AgriCos e-Newsletter
ISSN: 2582-7049
AgriCos e-Newsletter
Open Access Multidisciplinary Monthly Online Magazine
Volume: 04 Issue: 09 September 2023 Article No: 16

Heavy Metal in Marine Environment: Bioaccumulation, Tropical Transfer and Health Risk Implications

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SUMMARY

Heavy metals (HMs) refer to metallic elements with an atomic weight higher than 40.04 and a specific gravity of more than 5.0. HMs is extremely toxic, abundant in nature, persistent, non-biodegradable, and have higher accumulation potential. HMs may be either essential or non-essential. Non-essential HMs include cadmium, chromium, mercury, lead, arsenic, and antimony. HMs such as cobalt, copper, iron, manganese, molybdenum, and zinc are essential in trace amounts. The vital metals can also produce a toxic effect upon elevated intake. HMs enters the marine environment through various natural and anthropogenic activities, as they dissolve in water and are associated with suspended sediments. They are persistent in the environment and can bioaccumulate in the food chain. Some non-essential trace metals pose a hazard even at a negligible level, and their accumulation in humans leads to cellular and tissue damage, decreased fertility, dysfunction of different organs, intoxication, and metabolic alteration.

INTRODUCTION

The source of HMs in the environment is various natural and anthropogenic activities. The natural sources include weathering of rock, seepage from rocks, volcanic activity, forest fires, agriculture run-off, etc. The growing population, urbanization, and industrialization have increased the pollution caused due to HMs. Industrial pollution occurs both at the production level, end-use of the products, and run-off (Joy et al., 2019). The main sources of contamination include mining wastes, landfill leaches, municipal wastewater, use of pesticides and (phosphate) fertilizers as well as biosolids in agriculture, sludge dumping, industrial discharge, atmospheric deposition, etc. and industrial wastewaters, particularly from electroplating, electronic and metal-finishing industries. The problem of waste disposal has become important with increasing metal generation from technological activities. Some of the oldest causes of environmental pollution globally are heavy metals such as Cu, Hg, and Pb mining, smelting, and utilization by ancient civilizations (Bonanno et al., 2020).

Heavy metal toxicity in sediments

Sediments are a mixture of various sorbent phases such as organic matter, oxides, sulphides, carbonates, and clay or stilt minerals. Their abundance is based on pH, redox conditions, hydrological level, and the depositional environment. Sediments can be a long-term source of metal pollution. Sediment contamination with metals severely threatens the soil ecosystem, particularly the organisms in direct contact with the environment, affecting their survival, reproduction, and growth. Heavy metal toxicity in sediments can be present longer since sediments act as sinks for all kinds of pollution, both organic and inorganic. Sediments not only store potentially toxic metals but also enhance the transportation of the same. Especially aquatic sediments are likely to attract heavy metals due to their finer texture and store metals through adsorption, complexation, and precipitation processes. Most of the metals present as free metal ions remain in waters surrounding the sediment. The form of the metals present (speciation) impacts the toxicity level of the metals in sediments. Thus, speciation and distribution of heavy metals in sediment are of major concern when indicating metal toxicity in sediments.

Physio-chemical factors such as temperature, hydrodynamic conditions, redox state, organic matter content and microbes, salinity and particle size affect the chelation process at the sediment level. However, the distribution of heavy metals in the sediment is highly based on the composition of the sediment, particle size and organic matter content. In finer sediments, organic carbon plays a vital role in the binding of the metals, and higher organic carbon reduces metal solubility and toxicity. Especially humus in soil binds metals more than any other organic matter. This is due to the humic substances' affinity towards heavy metals and their chelating properties. Any alteration in the sediment composition affects the benthic organisms, severely disrupting the habitat's normal functions such as exchanging organic matter or nutrients.

In terrestrial sediments, the toxicity depends largely on the sulphides in the sediment layers. These sulphides, termed acid volatile sulphides (AVS), are formed by sulfur-reducing bacteria from organic matter, which are more in anaerobic sediments. Other factors include soil pH, particle size, carbonates and Fe and Mn-oxy hydroxides. Differences in metal bioavailability are also affected by several other environmental factors, such as pH and redox, thereby affecting metal solubility and metal complexation with organic matter in the soil such as hummus. pH is the most important factor governing metal speciation. It affects the solubility of metal hydroxide minerals and the adsorption and desorption processes. Metal hydroxides have very low solubilities under pH conditions in water. Other factors include water hardness, organic carbon content and dissolved oxygen content. Due to this, differences in metal bioavailability exist, leading to metal toxicity. There are also substantial uncertainties in the data collected when bioavailability is considered one of the tools to measure soil bioaccumulation.

Bioaccumulation of heavy metals

The bioaccumulation factor is defined as the increase of contaminant concentrations in aquatic organisms following uptake from the ambient environmental medium. Different sources of exposure contribute to contaminant bioaccumulation. Toxicokinetic parameters, including the dissolved uptake rate constant, dietary assimilation efficiency, and efflux, are critical in bioaccumulation. Much study has been conducted on quantifying these biokinetic parameters in diverse marine organisms.

Bioaccumulation in benthic organisms

Benthic ecosystem often refers to the bottom of the ocean floor and in some cases the bottom sediment in any aquatic ecosystem, both fresh and salt water. Benthic organisms in such sediments are referred to as benthic organisms. These may include a variety of species from micro- to macro-organisms representing insects, polychaete worms, earthworms and snails. Benthic macroinvertebrates readily accumulate contaminants and have been suggested to be reliable indicators of metal bioavailability in metal-contaminated aquatic ecosystems. They are mostly sessile, have long life cycles and represent a range of ecological niches. Variations in season, functional feeding group and size of the organisms should be considered while measuring bioaccumulation in these organisms. They are also an important part of the food web in an aquatic ecosystem, serving as prey for many fish and birds and are potential candidates for biomagnification. The sediment-dwelling organisms can easily bioaccumulate as they are exposed to pollution by ingesting contaminated soil and food.

Bioaccumulation mechanisms (biological receptors)

Metals in the soil interact with the soil constituents so that over a period, the absorbed contents are not easily available for uptake by benthic organisms. For example, soil pH modifies metal solubility by controlling metal dissolution and precipitation and influences the ionization of pH-dependent ion exchange sites on organic matter and metal oxide clay minerals. The biological receptors in the soil-dwelling organisms readily absorb the available fraction of metals and store them either for detoxification or in the form of toxicological accumulation. The non-sequestered portion not modified by the soil constituents remains as bioavailable fractions for the organism's uptake. Metallotheniens and chromosomes are examples of biological receptors in earthworms. Cadmium exposure can produce cysteine-rich metalloproteins called metallothioneins and can be stored in a distinct subtype of sulfur-rich granule called cadmosomes. Metallotheniens are sulfur-rich proteins with a low molecular weight that bind metals. Chlorogosomes are phosphate-rich structures with significant cation exchange capacities. The organic matrix of chromosomes is a highly complex mixture of carbohydrates, amino acids, lipids, and redox pigments such as riboflavin, thiamine, carotene, and metalloporphyrins.

Arsenic concentration in Sundarbans wetland – A case studies

The general concern for arsenic in the marine environment is associated with its wide distribution and potential toxicity. Fattorini et al. (2013) studied concentrations and chemical speciation of arsenic in sediments and biota samples from the Indian Sundarbans, the largest continuous mangrove tract formed at the mouth of the Hugli (Ganges) River estuary. Arsenic concentrations in sediments did not exceed 4 ppm, dry weight, with the contribution of inorganic molecules (arsenate and arsenite) ranging from 61.7 to 81.3%. Total As (TAs) concentrations varied from less than 2 to 16 ppm in tissues of bivalves. Sarkar et al. (2017) examined the concentration of total arsenic and individual arsenic species in four soft-bottom benthic marine polychaetous annelids of diverse feeding guilds from the intertidal regions of the Indian Sundarban wetland. The concentration of arsenic (As) in polychaete body tissues exhibited a wide range of variations, suggesting species-specific characteristics and inherent peculiarities in arsenic metabolism. Arsenic was generally present in polychaetes as arsenate (As V, ranges from 0.16 to 0.50 ppm) or arsenite (As III) (from 0.10 to 0.41 ppm) (30–53% as inorganic As) and dimethylarsinic acid (DMAV < 1–25%).

Bioaccumulation factor and Bioconcentration factor

Sediments absorb heavy metals that enter water bodies and then transferred/exchanged between water and biota through biological and chemical processes. Heavy metals are usually not present at high concentrations in water, primarily due to the deposition in sediment and uptake by animals and plants (Edelstein and Ben-Hur, 2018; Liu et al., 2019). Heavy metal concentrations in sediments were 1000 times higher than in water. Heavy metal concentrations in sediments and benthic invertebrates were also reported as 1000–10000 and 10–100 times higher than in water (Yi et al., 2017). Heavy metal bioaccumulation in aquatic organisms is a complex process influenced by exogenous and endogenous factors. The exogenous factors include metal bioavailability, temperature, redox process, and alkalinity of the surrounding environment, while endogenous factors include species, age, size, habitat, and feeding behavior, which played crucial roles in the bioaccumulation (Anandkumar et al., 2020; Kato et al., 2020).

Heavy metals in aquatic organisms are majorly absorbed through two major routes.

(i) The primary absorption routes for these chemicals in fish are through gills (or) the transfer of dissolved pollutants in water/sediments across biological membranes, and

(ii) the secondary pathways are through food (or) sediment particle ingestion.

Bio-uptake factors	Definitions
• Bioconcentration factor (BCF)	: Ratio of fish to water concentrations with no dietary intake
• Bioaccumulation factor (BAF)	: Ratio of fish to water concentrations with dietary intake
• Biomagnification factor (BMF)	: Ratio of fish to diet concentrations
• Trophic magnification factor (TMF)	: Averaged BMF over a food web of several trophic levels

Harmful effects of bioaccumulation of heavy metals

Heavy metals adversely affect human health; therefore, heavy metal contamination of food chains deserves special attention. Many heavy metals and metalloids are toxic and can cause undesirable effects and severe problems even at very low concentrations. Heavy metals cause oxidative stress (Mudipalli, 2008) by forming free radicals. Oxidative stress refers to the enhanced generation of reactive oxygen species (ROS), which can overwhelm the cell's intrinsic antioxidant defenses and lead to cell damage or death. Furthermore, they can replace essential metals in pigments or enzymes, disrupting their function.

Regarding their toxicities, the most problematic heavy metals are Hg, Cd, Pb, As, Cu, Zn, Sn, and Cr. Hg, Cd, Pb, and As are non-essential heavy metals, while Cu and Zn are essential heavy metals (trace elements). Toxic heavy metals can cause different health problems depending on the heavy metal's concentration, oxidation state, etc.

Biomagnification in Trophic Level – Risk to Human Health

The first trophic level (seawater - phytoplankton) for most trace metals shows the highest concentration increase. In the next trophic level (zooplankton) only Cd, Cu, and Zn concentrations increase. Plankton-feeding fishes have higher Cu and Zn levels than fishes preying on invertebrates and fish. The Cu, Zn, and probably Cd concentrations are higher in shrimps feeding on invertebrates than in fishes feeding on shrimps. For these three trace metals, the concentrations at first increase along the food chain, reaching a maximum with crustaceans and then decreasing in fishes. The concentration of mercury increases with the size of the organisms. Its increase along the food chain does not become evident in short-lived organisms. This increase in size and the fact that long-lived organisms are at the top of the food chain are responsible for the mercury increase along the food chain. Mercury is also the only trace metal that poses a risk to heavy seafood consumers, especially in areas with high natural mercury levels, such as the Mediterranean.

The significance of these persons' elevated mercury levels in hair and blood must also be evaluated in light of the antagonistic action of the selenium present in seafood. The reevaluation of the lead levels in marine foods shows that only very little Pb enters man through the marine food chain and that Pb is not a marine pollutant of concern. Very high As concentrations have been observed, especially in benthic organisms. Although most of the As is in a very low toxic or nontoxic organic form in organisms with high total levels, still considerable amounts may be present in the toxic inorganic form. At present, not enough data are available to assess possible risks. Only for mercury and arsenic can speciation and bioavailability be considered: for the other trace metals discussed, the analytical tools are not developed sufficiently to allow the determination of the forms which are accumulated by the organisms.

CONCLUSION

The trophic transfer of non-essential heavy metals in food chains is a gateway for these contaminants to the human body and poses a risk to human health. Food grown in heavy metal-contaminated media is a source of these pollutants for humans. The trophic transfer of toxic heavy metals in food chains/webs has important implications for human health. Above safe limits, these contaminants cause various adverse effects on human health. Different studies have anticipated the human health risk of bioaccumulating heavy metals in human food. Consumption of fish contaminated with toxic heavy metals risks human health. The use of fish in the human diet is recommended since they provide omega-3 fatty acids. These fatty acids have cardio-protective effects and are thus associated with health benefits. However, the discovery of heavy metal contents in some fish creates questions about the dietary role of fish consumption. The trophic transfer of Cd from lettuce to the Chinese white jade snail (Achatina fulica) has been viewed as a public concern in South China because it is widely consumed there (Ke et al. 2015). Similarly, contamination of shrimp with heavy metals can be hazardous to public health (Sarkar et al. 2016).

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