

Sedimentary geochemistry of Chorao Island, Mandovi mangrove estuarine complex, Goa

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Present study highlighted significant anthropogenic contributions in terms of heavy metal pollution in Mandovi estuarine complex. Sediment core was collected which was analyzed for different physico-chemical parameters. Sediments were found to be mature, quartz rich and weathering does not seem to play any role. Biological activities were significant due to abundance of S and OC in the sediments which along with the redox conditions controlled the metal variability. Sediments were found to be enriched with respect to heavy metals like Pb and Mn indicating anthropogenic influence in this region.

[Key words: Sediments, Trace metals, Nutrient, Anthropogenic pollution, Chorao Island]

Introduction

Mangroves are highly specialized ecosystems restricted to the latitudes between 30°N and 30°S, they almost cover up to 75% of coastlines worldwide¹. Mangrove sediments are highly anaerobic rich in sulphides and organic matter². They, therefore, favour the retention of water-borne heavy metals and the subsequent oxidation of sulphides between tidal events, allowing metal mobilization and bioavailability^{2,3}.

Chorao Island in Mandovi is one of the best mangrove forests and houses most of the mangrove species found in Goa. It is situated at the confluence of Mandovi and Mapusa rivers and is a well-known tourist spot for the presence of Salim Ali Bird Sanctuary. The wildlife sanctuary supports rich mangrove forests, which are home to a host of birds, a sizeable population of flying foxes, jackals, crocodiles, turtles and some other life forms endemic to coastal wildlife.

Goa is rich in mineral deposits such as iron ore, manganese ore and bauxite. The open-cast mining operations in Goa are mainly export-oriented and these strongly affect the chemistry of the mangrove ecosystems⁴. Rivers of Mandovi and Zuari provide inland waterways and are extensively used to transport minerals ores from the mines to the ports⁵. Tourism is a major industry in Goa and is mainly concentrated along the coastal stretches of the state. Untawale *et al.*⁶ described the impacts of urbanisation on the coastal environments which are responsible for drastic changes in the coastal configurations. Also deforestation in the catchment areas and mining activity has added to the increased sedimentation and pollution load of the rivers and estuaries⁷. Present study was undertaken to assess the anthropogenic stress on the geochemistry of Chorao Island, Mandovi Mangrove estuarine ecosystem with the objectives (a) to assess the variability of nutrients in sedimentary environment, (b) to assess the heavy metals concentration in the core sediments and (c) to assess the anthropogenic stress on the Mangrove ecosystem.

Materials and Methods

Mandovi is confined between latitude 15° 09' and 15° 33' N and longitude 73° 45' and 74° 14' E and has a direct opening into the Arabian Sea (Fig. 1). Sediment core was collected from Chorao Island



Fig. 1–Map of the study area: Chorao Island, Mandovi Mangrove estuarine system

(15°31'5.00"N, 73°51'32.26"E) in the Mandovi estuarine system in the month of June 2009 in order to understand the nutrient and heavy metal status and variability. The sampling position was noted down by using the portable GPS (Global Positioning System, Germin etrex make model). The core was collected using an acrylic tube, about 25 cm long, with a diameter of 5.5 cm. The core was sub sampled on site with 1 cm intervals. The sliced samples were stored in ice box on field and were immediately transferred to laboratory for further analysis.

Sediments were analyzed for their mineralogy using X-ray diffraction (Powder) technique (XRD, PANalytical X'pert PRO).

The Moisture content and LOI were calculated using the following equations⁸.

$$\% \text{ Moisture content} = ((SW - DW_{105}) / DW_{105}) \times 100$$

$$LOI_{550} = ((DW_{105} - DW_{550}) / DW_{105}) \times 100$$

Where LOI_{550} represents LOI at 550°C (as a percentage) i.e. Sedimentary Organic matter, SW represents the sediment weight taken initially before overnight drying, DW_{105} represents the dry weight of

the sample before combustion and DW_{550} the dry weight of the sample after heating to 550°C (all in g). Further the sample was combusted again at 950° C for 2 hours and reweighed. LOI was calculated using the following equation:

$$LOI_{950} = ((DW_{550} - DW_{950}) / DW_{105}) \times 100$$

Where LOI_{950} represents LOI at 950°C (as a percentage) depicting the inorganic carbon viz. carbonate., DW_{105} represents the dry weight of the sample at 105°C and DW_{550} the dry weight of the sample after heating to 550°C and DW_{950} the dry weight of the sample after heating to 950°C (all in g).

Biogenic Silica (BSi) was extracted from the from oven dried samples (at 75°C) sediment (25 mg) in a 0.1 M Na_2CO_3 solution at 80°C. Subsamples for extracted BSi (as DSi) were taken after 180, 240 and 300 min. Dissolved silica was measured spectrophotometrically. BSi was calculated by linear extrapolation through the 3 extraction points in a time-extracted silica plot⁹.

Analyses of major and minor elements were carried out by the two solution methods¹⁰. Solution “A” (obtained by the alkaline digestion of the sediments) was used for silica, alumina and phosphorus analysis and solution “B” (obtained by the acidic digestion of the sediments) was used for metal analysis. The dissolved silica content was determined by the Molybdate silicate method¹¹. The Alumina content was determined by the standard protocol of APHA¹¹. Phosphorous was analysed as per the standard protocol of Presley¹². Solution B was used for analyzing Heavy metals (Fe, Mn, Cr, Pb, Zn, Cd) using Atomic Absorption Spectrophotometer (THERMO Scientific, M Series).

The sediment samples were analyzed for total carbon (TC), total nitrogen (TN) and total sulphur (S) using EURO EA elemental analyser. The observed results were statistically analyzed using computer aided packages viz. SPSS (Version 19).

The geoaccumulation index (I_{geo}) was originally defined by Müller¹³ for a quantitative measure of the metal pollution in aquatic sediments.

The Index of Geoaccumulation (I_{geo}) was computed using the equation^{13,14}:

$$I_{geo} = \log_2 (C_n / 1.5 B_n)$$

Where, C_n is the measured concentration of the element in the sample and B_n is the geochemical background value (average shale) in the earth's crust¹⁵. The constant 1.5 allows for natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. Six classes of geochemical index have been distinguished.

According to Salomons and Forstner¹⁶, the contamination in an area can be inferred from the Enrichment Factor (EF), which is the ratio between metal/Al in the sample and metal/Al in the average shale and this provides an effective tool to evaluate sediment quality and aids in making comparisons between different areas.

$$EF = \{ C_n(\text{sample}) / C_{ref}(\text{sample}) \} / \{ C_n(\text{background}) / C_{ref}(\text{background}) \}$$

Where, $C_n(\text{sample})$ is the content of the examined element in the examined environment. The $C_n(\text{background})$ is the content of reference element in the reference environment. Five contamination categories are recognized on the basis of enrichment factor¹⁷.

Results and Discussion

The XRD analysis of the core sediments samples indicated that sediments were rich in Quartz. The mineralogy did not show any significant variation with depth.

The depth variation of Si and Al is depicted in the Fig. 2. Silica concentrations in the core sediments were more or less uniform indicating presence of uniform quartz content supporting the mineralogical observations. Mean concentration of Si in the mangrove sediments was 31.92% with maximum and minimum values as 37.2 and 25.9 % respectively. Percentage of Al concentration varied from 4 to 18 % with mean as 12.5 %. The Si/Al ratios are an indicator of the sediment maturity in context of the extent of weathering. Ratio varied from 2-7 with a

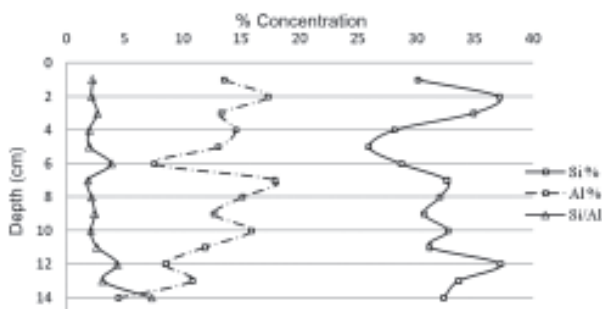


Fig. 2—Depth variations of Si, Al and Si/Al in the Mandovi core sediments.

mean value of 2.9 indicating that the sediments were well weathered and mature with higher Si content. The Si/Al ratio is also indicative of the variations in quartz content in the sediments¹⁸. Ratio increased with the depth and this can be related to enhanced input of quartz, which in turn may be due to Aeolian inputs¹⁹. Higher values can also be attributed as a consequence of the higher energy transport.

Depth variability of C, N, P and S

Figure 3 shows the variation of Total Carbon (TC), Organic Carbon (OC) and inorganic carbon (IC) in the Mandovi estuarine core sediments. Depth variation of OC in the sediments is a function of both the deposition rate of the sediment as well as decomposition and regeneration within the sediment. Reactivity of the decomposing organic matter (vegetation source) as well as prevailing sedimentary environment (burial rates, grain size, redox conditions, microbial populations etc.) plays an important role in governing carbon biogeochemistry in sediments²⁰. Mean concentration of TC in the sediments was 3.94 % ranging between 3.56 – 4.53 %. OC ranged from 2.48 – 3.28 % with a mean value of 2.77 %. Variation of IC with respect to depth was insignificant. OC constituted the major fraction of TC (nearly 70 %), governing the variability in TC (Fig. 3). TC and OC both showed the similar trend and increased with depth in general with maximum concentration peak at 9 cm, whereas, IC did not show much of variation. Dominance of OC can be attributed to the decomposition of organic foliage and other vegetative matter which contributed

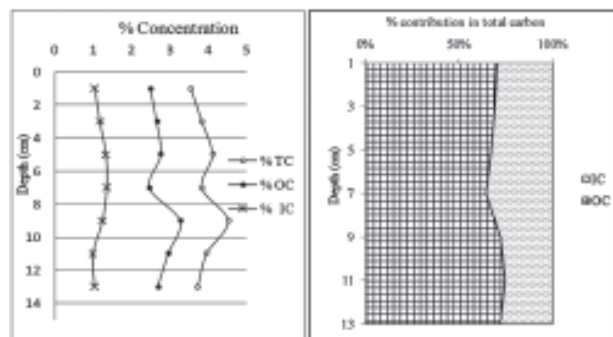


Fig. 3—Depth variation of C in the Mandovi core sediments and % contribution in TC

substantially to the organic matter content in the mangrove sediments²¹. Inherent biological productivity of the mangroves also contributes significantly to the organic content of the sediments²². Further, finely grained sediments favour the adsorptions of organic carbon²³.

Variations of TN in the sediments depend not only on the nature of the degrading organic matter but also on the sedimentary environment, hydrological conditions, microbial activities and anthropogenic input^{20,24}. In general TN concentration generally ranges from 0.2 to 0.4% of sediments dry weight in mangrove environment²⁵, though for Mandovi sediments it ranged between 0.39 – 0.56% (Fig. 4). Irregular pattern with depth for TN was observed with overall slight decrease in the concentration.

Phosphorus (P) plays an essential role in biological productivity of the aquatic ecosystems such as estuaries and coastal environment due to its limiting nature as compared to other nutrients^{26,27,28,29}. Global

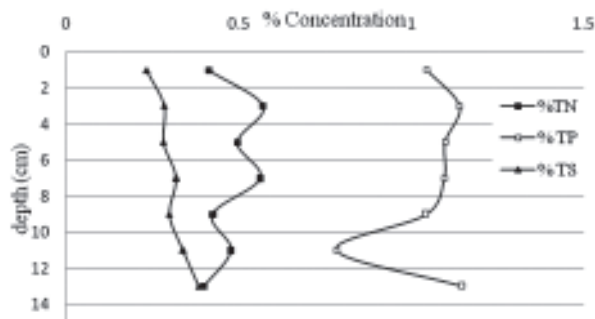


Fig. 4—Depth variations of TN, TP and TS in the Mandovi core sediments

average of phosphorus in the mangrove sediments varies between 100 – 1600 mg/kg²⁵. TP concentrations ranged from 0.7 – 1.1% and the values decreased as Fe levels control the P dynamics in the aquatic sediment. Iron (III) in oxic environment quenches phosphorus to form stable FeOOH-P³⁰. This could be considered as the possible reason for decreasing P concentrations with depth where increase in the reducing conditions would have prevented scavenging of P. Sulphur in the marine sediments has received considerable importance due to the pivotal role of sulphate reduction in the anaerobic respiration and the resultant production of authigenic sulphide minerals³¹. Total S concentrations showed a gradual increase in concentrations with the depth and its average concentration was 0.30%. Increase in concentration with depth can be attributed to the precipitation of sulphide sulphur in the sediments due to prevailing reducing condition.

Organic C/N elemental ratios have been employed as source indicators of sedimentary organic matter (OM) in numerous investigations based on the gross differences between respective organic matter pools and the general enrichment of marine derived organic material and elemental nitrogen relative to terrigenous matter^{32,33,34,35,36}. Vascular plants exhibit bulk chemical properties, which distinguish them from marine organisms. Presence of nitrogen-free biomacromolecule (like lignin, tannin, hemicellulose, cellulose, cutin, and suberin) over protein makes higher plant matter carbon-rich³³. Thus, marine phytoplankton have a mean C/N ratio ~7³², whereas terrestrial plants with soft tissue have C/N ratios from 10-100 and in woody material the ratio is from 100-1000³³. C_{org}/N values for the Mandovi sediments ranged from 4.4 – 7.7 indicating their source from the source of OM in Mandovi estuary is mainly derived from marine algae.

Depth variability of BSi

The most evident biological sink for Si is diatoms, single-celled organisms abundant in aquatic phytoplankton communities worldwide. Biogenic silica in sediments is known to be an important parameter to understand the biogeochemical

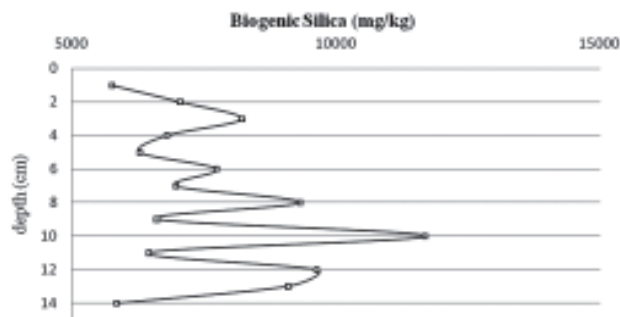


Fig. 5–Depth variation of BSi in the Mandovi core sediments

processes and paleo environmental records in estuarine and coastal ecosystems. Abiotic factors controlling BSi mobility are temperature, PH, and salinity³⁷. An increase of temperature, PH (over 6) or salinity has been reported to enhance BSi dissolution^{38,39,40}. Fig. 5 shows the depth distribution of BSi in the Mandovi sediments. BSi was found to be having an alternating trend with the depth. This alternative variation in the depth can be related to the algal (diatom) growth periods as they take up dissolved silicate and deposit it as BSi, within the protective coating of the diatom frustule⁴¹. The subsequent degradation of organic matter surrounding diatom cells and bacterial protease activity alters the BSi dissolution rates which vary vertically seasonally, and regionally to induce variation in BSi dissolution⁴².

Depth variability of Trace metals

Mangrove sediments are anaerobic and reduced, as well as are rich in sulphide and organic matter. They, therefore, favour the retention of water-borne heavy metals and the subsequent oxidation of sulphides between tides allows metal mobilization and bioavailability^{2,3}. Figure 6 represents the depth distribution of various trace metals in the sediments. High concentration of Iron (Fe), Manganese (Mn) and Lead (Pb) were observed in the core sediments whereas the concentration of Chromium (Cr) and Zinc (Zn) were low. Concentration of Fe was highest followed by Pb. High concentrations of Fe in sediments may be a result of prevalence mining activities in the Mandovi river basin⁵. Overall variation in Fe and Mn concentrations with respect to depth was insignificant even though irregular trends were observed. These irregular variations with respect

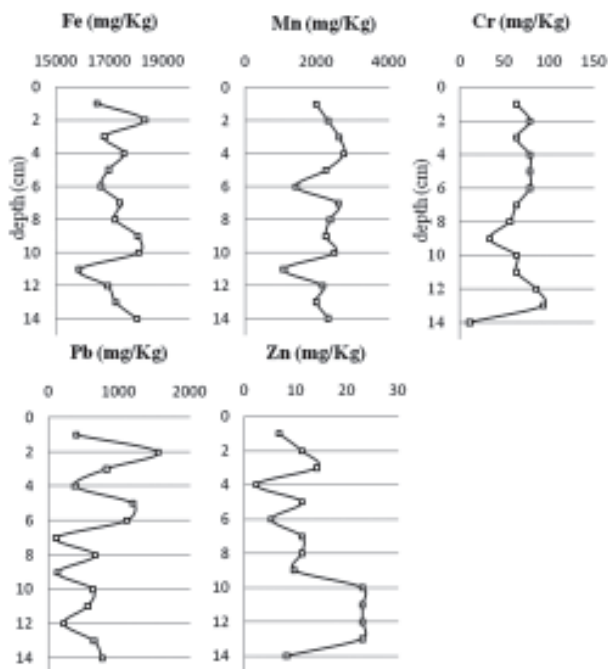


Fig. 6–Depth variation of Trace metals in the Mandovi core sediment

to depth can be attributed to the fact that Fe and Mn chemistry in sediments is largely influenced by redox conditions and microbiological activity⁴³. Tidal fluctuation and seasonal fluctuation may have resulted in these erratic trends, overall variations being insignificant.

The concentrations of Pb in sediments were considerably high. There has been heavy use of mechanised motorboats for recreational and transportation purpose in Mandovi estuary, Goa being a popular tourist destination. This may have also resulted in the localized deposition of lead. This, in turn, leads to the removal of Pb as sinking Pb-sulphides under reducing environment and subsequently enrichment in the core sediments. Pb showed somewhat similar trend like that of S with their concentrations increasing at deeper layers. Initial abrupt variation in Pb concentrations can be attributed to the changes in redox conditions in the upper core sediments due to tidal variations leading to oxidation of Pb sulphides. This can also be linked to the higher concentration of Pb in overlying water. In the deep sediments, the Pb values showed a decreasing trend.

The distribution pattern for the core (Fig. 7) was obtained by plotting organic carbon vs. metals and metal vs. metal for the sediments. Fe and Mn were associated with each other with no association with Cr. This indicated Fe and Mn share the same source

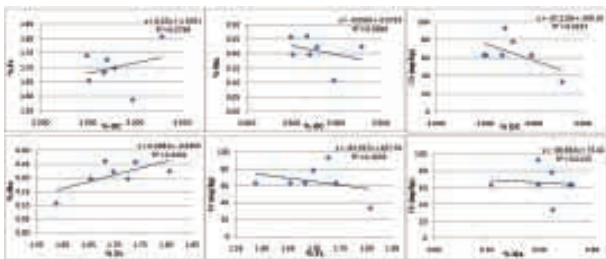


Fig.7–Distribution pattern and correlation – OC vs. metals and metals vs. metals of the core sediments.

that is due to the open cast mining activities carried throughout the estuary⁵. Fe and Mn in the sediments showed good association with P all through the depth whereas Cr and Zn showed association with OC (Figures 3, 4, 6). Specific association of different metals with P and OC reveals their role in remobilisation of the elements within the sediment. Mangrove sediments usually show a vertical redox zonation with an oxic upper layer where organic carbon is oxidized, overlying a reduced layer where generally sulphides are precipitated⁴⁴. Diagenetic reactions are important near the sediment–water interface, responding to redox changes and affecting metal concentration in vertical sediment profiles⁴⁵. Enhanced Fe and Mn values at the bottom are controlled by P⁴⁶. Significant correlation of Cr and Zn with OC suggest their preference for organic matter for chelation⁴⁷.

Table 2–Enrichment factor categorie

EF<2	Deficiency to minimal enrichment
EF=2-5	Moderate enrichment
EF=5-20	Significant enrichment
EF=20-40	Very high enrichment
EF>40	Extremely high enrichment

In order to understand the level of contamination with respect to trace metals, the values of trace metals were utilized to find geoaccumulation index (I_{geo}). While computing the I_{geo} of sediments of the study area, world average concentrations of these elements reported for Shale¹⁵ were taken as the background values. Increase of heavy metals in the mangrove sediment is primarily due to the enhanced organic matter content, abundance of fine particle with greater surface area¹⁶ precipitation of metals as hydroxide coating (mainly Fe and Mn) over finely dispersed particles⁴⁸, flocculation due to varying salinity regimes⁴⁹, transportation of deepshore sediments to the coastal zone etc.^{50,51}. Possible sediment enrichment of metals was evaluated in terms of the I_{geo} of Muller¹³. Geoaccumulation index (I_{geo}) was originally defined by Muller for a quantitative measure of the metal pollution in aquatic sediments⁵². This was applied for the Mandovi mangrove sediments shown in Table 3. Elevated I_{geo} values were identified for Pb and Mn. The I_{geo} indicates that the sediments are moderately to extremely contaminated with Pb and uncontaminated to moderately contaminated with Mn (Table 3). This was confirmed by the calculation of enrichment factor which was significant enough for

Table 1–Geo-Accummulation Index classes

Class	Value	Soil Quality
0	$I_{geo} < 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated
4	$3 < I_{geo} < 4$	Heavily contaminated
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

Table 3–Depth variation of Geo-accumulation index of the sediments

Depth (cm)	I _{geo} Classes						
	6	5	4	3	2	1	0
1	-	-	Pb	-	-	Mn	Fe, Cr, Zn
2	Pb	-	-	-	-	Mn	Fe, Cr, Zn
3	-	Pb	-	-	Mn	-	Fe, Cr, Zn
4	-	-	Pb	-	Mn	-	Fe, Cr, Zn
5	Pb	-	-	-	-	Mn	Fe, Cr, Zn
6	Pb	-	-	-	-	Mn	Fe, Cr, Zn
7	-	-	-	-	Mn, Pb	-	Fe, Cr, Zn
8	-	Pb	-	-	-	Mn	Fe, Cr, Zn
9	-	-	-	Pb	-	Mn	Fe, Cr, Zn
10	-	Pb	-	-	-	Mn	Fe, Cr, Zn
11	-	Pb	-	-	-	-	Fe, Cr, Zn, Mn
12	-	-	-	Pb	-	Mn	Fe, Cr, Zn
13	-	Pb	-	-	-	Mn	Fe, Cr, Zn
14	-	Pb	-	-	-	Mn	Fe, Cr, Zn

Table 4–Enrichment factor for the various metals in the core sediments

depth(cm)	Fe	Mn	Pb	Cr	Zn
1	0.21	1.37	11.52	0.42	0.04
2	0.18	1.25	35.91	0.40	0.05
3	0.22	1.86	24.74	0.42	0.09
4	0.20	1.78	10.29	0.48	0.01
5	0.22	1.61	36.59	0.53	0.07
6	0.38	1.76	58.69	0.92	0.06
7	0.17	1.36	2.38	0.32	0.05
8	0.19	1.47	17.41	0.33	0.06
9	0.24	1.68	3.84	0.24	0.06
10	0.19	1.47	15.84	0.35	0.12
11	0.23	0.85	18.60	0.47	0.16
12	0.34	2.38	9.90	0.90	0.23
13	0.27	1.72	23.84	0.77	0.18
14	0.69	4.91	68.63	0.22	0.16

Pb and Mn and insignificant for Fe, Cr and Zn (Table 4).

The correlation matrix was plotted for the core sediments (Table 5). It showed significant correlation between P and Fe & Mn which confirms the associations between the three. Fe and Mn correlations pointed out their source being the same and from the mining operations. Zn was found to be correlated with S indicating its presence and deposition in the form of sulphides. Cr-Pb-Zn correlation pointed out the same source for these elements. BSi was found to be correlated with Zn and S. Zinc is a chalcophilic element, but it complexes with OM⁵³. It mostly associates with OM through biological uptake as well as through adsorption and/ incorporation into the biologically resistant humic component in sediments. Zn correlates well with BSi and TS in mangrove sediments due to its affinity for biological uptake and with organic ligands in the mangrove forests and to form zinc sulphide with S ⁵⁴.

Conclusions

Overall the study highlighted that sediments were found to be mature, quartz rich and weathering does

Table 5–Correlation matrix for core sediments(n=14, p <0.05)

	OC	P	S	Si	Fe	Mn	Cr	Pb	Zn	BSi
OC	1.00									
P	-0.40	1.00								
S	0.18	-0.09	1.00							
Si	-0.21	0.19	0.40	1.00						
Fe	0.28	0.62	0.09	0.05	1.00					
Mn	-0.32	0.86	-0.30	0.19	0.67	1.00				
Cr	-0.57	0.28	0.42	0.03	-0.32	-0.11	1.00			
Pb	-0.12	0.16	-0.05	-0.35	-0.38	-0.04	0.60	1.00		
Zn	0.15	-0.35	0.86	0.38	-0.38	-0.58	0.50	0.22	1.00	
BSi	-0.13	0.49	0.68	0.72	0.22	0.25	0.49	0.16	0.59	1.00

not seem to play any role.The C/N ratio indicated marine origin of organic matter. The biological activities were significant due to abundance of S and OC in the sediments which along with the redox conditions controlled the nutrient variability. Metal concentrations were influenced by anthropogenic activities. High concentrations of Fe and Mn in sediments throughout the depth may have been a result of prevalence mining activities in the past as well as the present. Higher Pb concentration can be linked to the use of diesel for mechanised motorboats for recreational and transportation purposes apart from the sources from iron mining. However due to limited one time sampling and lesser data the conclusions cannot be generalised for overall characterisation of the Mandovi estuarine region. An extension of similar work in space and time is needed to improve the understanding of the nutrient and heavy metal dynamics for this region.

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References

1 Pernetta J C, Mangrove forests, climate change and sea level rise: hydrological influences on community structure

and survival, with examples from the Indo-West Pacific, *International Union for Conservation of Nature and Natural Resources*, (1993), pp. 45.

2 Silva C A R, Lacerda L D, Rezende C E, Heavy metal reservoirs in a red mangrove forest, *Biotropica*, 22 (1990) 339–345.

3 Tam N F Y & Wong W S, Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps, *Environ. Pollut.*, 110 (2000) 195–205.

4 De Sousa S N, Effect of mining rejects on the nutrient chemistry of Mandovi estuary, Goa, *Indian J. Mar. Sci.*, 28 (1999) 355-359.

5 Nayak G N, Impact of mining on environment in Goa: a review, *Environ. Geochem.*, 1 (1998) 97–100.

6 Untawale A G, Wafar S, Jagtap T G, Status of mangroves along the countries bordering the Arabian Sea, In: *Oceanography of the Indian Ocean*, edited by Desai B N, (Oxford and IBH, New Delhi, India) 1992, pp. 239 - 245.

7 Mascarenhas A, Oceanographic validity of buffer zone for the east coast of India: A hydrometeorological perspective, *Curr. Sci. India*, 86 (2004) 399-406.

8 Heiri O, Lotter A F, Lemcke G, Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results, *J. Paleolimnol.*, 25 (2001) 101–110.

9 Struyf E, Van Damme S, Gribsholt B, Middelburg J J, Meire P, Biogenic silica in tidal freshwater marsh sediments and vegetation (Schelde estuary, Belgium), *Mar. Ecol-Prog. Ser.*, 303 (2005) 51-60.

- 10 Shapiro L, Rapid analysis of silicate, carbonate and phosphate rocks, revised edition, *USGS Bull.*, 1401(1975) 1-54.
- 11 Clesceri L S, Eaton A D, Rice E W, Greenberg A E, *Standard methods for the examination of water and wastewater*, (American Public Health Association, Washington DC) 2005, pp. 1496.
- 12 Presley B J, Techniques for Analyzing Interstitial Water Samples. Part I: Determination of Selected Minor and Major Inorganic Constituents, In: *Initial Reports of the Deep Sea Drilling Project* edited by Winterer et al, (U.S. Government Printing Office Washington) 1971, pp. 1749-1755.
- 13 Muller G, Index of geoaccumulation in sediments of the Rhine River, *GeoJournal*, 2 (1979) 108–118.
- 14 Loska K., Wiechula D, Korus I, Metal contamination of farming soils affected by industry. *Environ. Int.*, 30 (2004) 159–165.
- 15 Turekian K K & Wedephol K H, Distribution of the elements in some major units of the earth crust. *Bull. Geol. Soc. Am.*, 72 (1961) 175– 92.
- 16 Salmons W& Forstner V, *Metals in the hydrocycle*. (Springer- Verlag, New York) 1984, pp. 347.
- 17 Sutherland R A, Bed sediment associated trace metals in an urban stream, Oahu, Hawaii. *Environ. Geol.*, 39 (2000) 611–627.
- 18 Calvert S E, Pedersen T F, Thunell R C, Geochemistry of the surface sediments of the Sulu and South China Seas, *Mar. Geol.*, 114 (1993) 207–231.
- 19 Werne J P, Sageman B B, Lyons T W, Hollander D J, An integrated assessment of a “type euxinic” deposit: evidence from multiple controls on black shale deposition in the Middle Devonian Oatka Creek Formation, *Am. J. Sci.*, 302 (2002) 110– 143.
- 20 Gonnee M E, Paytan A, Herrera-Silveira J. A, Tracing organic matter sources and carbon burial in mangrove sediments over the past 160 years. *Estuar. Coast. Shelf Sci.*, 61 (2004) 211–227.
- 21 Singh G, Ramanathan AL, Prasad M B K, Nutrient Cycling in Mangrove ecosystem: A brief overview, *J. Ecol. Environ. Sci.*, 30 (2005) 231-244.
- 22 Prasad M B K, Ramanathan AL, Sedimentary nutrient dynamics in a tropical estuarine mangrove ecosystem, *Estuar. Coast. Shelf Sci.*, 80 (2008) 60–66.
- 23 Ramanathan AL, Sediment characteristics of the Pichavaram mangrove environment, Southeast coast of India, *Indian J. Mar. Sci.*, 26 (1997) 319-322.
- 24 Ranjan R K, Ramanathan AL, Singh G, Chidamabaram S, Heavy Metal enrichments due to tsunami in Pichavaram Mangroves sediments, *Environ. Monit. Assess.*, 147 (2008) 389-411.
- 25 Alongi D M, Boto K G, Robertson A I, Nitrogen and phosphorus cycles, In: *Tropical Mangrove Ecosystems: Coastal and Estuarine Studies* edited by Robertson A I & Along D M, (American Geophysical Union, Washington DC), 1992, pp. 251- 292.
- 26 Fabre A, Fromard F R, Trichon V, Fractionation of phosphate in sediments of four representative mangrove stages (French Guinana), *Hydrobiologia* 392 (1999) 13–19.
- 27 Coelho J P, Flindt M R, Jensen H S, Phosphorous speciation and availability in intertidal sediments of a temperate estuary: relation to eutrophication and annual P-fluxes, *Estuar. Coast. Shelf Sci.*, 61 (2004) 583–590.
- 28 Liu S M, Zhang J, Li DJ, Phosphorus cycling in sediments of the Bohai and Yellow seas. *Estuar. Coast. Shelf Sci.*, 25 (2004) 209–218.
- 29 Prasad M B K, Ramanathan AL, Characterization of phosphorus fractions in the sediments of a tropical intertidal mangrove ecosystem, *Wetlands Ecol. Manage.*, 18 (2010) 165–175.
- 30 Hendricks S P, White D S, Streams and groundwater influences on phosphorus biogeochemistry. In: *Streams and Groundwater* edited by Jones J B & Mulholland P J, (Academic Press, London), 2000, pp. 425.
- 31 Goldhaber M B, & Kaplan I R, The sulfur cycle. In: *The Sea (Vol. 5): Marine Chemistry: The Sedimentary Cycle* edited by Goldberg E D, (Wiley-Interscience, New York), 1974, pp. 569–655.
- 32 Hedges J I, Ertel J R, Quay P D, Grootes P M, Richey J E, Devol A H, Farwell G W, Schmidt F W, Salati E, Organic carbon-14 in the Amazon River system, *Science*, 231 (1986) 1129–1131.
- 33 Hedges J I, Keil R G, Benner R, What happens to terrestrial organic matter in the ocean?, *Org. Geochem.*, 27 (1997) 195–212.
- 34 Thornton S F, Mcmanus J, Application of organic carbon and nitrogen stable isotopes and C/N ratios as source indicators of organic matter provenance in estuarine systems: Evidence from the Tay Estuary, Scotland, *Estuar. Coast. Shelf Sci.*, 38 (1994) 219-233.
- 35 Ruttenberg K C, Goni M A, Phosphorous distribution, C:N:P ratios, and $d^{13}C$ in arctic, temperate, and tropical coastal sediments: tools for characterizing sedimentary OM, *Mar. Geol.*, 139 (1997) 123– 145.
- 36 Ranjan R K, Routh J, Ramanathan AL, Bulk organic matter characteristics in the Pichavaram mangrove -estuarine complex, south-eastern India, *Appl. Geochem.*, 25 (2010) 1176-1186.

- 37 Roubex V, Rousseau V, Lancelot C, Diatom succession and silicon removal from freshwater in estuarine mixing zones: From experiment to modelling, *Estuar. Coast. Shelf Sci.*, 78 (2008) 14-26.
- 38 Yamada S S & D'elia C F, Silicic acid regeneration from estuarine sediment cores, *Mar Ecol-Prog Ser.*, 18 (1984) 113-118.
- 39 Van Cappellen P, Reactive surface area control of the dissolution kinetics of biogenic silica in deep-sea sediments, *Chem. Geol.*, 132 (1996) 125-130.
- 40 Hurd D C, Physical and chemical properties of siliceous skeletons, In: *Silicon Geochemistry and Biogeochemistry* edited by Aston S R, (Academic Press, London), 1983, pp.187-244.
- 41 Struyf E & Conley D J, Silica: an essential nutrient in wetland biogeochemistry, *Front Ecol. Env.*, 7 (2008) 88-94.
- 42 Beucher C, Tréguer P, Hapette A, Corvaisier R, Metzl N, Pichon J, Intense summer Si recycling in the surface Southern Ocean, *Geophys. Res. Lett.*, 31 (2004) DOI: 10.1029/2003GL018998.
- 43 Alongi D M, Ramanathan AL, Kannan L, Tirenti F, Trott LA, Prasad M B K, Human induced disturbances on benthic microbial metabolism in the Pichavaram mangroves, the Vellar-Coleroon estuarine complex, India, *Mar. Biol.*, 147 (2005) 1033-1044.
- 44 Zwolsman J J G, Berger G W, Van Eck G T M, Sediment accumulation rates, historical input, post-depositional mobility and retention of major elements and trace elements in saltmarsh sediments of the Scheldt estuary, S.W. Netherlands, *Mar. Chem.*, 44 (1993) 73-94.
- 45 Santschi, P H, Hohener P, Benoit G, Bucholtz Tenb Rink M, Chemical processes at the sediment-water interface, *Mar. Chem.*, 30 (1990) 269-315.
- 46 Cundy A B, Croudace I W, Cearreta A, Irabien M J, Reconstructing historical trends in metal input in heavily-disturbed, contaminated estuaries: studies from Bilbao, Southampton Water and Sicily, *Appl. Geochem.*, 18 (2003) 311-325.
- 47 Fernandes L, & Nayak G N, Distribution of sediment parameters and depositional environment of mudflats of Mandovi Estuary, Goa, India, *J. Coastal Res.*, 25 (2009) 273-289.
- 48 Degroot AJ & Allersma E, Field Observations on the Transport of Heavy Metals in Sediments, In: *Heavy Metals in the Aquatic Environment* edited by Krenkel P A, (Pergamon Press, Toronto), 1975, pp. 85-104.
- 49 Sholkovitz E R, Flocculation of dissolved organic and inorganic matter during the mixing of river water and sea water, *Geochim. Cosmochim. Ac.*, 40 (1976) 831-845.
- 50 Rubio B, Nombela M A, Vilas F, Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution, *Mar. Pollut. Bull.*, 40 (2000) 968-980.
- 51 Ramesh R, Kumar A, Inamdar A B, Mohan P M, Prithviraj M, Ramachandran S, Tsunami characterization and mapping in Andaman and Nicobar islands, In: *26th December 2004 tsunami : causes, effects, remedial measures, pre and post tsunami disaster management : a geoscientific perspective* edited by Rajamanickam G V, (New Academic Publisher, New Delhi), 2006, pp. 150-174.
- 52 Ridgway J & Shimmield G, Estuaries as repositories of historical contamination and their impact on shelf seas, *Estuar. Coast. Shelf Sci.*, 55 (2002) 903-928.
- 53 Achterberg E P, van den Berg C M G, Boussemart M, Davison W, Speciation and cycling of trace metals in Esthwaite Water: a productive English lake with seasonal deep-water anoxia, *Geochim. Cosmochim. Ac.*, 61 (1997) 5233-5253.
- 54 Kontas A, Trace metals (Cu, Mn, Ni, Zn, Fe) contamination in marine sediment and zooplankton samples from Izmir Bay (Aegean Sea, Turkey), *Water Air Soil Poll.*, 188 (2008) 323-333.