Review Paper:

Impact of Heavy Metals in Riverine and Estuarine Environment: A review

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Abstract

The significance of Riverine and Estuarine environment on the earth surface is very considerable. The Riverine and Estuarine environments support the plant growth and are the habitats of animals. In the present study, an attempt has been made to review the impact of heavy metal s in the riverine and estuarine environment. Besides natural disturbances to these environments, human induced interferences are more destructive in terms of degradation. Heavy metals present in environment are not toxic to a great extent as compared to human made compounds of heavy metals. Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni) and Zinc (Zn) are some of the examples of heavy metals added into the environment by polluted water through various anthropogenic activities such as manufacturing industries, mining and agricultural industries.

Collective depositions of material, minerals, wastage and bedload are transported to river system and also accumulate in the estuarine ecosystems. Estuaries are the most important source of food and many economic activities for coastal population. High content of heavy metals into the estuaries causes harmful effects on marine biota and produces high risk to the human health through the sea food. This review discusses the sources of heavy metals, its impact on environment and their limits/standard in the Riverine and Estuarine environment.

Keywords: Heavy metals, River, Estuary, Contamination, Consequences.

Introduction

Heavy metal contamination in soil on a large scale is now a global threat. Heavy metal contamination has increased in recent years in many inland waters as well as estuarine ecosystems[23]. Estuaries are most important to have enormous habitats like open water, reefs, sediments, sand and mud flats, sea grasses, salt marshes, mangroves associated with it. An estuary also supports various species of fish, marine plants and animals. The estuaries are also important for environment because they also filter pollutants like pesticides, herbicides and heavy metals present in the flow. 2/3rd population of the earth is associated with coast and coastal activities in which estuaries play the most important role. Industries like fisheries and tourism are major income sources in coastal region and therefore it becomes more crucial to maintain this unique ecosystem.

Heavy metals concentration is found in the leaves of halophytes (plants near salt marshes) and results show that heavy metal accumulated more in the low level salt marshes (near sea water) than the high level salt marshes (away from sea water)[14]. Quick civilization and the continuing reclamation also increase the amount of Fe, Cu and Mn[10,43] heavy metals in the surface water of the estuaries which affects the wetland vegetation[10]. E-waste burning adds the heavy metal to the soil and gets accumulated in nearby vegetation and through plants, it enters in the human and animals[8]. Oil exploitation activities near coastal region are increasing the heavy metal contamination in the estuaries and soil at the coast creates risk for the coastal ecosystem.[17,43]

Heavy metals: Though these heavy metals are present in the nature from several years, but their toxicity is increased due to anthropogenic activities like mining, urbanisation, oil extraction and reclamation of sea. This is one of the major parts of air, water and soil pollutants. Health of humans and plants depend on the surrounding they live, so it is very important to study the direct and indirect effects on environment due to heavy metals. Heavy metals are actually a group of metals or metalloids having an atomic number greater than 22 and specific gravity greater than 5. Examples are copper (Cu), lead (Pb), nickel (Ni), cadmium (Cd), mercury (Hg), arsenic (As), zinc (Zn) and chromium (Cr).[6,7,10,17]

There are essential elements in the heavy metal group for both plants and animals but some of them are toxic towards living organism. The proportion of the heavy metals must be balanced or else it will harmful in nature. As these metals are toxic, they dissolve in water and affect living organisms. Some of the effect of the heavy metal on human organs like kidneys, liver, lungs, hairs and skin may possibly cause severe damage and also affect high blood-pressure, cancer and many severe disease[37].

Although there are harmful effects of heavy metals, there are some positive effects of heavy metal to the environment, like plant having need of macro-nutrients (C, H, N, O_2, P, S, etc.) as well as micronutrients (B, Cl, Cu, Fe, Mn, Mo, Ni and Zn)

for their growth. Also, humans need heavy metals like Cu, Se and Zn playing several vital and favourable roles in metabolism and growth[24].

Sources of Heavy Metals

(1) Natural sources: Parent material or rock type is one of the most important natural sources of heavy metal. Atmosphere and triggering weathering activities decide the properties and accumulation of heavy metals[19].

(2) Agricultural sources: An anthropogenic activity leads to change in the natural availability of the heavy metals in the natural environment and that is the main cause of contamination. Plants also need some heavy metals to grow and for that purpose, farmers use fertilizers, pesticides and compost. These activities increase the amount of heavy metals such as Cu, Mn, Cd, Pb, Hg, F, As, Cr etc.[42]

(3) Industrial sources: Waste water of industries is also used for irrigation by the farmers and if it is used without proper treatment, they will contaminate the soil and water. Industries like mining, steel and paints etc. are large sources of heavy metals like Cd, Pb, As[33,45].

(4) Domestic sewage: Though this is not adding much heavy metal in the environment, but it is observed that domestic waste water adds Zn, Cu, Cd and Pb heavy metals in the soil through irrigation[12].

Heavy metal and its impact: Here we discussed heavy metal and their harmful consequences on humans in brief. Table 1 also shows the list wise details of heavy metals, sources and potential consequences[1, 26, 33].

a) Arsenic (As): Arsenic is easily available heavy metal everywhere in the form of oxides, sulphides and other compounds in polluted water and soil from the weathering of rocks and also by human activities. It is used in manufacturing of agricultural insecticides and fungicides and is also used as a drug to cure the diseases. Arsenic is mainly transported by the polluted water or air by the industries like smelting and refining metals and chemicals into the environment. Both the natural and human source of creations of arsenic and its other compounds accumulate in marine biota of the estuaries.

Accumulation of arsenic at certain level is not much harmful for the species in the estuaries but the excess concentration of arsenic could be toxic for all the organisms in the estuary and also for humans that consume fish and other products from the same estuary[20]. According to World Health Organization provisional guidelines, permissible value of arsenic in water is 0.01mg/L (WHO)[41]. Higher concentration of arsenic in drinking water can become a cause of lungs, liver, kidneys and skin diseases. Study also reveals that arsenic affects the growth of children and sometimes responsible for infant mortality[34].

Table 1
List of heavy metals, their sources and potential consequences

Heavy Metal	Source	Potential Consequences
Arsenic (As)	Metal Smelters, Pesticides, Fungicides, Paint, Textiles Industries, fossil fuel	Bronchitis, dermatitis (Skin irritation) [1]
Cadmium (Cd)	Welding, Electroplating, Pesticides, Fertilizers, CdNi batteries, Nuclear fission plant, PVC products	Kidney damage, Bronchitis, Gastrointestinal disorder, Bone marrow, Cancer [26]
Chromium (Cr)	Electroplating, Metallurgical industries, Textile, Tannery Industries, Rubber, Photography	Rapid hair loss, Respiration problem[1]
Copper (Cu)	Electroplating, Electronics waste, Pesticides, Mining,	Failure of Brain and Kidney, Severe anaemia, Intestinal irritation[1]
Lead (Pb)	Automobile emission, Mining, Burning of coal, Paint, Pesticide, Smoking, Waste water	Liver, kidney, Gastrointestinal damage, Mental retardation in children[33]
Manganese (Mn)	Welding, Fuel, ferromanganese production, Fertilizers	Inhalation or contact causes damage to central nervous system
Mercury (Hg)	Pesticides, batteries, paper industry, Polluted water, Scientific instrument, Chemical industries	Damage to nervous system[33]
Nickel (Ni)	Electroplating, Zinc base casting, Battery industries, Iron-steel industries, Fertilizers	Immunotoxic, Neurotoxic, Genotoxic, Hepatotoxic, Lungs, Throat and Stomach cancers, Rapid hair fall[1]
Zinc (Zn)	Refineries, Brass manufacture, metal Plating, Immersion of painted idols, Galvanisation	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane [26]

b) Cadmium (Cd): Cadmium is used in television screens, paints, cosmetics, welding, galvanising steel, electroplating, batteries, pesticides, fertilizers and many other purposes which are widely used by people. Cigarette smoking is also one of the sources of cadmium exposure to the human. Dust containing cadmium and contaminated water plays the role of conductor of cadmium through environment to the livings. Cadmium is the most toxic non-essential heavy metal added into the river by disposal of cadmium containing materials. Cadmium gets accumulated in sediments, particulate matter and water in the estuarine ecosystems. Bioaccumulation of cadmium into the marine organism depends upon the cadmium compounds structures, salinity and temperature of the marine systems[38].

Bay of Bengal is the largest delta and greatest estuary of Bangladesh and India, Cd is found to be the major pollutant in the same region that can damage the liver of fish and other marine organisms[13]. According to World Health Organization provisional guidelines, permissible value of cadmium in water is 0.003 mg/L (WHO)[41]. Higher accumulation of cadmium can harm vitamin D metabolism in kidneys with harmful impact on bones, heart and blood vessels, kidney damage, central nervous system and other organs[3].

c) Chromium (Cr): Various industries use chromium for different activities but 90% of chromium production is used in metallurgical industries. Tanning industries use chromium and the untreated waste water increases the contamination of chromium in the environment. Though it is an essential micronutrient for humans, the higher intake of chromium is toxic for human body. According to previous research[31], generally chromium does not get collected in the fish body, but if the amount of chromium increases, there are very harmful effects on fish gills at the discharge point. Oxidation state of chromium affects the uptake of chromium in the plants; Cr IV can penetrate through the cell membrane and high concentration in the plants may harm their metabolism and growth[5].

According to World Health Organization provisional guidelines, permissible value of chromium in water is 0.05 mg/L[41]. In animals, excessive amount of chromium harms the respiratory system and could become a cause of lung cancer. Skin sensitisation, liver and heart disorder are other effects of high chromium present in human body[27].

d) Copper (Cu): Pipe corrosion (Copper often used for manufacturing of water pipes or the alloys of brass and bronze which contain copper), electroplating, pesticides, mining, fibre productions, use of fertilizers, fungicidal spray activities are the source of copper contamination into the environment. Industrial waste as well as domestic waste added into the rivers leads to increase the concentration of heavy metals in the estuarine ecosystems and produces threat to the marine plants and animal species. The balance of heavy metals present naturally gets disturbed and provides high exposure of copper to the plant, species and sediments created. For example, two organisms *C. crangon* and *S. acus* from the black sea were found to be decreased in proportion due to increase in the amount of copper in the sea[2]. Copper used as a packaging material can also contaminate food and water. The permissible value of copper in water is 02 mg/L (WHO)[41]. Harmful effects of copper contaminations are failures of brain and kidney, liver damage, demolition of red blood cells and could be transferred into severe anaemia, intestinal irritation[15].

e) Lead (Pb): Humans generally get exposed to lead near mining activities due to inhalation in the human body. In case of fish and other marine organism, lead is collected indirectly from the food chain and directly from contaminated water. Lead is more toxic heavy metal and needs to have controlling measures on its use. The drinking water and sea food are one of the major exposures of lead to the humans[38].

Lead is found to be tolerable in the aquatic systems because it is slightly soluble in saline water and shows adaptability. This helps some kind of protection from lead to accumulate in the marine organisms[31]. Lead is harmful for all organs but specifically lung is the common organ attacked by the higher concentration of lead and possibly results into lungs cancer[15].

It is harmful for adults and children but children are affected at even lower level on accumulation of lead. The permissible value of lead in water is 0.02 mg/L (WHO) [41]. Nervous system is also damaged by the higher amount of lead in the body. Infertility of men, premature delivery in women and miscarriage are also the effects of higher levels of lead[27,34].

f) Manganese (Mn): Manganese is one of the easily available metals in the nature and soluble in water but if the concentration of manganese exceeds, it becomes toxic in nature. Therefore, risk of exposure of manganese to the marine organism increases as the amount of manganese increases in estuaries. Manganese accumulates in the liver of fish (bio accumulated manganese). Excessive amount of manganese in the aquatic systems leads to the disturbance in the metabolism of carbohydrates and affects the fish and other organisms[22]. Though manganese is essential element for well functioning of human body, there are different risk factors stated by scholars.

The anthropogenic sources of manganese exposure to the environment are mining wastes, fertilizers used in agricultural activities and other purposes. Higher concentration of manganese caused reduction in the photosynthesis in plants and damages the nervous system of human beings[30].

g) Mercury (Hg): Mercury used in thermometer, barometers, batteries, lights etc and combustion of fossil fuels such as coal is also a major anthropogenic source to

increase the amount of mercury in nature. Mercury has ability to form alloy with other metals such as gold, silver and tin called as amalgams used for filling the holes in the teeth. Contamination of mercury in water and soil increases the amount of mercury in the food and fishes.

It is a most toxic heavy metal found in the marine environment. Methyl mercury is the most toxic and common compound of mercury found in the sea foods and especially at Indian Ocean coasts[38]. Consumption of these sea foods leads the serious health risk to the humans and therefore quality assessment of sea foods becomes essential in such areas. The permissible value of mercury in water is 0.006 mg/L (WHO) [41].

Mercury is the harmful element for all the species and it is more dangerous for children. The major effect of high mercury in the human body is that it damages the nervous system. Mercury vapour may affect tissues of the lungs and turns blood-brain barrier and can be cause of neurological disorder[16].

h) Nickel (Ni): Nickel is used by human for lot of possessions such as jewellery, coins, metal plating, stainless steel alloy, welding, armour plating and rocket engines. Inhalation is the major transmission of nickel. More than the natural availability of nickel heavy metal in estuarine ecosystem causes harmful effect on marine plants and organisms[4]. The permissible value of nickel in water is 0.07 mg/L (WHO) [41].

Excessive amount of nickel in human body may harm the immune system and results into the asthma or dermatitis. Cancer of lungs and nasal has been reported amongst the nickel refinery workers at many places. Allergy, respiration problems, heart disorder, skin irritation are also the effects of higher levels nickel[15].

i) Zinc (Zn): Zinc is used in fertilizers and pesticide on a large scale as it is essential for plants growth. It is also useful for human but the overdose of zinc may cause fatigue or weakness. Zinc is used for different activities such as galvanisation of metals, paints, weapons, cosmetics, batteries, plastic, pharmaceuticals purpose etc[11].

Zinc gets added in to the estuaries by natural as well as anthropogenic sources. Zinc percentage in estuarine ecosystem could be raised by the use of lubricating oil containing zinc in it and this contamination of Zn can increase the health risk to aquatic plants and animals[28]. The harmful effects of over accumulation of zinc can cause nausea, anaemia, cholesterol and also may affect immune system of humans[11].

Heavy metals in environment and estuaries

Soil gets polluted by heavy metals after the use of sewage and waste water for irrigation. These heavy metals are absorbed by the plants and consumed by the animals or human and that is how it enters into the food chain. Increased amount of heavy metal in soil and water system due to the human actions leads to high risk to the environment as well as human health[33,46]. Contamination of heavy metals in soil and water system is studied by various scholars around the world and still it is a burning issue.

Sundaray et al[36] in their case study of Mahanadi basin, India, analysed risk assessment of heavy metal in the river estuarine sediments and concluded that marine system is highly affected by the availability of Cd, Ni, Co and Pb. Nowadays urbanisation and industrialisation growing at faster rate and proportionally the heavy metal runoffs from the industries, cities and towns get accumulated in the water bodies and toxicity is increasing. Estuarine ecosystems also get disturbed due to the excessive amount of heavy metals and proved as harmful for ecology by many scholars. Excavation of lateritic blocks from the lateritic plateau region of coastal Maharashtra is also one of the sources to increase the heavy metals in the downstream estuaries (Fig. 1).

Here also the risk of toxic elements imposition into fish and from fish to human increased[25]. An estuary has collective deposition of many rivers and of course it also contains heavy metals transported through the rivers. Estuaries associated with mangroves are very important for the protection of coastal ecosystem and the reproduction of mangroves is depending on the nutrition status of the region[18].

In recent studies of Thinh et al[39] it has been observed that mangroves play an important role to prevent the estuarine ecosystem from contamination of heavy metals through the surface runoff at the place where mangrove forests are located near upper region of an estuary. Heavy metals (e.g. Cadmium) can accumulate in the root and stems of the mangroves and also can replace the carbon and nitrogen ratio of the plants. This effect of heavy metal affects the carbon storage in estuarine plants and mangroves which also impacts the global climate[44].

Indian estuary of river Ganga (Hoogly) is a huge source of sediments to the ocean. River Ganga receives huge anthropogenic sewage contaminated by the heavy metals and therefore the potential risk has been increased for the aquatic biota present in that estuary. Suspended particulate matter and bed sediments of two consecutive years (2012-2013) were used to understand the heavy metal concentration[32].

In this study, concentrations of cobalt (Co) and nickel (Ni) were high in pre-monsoon and copper (Cu) in post monsoon. The trend shows that heavy metals concentration is increasing with salinity. Here the significant source of heavy metal to the estuary is anthropogenic activities and ground water supply[32].

Figure 1: Excavation of lateritic blocks from the lateritic plateau region

Bay of Bengal is the most important estuarine ecosystem for many marine organisms as well as humans due to its wide area covered. These are situated at the end of large rivers Ganga and Brahmaputra where they meet the ocean which forms a great delta in the world.

Lakshmanasenthil et al[13] in their research work analysed the fifteen different species of fishes and sediments from Bay of Bengal estuary. In this study, Fe, Zn, Cd, Mn, Pb, Cr, Ni and Co were determined in the fishes and sediments. From the above mentioned heavy metals, Cd, Cr, Ni and Mn were found as excess in derived limits and showed high health risk due to the marine organism and can be transferred to the human in future. Geochemical assessment of surface sediments of vellar and coleroon estuaries reveals that the Fe and Mn oxyhydroxides, mud and organic matter have triggered the accumulation of heavy metals in both estuaries. Here the sources of heavy metals are anthropogenic and geologically processed sediments presently which are not much harmful as compared to other heavy metals to the estuarine ecosystem[21].

Earlier works of Reddy et al[35] studied the estuaries of Pennar, Uppateru, Swarnamukhi and Kalangi rivers of eastern coast of India. The water samples were analysed for both pre-monsoon and post-monsoon season to analyse heavy metals. After analysing the water and sediment samples, it has been observed that heavy metal contamination is present in the estuaries and there are significant effects of heavy metals on the species in the estuaries. It is revealed that due to the effect of heavy metals, there is a drastic change in the number of species and diversity. Here we can understand that how the estuarine ecosystems have been disturbed throughout years. Ennore estuary which is connected to Pulicat Lake and meets the Bay of Bengal near Chennai was recently studied by Panneerselvam et al[25]. Samples of water, sediments and marine organism of Ennore estuary for two years (2014-2016) were analysed for this study. Water samples collected in monsoon and post monsoon show higher concentration of Cu, Cr, Cd, Pb and Ni than the summer.

Here the surface runoff is high in monsoon and transferred by river which probably increased the concentration of heavy metals in the estuary. Cr and Pb heavy metals are found in large scale in the sediment and the marine organism (crab, oyster, polychaete) collected from the estuary. Here the heavy metal concentration is higher than other estuaries in India and ecological risk is also high, so the continuous monitoring and remedial activities need to be done in case of Ennore estuary[25]. Eastern coast estuaries of India are contaminated by heavy metals but the western coast estuaries are not exception for it. Dudh creek and Konda creeks of northern Maharashtra are found contaminated by the heavy metals like Mn, Zn and Ni in their core creek region by analysing the mangrove sediments[40].

As compared to large estuaries, small creeks or estuaries respond quickly to certain changes in the environment and Dhudh creek is highly contaminated by the accumulation of heavy metals through the anthropogenic activities. There is a need to prepare a proper strategy to minimise the intake of pollutants into the creeks.

In recent studies of Raut et al[29], water samples of Ulhas river estuary near vasai fort in Thane District were studied to understand the heavy metal potential risk in the estuarine ecosystem. Samples were taken at monthly basis for six months. The amount of heavy metals (i.e. Pb, Cr, Ni, Cu, Zn, Cd and Hg) was increased in the Ulhas river estuary. This is very important to know the potential risk in this estuarine ecosystem because a core region has lot of population depends on the fishery and agriculture.[29]

Heavy metals can enter into the food chain through fishes and agricultural products. The rate of contamination of heavy metals in the estuarine ecosystems is increasing gradually and it has been proved in case of Cochin estuary in the research work of Harikumar and Nasir.[9] Here they used core sediments which represent the history of pollution in the estuary and study reveals that the concentration of heavy metals is high as compared to deep region sediments. Here authors concluded that due to the development of industries and anthropogenic activities in nearby region from the past few centuries, heavy metal accumulation increased.

As like soil and water, air is also contaminated by the heavy metals. Small particles of heavy metal emission by various industries are easily movable in the atmosphere due to their light weight. If the chimneys of industries are taller and the atmosphere is with higher wind velocities, the heavy metals can travel longer than at normal conditions. Acid rain is one of the effects of this air contamination of pollutants[11].

Conclusion

Rapid increase in the development of manufacturing industries, mining industries, agricultural industries and urbanisation causes to produce excess amount of heavy metals in the environment. Basically all deposited heavy metals in the environment in any form get concentrated into the surface runoff and river flows. Transportation of heavy metals ends at the estuaries and accumulates into the marine plants and organism. Heavy metals enter into the food chain through plants and fishes.

Many of the estuaries in the world already showed an alert of high contamination of heavy metals in the sediments, mangroves and other organisms in their ecosystems. Estuaries are significant in terms of economic activities at coastal areas and therefore it becomes essential to investigate the concentration of heavy metals and other pollutants into the estuarine ecosystems. This contamination of heavy metals in the sediments and marine ecosystem has potential of health risk to the humans and therefore strong remediation techniques and research should be promoted. Hazardous heavy metals must be trapped at the outlets of waste water discharged from the factories and industries.

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