Sedimentary Geochemistry of Chorao Island, Mandovi Mangrove Estuarine complex, Goa

Swati M. Sappal[1], AL. Ramanathan[1], Rajesh K. Ranjan[2], Gurmeet Singh[1]

[1]School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India

[2]School of Earth, Biological and Environmental Sciences, Central University of Bihar, Patna 800014, India

Abstract: The Mandovi mangrove estuarine systems are associated with anthropogenic activities (tourism, industrial etc.) and are also heavily influenced by the iron ore mining activities carried out in the state of Goa. ChoraoIsland in the Mandovi basin is a hub of tourist activities with famous Salim Ali bird Sanctuary situated in this island. There has been heavy use of mechanised motorboats, barges, trawlers etc. for recreational and transportation purpose in this region making it susceptible to heavy metal pollution. The present study was undertaken with an objective to assess the nutrient and trace metal status and its variability in the core sediments of Chorao Island, Mandovi estuarine region and to assess the stress on the biogeochemistry due to the prevailing anthropogenic/tourist activities. Sampling was carried out in the tourist season of 2009. A sediment core was collected which was analyzed for different physico-chemical parameters. Overall, the study highlighted significant anthropogenic contributions in terms of heavy metal pollution. Sediments were found to be mature, quartz rich and weathering does not seem to play any role. The biological activities were significant due to abundance of S and OC in the sediments which along with the redox conditions controlled the metal variability. The 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, mandovi estuarine mangrove complex, Chorao Island

Introduction:

Mangroves are highly specialized ecosystems, which are characterized by salt resistant plants growing in the intertidal areas along sheltered seacoasts and estuaries in the tropical and subtropical regions. Restricted to the latitudes between 30º N and 30º S, they almost cover up to 75% of coastlines worldwide[1]. Mangrove sediments are highly anaerobic rich in sulphides and organic matter[2]. 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].

The state of Goa is drained by seven major rivers of which the Mandovi and Zuari with the Cumbarjua Canal form the largest estuarine complex supporting a luxuriant growth of mangroves. The total area covered by the estuaries in Goa including the major Mandovi Zuari estuarine complex is approximately 120 km^2 of which the mangrove forests occupy 20 km^2.ChoraoIsland 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.

Increasing pressure on natural resources has led the mangroves being exploited beyond their sustainable potential. Reclamation and exploitation of mangroves for human settlements and agriculture have threatened a number of species. In the entire state, fishing using dragnets is common resulting in the damage to the young regeneration and plantations. Goa is also 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 ecosystems[4]. The rivers of Mandovi and Zuari provide inland waterways and are extensively used to transport minerals ores from the mines to the ports[5]. Tourism is a major industry in Goa and is mainly concentrated along the coastal stretches of the state. It poses a severe threat to the fragile and dynamic mangrove ecosystems. Their impact gets worse because of related anthropogenic activities that follow coastal tourism, and as a result Goa's coastal scenario is prone to fast changes.

Untawale[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 estuaries[7]. And, this problem is compounded by the petroleum residues from barges, tankers and trawlers in these regions. The discharges from the mining operations and other anthropogenic activities severely affect the diversity as well as chemistry of the estuarine regions.

Hence the 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 Mandovi mangrove estuarine ecosystem.

Study Area:

Mandovi is confined between latitude 15º 09' and 15º 33' N and longitude 73º 45' and 74º 14' E and has a direct opening into the Arabian Sea (Figure 2.1). It is one of the most important and largest rivers of the state of Goa running amidst a typical tropical setting along the mid-west coast of India. It covers a length of 81 km with a basin area of about 1530 km^2 and is remarkably influenced by monsoon maritime climate with its three distinct seasons, namely pre-monsoon (February–May), monsoon (June–September), and post-monsoon (October–January). The annual average annual rainfall is over 3000 mm whereas annual freshwater runoff of the Mandovi is approximated to be 16 km^3 (with a small summer runoff of 0.06 km^3). The river carries drainage from 435 km^2 of forestland. The soils in general are predominantly of lateritic nature, which manifests the underlying geology of the area. The coastal tracts are, however, alluvial flats.

The state of Goa is known for iron ore mining with two-thirds of the total mining activities located within the Mandovi estuarine region. There are about 27 large mines in this area that generate 1500–6000 tons of rejects per day per mine; a substantial portion of which is expected to ultimately end up in the basin. It flows through these mining areas and is heavily used to transport iron and manganese ores to the harbour from the hinterlands. Apart from these, the basin has been exclusively used for agriculture, farming, shell fishing, traditional fishing, tourism and recreational activities. A major portion of the Goa mangroves is supported by the Mandovi basin (7 km^2 out of the total 20 km^2) thus making these productive ecosystems susceptible to the existing anthropogenic activities.

Materials and Methods:

Sampling Location

The sediment core was collected from Chorao Island (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, Germinetrex make model).

Sample Collection and Preservation

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.

Analytical Procedures

Mineralogical Analysis

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

Sedimentary organic matter

The Moisture content and LOI were calculated using the following equations[8].

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

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

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 950º C for 2 hours and reweighed. LOI was calculated using the following equation:

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

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 950ºC (all in g).

Biogenic Silica (BSi)

BSi was extracted from the from oven dried samples (at 75°C) sediment (25 mg) in a 0.1M 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 spectro photo metrically. BSi was calculated by linear extrapolation through the 3 extraction points in a time-extracted silica plot[9].

Analysis of major and minor elements

Analyses of major and minor elements were carried out by the two solution methods[10]. Solution "A" was used for silica, alumina and phosphorus analysis and solution "B" was used for metal analysis.

Silica Analysis:

The dissolved silica content was determined by the molybdate silicate method[11].

Alumina Analysis

The Alumina content was determined by the standard protocol of[11].

Phosphorous Analysis

Phosphorous was analysedap per the standard protocol of[12].

Metals:

Solution B was used for analyzing Heavy metals (Fe, Mn, Cr, Pb, Zn, Cd) using Atomic Absorption Spectrophotometer (THERMO Scientific, M Series).

Total Carbon, Nitrogen, Sulphur

The sediment samples were analyzed for total carbon (TC), total nitrogen(TN) and total sulphur (S) using EURO EA elemental analyser.

Statistical Analysis

The observed results were statistically analyzed using computer aided packages viz. EXCEL (Microsoft Office version 2007).

Index of Geoaccumulation

The geoaccumulation index (I_{geo}) was originally defined by[13] for a quantitative measure of the metal pollution in aquatic sediments. The Index of Geoaccumulation (I_{geo}) was computed using the equation[13]:

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

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 crust[14]. The constant 1.5allows 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.

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

Enrichment Factor

According to[15], 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 (sample)/ C_{ref} (sample)} }/{ C_n (background) /C_{ref} (background) }

Where, C_n (sample) is the content of the examined element in the examined environment. The C_n (background) is the content of reference element in the reference environment. Five contamination categories are recognized on the basis of enrichment factor[16], which are as under:

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

Results and Discussion:

Mineralogical analysis

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.

Depth variability of Si and Al

The depth variation of Si and Al is depicted in the figure 3.6. Silica concentrations in the core sediments were more or less uniform indicating presence of uniform quartz content supporting the mineralogical observations. The mean concentration of Si in the mangrove sediments was 31.92% with maximum and minimum values as 37.2 and 25.9 % respectively. The 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. The ratio varied from 2-7 with a 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 sediments[17]. The ratio increased with the depth and this can be related to enhanced input of quartz, which in turn may be due to Aeolian inputs[18]. The higher values can also be attributed as a consequence of the higher energy transport.

Depth variability of C, N, P and S

Figure 3.7 shows the variation of total carbon (TC), organic carbon (OC) and inorganic carbon (IC) in the Mandovi estuarine core sediments. The 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. The 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 sediments[19]. The 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 %. The variation of IC with respect to depth was insignificant. The OC constituted the major fraction of TC (nearly 70 %), governing the variability in TC (Figure 3.7). The 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. The dominance of OC can be attributed to the decomposition of organic foliage and other vegetative matter which contributed substantially to the organic matter content in the mangrove sediments[20]. The inherent biological productivity of the mangroves also contributes significantly to the organic content of the sediments[21]. Further, finely grained sediments favour the adsorptions of organic carbon[22].

The 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[23]. In general TN concentration generally ranges from 0.2 to 0.4 % of sediments dry weight in mangrove environment[24], though for Mandovi sediments it ranged between 0.39 – 0.56 % (Figure 3.8). The 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[21]. Global average of phosphorus in the mangrove sediments varies between 100 – 1600 mg/kg[24]. 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 $FeOOH-P$[25]. 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 minerals[26]. Total S concentrations showed a gradual increase in concentrations with the depth and its average concentration was 0.30 %. The 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

8

material and elemental nitrogen relative to terrigenous matter[27-31].Vascular plants exhibit bulk chemical properties, which distinguish them from marine organisms. Presence of nitrogen-free bio-macromolecule (like lignin, tannin, hemicellulose, cellulose, cutin, and suberin) over protein makes higher plant matter carbon-rich[28]. Thus, marine phytoplankton have a mean C/N ratio ≈ 7[27], whereas terrestrial plants with soft tissue have C/N ratios from 10-100 and in woody material the ratio is from 100-1000[28]. 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 processes and paleoenviromental records in estuarine and coastal ecosystems. The abiotic factors controlling BSi mobility are temperature, pH, and salinity[32]. An increase of temperature, pH (over 6) or salinity has been reported to enhance BSi dissolution[33-34]. Figure 3.9 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 frustule[35]. 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 dissolution.

Depth variability of Trace metals

Mangrove sediments are anaerobic and reduced, as well as are rich in sulphide and organic matter[2]. 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 3.10 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. The concentration of Fe was highest followed by Pb. The high concentrations of Fe in sediments may be a result of prevalence mining activities in the Mandovi river basin[5]. Overall variation in Fe and Mn concentrations with respect to depth was insignificant even though irregular

9

trends were observed. These irregular variations with respect to depth can be attributed to the fact that Fe and Mn chemistry in sediments is largely influenced by redox conditions and microbiological activity[36]. Tidal fluctuation and seasonal fluctuation may have resulted in these erratic trends, overall variations being insignificant.

As mentioned earlier, 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 (Figures 3.11) 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 that is due to the open cast mining activities carried throughout the estuary[5]. Fe and Mn in the sediments showed good association with P all through the depth whereas Cr and Zn showed association with OC (Figure3.7, 3.8, 3.10). Specific association of different metals with P and OC reveals their role in remobilisation of the elements within the sediment. The 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 precipitated[37]. Diagenetic reactions are important near the sediment–water interface, responding to redox changes and affecting metal concentration in vertical sediment profiles[38]. Enhanced Fe and Mn values at the bottom are controlled by P[39]. The significant correlation of Cr and Zn with OC suggest their preference for organic matter for chelation[40].

In order to understand the level of contamination with respect to trace metals, the values of trace metals were utilized to find geo accumulation index (I_{geo}). While computing the I_{geo} of sediments of the study area, world average concentrations of these elements reported for Shale[14], 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 area[41,15], precipitation of metals as hydroxide coating (mainly Fe and Mn) over finely dispersed particles[42], flocculation due to varying salinity regimes[43], transportation of deep shore sediments to the coastal zone etc.[44,16,45]. Possible sediment enrichment of metals was evaluated in terms of the I_{geo} of[13]. The geoaccumulation index (I_{geo}) was originally defined by[13], for a quantitative measure of the metal pollution in aquatic sediments[46]. This was applied for the Mandovi mangrove sediments shown in Table 3.3. 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 3.5). This was confirmed by the calculation of enrichment factor which was significant enough for Pb and Mn and insignificant for Fe, Cr and Zn (Table 3.6).

Table 3.5 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 3.6 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

Table 3.7 Correlation matrix for coresediments(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

The correlation matrix was plotted for the core sediments (Figure 3.1.6). 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 OM[47]. It mostly associates with OM through biological uptake as well as through adsorption and/ incorporation into the biologically resistant humic component in sediments. The 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[48].

Conclusions:

The Mandovi mangrove estuarine systems are not only associated with tidal fluctuations, sea water inundation, anthropogenic activities (tourism, industrial etc.) but are also heavily influenced by the iron ore mining activities carried out in the state of Goa. There has been heavy use of mechanised motorboats, barges, trawlers etc for recreational and transportation purpose in the Mandovi basin making it susceptible to heavy metal pollution. The sediments were matured and weathered, rich in quartz which is supported by high Si/Al ratios. The OC constituted major fraction of TC throughout the depth. IC varied insignificantly with depth. TN showed irregular pattern with depth with slight decrease in concentration. The C/N ratio indicated marine origin of organic matter. The variation of TP in core sediment was supposedly influenced by redox condition and a decrease with the depth was observed. TS showed gradual increase with depth due to prevailing reducing conditions. BSi had alternating variation with depth with can be related to seasons of algal growth and diatom blooms. The core sediment showed higher concentrations of heavy metals namely Fe, Mn, and Pb. The 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. The 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. No good correlation was observed between OC and Fe, Mn however they were found to have significant correlations with P indicating their association as phosphate. Zn also had strong correlation with S indicating the preferential association as sulphides in reducing conditions. Fe- Mn and Cr- Pb- Zn correlation pointed out they have common sources. Values for I_{geo} and enrichment factor indicated that sediments were enriched in Pb (strongly to extremely contaminated) and Mn (moderately to uncontaminated).

Overall the study highlighted that sediments were found to be mature, quartz rich and weathering does not seem to play any role. 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. The metal concentrations were influenced by anthropogenic activities. 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.

References:

1. Pernetta, J.C., 1993. 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 (IUCN), p 45.

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

3. Tam, N.F.Y., Wong, W.S., 2000. Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. Environmental Pollution, 110: 195–205.

4. De Sousa, S.N., 1999. Effect of mining rejects on the nutrient chemistry of Mandovi estuary, Goa. Indian Journal of Marine Sciences 28, 355-359.

5. Nayak G.N., 1998. Impact of mining on environment in Goa: a review. Environmental Geochemistry, 1, 97–100.

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

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

8. Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonatecontent in sediments: reproducibility and comparability of results. Journal of Paleolimnology 25: 101–110.

9. Struyf, E., Van Damme S., Gribsholt B, Middelburg J.J., Meire P., 2005. Biogenic silica in tidal freshwater marsh sediments and vegetation (Schelde estuary, Belgium). Marine Ecology Progress Series 303: 51-6.

10. Shapiro, L., 1975. Rapid analysis of silicate, carbonate and phosphate rocks, revised edition. USGS Bulletin 1401: 1-54.

11. American Public Health Association, APHA 1995. Standard methods for the examination of water and wastewater, 19th Ed, APHA, Washington DC.

12. Presley, B.J., 1971. Appendix: Techniques for Analyzing Interstitial Water Samples. Part I: Determination of Selected Minor and Major Inorganic Constituents. In

Winterer et al (Eds.) Initial Reports of the Deep Sea Drilling Project, Washington, U.S. Government Printing Office VII: 1749-1755.

13. Muller, G.(1979) Schwermetalle in den sedimenten des Rheins e Vera̎nderungenseit 1971. Umschau 79:778-783.

14. Turekian K.K, Wedephol K.H 1961. Distribution of the elements in some major units of the earth crust. Bull GeolSoc Am 72:175– 92.

15. Salmons W and Forstner V 1984. Metals in the hydrocycle. Springer- Verlag Publisher, New York. pp 347.

16. Seralathan, P., Srinivasalu, S., Ramanathan, AL, Rajamanickam, G.V., Nagendra, R., Singarasubramanian, S. R., Mukesh, M. V., Manoharan, K., 2006. Post tsunami sediments characteristics of Tamilnadu Coast. In: G. V. Rajamanickam (Editor), 26th December 2004 Tsunami causes effects, remedial measures, pre- and post tsunami disaster management, a geoscientific perspective. Department of Science and Technology report, New Delhi, pp. 196–209.

17. Calvert, S.E., Pedersen, T.F., and Thunell, R.C 1993. Geochemistry of the surface sediments of the Sulu and South China Seas. Mar. Geol., 114:207–231.

18. Werne, J. P., Sageman B. B., Lyons T. W., & Hollander D.J. 2002. An integrated assessmentof a ''type euxinic'' deposit: evidence from multiple controls on black shale deposition in the Middle Devonian Oatka Creek Formation. Am. J.Sci., 302: 110– 143.

19. Gonneea, M. E., Paytan, A., Herrera-Silveira, J. A., 2004. Tracing organic matter sources and carbon burial in mangrove sediments over the past 160 years. Estuarine Coastal Shelf Science. 61: 211–227.

20. Singh, Gurmeet, Ramanathan, AL., Prasad, M.B.K., 2005. Nutrient Cycling in Mangrove ecosystem: A brief overview. Journal of Ecology and Environmental Sciences 30:231-244.

21. Prasad, M.B.K., Ramanathan. AL., 2008. Sedimentary nutrient dynamics in a tropical estuarine mangrove ecosystem. Estuarine, Coastal and Shelf Science 80: 60–66.

22. Ramanathan AL., 1997. Sediment characteristics of the Pichavaram mangrove environment, Southeast coast of India. Ind. J. Mar. Sci. 26: 319-322.

23. Ranjan, R.K., Ramanathan, AL, Singh, G., Chidamabaram, S., 2008. Heavy Metal enrichments due to tsunami in Pichavaram Mangroves' sediments, Environmental Monitoring and Assessment 147:389-411

24. Alongi, D.M., Boto, K.G., Robertson, A.I., 1992. Nitrogen and phosphorus cycles. In: Robertson, A.I. Along, D.M. (Eds.), Tropical Mangrove Ecosystems: Coastal and Estuarine Studies, vol. 41. American Geophysical Union, Washington DC, pp 251- 292.

25. Hendricks, S.P., White, D. S., 2000. Streams and groundwater influences on phosphorus biogeochemistry. In: Jones JB, Mulholland PJ (eds.) Streams and Groundwater. Academic Press, London: 425.

26. Goldhaber, M.B., and Kaplan, I.R., 1974. The sulfur cycle. In Goldberg, E.D.(Ed.), The Sea (Vol. 5): Marine Chemistry: The Sedimentary Cycle: New York (Wiley-Interscience), 569–655.

27. Hedges, J.I., Ertel, J.R., Quay, P.D., Grootes, P.M., Richey, J.E., Devol, A.H., Farwell, G.W., Schmidt, F.W, and Salati, E. 1986. Organic carbon-14 in the Amazon River system. Science 231: 1129–1131.

28. Hedges, J.I., Keil, R.G., Benner, R., 1997.What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27 195–212.

29. Thornton, S.F., Mcmanus, J., 1994. 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. Estuarine, Coastal and Shelf Science 38, 219-233.

30. Ruttenberg, K.C., Goni, M.A., 1997. Phosphorous distribution,C:N:P ratios, and d13Coc in artic, temperate, and tropical coastal sediments: tools for characterizing sedimentary OM. Mar.Geol. 139, 123– 145.

31. Ranjan, R.K, Routh, J., Ramanathan, AL., 2010. Bulk organic matter characteristics in the Pichavaram mangrove -estuarine complex, south-eastern India. Appl. Geochem. (in Press).

32. Roubeix V, Rousseau V, Lancelot C 2007. Diatom succession and silicon removal from freshwater in estuarine mixing zones: From experiment to modelling. Estuar Coast Shelf Sci. doi:10.1016/j.ecss.2007.11.007

33. Yamada, S. S., AND C. F. D'elia. 1984. Silicic acid regeneration from estuarine sediment cores. Marine Ecology Progress Series 18: 113–118.

34. Hurd, D. 1983. Physical and chemical properties of siliceous skeletons. In Aston, S. (ed.):

35. Struyf, E., Conley, D.J., 2008. Silica: an essential nutrient in wetland biogeochemistry. Frontiers in Ecology and Environment 7(2): 88–94,

36. Alongi, D.M., Ramanathan, A.L., Kannan, L., Tirenti, F., Trott, L.A., Prasad, M.B.K., 2005. Human induced disturbances on benthic microbial metabolism in the Pichavaram mangroves, the Vellar-Coleroon estuarine complex, India. Marine Biology 147, 1033-1044.

37. Zwolsman, J.J.G.; Berger , G.W., and Van Eck, G.T.M., 1993. 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. Ma-rine Chemistry, 44, 73–94.

38. Santschi, P.H.; Hohener , P.; Benoit , G., and BucholtzTenb Rink , M., 1990. Chemical processes at the sediment–water interface. Marine Chemistry, 30, 269–315.

39. Gaillard, J.F.; Pauwells, H., and Michard , G., 1989. Chemical diagenesis of coastal marine sediments. OceanologicaActa, 12,175–187.

40. Fernandes, L., and Nayak, G.N., 2007. Distribution of sediment parameters and depositional environment of mudflats of Mandovi Estuary, Goa, India.Journal of Coastal Research, 00(0), 000-000. West Palm Beach (Florida),ISSN 0749-0208.

41. Forstner V, Wittman GTW 1983. Metal pollution in the aquatic environment, 2nd edn. Springer, New York, 486 pp

42. DegrootAJ andAllersma, E 1975. Heavy metals in the aquatic environment , edited by P A Krenkel (Pergamon Press, Oxford) pp 85.

43. Sholkovitz, E.R. 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and sea water.GeochimicaetCosmochimicaActa 40: 831-845

44. Rubio, B., Nombela, M.A., Vilas, F. 2000. Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. Mar. Poll. Bull. 40:968-980.

45. Ramesh, R., Kumar A., Inamdar, A.B., Mohan, P.M., Prithviraj, M., Ramachandran, S., and others 2006. Tsunami characterization and mapping in Andaman and Nicobar islands. 26 th December 2004 Tsunami Causes, Effects Remedial Measures, Pre and Post Tsunami Disaster Management, A geoscientific Perspective (Edi. by G V Rajamanickam) New Academic Publisher, New Delhi.

46. Ridgway, J., Shimmield, G. 2002 Estuaries as repositories of historical contamination and their impact on shelf seas. Estu.Coast Shelf Sci. 55: 903-928.

47. Achterberg, E.P., van den Berg, C.M.G., Boussemart, M., Davison, W., 1997. Speciation and cycling of trace metals in Esthwaite Water: a productive English lake with seasonal deep-water anoxia. Geochim.Cosmochim.Acta 61, 5233-5253.

48. Kontas, A., 2008. Trace metals (Cu, Mn, Ni, Zn, Fe) contamination in marine sediment and zooplankton samples from Izmir Bay (Aegean Sea, Turkey). Water Air Soil Pollut.188, 323-333.

Figure

Figure 2.1 Map of the study area: Chorao Island, Mandovi Mangrove estuarine system

Figure 3.6 Depth variations of Si, Al and Si/Al in the Mandovi core sediments.

Figure 3.7 Depth variation of C in the Mandovi core sediments and % contribution in TC

Figure 3.8 Depth variations of TN, TP and TS in the Mandovi core sediments

Figure 3.9 Depth variation of BSi in the Mandovi core sediments

Figure 3.10 Depth variation of Trace metals in the Mandovi core sediments

Figure 3.11 Distribution pattern and correlation – OC vs. metals and metals vs. metals of the core sediments.