

Temporal and spatial variability of trace metals in suspended matter of the Mandovi estuary, central west coast of India

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Abstract Studies on the suspended particulate matter (SPM) in the Mandovi estuary, western India indicate that during the monsoon and pre-monsoon, the SPM increases, and the major and trace metals decrease from stations in the upstream to downstream of the estuary. SPM is consistently low at all stations during the post-monsoon. Trace metals (Cu, Ni, Zn, Cr, Pb) show strong inter-relationships. They correlate well with Fe and Mn only during the monsoon. The concentrations of Cr, Cu and Pb are high during the post-monsoon. Enrichment factors and I_{geo} values of metals indicate that Mn shows significant to strong pollution in all seasons, while Cr, Ni and Zn during monsoon and Cr during the post-monsoon show moderate pollution. SPM is controlled by the turbidity maximum, while major and trace metals are governed seasonally by a combination of river discharge, resuspension, spillage of Fe-Mn particulates, and anthropogenic contamination. Incursion of saline waters deep into the river channel during the dry season facilitates aggregation and settling of particulate-borne pollutants close to the discharge area, thereby keeping the estuarine waters free from major contamination.

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1 Introduction

The concentration and composition of the suspended particulate matter (SPM) in estuaries are controlled by seasonal changes in inputs from river-end and marine-end members, physico-chemical processes occurring at the mixing zone of freshwater and salt water and biological productivity (Boyden et al. 1979; Kennedy 1984; Balls 1990; Turner et al. 1991; Burton et al. 1994; Balls et al. 1997; Paucot and Wollast 1997; Zwolsman and van Eck 1999; Nolting et al. 1999; Hatje et al. 2001; Qiao et al. 2007; Kessarkar et al. 2009). Flocculation and coagulation of materials (Benoit et al. 1994), adsorption and desorption of metals in low salinity, high turbidity zone (Windom et al. 1988), resuspension of bottom sediments (Feely et al. 1986) and mobilization of metals from reducing sediments to the overlying water column (Liu et al. 1998) would modify the compositions of SPM. SPM contains inorganic and organic particulates bound by major and trace elements. Major elements usually form amorphous and crystalline solids and are derived largely from riverine inputs. Trace metals, on the other hand, can be derived from the weathering of rocks and/or anthropogenic sources derived from mining, industrial and urban development and other human practices near river and estuaries (Zhang et al. 1990; Zwolsman and van Eck 1999; Sutherland 2000; Zhang and Liu 2002; Zhou et al. 2003; Marmolejo-Rodriguez et al. 2007; Qiao et al. 2007). Atmospheric input and grain size also influence the distribution of trace metals (Windom et al. 1989; Zhou et al. 2003). As physical, chemical and biogeochemical processes are key factors in controlling the transport and fate of trace metals in estuaries, it is important to understand the mechanisms of their distribution in space and time to ascertain the health of the estuaries. Studies on the seasonal variations in particulate trace metal concentrations in Indian estuaries have been somewhat neglected. The purpose of this paper is to investigate seasonal changes in the concentration and composition of SPM in the Mandovi estuary, Goa, India and to identify the processes that control trace metal distribution. Previous studies in the Mandovi estuary have investigated the particulate Fe (Kamat and Sankaranarayanan 1975) and Al (Upadhyay and Sengupta 1995), As, Cu, Zn and Mn in marine flora and fauna of the estuarine waters (Zingde et al. 1976), organic carbon, trace metals (Alagarsamy 1991; 2006) and nutrients (Pratihary et al. 2009) in bottom sediments.

1.1 Study area

The Mandovi River of Goa, central west coast of India originates in the Western Ghats (mountain ranges), drains through the narrow coastal plains and joins the Arabian Sea with a wide bay (Aguada Bay) at its mouth (Fig. 1). Rainfall over the river basin is highly seasonal. The annual rainfall during the southwest monsoon (June – September) varies from an average of 286 cm at Panaji on the coast to an average of 661 cm at Gavali on the slopes of the mountains (Shetye et al. 2007). The rainfall is

negligible during the dry season, i.e., the remaining 8 months (October - May). The annual run-off measured in the Mandovi basin at Ganjem, located 50 km from the mouth, is 3400 M cum (million cubic metres), the standard deviation about the mean being 648 M cum (Shetye et al. 2007). The Mandovi estuary is mesotidal. The tidal ranges are 2.3 m and 1.5 m during the spring and neap tides, respectively (Manoj and Unnikrishnan 2009). The currents in the estuary are tide-dominated, and saline waters occur several kilometers upstream from the river mouth during the dry season (Shetye et al. 1995). Thus, water within the channels of the estuary change from mainly freshwater river flow during the monsoon to highly saline water from marine sources for several kilometers from the mouth during dry season. Fishing activity comes to a stand still during the monsoon and all the mechanized fishing boats are stationed at the lower estuary. About two-thirds of the mining activities for Fe-Mn ores in Goa are located in the Mandovi basin (Pathak et al. 1988). There are several points along the estuary channel, where Fe-Mn ore deposits from local mines are pulverized and stored on the shore (Fig. 2A), in order to load the deposits onto barges (Fig. 2B). Export of Fe-Mn ore through the river is active from October to May. A ship-building unit located on the shore of the lower estuary (Fig. 2C) is a potential contributor of metals. The municipal city, Panaji, is on the shores of the lower estuary. The Mandovi receives 5.21×10^6 m³ of sewage and their effluents per year (Qasim and Sengupta 1981). Sand mining is an important activity in the upstream channel of the estuary (Fig. 2D).

2 Materials and methods

The suspended particulate matter (SPM) from surface waters and bottom sediments collected in the mid-channel of the Mandovi estuary at fixed stations (Fig. 1) during June 2007–May 2008 were used for the present study. Five liters of surface water were collected every alternative day at one station from June to September (monsoon) 2007. This station (no. 2) is referred to here as the ‘regular station’ (Fig. 1). Surface water and bottom sediments were also collected fortnightly at five stations along the main channel of the estuary (referred here as ‘transect stations’) during June–September 2007, using a mechanized boat. From October 2007 to May 2008, two more stations were added towards upstream of the estuary. Salinity of the surface waters was measured invariably at all stations using a CTD profiler. Surface waters were filtered through a 0.45 µm Millipore filter paper. The SPM retained on the filter papers was dried and weighed and, expressed as milligram per liter.

Ninety filters containing SPM from the regular and transect stations of the estuary collected during different months were selected for major (Al, Fe and Mn) and trace (Cu, Ni, Zn, Cr, Pb and Co) metal determination. The SPM retained on the filter papers was removed carefully, re-weighed and transferred to teflon beakers. The samples were treated with a mixture of HF+HNO₃+HClO₄ solution,

kept overnight and then dried on a hot plate. This procedure was repeated till the sample in the beakers was completely digested. The residue was dissolved with 20 ml of 1:1 HNO₃ solution. Subsequently, 5 ml of 1 ppm Rh solution was added as an internal standard and made up the final volume (Govindaraju 1994). The aliquots were analyzed for trace metals with a Perkin Elmer SCIEX® (Model 6100ELAN DRC II) Inductively-coupled plasma mass spectrometer (ICP-MS) at the National Geophysical Research Institute, Hyderabad, India. Major elements were analyzed using ICP-AES at the National Institute of Oceanography, Goa. MAG1 (Marine mud) was used as an internal standard to check the reliability of the analysis. The reproducibility of the results was found to be better than 5% and 10% for major elements and trace metals, respectively.

Thirty eight sediment samples were selected along the transect stations of the estuary. The <2 µm fraction of the sediment was separated using Stoke's settling velocity principle, dried and powdered. Following the fore-mentioned procedure, the powders were digested and analyzed for their major and trace metal concentrations.

Statistical treatments were carried out for the metals. The test of significance and variability of major and trace metals are given in tables. For transect stations we considered seasonal variations in the mean concentrations of metals, i.e., the averages for four months, June to September (monsoon), October to January (post-monsoon) and February to May (pre-monsoon) at each station. The enrichment factor (EF) of metals (Taylor and McLennan 1995) with reference to the upper continental crust (UCC) was used to understand the behavior of metals and is defined as

$$EF = [X]/[Al]_{sam} / [X]/[Al]_{upper\ crust},$$

where [X] represents the concentration of the element X, and [Al] the Al concentration. The defined categories for the degree of pollution based on the EF of metals (Sutherland 2000) are as follows: EF value ~2 = no or minimal pollution, 2–5 = moderate pollution, 5–20 = significant pollution, 20–40 = very strong pollution and >40 = extreme pollution.

The Index of geoaccumulation (I_{geo}) was also used to measure the degree of pollution (Muller 1969) and defined as

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

where C_n is concentration of element n, B_n is the reference material (UCC) concentration of element n. The factor 1.5 in equation is used because of the possible variations due to lithogenic effects (Muller

1969; Loska et al. 2004). The defined categories of I_{geo} (cf. Förstner et al. 1990) are as follows: I_{geo} value ~ 0 = practically unpolluted; 0–1 = unpolluted to moderately polluted; 1–2 = moderately polluted; 2–3 = moderately to strongly polluted; 3–4 = strongly polluted; 4–5 = strong to very strongly polluted; and >5 = very strongly polluted.

3 Results

3.1. Characteristics of SPM at the regular station

The concentrations of SPM are ~ 5 mg/l during May (pre-monsoon month). SPM concentrations start increasing to ≥ 20 mg/l in June and July and to 8–20 mg/l in August and September. The concentrations of Fe, Mn, Al and Co are higher than those of the suspended particulate matter of the world rivers (SPMWR) (Viers et al. 2008) and Upper Continental Crust (UCC) (see Fig. 3). The concentrations of Cu, Ni, Zn, Cr and Pb are lower than those of the SPMWR in June and July, but higher during August and September (Fig. 3). The enrichment factors of metals reveal Mn and Cr are significant to moderately enriched, and Fe, Ni, Zn and Co are moderately enriched. There is no correlation between SPM and its metal concentrations (Table 1). Based on the correlation coefficient, we found that a strong inter-element relationship exists among metals of group 1 (Cu, Ni, Zn, Cr and Pb) and group 2 (Fe, Mn and Co), but moderate to low relationship between the metals of two groups (Table 1). Temporal variability of metals in group 1 (49 to 82%) is higher than those in group 2 (41 to 19%).

3.2 Characteristics of SPM at transect stations

The mean SPM concentrations are low at stations in the upstream and increase gradually towards downstream of the estuary, both during the monsoon and pre-monsoon. The SPM concentrations are consistently low at all stations during the post-monsoon (Fig. 4). The mean concentrations of metals are inverse to that of SPM and are high at stations in the upstream and decrease towards downstream, both during the monsoon and pre-monsoon (Fig. 4; Table 2). Metals such as Mn, Cr, Cu, Ni and Zn show progressive / sharp decrease, while Fe, Co and Pb show marginal decrease towards stations seaward of the estuary during the monsoon. A strong inter-element relationship and positive correlation exist between major and trace metals (Table 3). During the post-monsoon, the concentrations of Fe and Cr are high at stations in the downstream, and Cr, Pb and Cu at all stations are higher than those during the monsoon and pre-monsoon (Fig. 4). Al correlates well with Fe, Ni and Zn and, Pb with Cu in post-monsoon. Metal concentrations, except Mn, are low at all stations in pre-monsoon. A strong correlation exists among Fe, Mn and Co and, Zn, Ni, Cr, Cu and Pb, but not between the two groups. Organic carbon (OC) content varies from 4 to 6% and shows weak to moderate correlation with Al, Fe,

Mn, Co, Zn and Pb during the monsoon and good correlation with Al and Cr during the post-monsoon. OC shows positive correlation with Mn, Cr, Cu, Ni and Zn during the pre-monsoon. Statistical analysis (Analyses of Variance- ANOVA) suggests that the Cr, Ni, Zn and Pb are more significant ($P < 0.001$) seasonally and Mn spatially. Co is significant ($P < 0.05$), both spatially and seasonally, while Fe is spatially significant ($P < 0.05$).

3.3 Enrichment factors and I_{geo} values of metals in SPM

The mean enrichment factor (EF_m) of Mn ranges from 7 to 50 (Fig. 4) and increases from monsoon to post-monsoon to pre-monsoon, with extreme values in the upstream. During the monsoon, the EF_m of Fe (2.5 to 3.5) and Ni, Cr and Zn (3.5-11) are higher than those of Cu, Co and Pb (~2). During the post-monsoon, the EF_m of Cr (12-31), Cu (3-8) and Pb (4-10) are higher than those of Ni, Zn and Fe (3-8). During the pre-monsoon, except at station 7, the EF_m of Fe and Co range between 2 and 5, while that of Cu, Ni, Zn, Cr and Pb are < 2 .

I_{geo} values, calculated with reference to Upper Continental Crust (Fig. 5A), are in the range 2-3 for Mn, Zn and Cr during monsoon, Mn and Cr during the post-monsoon and Mn during the pre-monsoon. I_{geo} values are in the range 1-2 for Fe and Ni during the monsoon, Ni and Pb during post-monsoon, and Cr during pre-monsoon. I_{geo} values are least (0-1) for Fe, Cu, Zn and Co during the post-monsoon and for Fe, Cu, Ni, Co and Pb during pre-monsoon. Using Mag 1, I_{geo} values are highest (2-3) only for Mn in all seasons, followed by values of 1-2 for Zn and Cr during monsoon and Cr and Pb during the post-monsoon (Fig. 5B).

3.4 Al-normalized ratios of metals (M/Al) in SPM and bottom sediments.

Fig. 6 shows the mean M/Al ratios in SPM and salinity along transect stations. The salinity of the surface water increases seaward of the estuary and varies from 0 to 15, 3 to 31 and 9 to 34 (Fig. 6) during the monsoon, post-monsoon and pre-monsoon, respectively. The Fe/Al and Mn/Al values decrease gradually downstream, both during monsoon and pre-monsoon. The M/Al values of Zn and Cr during monsoon and, Zn, Cu, Ni, Cr and Pb during pre-monsoon are high at the upstream station and decrease sharply at salinities > 1 in monsoon and at salinities > 10 during pre-monsoon. Peaks of high Fe/Al and Cr/Al coincide with high salinities at the downstream of the estuary during post-monsoon. The M/Al of Cu, Ni, Pb and Co exhibit similar values with increasing salinity (Fig. 6).

The mean M/Al of metals in suspended and bottom sediments at stations in the upstream and downstream of the estuary during a year are shown in Fig. 7. The M/Al values of Fe, Mn, Co, Zn, Ni, Cr

and Pb in sediments are lower, or similar to that in SPM. The M/Al of Mn, Fe and Co in SPM are relatively low during June-September, but increase sharply and maintain high values during October-May at the upstream station (Fig. 7). In the downstream station the Mn/Al values in SPM increase gradually from June to October and maintain high values during November-May. The Fe/Al and Co/Al values are also high in October-January, but decrease during February-May (Fig. 7). The Zn/Al and Ni/Al of SPM show an overall decrease from June 2007 to May 2008 at the upstream station. While in the downstream station these ratios increase gradually from June to October, decrease sharply in November and maintain low values from November to May. The M/Al of Cr, Cu and Pb in SPM increase marginally from June to September, reach highest values during October - January and then decrease sharply to low values during February - May, both in upstream and downstream stations.

4 Discussion

4.1 Controls on the characteristics of SPM at the regular station

Temporal variations at a station are helpful to understand the sources and processes controlling the compositions of SPM (Gaillardet et al. 2005). The concentrations of Al, Fe and Mn throughout the monsoon and trace metals in August and September are higher than those in the suspended particulate matter of World Rivers (Fig. 3). Trace metals exhibiting poor correlation with Al, and their higher variability compared to major metals suggest different sources of metals: First, SPM contributed by the river run-off comes from chemical weathering of tropical soils, including coastal laterites and Fe-Mn deposits in the river basin (Gokul et al. 1985). Furthermore, washing and leaching of these ore deposits stored along the shore (Fig. 2A) during heavy rainfall contribute abundant particulate Fe and Mn to the estuary. Second, Regular Station is located within the zone of maximum turbidity (see below). Resuspension of bottom sediment in the estuary by turbulence results in variations in SPM concentrations. The coincidence of high SPM concentrations with low trace metals during June-July (see Fig. 3) suggests that the trace metal concentrations are diluted by the SPM from the river discharge and resuspension. Nolting et al. (1999) suggested that sediment resuspension is a factor controlling the composition of SPM. Third, high inter-elemental relationship among trace metals (Table 1) suggests a common source. Except for Zn and Co, all the trace metals show weak correlation with major metals. As high variability of trace metals is an indicator of anthropogenic source (Viers et al. 2008) we hypothesize that these metals are partly contributed by anthropogenic sources (see Section 4.3) Therefore, the concentrations and composition of SPM are governed by river run-off, Fe-Mn ore deposits, resuspension of bottom sediments and anthropogenic sources.

4.2 Spatial and temporal variations of SPM and metals at transect stations

4.2.1 During the monsoon

The Mandovi River estuary receives high run-off only during the monsoon. In general, high SPM concentrations should be expected at stations in the upstream with a gradual decrease towards downstream of the estuary as salinity increases. The concentrations of SPM, however, increase and metal concentrations decrease from stations in the upstream to downstream, both during the monsoon and pre-monsoon (Fig. 4). Two processes appear to control SPM and metal concentrations: (a) the increase of SPM towards downstream can be attributed to the development of estuarine turbidity maximum (ETM) that results in resuspension of bottom sediments (Kessarkar et al. 2010). (b) The decrease in metal concentrations towards lower estuary indicates a change in the nature of suspended particles with increasing SPM concentrations. The SPM in the zone of turbidity maximum contains resuspended sediments that tend to be coarse-grained (such as quartz) and non-cohesive, with low-surface area and little sorptive capacity and thus are depleted in trace metals (Turner 1996; Liu et al. 1998; and Hatje et al. 2001, Hatje 2003; Zhou et al. 2003). Benoit and Rozan (1999), Zhou et al. (2003) and Wen et al. (2008) reported inverse relationship between SPM and metals in Texas, Conwy and Trinity River estuaries and suggested that resuspension and particle size controlled the composition of SPM. Therefore, the low metal concentrations in SPM toward lower estuary are attributable to the mixing of fluvial suspended particles with resuspended sediments.

High concentrations of Fe, Mn, Ni, Zn and Cr at stations in the upstream and their decrease towards downstream of the estuary (Fig. 4; Table 2) indicate that the river is the major source for these metals. Vijith et al. (2009) reported that the total run-off in the Mandovi River during the monsoon is large, well over an order of magnitude larger than the estuarine volume. During heavy spells of high rainfall saline waters are completely flushed out of the estuary. In other words, under heavy discharge conditions the stations in the upstream receive SPM and metals not only from the weathering of rocks but also resuspended material from the river channel and washed material from the banks of the river, where Fe-Mn ore deposits are stored. The strong inter-relationships of trace metals and good correlation between trace and major metals (Table 3) indicates that the high adsorptive capacities of clays (dominated by kaolinite, gibbsite and goethite - Kessarkar et al. 2010) and low degree of crystallinity of Fe, Mn-colloids and hydroxides (Chao 1984; Waren and Zimmerman 1993; Zhou et al. 2003) may have acted as good carriers for trace metals. The decrease in trace metal concentrations with increasing salinity (Fig. 6) simply reflects the influence of salinity in coagulation and deposition

and, dilution from the resuspended material. Zwolsman and van Eck (1993) showed that low concentrations of trace metals are primarily due to mixing of fluvial and marine particulates.

The low or identical concentrations of metals in sediments than in SPM (Fig. 7) may be due to the texture of the sediments. Sediments were collected within, or close to the main navigational channel of the river, wherein turbidity maximum prevails, both during the monsoon and pre-monsoon. The movement of barges carrying ores and mechanized fishing boats along the main channel may induce continuous disturbance of sea bed. Sand mining is also an important activity in the upstream of the river. As a consequence, resuspended, fine-grained clays rich in trace metals may have transported further and settled away from the channel. It is also likely that some trace metals may have been desorbed from clays because of continuous turbulence. Thus the sediments in the channel show low concentrations of trace metals. These sediments admittedly are not true representations of the estuarine sediments, and further close grid sampling needs to be carried out across the estuary to better understand the trace metals distribution in sediments.

4.2.2 During the post-monsoon

Low SPM at all stations (Fig. 4) during post-monsoon is in accord with the negligible river discharge. Loading of Fe-Mn ore deposits onto the barges at several shore stations along the estuary (Fig. 2B) and transferring the same onto large ships in the offshore for export is an important activity which begins from the month of October. Therefore, the spillage of Fe and Mn particulates from barges during transportation should be expected. The sharp increase in Fe/Al and Mn/Al in SPM from October, both at upstream and downstream stations (Fig. 7) is indeed a reflection of this activity. Similar distribution of Mn and Co (Fig. 7) during October to May may suggest their common source and, co-precipitation of Co with Mn (cf. Zwolsman et al. 1999). High values of Cr, Cu and Pb occur at stations in the downstream of the estuary (Figs. 4 and 7). Similar distribution of Cr and Fe (Fig. 6) and moderate correlation between the two (Table 3) may partly be due to the association of Cr with Fe-bearing minerals (cf. Nriagu 1988; Hatje et al. 2001). Pb shows negative correlation with Fe, Mn and OC during post-monsoon (Table 3). Other sources for Pb could be atmospheric deposition, industrial activity, waste water disposal and biogenic particles (Ip et al. 2007). Human-induced activities within the estuary may have contributed Pb (see Section 4.3). Primary productivity increases during this season. The positive correlation of Cu and OC (Table 3) suggests organic ligands released by algae during phytoplankton bloom at high salinity may have contributed Cu. The negative correlation of Cr, Cu and Pb with Al suggests that the trace metals are not solely detrital. Moreover, higher concentrations of Cu and Pb are found at mid-estuary (station 5) rather than at station (7) in the upstream (Fig. 4). Thus the

relatively high concentrations of Cr, Cu and Pb cannot be explained solely by low SPM or inorganic particles that serve as adsorptive surfaces. Therefore, the change in major and heavy metal concentrations from monsoon to post-monsoon is attributable to the increase in industrial activity (Fe-Mn ore transportation), contaminants from industrial effluent discharge and primary production.

4.2.3 During the pre-monsoon

Saline waters extend further into the river channel and salinity ranges between 9‰ and 34‰ (Fig. 6). Productivity of the estuarine waters increases from monsoon to post-monsoon to pre-monsoon (Pratihary et al., 2010). Despite negligible river discharge the concentrations of SPM increase while trace metal concentrations decrease at stations from the upstream to downstream (Fig. 4). This has been explained by the occurrence of estuarine turbidity maximum in the lower estuary (Kessarkar et al. 2010). Low SPM and, higher M/Al values of Zn, Cr, Cu, Ni and Pb in pre-monsoon than that of monsoon at upstream station (Fig. 6) and their strong inter-element relationship (Table 3) may suggest anthropogenic or industrial contamination. Very low concentrations of trace metals at the downstream station (Fig. 7) may be due to the influence of salinity ingress and precipitation close to the discharge point at the upstream station.

4.3 Contamination and pollution of different metals in SPM

Significant to extreme pollution of Mn in different seasons (see Figs. 4 and 5) is directly related to the Fe-Mn ore deposits and human-induced activity in handling and transportation of these ores through the estuary. The EF_m of metals show that Fe is moderately polluted and Mn is significantly polluted, even though the concentrations of Fe are much higher than that of Mn. This may be due to the reactivity of Fe and Mn to oxidation, wherein Fe is oxidized and precipitated much faster than Mn (see Zhou et al. 2003). Sholkovitz (1978) reported that Fe is rapidly removed in the early stages of estuarine mixing. Cr, Ni and Zn show moderate to strong pollution during the monsoon. These metals increase gradually from June to September in the lower estuary (Fig. 7). Numerous fishing boats are stationed in the estuary during the monsoon. Repair works, chipping and welding works and anti-fouling painting works are being carried out at the ship-building unit (Fig. 2C). Cr, Cu, Pb and Zn have been used in anti-fouling paints, and Ni and Zn in welding materials, galvanizing and metal plating. Tire wear and grease also contain some Ni and Zn (Sutherland 2000; Buggy and Tobin 2008). Therefore the increasing concentrations of trace metals during August - October (Fig. 7) can be attributed to the anthropogenic contamination. Cr is strongly polluted, whereas Cu, Zn, Co and Pb show uncontaminated to moderate levels of contamination during post-monsoon. As river discharge is

negligible in this season, trace metals from ore particulates, industrial discharge, organic wastes and effluents from municipal sewage become important sources for their contamination. During the pre-monsoon all metals, except Mn, are moderately contaminated. Saline waters extend until 40 km from the mouth and lower estuary acts as an extension of sea during pre-monsoon (Shetye et al. 2007). The increasing salinity of estuarine waters affects flocculation and coagulation of particulate material in suspension and favours quick settling of pollutant-borne particulates at the point close to the source of discharge in the upstream. This in turn keeps the estuary free from major contaminants and favouring marine life, thanks to the salinity egress during dry seasons.

5 Summary and conclusions

Seasonal variations in the concentration and composition of suspended matter and sediments in the Mandovi estuary, Goa were investigated. At the regular station high SPM coincides with low major and trace metals in June and July and vice versa in August and September. At transect stations, the concentrations of SPM increase, and major and trace metals decrease from stations in the upstream to downstream of the estuary during the monsoon and pre-monsoon. The SPM concentrations remain consistently low, with significant increase in Fe, Mn and Co at all stations during the post-monsoon. A strong inter-relationship exists among trace metals, which also correlate with Fe and Mn only during the monsoon. Mn is the most important pollutant in all seasons. Cr, Ni and Zn in the monsoon and Cr in post-monsoon exhibit moderate pollution. SPM distribution is largely controlled by the estuarine turbidity maximum. Whereas the controls on the distributions of major and trace metals are seasonal and influenced by river discharge, resuspension of bottom sediments, spillage of Fe-Mn particulates and anthropogenic contamination. The low trace metal concentrations despite heavy industrial discharge and sewage waste disposal during dry seasons is attributed to the incursion of saline waters deep into the river channel, which facilitate aggregation of particulates and settling of pollutant-borne particulates close to the discharge points, thereby allowing a large part of the estuary to be free from major contamination.

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Figure captions

Fig. 1. Location of stations in the Mandovi estuary, central west coast of India.

Fig. 2. Photographs showing heaps of pulverized Fe-Mn ores on the shores of the estuary (A), loading of Fe-Mn ores onto barges (B), Ship-building unit at a point in the lower estuary (C), and sand mining in the river channel at the upstream station (D).

Fig. 3. Variations in the concentrations of SPM, major elements and trace metals on different dates at the regular station. Solid horizontal line on each graph represents the value of the metal in suspended matter of the World Rivers (SPMWR). Dashed horizontal line is the concentration value of the metal in the upper continental crust (UCC). The mean value of Fe for the SPMWR (5.8%) and UCC (3.5%) could not be shown on Fe graph.

Fig. 4. Variations in the mean concentrations of SPM, major and trace metals (black histograms) and EF_m of metals (red histograms) at transect stations. The defined categories of pollution (cf. Sutherland 2000) are also shown. U.Es – upper estuary, L.Es – lower estuary.

Fig. 5. The index of geoaccumulation (I_{geo}) values of major and trace metals during the monsoon, post-monsoon and pre-monsoon with respect to (A) upper continental crust (UCC), and (B) Marine Mud (Mag1). The defined categories of pollution (cf. Förstner et al. 1990) are also shown.

Fig. 6. Seasonal distribution of the mean M/Al ratios of major and trace metals along transect stations. Mean salinity at each station is also given. U.Es – upper estuary, L.Es – lower estuary.

Fig. 7. (A) Monthly variations in the M/Al ratios of major and trace metals in suspended particulate matter (SPM) and bottom sediment (SED) at station in the upstream (mean value at stations 4 and 5) and downstream (mean value at stations 1 and 2) of the estuary.

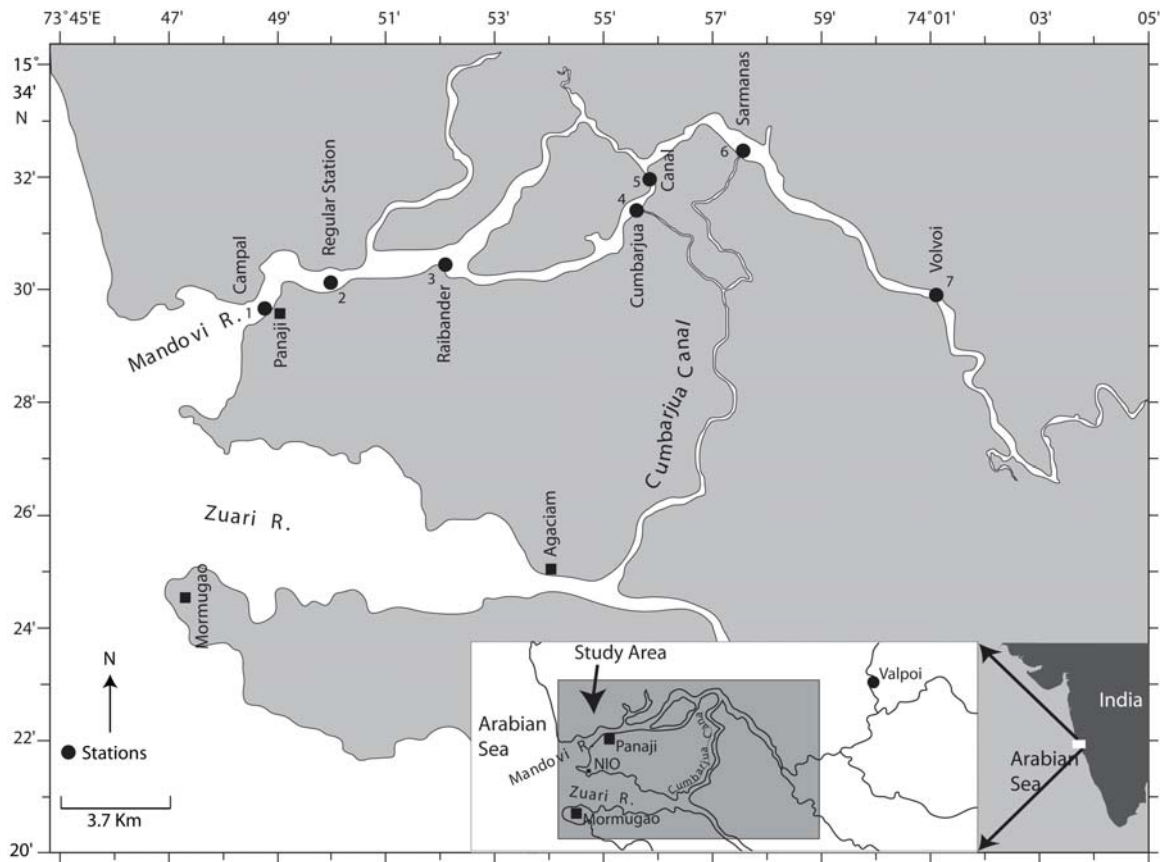


Fig. 1

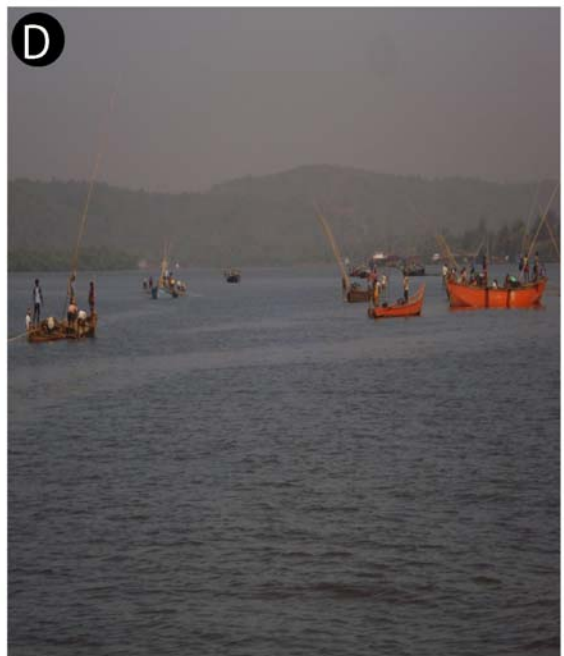
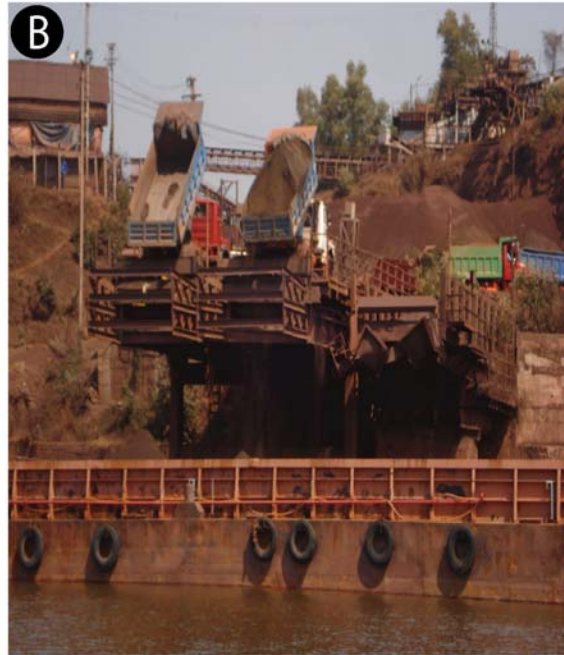


Figure 2

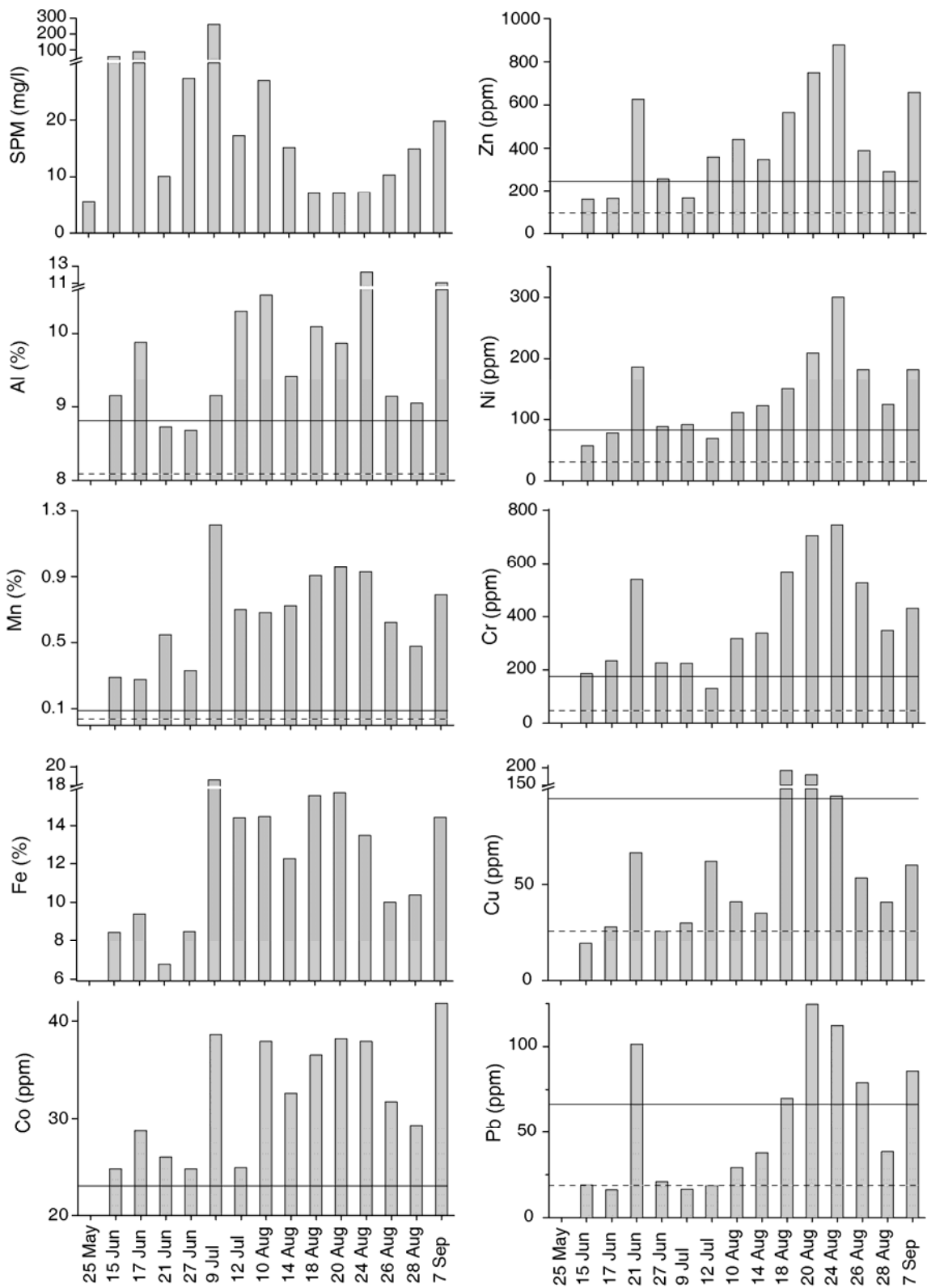


Figure 3

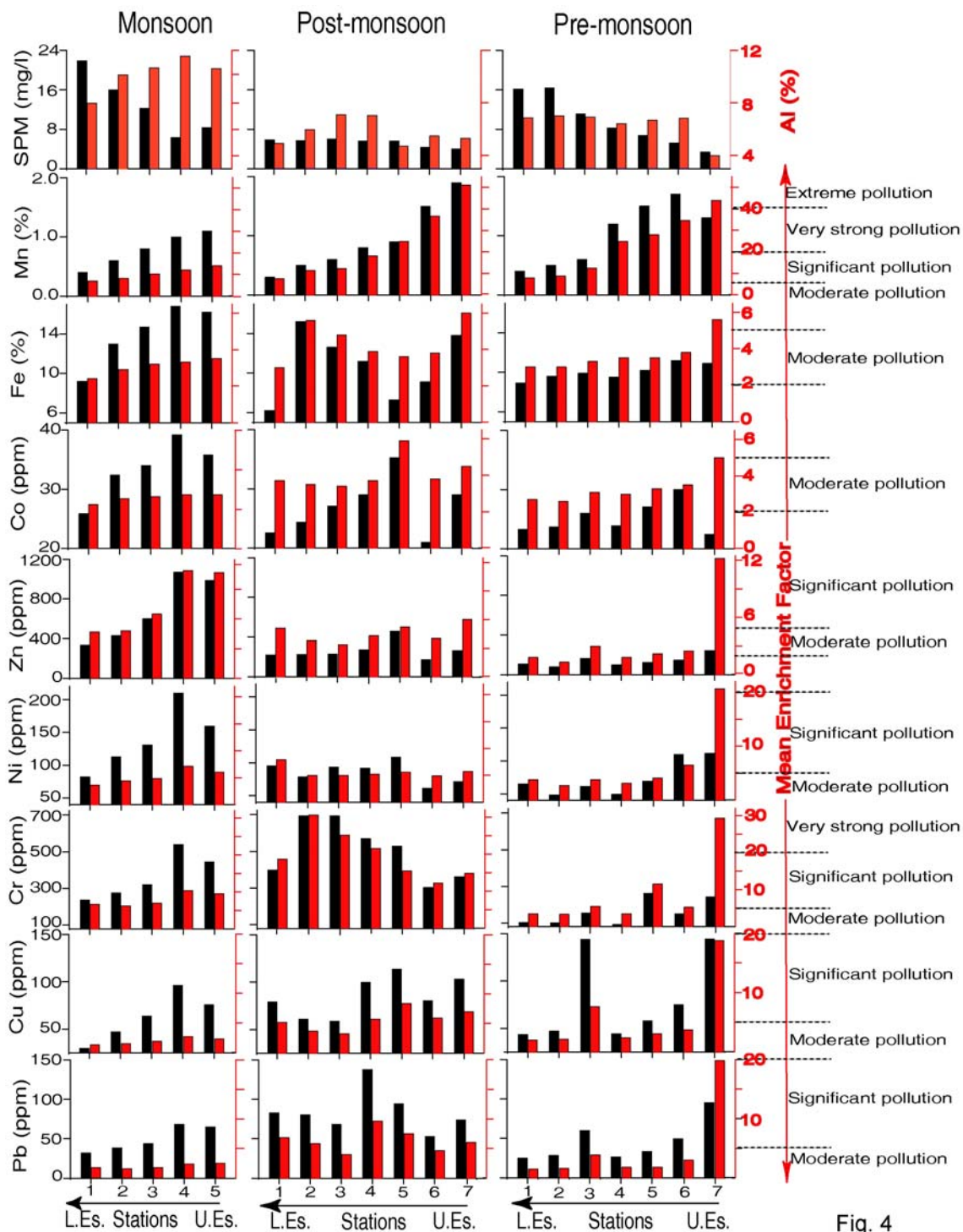


Fig. 4

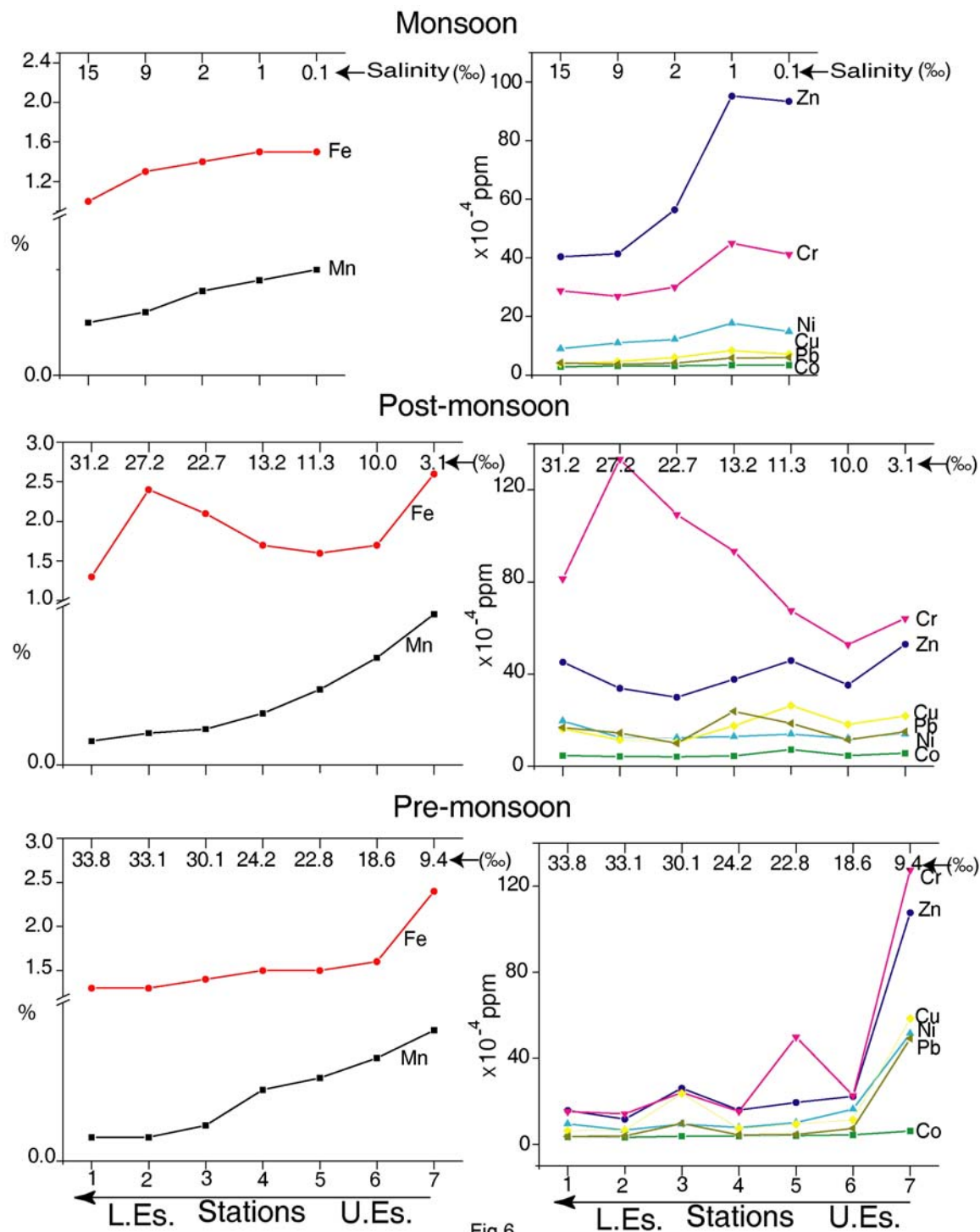


Fig.6

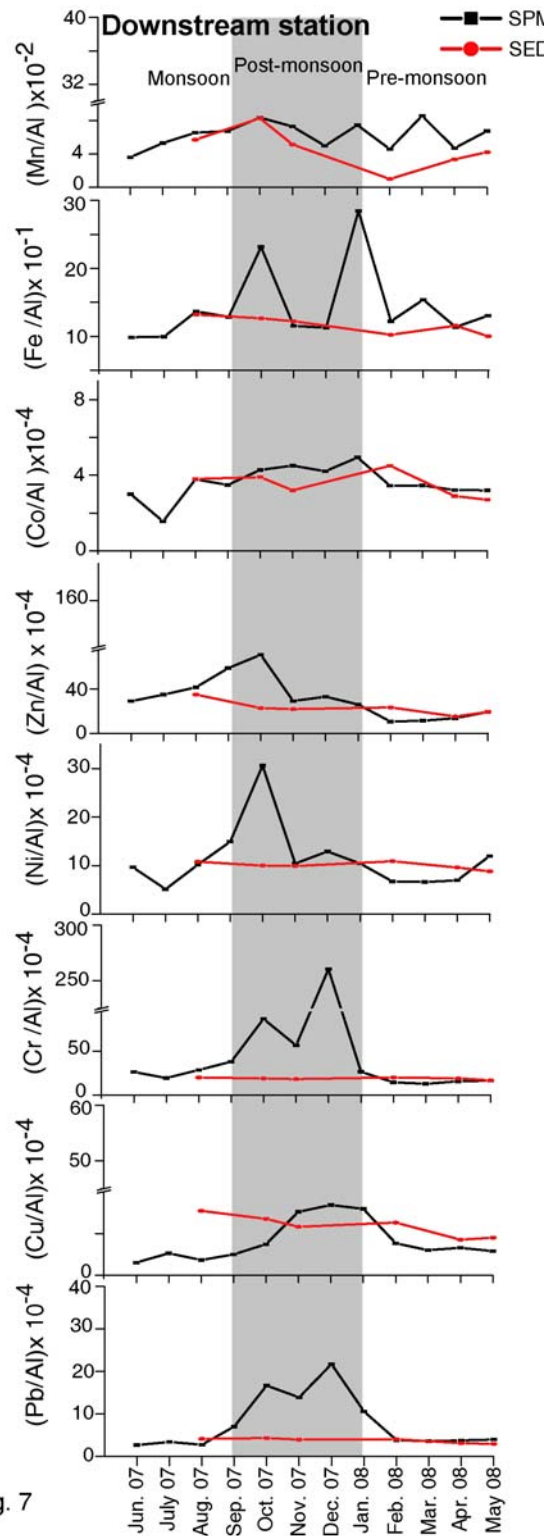
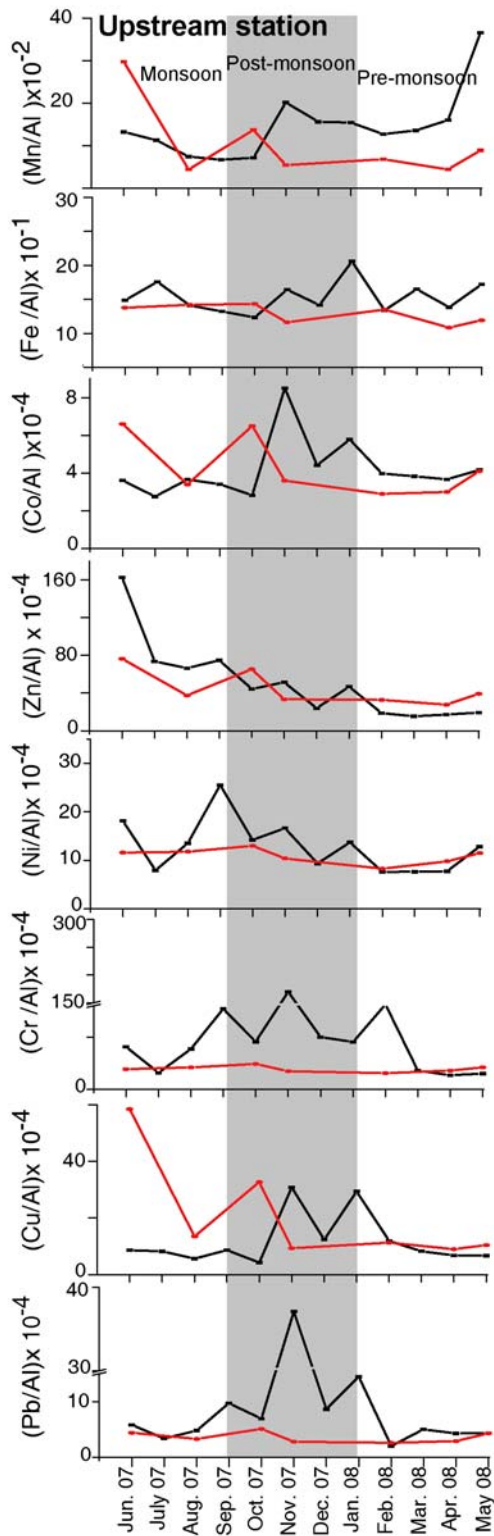


Fig. 7

Table 1: Correlation coefficient matrix for selected elements at the regular station. Correlations <-0.51 or $>+0.51$ are statistically significant at $\alpha \leq 0.05^*$; <-0.64 or $>+0.64$ are at $\alpha \leq 0.01^{**}$ and <-0.76 or > 0.76 are at $\alpha \leq 0.001^{***}$. Number of samples=14.

Elements	SPM#	Al	Mn	Fe	Co	Zn	Ni	Cr	Cu	Pb
SPM	1									
Al	-0.22	1								
Mn	0.33	0.40	1							
Fe	0.37	0.46	0.88 ^{***}	1						
Co	0.16	0.58 [*]	0.77 ^{***}	0.76 ^{***}	1					
Zn	-0.52	0.64 ^{**}	0.77 ^{***}	0.25	0.53 [*]	1				
Ni	-0.39	0.56 [*]	0.45	0.14	0.53 [*]	0.90 ^{***}	1			
Cr	-0.43	0.41	0.44	0.14	0.51 [*]	0.88 ^{***}	0.94 ^{***}	1		
Cu	-0.35	0.32	0.51 [*]	0.43	0.43	0.68 ^{**}	0.53 [*]	0.73 ^{**}	1	
Pb	-0.47	0.37	0.40	0.09	0.44	0.91 ^{***}	0.92 ^{***}	0.95 ^{***}	0.67 ^{**}	1

SPM- suspended particulate matter

Table 2: Mean concentrations of major (%) and trace metals (ppm) in different seasons.

St.No	Al	Mn	Fe	Co	Zn	Ni	Cr	Cu	Pb
Monsoon									
St.1	8.0	9.2	0.4	25.9	334.5	81.9	235.8	29.9	31.9
St.2	10.1	13.0	0.6	32.4	428.8	112.6	276.2	47.2	38.7
St.3	10.7	14.7	0.8	34.0	597.8	130.8	320.4	63.7	43.9
St.4	11.6	16.8	1.0	39.2	1071.9	209.7	538.5	96.3	68.3
St.5	10.6	16.2	1.1	35.8	984.4	159.4	444.2	75.9	64.9
Mean	10.2	14.0	0.8	33.4	683.5	138.9	363.0	62.6	49.5
S.D	1.3	3.0	0.3	4.9	329.9	48.6	125.4	25.6	16.2
Var.(%)	13.2	21.7	34.2	14.7	48.3	35.0	34.6	40.9	32.7
Post-monsoon									
St.1	4.9	6.2	0.3	22.6	220.1	95.5	397.9	79.0	83.0
St.2	6.0	15.2	0.5	24.4	226.2	78.7	694.2	61.1	80.3
St.3	7.1	12.6	0.6	27.1	230.2	93.4	692.4	58.6	68.3
St.4	7.1	11.2	0.8	29.0	271.8	92.0	568.5	99.7	137.8
St.5	4.7	7.3	0.9	35.3	456.0	108.3	528.8	113.7	94.4
St.6	5.5	9.1	1.5	21.0	172.9	61.4	302.3	80.3	53.0
St.7	5.3	13.8	1.9	29.0	266.1	71.2	361.5	103.2	73.9
Mean	5.8	10.8	0.9	26.9	263.3	85.8	506.5	85.1	84.4
S.D	1.0	3.4	0.6	4.8	91.1	16.1	157.4	21.2	26.8
Var.(%)	16.6	31.2	61.9	17.9	34.6	18.8	31.1	24.9	31.8
Pre-monsoon									
St.1	6.9	8.9	0.4	23.3	108.6	65.3	104.0	43.6	25.1
St.2	7.0	9.3	0.5	22.7	81.7	46.5	99.4	46.4	27.1
St.3	6.9	9.9	0.6	26.0	165.7	61.7	154.3	143.8	60.1
St.4	6.4	9.5	1.2	23.9	100.4	49.2	92.6	44.4	26.8
St.5	6.7	10.2	1.5	27.1	126.8	69.3	261.4	57.8	33.5
St.6	6.8	11.2	1.7	30.0	149.2	109.7	151.2	75.2	49.4
St.7	4.0	10.2	1.2	21.0	237.6	106.8	269.7	130.1	102.6
Mean	6.4	9.9	1.0	24.9	138.6	72.6	161.8	77.3	46.4
S.D	1.1	0.8	0.5	3.1	52.2	25.7	75.0	42.4	28.1
Var.(%)	16.9	7.8	51.1	12.3	37.7	35.3	46.4	54.8	60.5

S.D.- standard deviation;Var.- variability, calculated following the equation of Viers et al. (2008)

Table 3: Correlation coefficient matrix for selected elements at the transect stations. Correlations <-0.43 or >+0.43 are statistically significant at $\alpha \leq 0.05$; <-0.54 or >+0.54 are at $\alpha \leq 0.01^{**}$; <-0.66 or > 0.66 are at $\alpha \leq 0.001^{***}$ for monsoon, <-0.38 or >0.38 are at $\alpha \leq 0.05$; <-0.48 or >+0.48 are at $\alpha \leq 0.01^{**}$; <-0.59 or >+0.59 are at $\alpha \leq 0.001^{***}$ for post-monsoon, <-0.36 or >0.36 are at $\alpha \leq 0.05$; <-0.47 or >+0.47 are at $\alpha \leq 0.01^{**}$; <-0.57 or >+0.57 are at $\alpha \leq 0.001^{***}$ for pre-monsoon.

		Monsoon (n=20)										
		a										b
	SPM	Al	Mn	Fe	Co	Zn	Ni	Cr	Cu	Pb	OC	
SPM	1											
Al	-0.35	1										
Mn	-0.47	0.56 ^{**}	1									
Fe	-0.42	0.87 ^{***}	0.80 [*]	1								
Co	-0.25	0.88 ^{***}	0.48 [*]	0.72 ^{***}	1							
Zn	-0.50	0.36 ^{**}	0.74 ^{***}	0.46 [*]	0.45 ^{***}	1						
Ni	-0.53	0.65 ^{**}	0.36	0.49 [*]	0.70 ^{**}	0.53 [*]	1					
Cr	-0.48	0.57 ^{**}	0.21	0.37 ^{**}	0.65 ^{**}	0.43 [*]	0.97 ^{***}	1				
Cu	-0.64	0.58 [*]	0.66 ^{***}	0.65	0.47 ^{**}	0.78 ^{***}	0.69 ^{***}	0.60 ^{**}	1			
Pb	-0.61	0.50 ^{**}	0.28 ^{**}	0.38 ^{**}	0.59 ^{***}	0.52 ^{***}	0.91 [*]	0.92 [*]	0.68 ^{***}	1		
OC	-0.69	0.62 ^{**}	0.55 ^{**}	0.59 ^{**}	0.78 ^{***}	0.71 [*]	0.53 [*]	0.46 [*]	0.35	0.69 ^{***}	1	
		Post-monsoon(n=26)										
	SPM	Al	Mn	Fe	Co	Zn	Ni	Cr	Cu	Pb	OC	
SPM	1											
Al	0.06	1										
Mn	-0.34	0.16	1									
Fe	0.20	0.53 ^{**}	0.28	1								
Co	-0.08	0.41 [*]	0.34	0.16	1							
Zn	-0.11	0.68 ^{***}	0.15	0.43 [*]	0.53 ^{**}	1						
Ni	-0.05	0.64 ^{***}	-0.02	0.30	0.50 ^{**}	0.88 ^{***}	1					
Cr	-0.08	0.14	-0.19	-0.15	0.21	0.34	0.33	1				
Cu	-0.32	-0.40	0.08	-0.30	0.10	0.11	-0.08	-0.02	1			
Pb	-0.16	0.03	-0.09	-0.10	0.32	0.40 [*]	0.41 [*]	0.44 [*]	0.66 ^{***}	1		
OC	-0.40	0.53 ^{**}	0.40 [*]	-0.11	0.45 [*]	0.27	0.24	0.55 ^{**}	-0.09	0.07	1	
		Pre-monsoon(n=28)										
	SPM	Al	Mn	Fe	Co	Zn	Ni	Cr	Cu	Pb	OC	
SPM	1											
Al	0.22	1										
Mn	-0.53	0.22	1									
Fe	-0.18	0.64 ^{***}	0.63 ^{***}	1								
Co	-0.17	0.76 ^{***}	0.66 ^{***}	0.78 ^{***}	1							
Zn	-0.57	-0.52	0.18	-0.17	-0.05	1						
Ni	-0.43	-0.29	0.46 [*]	-0.04	0.09	0.58	1					
Cr	-0.31	-0.57	-0.10	-0.35	-0.29	0.49 ^{**}	0.12	1				
Cu	-0.29	-0.43	-0.07	-0.23	-0.08	0.83 ^{***}	0.25	0.45 [*]	1			
Pb	-0.43	-0.66	0.02	-0.26	-0.19	0.92 ^{***}	0.41 [*]	0.97 ^{***}	0.85 ^{***}	1		
OC	-0.71	-0.09	0.68 ^{***}	-0.09	0.42 [*]	0.49 ^{**}	0.53 ^{**}	0.51 ^{**}	0.60 ^{***}	0.46 [*]	1	

^asuspended particulate matter ^borganic carbon