Assessment of Heavy Metal Contamination and Sediment Quality of Thengapattinam Estuary in Kanyakumari District

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Abstract

Risk analysis of heavy metals in urban aquatic systems turns significant due to their persistence, non-degradability, toxicity and accumulation. Thengapattinam estuary in Kanyakumari district is subjected to various environmental stresses due to multiple waste discharges through the AVM canal. The distribution and accumulation of heavy metals - Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn) and Zinc (Zn) in the sediments of this estuary were investigated from April 2011 to March 2013. The mean concentration of these metals was 0.080 ppm for Cd; 21.82 ppm for Cr; 24.15 ppm for Cu; 5378 ppm for Fe; 6.833 ppm for Pb; 54.59 ppm for Mn and 52.19 ppm for Zn. The result showed that the mean concentration of heavy metals was ranked as: Fe> Mn> Zn> Cu> Cr> Pb> Cd. In this study, a comprehensive approach is adopted for ecological risk assessment using toxicity units based on numerical sediment quality guidelines (SQGs) and potential ecological risk indices. The mean concentrations of Cd, Cr, Cu, Fe, Mn, Pb and Zn in the sediment samples were lower than the proposed threshold effect concentration (TEC), indicating that there were no harmful effects due to the presence of these metals. On the basis of the mean values of Geo – accumulation Index (I_{geo}), sediments were enriched with metals in the following order: Cd> Cu> Zn> Pb> Cr> Fe> Mn, while according to Contamination factor (C_f), the order was Zn> Cu> Pb> Cd> Cr> Fe> Mn. According to Degree of contamination (C_d), station 3 was the hot spot which received water from AVM canal. The mean Enrichment factor (EF) for Cd, Cr, Cu, Fe, Pb, Mn and Zn vary between 0 and 10, indicating that the Thengapattinam sediments were not affected by anthropogenic influences. The Pollution load index (PLI) for the samples collected from all the stations were found to be less than unity indicating perfection.

Keywords: Contamination factor, degree of contamination, heavy metals, risk indices, toxicity

Introduction

Aquatic system, an important basic component of our environment, provide food and shelter for flora and fauna as well as act as a sink for a wide variety of pollutants. Aquatic sediments, especially of urban environment, accumulate metal pollutants from various sources to much higher concentrations than corresponding water columns. Weathering of rocks and soils and multiple anthropogenic activities, discharge of industrial and urban wastes into water bodies [1] are the major pollutant contributors. Among these pollutants, heavy metals have been of great concern due to their toxicity, abundance, persistence, and subsequent accumulation in aquatic habitats [1, 2, 3, 4]. The adsorbed contaminants may be later released into the water column with changing environmental conditions and may pose threat to biota [5]. Some of the metals such as calcium, magnesium, potassium and sodium are essential minerals for sustaining life and must be present for normal body functions while presence of other metals such as cobalt, copper, iron, manganese, molybdenum and zinc at low levels are essential to catalyze enzyme activities [6]. Excess exposure to these essential metals can however, be toxic. Water is unique in its chemical properties due to its polarity and hydrogen bonds which makes its ability to dissolve, absorb, adsorb or suspend different compounds [7].Thus, in nature, water is not pure as it acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities [8].

Contaminated sediments are known to be responsible for degradation of water quality in the natural waters especially in the shallow and enclosed water systems [9,10]. In order to protect the aquatic life community, comprehensive methods for identifying and assessing the severity of sediment contamination have been introduced [11, 12, 13]. Exposure to heavy metals has linked to several human diseases such as development retardation or malformation, kidney damage, cancer, abortion, effect on intelligence and behavior and even death in some cases of exposure to very high concentrations. For these reasons, it would be desirable and imperative to investigate their distribution in Thengapattinam estuary which can provide valuable information of heavy metal pollution and help to evaluate potential environmental risks. The aim of this study was to investigate the contamination levels and distributions of heavy metals in surface sediment and evaluate the potential toxicity of the metal concentrations based on sediment quality guidelines.

Study area

Thengapattinam estuary (8^o 14’ N latitude and 77^o 10’ E longitude) on the south-west coast of India is situated in Paimkulam village of Vilavancode Taluk of Kanyakumari district (Fig 1). It is the largest estuary in Kanyakumari district, situated at a distance of about 35 km from Nagercoil. The estuary spreads over an area of 400 hectares and extends over 5 km. It is a bar-built estuary formed by the confluence of river Tamiraparani with the Arabian Sea at Thengapattinam. The climate of this region is greatly influenced both by the south-west and north-east monsoons. Along the west coast line, the AVM canal with water inflow from nearby land and streams, is used for coconut husk retting activities. The estuary is connected with the sea during the rainy season and land locked for the rest of the year by sand bar.

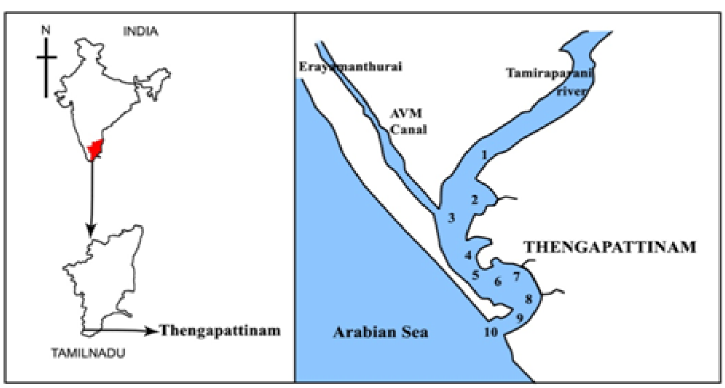

Fig.1 – Location map of the area of study

Materials and Methods

Ten stations were selected based on different ecological conditions for the collection of sediment samples from estuarine mouth bed to river basin in the Thengapattinam estuary as shown in Fig 1. Sediment samples were collected from ten stations quarterly for a period of two years from April 2011 to

March 2013. The collected samples were initially air dried and finely powdered using agate mortar. The air dried samples were analyzed for heavy metals (Cd, Cr, Cu, Fe, Pb, Mn and Zn) in the sediment samples using an Atomic Absorption Spectrophotometer (Perkin Elmer Model 2380) [14]. The digested samples were directly aspirated into the flame (Air-Acetylene fuel mixture). Using the absorption mode, the concentration corresponding to the absorption in the digest was determined.

Results and Discussion

The mean concentration of selected heavy metals in the surface sediments is given in Table 1. Generally, the metal concentrations exhibit fluctuations between different stations. Elemental concentration of Fe was highest in Thengapattinam sediments followed by Mn, Zn, Cu, Cr, Pb and Cd i.e. Fe> Mn> Zn> Cu> Cr> Pb> Cd. Cadmium was the least concentrated heavy metal in all the stations sampled and the results are consistent with those of Ennore - Pulicat stretch [15]. Of the various sampling stations, station 3 showed maximum concentration of all metals, the station where pollutants from AVM canal entered into the estuary, and it was identified as hot spot.

Table 1 - Mean Concentration of Heavy Metals (ppm) in sediments of Thengapattinam estuary

Station	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Zinc
1	bdl	21.65	27.64	4455	5.423	48.44	45.21
2	0.187	23.56	21.23	5996	2.447	52.82	48.20
3	0.494	27.06	33.56	14111	21.56	136.1	132.8
4	bdl	23.41	22.54	3647	2.492	12.51	64.21
5	bdl	26.45	26.09	2611	7.734	9.962	36.80
6	bdl	21.47	25.73	3121	4.302	50.89	35.12
7	bdl	18.52	23.35	3034	4.602	32.65	32.08
8	bdl	20.69	19.66	7682	7.392	89.02	43.54
9	bdl	22.32	25.67	8201	8.737	100.6	55.66
10	0.1203	13.10	15.99	921.6	3.641	12.93	28.34
Maximum	0.494	27.06	33.56	14111	21.56	136.1	132.8
Minimum	bdl	13.10	15.99	921.6	2.447	9.962	28.34
Mean	0.0801	21.82	24.15	5378	6.833	54.59	52.19
TEC	0.99	43.4	31.6	20000	35.8	460	121
PEC	4.98	111	149	40000	128	1100	459

TEC – Threshold Effect Concentration; PEC – Probable Effect Concentration; bdl – below detectable limit.

Assessment of Sediment Contamination

TEC/PEC guidelines

An assessment of heavy metal contamination in sediments is an indispensable tool to assess the risk of an aquatic environment. To assess metal concentrations in sediment, Numerical Sediment Quality Guidelines (SQGs) were applied. The metal concentrations were thus compared with TEC/PEC guidelines [16]. SQGs include a threshold effect concentration (TEC) and a probable effect concentration (PEC) (Table 1). If the metals in sediments are below the TEC, harmful effects are unlikely to be observed. If the metals are above the PEC, harmful effects are likely to be observed [17]. In Thengapattinam estuary, the mean concentrations of Cd, Cr, Cu, Fe, Mn, Pb and Zn in the sediment samples were lower than the proposed TECs, indicating that there are no harmful effects from these metals (Table 1). On the other hand, the concentrations of Cu (33.56 ppm) and Zn (132.8 ppm) in the samples collected at station 3 exceeded TEC indicating that the station 3 was the hot spot which received water from AVM canal.

United States Environment Protection Agency (USEPA) and World Health Organization (WHO)

The chemical contamination in the sediments was evaluated by comparison with the sediment quality guidelines proposed by USEPA/WHO. These criteria are shown in Table 2.

In Thengapattinam estuary, the highest concentration of Cadmium (0.494ppm) was observed at station 3 and the lowest was below the detectable level at stations 1, 4, 5, 6, 7, 8 and 9 with a mean value of 0.080 ppm. Cadmium is used in the production of inorganic fertilizers from phosphate ores which constitute a major source of diffuse cadmium pollution [18,19]. Moreover, when ingested by humans, cadmium accumulates in the intestine, liver and kidney [20]. Cadmium has a range of negative physiological effects on organisms such as decreased growth rates and negative effects on embryonic development [21]. The levels of cadmium in the sediment samples of the estuary were below the WHO standard value of 6 ppm. The concentrations of chromium in the sediment samples of station 3(27.06 ppm) and station 5 (26.45 ppm) exceeded the regulating limits but the mean concentration of Cr in the estuary was below the WHO/USEPA standard value of 25 ppm. The mean concentration of Cu in the Thengapattinam estuary was below the WHO standard value of 25 ppm. Copper is an essential element to human life, but, in high concentrations, it can cause anemia, liver and kidney damage, stomach and intestinal irritation [22].

Table 2 SQG and Concentration of heavy metals (ppm) in the sediment samples of Thengapattinam estuary

Metal	Minimum	Maximum	Mean	Geochemical Background		WHO SQG	USEPA SQG
				World surface rock average*	Mean shale concentration**		
Cd	bdl	0.494	0.0801	0.2	0.3	6	0.6
Cr	13.10	27.06	21.82	71	90	25	25
Cu	15.99	33.56	24.15	32	45	25	16
Fe	921.6	14111	5378	35900	46700	-	30
Pb	2.447	21.56	6.833	16	20	-	40
Mn	9.962	136.08	54.59	750	850	-	30
Zn	28.34	132.8	52.19	127	95	123	110

Values are in ppm; *****Martin and Meybeck ; ******Venkatesha Raju

In Thengapattinam estuary, the maximum concentration of 14111 ppm for iron was observed at station 3, while the minimum level of 921.6 ppm was detected at station 10 with a mean value of 5378 ppm. The USEPA guideline value 30 ppm of Fe in sediment is acceptable [23]. Above 30 ppm, a condition known as haemo-chromatosis could result. From the result of this study, the concentration of iron in the sediment samples exceeded the guideline limit indicating pollution of Thengapattinam estuary with iron.

The concentration of lead varied between 2.447 ppm (station 2) and 21.56 ppm (station 3) with a mean value of 6.833 ppm. The levels of lead in the analyzed sediment samples showed that they are far below the limiting values by USEPA of 40 ppm [24]. The concentration of manganese varied between

9.962 ppm (station 5) and 136.1 ppm (station 3) with a mean value of 54.59 ppm. The common manganese species found in water is predominantly Mn^{2+} and Mn^{4+}. Manganese compounds are used in fertilizers, varnish and fungicides and as livestock feeding supplements. Manganese can be adsorbed onto sediment; the extent of adsorption depends on the organic content and cation exchange capacity of the soil. The levels of manganese in the sediment samples exceeded the USEPA limit of 30 ppm. It can bioaccumulation in lower organisms (e.g., phytoplankton, algae, mollusks and some fish) but not in higher organisms; biomagnifications in food chains is not expected to be very significant [19,20]. The mean value of zinc was found to be 52.19 ppm and the variation was between 28.34 ppm (station 10) and 132.8 ppm (station 3). Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life [20]. In addition, Zn is involved in a variety of enzyme systems which contribute to energy metabolism, transcription and translation. Zinc is also potentially hazardous and excessive concentrations in sediment lead to phytotoxicity as it is a weed killer [18,20,25]. The mean value of zinc in the sediment samples was below the WHO guideline value of 123 ppm.

Geo-accumulation index (I_{geo})

Geo-accumulation index introduced by Muller was used to assess the degree of metal pollution in aquatic sediment studies [26,27,28]. I_{geo} was used to determine metal contamination in sediments, by comparing current concentrations with pre- industrial levels and can be calculated by the following equation [29].

$$Igeo = \log2 (Cn/1.5Bn)$$

Where, Cn is the measured concentration of a heavy metal in sediments, Bn is the geochemical background value in average shale of element n and 1.5 is the background matrix correction due to terrigenous effects. The geo-accumulation index classification consists of seven classes (0-6), ranging from unpolluted to extremely polluted: ≤ 0 (class 0) unpolluted, 0-1 (class 1) unpolluted to moderately polluted, 1-2(class 2) moderately polluted, 2-3(class 3) moderately to strongly polluted, 3-4 (class 4) strongly polluted, 4-5 (class 5) strongly to extremely polluted, 5-6 (class 6) extremely polluted [30].

In Thengapattinam estuary, the calculated results of I_{geo} values (Table 3) indicated that for Cd, sediment quality ranges from unpolluted to moderately polluted ($0 \leq I_{geo}<1$) for station 3 and unpolluted ($I_{geo} < 0$) for all other stations . I_{geo} values of Cr, Cu, Fe, Mn, Pb and Zn ($I_{geo}<0$) in the estuary indicated that all the stations were unpolluted with these metals. On the basis of the mean values of I_{geo}, the sediments were enriched with metals in the following order: Cd> Cu> Zn > Pb > Cr > Fe> Mn.

Table 3 Geo-accumulation index for heavy metals in sediments of Thengapattinam Estuary

Station	Cd	Cr	Cu	Fe	Pb	Mn	Zn
1	-	-2.6405	-1.2881	-3.9748	-2.4675	-4.7179	-1.6561
2	-1.2667	-2.5185	-1.6689	-3.5462	-3.6158	-4.5932	-1.5641
3	0.1349	-2.3190	-1.0081	-2.3119	-0.4765	-3.2284	-0.1018
4	-	-2.5278	-1.5825	-4.2637	-3.5895	-6.6712	-1.1501
5	-	-2.3518	-1.3715	-4.7458	-1.9557	-6.9999	-1.9534
6	-	-2.6529	-1.3914	-4.4884	-2.8019	-4.6471	-2.0203
7	-	-2.8656	-1.5316	-4.5292	-2.7046	-5.2871	-2.1514
8	-	-2.7056	-1.7794	-3.1884	-2.0209	-3.8402	-1.7108
9	-	-2.5968	-1.3948	-3.0942	-1.7799	-3.6638	-1.3562
10	-1.9035	-3.3653	-2.0776	-6.2477	-3.0422	-6.6238	-2.3299
Mean	-0.3035	-2.6544	-1.5094	-4.0390	-2.4455	-5.0273	-1.5994

Contamination factor (C_f) and Degree of contamination (C_d)

Contamination Factor (C_f) analysis is another important tool for the assessment of heavy metal pollution in estuarine study. For C_f computation, the values like Fe, Mn, Cd, Pb, Cu, Cr and Zn are normalized using the corresponding average metal values of shale [31]. This is because, the world shale average is considered as background values. The Contamination factor (C_f) was evaluated using the equation

C_f =Metal concentration in polluted sediment / Background value (shale) of the metal.

$C_f < 1$ refers to low contamination, $1 \leq C_f < 3$ means moderate contamination, $3 \leq C_f < 6$ indicates considerate contamination and $C_f > 6$ indicates very high contamination [32].

Hakanson analysed seven specific heavy metals (As, Cd, Cu, Cr, Hg, Pb, Zn) and the organic pollutant, polychlorinated biphenyls (PCB) and thus considers eight possible measures of contamination. Hakanson's study also proposed that the numeric sum of the eight specific contamination factors expressed the overall degree of sediment contamination (C_d) using the following formula

$$C_d = \sum_{i=1}^{n} C_{f\,i}$$

The C_d is aimed at providing a measure of the degree of overall contamination in surface layers in a particular core or sampling site. The assessment of sediment contamination was carried out using the contamination factor and the degree of contamination and the data are presented in Table 4.

Table 4 Contamination factor (C_f) and Degree of contamination (C_d) for Thengapattinam Estuary

Station	Cd (C_f)	Cr (C_f)	Cu (C_f)	Fe (C_f)	Mn (C_f)	Pb (C_f)	Zn (C_f)	Degree of contamination (C_d)
1	0	0.2406	0.6142	0.0954	0.0570	0.2712	0.4759	1.7543
2	0.6233	0.2618	0.4718	0.1284	0.0621	0.1224	0.5074	2.1772
3	1.6467	0.3007	0.7458	0.3022	0.1601	1.0780	1.3979	5.6314
4	0	0.26017	0.5009	0.0781	0.0147	0.1246	0.6759	1.6544
5	0	0.2939	0.5798	0.0559	0.0117	0.3867	0.3874	1.7154
6	0	0.2386	0.5718	0.0668	0.0599	0.2151	0.3697	1.5219
7	0	0.2058	0.5189	0.0650	0.0384	0.2301	0.3377	1.3959
8	0	0.2299	0.4369	0.1645	0.1047	0.3696	0.4583	1.7639
9	0	0.2480	0.5704	0.1756	0.1184	0.4369	0.5859	2.1352
10	0.4010	0.1455	0.3553	0.0197	0.0152	0.1821	0.2983	1.4171
Mean	0.2671	0.2425	0.5366	0.1152	0.0642	0.3417	0.5494	2.1167

In Thengapattinam estuary, maximum mean contamination factor was observed for Zn for which $C_f = 0.5494$ (Table 4).The degree of contamination was found to be high (5.6314) in station 3. In station 3, the C_f for Cd, Pb and Zn was greater than unity indicating that the sediment at station 3 was moderately contaminated with these metals. Mean contamination factor of all the metals indicated that the estuary was contaminated with metals only to a lower degree. Based on the values of C_d, all the stations were found to be of low contamination with metals. On the basis of the mean values of C_f, Thengapattinam sediments were enriched with metals in the following order: Zn> Cu> Pb> Cd> Cr> Fe> Mn.

Enrichment factor of heavy metals (EF)

Enrichment factor [33] was employed to assess the degree of contamination and to understand the distribution of the elements of anthropogenic origin from sites by individual elements in sediments. Fe was chosen as the normalizing element while determining EF values, since in wetlands it is mainly supplied from sediments and is one of the widely used reference element [15,28,34]. Other widely used reference metal elements include Al and Mn [35]

Enrichment factor = (C_n/Fe) sample/ (C_n/Fe) background,

where, C_n is the concentration of element "n". The background value is that of average shale [30]. An element qualifies as a reference one if it is of low occurrence variability and is present in the environment in trace amounts [34]. Elements which are naturally derived have an EF value of nearly unity, while elements of anthropogenic origin have EF values of several orders of magnitude [36]. A value of unity denotes no enrichment or depletion of elements relative to earth's crust. Six categories are recognized: < 1 background concentration, 1- 2 depletion to minimal enrichment, 2 –5 moderate enrichment, 5 – 20 significant enrichment, 20– 40 very high enrichment and > 40 extremely high enrichment [37].

EF values greater than 1.5 is a clear indication that the heavy metals derived from other sources suggesting environmental contamination by those particular heavy metals [38]. It is presumed that high EF values indicates an anthropogenic source of trace metals mainly from activities such as industrialization, deposition of industrial wastes etc. [38]. Measuring enrichment factor (EF) is an essential part of geochemical studies and is generally used to differentiate between the metals originating from anthropogenic and geogenic sources, and to assess the degree of metal contamination [39].

Table 5- Enrichment factor (EF) and Pollution load index (PLI) of heavy metals in sediments of Thengapattinam Estuary

Station	Cd	Cr	Cu	Fe	Mn	Pb	Zn	PLI
1	0.0000	2.5216	6.4386	1.000	0.5974	2.8424	4.9886	0.0000
2	4.8548	2.0389	3.6744	1.000	0.4840	0.9529	3.9517	0.2337
3	5.4496	0.9950	2.4681	1.000	0.5299	3.5676	4.6263	0.5967
4	0.0000	3.3307	6.4139	1.000	0.1885	1.5955	8.6549	0.0000
5	0.0000	5.2565	10.370	1.000	0.2096	6.9165	6.9284	0.0000
6	0.0000	3.5695	8.5556	1.000	0.8959	3.2186	5.5316	0.0000
7	0.0000	3.1674	7.9869	1.000	0.5912	3.5418	5.1977	0.0000
8	0.0000	1.3975	2.6559	1.000	0.6367	2.2469	2.7862	0.0000
9	0.0000	1.4122	3.2484	1.000	0.6740	2.4876	3.3363	0.0000
10	20.320	7.3757	18.006	1.000	0.7708	9.2250	15.116	0.1189
Max	20.320	7.3757	18.006	1.000	0.8959	9.2250	15.116	0.5967
Min	0.0000	0.9950	2.4681	-	0.1885	0.9529	2.7862	0.0000
Mean	3.0624	3.1065	6.9817	1.000	0.5578	3.6595	6.1118	0.0949
SD	6.4323	1.9677	4.7267	0.000	0.2226	2.5259	3.5946	0.1928

Also EF is a convenient measure for making comparisons between areas. Table 5 shows that the mean enrichment factors for Cd, Cr, Cu, Fe, Pb, Mn and Zn vary between 0 and 10, indicating that the Thengapattinam sediments are not affected by anthropogenic influences. At station 10, the enrichment factor for Cd, Cu and Zn were high indicating anthropogenic source of trace metals, Cd, Cu and Zn mainly from activities such as discharge from agricultural fields and deposition of industrial wastes etc. The results indicate that station 10 was affected by the anthropogenic heavy metal loading from AVM canal and Tamirabarani River and it was the bar mouth which discharge these metals into the Arabian sea. Based on the EF values it may be concluded that all the stations of Thengapattinam estuary were equally enriched with one or more metals.

Pollution Load Index (PLI)

Pollution load index for each sample was evaluated as indicated below [40]

Pollution load index= $(C_{f\,1} \times C_{f\,2} \times ..... \times C_{f\,n})^{1/n}$

Where, n is the number of metals and C_f is the contamination factor. The PLI value > 1 indicates pollution whereas PLI value < 1 indicates no pollution [15,28]. This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. A value of zero indicates perfection, a value of one indicates only baseline levels of pollutants present and values above one would indicate progressive deterioration of the site and estuarine quality [40].

The PLI values for heavy metals Cd , Cr, Cu, Fe, Mn, Pb and Zn in the Thengapattinam estuary sediments are listed in Table 5 and they ranged from 0 to 0.5967 with a mean value of 0.0949. At all sampling stations in the estuary, the PLI value was less than 1 suggesting perfection.

Conclusion

The results of this study provide valuable information on the metal contents of sediments from different stations of Thengapattinam estuary. Moreover these results can also be used to test the quality of the surface water and presence of chemical components in the sediment in order to evaluate the possible risk to the estuary. The assessment of the ecological risk using toxicity units based on numerical sediment quality guidelines (SQGs) and potential ecological risk indices indicated perfection in all sampling stations of Thengapattinam estuary. Therefore it can be concluded that the input of AVM canal into the Thengapattinam estuary is alone responsible for the pollution of the sediment and must be regarded as a major concern.

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