The Biogeochemical Behavior of Heavy Metals in the Aquatic Environment and their Effects on Health

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ABSTRACT

The contamination of aquatic environment by various types of pollutants and, mainly, by heavy metals seems to affect dramatically both human health and the lives of all organisms living into this environment, not to mention the social impacts of this phenomenon as is indicated in recent researches conducted especially in U.S.. So, this article concentrates on the study of the conditions of contamination of the aquatic environment by heavy metals, as well as the impacts of the latter on human health and much more on health of any organism. In any case, human health is closely related to its environment and all the living organisms. Taking into consideration all this, eight heavy metals, namely cadmium, copper, chromium, iron, lead, nickel, manganese and zinc, are examined in terms of their biochemical properties, their behavior and toxicity in the aquatic environment. The endeavor aims to point out heavy metals` role in the contamination process, their impact on human health and to indicate measures that ought to be taken or rather researches that ought to be further conducted.

Keywords: Heavy Metals; Water Pollution; Toxicity; Bioavailability; Bioaccumulation; Aquatic Environment; Trace Metals; Health Effects.

1. Introduction

The term heavy metals is general and is used for a large group of elements, metals and metalloids, with a density greater than 6 [1] or 5 g/cm^3 [2]. Certain metals, such as iron and aluminum are naturally present in coastal water systems in high relative concentrations, while others are particularly rare and usually found in low concentrations such as mercury, cadmium, selenium, etc. These metals are called trace elements or even micro-nutrients (as their presence is important for the growth of plant and animal organisms). Various metals such as mercury and lead can be highly toxic in high concentrations, significantly affecting the biological processes of organisms. Human activities increase concentrations of heavy metals above their natural levels. Industrial and municipal wastes, agricultural residues, fine sediments, erosion products, atmospheric precipitation, ship paints, mine by-products, etc. are sources of heavy metals originating from human activities [3], [4], [5]. In particular the term heavy metals is applied to the elements Cd, Cr, Cu, Hg, Ni, Pb and Zn, which are related to pollution and toxicity problems. An alternative and more accepted term for these elements is trace metals, but is less commonly used [6].

Unlike organic pollutants, heavy metals are found in the minerals that make up rocks and thus have natural background concentrations in soils, sediments, water and living organisms. Metal pollution results in concentrations much higher than natural background levels. So, the presence of metals in an environmental compartment is not sufficient evidence of pollution, but the relationship of existing concentrations to background concentrations must be considered [1], [6].

Water is the medium that contributes to the disintegration of land and the transport of metals. During the transport of metals, environmental changes affect their distribution between the soluble and particulate phases. After being

transported from rivers and the atmosphere to the oceans, metals participate in complex biogeochemical cycles and become incorporated into oceanic sediments. In the sediments, the metals are more inert, but with a change in the environmental conditions their re-dissolution is possible. In oceanic sediments, however, the metals will remain there until they take part in the next hydrological cycle [1], [6].

Heavy metals occur in coastal water bodies in dissolved phase, suspended phase, bottom sediments and aquatic organisms. Their main transformation processes include adsorption, complexation, precipitation and biological uptake. Adsorption is usually the dominant process, since metals tend to participate in iron and manganese oxides, adsorbed by organic materials and fine suspended solids, such as silt and clay. This means that heavy metals tend to accumulate in bottom sediments. The dissolved phase of metals represents the main bioavailable source of metals for a coastal system. The dissolved phase of heavy metals is favored when there are conditions of low pH, low suspended particulate load and high concentrations of dissolved organic material. The low pH is particularly important because [3]:

1. The solubility of metal hydroxides increases as the pH decreases.

2. Adsorption of suspended particles to solid surfaces is reduced.

3. Hydrogen cations compete with metals for participation in molecules of organic substances.

Furthermore, an increase in salinity usually leads to a decrease in dissolved concentrations of heavy metals, as fine suspended materials and organic molecules form aggregates, acquiring a high settling velocity. The presence of high pH values and increased concentrations of suspended organic matter favor the suspended phase of heavy metals and thus their final transport to the bottom [3].

The bioavailability of metals, i.e., the concentrations of metals available for uptake by terrestrial, aquatic and marine organisms depends on the one hand on the contribution from the atmosphere and the direct discharge of wastes into the waters, but also on the dissolution of metals from minerals and their adsorption and deposition in soils and sediments [1], [6].

Although metals differ in their chemical properties, they are widely used in machinery, electronics, and various objects of daily life. So, they end up in the environment from many anthropogenic activities, in addition to natural geochemical processes [1], [6].

2. Heavy Metal Sources

The natural sources of metals in the sea are soil erosion, corrosion and volcanic activity. Anthropogenic sources are mining, industrial activity, fuel use, combustion processes at high temperatures. Also, deforestation and the construction of deep harbors and artificial lakes increase the transport of metals with particles [1], [6], [7].

2.1. Natural - Geochemical Sources

Heavy metals or trace elements make up 1% of the earth's crust, while macroelements (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, P, S) make up 99%. Usually trace elements are found as impurities in minerals, having replaced various macro elements in the crystal lattice.

Primary minerals are those found in volcanic (explosive) rocks and have crystallized directly from magma. In sedimentary rocks, trace elements are adsorbed to secondary minerals, which are the weathering products (physical weathering and chemical decomposition) of primary minerals [1], [6].

2.2. Anthropogenic Sources

Mines: Either operating or abandoned, mineral processing and metal receiving activities are important sources of metals in the environment and affect the wider area around them.

Agricultural materials: Are a non-point source of metals. Metals are contained as impurities in fertilizers (Cd, Cr, Mo, Pb, U, V, Zn, e.g., Cd and U in phosphate fertilizers), in herbicides - fungicides (Cu, As, Hg, Pb, Mn Zn), in wood preservatives (Cu, As, Cr), waste from pig and poultry farms (Cu, As, Zn), in compost and manure (Cd, Cu, Ni, Pb, Zn, As), in sewage sludge (Cd, Ni, Cu, Pb, Zn etc.) and finally from the corrosion of metal objects (metal roofs and fences).

Combustion of fossil fuels: Fuels contain several metals that are either released into the atmosphere in particulate matter during combustion or accumulate in the ash, where they can again become airborne or leached from the ash where it is produced. Some of the metals that emerge as pollutants from fuel combustion are Pb, Cd, Zn, As, Sb, Se, Ba, Cu, Mn and V. Combustion of gasoline, containing lead additives, produces lead-enriched particles. Coal combustion produces U and Cr. Crude oil contains significant amounts of V.

Metallurgical industries: Many metals are used in special alloys and steels and thus the production, disposal or recycling of these materials leads to environmental pollution from various metals. The same applies to the production of non-ferrous metal products.

Electronics: Many heavy metals are used to make semiconductors and other electronic components. Metals are released both during the production of these materials and from their disposal as waste after their use.

3. Heavy Metals Pollution

The starting point of environmental pollution from heavy metals can be considered the period of discovery and use of fire by man. The deposition of small amounts of trace elements released during the burning of wood changed the levels of metals in the cave environment. Human civilization is increasingly based on the use of various forms of metals. The first metals used by humans are Cu and Pb [8]. Metallurgy in ancient times, with the discovery of metal mining and processing techniques, led to the use of heavy metals but also to their pollution. In the Roman Empire, large amounts of heavy metals, mainly Pb, Cu, Zn and Hg, were produced to maintain a high standard of living [6]. During the Industrial Revolution, the need for heavy metals increased dramatically. This need was met with more intense mining and production. However, the release into the environment of metals such as Cd, Cr, Ni, Cu, Zn and Pb causes great environmental concern [8]. The world production of metals, except for Hg and Pb, increased at the beginning of the 20th century, while a steep increase in their production was observed in the period 1960-1990. The rapid increase in production of Cr in the period 1975-1990 is due to extensive military use. After the 1970s, Pb production stabilized. At the end of the 20th century, the rate of Pb production decreased significantly, after the use of unleaded gasoline was established [9]. The order of annual global metal production in the 20th century was as

follows: Cr > Cu > Zn > Pb > Ni > Cd > Hg [8]. Environmental pollution from heavy metals is also characterized by their biochemical properties, namely, bioavailability – bioaccumulation and toxicity.

3.1. Bioavailability – Bioaccumulation

Bioavailability is defined as the percentage of the total metal that is available for incorporation into organisms [6], [7]. The metals of major interest for bioavailability studies, according to the US Environmental Protection Agency (EPA) are: Al, As, Be, Cd, Cr, Cu, Ni, Pb, Hg, Se, and Sb. Heavy metals show an increased ability to bioaccumulate in organisms, but few of them tend to biomagnify. Bioavailability in surface and groundwater, sediments and the atmosphere is a complex function of many factors. These include total metal concentration, mineralogy, pH, redox potential, temperature, total organic matter content, suspended particulate matter content, as well as water volume, velocity and availability over time, especially in arid and semi-arid environments [6]. Another factor is the climate, which seems to affect the shape of the soil, which in turn significantly affects the mobility and bioavailability of elements, especially metals. Many of the above factors vary seasonally and over time, while most are interdependent.

Bioaccumulation is a general term that describes the net amount of uptake of chemicals from the environment through one or all possible routes (e.g., breathing, skin, food), from any source in the aquatic environment where the chemicals are present [10].

3.2. Toxicity

The toxic effect that a metal can have depends on its total concentration, but mainly on its bioavailability, i.e., on the forms in which it is found in the environment. The order of toxicity starting from the most toxic to the least toxic is: $Hg^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Pb^{2+} > Cd^{2+} > As^{3+} > Cr^{3+} > Sn^{2+} > Fe^{3+} > Mn^{2+}$. The combined action of several metals in an organism can create synergistic effects. Thus, for the combinations of the metals Ni-Zn, Cu-Zn, Cu-Cd, an increase in the toxic effect can be observed up to a value five times that resulting from the sum of the individual actions [6]. In conclusion, toxicity seems to be influenced by the type of pollutant, the abiotic factors of the environment (pH, temperature, forms of metals etc.) and the biological factors (age, type of organism etc.) [6].

According to the EPA/ATSDR list of most hazardous chemicals, hazardous chemicals are not necessarily just heavy metals. Hazardous chemicals can also be metalloids, radioactive ones (U, Ra, Th and Pu) or even noble metals (Pd). First on the list of EPA/ATSDR, and according to the directive 98/83/EC (of the European Union) for the quality of drinking water, is As (metalloid), whose concentrations greater than 10 μg/l are considered toxic [9]. At a biochemical level, the toxic effects caused by heavy metals are due to competition for binding sites with important metabolites, replacement of necessary ions, reactions with methiolic groups (–SH), damage to cell membranes and reactions with the phosphate groups of ATP and ADP. Organisms have homeostatic mechanisms that allow them to tolerate small fluctuations in exposure to non-essential metals. But long-term exposure to higher concentrations results in the inability of the mechanisms to cope and eventually the appearance of toxicity, which can even lead to death [11].

4. Inquired Metals

4.1. Copper (Cu)

The distribution of copper in the surface layers of seawater decreases with increasing distance from the coastal area. Copper is considered a nutrient and is a trace metal of vital biological importance. Copper shows a selective tendency to accumulate in plant and animal tissues. Very high concentrations of copper are toxic to marine organisms. It shows a decrease in its concentration in surface water bodies due to its capture by phytoplankton populations. These populations show strong growth rates in the surface layers, due to the greater possibility that sunlight has to enter these layers. With increasing depth, the concentration of copper increases due to recycling of copper, resulting from its release from decaying organic matter. Copper compounds used in agriculture and usually soluble in water are more dangerous to human health. Copper is an essential trace element for the health, growth and metabolism of all living organisms, because it is incorporated into several enzymes. However, exposure to higher doses can be harmful. Copper enters the human body either through food or water intake, or by inhaling copper-containing dust (e.g., by workers in copper processing facilities). Long-term exposure to copper dust causes nose, mouth, eye irritation, headaches, nausea and diarrhea. Drinking copper-laden water can cause nausea, vomiting, or diarrhea. It takes a few days for copper to be removed from the body through urination and mainly feces. Ingestion of very high concentrations can cause liver and kidney damage, and even death. Copper deficiency can cause hypochromic anemia, leukopenia and osteoporosis. In the diet, zinc significantly affects the absorption of copper, but in high concentrations it can lead to copper deficiency. It is not known whether it causes cancer in humans, so the International Agency for Research on Cancer (IARC) and the EPA do not classify it as a human carcinogen [9].

4.2. Cadmium (Cd)

In the marine environment, Cd tends to bind quite strongly to organic substituents [6]. Compared to other metals, cadmium is considered to be the most mobile, both in the aquatic environment and in the soil [12]. In the case of high-temperature processes, cadmium oxides, chlorides and sulfates may be present in the air as particles or vapors. In this form it can be transported to a considerable distance and precipitate on the ground and on water surfaces. In the case of seawater, cadmium forms chloride compounds, is a more unstable metal than zinc or lead, and its solubility is significantly affected by pH, but also by its chemical form. Studies in lake sediment have shown that cadmium is mainly detected in the exchangeable fraction, carbonates and iron and manganese oxides [6]. Finally, it has been shown to be one of the most mobile [13] and potentially bioavailable metals [6], as demonstrated by the application of various sediment leaching tests [14]. High concentrations of Cd can still be detected in rivers and estuaries near mining sites. In sediments, Cd either accumulates on the precipitated iron oxides through adsorption or occurs as insoluble CdS. According to recent researches along Mediterranean Sea coast it is considered the most abundant element in the coastal marine sediments [15]. Cadmium is taken up by organisms through food and water consumption or by inhalation. It does not enter the body through the skin. It is an element that accumulates in the body, particularly affecting the kidneys and the cardiorespiratory system, the spleen and the thyroid gland. In case of deficiency of iron or other nutrients, there is a high possibility of intake of

a larger amount of cadmium from the diet. It replaces zinc, an essential trace element in the body, affecting various biological and physiological reactions. The largest amount of cadmium that enters the body is transported to the kidneys and liver and can remain there for several years. A small amount of cadmium is removed from the body through urine and faeces. In addition, the human body can convert cadmium into a harmless form. But too much cadmium in the body can inhibit the ability of the kidneys and liver to convert cadmium into a harmless form. Exposure to low levels of cadmium over a long period of time can make bones weak, making them easily fractured. The International Agency for Research on Cancer (IARC) classifies cadmium and its compounds as "Group 1" carcinogens to humans [9].

4.3. Chromium (Cr)

Chromium (Cr) occurs in the sea in well oxygenated waters. It is considered a nutrient and is recycled in the liquid column. It participates in many biogeochemical cycles with the result that it is deficient in surface waters and enriched at some depth of the water column. Chromium is an essential trace element for humans and mammals, but in high concentrations it can be toxic, mutagenic, carcinogenic and can also cause teratogenesis. Hexavalent chromium is toxic and a known carcinogen, having been associated with respiratory tract cancer in workers chronically exposed to dusts containing chromic ions. The International Agency for Research on Cancer (IARC) classifies hexavalent chromium as Group 1, as a human carcinogen, and metallic and divalent chromium are classified as Group 3, i.e., not classified as human carcinogens, due to insufficient evidence from human and animal studies. Chromium is weakly adsorbed to soils, making it more mobile. Benthic organisms are exposed to dissolved and particulate chromium in pore water and surface water, as well as bound chromium in sediments, through contact and ingestion. Important reviews have been published regarding the hazards and effects of chromium on invertebrates, fish, animals and humans. In the soluble phase, hexavalent chromium predominates, and its removal is controlled by adsorption and reduction processes to trivalent chromium. Because trivalent chromium is strongly adsorbed to particles, it accumulates and persists in sediments. Therefore, the transport and deposit of chromium in the aquatic environment depends significantly on its chemical form, with hexavalent chromium being the predominant form in oxygenated waters, and trivalent chromium in sediments, anoxic waters, and low pH waters [6].

4.4. Iron (Fe)

Iron is the most abundant element on Earth. It makes up 30% of its total mass and 80% of its core. It is also the fourth most abundant element in the earth's crust. It is not considered a significant pollutant of the marine environment and is mainly released by the erosion of rocks. Trivalent Fe oxides show little solubility, with the result that Fe concentrations in water are low. These low concentrations in surface waters also show that its uptake by organisms is satisfactory. In coastal areas, iron concentrations are higher due to sediments, while in the open sea, airborne dust is the main source [6]. Its concentrations in sediments are very low and depend on the prevailing redox conditions [16]. During the mixing processes of water masses in estuaries, Fe is removed to a significant extent in the low salinity part of the estuary (0-5‰), while its removal occurs almost entirely when the salinity reaches 15‰. Iron (Fe) occurs in the sea in well-oxygenated waters [6]. Iron is a seawater trace element of great

importance for normal phytoplankton growth. Iron in the sea comes mainly from the weathering of minerals. In general, there is an increase in concentrations in coastal waters, while there are seasonal fluctuations. In a vertical distribution of seawater iron content, iron concentration usually increases with increasing depth of the liquid column, while both in the surface water layer and near the bottom it shows a decrease. In surface waters, solar radiation can penetrate more easily, and consequently a shallow water depth corresponds to a higher degree of productivity and phytoplankton growth, resulting in the sequestration of iron, which implies a reduction of its content in the corresponding water layers. Conversely, the decay of organic matter at greater depths releases iron. This recycling is responsible for increasing the concentration of iron with increasing depth. Also, iron in the sea is found in ferromanganese nodules [9].

4.5. Lead (Pb)

Lead (Pb) occurs in the sea in well-oxygenated waters mainly as $PbCO_3^{2-}$, $Pb(CO_3)_2$- and PbCl-. Salinity does not significantly affect soluble lead levels. The study of lead is of great importance because its high concentrations cause significant effects, such as inhibitory effects on the growth of planktonic organisms, toxic effects on higher organisms, while it tends to accumulate in plant and animal tissues. The distribution of lead in the surface layer of the Pacific Ocean shows the lowest concentrations in the waters corresponding to the depths of the continental shelf and which are characterized by intense biological activity. At greater depths, an increase in lead content is generally observed. According to Schaule & Patterson [6], the distribution of lead in Pacific surface waters depends on its atmospheric origin, both in the coastal area and in the open ocean. Then, in coastal waters, lead is removed at a faster rate than in deeper waters, because the rate of biological productivity is higher in shallow waters. Lead is a non-essential trace element, where in high concentrations it can be toxic to aquatic organisms. It is the most common of the toxic elements. Organic compounds of lead are more toxic to aquatic organisms than are its inorganic compounds. Sediments are important areas of exposure of microorganisms to lead. Adsorption of lead to organic material, clay, co-precipitation and adsorption to iron (hydro) oxides and manganese oxides increases with increasing pH value. Lead bioaccumulates in plants and animals but does not biomagnify in the food chain [6] [17], [18]. Filter-feeding animals, such as mussels, are capable of accumulating large amounts of lead. Therefore, benthic organisms in sediments may show a higher concentration of lead than species at higher levels of the food chain. Reviews have been published that address the toxicological profile of lead [17], [18] and its effects on invertebrates, fish, livestock and humans [6]. Lead is a toxic metal [12]. Whether lead intake is by inhalation or ingestion, the effects are the same. The human body does not convert lead into any other form. The effects on the nervous system of adults and children are particularly important. In high concentrations, it can cause significant damage to the brain and kidneys, and is likely to cause death. Exposure of the male population to high concentrations causes damage to the organs responsible for sperm production, reducing fertility. In pregnant women, high lead concentration can lead to miscarriage. Exposure of children, even to low levels of lead, can affect their mental and physiological development. There is insufficient evidence to conclude that it is carcinogenic to humans. The International Agency for Research on Cancer (IARC) classifies lead in Group 2B, i.e., possibly carcinogenic to humans, inorganic lead compounds in Group 2A, as possibly carcinogenic to humans,

while organic compounds are classified in Group 3, i.e., not classified as carcinogenic to humans, due to insufficient evidence from human and animal studies. The only lead compounds that easily penetrate the skin are gasoline additives. When lead enters the body, it is carried through the blood to tissues and organs such as the liver, kidneys, lungs, brain, spleen, muscles and heart. Once taken up and distributed to the organs, lead that is not stored in the bones is removed in the urine. About 99% is removed from an adult's body within a few weeks, but only 32% is removed from a child's body. Children absorb about 50% of ingested lead. After a few weeks, it is transferred to the bones and teeth. It is possible that some of the lead is removed from the bones and carried into the blood and other organs [6].

4.6. Manganese (Mn)

Manganese is found in the sea mainly as Mn^{2+} and $MnCl^+$, with a concentration range of 0.2-3 nmol/kg. The concentration of soluble Mn in the marine environment shows in most cases a maximum in surface waters, due to the indirect photochemical reductive dissolution of its oxides. Manganese is generally deficient near the bottom. In the Pacific Ocean, the distribution of manganese in the surface layers shows the highest concentrations in the coastal areas, while the values decrease towards the open sea. This result is probably due to the manganese enrichment of the coastal zone, due to brought river materials or due to diffusion of bottom sediments. The greater percentage of this contribution in manganese enriches the coastal waters, while the percentage that manages to reach the open sea is small. Although the oxidation of Mn^{2+} to Mn^{4+} by oxygen is thermodynamically favored, it is an extremely slow process at common ocean pH. This oxidation occurs mainly due to biological action. Its effect on the lower members of the food chain is different. A concentration of Mn above 5 μg/L has a toxic effect on various algae in the reservoirs, while a concentration of 0.5 μg/L in the sea stimulates the growth and proliferation of phytoplankton. In the marine environment, concentrations below 20 μg/L are harmless, while above 100 μg/L are considered a serious risk for organisms [6].

4.7. Nickel (Ni)

Nickel is found in seawater in well oxygenated waters, with concentrations ranging from 2 to 12 nmol/kg and a mean value of 8 nmol/kg. It is considered a nutrient. The concentration of nickel in the surface layers of seawater decreases from the coastal region to the open ocean. Nickel can be transported to the coastal area by rivers, atmospheric precipitation, as well as by diffusion from sediments and upwelling mechanisms. Only a small percentage of the total amount of nickel added to the coastal area manages to move away from it, through horizontal drift to the open ocean. Ni is considered an essential element, although its role in mammals is limited. Often high concentrations can be found in oil, while plant growth is significantly inhibited in Ni-rich soils [6]. Nickel has not been shown to accumulate in fish. Nickel-laden particles can enter the human body by inhalation and end up in the lungs for a long time. In high concentrations it can cause significant damage to the lungs, affecting their function. A small amount of it can be introduced into the blood by contact with the skin. The nickel introduced into the body is transferred to other organs and mainly to the kidneys. The most common health effect is an allergic reaction. About 10-20% of the population is sensitive to nickel (jewelry or other items containing nickel). The International Agency for Research on Cancer (IARC) classifies nickel compounds in Group 1, as

carcinogenic to humans, while metallic nickel and its alloys are classified as Group 2B, possibly carcinogenic to humans [9].

4.8. Zinc (Zn)

Zinc (Zn) occurs in the sea in well-oxygenated waters, with a concentration range of 0.05-9 nmol/kg and a mean concentration of 6 nmol/kg [6]. It is considered a nutrient, i.e., it is recycled in the liquid column. It participates in the oceanic biogeochemical cycles, resulting in a deficiency in the surface waters and an enrichment at a greater depth of the liquid water column. In closed polluted bays, it is found bound to inorganic and organic substitutes through complexation, coprecipitation and simple adsorption mechanisms [6], [9], [19]. It is a necessary trace element for humans and plants [12], but in high concentrations it can become toxic. Zinc moderately bioaccumulates in aquatic organisms, does not accumulate in plants, and does not biomagnify through the food chain. Sediments are an important source of exposure of microorganisms to zinc. Benthic organisms are exposed to both particulate and soluble zinc in pore water and surface water. Adverse biological effects from zinc exposure include reduction in benthic biodiversity and abundance, increased mortality, and behavioral changes. Biological activity influences the mobility of zinc in the aquatic environment, although organisms contain a low amount of zinc relative to its concentration in sediments. The toxicity of zinc in sediments is moderated by the presence of various sediment components, such as organic matter and sulfides, which have been found to reduce the availability and toxicity of zinc. Zinc is an essential element in humans and animals, for the functioning of a large number of metalloenzymes. Zinc deficiency has been associated with problems such as dermatitis, anorexia, growth problems, difficulty in wound healing, reduced reproductive capacity and mental function. Reviews have been published addressing the toxicological profile of zinc and the effects of zinc on invertebrates, fish, animals and humans. Exposure to zinc can be through breathing, diet (food, water) or skin contact. The removal of zinc from the human body is done through urination. In most cases, dermal exposure to zinc and its compounds does not cause significant effects. Skin exposure is achieved even with sunscreens, creams and deodorants, where it is included in their ingredients. The levels of zinc that cause adverse health effects are much higher than the recommended permissible amount of intake, 11 mg/day for men and 8 mg/day for women. Short-term intake of large amounts of zinc causes nausea and vomiting, while intake of large amounts over several months can cause anemia and damage to the pancreas. A significant effect is caused by the vapors of zinc and its compounds, mainly zinc chloride, which is more corrosive, causing shortness of breath, coughing, acute pneumonitis, but also death in very high concentrations. However, there are differences in toxicity between the various zinc compounds when exposure is by inhalation. The Environmental Protection Agency (EPA) classifies zinc and its compounds in Group D, i.e., it is not classified for causing cancer in humans [6].

5. Conclusion

Metals are mobile in the atmosphere-water-organisms environmental system. In the aquatic environment, movement of metals from the water column, particulate matter, pore water and sediments is observed. The water interacts with the particulate matter, resulting in the metals participating in adsorption-desorption and co-precipitation processes. The weathering of sedimentary and other rocks produces particulate material, which

settles and then participates in the process of sedimentation. Diagenesis processes in sediments increase metal concentrations in pore water. Metals end up in the aquatic environment through several processes. When they enter it, they undergo changes (physical or chemical), resulting in them appearing in various forms. In water, metals are found either in the form of free ions (Cu^{2+}, Zn^{2+}, Hg^{2+}) or ionic compounds ($HgCl_4^{2-}$, H_2AsO^{3-}, H_2AsO^{4-}), depending on the prevailing conditions, or they are incorporated into inorganic particles or organic matter, and precipitate with them. Some metal ions are adsorbed or precipitated with hydrated Fe, Mn and Al oxides in soils and sediments. The influence of aquatic organisms often contributes to the conversion of metals from one form to another. The high concentration of metals, when absorbed by aquatic plants and animals, can lead to toxic effects [6].

Redox potential, pH and temperature are factors which, individually, but mainly in combination, determine the chemical forms in which metals enter the aquatic environment. The above factors, aided by bacterial processes, affect the solubility, mobility and precipitation-deposition of metals. At neutral pH of the aqueous solution, the solubility of the elements depends on the temperature. An increase in temperature also implies an increase in solubility. Different metals exhibit different behaviors at different pH values. For example, Zn and Cu are inert at neutral pH unlike Mo. According to studies on the effect of pH on the mobility of Zn and Cd, it was found that for pH < 5 the mobility of Zn increases while for pH < 6 the mobility of Cd increases [6].

In the marine environment, some metals may undergo methylation. Methylation occurs either through the ability of organisms to methylate metals or through chemical reactions. This change increases the mobility of heavy metals and can play an important role in environmental cycles. Methylation can also increase metal toxicity. A case in point is the Minamata region of Japan, where Hg was methylated to CH_3Hg^+ (the most toxic form of Hg) and was detected in waste from a plastics manufacturing industry, which entered Minamata Bay from an adjacent river [6].

Concluding, recent researches, especially in the Mediterranean area [15], [20], claim that heavy metals exist in great quantities in seawaters and aquatic environments in general and as such remain a constant hazard for organisms that live not only in water but also from it. At the same time, others draw attention to the social inequalities [21] accompanied or even caused by this environmental crisis – if such a term can be used. For all the above reasons, the scientific community ought to focus on the more intensive study of the above-mentioned elements as well as on the development and improvement of more sensitive detectors and methods to eliminate or rather decrease the existence of them in our aquatic environments. Much more, governments ought to support such attempts. Regarding this research directions, some members of the herein research team proceed in the development of electronic sensors, attached to robotic vessels, able of detecting pollutants "in situ", i.e., without the need of taking samples of water for chemical analysis in laboratory premises. This method under development will hopefully provide fast and accurate detection of dangers to the environment and to the public health pollutants.

Competing Interests Statement

The authors have declared that no competing financial, professional or personal interests exist.

Consent for publication

All authors contributed to the manuscript and consented to the publication of this research work.

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