CLIMATE CHANGE & SUSTAINABLE DEVELOPMENT: NEW CHALLENGES OF THE CENTURY

TEXTBOOK

supported by
Visegrad Fund

Petro Mohyla Black Sea National University, Ukraine

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edited by
prof. Olena Mitryasova

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The textbook is devoted to problems strategy of sustainable development as a road map of civilization; main components supporting the sustainable development of the planet; environmental ethics and economics as key instruments for sustainable development; inland waters: types, threats, challenges; water management: history; water purification; wastewater and sewage treatment; sustainable and environmental land management; green chemistry: principles, metrics and examples.
The book is written for students, postgraduate students, lecturers who are specialized and interested in the field of environmental research.

**Chapter I. − prof. Olena Mitryasova; Chapter II − assoc. prof. Pavel Nováček;
Chapter III. – prof. Piotr Koszelnik, Ph.D Małgorzata Kida; Chapter IV. – prof. Eva Chmielewská;
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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 book 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 chapters of the textbook:

- ✓ Main components supporting the sustainable development of the planet;
- ✓ Environmental ethics and economics as key instruments for sustainable development;
- ✓ Inland waters: types, threats, challenges;
- ✓ Water management: history; water purification; wastewater and sewage treatment;
- ✓ Sustainable and environmental land management;
- ✓ Green chemistry: principles, metrics, examples;
- ✓ The role of the environmental ethics and project-based learning in the education of environmental engineers.

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. The textbook is the result of the work of scientists, leading experts from universities:

Chapter I. – prof. Olena Mitryasova, Ecology Department of the Petro Mohyla Black Sea National University, Mykolaiv, Ukraine;

Chapter II. − assoc. prof. Pavel Nováček, the Environmental Studies Department, Faculty of Science Palacký University in Olomouc, Olomouc, Czech Republic;

Chapter III. – prof. Piotr Koszelnik, Ph.D Małgorzata Kida, the Department of Chemistry and Environmental Engineering, Rzeszow University of Technology, Rzeszow, Poland;

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Chapter VII. – assoc.prof. Rita Bodáné-Kendrovics; emeritus prof. Zoltán Juvancz, Department of Environmental Engineering, Óbuda University, Budapest, Hungary.

The content of the book does not cover all questions of climate change and sustainable development problems.

We express our sincere thanks to all the authors, who have presented the own, interesting chapters on the problems of climate change and sustainable development, contributing to this book was published.

In the future we hope that the content is 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.

Professor Olena Mitryasova

Mykolaiv, Ukraine,

March 2022

Chapter I

MAIN COMPONENTS SUPPORTING THE SUSTAINABLE DEVELOPMENT OF THE PLANET

In this section you will learn about

- ✓ Scientific view of the Earth.
- ✓ Systems that determine the stability of our planet.
- ✓ Biodiversity as a major factor in the stability of the planet.
- ✓ The water cycle as a factor in the stability of the biosphere.
- ✓ Circulation of nutrients as a condition for the existence of the biosphere.
- ✓ Anthropogenic pollutants.
- ✓ The ozone layer.
- ✓ The limits of sustainability of the planet.
- ✓ Zero Carbon emission target.

Key words:

the Holocene
the Anthropocene
Biome
Biodiversity
Water cycle
Nutrients

Desertification
Eutrophication
Dead zones
Anthropogenic pollutants
Aerosol
The ozone layer
Carbon neutrality
Circular (green) economy

Understandings of how our planet works are constantly changing. Since the appearance of the first people in ten years, the average temperature has reached 10^{o}C. The temperature-stabilized only 10 thousand years ago. It was a stable interglacial period called the Holocene. The stability of the planet is due to the stable temperature of the Holocene. The sea level stabilized. Predictable seasons began to exist. Stability was very important, which made possible the rapid development of human civilization. The exponential growth of human pressure on the planet has allowed us to reach the limit at which our geological epoch, which has been called anthropogenic, has already formed.

The most alarming sign is the melting of glaciers. Since 1980, significant global warming has led to new much faster melting of glaciers around the world, leaving many extinct and many others in jeopardy. According to scientists, if the glaciers of Greenland melt, the sea level will increase by 7 m. The planetary climate limit is a warming of 1.5^{0}C.

The stability of our planet depends not only on climate. Additional research by scientists has shown that there are four more boundaries in the planet's biosphere, namely: terrain; biodiversity; water cycle; nutrients.

Mankind continues to degrade tropical rainforests at a rate that threatens to cross critical ecological boundaries. It's not just tropical forests, all the trees on our planet play a role in maintaining their stability. The loss of 25% of the Earth's forest can lead to catastrophic consequences.

In just 50 years, humanity has wiped out 68% of the world's wildlife population. About 70% of crops depend on insect pollination. Deterioration of nature is not limited to insects. Today, only 30% of all birds on the planet are wild. Among all mammals on the planet, wild species make up only 4% by weight.

The next boundary of the biosphere is related to the circulation of water on the planet. It is determined that for 1 person per day requires about 3000 liters of freshwater, for drinking and personal hygiene requires 50 liters; for household needs a person uses about 100 liters per day and for industrial needs 150 liters. The remaining 2,500 liters are needed for food, ie for growing everything that a person eats. Every person on the planet uses about 1.5 million liters of water a year! By 2025, about 2.8 billion people from 48

countries will be short of water, and by 2050 the number of people who are constantly short of water will reach 7 billion.

The combination of climate change and increased nutrient consumption will lead to a decrease in ocean oxygen levels by an average of 3% −4% by 2100. Two main causes of deoxygenation are outlined: ocean warming from fossil fuel combustion and excessive algae growth (eutrophication). Ocean deoxygenation has a wide range of implications for marine biodiversity and the day-to-day functioning of ocean ecosystems.

According to forecasts, in the future the oceans will continue to absorb CO_2 and become more acidic. Estimates of future CO_2 levels show that by the end of the XXI century. the acidity of ocean surface waters can increase by almost 150%. This will lead to unprecedented pH levels in the oceans in 20 million years.

Aerosols are one of the most dangerous forms of pollutants that globally affect the state of the biosphere. 75% of aerosols are formed due to the combustion of fossil fuels. Aerosols can to capture sunlight and scatter it. These particles can to affect the climate, absorbing solar radiation and thus cause cooling of the planet. The cooling effect of aerosols masks 45% of the effects of global warming. Every year, about 7 million people die from air pollution. Life expectancy in large cities is reduced by an average of 3 years. However, scientists have not yet determined where the limit of air pollution passes, but it is estimated that 7 million deaths from air pollution are the limit for aerosols. Aerosols are dust, particles of smoke and ash from fires, fuel combustion, volcanic eruptions, pollen and plant spores, and others. On average, each square centimeter of the earth's surface contains about 109 aerosol particles.

The question of the ozone screen, predicting its depletion and the consequences of this process affects the stability of the Earth's ecosystem and, above all, all living things on Earth.

Currently, scientists have defined a clear structure of planetary boundaries. There is strong evidence that humanity is at risk of climate change and biodiversity loss. There is a frequency of droughts, the number of fires on many continents, the negative impact on the Amazon rainforest, the acceleration of melting glaciers, the catastrophic state of coral reefs. Corals are a kind of indicator of the state of the environment, they fade when the water becomes too warm. Under conditions of global warming there is a mass extinction of corals. The effects of discoloration are 10 times greater than those of a large-scale tropical cyclone of the fifth category.

The planet will experience harsher and more devastating weather events over the next 30 years. To stop the deterioration of weather conditions by 2050, the increase in global temperature should be limited to about 1.5 ° C according to the pre-industrial level.

1.1. Scientific view of our planet.

Recent discoveries by scientists studying how our planet works are certainly important for all the inhabitants of the Earth. On the one hand, these discoveries are very disturbing, but on the other hand, they give us hope for the best and knowledge of how to fix everything.

Scientists say there are ways to overcome the global environmental crisis. It is not about the planet, but about humanity and the future of mankind. We still have a chance, we have a chance for a better future! And it's great that today we have such an opportunity (Fig. 1.1.)!

Fig. 1.1. Man and the Universe.

Understandings of how our planet functions are constantly changing. We now understand better than ever how the relationships in the environment are important to human survival. But biodiversity is shrinking and our climate is changing.

What factors support the stability of the planet Earth? It is thanks to science that we have become the first generation to learn what factors support the stability of the planet and what undermines its existence.

Thus, the graph of the state of ice objects shows how the temperature of our planet has changed over the past millennia (Fig. 1.2).

Since the appearance of the first people in ten years, the average temperature has reached 10oC. These were very difficult times. It should be noted that the temperature stabilized only 10 thousand years ago. It was a stable interglacial period. Geologists gave this period a special name − the **Holocene**.

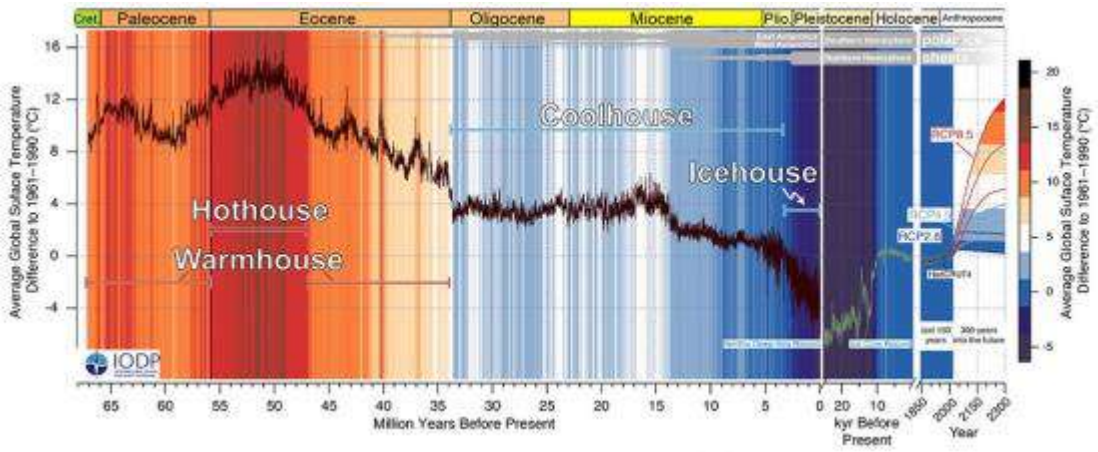


Fig. 1.2. The average global temperature for the last 66 million years.

The Holocene (from the Greek ὅλος − whole, whole; and the Greek Καινός − new, recent) − a modern, latest epoch of the Quaternary period, which covers the postglacial period. It began 11,700 years ago and continues to this day. During this period, land and sea acquired modern contours, formed geographical areas, formed riverbeds and peatlands. The Holocene is an incredible phenomenon, a period during which the average global temperature varies within 1^{o}C. Only 1^{o}C! Due to this period, our planet has acquired the form it has today (Fig. 1.3).

Fig. 1.3. Thanks to the Holocene, our planet has acquired the appearance that it has now.

The stability of the planet is due to the stable temperature of the Holocene. The sea level stabilized. Predictable seasons began to exist. Stability was very important, which made possible the rapid development of human civilization. And humanity, without wasting time, took advantage of this. Intensive development of agricultural production began with the cultivation of such crops as rice, wheat, corn, sorghum,

and others. This interglacial period helped to reach the modern level of civilization. Thus, the Holocene is the only state on the planet that can support the modern form of life.

Since the beginning of human civilization, we have depended on the stable state of the planet, on its constant two ice sheets, the flow of rivers, forests, stable weather and a variety of life forms. Throughout the Holocene, a stable planet provided humanity with food, clean water, and clean air. But this period is behind us.

The exponential growth of human pressure on the planet has allowed us to reach the limit beyond which our geological epoch has already formed. Scientists have recently announced that the Holocene has ended and a new period has begun − **Anthropocene**.

Anthropocene − a geological era when the level of human activity plays a crucial role in the Earth's ecosystem. The term was introduced into scientific practice in the 1980s by ecologist Eugene Stormer, and was widely popularized by atmospheric chemist Paul Krutzen, a Nobel laureate in chemistry, who first used the term anthropocene in 2000. Since mid-2015, the term has been considered by special workers. groups of geological scientific societies.

Thus, humanity is now the main driving factor on the planet Earth (Fig. 1.4). We have turned half of the habitable areas into agricultural fields. We move more sediment and rocks than all-natural phenomena combined. We catch most of the fish in the ocean. Nine out of ten people breathe polluted air.

Fig. 1.4. Humanity is the main driving factor on the planet Earth.

What does the future of greenhouse gas emissions look like?

In fig. 1.5. presents some potential future scenarios of global greenhouse gas emissions (measured in gigatons of carbon dioxide equivalent) based on Climate Action Tracker data. There are five scenarios:

• Lack of climate policy: projected future emissions, if climate policy is not implemented, will lead to warming of 4.1–4.8° C by 2100 (compared to pre-industrial temperatures);

• Current climate policy: projected warming of 2.8−3.2° C by 2100 based on current climate policy;

• National promises: if all countries achieve their current goals and promises set out in the Paris Climate Agreement. It is estimated that the average warming by 2100 will be between 2.5 and 2.8° C. This will far exceed the overall goal of the Paris Agreement to keep warming "well below 2 ° C".

• 2 ° C consecutive: limit the average warming to 2° C by 2100. This would require a significant increase in the ambitions of current commitments under the Paris Agreement.

• 1.5 ° C consecutive: limit the average warming to 1.5° C by 2100. This requires a very urgent and rapid reduction in global greenhouse gas emissions.

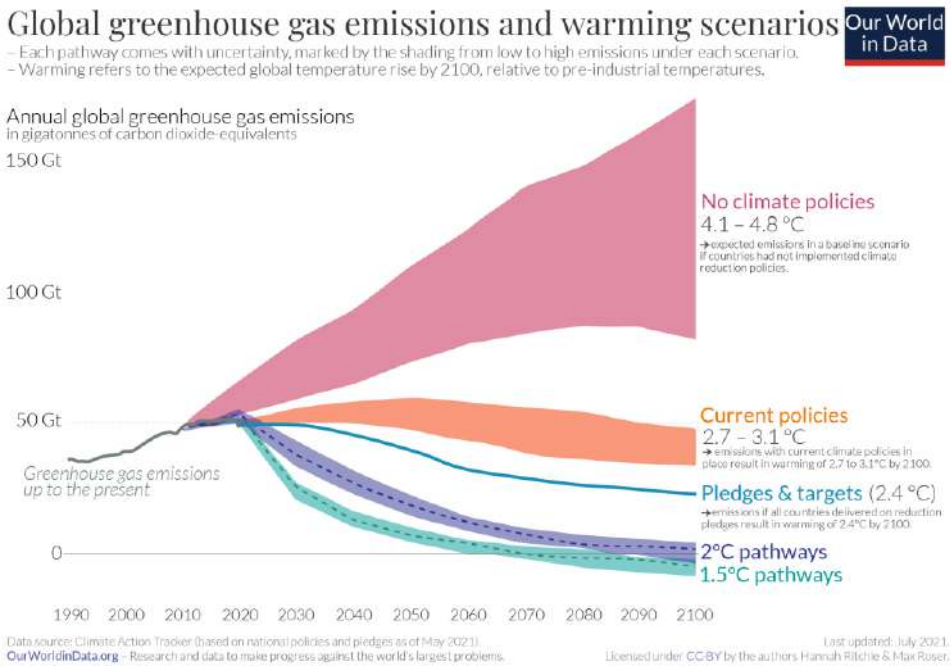


Fig. 1.5. Future greenhouse gas emissions scenarios.
(https://ourworldindata.org/future-emissions)

During the life of one person, we heated the Earth by more than 1^{o}C. In just 50 years, humanity has changed the state of the Earth's ecosystem, which our planet has been for the last 10,000 years. Mankind risks destabilizing the entire planet.

Indeed, today's human civilization must seriously consider the risk of destabilizing the entire planet.

1.2. Systems that determine the stability of the Earth.

What systems determine the stability of our planet? These systems maintained the stable state of the planet throughout the Holocene. The more impact we have on Earth, the more likely it is that these systems will fail if we cross certain boundaries. This will be the collapse of the stability of the Earth on which we depend. Scientists are now working to find the point at which humanity will cause nonlinear changes in the planet's ecosystem.

If scientists can define planetary boundaries, will they be able to provide a roadmap, a plan for overcoming this global crisis?

The first limit is quite well defined. Now, when the temperature is higher than at the beginning of human civilization, there is a possibility that humanity has already crossed the Earth's climate.

The most alarming sign is the melting of glaciers (Fig. 1.6). Since 1980, significant global warming has led to a new much faster melting of glaciers around the world, leaving many of them extinct and the existence of many others under significant threat.

In certain parts of the Andes and the Himalayas, the disappearance of glaciers will have significant consequences for the supply of freshwater to the surrounding population and local ecosystems. The current rapid destruction of the Greenland and West Antarctic glacier glaciers, which began around 1985, could have the effect of rising ocean levels, affecting coastal areas around the world.

Fig. 1.6. View of the Whitchack Glacier in the Glacier Peak Wilderness in 1973 and 2006.

What we see in Fig. 1.5 does not yet destabilize the planet, but the presence of two ice masses in the Arctic and Antarctica is an important condition for the planet to remain stable. So, the melting of glaciers is an alarming signal of destabilization of our planet, as all the glaciers of the Earth are cooling it.

This cooling effect from the two Arctic and Antarctic massifs maintained the planet's stable temperature throughout the Holocene and reflected excess energy into space. This huge white surface of glaciers (Fig. 1.7) reflects 90-95% of the heat coming from the Sun. As these ice sheets begin to melt, they shrink in size, causing their edges to darken and absorb heat. The fact that liquid is formed on the surface of glaciers leads to the fact that glacial shields cease to cool themselves and begin to heat up. This is a critical point, the point when change begins to become irreversible and humanity loses control over processes or phenomena.

Fig. 1.7. The surface of glaciers reflects 90-95% of the heat coming from the Sun.

Snow that has accumulated in Greenland for thousands of years has formed a 3 km long ice dome. Due to the melting of the dome is lowered into warmer air, which accelerates this process. The more the glacier melts, the colder the climate must become to compensate for these changes, but the climate in Greenland is too warm right now. Today, this island has already crossed the border, through which 10 thousand m^3 of ice melts in one second. This is the average rate of melting, and it will continue to increase as the climate gets warmer.

Thus, scientists claim that Greenland is almost lost due to the irreversible climate change that is happening today. The danger of a critical point is that after crossing it, the process can be stopped. After a critical point, the planet may fall into a state of irreversibility, which will pose a complete threat to human existence.

According to scientists, if the glaciers of Greenland melt, the sea level will increase by 7 m. Rising sea levels threaten hundreds of coastal cities. After all, a stable sea level was very important for the development of civilizations. The Greenland Glaciers are not the only ones on our planet that maintain the stability of their temperature. There are also glaciers in Antarctica, which until recently were

considered a stable glacial system. But due to climate change, the area of Antarctic glaciers is also declining. The water formed by this melting flows into the ocean.

If West Antarctica melts completely, the sea level will rise by more than 5 m, and if the East, the sea level will rise by more than 50 m.

Everything in the Earth's ecosystem is interconnected. If one part of the system crosses a critical point, there is a high probability that other parts of the system will cross this limit. This is similar to the domino effect. Thus, if global warming continues, there is a high probability that Earth's systems will cross critical points.

Crossing critical points, we trigger irreversible changes. This means that our planet will turn into a sphere that will relieve stress by absorbing carbon dioxide and absorbing heat. Climate warming is due to the absorption of greenhouse gases. Long before the advent of human civilization, the concentration of carbon dioxide in the Earth's atmosphere precisely regulated the temperature on the planet. During the Holocene, the CO_2 concentration was relatively stable (Fig. 1.8).

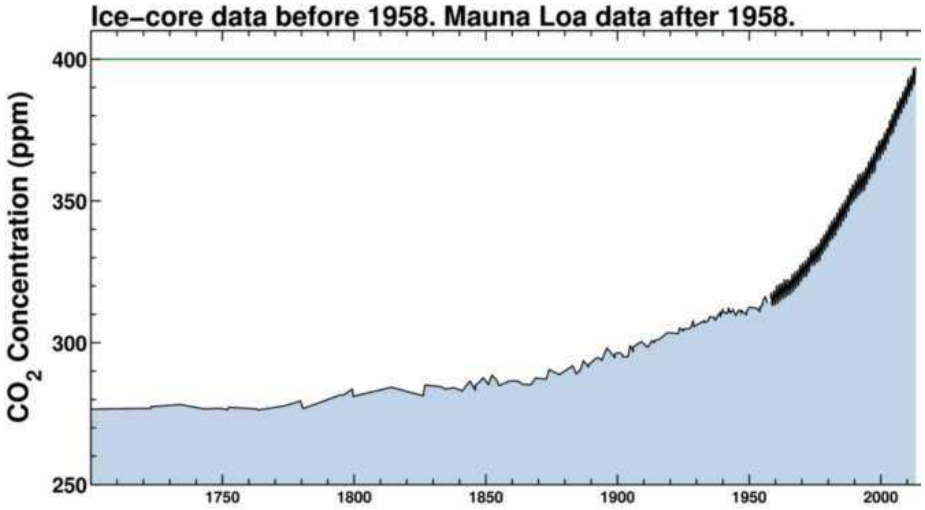


Рис. 1.8. Carbon dioxide concentration.

With the industrial revolution, everything changed. In 1988, we achieved emissions of 350 parts per million of carbon dioxide into the Earth's atmosphere. Then humanity crossed the critical line, causing rapid climate change. Therefore, at a concentration of CO_2 of 350 ppm in the atmosphere, the planet falls into the danger zone. This is the so-called first mess that humanity crossed more than 30 years ago.

We have now reached a point where the concentration of carbon dioxide in the atmosphere is 415 parts per million and we are already seeing the effects of being within the critical zone of climate change. Thus, the frequency of droughts and floods has significantly increased, ice melting has accelerated, permafrost has thawed, and the frequency of forest fires has increased.

Ahead is the second limit, and humanity is rapidly approaching the mark of 450 parts per million. The dangerous zone of planetary boundaries is marked by a range of uncertainty in science. Currently, scientists claim that this range is within 550 ppm. Thus, an area where the concentration of carbon dioxide is 550 parts per million and more is defined as a high-risk area, where irreversible critical points are quite probable and inevitable.

The planetary limit of the climate is warming by 1.50C. And the only way not to cross this line is to completely abandon mining for 30 years. This topic has now received a very wide discussion among scientific, governmental, and public circles.

The stability of our planet depends not only on climate.

Additional research by scientists has shown that there are four more boundaries in the planet's biosphere. The first is the terrain. Thus, the Earth's biome consists of three tropical forests, mixed forests, taiga, meadows, and swamps.

A **biome** is a large regional or subcontinental system. The classification of terrestrial ecosystems by biomes is based on vegetation types and the main unchanging physical characteristics of the landscape. The geographical distribution of biomes corresponds to the soil and climatic zones of the continents. They have existed for a long time and are sufficiently adapted to the specific physical and geographical conditions of the environment.

Secondly, it is biodiversity, all forms of life at all levels of biological organization.

Third is the water cycle.

Fourth, these are nutrients that are essential for the existence of the biosphere.

The first of the boundaries of the biosphere is the composition of the Earth's habitats. It is about how humanity is changing these habitats. We are fast approaching a critical point in one of the largest wildlife areas in the Amazon. After all, tropical forests play an important role in maintaining the stability of the planet. Vast areas of the Amazon were cleared for growing crops.

A large-scale scientific project has been underway since 1998, which has determined that a large area of tropical forests is experiencing drought. In the Amazon, the drought season usually lasts three months. Due to changes in global temperatures, plowing, the drought season has increased by 6 days every decade since the 1980s.

Due to the reduction of forest area, its ability to recycle water is reduced. If the dry season lasts more than four months, the trees in the jungle will die and be replaced by the savannah. This phenomenon is called **savannization**, or **desertification**.

Desertification is a phenomenon of reducing the natural resource potential of the territory below the conditional (permissible) level, which affects the degradation of vegetation, deterioration of biological productivity of lands, can lead to conditions similar to desert.

If deforestation exceeds 20–25% of their area, then with increasing global warming, there is a high probability that the process of savannization (desertification) will become irreversible. This will be possible for 50−60% of the Amazon area. As of now, about 20% of the Amazon rainforest has been lost.

The Amazon jungle is capable of absorbing up to 200 billion tons of carbon dioxide over the next 30 years, which is equivalent to the amount of CO_2 emitted into the atmosphere over the past 5 years. And this is a significant reason for decisive action to address the problems of declining rainforest and global warming.

Fig. 1.9. The Amazon jungle is capable of absorbing up to 200 billion tons of carbon dioxide over the next 30 years.

Mankind continues to reduce rainforests at a rate that threatens to cross critical levels. It's not just tropical forests, all the trees on our planet play a role in maintaining their stability. The loss of 25% of the Earth's forest can lead to catastrophic consequences.

1.3. Biodiversity as a major factor in the stability of the planet.

Reducing the forest area of the Earth causes the next important consequence - the reduction of biodiversity. Biodiversity itself is another important condition for the sustainability of the planet's existence. About 1 million species of plants and animals from 8 million are threatened with extinction. If this negative trend continues, it could lead to the sixth mass extinction of species.

In just 50 years, humanity has wiped out 68% of the world's wildlife population. The planet is at the epicenter of a crisis to reduce biodiversity. Due to the

tendency to reduce biodiversity, humanity will not be able to feed the entire planet, because for this the ecosystem must function properly. For example, in the United Kingdom in the 1990s, the complete extinction of jamals, which are the main pollinator of crops, was recognized.

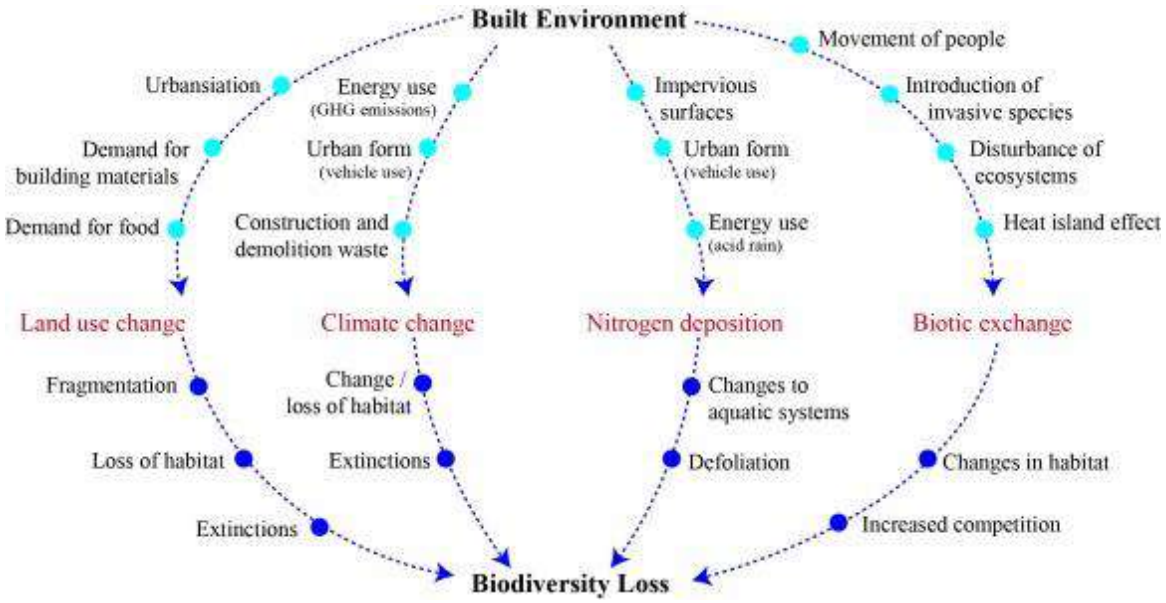


Fig. 1.10. Ecosystem services analysis in response to biodiversity loss.

About 70% of crops depend on insect pollination. However, due to the increase in sowing areas by monocultures, the insect population decreases sharply. Paradoxically, an increase in arable production capacity nullifies the foundations on which this industry is based. The harmonious existence of flora and fauna is a set of tools for the existence of human civilization.

Scientists have tried to calculate the benefits of insects that perform various functions in the Earth's ecosystem. However, their value cannot be calculated until the insects suddenly disappear.

Of course, the deterioration of nature is not limited to insects. Mankind has displaced wildlife, expanding agricultural land to most of the habitable Earth. Today, only 30% of all birds on the planet are wild. Among all mammals on the planet, wild species make up only 4% by weight.

What other part of the natural world can humanity lose? There are many critical points regarding the loss of biodiversity, because life is very difficult. The single boundary of an ecological catastrophe is difficult to determine due to the scarcity of nature itself, the relationships between the many natural components. However, today humanity is in the red zone, when species are disappearing and its

ecosystems are being destroyed.

At the beginning of the decade of 2022, it is time to set a strategic goal − zero losses of natural resources.

The value of global warming at 1.5^{o}C will be zero loss of natural resources.

1.4. The water cycle as a factor in the stability of the biosphere.

The next boundary of the biosphere is related to the circulation of water on the planet. This is another fundamental factor on which humanity depends.

Thus, scientists have estimated that 1 person a day requires more than 3,000 liters of freshwater to survive. Does it seem like so much ?! After all, 50 liters are required for drinking and personal hygiene; for household needs a person uses about 100 liters per day, and for industrial needs 150 liters. The remaining 2,500 liters are needed for food, ie to express everything that a person eats.

Every person on the planet uses about 1.5 million liters of water a year!

Every product we buy, from t-shirts, bread to electrical appliances, requires water to produce.

For example, water footprint indicators for some products:

- ✓ tea − 90 liters of water per 1 teapot;
- ✓ wheat − 650 liters of water per 500 g;
- ✓ milk − 1000 liters of water per 1 liter;
- ✓ hamburger − 2500 liters of water per 1 hamburger (150 g of beef);
- ✓ beef − 4650 liters of water per 1 chop (300 g);
- ✓ 1 kg of chocolate − 24,000 liters of water;
- ✓ 1 kg of sugar − 1500 liters of water;
- ✓ 1 cup of coffee − 140 liters of water.

The water footprint covers three components:

- ✓ blue;
- ✓ green;
- ✓ gray.

The blue water footprint includes the amount of surface and groundwater

consumed during the production of goods or services.

Green water footprint is the amount of rainwater consumed in the production process, which is especially relevant for agricultural and forestry products.

Gray water footprint is an indicator of freshwater pollution that may be associated with production. It is defined as the amount of freshwater required to absorb the load of pollutants based on current environmental quality standards.

The comparison of the planet's population by continent with the percentage of water supply is given in Fig. 1.11.

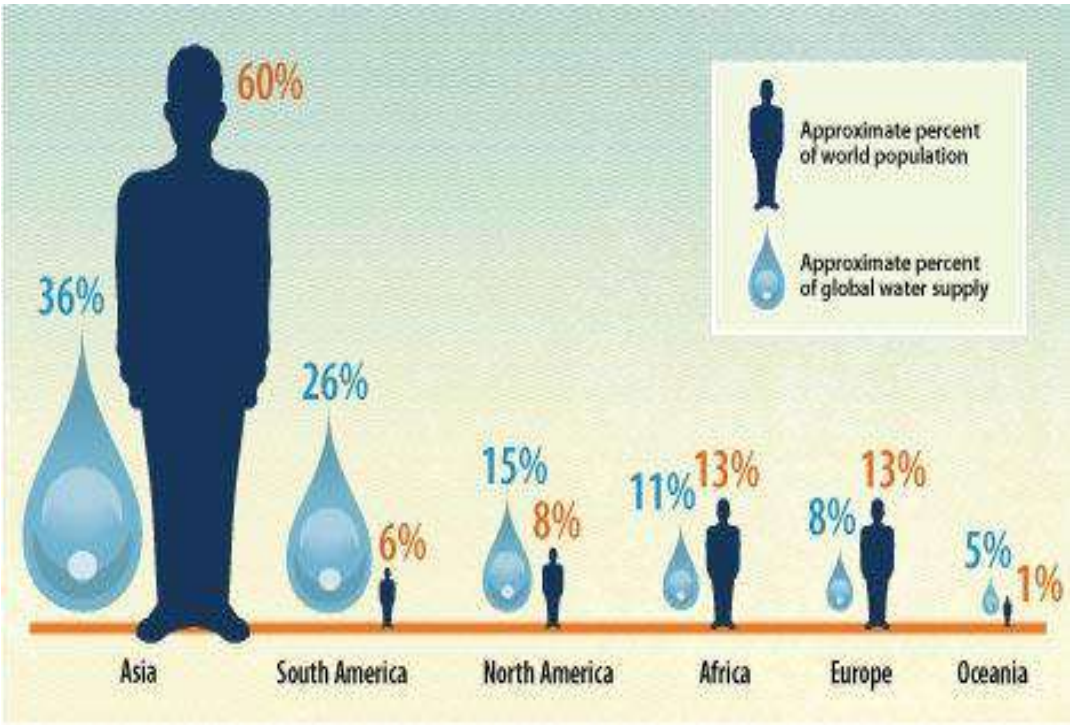


Fig. 1.11. Approximate percentage of the world's human population and approximate percentage of the world's water supply (water drop)
(http://www.climateinfo.org.ua/content/chomu-slid-dbati-pro-svii-vodnii-slid)

The following countries have the largest water footprint: USA (2.483 m^3/year); Greece (2.389 m^3/year); Malaysia (2.344 m^3/year); Italy (2.322 m^3/year); Thailand (2.223 m^3/year).

The countries that are most dependent on water imports include: Kuwait (87%); Malta (87%); The Netherlands (82%); Bahrain (80%); Belgium (80%).

The richest in renewable water resources: Brazil (8233 km^3/year); Russia (4507 km^3/year); USA (3069 km^3/year); China (2896 km^3/year); Indonesia (2838 km^3/year).

By 2025, about 2.8 billion people from 48 countries will be experiencing water

shortages, and by 2050 the number of people who are constantly experiencing water shortages will reach 7 billion.

In Ukraine, the average water footprint is 1575 m^3/year per capita, but the world average is 1240 m^3/year per capita. In terms of water, Ukraine ranks 51st among the countries of the world. Thus, Ukraine has a fairly significant water footprint, but belongs to one of the low-water countries in Europe.

Pure water is a colorless transparent liquid, the density of which is at a temperature of 4°C, Max 1,00 g/cm3. Water has an abnormally high heat capacity of 4,17 J/(g •K).

The high dipole moment of water molecules (1,82 D) and the ability to form four hydrogen bonds: two – as the donor protons and two as acceptor protons, that is not only increases the ability of the water as the solvent, but also contribute to the formation of certain structures of water associates, as well as molecules of biopolymers in aqueous solutions.

A high dielectric water constant (ε=78,5) promotes the opening of salts, acids, bases and their dissociation on ions. An ionic state of substances in the aquatic environment contributes to high speed flow of biochemical reactions.

At standard conditions about 30% of all the molecules of water are in the form of individual molecules, 70% included in the associates. 40% of them are stabilized associates with the structure that is «structured water» and 30% of them are random associates that do not have a specific structure.

Ordinary clean water is a complex dynamic system! On the state of equilibrium in the water environment influence: temperature; acoustic, magnetic and electric fields; ions H+ and OH-, which arise due to the dissociation of water; radicals, which are generated in the process of radiation exposure in the water.

To increase content of structured water may: melting ice (meltwater) with support for low temperature (below 10oC); long contact with the surface of insoluble in water minerals: apatite, calcite, quartz; shungit; silica; flint; clay and some others, which leads to the formation of spring water; dissolve in water of substances for ions or molecules which characterized positive hydration; effect of vibration and the different fields with certain characteristics: acoustic, magnetic, electric; effect of supercritical temperature and pressure.

Water with high content of «structured» water is useful for living organisms and therefore often referred to as «alive water». This water is better absorbed by organisms because without significant adjustment used for the hydration of tissues, proteins and other biological substratums.

The presence in water of various associates which have a different structure

and a different time of life, allows justifying yet another feature of water - structural-information memory. The ability to transition to different structural-information states is characteristically not only for clean water, but for water systems in living organisms.

There are positive and negative hydrations depending on the time of water molecules' life. Positive hydration characteristic for ions with a large charge and a small radius: Li^+; Na^+; Mg^{2+}; Al^{3+}; Fe^{3+}; Cr^{3+}; F^-; Cl^-; CO_3^{2-}; HCO_3^- . A lifetime of water molecules in a hydration shell is larger than the "free" water. Ions with positive hydration contribute an increase in the solution of the «structured» water. Probably, ions Na^+ and Cl^- are concentrated in the intercellular fluid. Negative hydration is characteristic for ions with a low surface density charge: K^+; Cs^+; NH_4^+; I^-; Br^-; HPO_4^{2-}; $H_2PO_4^-$; NO_3^-; ClO_3^-. These ions weakly attract water molecules and have in hydrate shell a thin dense structured layer and a big destructured layer. Probably, K^+; HPO_4^{2-}; $H_2PO_4^-$ ions are concentrated in the intracellular fluid, contributing to the increase in its destructured water.

The unique property is that the water is at the same time for all organisms are the substrate and metabolite.

The water on the way to the human body: absorb from air gases, volatile organic substances; extract organic and mineral substances from plants; dissolves the salt, minerals, organic compounds from soil; enriched by viruses, bacteria, fungi, algae and other aquatic and their metabolites; team up with metabolic water; is irradiatehaving by the electromagnetic fields; accumulate the possible information. Drinking water should have a «memory»: about diverse life that it created; about the myriad of living creatures that inhabit the surface water; about close contacts which water had with live and inert matter for natural conditions; but not about the «high-tech treatment» technology. Any chemical and/or physical-chemical treatment ("clearing") of natural water degrades its quality and moves away from the drinking water, destructured water. Drinking water has a «memory»: about diverse life that it created; about the myriad of living creatures that inhabit the surface water; about close contacts which water had with live and inert matter for natural conditions; about the «high-tech treatment» technology.

A human body 60% consists of water, of which 42% falls on the intracellular liquid, others on the intercellular fluid, which is divided into intravascular and intracellular liquid. Water is not only the environment, but also an active participant in the processes of life.

Factors such as land use, population growth, water pollution and climate change are harming on the quantitative and qualitative state of water resources almost all over the world. Climate change is a major global problem that threatens

the existence of both humanity and biodiversity on Earth. Since the beginning of the industrial revolution, the global temperature of the planet has increased by almost 1.5°C. Such slight warming is already leading to serious problems − the area of glaciers is decreasing, sea levels are rising, severe storms, tornadoes, heavy floods and droughts have become more frequent.

Among European countries, Ukraine ranks 17th in terms of water supply and 124th in the list of 181 countries in the world. On average, there is only 1 thousand m^3 of local runoff per capita in Ukraine, however, in Canada this figure is 94.3 thousand m^3, Russia − 31.0 thousand m^3, the United States − 7.4 thousand m^3, Germany − 1,9 thousand m^3.

Provision of local water resources in some areas country differs almost 60 times: from 0.14 km^3/year in the Kherson region, to 7.92 km^3/year − in the Zakarpatska region. The least supplied water resources are Donbas, Kryvyi Rih, Crimea and southern regions Ukraine, where the largest consumers of water are concentrated.

There are different scenarios about the future of water resources.Thus, according to the National Meteorological Service of Great Britain in Central and Eastern Europe, including Ukraine, the flow of rivers in the middleXXI century will decrease by 50% in summer. According to the results of the assessment of possible changes in the water resources of Ukraine in the context of global warming during the XXI century (except for river basins within the Ukrainian Carpathians and Zakarpatska) there will be a reduction in water runoff by 25−50%. According to researchers, by the middle of this century there will be a significant reduction in water resources of the plains of Ukraine (up to 70% in the southeast), and the Ukrainian Carpathians will stabilize and even increase water resources.

By 2050, the semi-arid zone will expand to the north. In the period 2031–2050, the reduction of water resources in the south of Ukraine may reach 60–70%, and in the north − at least 30–40%.

The question is to determine the critical threshold of freshwater content, crossing which the system will collapse. The volume of river water currently in use is the reason for their drying up. In general, scientists estimate that freshwater reserves are still out of risk, but humanity is rapidly approaching the risk zone.

1.5. Circulation of nutrients as a condition for the existence of the biosphere.

The last limit of the biosphere is the circulation of nutrients. The main nutrients for plants are compounds of Nitrogen and Phosphorus. However, the consequences of increasing the use of these compounds as fertilizers lead to

disruption of the circulation of elements in the aquatic ecosystems of the planet.

For example, in the Baltic Sea, the biodiversity of predatory fish, including cod, has declined significantly in recent decades due to the removal of fertilizer residues from fields that then end up in the sea. Today, the Baltic Sea is the most polluted in the world, and there are many such examples.

The process of getting Nitrogen and Phosphorus compounds into water bodies, which leads to its gradual decrease in productivity and destruction, is called **eutrophication** (Fig. 1.12). This phenomenon is accompanied by intense flowering of blue-green algae, which leads to a significant reduction in the amount of soluble oxygen in the water. The amount of phosphorus compounds in the water body is increasing.

As a result of massive and unbalanced eutrophication, most of the flora and fauna of the reservoir can be destroyed, and the ecosystem of the reservoir - dramatically and catastrophically changed.

Fig. 1.12. Eutrophication of the reservoir.

✓ By 2100 the population of the Earth will increase by 50%. This will increase the amount of wastewater that enters the reservoirs. The current rate of population growth means that by 2100 eutrophication will increase 2-4 times.

✓ Increased storms and stormwater runoff will increase nutrient losses on land and into water bodies. This will promote the growth of algae, zoo- and phytoplankton in the lakes, rivers and seas of the planet.

✓ Global warming will lead to water warming. Warm water will promote the rapid growth of algae. In addition, the melting of ice at the poles of the Earth will increase the area of water bodies, which will lead to an even greater increase in methane emissions.

The same, eutrophication, occurs in the ocean when dead zones form (Fig. 1.13). **Dead zones** are areas with low oxygen content. They are formed due to the ingress of nitrogen-phosphorus fertilizers from wastewater into the world's oceans.

Such sites already exist in several parts of the world. The eutrophication of the ocean was to be one of the causes of previous periods of mass extinction of living organisms. Today, such areas are spread over tens of thousands of square kilometers.

O_2 levels in the ocean have fallen by about 2% since the 1950s, and the amount of water completely depleted of oxygen has quadrupled since the 1960s. Sixty years ago, only 45 marine areas suffered from low oxygen levels, and in 2021 the number was over 700. About 50% of the oxygen loss in the upper ocean is the result of rising temperatures.

The combination of climate change and increased nutrient consumption will lead to a decrease in ocean oxygen levels by an average of 3% −4% by 2100. Researchers have named two main causes of deoxygenation: ocean warming from burning fossil fuels and excessive algae growth (eutrophication). Ocean deoxygenation has a wide range of implications for marine biodiversity and the day-to-day functioning of ocean ecosystems.

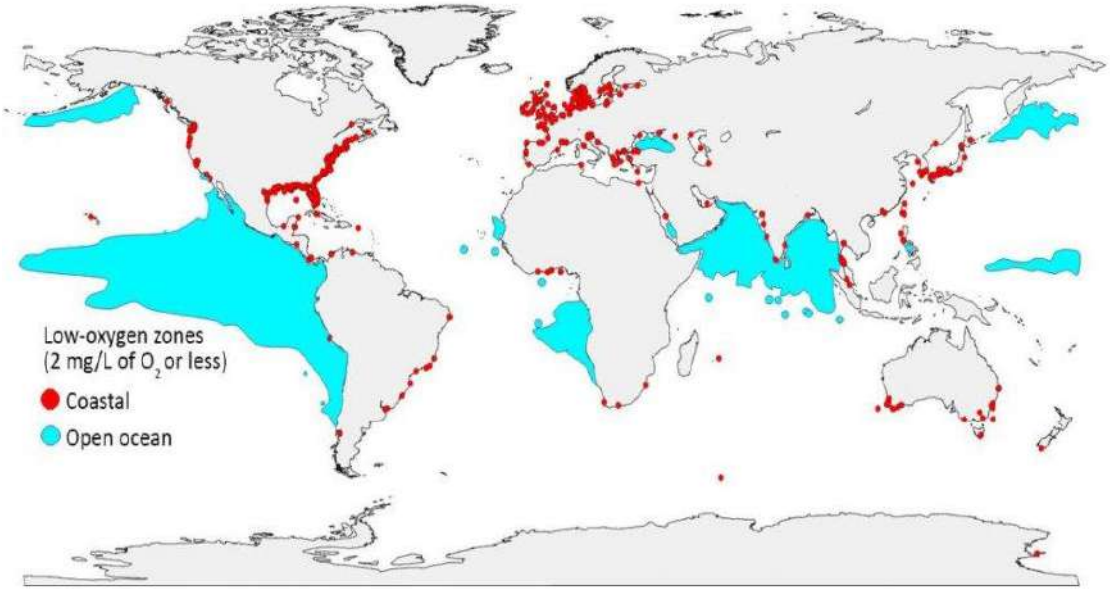


Fig. 1.13. The largest dead zones are found in the Gulfs of Mexico, Chesapeake, Black and Baltic Seas.

Declining oxygen levels in the ocean are one of the most serious environmental problems. If the temperature continues to rise, the ocean will continue to lose oxygen. So, humanity has already crossed the limit of nutrient consumption!

- ✓ Nutrients;
- ✓ Water;

- ✓ Forests;
- ✓ Biodiversity, and
- ✓ climate are the main components that supports the stability of our planet.

1.6. Acidification of the oceans.

When carbon dioxide is released into the atmosphere, about 2/3 of the amount of this gas enters the oceans. This phenomenon changes the chemical composition of the ocean, in particular the pH level. The result is a decrease in the acidity of the environment, it makes the pain sour. The chemistry of this process is as follows:

$$CO_2 + H_2O \leftrightarrow H_2CO_3.$$

During the dissolution of carbon dioxide in water, carboxylic acid is formed. In recent decades, the acidity of the world's oceans has fallen by 26%. This process continues today.

Then the acid interacts with chemical compounds, carbonate ions, reducing their concentration. This affects various living organisms, especially those that require carbonate (CO_3^{2-}) to form the skeleton. Ocean acidification, changing chemical characteristics of seawater, affects for growth, reproduction and metabolic processes of many marine organisms. Plants and animals whose shells are formed, in particular, of calcium carbonate are the most vulnerable, because lowering the pH leads to deterioration of calcification conditions. Low saturation with calcium carbonate ($CaCO_3$) it’s mineral components − aragonite and calcite − can adversely affect the rate of calcification of many marine species. A more acidic environments will harm the sea species such as mollusks, corals and some species of plankton. The shells and skeletons of these animals may become less dense or strong, and coral reefs are more vulnerable to damage by storms and slow down restoration.

Acidification can affect other physiological processes that affect, in particular, growth and survival in the early stages of life of organisms. In addition, acidification changes the behavior of living organisms. For example, it can affect the formation of shoals of fish due to their deterioration of sensory mechanisms, hearing, smell and sight.

Ocean acidification has different effects on different species. Increasing CO_2 concentrations in the ocean can have a positive effect on some species of algae and seaweed as it can increase the rate of their photosynthesis and growth. In any case, the acidification of the ocean changes food chains as a result affects ecosystems. These changes can intensify in combination with the effects of other new climate risks. So, for example, a decrease in oxygen levels in the ocean (state ocean deoxygenation) in some regions already affects marine flora and fauna. Moreover, all

these influences are amplified globally warming. Rising temperature in the ocean affects marine species and ecosystems, causes discoloration of corals and loss of space reproduction of marine fish and mammals (Fig. 1.14).

Ocean acidification affects all parts of the world's oceans, including coastal estuaries. Many economies depend on fish and shellfish. Food from the ocean is a major source of protein for people around the world.

Ocean acidification is a new global problem. According to forecasts, in the future the oceans will continue to absorb CO_2 and become more acidic. Estimates of future CO_2 levels show that by the end of the XXI century. the acidity of ocean surface waters can increase by almost 150%. This will lead to unprecedented pH levels in the oceans in 20 million years.

As the rate of ocean acidification increases, scientists, conservationists and politicians recognize the urgent need to strengthen the scientific basis for decision-making and action.

An effective policy to combat ocean acidification should encourage the rapid phasing out of fossil fuels, given its significant role in this problem.

Thus, the oxidation of the ocean, which leads to changes in the pH of the environment, can cause the mass extinction of certain species of flora and fauna, which was observed in the geological record. Therefore, increasing the amount of carbon dioxide in the atmosphere is a "game with fire" given the unpredictable future scenarios of the planet's ecosystem. While the planet is in a safe zone, in terms of ocean acidification, but risks becoming dangerous.

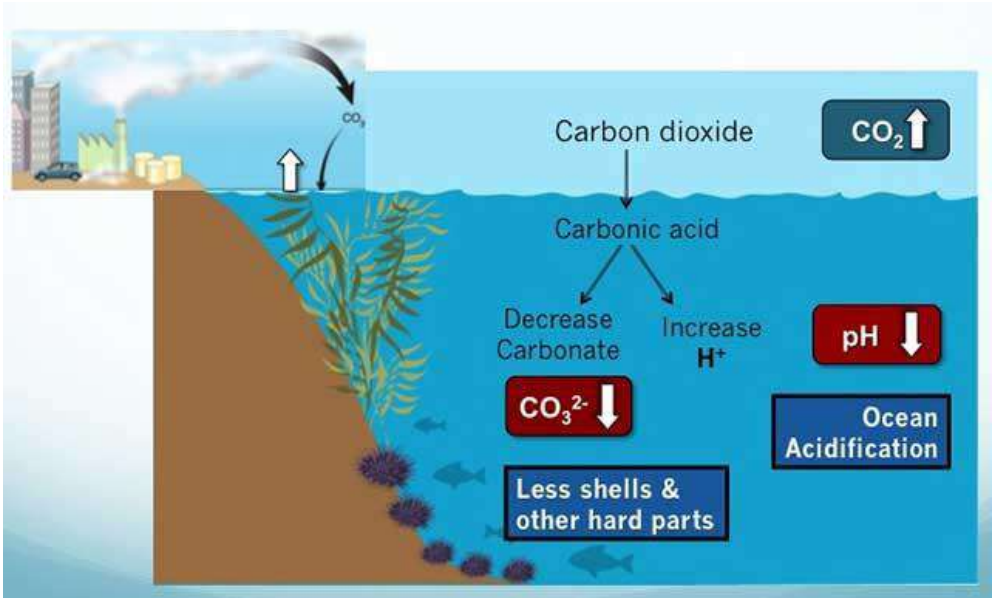


Fig. 1.14. The process of ocean acidification.

1.7. Anthropogenic pollutants and the ozone layer.

Although the Earth is a complex structure, only a few systems have been identified that support its stability.

One of them is the classification of anthropogenic pollutants. These are the so-called new compounds, which include nuclear waste, persistent organic pollutants. As well as heavy metals and microplastics. Human civilization is constantly creating new synthetic materials that can interact catastrophically with the environment. At present, it is impossible to determine the extent of these pollutants. So far, the cumulative effect of these pollutants has been little studied. However, most anthropogenic pollutants can cause global destabilization if left unchecked.

Currently, one of the forms of pollutants that globally affect the state of the biosphere is **aerosols**. These are dispersed systems consisting of fine solid or liquid particles (dispersed phase) and a dispersed gaseous medium (eg air). 75% of aerosols are formed due to the combustion of fossil fuels.

Aerosols can capture sunlight and scatter it. These particles can affect the climate, absorbing solar radiation and thus cause cooling of the planet. The cooling effect of aerosols masks 45% of the effects of global warming. Every year, about 7 million people die from air pollution. Life expectancy in large cities is reduced by an average of 3 years. However, scientists have not yet determined where the limit of air pollution passes, but it is estimated that 7 million deaths from air pollution are the limit for aerosols.

Aerosols are dust, particles of smoke and ash from fires, fuel combustion, volcanic eruptions, pollen and plant spores, and others. On average, each square centimeter of the earth's surface contains about 109 aerosol particles.

The total level of man-made air pollution reaches about 1 billion tons of aerosols and gaseous emissions, as well as 300−5000 million tons of dust. This amount is still a small part of the total mass of the atmosphere. But the intensity of pollution is growing, and the bulk of pollutants are concentrated in the lower atmosphere and concentrated in areas of accumulation of industry and transport.

Sulfur (IV) oxide is emitted mainly by thermal power plants and chemical plants. Sulfur dioxide CO2 is a colorless gas with a pungent odor. It is well soluble in water, thus forming sulfuric acid. A similar process occurs in the humid air. Sulfur(IV) oxide can oxidize in air, forming sulfuric acid according to the scheme:

$$2SO_2 + O_2 \rightarrow 2SO_3;$$

$$SO_3 + H_2O \rightarrow H_2SO_4.$$

Oxidation of SO_2 in SO_3 is facilitated by:

- oxides and salts of metals in the air in the form of dust, which play a role

catalysts;

- drops of water, fog;
- photons of solar radiation (photochemical oxidation).

Acid rain causes significant damage to the environment (Fig. 1.15).

Nitrogen oxides act similarly according to the scheme:

$$2NO + O_2 \rightarrow 2NO_2 ;$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2.$$

Precipitates that contain acids ("acid" rains) have a detrimental effect on the environment. For example, sulfur dioxide irritates the mucous membranes of the nose and eyes, causes coughing, sore throat, bronchitis. In large quantities, this gas is life threatening. It is environmentally dangerous for plants, especially fruit trees. Also, this gas can destroy works of art made of marble, cladding (marble turns into plaster). Forests suffer from "acid rain", defoliation is often carried out (artificial dropping of needles or leaves).

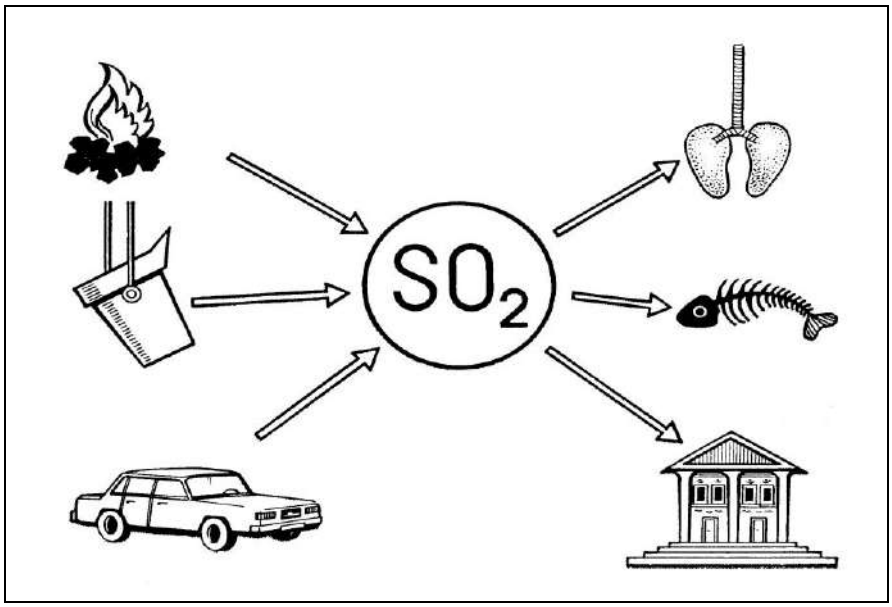


Fig. 1.15. Sources and harmful effects of sulfur dioxide on humans and the environment.

Sulfate aerosols in the stratosphere can scatter the sun's ultraviolet radiation, thus "helping" the ozone layer to absorb UV rays. This indicates the complexity of the interactions of different pollutants and the need to study the chemistry of the atmosphere in a single complex.

Nitrogen oxides can enter the atmosphere as a result of the activity of soil bacteria (mainly N_2O and NO). Human economic activity also makes a significant contribution to the emission of nitrogen oxides. In addition to participating in the formation of "acid rain", nitrogen oxides affect the formation of photochemical smog

(a word derived from the English smog − smoke and fog − dust) − complex air pollution due to the concentration of air masses in large cities.

Car internal combustion engines are a major source of pollution. In addition to nitrogen oxides NO_x and ozone, in the photochemical smog there are:

• carbon(II) oxide CO (product of incomplete combustion of gasoline fuel);

• C_xH_y hydrocarbons;

• aldehydes and more complex organic compounds.

All this "bouquet" in wet weather is in the air of big cities. This phenomenon was often observed in London, Los Angeles, Buenos Aires, Sao Paulo, Rio de Janeiro, Mexico City, Ankara, Tokyo, Moscow, St. Petersburg, and in Ukraine - in the cities of Dnieper and Donbas (Zaporizhzhia , Dnieper, etc.). Photochemical smog is now more common. Unlike conventional smog, which is formed in low clouds and high humidity in cold weather, photochemicals are formed on clear, sunny days. They occur in a polluted atmosphere under the influence of solar radiation. This creates new substances that are more toxic than those that enter the atmosphere. This smog dramatically reduces the transparency of the air, irritating of the mucous membranes, nose and mouth, exacerbation of lung and allergic diseases. Vegetable and ornamental plants wither quickly. Smog causes corrosion of metals, cracking of paints, rubber products, damage to clothing, etc.

Atmospheric carbon(II) oxide is formed mainly (70%) naturally, mainly during incomplete oxidation of methane:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O.$$

CO is also formed during the incomplete combustion of gasoline. A car emits up to 3 m^3 of carbon monoxide per hour, and a truck emits up to 6 m^3. The annual share of CO emissions from incomplete combustion of fuel, vehicles, thermal power plants is an additional 20-30%. But the concentration of carbon(II) oxide in the atmosphere increases slowly. This is because in nature there are processes that lead to the absorption of the latter. Binding of CO in the biosphere is carried out in the following ways:

• oxidation to CO_2 (partially and very slowly);

• absorption by soil organisms;

• dissolution in ocean waters;

• diffusion into the stratosphere and interaction there with more reactive molecules and atoms according to the scheme:

$$HO\cdot + CO \rightarrow CO_2 + H\cdot;$$

$$HOO\cdot + CO \rightarrow CO_2 + HO\cdot.$$

Carbon monoxide has a very harmful property for humans: it can specifically bind to hemoglobin Hb blood − a protein − a carrier of oxygen in the body, forming a

stable complex of carboxyhemoglobin HbCO. Carbon monoxide molecules compete with oxygen molecules for the right to bind to blood hemoglobin and are 210 times superior to oxygen!

The molecules of CO and O_2 are very similar in electronic structure, but CO has a greater than O_2 chemical affinity for the Fe^{2+} ion in hemoglobin.

Almost a small amount of CO can remove most of the hemoglobin from the blood, and the body receives less oxygen. For example, a person who inhales air with a CO content of only 0.1% for several hours absorbs it so much that most of the hemoglobin (60%) binds to the COHb complex (the same reduces the normal function of blood with O_2 transfer). This process is accompanied by tinnitus, dizziness, loss of consciousness. Smokers are subject to a similar action of CO. There is a direct relationship between smoking and the level of carboxyhemoglobin in the blood. The high content of CO in the atmosphere of megacities contributes to the growth of cardiovascular disease, because the heart is forced to distill in a more "hard" rhythm poisoned by carboxyhemoglobin blood.

Atmospheric pollutants also include solid suspended particles. The main sources of their entry into the atmosphere are metallurgical plants, construction industry, transport and others. The problem of these pollutants is extremely relevant. They can be allergic, carcinogenic (asbestos), cause respiratory diseases.

Due to air pollution, large industrial cities receive 15% less sunlight and 10% more precipitation in the form of rain, hail and snow.

There was a significant (by 25−30%) reduction in the yield of most crops by 2−3 km around the source of pollution. Some plant species respond to even small concentrations of pollutants. For example, conifers, walnuts, tobacco, clover are very sensitive to sulfur dioxide, and onions, strawberries, spruce and pine - to fluoride. Cases of mass death of cattle and poultry during smog have been noted. Bees are very sensitive to air pollution.

For a long time, the only way to solve air pollution problems was the ability of the atmosphere to self-clean. Mechanical particles and gases dispersed in the air, fell to the ground with rain and snow, and were neutralized by interacting with natural substances. However, the ability of the atmosphere to self-clean. The magnitude and speed of industrial, transport and domestic emissions far outweigh the natural possibilities for self-organization. Therefore, the processing of industrial waste, the installation of gas and dust treatment plants at all existing enterprises, the transition to waste-free technological processes, the improvement of internal combustion engines in cars and others are important.

One of the important measures to be taken for air purification is landscaping. The composition of harmful substances should be taken into account, because

different plants purify the air differently. Where the air is polluted with smoke, it is best to plant white acacia, mulberry, Canadian poplar, and where dust - elm. Horse chestnut cleans the air very well from vehicle emissions, and Karelian birch, sharp-leaved maple, weeping willow, etc. from gasoline and gas.

It is necessary to control the concentration of harmful substances in the air at the level of maximum permissible levels, ie those indicators at which these substances do not show toxic effects.

Atmospheric pollution is a global phenomenon. The atmosphere knows no borders and therefore requires the mobilization of people around the world to protect it from pollution.

Solar radiation, especially its short-wave ultraviolet part, is one of the strongest factors in the environment that determine the conditions for the development and existence of all living things on Earth. It is known that the biological activity of radiation is greater the shorter the wavelength. Therefore, UV radiation quanta have a particularly high radiological activity. Almost a small amount of radiation is enough to quickly destroy all living things on the earth's surface, but the atmosphere does not reliably protect the biosphere from UV radiation (Fig. 1.16).

The question of the ozone screen, predicting its depletion and the consequences of this process affects the stability of the Earth's ecosystem and, above all, all living things on Earth.

Ozone − translated from Greek fragrant. It is a gas whose molecule contains three atoms of Oxygen − O_3 (one of the forms of existence of Oxygen in the free state). Its smell can be felt after a thunderstorm, because in the lower atmosphere it is formed during lightning discharges, and in the stratosphere it is formed under the action of the Sun.

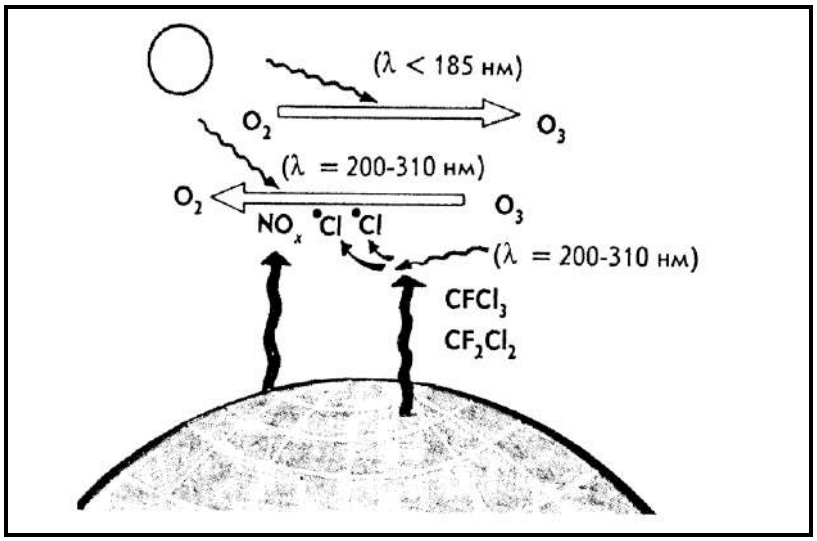


Fig. 1.16. Scheme of influence of fluorochlorocarbons and nitrogen oxides on the ozone layer.

Ozone in the atmosphere is very small - millionths of a percent. The largest amount of this gas at an altitude of 20−25 km − 0.001%. At this altitude, ozone forms a shell, which is called the ozone "screen" of the Earth. The thickness of this layer is only a few millimeters. In small quantities, ozone is very useful for living organisms. People experience a noticeable improvement in well-being when breathing "ozone" air after a thunderstorm. But when the amount of ozone increases significantly, there is an increase in human morbidity. A small decrease in the thickness of the ozone layer increases the likelihood of skin cancer. Reducing this layer twice would have disastrous consequences for the earth's funds.

The ozone problem consists of the following aspects.

1) This layer protects our planet from the harmful effects of ultraviolet radiation from the Sun. Small doses of such radiation are useful because they promote the formation in the human body of vitamins "D", which increase the body's resistance (immunity). However, significant doses of this radiation can kill living organisms, especially humans.

The ozone layer in the lower stratosphere absorbs significant amounts of the sun's ultraviolet radiation.

2) In recent decades, a zone with very low ozone concentrations over Antarctica has emerged and is expanding rapidly. This area was called the "ozone hole". There are many reasons for the depletion of the ozone layer. For example, nitrogen oxides pose a significant risk to the ozone layer. In the Northern Hemisphere, the amount of ozone decreased by 3–6%. After the major powers of the world agreed to end nuclear tests, this danger disappeared.

Ozone is also lost during the launch of artificial satellites of the Earth, because it forms a hole for several kilometers, which disappears very slowly.

Chlorine and its compounds are involved in the process of ozone depletion. Chlorine compounds, the sources of which are chemical plants, as well as the operation of household appliances, rise to the heights of the ozone layer. Freons (polyhydric chloro-, bromoorganic compounds such as: methylchloroform − CH_3Cl_3, Freons-11 ($CFCl_3$), −12 (CF_2Cl_2), methyl bromide (CH_3Br), gallons − 1301 (CF_3Br) and 1211 (CF_2ClBr) are widely used The latter are released into the atmosphere as sprays, solvents, refrigerants in refrigerators and air conditioners, and organically brominated substances are widely used for firefighting, military, and agricultural purposes, and have been banned since 1995, but are currently banned. no effective replacement was found.

In the lower atmosphere, chloro- and bromo-organic compounds remain inert. But under the action of solar radiation in the stratosphere, freons decompose and destroy ozone when they interact with ozone. The chemistry of ozone depletion in

catalytic cycles is as follows:

$$O + XO \rightarrow X + O_2;$$
$$O_3 + X \rightarrow XO + O_2.$$

$$O + O_3 \rightarrow 2O_2,$$

where X – catalyst (–OH, NO_x, Cl, Br, Me etc.).

The most common CFCs have a long "relaxation time" (the time of their "life" in the stratosphere, which is defined as the average time from entry into the atmosphere or the formation of a molecule to its photochemical destruction). For example, for CFCs-11, -12 it is 60 and 120 years, respectively. Thus, freons-11 and -12 almost after the cessation of their production and use will be present in the atmosphere for many decades. As for bromine atoms, their ozone-depleting properties are 10 times greater than chlorine atoms. In addition, if chlorine depletes ozone at an altitude of about 40 km, where its amount is relatively small, the maximum effect of bromine on ozone falls on the layer of 14-22 km, which is close to the ozone maximum. Scientists have determined that each chlorine atom destroys almost 100,000 ozone molecules.

As already noted, nitrogen oxides can also destroy ozone molecules. One of the sources of supply of nitrogen oxides to the atmosphere is agro-industrial production. In soils treated with nitrate fertilizers, anaerobic bacteria reduce nitrate ions to molecular nitrogen and nitrogen(I) oxide N_2O.

Cultivated soils seem to "breathe" this oxide, which enters the stratosphere and interacts with oxygen atoms according to the scheme:

$$N_2O + O \rightarrow 2NO.$$

It is known that nitrogen(II) oxide is a catalyst for the destruction of ozone molecules.

Thus, in a few decades, ozone has evolved from a little-known component of atmospheric air into gas, which has one of the main roles in ensuring life on Earth.

Among the chemical measures to restore the ozone layer, scientists suggest the following:

• increasing the photochemical source of ozone by excitation of molecular oxygen and the rate of its photolysis by laser radiation in the lower stratosphere;

• destruction of fluoro-, chlorocarbon molecules in the upper layers of the stratosphere during a gas discharge that occurs at the intersection of several strong microwave rays;

• reduction of the use of fluoro-, chlorocarbons and search for environmentally friendly substitutes.

Scientists who have studied the ozone layer have found that the amount of

ozone decreases by about 1% over a decade. But as early as 1985, there were unexpected reports of ozone depletion over Antarctica almost halving in seven years. This phenomenon has been studied by scientists from all countries exploring Antarctica. The greatest losses of ozone are observed at an altitude of 16.5 km, where it remains 3% of the normal amount.

Scientists around the world are trying to draw the attention of governments and industrialists to the protection of the ozone layer. They have proven not only the harmfulness of CFCs for the ozone layer, but also the use of solid fuels in rockets, and are seeking a ban on some ozone-depleting chemical technologies. In addition, there is an urgent need to reduce the use of nitrogen fertilizers and take measures to introduce more environmentally friendly tillage methods.

1.8. The limits of sustainability of the planet1 and zero Carbon emission target.

It is unbelievable that the warning of scientists could turn into political action. This is an example of the fact that humanity can still control the processes on the planet.

So, our planet has several boundaries, beyond which there are certain global environmental risks. There are problems −

- ozone layer;
- freshwater;
- ocean acidification;
- aerosol air pollution;
- climate;
- forests;
- nutrient intake;
- conservation of biodiversity.

So far, humanity is in a safe zone against the problems of the ozone layer, the acidification of the ocean and freshwater. The risks to air polluted by the new compounds are still unknown. However, humanity has already crossed dangerous zones of environmental risk in terms of climate, forests, nutrient supply and biodiversity conservation.

Currently, scientists have defined a clear structure of planetary boundaries. There is strong evidence that humanity is at risk of climate change and biodiversity loss. There is a frequency of droughts, the number of fires on many continents, the negative impact on the Amazon rainforest, the acceleration of melting glaciers, the

catastrophic state of coral reefs.

Corals are a kind of indicator of the state of the environment, they discolor when the water becomes too warm (Fig. 1.17). So, the Great Barrier Reef − the world's largest network of coral reefs is located off the coast of Australia. However, its area is rapidly declining: over the past three decades, the ecosystem has lost much of its coral. The reef is affected by several factors: tropical hurricanes; starfish that feed on polyps; rising water temperatures and ocean pollution. All this leads to discoloration of the corals, which is a sign that the colony is left by microscopic algae that live in their tissues. Such coral becomes vulnerable and soon dies (Fig. 1.18).

Under conditions of global warming there is a mass extinction of corals. The effects of discoloration are 10 times greater than those of a large-scale tropical cyclone of the fifth category.

Fig. 1.17. The Great Barrier Reef is the largest reef system in the world.

The reef system has already experienced several mass extinctions of coral, and in addition, it has adapted to changes in ocean levels. In particular, during ice ages, ocean levels and temperatures are at minimum levels (about 118 meters lower than now), and at this time the reef "crawled" to the outer limit of the shelf. But with the departure of ice and rising temperatures, corals began to move in the opposite direction, capturing areas that became comfortable for them. The fact is that rising ocean levels lead to an increase in the rate of formation of carbonate deposits, which degrades water quality, but the reef has learned to respond quickly to new conditions.

However, recent changes in global temperature significantly reduce the time intervals between mass extinctions of corals, which creates a risk of their

reproduction.

However, recent changes in global temperature significantly reduce the time intervals between mass extinctions of corals, which creates the danger of their reproduction. Today, half of the coral reef is dead. According to scientists, due to climate change and environmental pollution, 70−90% of coral reefs will disappear within the next 20 years, and completely coral reefs will disappear by 2100.

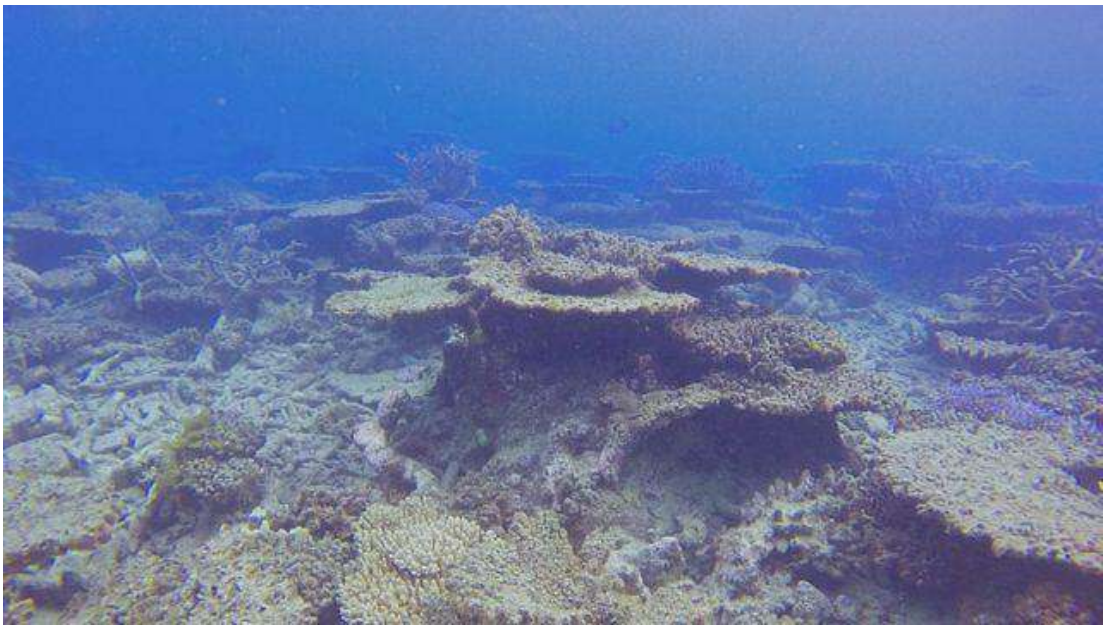


Fig. 1.18. Coral discoloration is caused by an increase in water temperature.

Today, the Great Barrier Reef is almost completely discolored and will become a coral graveyard soon. Mankind has crossed the critical precision of coral discoloration.

Thus, scientists are struggling to determine the effects of global warming over the next thirty years.

In 2020, Australia had a hell of a summer. Due to the record high temperature and months of drought, 20 million hectares of land were burned. Scientists estimate that 3 billion animals died or were displaced by the fires: 1.43 million mammals; 2.46 billion reptiles; 187 million birds; 51 million frogs. These are huge numbers that show the enormous consequences for the planet's ecosystem.

In 2021, abnormal heat was recorded in Canada and the Northwestern United States. The air temperature in the Canadian province of British Columbia reached a record 49.5°C, and in the States this year's heat has already been called "historic" (Fig. 1.19). Meteorologists have linked the extreme heat in Canada and the United States to the "thermal dome" effect due to high atmospheric pressure.

About 500 sudden deaths have been linked to abnormal heat in Canada, where temperatures in some regions have reached 49.5 ° C. However, the record

temperature for the country affected the animals. Scientists estimate that the heat in Canada has killed about a billion marine animals, including a huge number of mussels, mollusks and starfish.

On the coast, scientists have recorded temperatures above 50°C. Because of this, much marine life had no chance of surviving, they just boiled. Empty shells of animals covered the shore. Mass deaths of fish, oysters and other representatives of flora and fauna affected by abnormal heat have been recorded.

Such anomalies lead to significant changes in the ecosystem, because the same mussels and mollusks filter the water in the sea and, thanks to their work, other species of animals have a chance to live. And if mussels can rebuild their population in a few years, other marine life will need much more time.

Fig. 1.19. In 2021, abnormal heat was recorded in Canada.

In 2021, catastrophic floods killed 160 people in Germany, while more than 50 people died after floods swept through the Chinese province of Henan. At the same time, forest fires engulfed one of the coolest places in the world − Siberia.

Every year, factories, power plants and vehicles pump tens of billions of tons of carbon dioxide into the atmosphere, which absorbs solar radiation, which will further raise the global temperature.

Even if all greenhouse gas emissions are reduced to zero tomorrow, the carbon dioxide already in the atmosphere will remain there for decades and continue to heat the planet, drying out vegetation and allowing air to retain more moisture and then emit precipitation with sudden devastating effects.

Human society fears that this may become a new norm, but scientists predict

that the concept of the norm will not be.

It is very doubtful that humanity will quickly destroy its dependence on fossil fuels. At best, this goal can be achieved by 2050, a date set by world leaders to achieve zero greenhouse gas emissions.

In other words, the planet will experience harsher and more destructive weather events over the next 30 years. Floods, fires and storms, along with melting glaciers, rising sea levels, the disappearance of coral reefs and the spread of deserts, may be the norm. And this is the best that can be hoped for over the next three decades.

The problem, scientists say, is that to stop the deterioration of weather conditions by 2050, the rise in global temperature should be limited to about 1.5°C according to pre-industrial levels. However, the world has already warmed to 1.2°C, thanks to greenhouse gases emitted into the atmosphere, and the prospect of limiting further temperature rises over the next 30 years looks remote. Estimates based on countries' current promises to reduce emissions suggest that temperatures are likely to rise more than 2°C above pre-industrial levels by the middle of the century.

In such a future, most of the planet is likely to suffer from drought; tropical forests are at risk of extinction, and melting ice sheets will lead to dangerous sea levels and major changes in the behavior of ocean currents such as the Gulf Stream. In addition, the loss of ice cover will cause the oceans to absorb more solar radiation, while the melting of permafrost will lead to increased methane emissions. The inevitable temperature will rise even more.

This disappointing prospect is because politicians and business leaders for decades have failed to assess the risks associated with the massive impact of human activities on the planet, and have not begun to act in time to limit harm. As a result, the world may face a climate catastrophe, and there is little time left to resist the threat.

The prospects look very problematic. As demonstrated in the Naples talks, when the G20 energy and environment ministers, who together account for 85% of annual emissions, failed to agree on a full package of commitments to combat climate change.

In addition, rich and developing countries cannot agree on cost-sharing to combat global warming. This was one of the problems of the international climate negotiations on the eve of the Paris Agreement of 2015, which obliged the world to keep global warming below 1.5°C, but rich countries have not fulfilled these commitments.

Mankind has crossed the line of climate, causing droughts, fires, coral discoloration and other consequences. The decline of Nature was the main reason for

the large-scale destabilization of the planet, namely the COVID-19 pandemic. It has affected the lives of all mankind. Many were surprised that the WHO warned of this situation in advance. Indeed, human society continues to destroy nature, conducts very aggressive arable production, destroys large-scale forests. Added to this is the fact that most people live in highly polluted cities with a high population density. All these factors became the basis for the ideal scenario of the spread of a new virus.

New viruses emerge and spread among humans as nature's resilience declines. Transmission of diseases occurs only in certain species and under certain conditions, when humanity aggressively interferes with their habitat. As a result, human, animal health and environmental state are closely linked.

The COVID-19 pandemic, which has affected the entire world economy, has caused humanity to think about the future scenarios of society. The emergence of the COVID-19 virus was a warning that the planet's ecosystem is in danger, but humanity has also been able to change the vector of development towards a stable future.

Today, it is no longer a question of reducing economic growth along with reducing anthropogenic pressure. Mankind must build a new planetary model of development for its stability.

First of all, it is necessary to achieve zero carbon emissions and achieve the lowest possible stable temperature in the world. Of the energy used by mankind today, 34% of the world's energy comes from burning oil, 27% from coal, and 24% from natural gas. Nuclear energy, as well as hydroelectric power and other renewable sources, together now account for only 15%. The result of burning fossil fuels is the current industrial economy, and for the planet as a whole it is 9.5 billion tons of carbon annually, which is released from the ground into the atmosphere.

After the beginning of the industrial revolution, carbon dioxide emissions amounted to 2.400 billion tons. In order not to exceed the threshold of 1.5oC, we must emit 300 billion tons less. If humanity continues to emit 40 billion tons of CO_2 per year, it will reach a critical level in 7 years!

Currently, the Carbon cycle is unbalanced. In fig. 1.20 the schemes of Carbon flows in gigatons in the pre-industrial period, Holocene (A) are given. On the left is the biosphere; in the center − the atmosphere; on the right − the ocean; below − the geosphere.

Figure (B) shows the period of the early Anthropocene, modernity. 325 gigatons of carbon were taken from the geosphere, 240 of which were in the atmosphere. We can see how the exchange between the atmosphere and the oceans and the biosphere has increased accordingly.

The lower (C) figure shows the late Anthropocene, the desired "almost zero"

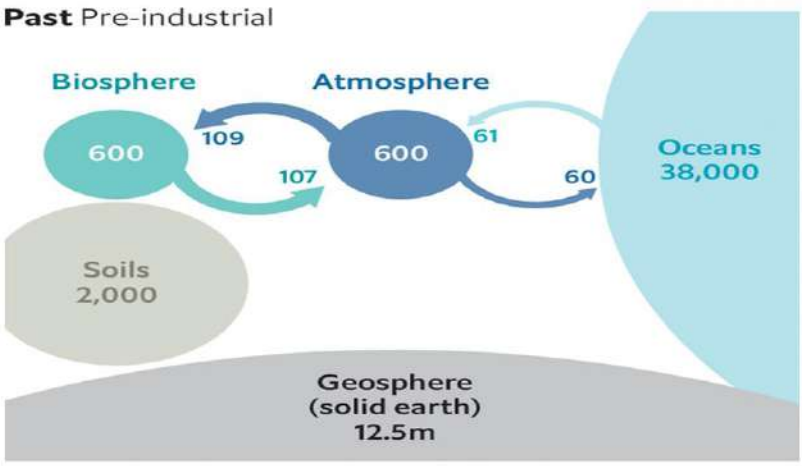
future. In particular, the means of "negative emissions" (ie, carbon sequestration due to anthropogenic activities):

- increased weathering (carbon binding in minerals);
- reproduction of forests;
- soil improvement.

However, all figures for the future model (Figure C) are unknown.

The current intensification of the Carbon cycle has side effects. Plants grow better. Thus, according to scientists, the level of photosynthesis on the planet is 3-7% higher than it was 30 years ago. Satellite images show that the Earth is turning green. This "carbon fertilizer" has improved the yields of some crops, as well as the growth of some forests and other ecosystems. This is not enough to compensate for the damage caused by climate change due to rising temperatures and changing rainy cycles.

However, increasing the amount of soluble carbon dioxide for the oceans means more acid. Even if fossil fuels do not heat the planet, the oxidation of the ocean is a change on a planetary scale.



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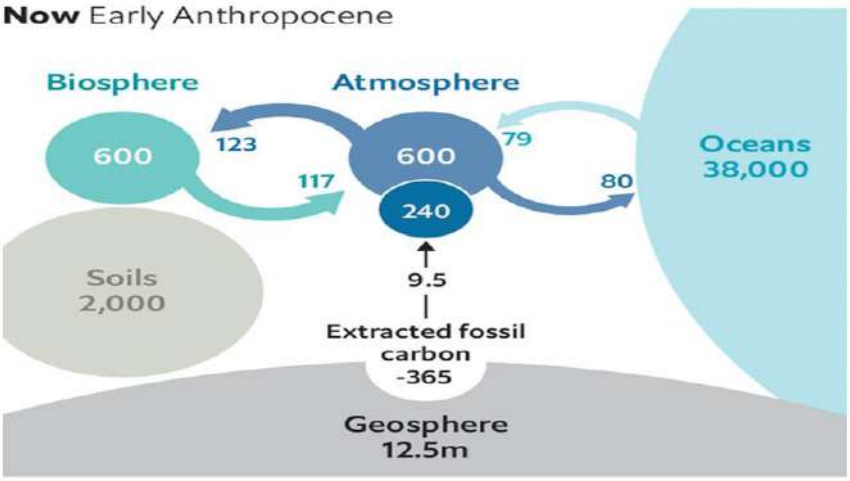

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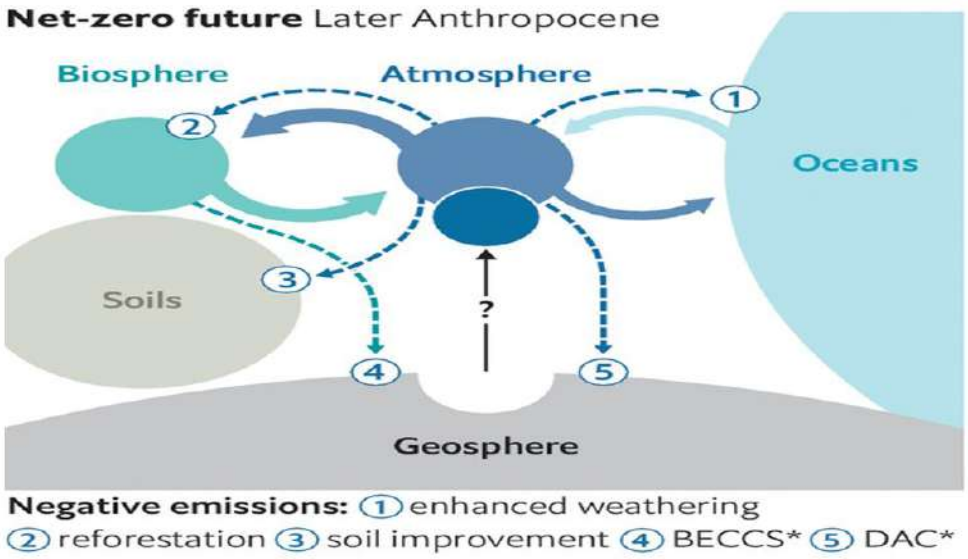


C

Fig. 1.20. Schemes of Carbon flows in gigatons in the pre-industrial period, in the early Anthropocene and late Anthropocene.

(https://inlnk.ru/577ZBx)

The 2015 Paris Agreement aims to halt rising levels of carbon dioxide in the atmosphere by burning fossil fuels by the middle of the 21st century.

However, the planet is undergoing erosion, during which silicates are bound to the surface, which binds carbon dioxide, eventually forming solid minerals, from which carbon is not released as easily as from coal or oil. Such "chemical weathering" is much slower than the ocean and biosphere uptake. According to geochemists, it will take a thousand years just to bring the level of carbon dioxide, which will occur after the end of the fossil fuel era, to the level of the mid-20th century.

Today, humanity is facing the problem of developing technologies for "negative emissions", ie the absorption of carbon, which will reduce CO_2 emissions.

Such forms of "negative emissions" exist. This is the cultivation of agricultural plants; reforestation and planting new ones; growing plants for combustion and electricity − while chemically binding CO_2 and accumulating it underground.

This approach is called "carbon capture and storage bioenergy" (BECCS). Next, there is the idea of capturing CO_2 from the atmosphere using chemical engineering, "direct capture from the air" (DAC).

So, if by 2060 the world refuses to use 90% of fossils compared to the current level, to balance the remaining 10% it is necessary to absorb about a billion tons of carbon per year. So far, Carbon absorption systems of this magnitude are barely able to absorb only one-thousandth of this amount. Ensuring the necessary absorption by

photosynthesis will require additional forest cover of large areas.

Mankind can avoid raising the global temperature by $2^{o}C$, even by $1.5^{o}C$, although this possibility is incredible and requires the efforts of all countries.

What is the greatest level of emission reductions that humanity can achieve?

Scientists have proved that if it is 6−7% per year, it will be reduced by 2 times in a decade. Reducing emissions 2 times every 10 years is an exponential rate of change. If everyone on our planet maintains this rate of emission reduction, we can give up fossil fuels in one generation (about 30 years).

The abandonment of fossil fuels could return humanity to a safe zone for climate change. This will significantly reduce air pollution, ocean acidification, and reduce the pressure on biodiversity. However, zero-emissions are not enough. Mankind must reduce the level of Carbon, which is already overheating the planet.

There is a way to reduce Carbon − the preservation of forests, greenery and their increase. In Scotland, for example, 22 million seedlings have been planted a year to adapt to climate change. Local forests annually extract almost 9.5 million tons of carbon dioxide from the atmosphere.

Studies show that planting additional trees to adapt to climate change in Europe can increase rainfall. According to the BBC, the conversion of agricultural land to the forest will increase the number of summer rains by an average of 7.6%. Scientists argue that additional rains may partially offset the increase in drought expected due to climate change. Conclusions on the increase in precipitation are partly based on observations of existing models. However, the main reasons are less clear - they are probably related to how forests interact with cloudy air.

Planting trees has become one of the main focuses of many countries' efforts to adapt to climate change around the world (Fig. 1.21).

Thus, in the UK by 2025 it is planned to plant about 30 million new trees annually.

Researchers have found that if forests increased by 20% evenly across Europe, it would lead to an increase in local rainfall, especially in winter and with a large impact that would be felt in coastal regions. In addition to local rains, planting new forests affects the leeward side. Scientists have found that rainfall in these places has increased, especially in the summer months. Combining these two effects, it was found that the total amount of precipitation in the summer increased by 7.6%.

The global initiative to plant a billion trees could be the most powerful way to address the climate crisis. In addition, increasing the number of trees can reduce the amount of carbon dioxide in the atmosphere.

Forests help reduce soil erosion, increase rainfall and therefore can guarantee

the sustainable development of the biosphere. Deforestation will not only have a positive impact on the planet's biodiversity, but will also help stabilize the planet's climate and freshwater levels, as well as benefit food and other resources.

Fig. 1.21. Planting trees has become one of the main focuses of many countries' efforts to adapt to climate change around the world.

Another very simple transformation will help humanity stay within planetary boundaries. This is a change in diet, namely, a reduction in the consumption of red meat, more vegetable protein, fruits, nuts, less food containing starch. If you follow this diet, you can also approach a safe zone not only for climate but also for biodiversity, nitrogen and phosphorus levels. Interestingly, a healthy diet can be the most effective way to adapt to climate change.

The next important transformation that will help return the panel to a security environmental zone is zero waste.

The next important transformation that will help return the panel to a safe ecological zone is zero waste. Therefore, a closed-loop economy (circular green economy) is fundamental to the sustainable development of the planet's ecosystem.

Circular (green) economy is based on the restoration and rational consumption of resources, an alternative to a traditional, linear, economy. It is characterized by the creation of new alternative economic approaches, the task of which is to minimize the negative human impact on the environment. The closed-loop economy is designed to change the classic linear model of production, focusing on products and services that minimize waste and other types of pollution. The basic principles of the closed-loop economy are based on the recovery of resources, recycling, the transition

from fossil fuels to the use of renewable energy sources. This type of economy is seen as part of the Fourth Industrial Revolution, which will increase the overall rational use of resources, including natural resources, the economy will be more transparent, predictable, and its development systemic.

Waste minimization, as well as their complete elimination, will allow humanity to achieve a secure environmental zone, reduce the pressure on biodiversity and reduce nutrient consumption.

Planetary boundaries, in other words environmental risks, have identified ways to restore and conserve biodiversity. Things like using renewable energy, eating healthy food, planting trees, disposing of waste can change the future of the Earth. Such transformations will already help to improve the environmental situation, both locally and globally. Returning to the planetary borders will be a guarantee of sustainable development of society in all its forms, especially environmental, as well as economic and social. This will reduce the risks of conflict and instability in the regions.

What will humanity do in the next 10 years? Given the current environmental challenges, this will be a crucial decade for the future of human society. Thus, the future of the planet for the next century depends on the choice of direction for the current 10 years. The issue of planned borders must become a priority at the highest level in the world, developed by the UN Security Council.

Today, human society dominates the planet, which has not been observed for 4.5 billion years. Scientists have learned to observe planned processes, to determine their ecological status. The digitalization and hyperconnectivity of world science determine the complex knowledge of the planet. Today there is a new geological epoch, which is determined not only by the physical content, but also by the creation of a new consciousness, which will be built into the future vector of development of the planet.

Conclusions

So, our planet has several boundaries, beyond which there are certain global environmental risks. These are the problems of the ozone layer; freshwater; ocean acidification; air pollution by aerosols; climate; reduction of forest area; nutrient

intake; biodiversity conservation.

So far, humanity is in a safe zone against the problems of the ozone layer, the acidification of the ocean and freshwater. The risks to air polluted by the new compounds are still unknown. However, humanity has already crossed dangerous zones of environmental risk in terms of climate, forests, nutrient supply and biodiversity conservation.

Currently, scientists have defined a clear structure of planetary boundaries. There is strong evidence that humanity is at risk of climate change and biodiversity loss. There is a frequency of droughts, the number of fires on many continents, the negative impact on tropical forests, the acceleration of melting glaciers, the catastrophic state of coral reefs.

Under conditions of global warming there is a mass extinction of corals. The effects of discoloration are 10 times greater than those of a large-scale tropical cyclone of the fifth category.

The planet will experience harsher and more devastating weather events over the next 30 years. Floods, fires and storms, along with melting glaciers, rising sea levels, the disappearance of coral reefs and the spread of deserts, may be the norm.

To stop the deterioration of weather conditions by 2050, the increase in global temperature should be limited to about 1.5°C according to the pre-industrial level. However, the planet has already warmed up to 1.2°C, thanks to greenhouse gases.

Estimates based on countries' current promises to reduce emissions suggest that temperatures are likely to rise more than 2°C above pre-industrial levels by the middle of the century.

In such a future, most of the planet is likely to suffer from drought; tropical forests are at risk of extinction, and melting ice sheets will lead to dangerous sea levels and major changes in the behavior of ocean currents such as the Gulf Stream. In addition, the loss of ice cover will cause the oceans to absorb more solar radiation, while the melting of permafrost will lead to increased methane emissions. The inevitable temperature will rise even more.

Mankind's primary goal is to achieve zero carbon emissions. Of the energy used by mankind today, 34% of the world's energy comes from burning oil, 27% from coal, and 24% from natural gas. Nuclear energy, as well as hydroelectric power and other renewable sources, together now account for only 15%. The result of burning fossil fuels is the current industrial economy, and for the planet as a whole it is 9.5 billion tons of carbon annually, which is released from the ground into the atmosphere.

After the beginning of the industrial revolution, carbon dioxide emissions

amounted to 2,400 billion tons. In order not to exceed the threshold of 1.5°C, we must emit 300 billion tons less. If humanity continues to emit 40 billion tons of CO_2 per year, it will reach a critical level in 7 years! Currently, the Carbon cycle is unbalanced.

If by 2060 the world abandons the use of 90% of fossils compared to the current level, to balance the remaining 10% it is necessary to absorb about a billion tons of carbon per year. So far, carbon absorption systems of this magnitude are barely able to absorb only one-thousandth of this amount. Ensuring the necessary absorption by photosynthesis will require additional forest cover of large areas.

Mankind can avoid a global temperature increase of 2oC, even 1.5oC, although this possibility is incredible and requires the efforts of all countries.

Abandonment of fossil fuels could return humanity to a safe zone for climate change. This will significantly reduce air pollution, ocean acidification, and reduce the pressure on biodiversity.

There is a way to reduce Carbon - the preservation of forests, greenery and their increase. Planting additional trees to adapt to climate change in Europe can increase rainfall.

It is estimated that if forests increased by 20% evenly across Europe, this would lead to an increase in local rainfall, especially in winter and with a large impact felt in coastal regions. In addition to local rains, planting new forests affects the leeward side. Scientists have found that rainfall in these places has increased, especially in the summer months. Combining these two effects together, it was found that the total amount of precipitation in the summer increased by 7.6%.

A global initiative to plant a billion trees could be the most powerful way to address the climate crisis. In addition, increasing the number of trees can reduce the amount of carbon dioxide in the atmosphere.

Another very simple transformation will help humanity stay within planetary boundaries. This is a change in diet, namely, a reduction in the consumption of red meat, more vegetable protein, fruits, nuts, less food containing starch. If you follow this diet, you can also approach a safe zone not only for climate but also for biodiversity, nitrogen and phosphorus levels. Interestingly, a healthy diet can be the most effective way to adapt to climate change.

The next important transformation that will help return the panel to a safe ecological zone is zero waste. Therefore, a closed-loop economy (circular green economy) is fundamental to the sustainable development of the planet's ecosystem.

The basic principles of the closed-loop economy are based on the recovery of resources, recycling, the transition from fossil fuels to the use of renewable energy

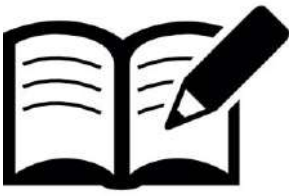
sources. This type of economy is seen as part of the Fourth Industrial Revolution, which will increase the overall rational use of resources, including natural resources, the economy will be more transparent, predictable, and its development systemic.

Waste minimization, as well as their complete elimination, will allow humanity to achieve a safe ecological zone, reduce the pressure on biodiversity and reduce nutrient consumption.

Planetary boundaries, in other words environmental risks, have identified ways to restore and conserve biodiversity. Things like the use of renewable energy, healthy eating, planting trees, waste disposal can change the future of the Earth. Such transformations will already help to improve the environmental situation, both locally and globally.

Questions for self-control

1. What factors support the stability of the Earth?
2. Define the Holocene and Anthropogenic. What is the fundamental difference between the epochs?
3. What is the main driving factor in the development of the planet?
4. Describe potential scenarios for the effects of global greenhouse gas emissions?
5. Describe the dynamics of melting glaciers?
6. What ecosystems do the biome consist of?
7. Name the basis of the biosphere.
8. What is the limit of the non-painful process of desertification?
9. What is the limit of global warming?
10. Describe the concept of water footprint.
11. Which countries in the world have the largest environmental footprint?
12. Which countries in the world are the richest in water resources?
13. Describe the unique properties of water.
14. How is the phenomenon of eutrophication related to the circulation of nutrients?
15. Name examples of "dead zones" in the oceans.
16. Describe the chemistry of the process of ocean acidification.
17. How does an increase in CO2 affect the acidification process?
18. Describe the main air pollutants. Why are aerosols the most dangerous in terms of climate change?
19. Describe the main aspects of the ozone problem.
20. Describe the main ways to adapt to climate change.



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Chapter II

ENVIRONMENTAL ETHICS AND ECONOMICS AS KEY INSTRUMENTS FOR SUSTAINABLE DEVELOPMENT

In this section you will learn about

- ✓ **Nowadays new challenges**
- ✓ **Cultural evolution**
- ✓ **Sustainable development – general background**
- ✓ **Value orientations**
- ✓ **Environmental Economics**

Key words

sustainable development
environmental ethics
environmental economics
cultural evolution

You will learn about principles of sustainable development, including human values compatible and uncompatible with sustainable development and economical aspects of sustainable development.

Exponential growth in production and consumption within the restricted Earth ecosystems is not sustainable in the long term. Therefore the international commission was established, that would attempt to do the seemingly impossible – propose how to enable people and whole nations to

develop while sustaining functioning ecosystems and a healthy environment. The efforts of the UN World Commission on Environment and Development resulted in a report called „Our Common Future“ published in 1987. The key term was „sustainable development“, a phrase central to world politics at the end of the last millennium and the beginning of the 21st century.

According to the UN World Commission on Environment and Development, sustainable development is „development that meets the needs of the present without compromising the ability of future generations to meet their own needs“. Although the concept of sustainable development has been evolving for more than 30 years, it is still extremely vague. On the other hand, despite the concept of sustainable development is far from flawless and is not a scientific theory, there is no better way to attempt to respond to the ever more acute problems of global scale.

The values which people hold and base their conduct on are probably the most important factor deciding whether we do or do not endorse sustainable development. Value orientations are likely to change over long time periods. We must strive for a substantial change in our value orientations and lifestyle if we want people in the future to have the chance to live their lives with dignity, quality, and creativity.

Economic instruments, unlike value orientations, can be implemented very quickly and they become effective virtually immediately. Nevertheless, political will is necessary to promote and adopt them. Until recently, economists and politicians focused exclusively on solving the problem of labor and capital productivity and investigating their mutual relationship. The productivity of natural riches was neglected, which led to the inefficient use of natural resources. Humanity is facing a historical turning point. For the first time in history the limits to the growth of prosperity are not caused by the lack of man-made capital, but natural capital. We are at the point where further growth of the economy does not make us richer, but poorer.

Sustainable development in this sense does not mean the end of economics. On the contrary, when economic growth reaches its limits, economics becomes a more important discipline than ever before, but it is an economics of solidarity, frugality, humility, and adaptation to the limits which nature puts to us. It is an economics which seeks quality, not expansion.

2.1. Nowadays new challenges.

„That´s one small step for a man, one giant leap for mankind.“ These were the words of Neil Armstrong, the first person to set foot on the Moon on July 20, 1969. It was a triumph of human hope, will, and creativity in the best possible sense.

The Apollo 11 flight and the landing of a human on an extraterrestrial body should remind us that once people have a vision and the will to implement it, they are capable of great things.

Nowadays we are facing a similar challenge, but of a much greater, global extent. We are confronted with massive poverty in the world. More than fifty years ago we managed to send people ot the Moon yet we remain unable to prevent people from dying of hunger. In many regions the environment is damaged or being destroyed. Many animal and plant species are irretrievably disappearing due to human activities. The world´s population continues to grow, increasing the anthropogenic pressure on the ecosystems and natural resources.

We need a vision of what to do next, and maybe more than that. We need to search for and find (on the individual as well as societal level) the „will to meaning". The Austrian psychiatrist Viktor Frankl (2006) says: „A society of prosperity or a nation of prosperity are able to meet basically all the needs of many, while the consumer society only generates individaul needs. Alas one need remains unsatisfied – the will to meaning – a need to find a meaning in one´s life, or better still in every situation – and devote oneself to it, fulfill it!"

In the history of Earth there occurred many times catastrophic situations, causing the extinction of the overwhelming majority of species. Surprisingly, however, the process of evolution was not set back by them. On the contrary, after each such „catastrophe" life developed into higher, more diverse and more advanced forms.

The cause of these extinctions was a collision with an asteroid or intensive volcanic and tectonic activity triggered by the movement and collisions of tectonic plates.

Even today relatively common phenomena, like a hurricane or an ordinary storm, release an enormous amount of energy which has, on a local or regional basis, a considerable impact on life. A tropical hurricane can in twenty-four hours release as much energy as all the inhabitants of France use in a year. One thunderstorm can contain an amount of energy equivalent to four days´ use of electricity for the whole United States.

From the beginning the Earth, and subsequently the biosphere, has been formed and influenced by a series of powerful natural elements. Life on Earth has several times been pushed to the edge of extinction, but it has never disappeared. It is human beings that have recently become another power (comparable to natural elements) influencing the state of the biosphere. From the geological point of view, their onset has been very fast.

When the Earth collided with an asteroid 65 million years ago, causing the extinction of 70 – 75 % of all animal and plant species, it was not just the annihilation of the existing state, but at the same time, a chance of creating something new.

Evolution seized the opportunity. The dominant dinosaurs disappeared from the scene, being gradually replaced by mammals.

The first ancestor of the Hominidae, which developed in the Tertiary period 15 million years ago, was the herbivorous Ramapithecus living in Africa and Asia. Seven million years ago, a new group of creatures emerged from the tropical forests of Africa and began to live on the savannahs. These were the Australopithecines, and for 5 million years they would be the world´s dominant hominid species.

Between two and three million years ago, there may have been as many as six hominid types coexisting in Africa. But only one was fated to last – the genus Homo.
The first member of the genus Homo was Homo habilis, an omnivore living in Africa about 2 – 3 million years ago. A higher species of hominid was Homo erectus that appeared one million years ago and gradually settled in Africa, Asia and Europe.
The only living species of the genus Homo, having appeared about 200 000 – 280 000 years ago, is Homo sapiens. At that time also Homo neanderthalensis existed, which disappeared relatively recently, i.e. 24 000 years ago. Modern humans, called Cro-Magnons could make stone and bone tools and were good hunters, not only gatherers of fruit. They mastered the art of speech, which further stimulated brain development. Moreover, with the first artistic works (cave paintings and figurines) they were able to think abstractly (they probably believed in an afterlife and hence were able to contemplate the future, an ability no other species on the planet appears to have).

Modern humans show remarkably little genetic variability. The reason is that we are the descendants of a small founding population.[1]

2.2. Cultural evolution.

Man is different from other creatures. Minds meet and communicate, and the feedback begins; the mind affects the body. Biological evolution is transformed in human beings into cultural evolution. which proceeds much faster.
With the Ice Age (10 000 – 12 000 years ago) coming to end, the climate underwent a change. The landscape acquired a new character and fauna and flora changed as well. As a result, man-the hunter was forced to search for additional sources of sustenance. He became a nomad and domesticated animals (dogs, sheep, goats, pigs, cattle, and others) on the way.

People developed fishing and collected grains of selected plants. This was followed by the artificial cultivation of wild growing grasses and cereals. This marked the beginning of the Neolithic (agricultural) revolution.

[1] This could be connected to the supervolcano eruption in Sumatra 75 000 years ago, followed by six global „volcanic winters“, which it is thought only a few thousand Homo sapiens survived. (Bryson, 2003)

People settled predominantly in warm areas. They built permanent settlements that would slowly grow larger. The new source of sustenance supported many more people than collecting and hunting ever could. Thanks to population growth, human clans united with groups of blood related families, associating in tribes and later in tribal unions. Tribe and tribal union members shared the same language, customs, religious ceremonies, and jointly defended the settled areas.

Providing the basis for future civilizations, the centers of these large communities emerged in the fertile silts of mighty rivers in the subtropical and temperate climatic zone (the Nile, Euphrates, Tigris, Indus, Ganges, Yellow River, and other rivers).

Four or five thousand years ago people began making the first tools, bronze weapons, and glass vessels. Three thousand years ago, iron was put to use. People were building farms, irrigation systems, water piping, and roads.

In those times, humans were able to adjust their environment (whether in a positive or negative way) on a regional scale. In ancient times our ancestors did not act any better or worse than we do now. However, their chances of affecting their environment were significantly more limited than ours.

In the 18th century, a „revolution“ broke out in Europe (spreading around the whole world), the importance of which can be compared to the Neolithic revolution. The symbol of the Industrial Revolution is the steam engine. But it is symbolized also by another two features: dependency on fossil fuels and exponential growth.

People were using more and more energy and so exponential growth became typical for the Industrial Revolution, whether it involved the increasing number of the population, the consumption of raw materials, energy, or pollution of the environment. Only in second half of the 20th century did people notice something was wrong and realize that this growth was not sustainable. There is a limit and exhaustion point to our space, defined approximately by the extent of the biosphere, and our stock of raw materials and energy. Therefore, the economic growth started by the Industrial Revolution must either come to an end or change in terms of quality.

The Industrial Revolution brought us much good, and the vast majority of people of the developed world now probably have a better standard of living (whether it concerns the level of hygiene, nutrition or the energy we use for heating, light, and transportation) than the one enjoyed by the nobility prior to the arrival of the industrial age. But there are two sides to every coin. We have collided with the „limits to growth“; the exponential increase in resource consumption and the related pollution production are no longer sustainable.

2.3. Sustainable development – general background.

Reports to the Club of Rome[2] and some other globally oriented reports of the 1970s and early 1980s demonstrated that the exponential growth in production and consumption within the restricted Earth ecosystem is not sustainable in the long term.[3] It was also more and more obvious that it was necessary to respect the different views held by developed and developing countries, as the developing countries were justly expressing their wish to establish first better living conditions and only then perhaps adopt restrictions in respect of the ecosystems´ sustainable capacity.

Therefore in 1983 the UN Secretary-General Javier Perez de Cuellar invited the Prime Minister of Norway (former Minister of the Environment) Gro Harlem Brundtland to establish international commission that would attempt to do the seemingly impossible – propose how to enable people and whole nations to develop while sustaining functioning ecosystems and a healthy environment. The efforts of the UN World Commission on Environment and Development over the course of four years resulted in a report called „Our Common Future" (widely referred to as the „Brundtland Report"), published in 1987. The key term of probably the most important UN report of the 1980s was „sustainable development", a phrase central to world politics at the end of the last millennium and the beginning of the 21st century.
According to the UN World Commission on Environment and Development (1987), sustainable development is „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".

The above definition is anthropocentrically oriented (meeting the needs of people) but that is not what is fundamentally wrong here. Above all, it is so vague and „all-embracing" that it is impossible not to agree with. Its biggest deficiency is the fact that it fails to attempt to even define human needs.

No unified, generally accepted definition has been provided as yet. Instead, there are dozens and probably hundreds of various sustainable development definitions, of which many are available in the Internet. We do not intend to present and evaluate these definitions. Let us mention only few of them.

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[2] The Club of Rome is an independent association of politicians, scientiests and artists founded by the Italian industrialist Aurelio Peccei that achieved the greatest popularity in the research of the global problems of the 1970s.

[3] The reports involved the first report to the Club of Rome „The Limits to Growth" (1972) as well as some of the other reports: „Mankind at the Turning Point" (1975), „Reshaping the International Order" (1976), „Beyond the Age of Waste" (1977), „Goals for Mankind" (1977), „No Limits to Learning" (1978), „Road Maps to the Future" (1980). Apart from activities of the Club of Rome and its associates, other publications included e.g. „To Have or To Be" by Erich Fromm (1976), „The Turning Point" by Fritjof Capra (1982), „Small is Beautiful" by Ernst Friedrich Schumacher (1973), „Gaia: A New Look at Life on Earth" by James Lovelock (1979), „The Global 2000 Report to the President" by Gerald O. Barney (1980) and others.

The European Parliament defines sustainable development as such development that gives rise to improvement in the living standard and welfare of people within the capacity of ecosystems while sustaining natural values and biological diversity for the present and future generations.

The Organisation of Economic Co-operation and Development (OECD) defines sustainable development as a dynamic balance between the economic, social, and environmental aspects of development in globalization, or as economically efficient, socially tolerable, and environmentally friendly development in all fields of human activity.

The former Czechoslovak Federal Minister of the Environment Josef Vavroušek (1993), defined sustainable development as follows: „Sustainable development, or a sustainable lifestyle, aims at the ideals of humanism and harmonious relationships between human beings and nature. It is a way of life that searches for a balance between the freedom and rights of each individual and his or her responsibility to other people and nature as a whole, including responsibility to future generations."

The last definition to be mentioned is by Slovak author Ján Topercer Jr. (Topercer in Nováček, Mederly et al., 1996): „Sustainable development is a purposeful process of changes in the way human society treats itself and its environment (the land and its resources), directed at increasing the present and future potential for meeting the needs of people and other beings while respecting the capacities (limits) of the land and its resources."

A definition should be concise and threfore can never capture the concept of sustainable development in its wider scope. In order to clarify this vague concept, the definitions are often complemented with the main principles of sustainable development.

Let us stress one principle we consider crucial – the precautionary principle. It is explicitly contained and defined also in Principle 15 of the Rio Declaration:[4] „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."

Although the concept of sustainable development has been evolving for more than 30 years, it is still extremely vague, which stems from the effort to capture and respond to highly complex global (not only environmental) problems. Ján Topercer Jr. (Mederly, Topercer, Nováček, 2004) characterized the key weak point of the concept of sustainable development as follows: „Sustainable development anticipates

[4] The Rio Declaration is a non-binding convention adopted at the United Nations´ Conference on Environment and Development in June 1992.

development that would not compromise the ability of future generations to meet their needs as viewed from the perspective of today´s generation. This concept of development is considered desirable, which makes it assume a prescribing rather than predicting role. However, the above concept lacks a reliable basis for prescription for the following reasons:

- The idea of a universal hierarchy of needs has not been sufficiently empirically documented (Smelser, 1994), which applies to space (geographically) but perhaps even more to time.
- In addition, our standards of what is optimal and desirable develop over time.

The concept of sustainable development encompasses one of the striking forms of a universal desire held by the majority of people: the desire to see the world from the perspective of „God´s eye“ (Putnam, Rorty, 1997), which is capable of an undistorted view and assessment of the needs and capacities of the past, present, and future generations.

Sustainable development can thus be preliminary classified under the category of „science&art”, i.e. among fields falling between science and art.

Although the concept of sustainable development is far from flawless and is not a scientific theory, there is no better way to attempt to respond to the ever more acute problems of global scale.

We (individuals and the society) have three options how to respond to the current global challenges:

1. We can underestimate, trivialize, or ignore the problems. We can honestly believe, that the situation (the consequences of climate change, high population increases in developing countries, resources exhaustion, poverty, etc.) is not serious and we need not worry. This logically suggests that there is no need for a response and everything can stay as it is, without any change. But that does not solve the problems. Quite the opposite, putting off an efficient action only makes them worse, while we are wasting perhaps the most precious and „exhaustible“ resource – time.

2. We can acknowledge the seriousness of the matter without trying to solve it. We fear a disaster but do not believe that our efforts could make a difference, that we ourselves could do anything to avert it. Therefore, we remain passive and resign ourselves to our fate, hoping things will sort themselves out. Or, even worse, we act regardless of what comes next, trying to seize as many pleasures as we can for ourselves before everything is lost. Thus we suppress the instinct of self-preservation and behave cruelly especially to our children, to future generations.

3. We can actively try to affect and alter the present adverse trends, to formulate and assert alternative, positive, and democratic visions of society´s development. However, no one can find the answer to: „What are the chances of

success?“ The chance can be eighty percent or just one percent and still we should take it. Although as individuals we are not that responsible for the outcome (usually, our capacity to affect that is very limited), we all are definitely responsible for our individual efforts, for how much time, energy, and skills we dedicate to what.

Let us try now to sum up the main ideas contained in the definitions and principles of sustainable development into four generalizing basic requirements.

1. Requirement for all people on Earth to be able to meet their (at least elementary) needs.

The trouble starts already when trying to define elementary human needs. We need food, water, clothes, and shelter for bare survival. Just surviving on a long-term basis is naturally not an option. Despite that, unfortunately about one billion people around the world suffer from acute hunger and 1.2 billion people have no access to safe water. In developed countries, we would certainly loathe it if we could cover but the most essential needs facilitating survival. But where is the limit to human needs? Probably in „infinity“.

Are there any limits to justified human needs? And do they differ in time and space? Abraham Maslow (1954) proposed a hierarchy (pyramid) of human needs, now widely known and accepted:

- Basic physical, physiological needs.
- Need for security and safety.
- Social needs (a need for belonging and love).
- Need for esteem and respect.
- Need for self-realization.

Unfortunately, not even Maslow´s hierarchy of human needs can help us determine a reasonable limit for human desires, which are often perceived as needs or even as something we are entitled to.

The communist ideology carried an appealing motto it never managed (nor was it possible) to honor: „From each according to his abilities, to each according to his needs.“ But is a car, a private yacht, a tourist trip into orbit a justifiable need?

I think the requirement for the satisfaction of needs as stated in the definition of the UN World Commission on Environment and Development is appealing but unfeasible and impossible to define. It seems more logical and adequate to condition the satisfaction of human needs by respecting the ecosystems´ carrying capacity while preserving natural values and biological diversity for the present and future generations.

The elementary requirement of sustainable development should not be formed by the satisfaction of human needs but by the respect for the ecosystems´ carrying

capacity upon which the activities of people living in individual regions and time periods must be based.

2. Requirement for the rights of future generations to meet their needs

This is a great new challenge. In history, various groups of inhabitants strived (whether by violent or non-violent means) to assert their rights – slaves, serfs, colonized nations, etc. Nowadays the problem is whether we will be able to respect the rights of those who are not here yet but will be – our children and all generations to come. This general statement can be specified with the help of Heman Daly´s (1977, 1989) three principles suggesting how to use Earth´s natural resources and ecosystems sustainably:

a) Explotation of renewable resources (forest, fish populations, etc.) does not exceed the rate at which they regenerate.

b) The rate of depleting non-renewable natural resources (e.g. fossil fuels) does not exceed the rate of growth of the renewable substitutes.

c) Waste emissions do not exceed the renewable assimilative capacity of the local environment (and therefore will not exceed the ecosystems´ carrying capacity).

3. Requirement for respecting the rights of other living beings

This is another great challenge that did not receive much attention in the 20th century, when people were „conquering“ nature. Similarly to the first requirement of sustainable development, we are unable to define the optimum status here either. Should humankind use its dominant position among other living beings and act as the „lord of creation“ or should it rather be a responsible manager of this planet? Or should we consider other beings equal to us (regardless of the fact that this radical requirement could not be implemented at any rate)?

Should we differentiate between individual species depending on what place they occupy in evolution?

These are questions we have no answer to, nor can we determine clearly what is good and what is wrong. However, we should not ignore the above challenges and instead formulate the answers gradually, even if it takes decades and perhaps even longer. We should gradually approach harmony in relationships between human beings and both animate and inanimate nature, as Josef Vavroušek states in his definition. Full harmony we will probably never reach. But we can always feel respect for life and nature in the sense of the legacy of Albert Schweitzer (see the ethics of reverence for life later in this text).

4. Requirement for learning from the future

This requirement does not ensue from the aforementioned definitions but I believe that it is indispensable for the implementation of sustainable development. The report to the Club of Rome „No Limits to Learning“ (1978) elaborates on the

idea of „anticipatory learning“, that is learning based on anticipating the possible consequences of our current activities. Anticipatory learning is thus a path leading to fulfilling the key principle of sustainable development, the precautionary principle.

Throughout all their history, human beings have learnt from their past experience or the past experience of their fellow humans. This model functioned well for thousands of years, as long as the consequences of our deeds (and errors) were space and time limited. Scientific knowledge and technological development have provided us with such powers that potential errors may now lead to a severe aftermath, whether it concerns e.g. the peaceful or military use of nuclear energy, genetically modified organisms, climated change, etc. Therefore it is necessary to learn not only from the past but also from possible futures and behave and act accordingly.

Society´s transition to sustainable development, to a sustainable lifestyle, implies major changes in its functioning. Owing to its importance, this transition could be called „the third global revolution“. Could such a change be truly global though? Is the vision of sustainable development applicable in various cultures and populations, despite all their dissimilarities?

If anyone will take the trouble to compare the moral teaching of, say, the ancient Egyptians, Babylonians, Hindus, Chinese, Greeks and Romans, what will really strike him will be how very like they are to each other and to our own. Men have differed as regards what people you ought to be unselfish to, whether it was only your own family, or your fellow contrymen, or everyone. But they have always agreed that you ought not to put yourself first.

Clive Staples Lewis

2.4. Value orientations.

The values which people hold and base their conduct on are probably the most important factor deciding whether we do or do not endorse sustainable development. Value orientations are likely to change over long time periods (decades to hundreds of years).

The sociologist Stanislav Hubík states that „value orientation is subject to inertia, it changes as slowly as possible and a revolution in value orientation is in progress silently, although it is the most revolutionary revolution“.

The set of principles and rules which indicate to people how they should behave in their interaction with others is called ethics. Ecological ethics, or rather environmental ethics is the set of principles and rules which indicate to people how they should behave in their interaction with the entire non-human world.

Value orientation of people in their everyday reality stems from what the phylogenesis[5] of hunters and gatherers equipped them with. Anthropologists point out that Homo sapiens has spent in this evolutionary stage 90 % of the time it has existed. Therefore, we tend to see nature, the world around us, as something which not only surrounds us, but also still potentially endangers us. That is why we must fight with nature, conquer it.

The 16th and 17th centuries gradually established the conception of the world as a machine. This radical change was triggered by new discoveries in physics, astronomy, and mathematics. Galileo Galilei restricted science to the study of phenomena which could be measured and quantified.

Galileo Galilei, René Descartes and Immanuel Kant influenced our perception or the world. Descartes and Kant separated reason from nature. Kant was convinced that the only thing deserving of respect was reason, which he considered the foundation of our freedom.

Descartes narrowed the concept of reason down to a purely mathematical arrangement of ideal entities and, in nature, to the mathematical and mechanical arrangement of particles in spacetime.

The first strong opposition to the mechanistic Cartesian paradigm originates in the Romantic movement[6] in art, literature, and philosophy. Nevertheless, a real shock for science came according to Capra, only in the 20th century when system theory was elaborated. Systems cannot be understood by means of their analyses. From the system perspective, it is the characteristics of the whole which none of its components has which are regarded as the fundamental, essential characteristics of an organism or living system. These characteristics originate in interactions among the components.

What actually makes humans fundamentally different from other living beings? According to the Judeo-Christian conception, humans, like everything else, have been created by God, but unlike animals, they possess immortal souls.

Early Modern Era the animal has ceased to be regarded as kin and a conception of the animal as raw material has been forming instead.[7] Whether humans are created by God and whether they, unlike animals, have souls is, at least for now, a question of faith. Intellectually, we can specify three basic features of humanity:

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[5] Phylogeny (phylogenetic evolution) is the evolution of species in historical sequence as understood by the theory of evolution. In contrast, ontogeny is the development course of a human individual.

[6] Romanticism – an artistic movement and philosophical school of thought as well as the life stance in the Euro-American culture of the end of the 18th and early 19th century.

[7] Kohák harshly but fittingly remarks: „Many people were shocked to read, after the war, about the medical experiments on children in Nazi concentration camps. Few of them noted that the only difference between Dr. Mengele´s experiments and the experiments we accept without hesitation is that Dr. Mengele drew the line between prohibited and permitted experimental animals between „Aryans“ and „non-Aryans“ while we draw it between humans and chimpanzees.“

a) Speech – the ability to capture the fleeting moment in concepts. This ability, dramatically intensified by the written word, makes possible far more rapid and effective cumulation of knowledge than the growth of customs and tradition.
b) Reason – because humans can capture immediate experience in words, they can grasp not only immediate spatiotemporal relations of continuity, contiguity, and resemblance, but also of logical and ideal relations. Defining ideal relations among components of experience is precisely what we call reason. There is one more thing related to reason: imagination, which is possible only because humans are capable not only of seeing a given state, but also of imagining it in ideas and concepts.
c) Freedom – reason and imagination enable humans to recognize moral responsibility. They do not live in the innocence which modernity attributed to other animals, said to accept uncritically whatever there is. Humans are aware of moral duties and are capable of worshipping God, thereby manifesting their „immortal soul" (or, more precisely, immortal spirit).

„Between humans and animals there is only one morally relevant difference, and that is freedom. Humans are beings who can imagine that things could be otherwise, the only beings that do not live within firmly established instinctual parameters. Freedom, though, does not mean privilege.

Peter Singer is a leading advocate of granting certain rights to other beings. In 1975 he published „Animal Liberation", a ground-breaking study on the relationship of humans and animals. According to Singer, the ability to suffer and feel pain (which is common to humans and animals) is sufficient reason for consideration. In Singer´s conception we are equal with animals, even though it does not mean that we are the same.

None of the differences between humans and their non-human fellows is morally relevant. None justify domination and discrimination. Societies for the protection of animals generally recognize four basic needs common to all higher animals (as a matter of fact, they were denied even to African slaves as recently as two centuries ago):

1. The possibility of free movement in sufficient space.
2. The natural cycle of day and night, of activity and rest.
3. The fellowship of their kind, including family relations.
4. A diet natural to the animal.

What attitudes do people have to living and non-living nature? To put it very simply, we have three options: the anthropocentric, the biocentric, and the theocentric attitudes.

Erazim Kohák (1998) provides an alternative division which is based on ecological or, rather, environmental ethics:

1. Ethics of the fear of the Lord

The kind of short-sighted egoism which we today call „anthropocentrism“ is something we normally encounter first in highly advanced civilizations, typically as a sign of decadence.

Early humans, hunters, herdsmen, farmers, were painfully aware of their own vulnerability and unimportance. Everything appears to them as a gift. Nature, which surrounds them, appears to them as infinitely powerful, unfathomable, evoking a holy fear which in a later religious conception will figure as the fear of the Lord.

In modern terminology, it is called theocentrism[8], its fundamental stance is that all value derives from God, and humans are but dependent parts of God´s creation.

Polish-American Catholic thinker Henryk Skolimowski (in Kohák, Kolářský and Míchal, 1996) considers contemporary fashionable attitudes, egoism, narcissism, snobbery, simply everything that leads the consumer society to destruction and self-destruction, a product of the ethical vacuum which ethical relativism generates around us.

2. Ethics of noble humanity

Annie Dillard (in Kohák, Kolářský and Míchal, 1996) and Charles Sherrington (1953) claim that nature is neither good nor evil, it is only completely insensitive. They give examples:

A wasp stings a caterpillar in seven nerve nodes to paralyze it, but not kill it. Only after that does the wasp lay eggs in the body of the caterpillar. It is necessary that the caterpillar lives long and suffers while bearing foreign eggs.

A cat plays with a mouse: it does not kill, only cripples and goes on playing.

Life is a constant escape from death. Those who survive bear the scars at the end of the summer – butterflies with torn wings, spiders missing a leg. And Mother Nature? It does not care about suffering. Only humans observing the insensitivity of nature suffer from empathy.

According to Sherington and Dillard alike, only with humans does altruism – freedom and the ability to act for the good of nature – enter into the world.

3. The ethics of reverence for life

All life is a source of meaning and value. Albert Schweitzer (1974) developed this concept under the title „the philosophy of reverence for life“. Reverence for life began with wonder over the miracle that there is life at all. An ethics which restricts itself to human interactions with each other is incomplete. A broader outreach is

[8] Theocentrism does not mean the centrality of God in the traditional European concept, but the centrality of sacred transcendence and awe.

needed, a reverence for all living beings. Only such a broad outreach, as wide as life itself, could provide the framework for avoiding harm and doing good as a general posture.

The ethics of reverence for life (or the biocentric approach to world) was developed by the American philosopher Paul Taylor (1986) in four propositions:

- People, animate beings of the subspecies Homo sapiens sapiens, are equal members of the community of all beings.
- The Earth is a web of mutual dependence.
- Every member of the biotic community is valuable simply because it is.
- The three previous propositions lead to the conclusion that the idea of human superiority is only an expression of human racism.

4. The land ethic

The land ethic comes from the work of ecological thinker Aldo Leopold.[9] This concept is not concerned only with respect for life itself, but with respect for the presuppositions of life, the whole community of all life, and conditions of its sustainability.

Value does not derive from humans or from life. It is a function of the balance of the entire ecosystem. In Leopold´s words, „a thing is right when it tends to preserve the integrity, stability, and beauty of the biotic community. It is wrong when it tends otherwise".

5. Lifeboat ethics

Economist Kenneth Boulding (1966) pointed out that the planet ceased to be „endless" a long time ago. He proposed the metaphor of a spaceship. Like in a spaceship, we on the Earth have only a limited amount of resources, and like in a spaceship, all our waste stays onboard. Garrett Hardin (1985) builds of Boulding with a reminder that a ship must have a captain – which the Earth does not.

Garrett Hardin concludes that where there is a surplus of demand it is essential to limit the availability of supply. Limited resources (of the planet) are incompatible with unlimited demands (of people).

The starting point of lifeboat ethics is that there are too many of us and that we share limited resources. Generosity will lead to tragedy. Therefore let us help no one, only make sure that we shall use our privileges for the preservation of common cultural values, not only personal consumption. Attempts to help others beyond that only prolong the misery. For instance the green revolution, which doubled agricultural yields, temporarily prevented famine but brought about a catastrophic

[9] Aldo Leopold was a forester and the first American university teacher of conservation ecology as a separate subject. His most famous work is „A Sand County Almanac" (1949).

rise in populations in which each extra mouth represents a further burden on the environment.

In addition to this division in attitudes towards nature based on Erazim Kohák, we shall also mention the concept of „deep ecology“ used first by Arne Naess (1996) from Norway in 1973. The distinction between „shallow“ and „deep“ ecologies is often used to distinguish between the ecology that is interested only in the technology of environmentally friendly production and the ecology which goes to the roots of the ecological crisis in human attitudes, especially in the consumer orientation of Euro-American civilization.

We are in the period of the sixth catastrophic extinction when species are disappearing because of the habitat loss caused by humans. Human genetic memory does not prepare humans for the conditions of a purely culturally determined life. Humans experience a deeply encoded fear of what had been dangerous in nature (e.g. of serpents). The incredible speed of modern development means, however, that humans do not even begin to develop a similar instinctive fear of far more dangerous things like automobiles and firearms.

Is it realistic to expect that values compatible with sustainable development will assert themselves in the behavior and activities of people? International long-term research conducted by Ronald Inglehart (1977, 1990) in the 1970s tried to capture the shift from material to post-material values. He performed a large-scale representative survey in all countries of Western Europe, North America, Japan, South Africa, and later in some countries of Central and Eastern Europe.

The basic finding is the gradual shift of emphasis from the needs of material nature to the non-material needs. Inglehart understands the material values primarily as material affluence and security, focus on economic prosperity, and stable economic growth. Post-material values include according to him, the unrestricted self-realization of an individual, the opportunity to participate in the administration of public affairs, to contribute to a more humane society in which ideas have higher importance than money, and also to create a better environment.

Inglehart calls this subtle but crucial change a „quiet revolution“ and demonstrates it in statistically reliable figures. He observes the shift in values especially in younger age groups. In the post-war generation, the proportion of „post-materialistic“ is already quantitatively higher than the proportion of people with a „materialistic“ orientation. A growing non-consumerist orientation can be found most frequently in the „middle class“.

With respect to a sustainable lifestyle the research revealed a problem: there is a relationship between post-materialistic attitudes and the level of gross domestic product (and the level of consumption in a given country).

This takes us back to the dilemma faced by the Brundtland Commission. What can be done to preserve a reasonable quality of the environment and at the same time allow countries to develop and prosper economically? With respect to value orientation: what can be done to shift from material towards post-material values if this shift depends on the level of GDP and 80% of the global population lives in poor, developing countries?

Values compatible and uncompatible with sustainable lifestyle

Josef Vavroušek (1993) attempted to define a framework of key values which are typical for industrial society and stimulate the emergence of global and regional problems (values of type A). He assigned alternative values to them which should be compatible with a sustainable way of life (values of type B):

1. Attitude of humans to nature
   A. Predatory attitude to nature.
   B. Awareness of unity with nature.
2. Attitude of human individuals to society
   A. One-sided emphasis on individualism and competitiveness (typical for „real capitalism“) as well as a one-sided emphasis on collectivism (typical for „real socialism“).
   B. Balanced emphasis on the individaul and the collective, supplementing competitiveness with cooperation.[10]
3. Attitude to the passage of time and a sense of history
   A. Obsession with the ideas of quantitative growth.
   B. Emphasis on the qualitative development of human society.
4. Attitude to the sense of our lives
   A. Hedonistic orientation to the consumer lifestyle.
   B. Emphasis on the quality of life, conscious modesty, and the self-denial of superfluous things.
5. Attitude to freedom and responsibility
   A. One-sided emphasis on human rights and freedoms, the erosion of common responsibility for the course of public affairs.
   B. Development of human rights and freedoms while respecting the symmetry between them and the responsibility which is connected with them.
6. Attitude to the level of our knowledge

[10] The American ecologist Eugene P. Odum (1977) says that the relations in nature evolve from parasitism to mutualism, that is, to mutual cooperation. Alternative economists talk about a „win-win strategy“, that is, a strategy by which individual subjects gain more in the long term through mutual agreement than if they competed and lived at the expense of one another.

   A. „Pride in reason“ resting on the one-sided emphasis on rationality and on the overestimation of the complexity, depth, and reliability of our knowledge and our ability to foresee and shape future development.
   B. Caution in all interference with nature and society.
7. Attitude to our lives
   A. Our alienation from our own lives, the weakening of the human instinct of self-preservation and of the feedback which makes the correction of our inappropriate or unsuccessful action possible.
   B. Restoring the human instinct of self-preservation.
8. Attitude to future generations
   A. Preference for short-term goals over long-term and permanent goals, life at the expense of future generations.
   B. Awareness of the long-term consequences of human activities.
9. Attitude to other opinions and other civilizations
   A. Lack of respect for other opinions, ideological, religious, racial, or other intolerance and the tendency to solve problems by force.
   B. Mutual tolerance, endeavoring to understand the situation of the citizens of other countries, solving problems by negotiation.
10. Attitude to common issues
   A. Withdrawal from common decision making.
   B. Development of participatory democracy combining the advantages of representative democracy with self-government.

According to Josef Vavroušek, our future depends largely on how high we will place values of type B in our individual and group value systems and to what extent we will suppress the values of type A. Suppressing values of type A in our behavior sounds rational, but unfortunately humans often do not behave rationally. It is a race against time; time is perhaps our scarcest resource.

In conclusion we may say that we must strive for a substantial change in our value orientations and lifestyle if we want people in the future to have the chance to live their lives with dignity, quality, and creativity.

Throughout the existence of the Homo sapiens sapiens subspecies, humanity has been immediately and existentially dependent on the surrounding nature as children are dependent on their parents. In the course of their evolution, for millenia, people have struggled with a shortage of food, diseases, and natural disasters; they have felt constantly threatened by the surrounding natural world. Only in the last few centuries has the situation been gradually changing (especially in the developed countries). Like those who have starved and suffered for a long time have a tendency to overeat excessively, to the point where they endanger themselves, also the current

majority of society considers accumulating wealth and entering into a „paradise of consumption“ almost the meaning of life.

Today we have become the new „geological force“ on Earth; to put it arrogantly, we have become the „masters of the Earth“, with the ability to deplete the non-renewable resources of the biosphere and destroy the renewable resources of the biosphere.

Now the goal is not only to recognize our strength in time, but also admit our dependence on the surrounding environment, on nature. Similar to and individual developing from child´s one-sided dependence on its parents into rebellious puberty and then into adulthood, human society too may now be experiencing the „stage of puberty“. Individuals want to outgrow their parents and become free and independent, people have the need to conquer nature, their environment. If that is the case, there will be much at stake in the first half of the 21st century.

At puberty, individuals are most vulnerable and can easily hurt themselves and others. Their outwardly self-assured and even arrogant behavior actually shows insecurity and weakness. It is this stage which substantially determines what kind of people they will become and how they will behave in adulthood, which is in fact already at the door.

If all goes well, they will recognize their power which has surpassed the power of their parents, but they will not misuse it against them. On the contrary, they will respect their parents, not as a child any more but as an equal partner. Perhaps it is possible, not only to believe, to hope, that the relationship of humanity to nature will ripen and mature, but also to actively seek to accomplish that aim, even though it will be a difficult and by no means painless process.

Shifts in value orientations – stories of success

Value orientations shift „silently“ and slowly, over decades or centuries, but there is no need to despair. There are several examples of positive changes in behavior and thoughtful readers can surely recall a few more hopeful signs from their neighborhood.

1. Abolition of slavery

Slavery has accompanied human society since time immemorial. In the United States it became the source of the most devastating war in its history, the Civil War between 1861 and 1865. When slavery was abolished, many people were afraid that the economy based on agriculture in the southern states would collapse. It did not happen. Today, one hundred and sixty years later, slavery is unacceptable from the perspective of values in the developed world. An advocate of slavery, for instance in an election campaign, would not be dangerous any more today, but ripe for the madhouse. The United States have certainly not resolved all the traumas originating

in the historically unequal and unjust relations of blacks and whites, but a shift in value orientations in a positive direction no doubt occurred.

2. Restrictions on smoking

Tobacco corporations earn billions of dollars from our addiction to smoking. When some civic initiatives in the Western countries started to campaign for restrictions on tobacco advertising in the 1970s, it had all the signs of tilting at windmills. A couple of hundred or maybe a few thousand zealots stood up against economic giants with sophisticated marketing strategies and effective lobbying. Yet it is now apparent in the developed countries that smoking has been restricted, especially there are fewer smokers among young people, and in many countries smoking is banned in public buildings and public areas where nonsmokers might be inconvenienced. This makes the multinational tobacco corporations push their way all the more aggressively into the former socialist and developing countries, but that is another story.

3. Recycling

I am convinced that if during my childhood and youth (the 1960s and 1970s) someone had suddenly started to ask people to sort waste voluntarily and for free, the results would have been woeful. Due to the increased attention to environmental issues in the following years and due to environmental education and campaigns, the sorting of waste works well in the majority of the developed countries today. Some people may take it as an alibi for an otherwise dissolute consumerist lifestyle („I sort waste, that means I have already done enough for the environment, let those who are paid for it take care of the rest.“), but nothing is perfect. I think that the recycling of waste can be included among the success stories showing a change in the behavior of people for the better which has occurred over a relatively short period of time.

4. Relations between France and Germany

I am not a historian and I may be simplifying the situation, but I chose as the last example the transformation of the relations between two powerful and ambitious nations, or rather countries. France and Germany were mortal enemies in both World Was I and II. Millions of dead on both sides could have led to the rational assumption after World War II that there was enough hatred sown for several generations ahead. Instead of that, the two countries have been, for two decades at least, the major driving force of European integration. One of the reasons for this success is perhaps the Marshall Plan and the subsequent economic prosperity of both countries. Nevertheless, it is not important for us at this point. What is important is that the mortal enemies have become friends, or at least reliable partners in building a united Europe and that it occurred within two or three generations.

Infobox: Virtues and vices

The values of Euro-American culture and civilization stem from the heritage of Judaism and Christianity (it applies similarly to Hispanic and Orthodox civilization groups). Judaism and Christianity find fundamental ethical importance in the Ten Commandments. The fourth through the tenth commandments are generally considered in these societies (even beyond religion) the „ethical minimum“ which defines the basic human relations.

According to the Old Testament, Moses received the Ten Commandments in the Sinai desert. A brief, catechetical version of the Ten Commandments is as follows:

1. I am the Lord, your God: you shall not have strange Gods before me.
2. You shall not take the name of the Lord your God in vain.
3. Remember to keep holy the Lord´s Day.
4. Honor your father and your mother, so that you may live long and that it may go well with you in the land.
5. You shall not kill.
6. You shall not commit adultery.
7. You shall not steal.
8. You shall not bear false witness against your neighbor.
9. You shall not covet your neighbor´s wife.
10. You shall not covet your neighbor´s goods.

Around 600 A.D. Pope Gregory I created a list of seven deadly sins. They are: pride, envy,
greed, wrath, lust, gluttony, and sloth.

Contrasting with the seven deadly sins there are seven main virtues in Christianity: humility, charity, kindness, patience, chastity, temperance, and diligence.

Moder time, however, bring new challenges and it is not easy to distinguish what is good (or what is still acceptable) and what is not. In March 2008, Gianfranco Girotti, a bishop from the Vatican, outlined in the newspaper L´Osservatore Romano which other vices connected with the process of globalization could be in the 21st century considered by the Catholic Church serious offenses against God and our neigbors.[11] They are: genetic engineering, experiments on humans, polluting the environment, contributing to social inequality, contributing to the poverty of others, lives in excessive wealth, drug trafficking and use.

„You offend God not only by stealing, blaspheming or coveting your neighbor´s wife, but also by ruining the environment, carrying out morally debatable scientific

[11] It is not, of course, the official position of the Catholic Church, but the personal statement of influencial Vatican bishop.

experiments, or allowing genetic manipulations that alter DNA or compromise embryos", says Bishop Girotti.[12]

Some of these „new sins" are hard to define because in the developed countries we are all contributing to social inequality and the degradation of the environment in the developing countries by buying cheap products which people in the developing countries have produced in appalling social conditions and the production of which is damaging the local environment. Nevertheless, it is certainly positive that after 14 centuries the Catholic Church (and let us hope not only it) seems to be opening a debate on the ethical aspects of emerging development opportunities and threats.

Hans Küng (1992, 1997, 2000) deals with values and ethical principles in his work devoted to the world´s ethos. He mentions „the golden rule of humanity", encountered in all major religious and ethical traditions. It can be worded negatively („Do not treat others in ways you would not like to be treated") or positively („Treat others as you would like them to treat you"). Hans Küng lists variations of this meesage as it appears in various environments which differ historically, culturally, and religiously:

- Confucius (c. 551 – 489 BC): „What you yourself do not want, do not do to another person" (Sayings 15, 23).
- Rabbi Hilel (60 BC – 10 AD): „Do not do to others what you would not want them to do to you" (Shabbat 31a).
- Jesus of Nazareth: „Whatever you want people to do to you, do also to them" (Matt. 7.12; Luke 6.31)
- Islam: „None of you is a believer as long as he does not wish his brother what he wishes himself" (Forty Hadith of an-Nawawi, 13).
- Jainism: „Human beings should be indeferent to wordly things and treat all creatures in the world as they would want to be treated themselves" (Sutrakritanga I, 11, 33).
- Buddhism: „A state which is not pleasant or enjoyable for me will also not be so for him, and how can I impose on another a state which is not pleasant or enjoyable for me?" (Samyutta Nikaya V, 353.35 – 342.2).
- Hinduism: „One should not behave towards others in a way which is unpleasant for oneself: that is the essence of morality" (Mahabharata XIII 114,8).

2.5. Environmental Economics.

Economics is the science of the economy of human society. Economics attempts to discover and formulate the laws governing economic activity in society.

[12] Taken from an article „Seven new deadly sins: are you guilty?" published in the Times on March 10, 2008.

As the economist Zdeněk Štěpánek (1997) puts it, economics is the science which primarily deals with the issue of how different societies use scarce resources to produce useful goods and how they distribute them among various population groups. Environmental economics developed relatively recently. It studies the ways in which the main economic activities (the production and consumption of goods and services) influence the environment, as well as the ways in which the condition of the environment and its protection influence the economy (economic growth, resource availability, distribution of goods, etc.).

Economic instruments, unlike value orientations, can be implemented very quickly and they become effective virtually immediately. Nevertheless, political will is necessary to promote and adopt them.

Arthur Rich (1994) distinguishes four purposes of the economy: fundamental, humane, social and environmental.

a) The fundamental purpose of the economy

The most fundamental need of humans is the need to live, to grow, to develop themselves, which are basically concepts synonymous with life. We share this need with plants and animals.

The purpose of the economy is satisfying basic existential needs. The truest purpose of the economy therefore rests in service to life and because it has a service purpose, the economy must be oriented towards the needs of humans, not humans towards the needs of the economy. The economy must always be only a means, not an end.

b) The humane purpose of the economy

The human purpose of the economy is connected with the efficiency and organization of work. Humans need an efficient economy which is able to secure their material basis of life, but they also need an economy with a humane structure which gives them room for the development of their personalities: personalities created in the image of God, not humanly stunted robots.

c) The social purpose of the economy

If an economy creates on a national or global scale social inequality of such a kind that there exists, on the one hand, an unnecessary surplus and, on the other hand, a shortage of the most necessary goods, it is experienced as an absurd, unjust, and unsustainable state.

d) The ecological purpose of the economy

It is the nature of humans that they are a part of creation, embedded in the ecological cycle of nature, in which everything is related to everything else. It is also their nature to have a special place within creation that enables them to intervene in nature. Insofar as we find the purpose of the economy in using natural resources for

the good of humans without thereby endangering or even destroying nature as the universal basis of life, we can speak of the ecological purpose of the economy. Natural resources should, not only be used in the service of life, but also carefully preserved.

If the economy grows, the funamental and social purspose converge, but it can also mean a divergence from the humane or ecological purpose of the economy. For instance, an increase in the economic efficiency of a company may eliminate jobs, deprive work of its content, or strengthen the burden of the already overloaded ecosystems.

Complete harmony among the different purposes of the economy may not be possible, but humans are certainly capable of reducing the tension and eliminating what Rich calls the „imperialism of a single purpose".

As Arthur Rich distinguishes several purposes of the economy, it is useful to distinguish several kinds of capital. Traditionally, capital is understood as resources (material goods, means of production, money, shares, etc.) which are not consumed by their owner, but used to generate profits.

, Lovins and Lovins (2003) distinguish four kinds of capital:

- Human capital – in the form of labor, intelligence, culture, and organization.
- Financial capital – consisting of cash, investments, and monetary instruments.
- Manufactured capital – including infrastructure (transport, energy, etc.), machines, tools, and factories.
- Natural capital – made up of the resources of living systems and the services provided by the ecosystem.

This list needs complementation with an additional item: social capital, which can be characterized as a set of social contacts and relationships. Robert Putnam defines it as „features of social organization, such as networks, norms, and trust, that facilitate coordination and cooperation for mutual benefit".

Especially natural capital has been neglected up to now despite it plays a key role in sustainable development.

Natural capital includes water, minerals, fossil fuels, fish, soil, air, etc. But it also encompasses living systems, which include grasslands, savannas, wetlands, estuaries, oceans, coral reefs, riparian corridors, tundras, rainforest, and so on.

The Czech economist Zdeněk Štěpánek (1997) presents similar ideas when outlining what we gain from a balanced natural system which has been evolving for hundreds of millions of years:

- protection against cosmic influences;
- relatively stable physical and chemical conditions for life;
- clean water provided by the natural water cycle;

- material resources;
- natural decontamination;
- fertile soils;
- energy resources;
- biological resources;
- room for life.

Herman E. Daly (1996) claims that until recently, economists and politicians focused exclusively on solving the problem of labor and capital productivity and investigating their mutual relationship. The productivity of natural riches was neglected, which led to huge wastage and the inefficient use of natural resources. In the past, this approach had its logic. The resources of energy and raw materials were seemingly inexhaustible and ecosystems were able to absorb waste and gas emissions. Today the situation is different.

The scarcest (because the shortest in supply) factor today is not man-made capital (such as fishing boats and chainsaws) but the remaining natural capital (such as the remaining fish populations and forests). Larger amounts of capital (chainsaws, fishing boats) cannot replace the decreasing amounts of resources (forests, fish populations). As Daly points out: „You cannot make the same house by substituting more saws for less lumber."

If we accept the argument that natural capital and man-made capital are complements rather than substitutes, then the factor in shortest supply (the scarcest) will also be the limiting factor.

Keller, Gál, and Frič (1996) argue that conventional economists reduced nature to many isolated items, like soil, raw materials, food, and most recently biotechnology. Ignoring the unity and uniqueness of nature, reducing it to a sum of mere objects to be possessed did not reflect the most fundamental quality of nature – its powerful productive capacity.

The physical growth of the economy leads to the transformation of natural capital into man-made capital. When we cut down a tree, we can make a table from it. We gain the benefits which the table provides. On the other hand we lose the benefits which the tree had provided before. In a sparsely populated world with limited economic activity, the benefits we lost by cutting down a couple of trees was insignificant, but the benefits we gained by the production of tables was significant. However, in today´s densely populated world with high economic activity the more trees we cut down, the more problems related to their shortage (and the shortage of the benefits they provide) we cause.

Growing total consumption (the total scale of the economy) is linked to both costs and benefits. Benefits are services which a greater number of tables provide us.

Costs arise from the inability of the ecosystem to continue providing certain services (cutting down trees leads to an increase in CO_2 emissions, the loss of biodiversity, soil erosion, etc.).

With growing consumption marginal costs tend to increase and marginal utility tends to decrease. If the value of marginal costs equals the value of marginal utility, the scale has reached its optimum and further growth of the economic scale (total consumption) would be uneconomical. The more the economy grows, the higher are the costs of its reproduction.

Traditional economists believe that we consume only the value that we ourselves have added to the natural riches. In their model we first add the value, subsequently we consume it, and this cycle is repeated again and again.All attention is focused on the added value, but the object to which the value is added, i.e. nature with its riches, suffers somewhat from a lack of interest.

The exploitation of nature, or more precisely natural capital, is analogous to the depreciation of man-made capital. Daly distinguishes two categories of natural capital: geological (non-renewable) and biological (renewable). Both these categories are exhaustible.

According to Keller, Gál, and Frič (1996), as a result of our treatment nature loses its productive capacity. All our wealth originates in nature and in human labor, whether physical or mental. Conventional economists know that the productivity of human labor can be sustained only if employees can renew their physical and mental strength, their productivity, but classical economic theory denies nature any means of sustaining its productivity. Nature is expected to regenerate somehow by itself, no matter how much we squeeze out of it for our needs.

Each employee under such treatment would have died from exhaustion a long time ago. In this respect, the ecological crisis is the cruel suffering of exhausted nature which has neither the means nor the time to regenerate its productivity.
It means the end of the period in which man-made capital was the limiting factor and the beginning of the phase where it is the remaining natural capital which becomes the limiting factor. „The production of caught fish is currently limited by remaining fish populations, not by the number of fishing boats; timber production is limited by reamining forests, not by sawmills; barrels of pumped crude oil is limited by petroleum deposits (or perhaps more stringently by the capacity of the atmosphere to absorb CO_2), not by pumping capacity; and agricultural production is frequently limited by water availability, not by tractors, harvesters, or even land area.

According to Daly (1996), humanity is facing a historical turning point. For the first time in history the limits to the growth of prosperity are not caused by the lack of man-made capital, but natural capital. Whenever new limiting factors have appeared

in history, the economy has usually undergone a profound restructuring in response. We are once again in a period of restructuring.

When something grows it gets quantitatively bigger; when it develops it gets qualitatively better, or at least different.

Quantitative growth and qualitative improvement follow different laws. Our planet develops over time without growing. Our economy, a subsystsem of the finite and non-growing Earth, must eventually adapt to a similar pattern of development. While there are limits to growth, it is necessary that there are no limits to development.

The American economist Kenneth Boulding (1966) distinguished between a „cowboy economy“ and a „spaceman economy“. Cowboys on the endless plains lived from the one-way flow of materials and energy in the ecosystem from the original source to the outlet holes. They did not need to recycle anything. By contrast, the crew of a spaceship lives in a small cabin which has a fixed and very limited cycle of material in a system of immediate feedback. It is therefore necessary to have everything under control, economize processes and make them efficient. While expense is irrelevant for the cowboy, it is absolutely essential for the crew of the spaceship.

The market is competent to solve the problem of optimal resource allocation but it is not able to solve the problem of optimal resource distribution (redistribution) and especially the optimal scale of economic activities.

The above mentioned is not an attempt to reject the market economy as the most perfect instrument known which serves the optimal distribution of resources among different uses. However, there is no type of economy, not even the market economy itself, with built-in sensors which would signal to us that the scope of our activities has already exceeded the carrying capacity ensuring the survival of the surrounding natural systems. The absence of such sensors is the more dangerous the more rapidly the economy turns natural resources into waste.

Economic growth in the physical sense does not generate only positives. It can cause the environmental costs (damage) to grow faster (and their extent to be much more serious) than the resulting benefits. In that case, we are in fact not getting richer, but poorer. So the question is whether such growth can still be called economic and whether the term „uneconomic growth“ would not be more appropriate. There may be nothing bad about getting rich at all. What is bad is when people get poorer due to uneconomical growth while it looks as if it was economic growth.

Alternative economists believe that the first thing which must be changed in economic theory is the conception of the economic process as a separate cycle

completely independent of its environment which does not mention the input and output of raw materials and energy. It is the same as if a biologist describing the body of an animal gave a detailed description of the circulatory system without mentioning the digestive track. An animal with an isolated circulatory system without a digestive tract would be a kind of a perpetual motion machine.

Together with Herman Daly, we can conclude these considerations by saying that we are at the point where further growth of the economy does not make us richer, but poorer. It seems that redistributive policies, a comprehensive (ecological) tax reform, and the efficient use of resources will have to be implemented as instrument for eliminating poverty.

Sustainable development in this sense does not mean the end of economics. On the contrary, when economic growth reaches its limits, economics becomes a more important discipline than ever before, but it is a subtle and complex economics of cultivation and quality improvements, an economics of solidarity, frugality, humility, and adaptation to the limits which nature puts to us. It is an economics which seeks quality, not expansion.

Ecological tax reform

Ecological tax reform occupies the prominent position among the environmental and sustainable development economic instruments. The idea is one hundred years old and its originator was the economist Cecil Pigou (so called Pigou tax).

The essence of the ecological tax reform is to shift the tax burden from what we want to have in sufficient amounts (e.g. labor) onto what we want to have in minimal amounts (e.g. 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 labor.

The principle of the ecological tax reform is fiscal (budget) neutrality. That is, what the state obtains from the higher taxation of natural resources is „dissolved“ in a decrease in labor taxes. It is therefore not a new tax, but a comprehensive tax reform which would increase primarily excise duty and environmental protection taxes and reduce (or even revoke) income tax and value added tax.

The ecological tax reform is a complicated strategic gambit. Therefore it is envisaged that the start of the ecological tax reform would be gradual and might take over a decade.[13]

[13] If, for example, the prices of energy and raw materials increased by 5 % annually, they would double in 14 years and they would increase four times compared with the original levels in 28 years.

The long implementation of the ecological tax reform is, however, also an obstacle to its political implementation. In democratic systems politicians are elected for 4 – 5 years and their considerations are bound to this time limit. It is difficult for them to embrace a comprehensive tax reform the significant benefits of which may materialize far beyond their mandate.

Another obstacle to the implementation of the ecological tax reform is that it should be introduced at one moment in a large and robust economic space. Ideally, it should be introduced globally, but this is unrealistic with respect to the present day profound economic, political and cultural differences. Considering this, it is perhaps the European Union that has the greatest chance for the implementation of the ecological tax reform. It is strong enough economically to implement it and prevent the collapse of its trade balance with those countries and regions which will not introduce the reform.

It may be expected that the benefits resulting from the implementation of a comprehensive ecological tax reform would significantly outweigh the potential risks and costs. The clear consequence of the reform would be that businesses and households would use natural resources in a more efficient way. Businesses would be motivated to use modern, more efficient technologies, households would invest primarily in energy savings (insulation of houses and apartments, energy efficient light bulbs etc.). The introduction of the ecological tax reform would provide a new impetus for using renewable energy resources, for the more thorough recycling of materials and for longer product lifetime. Nor can we forget the support of employment, because human labor subjected to lower taxation will be cheaper.

Carbon tax

The system of excise duties is a widely accepted tool for regulating human behavior. A carbon tax, i.e. a tax on fossil fuels the burning of which produces the greenhouse gas carbon dioxide could work similarly to excise duties. People whose lifestyle produces high CO_2 should pay by means of the carbon tax and its redistribution to people who do not produce such large quantities of CO_2.

The carbon tax should encourage not only the replacement of highly polluting sources with less polluting ones, but also savings.

It is desirable to introduce and gradually increase the carbon tax on fossil fuels to a level at which the price of energy generated from fossil fuels equals the price of energy from highly efficient renewable energy sources. Under such conditions, each subject will perceive the cost of energy as very high. It will increase the overall demand for efficient energy saving measures.

The patterns of human behavior will change in favor of lower energy demands and energy generating facilities using fossil fuels will be replaced with efficient sources employing renewable energy.

It is advisable to outline the carbon tax project on a worldwide scale, because climate change occurs globally as well. The tax should be collected by a „central world bank“ at the moment of fossil fuel extraction. Because the number of mining companies in the world is relatively small, it should be feasible to control the collection of taxes. After that, fossil fuels would be traded with the burden of the carbon tax, which would prevent tax evasion on imports and exports.

Initially, the carbon tax should be low in order to allow smooth reactions to various unexpected and unintended effects. It would grow gradually to an estimated target level somewhere between USD 100 – 200 per ton of CO_2.

The mechanism of carbon tax redistribution would include the principle of solidarity. Maximum solidarity would be achieved through the flat redistribution of the collected tax, i.e. each person in the world would receive the same amount. This would reflect the „right“ of everyone to contribute to CO_2 emissions produced by the country. The even distribution of the collected tax among the citizens could be administered through an increase in pensions and for working people through income tax deductions proportional to the number of their dependents.

The carbon tax would solve many social problems of a local and global character. It would create a flow of money from the rich countries producing large amounts of CO_2 emissions to the poor countries with low CO_2 production. If 80 % of the carbon tax was distributed by the amount of CO_2 emissions produced in the given country and 20 % by the size of the population, the carbon tax would bring benefit to everyone in a high CO_2 emission country who consumed less than 80 % of the countrywide average of CO_2 emissions. Because the majority of the population consumes less than 80 % of the countrywide emission average, this model could be politically acceptable.

The introduction of the carbon tax would change the market environment in favor of energy savings and low carbon technologies. It could also reduce the bureaucracy which has sprouted up around the problems associated with global climate change.

The introduction and gradual increase of the carbon tax would necessitate the discontinuation of all subsidies. Also, in a system with no subsidies, institutions which distribute them would become unnecessary.

Conclusion

If we are to ponder the concept of sustainable development thoroughly and honestly, we cannot avoid the elementary questions accompanying the pilgrimage of human life. Who are we? Where do we come from? Where are we going?

It all began with the Big Bang more than 13 billion years ago and with the formation of inanimate matter, which took 9 billion years. Then, less than a billion years after the planet Earth was botn, 3,85 billion years ago the first transgression took place: the evolution of inanimate matter transformed into biological evolution. The latter has been proceeding on Earth ever since and in spite of numerous turbulences and „disasters“ it has never stopped.

Life has been developing genetically, that is in information (genes) encoded in chromozomes, which govern the individual´s development from cell fertilization until the adult stage. In higher animals this development has continued even paragenetically, when the new individual must first learn from its parents or the species group to survive in the environment.[14] The third stage is metagenetic evolution, applicable only to humans.

The moment the „human mind evoke“ the second transgression took place: biological evolution transformed into cultural evolution (materialized through humans). Cultural evolution runs from the development of tools, the use of fire, agriculture, architecture, the invention of writing, philosophy, and science to the rapid expansion of the homosphere and subsequently the noosphere.[15]

In the noosphere, information, knowledge, and the ability to communicate spread breathtakingly fast. We have reached a technological stage when each of us can be identified at any given moment anywhere around the globe. We live in a stage of total globalization. This situation has two possible outcomes; either self-destruction or the third transgression and a shift to the next evolutionary stage, the stage of spiritualization.

[14] For example, a young bird of prey learns how to catch prey from its parents. The higher the organism, the longer the „education“ of the young ones takes.

[15] The homosphere is defined by the presence of humans and the extent of their influence. The homosphere is where the presence and influence of human beings predominates. The noosphere originates when the power of human intellect transforms the biosphere. It is the sum of knowledge and information accumulated by people throughout history. Human beings use this knowledge and information to change and transform their environment (biosphere).

This stage (if people manage to successfully enter it) should witness the realization of the biosociological self-organization of humankind, when people start determining and controlling their further development.

It is hard to imagine that one day the mind should prevail over matter, the spiritual over the physical world. In other words, human nature should transform. Perhaps this is precisely the meaning and final purpose of the extremely long process of transformations from the mineral, i.e. inorganic sphere Alpha (from the sphere of the inanimate physical world) through the biosphere (the revived world) to Omega, the sphere of spiritualization and pure spirit. Teilhard de Chardin[16] posits that arriving at the Omega Point is the ultimate goal of the evolution of the universe.

In order to eliminate risks, harm, and suffering as much as possible on our path to controlled evolution we need to change course. Changing course will require an immense amount of energy. Not the energy that comes from coal, gas, oil, or even nuclear fuel, but rather spiritual and emotional energy, enough to change the thinking and lives of more than eight billion people.

Questions for self-control

1. What is definition of sustainable development?
2. What are three basic features of humanity?
3. What are five different approaches to environmental ethics?
4. What are examples of positive shifts in value orientations?
5. What are four purposes of the economy according to Arthur Rich?
6. What are principal ideas of ecological tax reform and carbon tax?

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[16] Pierre Teilhard de Chardin (1881 – 1955) was a Jesuit who trained as geologist and paleontologist. In his important book „The Phenomenon of Man“ (1989) he introduces an original synthesis of the biblical idea of Creation and the end of the world with an evolutionary concept of development.

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Chapter III

INLAND WATERS: TYPES, THREATS, CHALLENGES

In this section you will learn about

- ✓ Inland water resources
- ✓ Hydrological and ecological characteristics of artificial water reservoirs.
- ✓ Large and small retention
- ✓ Types of artificial retention reservoirs
- ✓ Quality of inland waters
- ✓ The role of bottom sediments in the aquatic ecosystem
- ✓ Technological possibilities of removing organic pollutants from bottom sediments

Key words:

Inland water
Quality of inland waters
Organic pollutants
Bottom sediments

Inland waters are aquatic environments within land boundaries. This definition also covers transitional waters in coastal areas, even in the vicinity of marine environments. Inland water systems can be fresh, brine or mixed. Inland waters should not be equated with freshwater only. According to the common systematics, the Caspian Sea (freshwater) and the Dead Sea should be classified as such, while the Baltic Sea (also largely freshwater) will be excluded from this classification (UN 1982). In practice, however, inland water conditions focus on freshwater, in large part because freshwater

environments dominate inland waters, but also because of the importance of freshwater in the world. This definition covers all possible types of landward water bodies, including groundwater and groundwater. From an ecological and hydrological point of view, all groundwater and groundwater form an integral part of the inland water ecosystem, as freshwater from precipitation flows down the ground and feeds rivers, lakes and wetlands.

Inland waters, especially rivers, are part of all landscapes. On a smaller scale, inland aquatic ecosystems are also found in all terrestrial biomes - including meadows, mountains, forests, islands, agricultural areas, inland stretches of coastal zones, and deserts, where oases and seasonal or transitional rivers sustain life. Inland waters thus include lakes, rivers, ponds, streams, groundwater, springs, flood plains, as well as peatlands, wetlands and swamps that are traditionally grouped as inland wetlands.

Exploitation of water resources and neglect of issues related to their protection contributed to the progressive degradation of the environment. One of the main determinants of the severity of anthropopressure is the presence of organic and inorganic compounds in the bottom sediments, including heavy metals. They are not biodegradable but only biotransformed and can be immobilized in bottom sediments for a long time. However, the disruption of the structure of bottom sediments causes them to move to the upper layers of the water and to transport and deposit elsewhere. For this reason, pollution of bottom sediments is one of the most important environmental problems.

The coming years will be a time when Europe will be guided by the policy of the Green Deal. Its main goal is to reduce pollution by investing in environmentally friendly technologies. In recent years, there has been a significant increase in interest in the possibilities of stopping or reversing the ongoing degradation of the natural environment, caused by anthropogenic factors. The removal of pollutants from the aquatic environment is generally costly and very difficult. Effective activities in this area require knowledge of the types of pollution, in particular their physicochemical properties, as well as the geological structure of the catchment area, hydrological conditions of the water ecosystem, and the scope of activities and objectives required to achieve. Most anthropogenic chemicals, such as pesticides, phthalic acid esters, polycyclic aromatic hydrocarbons (PAHs) and many others, are poorly disposed of by conventional processes. As a result, new technologies based on the concept of green chemistry are implemented.

3.1. Inland water resources.

The earth's water resources are very large - but most of it is salt water in the oceans. Salt waters account for over 97% of the Earth's water resources. The remaining 3% is fresh water, which is largely trapped in glaciers and polar snows. Groundwater accounts for slightly more than 0.5% of water, and only 0.1% of water in rivers, although it is estimated that the outflow of inland waters to the seas this way

is approximately 37,000 km^3 annually (PFOZ 2019). About 0.4% of the world's water resources are closed in natural lakes, but interestingly, about 20-25% of this resource is retained in Lake Baikal, which, according to estimates, can provide a permanent water supply for over a billion people (PWN 2019). Tables 3.1 and 3.2 summarize the total distribution of waters and fresh waters in individual geocomponents occurring on the Earth.

Table 3.1

The world's water resources (Małecka and Staszewski 2015)

Types of waters	Volume x 1000 km³	% of the total
The waters of the world ocean	1338000.0	96.5
Glaciers and permanent snow cover	26064.1	1.74
Groundwater	23400.0	1.7
including active waters (up to 100 m)	10530.0	0.76
Permafrost	300.0	0.022
Lakes	176.4	0.013
Soil waters	16.5	0.001
Water vapor in the atmosphere	12.9	0.001
Swamps	11.47	0.0008
Rivers	2.12	0.0002
Biological water	1.12	0.0001
Total waters of the hydrosphere	1385984.0	100.0

Table 3.2

Freshwater resources (Małecka and Staszewski 2015)

Types of waters	Volume x 1000 km³	% of the total
Glaciers and permanent snow cover	24064.1	68.7
Groundwater	10530.0	30.1
Permafrost	300.0	0.86
Sweet lakes	91.0	0.26
Soil moisture	16.5	0.05
Water vapor in the atmosphere	12.9	0.037
Swamps	11.47	0.03
Rivers	2.12	0.006
Biological water	1.12	0.003
Total freshwaters	35029.21	100.0

All inland freshwater resources of the Earth could be sufficient to meet the needs of the entire population, but their uneven distribution and irrational management make the supply of people with water a huge problem in many countries

of the world. The countries of Central and Northern Africa, Central Asia and South America suffer the most from the water deficit. It is estimated that many European countries will soon struggle with the shortage of drinking water.

Poland's surface water resources vary from 40 km^3 in an extremely dry year to 90 km3 in an extremely wet year, with an average value of 63 km^3. In turn, the amount of groundwater is estimated at 15 km^3, of which 2 km^3 is available. Approximate water availability for one inhabitant is about 1600 m^3 of water per year and is up to 4.5 times lower than the global average. Additionally, access to these resources is heterogeneously distributed both seasonally and spatially. Most of the areas of the Polish Lowlands struggle with the deficit in the water balance for 6-9 months a year. On the other hand, the outflow from the submontane catchments during periods of intense rainfall or snowmelt results in a strong flood wave. The value of river outflow from Poland per capita in the nineties ranged between 1.1 and 1.9 thousand km^3, and only 6% of this load was retained under artificial conditions. The described situation determines the necessity to build water retention systems both as protection against drought and floods.

The climatic changes observed in recent years and the rationalization of the use of existing water resources, forced by increasing costs, determine the search for new water sources and ways of retaining rainwater and seasonal waters. The basic method of water retention is the construction of dam reservoirs. It is also connected with an additional element of eco-development, i.e. obtaining clean electricity for the needs of the developing world economy. Recognition and understanding of limnological and hydrological processes observed in dam reservoirs treated as river-lake ecosystems, will enable an appropriate policy of exploitation and protection of these objects. Human activity can significantly change the amount of natural retention of a specific area or element involved in the water cycle in nature.

There are different forms of water retention. The basic systematics distinguish between natural and artificial retention. Natural retention is created by natural landscape elements, such as forests and smaller trees or shrubs, peat bogs and swamps, lakes and ponds, but also snow and glaciers. It plays a huge role in the water management of the catchment area. Artificial retention is identified with the construction of artificial water reservoirs, but these are also agrotechnical or drainage treatments resulting in the accumulation of water in the environment. Artificial water reservoirs play a significant role. They improve the water balance of the catchment area by influencing the biological quality of the surroundings. Additionally:

- they can stop water rising;
- they play an important economic role as sources of municipal and irrigation water;

- are an element diversifying the landscape
- they form a permanent element of tourism infrastructure.

However, it should be remembered that artificial aquatic ecosystems radically change the nature of the catchment area. This change can be both beneficial and unfavorable for the environment and people. It is important to balance the needs and effects of building a water reservoir in accordance with the principles of sustainable development.

3.2. Hydrological and ecological characteristics of artificial water reservoirs.

As already mentioned, dam reservoirs are built for the purpose of storing water in connection with providing it for municipal and energy needs, or preventing floods. The unevenness of water supply and outflow related to these tasks causes that the water retention time in reservoirs is shorter than in natural lakes with similar morphometric parameters. Most often, within the reservoirs, the river zone (in the region of tributaries) and the lake zone (lacustral − in the region of the outflow) are distinguished. Polish dam reservoirs are classified as flowing waters, because this is the treatment of water reservoirs with a continuous inflow or outflow of surface waters, as well as artificial water reservoirs located in waters with variable flow. However, from the hydrological and ecological point of view, in some reservoirs, especially deep ones with a long retention time, conditions and phenomena similar to those in natural lakes, e.g. stratification or mixing. The basic features that distinguish dam reservoirs from natural lakes are (Fig. 3.1):

- one large, anthropogenically controlled runoff, located in the deepest part of the reservoir;
- deep water discharge, partially disturbing the stratification;
- seasonal, several-meter fluctuations in water level;
- depth systematically increasing from the inflow (tributaries) to the outflow;
- physico-chemical and biological parameters of the ecosystem changing along the reservoir, from purely river to lake;
- a long coastline, usually devoid of a littoral zone;
- catchment area, even several dozen times larger than the surface of the reservoir;
- duration (existence) of the order of only several dozen years due to faster sedimentation rates and siltation due to sediment deposition and eutrophication.

Some of these differences negatively affect the usability of the reservoirs. The fact that the freely flowing river is blocked by a dam causes that the resulting reservoir has a catchment area with a large area and often with a high degree of

development. This results in a significant load on its surface not only with solid material from soil erosion, but also a large supply of chemical compounds in a dissolved state, including biogenic ones.

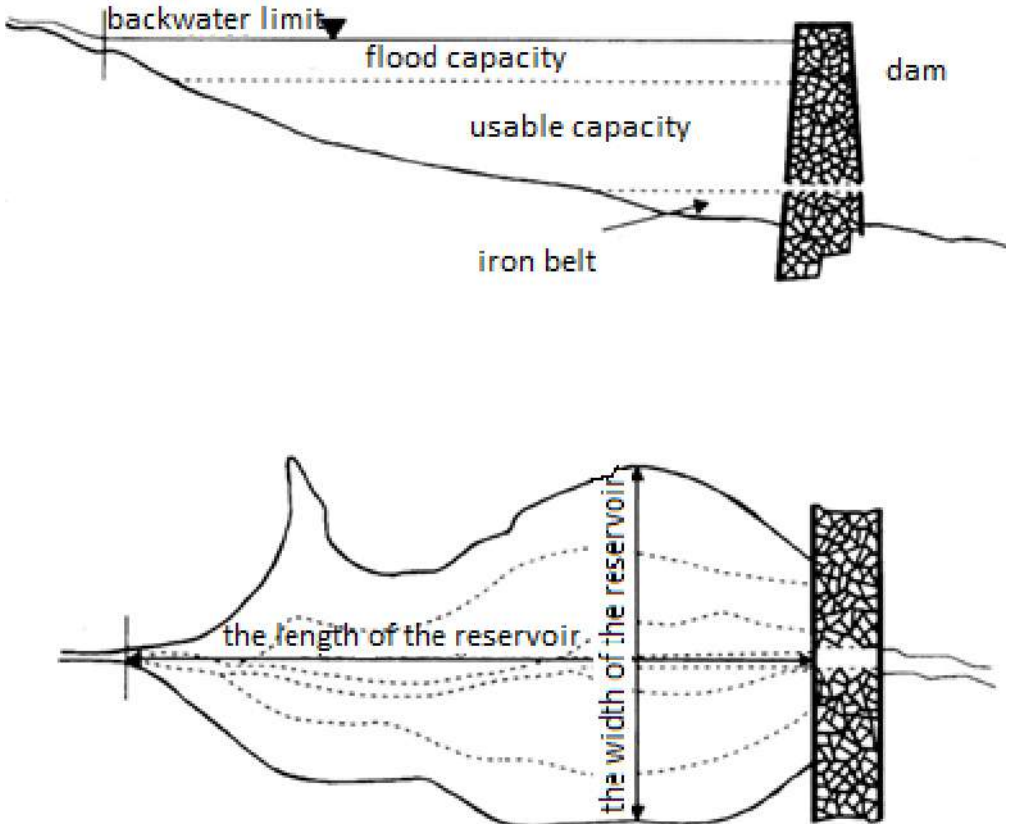


Fig. 3.1. Morphological and hydrological characteristics of dam reservoirs (Szczerbowski, 2008)

The consequence of this is the retention and deposition in the ecosystem of suspension particles supplied from the outside, as well as those produced as a result of autotrophic processes (e.g. eutrophication). Eutrophication is the most common and the most damaging anthropogenic disruption of the functioning of aquatic ecosystems. The waters are characterized by a different trophic state which determines the intensity of primary production. This leads to the formation of bottom sediments and a reduction in the usable capacity of the reservoirs. The process of shallowing having an external origin may be accelerated as a result of the accumulation of matter resulting from the processes of primary production processes in the waters (eutrophication). The time of water retention in the flooded section also increases, which further stimulates the processes of organic matter formation inside ecosystems. In this situation, the oxygen conditions in the tank deteriorate.

Reduction of water saturation with oxygen is most often observed in those

zones of reservoirs that are located closer to the dam, and is caused by its use for the degradation of indigenous matter, additional to the external matter supplied so far. This situation brings about three basic ecological problems that determine the need to balance both engineering and limnological activities at the stage of designing, building and operating reservoirs.

These problems are:

- the release of heavy metals from bottom sediments;
- emission of greenhouse gases to the atmosphere;
- modifications in the natural biogeochemical cycles of biogenic elements.

In the case of metals, one of the main issues currently being raised is the role of dam reservoirs as a specific source of mercury enriching the waters below them. This is especially true of newly built tanks. Inorganic mercury contained in flooded soils in concentrations that are often consistent with the geochemical background, undergoes biochemical transformation under anoxic conditions into the toxic mercury methyl (CH_3Hg^+), which is well soluble in the aquatic environment and undergoes bioaccumulation and biomagnification, constituting a very serious toxicological contamination.

Under low oxygenation conditions, the biomass delivered or produced within the reservoirs is decomposed into both carbon dioxide(IV) and methane. Also in this case, the production and emission of gases is intensified in the initial years of the dam reservoir's existence due to the decomposition of labile forms of terrestrial matter contained in flooded soils. A large amount of this matter determines the rapid depletion of oxygen, thanks to which the share of the fermentation product, which is methane, increases. In tropical ecosystems, greenhouse gas emission processes are intensified in the first 20 years of the reservoir's existence, for the temperate zone it may be even several dozen years.

The emission of carbon gases from dam reservoirs may constitute about 7% of the global production, and by about 60% exceeds the amount of coal retained within the reservoirs. The production of CO_2 and CH_4 is related to respiration and fermentation, respectively. The deterioration of the oxygen conditions of the reservoir shifts the balance of early diagenesis processes towards fermentation, which means that some other biogenic compounds bound in organic matter are retained in the bottom sediments or transformed into undesirable substances (e.g. S^{2-} instead of SO_4^{2-} or NH_4^+ instead of NO_3^-).

Modification of the natural cycles of transformation of biogenic elements is closely related to their easier inclusion in the trophic chain in lake ecosystems than in river ecosystems. In a sense, it is a positive phenomenon, because the excess loads of nutrients flowing from the overfertilised catchments are reduced, and the waters

leaving the reservoir are usually poorer in these compounds than the river before the dam was built. On the other hand, the collection of these elements for the purposes of biological production is associated with easier sedimentation, and the accumulated biogenic compounds cause the degradation of the ecosystem in which they have been retained. Anyway, many dam reservoirs are built precisely to retain nitrogen or phosphorus and protect other reservoirs/lakes/seas located below. The mechanisms of biogenic elements retention in dam reservoirs are similar to those that determine this phenomenon in other types of surface waters. Due to the widely observed anthropopressure in various ecosystems, they may be of different quantitative and qualitative nature.

A key and often unfavorable phenomenon accompanying the construction of artificial reservoirs is also the rising of the groundwater table in their vicinity and depends on the relief of the coastal zone, geological structure, as well as the damming height and the water management regime, i.e. damming and draining water. Preventing this negative phenomenon is difficult, costly and not always positive, therefore rational drainage solutions are needed in the adjacent areas.

3.3. Large and small retention.

In the hydrological nomenclature, there are non-standardized concepts of small and large retention. Small retention is described as a set of measures aimed at slowing down the runoff of rainwater from the catchment area, without the possibility of regulating the retained resource. Therefore, small retention is not only water reservoirs, but also all melioration activities resulting in an increase in the efficiency of soil and forest retention or regulation of watercourses. The most common border parameter to distinguish between low and large retention is retention capacity. It is considered that up to 5 million m^3, small retention should be considered, and above this value − high.

The working capacities of large retention reservoirs depend on their intended use and field conditions. Typically, reservoirs built for flood protection retain the largest amounts of water. They are located in the upper, i.e. mountain, parts of the catchment area, which means that, given their large capacity, the water surface area is not always very large. The formation of flooded mountain river valleys favors additional use for energy production. By the way, recreational functions of such reservoirs appear. The dams of the mountain reservoirs are tall but relatively short. They are deep tanks. Even slight fluctuations in the water level in these reservoirs expose the banks, thus preventing the formation of a littoral zone.

In Poland, examples of such reservoirs are the Solina-Myczkowce complexes on the San River (Fig. 3.2), Czorsztyn-Sromowce on the Dunajec River or Tresna-

Porąbka-Czaniec on the Sola River. Lowland reservoirs usually have a smaller capacity, but a larger area than mountain reservoirs. They are most often built in connection with the need to provide municipal water, e.g. Goczałkowice for Upper Silesia, Sulejów for Łódź or Dobczyce for Cracow.

Fig. 3.2. Solina high retention reservoir. Below the dam, the power plant with the upper part of the Myczkowce equalizing reservoir (photo by L. Mnich)

However, the lower the basin a reservoir is built, the greater the probability of contamination of its waters, mainly as a result of the application of eroded soil particles from the basin and eutrophic processes. Unlike natural lakes, they have drainage basins much larger than their own, which results in the deposition of large amounts of the above-mentioned pollutants and river sediment. The lower part of these types of tanks is often bounded by reverse shafts. Their dams are not high, but long. Fluctuations in the water level are smaller, lowering the damming level usually exposes large areas of the bottom of the reservoir (Fig. 3.3).

Fig. 3.3. Small retention water reservoir on the Służewiecki stream in Warsaw

3.4. Types of artificial retention reservoirs

The criteria for the division of tanks given in the literature mainly take into account the functions and tasks of tanks, as well as their parameters, location, geodynamic processes, and the method of obtaining capacity. Most of the large retention reservoirs that are currently being built are most often multi-purpose facilities, providing at the same time several detailed basic needs, including:

- electricity production;
- a place of rest and recreation;
- regulation of water conditions in the field (stabilization of the groundwater table);
- protection against floods and droughts by regulating flows;
- water supply for municipal needs;
- protection of rivers/reservoirs/lakes below.

On the other hand, small retention tanks are usually built to meet one or two of the above-mentioned needs. Due to the multiple water exchange, according to the systematics proposed by Starmach et al. 1978, there are rheolymnic (flow) and limnic (low flow) tanks. The multiple of the total water change during the year was assumed as the dividing line between these types of reservoirs. Water in rheolimic reservoirs is changed more than 10 times a year, while in limnic reservoirs less than 10 times a year. For these hydrological reasons, liminal reservoirs retain organic matter in bottom sediments, as opposed to rheolymic, where this retention is significantly lower. The division of reservoirs into rheolimic and limnic refers to both mountain and lowland reservoirs.

Flood protection reservoirs are designed to reduce the risk of flooding below the reservoir as a result of stopping and delaying the outflow of raised waters. In Poland, all major retention reservoirs are used for active flood protection. It is assumed that approximately 145 reservoirs and over-dammed lakes are used for this purpose. The total amount of the flood reserve in Poland amounts to about 800 million m^3, and it is at least twice lower than the needs.

Most of the flood control reservoirs are built as "wet" reservoirs with a fixed filling, but also "dry" reservoirs. They are mono-functional objects and their task is only to reduce the height of the flood wave. "Dry" tanks are created thanks to the construction of dams or dams, the overflows and outlets of which are not closed. In the periods between floods, the water flows naturally through the reservoir's bowl and outlets. When water flows into the tank with a flow exceeding its capacity, water accumulates in the tank. With large tributaries, water can also flow through surface overflows. Reducing the amount of water inflow from the catchment area leads to the emptying of the reservoir (Fig. 3.4).

In 2015, in the Podkarpackie Province, a "dry" reservoir with a capacity of up to 3.25 million m^3 was commissioned, near the town of Kańczuga on the Mleczka River. Currently, about 20 flood protection reservoirs are being built in Poland, including large ones, such as Świnna-Poręba (up to 160 million m^3), and projects of others, such as Kąty-Myscowa (up to 19.5 million m^3), are advanced, although the conclusions after the great flood from in 1997 indicated the need for much more intensive activities in this direction.

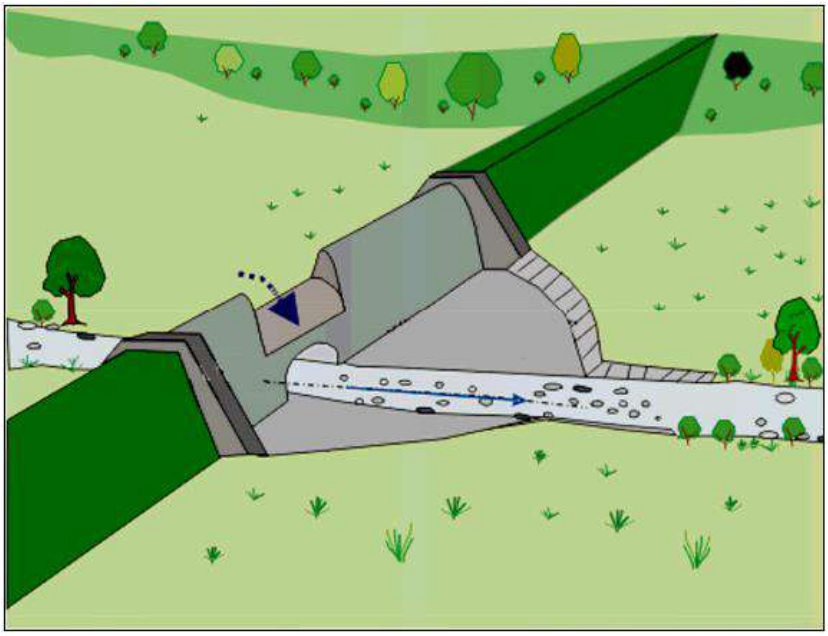


Fig. 3.4. The principle of operation of a dry reservoir dam with a central overflow

Utility tanks can be used for industrial, municipal, agricultural (irrigation), energy, shipping and recreational purposes. Industrial tanks collect water for production purposes. This water should be of a certain quality and must be supplied in the right quantity and at the right time depending on its production profile. The required capacity of the tank is determined on the basis of the projected and actual water consumption by its owner. These types of tanks, due to their work as part of the technological line, are exposed to contamination. A good example is the Rybnik reservoir, built in the 1970s as a power plant facility (at the normal water level, it has a capacity of 22 million m^3). It is a source of cooling water for the power plant, therefore the waste water returned to the reservoir is enriched with heavy metals and biogenic forms and with a stable (increased) temperature throughout the year, as a result of which contamination of bottom sediments and increased trophic status are observed.

Municipal reservoirs collect water for the purposes of supplying the population and small production plants located in cities and housing estates. The development and functioning of large cities, urban agglomerations and industry

requires water supply of appropriate quality and quantity. In Poland, about 70% of municipal water is provided by underground sources. However, for many, also large administrative units, surface waters are the main source. The Dobczyce reservoir (127 million m^3) provides about 55% of the water demand for Cracow. Additionally, it accumulates Raba's floods and supplies the hydroelectric power plant. Due to its tasks, it does not fulfill recreational functions.

Agricultural tanks are intended for storing water for irrigation and fish farming. The capacities of these tanks are in a wide range from 0.01 million m^3 to over 50 million m^3. Irrigation tanks store water in the autumn and winter period, while its use takes place in the period from May to September. Agricultural tanks are characterized by a large working layer and thus significant fluctuations in water levels. They influence the microclimate and the condition of water resources in the catchment area. They constitute a refuge for water and marsh birds and are an important element of the countryside landscape. In Poland, a model example of this type of tanks is Siemianówka on Narew. This lowland reservoir collects approx. 60−80 million m^3 of water, ensuring the irrigation of approx. 15 thousand. hectares of arable land and 20 thousand. hectares of valuable natural areas. At the same time, the reservoir is a habitat for numerous species of birds, including those protected as the black stork, and also provides about 15−30 tons of fish per year. It is a significant element of recreational infrastructure and cooperates with a hydroelectric plant.

In a large number of countries, dam lakes are the basis for the development of energy that uses the energy potential of rivers. Where energy is based on thermal or nuclear power plants, dam lakes together with hydroelectric power plants supplement the energy base. Compared to other utilities, hydropower plants deliver significant amounts of energy at low cost (Sørensen, 2004). Electricity from hydropower plants is classified as a renewable energy resource, although, as described above, it cannot be said that it is a zero-emission technology from the point of view of greenhouse gas emissions.

There are several types of hydroelectric power stations. Run-of-river power plants use the natural flow of water in slope conditions and do not require back-up and construction of a reservoir or reservoir. This technology is applicable to both large and small local (less than 5MW) power plants. The situation is slightly different in the case of pumped storage power plants, which include at least two tanks, upper and lower (equalizing). In the period of low energy demand, water from the lower reservoir is pumped to the upper reservoir, and in the period of peak energy demand, the drain from the upper reservoir generates energy production (Fig. 3.5).

The Solina and Myczkowce reservoirs located in the Podkarpackie Voivodeship together with the technical infrastructure constitute an element of the

Solina-Myczkowce S.A. Hydroelectric Power Plant Complex, which can provide an average of 262 GWh of ecologically clean electricity. It allows to save about 120 thousand tons of carbon and eliminate from the environment about 32 thousand tons of carbon(IV) oxide and 320 tons of sulfur(IV) oxide. Outflow from the upper reservoir, and thus supply to the lower one, are carried out through three overflow sections with overflows for emptying water or through the above-mentioned four pipelines concreted at a depth of 40 m with installed turbine sets. Discharges from the Solina Reservoir constitute about 90% of the total hydraulic load supplying the Myczkowce Reservoir, which means that its waters are characterized by low temperatures in summer and warmer in winter. Both reservoirs accumulate up to 500 million m^3 of water, which accounts for approx. 15% of the total artificial water retention in Poland.

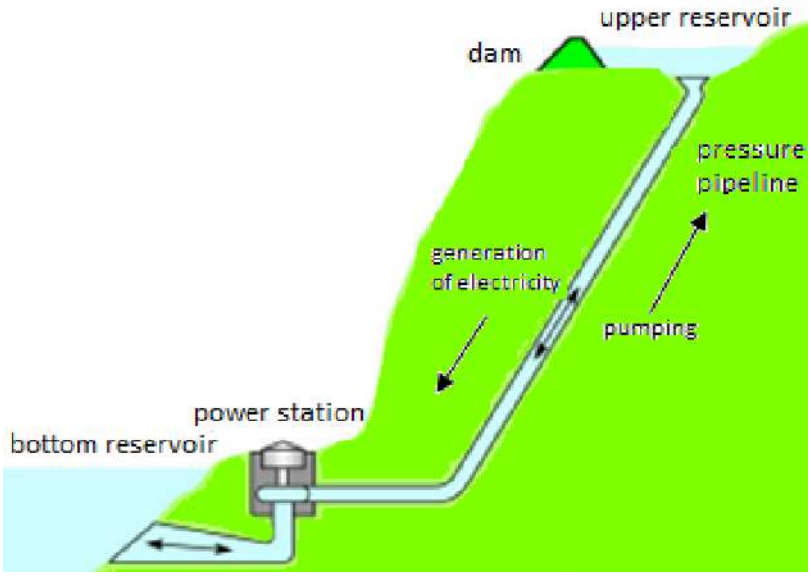


Fig. 3.5. Principle of water operation of a pumped storage power plant

3.5. Quality of inland waters.

Changes in the quality of inland waters

Quantitative and qualitative degradation of inland water systems has been initiated by many factors acting individually and synergistically or also cumulatively. Directly responsible are the changes resulting from the functioning of agriculture (irrigation, but also drainage), the spread of urban, industrial, tourist and recreational infrastructure. These changes mainly affect salinity and eutrophication. Global climate change, perceptible in recent decades, is likely to lead to even further degradation and exacerbation of existing pressures. Two phenomena are being observed and will continue to be: (i) changes in species diversity within aquatic habitats; (ii) emergence of new pollutants having a therapeutic effect at micro or nano

concentrations per dm^3.

Changes in species diversity within aquatic habitats are well described by the Living Planet Index (LPI) developed by the United Nations Environment Program. The LPI shows changes in 3,000 populations of 1,145 vertebrate species worldwide and in different types of aquatic habitats. For freshwater habitats, 93 populations of fish species, 67 amphibians, 16 reptiles, 136 birds and 11 mammals were observed. The LPI shows that freshwater populations declined systematically at a faster rate than other species groups, with an average decline of 50% between 1970 and 2000. In the same period, both land and marine fauna decreased by only 30% (Fig. 3.6). This is an extremely negative trend that proves that inland waters are becoming a habitat difficult to live in. The Water Framework Directive contains regulations based on many years of observations of the impact of chemical environmental pollutants on populations and species diversity. On this basis, the principles of monitoring the aquatic environment have been developed, where biological elements (indicators) determine the classification of the ecological status of surface waters, while physicochemical indicators - often treated as decisive - are only supporting elements (GIOŚ 2015).

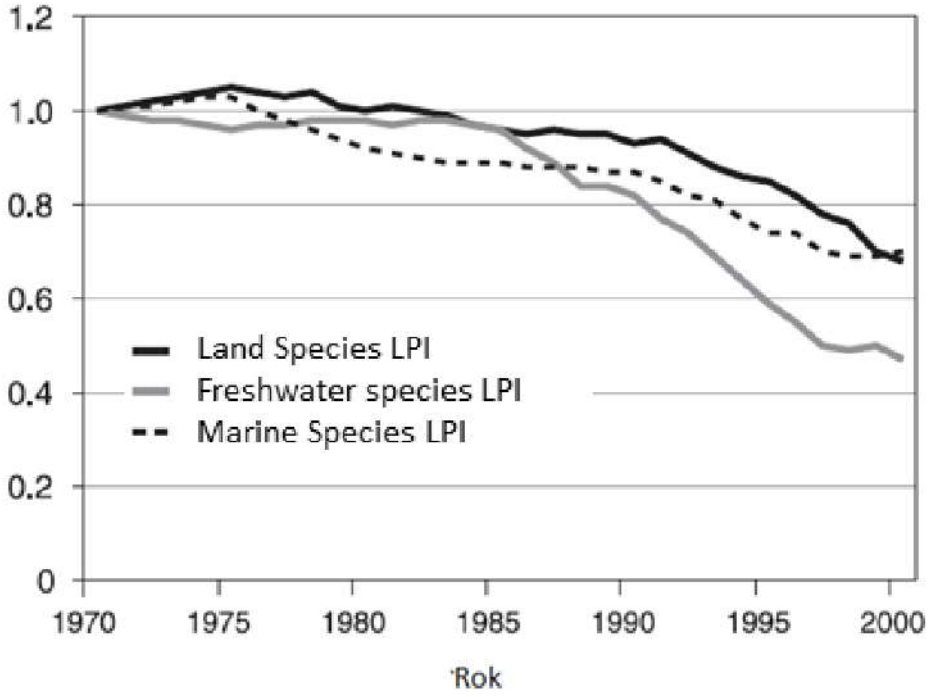


Fig. 3.6. Changes in the Living Planet Index for different types of water

It is well known that nutrient concentrations have increased significantly in inland waters around the world, resulting in progressive eutrophication, harmful algae blooms, and high levels of nitrate in drinking water. In industrialized countries, pollution with municipal wastewater has been largely eliminated, but unfortunately, more and more pollutants are appearing, the negative impact of which on the

condition of aquatic environments is still unknown. Developing countries, apart from growing micropollutants, are still struggling with large loads of biogenic compounds polluting surface waters. In Europe, it is believed that the agricultural sector generates around 50% of the total nitrogen and phosphorus load that feeds rivers. Municipal sources account for around 25%, and industry and atmospheric deposition for another 25%.

Meybeck (2003) provides an overview of water pollution problems in inland waters (Table 3.3). It is clearly visible that organic micropollutants are becoming a global problem. Identification of sources of origin and methods of their elimination in situ are today one of the main elements of water protection.

Table 3.3

The reasons for the deterioration of inland water quality
(Meybeck 2003, Finlayson et al. 2006)

Contaminant	**Rivers**	**Lakes**	**Artificial tanks**	**Groundwater**
Pathogens	xxx	x	x	xx
Suspensions	xx	na	x	na
Decomposable organic matter	xxx	x	xx	x
Eutrophication	x	xx	xxx	nd
Nitrates	x	0	0	xxx
Salinity	x	0	x	xxx
Heavy metals	xx	xx	xx	xx
Organic micropollutants	xxx	xx	xx	xxx
Acidification	x	x	xx	0
xxx – a serious global threat xx – significant threat x – occasional regional threat 0 – slight threat nd – not applicable				

Newly emerging pollutants

Reports on the presence of other, unusual pollutants in aquatic ecosystems are increasingly appearing in the scientific literature. These compounds are referred to as "emerging pollutants" (EC's), less frequently "emerging contaminants", "emerging substances", "contaminants of emerging concern". In Polish, they are most commonly referred to as "newly emerging pollutants/micropollutants".

'Newly emerging micropollutants' are trace pollutants, recently introduced or

found in the environment, largely due to the development of new analytical techniques that have allowed a significant reduction in the detection limit of micropollutants in environmental samples. Micropollutants in the environment appear and often have a therapeutic effect at the level of trace concentrations ranging from μg to below ng. Despite the fact that most of these substances are present in very low concentrations, they are a great threat to the environment because they are resistant to biodegradation and have a negative impact on living organisms. These are substances of both natural and anthropogenic origin, but the main threat to human health and life and to fauna and flora are anthropogenic micro-pollutants, which are part of products produced industrially on a large scale. Table 3.4 presents the main groups of newly emerging anthropogenic micropollutants detected in the environment and their exemplary impact on living organisms.

Table 3.4

Examples of newly emerging micropollutants in the environment and their impact on living organisms (Ziembowicz 2018)

Group of micropollutants	**Examples of substances**	**Effect on living organisms**
Antibiotics	Tetracycline, Erythromycin	Resistance to antibiotics
Disinfectants and disinfection by-products	Alcohols, aldehydes, oxidants and trihalomethanes	Genotoxicity, cytotoxicity, carcinogenicity
Personal hygiene products	Parabens	Bacterial resistance, endocrine disorders
Flame retardants	Polybrominated diphenyl ethers	Endocrine disorders, indicating an increased risk of cancer
Pesticides and insecticides	Permetryna, Fenitrotion	Zakłócenia endokrynologiczne
Plastyfikatory	Dioctyl phthalate, dibutyl phthalate, di(2-ethylhexyl) phthalate	Endocrine disorders, indicating an increased risk of cancer
Perfluorinated organic compounds	Perfluorooctanoic acid, perfluorooctane sulfonic acid	Hepatotoxic and teratogenic effects, negative influence on the reproductive and endocrine systems
Benzotriazoles	1H-benzotriazole, 5-methylbenzotriazole	Toxic, mutagenic and carcinogenic properties

The presence of groups of organic micropollutants in surface waters proves that conventional methods of wastewater treatment are insufficient and research on the development of an effective method of elimination of these compounds, which

are often very dangerous and toxic to the environment in small amounts, remains valid. Anthropogenic micropollutants most often do not biodegrade and are classified as difficult or non-degradable compounds. They are characterized by relatively long decay times, which depends on the type of pollution and natural conditions.

Due to the fact that the anthropogenic micropollutants occurring in the environment are very diverse in terms of their chemical structure, and thus − they have different physicochemical properties and have a different effect on living organisms present in the environment, there is no single pathway for the transformation of these pollutants in the aquatic environment. Under environmental conditions, they undergo multidirectional changes under the influence of physical, chemical and biological factors. Microorganisms play the main role in the mineralization of organic pollutants in the environment, however, the products of biological transformation may be more toxic than the original product. Transformation of pollutants in the environment may also occur as a result of abiotic factors, such as: UV radiation, free radicals or temperature.

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, Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 (Water Framework Directive) establishing the framework for Community action was developed in the field of water policy. 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 have been changed by Directive 2008/105/EC of December 16, 2008. 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 strongly changed water bodies.

The current legal act is Directive 2013/39/EU of 12 August 2013, which introduces the obligation to test the levels of certain hazardous chemical compounds in matrices other than waters, such as bottom sediments, fauna and flora, because the concentrations of pollutants in the water phase do not reflect the actual state. This document also updates the list of hazardous priority substances, recognizing, inter alia, di(2-ethylhexyl) phthalate is environmentally hazardous. Directive 2013/39/EU also extends the list of monitoring priority substances by another 12 substances or groups of substances, and tightens the environmental quality standards for seven applicable pollutants, and at the same time introduces the obligation to monitor

chemical compounds from the so-called watch list that may pose a risk to the aquatic environment. Some of them are also included in the so-called persistent organic pollutants (POPs), covered by the provisions of the Stockholm Convention, on the basis of which Regulation EC No 850/2004 and the amendment to Directive 79/117/EEC were developed. The first list contained twelve substances, most of which belong to the group of pesticides and PAHs. The list of these contaminants is open, and the most important are pharmaceuticals and substances contained in cosmetics, anti-ignition impregnates, products produced during water treatment (UPU) and water disinfection (UPD).

The harmfulness of pollutants on the natural environment is determined by many factors. One of the most important is the impact of pollutants on plant and animal organisms and on humans. Monitoring the pollution of bottom sediments allows for early identification of undesirable changes in the water ecosystem and for taking measures to reduce and eliminate pressures and negative environmental impacts. The greatest threat are organic substances such as phthalic acid esters, pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzodioxins (PCDDs), etc.

The presence of phthalic acid esters in bottom sediments can, to a large extent, select the biocenosis. Exposure to these types of compounds is related to, inter alia, with hormonal imbalance, reduced survival of aquatic organisms and reproductive problems. Phthalates belong to the group of exogenous endocrine disrupters (EDs), which disrupt the functioning of the endocrine glands and are toxic to the reproductive system of mammals. Changes in the species composition of benthos mean that some environmental processes, such as biodegradation and productivity, may be seriously disrupted. The loss of any population that is part of the biocenosis can directly or indirectly affect other components of the ecosystem. The extinction of species sensitive to the increase in environmental pollution may also lead to the dominance of species tolerating hazardous substances, which in turn may disturb the natural competitiveness and affect the dynamics of the population of higher organisms.

Contaminated sediment not only causes disease and extinction of aquatic species, but also poses a danger to humans and animals consuming contaminated fish flesh. Phthalic acid esters enter the human body mainly through the alimentary system, through the skin and as a result of inhalation. The amount of a substance that can be taken up by the human body is an indicator of exposure to a given chemical pollutant. Based on the measurements of the concentration of this substance in the environment, body weight and exposure time, it is possible to estimate the daily dose

of the substance taken up by the body. The tolerable daily intake (TDI) for DEHP is in the range of 40 - 140 μg/kg body weight/day. An example of a daily human consumption of di(2-ethylhexyl) phthalate is summarized in Table 3.5. The presence of DEHP in the highest levels has been found in dairy products, meat and fish, as well as in other products characterized by a high fat content.

Table 3.5

Human consumption of DEHP by age group (IARC, 2013)

Matrix	**DEHP dose (ng/kg body weight/day)**				
	0 – 0.5 years	0,5 – 4 years	5 – 11 years	12 – 19 years	20 – 70 years
Air	0.03 – 0.3	0.03 – 0.3	0.04 – 0.4	0.03 – 0.3	0.03 – 0.3
The air inside	860	990	1200	950	850
Drinking water	130 – 380	60 – 180	30 – 100	20 – 70	20 – 60
Food	7900	18000	13000	7200	4900
Soil	0.064	0.042	0.014	0.04	0.03
Sum	8900 – 9100	19000	14000	8200	5800

The only survey of the Polish population so far conducted by Struciński et al. (2006) showed that in all analyzed blood samples significant amounts of the most commonly used phthalates were found. The concentration of DEHP in most of the analyzed samples ranged from 49 to 293 ng/g of blood. According to the US EPA, phthalates are among the substances that are possibly carcinogenic to humans. Therefore, the EU Commission Regulation No. 143/2011 of February 17, 2011 on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) included six substances on the list, of which DEHP, DBP and BBP meet the criteria, which allow their classification as toxic for reproduction - category 1B. In addition, DNA damage has been found in humans exposed to these substances. Some of them cause genetic aberrations, adversely affect reproduction and further development, and lead to endocrine disorders. Phthalic acid esters block testosterone production in men, causing fertility problems, and in women, they lead to premature puberty. Exposure to phthalates in pregnant women is a significant concern as they are able to cross the placental barrier and easily enter the developing fetus. They disrupt the development of reproductive organs in male fetuses, in children they affect the development of the

brain and changes in the lungs.

Experiments by Swan et al. (2005) unequivocally showed that phthalic acid esters passing through the placenta into the child's body are metabolized much slower and their concentrations are twice as high as compared to the mother's body. Epidemiological data published in 2012 confirmed the role of di(2-ethylhexyl) phthalate in the development of mental disorders in children, such as autism and attention deficit hyperactivity disorder (ADHD). However, the role of phthalates in the formation of these disorders has not been clarified so far, as has the mechanism of their action in the nervous system. In addition, phthalates are toxic to the liver and kidneys, possibly increasing the risk of breast cancer, asthma and allergies. Exposure to phthalate metabolites has been associated with the observed infertility, toxicity and malformations in animals. Although di(2-ethylhexyl) phthalate is characterized by a lower acute toxicity compared to MEHP - the lethal dose of LD50 for rats is 25 g DEHP/kg body weight and 1.5 g MEHP/kg body weight, it should be taken into account that people are chronically exposed to DEHP throughout their lives.

3.6. The role of bottom sediments in the aquatic ecosystem

Bottom sediments are one of the elements of the environment into which the most pollutants are introduced and their number continues to increase in the environment. Additionally, bottom sediments are one of the most important components of any aquatic ecosystem. They arise as a result of the accumulation of allochthonous substances that flow into the water reservoir from the surrounding catchment area, and of indigenous substances, i.e. matter formed from mineral substances precipitated from the water phase and undecomposed organic matter. As a result of sedimentation of material suspended in the water column, sedimentary matter is formed, the three-phase structure of which makes it a natural geosorbent, accumulating pollutants introduced into the aquatic environment.

The content of pollutants in bottom sediments is influenced 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 the 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 the sediments is constantly changing. It is a consequence of the decomposition of organic matter, precipitation and exchange of components during the course of processes such as sorption − desorption, dissolution - precipitation, which are related to the change of physicochemical conditions (salinity, pH, temperature, oxygenation).

The chemical composition of bottom sediments is also significantly influenced by changes in the degree of water oxygenation, water balance, primary production and the intensity of photosynthesis processes, especially the persistence of periodic advantage of evaporation over supply and changes in the intensity of denudation in the catchment area, directly affecting the sedimentation rate. The method of the catchment management also determines the quality of bottom sediments. 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 as well as gas and dust pollution of the atmosphere are the source of information on the degree of anthropopressure in the water ecosystem. In turn, the analysis of the content of pollutants in bottom sediments is an important source of information to determine the origin, speed and distribution routes of chemical compounds in the aquatic ecosystem. Particularly high concentrations of chemicals in the sediments are detected near anthropogenic sources of pollution (Table 3.6).

Table 3.6

The origin of selected organic pollutants (Siebielec et al., 2015)

Organic pollutants	Source
organochlorine pesticides	plant protection products
polycyclic aromatic hydrocarbons (PAHs)	transport; hard coal processing; incineration of municipal waste; fires; crude oil processing
polychlorinated biphenyls (PCBs)	incineration of hospital waste; coal combustion in power plants; transport; technological processes; leaks from heat exchangers
phthalic acid esters (phthalates)	production of plastics; production of floors, roofs, walls, cable covers; medical devices

Although a significant part of low-solubility and low-degradable inorganic and organic pollutants entering the aquatic environment are retained in the bottom sediments at the final stage of the self-purification processes, some of them may be re-activated into the water phase as a result of the sediments of chemical and biochemical processes (molecular diffusion, dispersion, resuspension, bioturbation). The process of releasing the ingredients into the water column can be triggered, among others, by as a result of mechanical disturbance of the sediment structure as a result of natural processes (flood, high water levels, wind waves). Moreover, during a flood, contaminated sediments can be transported and deposited in other places, also

not included in the water ecosystem (except for the river bed in floodplains).

Another significant problem is the excessive accumulation of bottom sediments, which causes a number of adverse effects in water reservoirs, hindering their proper functioning. The results of the research on the silting process of medium and large dam reservoirs located in Poland confirm the occurrence of operational problems. The accumulation of bottom sediments is the basic factor influencing their service life. The increase in the thickness of bottom sediments primarily contributes to the reduction of the capacity and depth, limiting the usability of water reservoirs. In the part of the inlet to the water reservoir, there is shallowing and intensive overgrowing with vegetation, which contributes to flooding or flooding of the adjacent areas during floods. 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, which is particularly important in the case of reservoirs that are a source of drinking water, and which are not adapted to remove micropollutants. Recreational functions are also limited and, above all, it is difficult to properly conduct water management.

The intensity of silting of a water reservoir depends on many factors, resulting from the complex relations between the shape and surface of the catchment, the nature of its use, climate and the fluvial system (Table 3.7).

Table 3.7

The main factors influencing the silting process (Gwóźdź, 2007)

Hydrological parameters and hydrographic catchments	**Reservoir geomorphology**	**The geological structure of the catchment area**
• catchment area • way of using the catchment area • river network density • the state of watercourse regulation • basin hypsometry • the amount of rainfall in the catchment area	• development of edge abrasion	• susceptibility of the substrate to the development of erosive processes • mineral and petrographic composition of the substrate

These factors affect the course of erosion processes in the catchment area, the amount of sediment runoff denudation and ultimately the amount of mineral material flowing into the water reservoir. However, the accumulation of bottom sediments is primarily determined by the intensity of transport of particularly suspended sediment

and the ability of a water reservoir to retain it.

The phenomenon of reservoir silting has both a geochemical and a technical aspect and is often analyzed in terms of quantity and quality. Qualitative research includes, among others, the determination of the physical and chemical properties of bottom sediments and the assessment of their variability as they move away from the reservoir feeding point. In terms of quantity, changes in the thickness of sediments accumulated in the reservoir at specific intervals are determined. This allows to characterize the sedimentation dynamics and forecast the rate of decrease of the reservoir capacity during its operation.

Small retention reservoirs are characterized by more intense silting compared to large retention dam reservoirs. Measurements of the volume of river sediment retained in the reservoir were made after 10, 13 and 14 years of operation. The degree of silting was respectively 13.08%, 15.79% and 16.20%, while the annual average was 0.87%. 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%. The low value of the silting degree of the Wilcza Wola Reservoir, which is classified as a small water reservoir, despite the high intensity of transported sediment, may result from its considerable capacity (3,860,000 m^3).

Research aimed at determining the thickness increment of bottom sediments was also carried out by Madeyski et al. (2008), 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%. If the capacity of the tank is reduced by 80%, it does not fulfill its function. On the other hand, the functions of small water reservoirs are limited as soon as the capacity is reduced in the range of 40−60%. As a consequence of this, silting of water reservoirs necessitates the removal of sediments from the bottom, which primarily includes such aspects as: protection of water reservoirs against decreasing usable capacity, the need for proper management of the efficiency of watercourses to facilitate water outflow, optimal management in fish ponds, optimization of retention in reservoirs industrial and reducing clogging of infiltration ponds.

The restoration of the original capacity of the reservoir is carried out mainly by mechanical removal of sediments, less often they are biological or chemical methods. Desludging of dam reservoirs can be accomplished by:

- digging with excavators from the exposed bottom of the tank,
- dredging − mechanical removal with grab or multi-bucket dredgers, suction of

water with sediments using suction dredgers (dredgers), suction of water with sediments using a siphon thrown over the dam,

- draining water from the tank assisted by mechanical or hydraulic disturbance of sediments,
- quick drainage of water from the reservoir during high water levels or through large bottom flushing outlets,
- slowly draining the water from the reservoir and flushing with the natural flow of the river,
- controlled drainage of water from the tank through the rinsing outlet.

Removal of bottom sediments is considered to be one of the most effective methods of reclamation of water reservoirs, especially in the case of persistent organic pollutants, biogenic elements and heavy metals. Chmist and Hämmerling (2016) analyzed the five most commonly used methods of reservoir rehabilitation (biomanipulation, dredging, biostructures, bottom layer oxygenation and phosphorus inactivation) to determine the most effective. The criteria to be assessed were the individual type of reservoir, the effectiveness of the treatments due to the reason for degradation, the cost of works, the time needed to carry out the process and the source of contamination. Due to the time needed to achieve the intended goal, the immediate effect guarantees the correct removal of bottom sediments. On the other hand, the prospect of achieving the intended goal within a few years is realistic with the use of phosphorus inactivation. In the case of urbanized areas, which provide pollutants that are difficult to biodegrade in the biological way, it is necessary to use primarily mechanical methods, such as dredging. According to the authors, taking into account the overall assessment, dredging was the second best reclamation method, while the oxygenation of the bottom layers was considered the least effective. The use of off-tank removal methods is advisable for environmental and financial benefits. Research carried out on Lake Trummen in southern Sweden also shows the effectiveness of this procedure in the rehabilitation of water reservoirs. The research was carried out to observe the level of pollution with nitrogen and phosphorus compounds. After removing the sediments, a decrease in nitrogen concentration by about 80% and phosphorus by about 90% was observed, and an increase in water transparency from 0.2 m to 0.6−0.8 m. Currently, bottom sediments are removed only because of the excessive accumulation of matter in lakes, reservoirs or, if necessary, to restore the rivers. Unfortunately, the main reason for the removal of sediments from the seabed is not due to the presence of a large amount of contaminants.

Dredging water reservoirs is a necessary and commonly used procedure that allows to keep them in such a state that they fulfill their economic and economic

functions. First of all, it is an attractive method in many respects to remove dangerous organic pollutants from the aquatic ecosystem. During the implementation of this method, it is important to determine the physical and chemical properties of bottom sediments, which may indicate their ecological condition and the possibilities of their management.

3.7. Technological possibilities of removing organic pollutants from bottom sediments.

General characteristics

The decision to remove bottom sediments from the water ecosystem is made in the case of excessive shallowing of reservoirs, lakes or the necessity to restore the rivers. However, due to the rarity of implementing such a solution, there are few studies in the literature on the removal of organic pollutants from bottom sediments. The elimination of harmful pollutants from bottom sediments and their subsequent management is more advantageous than storage, taking into account the financial and environmental aspects. The technologies used for soil remediation were the basis for the development of methods for the treatment of bottom sediments. Physical, chemical, thermal, biological and combined methods are used for the treatment of bottom sediments extracted from the bottom of the aquatic ecosystem (ex situ methods). The processes of cleaning sludge from contamination are carried out on a specially prepared technological stand. The advantage of such a solution is the ease of their control and relatively short time of the process. In situ methods for removing pollutants from bottom sediments can also be carried out. Treatment of bottom sediments based on in situ methods, compared to ex situ methods, is much more difficult to implement and sometimes more expensive, which results, among others, from from the necessity to use environmentally non-invasive methods of cleaning and establishing and maintaining a base near the reservoir.

Biological methods are the most popular for removing contaminants from bottom sediments. However, the high content of hazardous organic substances makes it impossible to apply these methods. For example, the presence of heavy metals in bottom sediments has a toxic effect on organisms that prevent their development and, as a result, limit the possibility of removing pollutants from. The content of phthalic acid esters in the soil at the level of about 100 mg/kg inhibits the growth of microorganisms and the activity of the catalase enzyme. On the other hand, the increase in the content of diesel oil from 2,500 mg/kg to 20,000 mg/kg resulted in a decrease in the efficiency of bioremediation by 60% in soil.

The physicochemical parameters of the analyzed soil have a key impact on the process of removing both diesel oil and other pollutants. The optimal pH for the

effective course of soil bioremediation from petroleum products is 7.5. Extreme pH values resulted in a reduction in the activity of soil microorganisms towards the degradation of these products. Water content is also important in the biodegradation process. The humidity should be about 80% of the water capacity, the relative humidity should not be less than the value of 15%. Despite many advantages, in order to obtain satisfactory results of contamination removal, biological methods require a long process time (even several years). In this case, physical, chemical or physicochemical methods can be used first for the treatment of bottom sediments, followed by biological methods.

Thermal methods are considered to be one of the most effective methods for removing pollutants from bottom sediments. They are characterized by a short process time and are easy to carry out. A huge challenge for the design of these methods is the prevention of air pollution generated during the process. To protect the air, install scrubbers that clean the air before releasing the resulting gases into the atmosphere.

Another disadvantage of incineration of bottom sediments is also the excessive consumption of energy necessary to heat the soil to the required temperature and the presence of water, which significantly reduces the efficiency of the process. Thermal methods include the use of microwave radiation. The downside of this process is significant energy consumption and health risks. This method may also pose a safety risk, especially in the case of the remediation of bottom sediments rich in organic components. In order to use this process efficiently, further research on heat recovery is required.

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 might be:

- remediation of bottom sediments by resuspension,
- in situ removal of pesticides with the use of activated carbon and carbon nanotubes,
- in situ removal of petroleum substances with the use of zeolites combined with microbial decomposition.

The use of chemical methods, above all, increases the bioavailability of hazardous and hardly biodegradable chemical compounds by reducing their toxicity. Moreover, chemical methods very often completely decompose pollutants into simple products such as carbon(IV) oxide and water. In this case, the so-called advanced oxidation methods (AOPs). Unlike most methods, they do not transfer pollutants to another environment, but contribute to their degradation and are safe for the environment, which is a clear advantage over other methods used.

The effectiveness of APOs depends mainly on the type and concentration of the substance to be removed and the presence of other organic and mineral compounds. The hydroxyl radicals present in this process react quickly and non-selectively with almost all organic compounds. Thus, 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 so-called HO radical scavenger.

Advanced oxidation methods use different oxidation systems that can be divided into three groups:

- 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 Fenton's reagent assisted by ultrasound,
- processes using electromagnetic radiation with the use of electrodes with a high oxygen evolution overvoltage and Fenton's reagent assisted with electric current,
- photochemical processes, including photocatalytic degradation in aqueous semiconductor suspensions, Fenton's reagent assisted with UV light.

Each method 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.

The Fenton process in the remediation of bottom sediments

Due to the simple technological solution, the most popular method among AOPs is the Fenton reaction. It was first used to oxidize toxic pollutants in the 1960s. However, research on the application of this process in soil remediation began only at the end of the 20th century. Among the undisputed advantages of the Fenton process is the lack of formation of harmful products, which are formed, for example, in the case of chlorination and ozonation. It is believed that the Fenton reaction is particularly effective in degrading most pollutants and competitive with other advanced oxidation methods due to its simplicity, general availability of reagents and no need for specialized equipment. The mechanism of the classic Fenton reaction leads to the catalytic decomposition of hydrogen peroxide in the presence of iron ions, during which hydroxyl radicals are generated. The mixture of hydrogen peroxide and iron ions forms the so-called Fenton's reagent. Hydrogen peroxide is called the green oxidant because the by-product of the reactions involving water and oxygen. Moreover, it is relatively cheap and readily available in large quantities, and its use is an environmentally friendly alternative as opposed to oxidants such as ozone, $KMnO_4$, $K_2Cr_2O_7$. Hydrogen peroxide and other oxidants can also be used individually, but often turn out to be too weak to effectively degrade chemical

compounds that are difficult to decompose (Ferrarese et al. 2008). Therefore, iron ions are usually used which activate the decomposition of hydrogen peroxide and accelerate the overall rate of oxidation. Hydroxyl radicals formed in this process in an acidic environment (recommended pH in the range 2−4) oxidize organic substances with the diffusion rate in water 109−1010 1/M·s. At the same time, the addition of iron ions is not always necessary in the remediation of bottom sediments or soil, because the natural admixture of iron also takes part in the Fenton reaction.

The Fenton reaction is a complex process in which many side reactions take place. In soil, bottom sediment, these reactions include basic radical initiation (reactions (1) and (2), propagation (reactions (3) and (4) and termination (reactions (5)−(7) as well as with intermediates (reactions (8)−(15), with carbonate and bicarbonate ions (reactions (16)−(21) and with natural organic matter (NOM) (reaction (22).

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^{\cdot} + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (2)$$

$$HO^{\cdot} + RH \longrightarrow R^{\cdot} + H_2O \quad (3)$$

$$R^{\cdot} + H_2O_2 \longrightarrow ROH + HO^{\cdot} \quad (4)$$

$$HO^{\cdot} + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \quad (5)$$

$$HO^{\cdot} + H_2O_2 \longrightarrow H_2O + HO_2^{\cdot} \quad (6)$$

$$HO^{\cdot} + HO^{\cdot} \longrightarrow H_2O_2 \quad (7)$$

$$Fe^{2+} + HO_2^{\cdot} \longrightarrow Fe^{3+} + HO_2^- \quad (8)$$

$$Fe^{3+} + HO_2^{\cdot} \longrightarrow Fe^{2+} + O_2 + 2H^+ \quad (9)$$

$$HO_2^{\cdot} + H_2O_2 \longrightarrow H_2O + OH^{\cdot} + O_2 \quad (10)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O + O_2 \quad (11)$$

$$O_2^{\cdot -} + Fe^{3+} \longrightarrow Fe^{2+} + O_2 \quad (12)$$

$$O_2^{\cdot -} + Fe^{2+} + 2H^+ \longrightarrow Fe^{3+} + H_2O_2 \quad (13)$$

$$HO^{\cdot}_2 + O_2^{\cdot -} + H_2O \longrightarrow H_2O_2 + O_2 + OH^- \quad (14)$$

$$HO^{\cdot} + HO^{\cdot}_2 \longrightarrow H_2O + O_2 \quad (15)$$

$$CO_2(g) + H_2O \longleftrightarrow H_2CO_3(aq) \quad (16)$$

$$H_2CO_3(aq) \longleftrightarrow HCO_3^- + H^+ \quad (17)$$

$$HCO_3^- + OH^{\cdot} \longrightarrow CO_3^- + OH^- \quad (18)$$

$$CO_3^{\cdot-} + H_2O_2 \longrightarrow HO_2^{\cdot} + HCO_3^- \quad (19)$$

$$2CO_3^{\cdot-} \longrightarrow \text{products} \quad (20)$$

$$CaCO_3(s) + H^+ \longleftrightarrow Ca^{2+} + HCO_3^- \quad (21)$$

$$NOM + HO^{\cdot} \longrightarrow \text{products} \quad (22)$$

In addition to hydroxyl radicals, the process produces hydroperoxide radicals, superoxide anion radicals and hydroperoxide anions, which can act as their scavengers and have a very small share in the direct oxidation of organic pollutants, because they are much less reactive than OH radicals. An excess of hydrogen peroxide can lead to the formation of HO_2 radicals. Like too many Fe^{2+} and H^+ ions, it can also bind hydroxyl radicals. Bicarbonate and carbonate ions also act as radical scavengers. The radicals − carbonate ions produced in these reactions are also oxidants, and they are more selective, but much weaker than HO radicals. Natural organic matter present in bottom sediments also usually inhibits the action of hydroxyl radicals.

Hydroxyl radicals are formed not only in the presence of iron(II) ions. Iron(III) ions can also be used as a catalyst for the generation of hydroxyl radicals. Any change in the classic Fenton reaction is referred to as a "modified Fenton". The radicalation processes in this case take place in two or three stages, as a result of a slow reaction between H_2O_2 and Fe^{3+}, and then a rapid reaction between the produced ferrous ions and H_2O_2. The efficiency of removing petroleum products was higher in the case of using iron(III) ions as a catalyst compared to iron(II) ions. According to the authors, the reason for this is the partial loss of hydrogen peroxide in the oxidation phase of iron(II) to iron(III).

The use of the Fenton process is recommended in the remediation of soil and bottom sediments. However, usually the kinetics of the classical Fenton reaction is too slow to degrade the highly absorbed pollutants in soils and bottom sediments, and the heterogeneity of these matrices makes the process difficult. For example, the efficiency of removing 24 substances from the PAH group from the soil after 24 hours using the Fenton process ranged from 8.8 to 43% (Jonsson et al. 2007). In turn, Silva et al. (2009) achieved a degradation of phenanthrene in soil with a starting concentration of 700 mg/kg at 94%, but the content of pyrene (615 mg/kg) was only almost halved. At a comparable level (44%), the authors reported pyrene removal efficiency using photocatalytic degradation in the presence of TiO_2 after 25 hours, with the initial pyrene concentration being only 40 mg/kg.

In soil remediation, the Fenton process is especially recommended for the removal of pesticides. One of the first studies in this direction was conducted by

Miller et al. (1996). According to their reports, the efficiency of degradation of pendimethalin belonging to the group of herbicides as a result of the classic Fenton reaction was over 99%. Further studies confirmed the usefulness of this method for removing substances belonging to the group of pesticides. Although the effectiveness of the Fenton process in soil remediation is satisfactory, there are still limitations in applying this process individually. Sometimes, much higher doses of the oxidant are required due to the presence of natural organic matter in the soil, which may also undergo oxidation.

In order to eliminate or minimize disadvantages and limitations, various integrated methods using biological, physical and chemical methods in combination with the Fenton process are constantly being developed. Modifications of this process in soil remediation are mainly due to the lower availability of pollutants due to sorption on solid particles and the impeded operation of the iron catalyst in the natural soil environment. In the conventional Fenton reaction, the problem is the required low soil pH, which negatively affects the quality and properties and is incompatible with subsequent biodegradation. To extend the application of this method at a higher pH, a solution may be the use of chelating agents (e.g. EDTA, pyrocatechin) which keep the Fe3+ ions formed under these conditions in a dissolved form. The influence of these substances on the removal of pollutants from soil during the application of the Fenton process was investigated, among others. In many cases, however, the use of chelating substances is insufficient and it is necessary to use several methods together to obtain the desired end effects. For example, in the photo-Fenton reaction, hydroxyl radicals are formed under the influence of UV radiation and at the same time photo-reduction of iron(III) to (II) ions takes place, during which HO radicals are formed. In turn, in the electro-Fenton method, hydrogen peroxide is generated electrochemically or ions are formed iron(II) or combinations thereof. In soil remediation, however, the most popular is the use of biological methods in combination with chemical methods.

Ultrasonic field in the remediation of bottom sediments

A new method in the remediation of bottom sediments is the use of ultrasound (sonication), which can also be successfully used in situ. In environmental engineering, the ultrasonic field in the range of 20−100 kHz is most often used. This method is based on emitting ultrasounds to the water phase, which in contact with it cause the phenomenon of cavitation. The cavitation process consists in the formation of pulsating vacuum bubbles in the liquid or filled with gas dissolved in the liquid or with saturated vapor (Fig. 3.7).

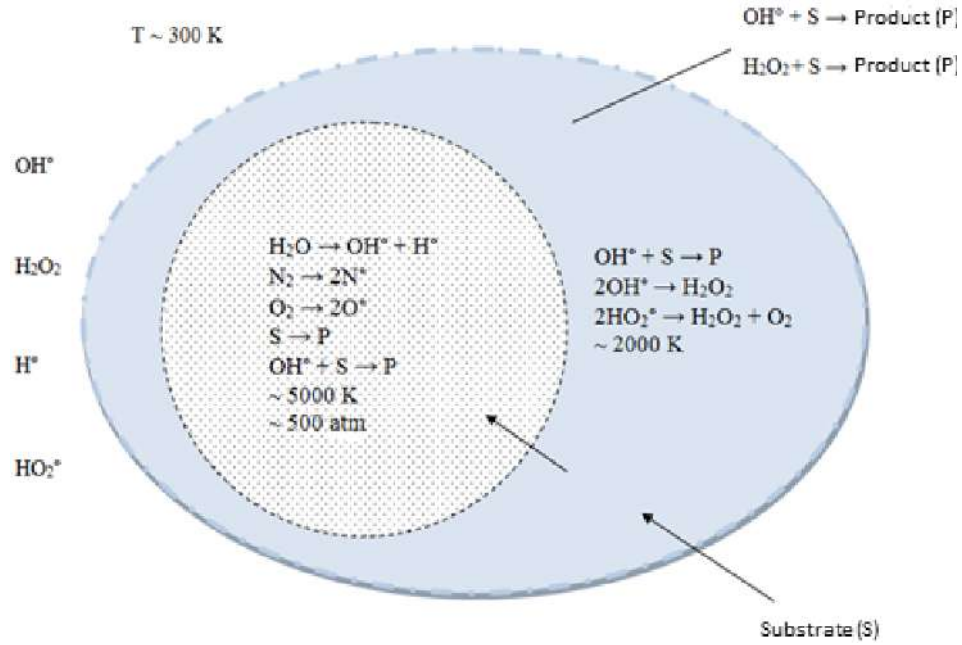


Fig. 3.7. Cavitation bubble (own elaboration based on Adewuyi, 2001)

Cavitation bubbles appear as a result of local ruptures of the medium under the influence of high tensile forces. During the operation of the ultrasonic field, the cavitation bubbles increase their radius twice or more. They then collapse rapidly, releasing a large amount of energy, resulting in a local increase in temperature and pressure. The rapid increase in pressure inside the bubble causes them to burst and the formation of a hydrodynamic shock wave. Extreme conditions are the cause of the thermal breakdown of water molecules, during which hydroxyl radicals are formed, which are the main source of the so-called sonochemical reactions (reactions 23−35). This phenomenon significantly accelerates the course of chemical and physical reactions.

$$H_2O +))) \longrightarrow HO\cdot + H\cdot \quad (23)$$

$$O_2 +))) \longrightarrow 2O\cdot \quad (24)$$

$$HO\cdot + O\cdot \longrightarrow HOO\cdot \quad (25)$$

$$O\cdot + H_2O \longrightarrow 2HO\cdot \quad (26)$$

$$H\cdot + O_2\cdot \longrightarrow HOO\cdot \quad (27)$$

$$OH\cdot + H\cdot \longrightarrow H_2O\cdot \quad (28)$$

$$2HO\cdot \longrightarrow H_2O\cdot + O\cdot \quad (29)$$

$$HOO\cdot + HO\cdot \longrightarrow O_2 + H_2O \quad (30)$$

$$2HO\cdot \longrightarrow H_2O_2 \quad (31)$$

$$2HOO\cdot \longrightarrow H_2O_2 + O_2 \quad (32)$$

$$H\cdot + H_2O_2 \longrightarrow HO\cdot + H_2O \quad (33)$$

$$HO\cdot + H_2O_2 \longrightarrow HOO\cdot + H_2O \quad (34)$$

$$2H\cdot \longrightarrow H_2 \quad (35)$$

Reactions that are initiated by cavitation can occur in three different areas. The interior of the collapsing bubble, subject to extreme pressure and temperature conditions, is the first area where the resulting hydroxyl radicals react with substances present in the gas phase as a result of thermal dissociation of water. The second area is the gas-liquid interface. There is still high temperature and pressure between the collapsing bubble and the liquid, but even low-volatile substances pyrolyze under these conditions. The effectiveness of thermal degradation of dissolved non-volatile substances depends mainly on their hydrophobicity and the activation energy necessary to break the bond. In turn, in the third area, which is the solution at ambient temperature, the hydroxyl radicals formed in the cavitation bubbles, which did not react in the border zone, react with the substance dissolved in the solution.

The production of hydroxyl radicals depends on many factors. Particular attention to the influence of pH, temperature, physicochemical properties of the removed substances, time, intensity and frequency of the ultrasonic field and the presence of inhibitory substances. According to his research, the pH is irrelevant to the amount of generated hydroxyl radicals and hydrogen peroxide. The impact of this parameter depends on the structure and chemical structure of the substance to be removed, it is important when the organic substance has a molecular and ionic form. The substance in the ionic form shows lower hydrophobicity, therefore its decomposition takes place in the third region (apart from the cavitation bubble), where less favorable conditions occur. In order for the degradation of the contaminant to take place inside the cavitation bubble, this substance must be present in the solution in a molecular form.

Henry's solubility and constant value are also important in this process. Temperature is also of great importance for the effectiveness of the removal of substances during the operation of the ultrasonic field. The increase in temperature causes an increase in the amount of cavitation bubbles, but they are filled with water vapor, which causes a decrease in the intensity of bubble collapse after exceeding the optimal temperature, which depends on the physicochemical properties of the pollutant removed. An increase in the process temperature from 15 to 35 °C has a positive effect on the efficiency of naproxen and paracetamol removal, while above 35°C a decrease in the amount of hydroxyl radicals was observed.

The literature also confirms the influence of the frequency of the ultrasound wave on the efficiency of pollutant removal. By using ultrasonic waves in the frequency range of 200−400 kHz, the best results are obtained for the decomposition of low-volatile substances. On the other hand, for volatile substances, increasing the frequency increases the efficiency of removal. The use of the ultrasonic field to

remove impurities that are difficult to decompose is a promising and recommended method, because ultrasounds, due to its high efficiency, significant reduction of the time of unit processes and low instrumental requirements, are treated as "green" technologies. The process can be carried out using a special sonotrode or in ultrasonic cleaners equipped with an ultrasonic transducer.

The available studies confirm the positive effect of sonochemical methods on the degradation of many organic compounds. Naddeo et al. (2007) analyzed the possibility of removing natural organic matter (NOM) from an aqueous solution as a result of an ultrasonic field with a frequency of 20 kHz and a field strength of 7 to 42 W/cm^2. The authors noted a reduction in the concentration of humic acids within the range of 24.5−34.9%. The degree of removal of these impurities depended on the intensity and duration of sonication. In turn, Shemer and Narkis (2005), using ultrasound with a field strength of 3.75 W/cm^2 and a frequency of 20 kHz, removed trihalomethanes from an aqueous solution. The efficiency obtained in these studies, during 180 min, was 100% for $CHCl_3$ (chloroform).

On the other hand, the removal of pollutants from soil and bottom sediments using an ultrasonic field was carried out by Collings et al. (2006). PCB 1254 removal efficiency from soil was 99% in 7−10 min (90% after 2 min), initial concentration - 45 ppm. The effectiveness of removing selected substances from the PAH group from bottom sediments was 70% after 2 minutes of sonication (initial concentration − 400 ppm). The research was carried out with the use of an ultrasound generator with high electrical power equal to 1.5 kW. According to the authors, this method is promising due to its high efficiency in removing pollutants, no formation of toxic by-products, and low energy consumption, assuming that similar results can be obtained on an industrial scale. The technology is also easy to move and, above all, it is possible to hydraulically transport the soil to the reactor. Moreover, during the process in suspension, the cavitation bubble collapses asymmetrically towards the surface of the solid. The shock waves generated as a result of this phenomenon are the cause of extreme conditions on the surface of the solid, which the fracture of the solids and the breakdown of the contaminants that are normally adsorbed on the solids. Mason et al. (2004) used the soil washing method to remove contaminants. Supporting this process with ultrasound significantly improves the efficiency of removing pollutants, e.g. as a result of the capillary phenomenon in the formed pores and crevices of solid particles.

Nevertheless, this method does not always produce satisfactory results, therefore a promising alternative in relation to conventional and unit oxidation methods is the combination of processes, e.g. the use of an ultrasonic field in combination with the application of the H_2O_2 oxidant or the Fenton process. A good

example is the research, where using the ultrasonic field to remove dichlorvos (insecticide) from an aqueous solution with an initial concentration of 20 mg/dm^3, achieved the removal efficiency of 6.4% after 120 minutes of sonication. As a result of the addition of hydrogen peroxide (500 mg/dm^3), this value increased to 20% using the Fenton process (80 mg H_2O_2/dm^3, 80 mg Fe^{2+}/dm^3) − 81.2%.

The combined process allows, among others to a significant increase in the efficiency of pollutants removal compared to a unit process, often shortening the time and, depending on the processes used, reducing the dose of oxidant and catalyst.

Conclusions

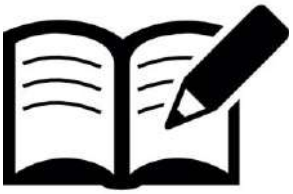
The analysis of the available data shows that both the qualitative and quantitative degradation of inland waters is progressing independently of the implementation of remedial programs, e.g. the Water Framework Directive, the slowing effect of which is visible mainly in developed countries. The protection and use of good-quality inland water resources is a constant challenge for societies, as is reducing the negative consequences of inland water degradation. Failure to act to reduce and reverse the processes of qualitative and quantitative degradation of inland water systems will have far-reaching consequences for humans, as this problem is both environmental and social − it can determine political consequences such as migration and wars.

Questions for self-control

1. What methods can we use to remove impurities that are difficult to decompose in bottom sediments?
2. What is the Fenton process?
3. What is the function of bottom sediments in the aquatic ecosystem?
4. What are the benefits of water retention?
5. What groups of organic pollutants are classified as difficult to degrade in the aquatic ecosystem?
6. Short describe the technological possibilities of removing organic pollutants from bottom sediments.

7. What is the the technological possibility of removing organic pollutants from bottom sediments more effective?

8. What is the sence of the Fenton process in the remediation of bottom sediments?



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Chapter IV

WATER MANAGMENT: HISTORY; WATER PURIFICATION; WASTEWATER AND SEWAGE TREATMENT

In this section you will learn about

- ✓ History of water supply and sanitation.
- ✓ Water purification.
- ✓ Wastewater and sewage treatment.

Key words:

Water supply systems, aqueducts
Cloaca Maxima
Sewage farms, indoor plumbing
Biological treatment and activated sludge process
Water purification, underground and surface waters
Water pretreatment, sedimentation, coagulation and flocculation
Water softening, pH adjustment, disinfection, drinking water quality
Solids, microorganisms, dissolved inorganic and organic substances

Sewage or municipal wastewater treatment
Sewage pretreatment: screening, grit, fat and grease removal, flow equalization
Primary and secondary clarifiers, activated sludge process
Nutrients removal and sludge handling

Major human settlements could initially develop only where fresh surface water was plentiful, such as near rivers or natural springs. Throughout history, people have devised systems to make getting water into their communities. Early human habitations were often built next to water sources. Rivers would often serve as a crude form of natural sewage disposal.

During the Neolithic era, humans dug the first permanent water wells, from where vessels could be filled and carried by hand. The size of human settlements was largely dependent on nearby available water.

Water purification means the process of removing undesirable chemicals, biological contaminants, suspended solids, and gases from water. The goal is to produce water that is fit for specific purposes.

The history of water purification includes a wide variety of methods. The methods used include physical processes such as filtration, sedimentation, and distillation and chemical processes such as slow sand filters or active carbon, flocculation and the use of electromagnetic radiation such as ultraviolet light. Water purification may reduce the concentration of particulate matter including suspended particles, parasites, bacteria, algae, viruses, and fungi as well as reduce the concentration of a range of dissolved and particulate matter. Simple procedures such as boiling or the use of a household activated carbon filter are not sufficient for treating all possible contaminants that may be present in water from an unknown source. Even natural spring water, considered safe for all practical purposes in the 19th century, must now be tested before determining what kind of treatment, if any, is needed. Chemical and microbiological analysis, while expensive, are the only way to obtain the information necessary for deciding on the appropriate method of purification.

The standards for drinking water quality are typically set by governments or by international standards. These standards usually include minimum and maximum concentrations of contaminants, depending on the intended use of the water.

Widely varied techniques are available to remove contaminants like fine solids, micro-organisms and some dissolved inorganic and organic materials, or environmental persistent pharmaceutical pollutants. The choice of method will depend on the quality of the water being treated, the cost of the treatment process and the quality standards expected of the processed

water. The processes below are the ones commonly used in water purification plants.

Sewage treatment (or domestic wastewater treatment, municipal wastewater treatment) is a type of wastewater treatment which aims to remove contaminants from sewage to produce an effluent that is suitable for discharge to the surrounding environment or an intended reuse application, thereby preventing water pollution from raw sewage discharges. Sewage contains wastewater from households and businesses and possibly pre-treated industrial wastewater. There are a high number of sewage treatment processes to choose from. These can range from decentralized systems (including on-site treatment systems) to large centralized systems involving a network of pipes and pump stations (called sewerage) which convey the sewage to a treatment plant. For cities that have a combined sewer, the sewers will also carry urban runoff (stormwater) to the sewage treatment plant. Sewage treatment often involves two main stages, called primary and secondary treatment, while advanced treatment also incorporates a tertiary treatment stage with polishing processes and nutrient removal. Secondary treatment can reduce organic matter (measured as biological oxygen demand) from sewage, using aerobic or anaerobic biological processes. With regards to biological treatment of sewage, the treatment objectives can include various degrees of the following: transform dissolved and particulate biodegradable components (especially organic matter) into acceptable end products, transform and remove nutrients (nitrogen and phosphorus), remove or inactivate pathogenic organisms, and remove specific trace organic constituents (micropollutants). Some types of sewage treatment produce sewage sludge which can be treated before safe disposal or reuse. Under certain circumstances, the treated sewage sludge might be termed "biosolids" and can be used as a fertilizer.

Sewerage (or sewage system) is the infrastructure that conveys sewage or surface runoff (stormwater, meltwater, rainwater) using sewers. It encompasses components such as receiving drains, manholes, pumping stations, storm overflows, and screening chambers of the combined sewer or sanitary sewer. Sewerage ends at the entry to a sewage treatment plant or at the point of discharge into the environment. It is the system of pipes, chambers, manholes, etc. that conveys the sewage or storm water.

4.1. History of Water Supply and Sanitation.

Wastewater reuse activities and drinking water supply since prehistoric time.

Reuse of untreated municipal wastewater has been practiced for many centuries with the objective of diverting human waste outside of urban settlements. Likewise, land application of domestic wastewater is an old and common practice, which has gone through different stages of development.

Domestic wastewater was used for irrigation by prehistoric civilizations (e.g. Mesopotamian, Indus valley) since the Bronze Age (ca. 3200-1100 BC). Thereafter, wastewater was used for disposal, irrigation, and fertilization purposes by Hellenic civilizations and later by Romans in areas surrounding cities (e.g. Athens and Rome).

The ca. 2400 BCE, Pyramid of Sahure, and adjoining temple complex at Abusir, was discovered to have a network of copper drainage pipes.

Some of the earliest evidence of water wells are located in China. The Neolithic Chinese discovered and made extensive use of deep drilled groundwater for drinking. Archaeological evidence and old Chinese documents reveal that the prehistoric and ancient Chinese had the aptitude and skills for digging deep water wells for drinking water as early as 6000 to 7000 years ago.

Devices such as shadoofs were used to lift water to ground level. Ruins from the Indus Valley Civilization had settlements with some of the ancient world's most sophisticated sewage systems. They included drainage channels, rainwater harvesting, and street ducts.

The ancient Greek civilization of Crete was the first civilization to use underground clay pipes for sanitation and water supply. Their capital had a well-organized water system for bringing in clean water, taking out waste water and storm sewage canals for overflow when there was heavy rain. It was also one of the first uses of a flush toilet, dating back to the 18th century BC. In addition to sophisticated water and sewer systems they devised elaborate heating systems.

The Ancient Greeks of Athens and Asia Minor also used an indoor plumbing system, used for pressurized showers. The Greek inventor Heron used pressurized piping for fire fighting purposes in the City of Alexandria.The Mayans were the third earliest civilization to have employed a system of indoor plumbing using pressurized water.

An inverted siphon system, along with glass covered clay pipes, was used for the first time in the palaces of Crete, Greece. It is still in working condition, after about 3000 years (Fig. 4.1).

Fig. 4.1. Pont du Gard, a Roman aqueduct in France.

In ancient Rome, the Cloaca Maxima, considered a marvel of engineering, discharged into the Tiber. Public latrines were built over the Cloaca Maxima (Fig. 4.2).

Beginning in the Roman era a water wheel device known as a noria supplied water to aqueducts and other water distribution systems in major cities in Europe and the Middle East.

The Roman Empire had indoor plumbing, meaning a system of aqueducts and pipes that terminated in homes and at public wells and fountains for people to use. Rome and other nations used lead pipes; while commonly thought to be the cause of lead poisoning in the Roman Empire, the combination of running water which did not stay in contact with the pipe for long and the deposition of precipitation scale actually mitigated the risk from lead pipes.

Roman towns and garrisons in the United Kingdom between 46 BC and 400 AD had complex sewer networks sometimes constructed out of hollowed-out elm logs, which were shaped so that they butted together with the down-stream pipe providing a socket for the upstream pipe.

Fig. 4.2. Ancient Rome factual approximation

There is little record of other sanitation systems (apart of sanitation in ancient Rome) in most of Europe until the High Middle Ages. Unsanitary conditions and overcrowding were widespread throughout Europe and Asia during the Middle Ages. This resulted in pandemics which killed tens of millions of people. Very high infant and child mortality prevailed in Europe throughout medieval times, due partly to deficiencies in sanitation.

In medieval European cities, small natural waterways used for carrying off wastewater were eventually covered over and functioned as sewers. London's River Fleet is such a system. Open drains, or gutters, for waste water run-off ran along the center of some streets. These were known as canals, channels and in Paris were sometimes known as “split streets,” as the waste water running along the middle physically split the streets into two halves. The first closed sewer constructed in Paris was designed by Hugues Aubird in 1370 on Montmartre Street and was 300 meters long. The original purpose of designing and constructing a closed sewer in Paris was less-so for waste management as much as it was to hold back the stench coming from the odorous waste water. In Dubrovnik, then known as Ragusa (Latin name), the Statute of 1272 set out the parameters for the construction of septic tanks and channels for the removal of dirty water. Throughout the 14th and 15th century the sewage system was built, and it is still operational today, with minor changes and repairs done in recent centuries. Pail closets, outhouses, and cesspits were used to collect human waste. The use of human waste as fertilizer was especially important in China and Japan, where cattle manure was less available. However, most cities did not have a functioning sewer system before the Industrial era, relying instead on nearby rivers or occasional rain showers to wash away the sewage from the streets. In some places, waste water simply ran down the streets, which had stepping stones to keep pedestrians out of the muck, and eventually drained as runoff into the local watershed.

In the 16th century, Sir John Harington invented a flush toilet as a device for Queen Elizabeth I (his godmother) that released wastes into cesspools. After the adoption of gunpowder, municipal outhouses became an important source of raw material for the making of saltpeter in European countries. In London, the contents of the city's outhouses were collected every night by commissioned wagons and delivered to the nitrite beds where it was laid into specially designed soil beds to produce earth rich in mineral nitrates. The nitrate rich-earth would be then further processed to produce saltpeter, or potassium nitrate, an important ingredient in black powder that played a part in the making of gunpowder.

Sewage farms (i.e. wastewater application to the land for disposal and agricultural use) were operated in Silesia in 1531, in Scotland in 1650, in Paris in 1868, in Berlin in 1876 and in different parts of the USA since 1871, where wastewater was used for beneficial crop production. In the 16th and 18th centuries in many rapidly growing countries/cities of Europe (e.g. Germany, France) and the United States, “sewage farms” were increasingly seen as a solution for the disposal of large volumes of the wastewater, some of which are still in operation today. Irrigation with sewage and other wastewater effluents has a long history also in China and

India; while also a large “sewage farm” was established in Australia in 1897 (Fig. 4.3).

Modern age. Sewer systems

A significant development was the construction of a network of sewers to collect wastewater. In some cities, including Rome, Istanbul (Constantinople) networked ancient sewer systems continue to function today as collection systems for those cities modernized sewer systems. Instead of flowing to a river or the sea, the pipes have been re-routed to modern sewer treatment facilities.

Basic sewer systems were used for waste removal in ancient Mesopotamia, where vertical shafts carried the waste away into cesspools. Similar systems existed in the Indus Valley civilization in modern-day India and in Ancient Crete and Greece. In the Middle Ages the sewer systems built by the Romans fell into disuse and waste was collected into cesspools that were periodically emptied by workers known as 'rakers' who would often sell it as fertilizer to farmers outside the city.

The tremendous growth of cities in Europe and North America during the Industrial Revolution quickly led to crowding, which acted as a constant source for the outbreak of disease. As cities grew in the 19th century concerns were raised about public health.As part of a trend of municipal sanitation programs in the late 19th and 20th centuries, many cities constructed extensive gravity sewer systems to help control outbreaks of disease such as typhoid and cholera. Storm and sanitary sewers were necessarily developed along with the growth of cities. By the 1840s the luxury of indoor plumbing, which mixes human waste with water and flushes it away, eliminated the need for cesspools.

Modern sewerage systems were first built in the mid-nineteenth century as a reaction to the exacerbation of sanitary conditions brought on by heavy industrialization and urbanization. Baldwin Latham, a British civil engineer contributed to the rationalization of sewerage and house drainage systems and was a pioneer in sanitary engineering. He developed the concept of oval sewage pipe to facilitate sewer drainage and to prevent sludge deposition and flooding. Due to the contaminated water supply, cholera outbreaks occurred in 1832, 1849 and 1855 in London, killing tens of thousands of people. This, combined with the Great Stink of 1858, when the smell of untreated human waste in the River Thames became overpowering, and the report into sanitation reform of the Royal Commissioner Edwin Chadwick, led to the Metropolitan Commission of Sewers appointing Joseph Bazalgette to construct a vast underground sewage system for the safe removal of waste. Contrary to Chadwick's recommendations, Bazalgette's system, and others later built in Continental Europe, did not pump the sewage onto farm land for use as

fertilizer; it was simply piped to a natural waterway away from population centres, and pumped back into the environment.

From as early as 1535 there were efforts to stop polluting the River Thames in London. Beginning with an Act passed that year that was to prohibit the dumping of excrement into the river. Leading up to the Industrial Revolution the River Thames was identified as being thick and black due to sewage, and it was even said that the river “smells like death.” As Britain was the first country to industrialize, it was also the first to experience the disastrous consequences of major urbanization and was the first to construct a modern sewerage system to mitigate the resultant unsanitary conditions. During the early 19th century, the River Thames was effectively an open sewer, leading to frequent outbreaks of cholera epidemics. Proposals to modernize the sewerage system had been made during 1856 but were neglected due to lack of funds. However, after the *Great Stink* of 1858, Parliament realized the urgency of the problem and resolved to create a modern sewerage system.

Joseph Bazalgette, a civil engineer and Chief Engineer of the Metropolitan Board of Works, was given responsibility for the work. He designed an extensive underground sewerage system that diverted waste to the Thames Estuary, downstream of the main center of population. Six main interceptor sewers, totaling almost 160 km in length, were constructed, some incorporating stretches of London's 'lost' rivers. Three of these sewers were north of the river, the southernmost, low-level one being incorporated in the Thames Embankment. The Embankment also allowed new roads, new public gardens, and the Circle Line of the London Underground.

The intercepting sewers, constructed between 1859 and 1865, were fed by 720 km of main sewers that, in turn, conveyed the contents of some 21000 km of smaller local sewers. Construction of the interceptor system required 318 million bricks, 2.7 million cubic metres of excavated earth and 670000 cubic metres of concrete. With only minor modifications, Bazalgette's engineering achievement remains the basis for sewerage design up into the present day.

In 1802, Napoleon built the Ourcq canal which brought 70 000 cubic meters of water a day to Paris, while the Seine river received up to 100 000 cubic meters of wastewater per day. The Paris cholera epidemic of 1832 sharpened the public awareness of the necessity for some sort of drainage system to deal with sewage and wastewater in a better and healthier way. Between 1865 and 1920 Eugene Belgrand lead the development of a large scale system for water supply and wastewater management. Between these years approximately 600 kilometers of aqueducts were built to bring in potable spring water, which freed the poor quality water to be used for flushing streets and sewers. By 1894 laws were passed which made drainage

mandatory. The treatment of Paris sewage was left to natural devices as 5000 hectares of land were used to spread the waste out to be naturally purified.

The first comprehensive sewer system in a German city was built in Hamburg in the mid-19th century. In 1863, work began on the construction of a modern sewerage system for the rapidly growing city of Frankfurt am Main, based on design work by William Lindley. 20 years after the system's completion, the death rate from typhoid had fallen from 80 to 10 per 100 000 inhabitants.

The first sewer systems in the United States were built in the late 1850s in Chicago and Brooklyn. Initially the gravity sewer systems discharged sewage directly to surface waters without treatment. Later, cities attempted to treat the sewage before discharge in order to prevent water pollution and waterborne diseases. During the half-century around 1900, these public health interventions succeeded in drastically reducing the incidence of water-borne diseases among the urban population, and were an important cause in the increases of life expectancy experienced at the time.

Early techniques for sewage treatment involved land application of sewage on agricultural land. One of the first attempts at diverting sewage for use as a fertilizer in the farm was made by the cotton mill owner James Smith in the 1840s. He experimented with a piped distribution system initially proposed by James Vetch that collected sewage from his factory and pumped it into the outlying farms, and his success was enthusiastically followed by Edwin Chadwick and supported by organic chemist Justus von Liebig.

The idea was officially adopted by the Health of Towns Commission, and various schemes (known as sewage farms) were trialled by different municipalities over the next 50 years. At first, the heavier solids were channeled into ditches on the side of the farm and were covered over when full, but soon flat-bottomed tanks were employed as reservoirs for the sewage; the earliest patent was taken out by William Higgs in 1846 for tanks or reservoirs in which the contents of sewers and drains from cities, towns and villages are to be collected and the solid animal or vegetable matters therein contained, solidified and dried. Improvements to the design of the tanks included the introduction of the horizontal-flow tank in the 1850s and the radial-flow tank in 1905. These tanks had to be manually de-sludged periodically, until the introduction of automatic mechanical de-sludgers in the early 1900s.

Chemical treatment and sedimentation

As pollution of water bodies became a concern, cities attempted to treat the sewage before discharge. In the late 19th century some cities began to add chemical treatment and sedimentation systems to their sewers. In the United States, the first sewage treatment plant using chemical precipitation was built in Massachusetts in 1890. During the half-century around 1900, these public health interventions

succeeded in drastically reducing the incidence of water-borne diseases among the urban population, and were an important cause in the increases of life expectancy experienced at the time.

Fig. 4.3. A Chinese ceramic model of a well with a water pulley system, excavated from a tomb of the Han Dynasty (202 BC - 220 AD) period (left) and typical old medieval water wells (right).

Odor was considered the big problem in waste disposal and to address it, sewage could be drained to a lagoon, or "settled" and the solids removed, to be disposed of separately. This process is now called "primary treatment" and the settled solids are called "sludge." At the end of the 19th century, since primary treatment still left odor problems, it was discovered that bad odors could be prevented by introducing oxygen into the decomposing sewage. This was the beginning of the biological aerobic and anaerobic treatments which are fundamental to wastewater processes.

The precursor to the modern septic tank was the cesspool in which the water was sealed off to prevent contamination and the solid waste was slowly liquified due to anaerobic action; it was invented by L.H Mouras in France in the 1860s. Donald Cameron, as City Surveyor for Exeter patented an improved version in 1895, which he called a 'septic tank'; septic having the meaning of 'bacterial'. These are still in worldwide use, especially in rural areas unconnected to large-scale sewage systems.

Biological treatment

It was not until the late 19th century that it became possible to treat the sewage by biologically decomposing the organic components through the use of microorganisms and removing the pollutants. Land treatment was also steadily becoming less feasible, as cities grew and the volume of sewage produced could no longer be absorbed by the farmland on the outskirts.

Edward Frankland conducted experiments at the sewage farm in England, during the 1870s and was able to demonstrate that filtration of sewage through porous gravel

produced a nitrified effluent (the ammonia was converted into nitrate) and that the filter remained unclogged over long periods of time.This established the revolutionary possibility of biological treatment of sewage using a contact bed to oxidize the waste.

From 1885 to 1891 filters working on this principle were constructed throughout the UK and the idea was also taken up in the US at the Lawrence Experiment Station in Massachusetts, where Frankland's work was confirmed. Contact beds were tanks containing an inert substance, such as stones or slate, that maximized the surface area available for the microbial growth to break down the sewage. The sewage was held in the tank until it was fully decomposed and it was then filtered out into the ground.

Activated sludge process

Most cities in the Western world added more expensive systems for sewage treatment in the early 20th century, after scientists at the University of Manchester discovered the sewage treatment process of activated sludge in 1912.

The activated sludge process was discovered in 1913 in the United Kingdom by two engineers, Edward Ardern and W.T. Lockett, who were conducting research for the Manchester Corporation Rivers Department. In 1912, Dr. Gilbert Fowler, a scientist at the University of Manchester, observed experiments being conducted at the Lawrence Experiment Station at Massachusetts involving the aeration of sewage in a bottle that had been coated with algae. Fowler's engineering colleagues, Ardern and Lockett, experimented on treating sewage in a draw-and-fill reactor, which produced a highly treated effluent. They aerated the waste-water continuously for about a month and were able to achieve a complete nitrification of the sample material. Believing that the sludge had been activated the process was named *activated sludge*. Not until much later was it realized that what had actually occurred was a means to concentrate biological organisms, decoupling the liquid retention time from the solids retention time.Their results were published in their seminal 1914 paper, and the first full-scale continuous-flow system was installed at Worcester two years later.

Water treatment

The first documented use of sand filters to purify the water supply dates to 1804, when the owner of a bleachery in Scotland, John Gibb, installed an experimental filter, selling his unwanted surplus to the public. This method was refined in the following two decades by engineers working for private water companies, and it culminated in the first treated public water supply in the world, installed by engineer James Simpson for the Waterworks Company in London in 1829. This installation provided filtered water for every resident of the area, and the

network design was widely copied throughout the United Kingdom in the ensuing decades. Early attempts at implementing water chlorination at a water treatment plant were made in 1893 in Germany, and in 1897 in England, was the first to have its entire water supply treated with chlorine. Permanent water chlorination began in 1905, when a faulty slow sand filter and a contaminated water supply led to a serious typhoid fever epidemic in England. Founders of microscopy, Antonie van Leeuwenhoek and Robert Hooke, used the newly invented microscope to observe for the first time small material particles that were suspended in the water, laying the groundwork for the future understanding of waterborne pathogens and waterborne diseases.

Water supply and sanitation in medieval Pressburg (Bratislava)

During the 16th century Pressburg (Bratislava) inhabitants used plenty wells, such as on the streets Hlavné námestie, Zámocká, Kapitulská, Michalská brána and the others (Fig. 4.4; 4.5.).

Fig. 4.4. The first digged well on the Sihoť Island for Pressburg (upper left), Water Works at the Sihoť(upper right), Inventor of drinking water pumping to the castle of Pressburg Wolfgang von Kempelen (lower left) and Company which constructed the first 4.1 km of sewerage for the city of Pressburg (lower right).

Drinking water was supplied also from surrounded Malé Karpaty mountains using for transportation firstly stone and wooden and later on copper pipes and

troughs. Around the year 1760 there was digged some well on the Danube river embankment which supplied with drinking water and horse drive the castle reservoir. Construction of the first objects of the city plumbing was started on the August 25, 1884 by C. Corte Company which managed Bernard Salbach. Since the February 1886 started the operation of the first city plumbing for 50 000 inhabitants with the capacity of 1059 m^3/d (20 liter/d/inhabitant) using the steam pump.

Fig. 4.5. Prešporok (Bratislava), Pressburg, Pozson in the middle-age time.

The first water pumping station was constructed on the left bank of the Danube River in Karlova Ves in 1886. Together with the well on the island of Sihoť and the water reservoir near Bratislava Castle, the pumping station forms the base of the waterworks for Bratislava.

Drinking water was supplied from underground sources on the island of Sihoť.These sources have been rich in naturally filtered water from the Danube. Water was supplied from the water well on Sihoť to the main pumping station in Karlova Ves via a 1.7 km pipeline. From there, water was distributed by steam pumps to the entire city and then into the main water reservoir near Bratislava Castle. Designed and engineered by Bernhard Salbach and Zdenko Ritter von Wessely, Bratislava's waterworks use a pressure-gravity system and were the first of their kind in Slovakia. The island's first water well from 1886 is surrounded by a high bank and lined with granite to protect it from floods (Fig. 4.4.). In the past, 3000 m^3 of water could be pumped from this well. The first pumping station with electric pumps was built on the island in 1912. Leading from here is a 100 meter concrete tunnel with water pipes, located beneath the arm of the Danube river. The Karloveské rameno is one of the few free-flowing arms of the Danube along the entire section of the

Danube flowing through Slovakia. Its total length is 4 800 m and it flows around the island of Sihoť, one of the most important sources of drinking water in Bratislava. The original vegetation of the floodplain forest and natural willow-poplar forests which complement it are preserved in the surroundings of the Karloveské rameno. It is the home of many rare plant and animal species.

The first 4.1 km long sewerage system was constructed in Pressburg (old Bratislava) during the years 1897 – 1900 by Pittel & Brausenwetter Company (Fig. 4.4. and 4.5.).

3.2. Water purification.

Water purification means the process of removing undesirable chemicals, biological contaminants, suspended solids, and gases from water. The goal is to produce water that is fit for specific purposes. The history of water purification includes a wide variety of methods. The methods used include physical processes such as filtration, sedimentation, and distillation and chemical processes such as slow sand filters or active carbon, flocculation and the use of electromagnetic radiation such as ultraviolet light. Water purification may reduce the concentration of particulate matter including suspended particles, parasites, bacteria, algae, viruses, and fungi as well as reduce the concentration of a range of dissolved and particulate matter. Simple procedures such as boiling or the use of a household activated carbon filter are not sufficient for treating all possible contaminants that may be present in water from an unknown source. Even natural spring water, considered safe for all practical purposes in the 19th century, must now be tested before determining what kind of treatment, if any, is needed. Chemical and microbiological analysis, while expensive, are the only way to obtain the information necessary for deciding on the appropriate method of purification.

The standards for drinking water quality are typically set by governments or by international standards. These standards usually include minimum and maximum concentrations of contaminants, depending on the intended use of the water. Table 4.1. illustrates individual element concentrations valid according to Slovak Water Act in drinking water.

Widely varied techniques are available to remove contaminants like fine solids, micro-organisms and some dissolved inorganic and organic materials, or environmental persistent pharmaceutical pollutants. The choice of method will depend on the quality of the water being treated, the cost of the treatment process and the quality standards expected of the processed water. The processes below are the ones commonly used in water purification plants.

Pretreatment of water

The majority of water must be pumped from its source or directed into pipes or holding tanks. To avoid adding contaminants to the water, this physical infrastructure must be made from appropriate materials and constructed so that accidental contamination does not occur. The first step in purifying surface water is to remove large debris such as sticks, leaves, rubbish and other large particles which may interfere with subsequent purification steps. Most deep groundwater does not need screening before other purification steps.

Table 4.1

Drinking water quality indicators (physico-chemical) according to Slovak Water Act

Sedimentation

Waters exiting the flocculation basin may enter the sedimentation basin, also called a clarifier or settling basin (Fig. 4.6). It is a large tank with low water velocities, allowing floc to settle to the bottom. The sedimentation basin is best located close to the flocculation basin so the transit between the two processes does not permit settlement or floc break up. Sedimentation basins may be rectangular, where water flows from end to end, or circular where flow is from the centre outward. Sedimentation basin outflow is typically over a weir so only a thin top layer of water - that furthest from the sludge - exits. In general, sedimentation basin efficiency is not a function of detention time or depth of the basin. Although, basin depth must be sufficient so that water currents do not disturb the sludge and settled particle interactions are promoted. As particle concentrations in the settled water

increase near the sludge surface on the bottom of the tank, settling velocities can increase due to collisions and agglomeration of particles. Typical detention times for sedimentation vary from 1.5 to 4 hours. As particles settle to the bottom of a sedimentation basin, a layer of sludge is formed on the floor of the tank which must be removed and treated. The amount of sludge generated is significant, often 3 to 5 percent of the total volume of water to be treated. The cost of treating and disposing of the sludge can impact the operating cost of a water treatment plant. The sedimentation basin may be equipped with mechanical cleaning devices that continually clean its bottom, or the basin can be periodically taken out of service and cleaned manually.

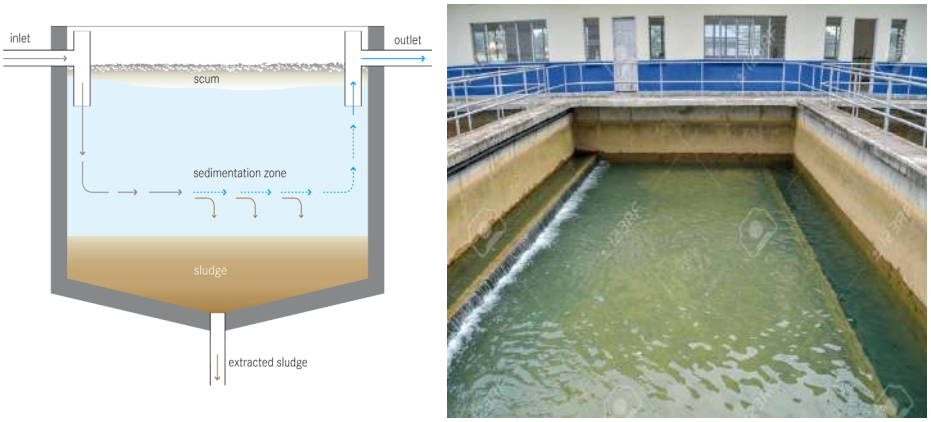

Fig. 4.6. Sketch of sedimentation tank (left) and sedimentation basin in real waterworks (right).

Sand filtration

The most common type of filter is a rapid sand filter. Water moves vertically through sand which often has a layer of activated carbon or anthracite coal above the sand. The top layer removes organic compounds, which contribute to taste and odour. The space between sand particles is larger than the smallest suspended particles, so simple filtration is not enough. Most particles pass through surface layers but are trapped in pore spaces or adhere to sand particles. Effective filtration extends into the depth of the filter. This property of the filter is key to its operation. If the top layer of sand were to block all the particles, the filter would quickly clog (Fig. 4.7).

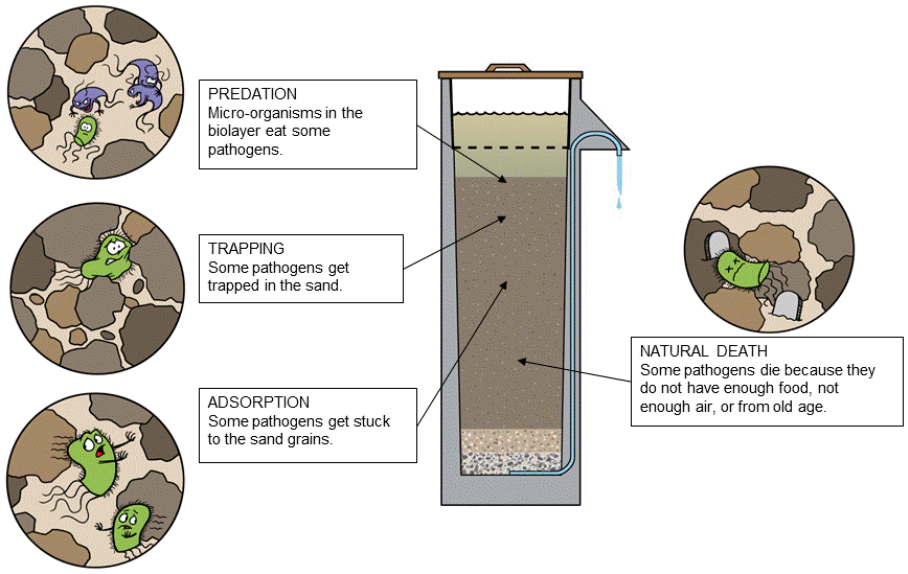

Fig. 4.7. Principle of mechanical sand filtration.

To clean the filter, water is passed quickly upward through the filter, opposite the normal direction (called *backwashing*) to remove embedded or unwanted particles. Prior to this step, compressed air may be blown up through the bottom of the filter to break up the compacted filter media to aid the backwashing process; this is known as *air scouring*. This contaminated water can be disposed of, along with the sludge from the sedimentation basin, or it can be recycled by mixing with the raw water entering the plant although this is often considered poor practice since it re-introduces an elevated concentration of bacteria into the raw water. Slow sand filters may be used where there is sufficient land and space, as the water flows very slowly through the filters. An effective slow sand filter may remain in service for many weeks or even months, if the pretreatment is well designed, and produces water with a very low available nutrient level which physical methods of treatment rarely achieve. Some water treatment plants employ pressure filters (Fig. 4.8). These work on the same principle as rapid gravity filters, differing in that the filter medium is enclosed in a steel vessel and the water is forced through it under pressure.

Coagulation and flocculation

One of the first steps in most conventional water purification processes is the addition of chemicals to assist in the removal of particles suspended in water. Particles can be inorganic such as clay and silt or organic such as algae, bacteria, viruses, protozoa and natural organic matter. Inorganic and organic particles contribute to the turbidity and color of water.

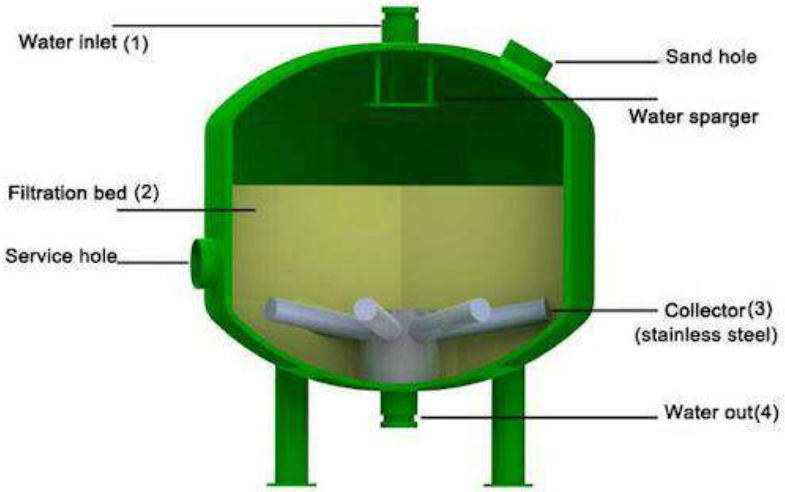

Fig. 4.8. Commercial steel pressure filter composition.

The addition of inorganic coagulants such as aluminum sulfate (or alum) or iron(III) salts such as iron(III) chloride cause several simultaneous chemical and physical interactions on and among the particles. Within seconds, negative charges on the particles are neutralized by inorganic coagulants. Also within seconds, metal hydroxide precipitates of the iron and aluminium ions begin to form (Fig. 4.9.).

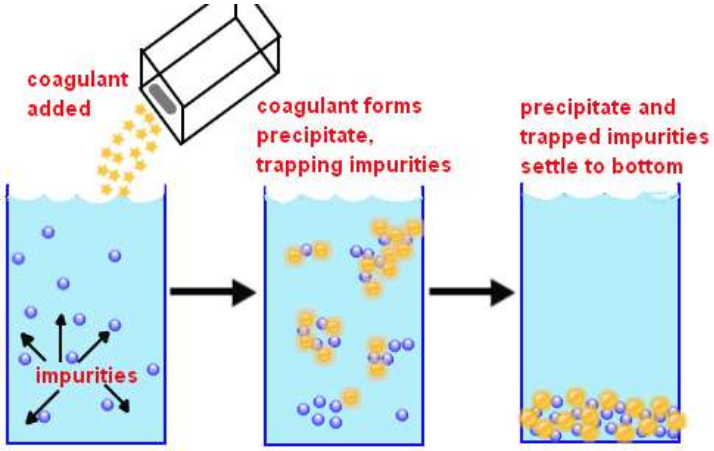

Fig. 4.9. Basic process explanation for coagulation and flocculation.

These precipitates combine into larger particles under natural processes such as Brownian motion and through induced mixing which is sometimes referred to as flocculation. Amorphous metal hydroxides are known as "floc". Large, amorphous aluminum and iron (III) hydroxides adsorb and enmesh particles in suspension and facilitate the removal of particles by subsequent processes of sedimentation and filtration. Aluminum hydroxides are formed within a fairly narrow pH range, typically: 5.5 to about 7.7. Iron (III) hydroxides can form over a larger pH range including pH levels lower than are effective for alum, typically 5.0 to 8.5. In water purification plants, there is usually a high energy, rapid mix unit process (detention

time in seconds) whereby the coagulant chemicals are added followed by flocculation basins (detention times range from 15 to 45 minutes) where low energy inputs turn large paddles or other gentle mixing devices to enhance the formation of floc. In fact, coagulation and flocculation processes are ongoing once the metal salt coagulants are added (Fig. 4.10. and Fig. 4.11).

Organic polymers were developed in the 1960s as aids to coagulants and, in some cases, as replacements for the inorganic metal salt coagulants. Synthetic organic polymers are high molecular weight compounds that carry negative, positive or neutral charges. When organic polymers are added to water with particulates, the high molecular weight compounds adsorb onto particle surfaces and through interparticle bridging coalesce with other particles to form floc.

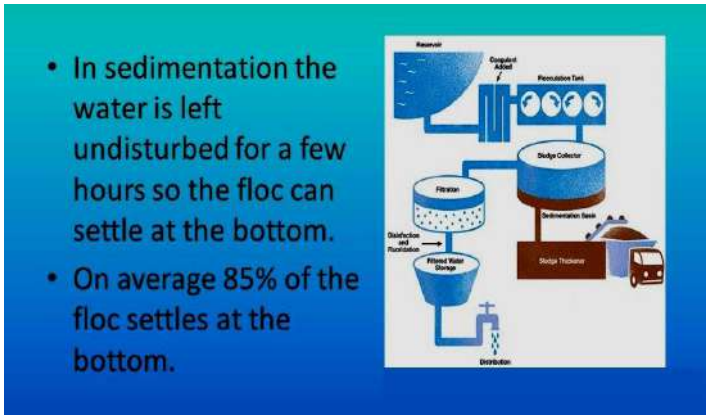

Fig. 4.10. Sketch of surface water purification incl. coagulation and flocculation.

Fig. 4.11. View of coagulation & flocculation process in real waterworks.

Water softening

Water softening is the removal of calcium, magnesium, and certain other metal cations in hard water. The resulting soft water requires less soap for the same cleaning effort, as soap is not wasted bonding with calcium ions. Soft water also extends the lifetime of plumbing by reducing or eliminating scale build-up in pipes and fittings. Water softening is usually achieved using lime softening or ion-

exchange resins but is increasingly being accomplished using nanofiltration or reverse osmosis membranes. Hard water contains calcium or magnesium ions that form insoluble salts upon reacting with soap, leaving a coating of insoluble stearates on tub and shower surfaces, commonly called soap scum (Fig. 4.12 and 4.13).

Fig. 4.12. Limescale in a PVC pipe.

Fig. 4.13. Ion exchange resin in the form of beads.

Water rich in hardness (calcium and magnesium ions) is treated with lime (calcium oxide) and/or soda-ash (sodium carbonate) to precipitate calcium carbonate out of solution utilizing the common-ion effect. Lime softening is the process in which lime is added to hard water to make it softer. It has several advantages over the ion-exchange method but is mainly suited to commercial treatment applications. In this method, water is treated with a calculated amount of washing soda (Na_2CO_3), which converts the chlorides and sulfates of calcium and magnesium into their respective carbonates, which get precipitated:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl;$$

$$MgSO_4 + Na_2CO_3 \rightarrow MgCO_3 + Na_2SO_4.$$

Ion exchange resins in the form of beads **(**Fig.3.12) are organic polymers containing anionic functional groups to which the divalent cations (Ca^{2+}) bind more strongly than monovalent cations (Na^+). Inorganic materials called zeolites also exhibit ion-exchange properties (Fig. 4.14). These minerals are widely used in laundry detergents. Resins are also available to remove the carbonate, bicarbonate, and sulfate ions that are absorbed and hydroxide ions that are released from the resin.

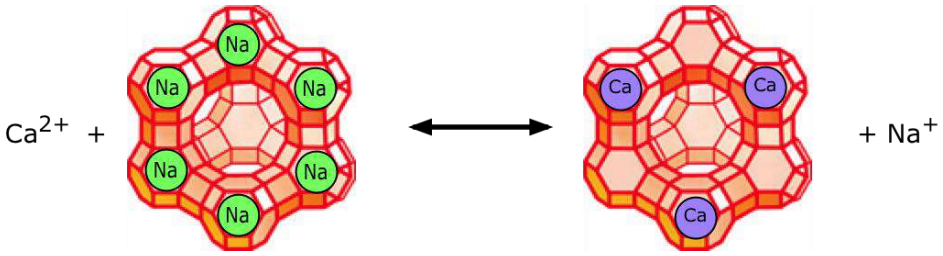

Fig. 4.14. Synthetic zeolites NaA, NaX or NaP in micrometric size used to be applied for detergents production since 1970.

When all the available Na^+ ions have been replaced with calcium or magnesium ions, the resin must be recharged by eluting the Ca^{2+} and Mg^{2+} ions using a solution of sodium chloride or sodium hydroxide, depending on the type of resin used. For anionic resins, regeneration typically uses a solution of sodium hydroxide (lye) or potassium hydroxide. The waste waters eluted from the ion-exchange column containing the unwanted calcium and magnesium salts are typically discharged to the sewage system.

pH adjustment

Pure water has a pH close to 7 (neither alkaline nor acidic). Sea water can have pH values that range from 7.5 to 8.4 (moderately alkaline). Fresh water can have widely ranging pH values depending on the geology of the drainage basin or aquifer and the influence of contaminant inputs (acid rain). If the water is acidic (lower than 7), lime, soda ash, or sodium hydroxide can be added to raise the pH during water purification processes. Lime addition increases the calcium ion concentration, thus raising the water hardness. For highly acidic waters, forced draft degasifiers can be an effective way to raise the pH, by stripping dissolved carbon dioxide from the water. Making the water alkaline helps coagulation and flocculation processes work effectively and also helps to minimize the risk of lead being dissolved from lead pipes and from lead solder in pipe fittings. Sufficient alkalinity also reduces the corrosiveness of water to iron pipes. Acid (carbonic acid, hydrochloric acid or sulfuric acid) may be added to alkaline waters in some circumstances to lower the pH. Alkaline water (above pH 7.0) does not necessarily mean that lead or copper from the plumbing system will not be dissolved into the water. The ability of water to precipitate calcium carbonate to protect metal surfaces and reduce the likelihood of toxic metals being dissolved in water is a function of pH, mineral content, temperature, alkalinity and calcium concentration.

Disinfection

Disinfection is accomplished both by filtering out harmful micro-organisms and by adding disinfectant chemicals. Water is disinfected to kill any pathogens which pass through the filters and to provide a residual dose of disinfectant to kill or inactivate potentially harmful micro-organisms in the storage and distribution systems. Possible pathogens include viruses, bacteria, including *Salmonella*, *Cholera*, *Campylobacter* and *Shigella*, and protozoa, including *Giardia lamblia* and other *cryptosporidia*.

After the introduction of any chemical disinfecting agent, the water is usually held in temporary storage, often called a contact tank or clear well, to allow the disinfecting action to complete. The most common disinfection method involves some form of chlorine or its compounds such as chloramine or chlorine dioxide.

Chlorine is a strong oxidant that rapidly kills many harmful micro-organisms. Because chlorine is a toxic gas, there is a danger of a release associated with its use.

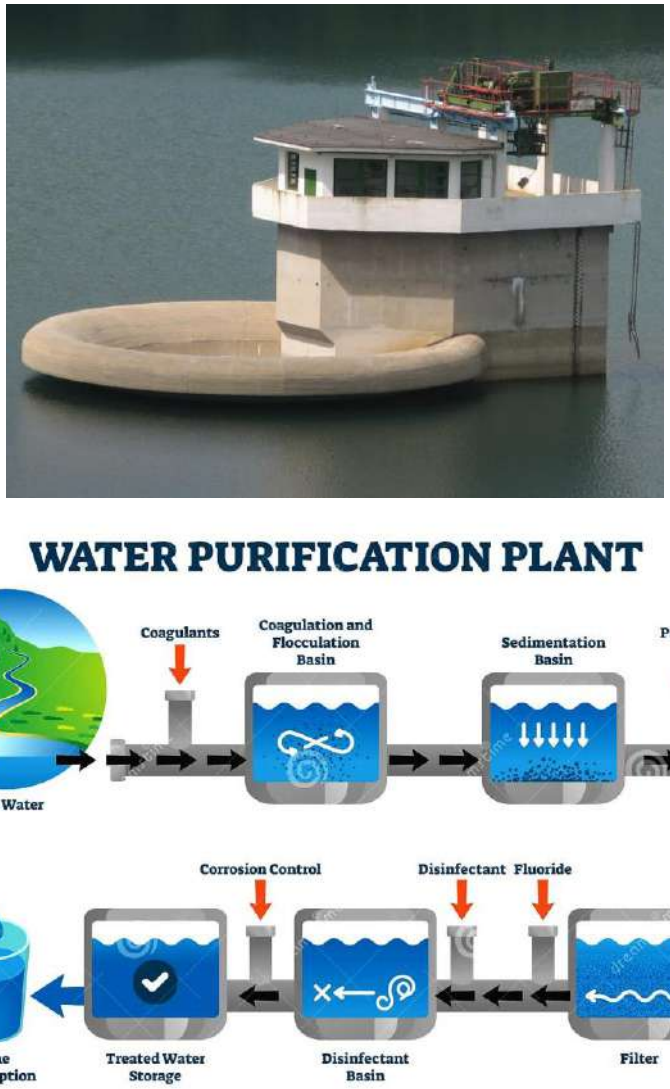

Fig. 4.15. Scheme of conventional surface water purification in waterworks (upper figure a typical surface water pumping into waterworks from the middle of reservoir).

This problem is avoided by the use of sodium hypochlorite, which is a relatively inexpensive solution used in household bleach that releases free chlorine when dissolved in water. Chlorine solutions can be generated on site by electrolyzing common salt solutions. A solid form, calcium hypochlorite, releases chlorine on contact with water. Handling the solid, however, requires more routine human contact through opening bags and pouring than the use of gas cylinders or bleach, which are more easily automated. The generation of liquid sodium hypochlorite is inexpensive and also safer than the use of gas or solid chlorine. Chlorine levels up to

4 milligrams per liter are considered safe in drinking water. One drawback is that chlorine from any source reacts with natural organic compounds in the water to form potentially harmful chemical by-products. These by-products, trihalomethanes (THMs) and haloacetic acids (HAAs), are both carcinogenic in large quantities. Although chlorine is effective in killing bacteria, it has limited effectiveness against pathogenic protozoa that form cysts in water such as *Giardia lamblia* and *Cryptosporidium*.

Chlorine dioxide is a faster-acting disinfectant than elemental chlorine. It is relatively rarely used because in some circumstances it may create excessive amounts of chlorite, which is a by-product regulated to low allowable levels. Chlorine dioxide can be supplied as an aqueous solution and added to water to avoid gas handling problems. Ultraviolet light (UV) is very effective at inactivating cysts, in low turbidity water. UV light's disinfection effectiveness decreases as turbidity increases, a result of the absorption, scattering, and shadowing caused by the suspended solids. The main disadvantage to the use of UV radiation is that, like ozone treatment, it leaves no residual disinfectant in the water; therefore, it is sometimes necessary to add a residual disinfectant after the primary disinfection process.

3.3. Wastewater and sewage treatment

Sewage treatment (or domestic wastewater treatment, municipal wastewater treatment) is a type of wastewater treatment which aims to remove contaminants from sewage to produce an effluent that is suitable for discharge to the surrounding environment or an intended reuse application, thereby preventing water pollution from raw sewage discharges. Sewage contains wastewater from households and businesses and possibly pre-treated industrial wastewater. There are a high number of sewage treatment processes to choose from. These can range from decentralized systems (including on-site treatment systems) to large centralized systems involving a network of pipes and pump stations (called sewerage) which convey the sewage to a treatment plant. For cities that have a combined sewer, the sewers will also carry urban runoff (stormwater) to the sewage treatment plant. Sewage treatment often involves two main stages, called primary and secondary treatment, while advanced treatment also incorporates a tertiary treatment stage with polishing processes and nutrient removal. Secondary treatment can reduce organic matter (measured as biological oxygen demand) from sewage, using aerobic or anaerobic biological processes. With regards to biological treatment of sewage, the treatment objectives can include various degrees of the following: transform dissolved and particulate biodegradable components (especially organic matter) into acceptable end products, transform and remove nutrients (nitrogen and phosphorus), remove or inactivate

pathogenic organisms, and remove specific trace organic constituents (micropollutants). Some types of sewage treatment produce sewage sludge which can be treated before safe disposal or reuse. Under certain circumstances, the treated sewage sludge might be termed "biosolids" and can be used as a fertilizer.

Sewerage (or sewage system) is the infrastructure that conveys sewage or surface runoff (stormwater, meltwater, rainwater) using sewers. It encompasses components such as receiving drains, manholes, pumping stations, storm overflows, and screening chambers of the combined sewer or sanitary sewer. Sewerage ends at the entry to a sewage treatment plant or at the point of discharge into the environment. It is the system of pipes, chambers, manholes, etc. that conveys the sewage or storm water.

Types of treatment processes

Sewage can be treated close to where the sewage is created, which may be called a "decentralized" system or even an "on-site" system (on-site sewage facility, septic tanks, etc.). Alternatively, sewage can be collected and transported by a network of pipes and pump stations to a municipal treatment plant (Fig. 4.16).

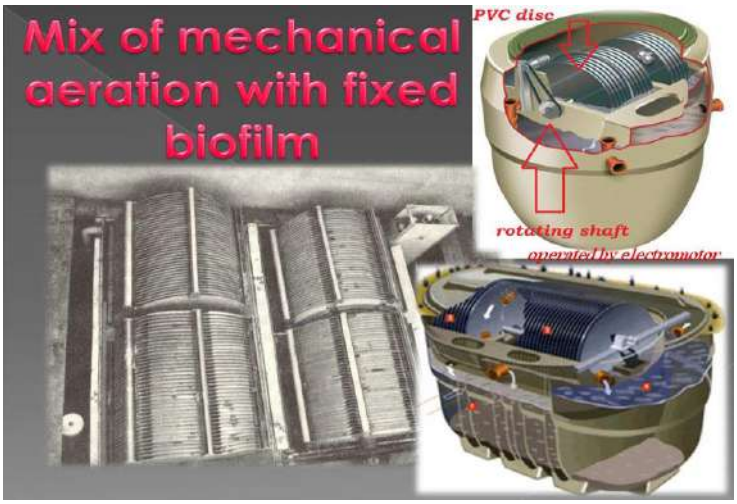

Fig. 4.16. Municipal wastewater treatment using biodiscs.

This is called a "centralized" system (see also sewerage and pipes and infrastructure). A large number of sewage treatment technologies have been developed, mostly using biological treatment processes (see list of wastewater treatment technologies). Very broadly, they can be grouped into high tech (high cost) versus low tech (low cost) options, although some technologies might fall into either category. Other grouping classifications are "intensive" or "mechanized" systems (more compact, and frequently employing high tech options) versus "extensive" or "natural" or "nature-based" systems (usually using natural treatment processes and occupying larger areas) systems. This classification may be sometimes oversimplified, because a treatment plant may involve a combination of processes,

and the interpretation of the concepts of high tech and low tech, intensive and extensive, mechanized and natural processes may vary from place to place.

There are other process options which may be classified as disposal options, although they can also be understood as basic treatment options. These include: Application of sludge, irrigation, soak pit, leach field, fish pond, floating plant pond, water disposal/groundwater recharge, surface disposal and storage. Application of sewage to land can be considered as a form of final disposal or of treatment, or both. It leads to groundwater recharge and/or to evapotranspiration. Land application include slow-rate systems, rapid infiltration, subsurface infiltration, overland flow. It is done by flooding, furrows, sprinkler and dripping. It is a treatment/disposal system that requires a large amount of land per person.

Population equivalent

The "per person organic matter load" is a parameter used in the design of sewage treatment plants. This concept is known as population equivalent (PE). The base value used for PE can vary from one country to another. Commonly used definitions used worldwide are: 1 PE equates to 60 gram of BOD per person per day, and it also equals 200 liters of sewage per day. This concept is also used as a comparison parameter to express the strength of industrial wastewater compared to sewage.

Available process steps

Sewage treatment often involves two main stages, called primary and secondary treatment, while advanced treatment also incorporates a tertiary treatment stage with polishing processes. Different types of sewage (Fig. 4.17) treatment may utilize some or all of the process steps listed below. Preliminary treatment (sometimes called pretreatment) removes coarse materials that can be easily collected from the raw sewage before they damage or clog the pumps and sewage lines of primary treatment clarifiers.

Screening and grit removal

The influent in sewage water passes through a bar screen to remove all large objects like cans, rags, sticks, plastic packets, etc. carried in the sewage stream. This is most commonly done with an automated mechanically raked bar screen in modern plants serving large populations, while in smaller or less modern plants, a manually cleaned screen may be used. The raking action of a mechanical bar screen is typically paced according to the accumulation on the bar screens and/or flow rate. The solids are collected and later disposed in a landfill, or incinerated. Bar screens or mesh screens of varying sizes may be used to optimize solids removal. If gross solids are not removed, they become entrained in pipes and moving parts of the treatment plant, and can cause substantial damage and inefficiency in the process (Fig. 4.17).

Grit consists of sand, gravel, rocks, and other heavy materials. Preliminary treatment may include a sand or grit removal channel or chamber, where the velocity of the incoming sewage is reduced to allow the settlement of grit. Grit removal is necessary to (1) reduce formation of deposits in primary sedimentation tanks, aeration tanks, anaerobic digesters, pipes, channels, etc. (2) reduce the frequency of tank cleaning caused by excessive accumulation of grit; and (3) protect moving mechanical equipment from abrasion and accompanying abnormal wear. The removal of grit is essential for equipment with closely machined metal surfaces such as comminutors, fine screens, centrifuges, heat exchangers, and high pressure diaphragm pumps.

Fig. 4.17. Manually-cleaned screens (left); sewage pumping into the next technology units of wastewater treatment plant (middle); horizontal flow grit chambers (right).

Grit chambers come in three types: horizontal grit chambers, aerated grit chambers, and vortex grit chambers. Vortex grit chambers include mechanically induced vortex, hydraulically induced vortex, and multi-tray vortex separators. During periods of high flow deposited grit is resuspended and the quantity of grit reaching the treatment plant increases substantially. It is therefore important that the grit removal system not only operates efficiently during normal flow conditions but also under sustained peak flows when the greatest volume of grit reaches the plant.

Flow equalization

Equalization basins can be used to achieve flow equalization, with the aim to reduce peak dry-weather flows or peak wet-weather flows in the case of combined sewer systems. The benefits are performance improvements of the biological treatment processes, the secondary clarifiers and any effluent filtration equipment.

Disadvantages include the basins' capital cost and space requirements. Basins can also provide a place to temporarily hold, dilute and distribute batch discharges of toxic or high-strength wastewater which might otherwise inhibit biological secondary treatment (such was wastewater from portable toilets or fecal sludge that is brought to the sewage treatment plant in vacuum trucks). Flow equalization basins require variable discharge control, typically include provisions for bypass and cleaning, and may also include aerators and odor control.

Fat and grease removal

In some larger plants, fat and grease are removed by passing the sewage through a small tank where skimmers collect the fat floating on the surface. Air blowers in the base of the tank may also be used to help recover the fat as a froth. Many plants, however, use primary clarifiers with mechanical surface skimmers for fat and grease removal.

Primary treatment

Primary treatment is the "removal of a portion of the suspended solids and organic matter from the sewage". It consists of allowing sewage to pass slowly through a basin where heavy solids can settle to the bottom while oil, grease and lighter solids float to the surface and are skimmed off (Fig. 4.18). These basis are called "primary sedimentation tanks" or "primary clarifiers" and typically have a hydraulic retention time of 1.5 to 2.5 hours. The settled and floating materials are removed and the remaining liquid may be discharged or subjected to secondary treatment. Primary settling tanks are usually equipped with mechanically driven scrapers that continually drive the collected sludge towards a hopper in the base of the tank where it is pumped to sludge treatment facilities.

Fig. 4.18. Primary clarifier.

Secondary treatment

The main processes involved in secondary sewage treatment are designed to remove as much of the solid material as possible. They use biological processes to digest and remove the remaining soluble material, especially the organic fraction. This can be done with either suspended-growth or biofilm processes. The microorganisms that feed on the organic matter present in the sewage grow and multiply, constituting the biological solids, or biomass. These grow and group together in the form of flocs or biofilms and, in some specific processes, as granules. In several treatment processes, the biological floc or biofilm and remaining fine solids can then be settled as a sludge, leaving a liquid substantially free of solids, and with a greatly reduced concentration of pollutants.

Secondary treatment can reduce organic matter (measured as biological oxygen demand) from sewage, using aerobic or anaerobic processes. The organisms involved in these processes are sensitive to the presence of toxic materials, although these are not expected to be present at high concentrations in typical municipal sewage (Figs. 4.19 and 4.20).

Fig. 4.19. Sketch of secondary sewage treatment in activated sludge tank connected with secondary clarifier (activation – intensification of processes ongoing in nature).

Secondary treatment is the removal of biodegradable organic matter (in solution or suspension) from sewage or similar kinds of wastewater. The aim is to achieve a certain degree of effluent quality in a sewage treatment plant suitable for the intended disposal or reuse option. A "primary treatment" step often precedes secondary treatment, whereby physical phase separation is used to remove settleable solids. During secondary treatment, biological processes are used to remove

dissolved and suspended organic matter measured as biochemical oxygen demand (BOD). These processes are performed by microorganisms in a managed aerobic or anaerobic process depending on the treatment technology. Bacteria and protozoa consume biodegradable soluble organic contaminants (e.g. sugars, fats, and organic short-chain carbon molecules from human waste, food waste, soaps and detergent) while reproducing to form cells of biological solids. Secondary treatment is widely used in sewage treatment and is also applicable to many agricultural and industrial wastewaters.

Fig. 4.20. Plate membrane reactor for N – microorganisms retention and high sludge age reaching (simultaneously cleaned using the air).

Biological nutrient removal

Excessive release to the environment can lead to nutrient pollution, which can manifest itself in eutrophication. This process can lead to algal blooms, a rapid growth, and later decay, in the population of algae. In addition to causing deoxygenation, some algal species produce toxins that contaminate drinking water supplies. Ammonia nitrogen, in the form of free ammonia (NH_3) is toxic to fish. Ammonia nitrogen, when converted to nitrite and further to nitrate in a water body, in the process of nitrification, is associated with the consumption of dissolved oxygen. Nitrite and nitrate may also have public health significance if concentrations are high in drinking water, because of a disease called metahemoglobinemia.

Phosphorus removal is important as phosphorus is a limiting nutrient for algae growth in many fresh water systems. Therefore, an excess of phosphorus can lead to eutrophication. It is also particularly important for water reuse systems where high phosphorus concentrations may lead to fouling of downstream equipment such as reverse osmosis. A range of treatment processes are available to remove nitrogen and phosphorus. Biological nutrient removal is regarded by some as a type of secondary treatment process, and by others as a tertiary (or "advanced") treatment process.

Nitrogen removal

Nitrogen is removed through the biological oxidation of nitrogen from ammonia to nitrate (nitrification), followed by denitrification, the reduction of nitrate to nitrogen gas. Nitrogen gas is released to the atmosphere and thus removed from the water. Nitrification itself is a two-step aerobic process, each step facilitated by a different type of bacteria. The oxidation of ammonia (NH_4^+) to nitrite (NO_2^-) is most often facilitated by bacteria such as *Nitrosomonas, Nitrosocystis, Nitrosospira*. Nitrite oxidation to nitrate (NO_3^-), though traditionally believed to be facilitated by *Nitrobacter* (Figs. 4.21 and 4.22).

Denitrification requires anoxic conditions to encourage the appropriate biological communities to form. "Anoxic conditions" refers to a situation where oxygen is absent but nitrate is present. Denitrification is facilitated by a wide diversity of bacteria. The activated sludge process, sand filters, waste stabilization ponds, constructed wetlands and other processes can all be used to reduce nitrogen.

Fig. 4.21. Layout of nitrification process by chemical equations.

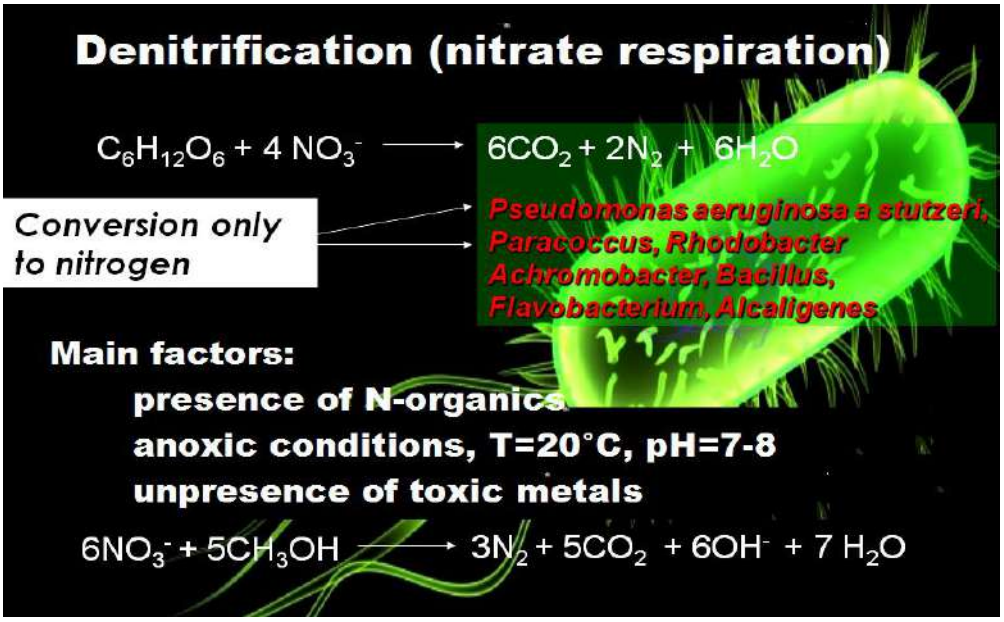

Fig. 4.22. Layout of denitrification process by chemical equations.

Since denitrification is the reduction of nitrate to dinitrogen (molecular nitrogen) gas, an electron donor is needed. This can be, depending on the wastewater, organic matter (from the sewage itself), sulfide, or an added donor like methanol. The sludge in the anoxic tanks (denitrification tanks) must be mixed well (mixture of recirculated mixed liquor, return activated sludge, and raw influent) e.g. by using submersible mixers in order to achieve the desired denitrification. Over time, different treatment configurations for activated sludge processes have evolved to achieve high levels of nitrogen removal. An initial scheme placed an anoxic treatment zone before the aeration tank and clarifier, using the return activated sludge from the clarifier as a nitrate source. The sewage (either raw or as effluent from primary clarification) serves as the electron source for the facultative bacteria to metabolize carbon, using the inorganic nitrate as a source of oxygen instead of dissolved molecular oxygen (Figs. 4.22 and 4.23).

Phosphorus removal

Phosphorus can be removed biologically in a process called enhanced biological phosphorus removal. In this process, specific bacteria, called polyphosphate-accumulating organisms (PAOs), are selectively enriched and accumulate large quantities of phosphorus within their cells (up to 20 percent of their mass) − Fig.4.24.

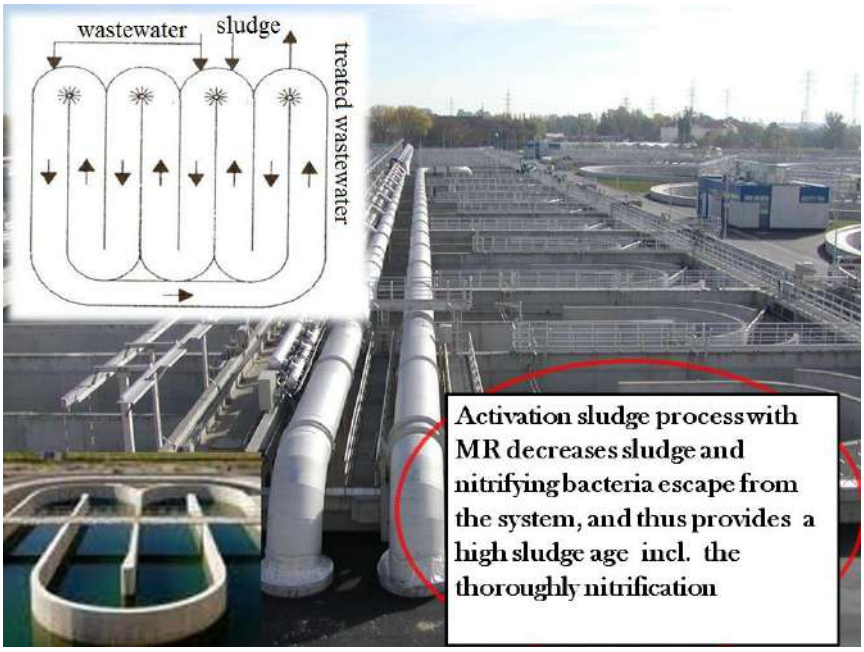

Fig. 4.23. Carrousel system as the most simple arrangement for the carbonisation, nitrification and denitrification of wastewater in wastewater treatment plants.

Phosphorus removal can also be achieved by chemical precipitation, usually with salts of iron (e.g. ferric chloride) or aluminum (e.g. alum), or lime. This may lead to a higher sludge production as hydroxides precipitate and the added chemicals can be expensive. Some systems use both biological phosphorus removal and chemical phosphorus removal. The chemical phosphorus removal in those systems may be used as a backup system, for use when the biological phosphorus removal is not removing enough phosphorus, or may be used continuously. In either case, using both biological and chemical phosphorus removal has the advantage of not increasing sludge production as much as chemical phosphorus removal on its own, with the disadvantage of the increased initial cost associated with installing two different systems.

Advanced and complementary sewage treatments

Advanced sewage treatment generally involves three main stages, called primary, secondary and tertiary treatment but may also include intermediate stages and final polishing processes. The purpose of tertiary treatment (also called "advanced treatment") is to provide a final treatment stage to further improve the effluent quality before it is discharged to the receiving water body or reused. More than one tertiary treatment process may be used at any treatment plant. If disinfection is practiced, it is always the final process. It is also called "effluent polishing". Tertiary treatment may include disinfection and removal of micropollutants, such as environmental persistent pharmaceutical pollutants.

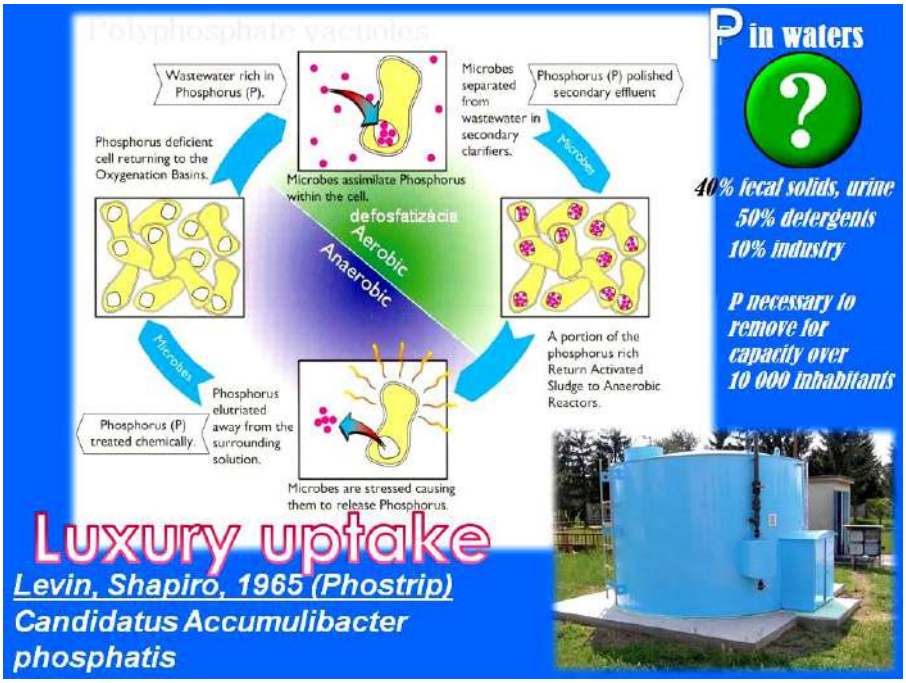

Fig. 4.24. Scheme of Luxury uptake phosphorus removal.

Advanced sewage treatment is defined as anything more than primary and secondary treatment in order to allow discharge into a highly sensitive or fragile ecosystem such as estuaries, low-flow rivers or coral reefs. Treated water is sometimes disinfected chemically or physically (for example, by lagoons and microfiltration) prior to discharge into a stream, river, bay, lagoon or wetland, or it can be used for the irrigation of a golf course, greenway or park (Fig. 4.25). If it is sufficiently clean, it can also be used for groundwater recharge or agricultural purposes.

Sand filtration removes much of the residual suspended matter. Filtration over activated carbon, also called carbon adsorption, removes residual toxins. Micro filtration or synthetic membranes are also used, for example in membrane bioreactors which also remove pathogens. Settlement and further biological improvement of treated sewage may be achieved through storage in large man-made ponds or lagoons. These lagoons are highly aerobic, and colonization by native macrophytes, especially reeds, is often encouraged.

Disinfection

Disinfection of treated sewage may be attempted to kill pathogens (disease-causing microorganisms) prior to disposal, and is increasingly effective after more elements of the foregoing treatment sequence have been completed. The purpose of disinfection in the treatment of sewage is to substantially reduce the number of pathogens in the water to be discharged back into the environment or to be reused. The effectiveness of disinfection depends on the quality of the water being treated (e.g. turbidity, pH, etc.), the type of disinfection being used, the disinfectant dosage

(concentration and time), and other environmental variables. Water with high turbidity will be treated less successfully, since solid matter can shield organisms, especially from ultraviolet light or if contact times are low. Generally, short contact times, low doses and high flows all militate against effective disinfection. Common methods of disinfection include ozone, chlorine, ultraviolet light, or sodium hypochlorite. Monochloramine, which is used for drinking water, is not used in the treatment of sewage because of its persistence.

Fig. 4.25. Further biological improvement of treated sewage may be achieved through storage in large man-made ponds or lagoons.

Chlorination remains the most common form of treated sewage disinfection in many countries due to its low cost and long-term history of effectiveness. One disadvantage is that chlorination of residual organic material can generate chlorinated-organic compounds that may be carcinogenic or harmful to the environment. Residual chlorine or chloramines may also be capable of chlorinating organic material in the natural aquatic environment. Further, because residual chlorine is toxic to aquatic species, the treated effluent must also be chemically dechlorinated, adding to the complexity and cost of treatment.

Ultraviolet (UV) light can be used instead of chlorine, iodine, or other chemicals. Because no chemicals are used, the treated water has no adverse effect on organisms that later consume it, as may be the case with other methods. UV radiation causes damage to the genetic structure of bacteria, viruses, and other pathogens, making them incapable of reproduction. The key disadvantages of UV disinfection are the need for frequent lamp maintenance and replacement and the need for a highly treated effluent to ensure that the target microorganisms are not shielded from the UV radiation (i.e., any solids present in the treated effluent may protect microorganisms from the UV light). In many countries, UV light is becoming the most common means of disinfection because of the concerns about the impacts of

chlorine in chlorinating residual organics in the treated sewage and in chlorinating organics in the receiving water.

Membranes can also be effective disinfectants, because they act as barriers, avoiding the passage of the microorganisms (Fig. 4.26). As a result, the final effluent may be devoid of pathogenic organisms, depending on the type of membrane used. This principle is applied in membrane bioreactors.

Micropollutants such as pharmaceuticals, ingredients of household chemicals, chemicals used in small businesses or industries, environmental persistent pharmaceutical pollutants or pesticides may not be eliminated in the commonly used sewage treatment processes and therefore lead to water pollution. Although concentrations of those substances and their decomposition products are quite low, there is still a chance of harming aquatic organisms. For pharmaceuticals, the following substances have been identified as "toxicologically relevant": substances with endocrine disrupting effects, genotoxic substances and substances that enhance the development of bacterial resistances. Techniques for elimination of micropollutants via a fourth treatment stage during sewage treatment are implemented in Germany, Switzerland, Sweden and the Netherlands and tests are ongoing in several other countries. Such process steps mainly consist of activated carbon filters that adsorb the micropollutants (Fig. 4.27). The combination of advanced oxidation with ozone followed by granular activated carbon has been suggested as a cost-effective treatment combination for pharmaceutical residues. For a full reduction of microplasts the combination of ultrafiltration followed by GAC has been suggested.

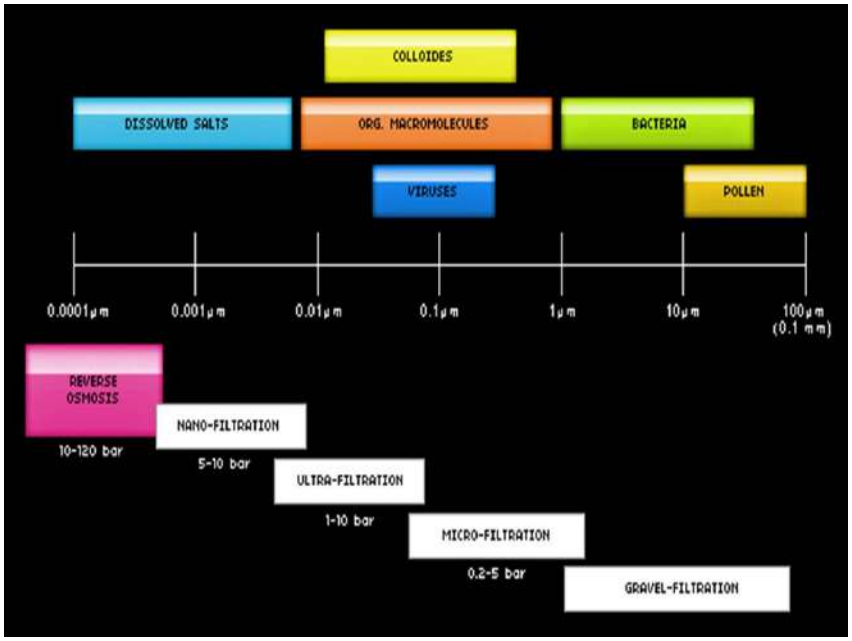

Fig. 4.26. Depending on the type of membrane used various pollutants incl. microplasts can be removed from water.

Fig. 4.27. Principal sketch of presure filter (left) which may be filled with activated carbon (right).

Sewage sludge treatment and disposal

Sewage sludge treatment describes the processes used to manage and dispose of sewage sludge produced during sewage treatment. Sludge treatment is focused on reducing sludge weight and volume to reduce transportation and disposal costs, and on reducing potential health risks of disposal options. Water removal is the primary means of weight and volume reduction, while pathogen destruction is frequently accomplished through heating during thermophilic digestion, composting, or incineration. The choice of a sludge treatment method depends on the volume of sludge generated, and comparison of treatment costs required for available disposal options. Air-drying and composting may be attractive to rural communities, while limited land availability may make aerobic digestion and mechanical dewatering preferable for cities, and economies of scale may encourage energy recovery alternatives.

Sludge is mostly water with some amounts of solid material removed from liquid sewage. Primary sludge includes settleable solids removed during primary treatment in primary clarifiers. Secondary sludge is sludge separated in secondary clarifiers that are used in secondary treatment bioreactors or processes using inorganic oxidizing agents. In intensive sewage treatment processes, the sludge produced needs to be removed from the liquid line on a continuous basis because the volumes of the tanks in the liquid line have insufficient volume to store sludge. This is done in order to keep the treatment processes compact and in balance (production of sludge approximately equal to the removal of sludge).

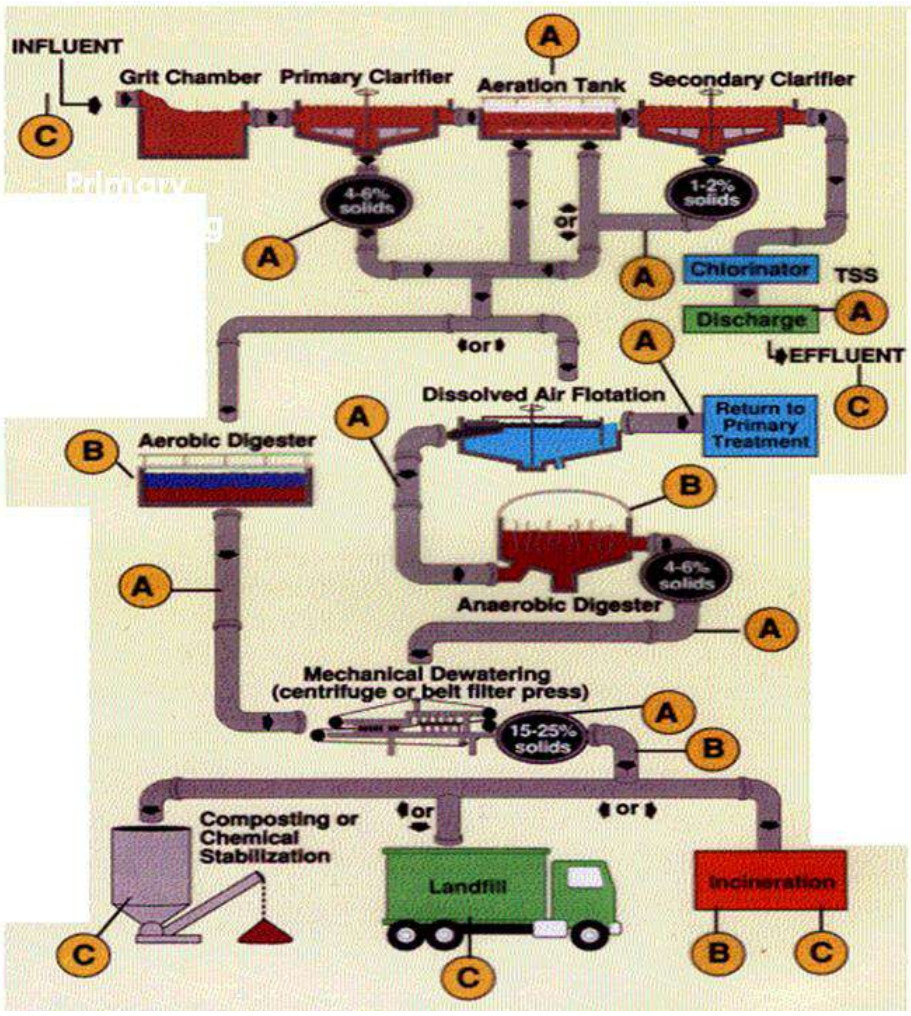

Fig. 4.28. Scheme of the entire wastewater treatment plant incl. sludge handling.

The sludge removed from the liquid line goes to the sludge treatment line. Aerobic processes (such as the activated sludge process) tend to produce more sludge compared with anaerobic processes. On the other hand, in extensive (natural) treatment processes, such as ponds and constructed wetlands, the produced sludge remains accumulated in the treatment units (liquid line) and is only removed after several years of operation.

Sludge treatment options depend on the amount of solids generated and other site-specific conditions. Composting is most often applied to small-scale plants with aerobic digestion for mid-sized operations, and anaerobic digestion for the larger-scale operations (Figs. 4.28 and 4.29). The sludge is sometimes passed through a so-called pre-thickener which de-waters the sludge. Types of pre-thickeners include centrifugal sludge thickeners, rotary drum sludge thickeners and belt filter presses. Dewatered sludge may be incinerated or transported offsite for disposal in a landfill or use as an agricultural soil amendment (Fig. 4.30).

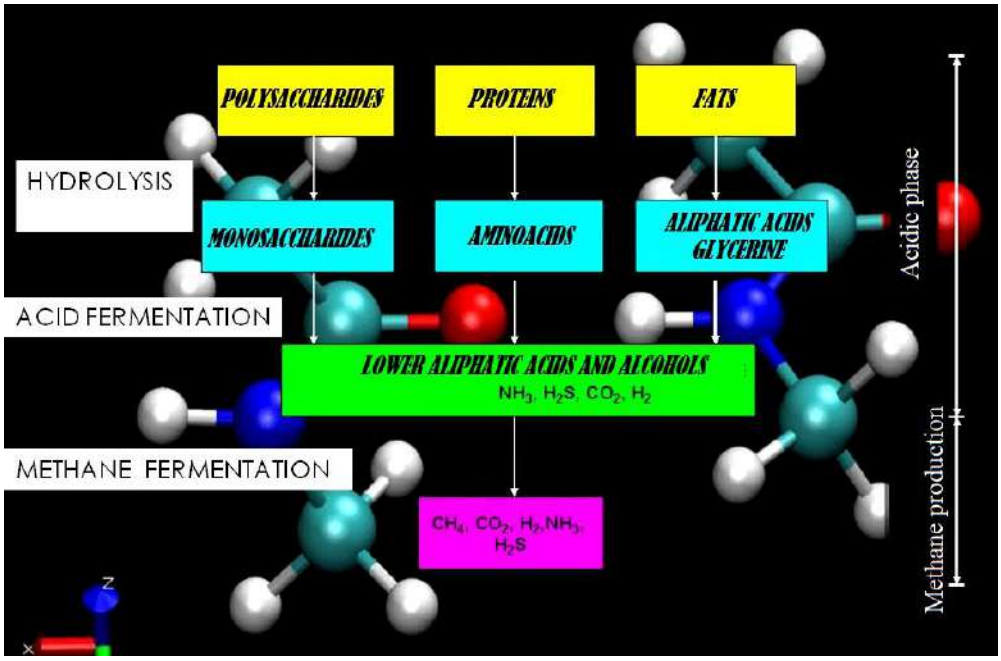

Fig. 4.29. Biochemical process layout for the anaerobic digestion.

Energy requirements

The energy requirements vary with type of treatment process as well as sewage strength. For example, constructed wetlands and stabilization ponds have low energy requirements, associated mainly with the occasional presence of pumps and other equipment. On the other hand, the activated sludge process includes an aeration step, which is highly energy consuming. Sewage treatment plants that produce biogas in their sewage sludge treatment process with anaerobic digestion can produce enough energy to meet most of the energy needs of the sewage treatment plant itself (Fig. 4.31). Most of this electricity is used for aeration, pumping systems and equipment for the dewatering and drying of sewage sludge. Advanced sewage treatment plants, e.g. for nutrient removal, require more energy than plants that only achieve primary or secondary treatment. Small rural plants using trickling filters may operate with no net energy requirements, the whole process being driven by gravitational flow, including tipping bucket flow distribution and the desludging of settlement tanks to drying beds. This is usually only practical in hilly terrain and in areas where the treatment plant is relatively remote from housing because of the difficulty in managing odors.

Fig. 4.30. Sewage sludge dewatering.

Co-treatment of industrial effluent

In highly regulated developed countries, industrial wastewater usually receives at least pretreatment if not full treatment at the factories themselves to reduce the pollutant load, before discharge to the sewer. The pretreatment has the following aims: to remove constituents that may pose risks to the sewerage system and its workers; prevent toxic or inhibitory compounds to the microorganisms in the biological stage in the municipal treatment plant; hinder beneficial use of the produced sewage sludge; or that will still be present in the final effluent from the treatment plant. Some industrial wastewater may contain pollutants which cannot be removed by sewage treatment plants. Also, variable flow of industrial waste associated with production cycles may upset the population dynamics of biological treatment units.

Fig. 4.31. Anaerobic digestion towers (upper figure municipal wastewater treatment plant for the city residence Petržalka of Bratislava capital where biogas production during sludge digestion process is combined with electricity co-generation unit).

Environmental impacts

Sewage treatment plants can have significant effects on the biotic status of receiving waters and can cause some water pollution, especially if the treatment process used is only basic. For example, for sewage treatment plants without nutrient removal, eutrophication of receiving water bodies can be a problem.

Water pollution (or aquatic pollution) is the contamination of water bodies, usually as a result of human activities, in such a manner that negatively affects its legitimate uses. Water pollution reduces the ability of the body of water to provide the ecosystem services that it would otherwise provide. Water bodies include for example lakes, rivers, oceans, aquifers, reservoirs and groundwater. Water pollution results when contaminants are introduced into these water bodies. For example, releasing inadequately treated wastewater into natural waters can lead to degradation of these aquatic ecosystems. All plants and organisms living in or being exposed to polluted water bodies can be impacted. The effects can damage individual species and impact the natural biological communities they are part of. Water pollution can also lead to water-borne diseases for people using polluted water for drinking, bathing, washing or irrigation.

Increasingly, people use treated or even untreated sewage for irrigation to produce crops. Cities provide lucrative markets for fresh produce, so are attractive to farmers. Because agriculture has to compete for increasingly scarce water resources with industry and municipal users, there is often no alternative for farmers but to use water polluted with sewage directly to water their crops. There can be significant health hazards related to using water loaded with pathogens in this way. The World Health Organization developed guidelines for safe use of wastewater in 2006. They advocate a ‘multiple-barrier’ approach to wastewater use, where farmers are encouraged to adopt various risk-reducing behaviors. These include ceasing irrigation a few days before harvesting to allow pathogens to die off in the sunlight, applying water carefully so it does not contaminate leaves likely to be eaten raw, cleaning vegetables with disinfectant or allowing fecal sludge used in farming to dry before being used as a human manure.

Water reclamation (also called wastewater reuse, water reuse or water recycling) is the process of converting municipal wastewater (sewage) or industrial wastewater into water that can be reused for a variety of purposes. Types of reuse include: urban reuse, agricultural reuse (irrigation), environmental reuse, industrial reuse, planned potable reuse, de facto wastewater reuse (unplanned potable reuse). For example, reuse may include irrigation of gardens and agricultural fields or replenishing surface water and groundwater (i.e., groundwater recharge). Reused water may also be directed toward fulfilling certain needs in residences (e.g. toilet

flushing), businesses, and industry, and could even be treated to reach drinking water standards. Treated municipal wastewater reuse for irrigation is a long-established practice, especially in arid countries. Reusing wastewater as part of sustainable water management allows water to remain as an alternative water source for human activities. This can reduce scarcity and alleviate pressures on groundwater and other natural water bodies.

Global targets

Sustainable Development Goal has a Target which is formulated as follows: "By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally." The corresponding Indicator is the "proportion of wastewater safely treated".

Data in 2020 showed that there is still too much uncollected household wastewater: Only 66% of all household wastewater flows were collected at treatment facilities in 2020 (this is determined from data from 128 countries). Based on data from 42 countries in 2015, the report stated that "32 per cent of all wastewater flows generated from point sources received at least some treatment". For sewage that has indeed been collected at centralized sewage treatment plants, about 79% went on to be safely treated in 2020.

Conclusions

Early human habitations were often built next to water sources. Rivers would often serve as a crude form of natural sewage disposal. Some of the earliest evidence of water wells are located in China. The Roman Empire had indoor plumbing, meaning a system of aqueducts and pipes that terminated in homes and at public wells and fountains for people to use. Rome and other nations used lead pipes; while commonly thought to be the cause of lead poisoningin the Roman Empire, the combination of running water which did not stay in contact with the pipe for long and the deposition of precipitation scale actually mitigated the risk from lead pipes. In the 16th and 18th centuries in many rapidly growing countries/cities of Europe (e.g. Germany, France) and the United States, “sewage farms” were increasingly seen as a solution for the disposal of large volumes of the wastewater, some of which are still in operation today. Irrigation with sewage and other wastewater effluents has a long

history also in China and India; while also a large “sewage farm” was established in Australia in 1897. It was not until the late 19th century that it became possible to treat the sewage by biologically decomposing the organic components through the use of microorganisms and removing the pollutants. The activated sludge process was discovered in 1913 in the United Kingdom by two engineers, Edward Ardern and W.T. Lockett, who were conducting research for the Manchester Corporation Rivers Department.

The water emerging from some deep ground water may have fallen as rain many tens, hundreds, or thousands of years ago. Soil and rock layers naturally filter the ground water to a high degree of clarity and often, it does not require additional treatment besides adding chlorine as secondary disinfectant. Such water may emerge as springs, artesian springs, or may be extracted from boreholes or wells. Deep ground water is generally of very high bacteriological quality (i.e. pathogenic bacteria or the pathogenic protozoa are typically absent), but the water may be rich in dissolved solids, especially carbonates and sulfates of calcium and magnesium. Depending on the strata through which the water has flowed, other ions may also be present including chloride and bicarbonate. There may be a requirement to reduce the iron or manganese content of this water to make it acceptable for drinking, cooking, and laundry use. Primary disinfection may also be required. Typically located in the headwaters of river systems, upland reservoirs are usually sited above any human habitation and may be surrounded by a protective zone to restrict the opportunities for contamination. Bacteria and pathogen levels are usually low, but some bacteria, protozoa or algae will be present. Where uplands are forested or peaty, humic acids can colour the water. Many upland sources have low pH which require adjustment.

Sewage (or domestic wastewater) consists of wastewater discharged from residences and from commercial, institutional and public facilities that exist in the locality. Sewage is a mixture of water (from the community's water supply), human excreta (feces and urine), used water from bathrooms, food preparation wastes, laundry wastewater, and other waste products of normal living. Sewage from municipalities contains wastewater from commercial activities and institutions, e.g. wastewater discharged from restaurants, laundries, hospitals, schools, prisons, offices, stores and establishments serving the local area of larger communities. Sewage can be distinguished into "untreated sewage" (also called "raw sewage") and "treated sewage" (also called "effluent" from a sewage treatment plant).

The term "sewage" is nowadays often used interchangeably with "wastewater" - implying "municipal wastewater" − in many textbooks, policy documents and the literature. To be precise, wastewater is a broader term, because it refers to any water after it has been used in a variety of applications. Thus it may also refer to “industrial

wastewater", agricultural wastewater and other flows that are not related to household activities.

The sewage is composed of around 99.9% pure water, and the remaining 0.1% are solids, which can be in the form of either dissolved solids or suspended solids. The suspended and dissolved solids include organic and inorganic matter plus microorganisms. About one-third of this solid matter is suspended by turbulence, while the remainder is dissolved or colloidal. The organic matter in sewage can be classified in terms of form and size: Suspended (particulate) or dissolved (soluble). Secondly, it can be classified in terms of biodegradability: either inert or biodegradable. The organic matter in sewage consists of protein compounds (about 40%), carbohydrates (about 25−50%), oils and grease (about 10%) and urea, surfactants, phenols, pesticides and others (lower quantity).

In order to quantify the organic matter content, it is common to use "indirect methods" which are based on the consumption of oxygen to oxidize the organic matter: mainly the Biochemical Oxygen Demand (BOD) and the Chemical Oxygen Demand (COD). These indirect methods are associated with the major impact of the discharge of organic matter into water bodies: the organic matter will be food for microorganisms, whose population will grow, and lead to the consumption of oxygen, which may then affect aquatic living organisms. In raw sewage, nitrogen exists in the two forms of organic nitrogen or ammonia. The ammonia stems from the urea in urine. Urea is rapidly hydrolyzed and therefore not usually found in raw sewage. Total phosphorus is mostly present in sewage in the form of phosphates.They are either inorganic (polyphosphates and orthophosphates) and their main source is from detergents and other household chemical products. In most practical cases, pathogenic organisms are not directly investigated in laboratory analyses. An easier way to assess the presence of fecal contamination is by assessing the most probable numbers of fecal coliforms (called thermotolerant coliforms), especially *Escherichia coli*. *Escherichia coli* are intestinal bacteria excreted by all warm blooded animals, including human beings, and thus tracking their presence in sewage is easy, because of their substantially high concentrations (around 10 to 100 million per 100 ml).

Questions for self-control

1. How can you characterize history of water supply and sanitation?
2. What do you understand under the Cloaca Maxima?
3. How can you define sewage farms and how cesspool?
4. Who are inventors of activated sludge process?
5. Define sewage system and population equivalent.

6. Which preliminary sewage treatment steps do you know?
7. Describe sewage primary and secondary treatment in wastewater treatment plant.
8. How would you explain biological nutrient removal in wastewater treatment plant?
9. Which advanced and complementary sewage treatments do you know?
10. How would you remove contaminants like fine solids, micro-organisms and some dissolved inorganic and organic substances from waters?
11. Describe individual treatment steps in conventional water purification process.
12. Explain the principle of coagulation and flocculation process.
13. What means disinfection and which disinfectants do you know?
14. Define sewage system and population equivalent.
15. Which preliminary sewage treatment steps do you know?
16. Describe sewage primary and secondary treatment in wastewater treatment plant.
17. How would you explain biological nutrient removal in wastewater treatment plant?
18. Which advanced and complementary sewage treatments do you know?

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Chapter V

SUSTAINABLE AND ENVIRONMENTAL LAND MANAGEMENT

In this section you will learn about

- ✓ Soil ecosystem: definition, composition and its functions
- ✓ Soil physical, chemical and biological properties
- ✓ Contamination in soil ecosystem: the sources of pollution, causes of contamination and the reducing of soil contamination
- ✓ Soil degradation: definition and what can involve
- ✓ Soil quality indicators of sustainable soil management
- ✓ General principles of sustainable land management

Key words:

Soil ecosystem
Indicators of soil quality
Soil degradation
Soil sustainability

Soil is one of the earth's most important natural resources. It is a biologically active, complex mixture of minerals, organic materials, living organisms, air and water. It underpins human food production systems, supports the cultivation of vegetation for feed, fibre and fuel, and has the potential to help combat and mitigate climate change. Human activity and related land use changes are the primary cause of soil degradation, which has substantial implication for nutrient and carbon cycling, land productivity and in turn, worldwide socio-economic conditions. Land occupies 38% of the total space, where approximately 30% represents agricultural land, approximately 30% represents forest ecosystem, 36% is represented by

deserts and 4% represents other land (rocks etc.). More than 90% of our food is grown on soil. One hectare of fertile, no compacted soil can cover the annual bread consumption of more than 120 people. Many hectares of fertile soil in Europe are still transformed into settlement and circulation areas every day. Nearly half of that area is sealed: streets, paths, parking lots and buildings are erected, asphalted, covered in concrete, paved or compacted. These settlement and circulation areas are then lost for the cultivation of agricultural or forestry products.

After reading this chapter, we hope you will have a greater appreciation and understanding of soil ecology, the function of soil in the natural environment and the role of soil organisms in affecting our daily lives.

5.1. Soil ecosystem: definition and function.

Soil is the biologically active, porous medium that has developed in the uppermost layer of Earth's crust. It is one of the principal component of life on Earth, serving as a reservoir of water and nutrients, as a medium for the filtration and breakdown of injurious wastes, and as a participant in the cycling of carbon and other elements through the global ecosystem. It arises at the interface of the atmosphere, lithosphere, hydrosphere and the biosphere, and thus its composition is significantly affected. In soil-forming processes, abiotic and biotic environmental factors are applied, and the result of their action is the component of the environment - **soil**.

Soil is a material composed of five ingredients — **minerals**, **soil organic matter**, **living organisms**, **gas** (soil air), and **water** (Fig. 5.1). Soil minerals are divided into three size classes — clay, silt, and sand, the percentages of particles in these size classes is called soil texture. Mineral matter contains three fraction: *sand*, *silt*, and *clay*. Organic matter contains appreciable quantities of nitrogen, phosphorus and sulphur. Soil organic matter consists of:

1. **Litter** – plant debris, animal carcasses, excreta,
2. **Leachates** – soluble organic compounds,
3. **Roots**,
4. **Soil organisms** – e.g. bacteria, acetomycetes, fungi, algaea, protozoa.

Air and water occupy pore spaces in soil. Soil water we can be devided into two groups:

1. **Gravitational water** – it fills all the pore-space, and leaves no room for oxygen and gaseous exchange,

2. **Capillary water** – is held in pores that are small enough to hold water against gravity, but not so tightly, that roots cannot absorb it. This water occurs as a film around soil particles and in the pores between them and is the main source of plant moisture.

3. **Hygroscopic water** – this water is held so tight (by surface tension) to the soil particles that the plant roots cannot take it up.

The main abiotic factors involved in soil formation include *parent material* (soil forming material), *relief*, *water* and *climatic conditions*.

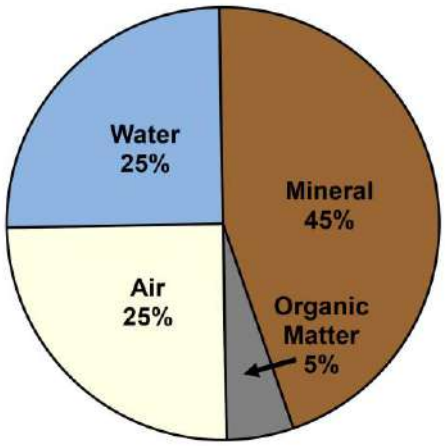


Fig. 5.1. Soil composition

The ***chemical composition*** of the soil depends mainly on the parent material from which the soil originated, from the processes taking place in the soil and from the human activities. The soil contains the most oxygen (about 50%) and silicon (about 25%), of the other elements it is mainly aluminium (clay), iron, calcium (limestone, gypsum), sodium, potassium, magnesium, hydrogen, titanium, in small amounts carbon, chlorine, phosphorus, sulphur and manganese.

Biotic factors include soil edaphon. These factors are called soil-forming factors. Edaphone is a living component of the soil. It is a set of soil microorganisms, fungi, plants and animals. Soil organisms (geobionts) live in washed-up crevices in soil air or water, especially in the topsoil. For humification processes are the most important plants, bacteria and mycophytes. Bacteria decompose organic matter in the soil. Both autotrophic and heterotrophic bacteria are found in the soil and can have a variety function in the soil ecosystem.

Decomposition of animal, plant and microbial residues is performed by heterotrophic bacteria. Chemoautotrophic bacteria are predominant in the soil that are represented by nitrifying bacteria and iron (Fe) oxidising bacteria. The most common microbial cells in the soil system are unicellular prokaryotes. Despite their high concentration in soil, fungal biomass predominates over bacterial biomass. Soil bacterial flora is extremely diverse, but fungal groups dominate in the soil in terms of biomass. They are eukaryotic organisms and have a mycelial morphology consisting of the mycelium that surrounds the multinucleated cytoplasm. They live in symbiosis

with most plant roots providing increased water and nutrient absorption capabilities. The production of spores by soil fungi allows them to survive to a certain extent adverse soil conditions. Fungi also include many important plant pathogens. Bacteria, worms, insects and other animals process plant residues in healthy soil. This is how the soil is enriched with substances that are vital for vegetation. However, if the soil is acidified by the rain, the animals cannot live in it. In this case, dead plant material remain lying down on earth, no nutrients are produced for the animals and the food chain is broken.

Healthy soil is the foundation of agriculture and as essential resource to ensure human needs in the 21st century, such as food, feed, fibre, clean water and clean air. It is vital part of ecosystem and earth system functions that support the delivery of primary ecosystem services. Soil have various unique **soil functions**. It is:

1. an essential natural resource,
2. an integrator of all parts of ecosystems,
3. a medium for plant growth,
4. a home for organisms,
5. a storehouse of water, heat and chemicals,
6. a decomposing medium for wastes,
7. a source material for construction of shelter and
8. a buffer system to neutralize harsh environmental changes.

5.2. Soil physical, chemical and biological properties.

There are three basic categories of soil properties that include:

1. **Physical properties** – texture, structure, bulk density, moisture, infiltration, porosity, water holding capacity, temperature, colour, etc.;

2. **Chemical properties** – nutrient content, salinity, pH, organic matter content, mineral content, cation exchange capacity, calcium carbonate content, etc.;

3. **Biological properties** – activity of microbes (bacteria, fungi), microbial biomass, biodiversity, biological activity (e.g. soil enzymatic activity).

Soil physical properties

Soil texture represents the relative proportion of sand, silt, and clay in the soil. These proportions affect how soil feels to the touch, thus the term texture. Sand are the largest particles, silt are medium sized and clay are the smallest sized particles. The proportion of different sized mineral particles in the soil or the relative amount of sand, silt, and clay present in the soil is expressed as percentage. On this base, we can recognize 12 textural class categories (Fig. 5.2.).

Soil structure refers to how particles of soil are grouped together into aggregates. They are cemented or bound together by physical, chemical and biological processes. Together, soil structure and texture have the greatest influence on pore spaces in soil, and how easily air, water, and roots can move through a soil. Soil structure is classified by type (shape) of peds, and grade (strength of cohesion) of aggregates. Soil aggregate stability is an indicator of organic matter content, biological activity and nutrient cycling. It is important for many other physical properties, such as infiltration and water movement, root penetration and growth, resistance to erosive forces of wind and water.

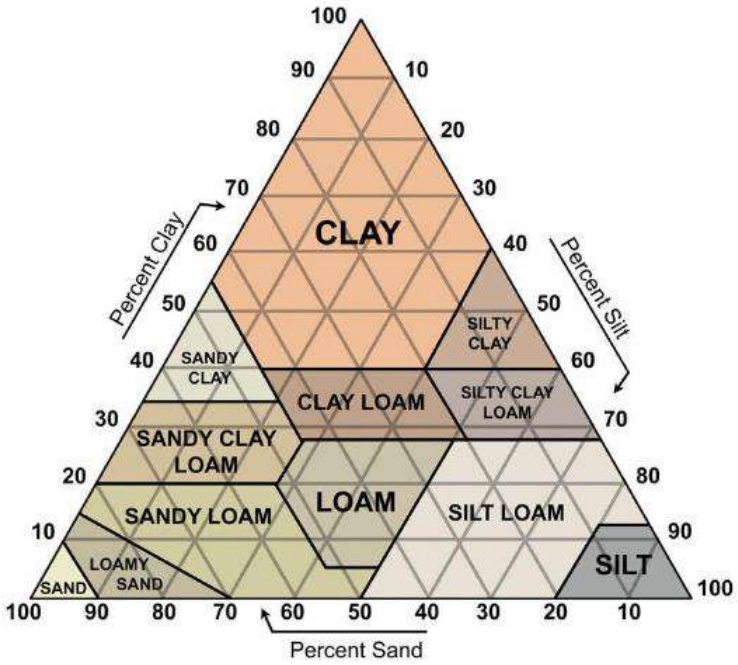


Fig. 5.2. Soil structure (Rowell, 1994)

Soil bulk density is defined as the dry weight of soil per unit volume of soil. Bulk density considers both the solids and pore spaces, whereas, particle density considers only the mineral solids. It is the indicator of soil compaction and tends to increase with the soil depth. Most soils have bulk densities between 1 and 2 g/cm^3. Soils with bulk densities higher than 1.6 g/cm^3 tend to restrict root grown.

Soil chemical properties

Soil reaction (soil pH) is an indication of the acidity or alkalinity of soil and is measured in pH units. Soil pH is defines as the negative logarithm of the hydrogen ion concentration. The pH scale goes from 0 to 14, with pH 7 as the neutral points (Table 1.). The effect of soil Ph is great on the solubility of minerals or nutrients. Before a nutrient can be used by plants it must be dissolved in the soil solution. Most minerals and nutrients are more soluble or available in acid soils

than in neutral or slightly alkaline soils. Extremely and strongly acid soils (pH 4.0-5.0) can have high concentrations of soluble aluminium, iron and manganese that may be toxic to the growth of some plants. The soil pH can also influence plant growth by its effect on activity of beneficial microorganisms Bacteria that decompose soil organic matter are hindered in strong acid soils. This prevents organic matter from breaking down, resulting in an accumulation of organic matter and the tie up of nutrients, particularly nitrogen, that are held in the organic matter. Soils tend to become acidic as a result of:

1. rainwater leaching away basic ions (calcium, magnesium, potassium and sodium);
2. carbon dioxide from decomposing organic matter and root respiration dissolving in soil water to form a weak organic acid;
3. formation of strong organic and inorganic acids, such as nitric and sulphuric acid, from decaying organic matter and oxidation of ammonium and sulphur fertilizers.

Strongly acid soils are usually the result of the action of these strong organic and inorganic acids. Generally, at low pH, many nutrients become very soluble and are readily leached from the soil profile. At high pH, nutrients become insoluble and plants cannot readily extract them. Maximum soil fertility occurs in the range 6.0 to 7.2 (Table 5.1).

Table 5.1

Soil quality categories based to pH index

Soil Category	**pH/H_2O**	**pH/KCl, $CaCl_2$**
Extremely acid	< 3.5	< 4.5
Very strong acid	3.5-4.5	4.6-5.0
Strongly acid	4.6-5.5	5.1-5.5
Moderately acid	5.6-6.5	5.6-6.5
Slightly acid to neutral	6.6-7.2	6.6-7.2
Slightly alkaline	7.3-8.5	7.3-7.7
Alkaline	> 8.5	> 7.7

Organic matter content (soil humus) makes up just 2-10% of most soils mass and has an important role in the physical, chemical and biological function of agricultural soils. Organic matter contributes to nutrient retention and turnover, soil structure, moisture retention and availability, degradation of pollutants, and carbon sequestration. Soil organic matter is composed mainly of carbon, hydrogen and oxygen, and has small amounts of other elements, such as nitrogen,

phosphorous, sulphur, potassium, calcium and magnesium contained in organic residues. It is divided into '*living'* and '*dead'* components and can range from very recent inputs, such as stubble, to largely decayed materials that are thousands of years old. About 10% of belowground soil organic matter, such as roots, fauna and microorganisms, is 'living'.

Cation exchange capacity (CEC) is the maximum quantity of total cations that a soil is capable of holding, at a given pH value, available for exchange with the soil solution. CEC is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination. It is expressed as centimol of Hydrogen per kg ($cmol_c$/kg or 100 meq_c/100g). Most of the soil's CEC occurs on clay and humus.

Calcium carbonate content $CaCO_3$ is a salt that is not very soluble and occurs in various forms and concentration in soils. Calcium carbonate in moderate amounts is favourable for soil structure and is often used to correct the pH of acidic soils, but when the level of calcium in the soil exceeds the capacity of the soil to absorb it, it binds with other elements and forms insoluble compounds that are difficult for plants to absorb. Excess amounts of calcium may restrict the availability of phosphorous, boron and iron to plants.

Soil biological properties

Soil biota consist of the:

1. **Micro-biota** – soil algae, bacteria, fungi, archaea, protozoa;
2. **Meso-biota** – nematodes, oligochaetes, insect larvae, collembolan;
3. **Macro-biota** – earthworms, rats, snakes.

As soil organisms consume organic matter and each other, nutrients and energy are exchanged through the food web and are made available to plants. Each soil organism plays a role in the decomposition of plant residue, dead roots, and animal remains. Soil biota depend on the soil environment for their energy and nutrient supply. Five **functions** mediated by the soil biota are:

1. The formation and turnover of soil organic matter that includes mineralization and sequestration of carbon;
2. Nutrient cycling;
3. Disease transmission and prevention;
4. Improvement of soil structure.

The soil environment hosts a complex and diverse biological community likely because of its extremely high physical and chemical heterogeneity at small scales, microclimatic characteristics, and phenologies of organisms that promote the development and maintenance of an extremely large number of niches. Soil organisms have been classified on the basis of body width into **microflora** (1–100

μm, e.g. bacteria, fungi), **microfauna** (5–120 μm, e.g. protozoa, nematodes), **mesofauna** (80 μm–2 mm, e.g. collembola, acari) and **macrofauna** (500 μm–50 mm, e.g. earthworms, termites) (Fig. 5.3.).

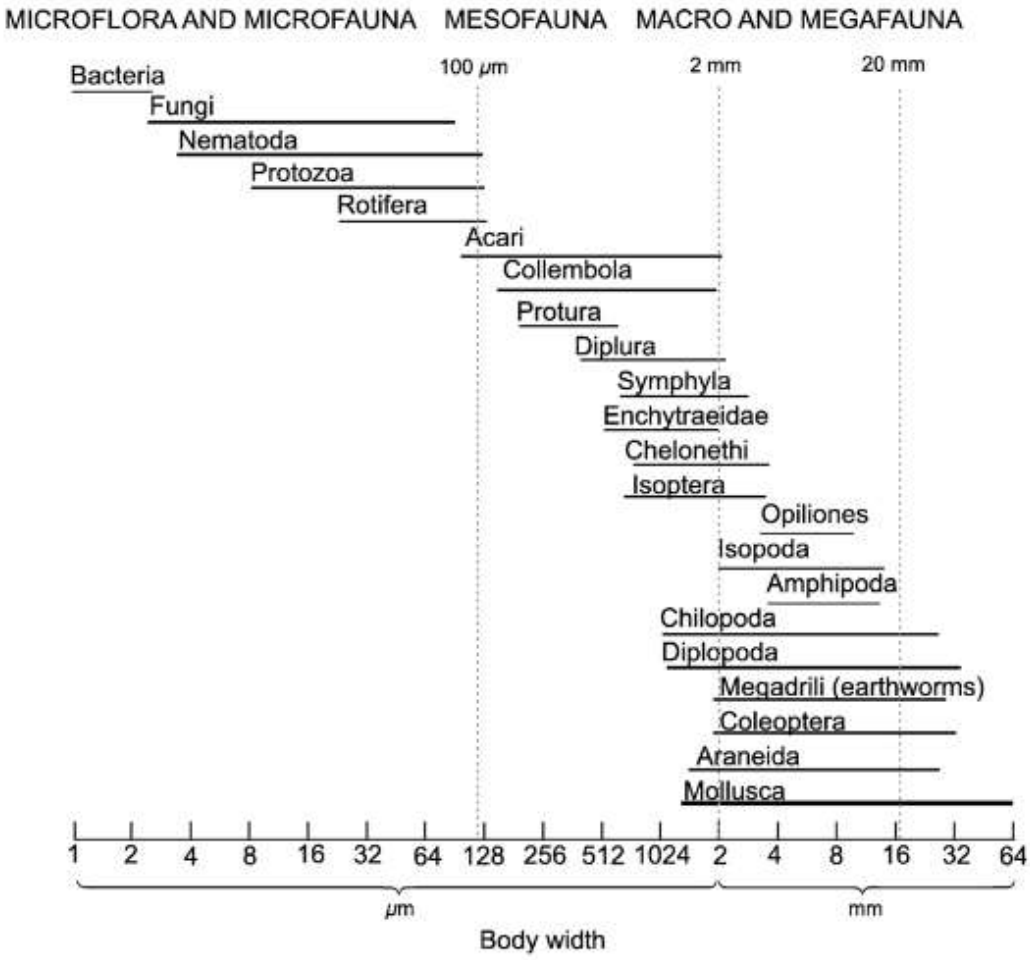


Fig. 5.3. Size classification of soil organisms according to body width
(Swift et al., 1979)

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). The functionality of soil processes can be measured by determining the activity of soil enzymes, nutrient mineralization, potential nitrification, soil respiration, etc. 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, mites, springtails, earthworms, etc. Very suitable indicator of an active nematode community, microflora and decomposition activity in grasslands is the high diversity of nematodes. These communities can also serve as bioindicators of climate change. The influence of heavy metals can also be determined on the basis of changes

in the occurrence of nematode groups. They react very sensitively to the content of SO_2 in the soil and sludge, which can signal environmental stresses in the soil ecosystem in time. Some representatives of mites are considered to be bioindicators of habitat and soil conditions and, together with springtails, they are among the most numerous representatives of soil fauna. Due to the fact that they accumulate heavy metals, they are suitable for bioindication of metal contaminated soils. Earthworms are considered to be the best indicators of soil quality due to their easy identification. They can be used as biomarkers to detect the effects of pollutants or to monitor sublethal doses of toxicants. Some types of earthworms are able to increase the availability of nutrients in the soil (phosphorus and potassium) to 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.

Biological properties in soil ecosystem represent the direct and indirect influence of the living organisms habituating a particular soil. They reflect how well suited a soil is to support life. Most of the properties require specialized and hig powered equipment for observations or measurements.

Mineralization of carbon (soil respiration) is a measure of the metabolic activity of the soil microbial community. It is measured by capturing and quantifying carbon dioxide (CO_2) released from soil. Respiration is a direct measurement of biological activity, integrating abundance and activity of microbial life. Thus, it is an indicator of the biological status of the soil community, which can give insight into the ability of soils microbial community to accept and use residues or amendments, to mineralize and make nutrients available from them to plants and other organisms, to store nutrients and thus buffer their availability over time, and to develop good soil structure, among other important functions. Soil biological activity influences key physical, biological and chemical soil processes, and is also influenced by constraints in physical and chemical soil functioning. The source of soil respiration is the decomposition of soil organic waste, respiration of roots, respiration of microorganisms in the rhizosphere and oxidation of soil organic matter. Its change is greatly influenced by temperature, humidity and the presence of the substrate. All CO_2 produced by microorganisms does not enter the atmosphere, but some remains in the soil, where it performs important functions. Soil respiration is positively correlated with soil organic matter content, microbial biomass and microbial activity (e.g. soil enzyme activity). It is highly variable and may indicate natural fluctuation depending on a number of environmental factors.

Mineralization of nitrogen is the process by which inorganic nitrogen is obtained by decomposition of dead organisms and degradation of organic nitrogenous compounds. As this process releases ammonium, it is also known as ammonification,

although this term is also used for other dissimilatory processes.

Nitrification is the biological oxidation of ammonia to nitrite followed by the oxidation of the nitrite to nitrate occurring through separate organisms or direct ammonia oxidation to nitrate in comammox bacteria. The transformation of ammonia to nitrite is usually the rate-limiting step of nitrification. Nitrification is an important step in the nitrogen cycle in soil. Nitrification is an aerobic process performed by small groups of autotrophic bacteria and archaea.

Soil enzymatic activity are the indicators of microbial community and functions. They reflect changes in soil biochemical processes and soil organic matter dynamics attributed to human-induced variation in abiotic and biotic factors in soil. Activity of soil enzymes is proposed to be an important determinant of soil and water quality improvement in different types of ecosystems 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. 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. Diversity of soil enzymes is very high and it correlates with the diversity of soil microbial community because the most enzymes originated with microorganisms. The presence and activity of soil enzymes are related to soil physical and chemical properties, microbial population composition, vegetative cover, land management, land use, etc. There are more than 500 enzymes in soil systems that play a role in soil cycles C, N, P and S. The high diversity of enzymes existing in the soil correlates with the diversity of soil microbial communities, as most enzymes come from microorganisms.

Microbiological characteristics are very often and effectively used as soil quality indicators, because the large surface area, reactivity, distribution, generation time and diversity of the soil microflora allow a virtually immediate response to any stimulus. Microbial parameters (e.g. soil respiration, soil microbial biomass, soil enzyme activity, fixation of biological N_2, etc.) appear to be useful in monitoring soil contamination by heavy metals, but the determination of only one attribute has no significance for soil and its changes in the environment. Therefore, several important microbial activities need to be taken into account. The soil environment is the largest complex of the biological community, which is highly diverse and contributes to a wide range of services for the soil ecosystem, which is beneficial for the sustainable

living of the natural and managed ecosystem. Activities of soil biota contribute significantly to increasing the quality and fertility of the soil. Most of these soil organisms are sensitive to various changes and are therefore used in soil biomonitoring. The most active component of soil biocenosis is microorganisms and their role in the soil ecosystem is irreplaceable.

5.3. Contamination in soil ecosystem: the sources of pollution, causes of contamination and the reducing of soil contamination

Soil contamination (soil pollution, land pollution) is the presence of man-made chemicals or other alteration to the natural soil environment. There is urgency in controlling the soil pollution in order to preserve the soil fertility and increase the productivity. Pollution may be defined as an undesirable change in the physical, chemical and biological characteristics of air, water and soil that affect human life, lives of other useful living plants and animals, industrial progress, living conditions and cultural assets. It is typically caused by industrial activity, agricultural chemical, or improper disposal of waste. The biggest risks for soil contamination are in urban areas and former industrial sites. The most common chemical of soil contamination are Petroleum hydrocarbons, heavy metals, pesticides and solvents. The most sources of contaminants are:

1. **Industrial pollution** – active mines, solid wastes, waste waters, etc.;
2. **Oil pollution** – consumption of fossil fuels;
3. **Agricultural pollution** – pesticides, fertilizers.

Sources of solid wastes that cause land pollution include wastes from *agriculture* (crop and farm residues, anima manure), wastes from *mining* (coal wastes, metal ore wastes), *industrial* wastes (solvents chemicals, paints), *solids* from sewage treatments-biomass sludge, settled solids, *ashes* (residues from solid fuels) and *garbage* (glass, metals, clothes, plastic, wood, papers).

When soil is contaminated with these substances, it can hurt the native environment. Many of these substances are just as toxic to plants as they are to humans. In addition, since soil is the "*earth's kidney*," contaminants can trickle through the soil and get to our water supply. Soil contamination have a strong effect on agriculture in reduced soil fertility, low crop yield, reduced soil biodiversity and reduced nitrogen fixation. Where and how much contamination is added to soils will largely determine how that contamination spreads throughout an area. The type of soil will also play a role in its distribution. For example, certain contaminants may reach groundwater sources more easily in sand than clay. This is because of faster infiltration rates of coarse-grained sandy soil types. Fine-grained clay soils or organic material in surface soils can hold contaminants tightly, which means the

contaminants will accumulate if left undisturbed. Not unexpectedly, soil contaminants can have significant deleterious consequences for ecosystems. There are radical soil chemistry changes, which can arise from the presence of many hazardous chemicals even at low concentration of the contaminant species. Effects occur to agricultural lands that have certain types of soil contamination. Contaminants typically alter plant metabolism, often causing a reduction in crop yields. This has a secondary effect upon soil conservation, since the languishing crops cannot shield the Earth's soil from erosion. Some of these chemical contaminants have long half-lives and in other cases, derivative chemicals are formed from decay of primary soil contaminants.

Contaminated or polluted soil directly affects human health through direct contact with soil or via inhalation of soil contaminants, which have vaporized. This tends to results in the development of pollution-related diseases. Exposure to heavy metals in soil and industrial toxins may cause nervous system disorders, kidney damage, liver toxicity, cancer, infertility, birth defects, and many other serious impacts on human health. There are several ways humans can be exposed to soil contaminants. The most common are:

1. **Ingesting soil** – the soil can be ingested in a variety of ways. Children that play in bare soil, might breathe in dust particles and if the soil is contaminated, it can cause serious problems. Contaminated soil dust may also affect our food supply. For example, contaminated soil could be present on products. If the vegetables are grown in soil with contaminants, the leaves, fruits and other parts could be covered. In addition, root crops like carrots and potatoes usually have soil on them in the store. The biggest risk of ingesting soil happens when the soil is left bare. Covering soil with grass or other plants and mulching well reduces the risk of contamination. If people are eating outdoors near windy soil on a windy day, airborne contaminants may land on food before it is eaten.

2. **Breathing volatiles and dust** - when soils are uncovered, small particles can become airborne with wind or other disturbance. Construction or demolition work, mining operations, or poor landscaping efforts can make soil dust. Breathing in contaminated dust may cause physical or chemical damage to humans. For example, asbestos fibres can puncture the lungs. Chemicals such as lead can hurt the nervous system, including the brain.

3. **Absorbing through skin**

4. **Eating food grown in contaminated soil** - Many vegetables and herbs can absorb contaminants as they grow. That puts us at risk if we eat them. In additon, vegetables and herbs can have soil dust on them. Without proper washing, contaminants remain.

Environmental remediation

Assessing the ecological risk of contaminated soil, pesticide application, sewage sludge amendment, and other human activities leading to exposure of the terrestrial environment to hazardous substances is a complicated task with numerous associated problems. A solution to the problem of soil contamination is **soil remediation**. Soil remediation is a way of purifying and revitalizing the soil. It is the process of removing contaminants in order to protect both the health of the population and the environment. In short, the goal of the process is to restore the soil to its natural, pollution-free state. Traditionally, there are three main soil remediation technologies: soil washing, thermal desorption and bioremediation.

Soil washing is a process that uses surfactants and water to remove contaminants from the soil. The process involves either dissolving or suspending pollutants in the wash solution and separates the soil by particle size.

In **thermal desorption**, heat is used to increase the volatility of contaminants, so that they can be separated from the solid material. The contaminants are then either collected or destroyed. Thermal desorption is the most proven and successful technology used for hydrocarbon contamination, and typically direct fired plants have been used for low levels of contamination. Lately, indirect fired units are more commonly used because of their versatility and their ability to recapture the hydrocarbons. A typical thermal desorption unit consists of two main processes. In the first, contaminated solids are heated to the boiling point of the contaminants. The volatized contaminants are then pumped to the second part of the process, where the vapour is either destroyed by a thermal oxidizer or condensed in a vapour recovery unit.

Bioremediation involves the use of living microorganisms, such as bacteria and fungi, to break down organic pollutants in the soil.

The **microbial treatment methods** appear to be more promising which can deal with whole range of organic contaminants including phenol, polychlorinated hydrocarbons, oil and oil products, dioxins, etc. There are two different ways of approaching the problems. A community of microbes already existing on the site is collected and cultured in the laboratory. Strains of microbes are developed in the laboratory that is capable of metabolizing particular chemicals. Excavation of the soil prior to treatment offers the greatest scope for creating optimum conditions. The excavated soil can be placed on thin layers to various depth using standard earth moving techniques and microbes and nutrients applied using standard agricultural techniques such as fertilizing, ploughing, harrowing, etc. Applying bio-fertilizers and manures can reduce chemical fertilizer and pesticide use. Biological methods of pest control can also reduce the use of pesticides and thereby minimize soil pollution.

5.4. Soil degradation: definition and what can involve.

Soil degradation is the physical, chemical and biological decline in soil quality. It can be the loss of organic matter, decline in soil fertility, and structural condition, erosion, adverse changes in salinity, acidity or alkalinity, and the effects of toxic chemicals, pollutants or excessive flooding. Degradation of soil is caused by soil deterioration, negative use of land management, usually for agricultural and industrial purposes. It is a serious environmental problem and the early detection of changes in the quality of the soil environment and its subsequent revitalization is crucial not only for the proper functioning of ecosystems, but also for humans. Currently, up to 60% of the world's ecosystems are reported to be degraded and exploited unsustainably. Intensification of agriculture associated with the cultivation of monocultures, intensive tillage and fertilization, application of phytopharmaceuticals, drainage activities, or biological invasions can have a dramatic impact on the activity and diversity of the natural community. In Slovakia and worldwide, ecosystems are still being destroyed, fragmented and degraded largely as a result of agricultural and forestry activities, transport and tourist infrastructure. Acidification, chemical pollution, invasive species, climate change and the growing ecological footprint also put increasing pressure on ecosystems largely. The impact of invasive plants on soil ecosystems has attracted worldwide attention in recent decades. Invasions of exotic plants often have a dramatic effect on the structure of natural vegetation and invasive plants are reported to alter soil abiotic properties, nutrient availability, organic carbon content, soil microflora composition and soil mesofauna. Particular attention is paid to the highly vulnerable and endangered ecosystems of the world, which include e.g. peat bogs, heaths, coastal ecosystems, etc. It is therefore very important to use methods that are reliable and sensitive to the early detection of adverse changes in ecosystems caused by anthropogenic influences. Soil degradation can involve:

- **water erosion** (includes sheet, rill and gully erosion),
- **wind erosion**,
- **salinity** (includes dryland, irrigation and urban salinity),
- **loss of organic matter**,
- **fertility decline**,
- **soil acidity** or **alkalinity**,
- **structure decline** (includes soil compaction and surface sealing),
- **mass movement**,
- **soil contamination** (including effects of toxic chemicals and pollutants).

5.5. Soil quality indicators of sustainable soil management.

Scientists use **soil quality indicators** to evaluate how well soil functions since soil function often cannot be directly measured. A **bioindicator** is defined as an organism, part of an organism, its product (e.g. enzyme), a set of organisms or a biological process that can be used to obtain information on the state and quality of all or part of the environment. The study and monitoring of these indicators is very important for understanding ecological changes within the soil ecosystem. **Principal requirements for soil indicators should**:

- be sensitive to human-induced changes to the environment,
- be simple and cost effective to measure, and applicable to the majority of soil monitoring networks,
- integrate soil physical, chemical, and biological properties and processes,
- indicate responses that can be distinguished from natural variability,
- be interpretable,
- provide both diagnostic and prognostic information.

Maintaining of soil quality is crucial for environmental sustainability. It depends partially on the natural composition of the soil, but also on changes caused by human activity and soil management. Soil quality cannot be determined directly, but must 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 processes in the ecosystem and integrate the physical, chemical and biological properties of soils as mentioned above. The selection of key indicators and their critical limits (threshold values) that must be met for normal soil functioning are needed to monitor changes and identify trends in improving or deteriorating soil quality for different agro-ecological zones for use at national and global levels. Many soil indicators interact with each other, and therefore the value of one is affected by one or more other selected parameters.

There are three main categories of soil indicators: **chemical**, **physical** and **biological**. Typical soil tests only look at chemical indicators. Soil quality attempts to integrate all three types of indicators. The categories do not neatly align with the various soil functions, so integration is necessary. Some indicators are descriptive and can be used in the field as part of a health card. Others must be measured using laboratory analyses (Table 5.2).

Organic matter, or more specifically soil carbon, transcends all three indicator categories and has the most widely recognized influence on soil quality. Organic matter is tied to all soil functions. It affects other indicators, such as aggregate stability (physical), nutrient retention and availability (chemical), and nutrient cycling (biological); and is itself an indicator of soil quality.

Table 5.2

Relationship between indicator type and soil function

Indicator category	Related soil function
Chemical	nutrient cycling, water relations, buffering
Physical	physical stability and support, water relation, habitat
Biological	biodiversity, nutrient cycling, filtering

Chemical indicators can give the information about the equilibrium between soil solution (soil water and nutrients) and exchange sites (clay particles, organic matter); plant health; the nutritional requirements of plant and soil animal communities; and levels of soil contaminants and their availability for uptake by animals and plants. **Physical indicators** provide information about soil hydrologic characteristics, such as water entry and retention that influences availability to plants. Some indicators are related to nutrient availability by their influence on rooting volume and aeration status. Other measures tells us about erosional status. **Biological indicators** can tell us about the organisms that form the soil food web that are responsible for decomposition of organic matter and nutrient cycling. Information about the numbers of organisms, both individuals and species, that perform similar jobs or niches, can indicate a soil's ability to function or bounce back after disturbance (resistance and resilience). Indicators include measures of earthworms, particulate organic matter, soil respiration, soil enzymes, total organic carbon, microbial biomass, etc.

Soil microbial and biochemical parameters in soil ecosystem monitoring

Compared to higher organisms, **microorganisms** respond very quickly to environmental stresses because they are closely related to the surrounding environment. In certain situations, changes in microbial diversity, or its activity, can lead to changes in the physical and chemical properties of the soil, leading to early detection of soil degradation. Accessibility of chemicals, such as heavy metals or pesticides, is an important soil health issue and it is microbial activity that significantly influences this process. The concentration of heavy metals in the soil does not change in a short time, but their accessibility to living organisms may change. Soil microorganisms and enzymes are the primary mediators of soil biological processes, including soil organic matter degradation, mineralization and nutrient cycling. They play an important role in maintaining the quality of the soil ecosystem and soil functional diversity. These microbiological and biochemical indicators are able to provide reliable indications of changes in soil quality and

nutrient cycles. Microorganisms are of the greatest importance in the biological cycle of substances due to their large active surfaces in relation to biomass volume, high degree of reproduction, large number of physiological groups with differentiated ability to decompose, transform and synthesize matter in the soil system. Substances that adversely affect soil organisms or alter the quality or quantity of organic matter may impair the functioning of the soil-plant system. Temperature fluctuations, extreme pH, disturbing physical factors, reduced soil gas exchange, low nutrient content and increased incidence of inhibitors, predators and antagonists are considered to be the most important environmental factors that adversely affect soil microbial biomass and its activity. Significant change of soil reaction and its reduction is also caused by lower amount of soil organic carbon, organic nitrogen, lower proportion of soil microbial biomass, changes in microbial activity and composition of microbial community, which is due to lower input of soil organic matter into acidic environment. The ecology, activity and population dynamics of microorganisms in the soil are affected by 15 environmental factors: carbon and energy sources, minerals, growth factors, ion composition, water accessibility, temperature, pressure, air composition, electromagnetic radiation, pH, redox potential, surfaces, spatial distribution, genetics of microorganisms and interactions between microorganisms. When determining soil quality and microbial soil activity, it is not appropriate to use individual microbiological and biochemical properties, because their size varies in time and space. Therefore, a combination of different soil properties is used to assess soil quality, which most closely reflects important microbiological and biochemical processes in the soil. Soil health microbial indicators include a set of microbial measurements to comprehensively assess all of their properties in the soil ecosystem. The evaluation of soil biological activity, and thus the assessment of management systems, encounters more serious problems in microbiological practice in connection with the selection and use of appropriate and available biological indicators for its monitoring. The effect on microbial activity, the movement of organic matter and the sequestration of N and C in the soil are also influenced by different tillage methods.

5.6. General principles of sustainable land management.

Sustainable land management was defined by the UN 1992 Rio Earth Summit as "*the use of land resources, including soils, water, animals and plants, for the production of goods to meet changing human needs, while simultaneously ensuring the long-term productive potential of these resources and the maintenance of their environmental functions*." The productivity and sustainability of a land-use system is determined by the interaction between land resources, climate and human activities.

Especially in the face of climate change and variability, selecting the right land uses for given biophysical and socio-economic conditions, and implementing sustainable land management, are essential for minimizing land degradation, rehabilitating degraded land, ensuring the sustainable use of land resources (i.e. soils, water and biodiversity) and maximizing resilience (Fig. 5.4).

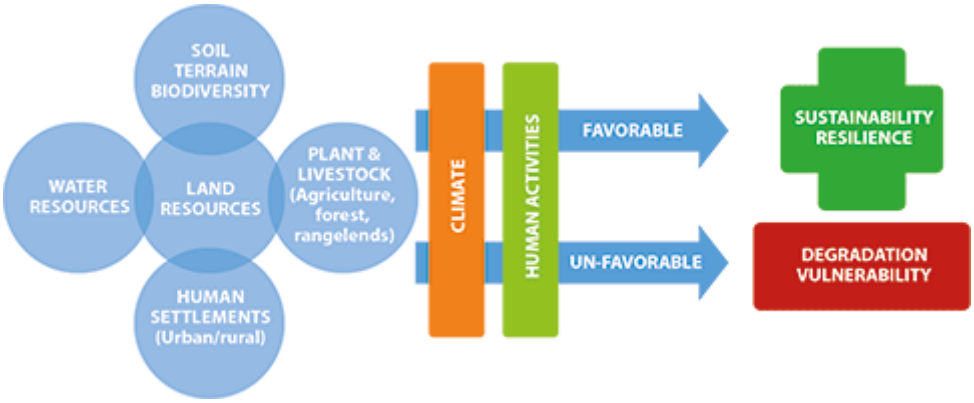


Fig. 5.4. Sustainable soil/land management for climate-smart agriculture (FAO, Climate-Smart Agriculture Sourcebook)

Sustainable land management is crucial to minimizing land degradation, rehabilitating degraded areas and ensuring the optimal use of land resources for the benefit of present and future generations. Sustainable land management involves using the land within its capability to ensure the productivity and economic potential of the land is maintained, whilst its ecological function, such as the ability of the soils to retain water or the landscape to support biodiversity, is not diminished.

General land management principles includes:

1. Management the soil according to the capacity and limitations of the land - this is based on an understanding of land resource areas and ecological processes. Consider soil structure, depth and type, slope and drainage in the management decisions. Critical processes include the ability of the soil to retain water or resist erosion.

2. Ensure appropriate placement and maintenance of infrastructure - this could include roads, bridges, drains, soil conservation features such as contours and waterways, fences, yards and water points to minimise land degradation. A property management plan can guide in making these decisions from a whole of property perspective.

3. Protect and rehabilitate areas that are degraded or at risk from erosion and salinity.

4. Control weeds and pests.

5. Respect and protect Indigenous and European cultural heritage sites.

6. Manage native forests for multiple purposes - implementing sustainable forest practices can improve timber production and grazing whilst maintaining or enhancing biodiversity values.

7. Minimizing on-farm energy use and waste.

Maintaining the healthy soil is made through managing soils and pastures. Sustaining good vegetation cover helps keep soils healthy, as the roots help bind the soil together, controlling run-off and preventing erosion. The quality of groundwater and run-off water entering watercourses are also largely influenced by vegetation cover and soil health. The soil should be kept at least 90% of the soil surface covered at all times of the year by managing your stocking rate. This will help prevent erosion, improve water quality and the pasture is able to quickly respond to any rainfall.

There are also other important points to considered when **managing soils and pastures**:

1. Maintaining high levels of groundcover.
2. Regularly monitoring the pastures.
3. Adopting grazing management practices which maintain good land condition - maintain healthy, diverse pastures dominated by perennial, productive and palatable) species by managing utilisation, matching stock numbers to available forage and routine spelling.
4. Adopting sustainable cropping practices - this includes reduced tillage, stubble retention, use of green manure crops, legumes and ley pastures, crop rotations, and regular soil analysis to match inputs to crop and soil needs, prevent soil health decline, soil acidification and erosion.
5. Adopting sustainable irrigation and farming practices - implement irrigation and farming practices which improve water use efficiency, minimise nutrient losses, run off and deep drainage and conserve limited water supplies.

Soil protection and sustainable land management practices for croplands are usually considered to be cost-effective. Soil protection practices are generally considered as desirable actions and an appropriate approach to prevent, reduce and reverse soil and land degradation. These practices and policies aim to maintain the long-term productivity of ecosystems through integrated management of soils, water, vegetation and biodiversity within their specific biophysical and socio-economic contexts. Managing for soil health allows producers to work with the land – not against – to reduce erosion, maximize water infiltration, improve nutrient cycling, save money on inputs, and ultimately improve the resiliency of their working land.

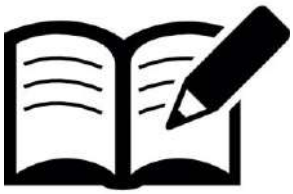
Moreover, healthy soils are the basis for healthy food production. It is estimated that 95% of our food is directly or indirectly produced on our soils. With a global population that is projected to exceed 9 billion by 2050, compounded by competition for land and water resources and the impact of climate change, our current and future food security hinges on our ability to increase yields and food quality using the soils that are already under production today. Healthy soils are the foundation of the food system. Our soils are the basis for agriculture and the medium in which nearly all food-producing plants grow. Healthy soils produce healthy crops that in turn nourish people and animals. Indeed, soil quality is directly linked to food quality and quantity. Farmers play a central role in this aspect. Numerous and diverse farming approaches promote the sustainable management of soils with the goal of improving productivity, for instance: agroecology, conservation agriculture, organic farming, zero tillage farming and agroforestry. Ultimately, a better understanding of the linkages between soil life and ecosystem function and the impact of human interventions will enable the reduction of negative impacts and allow to capture the benefits of soil biological activity more effectively for a more sustainable and productive agriculture.

Conclusions

Sustainable land management is proposed as a unifying theme for current global efforts on combating desertification, climate change and loss of biodiversity in any type of ecosystems. Where land is managed in a way that either conserves or enhances native vegetation, providing habitat for wildlife, the results can also be highly beneficial for sustainable farm production. A well balanced ecosystem has a key role in functions such as soil health, water quality, pest management and salinity control. Improved agronomic practices include organic fertilization, minimum soil disturbance, and incorporation of residues, terraces, water harvesting and conservation, and agroforestry. These practices can also deliver co-benefits in the form of reduced greenhouse gas emissions and enhanced carbon storage in soils and biomass. All parameters of microbial activity are more sensitive in monitoring changes in land use and such indicators are important for assessing the intensity of soil degradation as well as the other anthropogenic disturbances.

Questions for self-control

1. Define the soil system, soil function and its composition.
2. What are the main soil properties?
3. What is bioindicator and why soil biota (its activity and diversity) is considered to be the most effective indicator of soil health and quality?
4. What are the most sources of soil contamination? Think how this problem can be resolved.
5. State the general principles of sustainable soil use with the specific examples.



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Chapter VI

GREEN CHEMISTRY: PRINCIPLES, METRICS, EXAMPLES

In this section you will learn about

- ✓ Principles of green chemistry
- ✓ Green chemistry metrics: Atom economy, E-factor, calculation Waste prevention
- ✓ Green solutions in the chemical syntheses.

Key words:

Green chemistry
Alternative technologies
Green chemistry metrics
Green technologies

The green chemistry movement have been obtained popularity in the early 1990s. Since that time, there have been major contributions from all around the globe, with thousands of publications in this area. Numerous scientific journals related to green chemistry have achieved high impact factors due to new trend research. The evaluation of the environmental impact of a chemical process requires the consideration of numerous factors, such as processing efficiency, safety, and cost effectiveness. These criteria have historically been the primary consideration of the development of new chemical processes. The green chemistry principles also demand a detailed

analysis of environmental and health impacts. Each of these components must be evaluated across an average of numerous synthetic steps, across a wide range of functional group transformations and considering hundreds of options for reagents, catalysts and solvents.

A chemist needs to have the tools to conduct the selection of reagents and metrics to assess the changes being made to achieve an efficient, environmentally benign synthesis.

Many tools have been developed for measuring how green the processes are during recent years. First, the concept of atom economy which measures the efficiency of raw material use was introduced. Then, the E-factor analysis that quantities waste generation was developed. Later, twelve principles of green chemistry which claims that prevention is better than cure were formulated.

6.1. Principles of green chemistry.

The 12 Green Chemistry Principles:

1. ***Wastes prevention.*** Waste prevention is better and easier than waste treatment is the first and most important principle.

2. ***Atom economy.*** Maximal incorporation of starting materials into the final product is a fundamental principle to design and development of synthetic methods.

3. ***Safer synthesis.*** The designing of chemical methods with utilization and generation of substances with low or no toxicity to people and the environment is major priority.

4. ***Safer chemicals.*** Chemical products and side products should be designed to achieve a desired function with minimal toxicity.

5. ***Safer solvents and auxiliaries.*** Auxiliary substances such as solvents and separation agents should be minimized or eliminated whenever possible and made innocuous when used.

6. ***Energy efficiency.*** The minimization of the economic and environmental impacts associated with energy use in chemical synthesis is point of importance. The development of methods conducted at ambient temperature and pressure whenever it is possible is invited.

7. ***Renewable feedstocks.*** Starting materials from renewable origins should be used whenever economically and technically practicable.

8. ***Derivatives minimization.*** The utilization of protection/deprotection, blocking groups, and temporary modification of physical/chemical processes should be excluded or at least minimized with purposes of waste reduction.

9. ***Catalysts.*** Catalytic reagents that are engineered for high selectivity and efficiency for less waste production are needed.

10. ***Design for degradation*.** The design chemical products which break down into innocuous degradation materials at the end of their function and not dangerous for the environment is important.

11. ***Real-time analysis*.** It is important to develop and adopt real-time analytical methods that provide continuous process monitoring and control of the formation of hazardous compounds.

12. ***Accident prevention for safer chemical production*.** The potential for chemical accidents such as releases, explosions, and fires should be minimized by choosing inherently safer substances.

Following the formulation of these principles, more specific guides were published for process chemists and engineers. Efforts have continued in academia and industry to further development of metrics and educational tools that help chemists develop greener processes. Some of the recently published tools include the development of a series of solvent and reaction selection guides to help chemists during route development, even as early as the first medicinal chemistry route.

The 12 Green Principles of Chemical Processes Engineering:

1. Designers need to ensure that material and energy sources and outputs are as non-hazardous as possible.

2. It is better to prevent the waste production than as the waste treat or clean up after it is produced.

3. The minimization of materials and energy consumption for separation and purification operations should be designed.

4. Products, processes, and systems should be designed to maximize energy, mass, time, and space efficiency.

5. Products, processes, and systems should be “output pulled” rather than “input pushed” using materials and energy.

6. Embedded entropy and complexity must be involved when making design choices on reutilization, recycling, or beneficial disposition.

7. The goal of design should be targeted durability but not immortality.

8. Developing solutions for unnecessary capacity or capacity (for example, "one size fits all") should be considered a shortcoming of the project.

9. Diversity of materials in multi-component products should be minimized to facilitate disassembly and preservation of value.

10. The design of products, processes and systems should include integration and interconnection with existing flows of energy and materials.

11. Products, processes and systems must be designed to work in commercial "afterlife".

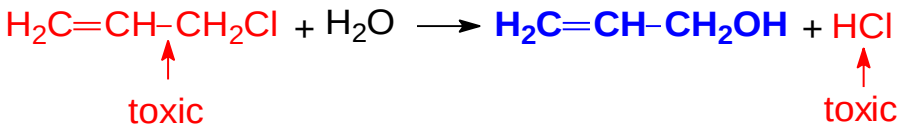
12. Material and energy resources must be renewable, not depleting.

6.2. Green chemistry metrics: Atom economy, E-factor, calculation Waste prevention.

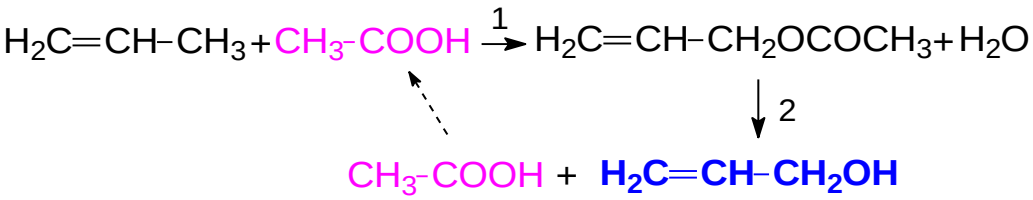
Waste prevention. The main idea is that it is better to prevent waste formation than invest to the treatment, clean up or storage of waste after it is formed. According to this principle, the traditional routes for synthesis of organic compounds must be substituted by an alternative, which minimize or even eliminate the use and production of toxic compounds.

For example, the production of allyl alcohol. The traditional route consists in hydrolysis of allyl chloride.

Despite the advantage, that this is one step production, this route involves the usage of toxic reactant (allyl chloride) and production of toxic side product (hydrochloric acid). Both compounds are toxic and harmful for the environment in case of an accidental release during the transportation, storage, or manipulation.



However, there is an alternative two step route is available. Allyl alcohol can be synthesized using propylene (CH_2=$CHCH_3$), acetic acid (CH_3COOH) and oxygen.



Only the side-product (acetic acid) produced in the second reaction can be received and used again for the first reaction. Therefore, no unwanted by-product in this route.

Atom economy. Synthetic methods should maximize the incorporation of all materials used into the final product. The synthetic routes should be designed to maximize the incorporation of all materials used in the process into the final product. Several green chemistry metrics are proposed for evaluation of “greenness” of chemical production.

Percentage of yield

The selection of chemical reactions for production of chemical compounds usually is based on the Percentage of yield. This is a very important matter for a chemist that provides a means of comparison of the theoretical and actual quantity of product. Percentage of yield evaluates the reaction efficiency.

Chemists commonly calculate Percentage yield to ascertain the efficiency of a particular reaction and defined by measuring the actual amount of a product produced

in a chemical reaction and comparing it to the mass predicted from the stoichiometric yield it is possible to calculate the percent yield.

$$\% \textbf{ Yield} = \frac{\textbf{Actual yield}}{\textbf{Stoichiometric yield}} \times \textbf{100\%}$$

The stoichiometric yield of a chemical reaction is the mass of product calculated from the mass of limiting reactant in a chemical reaction.

For example, the reaction below shows the formation of $CaSO_4$ by reacting $CaCl_2$ with Na_2SO_4

$$CaCl_2 + Na_2SO_4 \rightarrow CaSO_4 + 2\ NaCl.$$

In one run of this reaction in a water solution, the limiting reagent is $CaCl_2$. When 100 g of $CaCl_2$ was mixed with an extent of sodium sulphate solution, an actual yield of 120 g of the $CaSO_4$ participate was obtained after filtration, washing, and drying. In the begin, we need to find the stoichiometric yield. According to equation of the reaction, 1 mole of $CaCl_2$ transfers into 1 mole of $CaSO_4$.

$$n(CaCl_2) = \frac{m(CaCl_2)}{FW(CaCl_2)} = \frac{100g}{111g/mole} = 0.9\,mole\ CaCl_2 = n(CaSO_4)$$

where *FW* - formula weight of chemical compound,
n – quantity of chemical compound,
m – mass of chemical compound.

Stoichiometric yield of the reaction is

$$m(CaSO_4) = n(CaSO_4) \times FW(CaSO_4) = 0.9\ mole \times 136g/mole = 122.4\ g.$$

It is the maximum possible amount of product we can get in this reaction. In terms of percentage yield, this is 100%. The Actual yield (experimental) is 120 g. Thus, the Percentage of yield is

$$\%Yield = \frac{120g}{122.4\ g} \times 100\% = 98\%.$$

Such calculations show the completeness of the transformation of reagents into desired products. However, provides no information about the extent to which unwanted products are formed in the reaction pathway. In the chemical industry, there are many examples of highly “efficient” reactions that generate waste far greater in mass and volume than the desired product.

Therefore, the alternative criteria for evaluation of accordance to the Green chemistry principles were developed. One of them is Atom economy which measure the amount of atoms from the starting material that are present in the final product at the end of a chemical process. Hight Atom economy means most of the atoms of the

reactants are incorporated in the desired products. Only small amount of waste is produced, hence lesser problem of waste disposal.

The Atom economy of a process can be calculated using the following formula:

$$\% \textbf{ Atom economy} = \frac{\sum(\textbf{FW of the desired products})}{\sum(\textbf{FWs of all the reactants})} \times 100\%$$

High Atom economy (100%)

$$A + B \rightarrow C,$$

where A and B are reagents,

C is desired product.

Low Atom economy (<100%)

$$A + B \rightarrow C + D,$$

where D is side product.

Let's compare two industrial reactions. Preparation of the material for fire resistant coating (MgO)

$$2Mg + O_2 \rightarrow 2\ MgO,$$

FW(Mg) = 24 g/mole; *FW*(O) = 16 g/mole; *FW*(MgO) = 40 g/mole.

Reagents are quantitatively transformed on the desired product.

$$\% \, Atom \, economy = \frac{2 \times \mathrm{FW\ (MgO)}}{2 \times \mathrm{FW(Mg)} + \mathrm{FW(O_2)}} \times 100\% = \frac{80}{80} \times 100\% = 100\%.$$

Preparation of calcium oxide, the important compound for building industry

$$CaCO_3 \rightarrow CaO + CO_2,$$

FW($CaCO_3$) = 100 g/mole; *FW*(CaO) = 56 g/mole; *FW*(CO_2) = 44 g/mole.

In addition to desired product CaO, the preparation as followed by formation of side product CO_2.

$$\% \, Atom \, economy = \frac{FW\ (CaO)}{FW(CaCO_3)} \times 100\% = \frac{56}{100} \times 100\% = \ 56\%.$$

Example 1: Conversion of butan-1-ol to 1-brombutane

$$H_3C{-}CH_2{-}CH_2{-}CH_2{-}OH + \ HBr + H_2SO_4 \ \rightarrow$$

$$\rightarrow H_3C{-}CH_2{-}CH_2{-}CH_2{-}Br \ + \ NaHSO_4 \ + H_2O$$

$$\% \, Atom \, economy \ = \frac{FW\ (C_4H_9Br)}{FW\ (C_4H_9OH)) + FW(HBr) + FW(H_2SO_4)} \times 100\% =$$

$$= \frac{137}{275} \times 100\% = 49.81\%.$$

Example 2: Fermentation of sugar (glucose) to ethanol:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$$

$$\% \, Atom \, economy = \frac{2 \times FW\ (C_2H_5OH)}{FW\ (C_6H_{12}O_6)} \times 100\% = \frac{2 \times 46}{180} \times 100\% = 51.1\%.$$

Example 3: Dehydration of ethanol:

$$C_2H_5OH \rightarrow CH_2{=}CH_2 + H_2O$$

$$\%\ Atom\ economy = \frac{FW\ (C_2H_4)}{FW\ (C_2H_5OH)} \times 100\% = \frac{28}{46} \times 100\% = 60.9\%.$$

Example 4: Obtaining of the hydrogen from methane (stream methane reforming):

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

$$\%\ Atom\ economy = \frac{3 \times FW\ (H_2)}{FW\ (CH_4) + FW\ (H_2O)} \times 100\% = \frac{6}{34} \times 100\% = 17.6\%.$$

Example 5: Industrial production of iron:

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2.$$

$$\%\ Atom\ economy = \frac{2 \times FW\ (Fe)}{FW\ (Fe_2O_3) + 2 \times FW(CO)} \times 100\% =$$

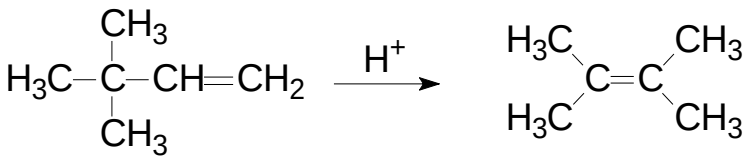
$$= \frac{112}{244} \times 100\% = 45.9\%.$$

Example 6: Production of hydrogen by reacting coal with steam:

$$C + 2H_2O \rightarrow CO_2 + 2H_2$$

$$\%\ Atom\ economy = \frac{2 \times FW\ (H_2)}{FW\ (CO_2) + 2 \times FW(H_2)} \times 100\% = \frac{4}{48} \times 100\% = 8.3\%.$$

Example 7: Reaction of 3,3-dimethylbutene-1:



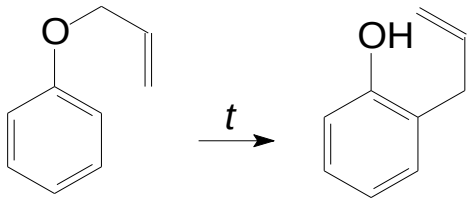
$$\%\ Atom\ economy = \frac{FW\ (C_6H_{12})}{FW(C_6H_{12})} \times 100\% = \frac{84}{84} \times 100\% = 100\%.$$

Example 8: Production of methanol:

$$CO + 2H_2 \rightarrow CH_3\text{-}OH$$

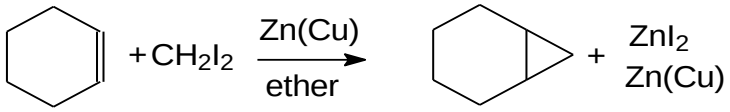
$$\%\ Atom\ economy = \frac{FW\ (CH_3OH)}{FW(CH_3OH)} \times 100\% = \frac{32}{32} \times 100\% = 100\%.$$

Example 9: Claisen rearrangement:



$$\%\ Atom\ economy = \frac{FW\ (C_9H_{10}O)}{FW(C_9H_{10}O)} \times 100\% = \frac{144}{144} \times 100\% = 100\%.$$

Example 10: Simmons-Smith cyclopropanation (assume the yield 87%):



When the yield is 100%, Atom economy is

$$\%\ Atom\ economy = \frac{FW\ (C_7H_{12})}{FW(C_6H_{10}) + FW(CH_2I_2) + FW(Zn(Cu), ether)} \times$$

$$\times 100\% = \frac{96}{82 + 267 + 129} \times 100\% = 20\%.$$

If the yield for target product is 87%, the obtained amount is 96×87%/100% = 83.5. Then

$$\%\ Atom\ economy = \frac{83.5}{82 + 267 + 129} \times 100\% = 17.4\%.$$

It's clear through these three calculations that the route I for bromination of stilbene is much more atom economical (100%), compared to route II (68%) and route III (90.4%). It means that 32% of the reagents used in the bromination of stilbene in route II and 9.6% in route II were wasted. Despite the fact the Atom economy is 100%, E-factor is not 1 because it considers the use of solvent.

Atom economies are theoretical but do not consider the reaction yield or selectivity, or the nature (toxic / benign) of the waste stream. It takes into account stoichiometric reagents, but do not consider the utilization of catalysts and solvents, as well as, other green chemistry concerns, e.g., energy, toxicity.

Atom economies are a useful way of comparing the waste production of alternative pathways, but other factors should still be considered.

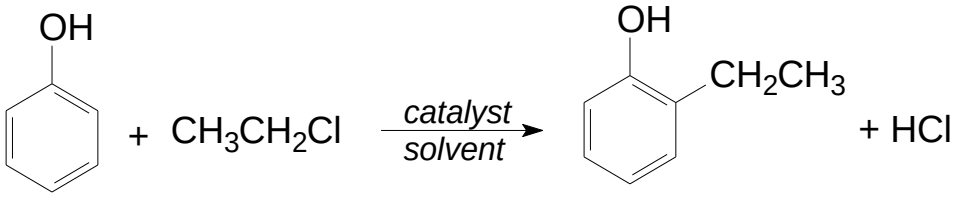
E-Factor

E-Factor (environmental factor) is another Green chemistry metric. The E-Factor is calculated as the ratio of total weight of waste generated to the total weight of product isolated.

$$\mathbf{E - Factor} = \frac{\sum \mathbf{m(waste)}}{\sum \mathbf{m(desired\ product)}}$$

This metric allows for rapid comparison of many different routes to the same product or across multiple products. It can also serve as a metric across different organizations in a similar field.

For reaction Friedel-Craft alkylation (preparation of 2-ethylphenol)



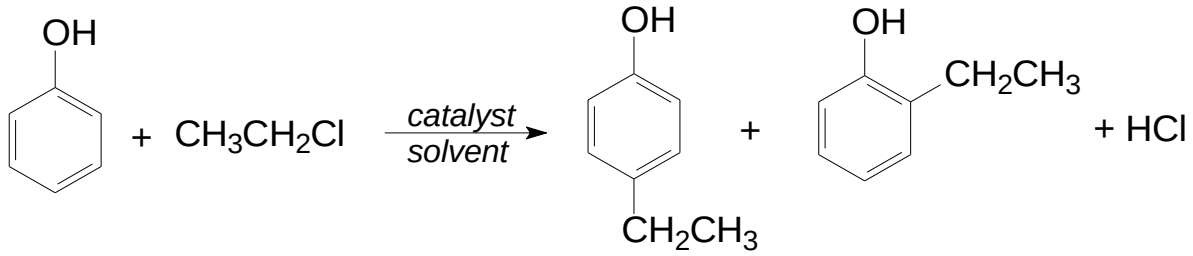
FW(C_6H_5OH) = 94 g/mole; *FW*(CH_3CH_2Cl) = 64.5 g/mole;

FW(HCl) = 36.5 g/mole; *FW*(OH-C_6H_4-CH_2CH_3) = 123 g/mole.

If the experimental data are not available, E-factor can be calculated using reaction equation. Thus, for obtaining of 1 mole of desired product, the mass of reactants and products are equal to *FW* multiplied on stoichiometric coefficients of equation. According to equation of reaction

$$E - Factor = \frac{m\,(HCl)}{m\,(OH - C_6H_4 - CH_2H_3)} = \frac{36.5}{123} = 0.3.$$

However, the realisation of the reaction involves the utilization of catalyst and solvent, as well as formation of 4-ethylphenol (side product):



Therefore, the more correct calculations can be done only when experimental data are available.

For example, during the synthesis of 60.0 g 2-ethylphenol, the 400 g of solvent and 2 g of catalyst were used. Additionally, 18.25 g of HCl and 63 g 4-ethylphenol (both are the side products) are obtained.

$$E - Factor = \frac{m\,(catalyst) + m\,(solvent) + m\,(4 - ethylphenol) + m\,(HCl)}{m\,(2 - ethylphenol)} =$$

$$= \frac{2\ g + 400\ g + 63\ g + 18.25\ g}{60\ g} = 8.05.$$

Example 1: Production of hydrazine:

$$2\ NH_3 + NaOCl \rightarrow N_2H_4 + NaCl + H_2O$$

FW(NH_3) = 17 g/mole; *FW*(NaOCl) = 74.5 g/mole; *FW*(N_2H_4) = 32 g/mole; *FW*(NaCl) = 58.5 g/mole; *FW*(H_2O) = 17 g/mole.

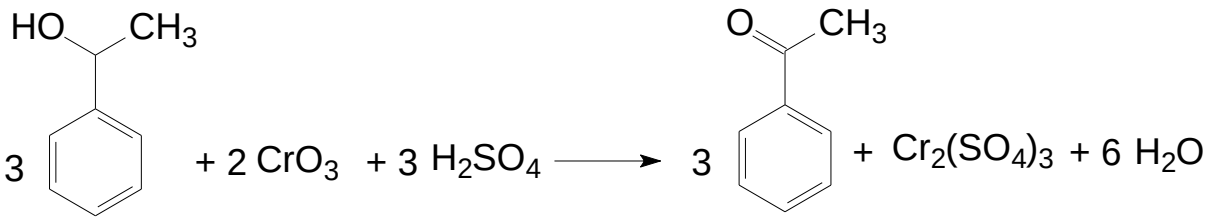
$$\%\ Atom\ economy = \frac{FW\ (N_2H_4)}{FW\ (N_2H_4) + FW\ (NaCl) + FW(H_2O)} \times 100\% =$$

$$= \frac{32}{108.5} \times 100\% = 29.5\%$$

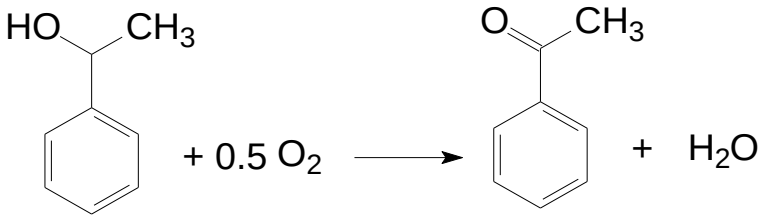
$$E - factor = \frac{FW\ (NaCl)\ +\ FW\ (H_2O)}{FW\ (N_2H_4)} = \frac{76.5}{32} = 2.39$$

Example 2: Compare two methods of methylphenylketone production:

a) stoichiometric oxidation (Jones Reagent)



b) catalytic oxidation



FW($C_6H_5C(OH)CH_3$) = 121 g/mole; *FW*($C_6H_5C(O)CH_3$) = 120 g/mole; *FW*(O_2) = 32 g/mole; *FW*(CrO_3) = 100 g/mole; *FW*(H_2SO_4) = 98 g/mole; *FW*($Cr_2(SO_4)_3$) = 392 g/mole; *FW*(H_2O) = 18 g/mole.

Route a)

$$\%\ Atom\ economy = \frac{3 \times FW(C_6H_5C(O)CH_3)}{3 \times FW(C_6H_5C(O)CH_3) + FW(Cr_2(SO_4)_3) + 6 \times FW(H_2O)} \times 100\% = \frac{360}{860} \times 100\% = 41.9\%$$

$$E - factor = \frac{FW(Cr_2(SO_4)_3) + 6 \times FW(H_2O)}{3 \times FW\ (C_6H_5C(O)CH_3)} = \frac{500}{360} = 1.39$$

Route b)

$$\%\ Atom\ economy = \frac{FW(C_6H_5C(O)CH_3)}{FW(C_6H_5C(O)CH_3) + FW(H_2O)} \times 100\% = \frac{120}{138} \times 100\% = 87.0\%$$

$$E - factor = \frac{FW(H_2O)}{FW\ (C_6H_5C(O)CH_3)} = \frac{18}{138} = 0.13$$

It's clear through these three calculations that the route I for bromination of stilbene is much more atom economical (100%), compared to route II (68%) and route III (90.4%). It means that 32% of the reagents used in the bromination of stilbene in route II and 9.6% in route II were wasted. Despite the fact the Atom economy is 100%, E-factor is not 1 because it considers the use of solvent.

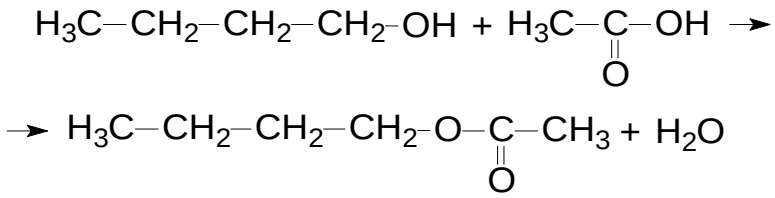
Effective Mass Yield

Effective Mass Yield (EMY) measures the environmental acceptability of a process. It is defined as the percentage of the mass of the desired product relative to mass of all non-benign materials used in its synthesis.

$$\mathbf{EMY} = \frac{\sum \mathbf{m(desired\ products)}}{\sum \mathbf{m(non-benign\ reagents)}}$$

This metric requires further definition of a benign substance - by-products, reagents or solvents that have no environmental risk associated with them, for example, water, low-concentration saline, dilute ethanol, autoclaved cell mass, etc.". This definition is not clear, as nothing is non-benign (which is a subjective term) and the substances listed in the definition have some environmental impact associated with them. Despite the formula also fails to address the level of toxicity associated with a process, EMY can be used as one of the Green chemistry metrics.

Let consider the esterification of n-butanol with acetic acid

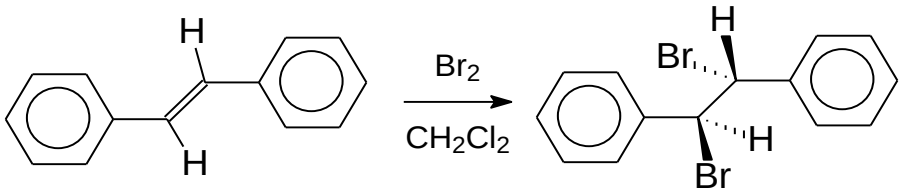


$m(C_4H_9OH)$ = 74 g; $m(CH_3COOH)$ = 120 g; $m(C_4H_9OOCCH_3)$ = 80 g.

$$EMY = \frac{m\,(C_4H_9OOCCH_3)}{m(C_4H_9OH)} = \frac{80}{74} = 108\%$$

Example: Comparison of Green chemistry metrics for the different synthesis methods. Bromination of stilbene can be carried out in three different routes:

1. Bromination in methylene chloride:

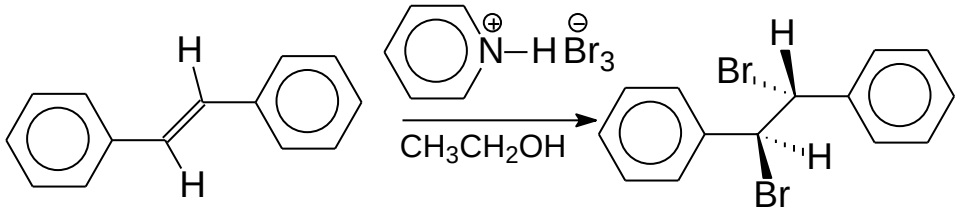


FW($C_{14}H_{12}$) = 180.25 g/mol, *FW*(Br_2) = 159.81 g/mol,

FW($C_{14}H_{12}Br_2$) = 340.05 g/mol.

Atom economy is 100.0%, E-factor = 7.46, EMY = 11.8%.

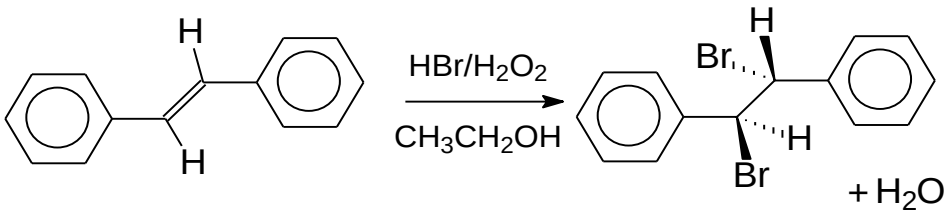
2. Pyridinium tribromide in ethanol:



FW($C_{14}H_{12}$) = 180.25 g/mol, *FW*($C_5H_6NBr_3$) = 319.82 g/mol, *FW*($C_{14}H_{12}Br_2$) = 340.05 g/mol, *FW*(C_5H_6NBr) = 160.01 g/mol.

Atom economy is 68.0%, E-factor = 8.96, EMY = 62.3%.

3. Hydrogen bromide and hydrogen peroxide in ethanol:



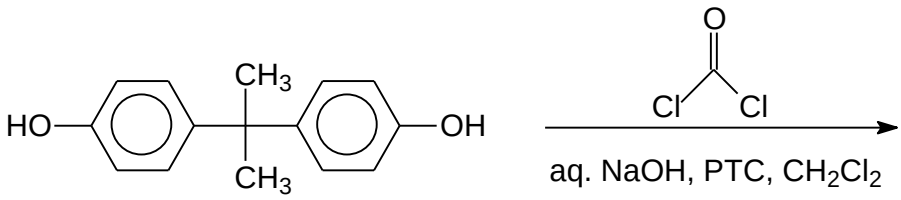
FW($C_{14}H_{12}$) = 180.25 g/mol, *FW*(HBr) = 80.92 g/mol, *FW*(H_2O_2) = 34.02 g/mol, *FW*($C_{14}H_{12}Br_2$) = 340.05 g/mol, *FW*(H_2O) = 18.01 g/mol.

Atom economy is 90.4%, E-factor = 9.81, EMY = 11.8%.

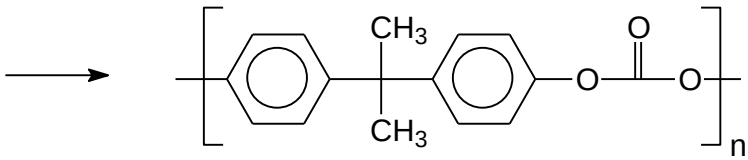
Reduced toxicity. Synthetic methods should use and generate substances that possess little or no toxicity to human health and the environment.

For example, the synthesis of polycarbonate. The first route through the phosgene process.

This route involves the utilization of a toxic reagent (phosgene) and large amounts of toxic solvent (dichloromethane). Produced polycarbonate is also contaminated with chlorine impurities.

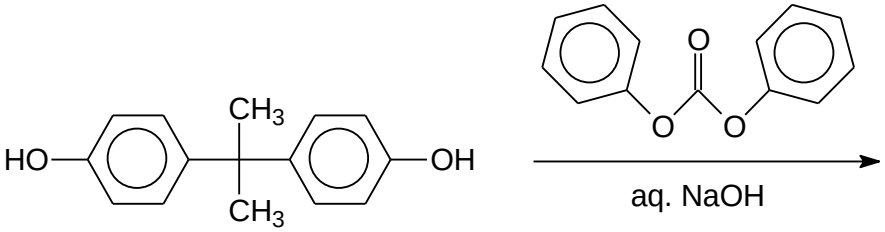


bisphenol A

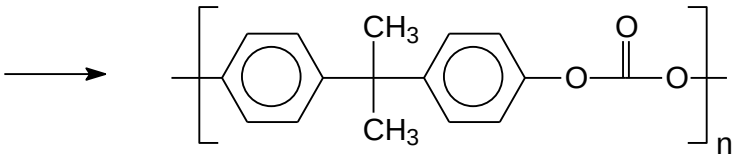


polycarbonate

An alternative route involves the use of diphenylcarbonate instead of phosgene, eliminates the use of dichloromethane and produces high-quality polycarbonates.

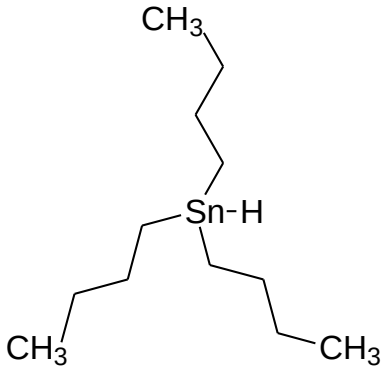


bisphenol A

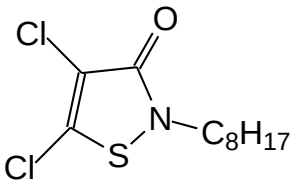


polycarbonate

Another example, the tributyltin was used as an additive for ship paint to prevent the growth of marine organisms on ships. However, organotin compounds are persistent organic pollutants with extremely high toxicity for some marine organisms. Endocrine disruption is visibly expressed in gonochoristic marine snails.



Tributyltin



Sea-Nine™

A novel antifoulant Sea-Nine™ was developed, which demonstrates high acute toxicity, but no chronic toxicity.

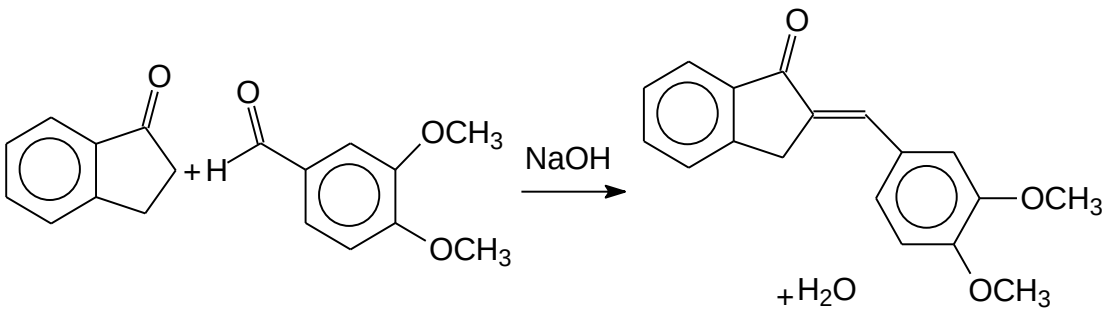
6.3. Green solutions in the chemical syntheses.

Safer solvents and auxiliaries

Organic solvents are commonly used in chemical syntheses, and these are the major sources of generated wastes. Such solvents are flammable, volatile and hazardous to human beings and the environment. There are two main approaches the problems caused due to these solvents can be solved. In the first approach, the solventless design. Many reactions can be carried out under the 'neat' conditions. But in solvent free techniques, many reactions are not possible, and many reagents and intermediates are not stable outside the solution.

The second approach is the replacement of organic solvents with greener solvents. Now a days, ionic liquids and supercritical fluids have been used quite commonly. There are some more compounds, which can serve as green solvents in chemical syntheses. The most popular among these green solvents are water, glycerol, polyethylene glycol, 2-methyltetrahydrofuran, cyclopentylmethyl ether, ethyl lactate, and so on.

Solventless Reactions. Solventless design of reaction can be used when all reagents and products are liquids which can react without solvent. For example, the Crossed-Aldol condensation:



Solvents are necessary for the synthesis of organic compounds, but their vapour creates air pollution. Therefore, efforts are being made to use solvents with high boiling points or to avoid solvent (solvent free reaction).

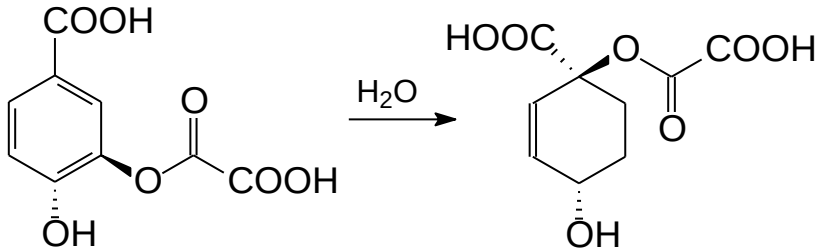
Solid state reaction is another alternative of solventless reaction. In such a situation, two fine grinded macroscopic solids interact directly and form a third, solid product without the intervention of a liquid or vapour phase (for example, oxidation, reductions, halogenations, hydrohalogenations, Aldol additions, elimination reactions, Aldol condensation reaction). However, not all reactions will work in the absence of solvent.

Green solvents

***Water*.** Water is one of the green solvents. It is easily available, not expensive, safe, and non-hazardous to environment. Water is also a "universal solvent" in nature. Living cells represent the most complex chemical reactions (termed as biochemical reaction) and all such reactions occur in environment with >90% water. Both, inorganic and organic reactions are also carried out using water as a solvent.

Most of the important reactions in organic synthesis have been tried using water as a solvent or one of the components in the solvent mixture; of course, with some modifications in the conventional methodologies.

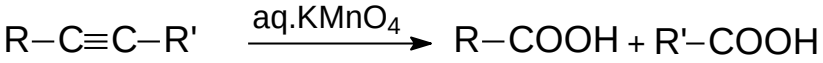
For example, in Claisen rearrangement of chorismic acid, pure water is used to promote the reaction.



Oxidation of alkene using aqueous solution of $KMnO_4$ and in presence of a phase transfer catalyst gives carboxylic acid with good yield.

$$R{-}(CH_2)_n{-}CH{=}CH_2 \xrightarrow[\text{Catalyst}]{\text{aq.}KMnO_4} R{-}(CH_2)_n{-}CH_2\text{-}COOH$$

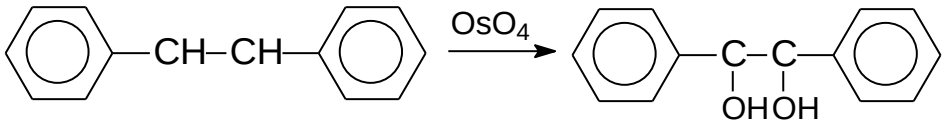
Alkynes can also be oxidized with formation of a mixture of carbonic acids



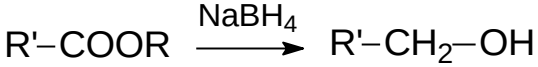
Polyethylene glycol. Polyethylene glycol is a linear polymer formed from the polymerization of ethylene oxide. It is available in a variety of molecular weights. The numerical designations of polyethylene glycol indicate the average molecular weight, for instance, PEG-200, PEG-400, PEG-2000 etc. Low molecular weight polyethylene glycols are liquid and completely miscible in water. Polyethylene glycols with high molecular weight are waxy white solids and highly soluble in water. The compound is inexpensive, non-flammable, biologically compatible, recoverable, non-toxic, thermally stable and biodegradable. Therefore, it can be considered not only as an environmentally benign solvent but also as biologically acceptable polymer, which has immense importance in drug delivery and approved for internal consumption.

Polyethylene glycols are used as the solvents for many organic reactions because they are stable to acids, bases, and high temperatures, not affected by oxygen, hydrogen peroxide or other oxidation systems.

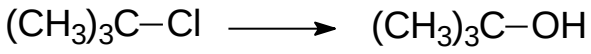
Can be used in the oxidation dihydroxy compounds of olefins



reduction of alkyl and acyl esters to the corresponding alcohols by sodium borohydride ($NaBH_4$)



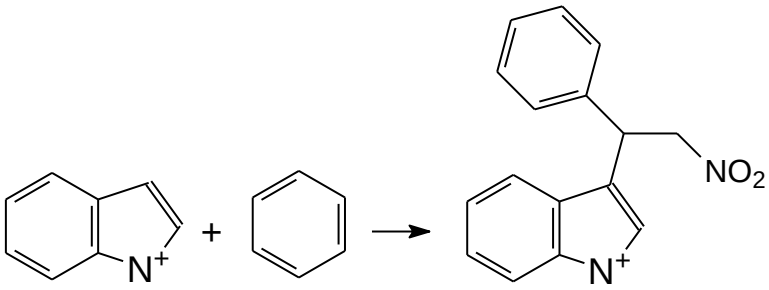
and substitution



and others.

Glycerol. Glycerol is another effective green solvent due to its polarity (capable for dissolving of polar and hydrophobic compounds low volatility (can easily be separated by distillation), low toxicity, low vapor pressure, low environmental impact, availability, easy handling, and storage.

For example, the addition reaction of indole to nitrostyrene was found with high yield under catalyst free conditions in glycerol.



***Cyclopentyl methyl ether*.** Cyclopentyl methyl ether is new hydrophobic ether solvent with some unique properties - high hydrophobicity (simple separation and recovering from water, reduced emissions and wastewater), wide liquidity range (applications from lower to higher temperatures for accelerating reaction rate), low heat of vaporization (low energy consumption for distillation and recovery), relatively hight stability to acids and bases,

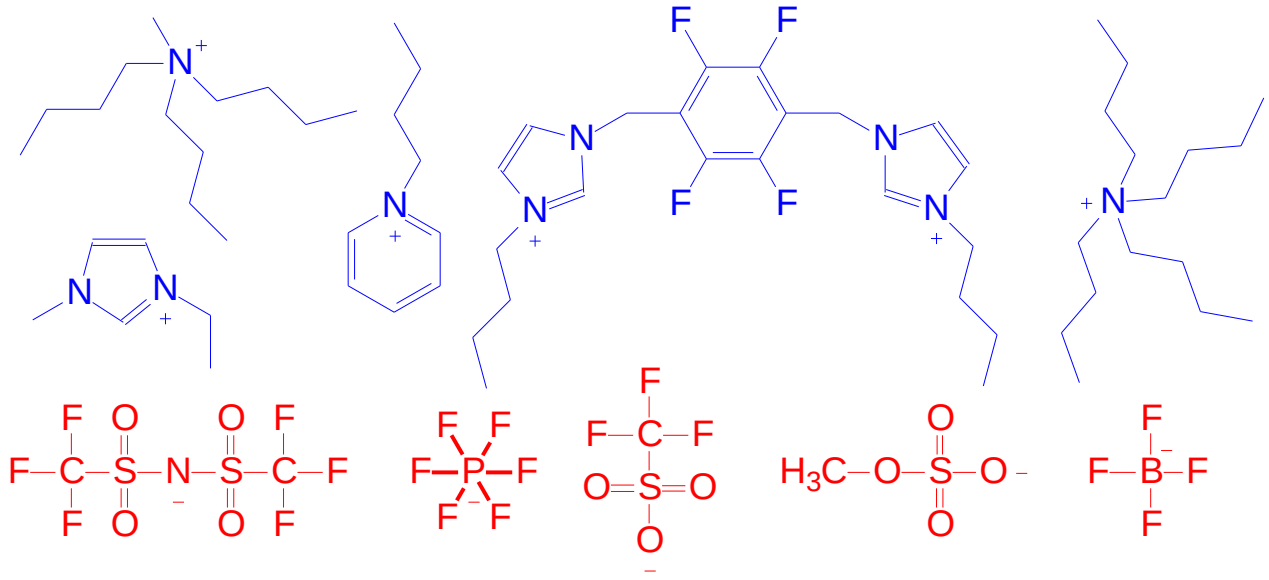
It has many properties that make it greener, easy to use and a more cost-effective process solvent for many types of synthesis.

***Perfluorinated solvents*.** Perfluorinated solvents are highly fluorinated hydrocarbons based upon sp^3 hybridized carbon (perfluorohexane C_6F_{14}, perfluoroheptane C_7F_{16}, perfluorodecalin $C_{10}F_{18}$, perfluoromethylcyclohexane C_7F_{14}, perfluorotributyl amine $C_{12}F_{27}N$). They are found to be unique solvents due to the immiscibility with water and most of the common organic solvents and form third liquid phase, nontoxic, non-flammable, thermally stable, recyclable and having high ability to dissolve oxygen. Fluorous fluids have high density, low intermolecular interaction, low surface tension, low dielectric constant and high stability Perflurous liquids for example, perfluoroethers, perfluoroalkanes, perfluroamines and so on, exhibit unique characteristics, which make them suitable alternative to most of the common organic solvents. The boiling point of these liquids depend on their molar mass, and it is lower than the corresponding alkanes. The density of perfluorous alkanes is higher than water and other organic molecules. Oxygen, carbon dioxide and hydrogen like gases are highly soluble in perfluorocarbons. Thus, these perfluorinated hydrocarbons permit some selective and efficient oxidation reaction under mild conditions.

Ionic liquids. A new class of solvents has emerged, which are fluid in a wide range of the temperature. As these solvents have high boiling point, it means lower vapour pressure of that solvent, and hence, no volatile organic compounds are escaped from these liquids at lower temperatures.

Ionic liquids are made-up of two components: cations and anions, which vary with different types of groups. Some examples of most common cations (blue) and anions (red). The nature of the cations and anions has a significant influence on the properties of

these ionic liquids. The most employed ionic liquid anions are polyatomic inorganic species, halogens, and organic anions.

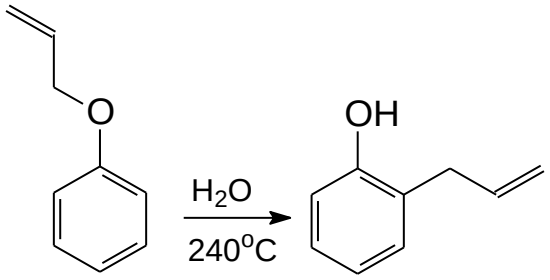


Ionic liquids are biodegraded via different pathways depending upon the length of the substituted alkyl chain. Biodegradation products are non-toxic to aquatic test organisms.

Supercritical fluids. Another green alternative of solvents are supercritical fluids. A supercritical fluid is a substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like gas and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature results in large changes in density allowing many properties of a supercritical fluid to be “fine-tuned”. Super-critical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids, and also being used for decaffeination and power generation, respectively.

Water is described as superheated water, subcritical water or pressurized hot water between 100°C and its supercritical point at 370°C. Subcritical water has been used in synthetic organic chemistry because of having some unique properties different from those of ambient water. Water has similar properties to an organic solvent such as methanol, but also has some unique properties and these characteristics are lower viscosity as compared to water that results in faster diffusion of the compound, lower surface tension, higher solubility of polar com-pounds due to lower hydrogen bonding, increased heat capacity (in 2-5 times compared to liquid water), which improves transfer of heat, single homogeneous phase results in no interfacial mass transfer limitation.

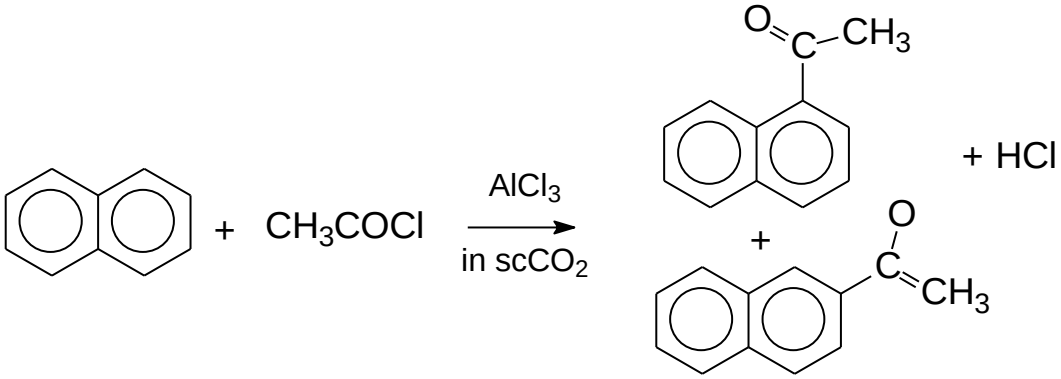
For example, Claisen rearrangement was reported in near critical water at 240°C in a microwave oven with 84% yield.



Carbon dioxide exists in three phases, that is, solid, liquid and gas. The solid phase of CO_2 is called 'dry ice' and it is used for cooling. The gas phase is well-known, and at atmospheric temperature and pressure the solid transforms to gas without liquification. Only in certain specified conditions, it can be liquefied. With the increasing pressure on gas or heating of solid CO_2, liquid phase can be achieved. The critical temperature of CO_2 is 31°C. At the temperature of -56°C and 5.1 atm, all three phases of carbon dioxide exist simultaneously. At 31°C and 73 atm, it exists as a supercritical fluid. At this condition, it has unique properties, that is, viscosity similar to the gas phase and density similar to the liquid phase.

Some advantages of supercritical carbon dioxide are a high diffusion rate offers potential for increased reaction rates, it has high compressibility (large changes in solvent properties with relatively small change in pressure), an excellent medium for oxidation and reduction reactions, no hydrolysis (which generally occurs in steam distillation), no thermal degradation products, high concentration of valuable ingredients and high extraction yield, environmentally benign solvent, high solubility toward hydrocarbons, ethers, esters, whereas polar compounds (sugars, tannins, glycosides etc.) are insoluble.

For example, the following transformation has been achieved by using Freidel-Crafts reaction in supercritical carbon dioxide:



The supercritical CO_2 is also used for extraction of natural products: essential oils from turmeric, coriander, ginger, ajowan, and extensively used for natural coffee decaffeination.

Renewable raw materials.

A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable. For example, plants are in use for the obtaining of pesticides, medicines or phytomediated synthesis of nanoparticles.

The production of metal and metal oxide nanoparticles is growing every year due to the interest to this kind of materials. Generally, convectional chemical methods of NPs synthesis involve using two groups of chemicals: reducing (sodium borohydride, methoxy polyethylene glycol, potassium bitartrate, hydroxylamine, and hydrazine) and stabilizing agents (polyvinyl alcohol, polyvinylpyrrolidone, hexadecyltrimethylammonium bromide). Some of them belongs to toxic compounds. This problem even more significant due to the fact, that synthesis of nanoparticles is the interaction of highly diluted solutions (<0.001 M). Therefore, the production of 1 g of nanoparticles resulted of large volume of solutions which are diluted but often still toxic.

Plant extracts usually contain bio-reductants, capping and stabilizing agents, obviating the need for additional reagents.

The variability of different classes of organic compounds in the plant extracts helps to design various sizes and shapes of final nanoparticles. For instance, Fig. 6.1 presents the electron transmission microscopy images of spherical silver, spherical gold and triangular gold nanoparticles prepared with various plant extracts.

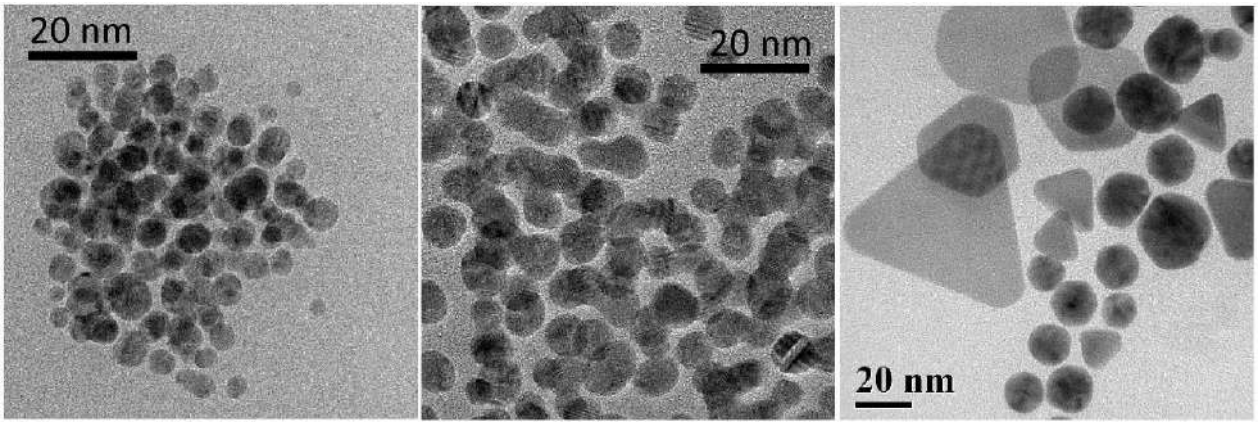


Fig. 6.1. Electron transmission microscopy images of spherical silver (left), spherical gold (middle) and triangular gold (right) nanoparticles.

The waste solutions after nanoparticle's synthesis contains the rest of plant extracts which normally are non-toxic.

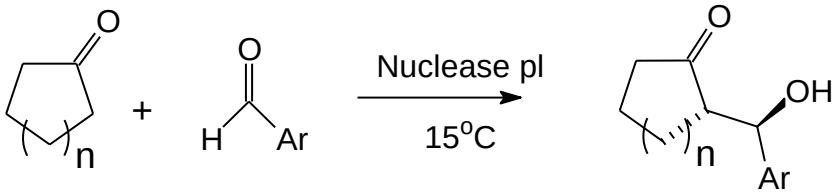
Catalysts

Many organic reactions of synthetic importance are slow, and catalyst need to be used to enhance their reaction rate. However, this catalyst may be toxic in nature, and it is important to find out some alternate catalyst, which is harmless or less toxic.

Such a job can also be done by any enzyme, which is also called biocatalyst or, in general, green catalyst.

Despite the fact, that homogeneous catalysis is preferable due to the higher reaction rate, heterogeneous catalysis, whenever possible, is a preferred and established method of waste reducing. This is because simple filtration or centrifugation facilitate the recovery of a heterogeneous catalyst from solution, leaving minimal impurities in the final product.

For example, nuclease p1 from *Penicillium citrinum* is able to catalyse asymmetric aldol reactions between aromatic aldehydes and cyclic ketones under solvent free conditions.



Green manufacturing involves production processes, which use inputs with low environmental impacts, which are highly efficient and generates little or no waste or takes care of pollution. It involves source reduction (also known as waste or pollution minimization or prevention), recycling and green product design.

Green products

Searching for green alternatives for the everyday products we consume, can have a beneficial impact on water and soil quality, reduce energy uses and the amount of pollution or waste by using concepts (catalysis by design, biodegradable consumer products) and accelerated application of green technologies and products. Therefore, the customers getting gradually concerned about the environment friendly products and the world market is drifting toward the recyclable or decomposable home appliances, hardware equipment and daily life products.

***Bioplastics*.** Recently, the trend of plastic polybags ban occurs across the world because plastic waste are almost non-biodegradable. This have a dramatic effect on animals.

Bioplastics are a form of plastics derived from renewable biomass sources, such as vegetable fats and oils, corn starch, cellulose, biopolymers, or microbiota displays a high-market potential because of their additional advantage of biodegradability in 10-15 years. Currently used plastics derived from petrochemicals, constitute a sustainable alternative to conventional oil-based plastics, which degrade in 100–150 years.

Naturally produced bioplastics are *polyhydroxyalkanoates* (poly-3-hydroxybutyrate, polyhydroxyvalerate, polyhydroxyhexanoate) and *renewable resource* (polylactic acid etc.). A novel and cost-effective polymerization technology

has been developed to produce high-quality bioplastics, with improved thermal stability up to 200ºC.

Green fuel. Hydrogen has attracted great attention of scientists, environmentalists, and industrialists as a benign fuel of future because of its capability to produce pollution free energy (no carbon emission and useful by-product of hydrogen fuel combustion that is only water) with highest energy density (140MJ/kg).

Despite that the transition will be very messy, and will take many technological paths but the hydrogen-fuel cells expected to be the future". The actual hydrogen production is derived from fossil fuels (coal, oil, and natural gas). Therefore, the success of hydrogen technology will depend on the efficient generation of hydrogen from water cleavage powered by renewable sources (such as solar or wind).

Green pesticides. The modern agriculture is dependent from the pesticides. Many of them are hazardous for human health and ecosystem. Therefore, there is a big interest to green pesticides that are derived from organic sources, which are considered environment friendly and causing less harm to human and animal health, and to habitats and the ecosystem.

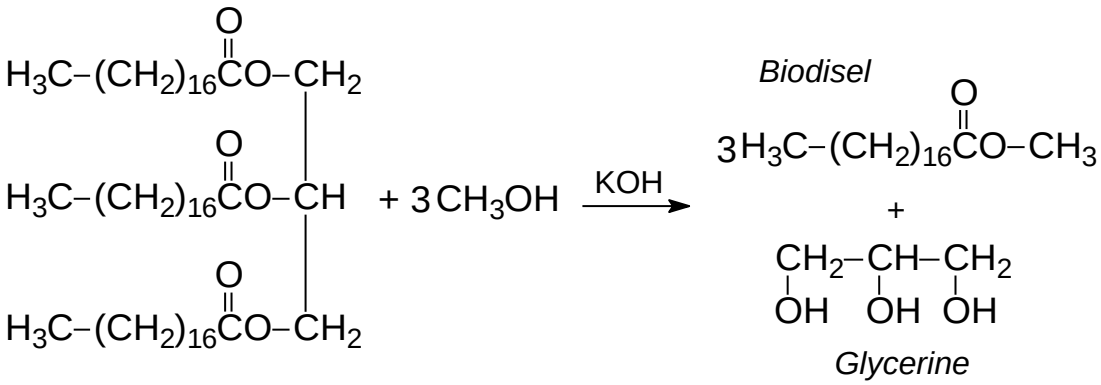
Biopesticides are generally safer than synthetic pesticides, but they are not always more safe or environment friendly than synthetic pesticides. Some examples: spinosad (shows high selectivity in destroying harmful pests and leaving beneficial insects alive), Wormwood extract, Chive extract, Summer tansy dust, Stinging nettle extract, Daffodil extract, Garlic extract, Rhubarb extract, Onion extract, Sambucus extract, Tobacco extract, and Stale beer. Sulfur (organic fungicide, pesticide, and acaricide), Bio-S (sulfur mixture), Pilzvorsoge, Spruzit, Carbolineum, Basalt dusting powder, Gene silencing pesticide, and Steam (Thermal pest control).

Green building construction materials. Green concrete (cements) is another resource saving structures with reduced environmental impact in term of CO2 emissions, energy saving, and waste water. The traditional cement making is environmentally destructive process that includes extraction and mining of limestone, transportation of materials and high energy consumption (over 7% of all green-house gas emissions worldwide are caused from the manufacturing of Portland cement).

The utilization of alternative raw materials and energy saving strategies, like use of fly ash, waste glass, waste fibre glass, blast furnace slag, volcano ash, metakaolin or calcined clay, calcined shale, rice hull ash, calcined shale, municipal solid waste incinerated product, and alternative fuels (sewage sludge, etc.) to develop or improve cement with low energy consumption belongs to main trends in the development of a new green cements.

The new types of cement with reduced environmental impact are more cost effective and friendly to environment. For example, geopolymer concrete. Geopolymers are amorphous alumino-silicate binding materials synthesized by polycondensation reaction of geopolymeric precursor, and alkali polysilicates. Main ingredients of geopolymers includes the fly ash, sand aggregates, alkaline liquid (sodium silicate and sodium hydroxide solution, water, and super plasticizer.

Biodiesel. One of the priorities of Green chemistry is utilization of benign and renewable feedstocks as raw materials. Therefore, combustion of fuels obtained from renewable feedstocks would be more preferable than combustion of the fossil fuels from depleting finite sources. The production of biodiesel oil is a promising green option. In this technology, fat embedded plant's oils are converted into the biodiesel via a transesterification reaction by using methanol and caustic or acid catalysts. The triglycerides are converted into the methyl ester and glycerol during these reactions. Production technology allow to use a greater range of feedstocks (i.e., used cooking oil). Another advantage, that product does not need to be washed to remove catalyst, and is it easier to design as a continuous process.



Conclusions

The green chemistry movement have been obtained popularity in the early 1990s. Since that time, there have been major contributions from all around the globe, with thousands of publications in this area. A chemist needs to have the tools to conduct the selection of reagents and metrics to assess the changes being made to achieve an efficient, environmentally benign synthesis.

Many tools have been developed for measuring how green the processes are during recent years. First, the concept of atom economy which measures the efficiency of raw material use was introduced. Then, the E-factor analysis that quantities waste generation was developed. Later, twelve principles of green chemistry which claims that prevention is better than cure were formulated.

There are 12 Green Chemistry Principles: wastes prevention; atom economy; safer synthesis; safer chemicals; safer solvents and auxiliaries; energy efficiency; renewable feedstocks; derivatives minimization; catalyst; design for degradation; real-time analysis; accident prevention for safer chemical production.

Searching for green alternatives for the everyday products we consume, can have a beneficial impact on water and soil quality, reduce energy uses and the amount of pollution or waste by using concepts (catalysis by design, biodegradable consumer products) and accelerated application of green technologies and products. A novel and cost-effective polymerization technology has been developed to produce high-quality bioplastics, with improved thermal stability up to 200ºC.

Hydrogen has attracted great attention of scientists, environmentalists, and industrialists as a benign fuel of future because of its capability to produce pollution free energy with highest energy density.

Biopesticides are generally safer than synthetic pesticides, but they are not always more safe or environment friendly than synthetic pesticides.

Green concrete (cements) is another resource saving structures with reduced environmental impact in term of CO_2 emissions, energy saving, and waste water.

The new types of cement with reduced environmental impact are more cost effective and friendly to environment. One of the priorities of Green chemistry is utilization of benign and renewable feedstocks as raw materials.

Questions for self-control

1. What is green chemistry?
2. What is the distinction between yield and atom economy?
3. What are the major basic principles of green chemistry?
4. Calculate the Atom economy and E-factor for the obtaining of hydrogen through the reaction:

a) $C + H_2O \rightarrow H_2 + CO$ *(assume 75% yield)*,

b) $2H_2O \rightarrow 2H_2 + O_2$ *(assume 80% yield)*.

5. Calculate the Atom economy and E-factor for the preparation of ethanol through the reaction:

$CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$ *(assume 85% yield)*.

6. Calculate the Atom economy and E-factor for the synthesis of bromoethane through the reaction

$C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$ *(assume 83% yield)*.

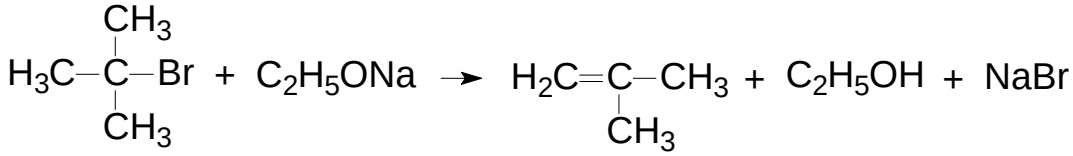
7. Calculate the Atom economy and E-factor to produce chlorbuthane through the reaction

$C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl$ *(assume 65% yield)*

8. Calculate the Atom economy and E-factor for the preparation of brombuthane through the reaction

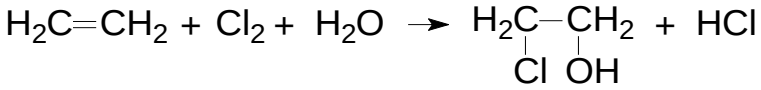
$C_4H_{10}OH + NaBr + H_2SO_4 \rightarrow C_4H_9Br + NaHSO_4 + H_2O$ *(assume 52% yield)*

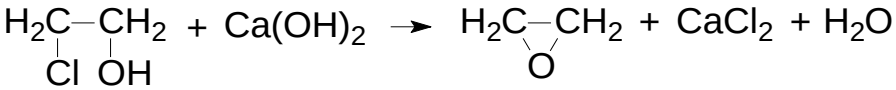
9. Calculate the Atom economy and E-factor for the obtaining of methylpropene through the reaction



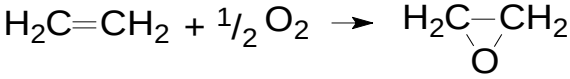
10. Compare the Atom economy and E-factor for the preparation of ethylene oxide through the different reactions:

a) the clorohydrin route *(assume 52% yield)*

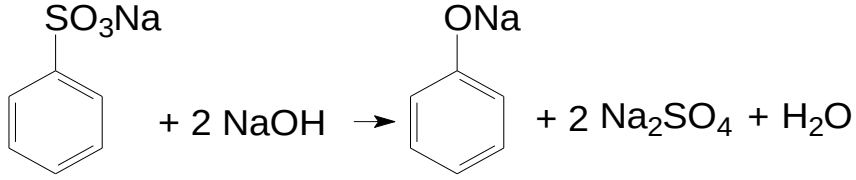




b) catalytic oxidation *(assume 72% yield)*



11. Calculate the Atom economy and E-factor for the preparation of sodium phenolate through the reaction



12. Calculate the Atom economy and E-factor for the synthesis of 2-chloro-2-methylpropane through the reaction

$(CH_3)C\text{-}OH + HCl \rightarrow (CH_3)C\text{-}Cl + H_2O$

13. Calculate the Atom economy and E-factor to produce 1-chlorohexane through the reaction

$CH_3(CH_2)_4\text{-}OH + SOCl_2 \rightarrow CH_3(CH_2)_4\text{-}Cl + SO_2 + H_2O$

14. Calculate the Atom economy and E-factor for the synthesis of propene through the reaction

$$CH_3\text{-}CHBr\text{-}CH_3 + t\text{-}BuO^-K^+ \rightarrow CH_2{=}CH\text{-}CH_3 + t\text{-}Bu\text{-}OH + KBr$$

15. Compare the Atom economy of reactions of preparation of copper

$$CuO + C \rightarrow Cu + CO_2 \text{ and } CuS + O_2 \rightarrow Cu + SO_2.$$

16. Production of ethanol from ethylene:

$$C_2H_4 + H_2O \rightarrow C_2H_5OH.$$

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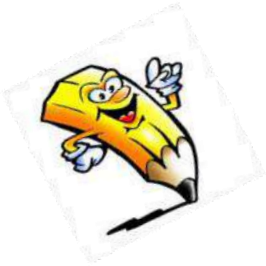
Chapter VII

THE ROLE OF THE ENVIRONMENTAL ETHICS AND PROJECT-BASED LEARNING IN THE EDUCATION OF ENVIRONMENTAL ENGINEERS

In this section you will learn about

- ✓ **Definition of environmental ethics and its trends;**
- ✓ **Pedagogical methods of environmental education;**
- ✓ **The strategy and methods of project-based education;**
- ✓ **Evaluation of a project based environmental course.**



Keywords:

Education of environmental engineers
B.Sc. level
Ethical environmental awareness
Project-based education

The engineers can act responsibly in their profession if they manage to combine high level of expertise with principled ethical behavior. This expectation is also phrased in the Code of Ethics of the Hungarian Chamber of Engineers, as well as in the Training and Output Requirements. Our education system contains the development of competencies: high theoretical knowledge, practical trainings and ethical point of view. This study focuses on the environmental engineering education (B.Sc.) from the point of view of ethical aspects. Principles of environmental ethics, incorporated into the various disciplines, can develop environmental awareness and formation of ecological thinking. Our teaching strategies, which achieve these goals, includes development of ethical thinking as a main aspect. The project-based education system is an effective way to get high-level theoretical and practical knowledge as well as ethical attitudes

The knowledge-based society of the 21st century expects up-to-date learning from the high-level educational institutes. This learning must be appropriate to answer the challenges of environmental difficulties of the last 50 years, and to give guidelines for solutions of these problems in the present time and the future. As Schumacher showed well in its book “Small is Beautiful” : The most important role of education is to teach, what we can do in our life perspectives. The key issues are non-technical, but ethical. The lack of wisdom will cause catastrophic situations. We can survive if we gain more wisdom with ethical attitudes.

The bases of right decisions are wisdom, prudent judgment for the truth, critical thinking and responsibility for the future. The educations, mostly the high-level educations can promote to get these abilities. The Report of Club of Rome has established the importance of skills-building innovative learning in 1972 . New attitudes need to be developed, which make the humankind to be appropriated for global responsibility and solidarity. Education has crucial role to build up the following virtues: foresight, estimations of consequences of present actions. A good learning program teaches team works, to built up mutual trust, and fair share of goods of humankind. The adaptation of the new type of learning is expected as a possible way of surviving. Can the society revise its traditional thinking, and preferences, and manage the necessary alterations? Every member of human society has to develop his or her ability for making the necessary changes. One of the most important parts of new thinking is the lifelong learning practice. The previously listed skills are particularly important for environmental engineers because they can directly influence environmental transformations and preservations. Namely,

improving our environment is the most emerging task of the humankind. There is no future without accepting the sustainability concept.

It is not enough to get knowledge in technical, natural, economy and law sciences for the environmental engineers, but it is also very important to get ethical thinking for them. It is good to note: the healing of the difficulties of humankind is not possible without moral basis.

There are two basic concepts of the environmental policy: technical conditions of environmental protection and ethical attitude, which are closely connected to each others. The environmental protection cannot be successful without technical and financial background. However, the previously mentioned conditions are not enough if the environmental attitudes and environmentally conscious behavior are missing. These are the reasons why it is so important to create an ethical and ecological attitude for environmental engineers in our education system.

The role of education has been already emphasized in United Nations Conference on Environment and Development, Rio de Janeiro, Brazil, 3-14 June 1992. The agenda for 21 century shows several targets in this field. For 40 years, the scientists and authorities have done a lot to draw attention for the environmental difficulties and they solved many of them. However, a lot of troubles have been unsolved. The better education can be an appropriate solution, to improve the environmentally conscious behavior of people. It is important to emphases the overwhelming parts of technical difficulties can be solved with recent methods, but the extinct species and ecological communities cannot be restored. Our future depends on us. The essence of the processes influencing the environment must be understood and these processes must be steered in the right direction. High-level education has a key role in the dissemination of environmental awareness attitudes and supporting the transformation of environmental ethics into social practices.

7.1. Definition of environmental ethics and its trends.

The role of the engineers is very important in environmental protections, water management, forestry, and agriculture. Namely, the environmental engineers make momentous strategic decisions, which influence of the environment to a large extent. The right decisions require deep ecological knowledge and ecological thinking. These attitudes are necessary to stop the fast destruction of natural values and other unfavorable changes in the environment.

The significant part of leading scientists and authorities have poor knowledge and sense in the field of environmental difficulties. They concentrate only on the

technical and financial aspects. Their education and socialization happened many years ago, when the troubles of the environment were not so obvious as today. This is one of the reasons why their plans decisions and actions underestimate the environmental difficulties. The troubles of environment can be solved only with new ecological sensitive thinking. To get more data is not enough to realize the real harm. New knowledge and new attitudes are required to solve the ecological difficulties. An up-to-date high-level education must emphasize the environmental issues, including environmental ethics.

The priority role of environmental ethics is to create a new type of thinking promoting the formation of an ecologically responsible society. Only a new environment conscious society can preserve our environment. For example, the water management actions must take consideration of the sport, drinking water, air quality, climatic aspects and mostly the ecological consequences. People, who build a cistern in their garden spare tap water, decreasing the volume of environment destruction water cleaning productions.

The ecological considerations have come to the forefront in the water management policy even in the inland water treatments. An inland water investment can decrease the volumes of flooded areas in the rainy periods, but these areas need water sprinklings in the dry seasons. Moreover, there are several water habitats die off, unwanted microclimatic changes happen, buffering effects of water bodies decrease toward to the point pollution sources, as a consequence of hydrological action. It is obvious a hydrological action on inland waters has ecological side effects, which can be managed with a good ecological attitude. The ecological troubles of Nasser dam are well known. Such cases can be avoided with an environmental cautious attitude in recent and future investments.

The necessity of a new environmentally friendly engineering attitude was already stated in 1931. The character of a good senior engineer consists of 50% moral strength, 25% general literacy and 25% technical knowledge. These requirements harmonize with the guidelines of the “Ethical Code of the Hungarian Chamber of Engineers”. The environmental ethics imposes obligations toward to the natural landscapes, animals, plants, and ecosystems, not only toward to humans. These are requirements that refer not only for the present, but for the future too. Environmental ethics deals with the human attitudes toward to biosphere and landscape in a philosophical basis. Its task is to judge the actions from moral aspects in the environment. The principles of environmental ethics define morally acceptable behaviors, and they can determine if an action is good or bad.

The environmental ethics has a double profile: it establishes the basic principles and judges the individual cases. The statements of the environmental ethics

are based on the scientific and social results of various branches of environmental sciences. The scientific and ethical bases are necessary to explain why something is good or bad.

The trends of various branches of environmental ethics differ from each other's in their concepts of the most important preserving goals and the moral status of a certain object. The "selfish" trend is human-centered, where the most important factor is the short-term human interests, and it does not care to much for the long-lasting effects on the environment. Ethical egoists keep the right to make decisions without caring for the environment. This trend also includes the deist concept, which declares the supernatural characters of humankind coming from divine will. The other trend is sustainability, which takes emphasized consideration to the long-lasting effects in the environment. Humanistic ethics keep in mind ecological factors emphatically.

The anthropogenic ethics concentrates for only the human beings. Biocentric environmental ethics preaches the sanctity of life, like the Buddhist philosophy. On the other hand, the ecocentric ethics trend takes care of the whole ecosystem without favoring any branch in a holistic way. The essences of this ethics is tolerance, the pursuit of understanding and cooperation, the acceptance and appreciation of the diversity of life. These factors must combine the responsible behavior and activities of the engineers. Such an ethics can be obtained effectively through a modern environmental education.

7.2. Pedagogical methods of environmental education.

The primary purposes of environmental education are environmental awareness, constructive lifestyle, high level of knowledge with high responsibility. The constructive lifestyle has a structured action scheme with responsibility in its center (Fig. 7.1).

The responsible behaviors manifest in the independence, freedom, and decisions of individuals. The self-determination expresses in self-controls, restraints, cooperation abilities and self-responsibility for actions. The individuals show-up to themselves in freedom taking consideration to the other's freedom. These individuals try to express their permanently developed inside values. They work out compromises with others. They do not subjugate the environment, but they harmonize their actions with the requirements of nature. Their deep knowledge helps them to solve the difficulties. The main aspects of cooperation are knowing and compile the disciplines without circumvention of the rules.

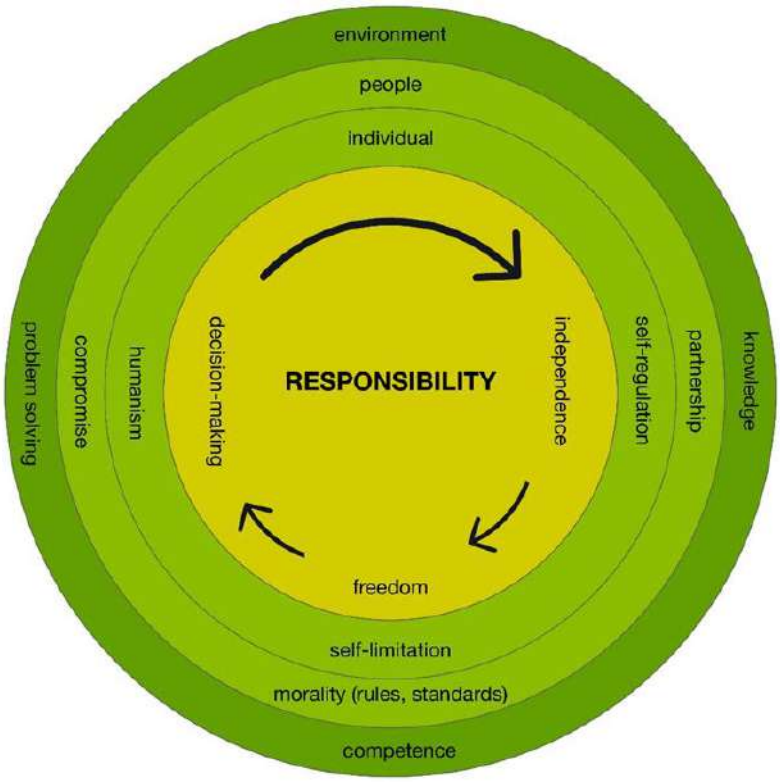


Fig. 7.1. Structure of constructive lifestyle.

The lack of deep knowledge and ecological thinking were the main reason for the red mud industrial catastrophe in Ajka. The walls of a giant storage reservoir of the red mud collapsed on 04.10.2010. The red mud flood swamped 1017 hectares and killed 10 people. The extremely alkaline flood destroyed the ecosystems along with flood (several tenths of kilometers). The catastrophe was caused by several reasons: too much amount of the highly basic mud in the cassette, lack of the alarming system, breaking several rules and standards. The ecological aspects were totally neglected, in the time of planning of the cassettes and during its operation. Moreover, the gypsum, which was applied for neutralization of basic sludge, also caused long-lasting ecological difficulties in several tenths of kilometers long. The red mud catastrophe made it obvious, that even a big economic advantage does not allow such economically dangerous practice.

Responsible people must have environmental awareness characters to avoid such catastrophes in the future. Their emotions have to play an important role. The will of preservation, protection of natural and environmental values, creativity, sense of responsibility are the most important requirements in the ecological correct actions. Deep knowledge of the environment promotes correct thinking and environmentally conscious behavior. These give appropriate behaviors toward to

environment, which are realized in in moral conducts.

The basics of environmental awareness education is illustrated in Fig. 7.2.

A large amount of knowledge is required to be familiar with the environment: rules of nature, sociological aspects, economic situations, and environmental law. Understanding the theory of sustainability and the importance of lifelong learning are also crucial to make the right decisions.

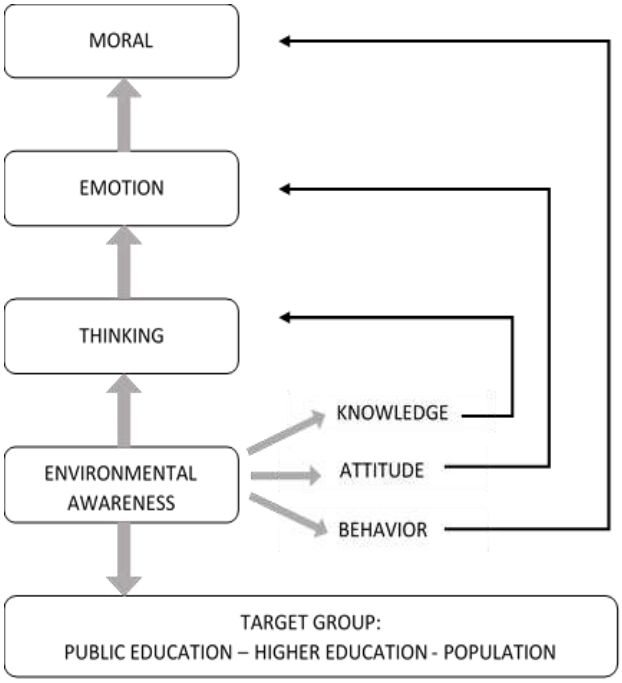


Fig. 7.2. The structure of environmental awareness education.

The theoretical knowledge is not enough for the appropriate decisions. It is necessary to learn examples, projects and tasks from real life for the decision-making persons. Experience, empathy, and self-examination are also required elements of gaining wisdom. The theoretical knowledge is crucial part of higher education, but they are not enough for wisdom. The practical trainings help to recognize the real situations and arouse the interests of students. Project-based education is an excellent method to get practical knowledge under real situations for years.

7.3. The strategy and methods of project-based education.

Project-based education is a problem-oriented open education strategy. It includes task-oriented structured student activities. These tasks improve the skills, knowledge, and abilities of students. This system guides the student from the wording of the problems to solving them. The result of the education processes is realized in successful solutions of certain problems. Moreover, project-based education helps to develop the environmental awareness attitude under real-life conditions. The

independently done explorations and solutions promote the lifelong learning attitude of the pupils. During self-regulated learning, the students can formulate their personal goals in accordance with their own needs and ability. A well-solved project gives positive motivations and suggests further learning and activity for people.

There are three well-separable activity groups during the project-based education.

1. The students choose a problem to solve which can be suggested by the teacher. The first step is to recognize and understand the subject of the project. Students have to establish the consequences of the problem to be solved. They recognize causal relationships and select the main target. The groups divide to subgroups with the determination of the responsibility and aims of different subgroups. Every individual gets their own defined task in the subgroups. Of course, the targets must be in accordance with conditions (time, money, instrumentation knowledge etc.).

2. The next steps are the detailed planning and workout periods of the actions. The detailed plan is constructed for the solution of the subtask. Data are collected, activities are divided to different persons, the appropriate experiments are chosen, timetables are laid down (what, who, how) in these periods. The group leaders and responsible persons are selected by participants. If it is necessary, some modifications are taken in the subtasks.

3. The gained data are collected, sorted, understood, and evaluated. Finally, the results are presented

The Table 7.1 summarizes the main features of project-based education methods in the different phases.

Table 7.1

The summary of project-based education

<table>
<tr><th colspan="3">The systematic structures of project-based education</th></tr>
<tr><th>Activities</th><th>Tasks</th><th colspan="2">Methods</th></tr>
<tr><td rowspan="8">Drafting of the project</td><td rowspan="8">Definition of problem
Determination of target
Choosing theme
Designations of main</td><td rowspan="8">Methods to help learn individual goals</td><td>consultative thinking</td></tr>
<tr><td>retrospective judges</td></tr>
<tr><td>target in a broader view</td></tr>
<tr><td>chats</td></tr>
<tr><td>prepared discussions</td></tr>
<tr><td>definition of the target</td></tr>
<tr><td>small lectures of the students</td></tr>
<tr><td>role plays</td></tr>
</table>

	and sub-objectives		reports
			explanations
			illustrations
Planning, elaboration	Gaining experiences Data collections Determination of duties Wording of causal relationships Sharing the tasks	Methods that promote independence, creativity and research	observations
			experiments
			measurements
			collections
			analyses
			planning's
			investigations
			data processing
			interpretations, comparisons
			sorting
			research
			surveys
			interviews
			explorations
			field works
			creations
			case studies
			learning contracts
			homework
			impact assessment
Implementation	Analysis and interpretation of data, Data processing, systematizations Problem solving Product preparations	Methods of cooperation's	project methods
			cooperative actions
			Games
			role plays
			situation role plays
			field practices
			quizzes
			competitions
			guided tours
			event organizations

7.4. Evaluation of a project based environmental course.

A project-based education program was launched for B.Sc. environmental engineer students, pursued the guidelines of table 7.1. The title of the project was "Evaluation of water pollution of a low water stream".

The project emphasized the following educational purposes:

- built-up and further develop the ecological thinking,
- acquisition the environmentally conscious behavior and lifestyles,
- adaptation of the systematic working approach,
- developing a holistic and global approach,
- educating theory of sustainability and promoting to accept its principles,
- teaching the environmental ethics to adopt the ethical engineering attitudes,
- developing tolerance and a supportive lifestyle,
- creating civic responsibility.
- developing the ability to recognize causal relationships,
- problem-solving thinking, development of decision-making skills,
- improving the communication skills,
- developing cooperative skills and helpfulness skills,
- building-up organizational skills, strengthening self-confidence,
- developing the critical thinking and creative problem solving,
- creating and developing the responsibility attitudes.

The actions of our project aimed at the observation of the sustainable use of water, recycling the water, and protection of ecosystems of water. These activities strengthened the environmentally conscious attitudes, ecological point of view, and environmental responsible characters of students.

The final result of the project showed the ecological status and ecological mapping of the chosen low water stream (Aranyhegyi patak). The project was made according to the guidelines of water framework directives (WFD), showing a good example for the survey of other low water streams.

The used methods followed the figures of table 7.1. because they were well constructed and practical orientated. The crucial parts of the project were the field surveys, field, and laboratory measurements of the students. The pupils could get experiences under realistic conditions, which will be useful in their further careers. The raw data were the measured, observed and literature parameters. The data were compared to the previous measurements and legal limits. Such comparisons show the ecological and chemical status of this low water stream.

The project significantly improved the positive attitudes of the students. They could also explore causal relationships, which were one of the most important duties of environmental engineers.

This case study guided the students from the recognition to the solution of a problem. This case study can be a supplement of the CV of the students. The objectivity, reliability, decision making ability characters of the students improved during the project, moreover they got a lot of knowledge.

The students worked independently on their chosen topics, but they consulted each other's to reach the common goals. The personal duties improved their sense of responsibility and sense of reliability.

The pupils learned cooperation during the group activity, recognizing the importance of common work to achieve their targets. The common activity helped the development of helpfulness tolerance emphatic characters. This cooperation ability will be also useful on their workplaces, to solve personal conflicts too.

The consultative thinking promoted opinion-forming, judgment-making, and step-by-step thinking methods. Listening to other opinions improved the tolerance, discussion skill, cooperation ability of members of the groups.

The intrinsic motivation method promoted getting as much knowledge as possible. This also supported the adaptation of the lifelong learning practice.

Project evaluation tasks were also very important. The lectures improved structured communication, verbal expressiveness, and willingness to debate. The written works helped to develop the structured presentation, systematic writing, structured well readable style and editorial skills. The statistical evaluations taught the student for using data sources, and the validation of their own data.

The success of the completed work gave pleasure, increased the student's self-confidence, and aroused the desire to do another research and work. The developed skills will be also realized in the future careers of the participants of the project.

Conclusions

One of the crucial requirements of engineering education is to harmonize theoretical knowledge to practical-orientated skills. These expectations are more emphasized in the education of environmental engineers because several of them will do fieldwork. Their educations must include environmental awareness, ethical thinking too. The unsolved environmental difficulties of the last decades draw our attention for the necessity of environmentally conscious attitudes. Probably the overwhelming part of the environmental difficulties do not result of the lack of appropriate technological knowledge.

The reason of these difficulties came from the lack of sense of responsibility toward to environment. The ethical attitude, the main competence, can only be the key to our survival in the future. According to the leading scientists, technical

knowledge is not enough for solving environmental troubles, but ethical attitudes are also necessary for success. The environmental ethics is dealing with not only humans, but the natural environment, animals, plants, whole ecosystem has also a central role in it. Moreover, the environment ethics takes into consideration the present as well as future. “We do not inherit the earth from our ancestors; We borrow it from our children”

The ethical aspects are very important in the engineer practices, and in more emphasized the way in the works of environmental engineers works. The ethical attitudes of environmental engineers must be evolved during their education. Competence-based higher education is an effective way to create ethical environmental attitudes. The effective environmental protection requires high-level professional knowledge, deep scientific background and ethical thinking.

Project-based education is appropriate to give theoretical knowledge as well practical skills. A project-based course combines the classroom, literature search, field practice, laboratory measurements, data processing, data evaluation, report writing and presentation studies. The students become also familiar with effective cooperation, good communication, realistic timing, and program management under realistic conditions. Project-based education is also an effective method to build up the environmental ethic attitudes of the students.

Questions for self-control

1. What is the environmental ethics?
2. Describe trends of the environmental ethics.
3. What pedagogical methods of environmental education do you know?
4. Short describe the strategy of the project-based education.
5. What are the major methods of project-based education?
6. What are the steps of the evaluation of a project based environmental course?
7. Formulate the essence of project-based education.

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