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Heavy Metals and the Environment

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Abstract

Global environmental contamination is one of the most significant environmental problems in contemporary society. Pollutants are entering the environment from different sources, and on the basis of their physico-chemical properties, they are transported and participate in biochemical cycles in the varied components of the environment, namely in the air, aquatic environment, soil and in rocks or segments. They enter the food chain through which they enter the human body, where they are transformed into either harmless metabolites (detoxification) that are easily excluded or else harmful, reactive products are formed. Heavy metals are one of the most dangerous groups of biologically important pollutants. The burden of the environment puts more significant burden on populations and ecosystems. They form integrant part of the earth's surface and therefore are present throughout the land. We can utter that contamination of the environment and its consequences for living organisms have long been in forefront of the interest in scientific as well as lay community.

Keywords: environment, heavy metals – Cd, Hg, risks of environmental pollution, food chain, health

1. Introduction

Modern civilization process brings on the one hand, better living standards, on the other hand, it has negative side effects in the form of impaired ecological, biological and natural conditions of life. Global environmental contamination is one of the most significant environmental problems at present. It is associated with an unprecedented boom in the utilization of chemicals in industrial and agricultural production. As a result, there is a relatively high concentration of toxic substances in the environment. These substances are not natural and are “strange” and „unfriendly “to the environment. Contaminants can be organic or anorganic compounds that are not naturally found in the environment; e.g., xenobiotics which can be found in unnaturally high concentrations (e.g. heavy metals) in individual environmental segments. The attention of professionals and lay public is mainly focused on hazardous substances, i.e. those that are difficult to decompose in natural surroundings, with high persistence and often exhibiting toxic effects on the environment [1–3].

Effects of environmental stress - sensitivity of a given organism to a certain stressor depends on its state of development and the conditions of its metabolism.

When humans are concerned, especially the fetus, the newborn and the mother during pregnancy should be protected. Sick, weakened or weak individuals react very sensitively to environmental pollution. Smog disasters threaten humans and animals, and soil changes adversely affect vegetation. Very often not one, but several factors stress and pollute the environment. The simultaneous action of multiple factors may be substantially different than in the case of an individual effect; antagonistic, summative, synergistic, potentiating effects are recognized in these cases. It is true that the responses of biological system to environmental pollution can be: *individual-level responses* - (metabolic disorders stimulation or inhibition depending on stress level), production of chemical stress agents, changes in hormone levels (vertebrate adaptation syndrome), reproductive disorders, impaired orientation and even death in cases of extreme stress, *population-level responses* - extinction of sensitive individuals, change in size and age structure of the population, strong selection of genetically resistant individuals, general decline in genetic diversity within the population, extinction of populations, *biocenosis and ecosystem level responses* - change in competition and predator - prey-victim ratio, change in the field of parasitism and disease, change of species spectrum and elimination of sensitive species and spreading of resistant species, decline in biomass and diversity of species, change of closed metabolism system into an open one (partial or complete loss of minerals from natural deposits), change from equilibrium to imbalance, from ecosystem stability to instability, collapse of biocenosis (in extreme cases). Toxic substances are particularly environmentally harmful to animal and human health, and thus, health risk assessment methods are particularly important in this respect.

Climate change, water, soil and health. *Climatic conditions* in Europe but also on other continents are changing. As a result of these changes, extreme weather-related events (floods, heat waves, droughts, forest fires, changes in vegetation, changes in the sea and ocean levels) are becoming more and more frequent. The change of the global climate, its impacts, and the need for solutions represent one of the most important and widely discussed environmental issues in human history so far. This change can be triggered by a number of internal and external factors, including human activity. Key effects caused by anthropogenic activity are the changes in greenhouse gas concentrations, ozonosphere disruption, local air pollution, land use and countryside exploitation. Given the complexity of the whole system, at present, it is extremely difficult to quantify precisely the human share on the total climate change. Subsequent assessment of the health consequences of the climate change is still relatively problematic, as most human health disorders are caused by several factors and take place against the backdrop of economic, social, demographic and overall environmental changes. *The area of climate change, water and soil - international commitments* - The UN Framework Convention on Climate Change, adopted in 1992 in New York, has become the basis for tackling climate change at international level. Its ultimate goal is to stabilize the impacts of the concentration of greenhouse gases in the atmosphere at a level that would prevent the dangerous consequences of human interaction and the Earth's climatic system. In 1997, the Kyoto Protocol to the Convention was adopted to tighten up the commitments of individual countries (officially adopted in 2005). This is the first binding UN legislation in the area of environment. Already in 1979, at the UNECE Convention in Geneva, the so-called "Convention on Long Range Transboundary Air Pollution", was signed. The basic aim is to protect the environment from air pollution respectively its gradual reduction. The Convention was supplemented by additional protocols related to the long-term funding of the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission (Geneva, 1984, Oslo, 1994), reduction of sulfur emissions or their transboundary

flows (Helsinki, 1985), reduction of nitrogen oxide emissions or their flows crossing the borders (Sofia, 1988), limiting the emissions of volatile organic compounds - VOCs (1991), reducing emissions of persistent organic pollutants, reducing acidification, eutrophication and ground-level ozone. In the context of water protection at international level, already in 1972, the European Council proclaimed the European Water Charter, which highlights the vital importance of water and the inevitable need to protect and use water resources. "the Directive no. 2000/60/EC of the European Parliament and Council", establishing the framework for the Community action in the field of water policy (WFD), which entered into force in 2000, provides the legislative framework for the introduction of a single policy in the countries of the European Union. Nowadays, the issue of water cleanliness and protection seems to be a priority, not only from a general and economic point of view, but above all from the fact that the quantity and quality of water is an essential factor in protecting and creating the environment [3–7].

2. Atmosphere

The word *atmosphere* comes from Greek (atmos -vapor, sfaira - sphere) and represents the gaseous layer around the Earth. It protects us from harmful cosmic radiation, harmful sunlight, solar winds and is the place where weather is created. There could be no life without the atmosphere. Gases forming the atmosphere are retained around the Earth by gravitational force. *The composition and properties of air*: Air is an essential component of the biosphere, without which the existence of various forms of life on Earth would not have been possible. The gases that create the atmosphere are kept around the Earth by gravitational force. The basic elements of the atmosphere are nitrogen (78.1%), oxygen (20.9%), argon (0.9%) and carbon dioxide (0.033%). The secondary components are noble gases (He, Kr, Ne, Xe), hydrogen, ozone, nitrogen oxides, ammonia, methane, iodine. The atmosphere provides protection from harmful cosmic radiation, harmful sunlight and solar wind. It has no significant upper boundaries, as it merges with space and rotates with the Earth. It is an essential condition for life as it transforms the radiant energy of the Sun, regulates the distribution of humidity and heat, and affects the spatial arrangement of the entire landscape. Based on the temperature-to-height dependence, the Earth's air cover is divided into individual layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere. *The troposphere* (from the Greek tropos - change) is the lowermost and the densest part of the atmosphere and makes up to 80% of its weight. It reaches 16–18 km above the equator, 8–10 km above the poles and 11 km in the temperate zone. With height, its temperature drops by an average of 0.65°C to 100 m. The temperature of this atmosphere layer is about 17 to –52°C. The composition of troposphere is quite constant. It contains about 78% nitrogen, 20% oxygen, small amounts of other gases and also contains virtually all water vapor. The troposphere is the most important layer of the atmosphere for life, with clouds being formed there and the occurrence of the majority of weather-related phenomena. *The Stratosphere* (from the Latin stratum - blanket) is the second major layer of the Earth's atmosphere after the troposphere. It reaches a height of 45–50 km above the Earth. About 20–30 km above the Earth's surface, the stratosphere contains ozone, which is called stratospheric ozone. It acts as a filter, trapping harmful ultraviolet radiation, and transmitting life-giving light and heat to the Earth. It completely absorbs UV-C radiation, which has lethal effects on the living organism and partially absorbs the short-wave UV-B radiation (wavelength of 280–315 nm), which is capable of causing many adverse effects. Although ozone in the stratosphere is naturally created and destroyed in a constant, balanced rate,

people are gradually breaking this balance by using ozone-consuming substances. Increased penetration of UV-B radiation through the ozone layer increases the risk of skin cancer, cataracts and also contributes to immune system disruption. In addition, it damages crops such as soybeans, beans, disrupting the food chain in the oceans as well. *Ozone* also occurs in the lower part of the atmosphere as tropospheric ozone. Ozone in the ground level atmosphere has a harmful effect on living organisms. Unlike stratospheric ozone, tropospheric ozone does not protect organisms but, on the contrary, damages the respiratory organs of plants and animals. In recent decades, “good” stratospheric ozone has been decreasing and “bad” tropospheric ozone has been increasing. Air conditioners, fire extinguishers and chemicals such as Freon used in refrigerators and freezers can get to the stratosphere where they decompose and the released bromine and chlorine molecules thus destroying “good” ozone. One molecule of chlorine or bromine can destroy up to 100,000 ozone molecules, so ozone in the stratosphere disappears faster than it can naturally be supplied. Volcano explosions contribute only with a tiny amount, about 3% of the total, of chlorine to the stratosphere, while people contribute with 82%. *The mesosphere* extends to a height of about 80 km. This atmosphere layer is characterized by a temperature drop down to -90°C , which represents the lowest temperature area in the whole atmosphere. The reason for the temperature drop is extremely thin air and the near absence of ozone. It should also be noted that in the mesosphere the temperature varies depending on the season of the year. The boundary within the mesosphere is known as mesopause. Most of the meteorites falling onto Earth mostly burn in the mesosphere. *The ionosphere* represents the ionized part of the atmosphere that affects the propagation of electromagnetic signals. Located between 80 and 600 km in the mesosphere and thermosphere, it consists of neutral gas, ions and electrons. *The thermosphere* extends to the height of 690 km. The temperature rises with increasing height. It reaches up to 1500°C at a height of around 300 km and is no longer changing at higher altitudes. The thermosphere has the lowest density, it contains only 0.001% of the mass of the whole atmosphere. *The exosphere* is sometimes not even distinguished as a separate layer but is assigned to the thermosphere. It represents the highest layer of the atmosphere, more than 800 km above the Earth's surface. In the exosphere, conditions for the release of atmospheric particles into the interplanetary space arise [8–10]. *Air Contamination, Causes, Consequences:* The air that mankind has not been paying attention to (and did not have to pay) in the past, is nowadays becoming an acute and widely discussed issue. Since air is not inexhaustible. Its pollution is more perceptible from year to year. There are always new ways and means of its pollution, which also affect their originators, people, animals and nature. A *pollutant* is any substance introduced by human activity directly or indirectly into the air that has or may have harmful effects on human health or the environment, except for a substance the introduction of which into the environment is governed by a specific regulation. *Emission* is any direct or indirect release of a pollutant into the air. A *stationary source of air pollution* is a technological complex, warehouse or landfill of fuels, raw materials and products, waste dump, quarry or other area with the possibility of steaming, burning or polluting or other construction, object, equipment and activity that pollutes or can pollute the air; it is defined as the sum of all facilities and activities within a functional unit and a spatial unit. A *mobile source of air pollution* is a mobile device with an internal combustion engine or other propulsion engine that pollutes the air. The air is polluted by the discharge of various substances into the atmosphere and the processes taking place directly in the air. The atmosphere is under increasing pressure from greenhouse gases, which represent climate change and under pressure from ozone depleting chemicals. Pollutants, including substances that cause acid rain, are often transferred over long distances, thus damaging soil and water. Air pollution is the

introduction of pollutants into the atmosphere which, either directly, after a chemical change or by interaction with another substance, adversely affects the environment. We know various sources of air pollution, namely anthropogenic and natural, which include: combustion of fossil fuels in electricity generation, transport, industry and households, industrial processes and the use of solvents, for example in the chemical and mineral processing industries, agriculture, waste treatment, volcanic eruptions, windblown dust, sea salt spray, and emissions of volatile organic compounds from plants are examples of natural emission sources. Within broader understanding of air pollution, we also include harmful electromagnetic radiation, noise, heat, etc., among pollutants. The following inorganic substances pollute the air: sulfur oxidation products (sulfur dioxide, sulfur trioxide, sulfuric acid, sulfates), which are introduced into the air by the combustion and processing of coal and oil. Nitrogen oxidation products (nitrogen oxide, nitrous acid, nitrates) that enter the atmosphere as products of biological processes (bacterial activity), from combustion processes in industry and transport. Carbon monoxide is produced in combustion processes where there is insufficient oxygen supply to the burning fuel (exhaust gases of motor vehicles and air planes, heating). *Anthropogenic emissions* - beryllium (Be), cobalt (Co), antimony (Sb), selenium (Se) - arise mainly from coal combustion, nickel (Ni) and vanadium (V) are predominant in the combustion of diesel, arsenic (As), cadmium (Cd), copper (Cu) and zinc (Zn) are emitted mainly when melting non-metallic ores. Chromium (Cr) and zinc (Zn) are released from the iron and steel works. Inhalable and respirable particles, which can penetrate up to the alveoli [11], are considered to be dangerous to health. Other important substances - volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins are measured selectively in targeted studies. In case of any harm to human health, animals and beasts by the action of pollutants, the emphasis is mainly on the effects of generally toxic, allergenic, carcinogenic, mutagenic, teratogenic substances. *Immissions* are substances that affect the soil, water, plants, animals and humanity. The composition of the air and its properties are variable, so its effect on the organism changes. In terms of place of origin, air pollution is divided into *primary and secondary*. *Primary air pollution* is the release of pollutants from the source of pollution. *Secondary air pollution* refers to chemical changes in some substances occurring in the process of spreading airborne exhalates. The level of air pollution is expressed by the instantaneous or average concentration of pollutants at a particular location and depends both on the emissions of pollutants and on the processes to which these emissions are subject in the air. This level is characterized by detected pollutant emissions. Polluted air damages the environment or its components, endangers or damages the human and animal organisms and impairs the environment by deteriorating odor, reducing visibility, etc. [2, 3, 10–13].

The Causes of Air Pollution: Increasing population and living standards, including energy requirements, are the main cause of the increase in air pollution. The global economy, which meets the demands of an advanced society, is characterized by increasing oxygen consumption and the release of gaseous, liquid and solid emissions. Depending on the volume of the polluted air, pollution can be divided into local (covering areas with units of tens of km² – i.e., air pollution of cities and industrial areas, changes caused by changes in local emission and meteorological conditions), regional (bottom troposphere pollution of entire territorial unit, in assessing regional air pollution, it is necessary to analyze the long-term impact and its consequences on soil, water and sensitive ecosystems) and global (pollution of the free atmosphere, changes in the composition of the atmosphere as a whole; the most serious pollutants being carbon dioxide and small particles of solid and liquid substances) [3, 9]. *Carbon dioxide* (CO₂) - the natural source of carbon dioxide

emissions is the breathing of aerobic organisms, while the process leading to its natural decrease is the photosynthesis of green plants and the oceans represent the ways to absorption. The mean residence time in the atmosphere is estimated to be 2–4 years. The total CO₂ content is increasing - over the last 100 years the CO₂ concentration has increased by about 10%. The increase in CO₂ in the atmosphere is responsible for the worsening of the greenhouse effect. *Anthropogenic sources* are mainly combustion processes. Other natural processes emitting carbon dioxide include fires and volcanic activity. Carbon dioxide is emitted wherever combustion processes of carbon fossil fuels (natural gas, petroleum products, coal, coke) occur. The source of emissions is also the combustion of fuels of biological origin (biomass, wood, biodiesel and biogas). Carbon dioxide in the atmosphere absorbs the infrared radiation of the Earth's surface and thus contributes to the greenhouse effect and consequently to global warming. In higher concentrations, in poorly ventilated areas, it may exhibit toxic effects. Short-term exposure may cause headache, dizziness, difficulty in breathing, confusion immediately or with a short delay. Higher exposure may cause cramps, coma, or death. Some more serious cases of poisoning can leave brain effects, cause personality changes, and impair vision. *Carbon monoxide* - has an uncontrolled radiation impact on the atmosphere in connection with increasing methane concentration and increasing of the ozone hole. CO belongs to the photochemically active gases contributing indirectly to the greenhouse effect of the atmosphere. It is known as a precursor of ozone because it affects the formation and breakdown of ozone in the troposphere. The atmospheric residence time estimates vary, with a range of 0.1–0.3 years, some 1 month to 5 years; this also depend on the carbon monoxide removal rate. The major part of CO is formed in the atmosphere during methane oxidation, chlorophyll decomposition and terpene photooxidation. Volcanic activity, forest fires and bacterial activity in the oceans contribute to the total amount produced by natural resources. Anthropogenic activity is letting into the air from 350 to 600 million tons of CO per year. The most important emission sources include imperfect combustion, e.g. in automobiles, industry, incinerators and heating plants and incomplete combustion of carbon-containing organic substances. It is one of the most common poisons. When inhaled, it is absorbed into the lungs and re-bound to the blood dye, producing carboxyhemoglobin. CO has 200 some literature reports up to 240–300 times more affinity for blood pigment than oxygen [13, 14]. *Hydrocarbons* - the largest share is methane gas from natural resources. The second largest group is represented by terpenes from natural sources. From human activity, comes less than 5% of the total volume of hydrocarbons, of which 38.5% comes from combustion, 11.3% from solvent evaporation, 8.8% from the evaporation of crude oil and transport losses, 7.1% from refinery waste. In terms of air pollution, the combustion of hydrocarbons is of the utmost importance. When hydrocarbons enter the atmosphere as products of combustion processes, they react with the components of the polluted atmosphere or undergo photooxidation or photolysis. The most serious ones are those that create photooxid smog. Significant hazard to ozone depletion is represented by freons and halons. *Nitrous oxide* belongs to stable atmospheric components. The only source of nitrous oxide are natural processes. When converted into nitrogen, nitrous oxide represents 97% of all nitrogen compounds, remaining present in the atmosphere approximately for 4 years. Its larger part returns to the Earth's surface, of which about 6% diffuses into the stratosphere, where it disappears in photodissociation. Of the total amount of N₂O that undergoes a reaction, 98% is changed to N₂ in the atmosphere and 2% is converted to NO. *Nitric oxide* - most of it comes from natural sources. From anthropogenic activity, combustion processes (emissions from energy, municipal sources and transport) contribute significantly to NO emissions. The residence time in the atmosphere is

estimated to be about 4 days. NO arises from combustion processes at sufficiently high temperatures. Under equilibrium conditions in the presence of oxygen, most NOs oxidize to NO₂, changing colorless nitric oxide to colored nitrogen dioxide. In the mesosphere and thermosphere, the photodissociation of nitric oxide is taking place, which presents the way of NO disappearance in the higher atmosphere. The photochemical conversion of NO to NO₂ can be of considerable importance for the air pollution in urban agglomerations. *Nitrogen dioxide* -Most of the nitrogen dioxide is produced directly in the polluted atmosphere by NO oxidation. Significantly less is released into air from anthropogenic sources. The removal of NO₂ from the atmosphere starts from its oxidation and hydration, resulting in nitric acid. Nitric acid in the polluted atmosphere can further react to form nitrates, which in the final phase are washed away by rain. In terms of air pollution, NO₂ photolysis, which can initiate photochemical smog, is of paramount importance. The formation and duration of photochemical smog depends on the chemical composition of the polluted atmosphere, the intensity and spectrum of the solar radiation. It is often created on warm sunny days at rush hours. *Ammonia* - the largest amounts of ammonia - are released into the atmosphere by the biodegradation of organic matter and by the reduction of nitrites or nitrates. Anthropogenic sources include the chemical industry, especially the production of fertilizers and urea and industrial waste. Ammonia gas reacts in an atmosphere with sulfuric acid, respectively nitric acid to form sulfates or nitrates. Self-cleaning processes occurring in the atmosphere such as sedimentation and rainwater rinsing allow the resulting salts to be removed from the air. The residence time in the atmosphere is estimated to be about 7 days. *Sulfur dioxide* is one of the typical and most common emission components. The largest amounts are produced by burning fossil fuels. Natural resources contribute to a lesser extent to total SO₂ emissions (emissions from volcanic activity). *Sulfur trioxide* is produced by burning fossil fuels. Small amounts get into the atmosphere due to the production of sulfuric acid, phosphate fertilizers or in galvanic plating. In the atmosphere, SO₃ reacts immediately with H₂O to form sulfuric acid. The sulfuric acid content increases with increased SO₂ concentration up to a certain critical value, from which the SO₂ content decreases further on. *Sulfane*-the main global source of sulfane emissions are natural processes such as volcanic activity and biological processes of substance degradation. Anthropogenic activity contributes to these sources only minimally, in the processes of oil, coal, pulp and paper processing. In the atmosphere, sulfate is gradually changing due to the oxidative effects of air oxygen with the contribution of solar radiation and due to the hydrolytic reactions with atmospheric moisture to form sulfuric acid. If other pollutants get into the air together with sulfate, the number of possible reactions is increased by combinations with primary and secondary pollution. *Consequences of air pollution:* ozone layer depletion (referred to as the ozone hole) is present in areas mainly above the Arctic and Antarctica with reduced ozone concentration due to anthropogenic pollution. In the ozonosphere there is a constant cycle of ozone formation and disappearance. In the presence of sunlight, photochemical processes occur, resulting in higher ozone concentrations. The most important thing concerning life on Earth is that most of the ultraviolet radiation is trapped in these processes and the visible light is transmitted to the Earth's surface. *Ozone* is a gas that is poisonous at higher concentrations. Therefore, in the troposphere where we live, it is undesirable, but in the stratosphere it is essential for life, as it absorbs dangerous UV radiation. Since 1970, we have been observing the depletion of the ozone layer around the entire globe. It is caused by civilization influences. At present, we know more than 200 chemical reactions of the ozone decomposition process. Depending on which parts of the atmosphere contain ozone, it can play a positive or negative role. *Tropospheric ozone* is ozone found in

lower parts of the atmosphere, which is harmful to living organisms. Unlike stratospheric ozone, its concentration in the troposphere is increasing. Excessive ozone amount in the troposphere is as harmful as its lack in the stratosphere. Tropospheric ozone can be of stratospheric origin or is a result of complex photochemical reactions of hydrocarbons, carbon monoxide and nitrogen oxides.

Stratospheric ozone - ozone found in the stratosphere prevents the penetration of harmful short-wave UV-B radiation with a wavelength of 280–315 nm. As a consequence of photochemical reactions in the stratosphere, besides the formation and decay of ozone, not only is there a significant attenuation of the incident solar ultraviolet radiation, but also the transmission (absorption) of energy, and thus an increase in temperature in the respective atmosphere layers. As a result of human activity, substances are released into the atmosphere, the amount of which exceeds the normal value of their occurrence in the atmosphere several times. This reduces the amount of ozone in the ozonosphere and disrupts the natural structure of the atmosphere, which permits much more UV-radiation at wavelengths that adversely affect living organisms. The stratospheric ozone layer is increasingly disrupted by the action of chlorofluorocarbons (CFCs or Freons). Freons have been developed in the 1930s, have a very wide use, are non-flammable, non-toxic, odorless, cheap and lighter than air. As a result of UV-radiation, the atoms of the halo elements (chlorine, bromine) are released, converting ozone to oxygen molecules that do not absorb UV. The decrease of ozone in the stratosphere allows ultraviolet rays to get to the Earth. Negative effects on living organisms include skin cancer, eye diseases, weakening of the immune system and others [3, 10, 13–15]. Ultraviolet rays do not only damage living organisms, but also contribute to the deterioration of plastics, wood, paper and cotton. The amount of both tropospheric and stratospheric ozone depends on the balance between the processes in which ozone is produced and the processes in which ozone is disposed of in the atmosphere. In the last quarter of the 20th century, it was found that stratospheric ozone was disappearing, while tropospheric ozone was increasing. Even though stratospheric ozone is naturally produced and destroyed by a constant, balanced rate, people are gradually disrupting this balance by using ozone-consuming substances.

Acid rain is the result of strong air pollution, where dirt absorbed by air humidity gets back to the ground through precipitation. Rainwater with a pH value of 5.0–5.6 is slightly acidic because carbon dioxide is found in the air and absorbed by the air humidity. Acid rain is considered to be rainwater with a pH of 2.0–5.0. *The occurrence of acid rain* is mainly due to coal and oil-fired power plants, metallurgical plants, the chemical industry and transport. Sulfur and nitrogen oxides emitted by these sources combine with atmospheric moisture to form sulfuric and nitric acids. These rains have a negative impact on flora and fauna. They kill fish in lakes in bulk. Acid rain threatens plants, forests (healthy coniferous trees lose their needles after 6–8 years, sick ones after 2–3 years, only the newest needles remain on damaged coniferous trees, plant roots absorb toxins more easily in acidic environment) worms, insects and other animals that process plant remnants in healthy soil (thus enriching the soil with substances that are vital to plant life). However, if the soil is acidified by acid rain, the animals cannot live in it. Dead plant residues remain lying on the ground and no animal nutrients are formed. The food chain is disrupted. Some of the nutrients such as calcium, manganese, sodium, potassium is diluted from the soil due to the effects of acidic components of the rain; groundwater and surface water are (acidified water has a negative effect on aquatic animals and aquatic plants). Under these conditions, phytoplankton gradually disappears and due to its reduction, the light gets deeper into the water, so the water of the affected lakes is almost unnaturally clear and clean. Today, for example, only in Sweden out of 100,000 lakes, (about 20,000 are dead, lifeless), acid rains are damaging buildings, artistic and cultural

landmarks. Not all sites respond to acid rain in the same way - it depends on the soil and water chemical composition. There are some sites with alkaline soil that can tolerate large doses of acid rain without significantly changing the overall pH of the environment. Acid aerosols also have a harmful effect on humans by entering the respiratory tract, irritating the mucosa and thus facilitating the entry of infections into the lungs. *The greenhouse effect* is the denotation of a phenomenon consisting of warming the lower layers of the atmosphere due to the fact that the atmosphere permits the passage of short-wave solar radiation to the Earth's surface during the day and absorbs Earth's long-wave radiation at night and thus becomes warmer. Larger wavelength heat radiation, which is emitted back from the planet's surface, is absorbed by the Earth effectively, its immediate release into space being prevented this way. The anthropogenic greenhouse effect is caused by the burning of fossil fuels, the excavation of forests, the global changes in the countryside, and contributes to global warming. Among the greenhouse gases currently having the greatest climate impact belongs carbon dioxide. It occurred naturally in the atmosphere. From 1850 to the present, its concentration increased by 27%. It is released in the burning of fossil fuels and its amount is growing due to massive deforestation too. Part of it is absorbed by the oceans and much of it by forested areas. Another significant greenhouse gas is *methane*. In the atmosphere it occurs naturally, as does carbon dioxide. It is produced by anaerobic bacteria in the digestive tract of ruminants and by the decomposition of organic matter. It is released from subsurface landfills and is also released into the atmosphere by escaping from gas pipelines. *Nitrous oxide* is a naturally occurring greenhouse gas. Its presence is increased by using nitrogen fertilizers and burning fossil fuels. *Freons* have anthropogenic origin. They are found in refrigerant gases and are part of the propellants. They disrupt the ozone layer. We are currently adding nearly 10 billion tons of carbon to the atmosphere annually. The biosphere is not capable of returning such an amount back to underground reservoirs as fossils, nor is the world ocean able to drain such an amount of carbon because of physical and chemical limitations. This is the main reason that the concentration of CO₂ but also of CH₄ in the atmosphere grows in parallel with the consumption of fossil carbon by various anthropogenic activities. *Nitrogen* is an indifferent part of the air in respect to health. Oxygen is the most important component of air, resulting from its role in respiratory physiology. The human organism is highly resistant to fluctuations in the amount of oxygen. Ozone is of little use for low concentration under natural conditions. However, it is harmful and even dangerous at high concentrations. *Carbon monoxide* is an unnatural admixture in the air. Its hygienic importance lies above all in the danger of poisoning. It is particularly dangerous because humans cannot smell it. *Sulfur dioxide* is produced by the combustion of sulfur and acts irritatingly and even as a strong poison. *Ammonia* occurs only in trace amounts in the atmosphere. It is harmful at a concentration of 0.5%, which it practically does not reach. Odorous substances are produced in an enclosed atmosphere by anthropogenic and animal activity. Further impurities in the air are e.g. mercury, and gasoline vapor, hydrogen cyanide [3, 6, 10, 14].

3. Hydrosphere

Hydrosphere (from Greek hydro - water) is a denotation that encompasses all water, whether on the surface of the Earth or below it and in any form... Water is the most widespread, under the surface of the Earth. Water occurs in different states and creates a discontinuous water layer of the Earth (hydrosphere). These include the waters of the oceans, seas, surface waters, and, in a broader sense, soil

and groundwater, water bound in glaciers and snow, atmospheric water, and water in living organisms. on the Earth and for the animals it is directly the environment for their living. It is the main means of transporting nutrients, receiving and excreting them. Water on Earth occupies about 2/3 of its total surface area (drinking water represents about 1% of the total water; 97% saltwater contained in seas and oceans; 2% water bound in glaciers). The total water volume is about 1385 billion km³. The origin and development of the hydrosphere is closely linked to the evolution of the rest of the Earth. Between the lithosphere, the atmosphere and the hydrosphere, there is a constant exchange of water causing changes in the chemical and isotopic composition of water. Continuous water circulation is caused by solar energy and gravity. Large (global) water cycle takes place between the ocean and the mainland, and a small water cycle arises over the oceans. In the various phases of the cycle, complex water conversion takes place [3, 6, 10].

Meaning, function, properties and distribution of water: The health of the population as a universal value and primary human rights represent the fundamental economic resource not only for the individual but also for the whole of society. In recent years, information has been gathering to warn of the catastrophic effects of unscrupulous industrial devastation of natural resources, water resources, and interventions in the ecological balance of flora and fauna. Water is an indispensable component of the human environment, as well as all plant and animal systems, and constitutes the basic condition of life on Earth. It is an important prerequisite for the existence of every living matter on Earth.

The importance of water for man and the environment was accurately defined in the 12 points of the European Water Charter, proclaimed by the European Council on 6 May 1948 in Strasbourg: The Water Charter underlines the necessity to maintain sufficient water for future generations and the fact that water does not recognize state borders. Therefore, the growing water problems require international cooperation. According to data from the United Nations, polluted water kills more people than war. Up to 2 billion tons of polluted waste is discharged daily into the water worldwide. About 2 million people die of dehydration in developing countries every year on our planet, with about one in five people having no access to drinking water. More than 3000 children younger than 5 years die from diarrhea, dysentery, dehydration and cholera daily. According to the UN, about 783 million Earth inhabitants does not have access to drinking water and about 2.5 billion people do not know sanitation systems, while the quality of water resources is worse. The human body contains more than 60% water (65–75%), which is about 2/3 of the body weight. This ratio is even higher in children and newborns. Water plays an irreplaceable and irredeemable role in the life and function of the body as it participates in the digestion and metabolism, body temperature regulation, excretion of body waste, transport of oxygen and nutrients to tissues and cells.

The amount of drinking water received depends on several factors: age, activity, environment in which a person lives, condition of the body, nutrition (composition of diet). Lack of water leads to serious damage to the human body after only a few days. In the case of excessive loss of water from the body, we feel drowsiness, weakness, confusion. Dry mucous membranes, constipation, headache, fatigue, somnolence, impaired movement coordination, pulse acceleration, drop in blood pressure and decreased performance are also *manifestations of water deficiency*. In case of excessive fluid loss, we are talking about dehydration. Loss of fluid above 6% can lead to collapse or death. In the case of insufficient water supply, harmful substances accumulate in the body, which puts the excretory organs under stress. The thicker the blood, the more difficult it becomes for the kidneys to deal with the waste. Water in tissues, blood, and lymph are thickened, weakening the immune system, failing to transmit nerve impulses, slowing cell renewal. Water is also important for thermoregulatory processes and protects the body from

overheating. *Water functions: biological function* – it is the essential condition for the life of organisms from microorganisms to higher animals to humans, it provides nutrition for humanity, for some animal species water is their living environment, water participates in photosynthesis, it is part of components in the cell as well as regulator of thermal properties, *health preserving function* - the quality of life, hygiene, health, healing properties of mineralized and otherwise enriched waters depend on it; *economic function* – it is applied in the agricultural industry, *esthetic-cultural functions* - spas, water bodies fulfill the appropriate function, *political function* - watercourses form borders between states. *Water properties:* The physical, chemical and biological properties of water result from its structure and chemical composition. From a physical and chemical point of view, water is a very complicated compound characterized by a number of special chemical and physical properties resulting from the electron structure of its molecules. Water properties are divided into chemical, physical, microbiological and sensory. *The chemical properties of water* - water contains a wide range of chemicals, some of which are only minuscule and desirable (carbonates); others should only be present in limited quantities because they could change the color and haze properties (turbidity) of water (iron, chlorine) and there is also a group of substances undesirable in water that indicates water pollution with nitrogenous substances (ammonia, nitrites, nitrates, phosphates, chlorides) of organic origin, etc.) [6, 14]. The chemical properties of water are determined by the content of substances dissolved in water. The main inorganic constituents of natural waters are calcium, magnesium and sodium, which are mostly present as cations such as bicarbonates, sulfates and chlorides. In natural waters, potassium, iron, manganese and small amounts of other metals are represented in small concentrations, by which the water is enriched in contact with the soil, with various minerals and rocks. From a chemical point of view, we divide the substances found in waters into inorganic and organic. From a physical point of view, these substances can be present as ionically dissolved (electrolytes), non-ionically dissolved (non-electrolytes) or as undissolved (non-miscible, miscible and buoyant or floating). *Physical properties of water:* ability to accumulate more heat; large water bodies such as lakes, seas and oceans are involved in the regulation of temperature on the Earth, electrical conductivity, which depends on ion concentration, their mobility and temperature, while the dissolved salts and gases increase the water conductivity, the water density increases from temperature of 0 to 3.98°C, at higher temperature it decreases continuously, surface tension - is the cause of capillary phenomena (capillarity of water in the soil and rocks, wetting ability, foam formation, etc.), viscosity, which together with density significantly affects hydraulic water behavior - for example, the speed of sand filtration of water depends on its value, sedimentation rate that decreases with temperature rise. Other physical properties of water include light absorption, water radioactivity, and state changes. *Biological properties of water:* The microbial recovery of natural waters consists of autochthonous (indigenous) species, for which water is the primary and natural habitat, where they participate in the circulation of substances in water and are thus reflecting natural water pollution without anthropogenic influence. Microorganisms that get into the aquatic environment by flushing from the soil, or through civilization wastes, whether communal, industrial, or agricultural, and survive for some time in this environment, represent an allochthonous (non-original) recovery, indicating not only external pollution by organic substances, but also the possibility of pathogenic germs. There are many microbial species in natural waters. Microbiological analyzes are carried out in a targeted manner, and indicator groups or individual species of microorganisms as indicators of water quality are selected purposefully according to ecological or hygienic criteria. Ecological classification of organisms expresses the behavior and

application of organisms in certain physiological conditions and their ability to survive and adapt in new and more difficult conditions. Systematic division of organisms is done either from the perspective of their development or family relationships. This includes microorganisms, plants and animals. Ecological division relates to the participation of organisms in the circulation of substances in the aquatic environment and recognizes producers, consumers and destroyers. Producers are organisms able to assimilate inorganic nutrients and synthesize organic substances such as carbohydrates, proteins and fats from them. These include autotrophic bacteria, higher plants, algae, cyanobacteria. The source of energy is either light radiation, e.g. for algae, photosynthesis in plants or some oxidation–reduction reactions. In the case of photosynthesis, in addition to organic substances, producers also generate oxygen which can enrich water and air. Producers are the bases of aerobic life on the Earth and their photosynthesis is significantly utilized in self-purification of water. Consumers feed on finished organic substances that are processed by endoenzymes inside their bodies. Consumers include animals from protozoa to arthropods. Together with destructants they represent an organotrophic (heterotrophic) diet. Consumers release the waste substances of their metabolism into the water, especially carbon dioxide. Decomposers feed on finished organic substances. Since they do not have any food intake organs, they decompose high molecular weight substances outside of their body by exoenzymes into simpler molecules that can penetrate the cell wall into a destructive cell [3, 10, 13–15].

3.1 Division of water by origin, pollution, causes

Precipitation (atmospheric) water forms - occur in the air in the form of clouds, water vapor, precipitation and fog. This type of water is considered the cleanest, but it is contaminated by passing through polluted air layers. The greatest influence on the chemical composition of atmospheric waters has a layer of atmosphere that extends from the Earth's surface to a height of 1000–1500 m. *Surface water* - represents water that is permanently or temporarily on the surface of the Earth and is divided into: *flowing* (natural - streams, rivers, artificial - canals, conduits), *stagnant* (natural - seas, oceans, lakes, artificial - ponds, water reservoirs). Pollution of surface waters – the so-called “Eutrophication” is a set of natural and man-made processes leading to an increase in inorganic nutrients in water, especially nitrogen and phosphorus compounds, followed by increased growth of cyanobacteria, algae and higher plant forms, resulting in worsened ecological stability and reduced water quality. Phosphorus in surface waters comes from sewage and phosphate fertilizers used in agriculture. Nitrogen and phosphorus compounds mainly come from waste related to animal husbandry, industrial production and from sewage “water”. An important source of surface water pollution is the excessive application of NPK fertilizers to the soil. It occurs mainly in stagnant, slow-flowing waters, but eutrophication can also occur in watercourses under favorable conditions (strong nutrient supply, increased water temperature and slowed flow of water). *Groundwater* is created by infiltration of rainwater and surface water into the Earth's crust. Groundwater is of fundamental importance in the hydrological cycle in supplying the population with drinking water. Groundwater pollution by nitrates is an issue that has been given increased attention in the area of groundwater protection against pollution. The increased level of nitrates in groundwater is contributed to by anthropogenic activity, e.g. the application of industrial and artificial fertilizers to agricultural land, discharge of waste water from settlements and industrial buildings. Increased concentrations of nitrates in groundwater have a negative impact on both the environment and human health, since groundwater is preferably used as a

source of drinking water. In particular, the prevention of groundwater pollution by nitrogen compounds is provided by integrated territorial protection of areas with potentially endangered groundwater bodies. Thus, *contamination of water resources* can be physical (occurrence of insoluble sludge and radioactive substances), chemical (water-soluble impurities), biological (germs present). Thus the pollution itself occurs by the already mentioned increased use of fertilizers and pesticide preparations, leakage of silage juices, leakage of liquid parts of fertilizers from farms, leakage of lubricating oils, fuels and so on. *Pollutants (substances contributing to pollution)* - substances directly toxic (heavy metals, cyanides, pesticides), water pollutants (dyes, oil and related substances), substances affecting the amount of oxygen in the water (high levels of degradable substances, at the decomposition of which large quantities of O_2 in water are consumed), inert inorganic substances dissolved, undissolved, non-toxic [3, 10, 13, 14]. *Causes of water source pollution*-Man affects the quantity and quality of water resources directly through uncontrolled discharge of wastewater into watercourses or through sewerage networks. Waste water producers in the Slovak Republic are mainly industry and municipal sphere - sewerage systems of towns and villages. Inadequate purification results in high concentrations of pollutants and substances supporting the development of algae and plankton - phosphorus (P), nitrogen (N) - into the surface waters, resulting in an overall deterioration of water quality in streams and in stagnant waters (eutrophication). In the area of groundwater quality in the Slovak Republic, the issue of adverse oxidation-reduction conditions is at the forefront, which is often indicated by increased concentrations of iron (Fe), manganese (Mn), and NH_4 . Almost all metals are naturally found in surface and groundwater. Many of them are indispensable to life but may be harmful at higher concentrations. Metals with toxic properties, which are among the most important inorganic contaminants of waters and soils, become hygienically serious. The presence of cadmium (Cd), mercury (Hg) and chromium (Cr) is currently one of the most recent risks. Toxic metals have a negative impact not only on the surrounding environment, but especially on human and animal health. They also have an impact on flora and fauna [3, 8, 15–17].

4. Pedosphere

Soil is a natural formation that arises directly on the Earth's surface as a product of the interaction of climatic conditions, organisms, humans, relief and parent rocks Act 34/2014 Coll., amending and supplementing Act 220/2004 Coll., On the (Protection and Use of Agricultural Land). Soil is a complex system of abiotic and biotic components and is the result of soil-forming factors. It is created on the interface of the atmosphere, the lithosphere, the hydrosphere and the biosphere, which to a great extent influences its composition. In the soil-forming processes, abiotic and biotic environmental factors are applied together, and the result of their action is the abiotic-biotic component of the environment - soil. *The main abiotic factors* involved in soil formation include: parent (soil-forming) rock, relief, water and climatic conditions. The chemical composition of the soil depends primarily on the parent rock from which the soil originated, from the processes running in the soil and from the activity of man. Soil contains most oxygen (about 50%) and silicon (about 25%), other elements are mainly aluminum (clay), iron, calcium (limestone, gypsum), sodium, potassium, magnesium, hydrogen, titanium, in lesser amounts carbon, chlorine, phosphorus, sulfur and manganese. *Biotic agents* include soil edaphone. These factors are collectively called soil-forming factors. Edaphone is a living component of soil. It is a set of soil microorganisms, fungi, plants and animals. Soil organisms (geobionti, edafonti) live in slots washed

out by air or water, especially in the surface layers of the soil. For humification processes, plants, bacteria, and mycophytes are the most important. The root system of higher plants ensures the mechanical movement of the soil and keeps it loose. Bacteria break down organic matter in the soil. The soil contains both autotrophic and heterotrophic bacteria. Bacteria can have diverse functions in the soil. Decomposition of animal, plant and microbial residues is performed by heterotrophic bacteria. Chemoautotrophic bacteria in the soil are predominantly represented by nitrifying bacteria and, to a lesser extent, sulfur-oxidizing bacteria. The most common microbial cells in the soil are single-cell prokaryotes. Despite their high concentration in soil, fungal biomass predominates over the biomass of bacteria. Soil bacterial flora is extremely diverse and is dominated by Gram-positive bacteria. Fungi dominate the soil in terms of biomass amount. They are eukaryotic and have a mycelial morphology consisting of mycelia that surrounds the multi-nuclear cytoplasm. They live in symbiosis with most plant roots, which are of great importance for regulating nutrient uptake, aquatic connections and ultimately the growth of a plant partner in this community. Soil spore production allows to some extent their survival under unfavorable soil conditions. Fungi also include many important plant pathogens. Bacteria, worms, insects and other animals process plant residues in healthy soil. In this way, soil is enriched with substances that are vital for plants. However, if the soil is acidified by acid rain, the animals cannot live in it. Dead plant residues remain lying on the ground, no nutrients are created for the animals, and the food chain breaks. *Soil contamination, causes, monitoring:* we consider soil to be one of the main components of the Earth's ecosphere. It forms the basis of the nutritional chain at the end of which man stands [2, 18]. The most important soil characteristic is fertility, the ability of the soil to provide plants with water, air, nutrients in optimal quantities throughout the vegetation [19]. The soil system is a very specific component and to some extent can effectively and naturally eliminate various foreign substances. Soil and ecosystem components - water and air - are basic indicators of pollution. The soil loses most due to contamination since its ability to eliminate the negative effects caused by the natural and anthropogenic activity of man become limited [20–22]. Major problem of consumer society is waste production. The issue of waste does not end with the disposal of waste in landfills. Precipitation waters that infiltrate through landfills are contaminated with waste materials. Such landfill leachates can then contaminate the soil or the bedrock where the landfill is located. Another factor that negatively affects soil environmental functions is the contamination of soil by water and air. Pollutants in air and water are mainly from industrial production. *Toxic heavy metals*, like biogenic metals, are present in the soil in two mobilities. They occur in the liquid phase as hydrated ions or as soluble organic and inorganic complexes. In the solid phase they are in the form of insoluble precipitates on the surface of organic and inorganic colloids in exchangeable and specifically absorbed form. A dynamic equilibrium is created between the various forms, in accordance with the characteristics of the system. If e.g., a large amount of toxic substance gets into the soil, absorption and precipitation reactions predominate. On the other hand, when the acidity of the soil increases, the number of mobile forms increases, i.e., the concentration of metal ions in solution increases. Contamination of the soil by sulfur dioxide exhalation leads to its *acidification*. Low pH causes increased mobility of cadmium and aluminum, which can intoxicate plants. Other contaminants also enter the soil through sedimentation: nitrogen oxides, lead, cadmium, arsenic, fly ash, chromium, nickel, organic compounds. Lead polluting soil comes mainly from automobile traffic. The source of cadmium is the burning of fossil fuels. The arsenic from the power plant ash dissolves well in the water and therefore does not accumulate in the topsoil but passes into the lower layers. Acidification of the soil in already contaminated areas

is particularly dangerous as heavy metal compounds are normally insoluble, but when mobilized, they can result in a serious environmental damage (*timed chemical bomb*). Soil is an important geochemical reservoir, which relatively easily accumulates heavy metals. They are removed only very slowly, by leaching processes into subsurface waters or by plant bioaccumulation. Soil is the starting point for the entry of risky elements into crops and through forage into animal products [23, 24]. Soil contamination with water occurs as a result of soil irrigation or rainfall activity. Erosion is one of the most serious problems threatening soil worldwide. The erosion is due to the spread of mountain farming, the excavation of forests, the deterioration of the soil's water regime, the plowing of grasslands, the artificial regulation of watercourses, the wrong land cultivation. The result of erosion is the drainage of soil parts, humus, nutrients, crop reduction. As reported by the authors [13, 15, 25, 26]. industrial emissions primarily affect the pollution of agricultural and forest land. Especially increased content of lead (Pb), zinc (Zn), tin (Sn), cadmium (Cd), aluminum (Al), copper (Cu), nickel (Ni), mercury (Hg), manganese (Mn), and arsenic (As) was found in the vicinity of metallurgical factories. All metals usually get into the soil, but increasingly those components that dominate the immission type. The most important metal pollutants of soil are mercury (Hg), cadmium (Cd) and lead (Pb), which are generally toxic to humans and animals [2, 3, 9, 16, 27].

4.1 Health risks of environmental pollution, risk analysis, evaluation

Increasingly polluted environment, preservatives, dyes and flavorings present in the food are heavily burdening the body. Pesticides for weed control, chemical fertilizers, and nitrates can be carcinogenic when getting into organism. Automobile exhaust gases, ozone, formaldehyde, wood disinfectants and preservatives, insecticides, paint solvents and the like contaminate air, damage the respiratory tract and weaken the immune system [26]. This is why methods for assessing health risks (e.g. questionnaires, risk assessment, analyses, diagrams, use of geographic information systems) are extremely important. *Risk Analysis* - [28] states that it is very important to determine the level of danger to human health and animals in a given location and at the same time to take account of future use of a respective area. In general, the principles of the health risk assessment, hazard determination and hazard identification, (evaluation of dose - response relationship, exposure evaluation & assessment, risk characterization are applied). In assessing the health risks and adverse effects of metals, it is important to evaluate not only their presence and overall concentration in the environment and in food, but also their chemical and mineral forms that affect their persistence and bioavailability. The effects of sudden metal uptake into organisms may have the character of "*acute disease*". Metals, with regard to the accumulation in target organs of the organism, cause disease manifestations after periods with different length (weeks to years) and the clinical picture has the character of "*chronic disease*" [11, 29]. *The aim of the assessment* is to determine the harmfulness of chemicals or other risk factors occurring on the site and to assess whether the substance or risk factor has the ability to damage the body. In general, this part of the risk assessment process describes the quantitative relationship between dose and extent of adverse effect (injury, disease, death). This step requires two basic types of extrapolation using different mathematical models. These are extrapolations - interspecific (experimental animal - human) and extrapolation to the low dose area [10]. At present, the *protection of environment* is seen as a necessary condition for the existence and further development of human society. It includes activities to prevent pollution or damage to the environment, respectively for the reduction and/or elimination of pollution. It is either general protection (air, soil, water), special protection (protected areas, plants, animals,)

or the protection of cultural monuments. *The creation of the environment* is understood as a purposeful human activity that is organized on a scientific basis, aiming at optimizing the natural and artificial components of the landscape. *The aim of environmental care* is to maintain or improve its quality with respect to all organisms, while respecting all principles of sustainable living. This environmental care is called environmentalism [7, 13, 30].

4.2 Heavy metals and their importance in environmental pollution, sources, form

Heavy metals are among the common environmental pollutants resulting from both industrial and agricultural production [31]. They are not subject to biological degradation, and their levels are gradually increasing in the individual environmental components: water, air, foodstuffs [29, 32]. They are released into the environment from natural sources (weathering) and by erosion of some minerals and rocks. As stated by [33] the natural increased incidence of heavy metals and other risk elements is mainly in the areas of geochemical anomalies. Regarding pesticides (containing heavy metals), their use has been suspended and is no longer the source of this type of pollution. Metal production (their heat treatment), chemical, engineering, energy production, fossil fuel combustion, waste, food production flushing, fertilization, etc. are among the major *anthropogenic sources* of environmental pollution. As [34] report, metallurgy of ferrous and non-ferrous ores (the impact of non-ferrous ore metallurgy is predominant in mercury) contributes most to emissions of mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu) and zinc (Zn). Combustion of fossil fuels contributes significantly to the emissions of most heavy metals, glass production is a significant source of lead (Pb) and cadmium (Cd) emissions, and transport, despite the dynamic increase in the use of unleaded petrol, complements these sources. In the past, alkyl lead compounds (tetra-ethyl lead) were used as anti-knock additives in gasoline, thereby increasing the concentration of lead in the air. Thus, pollutants are introduced into the environment from various sources and based on their physico-chemical properties. They are transported and participate in biochemical cycles in individual environmental components (air, water, soil, rocks, segments). [35] states that heavy metals constitute one of the most dangerous groups of pollutants. Their amount in the environment is given by content, quantity and movement in all spheres of the environment. The side effects of heavy metal emissions are dangerous, they usually get into the environment (the air) in an uncontrolled way. In the environment, they can occur as simple complexes with inorganic ligands (in the aqueous environment, the form of the metal is affected by physico-chemical properties: pH, temperature, ionic strength), as chelates with organic ligands (sorbed to solid surfaces), free metals. In the terrestrial environment, fate, bioavailability and mobility of metals are influenced by: soil type, oxidation–reduction processes and cationic solid phase capacity [36]. More detailed information on the specific effects of individual heavy metals on cells, tissues, and organs of animals is obtained and validated within laboratory animal experiments. However, the results of the experimental application cannot be considered generally valid. Mostly, the experiment only works with the substance being studied individually, which does not occur alone in the environment. All animal species may not respond to the toxic substance in the same way. In the response of the organism to the action of a toxic substance, the overall momentary state of the organism, its life phase and gender are important. Taking all these factors into account during an experiment is almost

impossible. Therefore, despite the systematic research, there is still some concern over formulating the environmental and hazardous concentrations of these substances. However, these doubts do not justify the presence of heavy metals in the environment being taken lightly or underestimated. The combination of overexploitation of natural resources, coercive forced population growth and economic developments, as well as a lack of government regulations can increase the flow of toxic metals into the environment in all countries. By 2010, a significant increase in emissions of mercury (Hg), cadmium (Cd), copper (Cu) and a decrease in lead (Pb) emissions and deposition was expected in Europe [2]. Heavy metals cause a wide range of toxic biochemical effects and thus adversely affect organs and systems in humans and animals [37, 38]. Therefore, they pose a serious risk to health regardless of the source from which they enter the body. Some heavy metals (e.g., manganese, copper, zinc) are needed for physiological processes, but other toxic heavy metals (especially cadmium, mercury, lead) are environmental pollutants [39] and do not have any known physiological roles. Conversely, they may adversely affect health [40] and thus induce a variety of adverse effects including reproductive disorders [41] nutritional deficiencies, endocrine disorders [42, 43] or immunodeficiency disorders; they can induce tumor formation and other health-damaging chronic conditions [32, 44]. Currently, there is also a strong focus on low-dose exposures (environmentally relevant concentrations) of these metals that may affect human and animal reproductive health [3, 45, 46]. Ecologists and environmentalists duly address this issue and take into account the contexts that have not yet been considered. Even if the concentrations of heavy metals with regard to the health safety of living organisms are limited within the monitored areas, environmentalists are the ones drawing attention to many natural processes that cause the concentration of toxic elements to become a real danger. Certain metals are needed for normal body function. They are part of the enzymes and take different roles in metabolic processes and electron transfer - manganese (Mn), copper (Cu), nickel (Ni), molybdenum (Mo), cobalt (Co), iron (Fe), zinc (Zn), however, at higher concentrations they can already become toxic. Heavy metals are characterized by varying degrees of toxicity and different effects on living organisms. The subject of world monitoring is strongly toxic elements - mercury (Hg), cadmium (Cd), lead (Pb), arsenic (As), which have almost no purpose in the organism [47]. Metals are found bound in various inorganic compounds, but can also enter complex organic systems. They are persistent, non-degradable, biologically active with high bioaccumulation potential. They form a natural part of the Earth's surface composition and therefore occur everywhere in various concentrations. The natural balance of elements is also impaired by human activity. Together with the development of modern technology, production and consumption of metals and metalloids are growing rapidly, too. This is particularly true for non-ferrous metals, some of which have until recently been produced in incomparably lower amounts (e.g. laboratory scale) - beryllium (Be), titanium (Ti) gallium (Ga), selenium (Se), molybdenum (Mo), wolfram (W). Also, the production of classic colored metals which are gradually finding new types of applications, is increasing. This is especially true for aluminum (Al), lead (Pb), nickel (Ni), chromium (Cr), antimony (Sb), mercury (Hg). Increasing the concentration of the above metals in the environment - air, water, soil and foodstuffs, is a serious hygiene problem and its scale is still becoming larger [23, 34, 48–50]. In general, metals are highly reactive elements which, on the one hand, are essential (they are components of some enzymes), on the other hand they are capable of damaging different enzymes or interfering with different levels of signal transduction processes in cells.

4.3 Heavy metals and food chain

There is a comprehensive versatile and complex network of food chains in nature. They are interconnected, while the function of the individual elements of the food chains may vary. This causes the symbiotic organism to become dysbiotic, useful changes to harmful, or pathogenic [51]. The common population is also contaminated with the food chain [52] since it has a major impact on human (but also animal) nutrition, lifestyle and life expressions. Animals are much more exposed to the impact of the geochemical environment than humans, as they serve as effective buffers in the nutritional chain, in reducing the adverse effects of the environment on the consumer. According to [53] optimizing the animal nutrition can affect the human food chain. Most heavy metals get into the organism by plant or animal food (the load from air or drinking water is significantly lower). They are converted either into harmless metabolites (detoxification) that are easily excreted, or harmful, reactive products are formed. [54] states that the increased content of especially cadmium (Cd), mercury (Hg), chromium (Cr), arsenic (As), lead (Pb) and nickel (Ni) in agricultural soils may pose a potential risk of contamination of agricultural production. In most countries, including, the applicable legislation determines the maximum permissible concentrations (MPCs) for individual heavy metals (drinking water, air, foodstuffs of plant or animal origin). Therefore, the protection of the food chain from heavy metal contamination, and its follow-up checks are considered to be important in terms of health security. As reported by [55] food safety is a set of measures (animal health and welfare section, food and feed sector) and with their implementation, the safety of all components within the food chain is ensured. According to [56] the occurrence of contaminants in environmental components and in agricultural and food production is monitored through random check-ups and regular monitoring. The relationship between animal health, human health and the environment has been known for a long time. Potential contaminants and their total amount for both veterinary and public health are broad and vary according to their source, chemical nature and mechanism of action on biological systems. [57] state that the prevention of human and animal health from chemical risks implies their control throughout the food chain - field-table. Food quality control with the participation of state health surveillance in the Slovak Republic is one of the essential tasks of food surveillance and the limits of foreign substances in food commodities are harmonized in accordance with the limits of the European Union [58–61].

4.4 Impact of selected heavy metals-Hg and Cd on humans, animals and the environment

The transport of heavy metals in the atmosphere and their subsequent deposition depends on the following factors: the form in which the metal is found to escape into the atmosphere (solid or gaseous phase), their chemical reaction in the atmosphere, the height and location of the point source of emission, local geographic conditions, speed and direction of wind, rain washing and other meteorological requirements [12]. Pollution of the environment is now a global phenomenon, not excluding the territory of Slovakia and contributes to the deterioration of living and working conditions [2]. Recently, great attention has been paid to the impact of toxic heavy metals and their compounds (especially mercury, cadmium, lead) on human and animal health, which are considered to be dangerous and non-degradable contaminants in the environment. However, a suitable marker for early diagnosis of heavy metal exposure (including drinking water sources) has not yet been developed, which is perceived as a relatively serious problem [62].

As reported by several authors [44, 63, 64] the main consequence of the negative effect of environmental contaminants is the disruption of the optimal immune reactivity of the organism, the occurrence of allergies, increased susceptibility to pathogenic agents, higher occurrence of tumors, affecting reproduction. History shows us a number of global industrial accidents pointing to the negative effects. An important part in creating a good living environment for both humans and livestock is active health creation. It is based on two fundamental phenomena. It is a principle of complexity of measures, respecting variability of the effects of relationships and factors - the internal and external environment of the organism [7].

4.5 Cadmium - sources of cadmium in the environment, the effects of its occurrence

The main sources of cadmium include volcanic activity, weathering of rocks, or forest fires [65]. It gets into the environment by mining and processing of fossil fuels, ferrous and non-ferrous ores, limestone, in cement production [66]. It can be found in Cd-Ni batteries, stabilizers of plastics, home appliances. Cadmium also occurs in synthetic superphosphate and in naturally occurring superphosphates. Cadmium (yellow-orange) paints are added to coatings, gums, textiles, glass and ceramics. Along with zinc (Zn), it occurs in ores and soil at a ratio of 1:100 to 1:1000. It is usually found in the form of cadmium sulfide (CdS) in ores which also contain lead (Pb), zinc (Zn) and copper (Cu). Unlike mercury, it is not subject to biotransformation and cannot be released as an alkyl derivative from the organism. It is now widely used for its anticorrosive effects and serves as a base for electroplating and nickel plating. It is also widely used in making jewelry. It can enter the atmosphere due to poor waste incineration technology (higher cadmium exposure is near the smelter where ores blended with Cd are melted) or oil products [67]. According to WHO, the largest part of cadmium is bound to fine particles ($<1\ \mu\text{m}$) in air, which can then spread up to 1–2 km. Thus, cadmium builds up in soil, water and then enters the food chain. In soil and in some plants, accumulation occurs especially at low soil pH (e.g. leaves, rice). In agricultural soils, the accumulation of cadmium may be associated with the application of (phosphate fertilizers, sewage sludge, some fungicides [66, 68, 69].). The concentration of cadmium in the soil ranges from 0.01 to 0.7 mg.kg^{-1} and is most cumulative in the 0–5 cm layer. With increasing depth there is a decrease in its concentration. In the process of weathering rocks (content not exceeding 0.3 mg.kg^{-1}), it is easily transformed into a solution and its occurrence is in the form of Cd^{2+} . According to [70], cadmium intake by plants increases with the presence of chlorine in the soil and the content is also significantly affected by soil microorganisms. The way of farming, the time of harvesting the crop and also the environment (climate) affects the cadmium transfer into the plants. This suggests that increased cadmium content in soil is the result of increased cadmium absorption by plants, but, as [71] states, the bioavailability of cadmium also depends on soil solution composition, soil pH, and redox potential. Soil has the ability to somewhat eliminate the negative effects of pollution [22]. Compared to other environmental components, soil status is exceptional. Air and water may move (dilution occurs), and if the source of pollution ceases to be active, there is also a limitation or total elimination of pollution. However, in case of soil contamination by risk elements, we have to realize that this is an irreversible process, it cannot be observed immediately and therefore it is all the more serious. In waters, cadmium accompanies zinc at substantially lower concentrations. According to the higher cadmium content (Cd) has been repeatedly detected in water flowing right by zinc mines. The solubility in water is determined by the solubility of CdCO_3 and $\text{Cd}(\text{OH})_2$. It is generally presumed that people

(but also animals) are the most sensitive cadmium intake group when environment is concerned. The main source of cadmium intake for humans and animals is food, feed and beverages. It is estimated that the average daily dietary intake of cadmium is 50 µg. Up to 25% of the daily intake is retained in the body. The content in dairy products is higher. The lethal dose for oral intake is 350–8900 µg [11].

The impact of the toxic effects of cadmium on the organism: Relative the toxic effect, cadmium is one of the elements that is of great concern for its toxicity and widespread environmental impact. In humans, the main source of Cd exposure is food [72] and the bioavailability of cadmium from food is an important determinant of its potential risk. Cadmium is one of the 10 most toxic substances for human and animal health [39, 73]. Cigarette smoking is also an important source of cadmium accumulation in the body. As reported by author [37] cadmium can cause functional and morphological changes in organs and tissues, and is also strongly neurotoxic. When the exposure to cadmium in environmental components is short term, there may be no health consequences, but from the perspective of long-term exposure (individuals who are more sensitive to toxic effects - infants and children) certain symptoms may occur [70]. The detoxification of the organism is slow (cadmium is characterized by a high accumulation coefficient) and there is a danger of chronic intoxication. Chemically, cadmium is very similar to zinc (it is a part of food), it has an important role for the proper development and health of the organism. However, the similar chemical form of these elements can cause problems as cadmium easily enters various enzymatic reactions instead of zinc, and biochemical processes take place in a different way (e.g., blocking the insulin cycle) and serious health complications occur [3, 74]. Cadmium gets into the organism in three ways: by inhalation, gastrointestinal tract and absorption through the skin. According to WHO, 50–2600 tons of cadmium are emitted annually from natural resources. The atmosphere is polluted by 3300–12,500 tons annually through human activity. In order to eliminate the negative effect on the living organism, [75] recommends a concentration of 5 ng.m⁻³ as a non-carcinogenic cadmium limit in the air. Current levels in rural areas usually do not exceed 0.4 ng.m⁻³, and in cities they range from 0.2 to 2.5 ng.m⁻³. According to in the vicinity of certain industrial agglomerations, this concentration can be significantly higher. WHO has determined a provisional tolerable weekly intake (PTWI) for cadmium at 7 µg.kg⁻¹ of body weight. Since food is a major source of cadmium for most of the population, attention has also been paid to its quality as well as to the reduction of cadmium contamination of the environment. With an average absorption of about 5% of the amount received, about 0.5–1 µg of cadmium is retained daily in the organism. Based on epidemiological studies, there has been an increase in lung cancer and prostate cancer in long-term cadmium inhalation. In hazardous operations, inhalation intake is currently strictly controlled. The human lethal dose is 0.3–8.9 g. IARC [100] (International Agency for Research on Cancer) classifies Cd as the first category carcinogen for humans and animals.

4.6 Mercury - sources of mercury in the environment, the effects of mercury

Mercury is commonly found in the natural environment as it is a part of the Earth's crust. Its origin can be geogenic and anthropogenic. Mercury gets into the environment during its production and processing of products (production of electrodes, electrical equipment, dyes, measuring and control equipment, use in dentistry, chemical laboratories, etc.). In a year, this is estimated at 10,000–30,000 tons of mercury; and it gets into the environment by evaporating from the surface of the Earth and the oceans (vapor of metallic mercury, volatile organic compounds), [48]. The conversion of mercury (present in the form of ions) in a volatile

form can theoretically occur in three ways: by chemical reaction to elemental mercury (not previously found in nature), by reduction to elemental mercury by microorganisms, plants, animals, and by biotransformation to more volatile organo-mercury compounds (alkyl compounds), [76]. According to the most recent data, 5207×10^6 g of mercury is released from the natural sources annually into the atmosphere, and 2909×10^6 g (total 8116×10^6 g) of mercury from anthropogenic sources. The main anthropogenic sources by which mercury enters the atmosphere is the combustion of fossil fuels (1422×10^6 g.year⁻¹), gold mining (400×10^6 g.year⁻¹), waste management (187×10^6 g.year⁻¹), production of non-ferrous metals (310×10^6 g.year⁻¹), cement production (236×10^6 g.year⁻¹) [34, 77]. Global mercury emissions from natural resources are estimated at 3.0×10^6 g.year⁻¹. The average mercury (Hg) content in the Earth's crust is about 0.067 ppm. *Air, water, soil* - elemental mercury vapors released from the Earth's crust rise to the atmosphere (amount of about 18 mg.m^{-3}), where they are oxidized to divalent mercury and from there the compounds get into the water reservoirs by rain. Divalent mercury in the sediments at the bottom of the seas and lakes is methylated to methyl mercury by the action of microorganisms. It enters the food chain - phytoplankton - zooplankton - small fish - big fish. At the top of this chain are animals (that feed on fish), including humans. Within this chain, the process of bioaccumulation of ethylmercury occurs. As reported by [11, 78], its concentration is gradually increasing, with the values at the top of the chain about a million times higher than the concentration of methylmercury in the surrounding water. In general, large and longer-living fish (shark, tuna, mackerel, pike) also contain more mercury [48, 79, 80]. Under "European Commission Decision 93/351", the value of Hg in the meat of fish living in relatively uncontaminated areas should be below 0.5 gg^{-1} . The concentration of mercury in the air ranges from 1 to 5 mg.m^{-3} in rural areas and $7\text{--}10 \text{ mg.m}^{-3}$ in cities. The enrichment of soils with mercury is caused by the burning of coal, the occurrence of cinnabar deposits, but also by applying mercury-based fungicides. The use of sewage and urban sludge and fertilizers is also a source of mercury soil pollution. However, this is not just about soil contamination, but also about secondary effect on vegetation growing on it [81]. Mercury gets into the soil in the range of $0.02\text{--}0.3 \text{ mg.kg}^{-1}$. The concentration of mercury in uncontaminated soils should be within the range of $0.02\text{--}0.2 \text{ mg.kg}^{-1}$ [82]. Average concentrations affected by human activity are in the range of $0.1\text{--}0.4 \text{ mg.kg}^{-1}$, and in the vicinity of industrial enterprises and crematoria up to 1.8 mg.kg^{-1} , in the third of Slovakia's territory the content of total mercury is higher in woody plants (the value exceeds 0.12 mg.kg^{-1}) [11, 83, 84]. The natural content in the soil is from several, up to tens of $\mu\text{g.kg}^{-1}$. The use of mercury and its compounds has spread rapidly, and this fact cannot remain without consequences for: the environment, living organisms, including humans and animals. Therefore it is important to create favorable living conditions also for livestock (active health creation) based on the fundamental phenomena - complexity of measures and respect for the variability of the effects of relationships and factors between the internal and external environment [7].

Effects of toxic action of mercury on the organism: Regarding the effects of toxic effects on the organism, mercury is given a relatively high attention. Its toxicity depends on the physical properties of the individual forms. However, there are differences among them, based on the way of exposure, the metabolism itself, the way of excretion. It is known that the more mobile the form of mercury is, the more toxic it becomes. These properties are due to the structure of the molecule (e.g., behavior in biosystems, stability, excretion rates, etc.) [49, 85]. The negative impact not only on the health of people but also on the health and the performance of the animals results from an increased incidence of mercury, especially in polluted areas. The hygienic quality of animal products is lower, the content of toxic elements in meat and dairy

products is higher and the reproductive and growth indicators get reduced [9, 86]. Mercury is the world's only liquid metal that gets into the body most often by inhalation of mercury vapor, and up to 80% of these is absorbed in the lungs. The absorption of elemental mercury in the GIT is very low, less than 1%. [87] report that compounds containing divalent mercury are absorbed in GIT more, even up to 10%. Further, it is taken into consideration that oral administration may be accidental, or in contact with skin. As stated by [88], this metal has a high affinity for phosphates, cysteine and histidiny side chains of proteins, but also for purines, porphyrins and pteridines. Mercury, along with its compounds, is one of the high-toxic poisons (5 times more toxic than lead). The harmful daily human dose is 0.4 mg, the lethal dose is 150–300 mg. The condition of its toxic effect is the oxidation of Hg^0 to Hg^{1+} up to Hg^{2+} . After oxidation, Hg^{2+} binds to -SH groups of proteins, which are thereby inactivated. Upon absorption, a large proportion of mercury (depending on the type of compound and the site of absorption) gets into circulation. A part enters the erythrocytes and another part binds to the ligands in the plasma. The ratio of mercury content in plasma and in erythrocytes is about 1: 1. In erythrocytes, mercury (Hg) binds to the -SH group of hemoglobin. Elemental mercury (e.g. in mercury vapor poisoning) is oxidized to divalent cation. In plasma, mercury binds to albumin and other plasma proteins that contain free -SH groups. Exposure to mercury increases the amount of metallothionein (low molecular weight protein), which to some extent prevents kidney damage [11, 89, 90]. Elemental mercury and some of its organic compounds easily cross membranes (e.g., the erythrocyte membrane) and, unlike some other heavy metals (e.g. cadmium), easily cross the placental blood–brain barrier, too. In the complex with glutathione it is excreted in the bile, but it also reaches the sweat, salivary and dairy glands. In humans, the mean half-life of excretion for inorganic mercury is 60 days, for alkyl compounds of mercury 70 days [73]. The kidneys are the site of the greatest accumulation of mercury and also the major site of its excretion. There are several hypotheses explaining the mechanism of mercury excretion in the kidneys. One of them is the hypothesis that part of it gets into the urine in binding to albumin and then is reabsorbed (by endocytosis) in the proximal tubule. Another part is excreted in binding to glutathione, which is, similar to bile, hydrolyzed to amino acids by γ -glutamyltransferase and dipeptidases, and such amino acids are then reabsorbed by the Na-dependent transport system [91]. Mercury is excreted in the feces and urine. For inorganic mercury, the excretion half-life (both acute and chronic) is 1–3 months, for methylmercury it is 50 days. Since methylmercury permeates the hair, the level is used as a marker of mercury exposure [11, 92]. Food that has been contaminated with methylmercury (especially fish) are among the most common sources of exposure to organic mercury. At the end of the 19th century, [93] described the so-called pink disease (acrodynia - sporadic and predominant pediatric syndrome associated with calomel in toothpaste and other forms of inorganic mercury) related to an allergic reaction in hypersensitive people. Abnormal reddening of the skin has occurred, as well as peeling of the skin (area of the hands, legs, feet), pain threshold reduction, swelling. Acrodynia has been found in infants but also in older children who have used diapers treated with phenylmercury (an organic form of mercury). In spite of the scientifically-based study, mercury is still a part of various cosmetics and pharmaceutical compositions. However, it should be noted that the skin reactions to mercury are relatively rare, even scarce. The concentration of mercury in the blood in the general population (the result of dietary intake) is mainly in the form of organic compounds, but it is present in the urine mainly in inorganic form. Why this is the case (difference in form) yet needs to be further explored in mammals. As reported by [94], mercury concentration in blood increases with fish consumption. However, larger areas of

amalgam fillers, which may be the source of increased urinary excretion, also need to be considered. Other so-called immunotoxic responses can also be induced when exposed to inorganic mercury - Kawasaki disease, rash, cracking of the lips, fever, photophobia, pharyngitis, peeling of the skin on the palms of the hands and feet, tachycardia, affection of the lymphatic tissue - these are symptoms afflicted by sufferers. Urine levels of mercury have been shown to be higher in the affected patients. [93] reports that infants but also older children have more sensitive organisms than adults, and that explains the higher absorption of inorganic mercury. Among the organic mercury compounds, thiomersal (thimerosal, mertiolate, sodium ethylmercurithiosalicylate) is known as being used as a preservative in childhood vaccination since the 1930s. The thiomersal composition is 49.6 wt% Hg - it is metabolized to EtHg and thiosalicylate. The vaccine dose for children contains about 2.5 mg Hg in 0.5 ml. [95, 96] have expressed concern that the developing CNS could be harmed in children in the first half year of life. Possible health consequences: delayed speech development, impaired concentration, local hypersensitive responses, the spectrum of autism disorders. With long-term administration of gamma globulin (containing thiomersal), acrodynia has occasionally been confirmed. Based on these findings, thiomersal was requested to be removed from vaccines. However, it continues to be used in some countries to these days. According to [97] at high doses of EtHg the undesirable effects are similar to high doses of MeHg. However, the effect of low dose of EtHg remains unclear, more recent data [98] describe EtHg to be less neurotoxic than MeHg. The effects of mercury on health depend on several factors (form, dose, duration of exposure). International organizations Health Care Without Harm and the Health & Environment Alliance advocate accelerated reduction of environmental pollution by mercury in the European Union as well as worldwide and raise awareness of its destructive impact on the human fetal brain (arises during the early development of the fetus by methylmercury). It has a damaging effect on the development of the nervous system, and such damage is mostly irreversible. [99] states that the source of intense interest in the scientific community is primarily three chemical forms as a source of exposure: methyl mercury in fish, mercury vapor from amalgam dental fillings, and ethyl mercury in vaccines. US EPA (Environmental Protection Agency) classifies inorganic mercury into Group D "substances that do not have carcinogenic effects on humans" but [100] is considering reviewing the inclusion of inorganic mercury according to EPA. Organic forms of mercury - methyl mercury and its compounds are, according to IARC, rated as possible carcinogens [63].

5. Conclusion

Population health, as a universal value and primary human rights, is a fundamental economic resource not only for the individual but also for the whole of society. One of the main starting points for solving the relationship between man and the environment is the planned nature protection. The environment is everything that creates natural conditions for the existence of organisms, including humans, and is a prerequisite for their further development. The work was supported by VEGA 2/0125/17.

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