Chapter 21
Role of Suspended Particulate Matter in Metal Distribution Within an Estuarine Environment: A Case of Mandovi Estuary, Western India

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Abstract Suspended matter in the estuary is an important factor influencing the bioaccumulation of inorganic contaminants. Considering that mining, dredging and transportation by barges as well as mechanized boats can influence the levels of suspended particulate matter in the estuarine environment, an attempt has been made to study the component composition and elemental concentration of suspended matter in the estuarine environment of the River Mandovi, western India. Surface and bottom water samples, collected along the estuarine channel during monsoon, postmonsoon and premonsoon seasons were analyzed for suspended particulate matter and particulate metals. Systematic seasonal variation of Total Suspended Matter (TSM) along the estuarine region was observed. During the monsoon, TSM concentration was high towards the lower portion of the estuary while higher concentrations were observed in upper portions of the estuary especially in the bottom waters during non-monsoon. On an average, TSM was higher in premonsoon followed by monsoon and postmonsoon in both surface and bottom waters. To understand inter-seasonal variation, the salinity and TSM data along with particulate metals (Fe, Mn, Ni, Zn and Co) were plotted on Isocon diagrams. When monsoon and postmonsoon data were compared, salinity is most prominent in postmonsoon whereas, TSM and particulate Fe are prominent in monsoon season in both surface and bottom waters. Comparison of postmonsoon and premonsoon data indicated that salinity and TSM concentrations were higher during premonsoon both in surface and bottom waters. Pronounced levels of particulate Fe, Mn and Co in surface waters and Fe, Mn and Zn in bottom waters are observed during postmonsoon. Plots of premonsoon and monsoon showed salinity and TSM dominant in premonsoon season and particulate Fe was significant in monsoon season in both surface and bottom waters.

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21.1 Introduction

Estuaries are highly dynamic environments within a coastal zone. Tide and river flow are major physical processes which transport sediment into the estuary (Verlaan et al. 1997, Hossain and McConchie 2001). Tidal currents move sediments via tidal asymmetry (Chen et al. 2006). Estuarine mixing, flocculation and primary particle properties control the depositional characteristics of sediment within estuary (Edzwald and O'Melia 1975). The distribution of suspended matter in estuaries is controlled by various processes like coagulation, aggregation and disaggregation, selective sedimentation, resuspension, adsorption, desorption, dissolution and co-precipitation. Coastal waters are characterized by high concentrations of suspended organic and inorganic materials. Natural processes such as weathering and erosion of rocks, windblown dust and anthropogenic inputs are major sources responsible for increasing the concentration of sediments and metals in the estuarine environment. After entering estuarine waters, most heavy metals are rapidly adsorbed on to suspended matter and ultimately removed to bottom sediments (Santschi et al. 1984). Suspended materials serve as a carrier and storage agent of pesticides, absorbed phosphorus, nitrogen and organic compounds. Thus, Suspended sediments act as sink for anthropogenic pollutants, where certain elements become immobilized and essentially "locked up" in the sediments derived from several sources. Therefore, it is very important to monitor and assess the concentrations of suspended materials in estuarine waters, as well as their spatial and temporal distribution. The metals associated with TSM represent an integrated picture of metal concentration, both temporally and spatially (Niencheski and Baumgarten 2000). Total suspended matter (TSM) also helps in maintaining chemical and biological gradients in the aquatic system. Its composition and concentration reflects the dynamic water-column processes such as primary production in surface waters, dissolution and degradation at bottom, and also vertical and lateral particle transport. Given cognizance to these, the seasonal variations of TSM concentrations, constituents along with its metal chemistry supported by insight into processes and factors involved in their distribution are analyzed for the Mandovi estuary, Western India.

21.2 Study Area

The River Mandovi (Fig. 21.1) originates at the Parwa Ghat of the Karnataka part of the Sahyadri hills and has a drainage basin area of about 1,895 km^2 (Qasim and Sengupta 1981).

After traversing a stretch of about 70 km, the river joins the Arabian Sea through Aguada bay. The Mandovi estuary is funnel shaped. Near the mouth, within the bay, it is characterized by the presence of two shoaling zones namely the Aquada Bar and Reis Magos Bar. The width of the main channel at its mouth is 3.2 km and gets

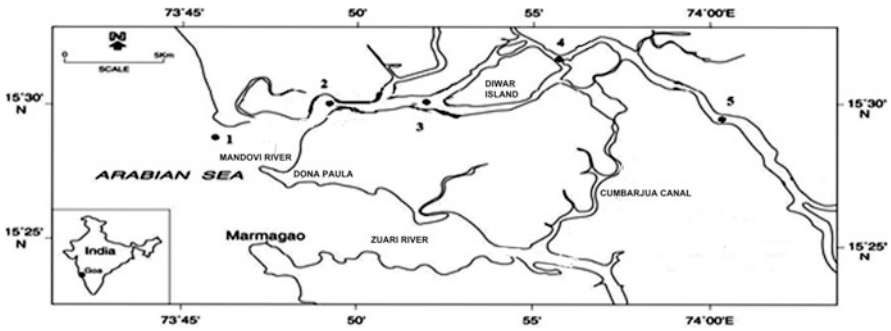

Fig. 21.1 Map showing the sampling locations

progressively narrower (to 0.25 km) and shallower upstream. The average depth of the river is 5 m. The flow in the estuary, however, is tide-dominated and saline waters occur several kilometers upstream from the river mouth (Shetye et al. 1995). The River Mandovi and its tributaries pass through regions of Iron and Manganese ore mining. There are 27 major mines within the Mandovi basin and the river provides an effective means of transport of iron ore from the hinterland to Marmugao harbor. The mining activities in this region influence the biological and geochemical conditions of the estuarine waters to a considerable extent. Industrial and mining activities are at a peak during October–May at several points along the estuary and discharge organic and inorganic industrial wastes, nutrients, heavy metals, and other pollutants (Alagarsamy 2006; Ramaiah et al. 2007).

21.3 Materials and Methods

Sampling was carried out in the Mandovi estuary during three seasons (Monsoon, Postmonsoon and Premonsoon). Five stations were selected covering lower, middle and upper regions of the estuary. 5 l of water samples were collected using Niskin sampler from surface and near bottom of each station and stored in pre-cleaned plastic containers. In the laboratory, the collected samples were analyzed for salinity, Total Suspended Matter, TSM constituents and Particulate metals. Salinity was measured by Mohr Knudsen chlorinity titration method (Grasshoff 1983). The water samples were vacuum filtered through pre-weighed millipore membrane filter having a pore size of 0.45 μm. The filter paper was then oven dried at 60 °C and reweighed on the four-decimal balance. Total suspended matter (TSM) concentration was then calculated using the sample volume and sample weight. TSM was expressed as mg/l. Digestion of filter papers containing suspended matter was carried out for the surface as well as for bottom water samples following the procedure given by Satyanarayana et al. (1985). Samples were analyzed for five selected elements viz. Fe, Mn Co, Ni and Zn using atomic absorption spectrophotometer (VARIAN – AA 240 FS model) equipped with deuterium background corrections. Blank corrections were applied for all the metals.

21.4 Results and Disscussion

21.4.1 Salinity

During monsoon, the salinity ranged from 0.1 to 26 psu (mean: 10.36 psu) and 0.2 to 29.2 psu (mean: 16.64 psu) in surface and bottom waters respectively. As could be observed elsewhere, the salinity showed a gradual increasing trend towards the estuarine mouth. Bottom waters showed higher salinity as compared to surface waters at all the five stations (Fig. 21.2a). This is due to retention of higher salinity in deeper waters and freshwater flow near the surface. The variation is significant at stations 2, 3 and to some extent at station 4.

During postmonsoon, the salinity of surface water varied from 16.66 to 34.02 psu (mean: 23.07 psu) and the bottom waters showed a range from 15.62 to 34.25 psu (mean: 22.99 psu). A gradual increasing trend was observed towards the mouth region in both surface and bottom waters (Fig. 21.2c). During premonsoon, salinity varied from 29 to 35.5 psu (mean: 33. psu) and 29.66 to 35.65 psu (mean: 33.73 psu) in surface and bottom waters respectively. Not much salinity variation could be observed between surface and bottom waters during postmonsoon and premonsoon. However, salinity values were higher in premonsoon indicating tidal control on the estuary (Fig. 21.2e). Average salinity was comparatively higher in premonsoon followed by postmonsoon and monsoon.

21.4.2 TSM

During monsoon, TSM of surface waters ranged from 1.8 to 12.30 mg/l (mean: 6.09 mg/l) and in bottom waters it varied from 1.88 to 36.4 mg/l (mean: 12.73 mg/l). Invariably, all the stations showed higher TSM values in bottom waters with an exception at station 3 (Fig. 21.2b). Increasing TSM with depth suggests that resuspension of bottom sediments was a significant source of input of suspended particles in the water column. The TSM of bottom water showed a gradual increase from station 5–2. The zone of higher suspended matter in lower portions of the estuary was related to the estuarine processes such as flocculation which might be a controlling factor in retaining maximum TSM in this region (Nayak and Bukhari 1992; Regnier and Wollast 1993). Rapid removal of terrigenous suspended sediments in the mixing zone indicated dilution by particle poor marine waters, or more possibly, by rapid deposition of riverine particles at an early stage of the mixing process as observed elsewhere by Zhang et al. (1998).

During Postmonsoon, TSM exhibited a range from 2.75 to 7.72 mg/l (mean: 4.81 mg/l) and 7.00 to 14.87 mg/l (mean: 9.29 mg/l). TSM of surface water showed a decreasing trend from station 5 to station 4 thereafter an increasing trend up to station 2, before showing a decrease towards the mouth of the estuary (Fig. 21.2d). However, while a decreasing trend was perceptible in the bottom waters from station

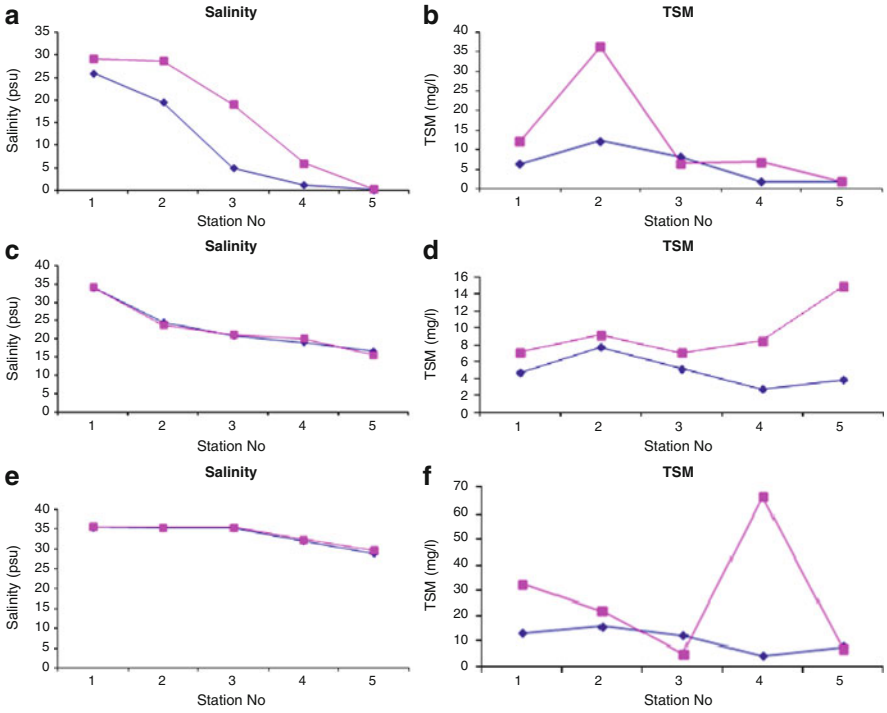

Fig. 21.2 Distribution of salinity and TSM profiles along the estuary from upstream (Staion 1) towards the head (Station 5). **Monsoon:** (**a**). Salinity, (**b**). TSM. **Post monsoon:** (**c**). Salinity, (**d**). TSM. **Premonsoon:** (**e**). Salinity, (**f**). TSM

5 up to station 3 and an increasing trend from station 2–1 was observed. The combination of tidal resuspension and mixing appeared to be the responsible factor in the hydrodynamic sorting of particles along the estuary (Goni et al. 2005). In addition, heightened transport activities of mined ores were observed during non-monsoon season, which could have also contributed suspended particulate matter to the estuarine waters.

TSM ranged from 4.68 to 16.09 mg/l (mean: 10.9 mg/l) and 5.38 to 66. 3 mg/l (mean: 26.7 mg/l) in surface and bottom waters respectively during premonsoon. TSM concentration increased from station 4 up to station 2 and showed lower values both towards the mouth (station 1) and upstream (station 4) in surface waters. In the case of bottom waters, TSM showed decreasing trend from station 4 to station 3 (Fig. 21.2f). Towards downstream, an increasing trend was observed from station 3 to station 1. Increasing tidal velocity towards the upper portion of the estuary due to constriction might have forced most of the sediment to overcome gravitational settling in this zone, and thus increased the residence time of the sediment in suspension, resulting in higher TSM concentration. In addition, ore loading and transport must have added the suspended material.

During monsoon, high concentration of TSM was observed towards the lower portion of the estuary while the upper portions of the estuary, particularly the bottom waters contained higher concentrations during non-monsoon. On the whole, highest TSM was observed in premonsoon followed by monsoon and postmonsoon in surface and bottom waters. During monsoon, the river discharge was high and little time was required to flush out the materials introduced into the estuary. During premonsoon, suspended matter introduced into the estuary could not be flushed out easily due to the insufficient buoyancy of incoming freshwater. Suspended matter was lower in winter months (postmonsoon) as compared to summer months (premonsoon) in the Mandovi estuary, as observed by Hatje et al. (2001a) elsewhere.

21.4.3 TSM Versus Salinity

Salinity and TSM showed an increasing trend from head to mouth region (Fig. 21.3a, b) in both surface and bottom waters during monsoon and in surface waters during postmonsoon (Fig. 21.3c) and premonsoon (Fig. 21.3e). However, at station 1, i.e. near the mouth, anti-sympathetic relationship between salinity and TSM values were observed. The salt induced flocculation phenomenon is often proposed as a major mechanism influencing the deposition of the suspended matter near the mouth of major rivers (Thill et al. 2001). Alternatively, high energy conditions prevailing in the mouth region could be responsible for transporting the particulate matter towards upstream regions during flood tide. In all the three seasons, the surface waters and, during monsoon, the bottom waters, showed high TSM concentration at station 2, supporting the transport of particulate matter from station 1 towards station 2. However, in bottom waters during premonsoon (Fig. 21.3f) and postmonsoon (Fig. 21.3d), higher TSM concentrations were observed at upstream, which could be due to the input from mining activities or due to resuspension of the bed sediments. Postma (1967) stated that the smaller size floccules are carried away by currents upstream where they tend to settle in calmer conditions thus increasing the TSM concentration near bottom in the upstream regions of the estuary.

21.4.4 Metals

Fe concentration ranged from 3.27 to 18.25 ppm (mean: 11.77 ppm) and from 5.19 to 53.10 ppm (mean: 18.18 ppm) in surface and bottom waters respectively during monsoon. In general, an increasing trend from upstream to station 2 and from then onwards decreasing trend towards the mouth in both surface and bottom waters could be observed. Highest Fe concentration was at station 2 in bottom waters which coincided with higher TSM. During postmonsoon, Fe ranged from 1.099 to

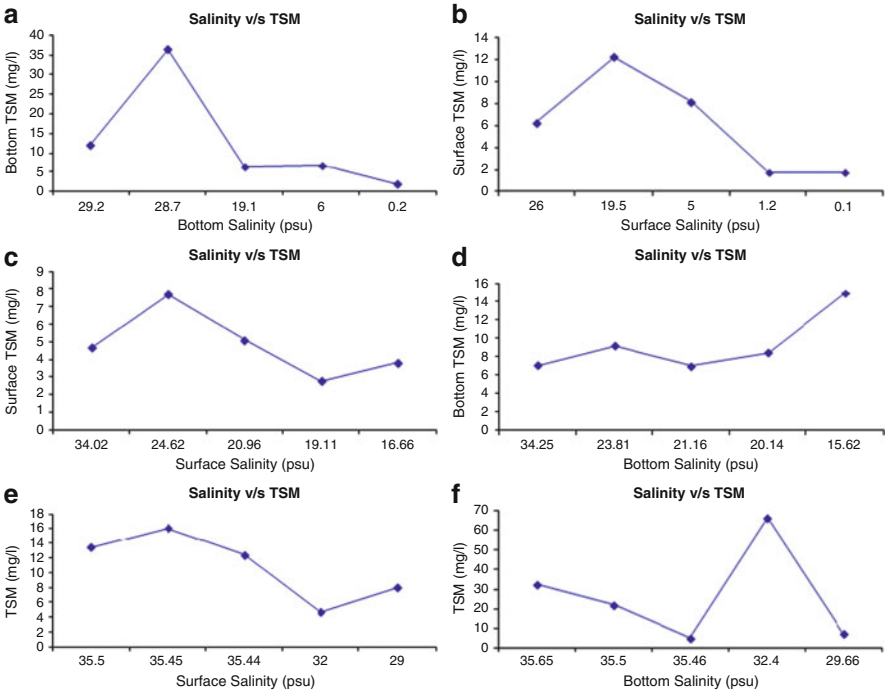

Fig. 21.3 Plots showing association of salinity and TSM. (**Monsoon** (**a**). Association of salinity and TSM (Surface waters) (**b**). Association of salinity and TSM (Bottom waters). **Post monsoon** (**c**). Association of salinity and TSM (Surface waters) (**d**). Association of salinity and TSM (Bottom waters). **Pre monsoon** (**e**). Association of salinity and TSM (Surface waters) (**f**). Association of salinity and TSM (Bottom waters))

11.12 ppm (mean: 5.58 ppm) and 4.76 to 30.09 mg/l (mean: 13.58 ppm) in surface and bottom waters. Higher concentration of Fe was observed at upstream in both surface (station 3) and bottom (station 5) waters. During premonsoon, particulate Fe ranged from 1.24 to 11.74 ppm (mean: 3.95 ppm) and from 1.47 to 33.89 ppm, (mean: 11.45 ppm) in surface and bottom waters respectively. In surface waters, similar values were observed at station 5 and 4 followed by a decreasing trend up to the station 2 and with a higher value at station 1. Fe concentration of bottom waters showed a decrease from station 5–4 followed by an increasing trend towards estuarine mouth. Seasonally, higher Fe during monsoon followed by postmonsoon and premonsoon could be observed. The bottom water had higher concentration of Fe than surface water.

Mn ranged from 0.46 to 2.72 ppm (mean: 1.39 ppm). It varied from 0.43 to 6.39 ppm (mean: 1.88 ppm) in surface and bottom waters during monsoon. Distribution of Mn is similar to that of Fe in both surface and bottom TSM during monsoon. Mn ranged from 0.019 to 2.06 ppm (mean: 1.06 ppm) and from 0.27 to 5.44 ppm (mean: 2.18 ppm) in surface and bottom waters respectively during postmonsoon. Distribution pattern of Mn resembled same as that of Fe except for

a few minor variations at station 1 and 5. Except for station 3, bottom water TSM was higher than surface waters. During premonsoon, particulate Mn ranged from 1.24 to 11.74 ppm (mean: 3.95 ppm) in surface waters whereas, in bottom waters, particulate Mn showed a range between 1.47 and 33.89 ppm (mean: 11.45 ppm). A largely decreasing trend was observed from station 5 towards the mouth of the estuary in surface waters. In bottom waters, particulate Mn showed a decreasing trend between station 5 and 4 followed by an increase downstream. On an average, higher particulate Mn was observed during premonsoon season followed by monsoon and postmonsoon in both surface waters and in bottom waters. Between seasons, the values showed a pattern of premonsoon > postmonsoon > monsoon. High concentrations of particulate Mn during summer (premonsoon) season resulted from enhanced oxidation at higher water temperatures (Morris et al. 1982; Cossa 1990; Turner 1999).

Zn value varied from 0.07 to 0.18 ppm (mean: 0.11 ppm) in surface waters and from 0.03 to 0.39 ppm (mean: 0.13 ppm) in bottom waters during monsoon. An increasing trend of Zn in surface waters from station 5 to station 3 followed by decrease at station 2 before showing a slight increase at station 1 was observed. In bottom waters an increasing trend of Zn from station 5 to station 2 and lower value at the mouth were observed, which ware similar to that of Fe and Mn. During postmonsoon, the particulate Zn value varied from 0.01 to 0.1 ppm (mean: 0.06 ppm) and from 0.04 to 0.10 ppm (mean: 0.076 ppm) in surface and bottom waters respectively. In surface waters, particulate Zn showed an increase from station 5–4 followed by a decrease up to station 2 and an increase towards the mouth. In bottom waters, decreasing trend was observed between stations 5 and station 3 followed by an increase up to station 2 and decrease from station 2 and 1. During premonsoon, particulate Zn ranged from 0.041 to 0.138 ppm (mean: 0.084 ppm) in surface waters and in bottom waters it ranged from 0.045 to 0.133 ppm (mean: 0.085 ppm). In surface waters, an increasing trend was observed between station 5 and 4 followed by a decrease between station 4 and 1 with slight variations at stations 3 and 2. At bottom, decrease of TSM was observed from station 5 to station 4 followed by an increase between station 4 and 2. Seasonally, the Zn values followed a decreasing trend from monsoon > premonsoon > postmonsoon in both surface and bottom waters.

During monsoon, the Ni varied from 0.012 to 0.028 ppm (mean: 0.019 ppm) and ranged from 0.013 to 0.056 ppm (mean: 0.025 ppm) in surface and bottom waters. Distribution pattern of Ni was similar to that of Fe and Mn in both surface and bottom waters. During postmonsoon, the Ni values ranged from 0.008 to 0.021 ppm (mean: 0.017 ppm) and from 0.018 to 0.039 ppm (mean: 0.028 ppm) in surface and bottom waters respectively. In surface waters, Ni value showd an increasing trend from station 5 to station 3 followed by decrease up to station 2 and further towards the mouth it showed a slight increase. In bottom waters, increasing trend was observed from station 5–4 followed by a decrease at station 3 and thereafter an increase at station 2 and then a decrease towards the mouth. Except at station 3, bottom TSM had higher concentration than surface waters. During premonsoon, Ni ranged from 0.02 to 0.037 ppm (mean: 0.028 ppm) and from 0.026 to 0.035 ppm

(mean: 0.033 ppm) in surface and bottom waters. Generally increasing trend was observed from upstream to mouth of the estuary with minor changes. Seasonally, the Ni values followed a decreasing trend from premonsoon > monsoon > postmonsoon in surface waters and in bottom waters the trend of premonsoon > postmonsoon > monsoon was observed.

During monsoon, the particulate Co ranged from 0.9 to 4.23 ppm (mean: 2.87 ppm) and from 1.46 to 10.23 ppm (mean: 3.86 ppm) in surface and bottom waters respectively. Distribution pattern of Co was similar to that of Fe and Mn with highest value at station 2 for bottom waters. During postmonsoon, the particulate Co varied from 0.25 to 3.2 ppm (mean: 1.49 ppm) and from 1.73 to 4.99 ppm (mean: 2.93 ppm) in surface and bottom waters respectively. The surface waters showed an increasing trend from station 5 to station 3 followed by a decrease up to station 2 and increase towards mouth. The bottom waters showed a decrease from station 5 and 3 followed by an increase at station 2 and then a decrease towards mouth. During premonsoon, Co ranged between 0.27 and 3.13 ppm (mean: 1.19 ppm) in surface waters whereas, in bottom waters, Co varied from 0.38 to 7.64 ppm (mean: 2.76 ppm). Increasing trend of Co in surface waters was observed between station 5 and station 4 followed by a decrease from station 4 and station 3 thereafter an increasing trend up to station 1. In bottom waters, decrease in particulate Co was observed between stations 5 and station 4 followed by an increase towards the mouth of the estuary. Seasonally, both the surface and bottom waters showed the trend of monsoon > postmonsoon > premonsoon.

21.4.5 TSM Versus Metals

The Mandovi River receives considerable volume of freshwater during monsoon season, in the form of runoff from catchment area and monsoon precipitation. The salinity remained almost negligible during monsoon in the upstream regions (Station 5) and showed a typical salt wedge feature in the downstream (Fig. 21.2a). During monsoon, salinity and TSM showed increasing trends from head to mouth in both surface and bottom waters with highest values at station 2 (Fig. 21.3a, b). All the elements studied also showed higher concentration during monsoon at station 2 in bottom waters. The salt induced flocculation phenomenon proposed by Thill et al. (2001) may be a mechanism for this trend, as could be observed elsewhere. The terrigenous particles carried by freshwater during monsoon when come in contact with saline waters near the estuarine mouth, salinity of waters influences the double layer dynamics at the particle surface and, hence, increases the probability of flocculation and the settling velocity of the particles. This could have been the reason for the observed spatio-temporal variations of TSM and metals.

Two factors thought to be important for the formation of a flocculation upon collision between two particles are: the organic coating of the particles (Van Leussen 1994), and salinity of the surrounding water influencing the double layer

dynamics. Flocculation at salinities ranging from 5 to 12 psu is well known. At higher salinity levels, organic coating on particles might facilitate adsorption of elements resulting in higher suspended matter at station 2. Alternatively, as stated earlier, high energy conditions prevailing in the mouth region could have been responsible for transporting the particulate matter towards upstream regions during flood tide. The distribution of particulate metal profiles in the Mandovi estuary with higher concentration at station 2 during the monsoon season especially in bottom waters suggested the addition of material from resuspension and remobilization from bottom sediments. Dissolved Fe released from sediments can rapidly get oxidized in the overlying waters, producing Fe oxide coatings. This coating of Fe might also facilitated adsorption of trace metals. Behaviour of many metals as that of Fe supports this inference.

Minor differences of salinity between surface and bottom waters during post and premonsoon were observed. However, bottom water showed slightly higher salinity than the surface waters. The quantity of freshwater discharge from the River Mandovi during post-monsoon and pre-monsoon period was negligible and the flow within the estuary during these seasons was regulated largely by tides of semidiurnal nature. Thus, the estuary remained partially mixed during post-monsoon and well mixed during pre-monsoon. The higher TSM values observed at upstream during these seasons in the Mandovi estuary was contrary to the distribution of TSM in the adjacent Zuari estuary wherein decrease in TSM content from mouth towards upstream during premonsoon and post-monsoon was reported (Nayak and Bukhari 1992). Higher TSM concentration observed towards the upstream especially in bottom waters during both premonsoon and postmonsoon could be due to the resuspension of the bottom sediments and/or input from mining activities. The highest TSM concentrations observed in the shallow upper reaches of the estuary reflected largely the resuspension of bottom sediments. Biological processes, such as primary productivity and algal mats formed on the sediment surface during winter, could have also contributed to TSM. However, as the area is under heavy mining activity, addition of material from mining cannot be ruled out in the upper estuary i.e. around station 5.

During postmonsoon season, as the freshwater input to the estuary was reduced drastically, saline water entered the estuary during flood tide which in turn enhanced significant mixing between saline and freshwater in the middle estuarine region. Saline water moving upstream near the sediment bed surface was responsible for resuspension and remobilization of metal upstream. In the process, smaller size floccules were carried away by currents upstream where they settled in calmer conditions. This phenomenon could explain the higher TSM concentration near bottom in the upstream regions of the estuary (Postma 1967). As stated earlier, dissolved Fe released from sediments rapidly got oxidized in the overlying waters, producing Fe oxide coatings. Manganese, which is also a redox-sensitive element, is oxidized but slowly than Fe in natural systems (Sung and Morgan 1980). The diagenetic mobilization of Fe and Mn in estuaries is widely recognized (Sundby et al. 1986; Owens et al. 1997; Zwolsman and Van Eck 1999). Most of the metals analyzed for the Mandovi estuary showed higher concentrations in the upper

estuary during postmonsoon. Based on the geochemical considerations, higher trace metal concentrations can be explained on TSM in the bottom waters during postmonsoon as Fe and Mn. These indicators of important host phases for particulate trace metals, exhibited significant enrichment in TSM.

During the premonsoon season, the Mandovi estuary was fully controlled by tidal influence and saline waters, and the estuary showed a well mixed nature. During this season Fe, Ni, Co and, to some extent Zn, showed higher concentrations near the mouth. It indicated that the distribution of these metals in TSM was completely influenced and controlled by the highly dynamic environment near the mouth. It also supported the interpretation of significant influence exercised by resuspension of bottom sediments over remobilization of metals in the Mandovi estuary.

21.4.6 Isocon Plots

In order to understand the seasonal variations of different elements associated with TSM, the data were plotted on isocon diagram. Isocon plots allow an easy visual comparison of average composition of each parameter studied in every season (Grant 1986; Cundy et al. 1997; Rosales-Hoz et al. 2003). Average concentration of metals in surface and bottom TSM were plotted separately along with respective salinity and TSM concentration.

Comparison of monsoon and postmonsoon data showed that the Ni and Mn fall on or near the isocon line in both surface and bottom TSM indicating lesser inter-seasonal variation (Fig. 21.4a, b). Salinity was more pronounced during postmonsoon than monsoon in both surface and bottom waters. TSM along with metals such as Zn, Co and Fe deviated away from the isocon line and showed higher values during monsoon in surface and bottom waters, indicating that these metals were adsorbd on to the surface of suspended matter during the monsoon season. Comparison of data of postmonsoon and premonsoon (Fig. 21.4c, d) indicated that Ni and Zn fall on or near the isocon line in surface waters and Ni, Co and Mn in bottom waters. In surface and bottom waters salinity and TSM concentrations were higher during premonsoon than postmonsoon whereas Fe, Mn and Co were more pronounced in surface and Fe and Zn were more pronounced in bottom waters during postmonsoon. It indicated the crucial roles played by Fe and Mn hydroxides in distribution of Co in surface waters. Higher concentration of Fe in bottom water indicated that particles settled slowly towards the bottom upon adsorption by Fe. When the data of monsoon and premonsoon (Fig. 21.4e, f) were compared, Ni, Mn, Zn and Co fall on or near the isocon line in both surface and bottom waters indicating minor seasonal variation. TSM along with salinity was more pronounced in premonsoon in both surface and bottom waters as compared to monsoon. High saline waters facilitated flocculation which allowed the particles to move to deeper levels resulting in increase of TSM in bottom waters.

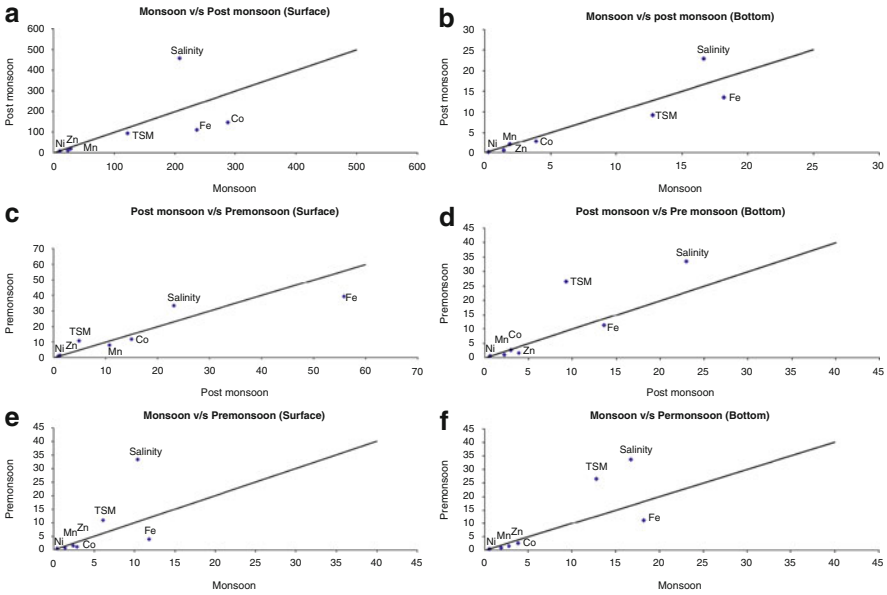

Fig. 21.4 Isocon diagam (Grant 1986) individual points represent average value of suspended component and element in each core. **Monsoon v/s Post monsoon** (**a**). Monsoon v/s Post monsoon (Surface waters) (**b**). Monsoon v/s Post monsoon (Bottom waters). **Post monsoon v/s Pre monsoon** (**c**). Post monsoon v/s Pre monsoon (Surface waters) (**d**). Post monsoon v/s Pre monsoon (Bottom waters). **Pre monsoon v/s Monsoon** (**e**). Pre monsoon v/s Monsoon (Surface waters) (**f**). Pre monsoon v/s Monsoon (Bottom waters)

21.4.7 Pearsons Correlation

In surface and bottom waters of the Mandovi estuary, salinity and TSM showed a significant correlation during monsoon season. TSM exhibited significant correlation with almost all the particulate metals (Tables 21.1 and 21.2). With the increase of salinity, most of the fine-particulate materials gradually flocculated and deposited creating maximum turbidity. Turbidity maximum is the main carrier of heavy metal in estuaries. The Fe and Mn of surface waters also exhibited significant correlation with Ni. Fe showed a significant association with Co. In bottom waters, Fe and Mn showed significant association with other metals. During postmonsoon, in surface waters, TSM and salinity showed negative correlation with most of the elements (Table 21.3). Mn and Fe showed significant correlation with Ni, Zn and Co. In bottom waters (Table 21.4), TSM showed significant correlation with Mn, Fe, Zn and Co. Fe and Mn showed positive correlation with Zn and Co. Zn and Co were sympathetic with Ni. Zn showed positive correlation with Co in both surface and bottom waters. During premonsoon in surface waters, salinity and TSM showed significant correlation. No significant correlation was perceptible in the case of Mn with other particulate elements (Table 21.5). Fe showed significant correlation with Ni and Co. In bottom waters, negative correlation was observed between salinity

Table 21.1 Pearsons correlation between parameters such as salinity, TSM and particulate metals (Fe, Mn, Co, Ni, Zn) in surface waters

Monsoon	Mn (ppm)	Fe (ppm)	Ni (ppm)	Zn (ppm)	Co (ppm)	SALINITY	TSM
Mn (ppm)	1.00						
Fe (ppm)	**0.65**	1.00					
Ni (ppm)	**0.76**	**0.97**	1.00				
Zn (ppm)	0.31	0.17	0.06	1.00			
Co (ppm)	0.60	**0.98**	**0.95**	0.12	1.00		
SALINITY	0.09	**0.72**	**0.68**	−0.41	**0.79**	1.00	
TSM	**0.73**	**0.93**	**0.97**	−0.02	**0.86**	**0.63**	1.00

Table 21.2 Pearsons correlation between parameters such as salinity, TSM and particulate metals (Fe, Mn, Co, Ni, Zn) in bottom waters

Monsoon	Mn (ppm)	Fe (ppm)	Ni (ppm)	Zn (ppm)	Co (ppm)	SALINITY	TSM
Mn (ppm)	1.00						
Fe (ppm)	**0.99**	1.00					
Ni (ppm)	**1.00**	**1.00**	1.00				
Zn (ppm)	**0.99**	**0.99**	**1.00**	1.00			
Co (ppm)	**0.97**	**0.99**	**0.99**	**0.97**	1.00		
SALINITY	**0.55**	**0.64**	**0.62**	**0.63**	**0.67**	1.00	
TSM	**0.95**	**0.97**	**0.96**	**0.94**	**0.99**	**0.70**	1.00

Table 21.3 Pearsons correlation between parameters such as salinity, TSM and particulate metals (Fe, Mn, Co, Ni, Zn) in surface waters

Post monsoon	Mn (ppm)	Fe (ppm)	Ni (ppm)	Zn (ppm)	Co (ppm)	SALINITY	TSM
Mn (ppm)	1.00						
Fe (ppm)	**0.85**	1.00					
Ni (ppm)	**0.93**	**0.94**	1.00				
Zn (ppm)	**0.98**	**0.80**	**0.90**	1.00			
Co (ppm)	**0.89**	**0.90**	**0.99**	**0.86**	1.00		
SALINITY	−0.73	−0.72	−0.63	−0.61	−0.54	1.00	
TSM	−0.67	−0.52	−0.50	−0.77	−0.44	0.33	1.00

and suspended matter (Table 21.6). Mn exhibited significant correlation with Fe, Ni and Co whereas Fe did so with Ni, Zn and Co. Ni exhibited positive correlation with Zn and Co in both surface and bottom waters. Zn was correlated with Co. Strong correlation between trace metals and Fe in TSM suggested that Fe oxides were the primary sorptive phases of the suspended matter. In bottom waters, Fe and Mn showed significant correlation with all the metals. Metal oxides along with organic coatings must be responsible for adsorbing trace metals on to the surface of suspended matter.

Table 21.4 Pearsons correlation between parameters such as salinity, TSM and particulate metals (Fe, Mn, Co, Ni, Zn) in bottom waters

Post monsoon	Mn (ppm)	Fe (ppm)	Ni (ppm)	Zn (ppm)	Co (ppm)	SALINITY	TSM
Mn (ppm)	1.00						
Fe (ppm)	**0.96**	1.00					
Ni (ppm)	0.43	0.42	1.00				
Zn (ppm)	**0.82**	**0.89**	**0.64**	1.00			
Co (ppm)	**0.93**	**0.97**	**0.61**	**0.90**	1.00		
SALINITY	−0.80	−0.63	−0.47	−0.42	−0.70	1.00	
TSM	**0.89**	**0.95**	0.47	**0.80**	**0.97**	−0.66	1.00

Table 21.5 Pearsons correlation between parameters such as salinity, TSM and particulate metals (Fe, Mn, Co, Ni, Zn) in surface waters

Pre monsoon	Mn (ppm)	Fe (ppm)	Ni (ppm)	Zn (ppm)	Co (ppm)	SALINITY	TSM
Mn (ppm)	1.00						
Fe (ppm)	0.20	1.00					
Ni (ppm)	0.18	**0.77**	1.00				
Zn (ppm)	0.08	0.12	**0.69**	1.00			
Co (ppm)	0.26	**0.99**	**0.85**	0.26	1.00		
SALINITY	−0.90	0.24	0.17	0.02	0.17	1.00	
TSM	−0.78	0.16	0.03	−0.32	0.07	**0.77**	1.00

Table 21.6 Pearsons correlation between parameters such as salinity, TSM and particulate metals (Fe, Mn, Co, Ni, Zn) in bottom waters

Pre monsoon	Mn (ppm)	Fe (ppm)	Ni (ppm)	Zn (ppm)	Co (ppm)	SALINITY	TSM
Mn (ppm)	1.00						
Fe (ppm)	**0.92**	1.00					
Ni (ppm)	**0.96**	**0.98**	1.00				
Zn (ppm)	0.73	**0.87**	**0.82**	1.00			
Co (ppm)	**0.91**	**1.00**	**0.97**	**0.87**	1.00		
SALINITY	0.28	**0.59**	0.43	**0.67**	**0.63**	1.00	
TSM	−0.19	0.03	0.04	−0.09	−0.02	−0.03	1.00

21.4.8 Cluster Analysis

During monsoon, two clusters formed (Figs. 21.5a, b) out of which one included salinity, TSM and Fe and the other comprised Co, Zn, Ni and Mn in both surface and bottom waters. Many researchers including Gibbs (1994) and Santiago et al. (1994) reported several metal associations with suspended particulate matter. Sondi et al. (1994) reported higher concentrations of Cd, Cu, Cr, Mn, Pb, Ti and Zn

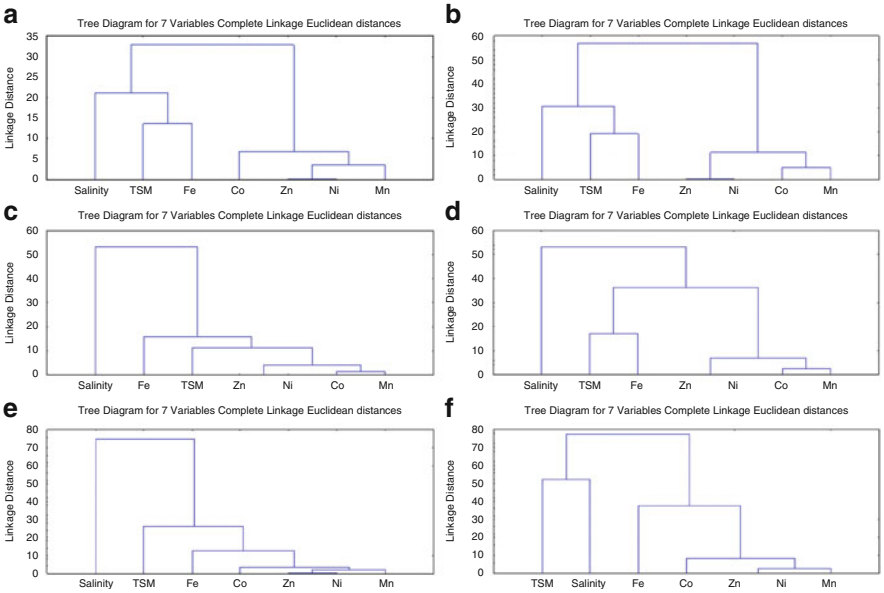

Fig. 21.5 Dendograms. (**Monsoon** (**a**). Surface waters (**b**). Bottom waters. **Post monsoon** (**c**). Surface waters (**d**). Bottom waters. **Pre monsoon** (**e**). Surface waters (**f**). Bottom waters)

with suspended matter. Fe coating on TSM seemed to act as adsorbing surface for other metals. Martino et al. (2002) reported Fe oxyhydroxide as a host phase on suspended matter for particulate trace metals.

During postmonsoon in surface waters (Fig. 21.5c) salinity seemed to have a direct control on particulate Fe. Distribution of other elements viz. Zn, Ni, Co and Mn were not directly controlled by Fe. In the bottom waters (Fig. 21.5d), Fe and TSM formed a single group. During premonsoon in bottom waters (Fig. 21.5f), salinity seemed to control TSM and metal relations.

Cluster groups were similar during monsoon in both surface and bottom waters. During this season, the large quantity of freshwater influx must be responsible for diluting salinity within the estuary. The estuary therefore acted as a river except in the lower portion wherein it showed a salt wedge character. Cluster groups during postmonsoon and premonsoon were similar in surface waters (Figs. 21.5c, e) and were different in bottom waters indicating the role of salinity in the concentration of trace metals in TSM and therefore in the formation of cluster groups. In waters of low salinity, a diffuse electrical double layer existed due to the lesser ionic strength and the colloidal particles repelled each other allowing conditions for the formation of stable suspensions (Edzwald et al. 1974). In the bottom waters, an increase in salinity contributed to a constriction of the double layer creating agglomerations known as flocs (Drever 1997). These characteristics of estuary explain the observed cluster groups in the Mandovi estuary.

21.5 Conclusion

The present study has demonstrated that the distribution pattern of TSM within an estuarine region was dependent on salinity variations, terrestrial and marine input and hydrodynamic conditions. Processes like resuspension of sediments, flocculation, along with fresh and marine water influx influenced the distribution of suspended matter. TSM distribution varied with space within the estuary. It is inferred that distribution of metals is distinct with respect to seasons and geographic locations. Ni and Mn showed higher concentration in premonsoon season whereas Zn, Fe and Co were enriched during monsoon in both surface and bottom waters. During postmonsoon, almost all elements showed higher concentration towards the upstream regions in bottom waters. During monsoon, salinity, TSM as well as Fe and Mn oxyhydroxides were effective in adsorption of most of the trace metals as indicated by correlation analysis and Cluster analysis. All these inferences also affirm that the TSM in estuary has overriding influence on the heavy metal concentrations.

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