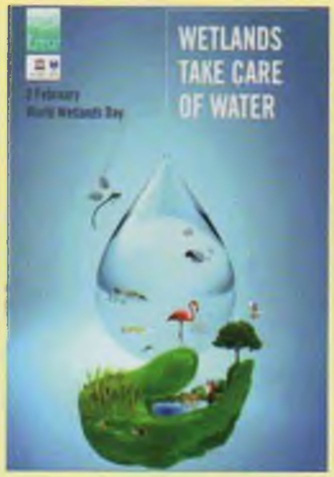
Uttara Kannada Jilla Vijnana Kendra, Karwar

Uttara Kannada District, Karnataka



WATER FOR LIFE
2005-2015

UN WATER
World Water Day
2013
International Year of
Water cooperation

National Conference on

Wetlands and Water

February 1-2, 2013

Sponsored by

Karnataka Science & Technology Academy

Bangalore

3. SEDIMENT AS AN INDICATOR OF HEALTH OF TIDAL WETLAND ECOSYSTEM

G. N. Nayak

Department of Marine Sciences, Goa University, Goa 403 206

Email: nayak1006@rediffmail.com

ABSTRACT

Wetlands are classified as tidal and non-tidal wetlands. Tidal wetlands as their name suggests, are closely linked to our nation's estuaries, where sea water mixes with fresh water to form an environment of varying salinities. Large variation in salinity facilitates processes which lead to sediment deposition and therefore estuaries and creeks are the ultimate repositories of land derived material including waste generated and released to the environment by the human population. Further, heavy metal contents in sediments are an accepted and widely used indicator of anthropogenic pollution over time. Tidal wetlands represent the largest component of the terrestrial biological carbon pool and thus play an important role in global carbon cycles. The health of wetlands depends on the quality and quantity of water that reaches them and also bioavailability of metals within sediments and water. Present study has proved that the bioavailable metals if released from sediment to water column due to processes of either natural or anthropogenic or both, can cause potential risk to water quality and associated biota and in turn health of the wetland ecosystem.

Introduction

'Wetland' is a generic term for water bodies of various types, and includes diverse hydrological entities, namely, lakes, marshes, swamps, estuaries, tidal flats, river flood plains, and mangroves. Wetland is a distinct ecosystem that is saturated with water, either permanently or seasonally. Ramsar international wetland conservation treaty defined wetlands under Article 1.1 as "wetlands are areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six metres". Further, under Article 2.1 it is stated that the "Wetlands may incorporate riparian and coastal zones adjacent to the wetlands, and islands or bodies of marine water deeper than six metres at low tide lying within the wetlands". World Wetlands Day is celebrated internationally each year on 2 February. It marks the anniversary of the signing of the Convention on Wetlands of International Importance (Ramsar Convention) in Ramsar, Iran, on 2 February 1971. World Wetlands Day was first celebrated in 1997.

The factor that distinguishes wetlands from other land forms or water bodies is the characteristic vegetation that is adapted to its unique soil conditions. Wetlands consist primarily of hydric soil, which supports aquatic plants. The water found in wetlands can be saltwater, freshwater, or brackish. Main wetland types include swamps, marshes, bogs and fens. Sub-types include mangrove, carr, pocosin, and varzea. Wetlands play a number of roles in the environment, principally water purification, flood control, and shoreline stability. Wetlands are also considered the most biologically diverse of all ecosystems, serving as home to a wide range of plant and animal life. The finite natural resources of our planet are under tremendous stress due to demographic pressures and economic growth. The UN Millennium Ecosystem Assessment determined that environmental degradation is more prominent within wetland systems than any other ecosystem on Earth. International conservation efforts are being used in conjunction with the development of rapid assessment tools to inform people about wetland issues.

Wetlands occur naturally on every continent except Antarctica. They can also be constructed artificially as a water management tool, which may play a role in the developing field of water-sensitive urban design. Wetlands are also classified as tidal and non-tidal wetlands. Tidal wetlands as their name suggests, they are closely linked to our nation's estuaries, where sea water mixes with fresh water to form an environment of varying salinities. The salt water and the fluctuating water levels, due to tidal action, combine to create a rather different environment for most organisms. Consequently, many shallow coastal areas are unvegetated mud flats or sand flats. Some plants, however, have successfully adapted to this environment. Certain grasses and grass like plants that adapt to the saline conditions form the tidal salt marshes that are found along the coasts. Mangrove swamps, with salt-loving shrubs or trees, are common in tropical climates. Some tidal freshwater wetlands form beyond the upper edges of tidal salt marshes where the influence of salt water ends. Non-Tidal wetlands are most common on floodplains along rivers and streams, in isolated depressions surrounded by dry land for example, playas, basins, and "potholes", along the margins of lakes and ponds, and in other low-lying areas where the groundwater intercepts the soil surface or where precipitation sufficiently saturates the soil. Inland wetlands include marshes and wet meadows dominated by herbaceous plants, swamps dominated by shrubs, and wooded swamps dominated by trees.

The international theme for World Wetlands Day 2013 is ***Wetlands take care of water***. Wetlands provide important hydrological functions such as groundwater recharge, water quality improvement and flood alleviation. The health of wetlands depends on the quality and quantity of water that reaches them and also bioavailability of metals within sediments are water. To secure their conservation and wise use it is essential that they are managed in the wider context of catchment-scale water resource management. Tidal wetlands represent the largest component of the terrestrial biological carbon pool and thus play an important role in global carbon cycles. Most global carbon budgets, however, have focused on dry land ecosystems that extend over large areas and have not accounted for the many small, scattered carbon-storing ecosystems such as tidal saline wetlands. In this paper an attempt is made to explain how sediment parameters act as indicator of health of wetland ecosystem. This paper has input from all our research work published on estuarine mudflats and specially the following research papers, **Singh and Nayak, 2009; Fernandes and Nayak, 2009; Fernandes and Nayak, 2010; Fernandes et al 2011; Fernandes and Nayak, 2012a; Fernandes and Nayak, 2012b; Fernandes et al., 2012.**

Research Methodology

A sediment sample in general is an accurate representation of the sediment in the area and it should resemble the original materials as closely as possible without loss of a particular size or geochemical fraction. It is necessary to understand the importance of and the relationship among individual steps of sediment sampling and analysis. Keeping all these in mind, a sampling plan was prepared in order to meet the objectives of the proposed study. The plan includes the field work and laboratory analysis need to be carried out to obtain all necessary data for the characterization of the sediments (**Fig. 1**).

Sediment cores were collected from mudflats within estuaries along central west coast of India, representing different hydrogeochemical environments. The cores were collected at low tide by pushing a hand-held PVC core (150 cm long and 6.5 cm diameter) in the intertidal region of each sampling location and transported to laboratory at low temperature. In the laboratory, the cores were sectioned at 2 cm interval, placed in polyethylene bags, immediately measured for pH (Thermo Orion 420 A model) and stored at 4^0 C till further analysis. The locations of sampling stations were obtained by a hand-held GPS.

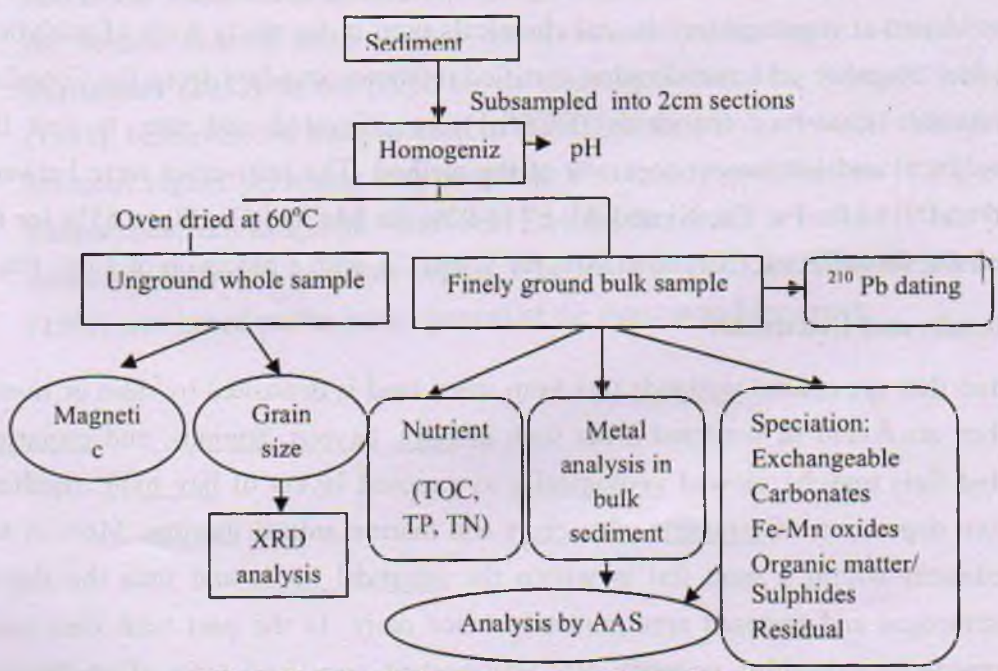


Fig.1. Flowchart of sample preparation and analysis

In order to analyze the sedimentological and geochemical parameters, the sediment samples were oven dried at 60^0C. Sediment component analysis was performed to separate silt and clay (<0.063 mm) and sand (>0.063 mm) fractions using standard sieve and pipette technique (**Folk, 1974**), after destruction of organic matter with 30% H_2O_2. Further, for geochemical analyses, the dried sediment samples were finely ground using mortar and pestle. Total organic carbon (TOC) was determined by exothermic heating and oxidation with potassium dichromate and silver sulphate, followed by titration of excess dichromate with 0.5 N ferrous ammonium sulphate solutions (**Walkley and Black, 1934; Gaudette et al., 1974**). Sediment samples for trace metal analysis were digested using $HF+HNO_3+HClO_4$ total dissolution technique (**Jarvis and Jarvis, 1985**). The digested samples were aspirated for Al, Ca, 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, Ca and V for which nitrous oxide/acetylene flame was employed at specific wavelengths. The instrument was calibrated by running blank and standard solutions prior to each element analysis. Recalibration check was performed at regular intervals. All chemicals used in the study were of analytical grade. 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 and 91% for Fe, Cu, Ni and Al; 87 to 92% for Mn and Co; 80 to 85% for Pb and Zn; 90 to 95% for Cr; 82 to 90% for V and Ca, with a precision of + or - 6%.

Results and Discussion

Mud flats are coastal wetlands that form when mud is deposited by tides or rivers. They are found in sheltered areas such as bays, bayous, lagoons, and estuaries. Mud flats may be viewed geologically as exposed layers of bay mud, resulting from deposition of estuarine silts, clays and marine animal detritus. Most of the sediment within a mud flat is within the intertidal zone, and thus the flat is submerged and exposed approximately twice daily. In the past tidal flats were considered unhealthy, economically unimportant areas and were often dredged and developed into agricultural land. Variability in sediment accumulation rates within marshes is a major control of carbon sequestration rates masking relationship with climatic parameters. Globally, these combined wetlands store at least 44.6 Tg C yr^{-1} and probably more.

When the metal concentrations of Thane creek and Ulhas river are compared (**Table 1**) with studies carried out in the other parts of the country, especially on the west coast of India (Mandovi and Zuari estuaries), it is seen that Fe exhibits lower percentage in Thane creek and Ulhas river as compared to the Mandovi estuary but higher than the Zuari estuary (**Fernandes, 2013**). In the case of Mn, the Thane and Ulhas show higher values than the study carried out by **Bhosale and Sahu (1991)** in the same region. However, Mandovi and Zuari estuaries project higher concentration of Mn than Thane creek and Ulhas estuary, maybe because of the mining activities being carried out in the Goa region. Among the trace metals, almost all of them show an increment in the Thane and Ulhas when compared to the study carried out by **Bhosale and Sahu (1991).** On the other-hand, the Cr concentrations in the Zuari estuary are found to be comparable with that of the Thane creek and Ulhas estuary. In general, it is observed that almost all the metals studied show higher concentration in the study carried out by **Fernandes (2013)** as compared to the study carried out by **Bhosale and Sahu (1991).** However, we have to keep in mind that the previous study carried out in Mumbai region presented only a spatial distribution and that our study covers temporal as well as spatial variations. Further, this study is based on the samples collected from the mudflats region whereas the study of **Bhosale and Sahu (1991)** was based on the main channel of the estuary and the creek.

Area	Fe	Mn	Cu	Pb	Co	Ni	Zn	Cr	V	Reference
Thane creek	-	210-1274	91-240	54-143	34-59	91-130	114-273	29-63	-	**Bhosale and Sahu, 1991**
Ulhas estuary	-	195-1024	61-150	30-68	31-61	70-133	96-183	30-51	-	**Bhosale and Sahu, 1991**
Mandovi estuary	2.2-49.7	<DL-1.61%	11.5-77.5	4.5-46.5	2.5-45.3	-	19.9-83.5	-	-	**Alagarsamy, 2006**
Zuari estuary	7.61-8.72	0.29-0.31	34.34-96.88	-	39.14-52.60	-	70.39-101.95	113-267	-	**Dessai and Nayak, 2009**
Thane creek	6.77-10.66	836-2405	83-286	51-120	42-74	99-220	99-521	81-231	115-526	**Fernandes, 2013**
Ulhas estuary	4.09-9.60	759-1904	138-257	54-165	43-105	66-190	125-200	175-288	184-449	**Fernandes, 2013**

Table 1. Range of different metals in surface sediments along west coast of India

Our study carried out in Kalinadi estuary on sedimentary and geochemical signatures of depositional environment of sediments in mudflats (**Singh and Nayak, 2009**) showed significant results and we concluded as follows. Grain size analysis indicated a highly variable depositional regime with fining up of the core. The analysis revealed the possibility of three episodes of deposition in the two cores studied. Organic carbon is comparatively high in the Core with high mud content, which was collected from a more sheltered creek with a narrow mouth interior to the estuarine environment; it is comparatively low in the core with high sand, which was collected from a creek with a wide mouth nearer to the sea. However, the distribution of organic carbon with depth in sandy core was controlled by the proportion of finer fraction, which was not the case in muddy Core. Organic carbon in mudflats is as high as 9% when average percentage in marine sediments is around 2%.Therefore it is stated that tidal wetlands represent the largest component of the terrestrial biological carbon pool and thus play an important role in global carbon cycles. Geochemical data showed an upper zone of marked enrichment of all trace metals, including Fe and Mn, in both cores. The distribution of Fe, Mn, Cu, and Cr in sandy core is partly controlled by clay fraction and organic carbon, while mud, Fe, and Mn controlled distribution of Zn, Cu, and Co in muddy core. The vertical profiles indicate that Mn, and to some extent Fe, in both cores have been remobilized and that these diagenetic processes have modified the vertical distributions of Cu, Zn, Cr, and Co. In sandy core, there is evidence of redistribution of metals by early aerobic degradation of organic matter, in addition to the role played by clay fraction and Fe and Mn oxyhydroxides, resulting in a gradual decrease in metal concentration with depth. The distribution of trace metals in muddy core is probably solely controlled by the mud and by redox-sensitive Fe and Mn oxides. Further, the geomorphological setup of the two creeks and therefore the tidal circulation would also have played an important role in the vertical distribution of sediments and their associated metals.

It is a known fact that the geochemical associations of metals provide useful information concerning the absolute levels, source, mobilization, mode of occurrence and biological availability of metal **(Fernandes, 2013).** Near the creek head, in Thane creek, Mumbai, sediment contains more than twice the concentration of metals as compared to the other cores and a reduction in metal content occurs with increasing distance from the creek head. Most of the industries are housed above and along the creek head. During periods of high rainfall and flooding, the core location at near creek head would receive the sediment-loaded water from the industrial and urban areas first and would therefore receive the larger proportion of contamination. The inner creek with reduced tidal influence, lower salinity and decreased current speed is relatively sheltered, making the conditions conducive for the settlement of suspended load. Further, the metal distribution in core near creek head revealed a general trend of decreasing metal concentration with increasing depth. Therefore, once incorporated into the sediments, it is unlikely that this detrital material is altered significantly by post-depositional processes. As the sediments in this part of the creek contain a greater quantity of fine particles and organic material than those downstream, it is probable that there is an increased potential for adsorption of metals to organic and inorganic particles. Generally, trace metals are more associated with the silt/clay sediment fraction, consisting of particles with a grain size <0.063 mm. The enrichment of the silt/clay fraction by anthropogenic trace metals is due to the large specific area of this fraction and to the strong adsorptive properties of clay minerals. Sediments collected near the mouth of the creek reveals a substantial reduction in most of the metal concentrations, as this location is more prone to wave action from the sea, causing the sediments to be more uniformly distributed **(Fernandes, 2013).** Therefore, there is evidence for a distance-concentration relationship in the sediment record, with concentrations decreasing with greater distance from the head/input. In general, sediments located within the northern reach of the creek have higher metal concentrations than those in the southern reach.

Variation in metal concentrations can result from natural differences in grain size, mineralogy, organic matter content, diagenetic reactions and anthropogenic inputs. Therefore, these factors must be considered collectively in any attempt to explain metal distribution or to identify the presence of anthropogenic input of metals in sediments. High Cr and Ni contents in the sediments are interpreted to reflect, in part, the weathering of basic-ultrabasic rocks of the region. Vertical profiles of Fe and Mn show rapid decrease in their concentrations from the surface which might be suggestive of a diagenetic enrichment during which Fe-Mn oxy-hydroxides dissolve in the partly reduced sediment layer producing Fe^{2+} and Mn^{2+} species, which migrate upwards in the sediment column and get precipitated near the oxic-suboxic interface. Other metals are likely to be chemically immobilised through formation of their insoluble sulphides. All these observations support that the early diagenetic remobilization has not significantly affected the vertical distributions of some heavy metals. Instead, they are probably due to contaminant inputs.

Pollution status of Thane creek

Human activities around coastal areas have significant negative impacts on the health of the ecosystems and the viability of resources. To know the extent to which the creek is getting polluted with time, Enrichment factor and Geo-accumulation index was computed. Enrichment Factor (EF) has been calculated

(Feng et al., 2004) for all the cores using Al as the reference element, to differentiate between the metals originating from anthropogenic (non-crustal) and geogenic (crustal) sources, and to assess the degree of metal contamination. The EF is given by equation (1)

$$EF = (C_n / C_{Al})_{sediment} / (C_n / C_{Al})_{background} \quad (1)$$

where, $(C_n/C_{Al})_{sample}$ is the ratio of concentration of the element (C_n) to that of Aluminium (C_{Al}) in the sediment sample; $(C_n/C_{Al})_{background}$ is the same ratio with background value taken of average shale **(Turekian and Wedepohl, 1961).** Aluminium was selected as the reference element as it is a major constituent of fine grained alumina silicates with which the bulk of the trace metals are usually associated. It is highly refractory and its concentration is generally not influenced by anthropogenic sources **(Schropp and Windom, 1988; Loring, 1991)** and also not affected by early diagenetic processes and strong redox effects observed in sediments **(OSPAR, 1998).** According to **Zhang and Liu (2002)**, EF values between 0.5 and 1.5 indicate the metal is entirely from crustal material or natural processes, whereas EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic.

Near the head region of the creek, except for Cr and to some extent Fe, almost all the metals are found to be highly enriched along the entire core length. In the upper middle region of the creek, sediment exhibits considerable enrichment of Mn while in sediments near the mouth except for Fe and Mn, almost all the other metals are found to be highly enriched. When the average EF values are calculated for the entire creek, the core collected near the creek head shows the highest values for almost all the elements except for Mn, Cr and V while core from upper middle creek region exhibits the lowest value. As already confirmed by statistical analysis, sediment core near the head is recipient of anthropogenic inputs which is supported by the results of EF values.

Index of Geoaccumulation (Igeo) which compares present day contaminant concentrations with pre-civilization background values, was used to quantitatively estimate the metal pollution status of the sediments. It is a semi-quantitative approach based on differences between current measurements and subtracted from average global shale measurement taken as background values **(Muller, 1979).** The Igeo is given by equation (2)

$$Igeo = \log_2 (Cn/1.5Bn) \quad (2)$$

Where, Cn = the measured concentration of the element n in the sediment fraction; Bn = geochemical background of element n, taken from literature (average global shale) as local or regional background values are unavailable for this region. The factor 1.5 is introduced to include the possible variations of the background values due to lithogenic variations.

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

Table 2. Geoaccumulation index proposed by Muller (1979)

Table 2 gives the classification for metal pollution. Class 0 to class 6 represents increasing intensity of pollution, i.e. from unpolluted to very strongly polluted. Figure 2 shows the distribution plots of Igeo for selected metals in Thane creek.

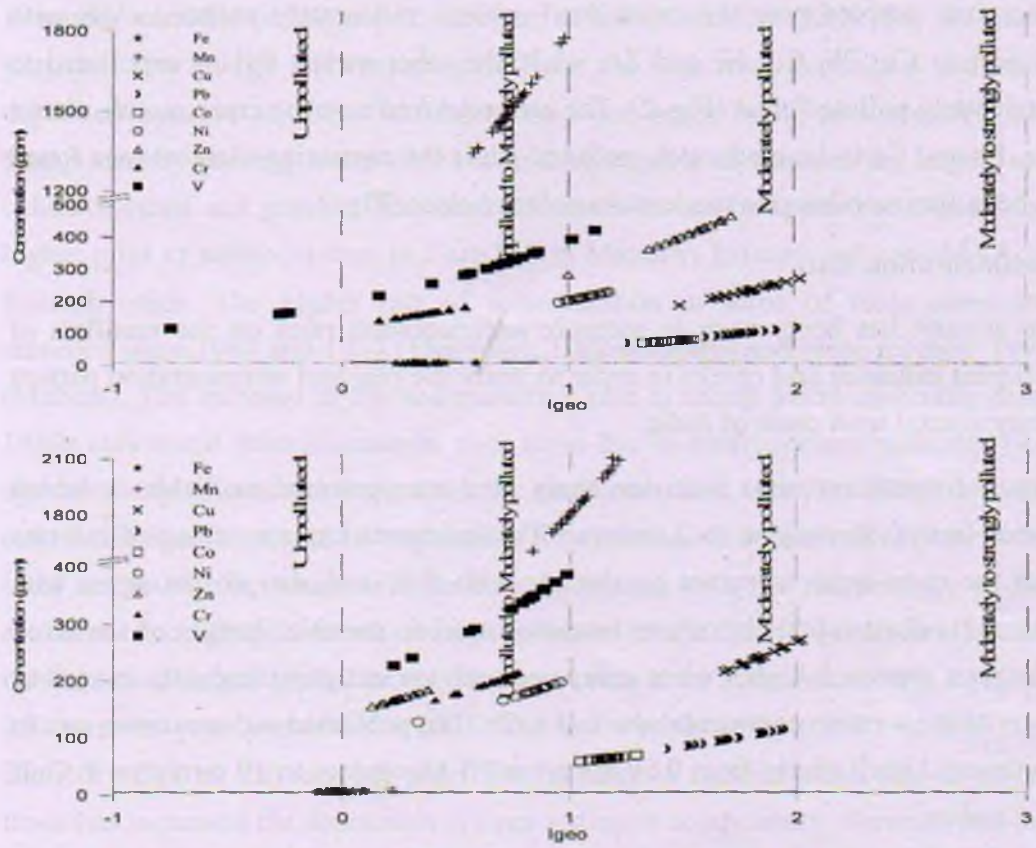


Fig. 2. Igeo plots for cores collected near the creek a) head and b) mouth of Thane creek

Core Name	Location	Sedimentation rate (cm/year)
MAA	Kolamb Creek Malvan	1.21 (0 – 10 cm), 0.31 (> 10 cm)
MAK	Karli River	0.34
MS		1.63 (0 – 28 cm), 0.13 (>28 cm)
MR	Mandovi Estuary, Goa	1.41 (0 - 36 cm), 0.14 (>36 cm)
KM		1.28
KH	Kalinadi Estuary, Karwar	0.55
GH	Tadri River, Gokarn	2.00 (0 - 26 cm), 0.16 (>26 cm)

Table 3. Sedimentation rates in different mudflats

The core sampled near the creek head exhibits moderately polluted class with respect to Cu, Pb, Co, Ni and Zn, while the other metals fall in unpolluted to moderately polluted class (**Fig. 2**). The core retrieved near the creek mouth, shows Cu, Pb and Co to be moderately polluted while the remaining elements are found to be in the unpolluted to moderately polluted class (**Fig. 2**).

Sedimentation Rate

An attempt has been made to measure sedimentation rates on the mudflats of different estuaries and creeks in order to study the regional sedimentation pattern along central west coast of India.

The sedimentation rates from the study area are presented in **Table 3**, which varies from 0.36 cm/year to 2 cm/year. The sedimentation rates obtained indicate that the river input were not persistence with time and also do not agree with general understanding, 1mm/year increase based on eustatic changes of sea level. The rates are much higher when compared with various published data of various parts of the western continental shelf of India. The published sedimentation rate in continental shelf varies from 0.56 mm/year off Mangalore to 19 mm/year in Gulf of Cambay.

The higher rate is expected in the present study area because the core sites are in the mudflats within the estuaries and creeks. It is a known fact that estuaries and tidal creeks are active reservoirs for sediments between land and ocean **(Salomons and Forstner, 1984).** High rate of sedimentation (2.96 cm/year) in Ulhas estuary was reported earlier by **Ram et al. (2003)** and cited the high sediment transport through Ulhas River during monsoon is possibly responsible for the high sedimentation rate. The mudflats of Karli River (Malvan) and Kali River (Karwar) show a single phase of sedimentation with time while mudflats in Mandovi Estuary (Goa), Tadri River (Gokarn) and Kolamb Creek (Malvan) show two phases of sedimentation, a relatively low to higher rate of sedimentation with time.

Interestingly, given the same longitude and within the same estuary, the two cores of Kali River show difference in sedimentation rates which is higher 1.28 cm/year in muddy mudflat (KM) to 0.55 cm/year of sandy mudflat (KH). So, the more protected low energy environments facilitate the high mud deposition and once deposited because of their 'stickiness' they can resist being re-suspended and transported by moving water which would be capable of transporting larger, un-cohesive sands and gravels. The same phenomenon can be applied to explain the higher rates of sedimentation in Core MS in Mandovi Estuary and core MAA of Kolamb creek. The higher rate of sedimentation in some of these areas are recorded since 1980 and 1987 (Mandovi), 1982 (Gokarn) and more recently 1996 (Malvan). The increase in the sedimentation rate in recent years especially from 1980s may result from increase in river input due to anthropogenic activities like agricultural practices, mining etc. in the catchment area. Another factor, besides river discharge, that could be responsible for variations in sedimentation rate is the local sea level rise, which will be directly related with the morphology of the estuaries. According to fourth assessment report of the Inter Governmental Panel on Climate Change, global average sea level rose at an average rate of 1.8 (1.3 to 2.3) mm per year over 1961 to 2003. The rate was faster over 1993 to 2003, i.e. about 3.1 (2.4 to 3.8) mm per year. The increase in sedimentation rate in recent times has increased the deposition of finer sediment components, elements and the magnetic minerals (**Table 4**). Marked changes are observed in values of different sediment components, elemental concentrations and magnetic susceptibility in the two phases of sedimentation. In all the four cores, it is observed that more finer fraction of sediments (mud) was deposited during the recent higher rate of sedimentation. The increase in finer sediments may reflect the periods of wet and cold climates. The organic carbon content in these two cores was also increased and higher during the recent phase of sedimentation. Similarly, the change in sedimentation has affected the elemental distribution too. All the elements except Pb are comparatively enriched in second phase of higher sedimentation in both the cores.

Metal Speciation and Bioavailability

Heavy metals are present in different chemical forms viz., metal carbonates, oxides, sulphides, organo-metallic compounds and lattice structure bound. However, only part of the metal present can be easily remobilized. Site-specific chemical and physical conditions greatly influence the form in which metals occur in the environment and thus the degree to which they are sorbed to sediments and soils. Chemical processes at the sediment-water interface are complex and are governed by physicochemical characteristics such as grain size, organic matter, redox potential or ionic strength change, resulting in the release of bound metal into solution **(Wepener and Vermuelen, 2005).** Unlike many organic contaminants that lose toxicity with biodegradation, *metals cannot* be degraded and their toxic effects can therefore be long lasting **(Clark, 1992).** Because, metals can be either adsorbed onto sediments or accumulated by benthic organisms to toxic levels, bioavailability and toxicity depend upon the amounts of metal bound to the sediment **(Yu et al., 2010).** Chemical speciation can be defined as the identification and quantification of the different chemical species, forms or phases present in the sediment.

Core TI, sampled near the creek head, showed higher concentration of most of the metals in the first three fractions as compared to the other cores. The sediment speciation results in all the cores display similar spatial distributions of each metal. Mn appears to have the greatest amount of variability among the fractions. Profiles of the different fractions of Cu and also Mn in core TV are similar and show significant positive correlations between the different fractions. This could be indicative of an equilibrated distribution of the high concentrations measured between the different sediment fractions **(Fernandes, 2013).**

Core	phase	Fe %	Mn ug/g	Zn ug/g	Cu ug/g	Cr ug/g	Co ug/g	Pb ug/g	Ca ug/g	K %	Mg %	Sand %	Silt %	Clay %	OC %	Mud %	Al %	χ (10^{-7} m^3 kg^{-1})
MAA	I	9.47	431	59.25	99.1	154.1	101.6	47.45	2419	0.85	1.14	11.78	33.13	55.09	3.11	88.22	5.48	25.50
	II	7.44	399	47.98	71.92	120.6	89.88	48.96	1088	0.68	0.76	43.12	16.39	40.49	2.8	56.88	4.29	9.29
MS	I	8.95	1382	88.52	57.64	219.5	84.34	28.52	320	1.07	1.32	16.7	29.88	53.42	2.02	83.3	6.14	8.38
	II	5.39	434	61.82	43.11	208.6	79.14	43.75	162.9	0.78	1.05	46.29	12.47	41.25	1.29	53.71	4.5	2.06
MR	I	15.4	3165	81.56	74.63	235.8	106.2	75.94	486.6	0.95	1.47	12.34	48.87	38.75	2.72	87.61	9.35	36.61
	II	8.36	931	75.44	77.06	281.6	51.38	83.75	549.1	0.97	1.54	17.95	42.67	39.38	4.25	82.05	8.06	6.24
GH	I	7.06	467	65.33	55.88	181.4	35.54	16	1084	1.16	1.36	8	38.24	53.76	2.19	92	5.26	5.19
	II	6.82	428	63	50.15	210.4	26.6	12	439.8	1.09	1.05	15.18	36.71	48.11	3.01	84.82	5.94	2.50

Table 4. Average values of different sediment components and metals in two phases of sedimentation.

Sediment Quality Guidelines

If the concentration of metals incorporated in sediments exceed threshold values, a direct risk to detrital and deposit-feeding benthic organisms can occur, which may represent a long-term contamination source to higher trophic levels **(Mendil and Uluözlü, 2007).** Therefore, eco-toxicological effects of heavy metal contaminations in sediments was determined using Sediment Quality Guidelines (SQGs) defined by **MacDonald et al. (2000),** developed for marine and estuarine ecosystem **(Bakan and Ozkoc, 2007).** Generally the primary purpose of SQG is to monitor and protect the aquatic biota from the harmful and toxic effects related with sediment-bound contaminants **(MacDonald et al., 2000; Spencer and Macleod, 2002; McCready et al., 2006).** These guidelines evaluate the degree to which the sediment-associated chemical status which might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality **(Caeiro et al., 2005).** Sediment quality criteria have also been derived using the Apparent Effects Threshold (AET) approach. This approach determines the concentration of a particular toxicant above which a statistically significant ($p<0.05$) biological effect is always observed, e.g. increase in toxicity in sediment toxicity tests, damage to benthic infaunal community structure, histopathological abnormalities in fish **(Chapman and Mann, 1999).** It is assumed that when the threshold AET concentration of a particular toxicant is exceeded under field conditions, any observed effects are due to the contaminant of interest. An advantage of the AET approach is that criteria are developed from field conditions using both chemical and biological information. As reported by many authors, both approaches have their own limitations, e.g. the SQG do not account for the physico-chemical attributes of the sediments such as grain size, organic matter content, sulphides, chemical species and complexes that may increase or decrease the potential for toxic effects at a specific area **(Ingersoll et al., 2000);** and limitations to AET approach are that a large data set is required, the criteria are developed on a chemical by chemical basis and that the method does not account for the effects of multiple toxicants **(Giesy and Hoke, 1990).** Therefore, a combination of these approaches can be a good option to give a more comprehensive and accurate assessment on the contamination status of heavy metals in the region.

Element	Thane Creek			Ulhas Estuary			TEL	PEL	ERL	ERM	Apparent effects threshold (AET)
	Near creek head(TI)	Lower middle (TV)	Near creek mouth (TIV)	Near estuary mouth (UI)	Lower estuary (UV)	Upper estuary (UIV)					
Fe (%)	1.97	0.51	0.45	0.61	0.48	0.53	-	-	-	-	22% (Neanthes)
Mn (ppm)	**866**	**1278**	**1208**	**609**	**1023**	**701**	-	-	-	-	260 (Neanthes)
Cu (ppm)	44.08	40.63	22.47	12	17	23	31.6	149	34	270	390 (Microtox and Oyster Larvey)
Pb (ppm)	27.94	34.97	33.76	24	25	34	35.8	128	46.7	218	-
Co (ppm)	18.33	22.02	17.99	15	16	22	-	-	-	-	10 (Neanthes)
Zn (ppm)	256.06	45.44	50.41	73	71	42	121	459	150	410	410 (Infaunal community)
Cr (ppm)	34.89	24.79	63.97	12	16	28	31.6	111	81	370	62 (Neanthes)

Table 5. Screening Quick Reference table for heavy metals in marine sediment (Buchman, 1999)

Analysis of the partitioning of metals in the sediments indicates that the percentage of metals associated with fractions 1 to 4 differ considerably between the sites and this may indicate relative differences in bio-availability. In general, bio-availability depends on the nature of metal particle associations, the mechanisms of metal release from sediments and the variation in exposure routes **(Chapman et al., 1998).** In the absence of anthropogenic influences, trace metals in sediments are mainly associated with silicates and primary minerals and therefore have limited mobility. Chemical elements introduced from human activity show greater mobility and are associated with other sediment phases, such as carbonates, oxides, hydroxides and sulphides **(Heltai et al., 2005).** Therefore, should significant agitation and mixing with oxygenated water occur, as would happen to material dredged from the shipping channel, oxidative degradation of organic matter would be enhanced resulting in potential mobilisation of Cu, Zn and Cr. Therefore, the elements Cu, Zn and Cr enriched in sediments near the creek head might be released to the water column if there is a change in the environmental condition (**Table 5**). Benthic invertebrates are an important link in the transfer of substances to higher trophic levels because of their close association with sediments and their ability to accumulate metals **(Burgos and Rainbow, 2001).** Further, although metal concentrations in the bio-available fractions are low in the Ulhas estuary, contaminated sediments at relatively shallow depths in estuary experiencing erosion, may present considerable risk to sediment dwelling biota.

Conclusion

Tidal wetlands namely estuaries and creeks are the ultimate repositories of land derived material including waste generated and released to the environment by the human population. Metals in sediments are widely used indicator of anthropogenic pollution. Tidal wetlands play an important role in global carbon cycles. Bioavailable metals if released from the sediment to water column due to processes of either natural or anthropogenic or both, can cause potential risk to water quality and associated biota and in turn health of the wetland ecosystem.

References

1. Alagarsamy, R. (2006). Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. Estuarine, Coastal and Shelf Science, 67, 333-339.
2. Bakan, G. and Ozkoc, H. B. (2007). An ecological risk assessment of the impact of heavy metals in surface sediments on biota from the mid-Black Sea coast of Turkey. International Journal of Environmental Studies, 64 (1), 45-57.
3. Bhosale, U. and Sahu, K. C. (1991). Heavy metal pollution around the island city of Bombay, India. Part II: Distribution of heavy metals between water, suspended particles and sediments in a polluted aquatic regime. Chemical Geology, 90, 285-305.
4. Buchman, M. F. (1999). NOAA screening quick reference tables. NOAA HAZMAT Report 99-1. Seattle, WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, 12p.

5. Burgos, M. G. and Rainbow, P. S. (2001). Availability of cadmium and zinc from sewage sludge to the flounder, Platichthys flesus via a marine food chain. Marine Environmental Research, 51, 417-431.

6. Caeiro, S., Costa, M. H., Ramos, T. B., Fernandes, F., Silveira, N., Coimbra, A., Medeiros, G. and Painho, M. (2005). Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. Ecological Indicators, 5(2), 151-169.

7. Chapman, P. M. and Mann, O. S. (1999). Sediment Quality Values (SQVs) and Ecological Risk Assessment (ERA). Marine Pollution Bulletin, 38, 339-344.

8. Chapman, P. M., Wang, F., Janssen, C., Persoone, G. and Allen, H. (1998). Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment and remediation. Canadian Journal of Fisheries and Aquatic Sciences, 55, 2221-2243.

9. Clark, R. B. (1992). Marine Pollution. Oxford University Press, Oxford.

10. Dessai, D. V. G. and Nayak, G. N. (2009). Distribution and speciation of selected metals in surface sediments, from the tropical Zuari estuary, central west coast of India. Environment Monitoring and Assessment, 158, 117-137.

11. Feng, H., Han, X., Zhang, W. and Yu, L. (2004). A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. Marine Pollution Bulletin, 49, 910-915.

12. Fernandes, L. (2013). Reconstructing pollution history from intertidal regions of estuaries along Mumbai Coast, India. Ph.D. Thesis submitted to Goa University, Goa.

13. Fernandes, L. and Nayak, G. N. (2009). Distribution of sediment parameters and depositional environment of mudflats of Mandovi estuary, Goa, India. Journal of Coastal Research, 25, 273-284.

14. Fernandes, L. and Nayak, G. N. (2012a). Heavy metals contamination in mudflat and mangrove sediments (Mumbai, India). Chemistry and Ecology, 1-21.

15. Fernandes, L., Nayak, G. N. and Ilangovan, D. (2012). Geochemical Assessment of Metal Concentrations in Mangrove Sediments along Mumbai Coast, India. International Journal of Civil and Geological Engineering, 6, 15-20.

16. Fernandes, L., Nayak, G. N., Ilangovan, D. and Borole, D. V. (2011). Accumulation of sediment, organic matter and trace metals with space and time, in a creek along Mumbai coast, India. Estuarine Coastal and Shelf Science, 91, 388-399.

17. Fernandes, L. and Nayak, G. N. (2012b). Geochemical assessment in a creek environment: Mumbai, west coast of India. Environmental Forensics, 13, 43-54.

18. Fernandes, L. and Nayak, G. N. (2010). Sources and Factors Controlling the Distribution of Metals in Mudflat Sedimentary Environment, Ulhas Estuary, Mumbai. Indian Association of Sedimentologists, 29, 71-83.

19. Folk, R. L. (1974). Petrology of sedimentary rocks. Hemphill, Austin, Texas, 177p.

20. Gaudette, H.E., Flight, W.R., Toner, L. and Folger, D.W. (1974). An inexpensive titration method for the determination of organic carbon in recent sediments. Journal of Sedimentary Petrology, 44, 249–253.

21. Giesy, J. P. and Hoke, R. A. (1990). Freshwater sediment quality criteria: Toxicity bioassessment. In Sediments: Chemistry and Toxicity of In-Place Pollutants (Baudo, R., Giesy, J., and Muntau, H., Eds), CRC Press Inc, Boca Raton, FL, 265-332p.

22. Heltai, G., Percsich, K., Halász, G., Jung, K. and Fekete, I. (2005). Estimation of ecotoxicological potential of contaminated sediments based on a sequential extraction procedure with supercritical CO_2 and subcritical H_2O solvents. Microchemical Journal, 79, 231-237.

23. IMD (2007). Annual climate summary 2007: Indian Meteorological Department, Govt. of India, Pune, India, 27p.

24. Ingersoll, C. G., Macdonald, D. D., Ning, W., Judy, L. C., Field L. J., Pam, S. H., Nile, E. K., Rebekka, A. L., Corinne, S. and Dawn, E. S. (2000). Prediction of sediment toxicity using consensus-based freshwater sediment quality guidelines. United States Geological Survey (USGS) final report for the U.S. Environmental Protection Agency (USEPA), Great Lakes National Program Office (GLNPO).

25. Jarvis, I. J. and Jarvis, K. (1985). Rare earth element geochemistry of standard sediments: a study using inductively coupled plasma spectrometry. Chemical Geology, 53, 335-344.

26. Loring, D. H. (1991). Normalization of heavy-metal data from estuarine and coastal sediments. ICES Journal of Marine Science, 48, 101-115.

27. MacDonald, D. D., Ingersoll, C. G. and Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology, 39, 20-31.

28. McCready, S., Birch, G. F. and Long, E. R. (2006). Metallic and organic contaminants in sediments of Sydney Harbour, Australia and vicinity - a chemical dataset for evaluating sediment quality guidelines. Environment International, 32, 455-465.

29. McDonald, T. J., Mahlon, K. C., Rafalska, J. K. and Fox, R. G. (1991). Source and maturity of organic matter in glacial and Cretaceous sediments from Prydz Bay, Antarctica, ODP Holes 739C and 741A. In Barron, J., Larsen, B., et al., Proc. ODP, Sci. Results, 119: College Station, TX (Ocean Drilling Program), 407-416p.

30. Mendil, D. and Uluözlü, O. D. (2007). Determination of trace metal levels in sediment and five fish species from lakes in Tokat, Turkey. Food Chemistry, 101, 739-745.

31. Muller, G. (1979). Schwermetalle in den sedimenten des Rheins - Veranderungen seit (1971). Umschau, 79, 778-783.

32. OSPAR (1998). OSPAR guidelines for the Management of Dredged Material. Annex 43 (Ref. B-8.2) of Ministerial Meeting of the OSPAR Commission, 32p.

33. Ram, A., Rokade, M. A., Borole, D. V. and Zingde, M. D. (2003). Mercury in sediments of Ulhas estuary. Marine Pollution Bulletin, 46, 846-857.

34. Salomons, W. and Forstner, U. (1984). *Metals in the Hydrocycle.* Berlin: Springer, 349p.

35. Schropp, S. J. and Windom, H. L. (1988). A guide to the interpretation of metal concentrations in estuarine sediments. Coastal Zone Management Section, Department of Environmental Regulation, Florida, 74p.

36. Singh, K. T. and Nayak, G. N. (2009). Sedimentary and Geochemical Signatures of Depositional Environment of Sediments in Mudflats from a Microtidal Kalinadi Estuary, Central West Coast of India. Journal of Coastal Research, 25(3), 641-650.

37. Spencer, K. L. and MacLeod, C. L. (2002). Distribution and partitioning of heavy metals in estuarine sediment cores and implications for the use of sediment quality standards. Hydrology and Earth Science System, 6(6), 989-998.

38. Turekian, K. K. and Wedepohl, K. H. (1961). Distribution of the elements in some major units of the Earth's crust. Geological Society of American Bulletin, 72, 175-192.

39. Walkey, A. and Black, J. A. (1934). The determination of organic carbon by rapid titration method. Soil Science, 37, 29-38.

40. Wepener, V. and Vermeulen, L. A. (2005). A note on the concentrations and bioavailability of selected metals in sediments of Richards Bay Harbour, South Africa. Water SA, 34(4), 589-595.

41. Yu, R., Hu, G. and Wang, L. (2010). Speciation and ecological risk of heavy metals in intertidal sediments of Quanzhou Bay, China. Environmental Monitoring and Assessment, 163, 241-252.

42. Zhang, J. and Liu, C. L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China–Weathering features, anthropogenic impact and chemical fluxes. Estuarine, Coastal and Shelf Science, 54, 1051–1070.