Chapter Four

SEDIMENT CHARACTERISTICS: KALINADI, TADRI AND KARLI ESTUARIES
SECTION 4A: KARWAR (Kalinadi)

Two shallow cores namely KH (Hiresitta) and KM (Madewada) were collected from the mudflats of the Kalinadi Estuary. Core KH was collected from the mudflat of a creek with a wide mouth nearer to sea while core KM was collected from the mudflat of a more sheltered creek with a narrow mouth interior to estuarine environment.

4A. 1 Field Observations

On the field, the sediment cores could be separated in to three vertical zones based on difference in sediment colour as follows:

1. A brown top layer of sediment, 17 cm in core KH and 18 cm in core KM.
2. A grey middle layer located in between 17-50 cm in core KH and 18 - 48 cm in core KM.
3. A mixed bottom layer in between 50-76 cm in core KH and 48-70 cm in core KM.

A distinct geochemical redox profile, which is visually evident, often develops in mudflats and salt marshes (Zwolsman et al., 1993; Williams et al., 1994; Cundy and Croudace, 1995b). The visual evidence is mainly due to the post depositional relocation of the major elements Mn and Fe in the Marsh profile, with formation of red/brown Mn (IV) and Fe (III) oxyhydroxides in an upper oxidized zone and of reduced black/grey Fe (II) sulfides in a deeper reducing zone (Thomson et al., 2002). These field observations are in agreement with the down core distribution profiles of analyzed grain size components and redox- sensitive elements (Fe and Mn), which are discussed below in detail.

4A. 2 Sediment Components (sand, silt, clay and organic carbon)

4A. 2a Results

The percentage of sand, silt and clay for each core are presented graphically (Fig. 4A. 1) and described below.
<table>
<thead>
<tr>
<th></th>
<th>Sand %</th>
<th>Clay %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Silt %</th>
<th>O.C. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.63%</td>
<td></td>
<td>0.63%</td>
</tr>
<tr>
<td>1.86%</td>
<td></td>
<td>1.86%</td>
</tr>
<tr>
<td>38 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68 cm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 4A.1.** Down core variation of sediment components: A – core KH, B – core KM

The data obtained shows a range of 38% - 80% sand, 4% - 35% silt, and 10% - 30% clay for core KH and range of 14% - 70% sand, 4% - 38% silt, and 24% - 59% clay for core KM. It is observed that in both the cores, sediment size decreases upward. However the difference between the two cores is that, the core KH, which was collected from a creek with a wide mouth nearer to sea, is typically sandy with an average of 64% sand, while core KM, which was collected from a more sheltered creek with a much narrow mouth to estuarine environment is muddy with an average of 64% of mud (<63μm) and 36% of sand. In both the cores, the clay fraction is nearly constant and the variations can be directly related to the increase in the sand fraction with depth replacing silt.

The organic carbon (OC) content of core KH (Fig. 4A.1A) varies from a minimum of 0.63% at 58 cm, where silt and clay content is also low, to a maximum of 1.86% at 12 cm depth. There are three maxima of organic carbon at depth 38 cm, 48 cm and 66 cm that are coincided with silt and clay maxima. Organic carbon values increase from base of the core to the surface as a whole but it is more pronounced in the top 32 cm from where it maintains a nearly constant profile with some fluctuations downwards. In core KM, the organic carbon value (Fig. 4A.1B) shows a maximum
of 2.59% at 20 cm depth and a minimum of 1.34% at 64 cm depth. As a whole, the organic carbon content increases from the base of the core with an exception of 62 - 54 cm where values suddenly rise before falling at 54 cm.

From the grain size profiles with depth (Fig. 4A. 1A) the core KH can be divided into three sections namely 76 - 46 cm, 46 - 18 cm and 18 - 0 cm. The bottom section 76 - 46 cm is marked by the gradual decrease of sand, which is compensated by the gradual increase in both silt and clay. In middle layer 46 - 18 cm, distributions of sand, silt as well as clay is near constant with some variations at few points. In the top 18 - 0 cm layer, there is decrease in sand accompanied by increase in silt but with ups and downs of clay content.

Similarly, in core KM (Fig. 4A. 1B), the whole core can be divided into three different sections but at different depths depending upon the sediment components. The bottom portion 70 - 40 cm is marked by the gradual decrease in sand content which is compensated by the gradual increase in both silt and clay. The middle portion 40 - 16 cm is characterized by a decreasing trend of sand compensated by the increase of silt and clay fraction. A nearly constant sand distribution and increasing and decreasing profiles of silt and clay respectively characterize the upper portion from 16 cm to surface with a break at 10 cm depth.

![Figure 4A. 2(A, B). Ternary diagrams for the textural classification of sediments on the basis of sand/mud ratios. A: after Reineck and Siefert (1980). B: Flemming (2000).](image)

Further, in order to understand the change in sediment characters throughout the core and hence the depositional environment, ternary diagram (Fig. 4A. 2A)
proposed by Reineck and Siefert (1980) was used. It is found that both cores (KH and KM) can be divided into two distinct classes as given below:

<table>
<thead>
<tr>
<th>CORE KH</th>
<th>CORE KM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (cm)</td>
<td>Class</td>
</tr>
<tr>
<td>0 - 14</td>
<td>Mudflats</td>
</tr>
<tr>
<td>14 - 70</td>
<td>Mixedflats</td>
</tr>
</tbody>
</table>

It is clear from the diagram that core KH has transformed to mudflat from mixedflat much later than core KM.

Further, a highly variable grain size characters with depth is also witnessed when the data was plotted in ternary diagram (Fig. 4A. 2B) of Flemming (2000). It is found that, both the cores can be divided in to three zones as follows:

<table>
<thead>
<tr>
<th>CORE KH</th>
<th>CORE KM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (cm)</td>
<td>Lithology</td>
</tr>
<tr>
<td>0 - 14</td>
<td>Sandy mud</td>
</tr>
<tr>
<td>14 - 66</td>
<td>Muddy sand</td>
</tr>
<tr>
<td>66 - 76</td>
<td>Slightly muddy sand</td>
</tr>
</tbody>
</table>

Further, the hydrodynamic condition of the depositional environment was inferred so as to validate the variations in depositional regime indicated by the different sediment component analysis. The components plotted in ternary diagram (Fig. 4A. 2C) of Pejrup (1988) falls in groups II(B) and III(C) for core KH, which represents a quiet to more violent hydrodynamic condition. On the other hand, core KM falls under groups I (B) and II (B and C), which represents the very calm condition to quiet hydrodynamic conditions.

Fig. 4A. 2C. Triangular diagram for the classification of hydrodynamic conditions after Pejrup (1988).
4A. 2b Discussion

It is argued that the composition of sediment simply reflects source related features. While this holds true for the mineralogical and textural composition of many sediments, it is equally true that the source controlled grain size spectra would still be subjected to size sorting in course of hydrodynamic transport, which would hence result in selective deposition along an energy gradient (Bagnold, 1968). In the present study, the sediment component variation shows a marked change with space and time which indicates the change in energy gradient and hence the depositional environment. In the cores studied, there are three distinct successive textural groups that are very well supported by the distribution profiles of different sediment components that may probably be suggesting the three episodes of deposition in three different environmental settings. From sediment component analysis explained above as well as from grain size profiles, an upward fining trend is witnessed i.e. finer sediments are deposited more in recent past. Most importantly, the ternary diagram of Reineck and Siefert (1980) showed the transformation of mixed mudflat to mudflat with time. All these ample evidences are enough to infer that the depositional environment was changing with time in terms of energy gradient of river current and ocean tides, proximity from the shoreline, supply of sediment and climate. In the same time the areas could have become more protected due to certain act of human interference in the form of construction of dams and bunds facilitating the deposition of finer fractions. The possibility of role played by the climate especially rainfall cannot be ruled out as grain-size fluctuations in sediment through time, particularly increase in sand sizes, may reflect low-level lake stands related to periods of dryer and warmer climate. Conversely, decrease in sand content may reflect periods of wet and cold climates (Alin and Cohen, 2003). But all these need to be validated with dating, rainfall data as well as with geochemistry data. Further there is a marked variation in sediment components between the two cores that could be because of difference in geomorphology and its enhanced processes. The creek from where core KH was collected has a wide mouth nearer to sea through which both the tidal as well as river action would be relatively pronounced resulting in the deposition of coarser fractions. On the other hand, the creek from where core KM was collected has a very narrow mouth interior to the estuarine environment by which the actions of both tides and river would be more restricted resulting in the deposition of finer
fractions. Grain-size variations in sediments reflect changes in the processes and energy of sediment transport. Particle size is closely linked to turbulence, wave energy, and proximity to shoreline. Increased grain size generally correspond to higher energy conditions, whereas decreased grain size indicate lower energies, which is well true in the present study as the muddy core KM sediments fall in very quiet to quiet conditions while sandy core KH sediments fall under more violent hydrodynamic conditions.

The decline in organic carbon with depth is generally attributed to degradation, and such profiles are frequently observed in sandy marine sediments. Although some degradation of organic matter must be occurring in the sediments, the dominant control on organic matter content in core KH seems to be due to the proportion of mud-size particles. The decrease in organic carbon with depth can be accounted for with the decrease of input of silt to which it shows a good correlation (R=0.69) to that of clay (R=0.48). So, individually distribution of organic carbon with depth is more controlled by silt than clay but more significantly by mud fraction (R=0.70). The strong correlation between organic carbon and finer fraction can be related to the process of organic matter preservation by sorption onto finer particles. However, in core KM, the organic carbon profile is different showing relatively poor correlation with mud.

4A. 3 Clay mineralogy

The XRD analysis was carried out for core KH and the identified clay minerals are kaolinite, illite, smectite and chlorite in order of decreasing abundance (Table 4A. 1). The clay mineralogy is similar throughout the core with no major changes in the proportions of clay minerals components, which would suggest little change in source or provenance over the observed sedimentation period. The composition of clay minerals, which are the weathering products of rocks and soil on land, largely depends on climate,
geology and topography of the region (Singer, 1984; Chamley, 1989). Intense chemical weathering and leaching of crystalline rocks under the tropical humid climate leads mainly to the formation of kaolinite and gibbsite (Chamley, 1989). A gneissic province is characterized by kaolinite and gibbsite that are the weathering products of Precambrian gneissic rocks and laterites of Southern India (Rao and Rao, 1995). In the present study, higher amount of kaolinite and illite clearly reflect their derivation from the catchment area, which consists mainly of Precambrian crystalline rocks that are lateritised at places. Chlorite content remained low throughout the core and can be attributed to the prevailing humid tropical climatic conditions in this region, wherein chlorite mineral is unstable.

**4 A. 4 Geochemistry**

**4 A. 4a Results**
The distribution of major elements (Al, K and Mg) in both the cores (Fig. 4A. 3A and 3B) is largely controlled by grain size. Al, K and Mg profiles agree with silt and clay and show a nearly increasing trend towards the surface. The Ca profile shows an erratic trend in core KH while in core KM, it shows a decreasing trend with some spikes from base to 22 cm from where values show sudden decreasing trend up to 6 cm before it increases towards the surface. The sudden decrease of Ca in the top portion of core KM is likely to be due to total dissolution of CaCO$_3$ as acidity is generated in the pore waters of the oxic zone of the sediments (Froelich et al., 1979). The vertical profiles of trace metals including Fe and Mn in both the cores show three zones supporting the results of sedimentary profiles but with variations in depth. In core KH (Fig. 4A. 3A), the bottom portion (76 - 56 cm) shows nearly steady low trends followed by a middle zone (56 – 18 cm) of increasing upward but very erratic trends and an uppermost zone (18 - 0 cm) marked by the enrichment of all the trace metals.
Fig. 4A. 3. Down core variation of metals: A - core KH, B - core KM.
In case of core KM (Fig. 4A, 3B), different metals show different patterns within these three portions probably reflecting the different post depositional behaviors. The profiles of Zn and Cu are similar to large extent with increasing upward trend with some ups and downs in the bottom portion (70 - 56 cm), followed by a middle portion (56 - 30 cm) of gradual upward increase and finally decreasing trend in the uppermost (30 - 0 cm) portion. Cr shows a decreasing trend in the bottom portion followed by an increasing trend in the second portion and finally an erratic distribution in the upper portion. Co values show an increasing trend in the bottom portion agreeing with Zn and Cu, then an erratic trend in the middle portion and gradually increasing upward trend in the top portion.

4A. 4b Discussion

4A. 4b i Vertical distribution

The homogeneity with depth of both the cores is illustrated by the profile of K normalized to Al (Fig. 4A, 3A and 3B) to account for the constant sum problem (Rollinson, 1992). The relative constancy of the K/Al profile with depth is interpreted to imply that the composition of the accumulated material has not fluctuated dramatically over time. Therefore, the observed trends of metal distribution are not because of the variation in source. At the same time, metals have been observed to be mainly associated with fine sediments (especially clay), associated Fe/Mn and organic coatings which provide reactive sites for metal sorption (Grant and Middleton, 1990; Cundy and Croudace, 1995a). The presence of a strong Fe and Mn peak may indicate redox mobilization and trace metals originally associated with Fe/Mn substrate (McCaffrey and Thomson, 1980; Zwolsman et al., 1993). Recognizing that the elements exhibiting the largest signals are Fe and Mn, the redox status of the cores will be inferred mainly from these elements together with the changes in color observed in the field. Analysis of the correlation coefficients among the different chemical components for core KH shows a significant correlation of Al with Fe (0.78), Mn (0.86), Cu (0.65), Cr (0.63), K (0.75) and Mg (0.63) while in the core KM, Al shows a significant correlation with Fe (0.90), Mn (0.81), Zn (0.66), Cu (0.75), Co (0.76) K (0.87) except with Mg (0.48). This strong correlation with Al indicates that metals are dominantly associated with clay minerals, probably as lattice-bound components (Rosales-Hoz et al., 2003). The profiles are, therefore, being normalized in order to remove the grain size effect as
suggested by Ackermann (1980) and Grant and Middleton (1990). However, the bulk profiles in core KM are almost similar with normalized ones indicating minor mineralogical variations with depth. But, the distribution may be due to early diagenetic processes (Berner, 1980) as well as environmental contamination (Anderton, 1985). On the other hand, the normalized profiles, except Mn, of core KH are considerably changed from bulk profiles suggesting the role played by the fine sediments in distribution of metals and therefore, the normalized trends will be considered for further discussion.

The concentration of Fe in core KH is steady from bottom to 54 cm and then erratic in nature up to 32 cm depth from where it drops suddenly and then increases towards the surface of the core. In core KM, the value decreases from base of the core to 50 cm from where value gradually increases towards the surface and enriched in top 8 cm of the core. However, Mn concentrations show enrichment in the upper 18 cm in core KH and 8 cm in core KM from where the values decrease up to 50 and 46 cm respectively before maintaining a steady trend to the bottom of their respective cores. These features are probably caused by the dissolution of Fe and Mn oxyhydroxides in the partly reduced sediment layer, upward migration and reprecipitation near the oxic-suboxic interface. The enrichment is more apparent in Mn than Fe in both the cores as diagenetic Fe enrichment starts at greater depth than diagenetic Mn enrichment because of the somewhat higher stability of Fe oxyhydroxides under mildly reducing conditions and the faster oxidation kinetics (Zwolsman et al., 1993; Selvaraj et al., 2003). The Mn maximum in the top layer of 18 cm in core KH and 8 cm in core KM may probably indicate an oxic condition which is followed by a suboxic zonation up to ~50 and 46 cm respectively, which is also supported by the brown and grey colour observed in the field and Ca profile, in core KM, described above.

Evidence of diagenetic modifications can be seen below the oxic suboxic interface of the cores due to the dissolution of Fe and Mn oxyhydroxides. In core KH, Fe and Mn show significant correlation with Cu (0.67, 0.71) and Cr (0.65, 0.72) suggesting Cu and Cr are associated with Fe and Mn oxyhydroxides. In case of core KM, Fe shows a significant correlation with Co (0.71) and Cu (0.80) while Mn shows a significant correlation with Co (0.79) only. The similarity in the profiles of Cu and Zn
with depth in core KM and their significant association with Fe only suggests the distribution of Cu and Zn may be strongly controlled by Fe cycling than Mn cycling. Allen et al. (1990) identified a similar pattern for Cu, Pb and Zn in sediments from the Severn Estuary. On the other hand Co shows a better association with Mn than Fe in the core KM and in the top oxic layer in core KH, reflecting that Co is more cycled along with Mn oxides at redox boundaries (Zwolsman et al., 1993). The exclusive role played by Mn oxides in the cycling of Ni and Co has been reported earlier by Klinkhammer (1980) and Shaw et al. (1990). This evidence of heavy metal coprecipitation with Fe and Mn oxides may be related to pore-water movement during the reduction and re-adsorption in oxic zone (Finney and Huh, 1989). Hence cycling of Fe and Mn may partly control the vertical profile of trace metals in these sediments.

Organic carbon and clay contents are the major controlling factors, which influence the binding of heavy metals (De Groot et al., 1976; Fletcher et al., 1994; Williams et al., 1994). The association of heavy metals including Fe and Mn with finer fractions in both the cores can be demonstrated through correlation of metal concentrations with sediment components. In core KH, mud (silt and clay) shows a significant positive correlation of 0.88 with Fe (0.87 silt, 0.60 clay); 0.90 with Mn (0.90 silt, 0.60 clay); 0.66 with Cu (0.60 silt, 0.55 clay) and of 0.74 with Cr (0.76 silt, 0.46 clay) whereas, sand shows the strong negative correlation with same elements (-0.89 Fe, -0.92 Mn, -0.69 Cu, and -0.74 Cr). In core KM, mud shows significant positive correlation of 0.88 with Fe (0.78 silt, 0.79 clay); 0.90 with Mn (0.77 silt, 0.83 clay); 0.67 with Zn (0.68 silt, 0.52 clay); 0.71 with Cu (0.67 silt, 0.60 clay) and of 0.80 with Co (0.70 silt, 0.74 clay) whereas sand shows strong negative correlation with the same elements (-0.88 Fe, -0.90 Mn, -0.67 Zn, -0.71 Cu and -0.70 Co). Similarly, association of organic carbon with heavy metals can be seen in core KH, even though overall organic carbon content is low. However, the degree of correlation does not support the control on heavy metals distribution in core KM. During initial deposition, trace metals may become associated with organic matter (Salomans and Forstner, 1984). Metals may be redistributed by early aerobic degradation of organic matter resulting in gradual decrease in metal concentration with depth (Allen et al., 1990; Valette-Silver, 1993). In core KH, values of organic carbon show a more or less decreasing trend with depth and the concentrations of metals Fe,
Mn, Cu and Cr show characteristic decrease with depth, which suggests that metals have been significantly redistributed by the degradation of organic carbon. It is also supported by significant correlation with organic carbon with Fe (0.61), Mn (0.72), Cu (0.62) and Cr (0.73). It can be probably accounted to the percolation of oxygen rich pore water in this sandy mudflat during high tides that allows the degradation of organic carbon. Selvaraj et al. (2003) has reported the clear early diagenetic signal due to percolation of oxygen rich pore water, which allow the oxidation-reduction changes in sand dominated intertidal region. However, the phenomenon cannot be applied for core KM, as there is little evidence to suggest the association of metals with organic carbon, which is revealed by poor correlation values (Fe, 0.23; Mn, 0.36; Zn, 0.03; Cu, 0.01; Cr, -0.09; Co, -0.21). This may probably be due to oxygen depleted, more protected and muddy sediment in which there is less chance of aeration and hence no degradation. Further, in this condition, the distribution of trace metals is probably controlled by the mud as well as by redox sensitive Fe and Mn oxides. Similar phenomenon has been reported elsewhere earlier by Ayyamperumal et al. (2006) and Spencer et al. (2003).

**4A. 4b ii Spatial distribution**

Geochemical data from surface sediments and cores frequently show variations due to one or more factors. These are mineral variations (change in clay, sand, carbonate or particulate organic matter inputs), redox-controlled element migration and pollution (Cearreta et al., 2000). A difference in sediment components, organic carbon and metal distributions are observed between two cores, which could be because of difference in source, sedimentary processes and depositing site. These variations can be clearly seen through isocon diagrams plotted (Fig. 4A. 4). The isocon diagram shows that there...
was little difference between the two cores in the major elements (Al, K) and heavy metals (Zn, Cu) which are plotted on or near the isocon line indicating little variations. The differences are most apparent with higher concentrations of Ca, Co and sand in core KH while Mg, Fe, Mn, Cr, clay and OC are higher in core KM. This higher amount of Fe, Mn and OC in core KM is clearly due to their association with finer fraction of sediments (clay and silt) which is also high in this core. In the intertidal flats where sulfate reduction is dominated, metal ions are more likely to be precipitated as insoluble through sediment if the extent of water percolation through that sediment is limited (Warren, 1981). This process may account partially for higher metal concentration in core KM, which is more protected and less porous. The marine influence is more visible in core KH by higher concentrations of Ca with an increase in grain size. Some metals such as Zn and Cr form strong complexes with chloride legands and therefore changes in salinity may have profound effects on their solubility (Forstner and Salomans, 1980). Infact Cr concentration in core KH is comparatively less than in core KM where the change in salinity is more pronounced. Further, there is higher concentration of Mn in the same core with enrichment in the upper portion. Mn oxides are reduced in anoxic sediments to the more soluble oxide forms like Mn$^{2+}$, which can enter the interstitial waters of the sediment (Beeftink and Rozema, 1988). The anoxic conditions present in the tidal flats may facilitate the reduction of Mn oxides in both the cores but with a higher amount of percolation facilitating removal of substantial amount of Mn in sandy core KH where the tidal actions and change in salinity is more pronounced.

4A. 5 Factor analysis

In core KH, three factors representing 70.67% of the total variance in the sample were identified with the loadings given in table 4A. 2. Factor 1 accounts for 52.60% of the total variance and is characterized by high positive loadings (> 0.5) on Fe, Mn, Cu, Cr, K, Mg, Al, silt, clay and organic carbon and high negative loadings on sand. This factor represents the association of metals with silt, clay and organic carbon which indicates detrital components of terrigenous origin. Factor 2 accounts for 9.89% of the total variance and is characterized by moderate positive loadings on Pb and negative loadings on Zn and Ca while Factor 3 accounts for 8.18% of the total variance and is characterized by high positive loadings on Co and Ca. Both the
factors do not show any association with either major elements or sediment components, that suggests different sources including an anthropogenic origin.

Table 4A. 2. Factor analysis matrix after varimax rotation showing correlations with principal components.

<table>
<thead>
<tr>
<th></th>
<th>KH</th>
<th>KM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Variance %</td>
<td>Factor 1</td>
</tr>
<tr>
<td></td>
<td>52.60%</td>
<td>9.89%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.90</td>
<td>-0.02</td>
</tr>
<tr>
<td>Mn</td>
<td>0.95</td>
<td>0.02</td>
</tr>
<tr>
<td>Zn</td>
<td>0.33</td>
<td>-0.60</td>
</tr>
<tr>
<td>Cu</td>
<td>0.76</td>
<td>-0.32</td>
</tr>
<tr>
<td>Cr</td>
<td>0.78</td>
<td>0.07</td>
</tr>
<tr>
<td>Co</td>
<td>0.35</td>
<td>-0.06</td>
</tr>
<tr>
<td>Pb</td>
<td>-0.01</td>
<td>0.45</td>
</tr>
<tr>
<td>Ca</td>
<td>0.02</td>
<td>-0.71</td>
</tr>
<tr>
<td>K</td>
<td>0.74</td>
<td>0.29</td>
</tr>
<tr>
<td>Mg</td>
<td>0.80</td>
<td>-0.25</td>
</tr>
<tr>
<td>Al</td>
<td>0.86</td>
<td>0.07</td>
</tr>
<tr>
<td>Sand</td>
<td>-0.97</td>
<td>-0.07</td>
</tr>
<tr>
<td>Silt</td>
<td>0.93</td>
<td>0.13</td>
</tr>
<tr>
<td>Clay</td>
<td>0.69</td>
<td>-0.08</td>
</tr>
<tr>
<td>OC</td>
<td>0.76</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

Similarly, in core KM, three factors representing 78.03% of the total variance were obtained with loadings given in Table 4A. 2. Factor 1 accounts for 60.85% of the total variance and is characterized by high positive loadings on Fe, Mn, Zn, Cu, Co, Pb, K, Mg, Al, silt and clay and negative loading on sand. This factor shows strong association of metals with finer fraction of sediments and is of detrital origin. Factor 2 accounts for 10.31% of the total variance and is dominated by high positive loadings on Ca while Factor 3 represents 6.87% of the total variance and is dominated by high positive loadings on Cr, which suggest an input from a different source.
4A. 6 Sedimentation rate and Enrichment Factor

The profiles of $^{210}\text{Pb}_{\text{excess}}$ are presented in figure 4A. 5. In both the cores, the $^{210}\text{Pb}_{\text{excess}}$ profile decreased exponentially with increasing depth indicating a constant sedimentation rate and no significant mixing. The absence of surface mixed layer agrees with the fact that bioturbation and physical reworking of the sediments are negligible in this core. Similarly, variations in distribution of sediment components observed in these cores seem to have not affected the rate of sedimentation. The sedimentation rate determined from $^{210}\text{Pb}_{\text{excess}}$ profile is of 0.55 cm/year for core KH and 1.28 cm/year for core KM. This result reveals that these cores represent up to last 138 and 55 years of sedimentation respectively. The EF values of all the metals show more or less similar trends in both the cores (Fig. 4A. 6). The EF values of Mn and Zn are less than 1.5 suggesting that these metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002). On the other hand, EF values of Fe, Cu, Cr, Co and Pb are more than 1.5 which suggests that a significant portion of metal is delivered from non-crustal materials, or non-natural weathering processes.
In core KH (Fig. 4A. 6A), the EF values of Fe, Cu, Cr, Co and Pb are enriched from base of the core up to 30 cm, which corresponds to the year 1951, where the values suddenly dropped and then increased gradually to the present. Similarly, in core KM (Fig. 4A. 6A), Fe, Cu and Cr are enriched from the base of the core to 50 cm, which corresponds to the year 1965, where values suddenly dropped. Subsequently, values of these metals along with Pb increased gradually to the present. So, the EFs of the present study show environmental contamination by Fe, Cu, Cr, Co and Pb throughout the cores.

4A. 7 Magnetic susceptibility

4A. 7a Results

The magnetic profiles of core KH and core KM are shown in figure 4A. 7(A and B). Down core profiles of magnetic parameters are broadly similar between the two cores. In general, the values of $S_{300}$ for both the cores are above 0.7, suggesting that the magnetic properties of the sediments are dominated by ferromagnetic magnetite together with strong contribution from anti-ferromagnetic minerals. The magnetic grain size indicators ($\chi_{ARM}/\chi$, $\chi_{ARM}/SIRM$) reflect the dominance of coarse
magnetite greater than Stable Single Domain (SSD) grains (Oldfield, 1994). Oldfield (1994) suggested that $\chi_{ARM}/\chi < 70$ indicates the dominance of grains coarser than 0.07um. The $\chi_{fd}$ % values indicated a moderate presence of the superparamagnetic (SP) component.

Fig. 4A. 7A. Magnetic profiles of core KH.

The concentration of magnetic minerals ($\chi$, $\chi_{ARM}$, SIRM) exhibited down core as well as inter-core variations. In core KH (Fig. 4A. 7A), below a sediment depth ~60 cm, all the concentration dependent parameters are uniform and strongly suggest a homogenous magnetic mineral assemblage, although there is some variation in granulometric index ratios ($\chi_{ARM}/\chi$, $\chi_{ARM}$/SIRM). Then $\chi$, $\chi_{ARM}$ and SIRM increase upward to surface with some low values in between. $S_{300}$ values are gradually decreasing upward suggesting that there is a gradual decrease in ferromagnetic magnetite with time. The concentration-independent ratios ($\chi_{ARM}/\chi$, $\chi_{ARM}$/SIRM) decline at 60 cm and maintain a nearly uniform trend up the core.
In core KM (Fig. 4A. 7B), a uniform low magnetic layer occurred at the base > 50 cm of the core. Then $\chi$, $\chi_{\text{ARM}}$ and SIRM increase suddenly upward to 40 cm and then maintain a uniform distribution until values increase from 20 cm to surface. $S_{300}$ values are gradually decreasing upward suggesting that there is a gradual decrease in ferromagnetic magnetite with time. The concentration-independent ratios ($\chi_{\text{ARM}}/\chi$, $\chi_{\text{ARM}}$/SIRM) decline from 50 cm to 40 cm from where they maintain a nearly uniform trend of relatively coarser size up the core.

Fig. 4A. 8. Representative thermal demagnetization curves for different sections of core KH and core KM.
The shape of the demagnetization curves of the selected three samples from each core are presented in Fig. 4A.8. The three samples are chosen from different depths of the cores in order to represent the full core. All the samples show somewhat similar trends with a smooth monotonic decay until their unblocking at 580°C and 690°C which are the characteristic of magnetite and hematite.

4A.7b Discussion
The measured susceptibility value depends, on the one hand, on the amount of the magnetic minerals provided by the parent material and, on the other hand, on the amount of newly formed magnetic minerals (Hanesch and Scholger, 2005). The data of this study reflect the influence of the catchment area processes on magnetic susceptibility. The significant correlation of dominant remanence carriers of the magnetic signal (e.g. SIRM) with geochemical indicators of erosion Mg (0.72, 0.57), K (0.69, 0.65) and Al (0.85, 0.67) in core KH and KM respectively probably hint the changes in the catchment area as the possible explanation of the profile (Mackereth, 1966). Evidence for an internally derived, diagenetic changes in the sediment magnetic assemblage is negated by the negative correlation (-0.92, -0.18) between S-ratio parameter and the sedimentary Mn (Anderson and Rippey, 1988).

The other factors like texture of the sediments and human impact can also change the conditions in the catchment area and hence the capability of retaining and/or forming magnetic minerals. Within the cores, significant correlations were noted between susceptibility with organic carbon and clay content probably indicating adsorption on clay particles and/or on organic matter (Hanesch and Scholger, 2005).

The change in magnetic properties that occur in both the cores points to quantitative and qualitative changes in the assemblage of magnetic minerals present. The increase in SIRM and decrease in $\chi_{\text{ARM}}/\chi$, $\chi_{\text{ARM}}/$SIRM ratios reflect an increase in both total magnetic mineral concentrations and in the relative importance of coarser magnetic grain sizes (Maher, 1988). Combined with the higher SIRM, the increased importance of the hardest remanence component points to an increase in hematite in both relative and absolute terms (Oldfield, 1990). The trend in 'soft' and 'hard' isothermal remanence was plotted separately on a mass-specific basis (Fig. 4A.7) and this isolates these two properties from all
other variables responsible for changes in magnetic properties. The trends confirm that both components increase significantly in the upper levels of the core. The increase is relatively much more in hematite than magnetite. So, it would appear that a different and additional source, presumably an input from the catchment area is contributing to the higher hematite and magnetite in recent time. Hematite is likely to be relatively more important than magnetite in recent years and the relative importance of the two may reflect changing anthropogenic source types. Within the catchment area of Kali River there are Iron and Manganese mines and also ferroalloy industries which must be responsible for additional contribution.

**Significance for environmental study:** The relationship between heavy metals and magnetic parameters provided interesting information on heavy metal sources and pathways (Lu et al., 2005). The considerable similarity between heavy metals and $\chi_{ARM}$ was reported from intertidal sediments of the Yangtze Estuary, China by Zhang et al. (2001). It has been suggested that certain magnetic parameters can be used as grain size proxy (Oldfield and Yu, 1994; Zhang et al., 2007). Zhang et al. (2007) reported a strong relationship between $\chi_{ARM}$ and heavy metals, and to a lesser degree between frequency dependent susceptibility ($\chi_{fd}$) and heavy metals, and explained the role of particle size and iron oxides in controlling metal concentration. In the present study, $\chi_{ARM}$ shows good correlation with Cu (0.78) and Cr (0.73) in core KH and with Zn (0.64), Cu (0.72), Co (0.78) and Pb (0.64) in core KM which indicates that there is close association between heavy metals and fine grained magnetite. Most significantly, there is parallelism in trends of 'soft' profiles with metals, which points a strong affinity of heavy metals with ferromagnetic minerals.
SECTION 4B: GOKARN (Tadri)

Two shallow cores namely GH (Hosakatta) and GN (Nusikote) were collected from the mudflats of the Tadri creek. Core GH was collected from the mudflat of a main channel at a distance of ~4.5 km from the mouth of the river whereas core GN was collected from a mudflat interior of estuary and located at a distance of ~6 km from the mouth of the river.

4B.1 Field observations
The cores exhibit clear vertical zonation and can be divided into two units (Zwolsman et al., 1993; Williams et al., 1994; Thomson et al., 2002) as following:
1. A brown oxidized surface layer of 0 – 32 cm for core GH and 0 – 68 cm for core GN.
2. A grey reduced layer of 32 – 66 cm for core GH and 68 – 92 cm for core GN.

4B.2 Sediment components (sand, silt, clay and organic carbon)

4B. 2a Results
In core GH, the sand, silt and clay data obtained show a range of 3.04 - 19.92%; 28.20 - 57.19% and 29.68 - 60.32% respectively and the sediment is muddy with an average value of 89.28% of silt and clay out of which clay (avg.47.32%) is dominated to silt (avg. 41.96%). The sand profile (Fig. 4B.1A) shows an increasing trend from the base of the core up to 52 cm depth with a plateau at 60 to 66 cm and then a gradually decreasing trend towards the surface. Silt shows nearly constant trend with some ups and downs whereas clay shows an opposite distribution to sand with a decreasing trend from base to 52 cm depth from where it increases till the surface of the core. So the core can be divided into two distinct zones marked by variations of sand and clay as lower 66 – 52 cm where the decrease in clay is compensated by the increase in sand and an upper 52 – 0 cm zone where sand decreases in the expense of clay. Organic carbon value ranges from 1.26 to 4.92% with an average value of 3.08%. The profile of organic carbon also shows two distinct zones with a nearly constant trend in the lower 66 – 52 cm portion then it suddenly increases up to 50 cm and then shows decreasing trend in the upper 50 – 0 cm portion. The organic carbon profile agrees with the sand profile except at top 8 cm where it agrees with clay.
In core GN, the data show a range of 9.00 to 67.38% sand, 11.95 to 45.50% silt and 17.40 to 54.13% clay and the clay is the dominating component with an average value of 38.24% followed by sand and silt with average values of 32.15% and 27.71% respectively. Sand and silt profiles (Fig. 4B.1B) with depth show an opposite distribution with three distinct portions, while clay shows a nearly decreasing trend with depth. In the bottom 92 – 64 cm portion sand decreases which is compensated by increase in silt. In the middle 64 - 26 cm portion, sand decreases in the expense of silt while the increase in sand is compensated by the decrease in clay in the top 26 – 0 cm portion. The organic carbon value ranges from a minimum of 0.25% to a maximum of 4.47% with an average value of 1.68%. The organic carbon profile shows a nearly constant trend of relatively high values from the base of the core to 74 cm from where values suddenly decrease up to 66 cm depth and then maintains a gradually increasing trend towards the surface. The distribution of organic carbon largely agrees with clay in the upper portion.
4B. 2b Discussion

The organic carbon content in core GH shows good correlation with sand ($r = 0.50$) and silt ($r = 0.53$) but very poor association with clay ($r = -0.73$). So, individually distribution of organic carbon is controlled by sand and silt. In core GN, organic carbon content showed no association with any of the sediment fraction (0.01, sand; -0.05, silt and -0.37, clay). The gradual increase in organic carbon towards the surface can be seen in the upper portion of the core GN and to some extent in the top most portion of core GH, which are generally attributed to degradation, and such profiles are frequently observed in sandy marine sediments. Although some degradation of organic matter must be occurring in the sediments, the dominant control on organic matter content in core GH seems to be due to the proportion of sand- silt particles.

Further, the changes in sediment characters within the cores are analyzed by plotting the sediment data in ternary diagram proposed by Reineck and Siefert (1980). According to this diagram (Fig. 4B. 2A), core GH falls in mature mudflat class throughout the core while core GN changes from mudflat to mixedflat and from mixedflat to mudflat with time.


Similarly, variation in grain size characters are also witnessed when the data is plotted in ternary diagram (Fig. 4B. 2B) of Flemming (2000). It is found that
sediments of core GH have undergone change from slightly sandy mud to mud with time while in core GN sediments are graded from sandy mud to slightly sandy mud again from slightly sandy mud to sandy mud with time. Therefore, it is clear that core GN shows high variations in sediment characters with repetitions of classes in between while core GH is showing gradually fining of sediments with time.

Further an attempt has been made to infer the hydrodynamic condition of the depositional environment by using the ternary diagram (Fig. 4B. 2C) developed by Pejrup (1988). In the present study, the components plotted for core GH, largely fall in group II (B and C), which represents a relatively quiet hydrodynamic condition. On the other hand, core GN falls under group II (C and D) and III (C and D), which represents the relatively violent hydrodynamic conditions.

4B. 3 Geochemistry
4B. 3a Results

Major element profiles, in core GH, do not agree with any of the sediment component profiles (Fig. 4B. 3A). Al profile shows three portions of distinct distribution with bottom portion 66 - 54 cm of high value but decreasing trend which is followed by middle 54 - 18 cm of constant trend while a low value but highly fluctuating trend characterized the top 18 - 0 cm upward. K shows a nearly constant trend throughout the core while Mg shows an erratic trend in the bottom portion of 66 - 48 cm and then a decreasing trend of ups and downs up to 34 cm before it maintains an increasing trend towards the surface. Ca shows an enriched bottom portion of 66 - 46 cm with spikes of high values in between and almost a constant trend in the top 46 - 0 cm towards the surface. In case of core GN, Al, Mg and K profiles agree with silt profile and to some extent with clay profile (Fig.4B. 3B). All these elements show three distinct portions with an enriched but decreasing bottom portion of 92 - 64 cm followed by middle portion 64 - 28 cm of
increasing trend and then decreasing trend towards the surface. Ca shows a constant trend from the base of the core up to 68 cm from where values increase suddenly before maintaining a more or less increasing trend towards the surface.

Fig. 4B. 3. Down core variation of metals: A — core GH, B — core GN.

In both the cores, almost all the heavy metals including Fe and Mn show broad similarities in distribution with depth. In core GH, geochemical data shows a range
of 6.03 – 7.92 % Fe, 362 - 574.75 μg/g Mn, 56.25 - 77.78 μg/g Zn, 41.50 - 79.00 μg/g Cu, 118.00 - 295.00 μg/g Cr, 12.50 - 43.75 μg/g Co and 0.75 - 30.75 μg/g for Pb. All the metals except Co and Pb show three distinct portions (Fig. 4B. 3A). The concentration of Fe decreases from base of the core to 44 cm from where it increases up to 8 cm before it maintains a decreasing trend towards the surface. Mn, Zn and Cu show increasing trend in the bottom 66 – 44 cm and then gradual increasing trend in the middle portion of 44 – 6 cm from where values decrease towards the surface. Cr shows a decreasing bottom portion of 66 – 52 cm and then an increasing trend in the middle portion of 52 – 28 cm from where it shows an erratic trend towards the surface. Co shows a more or less increasing trend from the base of the core towards the surface while Pb shows an erratic trend with ups and downs through out the core.

In case of core GN, the geochemical data shows a range of 3.77 - 8.43 % Fe, 204.25 -540.25 μg/g Mn, 37.50 - 118.50 μg/g Zn, 32.75 - 81.50 μg/g Cu, 105.75 - 191.25 μg/g Cr, 8 - 130 μg/g Co and 16.5 - 184.75 μg/g for Pb. All the metals except Pb agree with major elements and show three distinct portions with depth (Fig. 4B. 3B). The bottom portion 92 – 64 cm is characterized by plateau of enriched concentrations and decreasing trend which is followed by an increasing middle portion of 64 - 28 cm while the top portion of 28 cm to the surface is characterized by decrease in values. Pb shows overall an increasing trend from base of the core towards the surface.

**4B. 3b Discussion**

**4B.3b i Vertical distribution**

A measure of the compositional variability of the inorganic component delivered to a marsh is revealed by the down core profiles of the elements that are constituents of detrital mineral phases and therefore unaffected by diagenesis (Allen, 1987). The relative constancy of K/AI ratio with depth in both the cores is interpreted to imply that the composition of the accumulated material has not fluctuated dramatically over time. However, in core GH, there is slight change which may indicate change in input with change in grain size (Fig. 4B. 3A). No significant down core differences are observed in the X-ray diffraction spectra or in the clay mineral composition in the core GN (Fig. 4B. 4) and have therefore been derived from the same sediment.
source (Spencer et al., 2003). The identified clay mineral assemblage of kaolinite, chlorite, illite and smectite clearly reflects their derivation from the catchment area, which consists mainly of Precambrian crystalline rocks that are lateritised at places (Chamley, 1989; Rao and Rao, 1995).

The diagenetic cycles of Fe and Mn are well known as they are dominant participants in bacterially driven aquatic redox processes (Stumm and Morgan, 1981) and presence of strong Fe and Mn peaks may indicate redox remobilization. So, the oxidized conditions, as indicated by Mn profile in core GH and Mn and Fe profiles in core GN, do persist from the surface to 6 cm in core GH and 28 cm in core GN. Any post-oxic zone, if present must be in between 6 to 44 cm and 28 to 64 cm in core GH and GN respectively where the Fe and Mn profiles show some enrichment with an overall decreasing trend but lack clear and consistent peaks. This may probably indicate that a stable redox zonation has not developed, as the area is frequently flooded and so will be subjected to a fluctuating water table. This will vary daily and monthly in response to land runoff as well as tide. A dynamic water table will cause short term fluctuations in the redox boundary (Casey and Lasaga, 1987; Hines et al., 1989) which precludes the formation of sharp diagenetic Mn and Fe peaks (Zwolsman et al., 1993). The bases of the oxic - anoxic conditions in the cores are therefore inferred at 44 cm and 64 cm. The increase in Mn and Fe in the deeper zone in both the cores may demonstrate that they are trapped by authigenetic carbonate/sulfide formation where conditions are permanently reduced (McCaffrey and Thomson, 1980; Zwolsman et al., 1993). The calcium profiles in both the cores support the above described diagenetic phenomenon. The sudden decline of Ca profile from surface over 6 cm to leave a tail of low value upto 44 cm in core GH and the decreased trend from surface to 68 cm in core GN are likely due to dissolution of CaCO$_3$ as acidity is generated in the pore waters of the oxic zones of the sediments (Froelich et al., 1979). Decalcification occurs in oxic salt marsh sediments in response to a lowering of pH resulting from nitrification and
decomposition of organic matter (Luther and Church, 1988; Vranken et al., 1990). The organic carbon profiles in both the cores agree with decreasing trends in the oxic-anoxic zones leaving enriched reducing zone in deeper portions of the cores. However, the deep increase in Ca concentration at deeper portion of core GH is likely due to authigenic carbonate formation in response to increase in pore-water alkalinity as sulfate is consumed and sulfides formed (Gaillard et al., 1989; Zwolsman et al., 1993; Pye et al., 1997). However, the vertical distributions of major elements especially Ca in core GH are also likely affected by variation in sediment source as indicated by K/Al ratio profile. The decrease of K/Al ratio from 54 cm down the core which is accompanied by sudden drop but still high value in organic carbon content with high Ca and Mg concentration may probably indicate a comparatively more marine input in addition to the diagenetic precipitation. The sudden rise of organic carbon content at 50 cm and upward decrease with sudden decrease of Ca and Mg may again signify the more terrigenous input which is modified by diagenesis.

The heavy metal profiles in core GH show similar distribution with depth demonstrating similarities in sources and/or post depositional behaviour. Heavy metals are normally scavenged from solution by fine sediments specially clay minerals and associated Fe, Mn and organic coatings (Bendell-Young and Harvey, 1992; Cundy and Croudace, 1995a). However, heavy metals concentrations including Fe and Mn show poor association with Al (0.502, Fe; -0.043, Mn; 0.191 Zn, -0.151, Cu; 0.530, Co; -0.048, Pb) and clay (0.354, Fe; 0.573, Mn; 0.253, Zn; 0.526, Cu; 0.163, Cr; 0.478, Co; -0.065, Pb) indicating that observed profiles are not a result of mineral variations (Cearreta et al., 2000). The profiles are, therefore, presented in raw, rather than being normalized as suggested by Ackermann (1980) and Grant and Middleton (1990). However, the distribution profiles may be partially due to early diagenesis processes (Berner, 1980) as well as environmental contamination (Anderton, 1985). Even though the profiles of heavy metals seem to be similar with Fe and Mn distribution, Fe and Mn show no significant correlation with heavy metals except with Cu. Still Mn shows better correlation than Fe signifying its role in redistribution of heavy metals. Mn shows significant correlation with Cu (0.749) and moderate correlation with Cr (0.422) and Co (0.462) while Fe maintains a moderate association with Cu (0.545) and Cr (0.441). The better
association of Co with Mn than Fe reflects that Co is more cycled along with Mn oxides at redox boundaries (Zwolsman et al., 1993). The exclusive role played by Mn oxides in the cycling of Ni and Co has been reported earlier by Klinkhammer (1980) and Shaw et al. (1990). Evidence of digenetic modifications can be seen with the peaks of Zn, Cu, Cr and Co at depths 6 cm which coincides with Mn peak and peaks of Zn, Cu (28 and 40 cm) and Cr (28 cm) with Fe and Mn, which indicate the coprecipitation with Fe and Mn oxides.

In core GN, Al shows significant correlation with clay (0.818), Fe (0.672), Mn (0.633) and moderate correlation with heavy metals (0.314, Cu; 0.463, Cr and 0.343, Co) and hence heavy metals including Fe and Mn are normalized with Al in order to remove the grain size effect. However, the bulk profiles are almost similar with normalized ones indicating minor mineralogical variations with depth. Fe shows a significant association with Zn (0.648), Cu (0.698) and moderate correlation with Cr (0.574) while Mn shows moderate association with Cr (0.418) and Co (0.332). The similarity in the profiles of Cu and Zn without pronounced peaks and their significant association with Fe only suggests the distribution of Cu and Zn may be strongly controlled by Fe cycling than Mn cycling in this core. Allen et al. (1990) identified a similar pattern for Cu, Pb and Zn in sediments from the Severn estuary. On the other hand, Mn shows moderate association with coincident pronounced peaks with Cr (4, 36, 42, 56 cm) and Co (4, 22, 36 cm) reflecting that they are more cycled along with Mn oxides (Zwolsman et al., 1993). There is evidence for coprecipitation of all heavy metals with Fe and Mn oxyhydroxides as they show enrichment in the lower permanently reduced zone. So, in the oxidizing and partially reducing middle zone, they exhibit readsoption with Fe/Mn oxyhydroxides, and following early diagenetic movement of trace metals in the surface oxic layer and in the highly reducing lower layers (Zwolsman et al., 1993). However, the gradually increasing Pb profile towards the recent strata, which is totally in contrast with redox sensitive Fe and Mn profile, may suggest an anthropogenic source.

4B.3b ii Spatial distribution

The sediment characteristics and geochemistry of the two cores described above indicate considerable variations between them. The core GH is of mature mudflat
and consists of slightly sandy mud whereas core GN is characterized by comparatively coarser sediments of sandy mud of a mudflat environment. The difference in sediment characteristics may be due to the varying distances from the source. A simple yet effective way of showing the variations between sites is by using isocon diagrams (Grant, 1986; Cundy et al., 1997). These plots compare the average values of specific components from different sites.

The isocon diagram (Fig. 4B. 5) indicates that there is little difference in Al, K, Fe, Zn, Cu and Cr concentrations between the two cores. There are, however, significant differences in sediment components and more importantly in concentrations of Ca, Mg, Pb and Co. Core GH shows high concentrations of Ca, Mg, and Cr together with high percentage of silt, clay and organic carbon. The high concentrations of Ca and Mg are likely due to marine influence in this mudflat which is relatively nearer to sea while high organic carbon, Mg, to some extent Cr and Fe, may be caused by grain size effect. On the other hand, core GN shows relatively higher concentrations of Pb and Co together with higher value of sand. The higher values of sand and high concentrations of Pb and to some extent Co are likely to be caused due to its proximity to continental source reflecting a pollution origin.

4B. 4 Factor analysis

In core GH, three factors representing 64.33% of the total variance in the sample were identified with the loadings given in table 4B. 1. Factor 1 accounts for 32.38% of the total variance and is characterized by high positive loadings (>0.5) on Fe, Mn, Cu and clay, and high negative loadings on sand, silt and organic carbon. This factor represents the association of metals with finer fraction which indicates that the environmental dynamic conditions exert control over them and are probably of detrital origin. Factor 2 accounts for 19.07% of the total variance and is
characterized by high positive loadings on Co, Pb, and strong negative loadings on Al. The negative correlation with Fe and very low loadings on Mn negates the possibility of the diagenetic origin. So, this factor may represent the anthropogenic origin. Factor 3 accounts for 12.88% of the total variance and is characterized by high positive loadings on Zn, Ca, K, Mg and silt and negative loadings on sand and clay. This may suggest the strong association of metals with silt probably of marine origin.

Similarly, in core GN, three factors representing 73.54% of the total variance were obtained with loadings given in Table 4B.1. Factor 1 accounts for 40.66% of the total variance and is characterized by high positive loadings on Fe, Mn, Cr, K, Mg, Al silt, clay and moderate loadings on Co and high negative loadings on sand. This factor shows the association of metals with finer fractions and is of detrital origin. Factor 2 accounts for 23.90% of the total variance and is dominated by high

### Table 4B.1. Factor analysis matrix after varimax rotation showing correlations with principal components.

<table>
<thead>
<tr>
<th>Variance (%)</th>
<th>GH Factor 1</th>
<th>GH Factor 2</th>
<th>GH Factor 3</th>
<th>GN Factor 1</th>
<th>GN Factor 2</th>
<th>GN Factor 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.70</td>
<td>-0.49</td>
<td>0.07</td>
<td>0.67</td>
<td>0.62</td>
<td>0.25</td>
</tr>
<tr>
<td>Mn</td>
<td>0.82</td>
<td>0.05</td>
<td>0.11</td>
<td>0.70</td>
<td>-0.13</td>
<td>0.56</td>
</tr>
<tr>
<td>Zn</td>
<td>0.26</td>
<td>-0.16</td>
<td>0.75</td>
<td>0.12</td>
<td>0.87</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu</td>
<td>0.84</td>
<td>0.16</td>
<td>0.28</td>
<td>0.30</td>
<td>0.83</td>
<td>0.17</td>
</tr>
<tr>
<td>Cr</td>
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<td>0.16</td>
<td>0.64</td>
<td>0.37</td>
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</tr>
<tr>
<td>Co</td>
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<td>0.70</td>
<td>0.03</td>
<td>0.46</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>Pb</td>
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<td>0.13</td>
<td>-0.20</td>
<td>0.47</td>
<td>0.73</td>
</tr>
<tr>
<td>Ca</td>
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<td>0.63</td>
<td>0.33</td>
<td>-0.73</td>
<td>0.40</td>
</tr>
<tr>
<td>K</td>
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<td>0.24</td>
<td>0.54</td>
<td>0.90</td>
<td>-0.11</td>
<td>-0.03</td>
</tr>
<tr>
<td>Mg</td>
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<td>0.04</td>
<td>0.71</td>
<td>0.62</td>
<td>0.20</td>
<td>0.67</td>
</tr>
<tr>
<td>Al</td>
<td>0.02</td>
<td>-0.85</td>
<td>0.14</td>
<td>0.94</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Sand</td>
<td>-0.52</td>
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<td>-0.70</td>
<td>-0.91</td>
<td>-0.15</td>
<td>-0.22</td>
</tr>
<tr>
<td>Silt</td>
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<td>-0.13</td>
<td>0.54</td>
<td>0.85</td>
<td>0.00</td>
<td>0.49</td>
</tr>
<tr>
<td>Clay</td>
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<td>0.84</td>
<td>-0.20</td>
<td>-0.09</td>
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<tr>
<td>OC</td>
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<td>-0.02</td>
<td>-0.22</td>
<td>0.89</td>
<td>0.19</td>
</tr>
</tbody>
</table>
loadings on Fe, Zn, Cu, organic carbon and moderate loadings on Pb indicating their common anthropogenic origin. Factor three represents 8.98% of the total variance and is dominated by high positive loadings on Mn, Pb, Mg and moderate loadings on Ca and silt. This factor reflects the association of metals with silt and the probability of biogenic origin, as Ca and Mg are likely to be incorporated in the shells of the manganese/calcite or aragonite (Mil-Homens et al., 2006). The high positive loadings on Mn and moderate loadings on Fe suggest the presence of diagenetic processes.

4B.5 Sedimentation rate and Enrichment Factor

The profiles $^{210}$Pb$_{excess}$ are presented in figure 4B. 6. In case of core GH, there is a relatively log-linear decrease of $^{210}$Pb$_{excess}$ activity with depth but with a change in slope at 26 cm depth (Fig. 4B. 6A). Changing slope in the $^{210}$Pb$_{excess}$ profile indicates variation in accumulation rate or is due to bioturbation (Cundy and Croudace, 1995b). The assumption of closed system might be violated in salt marshes due to early diagenetic remobilization of $^{210}$Pb (Allen et al., 1993; Cundy, 1994). In the present study, there is no obvious change in the shape of $^{210}$Pb$_{excess}$ profile in the vicinity of the oxidized/reduced boundary, as would be expected if $^{210}$Pb migration had taken place. When the profiles of $^{210}$Pb are compared with Pb and redox sensitive elements, there are no similar peak concentrations negating the possibilities of mobilization of $^{210}$Pb. The higher values of $^{210}$Pb in top 26 cm do not coincide with the proposed oxidized/partially reducing boundary and not even with partially reducing/reducing boundary. However, the concentration minima occur below 35 cm, which are taken as background values, may highlight the possibility of diagenetic movement as 32 cm depth is the transition of colors recorded in field, but is apparently not significant enough to explain the change in slope at 26 cm depth. Therefore, the change in slope at 26 cm strongly suggests change in sedimentation as also supported by the K/Al ratio profile and not due to bioturbation. Hence the sedimentation was slower at 0.16cm/yr until 26 cm, which corresponds to the year 1982 and increased thereafter to 2cm/year.
To evaluate anthropogenic influences of heavy metals in sediments, enrichment factor (EF) has been used as an index. It is a useful indicator reflecting the status of environmental contamination. In core GH (Fig. 4B. 7A), the EF values of Mn and Zn are below 1 except at some points while Pb values are less than 1.5 with higher values at some points suggesting that these metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002). On the other hand, EF values of Fe, Cr and almost all the values of Co are higher than 1.5 which suggest that a significant portion of these metals are delivered from non-crustal materials, or non-natural weathering processes. Throughout the core, EF values of Fe is more than 1.5 which is gradually increasing upwards with the values more than 2 from 22 cm upwards corresponding to the period from 1994 to present. EF values of Cu are below 1.5 up to 22 cm which corresponds to the year 1994 from where it increases to present. Co starts enrichment (>1.5) from 48 cm which corresponds to the year 1904 to present day with a marked increase from 1994 onwards. Cr is the most enriched metal in the core with values greater than 2 throughout the core. So, the EF of the present study shows environmental contamination by Fe, Cu, Cr and Co in recent years especially from 1994.
In case of core GN, the total $^{210}$Pb profile does not show decay with depth (Fig. 4B. 6B). It shows some pattern in the top portion of 0 – 50 cm in which all the values are more or less same representing a zone of sediment mixing. Then the values suddenly drop below 1 (0.64 – 0.79 dpm/g) from 54 cm to the base of the core leaving a gap from 50 to 54 cm. This gap of depletion is probably caused by erosion or removal of sediments by human activities leaving mixed sediments. So, sedimentation rate of this core could not be calculated. The EF values of all the metals except Pb show more or less similar trend throughout the core except the down portion (< 68 cm) in which, interestingly, all the metals are enriched (Fig. 4B. 7B). As explained above, the enrichment of metals is probably caused by the diagenetic processes in the permanently reducing zone. So, the construction of pollution chronology in this core is limited by different processes. However, in the top portion, EF values Mn and Cu are less than 1 while the values of Fe and Cu are below 2. On the other hand, Cr and Co are highly enriched with values above 2. Pb, unlike in core GH, shows gradually increasing trend towards the surface with enrichment values above 5 which may signify higher degree of contamination nearer to land.
4B.6 Magnetic susceptibility

4B.6a Results

The rock magnetic parameters are shown in figure 4B. 8. Common features are observed in the rock magnetic parameters between the two cores. In both the cores, the concentration dependent magnetic parameters ($\chi$, $\chi_{ARM}$ and SIRM); magnetic mineralogy related parameters ($S_{300}$ in core GH and HIRM) and grain size indicators ($\chi_{ARM}/\chi$ and $\chi_{ARM}/$SIRM) have relatively high values in the middle and upper portion of the cores. The values show down core drop in the middle portion before maintaining an almost constant trend in the bottom portions of the respective cores. So, one can divide the entire core into three sections according to variations of the magnetic parameters.

In core GH (Fig. 4B. 8A), Section 1 (66 – 50 cm) has low values for all the parameters. The values of $\chi$, $\chi_{ARM}$, HIRM and grain size index ratios have almost constant trend whereas SIRM and $S_{300}$ show slight enrichment towards the bottom of the core. In section 2 (50 – 42 cm), all the parameters undergo a sudden increase especially in the upper 4 – 6 cm of this section and drop to their minimum values at ~50 cm. $S_{300}$ value increases sharply from 0.65 at about 50 cm depth to 0.75 at the top of this section. These changes indicate that the dominant magnetic minerals rapidly change up the core from high-coercivity components to low-coercivity minerals. HIRM values too, progressively increase up the core indicating that the partial increase of high-coercivity minerals took place in this section. $\chi$ value starts to increase to $3.4 \times 10^{-7}$ m$^3$ Kg$^{-1}$ at 42 cm from nearly constant value $1.3 \times 10^{-7}$ m$^3$ Kg$^{-1}$ below 50 cm depth. $\chi_{ARM}$ displays sudden increase of value $0.43 \times 10^{-5}$ m$^3$ Kg$^{-1}$ at 42 cm from $0.09 \times 10^{-5}$ m$^3$ Kg$^{-1}$ at 50 cm depth. The SIRM increases suddenly to $342.43 \times 10^{-5}$ Am$^2$ Kg$^{-1}$ at ~42 cm from its minimum value of $58.30 \times 10^{-6}$ Am$^2$ Kg$^{-1}$ below 50 cm. In section 3 (42 – 0 cm), all the parameters are enriched with highest values. $S_{300}$ values suggest that this section is magnetically dominated by low-coercivity ferromagnetic minerals together with a strong contribution from anti-ferromagnetic minerals. The magnetic granulometric index displays an almost constant value in this section.
In core GN, the profiles of concentration dependent parameters ($\chi$, $\chi_{\text{ARM}}$, and SIRM) and HIRM (Fig. 4B. 8B) agree with the geochemical profiles in all the three sections. In the bottom section 1 (92 - 60 cm), all the parameters except $S_{300}$ show a more or less constant trend. $S_{300}$ value maintains a high value and a nearly constant trend before it decreases in the upper portion of this section. In the second section (60 - 28 cm) all the parameters are gradually increasing upwards and
display highest value at 28 cm depth. $\chi$, $\chi_{\text{ARM}}$, SIRM and HIRM display the highest value of $2.54 \times 10^{-7} \text{ m}^3\text{Kg}^{-1}$, $0.25 \times 10^{-5} \text{ m}^3\text{Kg}^{-1}$, $181.99 \times 10^{-5} \text{ Am}^2\text{Kg}^{-1}$ and $52.68 \times 10^{-5} \text{ Am}^2\text{Kg}^{-1}$ respectively at 28 cm depth. In the last section 28 -0 cm, the values of concentration dependent parameters ($\chi$, $\chi_{\text{ARM}}$, SIRM) and HIRM gradually decrease towards the surface.

**Magnetic mineralogy:** The thermal demagnetization curves for selected samples from different sections are shown in figure 4B.9. In core GH, samples from section 3 and 2 show similar curves in which the IRM undergo a monotonic decay until their unblocking at ~680°C, which is indicative of hematite. The most distinct difference for samples from section 1, compared to those from higher parts of the core is that there is considerable decrease from 150 to 350°C. Gregite has higher coercivity than magnetite (Roberts, 1995) and is characterized by loss of most of its magnetization from 200°C to 350°C (Krs et al., 1992; Reynold et al., 1994; Roberts, 1995; Torri et al., 1996). In contrast, pyrrhotite undergoes rapid unblocking within a much narrower temperature range of 320 – 350°C (Dekkers, 1989; Torii et al., 1996).

There is a possibility that the loss in magnetization at around 200 - 320°C is due to maghemite or titanomagnetite. But the slight increase in the magnetic susceptibility at around 300°C in $\chi(T)$ curve may attribute the presence of gregite (Fig. 4B. 10).
Finally, the values are unblocked to near zero at about 580°C, which suggests that magnetite is also present and there is little hematite in this section. On the other hand, in core GN, samples from all sections (section 1 and 3 are represented) show similar curves in which the IRM undergo a monotonic decay until their unblocking at ~580°C, which is indicative of magnetite. So, it can be concluded that in core GH, the magnetic properties of section 3 and 2 contain substantial contributions from hematite as well as magnetite. In contrast, the magnetic mineralogy of section 1 is characterized by (titano)magnetite and gregite, with little hematite. However, core GN shows the uniform mineralogy throughout the core, which is characterized by magnetite with little hematite.

**4B. 6b Discussion**

The magnetic parameters are extremely sensitive and small changes in catchment area processes would be recorded in the sediments. It is clear from the correlation that there is no significant relationship between SIRM with Al (-0.49), Mg (-0.44) and K (0.07) in core GH indicating little supporting evidence of catchment area changes (Mackereth, 1966). However, changes in the catchment area processes can be the explanation for core GN as SIRM shows moderate correlation with Al (0.54), Mg (0.54) and K (0.75).

The data suggest that there has been a fining upwards of the magnetic grain size as well as increase in total concentration. This pattern is consistent with the suggestion that fine grains have been dissolved and the multi domain grains broken up into Stable Single Domain (SSD) grains. The finer component is believed to be dissolved first due to its high surface to volume ratio, which would result in a reduction in magnetic intensity as well as a shift in grain size towards the coarse end (Karlim and Levi, 1983; Bloemendal et al., 1993). Hence the precipitous down core drop of magnetic parameters from 42 cm and 28 cm in core GH and GN respectively, which is diagnostic of early diagenesis in deep water marine
sediments (Karlim and Levi, 1983; Robinson et al., 2000), and may reflect the onset of reducing condition.

The section 3 in core GH and part of sections 3 and 2 in core GN are marked by high values of all concentration dependent bulk magnetic parameters, nearly constant values of $S_{300}$ and granulometric index. These sections are therefore interpreted to be the least affected by early diagenesis influences. The main magnetic minerals in these parts of the cores (magnetite and hematite) can be regarded as the primary detrital magnetic minerals prior to diagenetic modifications in the underlying sections. The initial diagenetic stage, observed in section 2 of core GH, begins with sharp increase in ferrimagnetic mineral concentrations. These concentrations increase progressively upwards from absolute minimum abundance at the start of this section. This stage is associated with depletion of the high-coercivity components. The later diagenetic stage as observed in section 1 of core GH is characterized by authigenic production of fine-grained ferrimagnetic minerals. The section 1, which has been subjected to the initial diagenetic stages like the overlying sections would have retained, if any, the largest magnetic grains. On the contrary, however, there is enrichment of superparamagnetic (SP) grains as indicated by the increase of $\chi_{69}^d$ which can be reasonably interpreted to be of authigenetic origin. Thermomagnetic and temperature measurements suggested the possibility of gregite present in this section. Sedimentary gregite has been consistently found to have Single Domain (SD) like magnetic properties (Snowball, 1991; Roberts, 1995). On the other side, the section 1 of core is characterized by slight increase in $\chi$ and sudden increase in $S_{300}$ which also suggests the possibility of authigenetic origin. However, the similarity in monotonic decrease of thermal magnetization curve in different sections limited the explanation of possible gregite present in this section. The sudden increase in organic carbon content and ferromagnetic minerals together with high sand content may suggest the possibility of more terrigenous input during this time before it was subjected to diagenetic modifications in later stage.

**Significance for environmental study:** It has been demonstrated that environmental magnetism can be used as a proxy indicator of heavy metal concentration in a simple, quick and non-destructive way (Scoullos et al., 1979;
The considerable similarity between heavy metals and $\chi_{\text{ARM}}$ was reported from intertidal sediments of the Yangtze Estuary, China by Zhang et al. (2001). It has been suggested that certain magnetic parameters can be used as grain size proxy (Oldfield and Yu, 1994; Zhang et al., 2007). Zhang et al. (2007) reported strong relationship between $\chi_{\text{ARM}}$ and to a lesser degree, frequency dependent susceptibility ($\chi_{\text{fd}}$) with heavy metals and explained the role of particle size effects and iron oxides in controlling metal concentration. However, in the present study, even though $\chi_{\text{ARM}}$ in GH and both $\chi_{\text{ARM}}$ and $\chi_{\text{fd}}$ in GN show good correlation ($r > 0.5$) with clay, they show poor correlation ($r < 0.5$) with the metals studied except Co in GH; Mn and Pb in GN. Therefore, the changes in the heavy metal concentrations in this core cannot be accounted for by particle size alone. Hence, it is likely that the reduction of iron oxide plays a significant role in distribution of heavy metals. However, the change in magnetic properties in section 3 of both the cores, which are considered as the primary detrital minerals, point to both quantitative and qualitative changes in the assemblage of magnetic minerals present. The increase in SIRM reflects an increase in total magnetic mineral concentrations. In combination with SIRM, the increase of the hardest remanence component points to an increase in hematite in both relative and absolute terms. The trend in 'soft' and 'hard' isothermal remanence can be plotted on a mass specific basis and this isolates these two properties from all other variables responsible for changes. In the present study, it confirms that both components increase significantly in the upper levels of cores which are diagenetically least affected. The constant nature of grain size parameters in these sections indicate a nearly uniform grain size and hence suggest a similar condition of deposition with negligible post depositional modifications. When the calculated 'soft' i.e. mostly magnetite, 'hard' i.e. mostly hematite, and total i.e. SIRM trends were compared, there were interesting parallels and differences. The increase is much steeper in hematite to magnetite suggesting the relative higher deposition of hematite in recent years.

There is link between magnetic properties ($\chi$, $\chi_{\text{fd}}$, $\chi_{\text{ARM}}$ and SIRM) and metals (Fe, Mn, Zn, Cu and Co) in the upper section of the cores wherein the rate of sedimentation recorded is very high. Most importantly, there is parallelism in trends of 'hard' and 'soft' profiles with metals, which points to a possible common origin.
Gradual increase in $\chi_m$ value towards the surface along with metals is likely because of relative higher degree of weathering and erosion in recent years. This may reflect trace metal enrichment of the magnetically enhanced soil derived clays during weathering and transport in recent years with enhanced sedimentation rate especially in core GH.
SECTION 4C: MALVAN (Karli, Adari - Kolamb and Jetterwadi)

Three cores namely MAK (Karli River), MAA (Adari, Kolamb Creek) and MAJ (Jetterwadi) were collected from different mudflats in and around the Malvan area. Sediment component analysis was carried out for all three cores and then core MAK and core MAA have been subjected to further geochemical and rock magnetic analysis.

4C. 1 Field observations

The cores MAK and MAJ show almost uniform colour of brown throughout the core with some bands of grey colour in between. Core MAA exhibits clear vertical zonation and can be divided into two units (Zwolsman et al., 1993; Williams et al., 1994; Thomson et al., 2002) as follows:

1. A brown oxidized surface layer of 0 – 30 cm and
2. A dark grey reduced layer of 30 – 60 cm.

4C. 2 Sediment components (sand, silt, clay and organic carbon)

4C. 2a Results

The percentage of sand, silt, clay and organic carbon of three cores are presented graphically in figure 4C. 1 and are described below. In core MAK (Fig. 4C. 1A), the sand and clay profile show two distinct sections while silt maintains a more or less constant trend throughout the core. In the bottom section 84 – 32 cm of the core, trends are relatively steady with an upward decreasing trend of sand, which is compensated by increasing trend of clay. In the upper 32 – 0 cm, sand and clay values are comparatively slightly high with spikes of ups and downs throughout the portion and marked opposite point to point variations. The distribution of organic carbon largely agrees with the grain size profile. The values in the bottom section are comparatively high with some ups and downs and largely agree with silt while in the upper section, the organic carbon value is comparatively low in agreement with silt and clay in general but a point-to-point match trend with clay. Therefore, the distribution of organic carbon is mainly controlled by grain size distribution in this core.
In core MAA, the sand, silt and clay profiles show three distinct sections (Fig. 4C. 1B). The bottom section of 60 – 32 cm depth is characterized by increasing trend of sand and decreasing trends of silt and clay. The middle section of 32 – 18 cm depth is characterized by an erratic trend of all three parameters. In the top section from 18 cm depth to surface, sand shows a gradually decreasing trend which is compensated by increasing trend of silt and clay. So, silt and clay are broadly agreeing with each other throughout the core. The profile of organic carbon too shows three sections with a decreasing trend in the bottom section of the core. The middle section of the core is characterized by an erratic distribution while an increasing trend in the upper section of the core.

Fig 4C. 1. Down core variation of sediment components: A - core MAK, B - core MAA, C -core MAJ.

The sand, silt clay and organic carbon distribution in core MAJ show no distinct zones with depth but a simple trend rather (Fig 4C. 1C). Sand value is gradually
decreasing upwards while silt shows nearly increasing trend towards the surface. Clay agrees with sand to some extent and shows nearly decreasing trend upwards. Organic carbon shows a nearly constant trend from base to 8 cm from where values show gradually increasing trend towards the surface.

4C. 2b Discussion

Grain-size variations in sediments reflect changes in the processes and energy of sediment transport. Particle size is closely linked to turbulence, wave energy, and proximity to shoreline. Increased grain size generally corresponds to higher energy conditions, whereas decreased grain size indicates lower energies. In the present study, in general the decrease in grain size with time is witnessed in core MAA and MAJ in the upper portion whereas grain size slightly increases with time in the upper part in core MAK. Further, the changes in sediment characters within the cores are observed when the data were plotted on the ternary diagram proposed by Reineck and Siefert (1980).

According to this diagram (Fig. 4C. 2A), core MAK falls in mudflat class throughout the core while core MAA and MAJ changes from mudflat to mature mudflat with time. Similarly, variations in grain size characters are also witnessed when the data were plotted on ternary diagram (Fig. 4C. 2B) of Flemming (2000). It is found that sediments of core MAK showed a wide range of variation from sandy mud – slightly sandy mud – sandy mud – slightly sandy mud (not seen in figure) with time while in
core MAA and MAJ, sediments are graded from sandy mud to slightly sandy mud with time. From these diagrams, it is clear that core MAK show high variations in sediment characters with the repetitions of classes in between while cores MAA and MAJ are showing gradually fining of sediments with time.

Similarly, the variation in hydrodynamic conditions of the depositional environment between the different cores can be seen when the components are plotted in the ternary diagram (Fig. 4C. 2C) developed by Pejrup (1988). In the present study, the components plotted for core MAK fall in groups II (C) and III (C) and majority of the components of core MAJ falls under groups II (C) and III (C and D), which represents the relatively quiet to relatively violent hydrodynamic conditions. On the other hand, components plotted for core MAA fall under groups II (B, C and D), which indicates the relatively quiet hydrodynamic conditions.

The distribution of organic carbon in core MAK and MAJ is mainly controlled by silt \((r = 0.54, 0.44)\) than clay \((r = 0.15, -0.27)\). The strong correlation between organic carbon and silt fraction can be related to the relatively violent hydrodynamic conditions. However, in core MAA, though the overall distribution of the organic carbon is quite similar with those of silt and clay, it shows a very poor to moderate correlation with silt \((r = 0.197)\) and clay \((r = 0.487)\). The area is more protected and characterized by relatively quiet hydrodynamic conditions which may facilitate the deposition of high organic matter with clay. However, the moderate correlation of organic carbon with clay may be probably because of the extraordinarily high values of organic carbon in the lower section of the core. It is worth to mention here that below 32 cm, organic carbon content increases and suddenly reaches to > 11% below 52 cm. The higher amount of organic carbon in this area may be probably govern by factors such as source, sedimentation and post depositional
processes in addition to grain size parameters and energy conditions. Kumaran et al. (2004) have reported the lignite beds exposed in Kolamb well-section near Malvan area and further cited that these lignites are autochthonous and deposited in near-shore environment. Therefore, the high percentage of organic carbon in this particular core can be related to the lignite source which must have been deposited in calm energy and preserved under reducing conditions.

4C. 3 Clay mineralogy
Kaolinite, chlorite, smectite and illite in order of decreasing abundance, are the major clay minerals in core MAK whereas smectite, kaolinite, chlorite and illite are the major minerals in decreasing order of abundance in core MAA. Clay mineral compositions do not major changes with depth within the individual core (Fig. 4C. 3). However, compositional variations exist between and to some extent within the cores mainly due to kaolinite and smectite, which show opposite trends with depth.

![Fig. 4C. 3. Down core variation of clay minerals: A - core MAK, B - core MAA.](image)

The clay mineral assemblages of the study area clearly reflect their derivation from the hinterland, which are developed on a basement of basalt flows of the Deccan Volcanic province. Smectite is the predominant weathering product of basalts in
arid climates, and smectite and kaolinite in humid tropical climates (Chamley 1989). The clay mineral assemblage obtained largely corresponds to the clay minerals distribution of inner continental shelf of Ratnagiri - Goa along continental margin of India reported by Rao and Rao (1995), which they have concluded of hinterland origin. Smectite and kaolinite rich assemblages on the inner shelf of the Ratnagiri - Goa reflect a release from intense chemical weathering products. As the Western Ghats are with steeper western gradients and the area receives maximum rainfall (3000 mm) during SW monsoon, one would expect both mechanically derived residual clay minerals (illite and chlorite) and kaolinite and smectite (Rao and Rao, 1995). They have reported smectite of 55 %, kaolinite 21 %, chlorite 16 % and illite 8 % from the inner continental shelf. The observed difference between the dominance of smectite and kaolinite in two cores of estuarine region could be explained by dominant mechanical/physical size sorting together with differential sedimentation processes. The illite/chlorite ± kaolinite assemblage is typical for clastic sedimentary environments with a medium to high dynamics (Chamley, 1989). It is well known that amount of smectite increases with water depth, from the shore facies to the basinal ones. So, the significantly high amount of smectite in core MAA may suggest a low dynamics which was clearly indicated in ternary diagram (Fig. 4C.2C). This significant variation may be the result of differential sedimentation process. A rapid flocculation of kaolinite takes place under a 2% increase of salinity, leading to a fast sedimentation in slightly saline waters (Deconinck and Stresser, 1987). On the contrary, smectite undergoes a very slow sedimentation in waters with reduced salinity, but it flocculates fast in normal saline waters. Whitehouse et al. (1960) calculated theoretical clay association with varying salinity and reported a fast sedimentation of illite and kaolinite close to the shore, and a substantial sedimentation of dominant smectite in the proximal basinal areas. In addition to flocculation mechanisms, physical segregation of the particulate during transportation and sedimentation (Gibbs, 1977; Brockamp and Zuther, 2004) can partially explain the possible causes of such mineral association including those in continental shelf.

The clay mineralogy is similar throughout in both the cores with no major changes in the proportions of the mineral components, which would suggest little change in source or provenance over the observed sedimentation period. The relative
quantities of kaolinite and smectite, however, change little with depth. Together with salinity level, sedimentation rate seem to promote the flocculation and deposition of clay minerals in these cores. Moreover smectite is more affected than other clay minerals.

4C. 4 Geochemistry
4C. 4a Results
The distributions of major elements in core MAK, are largely controlled by grain size (Fig. 4C. 4A). Ca and Mg show association with sand fraction while Al and K are enriched in the finer fractions. As in the case of sediment component profiles, all the major element profiles show two distinct portions and all the elements are enriched in the upper portion where sand and clay are also enriched but with opposite peak variations. The high Ca and Mg and low organic carbon in the upper portion of the core when compared to purely detrital indicator i.e. K/Al (freshwater), which remains constant, may suggest more biogenic input through marine source. On the other side, in core MAA (Fig. 4C. 4B), grain size distribution does not control the metal distribution especially Ca and Mg. Ca value increases gradually towards the surface from the minimum and constant values up to 30 cm from the base suggests dissolution of CaCO₃. This is likely as total dissolution of CaCO₃ due to acidic nature which is generated in the pore waters of the oxic zone of the sediments (Froelich et al., 1979). A similar distribution trend is observed for Mg but with a plateau between 40 cm and 30 cm, after leaving a tail of constant values below 40 cm of the core.

In both the cores, Al shows moderate to good correlation with metals (r = 0.64, Fe; 0.4, Mn, 0.59, Zn; 0.50, Cu; 0.49, Cr; 0.62, Co for core MAK and r = 0.79, Fe; 0.83, Zn; 0.43, Cu and 0.54, Cr in core MAA), which indicates the association of metals with finer fraction of sediments and detrital source. So, the values of metals are normalized to Al in order to remove the grain size effect and presented graphically in figure 4C. 4.
In core MAK, the normalized metal profiles show similar distributions with depth suggesting that they are derived from the same source and/or that they have...
undergone similar post depositional behaviour. The vertical distributions of redox sensitive elements (Fe and Mn) show no indication of presence of diagenetic maxima and minima. However, the profiles can be divided into three sections with depth. The lower portion of the core 84 -52 cm is characterized by a trend of higher values. In the middle section 52 – 30 cm, both the metals maintain a steady trend with low values, which is followed by a top section of 30 - 0 cm where the values are relatively high for Mn but low for Fe with erratic trends. The distribution profiles of Zn and Cu are broadly similar with Fe in all three portions. Cr and Pb show erratic trend throughout the core with slightly increasing trend towards the surface while Co shows a nearly uniform distribution throughout the core.

In core MAA, Fe and Mn show an erratic trend from base to 18 cm upwards where values are suddenly enriched probably indicates the oxidized conditions resulting formation of oxyhydroxides. Again, any post - oxic zone (suboxic or weakly reducing), if present, must be in between 32 to 18 cm. The significant peak of both Fe and Mn at 32 cm depth from where values are suddenly enriched, which may suggests the onset of permanently reducing conditions in agreement with Ca profile and the transition of brown to grey colour observed in the field. The vertical distributions of Zn and Cr are nearly uniform with depth while Cu, Co and Pb, like the profile of Fe, show some increase and decrease in trend. Out of the heavy metals analysed, only Cu shows enrichment towards the surface importantly in upper portion of the core.

4C. 4b Discussion
4C. 4b i Vertical distribution
A measure of the compositional variability of the inorganic component delivered to a marsh is revealed by the down core profiles of the elements that are constituents of detrital mineral phases and therefore unaffected by diagenesis (Allen, 1987). The homogeneity with depth of both the cores (MAK and MAA) is illustrated by the profile of K normalized to Al (Fig. 4C. 4) to account for the constant sum problem (Rollinson, 1992). The relative constancy of the K/Al profile with depth is interpreted to imply that the composition of the accumulated material has not fluctuated dramatically over time.
The diagenetic cycles of Fe and Mn are well known as they are dominant participants in bacterially driven aquatic redox processes (Stumm and Morgan, 1981) and presence of strong Fe and Mn peaks may indicate redox remobilization. So, in core MAK, the Mn profile does suggest the possibility of diagenetic movement with the oxidized condition from the surface to 24 cm in core. The sudden decrease in Ca concentration at 32 cm depth is likely due to dissolution of CaCO₃ as acidity is generated in the pore waters of the oxic zones of the sediments (Froelich et al., 1979). However, Mg, K and Al also show almost same trend as that of Ca, which may point that the vertical distribution is probably due to the change in catchment area processes rather than diagenesis. Moreover, the Fe profile does not show any evidence of diagenetic modifications. Therefore the increase Ca and Mg concentration from ~32 cm towards the surface accompanied by increase in sand and decrease in organic carbon may indicate a comparatively more marine input.

The oxidized condition, as indicated by Mn and Fe profiles in core MAA, does persist from the surface to 18 cm in this core. Any post-oxic zone, if present must be in between 18 to 32 cm where the Fe and Mn profiles show maximum enrichment at 32 cm and then decrease with depth. This may probably indicates that a stable redox zonation has not developed, as the area is frequently flooded and so will be subjected to a fluctuating water table. This will vary daily and monthly in response to tide and land runoff. A dynamic water table will cause short term fluctuations in the redox boundary (Casey and Lasaga, 1987; Hines et al., 1989) which precludes the formation of sharp diagenetic Mn and Fe peaks (Zwolsman et al., 1993). The base of the oxic - anoxic conditions in the core is therefore inferred at 32 cm. The increase in Mn and Fe in the deeper zone may demonstrate that they are trapped by authigenic carbonate/sulfide formation where conditions are permanently reducing (McCaffrey and Thomson, 1980; Zwolsman et al., 1993). The calcium profile in this core supports the above described diagenetic phenomenon. Decalcification occurs in oxic salt marsh sediments in response to a lowering of pH resulting from nitrification and decomposition of organic matter (Luther and Church, 1988; Vranken et al., 1990). The organic carbon profile in the core agrees with decreasing trends in the oxic-anoxic zones leaving enriched reducing zone in deeper portions of the core.
The heavy metal profiles in both the cores, show similar distribution with depth demonstrating similarities in sources and/or post depositional behaviour. In core MAK, Zn, Cu and Co show significant correlation with Fe (0.81; 0.89; and 0.68) and Mn (0.69; 0.62 and 0.50) indicating their common source. The heavy metals do not show prominent enrichment towards the surface negating the possibility of more input in recent years. However, the slight enrichment of Mn, Cr, Pb and Zn can be seen in the recent past. In core MAA, the trend of heavy metals is erratic in distribution and does not show any enrichment towards the surface. Even though the profiles of heavy metals seem to be similar with Fe and Mn distribution, only Fe shows good correlation with Cu (0.93); Co (0.64) than Mn, (r < 0.4 with all heavy metals), signifying its role in redistribution of heavy metals. However, the strong correlation of Al with Fe (0.79) and subsequently with Cu (0.83) and Co (0.54) point their common origin rather than diagenetic precipitation.

4C. 4b ii Spatial distribution
The sediment characteristics of the two cores described above are nearly similar but show considerable variations in geochemistry between the two cores. A sediment texture in both the cores falls under mudflat environment (Reineck and Siefert, 1980) and consists of sandy mud (Flemming, 2000). The isocon diagram (Fig. 4C. 5) indicates that the values of all the metals both major and minor are markedly high in core MAK while organic carbon value is significantly high in core MAA. The difference in geochemistry may, therefore, be caused by the variation in catchment area processes, especially as MAK was collected from larger estuary and MAA from a creek.
4C. 5 Factor analysis

Table 4C. 1. Factor analysis matrix after varimax rotation showing correlations with principal components

<table>
<thead>
<tr>
<th>Variance (%)</th>
<th>MAK</th>
<th>MAA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Factor 1</td>
<td>Factor 2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.85</td>
<td>0.19</td>
</tr>
<tr>
<td>Mn</td>
<td>0.80</td>
<td>-0.27</td>
</tr>
<tr>
<td>Zn</td>
<td>0.85</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu</td>
<td>0.90</td>
<td>0.15</td>
</tr>
<tr>
<td>Cr</td>
<td>0.34</td>
<td>0.10</td>
</tr>
<tr>
<td>Co</td>
<td>0.45</td>
<td>-0.14</td>
</tr>
<tr>
<td>Pb</td>
<td>0.14</td>
<td>-0.10</td>
</tr>
<tr>
<td>Ca</td>
<td>0.32</td>
<td>-0.62</td>
</tr>
<tr>
<td>K</td>
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<td>-0.02</td>
</tr>
<tr>
<td>Mg</td>
<td>0.28</td>
<td>-0.33</td>
</tr>
<tr>
<td>Al</td>
<td>0.39</td>
<td>0.10</td>
</tr>
<tr>
<td>Sand</td>
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<td>-0.70</td>
</tr>
<tr>
<td>Silt</td>
<td>0.09</td>
<td>0.90</td>
</tr>
<tr>
<td>Clay</td>
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<td>0.10</td>
</tr>
<tr>
<td>OC</td>
<td>0.06</td>
<td>0.76</td>
</tr>
</tbody>
</table>

In core MAK, three factors representing 69.66% of the total variance were obtained with loadings given in table 4C. 1. Factor 1 accounts for 41.14% of the total variance and is characterized by high positive loadings on Fe, Mn, Zn and Cu, and moderate loadings on Co, K and Al. This factor shows strong association of heavy metals with Fe and Mn and moderate association with detrital metals which could be of diagenetic origin. Factor 2 accounts for 19.24% of the total variance and is dominated by high positive loadings on silt and organic carbon and high negative loadings on Ca and sand indicating the association of organic carbon with silt and Ca with sand. Factor 3 represents 9.28% of the total variance and is dominated by high positive loadings on Cr, Co, Al, Mg and clay and high negative loadings on sand. This factor reflects the association of metals with finer fractions of terrigenous origin.
Similarly, in core MAA, three factors representing 78.71% of the total variance in the sample were identified with the loadings given in table 4C. 1. Factor 1 accounts for 44.90% of the total variance and is characterized by high positive loadings (>0.5) on Fe, Cu, Co, Ca, K, Mg and Al. This factor represents the association of metals with major elements which probably indicates the detrital origin of both marine and terrigenous. Factor 2 accounts for 21.08% of the total variance and is characterized by high positive loadings on silt, clay and organic carbon and strong negative loadings on sand suggesting association of organic carbon with finer detrital components of sediments. Within this factor, two mutually exclusive groups of metals were distinguished, which are associated with clay and silt (Fe, Mn, Zn, Cu, Cr, Co, K, Mg and Al) and with sand (Ca and Pb). Factor 3 accounts for 12.72% of the total variance and is characterized by high positive loadings on Zn, Cr and Pb and negative loadings on Al, K and silt, that may suggest an anthropogenic origin.

4C. 6 Sedimentation rate and Enrichment Factor

The profiles 210Pbexcess are presented in figure 4C. 6. In core MAK, 210Pbexcess profile decreased exponentially with increasing depth indicating a constant sedimentation
rate and no significant mixing (Fig. 4C. 6A). The absence of surface mixed layer agrees with the fact that bioturbation and physical reworking of the sediments are negligible in this core. The sedimentation rate is determined from excess $^{210}\text{Pb}$ profile and is of 0.34 cm/y. The EF values of all the metals show more or less equal values throughout the core (Fig. 4C. 7A). EF values of Mn and Zn are less than 1.5 while the values of Fe, Cr, Co, Pb and Cu are above 2, which suggest that a significant portion of metal is delivered from non-crustal materials, or non-natural weathering processes.

In the case of core MAA, there is a relatively log-linear decrease of $^{210}\text{Pb}_{\text{excess}}$ activity with depth but with a change in slope at 10 cm depth (Fig. 4C. 6B). Changing slope in the $^{210}\text{Pb}_{\text{excess}}$ profile indicates variation in accumulation rate or is due to bioturbation (Cundy et al., 1995b). The assumption of closed system might be violated in salt marshes due to early diagenetic remobilization of $^{210}\text{Pb}$ (Allen et al., 1993; Cundy, 1994). If no diagenetic remobilization occurs then the annual flux will be relatively constant (Crozaz et al., 1964). In the present study, there is no obvious change in the shape of $^{210}\text{Pb}_{\text{excess}}$ profile in the vicinity of the oxidized/reduced boundary, as would be expected if $^{210}\text{Pb}$ migration had taken place. When the profiles of $^{210}\text{Pb}$ are compared with Pb and redox sensitive elements, there are no similar peak concentrations negating the possibilities of mobilization of $^{210}\text{Pb}$. The higher values of $^{210}\text{Pb}$ at the top 10 cm do not coincide with the proposed oxidized/partially reducing boundary and not even with partially reducing/reducing boundary. However, the concentration minima occur below 35 cm onwards, which are taken as background values, may highlight the possibility of diagenetic movement as 32 cm depth is the transition of colours recorded in field but is apparently not significant enough to explain the change in slope at 10 cm depth. Therefore, the change in slope at 10 cm strongly suggests change in sedimentation. Hence the sedimentation was slower at 0.31 cm/yr until 10 cm, which corresponds to year 1996 and increased thereafter to 1.21cm/year, which may be due to catchment area processes both natural and anthropogenic.

In core MAA (Fig. 4C. 7B), the EF values of Mn and Zn are less than 1.5 suggesting that these metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002). On the other hand, EF values of Fe, Cu, Cr, Co
and Pb are more than 1.5 which suggests that a significant portion of metal is
delivered from non-crustal materials, or non-natural weathering processes. Mn and
Zn values are dropped below 1 from 20 cm which corresponds to the year ~1964 to
the surface of the core while Fe and Cu show slight enrichment during this period.
So, the EF of the present study shows environmental contamination by Fe, Cu, Cr,
Co and Pb throughout the core.

Fig. 4C. 7. Down core trends of metal enrichment factors (EF): A – core MAK, B –
core MAA.

4C. 7 Magnetic susceptibility
4C. 7a Results
The rock magnetic parameters are shown in figure 4C. 8. No common features are
observed in the rock magnetic parameters between the two cores. In core MAK, the
core can be divided into two sections according to variations of the magnetic
parameters (Fig. 4C. 8A). In bottom section 84 - 30 cm, the concentration
dependent magnetic parameters (χ and SIRM) and magnetic mineralogy related
parameter (HIRM)) have relatively low values with a steady trend while values of χ50,
χARM, S300 and grain size indicators (χARM/χ and χARM/SIRM) are relatively high in this
section. The trends are reversed in the upper section 30 - 0 cm of the core.
On the other hand, in core MAA, the values are enriched in the upper portion and undergo down core drop in the middle portion before maintaining an almost
constant trend with low values in the bottom portions of the core (Fig. 4C. 8B). So, accordingly this core can be divided into three sections.

1. Section 1 (60 – 40 cm) – This section shows low values for all the parameters. The values of $\chi$, $\chi_{ARM}$, SIRM, HIRM and grain size index ratios have almost constant trend whereas $S_{300}$ show enrichment in the bottom section of the core.

2. Section 2 (40– 30 cm) – All the parameters except $\chi_{xd}$ undergo a sudden increase in the upper 4 – 6 cm of this section reaching minimum values at ~40 cm. $S_{300}$ values increase sharply to 0.93 at the top of this section from 0.87 at about 40 cm depth. These changes indicate that the dominant magnetic minerals rapidly change up the core from high -coercivity components to low-coercivity minerals. HIRM values too, progressively increase upwards indicating that the partial depletion of high-coercivity minerals took place in this section. $\chi$ value starts to increase to $19.23 \times 10^{-7}$ m$^3$ Kg$^{-1}$ at 30 cm from nearly constant value $1.6x \times 10^{-7}$ m$^3$ Kg$^{-1}$ below 40 cm depth. $\chi_{ARM}$ displays sudden increase in value to $0.82x \times 10^{-5}$ m$^3$ Kg$^{-1}$ at 30 cm from $0.05 \times 10^{-5}$ m$^3$ Kg$^{-1}$ below 50 cm. The SIRM quickly increases from lower section to 30 cm to $2141.97x \times 10^{-5}$ Am$^2$ Kg$^{-1}$ from $274.80x \times 10^{-5}$ Am$^2$ Kg$^{-1}$ at around 40 cm.

3. Section 3 (30 – 0 cm) - All the parameters are enriched with highest values in this section. $S_{300}$ values suggest that low-coercivity ferromagnetic minerals magnetically dominate this section. The magnetic granulometric index displays an almost constant value in this section.

**Magnetic mineralogy:** The thermal demagnetisation curves for selected samples from different sections are shown in figure 4C. 9. In core MAK, samples from two different sections show nearly similar curve with the IRM undergo a monotonic decay until their unblocking at ~ 580°C, which is indicative of magnetite. However, there are minor changes within and in between the sections. The curves show sudden decrease in magnetization in between 100 –320°C, which is more pronounced in the upper portion. The loss in magnetization to around 100 – 320°C is possibly due to presence of maghemite or titanomagnetite. Nevertheless, there is
uniform mineralogy throughout the core, which is characterized by magnetite with little hematite.

![Graphs showing thermal demagnetization curves for MAK and MAA cores.](image)

Fig.4C. 9. Representative thermal demagnetization curves for different sections in cores MAK and MAA.

In core MAA, samples from section 3 and 2 show similar curves, which shows that the IRM undergoes a monotonic decay until their unblocking at ~580°C, which is indicative of magnetite. The most distinct difference for samples from section 1, compared to those from higher parts of the core is that there is considerable decrease from 200 – 350°C. Gregite has higher coercivity than magnetite (Roberts, 1995) and is characterized by loss of most of its magnetization from 200°C to 350°C (Krs et al., 1992; Reynold et al., 1994; Roberts, 1995; Torri et al., 1996). In contrast, pyrrhotite undergoes rapid unblocking within a much narrower temperature range of 320 – 350°C (Dekkers, 1989; Torii et al., 1996). There is possibility that the loss in magnetization at around 200 -320°C is due to maghemite or titanomagnetite. Finally, the values are unblocking to near zero at about 580°C, which suggests that magnetite is also the dominant one in this section.
Representative $\chi$ (T) curves for heating – cooling cycles from room temperature up to 700°C from the section 3 and 1 of core MAA are shown in figure 4C. 10. In section 3, $\chi$ slowly increases up to 320°C and then decreases sharply to near zero at ~580°C, which suggests that magnetite is the dominant mineral. Upon cooling, there is a marked decrease in $\chi$ occurs, which indicates the loss of significant amount of magnetization during heating. For the sample from section 3, $\chi$ is low even to negative values in between and fluctuating from room temperature to 300°C, which suggests a dominant contribution from paramagnetic minerals. The decrease in $\chi$ up to ~300°C is followed by an increase in $\chi$ from 300 to 350°C and a marked increase in $\chi$ from 350 to 460°C. The increase in $\chi$ at ~300°C could be due to the presence of gregite, and might signal the onset of thermal alteration of gregite into magnetite or maghemite (Geiss and Banerjee, 1997; Dekkers et al., 2000). Upon cooling, there is a marked increase in $\chi$ occurs between ~580 and 450°C, which indicates the production of a significant amount of magnetite during heating. So, it can be concluded that in core MAA, the magnetic properties of section 3 and 2 contain substantial contributions from magnetite as well as hematite. In contrast, the magnetic mineralogy of section 1 is characterized by (titano) magnetite and gregite, with little hematite.

4C. 7b Discussion

The core sediments studied from Malvan area are mostly composed of slightly sandy mud with sandy mud in between. Therefore, the systematic difference between the rock magnetic parameters can be attributed partially to lithological differences between the upper and lower sediments. The magnetic parameters are
extremely sensitive and small changes in catchment area processes would be recorded in the sediments. If catchment area changes are the explanation, then one would hypothesize some relationship between geochemical indicators of erosion, i.e. Al, Mg, K and Na (Mackereth, 1966) and the dominant remanence carriers of the magnetic signal (e.g. SIRM). The good relationship between the dominant remanence carriers of the magnetic signal (SIRM) with Al (r = 0.59), K (r = 0.55) and Mg (r = 0.56) in core MAA suggests the catchment area processes as one of the explanations for the variations in magnetic properties with depth. However, surprisingly, SIRM in core MAK show poor correlation with Al (r = 0.14), Mg (r = 0.35) and K (r = 0.40) which suggests that the magnetic distribution is least influenced by the catchment area processes in this core.

Previous magnetic studies of deep-sea (Bloemendal et al., 1993) and lake sediments (Anderson and Rippey, 1988) have demonstrated the dissolution of magnetite under reducing conditions. The finer component is believed to be dissolved first due to its high surface to volume ratio, which would result in reduction in magnetic intensity as well as shift in grain size towards the coarser end (Karlim and Levi, 1983; Bloemendal et al., 1993). The iron oxide dissolution is a common feature in coastal sediments where organic input is high and this can be inferred from the magnetic profiles (Zhang et al., 2001).

In the present study, in core MAK, the magnetic intensity reduction accompanied by the coarsening of grain size, is not seen. On the contrary, there is an enhancement of magnetic intensity accompanied by slightly coarsening of grain size in the upper portion of the core. Similarly, the Fe and Mn profiles do not support the possibility of any diagenetic processes. However, in core MAA, the data suggests that there has been a coarsening of the magnetic grain size as well as reduction in total concentration. This pattern is consistent with the suggestion that fine grains have been dissolved and the multi domain grains broken up into Stable Single Domain (SSD) grains. Hence the precipitous down core drop of magnetic parameters at 30 cm, which is diagnostic of early diagenesis in deep water marine sediments (Karlim and Levi, 1983; Robinson et al., 2000), which may reflect the onset of reducing condition. The section 3 is marked by high values of all concentration dependent bulk magnetic parameters, nearly constant values of $S_{300}$ and granulometric index.
This section is therefore interpreted to be the least affected by early diagenetic influence. The main magnetic minerals in this part of the core (magnetite and hematite) can be regarded as the primary detrital magnetic minerals prior to diagenetic modifications in the underlying section. The initial diagenetic stage, observed in section 2 begins with sharp decrease in ferrimagnetic mineral concentrations. These concentrations decline progressively with depth until absolute minimum abundance is reached at the upper end of this section. This stage is associated with depletion of the high-coercivity components. The later diagenetic stage as observed in section 1, which is characterized by authigenic production of fine-grained ferrimagnetic minerals. The section 1, which has been subjected to the initial diagenetic stages like the overlying sections would have retained, if any, the largest magnetic grains. There is enrichment of magnetite in the lower portion of this section which can be reasonably interpreted to be of authigenic origin. Thermomagnetic and temperature measurements suggest the possibility of gregite present in this section. Sedimentary gregite has been consistently found to have Single Domain (SD) like magnetic properties (Snowball, 1991; Roberts, 1995). However, the sudden increase in organic carbon content and ferrimagnetic minerals together may suggest the possibility of more terrigenous input during this time before it was subjected to diagenetic modifications in later stage.

**Significance for environmental study:** The magnetic properties of sediments provide a useful tool for gaining information about the sedimentary processes affecting at least some population of metal carrying, terrigenous, volcanic or man-made particles (Scoullos and Oldfield, 1986). Scoulous et al. (1979) suggested that in marine environment where ferrimagnetic iron oxides are important components of the discharge from industrial or urban complexes, particulate pollution monitoring may be carried out using magnetic susceptibility ($\chi$) and saturation isothermal remanent magnetization (SIRM) measurements. At the same time, Hunt et al. (1984) have confirmed that several transition metals can be strongly enriched in the magnetic fraction of emission from industrial and automotive sources. In this study, in core MAK, the slightly enriched values of $\chi$ and SIRM in the top 30 cm accompanied by the coarsening of grain size may probably point towards an anthropogenic source. The close parallelism between magnetic susceptibility profiles ($\chi$ and SIRM) and metal content can be seen in this portion. It is also
observed that there is a slight decline in the percentage of the frequency dependent component ($\chi_{fd}$%) from ~38 cm to near surface. This insignificance of $\chi_{fd}$ value in the top portion may confirm the anthropogenic origin of the bulk of the most recently deposited magnetic oxides. The frequency dependent component results almost entirely from the presence of very fine grained magnetic crystals (0.03 μm diameter) just below the stable single domain/superparamagnetic size transition. These fine crystals are poorly represented both in anthropogenic particles generated by fossil fuel combustion and other industrial activities, and in common geological parent materials. They are derived almost exclusively from the weathered part of soil profiles (Oldfield and Bartington, 1982; Oldfield et al., 1985; Thompson and Oldfield, 1986). When the calculated ‘soft’ i.e. mostly magnetite, ‘hard’ i.e. mostly hematite, and total i.e. SIRM trends were compared, there were interesting parallels and differences. The increase is much steeper in hematite to magnetite suggesting the relative higher deposition of hematite in the recent years. The iron mineral deposition along the Ratnagiri areas and the Redi iron ore mines could probably be considered as the source which contributes considerable amount of hematite. However, soft remanence shows considerably good correlation with Fe ($r =0.41$), Mn (0.70), Zn (0.53), and Cu ($r = 0.44$) suggesting their association with ferrimagnetic than hard fraction which shows poor correlation with metals ($r < 0.3$).

In core MAA, $\chi$ and $\chi_{ARM}$ show poor correlation (- 0.24 and 0.17) with clay, but show good correlation ($r < 0.6$) with the Fe, Cu and Co. Therefore, the changes in the heavy metal concentrations in this core cannot be accounted by particle size alone. Hence, it is likely that the reduction of iron oxide plays a significant role in distribution of heavy metals. It has been demonstrated that environmental magnetism can be used as a proxy indicator of heavy metal concentration in a simple, quick and non-destructive way (Scoullos et al., 1979; Berry and Plater, 1998). The considerable similarity between heavy metals and $\chi_{ARM}$ was reported from intertidal sediments of the Yangtze Estuary, China by Zhang et al. (2001). It has been suggested that certain magnetic parameters can be used as grain size proxy (Oldfield and Yu, 1994; Zhang et al., 2007). Zhang et al. (2007) reported the strong relationship between $\chi_{ARM}$ and to a lesser degree, frequency dependent susceptibility ($\chi_{fd}$) with heavy metals and explained the role of particle size effects and iron oxides in controlling metal concentration. However, the change in magnetic
properties in the section 3, which are considered as the primary detrital minerals, point to both quantitative and qualitative changes in the assemblage of magnetic minerals present. The increase in SIRM reflects an increase in total magnetic mineral concentrations. In combination with SIRM, the increase of the hardest remanence component points to an increase in hematite in both relative and absolute terms. The trends in 'soft' and 'hard' isothermal remanence can be plotted on a mass specific basis and this isolates these two properties from all other variables responsible for changes. The present study confirms that both components increase significantly in the upper levels of diagenitically least affected upper portion of the cores. The constant nature of grain size parameters in this section indicates a nearly uniform grain size and hence similar condition of deposition with negligible post depositional modifications seems likely. When the calculated 'soft' i.e. mostly magnetite, 'hard' i.e. mostly hematite, and total i.e. SIRM trends were compared, there were interesting parallels and differences. The increase is much steeper in magnetite as compared to hematite suggesting the relative higher deposition of magnetite in the recent years. There is link between magnetic properties ($\chi$, $\chi_{ARM}$ and SIRM) with metals (Fe, Cu and Co) in the upper section of the core. Most importantly, there is parallelism in trends of 'hard' and 'soft' profiles with metals, which points towards a possible common origin. The $\chi_{d}$ values are also increasing gradually towards the surface along with metals, because of relatively higher degree of weathering and erosion in recent years. This may reflect trace metal enrichment of the magnetically enhanced soil derived clays during weathering and transportation in recent years with enhanced sedimentation rate.