

Geochemical Assessment of Metal Concentrations in Mangrove Sediments along Mumbai Coast, India

Lina Fernandes, G. N. Nayak and D. Ilangoan

Abstract—Two short sediment cores collected from mangrove areas of Manori and Thane creeks along Mumbai coast were analysed for sediment composition and metals (Fe, Mn, Cu, Pb, Co, Ni, Zn, Cr and V). The statistical analysis of Pearson correlation matrix proved that there is a significant relationship between metal concentration and finer grain size in Manori creek while poor correlation was observed in Thane creek. Based on the enrichment factor, the present metal to background metal ratios clearly reflected maximum enrichment of Cu and Pb in Manori creek and Mn in Thane creek. Geoaccumulation index calculated indicate that the study area is unpolluted with respect to Fe, Mn, Co, Ni, Zn and Cr in both the cores while moderately polluted with Cu and Pb in Manori creek. Based on contamination degree, both the core sediments were found to be considerably contaminated with metals.

Keywords—Creek, Igeo, Mumbai, trace metals

I. INTRODUCTION

MANGROVES dominate the world's coastline and are one among the most productive ecosystems, lying between the land and sea in the tropical and sub-tropical latitudes [1], [2]. Mangrove ecosystems are known for their activity viz. primary producers, shoreline protectors, nursery grounds and as habitats for a variety of animals. They play a crucial role in the biogeochemical cycling of phosphorus, carbon, nitrogen and other nutrients [3]. Throughout-welling of leaf litter and dissolved organic matter, mangroves act as detritus source to the adjacent oligotrophic marine food webs, supporting valuable estuarine and coastal fisheries [4]. Mangroves with their ability to trap sediments are believed to be an important sink of suspended sediments [5]-[8] which are introduced into coastal areas by river discharge. Mangrove sediments being anaerobic and reduced; with high sulphide and organic matter content, have a high capacity to retain heavy metals received from tidal water; river freshwater; stormwater runoff; atmospheric fallout and anthropogenic additions. Many mangrove ecosystems which are close to urban development areas [9] are therefore impacted by urban and industrial run-off, which contains trace and heavy metals in the dissolved or particulate form.

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Maharashtra, one of the important coastal states of India, is endowed with unique mangrove diversity spread all along its 720 km coastline, distributed in about 55 estuaries in five districts. Rapid developments like housing, industrialization and increasing population in and around Mumbai have resulted into degradation of most of the mangroves. In the present study, an attempt has been made to investigate the mangrove sediments of Manori and Thane creek with an aim to determine the concentration as well as the vertical distribution pattern of selected metals in sediment and, to understand the degree of anthropogenic influence on metal concentrations with the help of various pollution indices.

II. MATERIALS AND METHODS

A. Study Area

Manori Creek, located in north-western Mumbai, spreads around latitudes $19^{\circ}11'N$ to $19^{\circ}15'N$ and longitudes $72^{\circ}47'E$ to $72^{\circ}50'E$ (Fig. 1). The creek is fed by Dahisar River and has abundant mangroves, mudflats and low-lying marshy areas. The northern bank of the creek is relatively less developed and forms a natural beach. The upstream part of the creek is known as the Gorai Creek. The creek is shallow and receives semidiurnal tides with spring and neap of 3.5 and 1.8 m respectively, in the mouth area, that result in good tidal flushing of the lower reaches. There are no major industrial units in the area, however point discharges of domestic wastewater in the inner creek might exert some influence on water quality.

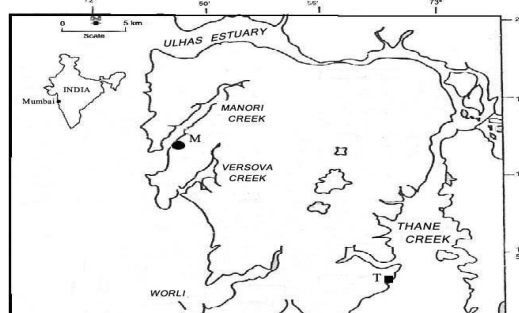


Fig. 1 Map showing Sampling locations

The Thane creek lies at latitudes $19^{\circ}00'N$ to $19^{\circ}15'N$ and longitudes $72^{\circ}55'E$ to $73^{\circ}00'E$. The creek is fringed with mangroves along both the banks coupled with heavy industrialization and urbanization. Geologically, Mumbai - Thane region is part of the Deccan trap that was formed by

volcanic effusions at the end of the cretaceous period [10]. The creek is narrow and shallow at the riverine end and broader and deeper towards the sea. It receives about 294 mld (million liters per day) and 145 to 260 mld of industrial and domestic wastes, respectively, within Thane city limits [11]. The diversified industries along the banks of the creek, which includes chemical, textile, pharmaceutical, engineering and major fertilizer complex, release through their effluents high levels of nitrates and phosphates into the creek [12]. Both the creeks are found to be dominated by *Avicennia* mangrove species. However, in the case of Thane more cutting of mangrove for various purposes such as for fuel, acquiring land for aquaculture ponds, solid waste dumping, reclamation of mudflat for road, bridge, building construction etc., have resulted in destruction of mangroves [13] as compared to Manori, which sustains a better coverage and harbours dense mangrove formation.

B. Sampling and Analysis

In order to meet the objectives of the study, sediment cores of 38 and 68 cm lengths were collected from the mangrove regions of Manori and Thane creek respectively (Fig. 1), by driving a hand held PVC tube (150 cm length and 6.5 cm diameter) into the sediment. The sampling was carried out at low tide when the regions were well exposed. Both the cores were collected to represent mangroves near creek mouths, however, Manori core was sampled at some distance away from the creek mouth while the Thane core was collected closer to the creek mouth. GPS was used to determine the geographical co-ordinates.

In the laboratory, the cores were sectioned at 2 cm interval, transferred to labeled polythene bags and maintained at low temperature (4°C) till further analysis. Later, the subsamples were oven dried at 60°C. Analysis of sediment component was carried out using standard sieve and pipette techniques [14]. For the remaining parameters, the sediment was ground and homogenized using mortar and pestle. Total organic carbon (TOC) content was determined based on Walkley and Black [15], Total Nitrogen (TN) and Total Phosphorus (TP) by Grasshoff [16] method. For elemental analysis, samples were completely dissolved and dried on a hot plate using mixed acid (HF: HNO₃: HClO₄) [17]. The digested samples were then aspirated for Al, V, Fe, Mn, Cu, Pb, Co, Ni, Zn and Cr with the help of Varian AA 240 FS flame atomic absorption spectrometry (AAS) with an air/acetylene flame for all of the above elements except for Al and V (nitrous oxide/acetylene flame was employed) at specific wavelengths. Together with the samples, certified reference standard from the Canadian National Bureau of Standards (BCSS-1) was digested and run, to test the analytical and instrument accuracy of the method. The recoveries were between 86-91 % for Fe, Cu, Ni and Al; 87-92 % for Mn and Co; 80-85 % for Pb and Zn; 90-95 % for Cr; 82-90 % for V, with a precision of +6 % standard deviation. Pearson's correlation test at p<0.05 was employed to verify the possible relation among the variables studied using the software STATISTICA 6.0.

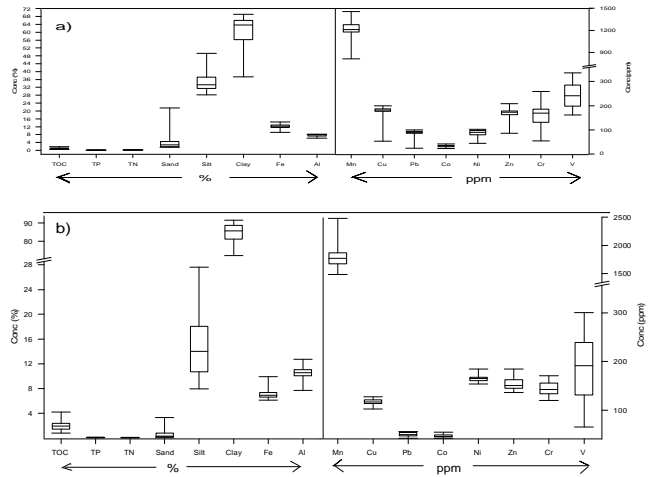


Fig. 2 Range and average for a) Manori core and b) Thane core

III. RESULTS AND DISCUSSION

A. Association of Metals with Organic Matter And Sediment Components

Organic carbon and clay contents are major controlling factors that have influence on the binding of heavy metals [18]-[20]. This can be demonstrated by correlating heavy metal concentrations with organic carbon and clay content. The significant correlations observed between TOC with TN ($r = 0.46$) and TN with Cu ($r = 0.51$), Ni ($r = 0.65$) and Zn ($r = 0.53$) in Manori core; TOC with Cu ($r = 0.61$), Co ($r = 0.36$) and Zn ($r = 0.59$), and TN with Mn ($r = 0.41$) in Thane core indicates that they have a common source. This suggests that, probably these metals may have been introduced to the creek via organic materials. In coastal environments such as in mangroves, the associations between organic matter, - granulometric fractions, heavy metals and base cations act as functions of ionic strength of sediment solution and surface cation complexation [21]. Also in Manori core, the concentrations of TOC, TN, Ni and Zn are found to increase near the surface as compared to the bottom. The increase of chemical material deposition to coastal waters can be related to intensive applications of inorganic fertilizers and also to the population growth [22]. Further, increasing inputs of land derived sedimentary matter [23]; and organic C and N-contained materials [24] associated with urban wastes, must have also contributed to the increase of these elements.

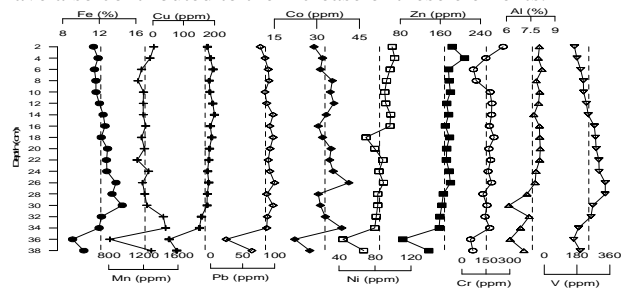


Fig. 3 Down core variations of metals for Manori creek

In the case of sediment components, all the elements studied show a strong correlation with clay in Manori core while in Thane core such association is not observed, even though, both the mangrove areas are found to exhibit dominance of finer sediment fraction (Fig 2). Therefore, it must be the difference in sediment composition and the proximity of the study area to the mouth of the creek that must be resulting in the above observation. Manori core was collected further away from the main channel of the creek mouth as compared to the Thane core, which was sampled closer to the proximity of the creek mouth. Due to lack of vigorous water motion in Manori, the fine sediments tend to settle on the bottom along with organic matter, rather than get widely dispersed by flushing which is the case for Thane. Fine material, with a larger surface to volume (or weight) ratio, has a greater potential to scavenge both inorganic and organic pollutants from the water column [25]. As a result, mud/silt/clay sediments with high organic content retain more contaminants than relatively coarse sandy sediment [26]. Fernandes and Nayak [27] found similar observation in a study carried out on estuarine mudflats of Mandovi River.

When the depthwise plot of metals (Fig 3) are observed in Manori core, the redox-sensitive elements viz. Fe and Mn are found to correlate well with each other and accordingly control the vertical distribution of most of the metals (Cu, Pb, Co, Ni, Zn, Cr and V), especially in the lower portion of the core. This significant correlation between Fe and Mn suggests the presence of Fe/Mn compounds and their strong association to the geochemical matrix. According to the study of Zabetoglou et al. [28], Fe and Mn oxides/hydroxides have high affinity with most trace metals and Fe often correlates with concentrations of other metals in aquatic environments. However, such a correlation is not seen in the case of Thane core (Fig 4), where only Mn is found to correlate well with most of the studied elements as compared to Fe indicating Mn is the major source for metal absorption at this location. The statistical analysis of intermetallic relationship reveals high degree of positive correlations among the metals studied for both the cores. However, Manori core shows a better metal-metal association as compared to Thane core. These associations can be explained in terms of identical source; identical behaviour of the metals during their transportation [29] and/or post depositional processes.

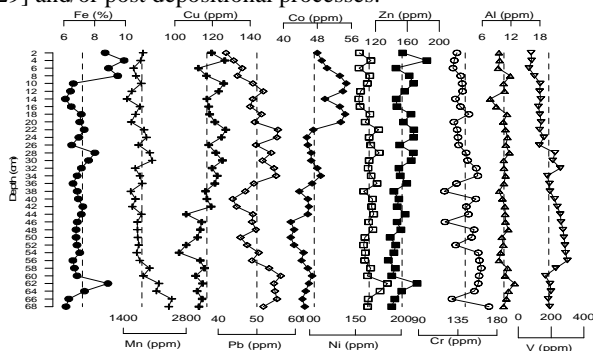


Fig. 4 Downcore variations of metals for Thane creek

B. Pollution Indices

Mangrove sediments have been extensively studied all over the world to assess the pollution status of the sediments. For example, a study carried out by Kehrig et al. [30] in Jequia mangrove forest, Brazil concluded that the mangrove forest had been polluted with heavy metals by the anthropogenic sources surrounding the estuary while, Ramanathan et al. [31] reported the concentration of heavy metals in Pichavaram mangrove forest in India were generally below the levels found in polluted and unpolluted estuaries and mangroves. Increase of heavy metals in the mangrove sediment was attributed to the abundance of fine particle with greater surface area by Forstner and Wittman [32] and precipitation of metals as hydroxide coating (mainly Fe and Mn) over finely dispersed particles [33]. In the present study, in order to evaluate the levels of sediment contamination, Enrichment factor (EF), Index of geoaccumulation (Igeo), Contamination factor (Cf) for each of the metals; Contamination degree (Cd) and Pollution load index (PLI) for each creek was calculated.

1. Enrichment Factor (EF)

The EF is a convenient measure of geochemical trends and is used for making comparisons between areas [34]. The values of EFs are obtained using equation 1,

$$EF = \frac{[(\text{metal}/\text{Al})]_{\text{sample}}}{[(\text{metal}/\text{Al})]_{\text{shale}}} \quad (1)$$

Where $(\text{metal}/\text{Al})_{\text{sample}}$ is the metal to Al ratio in the sample of interest, $(\text{metal}/\text{Al})_{\text{shale}}$ is the natural background value of metal to Al ratio [35]. The concentrations of average shale given by Turekian and Wedepohl [36] have been adopted as the background value for this study. EFs close to 1.5 indicate crustal origins while those greater than 1.5 are considered to be of non-crustal source [37].

The calculation of enrichment factor for both the cores show that most of the selected metals are enriched in the mangrove sediments. In Manori core, Pb and Cu (avg. 4.50 and 3.93) have the highest EF values among the metals studied. Co, Zn, Cr, V and Mn have minor enrichment (avg. 1.82, 1.86, 1.93, 1.98 and 2.14, respectively) whereas Ni exhibits the lowest EF value (avg. 1.31). In the case of Thane core, Mn shows the highest EF value (average 2.30) followed by Cu (avg. 1.99), Pb and Co (avg. 1.90), Ni (avg. 1.85), Cr (avg. 1.32) and Zn (avg. 1.23). V (avg. 1.09) exhibits the lowest EF value. Factors like enhanced organic matter content, flocculation due to varying salinity regimes [38] and transportation of sea sediments to the coastal zone [39]-[41] contribute significantly towards the enrichment of heavy metals in sediments. When the EF is observed for the entire length of Manori core, high values are seen in the upper portion compared to the lower portion of the core for all the metals except Mn and Co. This clearly indicates the creek is getting enriched with metals of anthropogenic origin. Study by Fernandes et al. [42] on mudflats along Manori creek showed high metal enrichment in recent sediments. On the other hand in Thane creek, the values are higher for Fe, Mn, Cu, Co and Ni in the upper few cm of the core. The enhanced values of trace metals might have resulted from an increase in

anthropogenic fluxes related to the urban and industrial development in recent years.

2. Index of Geoaccumulation (Igeo)

The Igeo introduced by Muller [43] is used to assess metal pollution in sediments given by equation 2,

$$I_{geo} = \text{Log}_2 (C_n/1.5B_n) \tag{2}$$

Where, C_n = measured concentration of heavy metal in the mangrove sediment, B_n = geochemical background value in average shale [36] of element n and 1.5 is the background matrix correction factor due to lithogenic effects.

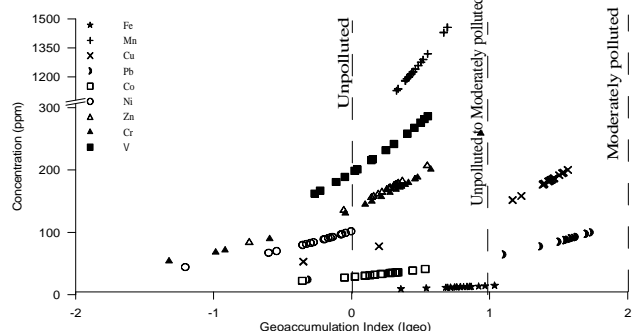


Fig. 5 Metal concentration and Igeo plot for mangrove core from Manori creek (Fe unit is %)

Karbassi et al. [44] elaborated that Igeo values can be used effectively and are more meaningful in explaining the sediment quality. The Igeo index, when computed for Manori core (Fig. 5), shows that all the metals fall within Class 1 and Class 2 of Muller’s grade scale (Table I). This suggests that the mangrove sediments of Manori creek are moderately polluted with Pb and Cu while unpolluted with respect to the remaining metals. From the values of Igeo calculated, vehicular traffic in the populated stretch of this creek as well as mechanized boats for fishing may have lead to the emission of Pb and its deposition at local scale. The increasing use of Cu as anti-fouling agent on fishing trawlers and other commercial boats being operated in the study area might be one of the reasons for the increase in Cu concentration in recent years [45].

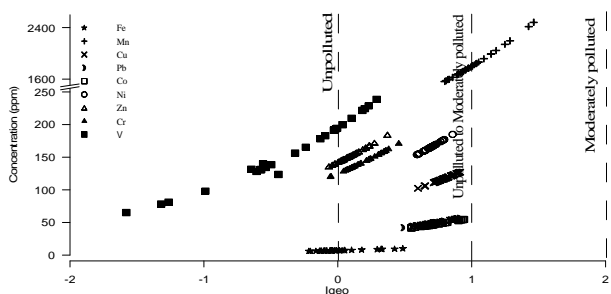


Fig. 6 Metal concentration and Igeo plot for mangrove core from Thane creek (Fe unit is %)

TABLE I
GEOACCUMULATION INDEX PROPOSED BY MULLER (1979)

Pollution Intensity	Sediment Accumulation	Igeo class
Very strongly polluted	>5	6
Strongly to very strongly polluted	4-5	5
Strongly polluted	3-4	4
Moderately to strongly polluted	2-3	3
Moderately polluted	1-2	2
Unpolluted to moderately polluted	0-1	1
Practically unpolluted	<0	0

In Thane creek, all the elements except for a few subsamples for Mn falls in unpolluted to moderately polluted class (Fig. 6). Also, the Mn value is found to fluctuate to the moderately polluted class as the depth increases. An extensive study carried out by Sharma et al. [46] in the Thane creek-Bombay harbour complex, reported higher concentration of Mn with depth in the coastal areas around Thane creek. This was attributed to authogenic source of Mn in the form of hydroxide floccules. Further, they suggested that the dissolved Mn when entering the sea comes in contact with alkaline and oxidizing environments and tends to precipitate as insoluble, finely divided MnO. However in the recent years, increase in organic pollutant loads might have resulted in the decrease of the authigenic Mn precipitation. The high organic matter must have lowered the dissolved oxygen content of water which consequently decreased the flocculation intensity of MnO in the water column resulting in observed lower Mn concentration.

3. Contamination Degree (Cd)

The assessment of the overall contamination of sediment was attempted based on the degree of contamination (Cd). The sum of the contamination factors of all elements examined represents the contamination degree (Cd) of the environment (Equation 3).

$$Cd = \sum_{i=1}^m Cfi \tag{3}$$

C_f = C_e/C_b, where C_e = concentration of the element in sediment samples, C_b = background value for the element taken from average shale [37], m are multiple metals. The following four classes [47], [48] have been used to define the degree of contamination of each creek in the present study.

$Cd < 7$ = low degree of contamination, $7 \leq Cd < 14$ = moderate degree of contamination, $14 \leq Cd < 28$ = considerable degree of contamination, $Cd \geq 28$ = very high degree of contamination. The values of contamination degree for metals for Manori and Thane cores (Table II) indicate considerable degree of contamination. However, the values are found to be higher in Manori creek as compared to Thane creek. This observation can again be attributed to the different sampling location of the core, with respect to mouth and tidal flushing influence on the locations.

4. Pollution Load Index (PLI)

Tomlinson et al. [49] employed a simple method based on PLI to assess the extent of pollution by metals in estuarine sediments [50]. PLI is calculated using the equation 4,

$$PLI = n \sqrt{Cf_1 * Cf_2 * \dots} \quad (4)$$

Where, Cf is the contamination factor, n the number of metals and world average concentration of elements reported for shale are taken as their background values [36]. The PLI represents the number of times by which the metal content in the sediment exceeds the average natural background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The PLI value of > 1 is polluted whereas < 1 indicates no pollution. In the present study, the PLI values of Manori core (Table II) are found to decrease with depth while that of Thane core (Table II) show an increase. In Manori creek, increase in recent sediments may be due to the influence of external discrete anthropogenic sources like agricultural runoff and atmospheric inputs.

IV. CONCLUSION

The results of the present investigation essentially contribute to the knowledge on the extent of pollution of sediments of Mumbai creeks. The present study carried out on sediment cores from mangrove ecosystem of Mumbai region, helped in understanding distribution and concentration of elements with time. The different indices of pollution computed indicate that the mangrove sediments are moderately polluted with Pb and Cu in Manori creek and with Mn in Thane creek; while unpolluted with respect to the other elements studied. Further, it is seen that finer sediment components and organic matter along with Fe and Mn oxides play an important role in concentration and remobilization of elements in the mangrove sediments especially in Manori core. From the study we can conclude that the core collected from Mangrove region of Thane creek being close to the proximity of the sea did not act as a sink for metal deposition. The wastewater discharged through drains and tidal tributaries get flushed into the sea before they could get absorbed onto the suspended matter and settle. On the other hand, the mangrove core sampled from Manori creek showed some signs of metal deposition especially for Cu and Pb. Pb from vehicular traffic and use of Cu in anti fouling paints must be the prime source of pollution.

TABLE II
POLLUTION LOAD INDEX OF MANORI AND
THANE CREEKS FOR SELECTED METALS

Depth (cm)	Manori		Thane	
	Cd	PLI	Cd	PLI
2	21.72	2.39	18.30	1.87
4	21.60	2.35	19.27	1.98
6	20.58	2.08	17.92	1.81
8	20.82	2.14	19.03	1.99
10	21.68	2.32	19.42	2.04
12	22.35	2.38	18.82	1.98
14	23.08	2.42	17.89	1.89
16	22.51	2.34	18.76	1.98
18	22.86	2.32	19.28	2.03
20	22.54	2.32	18.69	1.97
22	22.54	2.33	19.70	2.07
24	22.67	2.34	19.63	2.08
26	24.15	2.48	18.45	1.94
28	21.90	2.19	20.67	2.23
30	22.46	2.30	20.36	2.19
32	21.25	2.22	20.04	2.17
34	21.12	2.29	19.77	2.11
36	10.28	1.07	19.36	2.07
38	15.51	1.61	18.08	1.95
40			19.09	2.07
42			19.11	2.08
44			19.64	2.13
46			18.91	2.04
48			19.59	2.13
50			19.06	2.07
52			18.99	2.06
54			19.48	2.12
56			19.65	2.12
58			20.06	2.15
60			19.35	2.06
62			21.17	2.27
64			20.33	2.17
66			20.00	2.08
68			20.20	2.12

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