

Depositional record of trace metals and degree of contamination in core sediments from the Mandovi estuarine mangrove ecosystem, west coast of India

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Abstract

The concentrations of seven trace metals (Fe, Mn, Cu, Cr, Co, Pb and Zn) in three sediment cores were analysed to assess the depositional trends of metals and their contamination level in the Mandovi estuary, west coast of India. All sediment cores showed enrichment of trace metals in the upper part of core sediments and decrease in concentration with depth, suggesting excess of anthropogenic loading (including mining activities) occurred during the recent past. Scanning electron microscope (SEM) images distinguished the shape, size and structure of particles derived from lithogenic and anthropogenic sources in core sediments. The geo-accumulation index (I_{geo}) values indicate that Mandovi estuary is 'moderately polluted' with Pb, whereas 'unpolluted to moderately polluted' with Fe, Mn, Cu, Cr, Co and Zn. The comparative analysis of trace metals revealed that Fe and Mn were highly enriched in the Mandovi estuary compared to all other Indian estuaries.

Keywords: Trace metals, SEM, Geo-accumulation index, core sediments, Mandovi estuary

Goa is one of the highest mineral producing states in India, and its economy mainly depends on iron and manganese ore mining and export of the same (Goa exports 70.08% of India's iron ore). According to information provided by the Goa Mineral Ore Exporters Association (GMOEA), 54.45 million metric tonnes of mineral ore were exported from Goa in 2010-11, the highest by any state in India. The prospecting of Fe and Mn ore started in Goa as early as 1905, and the regular export commenced in 1947. During 1971–1980, Goa accounted for 32% of the country's total iron ore production and 55% of its export (Swaminathan, 1982). Goa is crisscrossed by seven rivers, out of which Mandovi and Zuari are the major drainage. The Mandovi estuary is one of the tropical estuaries along the west coast of India. Mangroves that fringe this estuary consist mainly of species like *Rhizophora mucronata*, *Pongamia pinnata*, *Cyperus spp.*, *Bruguiera gymnorrhiza*, *Avicennia officinalis*, *Caesalpinia spp.*, *Sonneratia caseolaris* and *Acanthus illicifolius* (Fernandes et al., 2012). Mandovi River is heavily used to transport large quantities of ferromanganese ores from mines located upstream to the Mormugao harbour (Figure 1). Mining associated activities such as ore loading, transportation of ore to platforms, effluents from beneficiation plants and barge-building activity were taking place during the sampling period. All these activities associated with mining contribute large quantity of material in the Mandovi estuary. Within the estuary, sediments are the major repositories of metals (Dessai et al., 2009).

Iron ore mines act as important sources of major metals, mainly Fe and Mn, and also associated trace metals into the environment (Ratha and Venkatraman, 1995). Mangrove sediments are rich in sulphide and organic matter, and these favour the retention of water-borne metals. Intertidal mangrove sediments act as traps and play an important role as sinks for heavy metals received from wide range of sources. Enrichment of metals in bottom sediments represents a critical measure of health for any mangrove ecosystem (Janaki-Raman et al., 2007). Trace metals in coastal and estuarine sediments are incorporated into the aquatic food webs through primary producers and then bio-magnified at higher trophic levels (Veerasingam et al., 2012).

The temporal variations in sediment cores reflect the geochemical history of a given region, including any anthropogenic impact (Szefer and Skwarzec, 1988; Venkatachalapathy et al., 2011a; Veerasingam et al., 2014). Though the impacts of iron ore processing on the surface sediments of the Mandovi estuary have been documented earlier (Alagarsamy, 2006; Shynu et al., 2012), the long term contamination history and impact of mining activities in estuarine sediments are sparsely understood. The objectives of the this study are: (i) to establish the spatial and vertical distribution of trace metals contamination in the Mandovi estuary, (ii) to assess the historical contamination trends of the Mandovi estuarine sediments

using the geo-accumulation index (I_{geo}) and (iii) to delineate the lithogenic and anthropogenic sources of metals in sediment cores using scanning electron microscopy analysis. The results of this study can be used for the improvement of new guidelines to mining related activities and future environmental monitoring programs in Goa.

Three sediment cores (D1, C1 and OG) were collected from the mangrove ecosystem along the Mandovi estuary using a hand-operated corer on 8 January 2013 (Figure 1). Sampling locations were identified using a hand-held Global Positioning System (GPS). Soon after collection, the cores were sectioned into 2.5 cm intervals using a plastic knife from the surface. The sub-samples were sealed in clean plastic bags, labelled and stored in an icebox for further laboratory analyses.

15 g of sediment samples were treated overnight by adding 20 ml of 10% Na-Hexa metaphosphate solution. The sand contents were determined after wet-sieving on 63 μ m sieve and subsequent weighing upon drying. The remaining mud fraction was made up to 1000 ml in a measuring cylinder. Silt (63 – 2 μ m) and clay (<2 μ m) content were determined by the standard pipette analysis (Folk, 1968). The separated fractions were oven-dried and weighed to calculate silt and clay contents.

50 mg of sediment samples were digested with 3 ml hydrofluoric acid and 9 ml nitric acid using PTFE Teflon bombs in a closed microwave digestion system (Multiwave 3000, Anton Paar). The procedure requires a 20–min temperature ramp (20–220 °C), followed by a 15–min 220 °C stage. After digestion, the obtained suspension was filtered through Whatman filter paper, and transferred to clean polypropylene vials, and diluted to 25 ml with ultra-pure water for analysis. The final solutions were used for trace metal analysis. Total trace metal concentrations were measured using a Perkin Elmer Analyst 200 Atomic Absorption Spectrometer (AAS). The instrument was calibrated using standard solutions and an internal standard was added to the samples. Standard reference material MESS–3 was used to ensure the quality control and accuracy of the analysis. All results showed good agreement with the certified data. Replicated measurements of standard reference material, reagent blanks and duplicated sediment samples were used to verify accuracy and precision.

The geo-accumulation index (I_{geo}) of seven elements (Fe, Mn, Cu, Cr, Co, Pb and Zn) was calculated according to the following equation (Muller, 1969):

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right).$$

Where, C_n is the measured concentration of metal 'n' in the sediment and B_n is the background value for metal 'n'. The factor 1.5 is used for the possible variations of the background data due to geogenic effects. The choice of the background value plays an important role in the interpretation of metal data. In this study, for the natural background value, we chose the deepest sediment layer of core D1 (i.e., pre-mining period).

Parts of the sediment samples were suspended in acetone, and the magnetic particles were extracted using a hand magnet. The magnetic extracts were coated with gold in a vacuum evaporator while the sample was being slowly rotated. Detailed typical micrographs were taken by using JEOL JSM-5800 LV scanning electron microscope.

Vertical distributions of sediment grain size showed the presence of relatively uniform fine-grained materials, i.e. silt and clay, exceeding 80%. The sand percentage is very small in these cores. The grain size distribution in estuarine sediments is closely related to the hydrodynamics of the estuary. The high content of silt and clay in the upper part of sediment core indicates that the recent sedimentation might be due to weak hydrodynamic conditions. The observations reveal that the presence of high amount of silt and clay particles in all core sediments is due to the existence of mangroves with areal root structures in this region. These root structures trap floating detritus and reduce the flow, and ultimately create conditions conducive to suspended clay and silt particles to settle in the estuary ([Veerasingam et al., in press](#)).

Vertical profiles of D1, OG and C1 show enrichment of Fe (0 – 45cm: 16.27 – 23.78%, 0 – 45cm: 19.3 – 29.22% and 0 – 25cm: 17.89 – 22.87%) and Mn (0 – 45cm: 1188 – 1994 μgg^{-1} , 0 – 45cm: 1605 – 2308 μgg^{-1} and 0 – 25cm: 1156 – 1624 μgg^{-1}) in the surface layers, which may be due to spillage of Fe and Mn ores during transportation in the Mandovi estuary. [Alagarsamy \(2006\)](#) also observed that the concentrations of Fe varied from 2.2% to 49.7% on the surface sediments of the Mandovi estuary, while the concentration of Mn ranged from below the detection limit to 1.61%. In D1 core, Fe and Mn show nearly the same concentration from the bottom (105 cm) to 85cm, followed by enriched and increasing trends till 15 cm and then decreasing trend towards the surface (Figure 2). Similarly in OG core, Fe and Mn show increasing trends from bottom to 7.5cm, followed by a gradual decreasing trend towards the surface.

Scanning electron microscopy (SEM) analysis of the separated sediment magnetic extracts demonstrated their morphology variations (size, shape and structure of iron minerals), primarily in the vertical sediment profiles. According to their shape, two groups of particles were specified, i.e., spherical particles and polyhedral particles (Figure 2). The morphology of iron oxides is indicative of susceptibility of the particles to the processes of physical and chemical weathering. The different morphological forms of iron oxides are well correlated with the sediment horizons. Spherical iron oxides predominate in the upper layers of sediment profiles due to deposition of iron spherules from the atmosphere. It is known that magnetic spherules are formed upon anthropogenic processes like combustion of coal and other fossil fuels from industries, boat, ships and other vehicles (Horng et al., 2009, Venkatachalapathy et al., 2011b). These magnetic spherules are less than 10 μm in size with smooth surface. These are iron-bearing silicate particles with admixture of manganese. The polyhedral particles iron oxides are predominant in the bottom parts of sediment cores. These are coarse particles with lithogenic titanomagnetite derived from natural weathering process (Zagurskii et al., 2009). The results of Fe and Mn concentrations and scanning electron microscopy images of different horizons of sediment cores reveal enrichment of iron oxides in the upper parts - derived from anthropogenic origin, whereas coarse grained iron oxides in the bottom parts – derived from lithogenic origin.

The vertical profiles of Cu, Cr, Co, Pb and Zn in sediment cores D1, OG and C1 are presented in Figure 3. The ranges of Cu, Cr, Co, Pb and Zn in D1 core are: 34.4 – 79 $\mu\text{g g}^{-1}$, 117 – 180.8 $\mu\text{g g}^{-1}$, 15.6 – 32.12 $\mu\text{g g}^{-1}$, 7.96 – 39.56 $\mu\text{g g}^{-1}$ and 47 – 69.4 $\mu\text{g g}^{-1}$, respectively. Distribution patterns of Cr and Zn are similar to those of Fe and Mn indicating that they are scavenged by Fe and Mn oxides. Laluraj and Nair (2006) found that the geochemical variations in metal distribution are associated with the extent to which the precipitation or dissolution of Fe and Mn oxides/hydroxides act as specific sink or source of metal. Vertical profiles of Cu and Co gradually increased from bottom to 35cm, followed by nearly constant pattern till 5 cm and then decreasing trend towards the surface. Down core profiles of all metals (except Pb) in D1 core showed a decreasing pattern in the upper sediments above 5 cm. In OG core, the ranges of Cu, Cr, Co, Pb and Zn are: 40.82 – 49.74 $\mu\text{g g}^{-1}$, 129 – 174.8 $\mu\text{g g}^{-1}$, 23 – 36.84 $\mu\text{g g}^{-1}$, 19.5 – 37.51 $\mu\text{g g}^{-1}$ and 68 – 72.9 $\mu\text{g g}^{-1}$, respectively. All metal profiles in OG core exhibit increasing pattern till 10cm and then decreased towards the surface, indicating the same sources of trace metals with nearly the same rate of deposition. In C1 core, Cu, Cr, Co, Pb and Zn ranges from 36.94 – 43.16 $\mu\text{g g}^{-1}$, 136 – 158.8 $\mu\text{g g}^{-1}$, 20 – 27.08 $\mu\text{g g}^{-1}$, 19.72 – 28.14 $\mu\text{g g}^{-1}$ and 69.5 – 72.2 $\mu\text{g g}^{-1}$, respectively. Cu, Co and Pb values increased towards the surface, whereas Zn was nearly uniform with depth. Cr shows an

increasing trend from the bottom to 5 cm, followed by a gradual decreasing trend towards the surface. This may reflect changes in the nature of industrial activity and compliance with legislation and directives aimed at reducing the discharge of effluents to the estuary (Owens and Walling, 2003). Recently, Hosono et al. (2010) have also found similar reduction trends in metal pollution in Asian developing countries. Unlike OG core, concentration of Pb in the upper layers showed increasing trend in C1 and D1, and are attributed to the local redox conditions, which allowed Pb to co-precipitate with Fe and Mn oxides. The presence of Pb in sediments might have been originated from the anthropogenic fly-ashes derived from the combustion of fossil fuels in industries, boat, ship and other vehicles as reported by Ayyamperumal et al. (2006).

Shetye et al. (2007) found that during pre-monsoon, saline waters extend upto 40 km upstream, and lower estuary acts as an extension of sea. 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 closer to the source of discharge in the upstream (Shynu et al., 2012). From 1980 onwards, industrialisation and urbanisation around Goa has accelerated, resulting in increase of pollution around the estuarine areas. The fact that trace metals increased generally and even enriched in the upper portion of the sediment cores indicate that the trace metals from anthropogenic sources have been deposited in the Mandovi estuarine sediments for the past few decades. Singh et al. (2014) recently collected a 76cm length of sediment core (near D1 core location in the Mandovi estuary) and found that the sedimentation rate was slower (0.14cm/y) from bottom to 35cm, which approximately corresponds to the year 1980 and the rate increased thereafter to 1.42cm/y. i.e., the bottom of the core (76 cm from the surface) date back to 1694. In this study, the age of bottom sediment layer of D1 core (105 cm) date back to 1565 (Based on the sedimentation rate estimated by Singh et al. (2014) using ^{210}Pb dating). Thus we find that the present results are very useful to reconstruct the past ~450 years record of the impact by human activities in the past, including mining.

The anthropogenic contribution of metals in estuarine sediments has been estimated using geo-accumulation index (I_{geo}). According to Muller (1969) I_{geo} values in estuarine sediments have been classified as: ≤ 0 : unpolluted; 0–1: unpolluted to moderately polluted; 1–2: moderately polluted; 2–3: moderately to strongly polluted; 3–4: strongly polluted; 4–5: strongly to extremely polluted; > 5 : extremely polluted. The highest class reflects at least 100-fold enrichment above background values. The geo-accumulation index (I_{geo}) calculated for trace metals indicates that the upper portion of core sediment samples can be characterised as ‘unpolluted to moderately polluted’ for Fe, Mn, Cu, Cr, Co,

and Zn, while I_{geo} values of Pb describe sediments 'moderately polluted' (Figure 4). The moderate pollution of Fe and Mn in the upper portion of sediment cores is directly related to the Fe-Mn ore deposits and human-induced activity in handling and transportation of these ores through the estuary. Shynu et al. (2012) and Alagarsamy (2006) also observed a high value of Fe and Mn in suspended matter and surface sediments, respectively in the Mandovi estuary. The moderate contamination of Cu, Co and Zn might be associated with the presence of boatyard and small vessel building yards. The sources of Zn contamination are derived from industries, liquid manure, composed materials and agrochemicals such as fertilizers and pesticides (Krishna and Kovil, 2004). The increase of Pb in sediments is caused by the use of anti-fouling paints, combustion of petroleum and diesel in boat, ferry and other traffic activities. The transfer of contamination and its dispersion in the aquifer is a very slow process, and changes in metal concentration in the upper aquifer layer are not manifested in a short time. However, metal contamination in the upper part of core sediments could directly affect the water quality of estuary, resulting in potential consequences to the sensitive lowest levels of the food chain and ultimately to human health. The trace metal concentration values in the sediments of Mandovi estuary reported herein were compared with those available in literature for various estuaries around the world (Table 1). The results show that Mandovi estuary is highly enriched with Fe and Mn compared to all other Indian estuaries.

Finally, based on the vertical distribution of trace metals and their geo-accumulation index (I_{geo}) values, the Mandovi estuarine sediments are 'moderately polluted' with Pb, whereas 'unpolluted to moderately polluted' with Fe, Mn, Cu, Cr, Co and Zn. It is envisaged that the present study shall help to develop environmental legislation and new guidelines for mining related activities in Goa.

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Figure 1. Location of sampling sites (marked with triangles) in the Mandovi estuarine mangrove ecosystem.

Figure 2. Temporal distribution of Fe and Mn concentrations with morphology of iron oxides in cores D1, OG and C1 sediments of Mandovi estuarine mangrove ecosystem.

Figure 3. Vertical profiles of trace metals (Cu, Cr, Co, Pb and Zn) in D1, OG and C1 sediment cores collected from Mandovi estuarine mangrove ecosystem.

Figure 4. Down core profiles of geo-accumulation index (I_{geo}) values in D1, OG and C1 core sediments.

Table 1. Comparison of metal concentration in the Mandovi estuary with other Indian and world estuaries (Fe in % and others in $\mu\text{g g}^{-1}$).

Figure 1

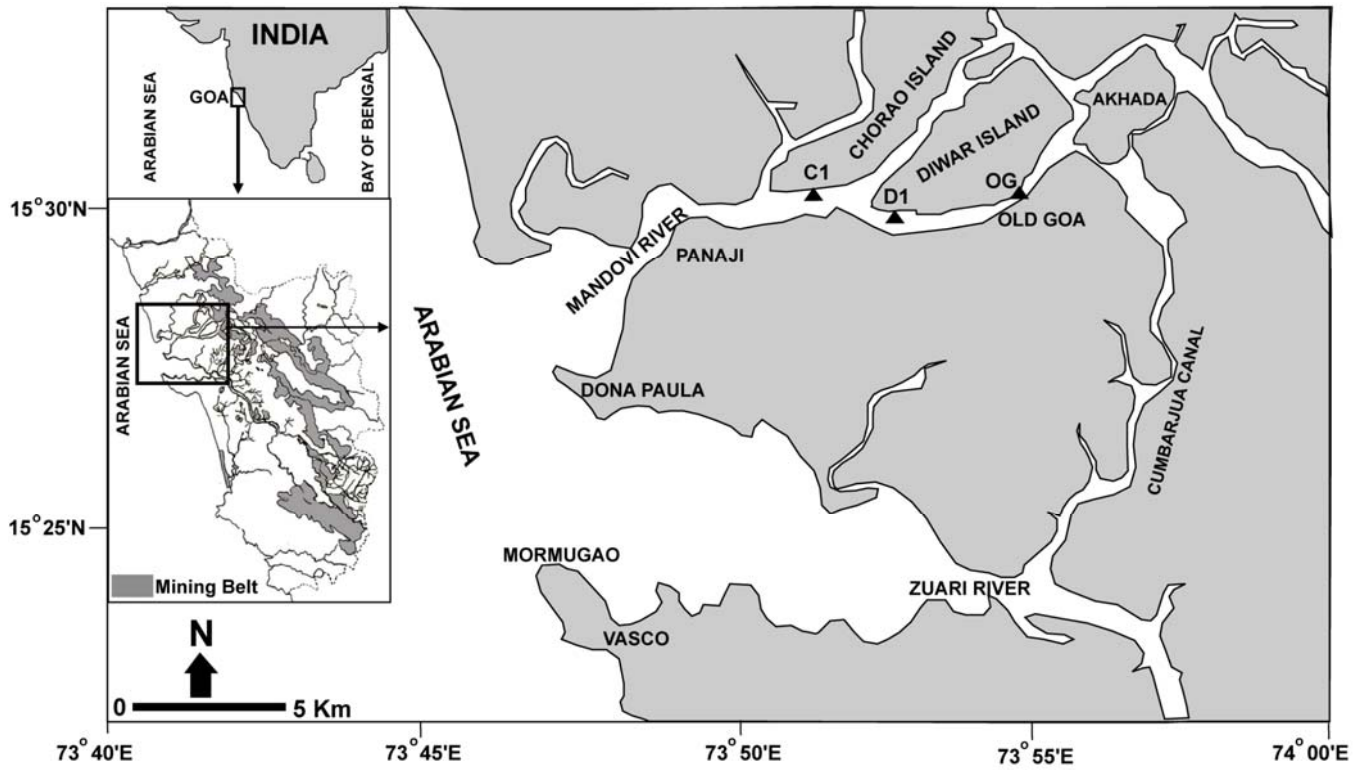
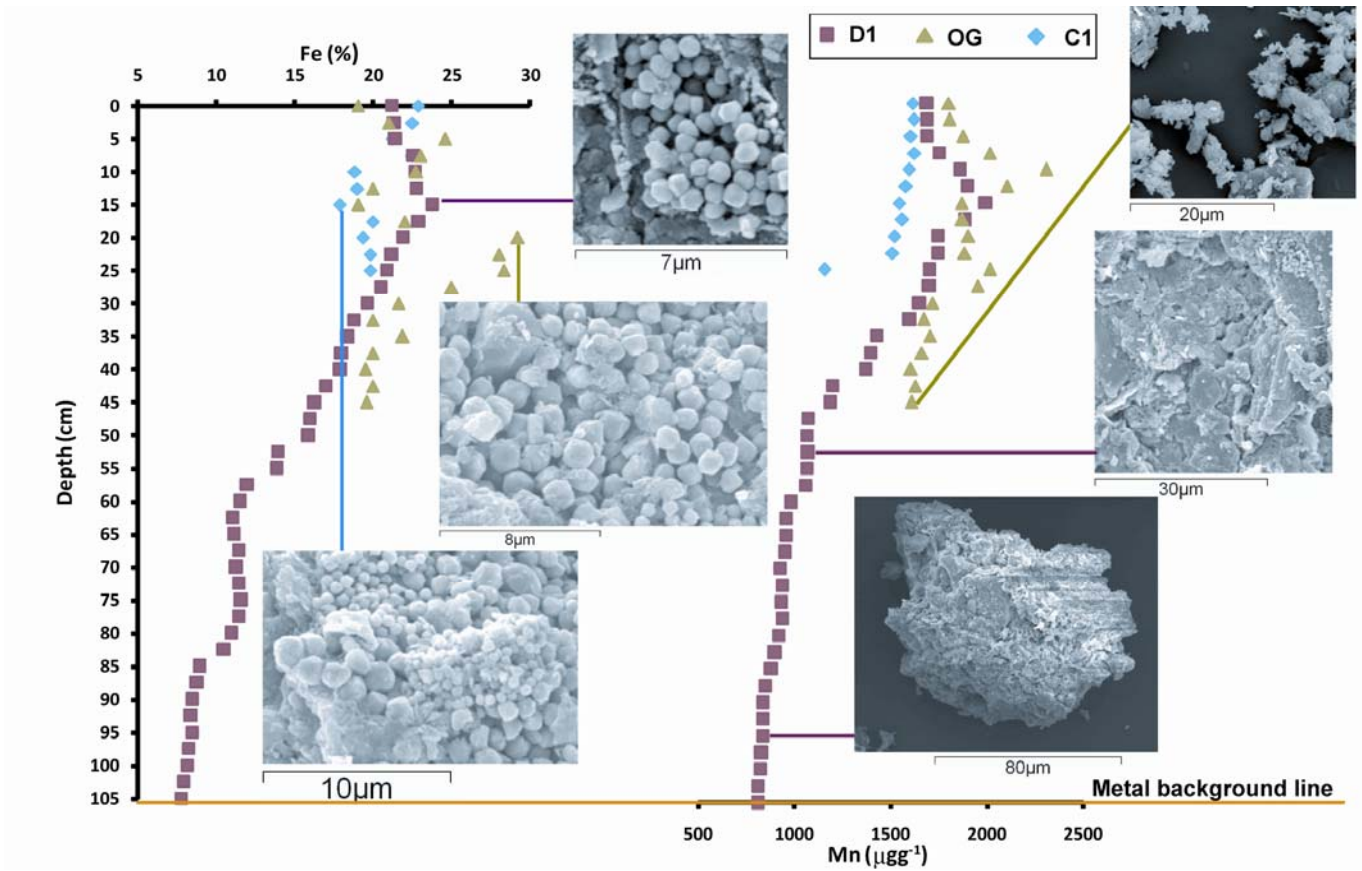


Figure 2



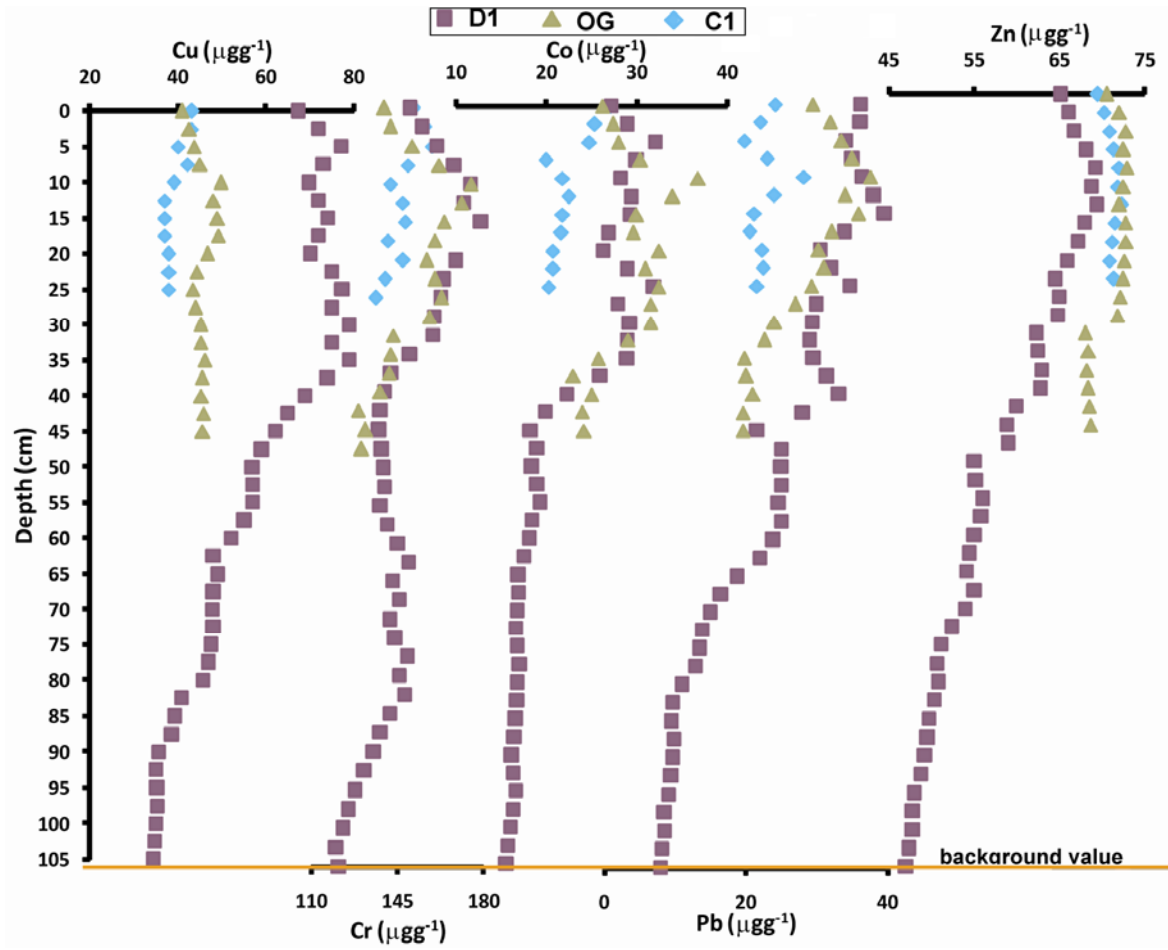


Figure 3

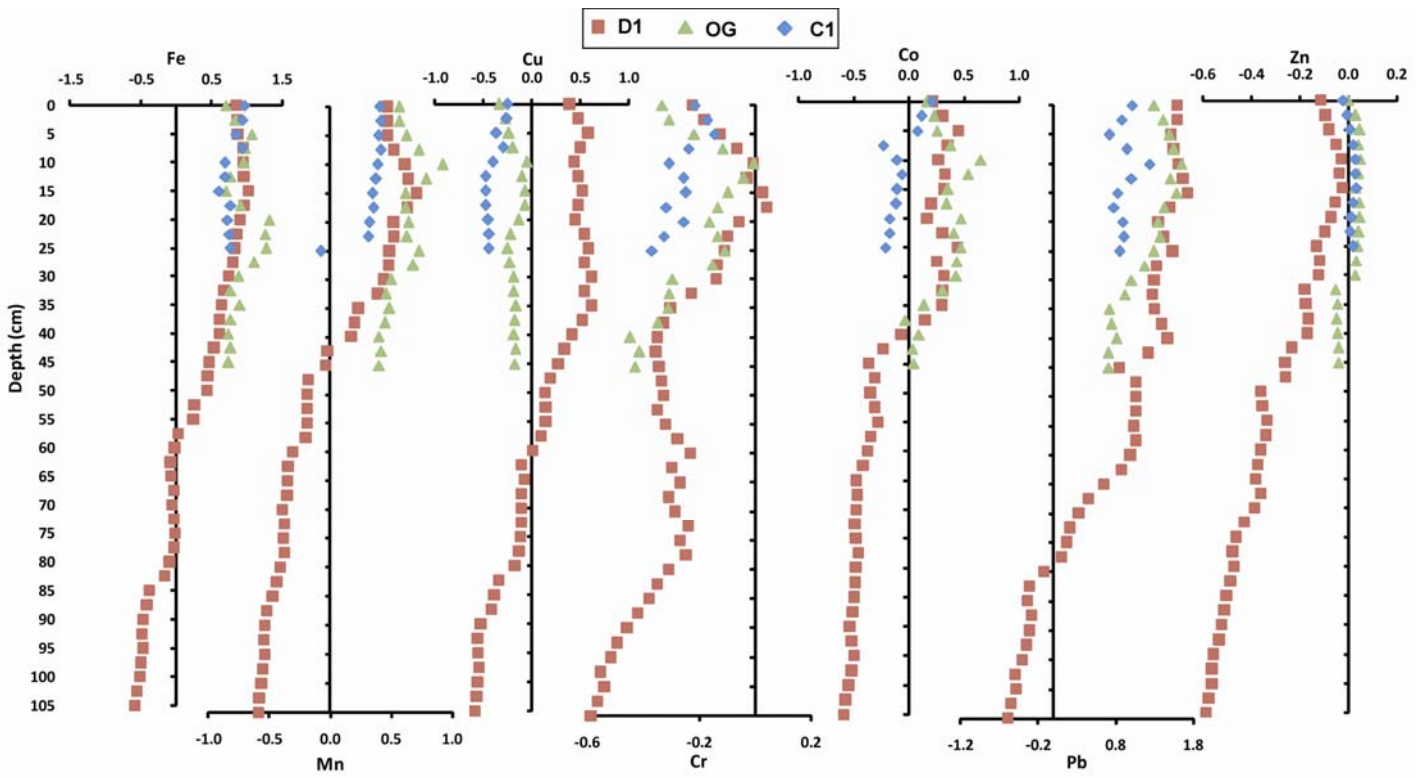


Figure 4

Table 1:

Location	Fe (%)	Mn	Cu	Cr	Co	Pb	Zn	References	
Indian estuaries									
Mandovi estuary	D1 OG C1	15.1 22.3 20.35	1244 1842 1539	57.23 45.51 39.23	145.89 150.42 146.93	21.7 29.09 22.45	22.8 28.06 22.62	57.7 71.03 71.15	This study This study This study
Narmada estuary		3.14	514	46	n.d	29	5	50	Biksham and Subramanian (1988)
Tapti estuary		6.79	n.d	148.32	55.2	18.34	56.69	143.55	Shah et al. (2013)
Zuari estuary		8.23	3000	58.67	186.6	48.40	n.d	87.51	Dessai et al. (2009)
Cauvery estuary		1.76	319	12	n.d	64	10	26	Subramanian et al. (1985)
Krishna estuary		4.23	1040	49	n.d	47	9	31	Biksham and Subramanian (1988)
Godavari estuary		6.03	1060	73	n.d	20	6	53	Biksham and Subramanian (1988)
Ganges estuary		2.16	400	21	n.d	22	25	46	Biksham and Subramanian (1988)
Brahmaputra estuary		2.90	644	17	n.d	31	13	47	Subramanian et al. (1985)
Thamiraparani estuary		1.64	668.5	40.19	4.23	3.62	26.16	198.6	Magesh et al. (2011)
World estuaries									
Medway estuary, UK		3.03	315	42	76	n.d	67	138	Spencer (2002)
Savannah estuary, USA		4.5	440	17	n.d	n.d	25	68	Goldberg et al. (1979)
Tijuana estuary, USA		n.d	n.d	26.3	25.4	n.d	36.1	107.1	Weis et al. (2001)
Estuaries of Texas, USA		n.d	n.d	20.5	132	n.d	122	295	Sharma et al. (1999)
Scheldt estuary		1.86	317	22.3	47.9	4.02	38.2	210	Bouezmarni and Wollast (2005)
Bakkhali estuary, Bangladesh		n.d	n.d	34.93	n.d	n.d	27.14	100.85	Siddique et al. (2012)
Pearl river estuary, China		n.d	n.d	70.8	102.3	19.9	47.3	146.6	Liu et al. (2011)
Seine river estuary, France		n.d	n.d	53	n.d	n.d	53.98	200	Hamzeh et al. (2013)
Tropical Pulau estuary, Malaysia		21.6	n.d	17.2	n.d	5.1	27.4	60.1	Khalik et al. (1997)
Tropical Kranji estuary, Singapore		n.d	n.d	17.27	n.d	n.d	26.13	62.12	Cuong and Obbard (2006)
Teifi estuary, UK		18.4	n.d	13	n.d	10	25	87	Bryan and Langston (1992)