breeding of a new generation (VI-VII)	5	7	7	7	7	6	10	8	6	7	7	–	7	5	8
Autumn migration (VIII-X)	10	10	9	10	7	6	11	9	9	11	9	8	8	7	10

Wintering is the longest (November-March), but there are quite warm days, when in January and February the evening temperatures can reach + 6-8 ºC, and in the first decade of March – +10ºC. During this period, we managed to record 8 species of bats on the territory of the Ukrainian Pryazovia. At points 2 (Chaplynka), 3 (Askaniia-Nova), 7 (Melitopol) and 8 (Mordvynivka), where most research was conducted, males and females of the *Plecotus* *austriac*us and *Plecotus auritus* were found during the winter, females of the Vespertilio murinus, males and females of the *Pipistrellus kuhlii* and the *Nyctalus noctula* (Table 5).

Table 5. Species diversity of bats at the sites of detection during wintering

№	Species	Chaplynka	Askaniia-Nova	Overianivka	Melitopol	Mordvynivka	Botiieve	Orlivka	Prymorsk	Manhush
1.	*Plecotus auritus*	+	+							
2.	*Plecotus austriacus*	+	+							
3.	*Nyctalus noctula*	+	+	+	+	+	+	+	+	+
4.	*Pipistrellus kuhlii*	+	+	+	+	+	+	+	+	+
5.	*P. nathusii*	+	+	+	+	+	+	+		+
6.	*P. pygmaeus*		+							
7.	*Vespertilio murinus*	+	+	+	+	+	+			+
8.	*Eptesicus serotinus*				+					+
Total:		6	7	4	5	4	4	3	2	5

Warm weather in years with frequent winter warming (2011/12; 2013/14; 2019/20) prompted bats to stop hibernation and search for food. As the concentration of the *Nyctalus noctula* at this time is too small to fully compensate for energy costs, this has resulted in the depletion and death of a significant number of animals. The *Pipistrellus kuhlii* is resistant to cold air and it is able to show activity at a temperature of + 7–10 ºC. We have repeatedly seen bats flying in late November – early December.

Transition of the average temperature through +10 ºC, which means the beginning of phenological spring, is a trigger signal to the beginning of spring migration. In Pryazovia in warm years, it begins in late March and lasts until early May. However, the bulk of bats migrates in April, and if in autumn the animals fly low above the ground, in the spring most of them fly at an altitude of about 100 m. Usually during the spring migration, clusters of bats are not expressed. In total, we recorded a temporary presence of 13 species of bats during this biological phase (Table 6).

Table 6. Species diversity of bats at the sites of detection during spring migration

№	Species	Armiansk	Chaplynka	Askaniia-Nova	Overianivka	Solone Lake	Melitopol	Mordvynivka	Stepanivka-I	Botiieve	Orlivka	Naberezhne	Prymorsk	Novopetrivka	Manhush
1.	*Plecotus auritus*			+											
2.	*Plecotus austriacus*			+			+	+		+					+
3.	*Myotis mystacinus*	+	+	+	+		+			+	+		+		+
4.	*Nyctalus lasiopterus*	+		+											
5.	*Nyctalus noctula*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
6.	*Pipistrellus kuhlii*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
7.	*P. nathusii*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
8.	*P. pipistrellus*	+	+	+	+	+	+	+		+	+	+	+		+
10.	*P. pygmaeus*		+												
11.	*Hypsugo savii*				+		+?			+					
12.	*Vespertilio murinus*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
13.	*Eptesicus serotinus*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Total:		8	8	10	8	6	9	7	5	9	7	6	7	5	8

Undoubtedly, interesting during the spring migration are isolated cases of detection of *Hypsugo savii* on 09 / 10.04.2020 near the villages of Overianivka and Botiieve and, with a certain amount of doubt, on 18 / 19.04.2020 in Melitopol (Table 6), as well as on 06 / 07.09.2018 in the village of Chaplynka (n = 3) and on 08 / 09.06.2020 near the village of Novopetrivka (n = 1) during the autumn migration (Table 8). After all, this species is quite rare even within the area on the southern coast of Crimea [6].

The summer fauna of bats in the Ukrainian Pryazovia is represented by 7-9 species (Table 7), which occurred at almost all vantage points. The most numerous everywhere were: *Nyctalus noctula, Vespertilio murinus, Eptesicus serotinus, Myotis mystacinus, Pipistrellus kuhlii, P. nathusii, P. pipistrellus. Plecotus auritus* and *Plecotus austriacus*, as well as *Nyctalus lasiopterus* and *Nyctalus leisleri* were rare. Given the randomness of the meetings and the singularity of the latter, we cannot confirm with much certainty the nature of their presence in the region in the summer.

Table 7. Species diversity of bats at the sites of detection during the birth and offspring rearing

№	Species	Armiansk	Chaplynka	Askaniia-Nova	Overianivka	Solone Lake	Sadky	Melitopol	Mordvynivka	Stepanivka-I	Botiieve	Orlivka	Prymorsk	Novopetrivka	Manhush
1.	*Plecotus auritus*							+							
2.	*Plecotus austriacus*							+	+						+
3.	*Myotis mystacinus*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
4.	*Nyctalus lasiopterus*			+											
5.	*Nyctalus noctula*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
6.	*Nyctalus leisleri*							+							
7.	*Pipistrellus kuhlii*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
8.	*P. nathusii*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
9.	*P. pipistrellus*		+	+	+	+	+	+	+	+	+	+	+	+	+
10.	*Vespertilio murinus*		+	+	+	+	+	+	+	+	+	+	+		+
11.	*Eptesicus serotinus*	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Total:		5	7	8	7	7	7	10	8	7	7	7	7	6	8

The largest species diversity of bats (n = 15) in the places of our research was recorded during the autumn migration (Table 8).

Table 8. Species diversity of bats at the sites of detection during the autumn migration

№	Species	Armiansk	Chaplynka	Askaniia-Nova	Overianivka	Solone Lake	Sadky	Melitopol	Mordvynivka	Stepanivka-I	Botiieve	Orlivka	Naberezhne	Prymorsk	Novopetrivka	Manhush
1.	*Plecotus auritus*	+			+			+			+					
2.	*Pl. austriacus*		+	+	+			+	+	+	+	+	+			+
3.	*Myotis mystacinus*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
4.	*M. daubentonii*										+					
5.	*Nyctalus noctula*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
6.	*N. lasiopterus*							+						+		

7.	*N. leisleri*	+						+			+					+
8.	*Pipistrellus kuhlii*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
9.	*P. nathusii*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
10.	*P. pipistrellus*	+	+	+	+	+		+	+	+	+	+	+	+	+	+
11.	*P. pygmaeus*		+	+	+		+	+	+	+	+	+				+
12.	*Hypsugo savii*		+													
13.	*Vespertilio murinus*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
14.	*Eptesicus serotinus*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
15.	*Barbastella barbastellus*	+														
Total:		10	10	9	10	7	7	12	9	9	12	9	8	8	7	10

If most of the animals found were expected migrants, the only meeting of the *Barbastella barbastellus* at the end of September, 2012 near Armiansk and registration of 3 *Myotis daubentonii* on 16 / 17.05.2014 near the village of Botiieve were a wonder. The "raids" of these species, which are not characteristic for field landscapes, testify to our limited knowledge about distribution of rare and not numerous bats in our country.

Of course, the transition from one phase of the biological cycle to another is gradual, as evidenced by the results of our research in Melitopol (Fig. 3). In March-April 2020, 5-180 sounds were recorded every night, which undoubtedly belonged to animals that wintered in the town. But in June, their number rose sharply to 125-470. When the peak reached in late June and early July (440-470), the migration wave subsided and the period of birth of young animals and their breeding began, which lasted until the last days of July. Already in mid-August 2020, the peak of the first autumn migration wave was registered in Melitopol, which generally lasts until August, 20-25 in the Ukrainian Pryazovia.

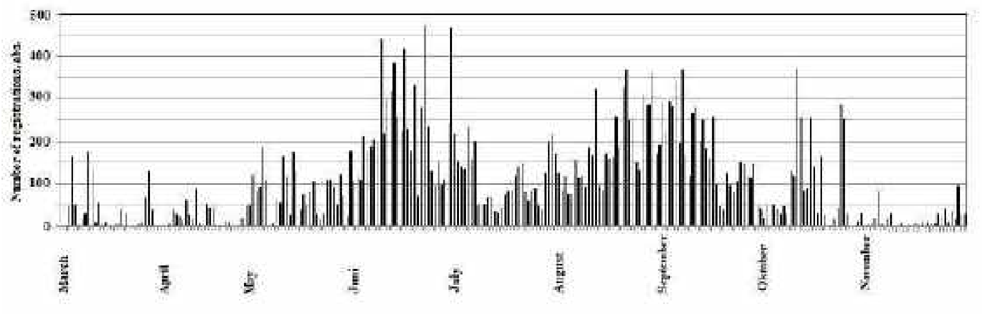

Fig. 3. Dynamics of activity of bats in Melitopol, 2020

From the beginning of July to the middle of August, there was a local increase in the number of bats due to birth, which was joined by other animals that appeared as a result of migration processes. In 2020, the second wave of migration lasted from late August to late September. It was characterized by 3 peaks (350 signals) and 3 depressive phases (120-180 signals per night), as well as a rapid decrease in animal activity (40-47 signals) at the end of the month, which could be caused by rapid cooling in much of Eastern Europe. In general, in many coastal areas, this wave becomes noticeable from late September to the third decade of October, but in cold weather it may not be. In the first decade of November this year, after a short migration surge, wintering of bats began. Although in some years in the last decade of October, no active individuals were found.

CONCLUSION

In 2010–2020 from Mariupol to the Sivash Lake, 15 species of bats were recorded at the locations planned for the construction of wind power plants using 6 certified ultrasonic detectors (Pettersson D240x, D500x; LunaBat DFR-1 PRO).

In the study area during the wintering, with limited research in this period, 8 species were found, during the spring and autumn migrations – 13 and in summer – 11 species. In all seasons, the least common were *Plecotus auritus, Myotis daubentonii, Nyctalus lasiopterus* and *Nyctalus leisleri, Hypsugo savii and Barbastella barbastellus.*

The greatest species diversity of bats (n = 10–12) was found in the narrowest gap between the Dnieper River and the Sea of Azov, as well as in the coastal strip, where the main flow of migrating animals takes place.

During migrations in the Ukrainian Pryazovia, bats willingly stop in tree hollows in parks, artificial forests and forest belts, various cliffs and buildings, which they use as temporary hiding places. In some of them they form small colonies and even overwinter.

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REFERENCES

1. Abelientsev V.I., Popov B. M. Order of bats – Chiroptera / Fauna of Ukraine. Mammals. Publishing house of the USSR Academy of Sciences, Kyiv, vol. 1 /issue 1, pp 229 – 446, 1956 (In Ukrainian).

2. Barataud M. Acoustic ecology of European bats. Species Identification and Studies of Their Habitats and Foraging Behaviour / Biotope Editions, Mèze. National Museum of Natural History, Paris, pp 1–340, 2015.

3. Bronskov O. Finding of the steppe whiskered bat *(Myotis aurascens* Kuzyakin, 1935) in the Southeast of Ukraine / Proceedings of the Theriological School, vol. 15 /issue 15, pp 154 – 155, 2017 (In Ukrainian).

4. Cheremisov A.I. Kuhl's Pipistrelle bat *(Pipistrellus kuhlii)* in the steppe regions of Ukraine / Vestnik zoologii, vol. 2, p 80, 1987 (In Russian).

5. Dietz Ch., von Helversen O., Nill D. Bats of Britain, Europe and Northwest Africa. A&C Black Publishers, London, pp 1– 400, 2009.

6. Dulickij A.I. Mammals (history, state, conservation, prospects) / Biodiversity of Crimea. Simferopol, Sonata, pp 1 – 208, 2001 (In Russian).

7. Gazaryan S.V., Bachtadze G. B., Malinovkin A. V. Current state of knowledge of bats in Rostov Region / Plecotus et al., vol. 13, pp 50 – 58, 2010 (In Russian).

8. Godlevskaja E.V. Bats. Landscapes, vegetation and fauna of the regional landscape park "Meotida". Donetsk, pp 84 – 87. 2010 (In Russian).

9. Horlov P.I., Volokh A. M., Polishchuk I. K., Siokhin V. D., Dolinnij V. I. Scientific and methodological principles of protection and environment impact assessment during the design, construction and operation of wind and solar power plants, power lines. Kyiv-Melitopol, pp 1 – 148, 2014 (In Ukrainian).

10. Kuzyakin V.P. Greater noctule bat *(Nyctalus lasiopterus)* in the USSR / Bats: Issues of theriology: Results of tagging mammals. Science, Moscow, pp 55 – 59, 1980 (In Russian).

11. Ognev S.I. Mammals of the Moscow province / Commission for the study of the fauna of the Moscow province, vol. 1 /issue 1, Moscow, 1913, pp 1– 310 (In Russian).

12. Patlyakevich L.D. Vespertilionidae location signals / Bats: Issues of theriology. Nauka, Moscow, pp 213 – 270, 1980 (In Russian).

13. Popov B.M. On seasonal migrations of bats / Priroda, vol. 2, pp 87 – 90, 1941 (In Russian).

14. Polishchuk I.K. Summer bat fauna of Askania-Nova (investigation with ultrasonic detector). Migration Status of Bats in Ukraine / Novitates Theriologicae, vol. 6, Kyiv, pp 102 – 105, 2001 (In Ukrainian).

15. Seljunina Z. Bats of the Black Sea Biosphere Reserve: European Bat Night '98 in Ukraine /Proceedings of the Theriological Schoo, vol. 1, Kyiv, pp 80 – 83, 1998 (In Russian).

16. Strelkov P.P., Unkurova V. I., Medvedeva G. A. New data on Kuhl's Pipistrelle bat *(Pipistrellus kuhlii)* and dynamics of its range in the USSR / Zoological. journal, vol. 64 /issue 1, pp 87 – 97, 1985 (In Russian).

17. Veretshchagin N.K. Mammals of the Caucasus. Publishing house of the USSR Academy of Sciences, Moscow-Leningrad, pp 1 – 704, 1959 (In Russian).

18. Vlaschenko A.S. The report *Nyctalus lasiopterus* in Ukraine: inventory of current status, proposals to revise the species status in IUCN Red List and conservation. Kharkiv, pp 1 – 26, 2012.

19. Volokh A.M. Forming of the Azov Sea Part of the Kuhl's Pipistrelle *(Pipistrellus kuhlii)* Range / Vestnik zoologii, vol. 36 /issue 1, pp 101 – 104, 2002 (In Russian).

20. Volokh A.M., Siokhin, V. D., Polishchuk, I. K., Horlov, P. I. The study of bats by ultrasound detector in the zone of influence of wind farms in Ukrainian Azov region / Transactions of the Azov-Black Sea Ornithological Station. vol. 17, pp 76 – 95. 2014 (In Ukrainian).

21. Volokh A., Horlov, P. Siokhin, V., Polishchuk, I. Species identification of the greater noctule bat *(Nyctalus lasiopterus)* by its records with detector / Novitates Theriologicae, vol. 11 pp 164–174, 2021 (In Ukrainian).

22. Yarmysh N.N., Kazakov A. B., Sonina N. Yu., Usvajskaya A. A. New finds of bats in the North Caucasus / Bats: Issues of theriology. Nauka, Moscow, pp 72 – 77, 1980 (In Russian).

23. Zagorodniuk I. (ed.). European Bat Night '98 in Ukraine / Proceedings of the Theriological School, vol. 1, Kyiv, pp 1 – 199, 1998 (In Ukrainian).

24. Zagorodniuk I. (ed.). Migration Status of Bats in Ukraine / Novitates Theriologicae, vol. 6, Kyiv, pp 1 – 172, 2001 (In Ukrainian).

25. Zagorodniuk I., Godlevska L., Tyshchenko V., Petrushenko Ya. Bats of Ukraine and adjacent countries: a guide for field investigations / Proceedings of the Theriological School, vol. 3, Kyiv, pp 1 – 108, 2002 (In Ukrainian).

26. Surveillance and Monitoring Methods for European Bats Guidelines produced by the Agreement on the Conservation of Populations of European Bats. Retrieved https://www.eurobats.org/official_documents/agreement_text

27. BatLib App web-site. URL:https://www.batlogger.com/en/products/batlib/

28. BatSound 4.1: Pettersson Elektronik AB; BatExplorer 2.1 (Analyse your recordings). https://www.nhbs.com/acoustic–ecology–of–european–bats–book/

THE IMPACT OF CLIMATE CHANGE ON WORKERS IN THE CONSTRUCTION AND ROAD INDUSTRIES WORKING OUTDOORS

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ABSTRACT

This paper presents the algorithm of the system model developed by the authors to assess and predict the acceptability of production risk for workers working outdoors in urban areas. When building the model, a comprehensive approach was used, which takes into account all the influential factors in the context of global climate change. The model consists of two levels of hierarchy. An example of this approach is given for a separate subsystem of the model, which takes into account the subsystem of interaction of temperature and air quality indicators on the health of workers on the example of Darnytska Square in Kyiv based on meteorological data 2013-2020. A scale of classifications between quantitative indicators of industrial risk and indicators of air pollution has been developed. On the example of some large road junctions in Kyiv, the classification of industrial risk from the level of secondary air pollution by formaldehyde due to photochemical transformations in the air under constant weather conditions in 2016 is given as one of the hottest observations in the city. The results will be useful in developing recommendations for the protection of workers' health in the context of global climate change.

Key words: climatic factors, risk, urban area, health of workers, air pollution, highways.

INTRODUCTION

In the context of global climate change, environmental factors pose an additional risk to the health of workers working outdoors. This is primarily workers in the construction and road industries. Factors such as air pollution against the background of abnormal temperatures and increasing noise pollution of urban areas, including due to an increase in the number of mobile transport sources of pollution that run on gasoline and diesel fuel. These factors have led to increased risks to the health of outdoor workers. This requires additional health and work-related measures, starting with personal protective equipment. There is also a need to adjust and bring into line urban planning norms and recommendations. It is necessary to note in addition such dangerous toxicological factor of influence as evaporation of dangerous substances at the raised temperature indicators, for example when working with bitumen and asphalt mix.

The work of many domestic and foreign scientists [1-4, etc.] is devoted to the relationship between global climate change, air pollution and environmental risk to public health in large cities. In these works, on the basis of mathematical processing of long-term monitoring data on air quality indicators and public health indicators, correlations were established, which showed a close relationship depending on temperature indicators. In [5,6] on the basis of a mathematical model of convective polluted jet over a warm surface of roads under constant meteorological conditions, a solution was obtained that allows to obtain data on carcinogenic and non-carcinogenic risks to public health from secondary air pollution by emissions from road transport. gasoline and diesel fuel. The passage of photochemical reactions in the air of urban areas in this case depends on the meteorological conditions of the area, the stability of the atmosphere, temperature, humidity and air velocity.

But in addition to meteorological factors, workers who work outdoors also experience the effects of noise pollution on the body. Works [7,8,9, etc.] are devoted to the risk of noise pollution impact. The research presented in these works concerns the determination of the levels of acoustic pollution from vehicles in large cities, the impact of the levels of this pollution on the human body and the justification of measures to reduce it. Based on the definition of noise, it is noted that noise from vehicles is one of the sources of negative impact on human life and work near noise pollution.

Characteristics of the impact of production conditions at elevated temperatures would be incomplete without taking into account the toxicological effects on workers. According to the latest technologies, the method of "cold asphalt" is used, it includes: PVA, modifier "MAK", Bitumen brand MG or SG 70/130 [10]. The bitumen used as a part of "cold asphalt" belongs to the III class of danger.

Bitumen is dangerous to the health of workers when: it is transported at the maximum temperatures specified in the conditions of transportation and operation; works higher than +60 C are performed [11]. According to the list of occupational diseases approved by the order of the Ministry of Health of Ukraine, the Ministry of Social Protection of Ukraine, the Ministry of Labor of Ukraine from February 2, 1995 N 23/36/9, employees of road repair organizations working in the open with vehicles, bitumen and crushed stone, hand ramming, or electric stove are susceptible to such diseases as: acute chronic intoxication, toxic respiratory damage, skin diseases, allergic diseases, pneumosilicosis, vibration disease, sensorineural deafness, etc. According to [12] recorded, as of 13.07.2016 at an air temperature of +31 C, the asphalt temperature was +53 C. It should be noted that the temperature in the warm season can reach over +31 C, thereby leading to an increase in asphalt temperature, as the effect of heating the asphalt from vehicles and increasing the risk of disease of workers on the above diseases.

The possibilities of these existing solutions allow to obtain relative and quantitative assessments of the impact of individual factors discussed in the above works on public health, but to date has not considered the issue of occupational risk and safety of workers working outdoors in the context of interaction. dangerous factors in the conditions of gradual average annual increase of temperature indicators.

To support management decisions in the planning and reconstruction of the urban environment in accordance with the "Strategy of low-carbon development of Ukraine until 2050" and the introduction of the latest technologies of construction and road works, it is necessary to take into account the degree of industrial risk for outdoor health. acceptability. An integral part of this important and urgent problem is the need to solve a scientific and applied problem, which is to develop a unit for assessing and forecasting the acceptability of industrial risk in the context of global climate change, taking into account all influencing factors for this assessment.

METHODS AND EXPERIMENTAL PROCEDURES

The aim of the work is to build a solution algorithm for assessing and forecasting the acceptability of industrial risk for workers working in the open air of urban areas in order to further make recommendations for the protection of workers' health in the context of global climate change.

To solve this problem, a comprehensive synergetic approach is needed, taking into account all the influential factors that pose a danger to the health of this category of workers. The solution of this problem is possible with the help of a systematic hierarchical two-level model of the formation of industrial risk on workers in the open air, taking into account long-term trends of rising temperatures in global climate change.

A systematic mathematical model for assessing and forecasting the impact of global climate change on employee health involves two basic operations: the formation of many alternatives to the factors of influence and comparison and the choice of options for influencing the value of occupational risk. The system model identifies a complex problem that is able to implement the following basic principles:

- analysis and evaluation of individual processes, elements in subsystems;

- assessment and forecast of the impact of temperature changes on the value of production risk according to regulatory criteria.

At the first level of the hierarchy, the proposed model contains three independent subsystems:

1- Interaction of temperature and air quality indicators on the health of workers.

2- Noise effects on employee health.

3- Toxicological effect on the background of elevated temperatures.

When modeling production risk, the method and accuracy of laying the source information is important

Each subsystem is characterized by its own set of criteria and indicators f_1, f_2, $f_3 \dots f_n$; q_1, q_2, $q_3 \dots q_4$; p_1, p_2, $p_3 \dots p_n$.

THE RESEARCH RESULTS AND DISCUSSIONS

Consider how the performance of each block at the first level of the system model on the example of meteorological factors.

It is known that a rise in temperature has a negative effect on human health, causing heat stroke; tachycardia, excessive sweating, which leads to water and salt imbalance, decreased blood flow to the brain, etc.

The relationship between the data of non-carcinogenic risk of contamination by the main components that exceed the reference doses and temperature indicators on the example of Darnytska Square in Kyiv in terms of 2013-2020 are presented in table 1. It should be noted that at the junction of Darnytska Square in Kyiv recently (2019) overhaul of the roadway was started, the lower layer of asphalt has already been installed.

The algorithm of this model is presented in fig. 1

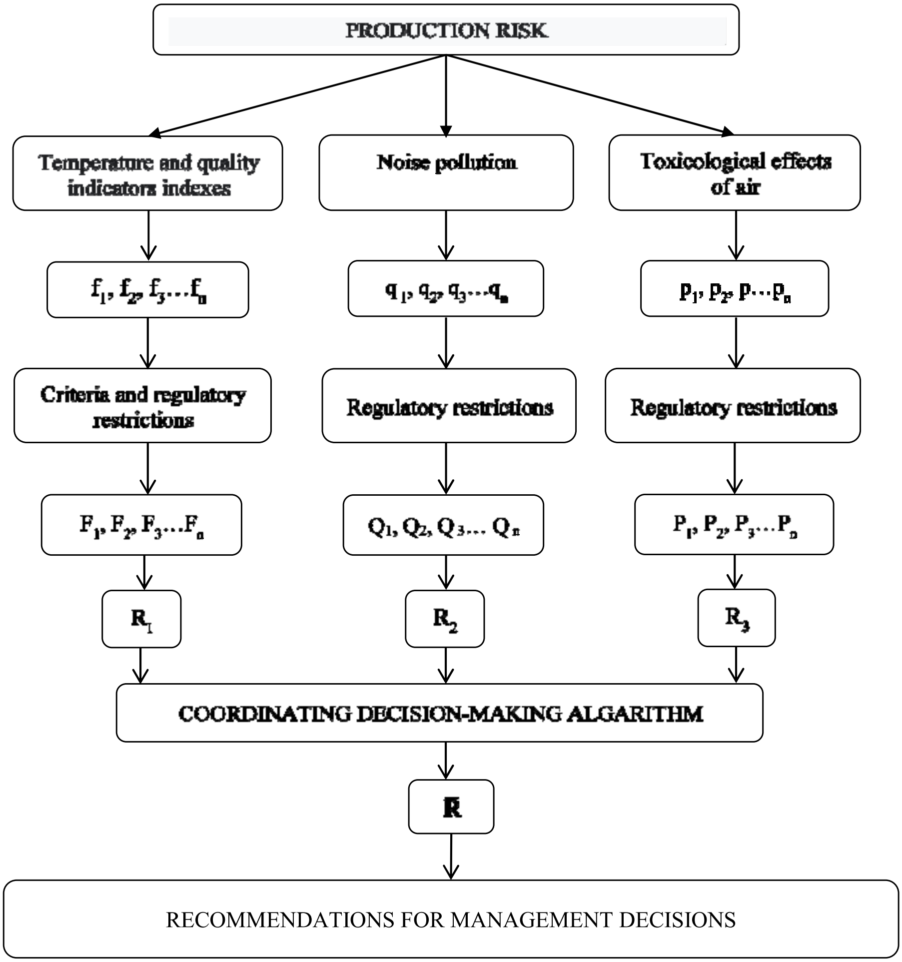

Fig.1. Algorithm of system hierarchical model of assessment and classification of production risk for workers working outdoors

On the example of some indicators of air pollution in urban areas according to individual stationary observation posts in Kyiv, the relationships between the main components of pollution and the average monthly temperature conditions in Kyiv according to the observations of the Central Geophysical Observatory. B. Sreznevsky in terms of 2013-2020 observations. These dependences showed a significant effect of temperature indicators on the indicators of air pollution, both primary and secondary indicators due to photochemical transformations in the air. Some dependences are given, which are a confirmation of this statement. Thus, Figure 2 shows the dependence of the stationary observations on Darnytska Square between the temperature and measurements of the toxic substance CHON in 2016, which was observed as one of the hottest years in recent decades.

Confirmation of the influence of temperature indicators and the dynamics of physicochemical transformations in the air are the dependences presented in Fig. 3, which show the dependences between temperature and NO_x indicators in the air, as well as the interaction of these pollutants, respectively. Moreover, in contrast to the graph CHON = f (t °), the dependence CHON = f (NO_x) is linear with a correlation coefficient of 0.73.

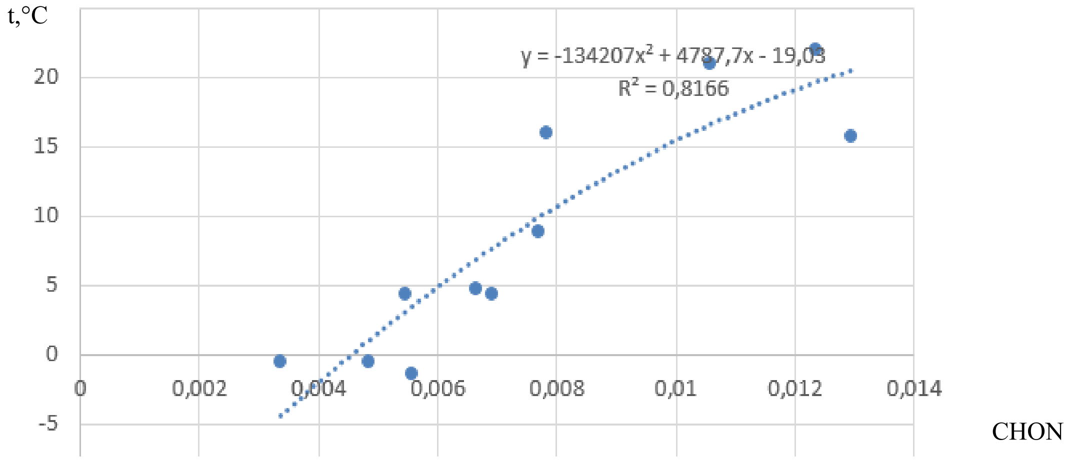

Fig. 2. Polygonal dependence between the indicators of CHON concentration in the air at the station of stationary observations in Kyiv (Darnytska Square) and the average temperature indicators in 2016.

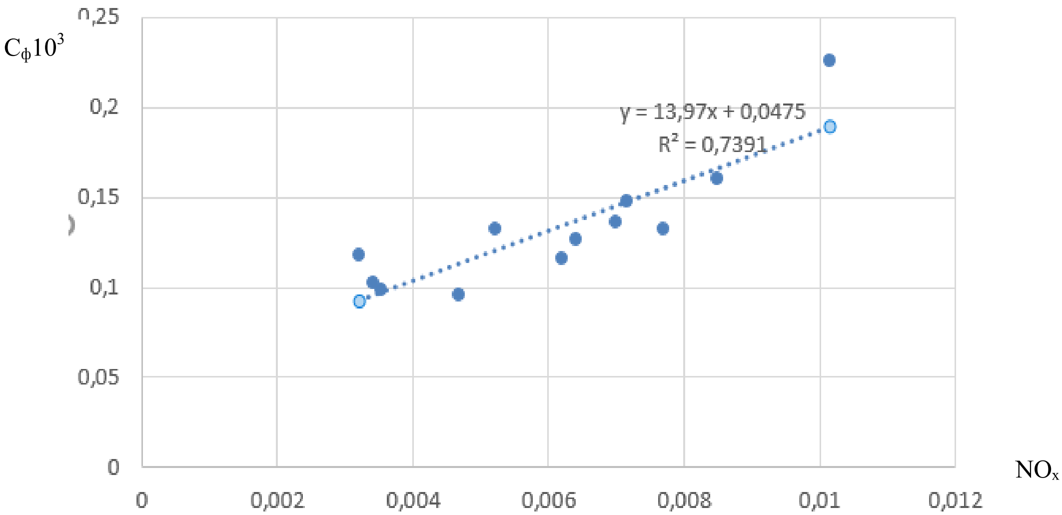

Fig.3. Relationship between the average monthly indicators of SNON concentration in the air at the station of stationary observations in Kyiv (Darnytska Square) and the average monthly NO_x concentrations in 2016

Risks to the health of the population were determined in accordance with the current in Ukraine Guidelines MR 2.2.12-142-2007 [13] on reference concentrations. Non-carcinogenic risk is calculated according to the total criterion of hazard index (HI), which is defined as the sum of hazard factors for exposure to substances (HQ).

As for the measurements of the current year, the average temperature in June 2021, according to the Central Geophysical Observatory. B. Sreznevsky, it was +21.3 °C, which is 1.8 °C above the climatic norm. From 23 to 26 June, as many as 10 temperature records were broken. Marked 6 days with a maximum air temperature above + 30.0 °C.

According to observations at the stationary posts of the Central Geophysical Observatory named after Borys Sreznevsky in the period from June 29 to July 5, 2021 in the air of Kyiv exceeded the maximum allowable concentrations (MPC) for the average daily content in the area of Darnytska Square: suspended solids - 1.0-1.2 times; nitrogen dioxide - 8.5; formaldehyde - 3.1-3.6 times.

Table 1. The value of non-carcinogenic risk under the conditions of chronic exposure to pollutants contained in the air (Darnytska Square) according to the data of July from 2013 to 2020

Substance/critical organs, system mg/m^3	CHON/ respiratory organs, immune.	NO_2/respiratory organs	Dust/respiratory system	Average monthly temperature, t°C	Year	∑HI = HQ
Reference concentration, mg/m^3	0,03	0,04	0,1		-	-
Measured concentration, mg/m^3	0,015	0,166	0,117	20,6	2013	-
HI	5,0	4,15	1,17	20,6	2013	10,32
Measured concentration, mg/m^3	0,016	0,176	0,128	22,3	2014	-
HI	5,3	4,4	1,28	22,3	2014	10,83
Measured concentration, mg/m^3	0,012	0,145	0,139	21,3	2015	-
HI	4,0	3,62	1,39	21.3	2015	10,01
Measured concentration, mg/m^3	0,014	0,172	0,1	22,4	2016	-
HI	4,67	4,30	1,0	22,4	2016	9,97
Measured concentration, mg/m^3	0,014	0,142	0,1	21,1	2017	-
HI	4,67	3,55	1,0	21,1	2017	9,22
Measured concentration, mg/m^3	0,006	0,112	0.09	21,4	2018	-
HI	2,0	2,8	0,9	21,4	2018	5,7
Measured concentration, mg/m^3				20,0	2019	-
HI	2,0	2,8	1,2	20,0	2019	6,0
Measured concentration, mg/m^3	0,0051	0,140	0,1	21,9	2020	-
HI	1,7	3,5	1,0	21,9	2020	6,2

According to estimates of non-carcinogenic risk, its value is 13.3.

Thus, the analysis of monitoring data on existing observation posts in Kyiv in 2013-2021 shows a stable excess of average monthly (from 1.5 and more in winter months and from 3 and more in summer), measured concentrations of such pollutants in the air as CHON, NO_2 and dust in the surface layer of atmospheric air. There is a tendency to increase over the years the concentrations of these pollutants against the background of increasing the number of personal vehicles with gasoline and diesel engines and long-term temperatures due to global climate change.

The data presented in Table 1 show that at elevated temperatures in one of the hottest months of the year, the value of non-carcinogenic risk to the health of workers working on the reconstruction of highways is in the range of 10-100. According to the classification of levels, this level of non-carcinogenic risk is defined as "significant". At this value, the risk is unacceptable for the population, and the production conditions require dynamic control and in-depth study of the sources and possible consequences of adverse effects to address the issue of risk management measures.

Carcinogenic risk according to the existing method [13] is defined as the product of the specific carcinogenic risk of a single pollutant multiplied by its average annual concentration. In the case of inhalation, the average daily intake m (dose rate), attributed to 1 kg of human body weight, is determined by the formula (1):

$$m = \frac{C \times V \times f \times T_O}{P \times T} \tag{1}$$

C - concentration of carcinogen in the environment - in the air, mg/m³;

V - volume of air entering the lungs during the day, m³/day;

f - is the number of days in the year during which the carcinogen is exposed;

T_O - the number of years during which the effect of the carcinogen;

P - average body weight of an adult, kg;

T - the average time of possible action of the carcinogen, ext.

To establish a scale of classifications between quantitative indicators of industrial risk and indicators of air pollution, the values of actual concentrations of pollutants are used and obtained during their statistical processing. To characterize air pollution on the basis of calculated data, the maximum single concentrations obtained for a specific area of the settlement are usually used in the calculations of emission scattering. Listed in table 2 scale of classifications between quantitative indicators of industrial risk and indicators of air pollution. The formation of this classification was based on the State Sanitary Rules for the Protection of Atmospheric Air of Settlements (from Chemical and Biological Pollution) of the Ministry of Health of Ukraine DSP-201-97.

In the case when you need to know the degree of danger of industrial risk in excess of the concentration of one of the most dangerous pollutants, we use a similar approach for a separate indicator.

As an example, we will give the value of the level of industrial risk from formaldehyde pollution at three road junctions: street Bohatyrska – street Lugova - Marshal Tymoshenko Avenue; street Shcherbakovsky - street Stetsenka - street M. Grechka, street Schuseva - street Olena Telihy - street Melnikova and street Olena Teliga - S. Bandera Avenue - Kurenivka, Kyiv at the level of 2016. The analysis data are presented in table 3. It should be noted that the tables show the value of non-carcinogenic risk of air pollution

Table 2. Levels of assessment of quantitative indicators of industrial risk and indicators of air pollution

Pollution level	Degree of danger (according to the value of production risk)	The frequency of exceeding the reference values of individual pollutants (taken by the largest value)	The value of production risk
Permissible	Safe At this level, the desired (target) value of risk in health and environmental measures	<1	<1
Unacceptable	Slightly dangerous The level of risk is acceptable for production conditions. With the impact on the whole population, dynamic control and in-depth study of the sources and possible consequences of adverse effects is needed to address the issue of risk management measures	>1-2,0	1,0 – 10,0
Unacceptable	Moderately dangerous Dynamic monitoring and in-depth study of the sources and possible consequences of adverse effects are needed to address risk management measures	>2-4,5	10,0 – 50,0
Unacceptable	Dangerous Risk - unacceptable for the population, the production conditions require dynamic control and in-depth study of the sources and possible consequences of adverse effects to address the issue of risk management measures	>4,5-8	50,0 – 100,0
Unacceptable	Very dangerous The risk is unacceptable for working conditions and the population. Measures to eliminate or reduce the risk are needed	>9	>100,0

.

Table 3. The average monthly value of non-carcinogenic risk of formaldehyde air pollution due to photochemical transformations near some car interchanges in Kyiv in 2016.

№	Car junction name	Multiplicity of exceeding the reference values of individual pollutants	Significance of non-carcinogenic risk
1	street Bohatyrska – street Lugova - Marshal Tymoshenko Avenue	January -2.13 February-1.81 March-2.19 April -2.93 May-3.7 June-6.93 July-4.63 August-4.46 September 4.0 October-3.23 November -2.53 December -2.47	January - Moderately dangerous February- Slightly dangerous March- Moderately dangerous April - Moderately dangerous May - Moderately dangerous June - Dangerous July - Dangerous August - Dangerous September - Moderately dangerous October - Moderately dangerous November - Moderately dangerous December Moderately dangerous
2	street Shcherbakovsky - street Stetsenka - street M. Hrechka	January-3.6 February-3.2 March-3.6 April -4.87 May-6.17 June-6.63 July-7.63 August-7.43 September-7.67 October-5.37 November –4.23 December -3.17	January - Moderately dangerous February- Moderately dangerous March - Moderately dangerous April - Dangerous May - Dangerous June - Dangerous July - Dangerous August - Dangerous September is safe October is dangerous November - Moderately dangerous December Moderately dangerous
3	street Schuseva - street Elena Teliga - street Mel′nykova	January-3.7 February-3.07 March-3.7 April -4.93 May-6.3 June-6.76 July-7.76 August-7.57 September-7.03 October-5.46 November –4.3 December -4.17	January - Moderately dangerous February- Moderately dangerous March - Moderately dangerous April - Dangerous May - Dangerous June - Dangerous July - Dangerous August - Dangerous September is dangerous October is dangerous November - Moderately dangerous December Moderately dangerous
4	street Olena Teliga - S. Bandera Avenue - Kurenivka	January-3.3 February-2.76 March-3.3 April -4.43 May-5.67 June-6.07 July-7.0 August-6.67 September-6.33 October-4.93 November –3.87 December -3.73	January - Moderately dangerous February- Moderately dangerous March - Moderately dangerous April - Moderately dangerous May - Dangerous June - Dangerous July - Dangerous August - Dangerous September is dangerous October is dangerous November - Moderately dangerous December Moderately dangerous

The data in Table 3 once again emphasized the interdependence of temperature conditions, the degree of air pollution and, accordingly, the importance of industrial risk for workers in the open air near road junctions. It should also be noted the need for dynamic control during the year on the magnitude of production risk and risk management.

When calculating the indicators of the second subsystem - noise pollution should be guided by a number of current regulations on the impact of excess noise pollution on the employee's body.

For the city of Kyiv today the biggest noise pollution is road transport. As of 2020, about 1,087 ml were registered in Ukraine. auto (subject to re-registration) [14]. This has led to excessive traffic jams and congestion at road junctions, excessive congestion of exhaust gases and excessive noise during congestion of cars and nearby areas. With the increase in the number of cars in the city of Kyiv there is a constant transport collapse [15] exhaust gases and noise pollution significantly reduce the quality of the ecological state of the city, life and work in the areas adjacent to the roads. To understand the origin of vehicle noise, it is necessary to determine what is the largest source of noise in a car. Based on the structure of the car is determined that the main source of noise in the car is the engine. The intensity of noise pollution depends on the type, design and mode of operation of the engine. [16].

Based on the definition of noise, it should be noted that noise from vehicles is one of the sources of negative impact on human life and work near noise pollution [17-20].

The third subsystem of the model uses the method of taking into account toxicological indicators on the degree of their impact on human health depending on temperature indicators, which is presented in [21,22].

The coordinating decision-making algorithm takes into account the significance of the risk to public health according to the formula (2):

$$R = \sum R_i \tag{2}$$

i= 1,2,3.

The value of formula (1) is the sum of the defined values of risk for each subsystem, climatic conditions are taken into account indirectly at the level of the first and third subsystems.

For workers working near highways, you can use a calculator developed by [6] to calculate the concentration of secondary formaldehyde pollution depending on weather conditions (temperature, solar radiation) and the concentration of hydrocarbons that are precursors of formaldehyde formation at constant temperatures.

CONCLUSION

Studies have shown the need to take global climate change into account when determining occupational risk for social workers working outdoors. The analysis of all the influencing factors for the health of workers (air pollution, noise pollution and increased toxic effects of hazardous substances used in the production process) proved the need for a systematic approach to this scientific and practical problem. The proposed hierarchical system mathematical model for determining industrial risk in the context of global climate change allows to take into account all factors and their interaction.

This model allows to improve the system of production risk management on the basis of preliminary assessment and forecasting in the design, construction and reconstruction of urban areas and correctly define measures for the safety of workers.

The calculation of non-carcinogenic risks of air pollution under high temperature conditions on the example of Darnytska Square and some transport interchanges in Kyiv carried out within the first subsystem of the model showed that there is a need for dynamic control for workers working in the open air and in-depth study of the sources and possible consequences of harmful effects on road service workers. Under such conditions, there is a need for further improvement of the air monitoring system in the area of highway overpasses and large intersections in Kyiv by the State Hydrometeorological Service of Ukraine and the State Sanitary and Epidemiological Service of the Ministry of Health of Ukraine. Achieving an acceptable level of risk for workers working outdoors in areas of maximum importance can be achieved by implementing appropriate measures, which in addition to strengthening personal protection measures must also include the organization of traffic, maximum introduction of environmentally friendly modes of transport and use of more environmentally friendly fuel.

Needs a separate further study of the strengthening of toxicological effects of evaporation of hazardous substances in conditions of rising temperatures.

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REFERENCES

1.Liao, T., Jiang, W., Ouyang, Z. *et al.* Evaluation of the health risk of air pollution in major Chinese cities using a risk-based, multi-pollutant air quality health index during 2014–2018. *Air Qual Atmos Health* (2021). DOI: https://doi.org/10.1007/s11869-021-01042-6

2. Voloshkina, O., Tkachenko, T. *et al.* The estimation and redaction of risk caused by air pollution in sities /Budownictwo o zoptymalizowanym potencjale energetycznym/ Constraction of Optimized energy potential, Vol.8, Nr2/2019.- 17-26. DOI: https://doi.org/10.17512/bozpe.2019.2.02

3. Ciencewicki J. *et al.*, 2007. Air Pollution and Respiratory Viral Infection. Inhalation Toxicology 19:14, 1135-1146. DOI: https://doi.org/10.1080/08958370701665434

4. Edoardo Conticini,Bruno Frediani, Dario Caro (2020). Can atmospheric pollution be considered a co-factor in extremely high level of SARS-CoV-2 lethality in Northern Italy? Environmental Pollution, Volume 261, June 2020, 114465 DOI: https://doi.org/10.1016/j.envpol.2020.114465

4. Kovaleva, A., Kravchenko, M., Klimova, I. Impact of elevated temperature and air pollution on urban air as a result of climate change on the health of social infrastructure workers/ Bulletin of the Dnieper State Academy of Civil Engineering and Architecture,No 6 (271-272), 2020. DOI: https://doi.org/10.30838/J.BPSACEA.2312.241120.104.704

5. Sipakov R., Trofimovich V. *et al.* Impact of Weather Factors on the Speed of the Reaction of Formaldehyde Formation Above Motorway Overpasses/ Environmental Problems, Volume 3, number 2, Lviv Politechnic National University, P. 97-102, 2018. Access mode: https://lpnu.ua/news/environmental-problems-volume-3-number-2-2018

6. Sipakov, R., Voloshkina, O., *et al.* Pollution of atmospheric air above the city highways. //USEFUL online journal, vol. 2, no. 4, pp. 01–08, December 2018. DOI: https://doi.org/10.32557/useful-2-4-2018-0001

7. Vnukova V. Estimation of acoustic pollution of the roadside territory of the highway. Eastern European Journal of Advanced Technology. Ecology. №4/6 (issue 52). Kharkiv, 2011. p. 42-47. Access mode: http://journals.uran.ua/eejet/issue/archive

8. Pukalo, M. Influence of road transport noise on the state of ecology and methods of reducing their indicators Materials of the first scientific-practical online conference, Lviv, 2016, P.32-38.

9.Гілета Л. Інтегроване поширення акустичного навантаження й виділення акустичних геосистем в урбогеосистемі Львова. Наукові записки ТНПУ ім. В. Гнатюка Серія. Географія. 2012. Вип. 1 (31). С. 199-204.

10. Electronic resource. Access mode: https://trivita.ua/ru/blog/holodnyj-asfalt-a-234

11. Electronic resource. Access mode: https://www.labadr.com.ua/news/page:12/sort:News.date/direction:DESC

12. Electronic resource. Access mode: https://kyivnews.24tv.ua/ru/asfalt_v_kieve_razogrelsja_do_nemyslimoj_temperatury_fotofakt_n704972

13. Electronic resource. Access mode: https://cfts.org.ua/news/2020/02/05/v_yanvare_2020_goda_v_ukraine_bylo_zaregistrirovano_28_tysyach_poderzhannykh_avto_57226

14. Electronic resource. Access mode: https://delo.ua/business/vechnyj-kollaps-na-dorogah-kiev-zanjal-3-mesto-v-364025/

15. Electronic resource. Access mode:https://os1.ru/article/7049-avtomobil-i-shum

16. Electronic resource. Access mode:https://nv.nltu.edu.ua/Archive/2013/23_12/126_Zub.pdf

17. Han J-H, Dimitrijevic A. Continuous noise maskers reduce cochlear implant related artifacts during electrophysiological testing. The Journal of Health Science. 2017;7(2):61-62. Access mode https://www.ncbi.nlm.nih.gov/pmc/journals/257/

18. Franklin M et al. Assessing the contribution of noise to the association between traffic-related air pollution and children's respiratory health. In: ISEE Conference Abstracts; 2018. Access mode https://ehp.niehs.nih.gov/doi/abs/10.1289/isesisee.2018.P03.0350

19. Zare S et al. Evaluation of the effects of occupational noise exposure on serum aldosterone and potassium among industrial workers. Noise & Health. 2016;18(80):1-6. Access mode https://pubmed.ncbi.nlm.nih.gov/26780955/

20. Electronic resource. Access mode: file:///D:/Comp/DskTop/%D0%BF%D0%BE%20%D1%88%D1%83%D0%BC%D1%83/klassifikatsiya-avtomobilnyh-dorog-po-urovnyam-shuma.pdf

21. Udod, V., Trofimovich, V., Voloshkina, O. Fundamentals of ecotoxicology, Kyiv, KNUBA, 2008. 88 p. Access mode: www.knuba.edu.ua

22. Fent K., Weston A., Caminada D. Ecotoxicology of human pharmaceuticals // Aquatic Toxicology. — 2005. — 76. — P. 122-159. Access mode: https://pubmed.ncbi.nlm.nih.gov/16257063/

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