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Assessment of Heavy Metals in Sediment Sample from Cauvery River Basin at Nagore Coastal Region, Southeast Coast of Tamil Nadu, India

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ABSTRACT: In the present study determine that the heavy metals such as Copper (Cu), Zinc (Zn), Cadmium (Cd), Mercury (Hg), Chromium (Cr) and Iron (Fe) were analyzed in the Sediment samples. The sample analysis was done by microwave assisted digestion and Atomic Absorption Spectrophotometer (AAS). The presence of heavy metals in brackish water causes hazardous impact on the aquatic organisms. They are released in large concentration through effluent discharges from fiber boat industry, dry fish form issue, metal processing, paints and pigment production, biocides production and through domestic sewage from nearby villages. The range of heavy metals in sediment ($\mu g g^{-1}$) Copper (Cu), Zinc (Zn), Cadmium (Cd), Mercury (Hg), Chromium (Cr) and Iron (Fe) were: 5.03-42.3; 26.4-75.26; 4.89-17.14; 0.012-0.112; 0.05-4.29 and 0.3-0.98 and 5.67-81.26; 26.45-69.32; 5.42-8.72; 0.016-0.163; 0.14- 5.2 and 0.4-0.64 respectively.

KEYWORDS: Heavy metals, Atomic Absorption Spectrophotometer and brackish water.

I. INTRODUCTION

Heavy metals in sediments are essential to assess the extent of metal pollution. The distribution of heavy metals in solution has been widely recognized as a major factor in the geochemical behavior, transport and biological effects of these elements in natural waters. Moreover, sediment has aptly been called as 'Trace element trap' because they eventually receive almost all the heavy metals, which enter the aquatic environment [1]. The scavenging by suspending particles results in large concentration of pollutants being retained in brackish water sediments. Sediment samples have also been widely used to monitor heavy metal pollution in coastal areas. Heavy metal contamination could frequently be identified through analysis. Some studies were carried out on the distribution of heavy metals in water and sediments from Indian regions are limited. Metal concentration in aquatic organism may be significantly influenced by temporal variations in metal levels within the ecosystem. Among the contaminants, heavy metals are of particular concern owing to their environmental persistence, biogeochemical recycling and toxicity risks. The accumulation of heavy metals in the coastal environment has considerably increased in recent times owing to anthropogenic activities [2, 3, 4, and 5].

The toxic pollution comes from heavy metals such as cadmium and mercury. Recently, a highly toxic chemical called Tri Butyl Tin (TBT) is used in paints to protect boats from the ravaging effects of the oceans. The best known example of mercury metal pollution in the oceans took place in 1984, when a Japanese factory discharged a significant amount of this metal into Minamata Bay and after a decade the effect of mercury (Hg) metal came to light. Minerals containing heavy metallic elements are of widespread occurrence in rocks and soils. Copper (Cu) and zinc (Zn) have been extensively mined, and whose environmental levels have been strongly influenced by man. All are toxic to living animals and are considered as serious pollutants [6].



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The wastes of anthropogenic and industrial origin are of complex characters and have considerable percentage of heavy metals. Since, rivers constitute the main inland water resources for domestic, industrial and irrigation purposes, it is imperative to prevent and control the river pollution and to have reliable information on the quality of water for effective management [7]. The heavy metals in the brackish water phase generally deposit on the sediment bed or remain in dissolved state in the water column, depending on nature of chemical species which are influenced by factors like aquatic salinity, pH etc. [8]. Assessment of heavy metal concentration in the coastal water can be made by using indicator organisms such as marine algae [9, 10] have reported that the trace amount of chromium (Cr) is necessary for the entire organism as it is needed for the proper utilization of iron (Fe) and its conversion into haemoglobin excessive discharge of chromium (Cr) into the aquatic environment can have an adverse effect both on animals and man who eat these animals as food. In animals, it reduces fertility.

Mohammed, [11] have observed Copper (Cu) is an essential trace element, which is widely distributed in nature and also widely used metal industries. Copper sulphate mixed with lime is used as a fungicide. Medicinally copper sulphate is used as an emetic; it is also used as an antiparasitic agent based on its astringent and caustic actions. Copper levels in human body vary with age. Copper levels in brain increase with age and Cu levels are high in new borns than in adults. Dara, [12] have reported Cadmium (Cd) contamination of water may also come from use of metallic and plastic pipes, while super phosphate fertilizers, sewage sludge and automobile tyres also contain some amount of this toxic metal. The main problem with Cd in human nutrition is that the body does not completely excrete whatever Cd is absorbed. Cd in water at 10ppm level can kill fishes in one day while at 2ppm level they will be killed in 10 days. Hardness and salinity of water provides some degree of protection. Zinc is nutritionally an essential element and is required for the activity of a number of enzymes. Mining, processing and smelting of ores for the extraction of zinc constitutes the chief source of zinc pollution in the environment. Zinc content in aquatic invertebrates in fresh unpolluted water ranges between 25-200mg per litre. Above 40ppm level this metal imparts a faint but definite metallic taste and milky appearance to fresh water [13].

Increased loads of nutrients, heavy metals and other compounds like pesticides, fertilizers have resulted from changes in land use and anthropogenic development of the Cauvery river basins. Since, rivers constitute the main inland water resources for domestic, industrial and irrigation purposes, it is imperative to prevent and control the river pollution and to have reliable information on the quality of water for effective management [7]. No paper has been published on the heavy metal assessment in Nagore coastal region. Hence, the present study has been undertaken to examine the heavy metals assessment (Cu, Zn, Cd, Hg, Cr and Fe) in sediments of Nagore coastal region. Station I is Nagore Cauvary river basin and Nagore pattanachcheri village is Station II. Monthly samplings were made during forenoon from October 2015 to September 2016 for four seasons viz. monsoon (October-December), post-monsoon (January-March), summer (April-June) and pre-monsoon (July-September).

II. MATERIALS AND METHODS

The study area (Figure-1) is located Cauvery river basin at Nagore Pattanachcheri village the southern part of Bay of Bengal in South East coast of Tamilnadu, India. It is extending from 10° 30' to 10° 55'N latitude and 79° 45' to 79° 55' E longitude and medium tropical transition climate, characterized by monthly average temperature of above 27° C. The relative humidity ranges from 70 - 77%. The Nagore brackish water is situated near Nagapattinam on the east coast of India. The Nagore brackish water has its source in the Cauvery river basin of Tamil Nadu. It has a year - round connection with the sea. This river flows in to the Bay of Bengal, near Nagapattinam of Tamil Nadu. In the harbor at Nagore, there are about many hundreds of mechanized boats and catamarans, employed for fishing. In the fishing vessels they are using paints and fuels from it the waste materials are released in to the harbor area. The domestic sewages agricultural drainages and the other sewage effluents are carried out into the Bay of Bengal through the small canals and rivers.

Sample preparation for chemical analyses

Heavy metals in sediments samples were prepared for six metals including Cu, Zn, Cd, Hg, Cr and Fe. Sediment samples were collected at monthly intervals (for a period of 12 months from October 2015 to September



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2016) and were collected in precleaned and acid washed polypropylene bottles of one litre capacity and were immediately kept in an ice box and transported to the laboratory to avoid contamination. Sediment samples were then filtered through a Millipore filtering unit using a Millipore filter paper (pore size 0.45µm). The heavy metals in sediments were analyzed in air-acetylene Atomic Absorption Spectrophotometer, undisturbed sediment samples were collected using a grab sampler placed in plastic containers for transport to the laboratory. Sample preparation for chemical analyses involved procedures for sub sampling during drying, sieving, crushing and storage. The metals were determined by plasma emission spectrophotometer at Centre of Excellence, Vapi (Gujarat) India. The resulting solution was then stored in acid washed Borosil glass vials for Hg and polypropylene containers for other metals. Concentrations of Cu, Zn and Cd in the solution were determined by aspirating the solution to a standard Flame Atomic Absorption Spectrophotometer (Perkin- Elmer model 373) and Hg was determined using a standard mercury analyzer (ECIL) by cold vapors Atomic Absorption Spectrophotometer. Blank digestions were also carried out. The mean and standard deviation was calculated.



Figure 1: Study area map



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III. RESULTS AND DISCUSSIONS

The presence of heavy metals in brackish water causes hazardous impact on the aquatic organisms. They are released in large concentration through effluent discharges from fiber boat industry, dry fish form issue, metal processing, paints and pigment production, biocides production, and through domestic sewage from nearby villages. Mendil and Uluozlu, [14] have reported that the sediment of heavy metals such as Copper, Zinc, Cadmium, Mercury, Chromium and Iron occur in coastal region in different forms and in different concentrations (Table 1 and 2). Heavy metals can enter a water supply by industrial and consumer waters or even from acidic rain, breaking down of soils and releasing heavy metals into aquatic environment [15]. In the present observation, the copper in sediment values ranged between 5.03 to 42.3µg g⁻¹, with minimum and maximum concentration of Cu during the monsoon and post monsoon season (Stn.1) and the minimum Cu concentration $5.67\mu g g^{-1}$ were recorded during monsoon and the maximum $81.26\mu g g^{-1}$ during summer season (Stn.2). Zinc in sediment values ranged between 26.4 to $75.26\mu g g^{-1}$ with minimum and maximum concentration of Zn during the monsoon and summer season (Stn.1) and 26.45 to 69.32µg g⁻¹, with minimum and maximum concentration of Zn during the summer and pre monsoon season (Stn.2). Cadmium in sediment concentration varied from 4.89 to 17.14 μ g g⁻¹, with minimum and maximum concentration of Cd during the summer season (Stn.1) and 5.42 to 8.72 μ g g⁻¹, with minimum and maximum concentration of Cd during the pre monsoon and summer season (Stn.2). Mercury in sediment values ranged between 0.012 to 0.112µg g⁻¹ with minimum and maximum concentration of Hg during the monsoon and summer season (Stn.1) and 0.016 to 0.163 μ g g⁻¹, with minimum and maximum concentration of Hg during the pre monsoon and post monsoon season (Stn.2). Chromium in sediment value varied from 0.05 to 4.29µg g⁻¹, with minimum and maximum concentration of Cr during the post monsoon and monsoon season (Stn.1) and 0.14 to 5.2µg g⁻¹, with minimum and maximum concentration of Cr during the pre monsoon and monsoon season (Stn.2). Iron in sediment values ranged between 0.3 to 0.98µg g⁻¹, with minimum and maximum concentration of Fe during summer and monsoon season (Stn.1) and 0.4 to 0.64µg g⁻¹, with minimum and maximum concentration of Fe during the summer and monsoon season (Stn.2), (Table 3 and 4).

Concentrations of heavy metals in sediments at the two stations varied seasonally. Variability in the distribution of metals appeared to be more related to hydrobiological conditions. Concentrations of dissolved metals especially Cu and Zn were high during the summer season. Cd and Hg concentrations were high during the summer and post-monsoon season. Cr and Fe concentrations were high during the monsoon season. Generally, the natural sources of heavy metals in coastal waters are through land and river runoff and the mechanical and chemical weathering of rocks. The components also were washed from the atmosphere through rainfall, windblown dust, forest fire, and volcanic particles, adding to the distribution of heavy metals in water.

Low levels of Cu in sediments during the monsoon could be due to the adsorption of Cu on to the particulate matter and consequent settlement to the bottom. Low level of Hg in sediments might have been caused by the higher ingestion rate of organisms, resuspension of sediments and absorption onto the particulates during the monsoon season at this station. In both stations, the same trend of abundance of different metals was observed in the present study: the essential metal (Zn) recording the maximum concentration and the non-essential metal (Hg) recording the minimum concentration, as observed in the Bay of Bengal along the Tamil Nadu coast. Low level of Cd and Cr in sediments during the pre-monsoon could be due to the adsorption of Cd in water at 10ppm level can kill fishes in one day while at 2ppm level they will be killed in 10 days. Chromium due to the observed that the highly toxic and responsible for several cases of poisoning through food. Low level of Fe in sediments during the summer due to the effects of iron is to brackish color, rusty sediment, better or metallic taste, brown green strains iron bacteria and discolored beverages. Our earlier investigations also noted the significant enrichment of heavy metals in the upper reaches of Cauvery river basin from agrochemical runoff [16].



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Table 1: Monthly variations in heavy metal assessment in sediments (µg g⁻¹) of Nagore Cauvery river basin during
October 2015 to September 2016 (Station I)

Parameters	2015			2016								
	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.
Copper (µg g ⁻¹)	6.32	17.81	24.12	5.03	42.3	24.7	14.5	18.5	24.52	13.2	16.82	20.95
Zinc (µg g ⁻¹)	26.4	46.31	55.06	48.54	55.46	67.45	28.79	58.76	75.26	27.7	63.15	70.43
Cadmium (µg g ⁻¹)	7.68	8.89	9.23	6.45	7.88	10.07	17.14	8.98	4.89	5.78	5.9	9.68
Mercury (µg g ⁻¹)	0.012	0.024	0.042	0.021	0.068	0.086	0.021	0.073	0.112	0.034	0.049	0.053
Chromium (µg g ⁻¹)	3.97	2.32	4.29	0.05	1.08	0.91	2.79	0.99	1.87	2.11	2.23	0.15
Iron (µg g ⁻¹)	0.68	0.49	0.98	0.54	0.66	0.42	0.3	0.5	0.12	0.16	0.25	0.32

Table 2: Monthly variations in heavy metal assessment in sediments (µg g⁻¹) of Nagore Pattanachcheri village duringOctober 2015 to September 2016 (Station II)

Parameters	2015			2016								
	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.
Copper (µg g ⁻¹)	5.67	19.4	14.5	6.92	53.65	18.26	15.82	81.26	65.6	24.73	27.89	25.64
Zinc (µg g ⁻¹)	48.5	41.5	34.08	43.4	51.1	62.16	26.45	48.64	63.2	28.6	48.5	69.32
Cadmium (µg g ⁻¹)	6.73	7.38	8.64	6.12	7.14	8.6	6.83	8.72	6.73	5.42	7.78	6.07
Mercury (µg g ⁻¹)	0.039	0.054	0.073	0.026	0.163	0.149	0.028	0.098	0.051	0.046	0.016	0.026
Chromium (µg g ⁻¹)	5.2	3.4	2.08	1.86	1.06	1.3	1.48	1.78	2.13	2.08	2.04	0.14
Iron (µg g ⁻¹)	0.56	0.29	0.64	0.42	0.29	0.31	0.4	0.7	0.10	0.15	0.19	0.18



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 Table 3: Mean values of heavy metal recorded in Cauvery river basin at Nagore during the period from October 2015 to September 2016 (station I)

Heavy metals	Monsoon	Post monsoon	Summer	Pre monsoon	
Copper (µg g ⁻¹)	16.08 ±7.36	24.01±15.22	19.17±4.11	16.99±3.16	
Zinc (µg g ⁻¹)	42.59±11.99	57.15±7.81	54.27±19.23	53.76±18.66	
Cadmium (µg g ⁻¹)	8.6±0.66	8.13±1.48	10.33±5.09	7.12±1.81	
Mercury (µg g ⁻¹)	0.02±0.01	0.05±0.02	0.068±0.03	0.045±0.008	
Chromium (µg g ⁻¹)	3.52±0.86	0.68±0.45	1.88±0.73	1.49±0.95	
Iron $(\mu g g^{-1})$	0.71±0.20	0.54±0.09	0.30±0.15	0.24±0.06	

 Table 4: Mean values of heavy metal recorded in Pattanachcheri village at Nagore during the period from October

 2015 to September 2016 (Station II)

Heavy metals	Monsoon	Post monsoon	Summer	Pre monsoon	
Copper (µg g ⁻¹)	13.19±5.68	26.27±19.90	54.22±27.89	26.08±1.32	
Zinc (µg g ⁻¹)	41.36±5.88	52.22±7.69	46.09±15.11	48.80±16.62	
Cadmium (µg g ⁻¹)	7.58±0.79	7.28±1.01	7.42±0.91	6.42±0.99	
Mercury (µg g ⁻¹)	0.05±0.013	0.11±0.06	0.059±0.02	0.02±0.01	
Chromium (µg g ⁻¹)	3.56±1.27	1.40±0.33	1.79±0.26	1.42±0.90	
Iron (µg g ⁻¹)	0.49±0.14	0.34±0.05	0.4±0.24	0.17±0.01	

When compared to sediments contained very high concentration of metals. Concentration of heavy metals in the sediments showed at Nagore coastal region during the study period. Cd, Fe and Zn concentrations were high at station I (Fig. 2) whereas Cu, Cr and Hg concentrations were high at station II (Fig. 3). At both stations, Cu and Cd concentrations were high during the summer and post-monsoon season. Zn and Hg concentrations were high during the summer and post-monsoon season. The higher concentration of metals observed during monsoon could be attributed to the heavy rainfall and subsequent river runoff, bringing much industrial and land derived materials along with domestic, municipal, and agricultural wastes, which include residues of heavy metal containing pesticides.

Zn and Cu always have a tendency to couple with organic carbon. Decomposition of the organic matter remain are found to release heavy metals back to sediments and accumulated; and this process might be responsible for the strong association of Zn and Cu with organic carbon. Higher organic carbon values recorded in the post-monsoon coincided with the elevated level of Zn and Cu in sediments. Besides, the release of organically bound heavy metals through influx from land runoff might have also contributed elevated level of Zn and Cu, despite they are meager in amount. Zn and Cu are generally good indicators of anthropogenic inputs. Rejomon [17] who reported that the Zinc concentration were high during the summer at both stations. High Zn concentration in water could have resulted due to



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the release of this metal from the sediments and abundant organic matter. Zn Concentration was low concentration during the monsoon season at both the stations. The extensive use of antifouling paints during the peak fishing season in post monsoon would have released cuprous oxide which in turn enriches the Cu content in the water [18]. Eventually, it would be settled from the water column by flocculation and sedimentation.

In summer, these metals might slightly elevate in content because the low salinity and high pH water might have caused the adsorption of these metals, leading to their removal from the water column. Significant variations observed in total heavy-metal concentrations, labile fractions and lithogenic fractions could be attributed to numerous factors, such as weathering, mineral transport, anthropogenic inputs, and physicochemical components of sediments [19]. The low concentration of Zn and Cu in monsoon might be due to the prevailing lower pH which renders dissolved metal carbonate complexes to release free metal ions into the water column. The relative enrichment of Cd (at station I) and Cu (at station II) in the near shore sediments during the post-monsoon could be attributed to the particulate fractions derived from the river runoff caused by monsoonal flow and occurrence of relatively higher percentage of particulate matter. Because Nagore brackish water is known for intensive fishing activities, the widespread use of antifouling paints in fishing boats could be a probable source of Copper.

Sediments are the principal sites of Hg accumulation in the aquatic environment. During the pre-monsoon season, less land drainage and rainfall and less turbulence resulted in stagnant condition rather than mixing thus facilitating higher accumulation of Zn and Hg in the sediments. In addition, excretion and elimination of exoskeletons by abundantly occurring plankton and by settlement of particulate matter probably have played a significant role in enhancing the concentration of Hg and Zn in the sediments. High metal concentrations in sediment at station I could have been resulted from the fresh water inputs through Cauvery river basin along with land drainages. Fishing activities and anthropogenic activities might have increased the Cd and Hg levels in near shore sediments. Metals in sediments at the two stations showed a similar trend of distribution. Among the essential metals, only Cu and Zn recorded the maximum concentrations whereas the non-essential metals Cd and Hg showed the minimum concentrations.

The heavy metals of Cr accumulation in the aquatic environment. Rajappa, [20] who observed that the Chromium is highly toxic and responsible for several cases of poisoning through food. Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces Zn biochemically and causes high blood pressures, kidney industrial discharge and Geological mining sites both stations show Cr concentrations high in monsoon season. A number of toxic elements are introduced into the aquatic environment from the effluents coming from the large industries resulting biodiversity and changes in water quality. For example effluents from textile mills and electroplating contained as much as 20-40ppm of chromium. Exposure of man to high concentration of Cr may cause dermatitis, ulcer, destruction of mucus of nose and cancer of the stomachs. The major source of Cr in water is via industrial effluents. Fe concentration was more during the monsoon season in stations due to various sources of pollution leaching of cast iron pipes in water distribution system and by natural process. The effects of iron is to brackish color, rusty sediment, better or metallic taste, brown green strains iron bacteria and discolored beverages. Fe is found in natural fresh and groundwater, but have no health-based guideline value, although high concentrations give rise to consumer complaints due to its ability to discolor aerobic waters. The pollutants that enter the inshore water and estuaries create serious problems causing extensive damage to the life and activities of the living aquatic organisms [21]. Trace element accumulation in aquatic consumers is of interest to ecologist and environmentalists so as to understand the fate and effects of contaminants in the food web dynamics as well as in the biogeochemical cycle of trace elements.



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Figure 1: Showing high concentration of heavy metal for each month at Nagore Cauvary river basin (Station I)







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IV. CONCLUSION

The data obtained for heavy metals such as Cu, Zn, Cd, Hg, Cr and Fe were dangerously higher than the maximum contaminant levels (MCL) recommended for unpolluted and drinking water. Heavy metals in sediments of the Cauvery river basin and Pattanachcheri village show its association with various geochemical forms. Cauvery river basin is a good example for a site where contributions of pollutants both from natural (lithogenic) sources and anthropogenic activities. The major sources of pollution of the Nagore Cauvery river basin are the industrial effluents, return flows, agricultural runoff, municipal and domestic sewage besides pedogenic background contributions. During the study period, the sediment samples during Monsoon season showed significantly lower values than Pre-Monsoon, Post-Monsoon and Summer season samples. The main reason behind the lower concentration during the Monsoon season is the dilution factor with the pollutant. The water body surrounding Nagore coastal region is contaminated with heavy metals especially Zn, Cr, Cu and Cd which can contaminate sea foods and hence humans. Fishing activities and anthropogenic activities might have increased the Cd and Hg levels in near shore sediments. Fe is found in natural fresh and groundwater, but have no health-based guideline value, although high concentrations give rise to consumer complaints due to its ability to discolor aerobic waters. Heavy metals parts and effluents from industrial and commercial activities such as fishing (nets, hooks, etc) shipping, timber processing and outboard engine boats influenced the levels of metals along the Nagore Pattanachcheri village while domestic activities (such as building materials, solid wastes). The area is contaminated with heavy metals and requires creation of awareness, periodic monitoring and evaluation of sea foods since most communities along the aquatic depend on sea foods and use the water for salt production after crystallization. Therefore the water was highly contaminated and polluted with heavy metals and not recommended as a drinking water for human consumption. Nevertheless, and looking for a global evaluation of the studied ecosystems, the addition of complementary information (*i.e.*, heavy metal concentrations in brackish water zooplankton suspended particulate matter and other organisms like fishes, mollusks, etc.) is recommended. We are recommended to ministry of environment to protect Nagore Cauvery river basin and Pattanachcheri village at Nagore polluted in improper industrial planning, unsaved disposal of industrial waste and urban waste. Otherwise high levels of pollutants in to brackish water ecosystem of Nagore and would greatly invite socioeconomic disaster.

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