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Toxic Heavy Metals Distribution Behaviour in Sediments of Mahul Creek Near Mumbai, India.

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ABSTRACT

The toxic heavy metals in aquatic environment have attracted great attention of environmental scientists and ecologist in recent years because of their long biological half lives, non-bio-degradable nature and accumulative properties. Hence, in the present investigation, we have selected Mahul Creek to investigate pollution load due to toxic heavy metals in an aquatic environment. The distribution coefficient (K_d) values (L/Kg) of different industrially important toxic heavy metals for Mahul Creek were calculated for sediment samples and the month wise variation in K_d values (L/Kg) of these metals for sediments from January 2013 to December 2013 were studied. A wide range in K_d values were observed for different metals. The K_d values for sediment samples in Mahul creek were in the increasing order for Zn, Pb, As, Ni, Cu, Hg, Cd, and Cr, respectively. The variation in K_d values of different metals can be attributed to the solubility of the metal in water as well as contribution of industrial pollution.

Keywords: sediments; toxic heavy metals; distribution coefficient; Mahul Creek; Mumbai.

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INTRODUCTION

Environmental pollution is a world-wide phenomenon. In a natural ecosystem there is a balance between input & output with hardly any accumulation of surplus or waste material. But rapid urbanization, industrialization and increasing human population, the problem of environmental pollution due to toxic heavy metals has begun to cause concern now in major metropolitan cities. These metals entering the ecosystem lead to accumulation and magnification. Trace metals are intrinsic natural constituents of our environment. Apart from the natural sources, several anthropogenic sources such as mining, smelting, production and use of the compounds and materials containing the metals, burning of fossil fuels, waste dumping and leaching of waste dumps, urban run-off, sewage effluents and agricultural run-off also contribute metal concentrations in the environment . Toxic metals are dispersed in the environment through industrial effluents, organic wastes, refuse burning, transport and power generation. They can be carried to places many miles away in the gaseous form or as particulates. Another means of dispersal of toxic heavy metals, especially in the hydrosphere is the transport of the effluent from catchment areas which have been contaminated by wastes from various industries. These toxic heavy metals entering in aquatic environment are adsorbed onto particulate matter, although they can form free metal ions and soluble complexes that are available for uptake by biological organisms [1]. The metals associated with particulate material are also available for biological uptake [2] and are deposited in estuarine sediments [3]. Once deposited, binding by sulfides or iron hydroxides immobilizes trace metals until a change in redox or pH occurs [4, 5]. Thus sediments accumulate trace metals and provide a means for evaluating the long term accumulation of heavy metal contaminants [4, 6]. The study of such toxic heavy metals in the environment is more important in comparison to other pollutants due to their non bio-degradable nature, accumulative properties and long biological half lives. It is difficult to remove them completely from the environment once they enter into it. With the increased use of a wide variety of metals in industries and in our daily life, there is now a greater awareness of toxic metal pollution of the environment. Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air [7]. There is considerable concern about the human health aspects of metal cycling in polluted coastal and inland waters that are in proximity to large population centers. For better understanding of heavy metal sources, their accumulation in the sediment and in water seem to be particularly important issues of present day research on risk assessments [8].Several domestic laws regulate what materials can disposed into a water body. In hydrosphere, trace metal concentrations are typically orders of magnitude greater in the sediments as compared to those in overlying waters. The capacity of the sediments to concentrate trace levels of most of the metals make them useful indicators for monitoring purposes and for detecting sources of pollution in the aquatic system. Therefore the analysis of sediment may provide a historical record of the heavy metal burdens.

Extensive studies were carried out over the years, on pollution in Mahul Creek which acts as a major sink for various municipal wastes and industrial discharges from the adjoining areas. As compared to other pollutants, toxic heavy metals in the environment are of serious concern due to their non-bio-degradable nature, accumulative properties and long biological half lives. These toxic metals not only pollute the creek waters but also pose a threat to the aquatic biota. The increase in levels of heavy metal content in water, sediments and biota, will result in decreased productivity and increase in health risk in case of human beings. During the past few years, attempts were made to develop strategies directed towards more integrated approach in coastal environments. Previous data on water pollution along creeks and lakes [7, 9,10, 11,12] points out to the need of systematic and regular monitoring of pollution level for further improvement in the industrial waste water treatment methods. Therefore in the present investigation we have selected Mahul Creek to study the pollution load toxic heavy metals in water and sediment.

Salient results of the investigations are presented and discussed in this paper.

EXPERIMENTAL

Study Area

Mahul creek (19°01‶N & 72°53‶E) lying on the east coast of Mumbai along the Arabian sea, is situated in Chembur suburban the north eastern corner of Mumbai about 15 km from Victoria Terminus (presently known as Chhatrapati Shivaji Terminus). The temperature of the area ranges between 13 °C to 39 °C. The south west monsoon (June to mid-October) brings rain to the area which is recorded maximum 747 mm during July. The climate is humid and relative humidity ranges between 29 to 96 % [13].

Water sampling and sample preparation

The study on pollution status along the Mahul creek of Mumbai was performed for the period of one year from January 2013 to December 2013. The sampling was done every month along different locations of the creek. The grab water samples were collected in polythene bottles of 2.5 L. The bottles were thoroughly cleaned with hydrochloric acid, washed with distilled water to render free of acid, rinsed with the water sample to be collected and then filled with the sample leaving only a small air gap at the top. The sample bottles were stoppered and sealed using paraffin wax. The samples thus collected were mixed to give gross sample. Such gross samples were analyzed every month for the toxic heavy metal content, so as to get the month wise variation in pollution level along the Mahul Creek. For estimation of dissolved heavy metal content in water, the collected sample was filtered using Whatman No. 41 filter paper. Filtrate was preserved with 2 mL nitric acid to prevent the precipitation of metals. The sample was concentrated to tenfold on a water bath and subjected to nitric acid digestion using the microwave assisted technique [14, 15].

Analysis of Heavy Metals

The water samples collected were analyzed for the heavy metal content. The analysis for the majority of the toxic heavy metals like lead (*Pb*), copper (*Cu*), zinc (*Zn*), nickel (*Ni*), cadmium (*Cd*) and chromium (*Cr*) in water samples was done by Flame Atomic Absorption spectrophotometer (*AAS*) technique, while analysis of mercury (*Hg*) and Arsenic (*As*) was performed by cold-vapour and by hydride generation techniques coupled with an atomic fluorescence detector [16].

Sediment Sampling

The study on pollution status along the Mahul Creek of Mumbai was performed for the period of one year from January 2013 to December 2013. The grab sediment samples were collected every month along different locations of the creek. The sampling was done by hand-pushing plastic core tubes with an intention to avoid metallic contamination. Samples so collected were kept in polythene bags which were free from heavy metals and organic contaminants. The samples were well covered while transporting from field to the laboratory to avoid contamination from the environment. The samples thus collected were mixed to give gross sample. The gross samples were air dried ground using agate mortar and sieved with a 0.5 mm mesh size sieve to uniform particle size. The thoroughly mixed sediment samples were packed in polythene bags and kept in a dry place until analysis. Such samples were drawn and analyzed monthly for their toxic heavy metal content, so as to get the month wise variation in pollution level along the Mahul Creek.

Sample Preparation

For analysis of heavy metal content in sediment samples, well mixed sample weighing 2 g was digested with 8 mL of aqua regia on a sand bath for 2 hrs. After evaporation to near dryness, the sample was dissolved in 2 % nitric acid, filtered through Whatman's No. 1 filter paper and then diluted with deionized water to give final volumes depending on the suspected level of the metals [17].

Analysis of Heavy Metals

The sediment samples collected were analyzed for the heavy metal content. The analysis for the majority of the trace metals like lead (*Pb*), copper (*Cu*), zinc (*Zn*), nickel (*Ni*), cadmium (*Cd*) and chromium (*Cr*) in sediment samples was done by Flame Atomic Absorption spectrophotometer (*AAS*) technique, while analysis of mercury (*Hg*) and Arsenic (*As*) was performed by cold-vapour and by hydride generation techniques coupled with an atomic fluorescence detector. [16].

RESULTS AND DISCUSSION

A number of metals are normally present in relatively low concentrations, usually less than a few mg/L, in aquatic environment. They are called heavy metals because in their metallic form, their densities are greater than 4 g/cc. Heavy metals are a special group of trace elements which have been shown to create definite health hazards when taken up by plants.

Concentrations of heavy metals in sediments

Heavy trace and toxic metals are not necessarily fixed by the sediments permanently, but may be recycled via biological and chemical agents both within the sedimentary compartment as well as in the water column. Behaviour of these metals in the coastal marine sediments is largely related to their capacity for complexation with organic matter in truly dissolved, colloidal, macro particulate phases. Persistence of trace metals in the environment may have possibilities for environmental transformation into more toxic compounds. Concentration of heavy metals by physical, chemical and biological processes is represented by a number generally known as 'concentration factor'. This concentration of heavy metals in sediment is represented by specific term known as distribution coefficient (K_d).

Distribution coefficient (K_d)

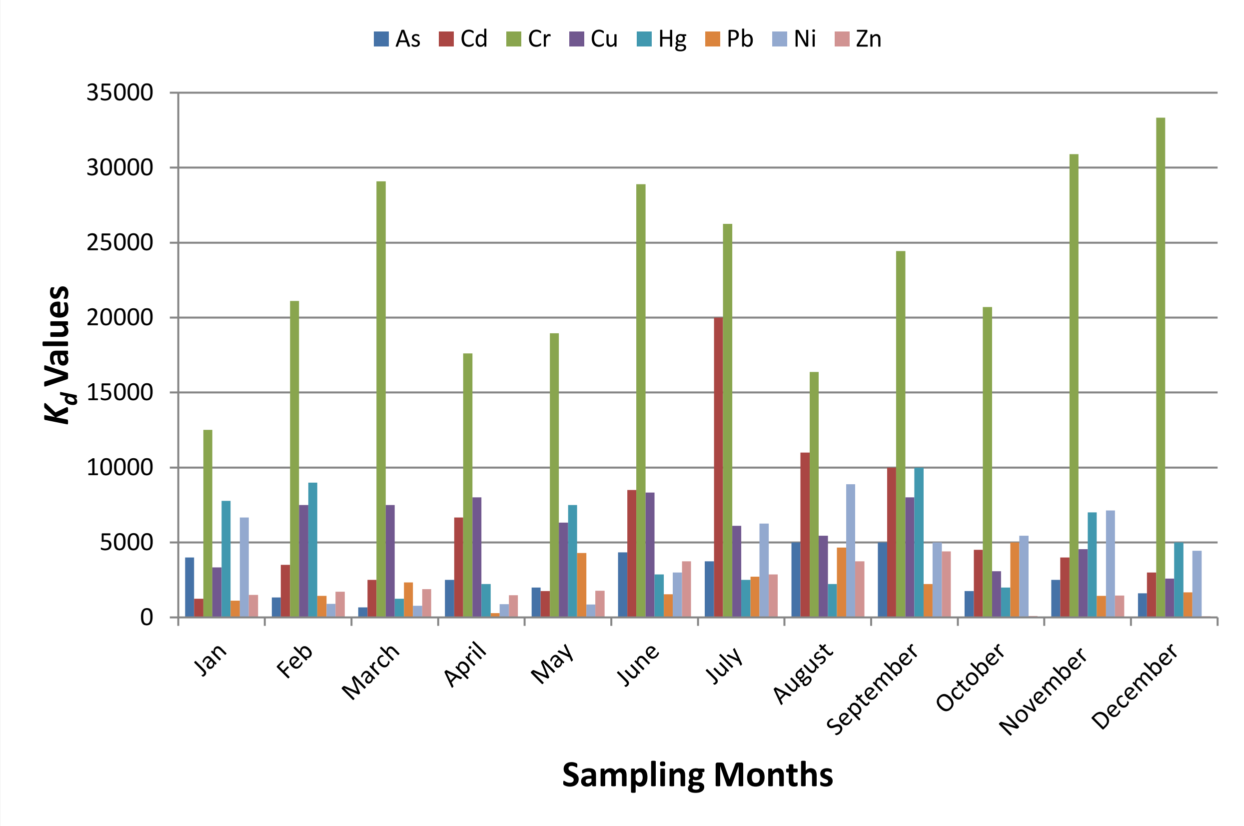
Coastal marine soil and to major extent sediments are a major repository as well as potential source of trace metals. Sediments are sinks for many inorganic and organic pollutants transported through the water column from various sources. Due to their particle reactivity, trace metals tend to accumulate in sediments, and, as a result, may persist in the environment long after their primary source has been removed. Distribution coefficient is expressed as the ratio of the concentration of an element in the sediment in (g/kg) dry weight to the concentration of the element in water in (g/L) under equilibrium conditions. The K_d values (L/Kg) of different industrially important toxic heavy metals such as Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Lead (Pb), Nickel (Ni) and Zinc (Zn) for Mahul Creek were calculated. The month wise variation in K_d values (L/Kg) of metals for sediments from January 2013 to December 2013 are presented in **Table 1**.

Table 1- Distribution coefficient K_d values (L/Kg) of various toxic heavy metals in sediments of Mahul creek.

	Toxic Heavy Metals							
Months	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Pb**	**Ni**	**Zn**
Jan	4000	1250	12500	3333	7777	1111	6667	1500
Feb	1333	3500	21111	7500	9000	1444	913	1722
Mar	667	2500	29091	7500	1250	2333	777	1875
Apr	2500	6667	17619	8000	2222	288	891	1481
May	2000	1750	18947	6316	7500	4286	857	1778
June	4333	8500	28889	8333	2857	1538	3000	3750
July	3750	20000	26250	6111	2500	2727	6250	2857
Aug	5000	11000	16364	5455	2222	4667	8888	3750
Sept	5000	10000	24444	8000	10000	2222	5000	4400
Oct	1750	4500	20714	3077	2000	5000	5455	99
Nov	2500	4000	30909	4545	7000	1429	7143	1467
Dec	1600	3000	33333	2581	5000	1667	4444	76
Average K_d (L/Kg)	2869	6389	23348	5896	4944	2393	4190	2063

A wide range in K_d values were observed for different metals. The K_d values (L/Kg) for different metals in sediment samples varied between 667 and 5,000 as minimum values in the month of March whereas 5,000 and 10,000 as maximum values in the month of September for Arsenic & Mercury respectively. In the month of January minimum K_d values (L/Kg) 1,250 for Cadmium and almost ten times higher that is 12,500 for chromium while maximum K_d values (L/Kg) varies with a vast difference as 20,000 for cadmium & 33,000 for chromium. Copper varies between 2,581 L/Kg and 8,333 L/Kg with an average K_d value 5,896 L/Kg. Lead and nickel varies in the range of 288-5,000 L/Kg and 777-8,888 L/Kg with an average K_d values 2,393 L/Kg and 4,190 L/Kg .Zinc varies drastically with lowest K_d values (L/Kg) in the months October and December as 99 and 76 as seen in bar graph **Figure 1** the bar for zinc metal is not visible for these two months whereas maximum value of 4,400 L/Kg is obtained in the month of September.

Figure 1 - Distribution behaviour of toxic heavy metals in sediments of Mahul creek



In comparison to other heavy metals, K_d value for Chromium was observed to be higher with an average of 23,348 L/Kg. The K_d values for sediment samples in Mahul creek were in the increasing order for Zn, Pb, As, Ni, Cu, Hg, Cd and Cr respectively. The variation in K_d values of different metals can be attributed to the solubility of the metal in water (less soluble is the metal, higher will be the K_d value) as well as contribution of industrial source. The distribution coefficient K_d is demonstrated to be highly sensitive to the concentration of the contaminant, cation-exchange capacity of the soil, and ionic species of the contaminant, in a decreasing order [18] whereas the distribution coefficients K_d values were higher for sediment as compared to that obtained for soil samples and also the K_d values of metals for soil and sediments were found to be lower in rainy and maximum in summer seasons studied for Thane creek [19].

Biological significance of heavy metals

Arsenic occurs naturally or is possibly aggravated by over powering aquifers and by phosphorus from fertilizers. Arsenic accumulates in water, soil and airborne particles, from which it is taken up by various organisms. The concentrations of the dangerous inorganic arsenics that are currently present in surface waters enhance the chances of alteration of genetic materials of fish. Plants absorb arsenic fairly easily, so that high-ranking concentrations may be present in food. High concentrations of arsenic in water can have an adverse effect on health [20, 21]. Organs affected by arsenic toxicity are those involved with absorption, accumulation or excretion, including the skin, circulatory system, gastrointestinal tract, liver and kidney. Arsenic is associated with multiple health effects, including Blackfoot diseases, diabetes, hypertension, peripheral neuropathy and multiple vascular diseases. Along with acute toxicity, long-term exposure to inorganic arsenic is associated with certain forms of cancer of the skin, lung, colon, bladder, liver and breast [22]. A few years back, high concentrations of this element was found in drinking water in six districts in West Bengal. A majority of people in the area was found suffering from arsenic skin lesions. Arsenic poisoning through water can cause liver and nervous system damage, vascular diseases and also skin cancer. The skin is quite sensitive to Arsenic and skin lesions are the most common and earliest non-malignant effects associated to chronic Arsenic exposure [23]. Higher values of cadmium in waste water effluent samples suggest the high level of pollution due to dyes paints and pigments manufacturing industries around. It is less toxic to plants than Cu, similar in toxicity to Pb and Cr. It is equally toxic to invertebrates and fishes [24]. Copper is highly toxic to most fishes, invertebrates and aquatic plants than any other heavy metal except mercury. It reduces growth and rate of reproduction in plants and animals. The chronic level of Cu is 0.02-0.2 mg/L, [24]. Aquatic plants absorb three times more copper than plants on dry lands [25]. Excessive copper content causes damage to roots, by attacking the cell membrane and destroying the normal membrane structure; inhibited root growth and formation of numerous short, brownish secondary roots. Copper becomes toxic for organisms when the rate of absorption is greater than the rate of excretion, and as copper is readily accumulated by plants and animals, its level has to be minimized in the waterway. Lead is discharged in the water through paints, solders, pipes, building material, gasoline etc. Combustion of oil and gasoline account for greater than fifty percent of all anthropogenic emissions, and thus form a major component of the global cycle of lead. Atmospheric fallout is usually the most important source of lead in the freshwaters, [24]. Lead enters in water of creeks and rivers through the vehicle washing and gasoline combustion. In plants, a concentration of 5 mg/L onwards, this is counteracted by severe growth retardation, discoloration and morphological abnormalities. There is an adverse influence on photosynthesis, respiration and other metabolic processes. Acute toxicity of lead in invertebrates is reported at concentration of 0.1–10 mg/L, [24]. Higher levels of lead pose eventual threat to fisheries resources. Exposure to mercury and its compounds can have acute adverse health problems. It may permanently damage the brain, kidneys and developing fetus. Effects on brain functioning may results in irritability, tremors, changes in vision or hearing, and memory problems. The acute lethal dose for most inorganic mercury compounds for an adult is 1–4g (or 14–57 mg/kg) for a 70 kg person [26]. In aquatic plants mercury compounds inhibit cell growth and impair permeability. The Canadian Global Emission Interpretation Center (*CGEIC*) has studied the spatial distribution of global emissions of mercury into air and has prepared a map of mercury emitted in different parts of the world. It shows that in India 0.1–0.5 T of mercury is released into the atmosphere every year. Emission rate of the metal in coastal areas is even higher (0.5–2 T/yr). According to the study, anthropogenic emission of mercury was estimated to have increased by 27% during 1990–2000 in the country. Thus India is one of the identified hotspots of mercury pollution in the world. Studies show that the aquatic ecosystem in India has significant amount of mercury [27]. Nickel (*Ni*) and nickel compounds have many industrial and commercial uses, and the progress of industrialization has led to increased emission of pollutants into ecosystems. Although *Ni* is omnipresent and is vital for the function of many organisms, concentrations in some areas from both anthropogenic release and naturally varying levels may be toxic to living organisms [28, 29]. Nickel compounds have been well established as carcinogenic in many animal species and by many modes of human exposure but their underlying mechanisms are still not fully understood [30]. It is observed that in mammals, exposure to zinc causes metal-fume fever with symptoms like fever, pain, fatigue, shivering, sweating, etc., while in plants; excessive zinc causes necrosis, chlorosis and inhibited growth [31].

CONCLUSIONS

Around the world as countries are struggling to arrive at an effective regulatory regime to control the discharge of industrial effluents into their ecosystems, Indian economy holds a double edged sword of economic growth and ecosystem collapse. Although in India the Central Pollution Control Board (*CPCB*) is responsible for restoration and maintaining the wholesomeness of aquatic resources under Water Prevention and Control of Pollution Act 1974 passed by Indian Parliament, it is expected that to maintain or restore the water quality at desired level it is important to have monitoring on regular basis. . The monitoring system for water quality needs to be strengthened both in terms of parameters monitored, water resources coverage and timely reporting to public domain. The present study on pollution due to toxic and trace heavy metals of the Mahul Creek of Mumbai will be useful for rational planning of pollution control strategies and their prioritization; to assess the nature and extent of pollution control needed; to evaluate effectiveness of pollution control measures already is existence; to evaluate water quality trend over a period of time; to assess assimilative capacity of a water body thereby reducing cost on pollution control; to assess the fitness of water for different uses. The present study on distribution coefficient of metals for sediments will also help to provide a means for evaluating the long term accumulation of heavy metal contaminants.

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