

# **Distribution and seasonal variation of trace metals in surface sediments of the Mandovi Estuary, West Coast of India.**

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## **Abstract**

The concentration and distribution of selected trace metals in surface sediments of the Mandovi estuary were studied to determine the extent of anthropogenic inputs from mining activities and to estimate the effects of monsoon on geochemical processes in this tropical estuarine system. Analysis of bulk sediments from the Mandovi estuary shows that the concentrations of iron, manganese, cobalt, copper, zinc and lead vary from 2.2-49.7%; <Detection Limit (DL)-1.61%; 2.5-45.3  $\mu\text{g g}^{-1}$ ; 11.5-77.5  $\mu\text{g g}^{-1}$ ; 19.9-83.5  $\mu\text{g g}^{-1}$ ; and 4.5-46.5  $\mu\text{g g}^{-1}$  respectively. An important observation is that, in general, lowest metal concentrations are found during the monsoon, compared to the pre- and post-monsoon. Comparison of the metal levels in the sediments from different areas of the estuary indicates that there is a detectable anthropogenic input to the Mandovi estuary. The enrichment of Fe and Mn reflects the intensity of anthropogenic inputs related to iron ore processing in the upstream region of the estuary, however, the highest enrichment levels were not found near the mouth region.  $I_{\text{geo}}$  values calculated for Fe (2.5) and Mn (3.4) showed higher values in the premonsoon period in the upstream region of the estuary than in the post monsoon and monsoon seasons. Cu and Zn enrichment in the river mouth region, associated with high organic carbon contents, is indicative of the influence of organic wastes from municipal sewage entering the estuary. The intermetallic relationship revealed the identical behaviour of metals during its transport in the estuarine environment.

Key words: trace metals; surface sediment; Mandovi estuary; anthropogenic input; mining; seasonal

## 1. Introduction

The Mandovi estuary is a tropical estuary on the west coast of India (Fig. 1) and its hydrological characteristics are governed by the monsoon regime. The estuarine channel of the Mandovi river is used to transport large quantities of iron and ferromanganese ores to Marmugao harbour (Arabian Sea) throughout the year. Its (length ~ 50 km; area ~ 29 km<sup>2</sup>; average depth ~ 5 m) width at the estuary is 3.2 km while, upstream, it narrows down to 0.25 km. The rich iron and manganese ore deposits are considered as a natural wealth of Goa. Goa is an important mineral producing area on its west coast of India and its economy is dependent mainly on iron ore mining and its export. The mining activities in this region may influence the biological and geochemical conditions of the estuarine waters to a considerable extent. A study of the distribution and seasonal variations of trace metals in the sediments is important to the assessment of the probable influence of the mining of iron ore in this region on the estuarine environment. The measurement of trace element concentrations and distribution in the marine environment leads to better understanding of their behaviour in the aquatic environment and is important for detecting sources of pollution (Förstner and Wittmann, 1979). Studies of various physico-chemical, biological and mineralogical aspects of the Mandovi estuary have been carried out (Varma and Rao, 1975; Murthy et al., 1976; Qasim and Sen Gupta, 1981; Upadhyay and Sen Gupta, 1995, de Sousa, 1999) but limited data are available on the distribution and seasonal variation of metal concentrations in the sediments of the Mandovi river. The trace metal data provide new information on the surface sediment geochemistry in the region whilst the study of element interrelationships, including organic carbon, gives information on their possible origin (Alagarsamy, 1991). The distribution of metals in sediments at 6 stations (Fig.1) in the Mandovi estuary has been examined, therefore, in order to enhance the data inventory for the region, characterize the geochemistry of Fe, Mn, Co, Cu, Zn and Pb in surficial sediments and to help understand the influence of anthropogenic activities and the monsoon on biogeochemical process in this tropical estuarine system. These impacts were assessed by means of the geoaccumulation index ( $I_{geo}$ , Müller, 1979) and  $I_{geo}$  classification is reported based on the chemical analysis of the bulk sediments. The  $I_{geo}$  has been widely utilised as a measure of pollution in freshwater (e.g. Müller, 1980; Singh et al., 1997; Kralik, 1999) and marine

sediments (e.g. Stoffers et al., 1986; Bryan and Langston, 1992; Dickinson et al., 1996). Sampling was carried out monthly, over a period of one year from January to December 1985. However the data are presented as pooled values covering premonsoon (February-May), monsoon (June-September) and post monsoon (October-January) seasons.

## 2. Materials and Methods

### 2.1. Collection and treatment of samples:

Surface sediments were collected monthly, using a Van Veen Grab from 6 stations in the Mandovi estuary (Fig. 1) across the upper, mid, and lower regions, covering a distance of ~50 km and a range of salinities from freshwater in the upstream area to seawater at the mouth. Sub samples were taken from the uppermost layer of the sediment taking care to minimise contamination. The samples were frozen after collection and later thawed, dried at 50-60° C in an oven and disaggregated in an agate mortar, before chemical treatment for total metal analysis. For each sample a known quantity (~ 1 g) of sediment was digested with a solution of concentrated HClO<sub>4</sub> (2 ml) and HF (10 ml) to near dryness. Subsequently, a second addition of HClO<sub>4</sub> (1 ml) and HF (10 ml) was made and the mixture was evaporated to near dryness. Finally, HClO<sub>4</sub> (1 ml) alone was added and the sample was evaporated until white fumes appeared. The residue was dissolved in concentrated HCl and diluted to 25 ml (Tessier et al., 1979).

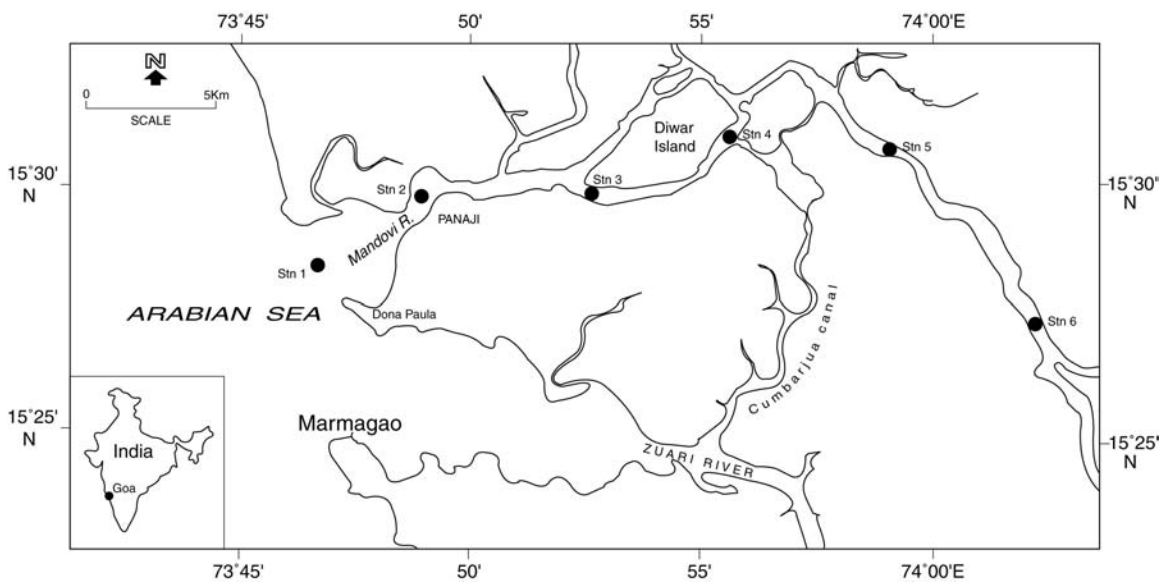


Fig.1. Location of sampling sites in the Mandovi estuary

## 2.2. Analysis of Trace Metals:

Trace metal concentrations (Fe, Mn, Cu, Co, Zn and Pb) were measured using a flame atomic absorption spectrophotometer (AAS, Perkin-Elmer Model 5000). The accuracy of the analytical procedures was assessed using the certified reference material BCR-1 and yielded results within the reference value range (Flanagan, 1973). For Fe, Mn, Cu and Zn the reproducibility, expressed as the coefficient of variation, was <5%; for Co and Pb it was 10 and 13% respectively.

## 3. Results and discussion

Concentration ranges in the sediments were: Fe 2.2-49.7%; Mn <DL-1.61% (DL referred from Perkin-Elmer Manual as recommended); Co 2.5-45.3  $\mu\text{g g}^{-1}$ ; Cu 11.5-77.5  $\mu\text{g g}^{-1}$ ; Zn 19.9-83.5  $\mu\text{g g}^{-1}$ ; and Pb 4.5-46.5  $\mu\text{g g}^{-1}$ . TOC values were referred from earlier studies (Alagarsamy, 1991).

### 3.1. Fe

The range in sedimentary iron values of between 2.2% and 49.7% are somewhat higher than that reported from other Indian estuaries (Table 1). During the premonsoon period, higher concentrations of iron are observed (Fig. 2a) throughout the estuary, which may be attributed to high spillage during transportation of iron and ferromanganese ores down the Mandovi estuary. Kamat and Sankaranarayanan (1975) observed a high value (5-44  $\text{mg l}^{-1}$ ) of particulate iron in the Mandovi estuary and low value in the nearshore water (0.65-12.7  $\text{mg l}^{-1}$ ).

### 3.2. Mn

Compared with other seasons, the Mn concentrations in the sediment were generally highest during the premonsoon period (Fig. 2b). Values showed an increase from the mouth to the freshwater upper regions as the water concentrations ranged varied from 6.2 to 102.2  $\mu\text{g l}^{-1}$  (Zingde et al., 1976). The high Mn concentrations observed for both water and sediment are related to high levels of manganese in the surrounding ore bearing landmass (Zingde et al., 1976) as the rivers flowing through the ore bearing (iron and manganese) terrain might be picking up the element (Sankaranarayanan and Reddy 1973). Zingde et al., (1976) observed a decrease in Mn concentration for water from 88.9

$\mu\text{g l}^{-1}$  at station 6 to only  $10.9 \mu\text{g l}^{-1}$  at the river mouth. Similarly sediment manganese also decreases from 0.76% upstream (St. 6) to 0.23% at the mouth of the estuary (based on the pooled values of monthly data for each seasons and stations). An important observation is that almost entire iron ore gets deposited in the upstream region and in contrast, only about 7% manganese is found in the sediments compared to the original composition of these ores as reported by Dixit et al. (1985).

### 3.3. *Co*

Generally, cobalt concentrations were the highest during the premonsoon period decreasing through to the post monsoon (Fig. 2c). No strongly elevated concentrations of Co were observed, although Co is apparently enriched above natural values. It should be noted that the choice of reference value for normalisation alters the degree of enrichment.

### 3.4. *Cu*

When the annual average for Cu in sediment was computed, a general increase from the marine to the riverine zone was seen. Sankaranarayanan and Reddy (1973) reported low concentrations of copper in water ( $2\text{-}14 \mu\text{g l}^{-1}$ ) in the Mandovi river as compared to Zuari river. There is a general trend observed that for copper (except for station 4) decreasing its concentration from the pre-monsoon to the monsoon and increasing again to the post-monsoon. During the monsoon period, when freshwater discharge is maximum, the copper level was  $74 \mu\text{g l}^{-1}$  (Sankaranarayanan and Reddy, 1973) and dissolved labile copper concentrations were also high both at the surface and in bottom waters of the Mandovi estuary in the river mouth (George et al. 1984). Higher level of sediment concentration ( $77.5 \mu\text{g g}^{-1}$ ) was observed during August. It may be mentioned here that there is no significant relation between salinity and the copper concentration for inshore and estuarine waters along the central west coast of India (Sankaranarayanan and Reddy, 1973). The values of copper concentrations in the sediment of the Mandovi estuary varied from  $11.5$  to  $77.5 \mu\text{g g}^{-1}$  and are lower or equal to those reported from various other estuarine sediments in India (Table 1).

### 3.5. Zn

As similar to Cu, there is a general trend observed that for zinc, decreasing its concentration from the pre-monsoon to the monsoon and increasing again to the post-monsoon. Zinc concentrations in the Mandovi estuarine sediments showed generally higher values than Cu. Zinc can enter the aquatic environment from a number of sources including industrial discharges, sewage effluent and runoff (Boxall et al., 2000). Zingde et al. (1976) reported that the average concentration for Zn ( $18.7 \mu\text{g l}^{-1}$ ) in estuarine waters around Goa. A gradual decrease of dissolved metals towards the Arabian Sea is observed (Zingde et al., 1976). This is particularly recognizable for Zn, which decreases from  $20.3 \mu\text{g l}^{-1}$  at station 6 to  $7.2 \mu\text{g l}^{-1}$  at the mouth (Zingde et al., 1976). The average concentrations of Zn in sediments in the mouth region are  $67.8 \mu\text{g g}^{-1}$ ,  $41.4 \mu\text{g g}^{-1}$  and  $49.0 \mu\text{g g}^{-1}$  in premonsoon, monsoon and post monsoon seasons respectively. Input of organic wastes into the estuary, which comes from municipal sewage, contributes to the Zn increase in sediments. This source also contributes to the high organic carbon content where a maximum value of 3% was observed in the mouth region (Alagarsamy, 1991).

### 3.6. Pb

In the present study lead concentrations varied from 4.5 to  $46.5 \mu\text{g g}^{-1}$ . Lead occurs in nature at an average crustal abundance of  $16 \mu\text{g g}^{-1}$ . Like soils in the terrestrial system, sediments are the primary sinks for lead in the aquatic environment. For deep ocean sediments the natural average value is about  $47 \mu\text{g g}^{-1}$  but with wide fluctuations (Craig, 1980). Lead values in bay, estuarine and other coastal sediments (marsh environments) have been much altered by man's activities. The average Pb levels in Indian river sediment is about  $14 \mu\text{g g}^{-1}$  (Dekov et al., 1999), which is lower than the world average. The average Pb in Indian river particulates are  $\sim 51 \mu\text{g g}^{-1}$  (Dekov et al., 1999) which are also lower than the world river particulates of  $150 \mu\text{g g}^{-1}$  (Martin and Meybeck, 1979). The present study showed that the variation of lead in the upstream regions and during post monsoon is small (Fig. 2f). Nolting et al., (1996) observed that the low and constant Pb concentrations indicating the minor importance of anthropogenic input from the Laptev Sea in contrast to other areas of world as anthropogenic inputs are considered to be the major source of elevated Pb concentrations in marine sediments (Nolting et al., 1999).

### 3.7. Index of geoaccumulation

Possible sediment enrichment of metals was evaluated in terms of the  $I_{geo}$  of Müller (1979). The formula used for the calculation of  $I_{geo}$  is:  $\log_2 (C_n/1.5*B_n)$ , where  $C_n$  is the measured content of element “n”, and  $B_n$  the element’s content in “average shale” (Turekian and Wedepohl, 1961). The geoaccumulation index ( $I_{geo}$ ) was originally defined by Müller (1979) for a quantitative measure of the metal pollution in aquatic sediments (Ridgway and Shimmiel, 2002) and is shown for the Mandovi sediments in the Figs. 3 (a-f). Elevated  $I_{geo}$  values identified for Fe and Mn in the same areas indicate that surface sediments are contaminated to some extent, most probably as a result of anthropogenic activities.  $I_{geo}$  values calculated for Fe (2.5) and Mn (3.4) showed higher values in the premonsoon period in the upstream region of the estuary than in the post monsoon and monsoon seasons. This trace metal enrichment is attributed to iron ore processing in the higher reaches. The sediments of the Mandovi estuary were found to be enriched in Fe and Mn according to the  $I_{geo}$  classification (Table 2). The sediment metal concentrations found in this study were of the same order of magnitude as metal concentrations found by diverse authors in sediments of Indian estuaries (Biksham and Subramanian, 1988; Ramesh et al., 1990; Subramanian et al., 1988; Ramanathan et al., 1993) except for Fe and Mn.

### 3.8. Factors controlling the distribution of trace metals in Mandovi estuary

It is well established that organic matter contents are important controlling factors in the abundance of trace metals (Rubio et al., 2000). The organic carbon content of the sediments showed that Co, Cu, Zn and Pb are significantly correlated and negatively correlated with Fe and Mn (Table 3). The statistical analysis of intermetallic relationship revealed the high degree of correlation and significant regression relation among the metals indicate the identical behaviour of metals during its transport in the estuarine environment. There are significant inter-elemental correlations (e.g., Fe-Mn, Fe-Cu, Co-Cu, Co-Zn, Cu-Zn, Cu-Pb, Zn-Pb) and inverse correlations (Mn-Zn) were observed in the estuarine sediments (Table 3). In the present study, the poor association of Mn with other metals (Co and Pb) suggests that Mn-oxide may be a only a minor host phase for these elements in the estuarine environment.

#### **4. Conclusions**

The elevated  $I_{geo}$  values identified for Fe and Mn in the Mandovi estuary indicate that the surface sediments are moderately or strongly contaminated to some extent, probably as a result of anthropogenic activities and provide a useful means of distinguishing between the natural and anthropogenic sources of metals entering the coastal zone through river inputs. It is observed that, in general, lowest metal concentrations are found during the monsoon, compared to the pre- and post-monsoon. The comparison of the metal levels in the sediments from different areas of the estuary indicated that there is a detectable anthropogenic input to the Mandovi estuary. Cu and Zn showed the influence of organic wastes from municipal sewage entering the estuary, in the river mouth region. Correlations with organic carbon have allowed to understand the distribution of metals and its association within the sediments. It is proposed that continuous monitoring and further studies in the area should be carried out in the near future to ascertain long-term effects of anthropogenic impact and to assess the effectiveness of minimising the human activity to upgrade the marine environment in the Mandovi estuary on the west coast of India as the mining activities influence the geochemical process in the estuarine systems.

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**Table 1**

Comparison of the metal levels ( $\mu\text{g g}^{-1}$  dry wt. except Fe in %) in the estuarine sediments from different areas of India (DL - Detection Limit)

Location	Fe (%)	Mn	Co	Cu	Zn	Pb	Reference
Cauvery estuary	1.76	319	64	12	26	10	Biksham and Subramanian, 1988
Ganges estuary	3.1	553	36	26	71	29	Subramanian et al., 1988
Krishna estuary	4.23	1040	47	49	31	9	Biksham and Subramanian, 1988
Godavari estuary	5.7	1070	47	82	54	11	Ramesh et al., 1990
Narmada estuary	3.14	514	29	46	50	5	Biksham and Subramanian, 1988
Tapti estuary	1.09	1300	36	126	118	5	Biksham and Subramanian, 1988
Mandovi estuary	2.2-49.7	<DL-1.61%	2.5-45.3	11.5-77.5	19.9-83.5	4.5-46.5	This study

**Table 2**

Description of sediment quality.  $I_{\text{geo}}$  classification (Müller, 1979)

$I_{\text{geo}}$	$I_{\text{geo}}$ class	Description of sediment quality
>5	6	Extremely contaminated
4-5	5	Strongly to extremely strongly contaminated
3-4	4	Strongly contaminated
2-3	3	Moderately to strongly contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated to moderately contaminated
<0	0	Uncontaminated

**Table 3**

Correlation coefficient matrix (r) for trace metals and organic carbon in surface sediments of Mandovi estuary ( $r > 0.23$ ,  $p < 0.05$ ,  $n = 69$  Bold figures are significant)

Elements	Fe	Mn	Co	Cu	Zn	Pb	TOC
Fe	1	<b>0.74</b>	0.19	<b>0.46</b>	-0.16	0.02	<b>-0.33</b>
Mn		1	0.23	<b>0.38</b>	<b>-0.48</b>	-0.17	<b>-0.46</b>
Co			1	<b>0.52</b>	<b>0.59</b>	-0.22	<b>0.27</b>
Cu				1	0.16	0.20	<b>0.41</b>
Zn					1	0.12	<b>0.62</b>
Pb						1	<b>0.42</b>

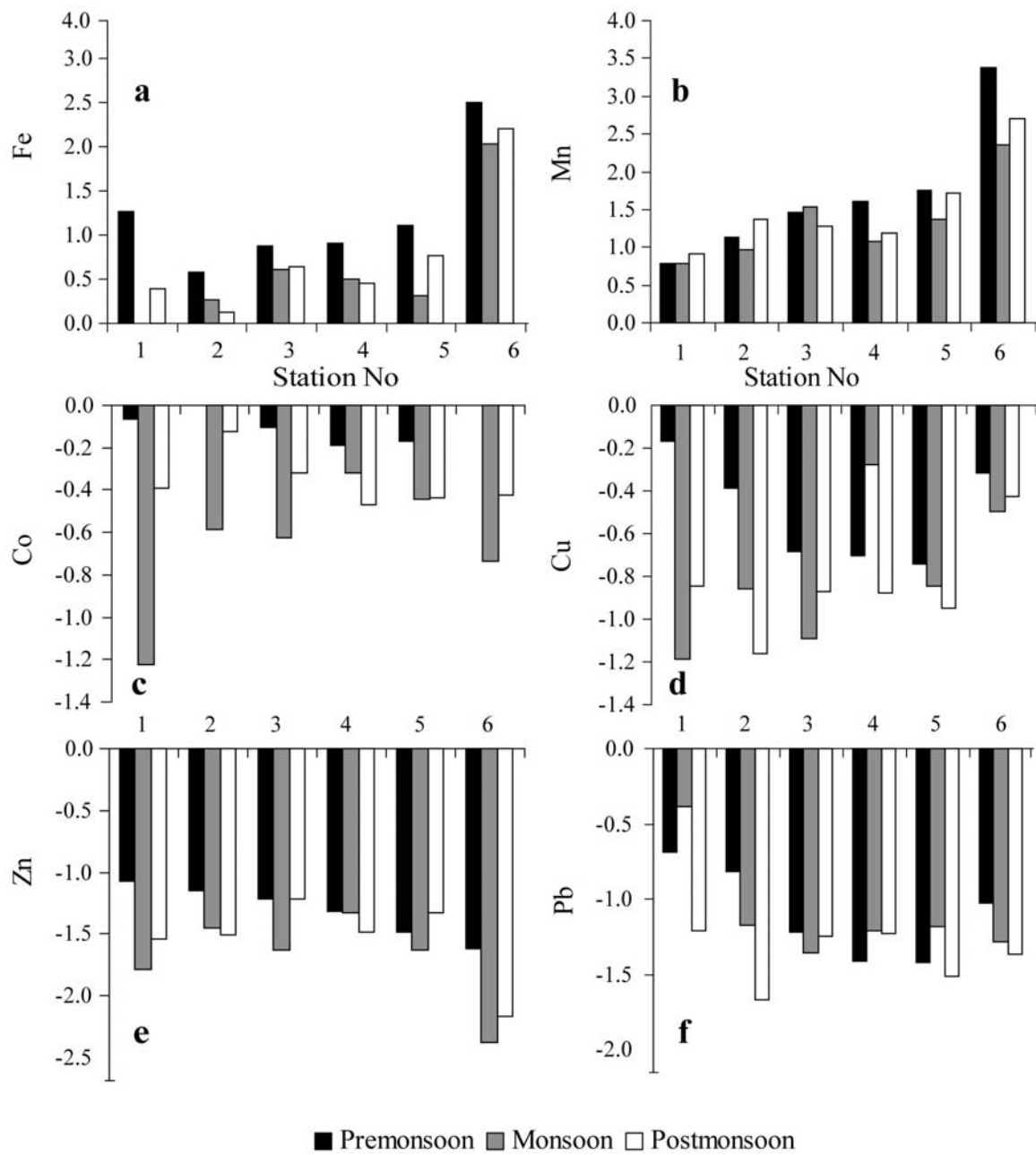


Fig. 2. Seasonal variation of Fe (a), Mn (b), Co (c), Cu (d), Zn (e) and Pb (f) in the Mandovi estuarine sediment.

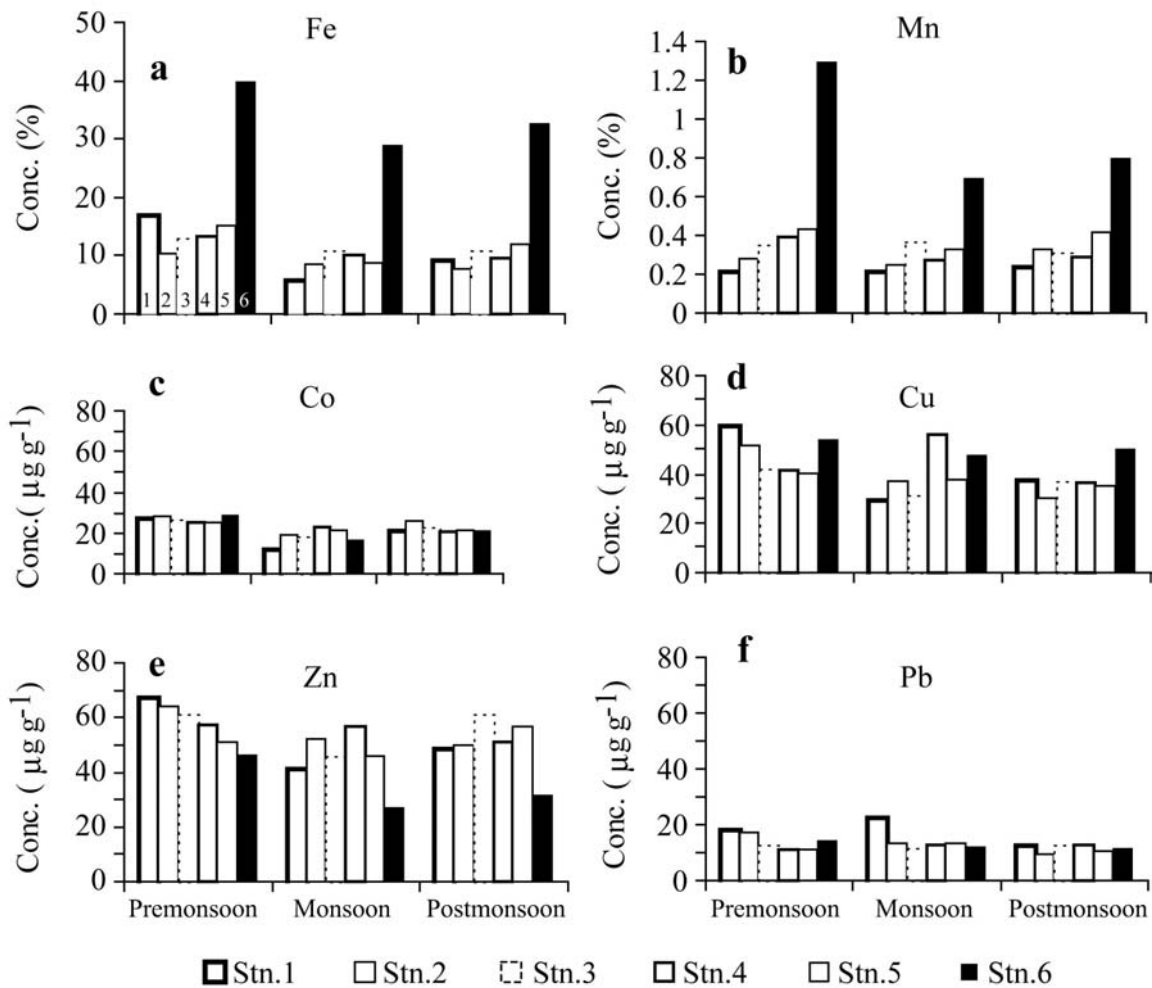


Fig. 3. Plots showing (a-f)  $I_{\text{geo}}$  seasonal values for each metal.