

**HEAVY METAL BURDEN IN COASTAL MARINE
SEDIMENTS OF NORTH WEST COAST OF INDIA IN
RELATION TO POLLUTION**

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Yours faithfully,

Controller of Examinations.

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CHAPTER 1

METALS IN MARINE ENVIRONMENT

Various contaminants released into the sea may significantly affect marine ecology, and in extreme cases, may lead to the destruction of whole ecosystems. The contaminants of major concern are sewage, nutrients, metallic compounds, substances disrupting endocrine functions, persistent organic pollutants and petroleum hydrocarbons (GESAMP, 1982, 2001). Many contaminants such as trace metals (also referred as heavy metals), though occur at extremely low concentrations in seawater, are accumulated by marine organisms and concentrations in their body tissue can be hundreds of times greater than the levels in seawater (Riley and Chester, 1971). Thus, consumption of contaminated fish can be harmful; the well-documented examples being Hg, Cd and Cu poisoning (Goldberg, 1992).

The outbreak of hitherto unknown neurological illness among the inhabitants living around Minamata bay, Japan was reported in 1953. The victims suffered from a weakening of muscles, loss of vision, impairment of cerebral functions and eventual paralysis and death. After intensive investigations it was found in 1959 that the cause of the disease was the consumption of fish and other foodstuffs contaminated with methyl-Hg, the source of which was traced to the effluent of a chemical industry manufacturing plastics. This disease became known as the Minamata disease. A second outbreak of the disease was reported in Japan during

1964-65 mainly among fishermen and their families living near Niigata. Several other alarming incidents of Hg poisoning have since been reported from other countries.

Contamination of aquatic environment by Cd is less widespread than by Hg. During 1947 an unusual and painful disease, subsequently became known as 'itai-itai', was reported among the villagers on the bank of the Jintsu River in Japan. Contamination of the river water by Cd was found to be the culprit and source of Cd was traced to a Zn mine situated some 50 km upstream from the afflicted villages. It is estimated that at least 100 deaths occurred due to the disease until 1965. An interesting episode of mass mortality of fish resulting from Cu poisoning occurred off the coast of Holland. Several kilograms of CuSO_4 buried under sand were identified as the source of Cu to the coastal water. In this area the seawater contained a Cu concentration of several hundred $\mu\text{g/l}$; the normal concentration of Cu in seawater being 1-3 $\mu\text{g/l}$ (Wittmann, 1979).

The study of metals in the marine environment has received considerable attention because of their biological significance as well as the possibility of their transfer to man through the food chains in quantities that can be harmful (GESAMP, 2001). The available information indicates that though the open oceans suffer from some contamination and ecological damage, they are still in a relatively healthy state as compared to some coastal areas. It is the waters nearest to the shore, particularly in estuaries and in semi-enclosed seas and bays bordering highly industrialised and urbanised zones that have suffered ecological degradation over the past few decades (GESAMP, 1982; 2001).

1.1 Sources of metals

Heavy metals, which include Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb, Cd, Hg, Ti and V enter the oceans as a result of natural processes and human activities via rivers, land runoff, dumping, atmosphere and the seabed. Major natural sources of these elements are rock weathering, degassing, emissions from terrestrial and submarine volcanoes and

dissolution from marine sediments. Hence, in areas characterized by metal-bearing formations these metals occur at elevated concentrations in water and bottom sediments of the marine zones receiving the runoff (Fernex *et al.*, 1984; Comacho-Ibar *et al.*, 1992; Weis *et al.*, 1993; Attrill and Thomes, 1995; Brooks, 1996; Borg and Jonsson, 1996; Gupta and Karuppiah, 1996; Balls *et al.*, 1997; Guo *et al.*, 1997; Vallius and Leivuori, 1999; Shumilin *et al.*, 2001; Munksgaard and Parry, 2002). The dominant inputs of most trace metals to coastal areas are through rivers and land runoff but for a few elements such as Hg, As and Pb the atmospheric route is also important, particularly in the open ocean, although even for these elements local discharges and rivers often dominate the coastal input. The important anthropogenic sources of metals like Cr, Mn, Co, Ni, Cu, Zn, Pb, Cd, Hg and As to coastal and inshore waters are industrial processing of ores and metals; ferrous and nonferrous metal industries including metal plating; industries producing both organic and inorganic chemicals; use of metal and metal components; leaching of metals from solid waste; and offshore dumping of domestic sewage, sludge and industrial wastes (Owens *et al.*, 1997).

1.2 Metals in seawater

Metals can exist in seawater at least in 4 different forms namely in true solution, as colloidal particles, adsorbed on other colloidal particles, and as a part of living organisms. Their dispersion in seawater is affected by properties such as their volatility, tendency to form insoluble complexes with inorganic and organic compounds, and their ability to form either soluble complexes with ions common in seawater or oxides or sulphides of low solubility (Forstner, 1979a). Difficulties in separating the dissolved and the solid phases of Fe by filtration result in a degree of uncertainty in determining the dissolved concentrations of other metals in seawater. Fe and Mn flocks absorb other metals thereby acting as scavengers (Tessier *et al.*, 1979; Forstner, 1979a). Trace metals dissolved in seawater are present at very low concentrations and contamination during sampling, storage and analysis often gives erroneous results. In fact much of the data on metals dissolved in

seawater pertaining to seventies and earlier are considered to be too high (Forstner, 1979b).

1.3 Metals in marine biota

Essential metals such as Cu, Zn, Fe and Co have important biochemical functions in the organism and form either an electron donor system or function as ligands in complex enzymatic compounds (Forstner, 1979c). In natural marine environment their enrichment in organisms does not exceed the level to interfere with the enzyme system functioning though their concentrations in organisms are generally higher than in seawater. However, if the ambient water or food contains high concentration of these metals, the homeostatic mechanism ceases to function and the essential trace metals act in an either acutely or chronically toxic manner (Nelson and Donkinn, 1985).

Simkiss and Taylor (1989) have discussed the pathways of metal accumulation by aquatic organisms and suggested six possible types of uptake. The most common is by a passive process of transfer from seawater down a concentration gradient into the tissues. In some cases uptake may also occur through ion pumps because of energy dependency. For many metals including Cd, Cu and Zn, the free metal ion is the most bioavailable form of the element (Goldberg *et al.*, 1976a, b). In case of metals such as Hg and As which can be alkylated in marine environment, the biological uptake is likely to occur in the alkylated form (Turner and Southworth, 1999). Autotrophic organisms probably accumulate trace metals directly from seawater. Hence, environmental parameters such as temperature, salinity, light and pH; and chemical factors such as speciation and complexation of the metal are of considerable significance. The presence of several potentially toxic trace metals can also affect their preferential uptake (FAO, 1976).

Variations in concentration of trace metals between species particularly in heterotrophs can be due to trophic level relationships (FAO, 1976). Though magnification of trace metals through the food web is

important, there are several other causes affecting the transfer of trace metals in marine organisms. There is also evidence of seasonal variations in the trace metal content within species (FAO, 1976). The biological uptake, retention and translocation of trace metals in marine biota are related to chemical changes in storage tissues within the organism (FAO, 1976). Thus, methyl-Hg assimilated through water or from metabolic conversion of Hg, accumulates in the muscle tissues of carnivore fish while the ionic Hg is preferentially transferred in their liver or spleen. Unlike Hg, Cd does not appear to concentrate in fish flesh, but accumulates in the gills, liver and gastro intestinal tract. Much of the As in marine organisms is in the form of organic As compounds (Culler and Reimer, 1989; Turner and Suathworth, 1999).

1.4 Metals in marine sediments

Metals in marine sediments can originate from several sources. In inshore and coastal areas the major source of metals is lithogenous associated with weathering products from the source rock. Hydrogenous formations that include precipitation products and metals adsorbed on particles formed due to physico-chemical changes in water also contribute to the metal burden in marine sediments (Riley and Chester, 1971). Anthropogenically introduced metals are ultimately transferred to the bed sediments (Simeonov *et al.*, 2000; Marchand *et al.*, 2006). Hence the environmental geochemistry requires knowledge of the naturally occurring metals in order to assess man's environmental impact. Although sediment analyses do not represent the extent of toxicity, they are useful to assess the burden of anthropogenic component over and above the lithogenic background and also in some instances, trace the sources of pollution long after input has taken place (Frignani *et al.*, 1997; Fukue *et al.*, 1999; Buccolieri *et al.*, 2006). San Francisco Bay, California, one of the largest estuaries on the west coast of America is an example of how anthropogenic activities changed the concentrations of potentially toxic metals (Flegal and Wilhelmy, 1991; Hornberger *et al.*, 1999).

Between 1850 and 1900 most of the Hg mining in the world occurred in the watershed of the San Francisco Bay. Hydraulic mining for gold mobilized sediments and deposited them in the bay. Activities in the Shasta mining district resulted in Cu, Cd and Zn contamination. Water management schemes on the Sacramento and San Joaquin Rivers between 1930 and 1970 changed sediment transport and hydraulic processes that affected the fate of metals in the bay. Rate of urbanization and industrialization increased after World War II and several industries including a Pb smelter released their effluents in the bay (Hornberger *et al.*, 1999). In 1980 approximately 100 t of trace metals (As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, Zn) were discharged to the south San Francisco Bay from 24 wastewater treatment plants (Hornberger *et al.*, 1999). Concentrations of many trace metals (Cu, Ni, Cd, Zn, Co) in surface water were anomalously high relative to the concentrations at comparable salinities in the northern reach. Mass balance calculations indicated that those excesses were primarily due to anthropogenic inputs and diagenetic remobilization from benthic sediments (Flegal and Wilhelmy, 1991). A marked decrease in the selenite concentration in the mid-bay compared to the past results has been attributed to a substantial decrease in the Se content in the effluents of the refineries to the bay (Cutter and Cutter, 2004).

Several sediment cores obtained from the San Francisco Bay were analyzed for the depth distribution of Ag, Al, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V and Zn. Baseline concentrations of metals were determined from horizons deposited before sediments were influenced by human activities and by comparing concentrations to those in a core from the Tomales Bay, a reference estuary. These concentrations have been estimated at 23.7-41.4 µg/g for Cu, 0.09 µg/g for Ag, 5.2 µg/g for Pb, 0.06 µg/g for Hg and 78 µg/g for Zn. The results indicated that the earliest anthropogenic influence on metal concentrations appeared as Hg contamination (0.3-0.4 µg/g) in sediment deposited between 1850 and 1880 apparently associated with debris from gold mining and the maximum concentrations were 20 times the baseline. Enrichment of Ag, Cu and Zn first appeared

after 1910, later than observed in Europe and North America. Early Hg contamination was perhaps a byproduct of the Pb smelting process. Maximum concentrations of Hg and Pb were 5-10 times the baseline and Cu and Zn concentrations were <3 times the baseline with large inventories of Pb in cores of proximity to the Pb smelter. Concentrations of Hg and Pb decreased since the 1970s, as expected (Hornberger *et al.*, 1999). Many other case studies of metal pollution assessment through sediment analysis are available in the literature (Frignani, 1997; Hornberger *et al.*, 1999; Fukue *et al.*, 1999; Simeonov *et al.*, 2000; Buccolieri *et al.*, 2006; Marchand *et al.*, 2006)

Although sediments are sink, trace metals may re-enter the water column under certain environmental conditions. Thus, the sediment acts as a buffer capable of keeping the metal concentration in water and biota above the background levels long after the input of the metal is stopped (Kremling, 1983; Cundy and Croudace, 1995; Gagnon *et al.*, 1997; Marins *et al.*, 1997; Conaway *et al.*, 2003). Mn, Fe and Al play a crucial role in the removal of metal ions from seawater as well as their behaviour in sediments. The oxyhydroxides of Mn and Fe have a high adsorption capacity and large surface area and can absorb cations such as Cr^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} and Cd^{2+} (Forstner, 1979a; Williams *et al.*, 1994).

Fe and Mn however, can migrate under redox gradients in sediments (Forstner, 1979a; Soetaert *et al.*, 2002). The nature of the diagenetic change occurring in marine sediments largely depends on the influx of decomposable organic matter to the sediment and the metabolic rate of oxidation. Three types of processes namely oxic diagenesis, suboxic diagenesis and anoxic diagenesis occur in sediments. When DO is present in the sediment pore waters, oxic diagenesis takes place and Mn concentration in the pore waters remains extremely low (about 2 $\mu\text{g/l}$). When DO in pore water depletes to very low levels, suboxic diagenesis dominates with the reduction of nitrate. When this occurs the concentration of dissolved Mn can increase by several orders of magnitude (>1000 $\mu\text{g/l}$) compared to the ocean bottom water (about 0.2

$\mu\text{g/l}$). When anoxic diagenesis takes over, reduction of Fe also occurs with high levels of both the metals in pore waters. Several trace metals that are bound to particle surfaces are also mobilized with Mn and Fe and their concentrations increase in the pore waters. These metal ions migrate upward through the pore water and precipitate along with Mn and Fe at a depth in the sediment where oxidising conditions prevail (Berner, 1980; Fernex *et al.*, 1984; Brannon and Patrick, 1987).

Oxidising conditions in marine sediments often occur at the sediment-water interface or a few centimetres below that level (Williams *et al.*, 1994). Thus, redox cycling tends to increase the metal content of the upper layers of the sediment, producing metal concentration profiles that show high concentrations near the sediment surface and lower concentration at depth in the sediment (Matty and Long, 1995). In sediments which are anoxic at the surface, the mobilized metals are released to the water column thereby enhancing their levels in water overlying the sediment. They may however reprecipitate if the water overlying the sediment is oxic (Williams *et al.*, 1994). Humic substances and microbial processes are also considered to influence mobilization of metals in the sediment matrix (Forstner, 1979c). Dissolved Cu, Co, Fe and Mn revealed (Kremling, 1983) dramatic changes (by factors of ≥ 100) across the $\text{O}_2\text{-H}_2\text{S}$ interface in anoxic Baltic waters, while, the concentrations of Zn, Cd and Ni at the redox front decreased by factors between 3 and 5. The findings supported the control of the solubility of Zn, Cd, Cu and Ni by the formation of bisulphide and (or) polysulphide complexes. Co was very mobile in anoxic regions with its concentration controlled by CoS precipitation. The concentrations of Fe and Mn in anoxic waters were controlled by total flux from sediment-water interfaces rather than by equilibrium concentrations of their solid phases (FeS and MnCO_3).

The concentration of trace metals in seafloor substratum tends to vary depending on factors such as sediment grain size contents of quartz and feldspar and organic carbon (C_{org}) etc. Different normalisation

techniques such as Enrichment Factor (EF), Geoaccumulation Index (I_{geo}) and sedimentary flux have been employed to assess the extent of metal accumulation in sediment over the lithogenic background (Muller, 1979; Loring and Rantala, 1992).

1.5 Metals in Arabian Sea and Bay of Bengal

The worldwide reports indicate relatively wide variations in metal concentrations in seawater and particulate matter from different oceanic areas (Chester *et al.*, 1978). According to Tappin *et al.* (1995) the factors governing the distribution of trace metals in the sea environment are boundary inputs, particle-water exchanges and advection and mixing within the basin. Physical mixing of fluvial and marine particulates leads to a continuous decrease in the trace element concentrations of the particulate matter with increasing salinity. A strong correlation between organic- and trace element-rich particles may indicate that organic matter effectively forms complexes with heavy metals (Jaspers *et al.*, 1999).

The abundance, geochemical and mineralogical composition as well as distribution pattern of metals in the Arabian Sea and the Bay of Bengal depend on the biogeography, hydrography and topography of brackish waters that transports these inputs to these seas. Inter comparison of results from different geographical sites is however difficult because of different methods and materials used for sampling, pre-treatment and final analysis used by various workers. This has also been acknowledged for other marine areas (Bernard *et al.*, 1989)

1.5.1 Metals in water

Published information on the concentration of dissolved metals in the Arabian Sea and the Bay of Bengal is rather limited and confined to only a few selected areas. These results are compiled in Table 1.5.1. The results reveal wide variation in the levels of dissolved metals, particularly in estuaries and nearshore coastal areas. Further, no trend is discernible in the variation of metals between the coastal waters of the west and the east coasts of India. The data on concentration of dissolved Cr are

available only for Mumbai Harbour (20 µg/l) and Kolak estuary (ND-102 µg/l) which received industrial effluents. High concentrations of trace metals such as Zn in the Kochi Backwaters, Ulhas estuary and Mahim Creek have been attributed to localized anthropogenic inputs (Kulkarni and Desai, 1980; Sabnis, 1984; Bhosale and Sahu, 1991; Ouseph, 1992).

The other trace metals which have been investigated in some specific areas and not included in Table 1.5.1 are Hg and As. The concentrations of Hg are distinctly high in Ulhas estuary (Bhosale and Sahu, 1991; Ram *et al.*, 2003), Thane Creek-Mumbai Harbour (hereinafter referred as Bay) (Zingde and Desai, 1981; Bhosale and Sahu, 1991; Jaiswar *et al.*, 2008), Rishikulya estuary (Sahu and Panda, 1987; Shaw *et al.*, 1988; Sahu *et al.*, 2002) and nearshore waters of Karwar (Krishnakumar and Pillai, 1990) and have been attributed to its release through the effluent of chlor-alkali industries. A standing stock of about 77 kg Hg in excess over the expected background has been reported in the Bay (Zingde and Desai, 1981). Concentrations of Hg as high as 108 µg/l as compared to the background level of 0.07 µg/l have been recorded in the vicinity of the outfall of the chlor-alkali industry in the Rishikulya estuary.

Due to the association of As with Fe and Mn ores mined in the hinterland of Goa and their estuarine and marine transport resulted in several investigations on its concentrations in waters of Mandovi and Zuari estuaries as well as coastal area of Goa (Sankaranayanan and Reddy, 1973; Fondekar and Reddy, 1974; 1976; Kamat and Sankaranayanan, 1975a, b; Zingde *et al.*, 1976, 1979; Singbal *et al.*, 1978; Fondekar *et al.*, 1981). The concentrations of dissolved As varied widely but no significant and consistent increase in areas of loading and unloading operations of ores has been found. The levels of metals were low in the Karwar region (Zingde and Singbal, 1983).

Only a few studies have been reported on the depth distribution of trace metals in the Northern Indian Ocean. The near surface Cd

concentrations varied from 0.04 to 0.26 $\mu\text{g/l}$ with an overall average of 0.15 $\mu\text{g/l}$. The average of intermediate and deep Cd enriched waters was 0.34 $\mu\text{g/l}$ (Sanzgiri *et al.*, 1981). As in all other oceans, the Pb concentrations were high in the surface waters of the Indian Ocean (0.04-0.5 $\mu\text{g/l}$). Recently Nakatsuka *et al.* (2007) have reported concentrations of Ni (3.0 $\mu\text{g/l}$), Cu (3.5 $\mu\text{g/l}$), Zn (9.5 $\mu\text{g/l}$), Cd (0.17 $\mu\text{g/l}$) and Pb (3.0 $\mu\text{g/l}$) in the open waters of the Indian Ocean.

The available results on the concentrations of metals in Suspended Particulate Matter (SPM) from coastal and offshore areas along the coast of India are compiled in Table 1.5.2. As in the case of dissolved metals, these concentrations also vary widely without any discernible trends. Often the concentrations of metals in SPM of shallow zones are comparable with those in the bed sediments as the SPM of shallow waters has its source in bed sediments.

1.5.2 Metals in organisms

Recent investigations on the concentration of metals in marine organisms of the Northern Indian Ocean are limited to only a few reports (Table 1.5.3). The past and recent data indicate general absence of bioaccumulation in the organisms studied except in localized areas receiving anthropogenic metals. The reported values of Cr, Co and Ni in organisms even in areas receiving industrial effluents are low. The concentrations of Cu and Zn are significantly high in molluscs. From the voluminous worldwide data available on Cu accumulation, it has been concluded that molluscs concentrate Cu to a high degree and are followed by crustaceans, macrophytes, annelids, tunicates, algae, achinoderms and coelenterates, in that general sequence (Eisler, 1979). High levels of Cu observed in lobster, crab etc is perhaps due to the storage of Cu in the liver and presence of haemocyanin in the blood. The limited data available from Mumbai region indicated variation of Cu in the range 0.88-34 $\mu\text{g/g}$ (dry wt) and for Zn 9.4-83.5 $\mu\text{g/g}$ (Matkar *et al.*, 1981). The concentrations of Zn for over 600 species of aquatic organisms have been tabulated by Eisler (1980). The greater concentration of Zn was

observed in filter-feeding bivalve molluscs, especially oysters. Oysters were reported to concentrate copper by 14000 times, zinc by 100000 times and cadmium by 300000 times the concentration in water. Though the average concentration of Cu dissolved in water of Goa was 4 µg/l, this was magnified by at least 15000 times on weight to weight basis in oysters (Zingde *et al.* 1976). In tissues of marine organisms Cr concentration usually varied in 0.1-2 µg/g (dry wt) (Fukai and Broquet, 1965). Relative high concentration of 4.5 µg/g (dry wt) reported in the tissue of fish from the Ulhas estuary was probably the reflection of anthropogenically added Cr in the estuary (Srinivasan and Mahajan, 1987).

Cd in the range 0.04-40 µg/g (wet wt) has been reported (Kureishy *et al.*, 1983) for marine organisms of the Andaman Sea. Estimates of mean concentrations of Cd found in different marine organisms from unpolluted areas have been published by Sanzgiri and Braganza (1981). Based on these estimates the concentrations of Cd of around 6 µg/g (dry wt) is expected in gastropod molluscs. Cd in the muscles of common food fishes off the coast of Bangladesh was in the range of 0.04-0.13 µg/g (dry wt) (Sengupta and Qasim, 2001). Cd was non-detectable in fish muscles from the strait of Malacca, while it was present (2.08-10.58 µg/g; dry wt) in shellfishes. The maximum permissible limit of Pb in the fishery products for human consumption, as set by FAO/WHO, lies in the range 1.0-2.0 µg/g (wet wt). Zooplankton from the coastal and open waters of the Northern Indian Ocean had concentrations in the range of 1.0-2.6 µg/g (wet weight) (Sengupta and Qasim, 2001). Wide ranges and highest concentrations of Pb were found in the livers and kidneys of some of the Northern Indian Ocean fishes. This indicates its greater affinity for fat solubility.

1.5.3 Metals in sediments

Table 1.5.4 indicates that the region has been, by and large, free from contamination by toxic metals though localised areas of enhanced levels of metals in sediment have been reported. Based on the

concentration of Cr in sediment of estuaries such as Cauvery and Godavari, the natural levels of this trace metal is of the order of 200 µg/g (Subramanian *et al.*, 1989). The concentrations of Co are generally below 60 µg/g and those of Ni are less than 100 µg/g in the coastal and estuarine sediments (Sabnis, 1984; Zingde *et al.*, 1989). Concentrations of Cu exceeding 130 µg/g in some locations is probably due to anthropogenic transfer (Sahu and Mukherjee, 1983; Sabnis, 1984; Bhosale and Sahu, 1991). The baseline concentration of Zn in the sediment of the region can be upto 150 µg/g while that of Cd appears to be about 1 µg/g. Likewise Pb concentration of around 25 µg/g probably represents the lithogenic fraction in these sediments (Subramanian *et al.*, 1989).

Due to release of Hg-containing effluent from chlor-alkali industry, high Hg burden in local sediments has been reported. In the zone of effluent release Hg concentration in sediment had increased to 456.7-2053.3 µg/g in the Rishikulya estuary (Shaw *et al.*, 1988). The Hg in sediment along Ulhas estuary decreased exponentially in the seaward direction with high concentrations (2.50-38.45 µg/g) confined to the inner 30 km segment and baseline (0.1 µg/g) had not attained even at 25 km off the estuary mouth (Ram *et al.*, 2003; Ram, 2004). High Hg concentration (49.19 µg/g) in the bottom section of a core from the effluent receiving site from Thane Creek has been shown to coincide with the commissioning of the chlor-alkali industry. Based on the concentration of Hg in sediments, depth of contamination, area of the region and sediment density total excess Hg in sediment has been estimated at 107.5 t for the Bay, 30 t for the Ulhas estuary and 77 t for the coastal area of Mumbai upto a distance of about 25 km from the shoreline (Ram, 2004).

1.5.4 Genesis of the study

Human activities in the marine environment of India are mainly confined to an area of about 1.8×10^5 km² associated with a long coastline of >7500 km, where the water depths are less than 50 m. Considering the vastness of the coastal area, the data on Al, Cr, Mn, Fe,

Co, Ni, Cu, Zn, Cd, Pb and P levels in seawater, marine sediments and biota is scanty and limited to a few areas. Of these, Mumbai-Bassein region that houses more than 8 % of the Country's industries has received relatively greater attention though exhaustive studies in recent years are missing. With this background the research scheme for the Thesis was planned to bridge the gaps as detailed below.

a) Metals in Thane Creek- Mumbai harbour

The Bay receives effluents from several industries established in the Chembur-Thane-Belapur belt and untreated domestic wastewater through several point sources. However, the contribution of Cr, Co, Ni, Cu, Zn, Cd, Pb and P to the anthropogenic loads by the industries and sewage have not been quantified. This information was necessary to assess relative contribution to metals in sediment by these 2 major polluting sources.

The past investigations on Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in the Mumbai-Bassein region were confined to the period when environmental awareness in India was in infancy whereby the industrial effluents entered the Bay without significant treatment. The scenario changed in early 1980s and industries were compelled to treat the effluent to the prescribed norms in a phased manner. The fluxes of metals and P through domestic wastewater, on the contrary would have gone-up due to increase in sewage throughput to the Bay from 2.5×10^5 m³/d in 1978 to 3.16×10^6 m³/d post-2000. Hence, it was considered worthwhile to revisit the Bay and freshly assess the metal burden in sediment with respect to the changed scenarios of anthropogenic fluxes of Cr, Co, Ni, Cu, Zn, Cd, Pb and P.

Taking the advantage of sedimentation rate reported for the Bay (Sharma *et al.*, 1994; Jha *et al.*, 1999; 2003) through ²¹⁰Pb dating it was possible to compare the reported sedimentation rates with the signature

of anthropogenic Cr, Co, Ni, Cu, Zn, Cd, Pb and P particularly in the zone of release of the effluent from industries and assess the extent of enrichment.

The Bay received high lithogenic flux estimated at $8.4 \times 10^5 \text{ m}^3$ annually through land runoff during monsoon (CWPRS, 1963) that is spread throughout the Bay under high tidal excursion and turbulence (Sharma *et al.*, 1994). Hence, it was interesting to quantify Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P content in soil and rock in the catchment and assess the influence of lithogenic flux of presumably low content of trace metals, on the Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P burden in sediments of the subtidal and intertidal zones of the Bay which could resolve seasonal changes if any.

Based on the distribution of selected metals in sediment cores from the Bay it has been suggested that the anthropogenic trace metals probably associated with the effluent streams either settled in the effluent drains prior to their entry in the Bay or the Bay was a passive link between the sources and the sink with much of the load transferred to the shelf (Patel *et al.*, 1985; Sharma *et al.*, 1994). With lack of data on industrial loads of metals to the Bay and high and variable natural levels of these metals in the sediment this issue had remained unresolved. If trace metals were transported to the sea their signature would be seen in sediments outside the Bay mouth. By estimating the sedimentation rate of a core of known metal profile, it would be also possible to establish the baseline metals in marine sediments of the region as well as the probable period of its excess accumulation in sediments.

It has been established that the bioavailability of trace metals in sediments depends on several factors (Lopez-Gonzalez *et al.*, 2008). To estimate the quantum of bioavailable metal in the sediment, surface and

selected core sections from the Bay were considered for investigating the extent of bioavailability of metals through sequential leaching.

b) Metals in Ulhas estuary

Cores retrieved from selected locations were investigated to establish the profile of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P distribution in the sediment column and evaluate inter-relationships. Historical time scale was introduced on the profiles of distribution of metals wherever possible by using available ^{210}Pb dating results.

c) Metals off northwest coast of India

In order to evaluate general distribution of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P, the inshore and openshore areas along the west coast were sampled at several transects in a direction perpendicular to the shoreline covering a maximum distance of about 25 km. It was therefore interesting to examine the trends in the variation of metals in these sediments and understand their association with the lithogenic constituents.

d) Metals in Gulf of Kachchh

The Gulf of Kachchh (Hereinafter referred as the 'Gulf') is one of the most bio-rich habitat along the west coast of India that has seen accelerated developments in terms of industries and ports in recent years (Chauhan *et al.*, 2000; Desa *et al.*, 2005). Apart from establishing the baseline Cr, Co, Ni, Cu, Zn, Cd, Pb and P levels in sediments of the Gulf, it was interesting to assess distinguishable variations if any in the metal content of sediments confined to its northern and the southern shores because of their predominantly different sources. It has been believed that the sediment of the northern coast finds its origin in the outflux of the Indus River while the sediment of the southern coast is largely derived from the adjoining landmass. Across the Gulf transport was considered to

be minor in view of the dynamic barrier of strong east-west currents to permit large-scale mixing (Nair *et al.*, 1982; Shetye, 1999)

All aforementioned issues form the base for this Thesis.

Table 1.5.1 : Concentration of dissolved metals ($\mu\text{g/l}$) along the coast of India											
Location	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Reference	
Mandovi Zuari (Goa)	-	-	-	-	-	2.0-63		-	-	Sankarayanan and reddy, 1973	
Mandovi-Zuari estuary	-	6-102	-	-	ND	3.0-8.0	6.0-42	-	-	Zingde <i>et al.</i> , 1976	
Mandovi-Zuari mouth	-	16-25	-	-	-	3.0-72	3.0-12	-	-		
Goa	-	42	19	0.8	5	4	16	-	-	Zingde and desai, 1987,	
Velsao Bay	-	13-16	27-56	-	ND	6.0-8.0	11.0-16.0	-	ND	Zingde <i>et al.</i> , 1979	
Cochin Backwaters	-	-	-	-	-	0.8-7.0	0.5-11.3	-	-	Sankarayanan <i>et al.</i> , 1978	
Periyar River	-	-	0.8-1.2	-	0.2	0.8-10.0	24-65	0.2	8	Ouseph, 1992	
Cochin estuary			0.2-0.8		0.3-0.6	2.2-22.2	105-385	1.8-4.2			
Karwar	-	2.3-10.2	9-26.2	-	-	0.8-4.2	3.1-20.1	-	-	Zingde and Singbal, 1983	
Thal	-	-	-	ND	ND	7	15	-	3	Zingde and desai, 1987	
Mumbai Harbour	20	8	3	0.5	0.5	16	27	0.1	4	Patel <i>et al.</i> , 1985	
Mumbai Harbour	-	8	3	0.5	0.5	6	27	0.1	4	Zingde and Desai 1987	
Thane Creek	-	5-169	8.0-35	ND-1.5	ND-9.5	10.0-66	17-121	-	-	Zingde, 1985	
Thane Creek	-	16	16	0.5	2.9	19	21	-	-	Zingde and Desai, 1987	
Thane Creek off	-	5	20	ND	ND	9	20	-	-		
Thane Creek/Bombay Harbour	-	-	7.0-29	ND-0.5	ND-1.8	8.0-15	15-28	-	4.0-12	Zingde <i>et al.</i> , 1989	
Thane Creek	-	2.4-17.5	27.0-147.2	1.0-6.7	3.3-12.3	5.8-21.5	21.7-132.0	1.1-1.8	7.8-27.2	Sahoo and Khopkar, 1987	
Thane Creek	-	3.3-99.5	16.5-40.3	2.5-4.9	6.8-14.3	5.2-15.6	38.7-93.6	1.3-2.8	19.2-25.1	Bhosale and Sahu, 1991	
Mahim coastal	-	-	17-44	0.9-0.9	3.0-6.0	12.0-15.0	103-121	-	-	Sabnis, 1984	
Mahim Bay	-	-	14-16	1.0-2.0	4.0-10.0	10.0-16.0	40-75	-	-		
Mahim Creek	-	-	14-186	0.6-1.0	3.0-12.0	2.0-5.0	23-112	-	-		

Table 1.5.1 (Continued...)										
Location	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Reference
Mahim (upstream)	-	-	43-1147	2.0-6.0	11.0-51	3.0-20	6.0-98	-	-	
Mahim coastal	-	4-169	-	ND-1.5	ND-9.5	10.0-66	17-121	-	-	Zingde, 1985.
Ulhas estuary	-	-	0.2-0.6	-	-	-	10-1000	-	-	Kulkarni and Desai, 1980
Ulhas River	-	4.5-10.8	27.5-34.4	3.2-4.8	14.5-18.4	7.9-15.5	18.7-76.0	1.4-2.1	20.4-29.8	Bhosale and Sahu, 1991 (part II)
Tarapur	-	8	17	2	1	25	57	-	-	Zingde and Desai, 1987,
Damanganga estuary	-	-	1.0-21	-		3.0-8.0	5.0-30	-	-	
Kolak estuary	-	-	2.0-30	-		1.0-8.0	3.0-19	-	-	
Kolak estuary	ND-102	3.5-106	-	ND-17.3	ND-22.6	1.2-17.2	1.9-34.6	-	-	Zingde <i>et al.</i> , 1980
Auranga	-	-	8.0-14	-		3.0-6.0	8.0-15.0	-	1.0-2.0	Zingde and Desai, 1987,
Ambika	-	-	10.0-22.0	-		2.0-7.0	7.0-18.0	-	-	
Purna	-	-	9.0-16.0	-		4.0-8.0	8.0-21.0	-	2.0-5.0	
Mindhola estuary	-	-	-	-	-	3.0-16.0	6.0-48.0	-	ND-6.8	
Tapi	-	-	0-50	-		1.0-10.0	1.0-20.0	-	-	
Veraval	-	-	12	ND	ND	9	13	-	3	
Arabian sea	-	-	7.2-66.9	ND-6.6	ND-11.5	2.5-7.9	5.5-42.4	-	-	Sen Gupta <i>et al.</i> , 1978
Northern Indian Ocean	-	-	-	-	-	-	-	0.04-0.26	0.04-0.5	Sen Gupta and Qasim, 2001
Bay of Bengal	-	3.33	3.06	0.67	4.81	3.94	18.31	-	-	Rajendran <i>et al.</i> , 1982
Bay of Bengal (Diamond Harbor)	-	90-350	30-560	-	-	7.0-90	150-710	-	12.0-62	Sarkar <i>et al.</i> , 2007,
Indian ocean open ocean	-	-	-	-	3	3.5	9.5	0.17	3	Nakatsuka seiji <i>et al.</i> , 2007
Central west coast of India	-	-	-	-	-	3.0-46	-	-	-	Sankarayanan and reddy, 1973
Andaman sea	-	2.7-24.7	2-21.7	-	-	1.0-5.0	2.1-12.7	0.3-2.0	ND-6.2	Sanzgiri and Braganga , 1981
Laccadive Sea	-	12-38.5	19.4-43.4		2.5-10.1	7.2-13.3	7.2-33	-	-	Sanzgiri S and Moraes, 1979

Table 1.5.2 :Concentration of metals ($\mu\text{g/g}$, dry wt) in SPM along the coast of India

Location	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Reference
Cochin estuary	-	-	9.4-9.8	-	5.0-53	76-298	318-3100	65-180	81-260	Ouseph, 1992
Thane Creek	-	1314-1932	7.0-7.4	-	-	212-276	155-224	-	-	Matkar <i>et al.</i> , 1981
Thane Creek	-	389-4485	10.4-67.0	11.3-43.4	34-209	54-304	123-709	0.9-6.2	16-200	Bhosale and Sahu, 1991
Ulhas estuary	-	102-1950	14.8-52.0	12.9-42.4	42-144	26-136	63-171	1.6-4.7	33-434	Bhosale and sahu, 1987
Thane Creek	-	-	-	-	-	-	-	2.05-5.10	-	
Ulhas estuary	-	-	-	-	-	-	-	1.80-3.75	-	
Mahim Creek(upstream)	275-2739	127-718	-	14-44	48-317	250-999	562-5187	8-143	62-340	Sabnsis, 1984
Mahim Creek	156-234	322-375	-	194-276	186-348	283-348	1284-2964	39-371	16-71	
Mahim coastal	92-354	555-646	-	0-310	0-1216	135-176	538-1577	135-342	134-277	
Mahim coastal	-	322-646	-	25-276	32-348	135-489	538-2964	1.35-4.27	1.34-37.1	Zingde, 1985.
Mindhola estuary	-	905-1362	-	-	54-131	87-213	102-332	-	3.0-62	Zingde <i>et al.</i> , 1988
Tapi estuary	-	1120-1569	-	-	64-94	129-208	93-299	-	-	Borole <i>et al.</i> , 1982
Narmada estuary	-	799-1482	-	-	54-97	78-147	84-184	-	-	Borole <i>et al.</i> , 1982
Arabian Sea	-	12.0-3333	260-69583	-	-	33-1417	305-204750	-	-	Sen Gupta <i>et al.</i> , 1978
Andaman Sea	-	ND-696	247-44182	-	-	ND-521	86-6160	ND-95	ND-1899	Sanzgiri and Braganga, 1981
Laccadive Sea	-	67-210	1247-3166	ND	25-44	58-233	573-1685	-	-	Sanzgiri and Moraes, 1979
Cauvery estuary	246	1968	39500	-	379	55	347	3410	38	Subramanian <i>et al.</i> , 1989
Bay of Bengal	-	-	-	ND-1.34	ND-0.79	-	-	-	ND-2.75	Rajendran <i>et al.</i> , 1982

Table 1.5.3: Concentration of metals ($\mu\text{g/g}$, dry wt) in biota										
Location	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Reference
Mandovi and Zuari Off	-	4.0-26.0	-	-	-	2.0-29	8.0-48	-	-	Zingde <i>et al.</i> , 1976.
Mandovi and Zuari	-	3.0-18	-	-	-	251-728	446-2800	-	-	
Mandovi and Zuari	-	15-21	-	-	-	22-48	22-70	-	-	
Mandovi (P. Malabarica)	-	-	105.7	-	-	13.5	36.6	3.8	30.3	Krishnakumari <i>et al.</i> , 2006
Velsao Bay (Molluscs)	-	10.0-62	362-820	-	0.5-4	280-362	1300-3000	-	1.5-12	Zingde <i>et al.</i> , 1979
Mumbai Harbour (Sewari)	2.7	49900	1500	3.5	10.8	11.1	132	2.8	-	Patel <i>et al.</i> , 1985
Thane Creek (fish)	-	-	-	-	0.3-1.2	1.2-4.8	20.7-45.3	0.03-0.18	0.03-0.1	Krishnamurti and Nair, 1999.
Bassein Creek (fish)	-	-	-	-	0.4-0.9	0.5-8.3	11.4-63.1	0.02-0.4	0.03-0.1	
Mumbai Harbour (fish)	0.78	-	-	-	0.68	0.31	8.36	0.02	0.08	Mishra <i>et al.</i> , 2007
Ulhas estuary	4.5	2.3	63	4.5	0.3	5.9	11.6	0.5	11.6	Srinivasan and Mahajan, 1987
Ulhas estuary	2.1-3.3	1.5-6.8	26-120	0.6-8.5	0.5-1.2	2.1-17.2	10-22.4	ND-0.7	7.0-32	
Northern Indian Ocean	-	ND-10.0	-	ND-3.8	ND-0.9	ND-4.5	ND-21.0	ND-2.0	0.06-6.02	Sen Gupta and Qasim, 2001
Damodar River (Ganga tributary)	5962	147-819	0.3-3.02	-	3.0-28	11.0-64	15-66	-	-	Abhay Kumar Singh, 1999.
Northern Indian Ocean	-	3.0-7.0	-	ND-4.0	0.06-3.0	0.7-24.0	8.0-31.0	0.002-5.99	ND-0.17	Sen Gupta and Qasim, 2001
Northern Indian Ocean	-	-	-	-	-	45	-	1.36	1	
Kenya (Oyster)	-	-	-	-	-	-	-	2.3-9.1	-	
Kenya (Scallop)	-	-	-	-	-	-	-	2.2-4.5	-	
Mombasa (Fish muscles)	-	-	-	-	-	-	-	0.1-0.9	-	
Mombasa (Fish scales)	-	-	-	-	-	-	-	0.8-0.21	-	

Table 1.5.4: Concentration of metals ($\mu\text{g/g}$, dry wt) (except Fe in %) in sediment along the coast of India											
Location	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Reference
Zuary estuary	-	-	-	-	-	-	-	-	-	0.1-0.3	Seralathan and Seetaramaswamy, 1979
Cochin Backwaters	-	72-256	-	10.0-38	22-83	17-47	102-348	-	-	-	Venugopal <i>et al.</i> , 1982
Vembanad Lake	-	183-387	-	37-49	28-41	21-60	-	-	-	37-1678	Murty and Veerayya, 1981
Bombay Harbour	-	460-2500	-	7.0-23	-	40-245	75-350	-	-	51-245	Gogte and Shah, 1976
Bombay Harbour Bay	-	746-1318	7.0-8.0	-	-	162-276	153-292	-	-	-	Matkar <i>et al.</i> , 1981
Mumbai Harbour	124	1140	8.6	50	111	105	155	10	48	-	Patel <i>et al.</i> , 1985
Bombay coast	102-120	886-1216	6.5-7.4	31-57	42-59	87-106	95-147	-	9.0-36	-	Dilli, 1986
Bombay Harbour	-	719-1059	6.7-8.1	35-51	112-146	105-142	127-206	-	20-48	-	Zingde <i>et al.</i> , 1989
Thane Creek	-	-	-	-	-	-	-	-	3.0-4.95	-	Bhosale and sahu, 1987
Thane Creek	-	860	7	37	105	103	170	2.29	54	-	Mahapatra, 1988
Thane Creek	-	-	-	-	-	231	169	1.2-2.0	31	-	Athale and Gokhale, 1989
Thane Creek	29-63	210-1274	-	34-59	91-130	91-240	114-273	1.7-6.1	54-143	-	Bhosale and Sahu, 1991
Mahim Bay	41-123	456-1132	-	19-35	49-82	71-150	48-345	1.5-4.5	15-41	790-1235	Sabnis, 1984
Mahim Creek	31-154	430-1002	-	20-36	38-67	70-327	75-799	2.4-8.2	13-41	698-1620	
Mahim upstream	31-950	300-996	-	10.0-90	30-183	100-3000	44-6740	1.6-14	20-510	873-3738	
Mahim coastal	29-200	422-1036	-	11.0-30	35-61	93-123	135-291	1.6-604	22-32	223-1105	
Mahim coastal	-	660-1059	-	43-59	89-175	105-198	110-308	0.5-3.3	25-42	-	
Ulhas estuary	-	-	-	-	-	-	-	-	1.69-5.10	-	Bhosale and sahu, 1987
Ulhas estuary	30-51	195-1024	-	31-61	70-133	61-150	96-183	1.7-5.3	30-68	-	Bhosale and Sahu, 1991
Ulhas estuary	64-104	139-285	5.4-6.9	35-47	65-91	77-109	74-187	1.0-2.9	28-41	-	Srinivasan and Mahajan, 1987
Ulhas estuary	250-662	-	-	-	-	100-306	500-1769	1.6-6.1	48-170	-	Sahu and mukharjee, 1983
Tapi estuary	-	1125	7.6	-	70	128	125	-	-	-	Borole <i>et al.</i> , 1982
Narmada estuary	-	1077	8.9	-	81	136	140	-	-	-	
Arabian Sea	-	1034-1212	-	-	66-87	99-130	109-204	-	-	-	Borole <i>et al.</i> , 1982
Caury estuary	229	1310	3.4	-	379	33	75	-	38	-	Subramanian <i>et al.</i> , 1989
Ganges estuary	98	732	4.2	-	49	44	151	-	32	-	
Krishna estuary	174	6978	10	-	149	69	1482	-	4	-	
Godavari estuary	128	1294	7.6	-	91	119	-	-	5	-	
Bay of Bengal	84	529	3.9	-	64	26	-	-	-	-	
Ganges estuary	147	1765	4	19	47	55	105	0.58	22	-	Singh <i>et al.</i> , 2003

CHAPTER 2

MATERIALS AND METHODS

The methods of sampling, processing, storage and analysis of sediment, SPM and organisms used for generating the data presented in this Thesis are discussed in this chapter.

2.1 Sampling locations

The sampling domain was confined to the coastal and inshore zones of the west coast of India between the Kori Creek in the north and Ratnagiri in the south over a distance of 3000 km (Figure 2.1.1). The sampling stations are illustrated in Figures 2.1.2 to 2.1.11.

2.2 Sediment

Surface sediment was obtained from all stations in Figures 2.1.2 to 2.1.11, while sediment cores were obtained from selected sites.

2.2.1 Collection

Surficial subtidal sediment was collected with the help of a van Veen type grab sampler, while the intertidal sediment was obtained using a plastic hand held shovel. The grab in open condition tied to a nylon rope was lowered in water and when it reached the seafloor, the rope was buzzed whereby the hook was released closing the grab halves thereby trapping the sediment within the grab. The grab was carefully retrieved on board the vessel and the contents were transferred to a clean polyethylene tub. The sediment was sub sampled in a plastic

bag/container, using a plastic scup. About 2-5 cm deep sediment from the intertidal zone was scooped with a shovel and directly transferred to a plastic bag/container.

Sediment cores were obtained with a gravity corer which is a device that is tied to a wire rope and allowed to freely fall from a ship. The corer penetrates the seafloor by gravity due to heavy weights (80 kg) at the top end and has a cutter at the other end. A 1.8 m long transparent acrylic liner with the inner diameter of 5.5 cm was inserted in the barrel of the corer to hold the sediment when the corer penetrates the seafloor. The catcher previously inserted in the barrel just above the core cutter, gets closed due to weight action of the sediment contained in the core liner, when the corer is hauled up on board the ship.

The gravity cores were retrieved from stations B23, B24, B25, U34, U35, U37 and R5 [Figures 2.1.2 and 2.1.6 (a)]. Cores from the shallow subtidal and intertidal zones of the Thane Creek (Figure 2.1.2), Ulhas estuary [Figure 2.1.6(a,b)] and the Gulf [Figures 2.1.8 (a,b)] were collected during low tide by pressing an acid clean acrylic tube in the soft sediment till it reached the hard stratum below. The tube was lifted carefully taking utmost care so that the material in the bottom portion of the tube did not slip out. The locations from where the cores were obtained are given in the table below:

Transect	Station	Latitude	Longitude
Thane Creek- Mumbai Harbour	B1	19° 10'646" N	72° 59'029"E
	B2	19° 08'031" N	72° 58'557"E
	B3	19° 07'566" N	72° 58'140"E
	B4	19° 04'059" N	72° 57'485"E
	B5	19° 03'714" N	72° 56'794"E
	B6	19° 59'198"N	72° 51'583"E
Thane Creek- Mumbai Harbour off	B23	18° 52'48"N	72° 44'48"E
	B24	18° 52'48"N	72° 39'48"E
	B25	18° 52'48"N	72° 33'48"E
Ratnagiri	R5	16° 59'00" N	73° 02'30"E

Transect	Station	Latitude	Longitude
Ulhas estuary	U3	19° 18'811" N	73° 11'007"E
	U4	19° 19'032" N	73° 11'189"E
	U5	19° 19'304" N	73° 11'95"E
	U23	19° 13'049" N	73° 00'539"E
	U30	19° 14'853" N	73° 07'078"E
	U32	19° 18'811" N	73° 00'007"E
Ulhas estuary off	U34	19° 18'24" N,	73° 44'48" E
	U35	19° 18'30" N	73° 39'16"E
	U37	19° 18'30" N	73° 33'00" E
Gulf of Kachchh	OD1	22° 23'323"N	69° 05'312"E
	OD2	22° 23'628" N	69° 05'212"E
	OD3	22° 23'343" N	69° 05'311"E
	OE	22° 23'623" N	69° 05'650"E
	OF	22° 23'628" N	69° 06'212"E
	OG	22° 23'628" N	69° 00'212"E
	VN16	22° 29'184" N	69° 45'302"E
Location of catchment area			
Mahableshwar		17°57'56" N	73°40.02' E
Lonavala		18°46'26" N	73°21'14" E
Khandala		18°45'26" N	73°21'51" E
Malshej		19°20'8" N	73°47'32" E
Igatpuri		19°41'49" N	73°30'58" E

After the corer was retrieved, the liner was removed from its barrel and was smoothly cut with a cutter at the interface with water in the tube. The open ends were capped and the liner was placed in a deep-freezer before transporting to the laboratory at Mumbai. In the laboratory the sediment core was carefully removed from the acrylic liner on a clean plastic sheet by holding the bottom end of the liner and carefully inserting a closely fitting wooden plunger. As the plunger pushed the sediment core out on the plastic sheet, the liner was pulled in the other direction till the core was completely freed from the liner. Extreme care was taken to minimise the disturbance to the sediment. The length of the core was measured and the sediment was sliced at every 1 cm interval using a clean non-metallic cutter. The sliced sub-samples were immediately transferred to clean wide mouth plastic jars. The required sub-sample was dried at <60° C in an oven as recommended (Loring and Rantala, 1992).

2.2.2 Storage

Dried sediment was manually ground in an agate mortar and stored in a screw capped plastic vial (20 ml capacity). The sample was sieved through a 63 µm sieve prior to analysis to ensure homogeneity.

2.2.3 Analysis

Metals were analysed by Atomic Absorption Spectroscopy (AAS), while, phosphorus and calcium carbonate were estimated by well-established procedures (Loring and Rantala, 1992; Barnes, 1959).

a) Metals

Flame AAS was used for estimating Al, Cr, Mn, Fe, Co, Ni, Cu and Zn while Graphite Furnace (GF) AAS was employed for analysing Cd and Pb.

i) Flame AAS

In flame AAS, aqueous metal solution is converted into an aerosol with the help of a nebulizer placed in the sample cell and the resulting fine droplets of the solution are injected into the flame. At the high temperature of the flame, the metal present in the solution is converted into its atoms in the path of a specific radiation source. The atoms of the metal absorb the radiation and the extent of radiation absorbed is directly proportion to the number of atom i.e. the concentration of the metal present in solution aspirated in the flame. This is mathematically described as

$$A = \log I_0/I_t$$

Where, A=absorbance;

I_0 =initial intensity of radiation; and

I_t =intensity of radiation after passing through the sample.

Resultant radiation from the hollow cathode lamp after absorption by the atoms of the metal under analysis is passed through a monochromator where selection of required path of dispersed spectra is achieved. Subsequently, the light signal passes through a photomultiplier detector. In the photomultiplier the light beam penetrates photocathode

and multiplies. At the end, the amplified light signal is converted into current and recorded by the recorder.

Sample digestion: About 0.5 g of the ground sediment was accurately weighed on a single pan analytical balance (Sortorius: BP2110; D=0.01 mg) and transferred to a clean Teflon beaker (50 ml) followed by the addition of HF (10 ml), HClO₄ (5 ml), HNO₃ and HCl (10 ml) to the contents. The beaker was heated continuously at elevated temperature on a sand bath mounted on a hot plate, till dryness. Subsequently, the beaker was removed from the sand bath, cooled and 25 ml of HCl (6 M) was added (Windom, and Cutshall, 1976). The solution was transferred to a 50 ml volumetric flask. The beaker was rinsed several times and rinsings were also transferred to the same flask. The reagent blank in triplicate was simultaneously prepared with each set of samples following similar procedure but without the sediment. The specifications of acids used in wet digestion are as follows:

Acid	Merck catalogue no
Nitric acid	17525
Perchloric acid	519
Hydrofluoric acid	338
Hydrochloric acid	10125

Calibration and analysis: Commercially available (Merck, Germany) standards were used to prepare 100 mg/l intermediate standard solutions of these metals in HCl (1%) while those for Al were prepared directly. The specifications of the standards used are given in the table below:

Element	Stock (mg/l)	Merck catalogue no	Working standard (mg/l)
Al	1000	1.1977.0500	40, 60, 80, 100
Cr	1000	1.19779.0500	0.25, 0.5, 1.0, 2.0
Mn	1000	1.19789.0500	0.25, 0.5, 1.0, 2.0
Fe	1000	1.19781.0500	0.25, 0.5, 2.0, 4.0, 6.0
Co	1000	1.19785.0500	0.25, 0.5, 1.0, 2.0
Ni	1000	1.19792.0500	0.25, 0.5, 1.0, 2.0
Cu	1000	1.19786.0500	0.25, 0.5, 1.0, 2.0
Zn	1000	1.19806.0500	0.1, 0.25, 0.5, 1.0

Auto pipette (Merck, Transferpette catalogue no 701782) was used for accurately pipetting the required quantity. Different working standard solutions were prepared by serial dilution of the stock solution in 100 ml volumetric flasks.

In the present study the light source was a hollow cathode lamp of the same element that was to be analysed. Either air-acetylene (Cr, Mn, Fe, Co, Ni, Cu, and Zn) or nitrous oxide–acetylene (Al) flame was used to obtain desirable temperature during analysis as recommended (Loring and Rantala, 1992; Hageman and Welsch, 1998).

The instrument was set for the best optimisation and maximum sensitivity by controlling the lamp and slit alignment to achieve maximum emission without sample and flame. Similarly, flame was adjusted during optimisation in the absence and the presence of the standard. Calibration range was selected for linear region where the Beer Lambert's law was applicable. Details of the instrumental parameters used are as follows:

Element	Wave-length (nm)	Oxidant/ Fuel	Slit (nm)	Detection limit (mg/l)	Sensitivity (mg/l)	Optimum working range (mg/l)
Al	309.3	N ₂ O-Acetylene	0.5	0.3	0.5	40 –100
Cr	357.9	Air-Acetylene	0.7	0.003	0.05	0.5-5.0
Mn	279.5	Air-Acetylene	0.2	0.01	0.05	0.25-2.0
Fe	248.3	Air-Acetylene	0.2	0.005	0.02	0.25-6.0
Co	240.7	Air-Acetylene	0.2	0.004	0.05	0.25-3.5
Ni	232.0	Air-Acetylene	0.2	0.009	0.04	0.25-2.0
Cu	324.8	Air-Acetylene	0.7	0.001	0.02	0.25-5.0
Zn	213.9	Air-Acetylene	0.7	0.005	0.008	0.1-1.0

Optimisation of the analytical condition for Al, Cr, Mn, Fe, Co, Ni, Cu and Zn was achieved with 40, 5, 2, 6, 2, 2, 2 and 1 mg/l concentration

of the metal respectively, against Milli-Q water for auto zero. Because of high concentrations of metals, the sample solutions were diluted with Milli-Q water as follows:

Metal	Dilution (times)
Cr, Co, Ni, Cu	50
Mn, Zn, Al	500
Fe	5000

The AAS used in the present study had the facility to directly display the concentration of the metal in the sample under analysis. From the knowledge of the sediment content taken for digestion and dilution of the digest, the concentration of the metal in sediment was calculated and expressed on dry weight basis.

ii) Graphite Furnace AAS

Graphite furnace is a flameless device. The energy required for atomization is supplied by passing a high electrical current through a graphite tube containing the sample. The furnace is aligned into the sampling area of spectrometer between hollow cathode lamp and photomultiplier tube in such a way that the light from the spectral lamp passes through the centre of graphite tube. The atomic vapour generated from the sample absorbs the light, which is proportional to the concentration of the element in the sample. With this technique elements can be determined typically at 1000 times lower concentration levels than those in flame AAS with a consumption of only a few microliters of the sample.

Components of the graphite furnace system: The graphite furnace is made up of three major components, the atomizer, the power supply, and the programmer. The atomizer is located in the sampling compartment of the atomic absorption spectrometer, where sample atomization and light absorption occur. The power supply controls power and gas flows to the atomizer under the direction of the programmer, which is usually built into the power supply or spectrometer. The major components of the graphite

furnace atomizer are graphite tube, electrical contacts, water cooled housing and inert purge gas control. A graphite tube is normally the heating element of the graphite furnace. The cylindrical tube is aligned horizontally in the optical path of the spectrometer and serves as the spectrometer sampling cell. A few microliters of samples are measured and dispensed through a hole in the center of the tube wall onto the inner tube wall. The tube is held in place between two graphite contact cylinders, which provide electrical connection. An electrical potential applied to the contacts causes current to flow through the tube, the effect of which is heating of the tube and the sample. The entire assembly is mounted within an enclosed, water-cooled housing. Quartz windows at each end of the housing allow light to pass through the tube. The heated graphite is protected from air oxidation by the end windows and two streams of argon.

The power supply and programmer control electrical power, temperature, gas and spectrometer functions. The spectrometer control functions can be programmed to occur at specified times within the graphite furnace programme. While the number of steps within each programme is variable, 6 steps namely drying, pyrolysis, cool down, atomization, clean out and cool down make up the typical graphite furnace programme.

Sample size: Since the graphite furnace signal depends on analyte mass, there is an effective degree of control on measured absorbance by controlling the sample volume. The sample volume up to 30 μl was used during the present study. Auto sampler was used for dispensing the sample as well as to generate working standards from stock solutions, add appropriate reagents, and provide method of addition and recovery measurements automatically.

In order to overcome difficulties due to physical and chemical mismatch between the sample and standards, generally the standard addition method was used for analysis. The built-in computer programme

calculates a least-squares regression line through the calibration points and computes the sample concentration directly by mathematical extrapolation. Instrumental sensitivity was checked as per the manual supplied by manufacturer.

Sample digestion: About 0.1 g of the ground sediment was accurately weighed and transferred to a clean Teflon beaker. The sample was brought into solution using Suprapure acids (Merck German).

Acid	Merck catalogue no
Hydrofluoric acid	1.00335.0500
Perchloric acid	1.00519.1000
Nitric acid	1.00441.1000
Hydrochloric acid	1.00318.1000

Details of the instrumental parameters used for the determination of Pb and Cd are as follows:

Element	Wave-length (nm)	Slit (nm)	Characteristic mass	Sensitivity check
Cd	228.8	0.7	1.3 pg/0.0044Abs	2.0 µg/l for 0.13 Abs
Pb	283.3	0.7	30 pg/0.0044Abs	50 µg/l for 0.15 Abs

The matrix modifier used for the estimation of these metals was a combination of 0.05 mg $\text{NH}_4\text{H}_2\text{PO}_4$ (0.05 mg) and $\text{Mg}(\text{NO}_3)_2$ (0.003 mg). For both metals 10 µl of sample volume, standard volume and matrix modifier was used. The concentration range for standards used were 0.2, 0.5 and 1.0 µg/l for Cd and 5.0, 10.0 and 20 µg/l for Pb.

Furnace programme for Cd and Pb was comparable except for temperature. The different parameters used are compiled in the following table with values for Pb in parentheses.

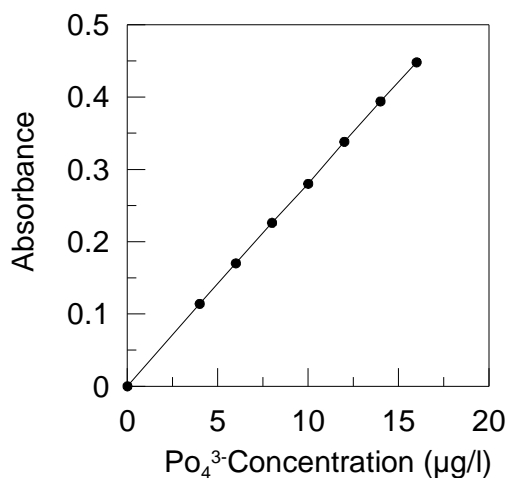
Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow (ml/min)
Dry 1	110 (110)	1	30	250
Dry 2	130 (130)	15	30	250
Pyrolysis	500 (850)	10	20	250
Atomization	1500 (1600)	0	5	0
Clean-out	2450 (2450)	1	3	250

The gas flow (argon gas) was maintained at 250 ml/min in all stages except atomization stage when the flow was stopped.

Sample analysis: A known volume of sample was dispensed into the furnace. The sample was then subjected to a multi-step temperature programme. When the temperature was increased to the point of atomization, absorption measurement was made.

b) Phosphorus

The sediment (0.5 g) was digested with conc HF, HClO₄, HNO₃ and HCl in order to release organic phosphorus. An acid-ammonium molybdate reagent was added to a suitable volume of the digested sample. The resulting phosphomolybdate complex was reduced to an intense blue complex using ascorbic acid reagent and the intensity of the colour was measured at 882 nm (Grasshoff, 1983). The calibration graph of P concentration versus absorbance is illustrated in the following figure:



c) Carbonate

Carbonate in sediment (0.5 g) was reduced to carbon dioxide with dilute HCl (1.0 N) and excess acid was estimated using NaOH (1.0 N) solution standardised against potassium hydrogen phthalate. The difference with the blank gives quantity of acid utilized by carbonate in sediment (Bernes, 1959). The percentage of carbonate in the sample was calculated using the following equation:

$$\text{CO}_3^{2-} (\%) = [\text{Br}(b) - \text{Br}(s)] \times 5 \times N / \text{wt of sediment}$$

Where, Br(b) = Mean burette reading for blank

Br(s) = Burette reading of sample

2.2.4 Quality control

The results of analysis were quality controlled through the determination of precision expressed in terms of standard deviation (SD). Wherever Certified Reference Materials (SRM_s) are available the accuracy of the results can be determined. In the present study SRM_s namely BCCS-1 and PASC-1 supplied by the National Research Council of Canada were used to ascertain the accuracy of analysis for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in sediment.

Replicates of SRM_s were analysed to determine precision and accuracy. The results are given in Tables 2.2.1. For constituents such as P and CO₃²⁻ in sediment where SRMs were not available, replicates of a representative sample was analysed to determine precision. These results are given in Table 2.2.2.

2.3 Sedimentation rate

Clay accumulation rate in cores B2, B23 and B24 was attempted through ²¹⁰Pb dating technique.

2.3.1 Sampling

Sediment cores obtained as detailed in Section 2.2.1 were used for the estimation of sedimentation rate. Dry powdered sediment from each section of the selected core was stored for more than 10 months to allow secular equilibrium between ^{210}Pb and its grand daughter ^{210}Po .

2.3.2 Analysis

About 2.0 g or more dried and grounded sediment was accurately weighed and transferred to a clean Teflon beaker (250 ml) followed by the addition of precisely known amount of ^{208}Po to the sample. Conc HF (10 ml) was added to the contents and the beaker was heated at 150 °C on a sand bath mounted on a hot plate. After some time (nearly 1-1.5 h) another aliquot of conc HF (10 ml) was added to the cooled sample and the beaker reheated on sand bath to decompose most of silicates as evident from the whitish residue left in the beaker. Conc. acids: HClO_4 , HNO_3 , HCl (each 10 ml; twice), were added successively followed by evaporation to achieve complete digestion of the sediment. After two times digestion with conc HCl , the residue became yellowish-orange. The solution was evaporated to dryness (3 times) with the addition of small quantities of conc HCl after each drying. Finally, the volume was made to 30-50 ml with 0.6 M HCl . Since Po is adsorbed strongly on glass surface, polyethylene bottles were used to store the solution and for analysis. The whole solution was quantitatively transferred to a polyethylene beaker and Po in the solution was plated on an Ag disc (1 cm diameter; 0.5 mm thick). To ensure plating only on one side, the other side of the disc was carefully covered by plastic tape. The surface, on which Po was to be deposited, was cleaned and buffed with silver-polish to make the surface smooth and scratch free.

The ^{210}Po in solution was plated on the Ag disc after masking Fe present in the solution with ascorbic acid (pinch). Due to the difference in electronegativity between Po and Ag , Po gets self-plated on the Ag disc. Plating was carried out in warm condition (60–65 °C) for 3 h by placing the beaker on a hot plate magnetic stirrer that also facilitated slow stirring

of the solution. After plating, the disc was removed, rinsed with Milli Q water and allowed to dry.

Each radioactive decay of ^{210}Po emits a α particle that has energy of 5.3 MeV. The tracer and the parent have different energy of emission and thus can be identified using a α spectrometer. The spectrometer consists of a surface barrier detector, preamplifier, amplifier, mixer router, analogue to digital converter, multi-channel analyzer and appropriate computer software. The sample was counted for a period of 6 to 48 h depending upon the activity of ^{210}Po in the sample. The activity of ^{210}Po in the sample was determined from the ratio of the total counts of ^{208}Po to ^{210}Po and from the quantity of sediment taken for analysis as well as ^{208}Po tracer added to the sample.

The activity of ^{210}Po was used to determine the total ^{210}Pb present in the sample. Subsequently, excess ^{210}Pb was estimated by subtracting supported ^{210}Pb from total ^{210}Pb . The ^{210}Pb content of sediment of the bottom sections of the core was considered as the supported ^{210}Pb . Sediment accumulation rate was determined from the slope of the least square fit for exponential decrease of excess ^{210}Pb as a function of depth of the sediment in the core, using constant initial concentration method (Robbins and Edginton, 1975; Goldberg *et al.*, 1977).

2.4 Domestic sewage

2.4.1 Sampling

Domestic sewage at selected pumping stations namely Bhandup, Colaba, Dharavi, Malad and Versova (Figure 2.1.2) was sampled using a clean polythene bucket and about 1000 ml was transferred to a clean polythene bottle. Conc HNO_3 (2 ml) was added to the bottle to lower the pH below 2 and the bottle was transported to the laboratory. The collections were made during June 1998, November 2001, February 2002, May 2002, April 2004, February 2005, March 2005, April 2005 and May 2005.

2.4.2 Storage

The bottle was stored in a refrigerator before analyses that was generally completed within 60 d from the collection.

2.4.3 Analysis

Metals and phosphorus

Method recommended by US EPA, (1979) was adopted for the estimation of metals in sewage samples. Unfiltered acidified sewage (400 ml) was transferred to a beaker and conc HNO₃ (3 ml) was added. The contents were evaporated to near dryness, cooled, another aliquot of conc HNO₃ (3 ml) was added and again evaporated. The process of adding conc HNO₃ and evaporation was repeated till the digestion was complete as signified by pale yellow residue in the beaker after evaporation. The residue was dissolved in dilute HCl (1:1) and the volume made to 25 ml in a volumetric flask. The blanks in triplicate were prepared following the same procedure but without sewage. These digests were used to estimate Al, Cr, Mn, Fe, Co, Cu, and Zn by flame AAS as described in section 2.2.3 (i); phosphorous estimation as described in Section 2.2.3 (b); and Cd and Pb by Graphite Furnace AAS as described in Section 2.2.3 (ii).

2.5 Sequential extraction

Selected surface and core sediments from the Bay were subjected to sequential extraction using the procedure developed by Tessier *et al.*, 1979.

2.5.1 Fraction I (Exchangeable phase)

Dry and powdered sediment (2 g) was taken into a 50 ml aged PVC centrifuge tube and MgCl₂ solution (1M) (16 ml) at pH 7.0 was added to it. The reagent blank in triplicate was simultaneously prepared following similar procedure but without sediment. The contents of the tube were continuously agitated at 90°C for 1 h, followed by centrifugation at 6000 rpm for 30 min to separate the aqueous phase. The aqueous solution

that contained the metals in the exchangeable phase was transferred to another tube by autopipette and kept in a refrigerator.

2.5.2 Fraction II (Biogenic or carbonate phase)

The left-over residue of Fraction I was leached for 5 h with sodium acetate (1 M) (16 ml) adjusted to pH 5.0 with acetic acid at ambient temperature by continuous agitation at 90 °C. The reagent blank in triplicate was simultaneously prepared following similar procedure. The leached solution was centrifuged and the aqueous extract separated. The aqueous extract containing the metals in the biogenic or carbonate phases was transferred to another tube by autopipette and kept in a refrigerator.

2.5.3 Fraction III (Hydrogeneous or reducible phase)

The residue obtained in Fraction II was treated with $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.04 M) (40 ml) in 25 % acetic acid at pH 2.0 for 6 h at 96 °C with occasional agitation. The reagent blank in triplicate was simultaneously prepared following similar procedure. The solution was diluted (20 ml) and continuously agitated for 10 min followed by centrifugation to separate the aqueous phase that contained metals in the hydrogenous or reducible phases. The extract was transferred to another tube by autopipette and kept in a refrigerator.

2.5.4 Fraction IV (Organic bound phase)

To the left over residue of Fraction III, HNO_3 (0.02 M) (6 ml) and 30 % H_2O_2 (10 ml) was added and the pH adjusted to 2 with HNO_3 . The resulting solution was heated at 85 °C for 2 h with occasional agitation. After cooling, 0.2 M ammonium acetate in 20% HNO_3 (10 ml) were added and the solution diluted to a final volume of 20 ml. The tube was then continuously agitated for 30 min, centrifuged and the aqueous extract separated by autopipette and stored in a refrigerator. The reagent blank in triplicate was simultaneously prepared following similar procedure.

2.5.5 Fraction V (Detrital)

The residue from Fraction IV was digested by the addition of concentrated HF, HClO₄, HNO₃ and HCl as described in Section 2.2.3 followed by dilution to 50 ml with 6 N HCl.

The metal concentrations in all the fractions were determined by AAS as described in Section 2.2.3.

Table 2.2.1 :Comparison of expected and observed concentrations of elements in certified reference materials										
	BCSS-1 (N = 13)									
	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Certified	11.83 ± 0.41	123 ± 14	229 ± 15	4.7 ± 0.14	11.4 ± 2.1	55.3 ± 3.6	18.5 ± 2.7	119 ± 12	0.25 ± 0.04	22.7 ± 3.4
Observed	13.52±0.19	122±9.8	248.5±5.6	4.45±0.23	10.7±2.8	54.3±1.2	19.3±0.91	102±6.4	0.28±0.03	20.9±2.6
RE (%)	2.8	8.4	2.1	5.2	26.2	2.3	4.9	1.2	10.8	12.6
	PACS -1 (N =13)									
Certified	13.08±0.18	113±8	461±8.3	6.80±0.35	17.5±1.1	44.1±2.0	452±16	824±22	2.38±0.2	404±20
Observed	12.23±0.22	81.2±2.0	470±12	6.96±0.12	17.86±0.48	38.6±2.6	462±3	862±22	2.67±0.47	311±69
RE(%)	2.7	2.5	1.8	7.3	2.7	6.9	14.4	2.6	18	22

Table 2.2.2 : Standard deviation and error used for estimating P and CO₃²⁻

Sr No	P	CO ₃ ²⁻
	(µg/g)	(%)
1	1275	30.6
2	1255	28.1
3	1223	30.6
4	1212	29.6
5	1196	31.5
6	1205	27.7
7	1217	30.3
8	1199	30.2
9	1204	29.6
10	1219	30.8
AV	1220	29.9
SD	±25.49	±1.19
RE(%)	2.09	4



Figure 2.1.1: Sampling area along the north west coast of India

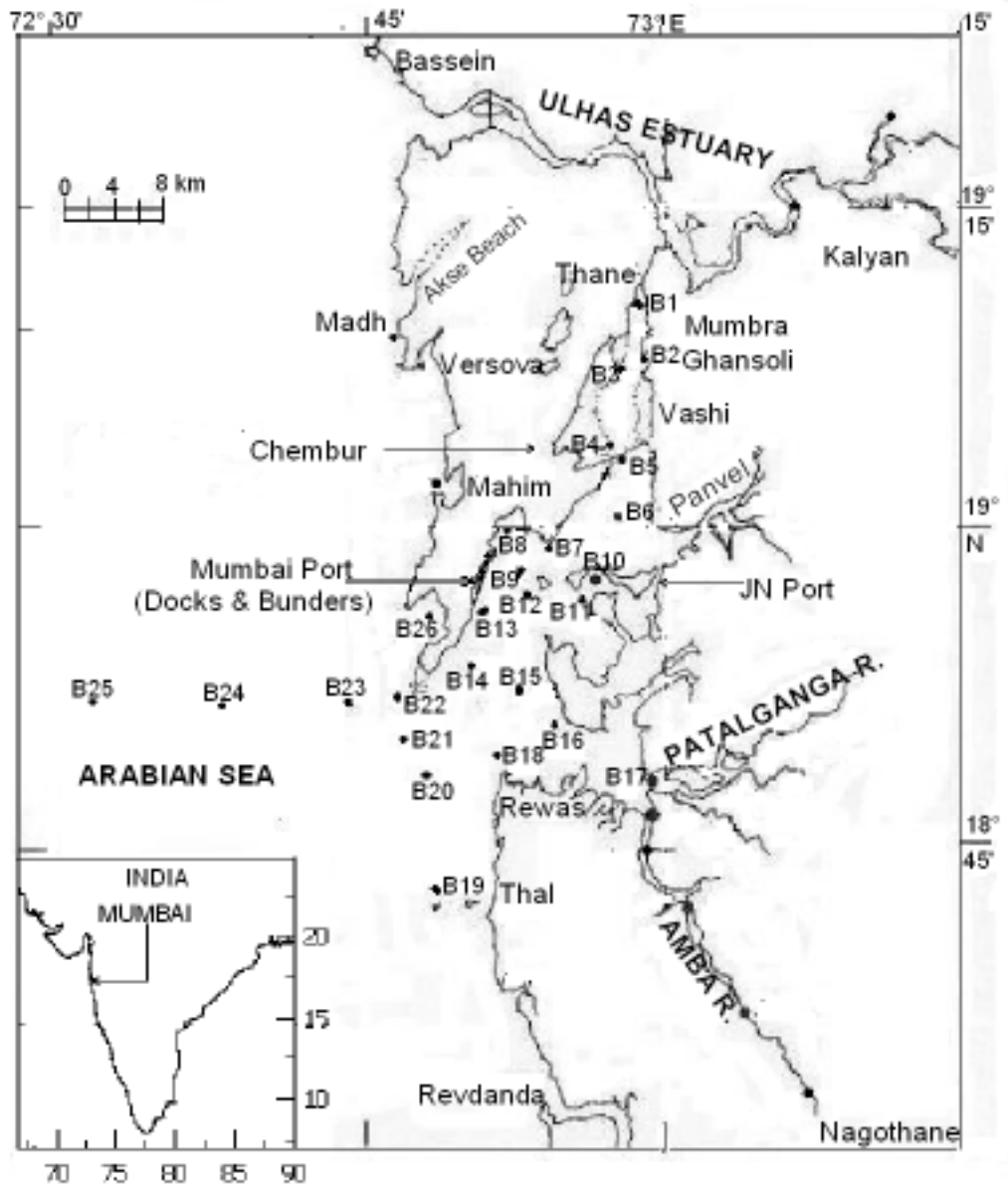


Figure 2.1.2 : Sampling stations in subtidal area of the Bay

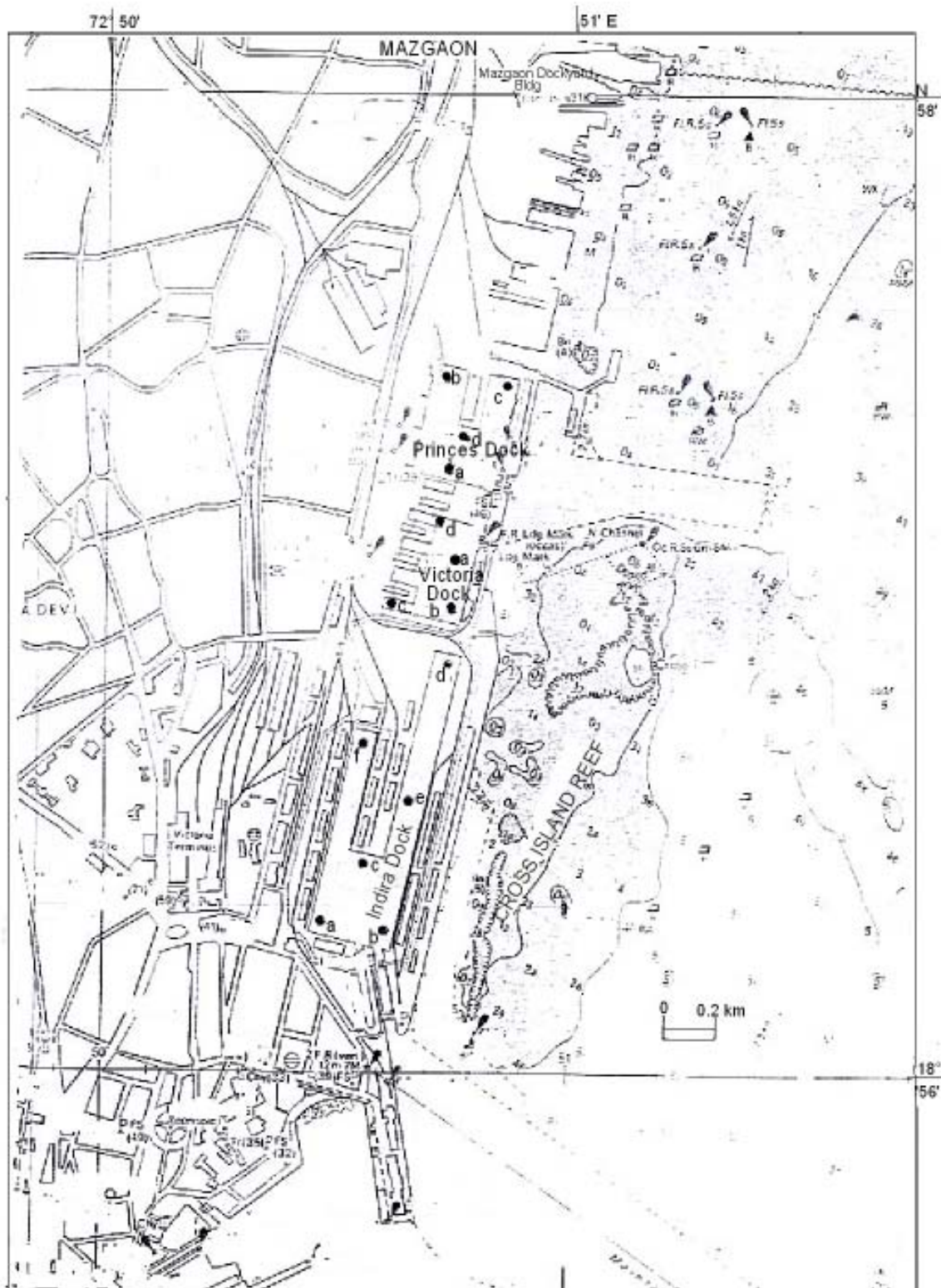


Figure 2.1.3 : Sampling stations within docks of the Mumbai port

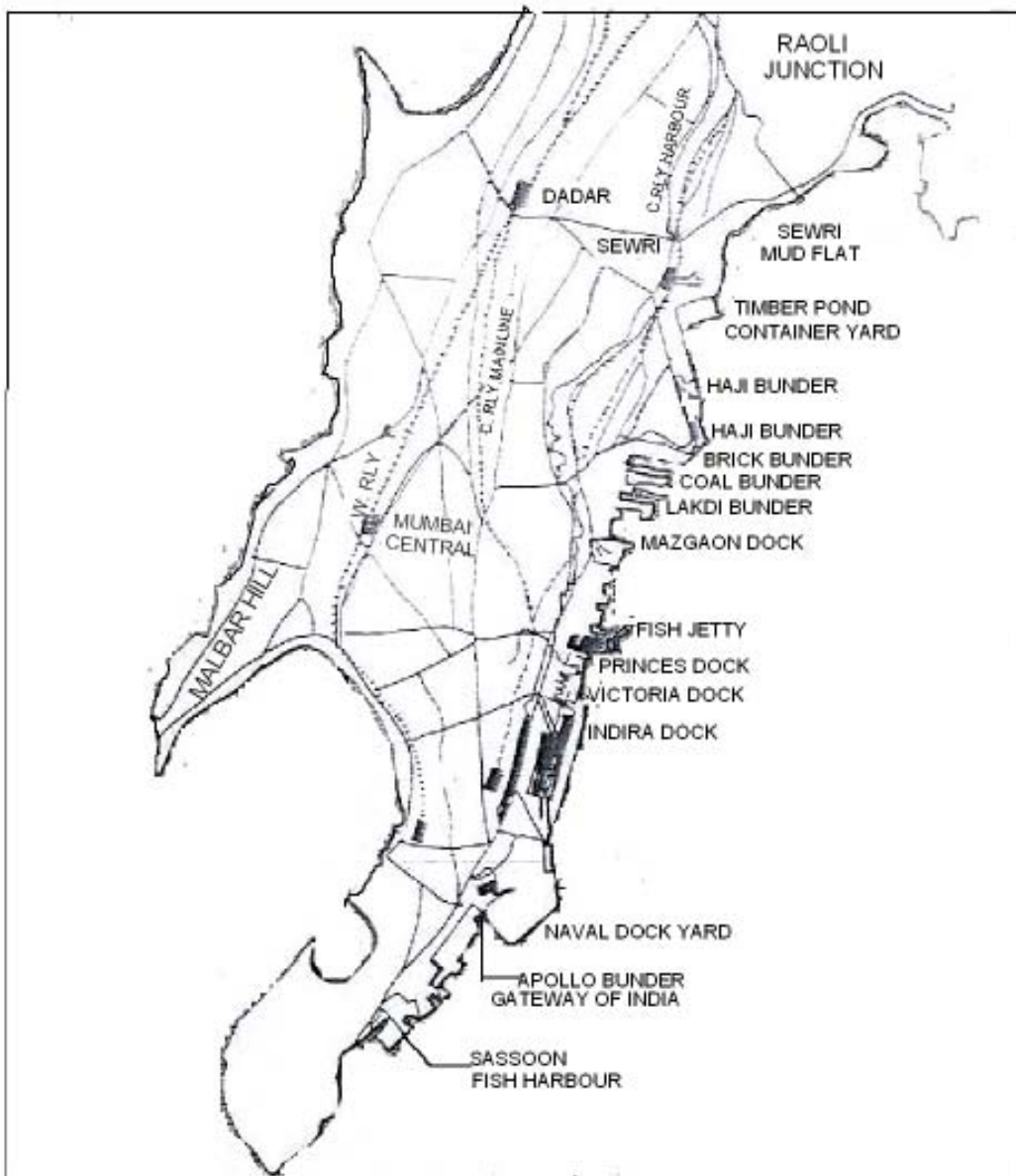


Figure 2.1.4 : Sampling stations in docks and Bunders of the Mumbai Port

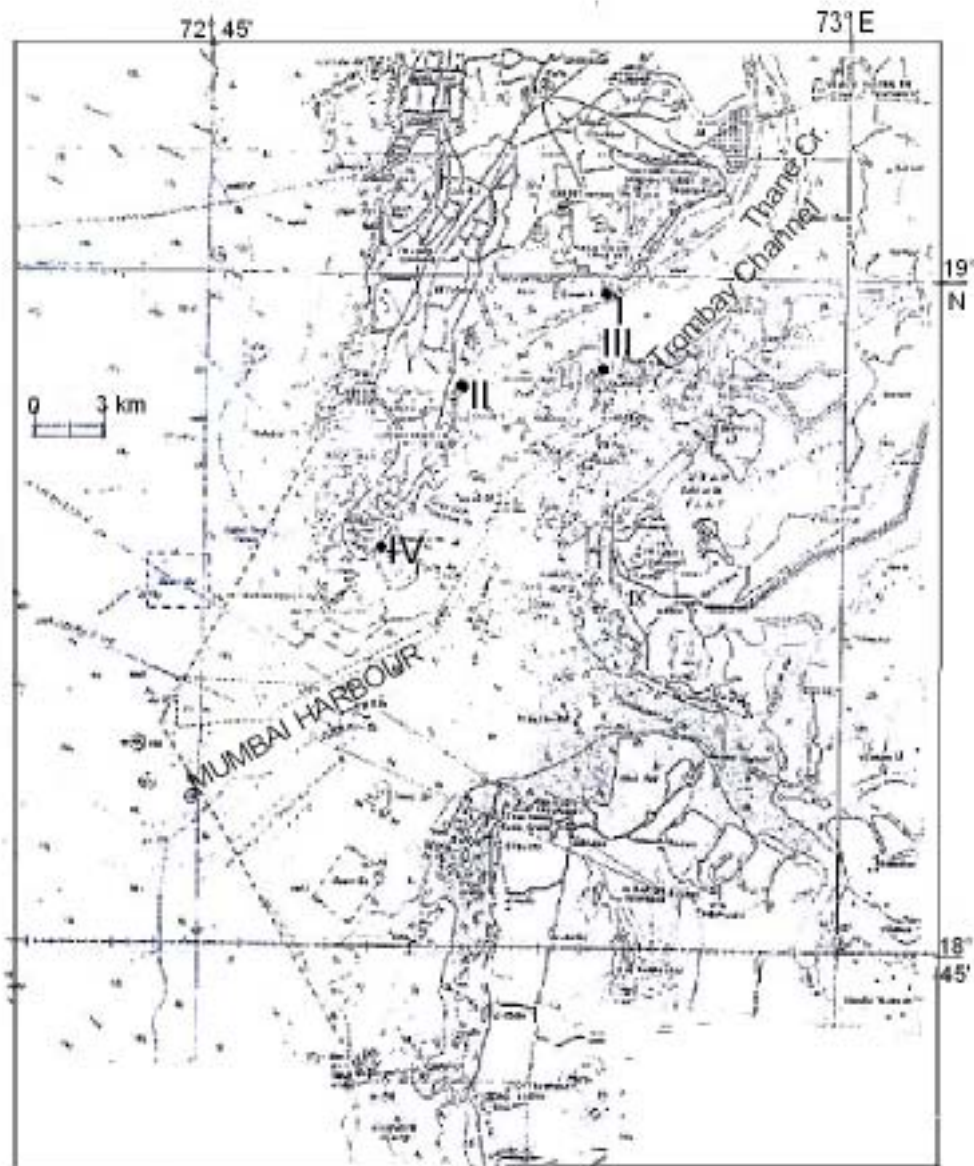


Figure 2.1.5 : Sampling transects at intertidal area of the Bay

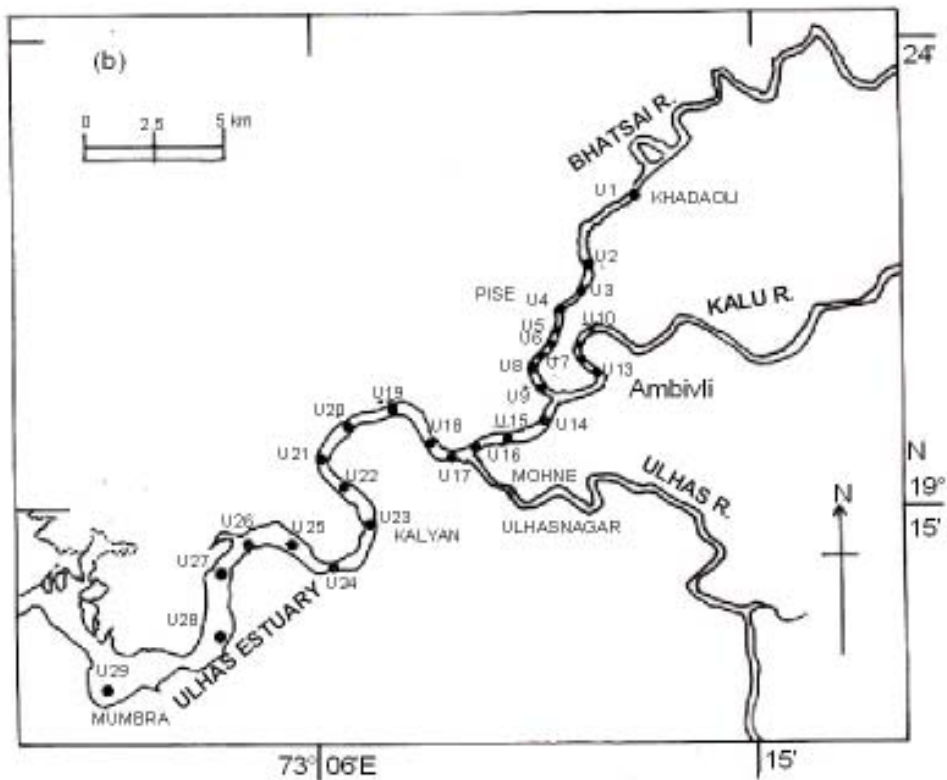
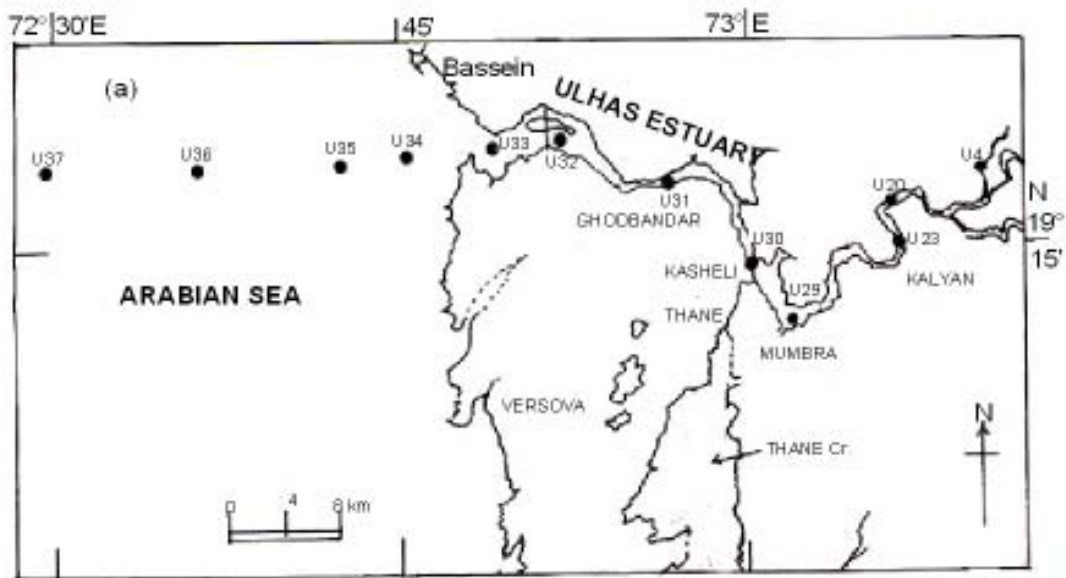


Figure 2.1.6 : Sampling stations in Ulhas estuary : (a) west of Kalyan
(b) east of Kalyan

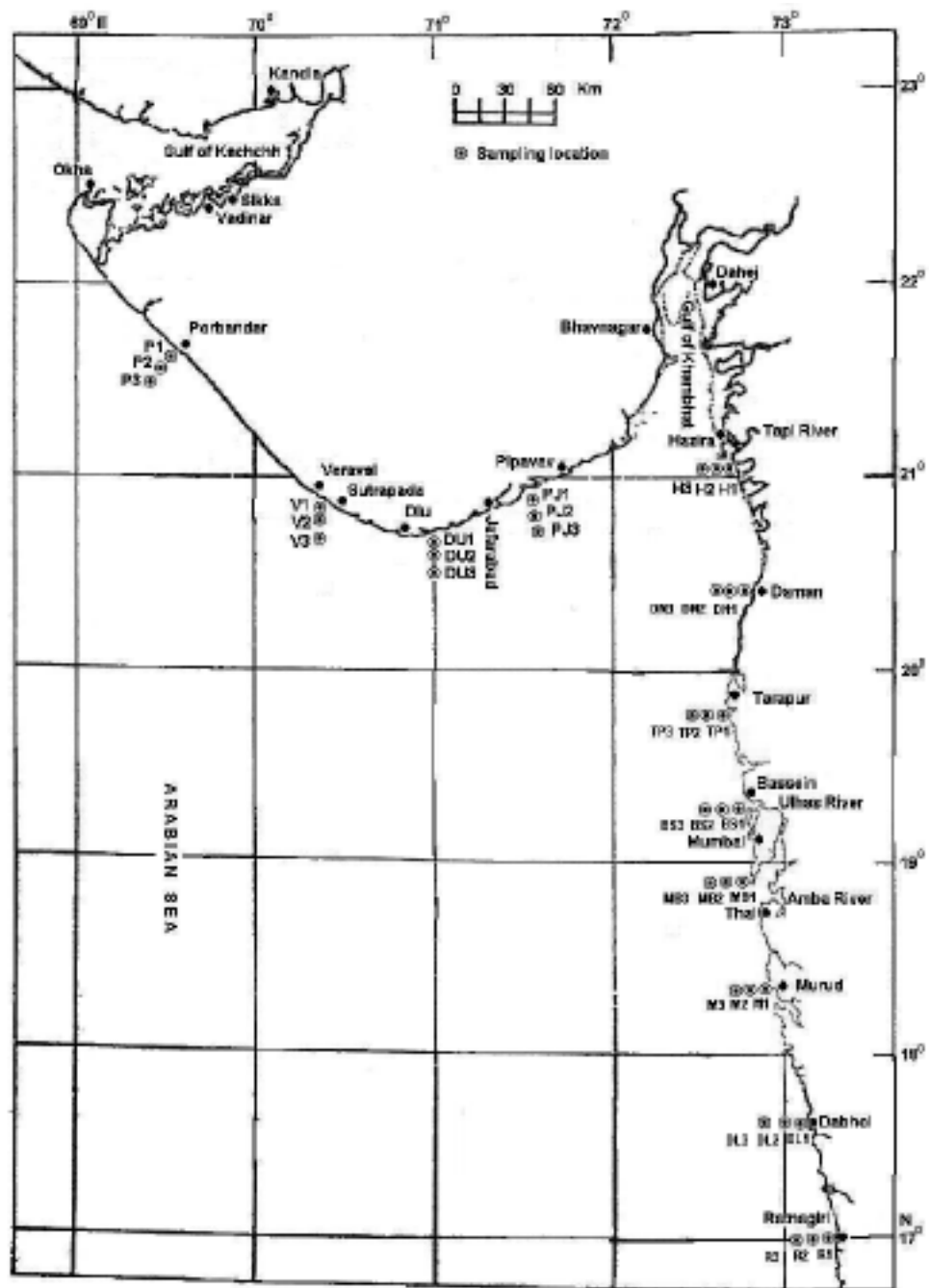


Figure 2.1.7 : Sampling transects along the northwest coast of India

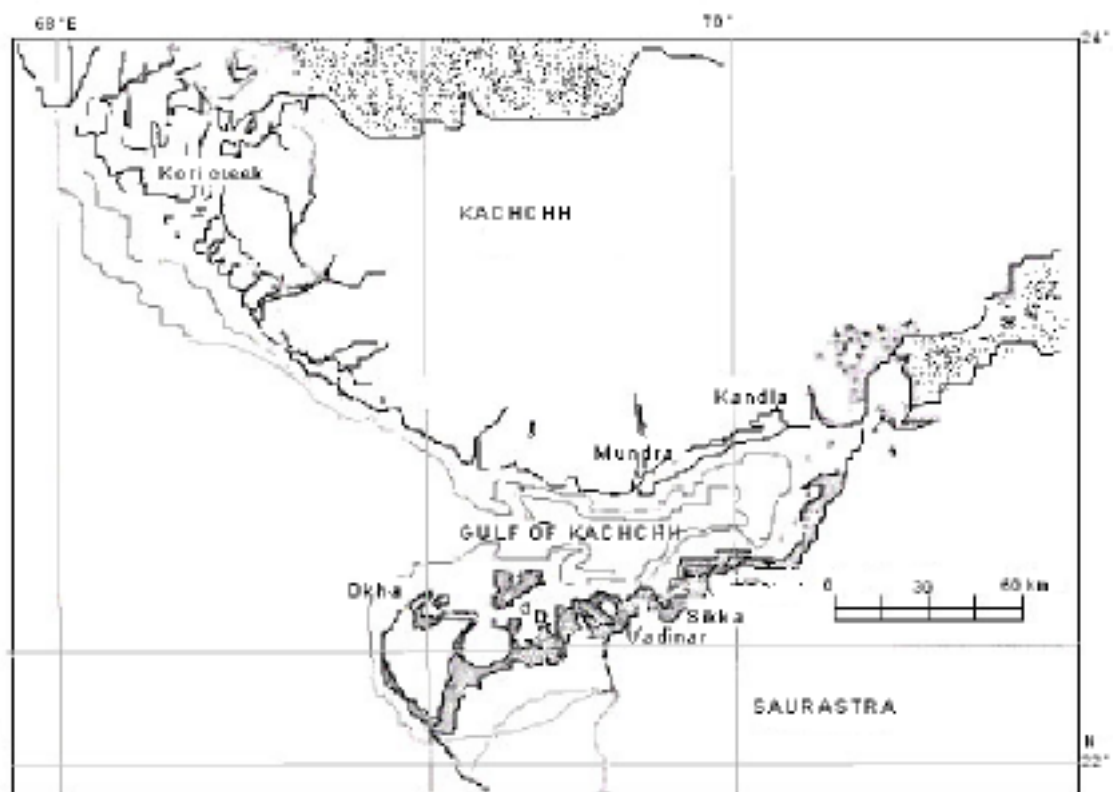


Figure 2.1.8: Sampling sites in the Gulf of Kachchh.

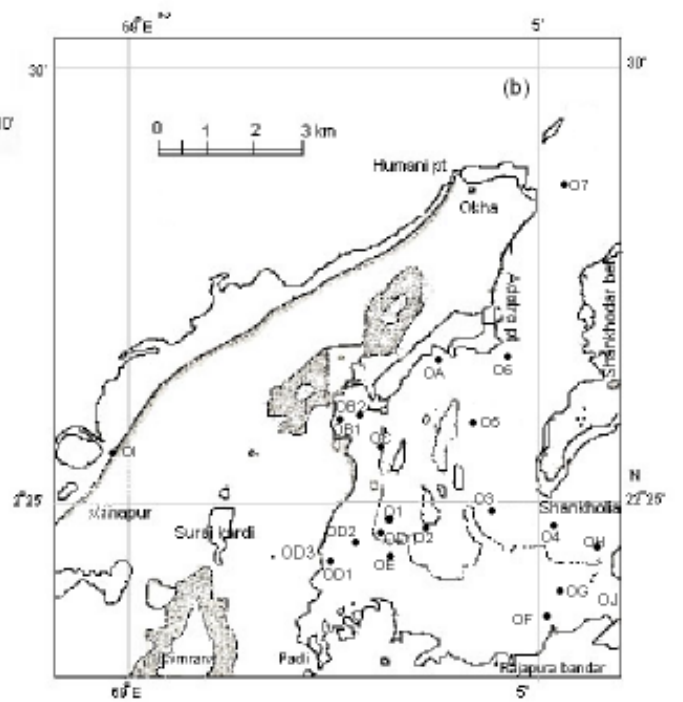
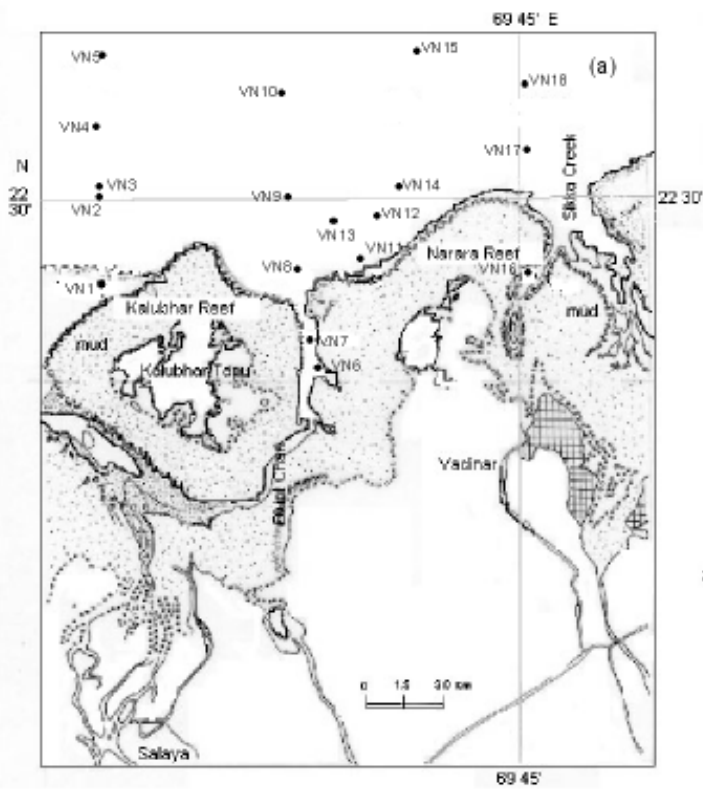


Figure 2.1.9: Sampling stations (a) off Vadinar and (b) in Positra bay

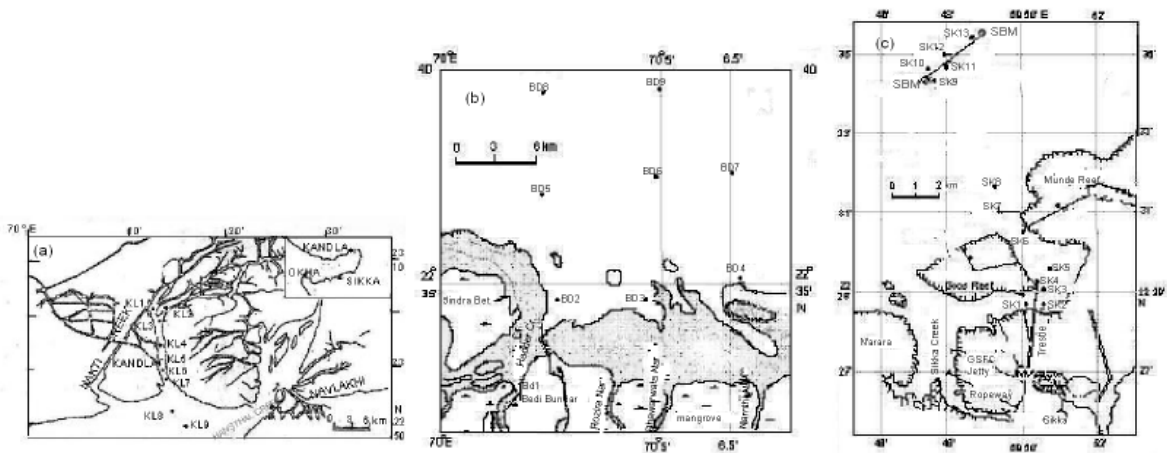


Figure 2.1.10: Sampling stations off (a) Kandla, (b) Bedi and (c) Sikka

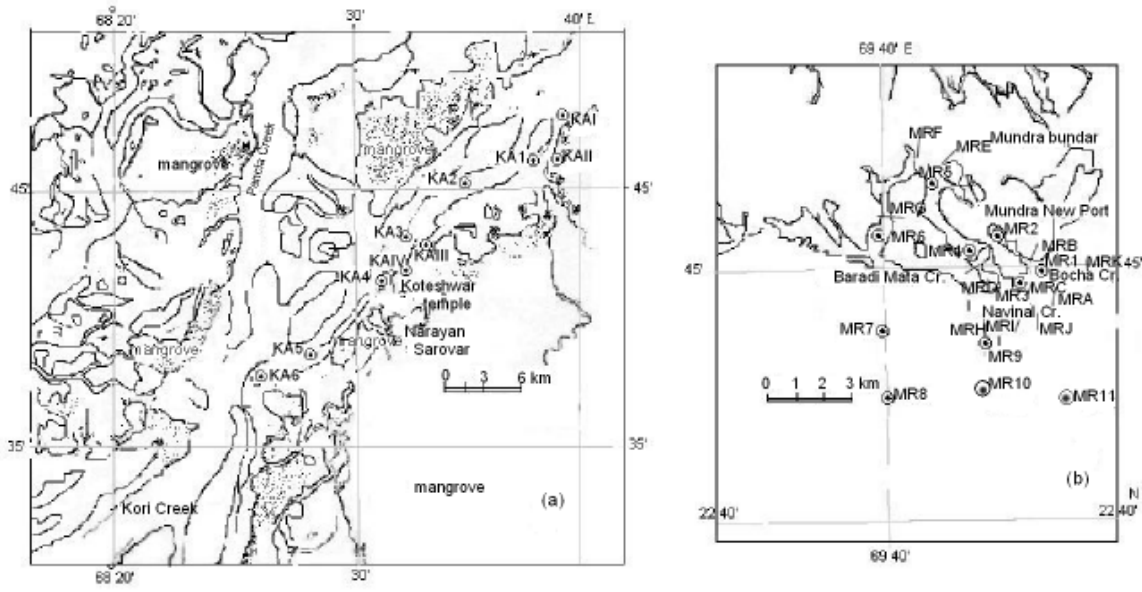


Figure 2.1.11 : Sampling stations in (a) Kori creek, and (b) Off Mundra

CHAPTER 3

METALS IN THANE CREEK-MUMBAI HARBOUR

3.1 Area description

Gifted with a sheltered natural deep-water harbour and located on the western shore of the Bay, the Mumbai Port since its inception 125 year ago, has been instrumental in the development of its vast hinterland and has played a key role in the economic growth of the country. To decongest the Mumbai Port, the Jawaharlal Nehru (JN) Port was established in late 1980s at Sheva on the eastern shore of the Bay. These ports are the major gateways for India's import and export and handle over 4.5×10^7 t of cargo annually which includes crude oil and its products, fertilizers, rock phosphate, sulphur, food grains, metals, chemicals, containerised cargo etc. The Mumbai Port has three wet docks (Indira, Victoria and Prince's) with lock/gate system and 11 major jetties (Bunders) that lie outside the dock areas. The JN Port has open berthing facilities and mainly handles containerised cargo. Crude oil and its products are handled at the Marine Oil Terminal off the docks and Bunders, at the Butcher Island.

The other prominent creeks opening along the western shore of Mumbai are the Mahim, Versova, Malad and Bassein Creeks. These creeks are shallow and mainly used by fishermen to shelter their vessels and in some instances to land their catch.

3.1.1 Bay

Both Mumbai and JN Ports are located in the mouth segment of the Bay. The Bay is a 24 km long, V-shaped semi-enclosed basin that opens to the Arabian Sea at its southwest approach and connected at its northern extremity to the Ulhas estuary through a narrow channel (Figure 2.1.1). The tides in the region are semi-diurnal type with an appreciable diurnal inequality. In the Bay the mean spring tidal range of 5.0 m in the mouth (station B13) decreases to 4.2 m at Vashi (station B5) but increases further north (4.9 m at station B1) due to the funneling effect. The tide at station B1 lags by 30-45 min with respect to the tide at station B13. The neap tidal range is 1.6, 1.2 and 1.5 m at the respective location. The impressive tidal influence generates swift water movements with excursion lengths of 5-11 km and average current speeds of 25-55 cm/s (NIO, 1999). Modeling of the residual circulation indicated that the western side of the Bay had ebb dominated flow as against slight flood-dominated currents along the eastern segment (Naidu and Sarma, 2001).

3.1.2 Openshore area

The shelf associated with the 50 km long coastline of Mumbai is gradually sloping and the 10 m depth contour is roughly 10 km off the coast. The high tidal influence resulted in swift water movements with the average current speeds often exceeding 50 cm/s. Circulation was elliptical with the major axis parallel to the shoreline (MCGB, 1979). Hence the inshore contaminated waters from creeks and bays draining into the coast tend to circulate before being transported offshore. The coastal water mass was well-mixed vertically even during monsoon and except for increase in the populations of pathogens and to some extent nutrients, the water quality was more or less comparable with the uncontaminated nearby coastal sites (Zingde, 1999a).

The prominent direct effluent release to the coastal water was of sewage amounting to 7.3×10^5 m³/d at Worli (Ram, 2004) though most effluents generated in the Mumbai region ultimately reach the sea. The integrated wastewater management scheme for the Mumbai city divides

the municipal area into 7 drainage zones. The plan envisages disposal of wastewater from Colaba, Worli and Bandra drainage zones after preliminary treatment through marine outfalls at a few kilometres from the coast. Wastewater from Ghatkopar and Bhandup zones would be treated in aerated lagoons and released in the Bay, while, that from Versova and Malad would be released in the Versova Creek after treatment in aerated lagoons. Though the Ghatkopar aerated lagoons have been operational, the comparison of the past and present data for the Bay did not indicate any substantial improvement in the water quality. Similarly, though aerated lagoons were operational at Versova, the recent monitoring results revealed that the creek continued to be under high environmental stress (NIO, 2003b). The environmental quality of the Mahim Creek is expected to improve considerably when the Bandra outfall that is under construction, becomes operational.

3.1.3 Effluent releases

Mumbai city with a human population density of 25,000 persons/km² generated 2.2x10⁶ m³/d of domestic sewage out of which about 2x10⁶ m³/d entered marine waters, largely untreated (Zingde, 1999a). The sewage generated in the city added 3.6x10⁶, 4.7x10⁵, 5.6x10⁵, 7x10⁴, and 1.2x10⁴ kg/d of dissolved solids, SPM, BOD, N and P to the coastal waters. Some of the sewage receiving creeks such as the inner Bay and Mahim and Versova Creeks were characterized by abnormally high and tide dependant levels of PO₄³⁻-P, NO₃⁻-N, NO₂⁻-N, NH₄⁺-N and chlorophyll *a*, variable DO falling to zero at low tides in some instances and markedly high and tide-dependant populations of pathogens. Often the contaminated low salinity water from the interior creek draining into the outer segment during ebb tide, lead to distinct vertical stratification with the surface, less saline water having low DO, low pH, high PO₄³⁻-P and low NO₃⁻-N. The levels of NO₃⁻-N and NO₂⁻-N decreased substantially when DO decreased below 0.5 ml/l suggesting active denitrification in these waters (Zingde, 1999a).

Nearly 8 % of industries in the country are located around Mumbai in three large industrial clusters namely, Chembur-Thane-Belapur-Taloja belt, Kalyan-Ulhasnagar-Ambarnath belt and Patalganga- Amba belt. A variety of industries, including a chlor-alkali plant, from Chembur-Thane-Belapur-Taloja belt have been releasing their effluents-largely untreated in the past, in the Bay. Patalganga and Amba estuaries that receive wastes from industries located around their banks drain the pollutants to the Bay in the southeastern area of the mouth segment. Reliable data on the industrial effluents entering the creeks is not available.

3.2 Lithogenic background of metals

Sediments are widely recognized as a suitable medium for assessing environmental quality as they both reflect an integrated contaminant inputs to the marine environment, thereby allowing sources and sinks to be identified (ICES, 1989). Much of the coastal marine sediment is of detritus origin and results from erosion of the surrounding landmass. However, unlike synthetic organic compounds such as DDT, PCBs and Heptachlor, trace metals occur naturally in terrestrial and marine geological deposits. The natural occurrence of metals in soils and rocks complicates the assessment of potentially contaminated marine sediments because the estimated concentration would be a total of the lithogenic as well as the anthropogenic sources (Loring and Rantala, 1992). Hence, as a first step it is necessary to establish the baseline concentration of trace metal under study. The assessment is further complicated because the concentration of a given trace metal tends to vary with the sediment texture. To overcome this difficulty several normalisation techniques have been used to account for natural mineralogical variations and to provide baseline relationships with which to assess the metal enrichment. These normalisers include grain size, C_{org} , Fe, Al, Li and radioisotope tracers (Muller, 1979; Loring, 1990; Din, 1992; Loring and Rantala, 1992).

Geology of the Mumbai region consists of dark coloured volcanic lava flows (Deccan Traps) and laterites. The Traps on weathering give

rise to a greyish to dirty green friable murum, which, on decomposition and decay yields fertile reddish-brown to coffee-brown soil deposits in the form of mudflats in the inshore areas. Such soils are expected to have relatively high concentrations of Fe and Al as well as some trace metals.

In order to establish the concentrations of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in the sediment of the drainage basin, several soil and rock samples from the catchment of the Bay and the Ulhas estuary were analysed. The results are given in Table 3.2.1. These concentrations though give an idea of expected baseline, they should be used with caution since considerable changes can occur during transport of denuded soils through runoff, in mixing zones of fresh-and seawaters and through authigenic precipitation of metal compounds (Meili, 1994).

Table 3.2.1 indicates wide variations in the concentrations of metals even at a given site. Thus, the concentrations of major metals Al and Fe in the soil at Mahableshwar vary in 8.2-14.2 % and 14.7-31.9 % ranges respectively. The highest concentration of Al (55.3 %) in a soil sample from Lonavala is also associated with the highest concentrations of Mn (12469 µg/g), Co (342 µg/g), Cu (1586 µg/g), Zn (907 µg/g), Cd (1.1 µg/g) and P (4874 µg/g). This sample however sustains the lowest concentration of Fe (11.3 %). Correlation coefficients of 0.62-0.95 and the high level of significance (<0.001) of trace metals namely Mn, Co, Ni, Cu, Zn and Cd with Al when all the samples are considered (Table 3.2.2) indicate their preferential association with Al. Unlike in several instances wherein the concentrations of trace metals varied with the Fe content (Loring, 1990), the correlation between a trace metal and Fe is poor in these sediments. The concentration of P in these sediments also varies directly with Al with the correlation coefficient of 0.81 ($p < 0.001$) and such a relationship is poor between P and Fe though a part of P is known to occur in Fe compounds in sediments (Berner, 1980).

The range and average metal concentrations based on the pooled samples of soil from different sampling sites are given in Table 3.2.3. One

sample from Lonavala which sustains abnormally high concentrations of metals was not considered in the above table. The average values in Table 3.2.3 gives an estimate of probable background concentrations in the soil of the catchment of the region. A comparison of average values of metals in the soil of the catchment investigated with average trace metals in shales, basalt, granite and continental crust (Table 3.2.4) indicates marked enrichment of these metals in the soil of the Mumbai catchment.

3.3 Metal fluxes through sewage

Sewage is a variable liquid mixture comprising material from sources such as human waste (faeces, paper, wipes, urine and other bodily fluids), washing water (personal, clothes, floors etc), ground and rain water infiltrated into sewage pipes, surplus manufactured liquids from domestic sources (drinks, cooking oil, pesticides, lubricating oil, paint, cleaning liquids etc) and industrial effluents when released in municipal sewers.

The composition of each sewage stream varies widely, but sewage derived from a large city such as Mumbai can be expected to contain water (>95%), non pathogenic bacteria ($>1 \times 10^6$ /ml), pathogens (bacteria, viruses, parasitic worms), organic particles (faeces, hair, food, vomitus, paper fibres, plant material, humus etc), soluble organic material (urea, fruit sugars, soluble proteins, drugs, pharmaceuticals etc), inorganic particles (sand, grit, metal particles, ceramics etc), soluble inorganic material (ammonia, sea-salt, cyanide, hydrogen sulphide, thiocyanates, thiosulphates), animals (protozoa, insects, arthropods, small fish, pets etc), macro-solids (sanitary towels, nappies/diapers, condoms, needles, children's toys, body parts, etc), gases (hydrogen sulphide, carbon dioxide, methane), emulsions (oils in emulsion, paints, adhesives, mayonnaise, hair colorants), toxins (pesticides, poisons, herbicides) etc (Atkins and Hawley, 1978).

Reliable estimates of quantities of domestic effluents entering the marine areas of Mumbai are not available. Estimates made in the past

vary between 1.5×10^6 and 2.2×10^6 m³/d (Zingde *et al.*, 1989; 1999a). Hence during the present study the information on the quantity of sewage released through treatment plants and pumping stations in the city was obtained by personal visits during the collection of sewage samples and presented in Table 3.3.1.

In order to decongest Mumbai, the satellite city of Navi Mumbai has been established and urbanisation has spread upto Panvel with high construction activity between Vashi and Panvel (Figure 2.1.2). This area developed along the east coast of the Bay releases 3.5×10^5 m³/d of domestic effluents to the Bay in addition to 8.1×10^5 m³/d discharged along the western shore, from the main city. Because of fund constrains and lack of marine environmental awareness, the pumping stations in the city have been located in the vicinity of creeks and bays for ease of marine disposal of sewage. Thus, out of the total sewage generated in the Mumbai city and surrounding area (3.16×10^6 m³/d), the Bay, Mahim Creek and the Versova Creek receive 1.16×10^6 , 8.3×10^5 and 4.4×10^5 m³/d respectively; the balance (7.3×10^5 m³/d) being released directly in the openshore area including the sea off Worli.

The levels of dissolved solids, suspended solids, BOD, N, P, Mn, Fe, Co, Ni, Cu, Zn and B associated with sewage generated in the Mumbai city have been estimated in the past (Zingde, 1985). Based on the concentrations of these constituents the loads associated with the increasing output of sewage have been periodically assessed (Zingde *et al.*, 1989). The fluxes of Hg through sewage of the city have been reported based on its concentration in samples from several pumping stations determined recently (Ram, 2004). In order to assess the present load of sewage-associated contaminants in the marine environment of Mumbai, the samples from the major sewage pumping stations during different months of the dry season were analysed for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P. These results are also included in Table 3.3.1. Monsoon period was not considered for sampling because of high rate of infiltration of groundwater in the sewage network thereby diluting the

sewage. Sewage from some pumping stations listed in Table 3.3.1 could not be collected. Hence, an average value obtained from the data in Table 3.3.1 was used to calculate the input of total metals through un-sampled pumping stations. The metals content in sewage represents both the soluble as well as acid leachable particulate fractions since the sample was treated with conc. HNO₃ soon after collection. The overall concentrations of metals recorded during the present study are compared with those reported 15 years back (Zingde *et al.*, 1989) in the following table.

Metal	Concentration (µg/l)	
	Present study	Zingde <i>et al.</i> (1989)
Al	0-35,581	-
Cr	0-234	-
Mn	29-1053	700
Fe	0-11,738	1800
Co	0-86	35
Ni	0-443	78
Cu	0-628	98
Zn	0-2200	201
Cd	0-3.32	-
Pb	0-19.8	48

These results indicate that the concentrations of metals reported in the past lie in the range of the present results though the ranges of variations are large. The concentrations of metals in sewage not only vary among pumping stations but also at the same station during different collections (Table 3.3.1). Examination of Table 3.3.1 however indicates certain broad trends. At the Malad pumping station the concentration of Cr is high on most occasions particularly in samples from February 2005 onwards, while, that of Ni, Pb and Cd is high in several instances. The average concentrations of Al (956-12790 µg/l) and Fe (0-5438 µg/l) are consistently high in all samples.

Unlike at all other pumping stations referred in Table 3.3.1, the sewage at Ghatkopar, Bhandup and Versova is treated in aerated lagoons and retained in settling tanks prior to release to the creek. This treatment given to sewage is reflected in the average concentrations of Al, Cr, Fe, and Ni which are generally lower as compared to those at the other pumping stations where such facilities do not exist. The concentration of Pb in sewage in 1976 was 7-99 µg/l averaging at 48 µg/l (Zingde *et al.*, 1989). The concentration has distinctly decreased (0-19.8 µg/l) in recent years and averages at 8.5 µg/l. This decline can be due to an impressive reduction in the production of tetraethyl lead over the past decade with changeover to unleaded petrol (Anagnostopoulon and Day, 2006). Based on the average wastewater flows and average concentrations of metals and P in sewage, the loads entering different water bodies around Mumbai are given in Table 3.3.2 and 3.3.3. Thus the maximum load of Mn (416.3 kg/d), Co (18.2 kg/d), Cu (53.4 kg/d), Zn (398.1 kg/d) and P (4393 kg/d) is associated with sewage entering the Bay. As against the sewage flow of 1.16×10^6 m³/d received by the Bay, the quantum released in the Versova Creek is just 4.4×10^5 m³/d, however, the maximum loading of Ni (50.4 kg/d), Cu (87.3 kg/d) and Cd (3.9 kg/d) through sewage is high in this creek.

Major industrial source of metals in sewage may be batteries, discarded electric equipment and wiring, paint residues, pharmaceutical wastes, hospitals discharges, small scale industries etc. High concentration of metals has been recently reported in sewage-associated SPM released to Patos Lagoon estuary from Rio Grande city in southern Brazil (Mirlean *et al.*, 2003). The physical and chemical characteristics of septic tank sewage, holding tank sewage and municipal sewage treated at the secondary level are compiled in Table 3.3.4. Comparison of the data in Table 3.3.3 and 3.3.4 indicates that the concentrations of metals are low in the Mumbai sewage suggesting that there is not much addition of metal-containing industrial effluents in the sewerage network. Moreover, bulk of the sewage is given only primary treatment before

release and concentrations of metals in sewage treated at the primary level are normally higher than that treated at the secondary level.

The correlations between different pairs of constituents of sewage studied during the present investigation are presented in Appendix-1 (a) and (b). When all the values are pulled (n=76) positive correlations at the level of significance of 0.001 are evident for the pairs Al:P, Cr:Ni, Fe:Pb, Fe:P, Co:Cd, Ni:Cu, Ni:Zn, Ni:Pb, Ni:P, Cu:Zn, Cu:Pb and Zn:Pb. When individual pumping stations are considered, the significant correlations (p=0.001) often differ [Appendix I-(b)] from the relations emerging when all the values are pulled [Appendix-I(c)]. Highest number of significant correlations is for the samples from the Bhandup pumping station among which Al is directly correlated with Cu, Zn and Cd, while, Cr directly varies with Co, Ni, Cu, and Pb. Other significant positive correlations at this pumping station are for the pairs Mn:Cd, Fe:Cd, Co:Cu, Co:Ni, Pb:Co, Cd:Co, Ni:Cu, Cu:Zn, Cd:Zn and Cd:P. Surprisingly, the majority of significant correlations is negative at the Malad pumping station. Number of times the positive correlation coefficients (p=0.001) for individual pairs occurring three times or more at the sites sampled are as follows:

pair	Number
Al:Pb	3
Cr:Co	3
Cr:Cd	4
Cr:Pb	3
Fe:Pb	3
Fe:Cd	3
Co:Cd	4
Zn:Pb	3
Zn:Cd	4
Pb:P	5

Thus, the significant positive correlations occurring at 50 % or more of the sites sampled are for the pairs Co:Cd, Pb:P, Cr:Cd and Zn:Cd.

Though the concentrations of metals are relatively low in sewage, considering the volume generated in the city, the fluxes to the marine

environment are fairly high (Table 3.3.3). As stated earlier, a considerable fraction of wastewater enters inshore creeks. The waste released is far in excess of the assimilative capacity of the receiving waters leading to high level of deterioration of ecological quality of these areas (Zingde, 1999a). Metals associated with sewage could accumulate in sediments, while, their accumulation in the openshore coastal sediment may be minor because the contaminants are widely dispersed. If the sewage is released through an adequately designed marine outfall that assures initial dilution by about 10-15 times and the currents are suitable to advect the sewage plume, the accumulation of sewage-associated metals in sediments would be insignificant. The metals of major concern in sewage from the human health point of view are Cd and Pb though the others such as Cr, Cu and Zn are also of interest. Al, Fe, and Mn occur in high concentrations in the soil and rock of the region (Section 3.2.1) and their fluxes through sewage would not influence their concentrations in marine sediments of sewage receiving sites. Hence, dilution of sewage by 10-15 times would reduce the concentrations of Cd and Pb near to the baseline of these metals in water in coastal areas. The general baseline concentrations of Cd and Pb ($\mu\text{g/l}$) in marine areas (Karl, 1991) are compared to Mumbai sewage diluted 15 times on release in the table below:

Area	Cadmium ($\mu\text{g/l}$)	Lead ($\mu\text{g/l}$)
Estuaries	0.05-0.2	0.12-10.0
Coastal waters	0.01-0.15	0.01
Open sea	0.01-0.1	0.003
Open ocean	0.01-0.1	0.01-0.03
Diluted sewage	0-0.22	0-1.32

To relieve inshore marine areas of the burden of sewage, the Municipal Corporation of Greater Mumbai has embarked on an ambitious project of releasing bulk of the sewage through two massive tunnels of 4.5 m diameter fully lined with precast concrete, 3.5 km off Worli and Bandra respectively in the Arabian Sea. The tunnels would be several metres below the seafloor and sewage would jet-out into the seawater through a series of riser pipes. The planning of the scheme that began in 1977 is

still under implementation. The marine outfall off Worli has become operational in June 1999 and the one off Bandra is under commissioning. In zones where release to creeks is inevitable, sewage would be treated in aerated lagoons to reduce BOD to acceptable levels, prior to release. Two sets of large single-cell aerated lagoons are under construction at Bhandup and Ghatkopar and sewage, after primary treatment, would be released to the Thane Creek. A post-commissioning study has been recently initiated off Worli to determine the extent of improvement in water quality in the near-shore area and the level of agreement of the observed values with those predicted based on modelling studies. The preliminary results have been reported to be encouraging (Gupta *et al.*, 2004)

3.4 Metals in surface sediment

The surficial sediment from the Bay and openshore coastal area was extensively investigated for their contents of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn and P, while, Cd and Pb could be analysed only in selected samples.

As discussed in Section 3.3 the sewage flow to the Bay has increased substantially (from 2.5×10^5 m³/d in 1978 to 1.16×10^6 m³/d in 2002). The industrial scenario in the Thane-Belapur belt; the major industrial input source of anthropogenic contaminants to the Bay from the eastern shore, has also undergone considerable transformation with several industries closing down and increasing treatment to the effluent enforced by the Maharashtra Pollution Control Board, for those which are functional. Hence, though the input of trace metals to the Bay through sewage has increased, that associated with the industrial effluents would have decreased.

In order to assess the extent of metals content of sediment with the changes in metal fluxes to the Bay over the years and to investigate their transport and redistribution within the Bay and the associated coastal area, annual monitoring of surficial sediment was undertaken at 10 stations spanning the innermost Bay (station B1) to 25 km off in the

Arabian Sea (station B25) over a distance of 65 km during April 1996-October 2000. The results are presented in Appendix-II(a) and II(b) and in Figure 3.4.1. In addition, pre-monsoon (May-June 1997) and post-monsoon (November-December 1996) monitoring of the surficial subtidal as well as intertidal sediments including docks and bunders in the Mumbai Harbour (outer Bay) was carried out for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn and P. These results are presented in Table 3.4.1 to Table 3.4.3.

The subsurface geology of the Bay and the nearshore area of Mumbai consists of three sedimentary units overlying the acoustic basement mainly representing the seaward extension of the Deccan Traps. The top 2.5-3 m thick sedimentary layer was relatively modern deposited during the past 600-700 years (Siddiquie *et al.*, 1985). The surficial sediment of the Bay is largely silty-clay or clayey-silt in character with low percentage of sand that increases from an average of 6 % off the western shore to 21 % along the eastern shore with the mid-segment of relatively low sand content averaging around 4 % (Desai *et al.*, 1986). The strong currents sweeping the Bay disperse the fine-grained sediment from the bed and extensive mud flats into the water column resulting in high SPM in water that is considered to be an efficient scavenger of heavy metals, entering the marine system. The SPM, though variable, is generally below 100 mg/l during dry season and may exceed 200 mg/l during monsoon (Zingde, 1989; 1994; NIO, 1999) in the Bay waters. The fine sediment of the Bay is dominated by montmorillonite, degraded chlorite, illite and to some extent silica and has the cation exchange capacity of 37.97-61.56 meq/100g that could aid in more efficient removal of trace metals from the water column (Sahu and Bhosale, 1991).

The results in Appendix-II(a) and Appendix-II(b) indicate marked variations in Al and Fe content even at a given location during different sampling events. Thus, the concentration of Al varies in ranges 6.5-9.0 % and 6.1-9.0 % at stations B6 and B23 respectively. These variations are in the ranges 6.0-7.9 % and 5.8-7.6 % for Fe at the respective location. The variations in concentrations of trace metals in these sediments can be

partly due to changing concentrations of Al and Fe as these metals are known to influence the concentration of trace metals in sediments (Forstner, 1979b). Increase in the concentration of Al from 7.4-7.7 % in April 1996 to 8.4-10 % in October 2000 indicates an enhancement in the flux of clay material to the Bay over the years. The trend also indicates a rise in the Fe content of the sediment as compared to the April 1996 results but the increase is less well defined than in the case of Al.

Among trace metals, Cr burden in the surficial sediment seems to have increased with the passage of time. Thus, at station B9 the concentration of Cr has gone up from 107 µg/g in April 1996 to 273 µg/g in October 2000. The increase is also seen in the coastal sediment at stations B24 and B25. The distribution of Cr in sediment along the length is not well defined in collections made in April 1996 and April 1998. However, a distinct gradation in the Cr content of sediment is evident with a marked decrease in the seaward direction. Thus, in March 2000 the concentration of chromium of 515 µg/g in the inner Bay (station B1) decreases to 273 µg/g in the mid-segment of the Bay (station B6) and falls to 194 µg/g at station B25 which is about 25 km off the coast. The high concentration of Cr in the inner Bay and its decrease in the seaward direction suggests a significant source of Cr to the inner Bay subsequent to April 1998. As in the case of Cr, distinctly high concentrations of Cu, Zn and Ni occur at station B1 with a trend of decrease in the seaward direction (Figure 3.4.1).

The inner Bay receives sewage from the Bhandup and Ghatkopar outfalls. The concentration of Cr in sewage from these stations has not increased between June 1998 and November 2001 [Appendix-I(a)] indicating that sewage may not be a major source of increase in the concentration of Cr. If sewage is the source of Cr because of increased flux of the metal to the Bay with considerable increase in sewage inflow, then the enhancement in trace metal content of the Bay sediment would be across the board for all trace metals (except for Cu and Zn). The results in Appendix-II(a) and Appendix-II(b) do not support this viewpoint.

The other possibility is an unidentified industrial source releasing effluent containing high concentration of Cr in the inner Bay. Contribution from the catchment soil associated with the runoff is another possibility in view of high Cr in several samples (Table 3.2.1). Querying of basalt ridges and spurt in construction activities have increased the transport of lithogenic flux to the Bay. However, in that event the increase in Cr concentration would occur more uniformly along the Bay since the land runoff is not only through the Ulhas estuary at the head of the Bay but also through Panvel, Nava-Sheva and Dharamtar Creeks which open in the middle and the outer Bay (Figure 2.1.2).

Relative high concentrations of Cu (123-171 µg/g) and Zn (192-321 µg/g) in sediments also occur in the inner Bay (station B1) with definite increase from April 1998 to October 2000. The trend of decreasing concentration of these metals in the seaward direction, as in the case of Cr, is also seen. An incremental increase in sewage load may be a factor influencing these trace metals due to their high concentration in sewage from Bhandup and Ghatkopar [Appendix-II(a)].

Assuming that the sediment at station B25 which is 25 km from the coast is not heavily influenced by anthropogenic trace metals and P, their concentrations at this site would largely represent the lithogenic component. The average concentrations of metals and P in sediment at station B25 and in the catchment soil are compared in the following table:

Constituent	Station B25	Catchment soil
Al (%)	7.4	10.8
Cr (µg/g)	157	263
Mn (µg/g)	817	2047
Fe (%)	7.1	18.6
Co (µg/g)	49	50
Ni (µg/g)	79	212
Cu (µg/g)	107	208
Zn (µg/g)	100	115
P (µg/g)	1086	726

These results reveal a marked depletion in concentrations of most metals in the sediment of station B25 as compared to their content in the catchment soil. This decrease is particularly prominent for Cr, Mn, Fe, Ni and Cu. The concentration of P has enhanced and as discussed later (Section 3.2), may not be solely due to the transfer of anthropogenic P to the sediments. Thus though several workers (Muller, 1979; Loring, 1990; Din, 1992; Loring and Rantala, 1992) have used trace metal contents of the catchment to assess their anthropogenic fractions in marine sediments, such an approach would be flawed in the present case.

Another approach to decide the baseline against which the observed concentrations of elements can be compared to assess anthropogenically introduced fraction, is to select representative sediment from the same region which was deposited prior to the influence of human activities in the region. Considering the developmental history of Mumbai, the sediment that might have been deposited off the coast about 100 years in the past can be a good source of baseline. This is possible by analyzing dated cores and selecting suitable sections of the core sediment. We used this approach for obtaining the baseline. The bottom sections of the cores B23, B24, B25, U34, U35, and U37 from the coastal area of Mumbai-Bassein and core R5 retrieved off Ratnagiri were used for this purpose. These results are presented below:

Constituent	Minimum	Maximum	Average
Al (%)	4.7	9.6	7.2
Cr ($\mu\text{g/g}$)	70	241	172
Mn ($\mu\text{g/g}$)	347	1102	796
Fe (%)	4.1	7.7	6.2
Co ($\mu\text{g/g}$)	31	60	49
Ni ($\mu\text{g/g}$)	34	112	70
Cu ($\mu\text{g/g}$)	27	111	85
Zn ($\mu\text{g/g}$)	26	185	98
Pb ($\mu\text{g/g}$)	8.8	52.0	21.7
Cd ($\mu\text{g/g}$)	0.1	0.6	0.3
P ($\mu\text{g/g}$)	620	1786	1129

The results in Appendix-II(a), Appendix-II(b) and Table 3.4.1 indicate marked decrease in the concentrations of Al, Mn, Fe and P in the subtidal as well as the intertidal sediment in postmonsoon as compared to the premonsoon. This may be due to the influence of the particulate load associated with the runoff during monsoon. High monsoonal precipitation in the region transports voluminous detritus to the Bay. A yearly load of $8.4 \times 10^5 \text{ m}^3$ of fine-grained sediment is estimated to be transported, largely during monsoon, to the Bay via Thane, Panvel and Dharamtar Creeks (CWPRS, 1963). Under the dynamic Bay environment the native bed sediment disturbed by turbulence mixes with the load delivered through the land runoff and the oscillating tidal movements probably spread this material fairly uniformly over the 240 km^2 area of the Bay (Patel *et al.*, 1985, Sharma *et al.*, 1994). The fine-grained sediment transported to the Bay is largely of terrestrial origin and based on the results given in Table 3.2.1 would have high metal content. Hence, under the influence of high lithogenic flux relative high concentrations of Al, Mn, Fe and P are recorded in the sediment in post-monsoon. However, with the withdrawal of monsoon during October, the lithogenic flux of high metal content to the Bay nearly ceases and results in relative low concentrations of these elements in the surficial sediment of the Bay.

Another prominent feature of the results in Figure 3.4.1 and Table 3.4.1 is the absence of discernible trend in the variation of metals and P in sediment across the Bay in the subtidal as well as the intertidal sediment. The variations of metals and P across an intertidal transect that is from HTL to LTL is also without any defined trend. It is possible that the sediment of the intertidal zone is periodically agitated and resuspended in the water column due to strong tidal movements and transferred over wide areas with good horizontal mixing thereby evening out the signature of accumulation of anthropogenic input of a constituent in the vicinity of the source. Naidu and Sarma (2001) have reported occurrence of anticyclonic eddies in the outer Bay particularly around Elephanta and Butcher Islands with high residual velocities that induce strong horizontal mixing. This is also supported by the salinity distribution during monsoon.

Dharamtar, Nhava-Sheva and Panvel Creeks transport large volume of fresh water to the eastern section of the Bay during July-August, while, there is no major creek opening along the western shore of the harbour. However, the horizontal salinity gradient between the eastern and the western segments of the Bay is not high (Zingde, 1989) suggesting good mixing across the Bay.

Indira, Victoria and Prince's Docks (Figures 2.1.3 and 2.1.4) where commercial ocean going ships berth for loading/unloading of cargo, are large semi-enclosed basins with navigational gates which limit water exchange between the docks and the Bay proper. To investigate spatial heterogeneity of the distribution of metals if any, these basins were sampled at several stations (Table 3.4.2). The harbour also has several Bunders with limited draft to facilitate cargo handling by small vessels. Some of the Bunders have degraded environment due to congestion and release of wastes by vessels and other shore establishments. Their sediment was also sampled (Table 3.4.3). The results do not indicate any clear trend of accumulation of trace metals in docks as well as Bunders.

Particle size of the Bay sediment may also be important for the observed levels of metals. The particle size in the Bay has been reported (Desai *et al.*, 1986) to vary in the range 63-2000 μm with higher percentage of particles in <400 μm range. In the inner Bay the grain size is generally in 2-63 μm range that would favour higher adsorption of trace metals. The larger particle size of the sediment of the outer Bay would reduce the availability of adsorption sites for trace metals. The levels of several trace metals in sediments are often correlated with its Al content that is considered as a good indicator of the amount of fine material (Windom *et al.*, 1989; Loring, 1991; Din, 1992). It has been suggested that detrital and authogenic Fe-Mn oxihydroxides which accumulate in oxic sediment layers can also be important scavengers of metals.

3.5 Metals in sediment cores

As discussed in Section 3.1.1, the Bay is known to receive a variety of anthropogenic pollutants through a number of sources. The high inherent suspended load in the Bay would facilitate efficient transfer of pollutants such as trace metals to the sediment where they would accumulate. Based on the distribution of selected metals (Al, Cr, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb) in sediment cores from the Bay it has been suggested that the anthropogenic trace metals associated with effluent streams either settled in the effluent drains prior to their entry in the Bay or the Bay was a passive link between the sources and the sink with much of the load transferred to the shelf (Sharma *et al.*, 1994). With lack of data on industrial loads of metals to the Bay and high and variable natural levels of these metals in the sediment this issue had remained unresolved.

In the intervening period the sewage flow to the Bay has increased substantially - from 2.5×10^5 m³/d in 1978 to 1.16×10^6 m³/d in 2002 (Ram, 2004). In order to assess the extent of metal content of sediment with the changes in metal fluxes to the Bay over the years and to investigate the transport and redistribution of metals and P within the Bay and the adjacent coastal area, sediment cores were retrieved from 9 stations spanning the innermost Bay (station B1) to 25 km off in the Arabian Sea (station B25) over a distance of 65 km during April 1996-October 2000.

The distribution of metals in cores from the Bay is neither uniform nor any definite trends common to all the cores are discernible (Figures 3.5.1 to 3.5.3). Factors such as episodic fluxes of metals, bioturbation and mixing of sediments due to physical disturbance including dragging of anchors, trawling and dredging can result in such irregular profiles. The vertical mixing of the sediment due to disturbance that can lead to erratic profiles of metals (Pillai *et al.*, 1987) are less likely since excess ²¹⁰Pb inventories in several cores from the Bay support undisturbed state of the sediment (Sharma *et al.*, 1994). The concentrations of C_{org} in sediments of the Bay and their variations in the sediment have been studied (Ram,

2004). The results indicate only small incremental increase in its concentration in sediments as compared to the baseline indicating efficient mineralization of organic matter transferred to the bed.

3.5.1 Sedimentation rate

In pollution assessment through accumulation of a contaminant in sediments, knowledge of the depositional history of the sediment column gives an advantage of introducing time scale on the depth profile of a contaminant. Radionuclides such as ^{210}Pb ($t_{1/2}=22.3$ year) are useful to evaluate sediment accumulation rates over the past several decades (Swami and Lal, 1982; Ivanovich and Harmon, 1982).

The ^{210}Pb activity in sediments is influenced by the atmospheric component which accounts for up to 1.5 dpm/cm²/y (Krishnaswami and Lal, 1982) and by the in-situ component which, in a water column of 20 m, contributes about 0.01 dpm/cm²/y, considering an average ^{226}Ra concentration of 0.15 dpm/l (Sarin *et al.*, 1994). High inventories are recorded in areas which are sinks for radionuclides. Thus the northern segment of the Thane Creek where there is preferential deposition of SPM, sustains relatively high inventories of ^{210}Pb , whereas, the adjacent Mumbai Harbour where currents are strong and accretion of sediment is limited, the inventories are low. (Sharma *et al.*, 1994). Similar high inventories have also been reported for the coastal reaches of southern California (Bruland, 1974; Huh *et al.*, 1987).

The radioactive isotope ^{210}Pb with atomic weight of 210 occurs in nature in the $^{238}\text{U} - ^{206}\text{Pb}$ decay chain, which is in abundance in the Earth's crust. Hence, ^{210}Pb is naturally present in sediments and rocks that contain ^{238}U . ^{226}Ra decays to ^{222}Rn , which subsequently decays through a series of short-lived daughters to ^{210}Pb . Rn is a noble gas and rapidly escapes into the atmosphere. Rn decays to ^{210}Pb in a matter of days. The ^{210}Pb is rapidly removed from the atmosphere (mean residence time of about 10 d) by rain or snow and transferred to the surface water. ^{210}Pb is removed from river and ocean waters by a combination of

inorganic and biochemical reactions. Its mean residence time in the aquatic systems is short, usually less than 1 year. This atmospheric flux of unsupported ^{210}Pb is presumed to have remained constant at a given locality. Thus, it accumulates in soils, and lake and ocean sediments (via water), and glacial ice where it eventually decays into a non-radioactive form of Pb. If the sediment layers are undisturbed, then as the sediment ages, it slowly loses its radioactivity associated with ^{210}Pb . Thus, the age of a sediment layer can be determined by estimating its content of ^{210}Pb . Because of its half-life of 22.3 year, it takes about 7 half-lives or 150 year for the ^{210}Pb in a sample to reach near-zero radioactivity.

^{210}Pb is chemically immobile in sediment and undergoes β decay to ^{210}Bi . This is very low energy decay, which make direct measurement of ^{210}Pb difficult. Two general methods have been used to determine ^{210}Pb activity in sediment; (a) measurement of the ^{210}Bi daughter which undergoes a more energetic beta decay to ^{210}Po (half-life 5 d) (Krishnaswamy *et al.*, 1971; Koide *et al.*, 1972; Sharma *et al.*, 1994) and (b) measurement of ^{210}Po grand-daughter which undergoes α decay to stable ^{206}Pb (half life 138 d) (Robbins and Edginton, 1975; Nittrouer *et al.*, 1979). Both methods require an assumption of secular equilibrium between ^{210}Pb and measured isotopes. Isolation of sediment sub-samples for a period of 2 - 3 half-lives (9 -14 months) of ^{210}Po , allows the in-growth of ^{210}Po from its grandparents ^{210}Pb and ensures that secular equilibrium is attained between the two radionuclides. Determination of the ^{210}Po activity by α counting then provides an indirect measurement of the ^{210}Pb activity.

The samples are counted for periods of 2 to 3 days depending upon the activity of ^{210}Pb in the samples. The activity of ^{210}Po in the sample is determined from the ratio of the total counts of ^{208}Po to ^{210}Po and from the quantities of sediment and ^{208}Po added to the sample. Blanks and standards are measured to verify the performance of all aspects of the procedures and the instrumentation.

Core B2 used for ^{210}Pb dating was collected in 1997, more than 10 year before the dating was done. Hence, it is reasonable to assume that the measured activity of ^{210}Po in the sediment is in secular equilibrium with that of its parent, ^{210}Pb . Total ^{210}Pb and excess ^{210}Pb activities for this core are given in Table 3.5.1 and illustrated graphically in Figure 3.5.4. The total ^{210}Pb activity in the bottom 39-45 cm segments of the core varies from 0.61 to 0.67 dpm/g. Using the average activity of 0.06 ± 0.04 dpm/g in the bottom layers, resultant excess ^{210}Pb activity in each sediment section of the core was calculated and plotted against depth (Figure 3.5.4). The ^{210}Pb activity decreases with depth up to 10 cm followed by the bottom segment of more or less constant and low activity. The sediment is therefore relatively undisturbed in the vertical. The observed ^{210}Pb concentration gradient profile as a function of depth of sediment can result if the source of ^{210}Pb accumulating in an area varies with time resulting in a ^{210}Pb profile resembling that of a decay profile, or due to decay of ^{210}Pb with sediment depth. In order to ascertain which of these two processes controls the ^{210}Pb decay profile, $^{210}\text{Pb}/\text{Al}$ ratios were plotted as a function of depth (Figure 3.5.4). The nature of the profile remains unchanged no matter which process dominates. Normalisation of the ^{210}Pb concentration to the Al content of the sediment also overcomes the uncertainties due to porosity changes with depth in the sediment. The results indicate sedimentation rate of 0.97 cm/y for core B2.

Clay accumulation rates of 0.18-1.9 cm/y in sediment cores from the nearshore to outer continental shelf and slope regions in water depths of 10-1246 m of India have been reported by Borole (1988). The sedimentation rate decreases southward from the mouth of the Gulf of Khambhat (1.9 cm/y) to Thal (0.62 cm/y), just south of Mumbai. The sedimentation rates reported for the Bassein-Ratnagiri region are as follows:

Station	Sed. rate (cm/y)	²¹⁰ Pb excess inventory in sediments (dpm/cm ²)	Reference
U-35	1.7	-	Ram, 2004
U-37	2.93	140	Ram, 2004
B1 (Bay)	0.92	26	Jha <i>et al.</i> , 1999
B2	0.92	26	Jha <i>et al.</i> , 2003
B2 (Bay)	0.97	32	Present study
B6	1.94	181	Sharma <i>et al.</i> , 1994
B25 (Bay)	1.4	80	Deorukhakar,
Thal	0.62	33.8	Borole, 1988
R5	0.21	41	Deorukhakar,

Inventories of excess ²¹⁰Pb in the core sections were calculated from the equation

$$\Sigma \text{dpm/cm}^2 = \int A_0 \rho \tau$$

Where A_0 = activity at the interface, ρ = insitu bulk density of sediment, $\tau = 33.3$ =radioactive mean for ²¹⁰Pb = $(1/\lambda)$ and $\lambda = 1/(0.639/22.3)$.

Inventory of ²¹⁰Pb depends upon fallout, terrigenous influence, 'boundary scavenging', water column processes etc. Inventories higher than those expected in an area are due to sediment focusing of high terrigenous material while lower values than atmospheric fallout are due to winnowing effects by bottom current activities. This suggests a diversified nature of sedimentation occurring along this margin.

The station in the first column in the table represents the nearest locations used for the present sampling (Figures 2.1.2 to 2.1.6) from where the cores were obtained. Majority of these cores were collected within a few metres from these locations. The high sedimentation rates of 0.73 to 1.94 cm/y occurred in the Bay (Sharma *et al.*,1994), while, sedimentation rate of 1.4 cm/y has been reported off the mouth of the Bay (B25) (Deorukhakar, 2003). The sedimentation rate of 2.93 cm/y for

Bassein (core U37) is markedly higher than reported north as well as south of core U37. Monsoonal transport of high sediment load via the Ulhas River to the coastal area and its deposition under the prevailing circulation along the coast is perhaps responsible for unusually high sediment accumulation rate in this zone (Ram *et al.*, 2003). Incidentally, the coastal area studied by Borole (1988) and Sharma *et al.* (1994) does not receive any direct riverine fluxes of SPM.

3.5.2 Distribution of major metals

The trends which are evident from the profiles of Al and Fe (Figure 3.5.1 to 3.5.3), the major metals investigated in the present study, are discussed in the following sections:

a) Aluminium

Aluminium is the third most abundant element of the earth's crust, occurring in minerals, rocks and clays. Al is present in all natural waters as a soluble salt, a colloid, or as insoluble compound. In soils Al exists almost exclusively in the form of silicates, hydroxides, and oxides. Al as such does not have detectable toxic effects. However content of Al in sediment is considered as a measure of clay percentage which is useful in calculating level of enrichment of other heavy metals.

Similar to most coastal areas Al is present in high concentration in these sediments and is the weathered product of the basaltic catchment (Subbarao *et al.*, 1988). Because of its high percentage of occurrence, its concentrations are unlikely to be influenced by anthropogenic additions (Schropp and Windon, 1988; Loring, 1991) and changes in its vertical profiles are often due to episodic events such as floods, cyclones, submergence etc; the period during which mass transfer and deposition of sediment with differing characteristics can occur. Geochemically, Al is not an active element and <1% of sediment-bound Al is exchangeable. Hence, it is often used as an index of argillaceous fraction of sediments. Murty *et al.* (1978) have concluded that the Al content of the shelf

sediment (northwest coast of India) is terrigenous in nature and its deposition was confined upto roughly 60-65 m water depth and lower concentrations associated with the relict sediments of the outer shelf was due to low percentage of terrigenous material in them.

The Al profile (Figure 3.5.1) in core B1 is irregular and suggests sporadic deposition of the metal in the sediment. This is possible because core B1 belongs to the innermost portion of the Bay and is at the confluence of the Thane Creek and the Ulhas estuary. The SPM transported by the Ulhas River during monsoon is variable and mixes with the native sediment of the creek in this segment which can result in widely varying concentration of Al in sediments of this zone. The Al profiles in cores B2 and B3 support a distinct decrease of metal over the depositional history of roughly 50 year. Thus the concentrations of Al at the surface (7.9 %) of cores B2 and B3 progressively increases into the sediment with values in the range (7.8-9.0 %) in the bottom section. Hence, it appears that the clay content of the sediment has progressively decreased with time at these locations with the sediment texture getting coarser. The cores B4 and B5 do not reveal any trend in variation of Al content with the overall profiles suggesting the absence of significant change in the concentration between the surface and bottom sections. The Al content in core B6 on the contrary has gradually increased from 5.7 % at 40 cm depth to 7.3 % in the near-surface 6-7 cm section (Figure 3.5.1). Thus, the trend of depth-wise variation of Al in the cores of the inner Bay indicates local changes in the depositional regime of the metal which can probably be due to changes in the hydrodynamics as a consequence of construction of structures such as the bridges across the creek, reclamation, port development etc.

The Al profiles in cores B23 and B24 do not reveal marked changes in the depositional history of Al. The core B25 however indicates a distinct and systematic increase in the Al content from 4.8 % at the bottom section to 9.0 % at the surface. Based on the sedimentation rate of 1.4 cm/y reported for a core from the same site (Deorukhakar, 2003)

the core B25 represents the history of deposition of about 114 year. The sharp fall of Al content at 60-62 cm which pertains to the year 1954 is probably an episodic event which is also reflected in the profiles of Cr, Mn, Fe, Co, Ni, Cu and Zn in this core.

The Core R5 retrieved from the coastal area of Ratnagiri about 300 km southeast of Mumbai represents the depositional history of 460 year based on the sedimentation rate of 0.21 cm/y reported for the site (Deorukhakar, 2003). In this sediment the Al content has remained more or less steady in the bottom 42 cm. The concentration decreases markedly at 41-42 cm (5.7-6.1 %) above which concentration increases steadily to attain maximum of 7.8 % at 5 cm depth. The minimum at 41-42 cm has probably occurred some 190 years in the past and hence unlikely to be associated with man-made modifications in the catchment since the region even this date is thinly populated and industrially less developed. The intermediate peak around 48-50 cm in the Al profile coincides with similar peaks in the depth profiles of Cr, Fe, Ni and Cu suggesting their common source.

b) Iron

As the fourth most abundant transition element in nature and probably the most well known metal in biological system, iron constitutes about 4.7 % of the earth's crust. In aqueous solution iron occurs as Fe^{2+} and Fe^{3+} or as organic ferrous and ferric complexes. Discharge of effluent containing Fe into waterways, results in formation of finely divided hydroxides of iron which on settling adversely affect bottom dwelling organism.

As in the case of Al, Fe is present in high concentration in these sediments and its concentrations are unlikely to be influenced by anthropogenic additions. In marine sediments Fe is mainly present (i) in lithogenous minerals such as augite, hornblende, magnetite ilmenite etc, (ii) as Fe incorporated in sediments directly from seawater, (iii) in association with the clay minerals either as an essential constituent or as

a minor constituent within the crystal lattice, (iv) as Fe oxide on the surface of the mineral platelets, and (v) as Fe derived through biological processes. Fe content of 5-7.5 % has been reported in the sediment of the inner shelf (water depth >20 m), and 9.8-10.8 % for coastal sediment of the northwest coast of India (Paropkari *et al.*, 1994) which is largely derived from the surrounding landmass. Based on the partition patterns of Fe in recent sediments of northwest continental shelf of India Rao *et al.*(1976) have concluded that (i) the major fraction of Fe in the sediments of the inner shelf was of terrestrial origin through the metal held in the lattice structure of the detrital minerals, (ii) lithogenous fraction contributed more than 90 % to total Fe in the shelf sediment, (iii) relatively higher concentration of Fe was associated with the nonlithogenous fraction in the fine-grained sediment of the inner shelf thereby indicating that the metal was being removed from the overlying water and fixed in sediments through other processes, and (iv) being a zone of intense tropical weathering, possibly Fe leached from rocks as well as their products of weathering such as regur and laterite were carried by rivers in the colloidal state to the sea and getting flocculated in the coastal region leading to higher concentrations of Fe in the nonlithogenous fractions of the sediment.

As in the case of Al profile, the depth distribution of Fe (Figure 3.5.1) in core B1 is irregular indicating its variable flux to the sediment with time. The trend of concentration of Fe increasing with depth is similar to the Al profile in cores B2 and B3. The concentration of Fe in core B6 does not vary appreciably throughout the length and averages at 6.4 %. The Fe profile in core 23 indicates a distinct increase in the concentration subsequent to the year 1954 based on the sedimentation rate of 1.4 cm/y reported for the site (Deorukhakar, 2003). Thus the trend of variation of Fe in this core is opposite of that of Al ($r=-0.41$; $p<0.001$). The Fe content in core B24 does not reveal specific trend unlike in cores B25 and R5 wherein the Fe concentration has increased with the deposition of sediment and its profile resembles that of Al in these cores. As in the case of Al the minimum at 41-42 cm in core R5 has probably occurred some

190 years in the past, and hence, unlikely to be associated with man-made modifications in the catchment. Generally, Fe and Al seem to co-vary in the area with significant correlations in cores B1 ($r=0.99$; $p<0.001$), B2 ($r=0.77$; $p<0.001$), B3 ($r=0.47$; $p<0.001$), B4 ($r=0.63$; $p<0.001$), B5 ($r=0.83$; $p<0.001$), B25 ($r=0.93$; $p<0.001$) and R5 ($r=0.84$; $p<0.001$) [Appendix-III(b)].

3.5.3 Distribution of minor elements

a) Chromium

Over the past several decades increased quantities of chromium compounds have been used by man and introduced into the environment. Cr can exist in different oxidation states like 2^+ , 3^+ , 5^+ and 6^+ and the danger of environmental contamination depends on the oxidation state of the metal. In its Cr^{6+} form it is 100 to 1000 times more toxic than the most common Cr^{3+} compounds (Gauglhofer and Gallen, 1991). Cr^{6+} compounds cause skin inflammation or eczema in fish, mammals and humans and after a longer latent time they can produce lung cancer (Gauglhofer and Gallen, 1991). The major source of Cr to the Bay is expected to originate from electroplating and tanning industries apart from the contribution due to sewage which is estimated at 4.82 kg/d [Appendix-I(c)]. Due to strong reducing conditions in sewage, Cr associated with it would be in the trivalent state. Although Cr does not form sulphide in water, its reduction to trivalent state accelerates the precipitation as hydroxide (Johnson *et al.*, 1992). Also, due to the extremely slow rate of oxidation of Cr^{3+} to Cr^{6+} even in oxidizing environment, no significant changes in concentrations of Cr are expected under changing redox condition in the sediment types (Johnson *et al.*, 1992).

The concentration of Cr in the cores under study varies considerably in some instances from surface to bottom while in others the changes in the vertical distribution are not marked thereby making the assessment of anthropogenic component of the metal a difficult task. The concentration of Cr in the catchment soil varies in 82-567 $\mu\text{g/g}$ range. Its concentration in the bottom sections of cores obtained from the coastal

area also varies considerably (Figures 3.5.1 and 3.5.2). Thus the concentration in the bottom sections of the cores B23, B24 and B25 is 202-241, 189-201, and 70-87 $\mu\text{g/g}$ respectively. This makes it difficult to fix the lithogenic background of Cr for the study area.

Cr concentration in the shale is reported to be 90 $\mu\text{g/g}$ (Turekian and Wedepohl, 1961). In regions unaffected by pollution the levels of this metal have been found to be normally below 100 $\mu\text{g/g}$ in marine sediments (Belmans *et al.*, 1993) while, highly variable concentrations have been observed in regions influenced by inputs of Cr (Szefer *et al.*, 1999). Thus for instance, in Weschnitz River (Germany) which is polluted by waste from tanning and other industries, the concentration of Cr in sediment was 493 $\mu\text{g/g}$ (Forstner, 1979b).

The core B23 reveals high concentration of Cr (174-245 $\mu\text{g/g}$) in the bottom 47-80 cm segment. The core obtained from this area has been dated and with the reported sedimentation rate of 0.72 cm/y (Deorukhakar, 2003), the sediment at 80 cm depth would have been deposited more than 110 year in the past. The variation of ^{210}Pb in sediment profile of this area indicates undisturbed nature of the sediment (Deorukhakar, 2003). Considering the history of industrialization in the region, the concentration recorded at the bottom of this core does not seem to be of anthropogenic origin. This suggests that the natural concentrations of Cr in sediment of the region vary widely and can be upto 250 $\mu\text{g/g}$ as observed in core B23. The concentration profiles of Cr in cores B1, B3, B4, B6, B23, B24 and B25 (Figures 3.5.1 and 3.5.2) therefore do not seem to support anthropogenic accumulation of Cr in the sediment.

The concentration of Cr in core B2 is uniformly high and generally exceeds 300 $\mu\text{g/g}$ throughout the core length. With the sedimentation rate of 1 cm/y recorded for this site (Jha *et al.*, 2003) the core represents the history of about 50 year before 1997 when the core was collected. This core was retrieved from the area adjacent to the Thane-Belapur industrial

belt and probably represents significant contribution of anthropogenic Cr. The trend of Cr variation in core B25 indicates systematic increase from 139 µg/g at 120 cm depth to 166 µg/g at the surface. However, Al and Fe concentrations also increase consistently from the bottom to the top (Figure 3.5.2). Hence, the upward increase in Cr in this core can be due to the grain-size effect or due to association of trace metals with Fe (Reuther, 1994). A small but prominent increase in the concentration of Cr at 42-58 cm segment of core R5 may be due to increase in Al and Fe content at that level.

The depth profile of Cr in core B5 is strikingly different (Figure 3.5.1) from all other cores investigated during the present study in that there are sharp peaks of abnormally high concentrations of the metal (1423-3308 µg/g) at 1, 10, 18, 19, 21, 22, 24, 25, and 27 cm. Similar unusually high concentrations of Mn, Co, Ni and Zn also occur at the same depths where high concentration of Cr are seen in the profile. Such peaks are however absent in the Cu profile and its concentration in this core is comparable with that observed in others. It therefore appears that the sediment at site B5 received sporadic input of anthropogenic material rich in Cr, Mn, Co, Ni and Zn. The Figure 3.5.1 also indicates high percentage of Al coinciding with the peaks of trace metals in the core profile while such peaks are absent for Fe. It is probable that the sediment at this site has been intermittently enriched with metallic particles such as Al-Si alloys which are mainly used in castings. Cr, Mn, Co, Ni and Mo are generally present in such alloys as correctives for Fe and their addition also improves strength at high temperature. Zn is a tolerated impurity in many such alloys; often upto 2 %. The Cu-free Al-Si alloys are used for low- to medium-strength castings with good corrosion resistance (Basavakumar *et al.*, 2008).

In cores B1, B5, B6, B23 and B25, Cr concentration directly varies with that of Al with the correlation coefficient (*r*) of 0.46-0.88 (*p*=0.001). The remaining cores reveal poor correlation. Excellent positive correlations also occur between Cr and Fe in cores B1, B2, B9 and B25

($r=0.58-0.94$; $p=0.001$). Cr-Fe relationship is negative in core B23 ($r=-0.76$; $p=0.001$). This type of behaviour of Cr is difficult to explain on the basis of the available data.

c) Manganese

Mining operation of Mn ores and industrial sources like manufacture of iron and steel, ferromanganese metals, dry cell batteries as well as fossil fuel burning are some of the source of environmental Mn. Use of pyrolusite in industry, and in uranium extraction from ores can also be the source of Mn input into the aquatic system.

Mn in trace amounts is an essential nutrient element, required for normal function of cell, however it is toxic in higher concentration. Chronic exposure to Mn can cause neurological disorder. Manganese exists mostly in the oxidation state 2^+ in natural salts and in stable native black manganese oxide, MnO_2 , its oxidation state is 4^+ . Synthetic compounds of Mn are known in nearly all valence stage between 3^- and 7^+ .

Understanding of the behaviour of Mn in oxic and anoxic sediments is essential to interpret Mn profiles in aquatic sediments. In shallow marine environment where water above the sediment is generally oxygenated, Mn oxides of higher oxidation states precipitate in the superficial sediment. If the subsurface sediment is anoxic and hence reducing which is often the case in areas receiving sewage, Mn oxides are reduced and mobilized and diffuse upwards through interstitial water. On reaching the superficial oxic layer the Mn gets oxidized and precipitated thereby enriching the surface sediment. This results in decrease in Mn content in the subsurface sediment and its subsequent enrichment in the surface layer. In natural marine sediments the enriched layer is often observed at subsurface depth due to the oxidation of upward diffusing Mn^{2+} by downward diffusing oxygen, both species being completely consumed within the sediment (Alvarez *et al.*, 2003).

The inner shelf area of the northwest coast of India exhibits low levels of Mn (500-750 µg/g) North of Dwarka and South of Ratnagiri, intermediate levels in segments Porbandar-Diu and Mumbai-Ratnagiri (750-1000 µg/g) and high concentrations (>1000 µg/g) between Diu and Mumbai (Murty *et al.* 1978). Occurrence of low concentration of Mn (<250 µg/g) in the sediments of the outer shelf suggests its terrigenous source with about 60 % of Mn associated with the lithogenous fraction of the sediments. Even within this fraction the major portion of the metal is associated with the clay minerals and a small percentage in the resistant detrital minerals (Murty *et al.*, 1973).

The Bay being shallow and tidal influence is substantial, the water column is generally oxygenated (Zingde and Govindan, 2000). Hence, the base of the oxidized layer is expected to be a few centimetres below the sediment-water interface. The profiles of Mn distribution in the cores however are irregular making it difficult to understand the behaviour of Mn in these sediments. The mean profile of Mn in core B1 which indicates an upward increase of the metal may not be due to mobilization of Mn and its transport through porewater. The Mn profile resembles closely with the trend in variation of Al and Fe in this core resulting in excellent correlations of the metal with Al ($r=0.93$; $p<0.001$) and Fe ($r=0.93$; $p<0.001$). It is possible that Mn is associated with these major elements and the observed profile of its variation in core B1 is due to changes in the contents of Al and / or Fe.

The variation of Mn in core B3 can be explained based on its mobilization in the sediment and its diffusion to the water column under anoxic conditions. However, as discussed earlier, the sediment-water interface is unlikely to be anoxic in the Bay and the mobilized Mn would precipitate in the surface sediment which is not supported by the metal profile. It is possible that Mn is associated with Fe in the sediment with which it has good positive relationship ($r=0.5$; $p<0.001$). The profiles of Mn and Al are also similar with trend of concentrations increasing with depth in this core. The unusual profile of trace metals in core B5 has

been discussed earlier and is attributed to anthropogenic addition of material such as an alloy of Al. As expected based on this assumption, Mn varies directly with Al ($r=0.60$; $p<0.001$), Cr ($r=0.97$; $p<0.001$), Co ($r=0.97$; $p<0.001$), Ni ($r=0.99$; $p<0.001$) and Zn ($r=0.99$; $p<0.001$). Its relationship with Fe, Cu and P is not significant in this core.

In the openshore core B23 the concentration of Mn averages around 903 $\mu\text{g/g}$ in the segment between 4 and 80 cm. The concentration is markedly high (1016-1402 $\mu\text{g/g}$) in the top 3 cm sediment section. Probably Mn reduced in the sediment and diffusing through the porewater is precipitated in the top section under oxic conditions. Enrichment of Mn in oxic layer of the sediment is well established in limonitic (Takematsu, 1979; Takematsu *et al.*, 1985; Mok and Wai, 1990) as well as marine (Farmer and Lovell, 1986; Yadav, 1996) sediments. Mn does not have any significant correlation with Al, Fe and other metals in core B23. The Mn profile in cores B4 and B6 does not indicate any trend while the concentration is generally uniform throughout the length in core B25. Mn indicates good positive relationship with Al ($r=0.48$; $p<0.001$) and Fe ($r=0.71$; $p<0.001$) in this core. The average concentration of Mn (359 $\mu\text{g/g}$) in core R5 is considerably lower than in cores B23, B24 and B25. The concentrations of Al and Fe are also relatively low in this core. The surface to bottom variation in Mn concentration in this core is irregular even though it indicates good positive relationship with Al ($r=0.46$; $p<0.001$), Fe ($r=0.46$; $p<0.001$) and Cu ($r=0.37$; $p>0.001$).

Mn concentration in cores from the upper slope of the Arabian Sea is in the range 285 - 350 $\mu\text{g/g}$ while, that in the cores of the lower slope is much higher (1900 - 10160 $\mu\text{g/g}$) on CaCO_3 free basis, in surface sections (Yadav, 1996). Low levels of Mn in the upper slope sediments have been explained on the basis of remobilisation in anoxic upper slope while only redistribution occurs in the lower oxic cores without net mobilization. Severe depletion of DO even at 100 m attaining near zero values at about 200 m throughout the Arabian Sea, is a common feature (Naqvi *et al.*, 2000). As the upper slope sediment is in contact with water

that is severely depleted in DO, Mn that is mobilised within the sediment is lost to the overlying water thereby depleting sediment Mn. Thandrup *et al.* (1994) have shown that mobilisation of Mn^{2+} resulted in elevated Mn concentration in the bottom water and much higher Mn/Fe ratios in SPM than surface sediment of Aarhus Bay, Denmark.

d) Cobalt

Common oxidation states of cobalt are 2^+ and 3^+ . However, compounds of Co^0 , Co^{1+} and Co^{1-} are also known. At low concentration Co is required for biological processes. With limited use of Co by industries around the Bay, the major source of input of the metal to the marine area can be through sewage (18.2 kg/d). Bombay Harbour sediments have been reported (Gogate *et al.*, 1976) to contain 7-23 $\mu\text{g/g}$ cobalt. The values emerging from the present study are somewhat higher but are comparable with its content in the catchment soil. The concentration of Co in core B1 is comparable throughout the core length with direct variation with Al ($r=0.56$; $p<0.001$), Mn ($r=0.57$; $p<0.001$), Cu ($r=0.58$; $p<0.001$) and Ni ($r=0.53$; $p<0.001$). Its profile of increase in concentration with depth in cores B2 and B3 is in line with the variation of Al and Fe in these cores. Thus, Co and Al ($r=0.74$; $p<0.001$) as well as Co and Fe ($r=0.6$; $p<0.001$) are positively correlated in core B2. A small increase in the concentration of Co from the bottom to the surface in cores B6 and B25 is in agreement with the decrease in Al content into the sediment. In core B25, Co varies directly with Al ($r=0.61$; $p<0.001$).

e) Nickel

The concentration of Ni in the catchment soil varies in 57-1181 $\mu\text{g/g}$ range and averages at 212 $\mu\text{g/g}$. With the exception of core B5 its concentration in the sediment cores is generally less than 150 $\mu\text{g/g}$ suggesting its removal from SPM during transport from the catchment and its deposition in the marine sediments of Mumbai. The concentration in the bottom sediment of cores B23, B24 and B25 which probably was deposited prior to industrial development of the Mumbai region, varies in the range 62-74 $\mu\text{g/g}$. Hence, the concentrations of Ni in cores from the

Bay in excess of 74 µg/g may be of anthropogenic origin. However, as discussed earlier, due to its high concentrations in the catchment soil the sporadic natural contribution is also a possibility.

Direct variation of Ni with Al ($r=0.96$; $p<0.001$), Cr ($r=0.84$; $p<0.001$), Mn ($r=0.92$; $p<0.001$), Fe ($r=0.97$; $p<0.001$), Cu ($r=0.62$; $p<0.001$) and Zn ($r=0.80$; $p<0.001$) in core B1 indicates its association with the major metals. Its profile of increase in concentration with depth in core B2 is in line with the variation of Al and Fe. The concentration of Ni in core B2 directly varies with significant correlations with Al ($r=0.74$; $p<0.001$), Fe ($r=0.7$; $p<0.001$) and Co ($r=0.8$; $p<0.001$). Likewise though the concentrations of Al and Fe decrease into the sediment in core B3, the concentration of Ni is relatively high throughout the core length probably due to anthropogenic contribution. The concentration of Ni is uniformly high in cores B4 and B6 with unusually high concentration (193-194 µg/g) in 26-27 cm segment. Its concentration in core B4 directly varies with that of Cr ($r=0.6$; $p<0.001$), Cu ($r=0.83$; $p<0.001$) and Zn ($r=0.79$; $p<0.001$), while, in core B6 its concentration is positively correlated with Al ($r=0.5$; $p<0.001$) and Cu ($r=0.56$; $p<0.001$). Vertical profiles of Ni in cores B23 and B24 are more or less uniform throughout the core length though the concentrations of Al, Fe and some other metals indicate considerable variations. The concentration of Ni varies directly with that of Fe ($r=0.55$; $p<0.001$) in core B24 while such a relationship is absent in core B23.

The depth profile of Ni in core B25 is similar to that of Al and Fe with significant correlations [Al-Ni ($r=0.87$; $p<0.001$); Fe-Ni ($r=0.98$; $p<0.001$)]. The concentration of Ni also varies directly with that of Cr ($r=0.93$; $p<0.001$), Mn ($r=0.72$; $p<0.001$), Co ($r=0.85$; $p<0.001$), Cu ($r=0.92$; $p<0.001$) and Zn ($r=0.71$; $p<0.001$) in this core. A sharp decrease in Al (4.0-4.9 %) and Fe (4.7 %) contents at 60-62 cm in this core is also reflected in decrease in the concentrations of most trace metals suggesting their lithogenic source. Similarly the peak at 11 cm in the Fe profile has resulted in similar spike in the profiles of all other trace

metals. Highest concentration of Cr (230 µg/g), Mn (1221 µg/g), Co (69 µg/g), Ni (79 µg/g) and Cu (71 µg/g) and second highest of Zn (226 µg/g) in this core occur at 32 cm depth. Profiles of Al and Fe do not have such prominent peak at 32 cm suggesting that the trace metals in this core segment are probably associated with Mn. The depth distribution profile of Ni in core R5 is similar to those of Al and Fe with which it appears to be closely correlated [Al-Ni ($r=0.36$; $p<0.001$); Fe-Ni ($r=0.61$; $p<0.001$)].

f) Copper

Cu mining and metallurgical operations contribute to contamination of aquatic environment. Cu is toxic to many aquatic plants at low concentrations. Lethal Cu concentration for fish and aquatic invertebrates range from 0.015 to 3.0 mg/l. The toxicity of Cu to aquatic organisms vary with the chemical species present in water and other environmental parameters like temperature, pH, turbidity, hardness etc.

The concentrations of Cu in the cores (98-198 µg/g) are considerably lower than that in the catchment soil (av. 208 µg/g). In the bottom sections of the cores B23 to B25 its concentration varies in 27-101 µg/g range. Considering this as the background, the levels of Cu in cores from the Bay are consistently high suggesting anthropogenic addition. Sewage released to the Bay contributes 53.4 kg/d of Cu and in view of its high industrial use its fluxes to the Bay could also be significant though estimates are lacking.

Cu forms highly insoluble sulphides and is therefore expected to remain fixed in the sediment (Forstner, 1979b). Its concentration in core B1 varies widely but these variations seems to be in accordance with the changes in Al and Fe contents. Evidently, its concentration co-varies with those of Al ($r=0.56$; $p<0.001$) and Fe ($r=0.56$; $p<0.001$). Its relationship with Co ($r=0.58$; $p<0.001$), Ni ($r=0.62$; $p<0.001$) and Zn ($r=0.64$; $p<0.001$) is also significant. As in the case of Ni, its profile in core B2 which is inverse of that of Al and Fe, indicates incremental increase of anthropogenic Cu in the sediment. Thus, its concentration of 119 µg/g in

the bottom sediment increases gradually and attains maximum (147 µg/g) at 19 cm – the sediment deposited around 1978-1981 based on the reported sedimentation rate of 1 cm/y (Jha *et al.*, 2003). The flux of the metal seems to have decreased marginally subsequently as reflected in decrease in concentration of the metal in the sediment above; the concentration of Cu in the surface sediment of this core being 135 µg/g. Similarly, though the concentration of Cu in core B3 varies considerably with depth, the trend suggests definite increase in concentration in the sediment deposited subsequent to 1963. Because of this incremental increase the concentration of Cu is inversely related with that of Al ($r=-0.43$; $p<0.001$) in core B3. Its concentration however varies directly with that of Cr ($r=0.53$; $p<0.001$), Ni ($r=0.5$; $p<0.001$) and Zn ($r=0.8$; $p<0.001$) in this core.

The depth variation of Cu in core B4 does not reveal significant trend though the profile resembles that of Cr, Ni and Zn with some increase in the mid-segment. The concentration of Cu in this core varies directly with that of Cr ($r=0.6$; $p<0.001$), Ni ($r=0.83$; $p<0.001$) and Zn ($r=0.95$; $p<0.001$) with inverse relationship with Mn ($r=-0.66$; $p<0.001$). Unlike other trace metals which reveal sharp high concentration peaks in their vertical profile (Figure 3.5.1), the concentration of Cu does not vary appreciably throughout the core length with good positive correlation. The concentration profiles of Cu in cores B23 and B24 are featureless with concentrations remaining more or less similar throughout the core length. It bears good positive correlation with Mn ($r=0.45$; $p<0.001$), Fe ($r=0.49$; $p=0.001$), Co ($r=0.37$; $p<0.001$) and Ni ($r=0.61$; $p<0.001$) in core B24 while its relationship with other metals is insignificant in core B23. The concentration profile of Cu in core B25 seems to be influenced by Al and Fe as in the case of other trace metals.

g) Zinc

Zinc is also an essential element and plays a vital role in the physiological and metabolic processes of many organisms. However, in high concentration, it is toxic to organisms. Zinc is very widely used metal

and its main sources of aquatic contamination are metal production units and other industrial uses of the metal and its compounds.

It is generally agreed that the oxidation-reduction environment of the sediment-water system influences the mobilization of Zn. However, the processes involved have not been fully understood. Some investigators have concluded that Zn was more soluble under reducing conditions because of the reduction of Fe and Mn oxide which have been considered to co-precipitate Zn under oxidizing conditions (Brooks *et al.*, 1968; Windom, 1972). Due to low solubility of Zn in the presence of sulphides, which occur under reducing conditions some other workers consider that Zn should be more soluble under oxidizing conditions (Holmes *et al.*, 1974; Lu and Chen, 1977).

The concentration of Zn in the catchment soil of the Mumbai region varies from 44 to 168 $\mu\text{g/g}$ averaging at 115 $\mu\text{g/g}$. Its concentration in the bottom sections of cores B23, B24 and B25 falls in the range 34-261 $\mu\text{g/g}$. Hence, it is reasonable to assume that its concentration in sediments higher than these values originates from anthropogenic sources. Sewage alone transports 398.1 kg/d of the metal to the Bay apart from other sources. In core B1 its concentration has doubled or even tripled in several sections. Similar to other trace metals, the concentration of Zn in core B1 shows good positive correlation with Al ($r=0.71$; $p<0.001$), Fe($r=0.72$; $p<0.001$), Cr ($r=0.61$; $p<0.001$), Mn ($r=0.7$; $p<0.001$), Ni($r=0.8$; $p<0.001$), and Cu ($r=0.64$; $p<0.001$). Similarly, its concentration has incrementally increased from 78 $\mu\text{g/g}$ at 50 cm depth to 146 $\mu\text{g/g}$ at the surface in core B2. Because of its anthropogenic addition and the trend of increasing concentrations of Al and Co into the sediment, its concentration is negatively correlated with Al ($r=-0.52$; $p<0.001$) as well as Co ($r=-0.6$; $p<0.001$). The profiles of Zn and Cu are strikingly similar in core B2 – both the metals being externally added, with good positive correlation between them ($r=0.9$; $p<0.001$). Zn also varies directly with Mn ($r=0.6$; $p<0.001$) in this core. Zn profile in core B3 is typical of incremental anthropogenic accumulation of the metal with the

bottom (87 µg/g) concentration considerably lower than at the surface (138 µg/g). As in the case of core B3, the concentration of Zn in this core varies inversely with that of Al ($r=-0.59$; $p<0.001$) and Co ($r=-0.5$; $p<0.001$) and directly with that of Cu ($r=0.8$; $p<0.001$).

The Zn profile in core B4 suggests accumulation of Zn throughout the length with values as high as 300-400 µg/g in the mid-segment. Its concentration varies directly with Cr ($r=0.6$; $p<0.001$), Ni ($r=0.79$; $p<0.001$) and Cu ($r=0.95$; $p<0.001$) and inversely with Mn ($r=-0.72$; $p<0.001$) in this core. Its concentration is higher than the expected baseline in core B6 with episodic additions of the metal represented by sharp peaks in its depth profile. Zn and Cu show significant positive correlation ($r=0.42$; $p>0.001$) in this core. The Zn profile in core B23 is unusual in that the concentrations are markedly high (120-156 µg/g) in the 48-56 cm segment as compared to the rest of the core except in the surface section. Its concentration seems to vary with that of Cr ($r=0.58$; $p<0.001$) and their high concentrations in the surface sediment which coincide with that of Mn seems to be due to their mobilization along with Mn. The Zn profile in core 25 with concentration decreasing into the sediment is similar to that of Al ($r=0.54$; $p<0.001$) and Fe ($r=0.64$; $p<0.001$) with significant correlations and its concentration does not indicate anthropogenic contribution. Zn also varies directly with Mn ($r=0.59$; $p<0.001$), Ni ($r=0.71$; $p<0.001$) and Cu ($r=0.70$; $p<0.001$) in this core. Unlike the peak at 13 cm in the Zn profile, the spike at 32 cm coincides with the peaks in the profiles of Cr, Mn, Co, Ni and Cu. Except for one value (166 µg/g) the concentration of Zn in core R5 is less than 70 µg/g.

h) Cadmium

Cd is a potential hazardous pollutant in the environment and chronic human exposure to low concentrations of this element in atmosphere, water or food may cause serious illness and possibly death. The sources of Cd are mainly through discharges from electro-plating, battery, dyes, fertilizer, photographic and chemical industries. Cd forms

strong complexes with bisulphide and chloride anions in solution but is only weakly attracted to organic ligands. Probably CdS controls cadmium solubility in anoxic estuarine sediments, but where high free sulphide concentrations prevail, Cd may exist in solution as bisulphide complexes (Davies-Colley *et al.*, 1985).

Cd was analyzed in selected cores namely B1, B2, B3, B23, B24 and R5 and its depth profiles are illustrated in Figure 3.5.3. The concentration of Cd in the catchment soil varies in the range 0.03-0.53 µg/g averaging at 0.2 µg/g. Its concentration in the bottom section of the cores B23 and B24 is 0.42 µg/g and 0.13 µg/g respectively. It is therefore reasonable to consider that the lithogenic baseline for the Bay sediment would be around 0.3 µg/g and the concentrations higher than 0.3 µg/g in the sediment result from anthropogenic sources. Less than 0.25 µg/g Cd have been reported in unpolluted Bermuda sediments (Lyons *et al.*, 1983) and Cd levels at 1 m depth were around 0.3 µg/g in the sediment core from the North Sea. The average shale concentration has been considered to be 0.3 µg/g (Turekian and Wedepohl, 1961).

Application of the sedimentation rate of 1 cm/y for the inner Bay to the Cd profile in core B1 indicates considerable increase in its concentration in the period 1975-1989 and decrease from 1993 to 1997. Based on the baseline of 0.3 µg/g, its concentration in core B1 is magnified at least 2 to 20 times which is due to the influence of industrial and sewage effluents. Anthropogenic Cd in core B2 has increased gradually from 0.3 µg/g in 1983 to a maximum of 1.02 µg/g in 1996. Likewise the average profile of Cd concentration in core B3 indicates an increase in concentration from 0.07 µg/g at 37 cm depth corresponding to the year 1950 to a high of 2.72 µg/g at 15 cm depth (1972) followed by a decrease. The signature of anthropogenic Cd entering the Bay is seen even in core B24 obtained 25 km off the Bay mouth wherein the concentrations in the top 10 cm sediment are relatively high as compared to levels below. The concentration of Cd in the bottom section of core R5 deposited some 450 years in the past is 0.55 µg/g which is relatively high

as compared to the baseline (0.3 µg/g) considered for the Mumbai region. Considering the period of deposition, the observed concentration can be considered as the lithogenic baseline. Its concentration profile in core R5 though irregular, indicates a trend of decrease in concentration over the past 65 year with the concentration in the surface sediment comparable to the baseline considered for the Mumbai area.

Unlike most other metals, Cd has no significant relationship with other metals in core B1. Its concentration in core B2 varies inversely with the Al content ($r=-0.42$; $p=>0.001$) but varies directly with Cu ($r=0.37$; $p=>0.001$) in core B3. Its concentration varies inversely with that of Al ($r=-0.38$; $p=<0.001$) but directly with that of Pb ($r=0.33$; $p=>0.001$) in core B24.

i) Lead

Pb is an element occurring naturally in the earth's crust, however, its concentration can be significantly elevated in the environment due to industrial activities, including mining and smelting of metalliferous ores, burning of leaded gasoline and the use of fertilizers, pesticides, sewage sludge and Pb-based paints. As soil contaminant, Pb is one of the more persistent heavy metal and it is extremely difficult to remediate because it is strongly bonded to organic and inorganic ligands and has therefore only limited bioavailability in the soil (Adriano, 2001). One major source of environmental lead and of lead exposure to humans, both through direct inhalation and from ingestion following contamination of food chains, has been from the combustion of leaded petrol. From the 1930s onward, tetra-alkyl lead additives have been used as antiknock agents in petrol for motor vehicles and, by the 1970s, lead fallout from the combustion of petrol accounted for around 90% of the atmospheric lead input in urban environments (Anagnostopoulou and Day, 2006).

Like Cd, Pb was analyzed in selected cores. From Table 3.2.3 it can be considered that the average concentration of Pb in the catchment soil is 21.7 µg/g though the values vary in a wide range. Its concentration

in the bottom section of the cores is generally around the catchment baseline but is nearly double (46.4 $\mu\text{g/g}$) in core B24. The available data is unable to explain this anomaly. It is presumed that the baseline concentration in these cores would be close to that recorded in the catchment soil.

In core B1 the concentration of Pb gradually increases from 28.7 $\mu\text{g/g}$ at the bottom to 35.7 $\mu\text{g/g}$ at 16 cm depth followed by an overall steeper increase in the 10-15 cm segment with the maximum value of 53.7 $\mu\text{g/g}$. From thereon the concentration decreases to 23.3 $\mu\text{g/g}$ at the surface. Unlike most other trace metals, Pb does not show significant relationship with others in this core. The Pb profile of core B2 reveals a similar trend as in core B1 with baseline concentration in the lower 34-50 cm core length that is sediment deposited prior to the year 1957. There is a sharp and abrupt rise in 33 cm segment of the core B2 (129.8 $\mu\text{g/g}$) and the concentration continues to be high until upto the year 1982 with value of 318.3 $\mu\text{g/g}$ at 15 cm depth of the sediment. The concentration sharply decreases (21.2-26.3 $\mu\text{g/g}$) in the top 3 cm of the core. The concentration of Pb in core B3 is variable, but, it is in the vicinity of the background throughout the core length except in the 27-31 cm section where the levels are mildly elevated. The Pb concentration varies inversely with that of Al ($r=-0.41$; $p>0.001$) in core B2 but varies directly with Mn ($r=0.62$; $p<0.001$), Cu ($r=0.76$; $p<0.001$) and Zn ($r=0.73$; $p<0.001$).

From the trend of distribution of Pb in the Bay sediments and core B2 in particular, it appears that there was an anthropogenic source of Pb in the vicinity of Ghansoli in the period 1964-1994, probably an industry, and that the flux of Pb to the Bay decreased progressively after 1982 possibly because of enforcement of treatment to effluents prior to release by the Maharashtra Pollution Control Board. The relative high concentration of Pb in core B1 is likely to be from the same source. The load of Pb (8.13 kg/d) associated with the release of sewage to the Bay may not be contributing significantly as compared to the industrial source since in that case the concentration profile of Pb is expected to indicate

decreasing concentration into the sediment since the volume of sewage released to the Bay has increased progressively over the years. From near baseline concentrations seen in core B3 it appears that Pb entering the Bay near Ghansoli is largely removed to the sediment in the vicinity of its entry. The decrease in Pb concentration in near-surface sediments in cores B1 and B2 is not due to prohibition in Pb in auto fuels since this was enforced only after 1996 (Elless *et al.*, 2007; Anagnostopoulou and Day, 2006) just an year prior to collection of cores.

Except in the top 3 cm, the concentration of Pb in core B23 is comparable to the baseline. The relative high concentration (31.4-69.2 µg/g) in the top 3 cm of the sediment is probably due to mobilized Pb along with Mn. The peak at 23 cm (36.3 µg/g) in the Pb profile also coincides with that of Mn in this core. Pb concentration varies inversely with Al ($r=-0.35$; $p=>0.001$) in this core but directly with Mn ($r=0.72$; $p=<0.001$), Co ($r=0.36$; $p=>0.001$) and Cd ($r=0.54$; $p=<0.001$). The background concentration of Pb in core R5 seems to be around 8 µg/g and hence lower than considered for the Mumbai region. The Pb profile in this core indicates an upward incremental increase in the concentration of Pb with the concentration of 16.9 µg/g in the surface sediment. Since the increasing trend is seen even in the sediment deposited some 200 year in the past it is unlikely to be due to anthropogenic Pb such as through atmospheric fallout and is possibly related to a large extent to increasing trend in the Al and Fe contents. This also supported by positive correlation of Pb with Fe ($r=0.42$; $p=<0.001$) as well as Al ($r=0.43$; $p=<0.001$) in this core.

j) Phosphorus

P is generally associated with Fe in marine sediments in complexes such as vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$, strengite, $FePO_4 \cdot 2H_2O$, hydroxyapatite $Ca_5OH(PO_4)_3$ and truvite $MgNH_4PO_4 \cdot 6H_2O$ which are almost insoluble compounds in aerobic environments (Matisoff *et al.*, 1975; Martins *et al.*, 1978; Kelderman, 1984) and the mechanism of its release from sediments has been established.

Fe-phosphate in sediments becomes more soluble when the redox potential falls low enough for ferric-Fe to be reduced to ferrous-Fe. Hence, P concentration in porewater of anaerobic sediment may be quite high (Masuda and Boyd, 1994). This pool of P is largely unavailable to the water column because Fe-phosphate reprecipitates when ferrous-Fe and phosphate diffuse into the aerobic layer normally existing at the sediment-water interface. P either precipitates directly as Fe-phosphate or it is adsorbed onto the surface of the floc of Fe^{3+} hydroxide precipitating from the oxygenated water. Solubilisation of FePO_4 , $\text{Ca}_3(\text{PO}_4)_2$, CaHPO_4 and $\text{Mg}_3(\text{PO}_4)_2$ during heterotrophic decomposition of organic matter is attributed to the formation of organic acids which function as chelating agents releasing free phosphate ions (Price, 1976; Berner, 1980; De Lange, 1986).

Sewage and agricultural runoff are considered to be the major anthropogenic sources of P to the coastal marine environment (Kumarsingh *et al.*, 1998). The hinterland of the study area being mountainous and rugged agriculture is limited and the rivers being short their basins are small. Hence, sewage that transports 4393 kg/d of P can be considered as the major anthropogenic source of P to the nearshore areas of Mumbai.

The P can be labile in aquatic sediments and its adsorption and desorption at the sediment water interface has been well established (Rochford, 1951). In fact aquatic sediments have been considered important in buffering the concentration of dissolved phosphate in estuaries and coastal areas (Pomeroy *et al.*, 1965). Desorption is dominant in unpolluted waters where phosphate concentration could be below the equilibrium value (Fox *et al.*, 1986; Froelich, 1988). The results however are contrary for the Bay and the coastal area of Mumbai. The concentrations of PO_4^{3-} -P in seawater of the region are variable but often high and in considerable excess than expected based on the N:P ratio (Bapardekar, 2004). The depth profile of dissolved PO_4^{3-} -P with distinctly

high concentrations in the bottom water indicated release of P from Mumbai Harbour and Baltic sediments (Zingde *et al.*, 1989; Hansen, 1990).

Arriving at the probable baseline for P in the sediment of Mumbai based on the available information is difficult. Published data for nearshore waters of India indicate variable levels in sediments. Total phosphorus in the range 96-372 $\mu\text{g/g}$ has been reported for the west coast of India (Gogate *et al.*, 1970) and 51-245 $\mu\text{g/g}$ for Bombay Harbour (Matkar *et al.*, 1981). While, concentrations in the range 390-1370 $\mu\text{g/g}$ have been reported for the surficial shelf sediment off Mumbai (Murty *et al.*, 1968). Paropkari *et al.* (1994) have reported P_2O_5 content of <0.25 % in the inner shelf sediment of the region between the mouth of the Indus and Murud that increases to 0.5-1 % in the zone between Murud and Karwar. Some of the P in sediments of the shelf area is detrital and a part of it is hydrogenous (Rao *et al.*, 1976; Paropkari, 1994). Though several views have been expressed to explain the occurrence of othigenic P, the popular one is that they are either primary chemical precipitates or incomplete replacement products formed from preexisting carbonates. According to the first view (Kazakov, 1950; Bjoerkman and Karl, 1994) the P in sea water is assimilated by phytoplankton and on death of the organisms is returned as orthophosphate to the subsurface water. This P released during the hydrolysis of organic matter is not precipitated as seawater is undersaturated with respect to apatite at pH of the surface water. As a result, phosphate saturation can be reached resulting in the precipitation of phosphate minerals. The second theory supports the inorganic replacement of CO_3^{2-} ions in carbonate materials present in seawater by PO_4^{3-} groups at the sediment water interface or at a depth in the sediment (Ame, 1959; Lopez and Morgui, 1992; Rao *et al.*, 2000). Intense seasonal upwelling occurs along the western continental shelf of India between Mumbai and Quilon with the intensity decreasing in the northerly direction.

The concentration of P in the catchment soil varies over a wide range of 120-1830 $\mu\text{g/g}$ (av 726 $\mu\text{g/g}$). Its concentration in the bottom sediments of the cores B23 deposited over a century ago is 1073 $\mu\text{g/g}$. The concentration of P in the 74-148 cm segment of core B24 which, probably was deposited over the period 1792 to 1897 based on the reported sedimentation rate for the region (Deorukhakar, 2003), varies in 1177-1646 $\mu\text{g/g}$ range. Hence, it can be considered that the concentrations of about 1500 $\mu\text{g/g}$ can naturally occur in the coastal sediments of the region.

The concentration of P in core B1 is variable but the average trend suggests an increase over the years of sediment deposition. P in this core directly varies with Al ($r=0.94$; $p<0.001$), Cr ($r=0.79$; $p<0.001$), Mn ($r=0.94$; $p<0.001$), Fe ($r=0.95$; $p<0.001$), Ni ($r=0.94$; $p<0.001$), Cu ($r=0.57$; $p<0.001$) and Zn ($r=0.79$; $p<0.001$). The average P profile in cores B2 and B3 also indicates concentration decreasing with depth in the sediment suggesting some accumulation with time. P varies directly with Mn ($r=0.56$; $p<0.001$), Cu ($r=0.54$; $p<0.001$), Zn ($r=0.49$; $p<0.001$) and Pb ($r=0.47$; $p<0.001$) in core B2 and with Mn ($r=0.62$; $p<0.001$), Cu ($r=0.52$; $p<0.001$) and Zn ($r=0.72$; $p<0.001$) in core B3. In core B4 the concentration of P is not significantly correlated with metals except for Fe ($r=0.75$; $p>0.001$) with which it varies directly. The depth profile of P in core B5 is devoid of definite trend though the concentrations are generally more than 1600 $\mu\text{g/g}$ and often exceed 2000 $\mu\text{g/g}$. The concentration of P in this core varies directly with that of Al ($r=0.77$; $p<0.001$), Fe ($r=0.89$; $p<0.001$) and Cu ($r=0.62$; $p<0.001$). As in the case of Cr and Zn, the concentration of P is relatively high in the 45-80 cm segment as compared to the top 8 cm section. P varies directly with Cr ($r=0.53$; $p<0.001$) and inversely with Fe ($r=-0.44$; $p<0.001$) in the core B3.

Considering that the Ratnagiri region is not industrialized and urbanized when compared to the Mumbai area, the high concentrations of P with value generally exceeding 1800 $\mu\text{g/g}$ in most instances is a natural phenomenon and is supported by published literature (Paropkari *et al*,

1994). Results of Paropkari *et al.* (1994) indicated wide variations in the concentration of P in sediments with a zone of high concentration off Ratnagiri. In core R5, P co-vary with Fe ($r=0.43$; $p>0.001$), Ni ($r=0.35$; $p>0.001$), Cu ($r=0.43$; $p<0.001$) and Pb ($r=0.35$; $p>0.001$).

3.5.4 Normalisation and enrichment factor

A variety of normalising techniques including grain size (Ackerman *et al.*, 1983), total organic carbon (Windom *et al.*, 1989), Fe (Morse *et al.*, 1993; Schiff and Weisberg, 1999) and Al (Din, 1992; Rubio *et al.*, 2000) have been used to quantify enhancement of trace metals over the lithogenic background. Using reference elements as conservative tracers of the natural-bearing phases in the fine sediment fraction requires several assumptions; first, that the reference element co-varies in proportion to the naturally occurring concentrations of the metal of interest; second, that the reference element is insensitive to inputs from anthropogenic sources, and third, that the reference element is stable and is not subject to environmental influences such as reduction/oxidation, adsorption/desorption and other diagenetic processes that may alter its sediment concentration.

Among reference elements, use of Al to normalise the metal data seems to be most consistent because it is a major constituent of fine-grained aluminosilicates with which the bulk of the trace metals are associated. It is highly refractory and its concentration is generally not influenced by anthropogenic sources (Schropp and Windom, 1988; Loring, 1991). Fe is another reference element commonly used. Though its geochemistry is similar to that of many trace metals, a potential difficulty with using Fe is that in certain circumstances this element can be mobilised such as during diagenesis. Some researchers have used C_{org} to normalise metal concentration (Windom *et al.*, 1989). However, C_{org} itself can be considered as a contaminant and the normalisation approach has no geochemical basis.

Due to high anthropogenic organic loading, the possibility of Fe getting reduced and mobilised at least below the zone of bioturbation precludes its use as a normalisation factor for the sediment of the Mumbai-Bassein region. Hence, we have used Al as a grain-size proxy. To quantify the results, Kemp *et al.* (1976) introduced a ratio that is designated as the Enrichment Factor (EF):

$$EF = (M/Al)_{\text{Sample}} / (M/Al)_{\text{Background}}$$

where 'M' is the trace metal and subscripts 'Sample' and 'Background' are the measured and background concentrations of M respectively. As discussed in Section 3.4.1 the following average concentrations of bottom section core of B23, B24, B25, U34, U35 and U37 were used as the background:

Constituent	Minimum	Maximum	Average
Al (%)	4.7	9.6	7.2
Cr ($\mu\text{g/g}$)	70	241	172
Mn ($\mu\text{g/g}$)	347	1102	796
Fe (%)	4.1	7.7	6.2
Co ($\mu\text{g/g}$)	31	60	49
Ni ($\mu\text{g/g}$)	34	112	70
Cu ($\mu\text{g/g}$)	27	111	85
Zn ($\mu\text{g/g}$)	26	185	98
Cd ($\mu\text{g/g}$)	0.1	0.6	0.3
Pb ($\mu\text{g/g}$)	8.8	52.0	21.7
P ($\mu\text{g/g}$)	620	1786	1129

The EF values calculated based on the above background and observed concentration of trace metal in sediment are plotted against depth in Figures 3.5.5 and 3.5.6 for the Bay. The EF exceeds with values as high as 30-40 in core B5 for Cr, Co, Ni and Zn. Core B1 exhibits the high EF between 2 and 40, for Cd.

3.5.5 Index of geoaccumulation

The geoaccumulation index (I_{geo}) was originally defined by Muller (1979) for metal concentrations in the $<2 \mu\text{m}$ fraction and developed for the global standard shale values. The index of geoaccumulation was calculated by the equation

$$I_{\text{geo}} = \log_2 C_M / 1.5 B_M$$

where C_M is the measured concentration of metals in a sediment sample and B_M is the background value. The factor 1.5 is used to compensate for possible variations with respect to background due to lithological variations. I_{geo} consists of seven grades or classes, with I_{geo} of 6 indicating almost a 100 fold enrichment above background value.

Average shale value (Sahu and Panda, 1987) as well as the regional background (Subramanian and Mohanachandran, 1990; Sahu and Bhosale, 1991) have been used to estimate I_{geo} . Figures 3.5.7 and 3.5.8 give the I_{geo} values of metals calculated for core sediments of the Bay. I_{geo} of 1 to 4 in the inner Bay is suggestive of moderate to high level of Cd accumulation in the sediment of this zone. I_{geo} in the core B2 in the Bay (Figure 3.5.8) is in class 1-5 indicating moderate to strong pollution in case of Pb.

3.6 Sequential extraction of metals

Anthropogenic trace metals entering marine environment get associated with the particulate matter and are eventually incorporated into sediments. However, under certain environmental conditions the sediment-bound metals may be released back to the overlying water column, influence biota exposed to these relatively high concentrations and also become available for bioaccumulation. It is therefore necessary to estimate the quantum of metal in the sediment that can become bioavailable (Berner, 1980; Luoma, 1983; Brumsack and Gieskes, 1983; Carignan and Lean, 1991). Trace metals in sediment are considered to exist in five important geochemical forms (Tessier *et al.*, 1979; Martin *et al.*, 1987; Salomons *et al.*, 1988) namely exchangeable, bound to carbonate phase, bound to iron-manganese oxides, bound to organic matter, and residual phase. These metal fractions have varying mobility, bio-availability and chemical characteristics. Selective sequential extraction methods have been devised to quantify the content of trace metals in different geochemical phases in the sediment and thereby

evaluate metal mobility and availability (Ajay and van Loon, 1989). Sequential extraction procedures, as opposed to bulk sample analysis, allow for the differentiation of the relative binding strengths of trace metals to the various solid phases by successive leaching with chemicals of increasing strength and selectivity (Kersten and Förstner, 1986).

In the present study metals namely Cr, Mn, Fe, Cu and Zn in various phases of the sediment were extracted using the selective chemical extraction procedure devised by Ajay and van Loon (1989). Surface sediment from stations B1, B2, B5, B6 and B12 and selected sections of core B2 from the Bay were subjected to sequential leaching that partitions the metals in five fractions as follows:

Exchangeable: The fraction that is adsorbed on major constituents of sediments such as clays, hydrated oxides of Fe and Mn and humic acids which can be easily desorbed under changes in water ionic concentration.

Bound to carbonates: A significant fraction of trace metals can be associated with sediment carbonates and hence susceptible to changes in pH and Eh. The mechanism for the association of heavy metals in carbonate phase is mainly by co-precipitation than surface adsorption. Co-precipitation with carbonate for removal of heavy metals from overlying water body has been reported by many authors (Calvert and Price, 1976; Stumm and Morgan, 1970; Jones and Turki, 1997).

Bound to Fe and Mn oxides: Fe and Mn oxides are excellent scavengers and efficiently remove trace metals from water. These oxides are thermodynamically unstable under anoxic conditions.

Bound to organic matter: Trace metals may be bound to organic matter such as living organisms, detritus, organic coatings on mineral particles etc. Organic matter such as humic and fluvic acids which occur in most natural waters have strong complexation and peptization properties and play an important role in the chemistry of trace metals dissolved in water.

Under oxidizing conditions in natural waters, organic matter is degraded resulting in release of metals to the water.

Residual: This is the residue left behind when above referred fractions are separated and mainly contains primary and secondary minerals, which may have trace metals within their crystal structure. These metals are generally not released in solution under the environmental conditions that normally occur in seawater.

3.6.1 Surface sediments

Bulk concentrations of trace metals at stations B1, B2, B5, B6 and B12 vary as follows: Cr (125-327 µg/g), Mn (658-951 µg/g), Cu (108-150 µg/g) and Zn (102-244 µg/g). The proportions of metals relative to the bulk concentration for the five leaching fractions are given in Table 3.6.1. The comparison of the sum of the five leachates with bulk analysis gives recovery rates for the leaching procedure between 55-119 %, 91-123 %, 63-82 %, and 51-118 % for Cr, Mn, Cu and Zn respectively. Except for one sample in each case the recovery is 70 % or more. Considering the numerous working steps and the difficult analyses of the leaching solutions, such variations are not entirely unexpected (Koschinsky *et al.*, 2001).

The results in Table 3.6.1 indicate that except for Mn the percentage of metals in the exchangeable fraction (Fraction 1) is extremely low and barely exceeds 2 % of the respective total metal content thereby suggesting that the sediment bound metals in the Bay may not be easily bio-available. Even in the case of Mn this value is low and varies in the range 1-6 %. Low concentrations of trace metals in exchangeable fraction of sediments even of areas receiving anthropogenic metals have been reported in many instances (Izquierdo *et al.*, 1988; Li *et al.*, 2001). In the non-lithogenous fraction the exchangeable or easily leachable fraction is geochemically insignificant, being less than 9 % of the total non-lithogenous fraction. Trace metals associated with carbonates in sediments may be released to water if the

pH of water overlying the sediment decreases. Decrease in pH can result in aquatic areas facing organic pollution such as that resulting from sewage releases which depletes DO and increases carbon dioxide in the system. From Table 3.6.1 it is evident that association of Cr with carbonates in the Bay sediments is extremely low (1– 2%) followed by Cu (3-4%), Zn (6-7%) and Mn (45-64%). Thus among the metals investigated nearly 50% of Mn is associated with the carbonate phase. The higher percentage of Mn in carbonate phase is most likely the result of similarity of its ionic radius to that of calcium which allows substitution of Ca with Mn in carbonates (Jones and Turki, 1997). Therefore, this fraction reflects heavy metals distribution of detrital origin as well as biogenic decomposition in the creek. The percentage of carbonate-associated Mn increases from 47% at station B1 to 64% at station B6 that is along the creek in seaward direction. The inner creek in the vicinity of station B1 receives substantial volume of untreated sewage resulting in depressed levels of DO and relatively low pH. The DO and pH levels improve in the seaward direction suggesting better oxidizing conditions away from the head of the Bay (Zingde and Govindan, 2000). It is possible that the loss of sediment carbonates and hence of Mn decreases from station B1 to B6. Station B12 falls in the harbour area which is frequently dredged and the relative low content of carbonate-associated Mn can be due to much coarser sediment in this region (Desai *et al.*, 1986). The influence of the type and grain size of sediments, organic matter contents, distance and location of the sampling site from the major source of sewage or industrial discharge on sediment metals has been reported (Jones and Turki, 1997).

Trace metals bound to Fe and Mn oxides can be mobilized and available for bio-uptake in reducing environment wherein Fe and Mn are reduced to water soluble species (Berner, 1980; Fernex *et al.*, 1984; Brannon and Patrick, 1987). About (1-5 %) of Cr is associated with Fe-Mn oxide phase in the sediments of the Bay without any spatial trends (Table 3.6.1). The association of Mn which varies from 15 to 24 % indicates a trend of concentration increasing from station B1 to B6 with a subsequent decrease at station B12. Similar trend of increase in the seaward direction

upto station B6 is also evident for Cu (10-15 %) and Zn (11-20 %). As discussed in Section 3.4.1, the surface sediment in the Bay is likely to be oxidic though the area receives large volume of sewage. Hence these trace metals bound to the oxide phases may not be released under the prevailing environmental conditions in the Bay.

It is rather surprising that Cr, Mn, Cu and Zn in the oxidizable phase are low suggesting that they are not bound to organic matter though the Bay receives a variety of organic substances. The content of these metals in the oxidizable phase is generally about 2 – 5 % except for Zn which seems to be associated to the extent of 5 – 11 %. As discussed in Section 3.4.1, much of the organic matter entering the shallow Bay is effectively consumed by its rich benthos and also oxidized aerobically leading to low levels of organic carbon in the Bay sediments.

High contents of Cr (36-94 %), Mn (22-30 %), Cu (49-60 %) and Zn (25-84 %) are associated with the residual phase and hence not easily available to biota except when consumed directly as sediment particles with food. This is in line with the literature reports for bulk sediment. About 60 % of Mn associated with the lithogenous fraction of the sediments has been reported by Murty *et al.* (1973). Even within this fraction the major portion of the metal was associated with the clay minerals and a small percentage in the resistant detrital minerals. A number of studies on speciation of trace metals in coastal sediments indicate that Cd, Cr, Pb and Zn are primarily in the reducible, residual and oxidizable phases, that Cu is preferentially associated with oxidizable and residual phases, and that Co and Ni are associated with residual and reducible phases (Jones and Turki, 1997). Our results differ to some extent from this general pattern in that in the Bay sediment, Cr is largely in residual phase (36-94 %) followed by reducible phase (5-15 %); Mn preferentially occurs in the carbonate phase (47-64 %) followed by residual (22-30 %) and reducible (15-24 %) phases; 49 to 60 % of Cu is in the residual phase with about 10 – 15 % in the reducible phase; and Zn mainly occurs in residual (25-84 %), reducible (11 -20 %) and oxidizable phases (5-11 %).

3.6.2 Core B2

The profiles of distribution of Cr, Mn, Fe, Cu and Zn in different phases in the sediment of core B2 are illustrated in Figures 3.6.1 to 3.6.5 and the results are given in Appendix-IV. The bulk concentrations of Cr (193-339 µg/g), Mn (721-958 µg/g), Fe (7.1-8.1 %), Cu (118-144 µg/g) and Zn (78-169 µg/g) vary in a fairly wide range in this core. The comparison of the sum of the five fractions with bulk analysis gives recovery rates for the leaching procedure between 37-69 %, 89-110 %, 104-111 %, 75-94 %, and 131-152 for Cr, Mn, Fe, Cu and Zn respectively. Thus in the case of Cr the recovery is poor as in the case of surface sediments while it is high in case of Zn.

In line with the surface sediments and literature reports (Jones and Turki, 1997; Li *et al.*, 2001; Koschinsky *et al.*, 2001) the concentrations of these metals are low and geochemically insignificant in the exchangeable phase with the order Cr; Fe < Cu < Zn < Mn. The concentration profile of Mn in the exchangeable phase with relatively elevated values in the mid-section coincides with the high concentration of the metal in the bulk sediment in this segment. The bulk concentration of Zn decreases down the core, however, the exchangeable Zn seems to increase with depth. Only small percentages of Cr (0-2 %), Fe (0.3-5.5 %) and Cu (3-7 %) occur in the carbonate phase, while, 29 - 44 % Mn and 12-31 % Zn are associated with the carbonate phase in this core. The sequence of leaching of heavy metals by NaOAC (pH=5.0) in the core sediment is Mn>Zn>Cu>Cr=Fe. The Zn profile of the carbonate phase mimics its bulk concentration in the sediment with decrease down the core length. The concentration of Fe in the carbonate phase is geochemically insignificant but interestingly the concentration abruptly increases in the sections below 30 cm though such trend is not seen in the bulk profile.

Unlike Cr, Mn, Fe and Cu, a significant amount of Zn (14-45 %) occurs in the reducible phase with high concentrations confined to the top

30 cm sediment. Likewise, except for Zn, the other metals do not indicate significant association with the organic material in these sediments. Zn is associated with the oxidizable phase to the extent of 15-19 % with no specific depth trend in its profile. Similar observations have been reported for the Pearl River (Li *et al.*, 2001). The concentrations of Cu and Zn in the five fractions remained stable among the different depths.

Table 3.2.1: Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%), dry wt) in soils and rocks from the catchment of Bay and Ulhas estuary.												
Location	Sample type	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
Mahabaleshwar	Soil	14.2	305	3383	24.7	125	1181	347	155	0.27	14.17	1830
	Soil	13.9	341	4729	29.5	20	72	223	44	0.14	23.2	629
	Soil	8.2	106	1423	18.3	50	79	280	145	0.18	27.8	155
	Soil	9.2	121	1438	14.7	49	96	215	110	0.09	17.9	829
	Soil	13.4	105	2113	25.7	72	108	365	119	0.13	97.5	219
	Soil	13	280	1893	15.2	52	108	171	84	0.14	2.1	120
	Rock	12.8	755	1082	31.9	24	64	86	103	0.09	27.5	1424
	Rock	6.6	91	1998	21.3	49	58	444	181	0.04	8.7	1316
	Rock	12.7	160	2408	21.5	68	134	306	153	0.14	11.1	969
	Rock	10	471	2124	18.7	91	249	250	164	0.11	16.7	347
Lonawala	Soil	8.6	217	1298	11.5	39	68	144	86	0.21	20	543
	Soil	55.3	798	12469	11.3	342	458	1586	907	1.1	<0.4	4874
	Rock	14.1	506	4699	23	100	248	197	145	0.02	3.4	948
	Rock	7.3	55	1483	19.6	56	51	235	178	0.18	15.9	1336
Khandala	Soil	10	82	2117	21.8	58	57	281	168	0.03	22.5	1487
	Rock	11.2	902	1593	24.2	52	268	171	154	0.11	22.5	2007
Malshej	Soil	12.2	525	1990	18.6	58	509	207	158	0.07	15.8	232
	Soil	8.3	366	1548	13.9	56	114	103	89	0.53	12.3	983
	Rock	10.9	97	3061	27.5	74	77	268	183	0.13	18.6	1147
	Rock	10	680	2373	18.5	88	159	100	134	0.13	5.7	827
	Rock	8.9	171	2067	18.7	64	73	95	199	0.07	4.8	911
Igatpuri	Soil	8.4	136	896	14.1	45	68	76	99	0.12	7.3	911
	Soil	10.3	567	1734	15.3	53	85	84	125	0.11	3	776
	Rock	8.2	117	1061	14.6	47	62	85	132	0.28	7.7	1522
	Rock	8.9	427	2468	13.7	53	77	70	102	0.15	8.6	525
	Rock	7.6	356	1868	14.1	50	77	148	125	0.21	24.7	932

Table 3.2.2: Correlation coefficient (r) and levels of significance (p) of metals and P in soils and rocks from the catchment of Bay and Ulhas estuary. (n=26)																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Cr	0.45	<0.02																		
Mn	0.94	<0.001	0.38	0.05																
Fe	-0.13	>0.1	0.07	>0.1	-0.07															
Co	0.93	<0.001	0.38	0.05	0.91	<0.001	-0.24	>0.1												
Ni	0.35	<0.001	0.28	<0.001	0.35	<0.1	0.11	>0.1	0.47											
Cu	0.93	<0.001	0.23	>0.1	0.89	<0.001	-0.13	>0.1	0.91	<0.001	0.33	<0.1								
Zn	0.93	<0.001	0.32	>0.1	0.88	<0.001	-0.25	>0.1	0.94	<0.001	0.28	>0.1	0.94	<0.001						
Cd	0.84	<0.001	0.34	<0.1	0.75	<0.001	-0.41	>0.02	0.82	<0.001	0.28	>0.1	0.79	<0.001	0.82	<0.001				
Pb	0.24	>0.1	0.15	>0.1	-0.05	>0.1	0.37	<0.1	-0.04	>0.1	-0.05	>0.1	0.4	>0.02	-0.1	>0.1	-0.01	>0.1		
P	0.81	<0.001	0.39	<0.05	0.75	<0.001	-0.08	>0.1	0.8	<0.001	0.34	<0.1	0.8	<0.001	0.86	<0.001	0.76	<0.001	-0.2	>0.1

Table 3.2.3: Range and average of concentrations of metals and P in soil* from the catchment.			
Constituent	Minimum	Maximum	Average
Al (%; dry wt)	8.2	14.2	10.8
Cr (µg/g; dry wt)	82	567	263
Mn(µg/g; dry wt)	896	4729	2047
Fe (%; dry wt)	11.5	29.5	18.6
Co (µg/g; dry wt)	20	72	50
Ni (µg/g; dry wt)	57	1181	212
Cu (µg/g; dry wt)	76	365	208
Zn (µg/g; dry wt)	44	168	115
Pb (µg/g; dry wt)	2.1	97.5	21.7
Cd (µg/g; dry wt)	0.03	0.53	0.2
P (µg/g; dry wt)	120	1830	726
*Soil sample from Lonawala with abnormally high concentration of metals is not considered.			
Total 12 samples considered			

Table 3.2.4: concentrations of metals in rocks and argillaceous, sandy and calcareous sediments ordered according to the metal content in shales**						
Constituent	Shales	Basaltic rocks	Granite rocks	Continental crust	Oceanic crust (ocean ridge basalt)	** (Karl, 1991)
Cr (µg/g; dry wt)	90	168	12	88	317	
Mn(µg/g; dry wt)	850	1390	325	800	1200	
Co (µg/g; dry wt)	19	48	4	19	45	
Ni (µg/g; dry wt)	68	134	7	45	144	
Cu (µg/g; dry wt)	45	90	13	35	81	
Zn (µg/g; dry wt)	95	100	50	69	78	
Pb (µg/g; dry wt)	22	3.5	32	15	0.89	
Cd (µg/g; dry wt)	0.13	0.1	0.09	0.1	0.13	

Ghatkopar	2804	ND	351	4125	ND	4	169	334	5351		Mulud outlet	1667	3	439	597	33	0	53	159	3.32	NA	3491	
Colaba	615	ND	149	1050	0.3	18	35	1873	5167		Versova inlet	6215	0	314	1108	7	0	18	238	0.39	NA	4760	
Dadar	1509	66.5	153	1775	ND	25	291	286	4891		Versova outlet	1088	0	330	285	6	13	15	47	0.27	NA	3518	
Dharavi	6209	15.6	498	11738	0.6	27	118	396	6112		Malad inlet	8770	69	257	1654	6	567	1136	3110	0.41	NA	5119	
Worli	1240	2.4	168	1613	ND	46	85	329	5482		Malad outlet	12310	75	352	1842	0	246	486	432	0.46	NA	6851	
Versova	1536	ND	311	2125	0.5	12	43	286	3990														
Table 3.3.1 (Contd..2)																							
Pumping station	Al	Cr	Mn	Fe	C0	Ni	Cu	Zn	P		Pumping station	Al	Cr	Mn	Fe	C0	Ni	Cu	Zn	Cd	Pb	P	
	2002 (February)											2005 (April)											
Malad	2838	51.6	323	5438	ND	443	628	644	6768		Bhandup inlet	2080	8	252	1933	20	9	53	588	0.39	10.9	4353	
	2002 (May)											Bhandup outlet	158	6	411	471	23	4	29	179	0.69	2.3	4022
Bhandup	2095	ND	325	2088	5.8	ND	38	293	4069		Colaba	2045	11	166	1318	17	2	47	437	0.45	12.8	6169	
Ghatkopar	2546	ND	276	2425	5.1	ND	102	286	5075		Dadar	2269	10	148	2775	19	8	141	588	1.96	13.6	4200	
Colaba	2899	ND	142	3575	ND	31	68	483	6611		Dharavi	2252	164	213	2095	19	7	67	492	0.61	13.2	4900	
Dadar	1776	78	117	1688	ND	6	53	253	3933		Worli	1990	21	183	2323	20	1	42	589	1.14	9.5	4843	
Dharavi	2831	34	371	3988	ND	10	80	403	4688		Mulud outlet	0	7	220	0	22	3	13	3	1.35	ND	2428	
Worli	1793	28	206	2325	ND	157	100	377	5157		Versova inlet	0	9	12	1309	3	0	42	0	0.66	2.7	5141	
Versova	810	ND	252	ND	ND	ND	21	76	3951		Versova outlet	44	2	229	347	0	0	6	71	0.16	0.5	3697	
Malad	956	ND	458	900	5.4	ND	44	169	4983		Malad inlet	-	-	-	-	-	-	-	-	-	-	-	
											Malad outlet	3105	234	290	1727	1	151	31	877	1.2	14.1	4659	
												2002 (February)											
											Bhandup outlet	0	3	39	0	3	0	7	2	0.16	ND	3325	
											Colaba	1051	5	177	1326	3	4	40	390	1.12	5.6	4681	

	Dadar	0	1	53	0	2	0	11	54	0.23	0.23	22
	Dharavi	1561	8	201	632	1	7	68	489	0.39	1.2	1203
	Worli	0	4	52	0	4	0	31	10	0.2	1.6	4266
	Mulud outlet	0	5	29	0	11	0	12	12	0.19	ND	525
	Versova inlet	0	3	4	0	2	0	15	0	1	ND	87
	Versova outlet	0	2	109	0	1	0	3	0	0.06	ND	197
	Malad outlet	1849	61	133	2588	3	101	329	674	0.79	40.4	3325

Table 3.3.2: Range and average (parentheses) of selected metals and P in sewage and their loading on the receiving water body

Pumping station	Metal	Concentration (range) (µg/l)	Concentration (average) (µg/l)	Sewage flow 10 ⁵ xm ³ /d	Receiving water	Load kg/d (range)	Load kg/d (average)	Pumping station	Metal	Concentration (range) (µg/l)	Concentration (average) (µg/l)	Sewage flow 10 ⁵ xm ³ /d	Receiving water	Load kg/d (range)	Load kg/d (average)
Bhandup	Al	0-3394	1298	2.8	Bay	0-950.3	363	Dadar	Al	0-12490	4172	0.4	Mahim Creek	0-499.6	166.9
	Cr	0-23	5			0-6.4	1.5		Cr	1.1-78	30.7			0.04-3.1	1.2
	Mn	29-1053	432			8.1-294.8	120.9		Mn	53-11756	1597.5			2.1-470.2	63.9
	Fe	0-2088	440			0-584.6	123.3		Fe	0-2775	1309.4			0-111	52.4
	Co	3.8-86	29			1.1-24.1	8.1		Co	0-19	5.4			0-0.76	0.2
	Ni	0-114	17			0-31.9	4.9		Ni	0-25	10.8			0-1	0.4
	Cu	9-101	35			2.5-28.3	9.8		Cu	11-291	86.3			0.4-11.6	3.5
	Zn	3-349	161			0.8-97.7	45.1		Zn	54-588	244			2.2-23.5	9.8
	Cd	0.19-3.32	1.72			0.05-0.93	0.48		Cd	0.23-1.96	0.75			0.01-0.08	0.03
	Pb	5-10.9	8.7			1.4-3.05	2.44		Pb	0.23-14.2	10.4			0.01-0.57	0.42
	P	525-4069	2616	147-1139	732.5	P	22-5985	4034	0.9-239.4	161.4					
Ghatkopar	Al	0-9350	2736	2.9	Bay	0-2711	799.1	Dharavi	Al	1561-35581	99172	7.9	Mahim Creek	1233-23109	7167
	Cr	0-10	2.8			0-2.9	0.81		Cr	8-164	42			6.3-129.6	33.4
	Mn	39-529	373			11.3-153.4	108.1		Mn	201-536	350			158.8-423.4	276.5
	Fe	0-4125	1424			0-1196.3	412.9		Fe	632-11738	3990			499.3-9273	3151.9
	Co	0-23	7.3			0-6.7	2.1		Co	0.6-19	9			0.47-15	6.8
	Ni	0-9	3			0-2.6	0.9		Ni	3.1-78	Jan-00			2.4-61.6	19.8
	Cu	7-169	603			2.0-49	17.5		Cu	7-118	63			5.5-93.2	49.7
	Zn	Feb-00	Mar-01			0.6-6638	130.3		Zn	317-722	451			250.4-570.4	356.4

	Cd	0-0.69	0.2			0-0.2	0.06		Cd	0.16-0.76	0.48			0.13-0.6	0.38
	Pb	0-102	2.45			0-2.96	0.71		Pb	1.2-14.6	9.65			0.95-11.5	7.6
	P	3115-5351	4033			903-1532	1170		P	1203-6377	4957			950-5038	3916
Colaba	Al	615-11630	4027	0.4	Bay	24.6-465.2	161.1	Worli	Al	0-12620	4866	7.3	Open shore	0-9213	3552
	Cr	0-11	4.8			0-0.4	0.2		Cr	0-121	28			0-88.3	20.6
	Mn	110-247	178.3			4.4-9.9	7.1		Mn	52-235	187			38-171.6	136.4
	Fe	1050-3575	1996			42-143	79.8		Fe	0-3900	2150			0-284.7	1596.2
	Co	0-17	5.9			0-0.68	0.24		Co	1.5-20	8.6			1.1-14.6	6.3
	Ni	2-246	39.3			0.1-9.8	1.6		Ni	0-234	61			0-170.8	44.6
	Cu	19-68	38.8			0.8-2.7	1.6		Cu	1-126	63			0.7-92.0	46.3
	Zn	70-1873	495.6			2.8-74.9	19.8		Zn	10-589	344			7.3-430	250.8
	Cd	0.27-1.12	0.58			0.1-0.05	0.02		Cd	0.2-1.14	0.63			0.15-0.83	0.46
	Pb	5.6-17.2	13.2			0.2-0.7	0.5		Pb	1.6-19.8	12.4			1.17-14.5	9.1
	P	4327-7149	5695			173-286	228		P	4266-5830	5110			3114-4256	3730

Table 3.3.3: Average loading of some metals and P on receiving water through domestic sewage					
Load (kg/d)	Bay	Mahim Creek	Versova Creek	Open shore	Total
Al	2804.9	7333.9	1495.9	3552.1	15186.7
Cr	4.82	34.7	21.3	20.6	81.4
Mn	416.3	340.4	140	136.4	1033.1
Fe	1323.6	3204.3	564	1569.2	6661.1
Co	18.2	7	1.3	6.3	32.7
Ni	18.2	20.2	50.4	44.6	133.4
Cu	53.4	53.1	87.3	46.3	240.1
Zn	398.1	366.1	135	250.8	1150
Cd	1.02	0.4	3.9	0.46	5.8
Pb	8.13	8	1.2	9.1	26.4
P	4393	4077.7	2056.6	3730.2	14257.5
Sewage discharge(10⁵ x m³ /d)	11.6	8.3	4.4	7.3	31.6

Table 3.3.4: Characteristics of sewage in septic and holding treated Municipal wastewater effluent (mg/l)*

	Metals	Septic sewage	Holding sewage
	Al	50	10-0.06
	Cr	1	7.9-0.01
	Mn	5	1.0-<0.01
	Fe	200	64-0.15
	Ni	1	44-<0.01
	Cu	8	1.7-<0.01
	Zn	40	8.1-0.03
	Cd	0.2	0.15-<0.01
	Pb	10	1.2-<0.01

* Atkins and Hawley, 1978; Perkins, 1984; EPA 625/6-84-009



Table 3.4.2: Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%), dry wt) in subtidal sediments of docks																			
during Post- and Pre-monsoon																			
Station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	Station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
1996 (November-December) (Post-monsoon)										1997 (May-June) (Pre-monsoon)									
Indira Dock										Indira Dock									
Ida	8.9	142	1087	7.7	44	89	128	199	1510	Ida	8.5	178	992	8.3	56	74	157	156	1644
Idb	7.9	137	1080	7.8	43	95	142	194	1916	Idb	8.2	227	358	8.8	56	74	154	274	1269
Idc	7.6	121	1106	7.7	44	93	136	167	2627	Idc	7.9	164	985	8.2	56	104	183	206	2620
Idd	7.9	154	957	7.7	44	92	175	249	2505	Idd	9	158	812	8.3	55	77	172	294	1966
Victoria Dock										Victoria Dock									
Vda	7.5	170	1057	7.6	43	93	122	152	1975	Vda	8.3	175	948	8.1	51	76	116	134	1251
Vdb	7.3	167	1062	7.5	43	94	125	156	1684	Vdb	8.3	171	901	8.4	52	76	121	161	1431
Vdc	7.5	156	973	7.5	42	92	120	153	1717	Vdc	7.9	148	776	7.7	50	75	126	175	1041
Vdd	6.6	156	1040	7.6	42	93	123	154	1702	Vdd	8.1	177	868	8.1	54	76	117	192	1186
Prince's Dock										Prince's Dock									
Pda	7.3	130	1123	7.9	45	93	111	195	1572	Pda	8.3	182	975	8.3	53	74	112	141	1130
Pdb	7.8	124	1015	7.8	43	91	111	376	1484	Pdb	7.8	178	853	8.1	55	76	123	204	1262
Pdc	7.8	131	921	7.5	43	89	116	150	1512	Pdc	8.2	198	425	8.3	55	76	117	222	1041
Pdd	8.3	123	1095	7.6	44	89	111	212	1536	Pdd	8.1	154	1037	8	53	73	109	145	1171

Table 3.4.3: Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%), dry wt) in subtidal sediments of bunders during																			
Post- and Pre-monsoon .																			
	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P		Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
Station	1996 (November-December) (Post-monsoon)									Station	1997 (May-June) (Pre-monsoon)								
Sasoon Fish Harbour	7.8	125	1375	7	42	79	99	114	1747	Sasoon Fish Harbour	7.6	173	836	8.4	51	79	110	192	867
Apollo Bunder	8.4	165	1014	7.6	47	92	110	113	1362	Apollo Bunder	8.2	166	929	8.9	51	78	111	131	1161
Naval Dock	8	139	981	7.6	44	94	107	129	1468	Naval Dock	7.7	134	941	9.2	52	78	111	146	471
Fish Jetty	6.9	131	926	7.6	44	92	152	208	1936	Fish Jetty	7.6	174	1029	8	50	78	119	160	-
Mazgaon Dock	7.1	-	930	6.7	42	85	757	243	1428	Lakdi Bunder	7.8	198	744	8.1	51	85	140	256	1138
Lakdi Bunder	8.5	194	944	7.4	46	100	156	262	2058	Coal Bunder	7.4	130	773	8.3	58	88	133	233	1090
Coal Bunder	8.9	198	1012	7.6	45	97	136	183	1704	Brick Bunder	9.1	194	827	10.2	49	85	126	191	791
Brick Bunder	8.1	-	1026	7.6	50	101	1054	496	1734	Hay Bunder	7.2	184	854	8.3	48	86	121	189	697
Haji Bunder	8.2	162	869	7.5	43	92	130	176	1330	Haji Bunder	8.1	195	902	8.7	51	89	126	193	-
Timber Pond	8.4	102	1085	7.9	45	103	121	143	1512	Timber Pond	7.2	172	783	8	49	78	115	160	1313
Sewri Bunder	8.1	160	958	7.5	44	96	117	132	-	Sewri Bunder	7.4	200	824	8.3	47	58	153	198	991

Table 3.6.1: Concentration of Cr, Mn, Cu, Zn ($\mu\text{g/g}$, dry wt) in leachates of surface sediment and percentage with respect to the total concentration in sediment of Bay.													
Depth (cm)	Leachate 1		Leachate 2		Leachate 3		Leachate 4		Leachate 5		F1+F2+F3 +F4+F5=	Bulk conc ($\mu\text{g/l}$)	% Recovery
	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)		
	Cr												
B1	2	1	2	1	18	12	7	5	126	81	156	155	100
B2	3	1	2	1	17	5	7	2	119	36	147	327	55
B5	2	2	2	2	19	15	8	6	118	94	149	125	119
B6	3	2	2	1	18	11	8	5	113	69	143	163	88
B12	2	1	3	2	14	7	5	3	134	67	158	200	79
Mn													
B1	40	4	441	47	152	16	33	4	234	25	900	930	97
B2	30	3	439	49	176	20	34	4	201	22	1056	899	117
B5	43	6	369	51	143	20	31	4	216	30	802	724	111
B6	24	4	418	64	159	24	35	5	176	27	812	658	123
B12	9	1	431	45	139	15	29	3	260	27	865	951	91
Cu													
B1	1	1	5	3	16	11	5	3	73	49	100	150	63
B2	1	1	4	3	15	11	5	4	71	53	95	135	70
B5	1	1	4	3	17	14	5	4	72	60	99	121	82
B6	1	1	4	4	17	15	5	4	67	59	93	114	82
B12	0	0	4	4	11	10	4	4	64	59	82	108	76
Zn													
B1	5	2	14	6	28	11	13	5	60	25	120	244	51
B2	3	2	9	6	23	16	14	10	118	81	167	146	114
B5	3	2	12	7	30	18	13	8	62	37	120	167	72
B6	3	2	10	7	28	20	14	10	119	84	168	142	118
B12	4	4	7	7	16	16	11	11	59	58	97	102	95

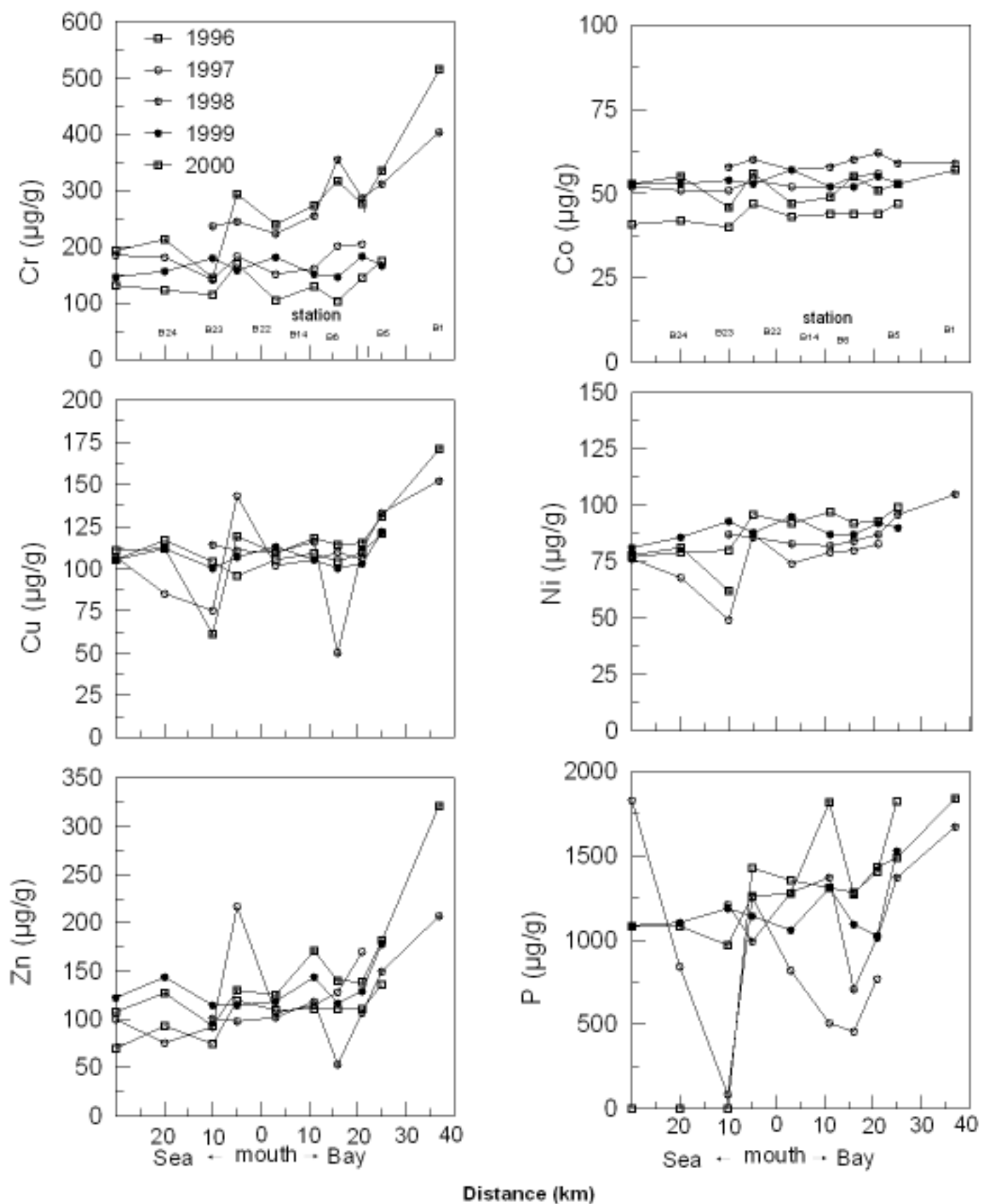


Figure 3.4.1: Variation of Cr, Co, Cu Ni, Zn and P ($\mu\text{g/g}$, dry wt) in surficial sediments of the Bay and the adjoining coastal area (Arabian Sea) during different sampling events

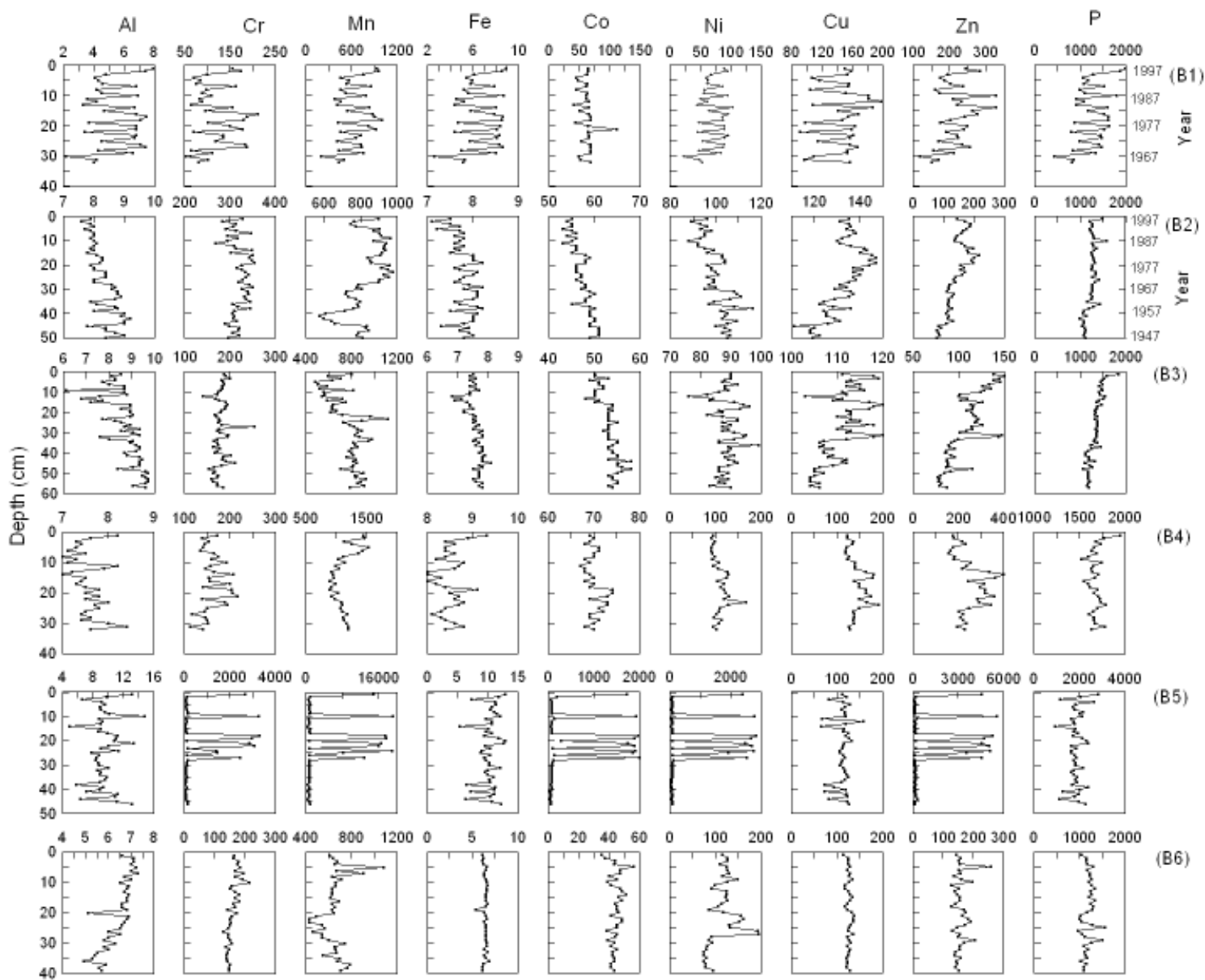


Figure 3.5.1: Depthwise variation of selected metals and P ($\mu\text{g/g}$; except Al, Fe (% dry wt)) in core sediments of the Bay

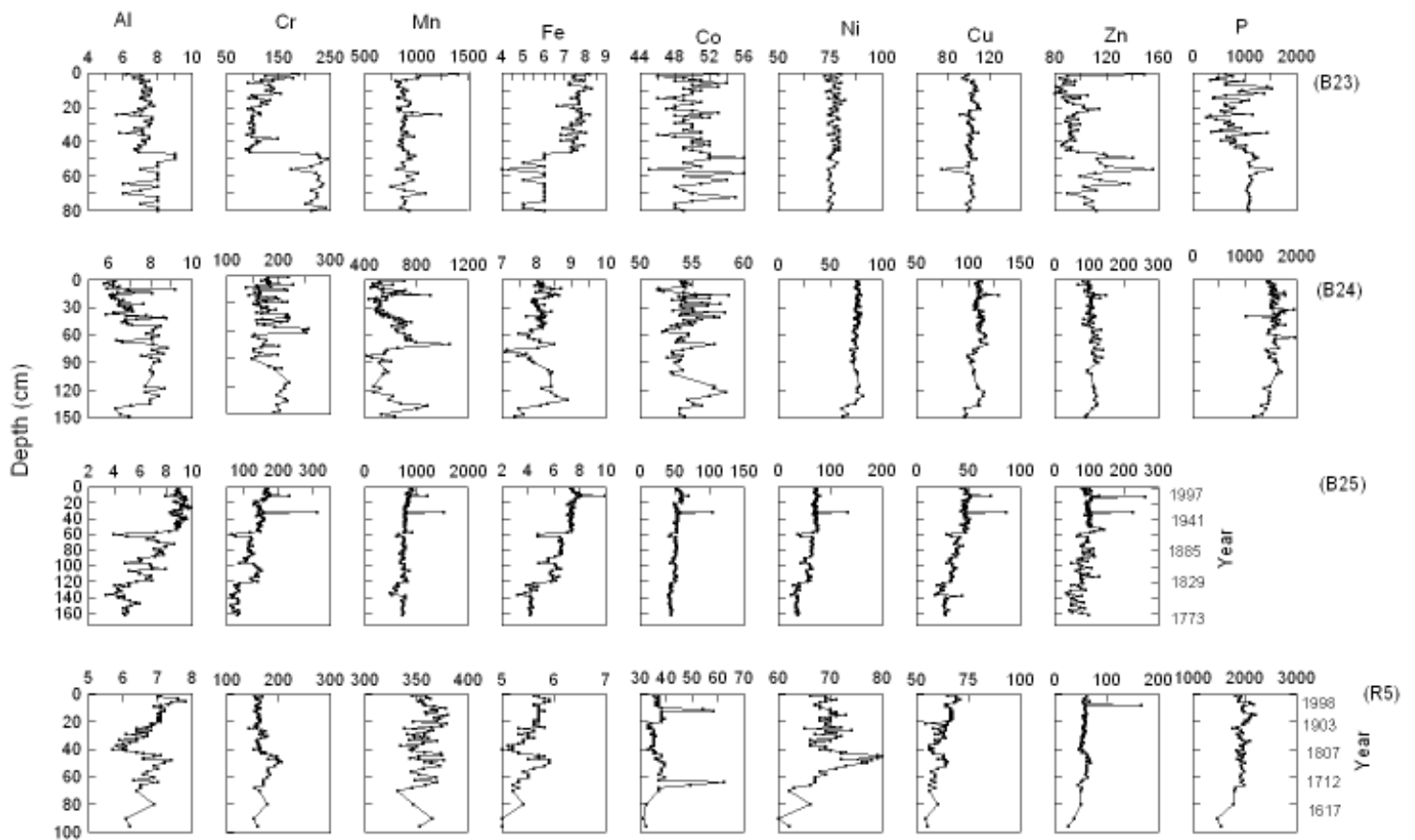


Figure 3.5.2: Depthwise variation of selected metals and P [$\mu\text{g/g}$, except Al, Fe (% dry wt)] in cores sediment of coastal area (Arabian Sea) of Mumbai

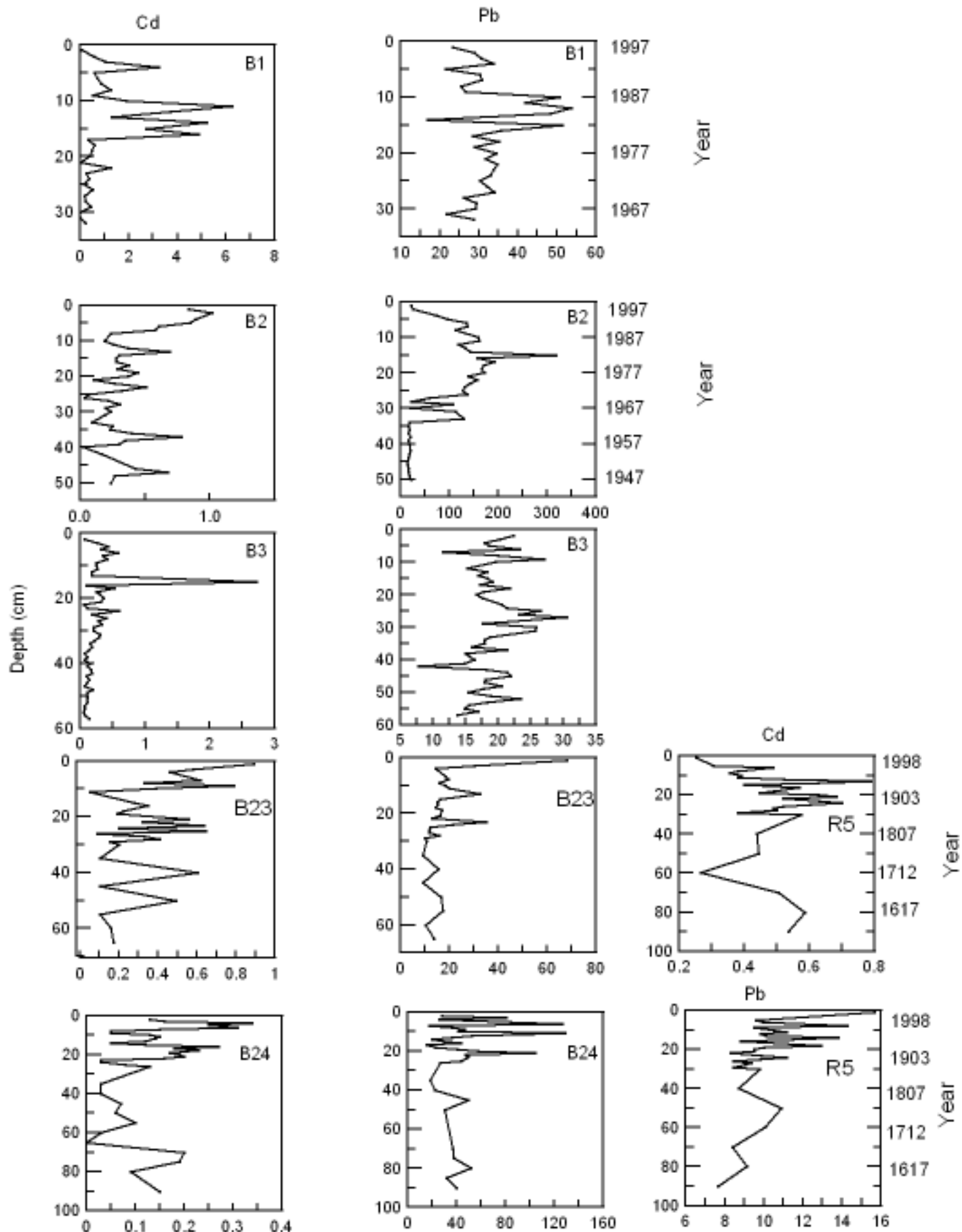


Figure 3.5.3: Depthwise variation of Cd and Pb ($\mu\text{g/g}$; dry wt) in core sediment of the Bay and adjoining coastal area (Arabian sea)

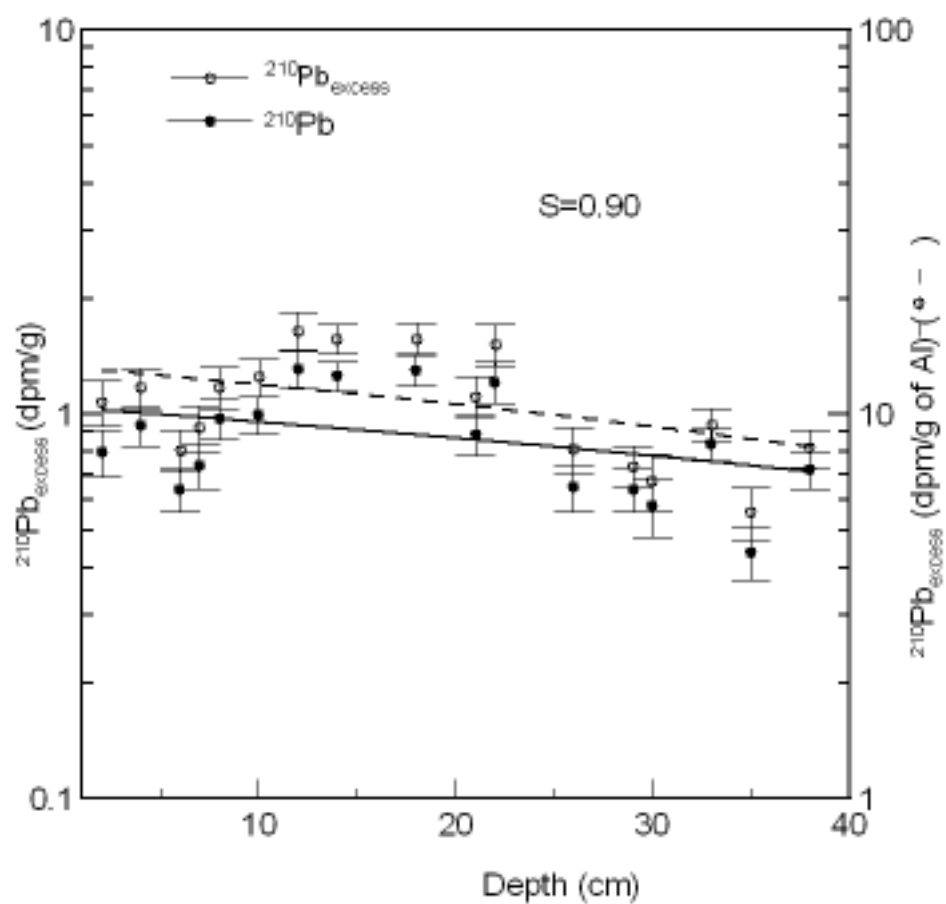


Figure 3.5.4 Excess ^{210}Pb concentration (dpm/g) in core B2 from the Bay

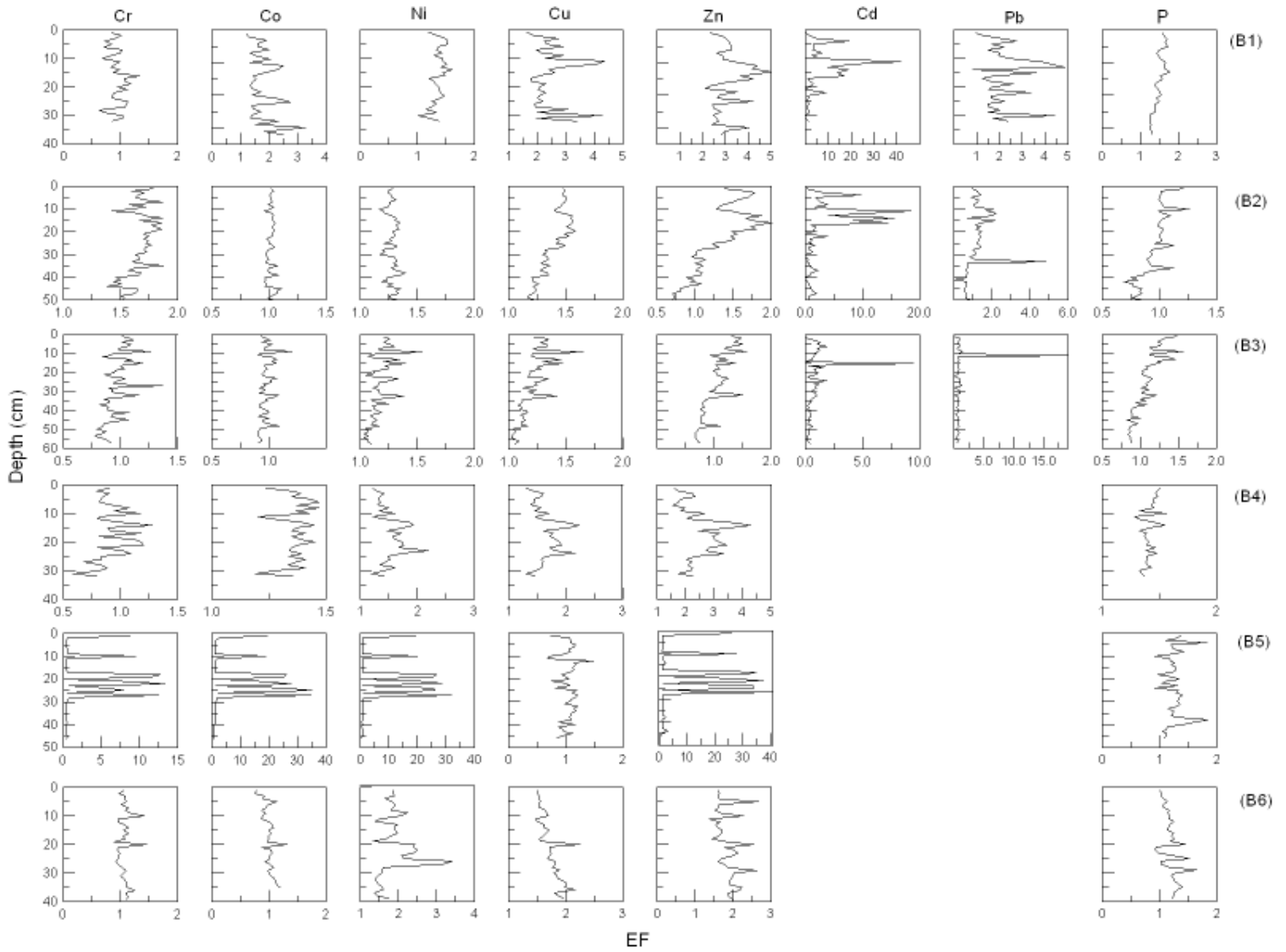


Figure 3.5.5: Enrichment Factor (EF) of some metals and P in core sediment of Bay

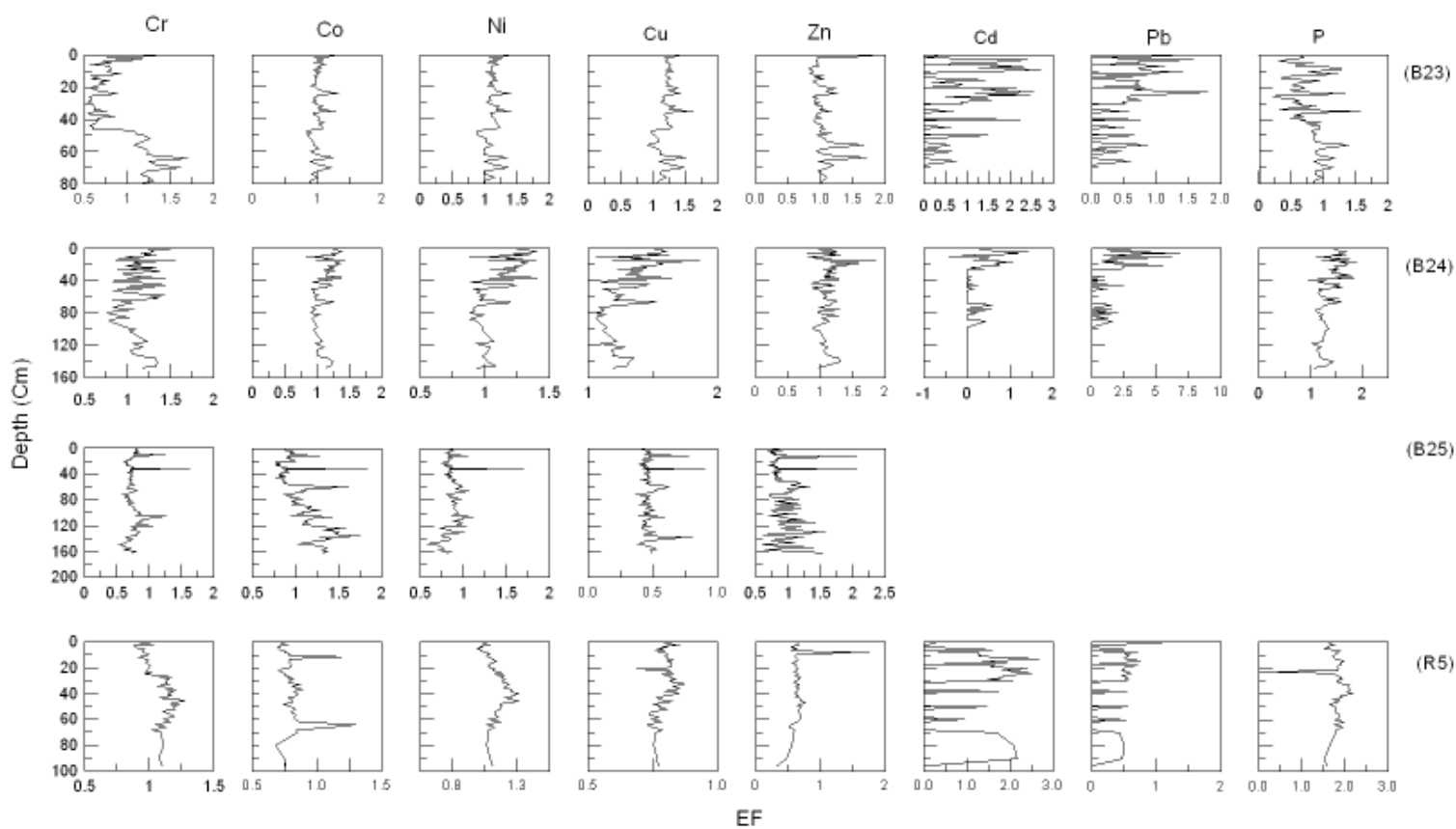


Figure 3.5.6: Enrichment Factor (EF) of some metals and P in core sediment of coastal area (Arabian sea) of Mumbai

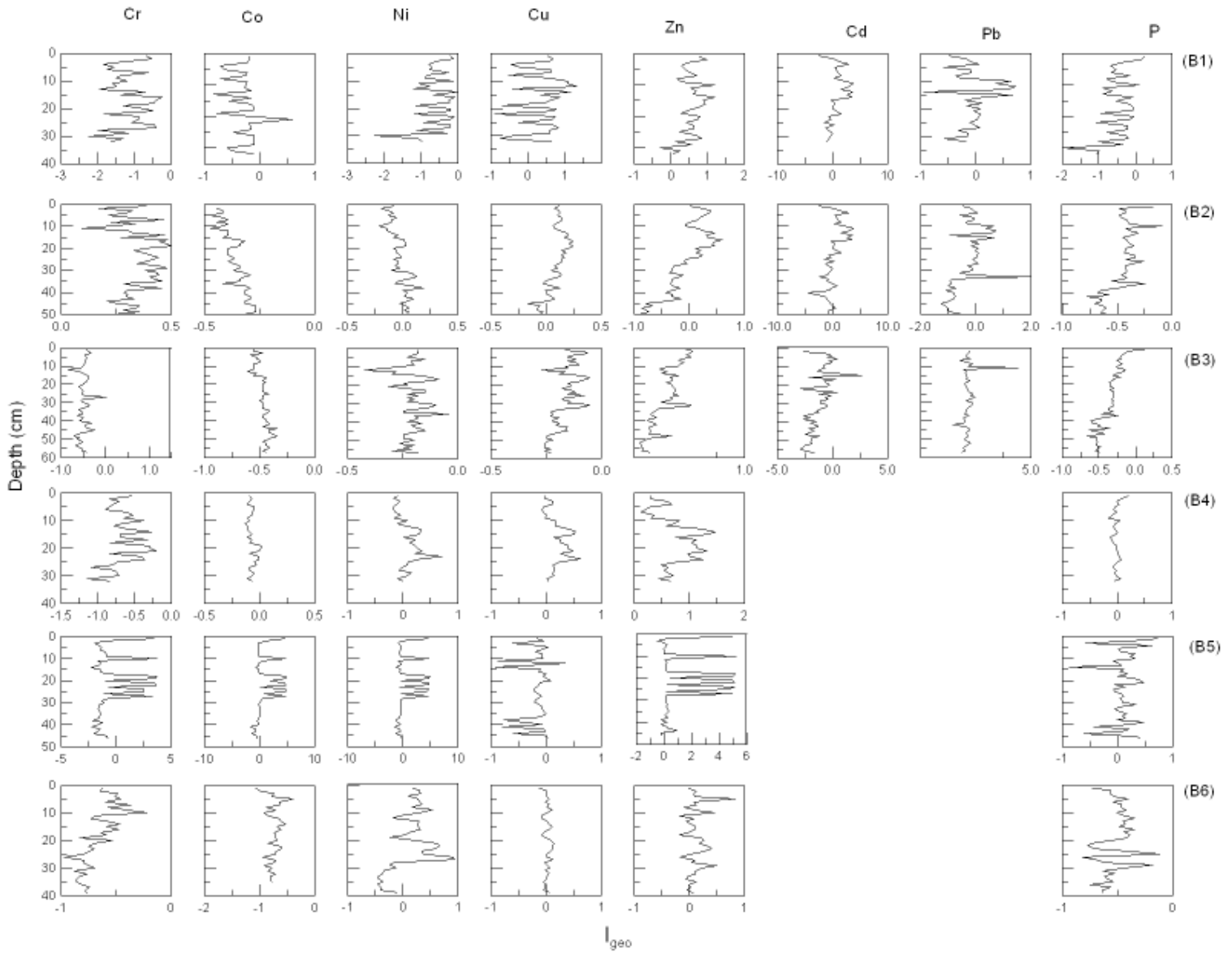


Figure 3.5.7: Geoaccumulation Index (I_{geo}) of some metals and P in core sediment of Bay

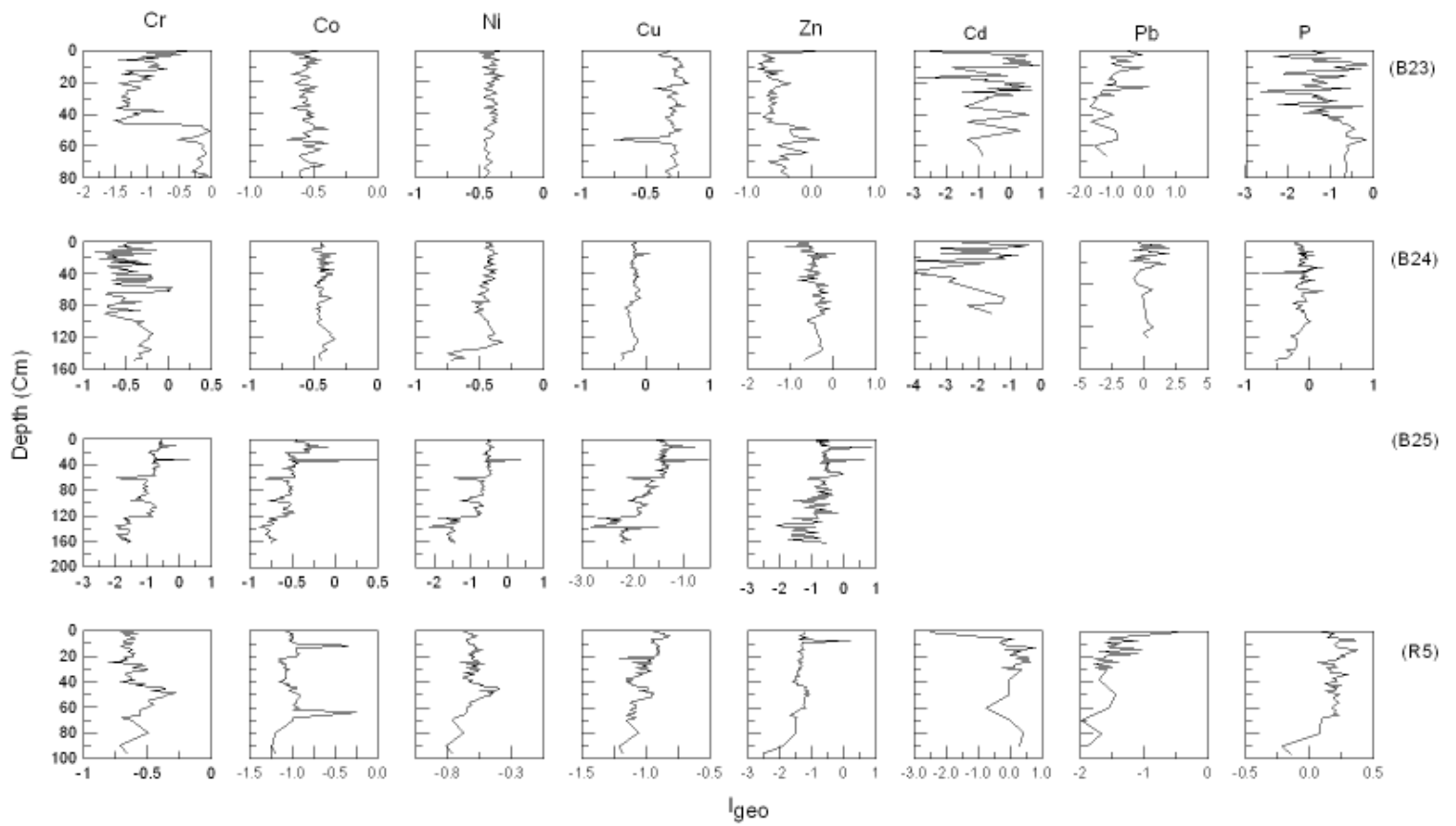


Figure 3.5.8: Geoaccumulation Index (I_{geo}) of some metals in sediment core of coastal area (Arabian Sea)

Cr (%; dry wt)

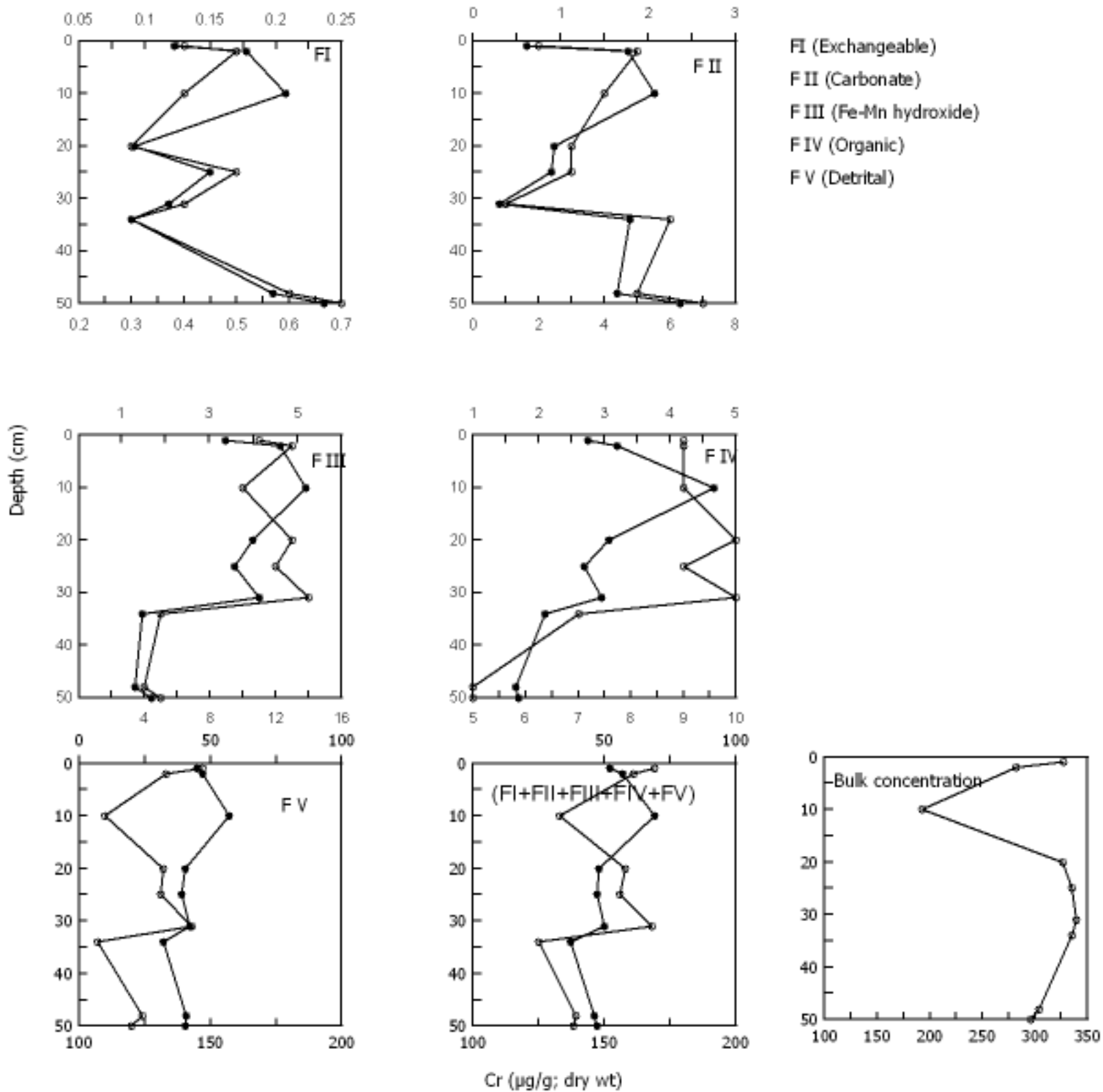


Figure 3.6.1: Concentration of Cr in the licheates ($\rightarrow\circ\leftarrow$) of sediment core B2 and its percentage ($\rightarrow\bullet\leftarrow$) with respect to the total concentration in sediment

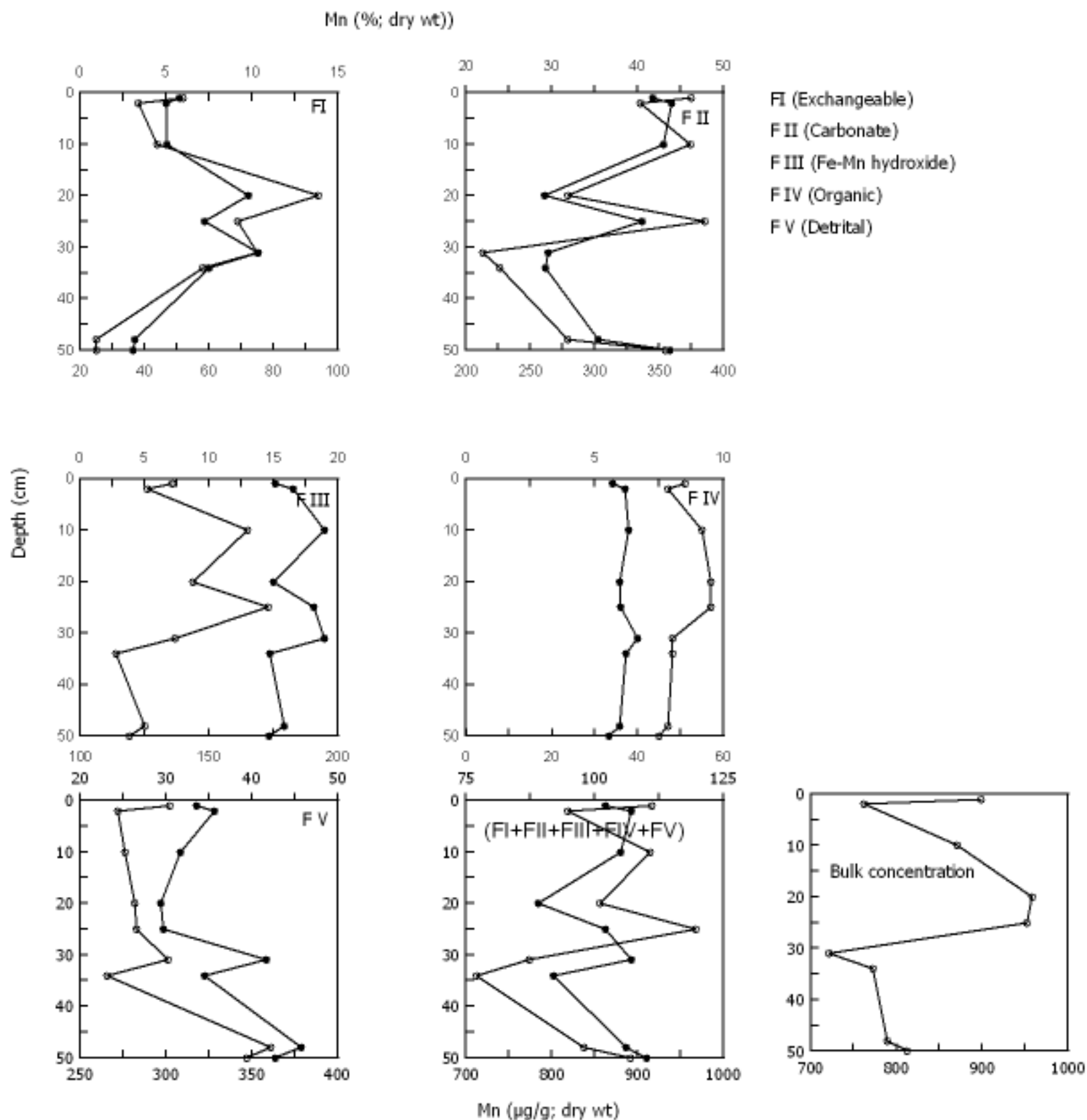


Figure 3.6.2: Concentration of Mn in the licheates (---) of sediment core B2 and its percentage (---) with respect to the total concentration in sediment

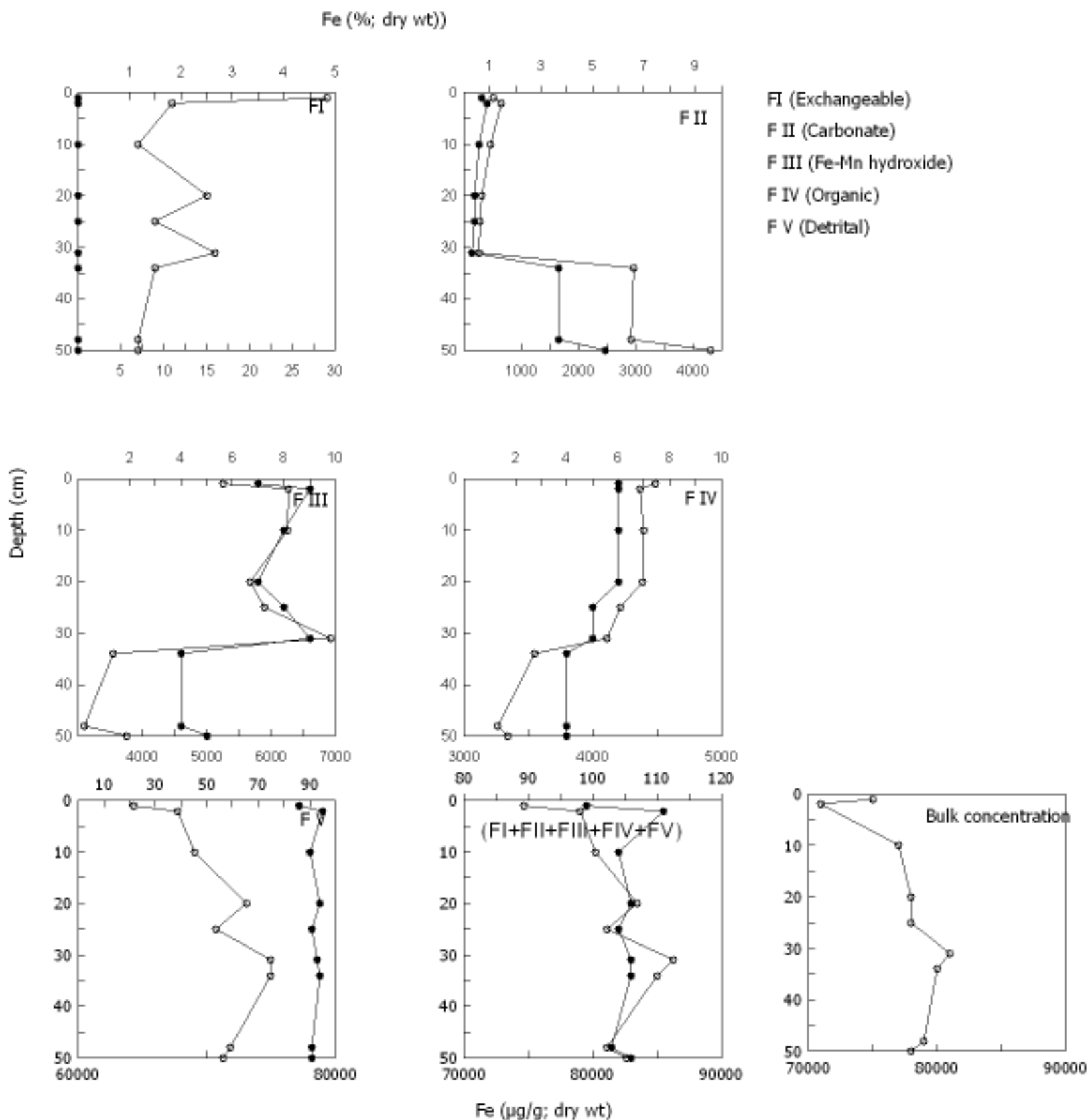


Figure 3.6.3: Concentration of Fe in the licheates (---○---) of sediment core B2 and its percentage (---●---) with respect to the total concentration in sediment

Cu (%; dry wt)

FI (Exchangeable)
 F II (Carbonate)
 F III (Fe-Mn hydroxide)
 F IV (Organic)
 F V (Detrital)

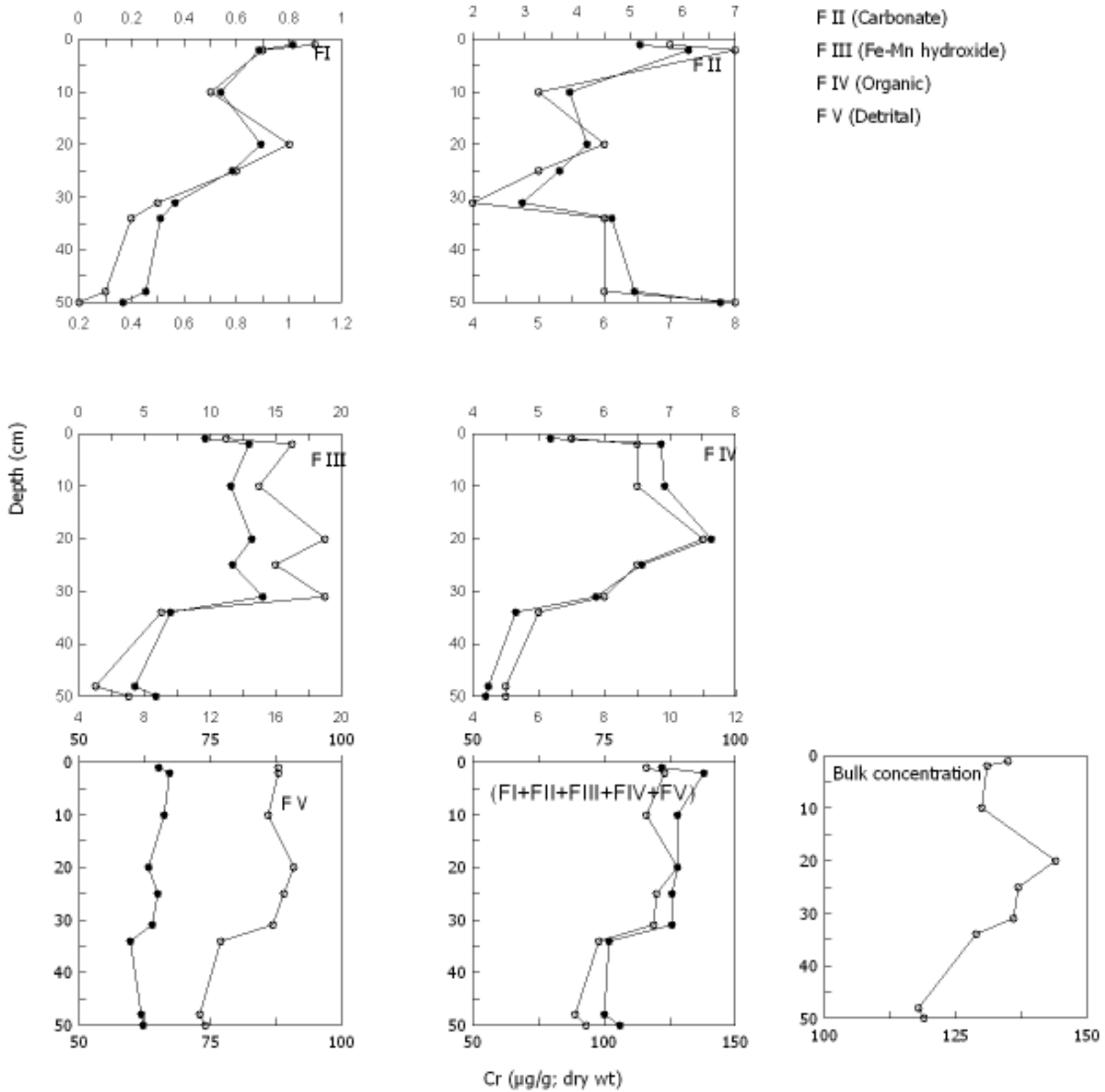


Figure 3.6.4: Concentration of Cu in the licheates (---○---) of sediment core B2 and its percentage (---●---) with respect to the total concentration in sediment

CHAPTER 4

METALS IN ULHAS ESTUARY

4.1 Area description

Ulhas River is the largest of the Konkan rivers and is divided into two well-marked sections: above and below the limit of the tide. Her upper course is steep and rugged with torrential waters flowing during the monsoon season.

4.1.1 Ulhas estuary

The Ulhas River originates in the western slope of the Sahyadrian range and after a westerly course of about 100 km through mountainous terrain, reaches Kalyan on the plains. From Kalyan onwards the river meanders through vast mudflats and extensive mangrove areas to join the Arabian Sea near Vasai through the Bassein Creek. Bhatsai and Kalu Rivers join the Ulhas in the upper tidal zone [Figure 2.1.6 (b)]. The high rainfall that the catchment receives during the monsoon period, leads to heavy runoff through these rivers to the Arabian Sea. The rivers have barrages constructed on them in the upstream that permit only limited river discharge (5×10^4 - 7×10^4 m³/d) in to the estuary during the early dry season and becomes scanty after December.

Before joining the Arabian Sea, an arm of Ulhas bifurcates at Mumbra and joins the Thane Creek head and diverts a small portion of its flow during monsoon and high tides to the Thane Creek. During dry season (October-May), the spring tidal range of about 4.5 m at the estuary mouth decreases to 2.8 m at 55 km inland [station U23 in Figure

2.1.6 (a)]; the corresponding neap tidal ranges being 3.0 and 1.7 m respectively. The high tidal influence generates strong currents with peak speeds typically exceeding 1 m/s. The dry season tidal excursion of 5-15 km in the lower estuary (Bassein-Kasheli segment) decreases to 2-5 km in the inner estuary (upstream of Mumbra). Thus, the estuarine reach is at least up to 55 km inland during dry season. The salinity varies considerably, temporally as well as spatially. Typically, the spring high tide salinity, which is close to the seawater value (35.5 psu) in the estuary mouth decreases to about 25 psu in the mid-estuarine zone and further down to 10 psu in the inner segment during May when the riverine flow is lean. The salinities are markedly lower during neap tide and values as low as 1 psu occur in the inner estuary during early dry season. The estuarine flushing time has been estimated to vary between 73 and 211 tidal cycles during dry season suggesting the possibility of build-up of contaminants in the inner estuary. Though no information on the dynamics of the estuary is available for the monsoon period, the estuary is considered to be effectively flushed by the voluminous river flow and occasional floods (NIO, 1994).

4.1.2 Openshore area

The shelf off the mouth of the Ulhas estuary is a continuation of the shelf off the Bay (Section 3.1.3) which slopes gradually with the 10 m depth contour roughly 10 km off the coast. Due to swift water movements and elliptical circulation the inshore contaminated waters from the estuary draining into the coast tend to circulate before being transported offshore. The coastal water mass is well-mixed vertically even during monsoon.

4.1.3 Effluent releases

Kalyan-Ulhasnagar belt is heavily industrialized and consists of chemical, metallurgical, pharmaceutical, textile and rayon industries which release their effluents in the Ulhas estuary and its tributaries. The human settlements, which have grown multifold around the industrial belt also dispose domestic wastewater in the estuary, often untreated.

Consequently, the quality of the estuary water deteriorates as the dry season progresses.

In May, the pH systematically decreases from 7.8-8.0 in the outer estuary to 6.7-7.9 in the inner segment due to enhanced aerobic microbial oxidation of organic matter. The DO is considerably under-saturated and tide-dependant with values falling below 1 ml/l in the inner estuary during low tide. The average concentrations of $\text{PO}_4^{3-}\text{-P}$ ($>2.5 \mu\text{mol/l}$) and $\text{NO}_3^-\text{-N}$ ($>30 \mu\text{mol/l}$) are considerably high in the inner estuary with abnormal levels of $\text{NO}_2^-\text{-N}$ ($>20 \mu\text{mol/l}$) and $\text{NH}_4^+\text{-N}$ ($>5 \mu\text{mol/l}$). The high nutrient content gives rise to high levels of chlorophyll *a* ($>25 \text{mg/m}^3$) in this segment where the SPM is relatively low (5-30 mg/l). The outer estuary, however, sustains low chlorophyll *a* ($<3 \text{mg/m}^3$) due to high SPM (100-700 mg/l) that results from dispersion of the sediment from the bed and mudflats by strong currents sweeping the shallow outer region of the estuary (NIO, 1994).

4.2 Metals in surface sediment

Surficial sediments from stations marked in Figures 2.1.6 (a) and (b) was sampled during May 1996, April 1998 and October 2000 for their contents of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn and P. The Ulhas River upstream of her confluence with the Bhatsai and Kalu Rivers has a rocky bed with no sediment deposits and hence could not be sampled. The weirs just upstream of stations U4 and U10 are an effective barrier for ingress of tidal water and the impacts of anthropogenic perturbations in the estuary are restricted up to the weirs. The profiles of distribution of Cr, Co, Ni, Cu, Zn, and P along the length of the estuary (Figure 4.2.1) indicate high concentrations of most metals just below the weir.

There are no substantial anthropogenic releases in the river upstream of the weir and the sediment metal concentrations can be considered to represent lithogenic background. The concentrations of metals and P at station U1 are compared with the average concentration

of the respective metal in the catchment soil discussed in Section 3.2, in the following table:

Constituent	Catchment soil			Station U1
	Minimum	Maximum	Averag	
Al (%)	8.2	14.2	10.8	7.2
Cr ($\mu\text{g/g}$)	82	567	263	302
Mn ($\mu\text{g/g}$)	896	4729	2047	1285
Fe (%)	11.5	29.5	18.6	10.1
Co ($\mu\text{g/g}$)	20	72	50	77
Ni ($\mu\text{g/g}$)	57	1181	212	114
Cu ($\mu\text{g/g}$)	76	365	208	89
Zn ($\mu\text{g/g}$)	44	168	115	180
P ($\mu\text{g/g}$)	120	1830	726	513

The concentrations of all the constituents are within the range observed for the catchment soil but often deviate from the average. Thus the sediment at station U1 appears to be depleted in Al, Mn, Fe, Ni, Cu, and P, while the remaining metals indicate higher levels as compared to the average concentration in the catchment soil.

The SPM in the estuary would remove considerable fraction of the anthropogenic metals entering the system as the *in-situ* SPM is fine (mean particle size 11.7 μm) with cation exchange capacity of 54.3-70.2 meq/100g (Bhosale and Sahu, 1991). The nature of the profiles of distribution of metals and P in surface sediment of the estuary (Figure 4.2.1) suggests high anthropogenic enrichment of Cr, Cu, Zn and P in the inner estuary. Data in Figure 4.2.1, indicate marked variation of a metal from one collection to the next. This can be due to the disturbance and redistribution of sediment because of several factors such as tidal movements, turbulence etc but largely influenced by high river runoff during monsoon.

Under high tidal excursion (NIO, 1994) the SPM enriched in metals would be transported in the inner estuarine segment of the Bhatsai and Kalu Rivers during flood tide where it probably settles under relatively

tranquil conditions created by the presence of weirs. The contaminated SPM transported downstream during ebb tide gets diluted by naturally occurring high SPM in the outer estuary and distributed over a large area as the estuary widens in the seaward direction thereby explaining significantly lower and decreasing levels of metals in the outer estuary.

The inner segment (particularly stations U4 to U9) was visited during July-September (monsoon), October-January (post-monsoon) and April-June (pre-monsoon). It was seen that the high freshwater flow over the weir during monsoon had completely eroded the sediment deposited in the inner segment (stations U4 to U9) exposing the rocky estuary bed. Accumulation of sediment in this zone commenced only after November when the weir discharge decreased substantially. Hence, we conclude that the sediment confined to the inner segment is fresh and accumulates over a period of only about 7 months from December to June. The sediment dislodged from the inner zone by the monsoonal flow would be transported to the middle and the outer estuary where it may get dispersed and eventually settle-partly or wholly, thereby influencing the metals content of the local sediment. A portion of the sediment would also be transported to the Arabian Sea where it would settle in the coastal area. The marked high concentration at station U4 is possibly due to preferential settling of the SPM due to tranquil conditions as the estuary broadens and curves in this zone (Figure 4.2.1). The Hg accumulation in the sediment of the inner estuary has been reported to increase as the dry season progresses (Ram *et al.*, 2003). Similar trends are seen for the metals investigated during the present study.

Among trace metals, Cr burden in the surficial sediment seems to have increased with the passage of time. Thus, at station U31 the concentration of Cr has gone up from 431 $\mu\text{g/g}$ in April 1996 to 843 $\mu\text{g/g}$ in October 2000. The increase is also in the coastal sediment at stations U36 and U37. The distribution of Cr in sediment along the length is well defined in collections made in April 1996, April 1998 and October 2000. A distinct gradation in the Cr content of sediment is evident with a marked

decrease in the seaward direction. Thus, in October 2000 the concentration of 877 $\mu\text{g/g}$ in the inner estuary (station U34) decreases to 421 $\mu\text{g/g}$ in the mid segment of the estuary (station U32) and to 166 $\mu\text{g/g}$ at station U37 which is about 25 km off the coast. The high concentration of Cr in the estuary and its decrease in the seaward direction suggests a significant source of Cr to the inner estuary subsequent to April 1996. Similar to Cr, distinctly high concentrations of Cu, Zn and P occur at station U4 with a trend to decrease in the seaward direction (Figure 4.2.1).

A marked change in the texture of the surface sediment of the Ulhas estuary from pre-monsoon to post-monsoon is also reported with a decrease in the clay and silt contents in the post-monsoon period. This decrease is attributed to the removal of fine sediment particles to the sea by the monsoonal discharge (NIO, 1994). High run off during monsoon period enhances resuspension of bottom sediment. The lighter clay particles are preferentially advected to the sea by strong currents during the receding tide thereby depleting the content of fine-grained material from the estuary sediments. As the river flow decreases with the withdrawal of monsoon, the ebb currents become relatively weak permitting the settlement of fine sediment in the estuary.

To assess which of the common variable controls the concentration of metals in the sediment of the estuary, we calculated correlations of metal pairs. Significant positive correlations among pairs Cr:Cu ($r=0.73$; $p=>0.001$), Cr:Zn ($r=0.75$; $p=>0.001$), Cr:P ($r=0.79$; $p=>0.001$), Mn:Ni ($r=0.80$; $p=>0.001$), Co:Ni ($r=0.93$; $p=>0.001$), Cu:Zn ($r=1.00$; $p=<0.001$), Cu:P ($r=0.99$; $p=<0.001$) and Zn:P ($r=1.00$; $p=<0.001$) are evident during April 1996. Inversely correlations among pairs Mn:Cu ($r=-0.92$; $p=>0.001$), Mn:Zn ($r=-0.92$; $p=>0.001$), Mn:P ($r=-0.92$; $p=>0.001$), Ni:Cu ($r=-0.78$; $p=>0.001$), Ni:Zn ($r=-0.78$; $p=>0.001$) and Ni:P ($r=-0.71$; $p=>0.001$) are also seen during April 1996.

Significant positive correlations among pairs Al:Fe ($r=0.70$; $p=>0.001$), Cr:Cu ($r=0.68$; $p=>0.001$), Cr:Zn ($r=0.67$; $p=>0.001$), Cr:P ($r=0.63$; $p=>0.001$), Mn:Co ($r=0.80$; $p=<0.001$), Mn:Ni ($r=0.75$; $p=>0.001$), Fe:Co ($r=0.68$; $p=>0.001$), Co:Ni ($r=0.93$; $p=<0.001$),), Cu:Zn ($r=0.97$; $p=<0.001$), Cu:P ($r=0.98$; $p=<0.001$), Zn:P ($r=0.99$; $p=<0.001$) are evident during April 1998. Significant positive correlations with pairs Al:Mn ($r=0.68$, $p=>0.001$), Cr:Ni ($r=1.00$, $p=<0.001$), Mn:Cu ($r=0.90$, $p=<0.001$), Mn:Zn ($r=0.78$, $p=<0.001$), Co:Ni ($r=1.00$, $p=<0.001$), Ni:Cu ($r=0.83$, $p=<0.001$), Cu:Zn ($r=0.76$, $p=>0.001$), Zn:P ($r=0.82$, $p=<0.001$) and inverse correlations with pairs Al: Ni ($r=-0.90$, $p=>0.001$) and Fe:Ni ($r=-0.73$, $p=>0.001$) are indicated in October 2000 (Appendix-V (b)).

4.3 Metals in sediment cores

Sediment cores were retrieved from stations U1, U3, U4, U23, U30, U34, U35 and U37 [Figure 2.1.6 (a), (b)].

4.3.1 Distribution of major metals

The trends which are evident from the profiles of Al and Fe (Figure 4.3.1 to 4.3.3), the major metals investigated in the present study, are discussed in the following sections:

a) Aluminium

The Al content in cores U1 and U3 from the river section upstream of the weir varies in the range 8.7-9.3 % and the profile (Figure 4.3.1) is devoid of any definite features indicating a more or less uniform depositional regime [Appendix-VI (a)]. Below the weir at the head of the estuary where the sediment deposition was transient and limited to the dry season, the Al concentration varies in a narrow range (4.6-5.9 %) but the overall concentration is markedly lower than in the riverine cores U1 and U3.

In the estuarine core U23 the concentration of Al varies randomly but overall profile reveals a definite decrease in concentration from 7.6 % at the bottom to 6.1 % at the surface. The trend of variation is reverse in

core U31 with the decrease in concentration in the bottom section (7.7 %) as compared to the surface (9.4 %). In the coastal cores U31 and U37 the overall concentration of Al seems to have remained unaltered throughout the core lengths unlike in core U35 where there is marginal but definite increase in concentration by about 1 % at the surface compared to the bottommost section. Relative high concentrations of Al are also seen in the 28-49 cm zone of core U34; the highest concentration of 10.1 % being at 43 cm section. Thus it is clear that the deposition of Al in the sediment of the estuary as well as the coast vary in space and time. Based on the sedimentation rate of 2.93 cm/y reported for a core from the same site (Ram *et al.*, 2003) the core U35 represents the history of deposition of about 50 years (Figure 4.3.1). Thus there seems to be absence of substantial change in the deposition of clay in the coastal sediment.

b) Iron

As in the case of Al, Fe is present in relatively high concentration in sediments of cores U1 (9.8-10.8 %) and U3 (11.1-11.7 %) but decreases markedly in core U4 (4-6.3 %) indicating that relatively heavy Fe-oxide particles are probably trapped in the reservoir upstream of the weir during transport. Generally, the vertical profiles of Fe are devoid of any systematic features except in core U23. In this core the concentration of Fe gradually increases from 6.9 % at the surface to 9.76 % at the depth of burial. In core U30 the concentration of Fe is centred around 8.7 % except for a sharp peak at 20 cm (15.0 %) suggesting an episodic event of high Fe deposition in the sediment at this site. Fe and Al co-vary with significant correlations in cores U23 ($r=0.69$; $p<0.001$) and U35 ($r=0.30$; $p<0.001$). The remaining cores revealed poor correlation (Appendix-VI (b)).

4.3.2 Distribution of minor elements

a) Chromium

The cores U1 and U3 sustain high concentration of Cr (450-602 $\mu\text{g/g}$) throughout the length which is on the higher side of the range recorded in the catchment soil. These concentrations are lithogenic since

the stations U1 and U3 are upstream of weir and are beyond significant influence of anthropogenic emissions. Because of high lithogenic Cr in the region it is difficult to conclude whether high concentrations observed in the inner estuary are natural or have anthropogenic component. Except for core U31 wherein the concentrations are abnormal in certain sections, the general trend of variation of the metal suggests a decrease from the inner to the outer estuary and the open coast. Thus, the concentrations of Cr are in the following ranges in the cores:

Core	Concentration range ($\mu\text{g/g}$)
U1	450-593
U3	511-602
U4	362-639
U23	254-408
U30	208-306
U34	137-247
U35	155-302
U37	70-139

Such a trend could result due to the dilution of the estuarine sediment with high Cr content with the sediment of marine origin sustaining relatively low concentration of Cr entering the estuary with the tidal ingress.

The depth profile of Cr in core U31 is strikingly different (Figure 4.3.1) from all other cores with sharp peaks of abnormally high concentrations (2801-3034 $\mu\text{g/g}$) at 11, 14, 17, 20, 23, 24, 25, 26 and 29 cm. Unusually high concentrations of Mn, Co, Ni and Zn also coincide with the high concentration of Cr. Such peaks are however absent in the Cu profile and its concentration in this core is comparable with that observed in other cores. As discussed for core B5 (Section 3.5.2) it is probable that the sediment at this site has been intermittently enriched with metallic particles such as Al-Si alloys which are mainly used in castings.

In cores U3, U31, U35 and U37, Cr concentration directly varies with that of Al with correlation coefficient (r) of 0.33-0.80 ($p=0.001$). The remaining cores revealed poor correlation. Excellent positive correlations also occur between Cr and Fe in cores U1 ($r=0.67$; $p=>0.001$), U35 ($r=0.51$; $p=<0.001$) and U37 ($r=0.28$; $p=>0.001$). Its relationship with Co in cores U1 ($r=0.85$; $p=<0.001$), U4 ($r=0.88$; $p=<0.001$), U31 ($r=1.00$; $p=<0.001$), U34 ($r=0.69$; $p=<0.001$) and U35 ($r=0.64$; $p=<0.001$) are significant.

b) Manganese

The Mn profiles in cores U1 and U3 indicate its lithogenic concentration variable in the range 1224-2165 $\mu\text{g/g}$ in the sediment transported to the estuary. Mn is depleted in core U4 as compared to upstream and downstream cores. In cores U23 and U30 the concentration of Mn throughout the length is centred on 1500 $\mu\text{g/g}$. The sharp peak at 39 cm (2559 $\mu\text{g/g}$) in core U23 and at 20 cm (2432 $\mu\text{g/g}$) in core U30 closely coincides with relative high concentration of Fe in these cores. The concentrations of Mn in coastal cores U34, U35 and U37 is lower than in the estuarine cores and the profiles are without any regular features.

Except for direct variation of Mn with Fe ($r=0.93$; $p=<0.001$) in core U3, there is no correlation with other metals and P in the riverine cores. In the estuarine and coastal cores Mn linearly varies with Ni ($r=-0.53$; $p=<0.001$) and Pb ($r= -0.38$; $p=>0.001$) in core 23; Co ($r=1.00$; $p=<0.001$), Ni ($r=1.00$; $p=<0.001$) and Zn ($r=0.99$; $p=<0.001$) in core U31; Zn ($r=0.33$; $p=>0.001$) and Cd ($r=0.30$; $p=<0.001$) in core U34; Fe ($r=0.38$; $p=<0.001$), Co ($r=0.65$; $p=<0.001$) and Cu ($r=0.32$; $p=>0.001$) in core U35; and Co($r=0.46$; $p=<0.001$) in core U37.

c) Cobalt

The concentration of Co in cores U1 (75-80 $\mu\text{g/g}$) and U3 (79-94 $\mu\text{g/g}$) is markedly higher than the average concentration in the catchment soil (50 $\mu\text{g/g}$) as in the case of Cr. The concentration decreases in core

U4 probably due to its low Al and Fe contents. Except for a few low values, the concentrations are abnormally high in core U30 with peaks of high concentrations coinciding with those of Ni, Cu and Zn. It is possible that this segment of the estuary receives very high input of these metals. The concentration of Co directly varies with that of Fe ($r=0.62$; $p<0.001$) and Cr ($r=0.85$; $p<0.001$) in core U1, while in core U4 Co varies with Cr ($r=0.88$; $p<0.001$) and Zn ($r=0.83$; $p<0.001$). The profile of its concentration with depth in core U23 is in line with the variation of Fe and Ni in the core. Thus, Co and Fe ($r=0.71$; $p<0.001$) as well as Co and Ni ($r=0.57$; $p<0.001$) are positively correlated in this core. Co varies directly with Al ($r=0.36$; $p<0.001$) in core U35 while it varies inversely with Al ($r=-0.27$; $p<0.001$) in core U37.

d) Nickel

Direct variation of Ni with Al ($r=0.78$; $p<0.001$) and Zn ($r=0.88$; $p<0.001$) in core U3 indicates its association with these metals. The concentration of Ni in core U23 directly varies with significant correlations with Cr ($r=0.72$; $p<0.001$) and Co ($r=0.8$; $p<0.001$). In core U30 its concentration directly varies with that of Co ($r=1.00$; $p<0.001$), Cu ($r=1.00$; $p<0.001$) and Zn ($r=0.99$; $p<0.001$), while, in core U31 its concentration is positively correlated with Al ($r=0.57$; $p<0.001$), Cr ($r=1.00$; $p<0.001$), Mn ($r=1.00$; $p<0.001$), Co ($r=1.00$; $p<0.001$) and Zn ($r=0.99$; $p<0.001$). The concentration of Ni varies directly with that of Cr ($r=0.35$; $p<0.001$) and Pb ($r=0.41$; $p<0.001$) in core U35 while such a relationship is absent in core U37.

e) Copper

Its concentration in core U1 varies in accordance with the changes in Al contents. Evidently, its concentration co-varies with that of Al ($r=0.70$; $p<0.001$). Cu concentration however varies directly with that of Al ($r=0.77$; $p<0.001$) in core U4.

The concentration profiles of Cu in cores U34 and U35 are featureless with a trend of increase in level towards the surface. It bears

good positive correlation with Cr ($r=0.70$; $p<0.001$), Co ($r=0.45$; $p=0.001$), Zn ($r=0.29$; $p<0.001$) and Pb ($r=0.64$; $p<0.001$) in core U34 while its relationship with Al ($r=0.55$; $p<0.001$), Cr ($r=0.60$; $p=0.001$), Mn ($r=0.32$; $p<0.001$), Fe($r=0.31$; $p<0.001$), Cr ($r=0.64$; $p=0.001$), Pb ($r=0.29$; $p<0.001$) is significant in core U35. The concentration of Cu in core U37 varies with Fe($r=0.29$; $p<0.001$).

f) Zinc

Zn concentrations in cores U1 and U3 are within the range of catchment soil concentration and the bottom sections of cores U34, U35 and U37 (88-185 $\mu\text{g/g}$). The concentration of Zn in core U1 and U3 does not indicate any correlation with other metals studied. Abnormally high concentrations of Zn in the estuarine cores indicate its anthropogenic release through the effluents. The concentration is as high as 4722 $\mu\text{g/g}$ at 7 cm depth and decreases to 2792 $\mu\text{g/g}$ in core U4 at surface. Its concentration directly varies with that of Co ($r=0.83$; $p=>0.001$) and Ni ($r=0.88$; $p<0.001$) in core U4. The concentrations are high (322-833 $\mu\text{g/g}$) throughout the length in core U23 with a trend to decrease towards the surface. In this core the concentration of Zn varies directly with Al ($r=0.46$; $p<0.001$), Fe ($r=0.57$; $p<0.001$) and Cu ($r=0.67$; $p<0.001$) but the relationship is inverse with Cr ($r=-0.60$; $p=>0.001$) and Ni ($r=-0.43$; $p=>0.001$). Accumulation of Zn to high levels in certain sections is also evident in cores U30 and U31 with the concentration varying directly with that of Co ($r=0.99$; $p<0.001$), Ni ($r=0.99$; $p<0.001$) and Cu ($r=0.99$; $p<0.001$). The high concentration of Zn in the estuarine sediment is not reflected in elevated levels in the cores from the open coast (Cores U34 to U37). In core U34 the concentration of Zn varies directly with that of Al ($r=0.30$; $p=>0.001$), Mn ($r=0.33$; $p<0.001$) and Cu ($r=0.29$; $p=>0.001$) and Cd ($r=0.54$; $p<0.001$) while in cores 35 and 37 the concentration of Zn does not seem to be correlated with other metals except with Cu ($r=0.34$; $p<0.0001$) in core 37.

g) Cadmium

Cd was analyzed in selected cores namely U23, U30, U34 and U35 and its depth profiles are illustrated in Figure 4.3.3. The concentration of Cd in the catchment soil varies in the range 0.03-0.53 $\mu\text{g/g}$ averaging at 0.3 $\mu\text{g/g}$. Its concentration in the bottom section of the cores U34 and U35 is 0.3 $\mu\text{g/g}$. It is therefore reasonable to consider that the lithogenic baseline for the estuary sediment would be around 0.3 $\mu\text{g/g}$ and the concentrations higher than 0.3 $\mu\text{g/g}$ in the sediment result from anthropogenic sources. The profiles of variation of Cd with depth indicate that its concentration in the sediment of the inner estuary has increased due to anthropogenic additions with the levels nearly doubled as compared to the baseline in core U23. The coastal sediment however seems to be free from anthropogenic Cd except for a few stray values. Cd has no significant relationship with other metals except in core U34. In this core its concentration varies directly with that of Mn ($r=0.50$; $p<0.001$) and Zn ($r=0.54$; $p<0.001$).

h) Lead

Like Cd, Pb was analyzed in selected cores (Figure 4.3.3). From Table 3.2.3 it can be considered that the average concentration of Pb in the catchment soil is 21.7 $\mu\text{g/g}$ though the values vary in a wide range. Its concentration in the bottom section of cores U34 and U35 (21.7 $\mu\text{g/g}$) is generally below the catchment baseline.

The concentration of Pb in core U23 is about double the concentration in comparison with the baseline. Unlike most other trace metals, Pb does not show significant relationship with other metals in this core. The Pb profile of core U30 indicates baseline concentration in the upper 1-20 cm core length. There is a sharp and abrupt rise in 21 cm segment of the core (274.1 $\mu\text{g/g}$) and the bottom section 353.9 $\mu\text{g/g}$ at 24 cm depth of the sediment. Except in the top 3 cm, the concentration of Pb in cores U34, U35 and U36 is comparable to the baseline. The Pb concentration varies inversely with that of Fe ($r=-0.35$; $p>0.001$) in core U35 but varies directly with Ni ($r=0.41$; $p<0.001$) and Cu ($r=0.29$;

$p < 0.001$) in these cores. The depth profile of variation of Pb in cores U34 and U35 also indicates increase in loading with the passage of time.

i) Phosphorus

The concentration of P in cores U1 and U3 though variable the average trend suggests the baseline concentration. The high concentrations of P in core U4 (average 5619 $\mu\text{g/g}$) indicates fast accumulation of P in only about 7 months from December to June as discussed elsewhere (Section 4.3). P varies directly with Mn ($r=0.79$; $p < 0.001$), and inversely with Fe ($r=-0.80$; $p < 0.001$) in core U4. The depth profile of P in core U30 is devoid of definite trend though the concentrations are generally more than 1100 $\mu\text{g/g}$. The concentration of P in core U31 averages around 1238 $\mu\text{g/g}$.

The concentration of P in the catchment soil varies over a wide range of 120-1830 $\mu\text{g/g}$; (av 726 $\mu\text{g/g}$). Its average concentration in the sediments of the cores U34, U35 and U37 deposited over 50 years ago is 966 $\mu\text{g/g}$, 875 $\mu\text{g/g}$ and 661 $\mu\text{g/g}$ respectively.

4.3.3 Enrichment Factor

The average values for the bottom sections of selected cores given in Section 3.4.1 were used as the background for calculating EF.

These are plotted against depth in Figures 4.3.4 and 4.3.5 for the Ulhas estuary. The EF is as high as 30-40 in the core U30 for Cr, Co, Ni and Zn. As discussed in Section 1.4, the maximum concentrations of Cd and Pb were 5-10 times the baseline and Cu and Zn concentrations were <3 times the baseline with large inventories of Pb in cores of proximity to the Pb smelter reported in the sediment core of San Francisco Bay (Hornberger *et al.*, 1999).

4.3.4 Index of geoaccumulation

I_{geo} is in class 0 to 1 for cores from the Ulhas estuary (Figure 4.3.6 and 4.3.7) reveals that the estuarine segment is moderately polluted, while, the sediment from the open-coast is unpolluted.

4.3.5 Overall assessment

When all the values are pulled (n=382) positive correlations at the level of significance of 0.001 are evident for the pairs Cr:Mn, Cr:Cd, Cr:Pb, Mn:Co, Mn:Ni, Fe:Ni, Mn:Zn, Mn:Cd, Fe:Cd, Co:Ni, Co:Zn, Ni:Zn, Zn:P and Cd:Pb. Negative correlations at the level of significance of 0.001 are evident for the pairs Al:Cd, Al:Pb, Al:P and Fe:P.

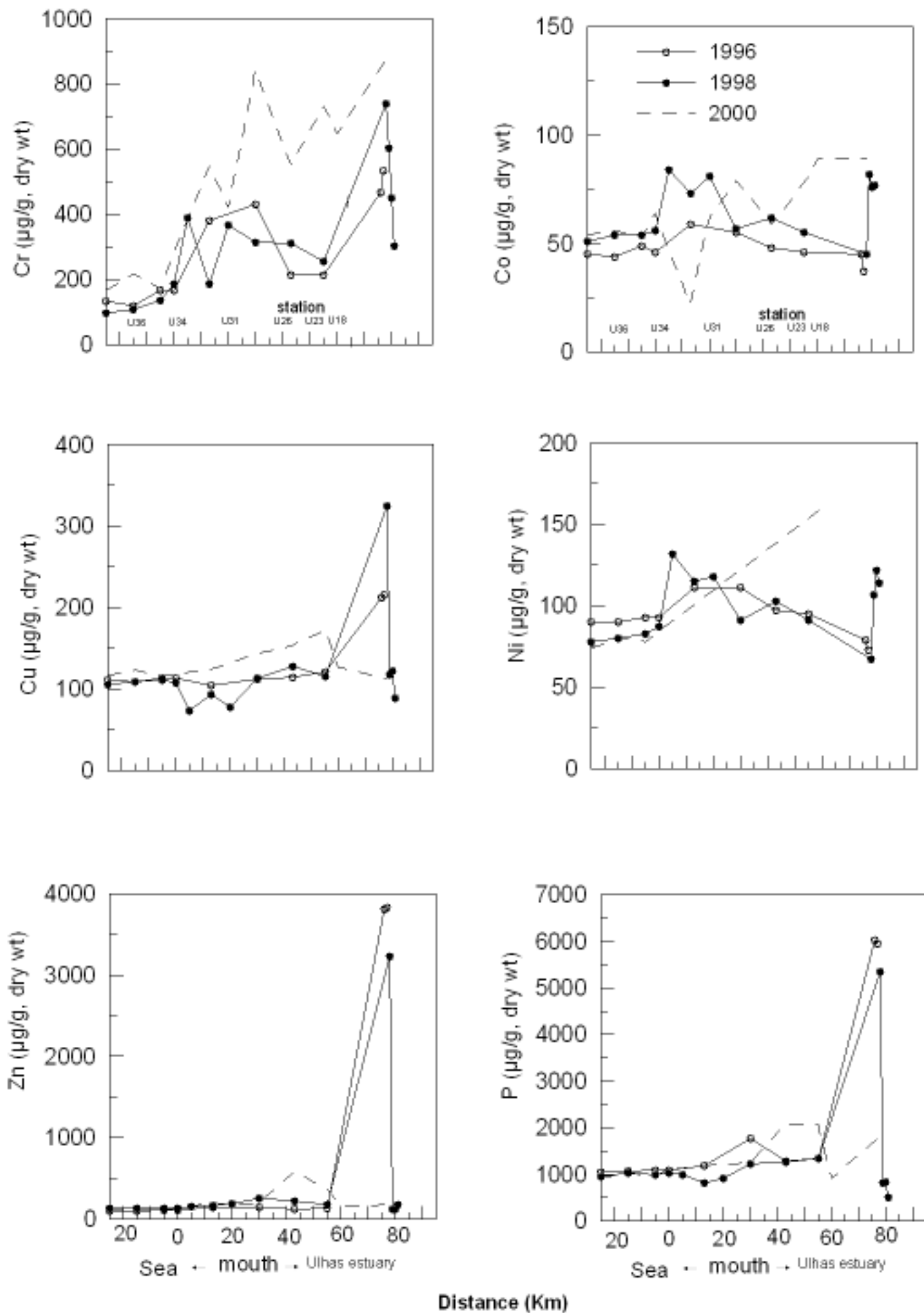


Figure 4.2.1: Variation of Cr, Co, Ni, Cu, Zn and P in surficial sediments of the Ulhas estuary and the adjoining coastal area (Arabian Sea) during different sampling events

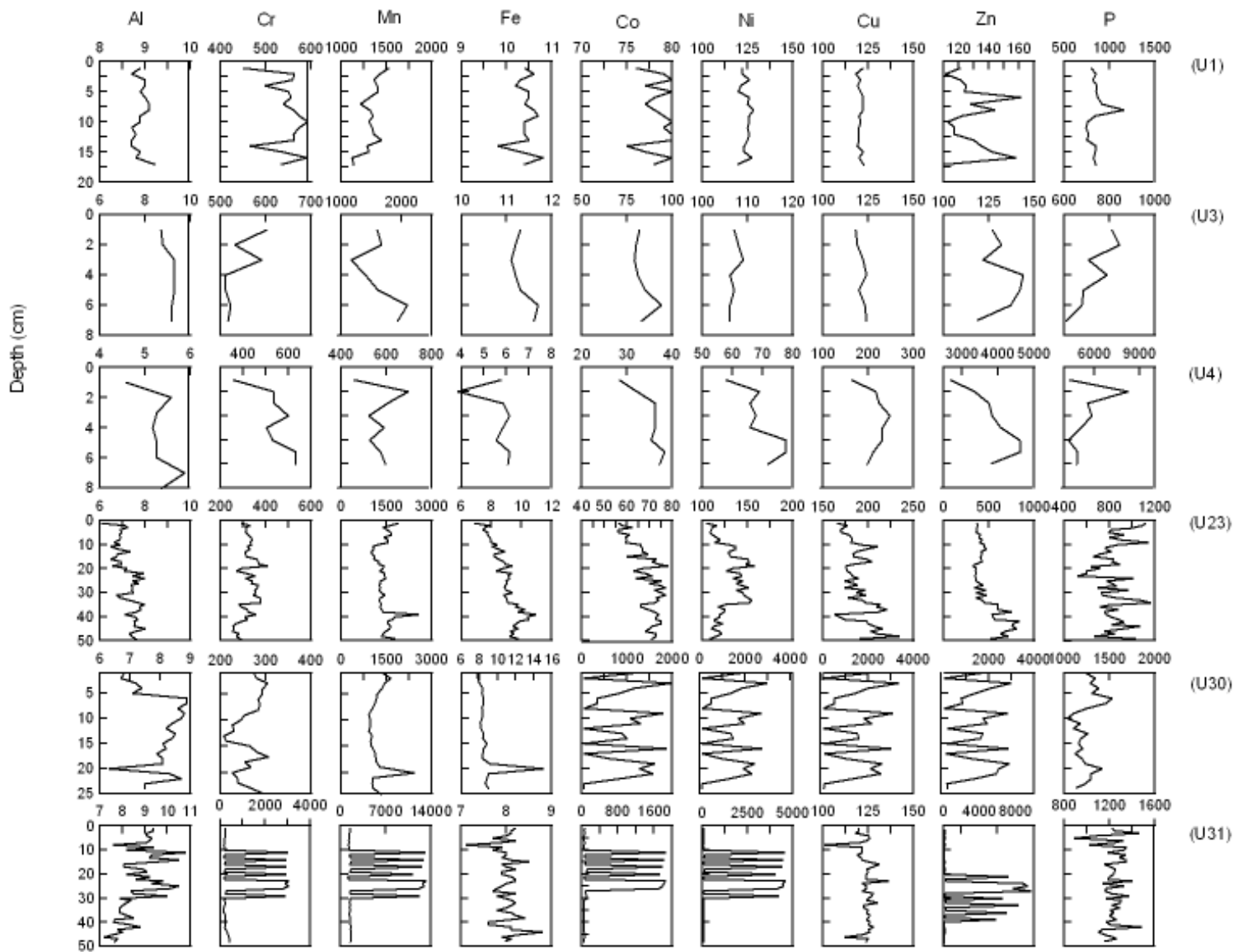


Figure 4.3.1: Depthwise variation of selected metals and P [$\mu\text{g/g}$; except Al, Fe (%), dry wt] in sediment cores from Ulhas estuary and adjoining coastal area (Arabian sea)

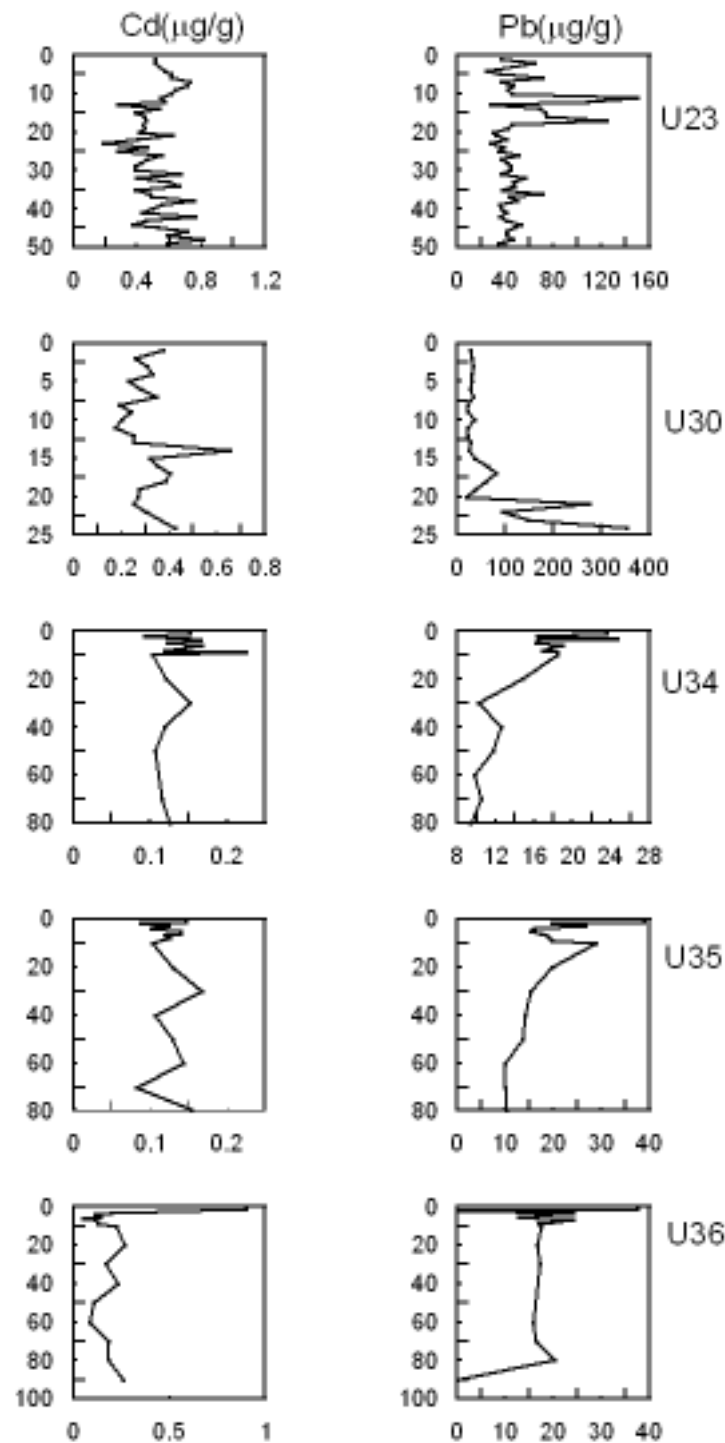


Figure 4.3.3: Depthwise variation of Cd and Pb ($\mu\text{g/g}$, dry wt) in core sediment of Ulhas estuary and adjoining coastal area (Arabian sea).

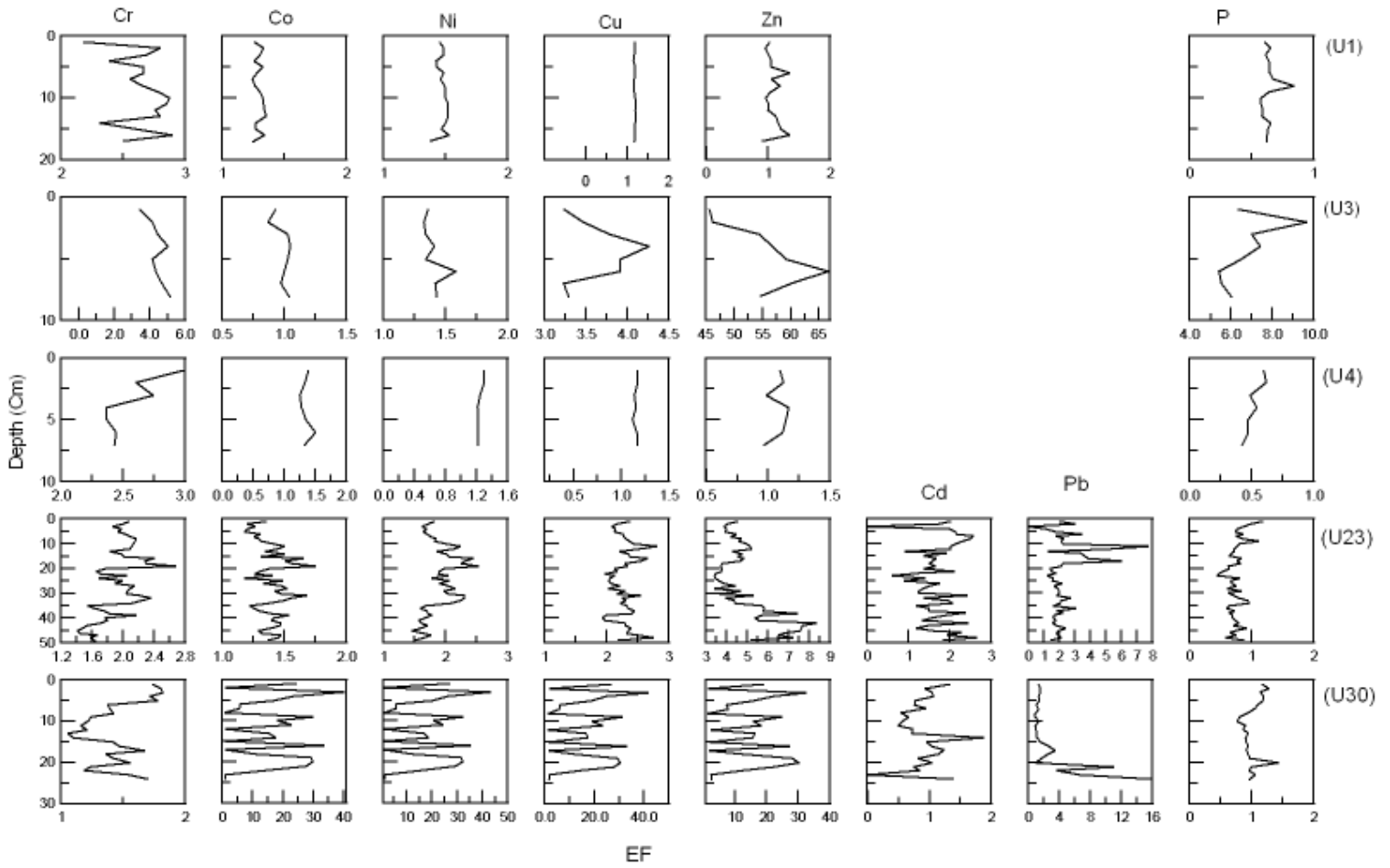


Figure 4.3.4 : Enrichment Factor (EF) of selected metals and P in sediment cores from Ulhas estuary

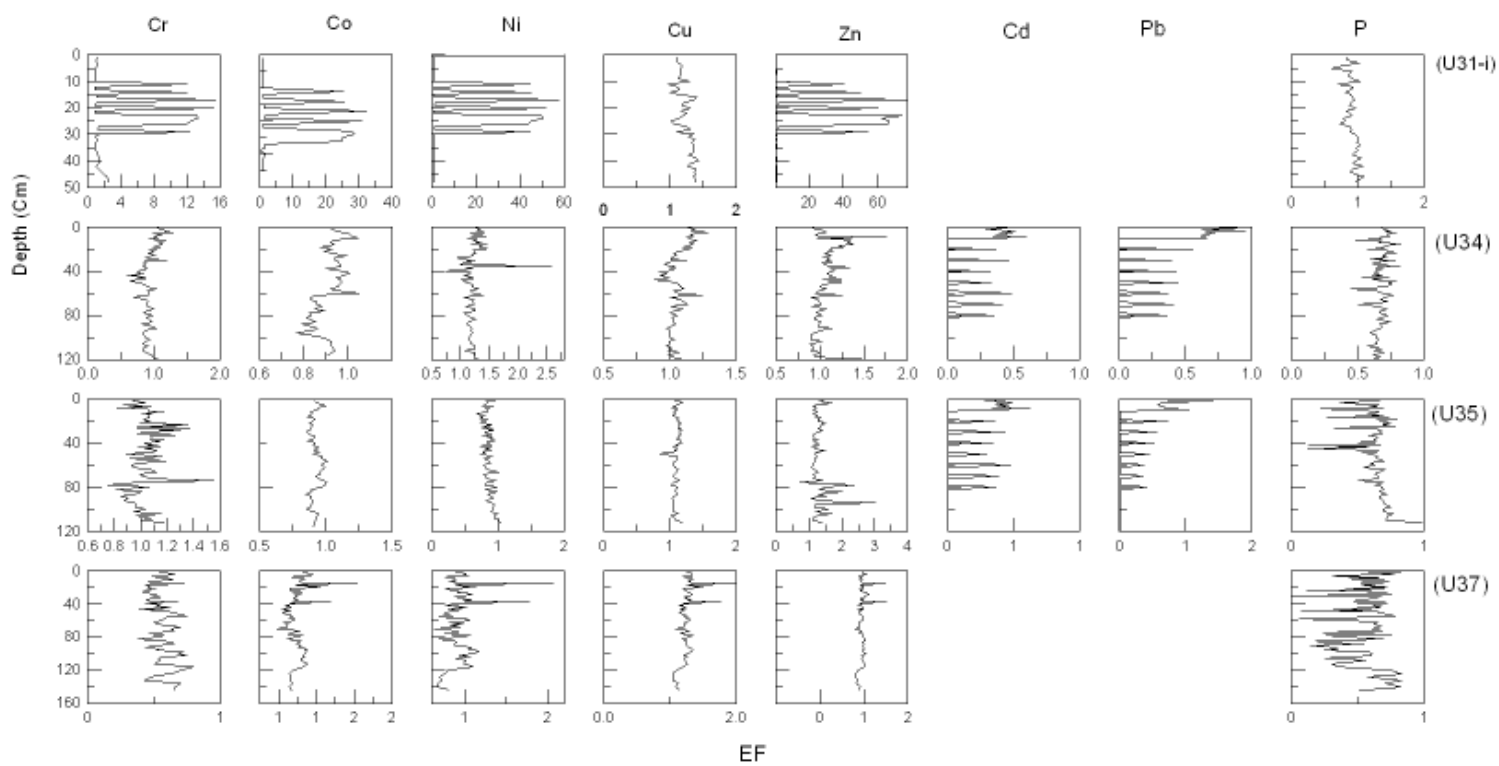


Figure 4.3.5 : Enrichment Factor of selected metals and P in sediment cores from Ulhas estuary

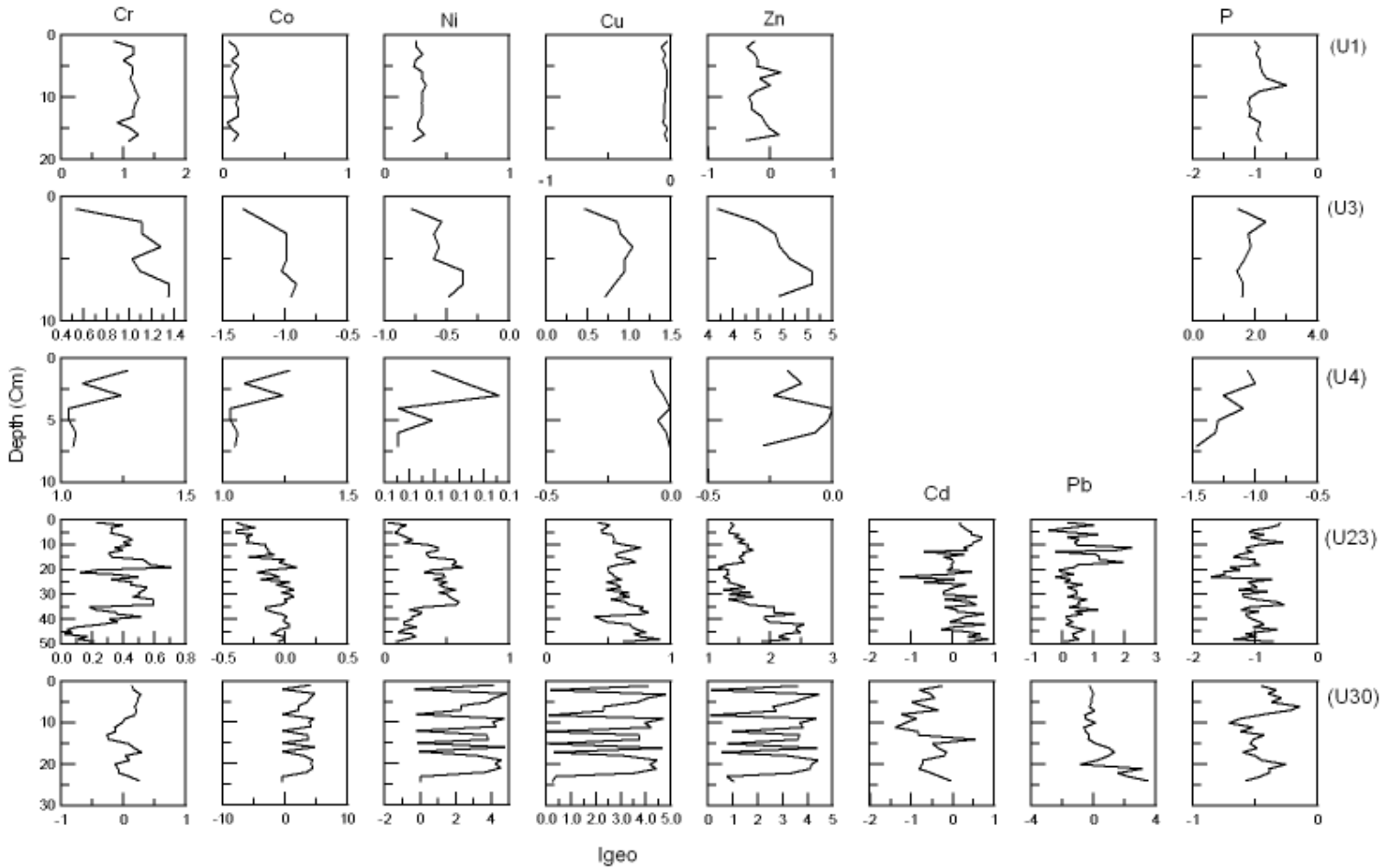


Figure 4.3.6 : Geoaccumulation Index of selected metals and P in sediment cores from Ulhas estuary

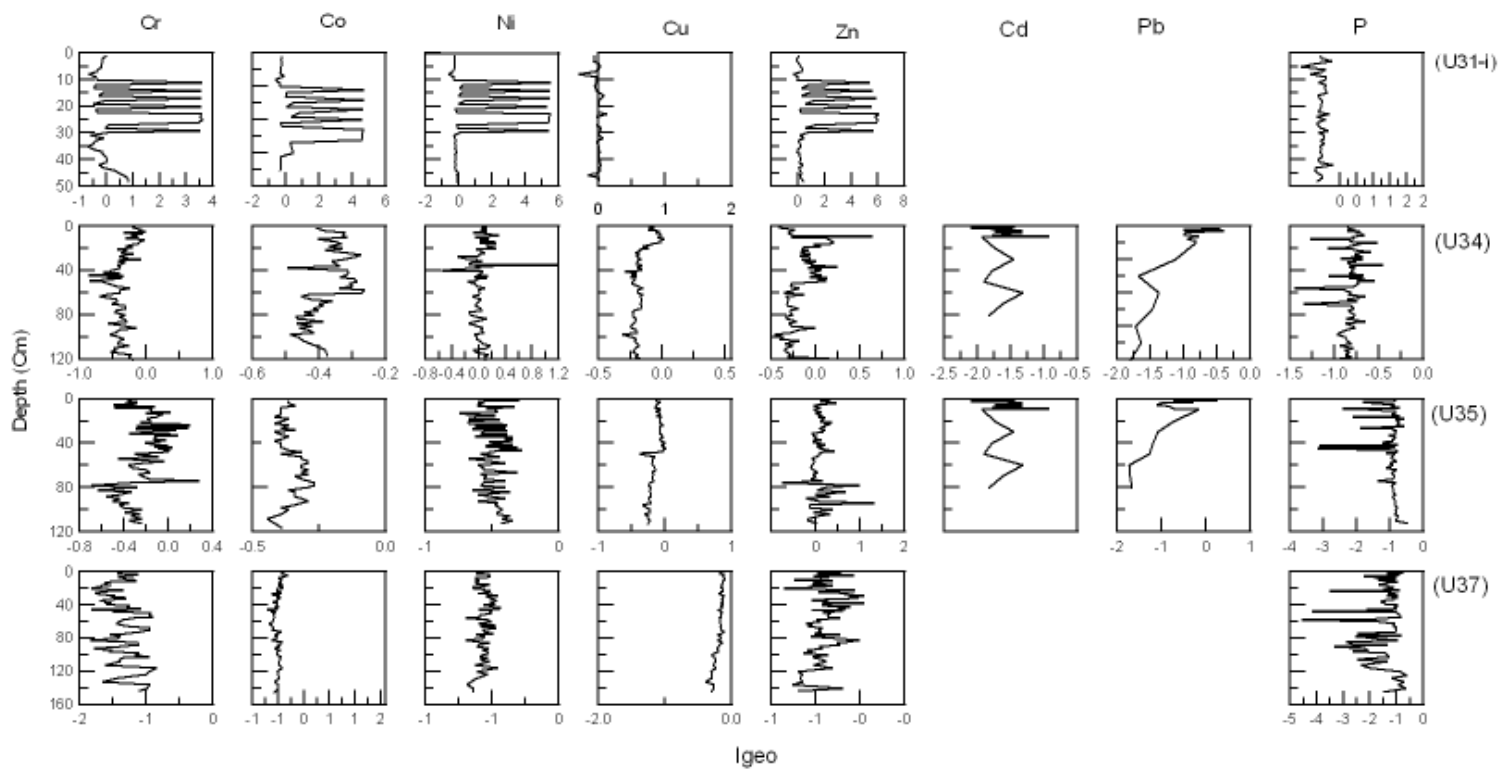


Figure 4.3.7 : Geoaccumulation Index of selected metals and P in sediment cores from Ulhas estuary

CHAPTER 5

METALS OFF NORTHWEST COAST OF INDIA

This chapter presents the investigations conducted along the coast between Porbandar in the north (Gujarat) and Ratnagiri (Maharashtra) in the south (Figure 2.1.1).

5.1 Study area

The study area essentially consists of the nearshore coastal belt of Gujarat and Maharashtra upto a distance roughly 25 km from the shoreline.

5.1.1 Coastal Gujarat

Gujarat has a coastline of 1663 km with associated continental shelf of 1.65×10^5 km². Four major, 5 medium, 25 minor, and 5 desert rivers annually add 7.1×10^{10} m³ runoff to the sea adjoining the state. There are 1 major, 11 intermediate and 28 minor ports, geographically dispersed across South Gujarat (13 ports), Saurashtra (23 ports) and Kachchh (4 ports) which collectively handled 6.5×10^7 t of cargo during 1997-98 (Desai, 1997).

Gujarat ranks second in the country after Maharashtra in industrial development and urbanization. The major industries consist of cement, chemicals, dyes and dye-intermediates, textiles, pulp and paper, rubber and plastics, dairy products, electronics, engineering goods, petroleum, natural gas and petrochemicals, food products, refineries, fertilisers, etc. The state cultivates 95,000 km² agricultural land producing a variety of

crops consuming around 6.0×10^6 t of fertilisers and 4300 t of pesticides, annually. The Saurashtra coast and the Gulf of Kachchh are rich in fishery resources as well as recruiting grounds for fisheries and account for more than 19 % in marine fish production of the national total (COF, 2005).

The hydro-meteorological conditions in the state change from arid to semi-arid to sub-humid to humid to very humid from the Kachchh District (Aridity index: 40) to the Valsad District (Aridity index: 10). The total mean annual rainfall within the coastal 20 km stretch is 2.168×10^{10} m³, which is 16.5% of the State's total of 13.1×10^{10} m³. The coastal zone is an area of extreme variation in temperature. It goes to a high of 47^o C during summer, inland of the two gulfs and a low at the freezing point in winter (Sen Gupta and Deshmukhe, 2000).

Semi-diurnal tide with large diurnal inequality and varying amplitude dominates the Gujarat coast. The mean high water spring of 3.5 m at Okha decreases to 2.6 m at Veraval but further down the coast steadily increases attaining 10.2 m at Bhavnagar. Along the South Gujarat coast, the mean high water spring of 8.8 m at Luhara Point decreases to 6.2 m at Daman and further to 5.4 at Umargam. Shallow depths, medium to high tidal amplitudes, moderately strong tidal currents with associated turbulence create a perennially homogenous one-layer water-mass all along the coast (Sen Gupta and Deshmukhe, 2000).

5.1.2 Coastal Maharashtra

The Maharashtra coast that stretches between Dahanu in the North and Terekhol in the South is about 560 km long and 30-50 km wide. The shoreline is indented by numerous West flowing river mouths, creeks, small bays, headlands, promontories and cliffs. Most of the coastal region is of Deccan Trap with an exception of pockets between Vengurla and Vijaydurg. There are about 18 prominent estuaries along the Maharashtra coast harbouring many mangrove floral and faunal species in varying densities. Of these Ulhas in the North is the biggest estuary.

A number of industrial areas established by the Maharashtra Industrial Development Corporation (MIDC) are located in the coastal belt and release their effluent in nearby water bodies (Zingde, 1989).

The climate of the coastal Maharashtra is cool and dry in winter with low intensity northeasterly winds from the land in November-February. The conditions are hot and humid in summer (March-May) followed by the rainy season (June-September). The Maharashtra coast receives average rainfall of about 3000 mm per annum and some of the wettest spots record more than 6,300 mm of precipitation. The winds are variable with higher wind speed upto 30 km/h in June-August as against 13-17 km/h during the remaining months of the year (Muraleedharan *et al.*, 2000).

The tidal amplitude is markedly lower than discussed earlier for the South Gujarat coast with the mean high water spring of 4.4 m at Mumbai decreasing to 2.7 m at Dabhol and further down to 1.8 m at Malvan. The coast shows relatively low annual net sediment transport (100,000 m³). Coasts near Malvan, Dabhol, Murud and Tarapur appear to be nodal drift points with equal volumes of transport in either direction annually (Chandramohan and Nayak, 1992).

The open shore water of Maharashtra, except off Mumbai, has good water quality though several inshore areas particularly Versova, Mahim and Thane Creeks and Ulhas, Amba, Kundalika and Vashisti Estuaries reveal deterioration in ecology to a varying degree due to the influx of anthropogenic discharges (Zingde *et al.*, 1979; Sabnis, 1984; NIO, 1996; NIO, 2000a; Zingde and Govindan, 2000).

5.2 Sampling locations

Grab sediment recovered from stations 1, 2 and 3 from transects off Porbandar Veraval, Diu, Pipavav-Jafarabad, Hazira, Daman, Tarapur, Bassein, Mumbai, Murud, Dabhol and Ratnagiri (Figures 5.2.1 to 5.2.3) were analysed for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P. These

sediments were studied during 1997 (February), 1998 (February), 2000 (January), 2001 (January), 2002 (January), 2003 (January), 2004 (January), 2004 (October), 2005 (April), 2005 (December), and 2006 (March). At each transect station 1 is near to the shoreline (3 – 5 km), station 2 at a distance of 12 – 15 km from the coast and station 3 at 22 - 25 km from the shore.

5.3 Surficial sediment

The physicochemical characteristics of sediments from the inner and outer shelf along the west coast of India have been investigated by several workers (Murty *et al.*, 1968; Rao *et al.*, 1974; 1976; 1978; Rao and Rajamanikam, 1976; Murty *et al.*, 1979; Paropkari, 1979; 1994; Wagle, 1979; Borole, 1982; 1988;). Much of these data pertain to the region westward of 20 m depth contour because the sampling was done on board deep-sea research vessels, which had depth limitations for navigation. Information on the sediment characteristics of the nearshore zone along the west coast is limited to site-specific studies (Murty *et al.*, 1973; 1978; Hashmi and Nair, 1976; Zingde and Desai, 1981; Borole, 1982; Patel *et al.*, 1985; Sharma *et al.*, 1994; Ram and Zingde, 2000; Ram *et al.*, 2003). The comprehensive information on variation of metals in the nearshore sediment over a large area however is largely lacking for the northwest coast of India.

The silt-clay fraction constitutes more than 95 % of the surface sediment at all the stations (Bapardekar, 2004). The sediment from the inner shelf between the Gulf of Kachchh and Quilon are characterized by low calcium carbonate (<25 %) unlike the sediments of the outer shelf, which contain high calcium carbonate (>75 %). This is attributed to the high rate of sedimentation of terrigenous influx on the inner shelf (Murty *et al.*, 1978; Chauhan *et al.*, 2006). Foraminiferans are significant carbonate contributors to the sediment and are distributed throughout the width of the shelf (Hashimi and Nair, 1976; Setty and Nigam, 1982). Three major rivers, namely the Indus, Narmada and Tapi, supply large amount of sediment to the western shelf. The Indus River has been estimated to

contribute 440 million t (Holeman, 1968), while the other two rivers together contributed 60 million t of SPM annually (Borole, 1982). Sediment deposition from the Indus is traced even in deep regions of the northwest continental shelf (Nair, 1984; Gupta and Hashimi, 1985). It is believed that the cross-shelf transport of sediment is insignificant on the western shelf, based on clay mineralogical studies (Ramaswamy and Nair, 1988) though there is considerable long-shore transport.

5.3.1 Distribution of major metals

a) Aluminium

The concentration of Al (Figure 5.3.1) decreases from 9.2 % at station P1, attains minimum at station H1 (3.3 %) and subsequently increases down the coast with the value of 10.1 % off Ratnagiri (Station R1). The profile of Al distribution at station 3 differs appreciably with respect to the one observed at station 1 with low concentration of the metal at station DU3 that increases southward attaining maximum (10.0 %) at station BY3. The overall concentration that falls in the range 3.3 – 10.8 % is more or less comparable with the values reported (Murty *et al.*, 1978) for the inner shelf sediment of the northwest coast of India. The high Al content of the nearshore and inner shelf sediment is probably associated with the fine-grained terrigenous material particularly clays which occur to the extent of 15.9 % in the shelf sediments of the West coast of India (Paropkari *et al.*, 1994). All clay minerals have Al in their crystal lattices. The clay minerals of the inner shelf South of the Gulf of Kachchh are dominated (Srivastava, 1970) by montmorillonite (50 – 70 %) followed by illite (0 – 20 %), chlorite (0 – 10 %) and kaolinite (0 – 10 %). Murty *et al.* (1978) have concluded that the Al content of the shelf sediment (northwest coast of India) is terrigenous in nature and its deposition was confined upto roughly 60 – 65 m water depth and lower concentrations associated with the relict sediments of the outer shelf was due to low percentage of terrigenous material in them.

The correlation between different constituents of sediment studied during the present investigation area are presented in Appendix-VII(a)

and Appendix-VII(b). When all the values are pulled (n=343) positive correlations at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Fe, Al:Ni, Al:Cu, Al:P, Fe:Cr, Fe:Ni, Fe:Cu, Fe:P, Mn:Cu, Cr:Ni, Cr:Cu, Cr:P, Ni:Cu, Ni:Zn, Ni:P, Cu:P, and Cd:P. When individual station are considered, the significant correlations (p=0.001) often differ [Appendix-VII(b)] from the relations emerging when all the values are pulled [Appendix-VII(c)]. Generally, Fe and Al seem to co-vary in the area with significant correlation (p<0.001) observed during the investigations in 1997, 1998, 2000, 2002 and 2005 (r=0.44-0.80).

b) Iron

Fe content of 5 – 7.5 % has been reported in the sediment of the inner shelf (water depth >20 m) of the northwest coast of India (Paropkari *et al.*, 1994). The present values for the coastal sediments agree well with these data and there seems to be no marked variation in the Fe content in the sediment with respect to that of the inner shelf (Figure 5.3.1). The overall trend indicates the concentration increasing southwards from Porbandar to Ratnagiri. The observed concentrations of Fe (3.3 – 10.2 %) except 13.8 % at Ratnagiri, compare favourably with the values reported (Paropkari *et al.*, 1994) for Deccan Traps (9.8 – 10.8 %) indicating that the Fe in the coastal sediment of the northwest coast of India is largely derived from the surrounding landmass. Based on the partition patterns of Fe in recent sediments of northwest continental shelf of India Rao *et al.* (1976) have concluded that (i) the major fraction of Fe in the sediments of the inner shelf was of terrestrial origin through the metal held in the lattice structure of the detrital minerals, (ii) lithogenous fraction contributed more than 90 % to total Fe in the shelf sediment, (iii) relatively higher concentration of Fe was associated with the nonlithogenous fraction in the fine-grained sediment of the inner shelf thereby indicating that the metal was being removed from the overlying water and fixed in sediments through other processes, and (iv) being a zone of intense tropical weathering, possibly Fe leached from rocks as well as their products of weathering such as regur and laterite were carried by rivers in the colloidal state to the sea and getting flocculated in the coastal region

leading to higher concentrations of Fe in the nonlithogenous fractions of the sediment.

5.3.2 Distribution of minor elements

c) Chromium

The concentration of Cr varies considerably and is in the range 56-244 µg/g in the nearshore zone. These levels are in the range observed for the catchment (Table 3.2.1). The average concentration of Cr seems to be uniform between Porbandar and Tarapur. Relative average high concentrations at stations BS1, BY1, BS2 and BY2 may be due to high anthropogenic loading from industries and urban centres around Bassein-Mumbai. Among trace metals, Cr burden in the surficial sediment seems to have increased with the passage of time at station BY1. At stations P2, P3, PJ2, H1, TP2, BS1, M3, DL1, DL2, DL3 and R1, the Cr concentration directly varies with that of Al with the correlation coefficient (r) of 0.86-1.00 ($p=0.001$). Cr-Al relationship is negative at station BS1 ($r=-0.96$, $p=0.001$). Excellent positive correlations also occur between Cr and Fe at stations V3, DI1, DL2 and DL3 ($r=0.77-1.00$; $p=0.001$). Cr-Fe relationship is negative at stations DU1, DN2 and TP2 ($r=0.79-0.90$; $p=0.001$).

d) Manganese

Unlike more or less uniform distribution of Al and Fe, in the sediments of the northwest coast of India, the concentration of Mn reveals a distinctive trend with concentrations increasing steadily southward upto about Bassein-Mumbai and then decreasing towards Ratnagiri. Such a trend is clearly seen in the profiles of all three transects. The concentration of Mn varies in the range 609-1528 µg/g in the nearshore zone (Figure 5.3.1). The variation of Mn at station 3 is in accordance with the trend reported for the inner shelf area of the northwest coast of India (Murty *et al.*, 1978) with low levels (500–750 µg/g) north of Dwarka and south of Ratnagiri, intermediate levels in segments Porbandar-Diu and Mumbai-Ratnagiri (750–1000 µg/g) and high concentrations (>1000 µg/g) between Diu and Mumbai (Murty *et al.*, 1978).

Occurrence of low concentration of Mn (<250 µg/g) in the sediments of the outer shelf suggests its terrigenous source with about 60 % of Mn associated with the lithogenous fraction of the sediments. Even within this fraction the major portion of the metal is associated with the clay minerals and a small percentage in the resistant detrital minerals (Murty *et al.*, 1973).

Mn varies directly with Al at stations P3, DU2, PJ2, PJ3, DN3 and BY3 ($r=0.75-0.95$; $p=0.001$). While, Mn:Al relationship is negative at station H1 ($r=-0.93$; $p=0.001$). Excellent positive correlations also occur between Mn and Fe at stations P2, DU2, and BS2 ($r=0.87-0.94$; $p=0.001$).

e) Cobalt

The concentration of Co varies in the range 17-88 µg/g in the sediment of the northwest coast of India (Figure 5.3.2) with the average concentration fairly uniform along the length. The concentration of Co is inversely related with that of Cu at stations P3, V2, V3, H1, H2, H3, TP2, BS1, BY1, and R3 ($r=0.-77$ to $0.-97$; $p=0.001$)

f) Nickel

The trend of variation of the concentration of Ni in the sediments (Figures 5.3.2) indicates a steady southerly increase. The observed concentrations of Ni (35-128 µg/g) compare favourably with the values reported (Paropkari *et al.*, 1994) for the shelf area of the west coast. Ni varies directly with Cu at stations P2, DU2, PJ1, H2 and TP2 ($r=0.78-0.93$; $p=0.001$). Its concentration is inversely related with that of Cu at stations BS1, BS2 and BS3 ($r=-0.84$ to -0.97 ; $p=0.001$). Excellent positive correlations occur between Ni and P at stations V2, V3, DU1, DU3, PJ1, H1, DN1 and BY2 ($r=0.81-1.00$; $p=0.001$).

g) Copper

Baseline concentration of Cu seems to be relatively low along the Gujarat coast and increases in the southerly direction. The present values of Cu (51-213 µg/g) agree well with the literature data (Paropkari *et al.*,

1994). Its concentration varied directly with Al and Fe during 1997, 1998 and October 2000 with significant correlation ($p < 0.001$). Positive correlations occur between Cu and P at stations P1, DU2, H2, BS2, BS3 and M1 ($r = 0.74-0.94$; $p = 0.001$).

h) Zinc

The average concentration of Zn is fairly uniform in the nearshore sediments of Gujarat and Maharashtra. The observed concentrations of Zn (63-237 $\mu\text{g/g}$) (Figure 5.3.3) compare favourably with the values reported by Paropkari *et al.* (1994) for the shelf area. Zn:Mn relationship is negative at stations TP2 and BS1 ($r = -0.94-1.00$; $p = 0.001$).

i) Cadmium

The Cd content of these sediments varies from 0.02-0.93 $\mu\text{g/g}$ (Figure 5.3.4) and the overall trend indicates no abnormalities in its distribution. Cd is known to be toxic in certain forms. As a result, materials which contain more than 0.6 $\mu\text{g/g}$ Cd in the solid phase are prohibited for marine disposal under the Canadian Ocean Dumping Control Act. Concentrations in coastal marine sediments worldwide usually fall below this level (Forstner, 1979a; Bloom and Crecelius, 1987). In the Ucluelet Inlet on the west coast of Vancouver Cd levels markedly exceed the 0.6 $\mu\text{g/g}$ concentration due to a natural phenomenon related to the unique sedimentary characteristics of the basin (Pedersen, 1989).

j) Lead

In general, the Pb concentration in the west coast sediments is relatively low and below 43 $\mu\text{g/g}$ (Figure 5.3.4). This is by a factor of 5 lower than the concentrations which have been analysed in marine sediments from other regions of the world, such as some areas of the Mediterranean Sea, (150-600 $\mu\text{g/g}$) (Palanques *et al.*, 1998), the North Sea (30-255 $\mu\text{g/g}$) and the Gulf of Thailand (23-180 $\mu\text{g/g}$). Yadav *et al.* (1994) have reported Pb content 40-64 $\mu\text{g/g}$ in the sediment of northwest coast of India.

k) Phosphorus

The distribution of P in the sediments of the northwest coast of India indicates a definite increase from north to south. At transect 1, the high concentration (1681 µg/g) at station DL1 decreases to 181 µg/g at station BS1 where it varies in the range 255 – 931 µg/g. Away from the coast (station 3), the P concentration follows a similar trend and increases steadily from station BS3 (938 µg/g) to station R3 (1996 µg/g). Paropkari *et al.* (1994) have reported P₂O₅ content of <0.25 % in the inner shelf sediment of the region between the mouth of the Indus and Murud that increases to 0.5 – 1 % in the zone between Murud and Karwar. Concentrations of P in the range 390 – 1370 µg/g have been reported for the surficial shelf sediment off Mumbai (Murty *et al.*, 1968).

5.3.3 Overall assessment

The overall trend of variation in concentrations of trace metals Cr, Co, Ni, Cu, Zn, Cd and Pb along the northwest coast of India indicates levels which can be explained based on the lithogenic component and there is no evidence for increase due to anthropogenic contributions.

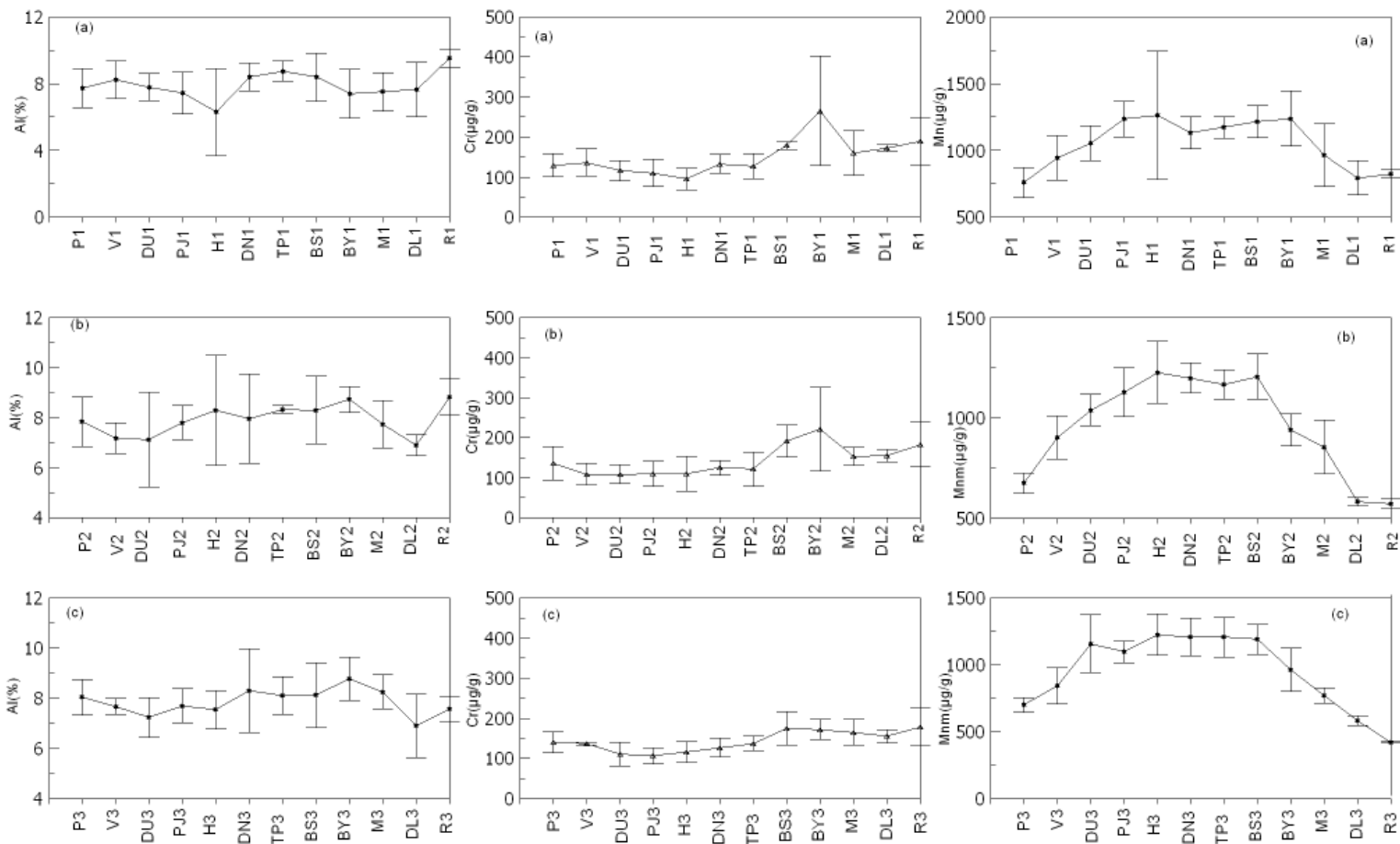


Figure 5.3.1: Average concentration of Al, Cr and Mn and their standard deviations in surface sediments of the north west coast of India: (a) near to the shore, (b) 12-15 km from the shore (c) 22-25 km from the shore during 1997-2003.

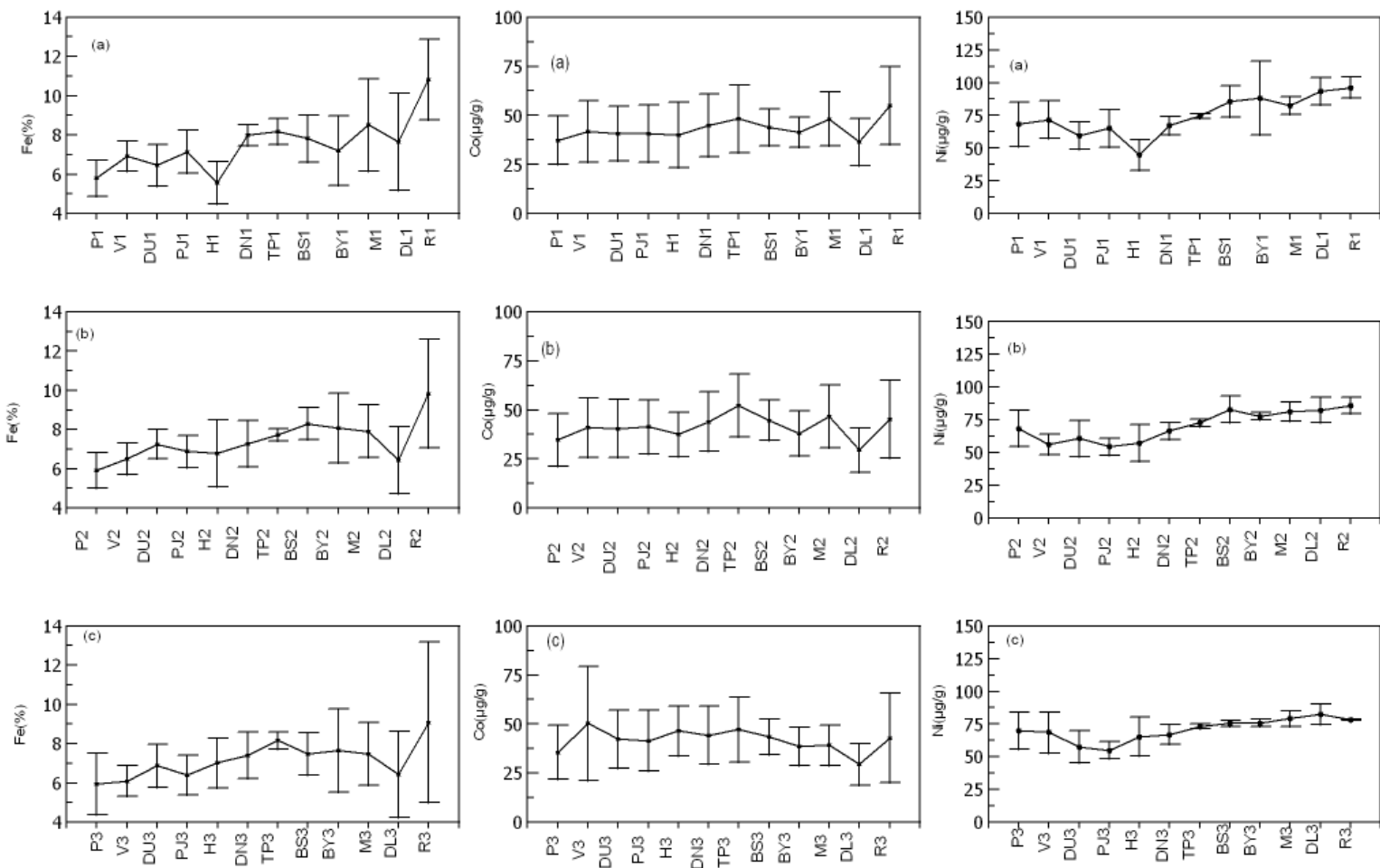


Figure 5.3.2: Average concentration of Fe, Co and Ni and their standard deviations in surface sediments of the north west coast of India: (a) near to the shore, (b) 12-15 km from the shore (c) 22-25 km from the shore during 1997-2003.

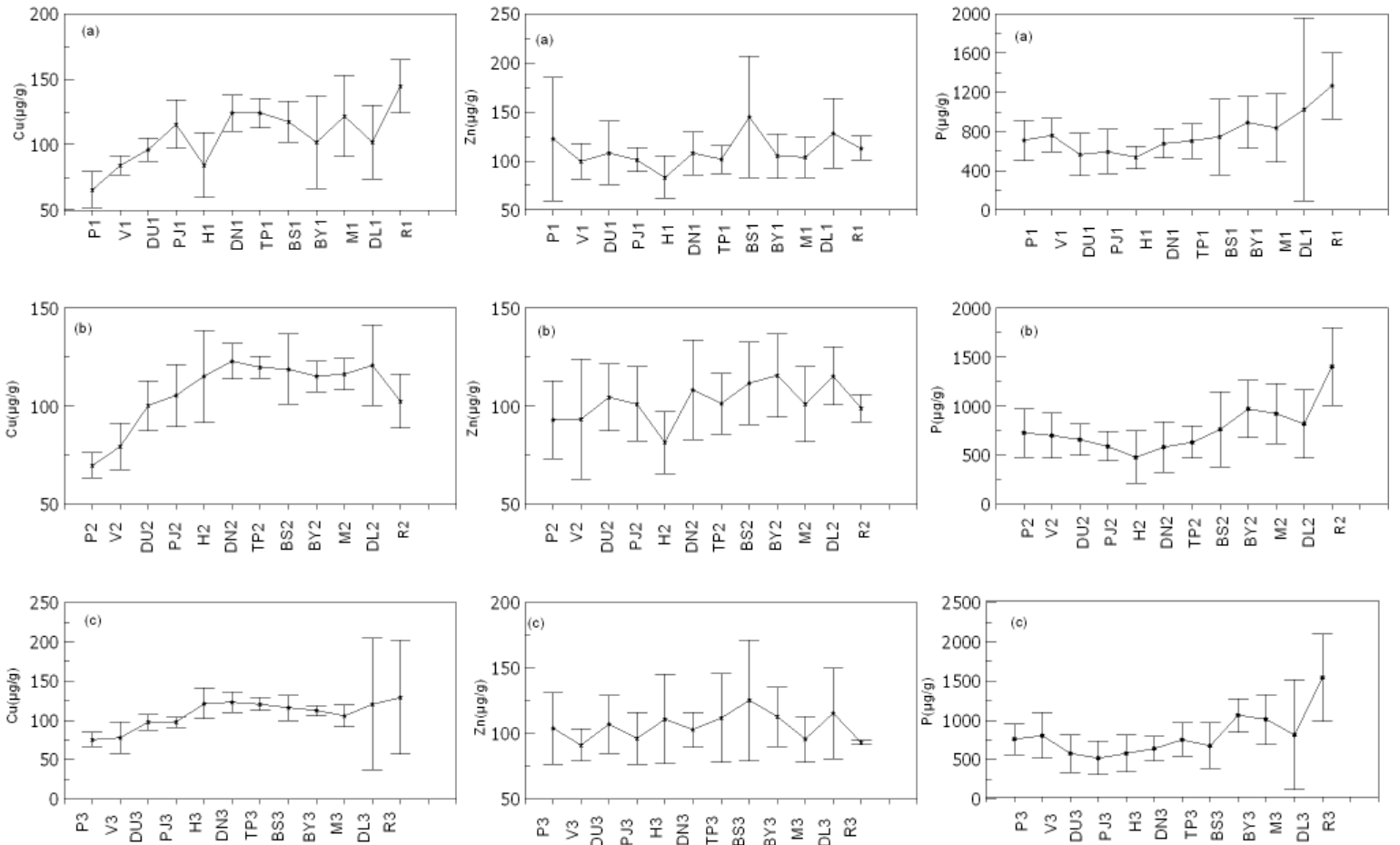


Figure 5.3.3: Average concentration of Cu, Zn and P and their standard deviations in surface sediments of the north west coast of India: (a) near to the shore, (b) 12-15 km from the shore (c) 22-25 km from the shore during 1997-2003.

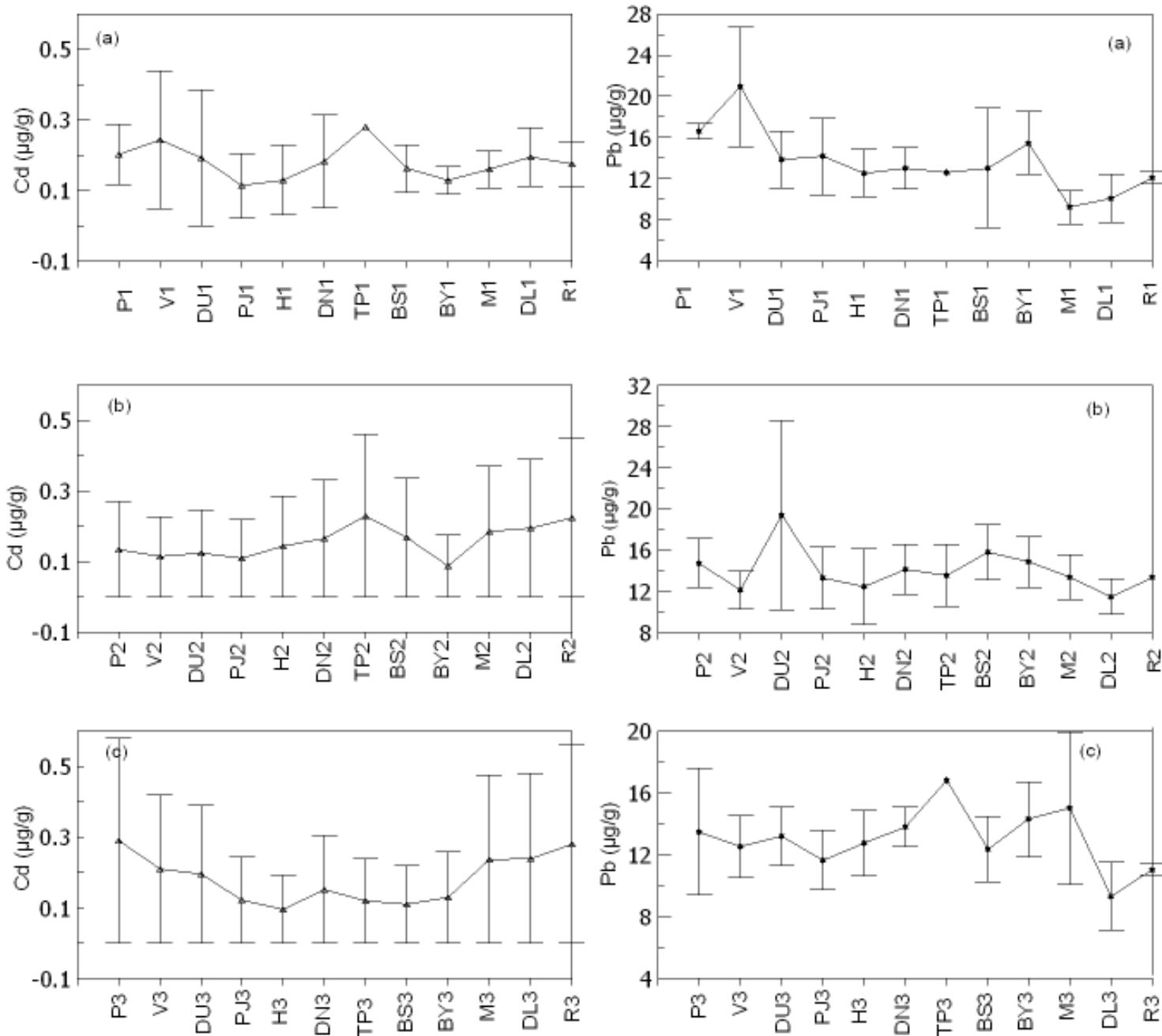


Figure 5.3.4: Average concentration of Cd and Pb and their standard deviations in surface sediments of the north west coast of India: (a) near to the shore, (b) 12-15 km from the shore (c) 22-25 km from the shore during 1997-2003.

CHAPTER 6

METALS IN GULF OF KACHCHH

6.1 Study area

The Gulf of Kachchh which is about 170 km long and 75 km wide occupies an area of 7500 km² (Figure 2.1.12). Though there are extensive fishing activities all along the coast the region, except for a few pockets such as Jamnagar, Sikka, Mithapur and Kandla, is underdeveloped. The maximum depth within the Gulf varies from 20 m at the head (Kandla-Navlakhi) to 60 m in the outer regions. The coastal configuration is very irregular with numerous islands, creeks, bays and pinnacles. The high tidal influx covers the low-lying areas of about 1500 km² comprising a network of creeks and alluvial marshy tidal flats in the interior region. The creek system consists of three main creeks Nakti, Kandla and Hansthal and the Little Gulf of Kachchh interconnecting through many other big and small creeks (NIO, 2000c). Based on the distribution maps of SPM and clays in the water column, it is deduced that a large segment of the Gulf is nourished by contributions from the Indus River (Chauhan *et al.*, 2005)

The tidal range in the Gulf increases dramatically from Okha to Navlakhi with the difference of 3.37 and 2.26 m during mean spring and mean neap tidal range respectively between the two sites. The phase lag between Okha and Kandla is 2 h to 2 h 25 min while between Okha and

Navlakhi it is 3 h to 3 h 20 min. Circulation in the Gulf is mainly controlled by tidal flows and bathymetry though wind effect also prevails to some extent. The maximum surface currents are moderate (0.7-1.2 m/s) but increase considerably (2.0-2.5 m/s) in the central portion of the Gulf (NIO, 2000b).

The concentrations of DO, BOD, nutrients, PHc and phenols in water are indicative of unpolluted coastal environment (Zingde and Desai, 1980; Zingde, 1993). The concentrations of PHc in sediment are also low though large quantities of petroleum crude and its products are off-loaded at Vadinar and Kandla respectively (Zingde, 1999b; Chouksey, 2002).

The marine flora is highly varied and includes sand dune vegetation, mangroves, algae, seagrasses, macrophytes and phytoplankton. Sheltered mud flats provide ideal sites for mangrove vegetation over an estimated area of about 1036 km². The marine fauna of the Gulf is rich, both in variety and abundance and includes zooplankton, sponges, sea anemones, molluscan fauna, polychaete worms, corals, echinoderm fauna, fishes, birds, etc. The corals are under extreme stress leading to vast areas of dead reefs, due to increased suspended solids as a result of mangrove deforestation and mining of coralline sand in the past (Pillai and Patel, 1988). Because of its high biogeographical importance and rich flora and fauna, several areas along the southern Gulf are notified under the Marine National Park (MNP) (16289 ha) and the Marine Sanctuary (MS) (45798 ha).

Compared to the land area available in the vicinity of the Gulf, the industrial development (except for traditional salt works) is sparse mainly because of lack of adequate infrastructure and scarcity of fresh water. Until early nineties, the development along the Gulf was limited to salt works and isolated industrial pockets at Mithapur, Vadinar, Sikka and Kandla apart from major port related activities at Okha, Navlakhi and Kandla. However, setting-up of a grass-root refinery with a refining capacity of 2.7×10^7 t/y at Sikka and another one under construction at

Vadinar, establishment of additional Single Buoy Moorings (SBMs) to evacuate crude oil imported through tankers including Very Large Crude Carriers (VLCCs), increase in handling of petroleum products at ports etc, have enhanced the risk of accidental spillage of petroleum that has potential to adversely affect the Gulf ecology. These complexes would use large volumes of seawater for desalination and for cooling purposes and release the high salinity (55–75 psu) and high temperature (4° C above ambient) return seawater to the Gulf (Zingde and Anand, 1994).

A chemical industry that manufactures soda ash, sodium bicarbonate, caustic soda, cement, bromine etc established at Mithapur in 1950s releases 28000 m³/d of high density effluent containing high concentration of SPM of inorganic origin through an open channel to the Positra Bay (NIO, 2000b). A fertiliser complex located at Sikka has a captive jetty on the Sikka Creek, which is largely utilised to unload phosphoric acid and liquid ammonia brought-in by deep-sea ships. A coal-based Thermal Power Station (TPS) situated nearby the fertiliser complex draws the Gulf water through an open channel to meet the cooling requirements. The warm return seawater containing fly ash is fed to a settling tank on the intertidal area within the MNP and the supernatant flow is released to the Sikka Creek. A cement factory also located at Sikka dredged the coralline sand from the Gulf as raw material in the past and has been responsible for severe destruction of coral reefs, particularly between Salaya and Bedi (Zingde and Anand, 1994).

Industrial developments along the northern coast of the Gulf are largely around the Kandla and Adani Ports. Apart from a number of fuel and chemical storages in and around the port premises, there is a fertiliser plant manufacturing DAP (Diammonium phosphate) and NPK for which phosphoric acid and liquid ammonia are imported via the nearby Kandla Port. In addition, there are several small-scale industries in the free trade zone near Gandhidham. A cement plant has been constructed recently near Jakhav, which uses locally available deposits of limestone. A lignite-based TPS is operational at Panandhro on the eastern bank of

the Kori Creek, which utilises lignite from mines in the vicinity. Another TPS nearby uses water from the Kori Creek for cooling purposes and also for desalination. The return effluent that contains the overflow from the ash pond is released back to the creek.

The surface sediment distribution map of the Gulf indicates that (i) the bed material of the Kandla Creek comprises of gravel, shelly sand and silty clay with shells and pieces of rock, (ii) the Sanu, Sara and Phang Creeks are carpeted by olive grey soft clay and silty clay with shells and mud stone in patches, (iii) the Little Gulf, the inner Gulf and the Chah Creek are covered by olive grey soft clay and silt, (iv) the Hansthal Creek comprises of olive grey clay on the flanks while the axial part is made up of sand with shells and shelly limestone, (v) the mouth of the Gulf is marked by extensive occurrences of calcareous sandstone rocks, algal limestone, aragonite cemented sand-stone and dead corals in the central part, while, sediments are confined to the margins, and (vi) the remainder of the Gulf consists of silt and clay with patches of fine sand (Hashimi *et al.*, 1978).

No information is available on the distribution of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in the sediments of the Gulf. Hence, sediment from selected areas in the Gulf prone to anthropogenic influence were analysed for their Al, Cr, Mn, Fe, Co, Ni, Cu Zn Cd, Pb and P content.

6.2 Sampling locations

With the functioning of refineries and modern ports as well as improvements in infrastructural facilities, there will be encouragement for establishing ancillary units and downstream industries. Many of these developments will be around Jamnagar and Vadinar along the southern coast and at Mundra on the northern coast. Hence, these sites were intensively studied at locations marked in Figures 2.1.13 (b) and 2.1.15 (a).

The sampling along the southern shore was conducted during March 1999 (Premonsoon), November 1999, December 2004 (Postmonsoon) at Positra Bay [Figure 2.1.15 (b)]. The sediment cores were collected from locations OG, OE, OF, OD1, OD2, OD3 and OC3 in March 1999 and November 1999, while, a single core was retrieved from Vadinar (VN16) during January 2000. Surface sediments were collected at Sikka, Vadinar, and Bedi during 2000-2007. The northern shore of the Gulf was sampled during 1996-2007 at Kandla, Mundra and Kori Creek.

6.2.1 Positra Bay

The natural sediment of the Intertidal area of the Positra bay has variable texture but generally composed of fine sand mixed with silt and clay. The subtidal sediment is highly heterogeneous and varies from very coarse sand and calcareous debris to fine silt and clay. The available information on stratigraphy indicates that the strata below the thin surficial layer of sediment are in general of limestone layer of thickness that varies from about 3 to more than 8 m.

The Bay is the recipient of 28000 m³/d of high density effluent from a chemical industry at Mithapur. The effluent has high concentration of SPM rich in carbonates and is released through an open channel to the Positra Bay. Much of the SPM settles on the intertidal area severely deteriorating the ecological quality of roughly 10 km² of the intertidal area around the effluent channel (Zingde, 1999b; NIO, 2000b). The aim of the present study was to identify changes if any in the metal profiles of the intertidal sediment due to settling SPM. As the SPM was rich in carbonates, this could be an indicator of SPM accumulation in the Bay.

6.2.2 CaCO₃

The Intertidal area around the effluent channel has thick deposits of effluent associated solids. The thickness of these deposits is estimated to be about 2 m in the vicinity of the channel and decreases to a few centimeters further to the east. To ascertain the extent of contamination, the surficial sediment and selected cores from the Intertidal locations

marked in Figure 2.1.15 (b) were analysed for CaCO₃ content. The results for the surficial sediment are given in the Table below while its depth distribution is illustrated in Figures 6.2.1 and 6.2.2.

Station	CaCO ₃ (%)			
	March 1999		November 1999	
	Content	Excess	Content	Excess
OA	32	20	43	31
OB	20	8	69	57
OC	56	44	81	69
OD	50	38	79	47
OE	55	43	-	-
OF	59	47	-	-
OG	88	76	-	-
OI	4	-	37	25
OJ	38	26	75	33

The biogenic contribution of CaCO₃ to the sediment of the Positra Bay is expected to be high in this bio-rich environment. This contribution is to be assessed to estimate excess CaCO₃ that would result from the SPM associated with the effluent. The background concentration of CaCO₃ was estimated from the depth profiles of the cores.

It is evident from Figure 6.2.2 that concentration of CaCO₃ though variable, is uniformly high in cores (OD1, OD2, OD3) obtained from the area of effluent release indicating that the solids associated with the effluent are present upto the bottom of the core. The cores OE and OG retrieved from the area away from the effluent channel clearly indicate a typical trend of low concentrations in the subsurface sections of these cores. Thus for instance the concentration of CaCO₃ in the bottom section of the core OE is 1.7 % that gradually increases to 70.6 % at the surface. These concentrations are 12.8 and 59.2 % respectively in core OG. The concentration in the bottom section of these cores can therefore be taken as the natural background in the sediment of the Positra Bay in the absence of contribution by the effluent associated SPM. An average concentration of 12 % is used as background in calculating the excess in the above table.

The surficial sediment from stations OD1, OD2 and OD3 which presumably contains solids settled from the effluent has CaCO_3 content of 34.8-54.1 % which agrees well with the content of 30 to 40 % of CaCO_3 in unwashed solids of waste from the industry (NIO, 2000b). However, the levels of CaCO_3 increase with distance to the east of the effluent channel with stations OE, OF and OG having CaCO_3 content of 43, 47 and 76 % respectively. East of station OF, the concentration decreases and is 26 % at station OJ. From these trends it appears that the effluent associated SPM is enriched with CaCO_3 as it is advected by the tidal currents. This is possibly because other constituents of the effluent associated SPM such as Fe_2O_3 , Al_2O_3 and SiO_2 which together constitute about 20-25 % of the solids, settle faster and hence removed from the suspension. Moreover the SPM in the effluent is also associated with CaCl_2 and NaCl upto the extent of 23 % (NIO, 2003) which would be quickly removed by dissolution as soon as SPM enter seawater.

The depth profiles of CaCO_3 distribution illustrated in Figure 6.2.2 indicate high concentration of CaCO_3 throughout the length upto which the core could be collected, as expected. The core from station OC3 which is to the west of the effluent channel reveals an average enrichment by about 20 % upto the depth of 30 cm below which the concentration falls close to the expected baseline (12 %). The cores obtained from the east of the channel OG and OE reveal considerable enrichment in the top 20-30 cm, with the excess CaCO_3 often exceeding 60 %. Hence, the Intertidal sediment atleast upto 5 km from the effluent channel is contaminated upto a depth of 20-30 cm with effluent associated SPM.

The concentration of CaCO_3 in the subtidal sediment is variable as evident from the Table 6.2.1. The station O1 which is in vicinity of the effluent channel sustains high concentration (42.9%) of CaCO_3 . Low concentrations of CaCO_3 at stations O2 (12.5%), O3 (11.3%) and O4 (19.1%) suggests minor transport of effluent associated SPM across the Bay towards Bet Shankhodhar. Station O5 which is in the flow path of the

ebbing water has high CaCO_3 (43.7%) while station O7 which is also in the path of the ebb flow but further away from station O6, has low levels of CaCO_3 (17.5%). It therefore appears that effluent associated SPM is confined to the area between station O2 and O6, and the subtidal area of the Bay is by and large free from the effluent associated SPM.

6.2.3 Metals

The CaCO_3 profiles (Figure 6.2.2) in cores OG and OE indicate incremental build-up of CaCO_3 over the years. Hence, these cores were analyzed for the contents of different metal to investigate the influence of CaCO_3 addition on their profiles. A core obtained from Vadinar (VN16) a location about 50 km to the east and free from the influence of the effluent released in the Positra Bay is considered for comparison. The concentrations of most metals are relatively low as compared to their respective concentration in core VN16 due to dilution by CaCO_3 . Thus, the concentration of Al which is more than 6 % in core VN16 is reduced to 1.8-3.6 % and 1.9-4.0 % respectively in cores OG and OE with the trend of concentrations decreasing with increase in the concentration of CaCO_3 . The concentration of Al (5.8 %) in the bottom section of the longer core OF probably represents the baseline concentration expected for the Positra Bay. The trend of concentration of Al increasing with depth is clearly evident in this core. Fe and Al seem to co-vary in the area with significant correlations in core OF ($r=0.94$; $P<0.001$). Excellent positive correlations occur between Cr and Fe in core OF ($r=0.90$; $p<0.001$). Cr:Fe relationship is negative in core VN16 ($r=-0.4$; $p>0.001$). Mn varies directly with Al ($r=0.82$; $p<0.001$), Cr ($r=0.88$; $p<0.001$), Fe ($r=0.85$; $p<0.001$), Co ($r=0.58$; $p>0.001$), Ni ($r=0.90$; $p<0.001$) and Zn ($r=0.59$; $p>0.001$) in core OF. The depth distribution profiles of Co in core OG and OE are reverse to those of Al with which it appears to be inversely correlated [Al:Co ($r=-0.77$; $p<0.001$); ($r=-0.75$; $p<0.001$)]. Its concentration however varies directly with that of Fe ($r=0.64$; $p>0.001$) and Cu ($r=0.91$; $p>0.001$) in core OG.

The Table 6.2.1 reveals wide variations in the concentrations of metals in the surface sediments. These variations are in part due to widely varying Al content (0.8-4.3 %). Thus, the concentrations of many metals are higher in the intertidal sediment because of relatively high Al levels (1.0-3.8 %). Comparison of these levels with those at station O7 unaffected by wastewater release, reveals that there is no gross contamination of sediment of Positra Bay by trace metals. The subtidal and intertidal sediments of November 1999 set indicate excellent correlation between Al and Cr ($r=0.99$; $p=>0.001$ and $r=0.88$; $P=>0.001$) respectively, while the other sets do not indicate any such relationship [Appendix -Viii(f)]. Fe and Al seem to co-vary in the area with significant correlations in intertidal sediment during November 1999 ($r=0.88$; $p=<0.001$). Excellent positive correlations also occur between Cr and Al in intertidal sediment during March 1999 and November 1999 ($r=0.76$; $p=>0,001$ and $r= 0.88$; $p= >0.001$). Cr:Fe relationship is also positive during November 1999 in subtidal and intertidal sediments ($r=0.93$; $p=>0.001$ and $r=0.91$; $p= >0.001$) respectively. CO_3^- varies inversely with Al during March 1999 ($r=-0.93$; $p= <0.001$). Mn varies directly with Al ($r=0.88$; $p= <0.001$), Cr ($r=0.84$; $p= >0.001$), and Fe ($r=0.91$; $p= >0.001$). The pairs Cr:Ni ($r=0.94$; $p= >0.001$), Cr:Cu ($r=0.91$; $p= <0.001$) and Cr:Zn ($r=0.92$; $p= <0.001$) also indicate excellent positive relation in the Intertidal sediment collected during November 1999. Direct variation of Co with Zn ($r=0.58-0.69$; $p=>0.001$) is evident during March 1999, for subtidal and intertidal sediment of Positra Bay. The concentration of Co in the subtidal sediment during November 1999 varies with Cu ($r=0.85$; $p=>0,001$) and P ($r=0.98$; $p=<0.001$). Cu also varies directly with Zn ($r=0.96$; $p=<0.001$) in the intertidal sediment collected during March 1999 while it varies with P ($r=0.87$; $p= <0.001$) in subtidal sediment during December 2004. Cd and Pb have no significant relation with other metals. When all the values are pulled ($n=102$) positive correlations at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Mn, Al:Ni, Al:Zn, Al:Cd, Al:Pb, Cr:Mn, Cr:Fe, Cr:Ni, Cr:Zn, Cr:Pb, Mn:Fe, Mn:Ni, Mn:Zn, Mn:Cd, Mn:Pb, Fe:Ni, Fe:Cu, Fe:Zn, Fe:Pb, Ni:Cu, Ni:Zn, Ni:Pb, Cu:Zn, Cu:Pb, and Cd:Pb [Appendix -Viii(f)].

6.3 Sikka-Vadinar

As discussed in Section 5.1 the Sikka region is relatively industrialised and with the setting-up of a refinery at Moti Khavdi, the developmental activities have accelerated in recent years. The water quality of the Gulf off Sikka however is comparable to that off Bedi and there is no gross change due to industrial activities (NIO, 2004). The texture of the sediment off Sikka-Jamnagar is broadly similar to that off Bedi with low Al (4.8-5.8 %) and Fe (1.9-4.7 %) contents (Zingde, 1999b).

The concentrations (Table 6.2.2) of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P is consistently low (1.4-7.0 %, 27-170 µg/g, 284-1218, 1.3-7.4 %, ND-26 µg/g, ND-74 µg/g, 5-145 µg/g, ND-119 µg/g, 0.21-1.26 µg/g, 5.7-21.0 µg/g and 414-942 µg/g respectively) off Sikka in the SBM area (stations SK9 to SK13), along the oil pipelines (stations SK5 to SK8), around the trestle (stations SK2 to SK4) and the effluent release site of the refinery (SK1). When all the values (n=52) are pulled, positive correlations at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Mn, Al:Fe, Al:Co, Al:Ni, Al:Cu, Al:Zn, Al:P, Cr:Fe, Cr:Co, Cr:Ni, Cr:Cu, Cr:Zn, Mn:P, Fe:Co, Fe:Ni, Fe:Cu, Fe:Zn, Fe:P, Co:Ni, Co:Cu, Co:Zn, Ni:Cu, Ni:Zn, Ni:P and Cu:Zn [Appendix-viii(g)].

The concentrations (Table 6.2.3) of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P are also low (0.1-11.0 %, 5-165 µg/g, 48-1359 µg/g, 0.1-8.4 %, 2-51 µg/g, 1-108 µg/g, 4-66 µg/g, ND-507 µg/g, 0.01-0.82 µg/g, 8.8-62.4 µg/g and 51-1255 µg/g respectively) in subtidal sediment off Vadinar including the areas (stations VN 7 and VN9) in the Pathfinder Creek (stations VN6, and VN8) where petroleum products are loaded. When all the values are pulled (n=145) positive correlations (Table 6.2.4) at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Mn, Al:Fe, Al:Co, Al:Ni, Al:Cu, Al:Zn, Al:P, Cr:Fe, Cr:Co, Cr:Ni, Cr:Cu, Cr:Zn, Mn:P, Fe:Co, Fe:Ni, Fe:Cu, Fe:Zn, Fe:P, Co:Ni, Co:Cu, Co:Zn, Ni:Cu, Ni:Zn, Ni:P and Cu:Zn [Appendix-viii(h)].

Number of times the positive correlation coefficients ($p=0.001$) for individual pairs occurring three times or more at the Vadinar site sampled seven times are as follows:

pair	Number	pair	Number
Subtidal			
Al:Cr	4	Mn:Fe	4
Al:Co	3	Fe:Co	5
Al:Ni	4	Fe:Ni	3
Cr:Mn	3	Co:Ni	3
Cr:Fe	4	Co:Cu	3
Cr:Co	4	Co:Zn	3
Cr:Ni	3	Ni:Cu	4
Cr:Cu	4	-	-
Intertidal			
Al:Cr	4	Mn:Fe	3
Al:Mn	3	Mn:Co	3
Al:Fe	3	Mn:Cu	4
Al:Co	4	Fe:Co	3
Al:Ni	3	Fe:Cu	4
Al:Cu	5	Fe:Zn	3
Cr:Mn	3	Co:Ni	3
Cr:Fe	3	Co:Cu	4
Cr:Co	3	Co:Zn	3
Cr:Ni	4	Ni:Cu	3
Cr:Cu	4	-	-

Thus, the significant positive correlations occurring at 50 % or more of the sites sampled at Vadinar indicate their preferential association with Al.

In core VN16 the Al content varies widely (5.8-9.0%) ((Appendix-VIII (d))). The Al profile however indicates a systematic decrease in the metal content from 9.0 % at the surface to 6.0 % at the bottom probably indicating that settlement of clay in the area might have increased with time. The concentration of Fe in this core does not vary appreciably throughout the length and averages at 5.3 %. Fe and Al inversely covary ($r=-0.4$; $p=>0.001$). Cr concentration directly varies with that of Al ($r=0.50$; $p=>0.001$), Co ($r=0.60$; $p=<0.001$), Ni ($r=0.60$; $p=>0.001$) and Cu ($r=0.50$; $p=<0.001$) but varies inversely with that of Mn ($r=-0.40$; $p=>0.001$), Fe ($r=-$

0.40; $p > 0.001$) and P ($r = 0.40$; $p > 0.001$). The concentration of Mn is inversely related to that of Al ($r = -0.4$; $p > 0.001$). The concentration of Co is comparable throughout the core length and varies directly with that of Al ($r = 0.4$; $p > 0.001$), Ni ($r = 0.7$; $p < 0.001$) and Cu ($r = 0.8$; $p < 0.001$). The concentration of Ni is in the range 57-86 $\mu\text{g/g}$ and varies directly with that of Al ($r = 0.6$; $p < 0.001$) and Cu ($r = 0.6$; $p < 0.001$). The concentration of Cu varies directly with Cr ($r = 0.5$; $p < 0.001$) and Co ($r = 0.8$; $p < 0.001$). Zn concentration falls in the range 105-197 $\mu\text{g/g}$. The concentration of P varies over a wide range of 230-1094 $\mu\text{g/g}$ and varies inversely with that of Cr ($r = -0.4$; $p > 0.001$) [Appendix-VIII (e)].

6.4 Bedi

The Bedi area is free from gross anthropogenic interventions except for the minor Bedi Bunder located in the Hadder Creek. Typically the salinities in the Gulf off Bedi are high (37.6-38.4 psu), waters are clear with low SPM (17-26 mg/l), DO is high (3.2-5.6 ml/l) and micronutrients in ranges expected for the Gulf. The sediment is mainly silty sand/clay with low content of Al (2.8-6.6 %) and Fe (2.0-5.2 %) (Zingde, 1999b).

The Al content in surface sediment during pre-monsoon (February-March 1997) and post-monsoon (November 1997) from Bedi varies in the range (3.1-7.5 %) and (2.9-5.9 %) (Table 6.2.4). Fe and Al co-vary with significant correlations in pre-monsoon ($r = 0.94$; $p < 0.001$) and post-monsoon ($r = 0.87$; $p < 0.001$). Excellent positive correlation also occurs between Cr and Fe in pre- ($r = 0.84$; $p > 0.001$) and post-monsoon ($r = 0.85$; $p < 0.001$). Its relationship with Ni ($r = 0.76$; $p > 0.001$) and Cu ($r = 0.88$; $p < 0.001$) in pre-monsoon and with Co ($r = 0.90$; $p < 0.001$), Ni ($r = 0.85$; $p < 0.001$) and Cu ($r = 0.84$; $p > 0.001$) in post-monsoon are significant [Appendix-VIII (i)].

The Mn concentration (490-858 $\mu\text{g/g}$) does not indicate any relationship with other metals during pre-monsoon. In the post-monsoon Mn linearly varies with Fe ($r = 0.87$; $p < 0.001$), Co ($r = 0.88$; $p < 0.001$), Ni ($r = 0.84$; $p > 0.001$) and Cu ($r = 0.93$; $p < 0.001$).

The concentration of Co directly varies with that of Fe ($r=0.97$; $p<0.001$), Ni ($r=0.95$; $p<0.001$) and Cu ($r=0.98$; $p<0.001$) during post-monsoon while such a relation is absent in pre-monsoon season. Direct variation of Ni with Al ($r=0.89$; $p<0.001$), Cu ($r=0.95$; $p<0.001$), and Zn ($r=0.75$; $p>0.001$) is seen in pre-monsoon while in post-monsoon Ni varies with Al ($r=0.75$; $p>0.001$) and Cu ($r=0.92$; $p<0.001$).

Copper concentration which is in the range (16-72 $\mu\text{g/g}$) co-varies with that of Al ($r=0.87$; $p<0.001$), Cr ($r=0.88$; $p<0.001$) and Ni ($r=0.95$; $p<0.001$) in pre-monsoon season. While, its relationship with Cr ($r=0.84$; $p<0.001$), Mn ($r=0.93$; $p<0.001$), Fe ($r=0.95$; $p<0.001$), Co ($r=0.98$; $p<0.001$) and Ni ($r=0.92$; $p<0.001$) is significant in post-monsoon season [Appendix-VIII (i)].

6.5 Kandla Creek

Kandla Port is operational for more than 40 year, however little published information is available on the impact of the port operations on ecology of the Kandla Creek. The outer creek area is periodically dredged to maintain navigation depth for deep-sea ships (Zingde, 1999b). The creek represents a highly dynamic marine area due to unusually high tides and fairly strong currents. Being a tributary to the inner Gulf and partially fed by the Little Gulf of Kachchh, the salinities are high and exceed 40 psu particularly in the inner segments. The waters are turbid and muddy with high SPM that averages at 128 mg/l. The levels of DO, BOD and micronutrients in water fall in the range observed for the inner Gulf. The sediment is largely sandy silt with low percentage of Al (ND-7.9 %) and Fe (ND-6.2 %). The concentrations of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P (Table 6.2.5) in sediment of the Kandla Creek (stations KL1 to KL7) closely compare with the concentrations at stations KL8 and KL9 which represents the inner Gulf.

When all the values are pulled (n=27) positive correlations at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Fe, Al:Co, Al:Ni, Al:Cu, Al:Zn, Cr:Mn, Cr:Fe, Cr:Ni, Cr:Zn, Mn:Co, Mn:Ni, Fe:Co, Fe:Ni, Fe:Cu, Fe:Zn, Fe:Pb, Co:Ni, Co:Cu, Co:Pb, Ni:Cu, Ni:Zn, Ni:Pb, Cu:Zn, Cu:Pb, Cu:P, and Zn:Pb [Appendix-VIII (j)].

6.6 Mundra

The coastal area of Mundra [Figure 2.1.13 (b)] is underdeveloped and sparsely populated and except for the ongoing development of the Mundra Port no other major industrial activity exists in the coastal belt. The core port area is confined to the open-coast (station MR3) and the Navinal Creek (stations MR1 to MR5) while the nearby Kotdi Creek (station MR6) is free from any developmental activity. The sediment texture along the openshore of the Navinal Island is generally sandy while the intertidal areas of the creeks are largely sandy of clayey silt with occasional sand patches. The shallow cores retrieved from the sea-face of the Mundra Port indicate the occurrence of greyish brown, dense nonplastic sandy silt upto the depth of 30 m. The surface 1.5 m layer typically contains 70-90% sand with silt and clay in minor proportions (NIO, 2000c).

The local sediment regime at Mundra is highly dynamic under the influence of strong tidal currents and wave action, particularly during monsoon. The littoral sediment transport is high with the movement induced by breaking waves (dominant cause of sediment transport) along the upper intertidal area. In the lower intertidal, the sediment mobilised by wave action is transported by tidal currents (Table 6.2.6). Computational modelling of sediment transport indicates a net drift rate of $3.2 \times 10^5 \text{ m}^3/\text{y}$ directed towards eastward at Mundra (NIO, 2000c).

When all the values are pulled (n=91) positive correlations at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Mn, Al:Fe, Al:Co, Al:Ni, Al:Cu, Al:Pb, Al:P, Cr:Mn, Cr:Fe, Cr:Co, Cr:Ni, Cr:Cu, Cr:Pb, Cr:P, Mn:Fe, Mn:Ni, Mn:Cu, Mn:Zn, Mn:Pb, Mn:P, Fe:Co, Fe:Ni, Fe:Cu,

Fe:Zn, Fe:Pb, Fe:P, Co:Pb,, Co:P, Ni:Cu, Ni:P, Cu:Pb, Cu:Zn and Pb:P [Appendix-VIII (k)].

Number of times the positive correlation coefficients ($p=0.001$) for individual pairs occurring three times or more at the Mundra site sampled five times are as follows:

pair	Number	pair	Number
Subtidal			
Al:Cr	5	Mn:Ni	4
Al:Mn	4	Mn:Cu	4
Al:Fe	5	Mn:Zn	4
Al:Co	3	Fe:Co	3
Al:Ni	4	Fe:Ni	4
Al:Cu	4	Fe:Cu	5
Al:Zn	4	Fe:Zn	4
Al:P	3	Fe:P	3
Cr:Mn	3	Co:Cu	3
Cr:Fe	4	Ni:Cu	4
Cr:Co	3	Ni:Zn	5
Cr:Ni	3	Ni:P	3
Cr:Cu	4	Cu:Zn	4
Cr:P	3	Cu:P	3
Mn:Fe	4		
Intertidal			
Al:P	3	Mn:Fe	3
Cr:Mn	3	Fe:Ni	3
Cr:Fe	3	Fe:Cu	3
Cr:Cu	3	Ni:Cu	3
Cr:P	3		

Thus, the significant positive correlations occurring at 50 % or more of the sites sampled at Mundra indicate their preferential association with Al.

6.7 Kori Creek

As stated earlier the Kori Creek receives effluent from a TPS near by. Nearly 11×10^6 t of lignite was used as fuel during the year 1998-1999 in the TPS on the shore of the Kori Creek. The lignite is high in ash content and roughly 3×10^6 t of fly ash was produced during 1998-1999 that formed about 25 % of lignite consumed. In the TPS, the fly ash was

converted into slurry with the return coolant water and conveyed to the fly ash slurry dyke. The overflows from the dyke containing leachates as well as particles of fly ash entered the Kori Creek. Although the major components (95 %) of fly ash are oxides of Si, Al, Fe and Ca, which are non-toxic, fly ash generally contains traces of toxic metals such as Hg, As, Cd and Cr (Shannon and Fine, 1974; Windom and Sander, 1981; Mohanpatra and Kanungo, 1995; Querol *et al.*, 2001) a fraction of which is released on interaction with seawater. The High concentrations of Hg have been reported at stations KA4 and KA5 (0.26 and 0.21 µg/g respectively) (Ram, 2004). Relative high concentration of As at these stations is considered to be due to high concentration of Fe and Mn in sediments (Deorukhakar, 2003).

Table 6.2.7 indicates wide variations in the concentrations of metals even at given site. Thus, the concentrations of major metals Al and Fe in the sediment of Kori Creek vary in 2.0-7.9 % and 1.5-4.3 % respectively. The correlations between different pairs of constituents studied during the present investigation are presented in [Appendix-VIII (I)]. When all the values are pulled (n=16) positive correlations at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Co, Al:Ni, Al:Zn, Al:P, Cr:Co, Cr:Ni, Cr:Zn, Cr:P, Mn:Fe, Mn:Co, Mn:Ni, Mn:Cu, Mn:Zn, Fe:Cu, Co:Ni, Co:Cu, Co:Zn, Ni:Cu, Ni:Zn, Cu:Zn, and Zn:P [Appendix-VIII (I)].

. The concentrations of Cd and Pb in the subtidal sediment vary in 0.07-0.14 µg/g and 13.2-23.4 µg/g ranges without significant spatial or temporal trends. These ranges are 0.07-0.10 µg/g and 14.7-26.8 µg/g for the intertidal zone of the Kori Creek and compare well with the range for the subtidal sediment. Cd and Pb are more or less uniformly distributed in the creek sediments and high level is not evident in the segment KA1-KA2 where the effluent from the TPS is released. The results indicate probable background concentrations of Cd and Pb as 0.3 and 20 µg/g respectively in the sediment of the Kori Creek that compares well with the background estimated for the sediment of the Mumbai-Bassein region (Sections 3.2).

6.8 Overall assessment

The Gulf is bordered by sedimentary formations, which are predominantly marine, tidal, littoral or sub-littoral fluvial and Aeolian deposits of quaternary age. Deccan Traps occur extensively in the area and some formations extend to the coast and can contribute to the SPM in the Gulf. Sediment from the Indus River and wave erosion of the coastal material are considered as the major sources of sediment in the Gulf (Chauhan *et al.*; 2005). Prograding sediments of the Indus Delta preferentially accumulate along the northern shore of the Gulf as their transport to the south is hindered by a dynamic barrier caused by the high velocity tidal stream flowing through the central channel of the Gulf (Kunte *et al.*, 2005). The proportion of sediments derived from hinterland is considered to be low as the region is arid and has little runoff. Moreover, as numerous streams that discharge into the Gulf are short and many have dams constructed across them due to which their net contribution to the sediment in the Gulf is expected to be minor (Nair *et al.*, 1982).

Since, the sediment along the northern shores of the Gulf is sourced largely from the outflow of the Indus transported into the Gulf and since significant north-south transport is considered minor, it was interesting to investigate whether there were differences in the metal composition of sediments of the two shores of the Gulf. Data presented in Tables 6.2.1 to 6.2.13 when collated reveal the absence of marked difference in the concentration of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in sediments between the northern and the southern shores of the Gulf. This suggests that the source rocks from which the Gulf sediment (along the northern and southern shores) is derived perhaps have comparable lithology.

The concentrations of trace metals namely Cr, Co, Ni, Cu, Zn, Cd and Pb in the sediment of the Gulf probably represents the baseline. These concentrations compare well with the baseline established for the Mumbai-Bassein region based on dated cores. Tables 6.2.1 to 6.2.7 indicate often varying concentrations of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn,

Table 6.2.1 : Concentration of selected metals and P [$\mu\text{g/g}$; except Al, Fe and Co_3^{2-} Fe in (%), dry wt] in surficial sediment of																								
Positra Bay during different sampling events.																								
station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	Co_3^{2-}	station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Co_3^{2-}	
March 1999 (subtidal)											November 1999 (Intertidal)													
	1.0	15	257	1	29	12	16	22	522	42.9	OA	2.3	13	204	0.9	27	9	9	17	-	-	464		
O2	2.0	12	339	1	22	17	9	25	469	12.5	OB1	-	-	-	-	-	-	-	-	-	-	-	-	
O3	1.8	39	519	1.1	23	13	88	25	559	11.3	OB2	3.8	62	431	2.2	39	32	31	35	-	-	676		
O4	2.0	16	550	1.1	28	13	12	33	519	19.1	OC	2.1	20	304	1.6	37	18	14	20	-	-	888		
O5	0.8	13	1696	0.9	21	11	9	17	736	43.7	OD1	-	-	-	-	-	-	-	-	-	-	-	-	
O6	1.8	25	475	1	20	13	8	20	425	9.4	OD2	-	-	-	-	-	-	-	-	-	-	-	-	
O7	-	-	-	-	-	-	-	-	-	-	OD3	2.7	47	378	1.9	40	24	20	34	-	-	689		
March 1999 (intertidal)											OE	2.2	34	301	1.5	39	15	18	28	-	-	620		
OA	1.4	35	205	0.6	26	10	11	19	529	63.3	OF	3.7	59	488	2.8	41	31	27	45	-	-	748		
OB1	3.2	89	440	2	35	31	24	45	353	31.8	OG	2.6	37	269	1.4	28	16	15	29	-	-	479		
OB2	3.0	62	270	1.5	28	23	20	30	506	29.8	OH	3.3	33	440	1.7	25	22	16	34	-	-	596		
OC	1.0	22	268	1.2	23	17	15	18	568	19.5	OI	1.2	6	207	0.3	33	5	7	13	-	-	683		
OD1	1.6	21	344	1.8	29	21	18	23	977	56	December 2004 (subtidal)													
OD2	1.5	29	356	1.5	29	21	16	22	126	48.7	O1	3	40	399	0.7	13	7	5	23	0.1	26	735	24.9	
OD3	1.5	16	317	1.4	28	20	16	19	601	50.6	O2	3.4	131	604	1.2	3.5	13	10	18	0.2	37	705	40.7	
OE	2.1	52	410	1.4	32	27	24	33	169	49.9	O3	3.1	153	675	0.9	0.1	8	8	26	0.1	14	644	35.6	
OF	1.6	40	359	1.4	31	24	21	29	401	54.6	O4	3.4	134	582	1	0.3	7	6	16	0	15	382	16.7	
OG	2.3	57	399	1.9	32	26	24	37	713	58.9	O5	2.4	127	242	1.4	0.2	15	11	28	0.1	11	663	20.1	
OH	2.3	56	348	1	14	17	9	21	454	87.6	O6	2.1	138	254	1.3	13	14	8	27	0.3	13	807	25	
OI	2.4	13	222	0.4	24	8	7	15	736	3.5	O7	2.8	9	272	1.4	2.8	16	17	46	0	11	875	17.5	
November 1999 (subtidal)																								
O1	1.6	16	290	1.3	35	21	16	20	588															
O2	2.4	ND	318	0.9	24	10	7	25	468															
O3	2.3	24	405	1.9	25	17	6	26	480															
O4	-	-	-	-	-	-	-	-	-															
O5	2.2	20	400	1.2	38	12	12	22	675															
O6	2.2	ND	444	0.9	21	11	5	15	410															
O7	4.3	55	479	2.6	38	28	24	44	709															

Table 6.2.2 : Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%) dry wt) in surficial sediment off Sikka during different sampling events																					
station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
2001(May)												2006 (January)									
SK1	6.9	142	768	6.1	9	37	145	66	-	-	664	SK1	5.6	117	666	4.6	22	54	48	77	650
SK2	6.2	124	721	5.4	6	21	51	44	-	-	694	SK2	3.4	51	1046	2.7	13	28	29	55	663
SK3	7	170	922	6.6	23	44	64	61	-	-	576	SK3	6.6	106	711	5.3	21	61	49	104	731
SK4	3.2	59	972	3.1	0	6	31	0	-	-	692	SK4	6.4	124	790	5.9	26	67	62	103	717
SK5	6.2	133	946	6	15	32	56	54	-	-	680	SK5	6.2	116	693	5.5	23	61	52	109	676
SK6	2.7	66	626	2.9	0	8	27	0	-	-	616	SK6	2.5	115	733	1.7	9	23	24	38	510
SK7	7.8	139	763	6.1	18	49	57	64	-	-	632	SK7	5.9	45	826	5	22	60	52	91	692
SK8	7.4	149	755	6.4	27	56	59	76	-	-	600	SK8	2	118	782	2.5	14	0	36	44	596
SK9	1.7	28	1218	3.3	6	8	14	0	-	-	942	SK9	5.8	110	866	6.2	30	74	66	96	613
SK10	5.2	82	809	5	15	37	31	24	-	-	732	SK10	2.8	166	698	2.9	15	34	33	52	414
SK11	4.8	82	747	4	14	35	26	4	-	-	740	SK11	4.9	101	749	4.7	23	55	51	82	596
SK12	6.3	113	1055	7.4	31	48	49	84	-	-	870	SK12	6.2	133	733	5.7	23	64	54	119	666
SK13	7.2	111	822	5.1	22	48	39	69	-	-	714	SK13	4	122	633	3.8	14	38	33	66	518
2005 (February)												2006 (May)									
SK1	1.4	27	609	1.3	5	7	5	31	0.77	17.2	530	SK1	5.4	117	638	3.7	20	54	43	84	653
SK2	1.8	73	995	4.1	13	19	17	57	0.21	17.2	465	SK2	2.8	48	1492	2.3	15	35	31	39	747
SK3	4.9	102	555	4.4	16	51	34	78	0.54	11.5	883	SK3	7.1	101	730	4.5	20	60	44	97	716
SK4	3.9	70	779	2.8	7	23	18	111	0.73	9	608	SK4	6.5	152	885	5.8	31	74	74	83	694
SK5	2.8	55	536	1.7	3	12	8	39	0.69	21	469	SK5	6.9	109	747	5.2	22	66	55	82	708
SK6	5.7	101	1150	4.2	10	49	33	78	0.38	6.1	816	SK6	6.8	120	734	4.8	22	64	53	80	736
SK7	2.7	74	853	2.9	6	27	22	76	0.43	7.2	487	SK7	5.5	105	721	4.3	20	55	49	73	682
SK8	1.9	42	557	1.6	7	9	8	32	1.04	5.7	358	SK8	4.6	100	982	4.1	21	49	48	58	372
SK9	2.7	46	498	1.9	6	9	9	42	0.75	10.5	296	SK9	6.2	159	940	5.6	31	68	64	72	620
SK10	5.4	64	671	3.1	12	24	17	67	1.26	6.2	590	SK10	6.7	122	801	4.8	26	66	57	80	659
SK11	3.4	36	389	2	8	16	15	52	0.17	14.3	450	SK11	4.3	103	613	3.3	18	39	34	49	757
SK12	2.3	37	284	1.5	5	6	9	35	0.09	13.2	467	SK12	7	141	897	5.5	27	62	52	100	764
SK13	4.8	91	858	3.7	14	16	29	79	0.57	7.6	631	SK13	5.4	117	638	3.7	20	54	43	84	653

Table 6.2.3 : Concentration of selected metals and P ($\mu\text{g/g}$ except Al and Fe in (%), dry wt) in surficial sediment off Vadinar during different sampling events.

station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
January 2000 (subtidal)												November 2005 (intertidal)									
VN1	9.2	122	718	5	50	65	49	94			832	Tr-I	2.6	24	205	1.2	23	11	17	26	
VN2	8.9	113	750	5	47	57	44	96			811	Tr-II	4	42	466	2.4	28	28	26	ND	
VN3	9.3	127	704	5	49	59	45	93			788	Tr-III	0.2	6	181	0.2	18	2	6	29	
VN4	9.7	119	677	5	47	55	40	91			808	Tr-IV	2	22	736	1.2	22	11	17	114	
VN5	8.4	109	785	4	47	48	43	65			786	Tr-V	0.5	8	153	0.5	28	12	9	104	
VN6	3.9	55	520	3	42	30	26	40			729	April 2006 (subtidal)									
VN7	9.3	118	764	5	49	58	44	100			786	VN4	5.2	165	913	5.7	114	64	43	114	964
VN8	11	118	766	5	49	58	46	86			807	VN6	7.8	119	755	5.8	125	96	66	125	745
VN9	7.4	112	700	4	48	51	47	73			789	VN7	3.7	79	515	3.2	129	56	34	129	777
VN10	2.9	38	366	2	36	19	20	49			891	VN8	6.7	115	705	5	126	84	49	126	755
VN11	0.3	0	148	0	32	1	4	11			1229	VN9	5	105	741	4.7	113	68	41	113	795
VN12	1.3	5	179	1	33	8	8	20			1029	VN11	7	121	662	4.9	124	81	48	124	686
VN13	8.1	104	428	4	43	53	37	82			678	VN12	7.1	115	662	5.1	123	81	49	123	750
VN14	8.8	127	587	6	47	59	50	87			871	VN13	7.4	101	682	5.1	121	78	49	121	758
VN15	8	146	695	6	51	59	57	97			874	April 2006 (intertidal)									
VN16	6.1	96	563	4	44	46	45	79			881	Tr-I	0.2	11	97	0.1	105	22	6	105	513
VN17	0.3	0	187	0	29	2	6	9			696	Tr-II	0.2	10	131	0.2	103	10	5	103	731
VN18	2.8	30	512	3	43	21	47	31			834	Tr-III	0.7	14	174	0.3	106	46	7	106	669
October 2004 (subtidal)												Tr-IV	1.6	25	182	1	103	41	14	103	657
VN4	7.5	118	688	5	23	61	59	154	0.3	62	985	Tr-V	0.2	11	120	0.3	115	68	4	115	752
VN6	10	118	498	5	22	64	53	152	0.5	31	688	November 2006 (subtidal)									
VN7	4.8	65	525	3	12	36	54	80	0.3	24	787	VN4	5.2	100	1084	5.1	31	67	33	22	584
VN8	5.6	114	1103	5	20	68	48	129	0	30	746	VN6	7.6	88	800	6.4	35	74	49	44	306
VN9	7.5	118	688	5	23	61	59	154	0.3	62	985	VN7	7.4	80	742	5.8	32	70	45	31	415
VN11	3.9	44	210	1	10	35	22	139	0.4	14	76	VN8	7	96	865	5.4	34	73	45	30	513
VN12	2.1	40	272	1	6	23	34	63	0.8	26	611	VN9	6.5	95	1359	6.9	37	75	48	36	562
VN13	11	114	471	5	20	69	48	136	0.2	38	696	VN11	6.5	84	1339	6	34	75	44	33	408
October 2004 (intertidal)												VN12	7.7	82	936	6	33	76	43	29	423
Tr-I	0.1	13	89	0	2	56	6	35	0.3	23	796	VN13	8	83	820	6	35	77	43	39	395
Tr-II	5.5	86	735	5	21	86	63	116	0.8	34	459	November 2006 (intertidal)									

Tr-III	0.8	19	157	1	2	53	9	46	0.5	20	809	Tr-I	5	80	715	5.6	33	72	47	31	51		
Tr-IV	3.1	87	624	6	14	13	40	119	0.6	34	627	Tr-II	0.8	12	124	0.4	17	26	8	ND	966		
Table 6.2.3 (Continued...)																							
station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P		
	October 2004 (intertidal)												November 2006 (intertidal)										
Tr-V	0.2	11	48	0	2	49	7	43	0.1	8.8	662	Tr-III	0.5	12	130	0.3	17	27	7	ND	707		
	April 2005 (subtidal)												Tr-IV	0.9	16	132	0.5	17	27	10	13	462	
VN4	3.7	45	296	2	23	48	19	61	1029			Tr-V	0.3	11	0	0.8	17	25	5	ND	462		
VN6	6.8	99	693	5	34	77	44	64				1188											
VN7	5.7	71	981	4	27	64	34	88				1013											
VN8	7.7	101	746	5	36	89	44	276				1096											
VN9	5.1	128	816	5	34	68	41	485				1143											
VN11	7.3	88	634	5	31	78	40	78				1076											
VN12	5.4	66	853	4	32	62	31	507				1121											
VN13	6.2	88	744	8	32	68	39	61				990											
	April 2005 (intertidal)											VN12	7.4	109	1025	4.8	31	76	46	65	234		
Tr-I	7.2	92	590	5	34	80	41	154	1133			VN13	7.9	105	1023	5.1	30	74	45	62	478		
Tr-II	3.7	39	306	2	22	48	19	22				1255											
Tr-III	0.2	0	138	0	16	28	4	10				1158											
Tr-IV	1.4	13	163	1	17	33	10	0				1054											
Tr-V	5.2	85	974	0	34	71	38	34				1159											
	November 2005 (subtidal)											Tr-III	0.2	10	143	0.3	13	3	5	ND	160		
VN4	5.4	66	586	4	34	42	35	34	1133			Tr-IV	0.5	13	261	0.4	14	21	6	ND	381		
VN6	7.8	81	853	6	41	70	51	46				Tr-V											
VN7	5.7	74	851	5	35	53	44	15				0.6											
VN8	7.2	87	1117	5	41	70	48	49				17											
VN9	5.1	66	999	5	37	52	38	26				252											
VN11	6.8	76	695	5	38	65	47	46				0.6											
VN12	8.8	76	705	5	37	65	47	84				14											
VN13	6.9	76	694	5	39	61	43	43				14											

Table 6.2.4 : Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%), dry wt) in surficial sediment off Bedi during different sampling events.																						
	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	
station	1997 (February-March)											1997 (November)										
BD1	6.6	133	490	4.2	40	67	51	97	0.2	25	975	BD1	4.4	176	617	4.1	39	53	54	53	330	
BD2	3.5	110	772	2.2	33	34	24	58	0.2	6.2	622	BD2	5.1	189	777	5.2	45	59	72	72	345	
BD3	7.1	148	712	3.8	43	60	42	79	0.2	29	785	BD3	5.5	152	683	4.7	41	54	56	69	334	
BD4	6.8	127	685	3.6	45	58	39	122	0.1	17	665	BD4	5.3	128	801	4.8	40	55	63	68	340	
BD5	7.5	140	643	3.7	47	54	39	83	0.1	-	709	BD5	5.9	152	652	4.6	39	58	53	73	402	
BD6	6.4	117	584	3.3	43	48	34	80	0.1	25	626	BD6	5.3	135	619	4.3	36	42	50	73	321	
BD7	6.8	174	775	4	49	56	49	74	0.2	12	718	BD7	3.2	78	513	2.7	29	34	35	55	221	
BD8	7.5	166	763	3.9	45	60	46	76	0.2	12	507	BD8	2.9	77	506	2.7	28	24	31	48	363	
BD9	3.1	48	502	2	53	32	16	39	0.2	12	813	BD9	4.5	146	858	4.8	43	60	66	71	337	

Table 6.2.5 : Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%) dry wt) in surficial sediment off Kandla during different sampling events.																					
1996 (October)												2004 (December)									
station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
KL1	-	-	-	-	-	-	-	-	-	-	-	KL1	0.7	26	113	3.9	3	8	4	38	51
KL2	-	-	-	-	-	-	-	-	-	-	-	KL2	ND	3	ND	ND	18	1	26	2	887
KL3	3.4	59	797	2.1	21	31	22	39	--	-	-	KL3	5.6	84	778	4.5	19	52	21	133	560
KL4	3.8	53	921	2.5	22	35	23	56	-	-	-	KL4	-	-	-	-	-	-	-	-	-
KL5	5.6	81	1314	3.2	27	54	33	86	-	-	-	KL5	-	-	-	-	-	-	-	-	-
KL6	6.3	103	1321	3.4	29	58	36	88	-	-	-	KL6	-	-	-	-	-	-	-	-	-
KL7	-	-	-	-	-	-	-	-	-	-	-	KL7	0.3	5	ND	0.1	1	1	ND	20	8
KL8	2.9	50	810	1.6	14	20	11	34	-	-	-	KL8	7.9	119	637	5.4	21	72	46	129	550
KL9	-	-	-	-	-	-	-	-	-	-	-	KL9	4.7	66	471	2.1	8	23	10	37	489
1998 (February)																					
KL1	5.8	51	662	5.1	31	47	41	54	0	19	784										
KL2	6.7	46	583	4.7	29	45	28	72	0.2	22	624										
KL3	7	56	724	6	32	54	39	72	0.2	22	760										
KL4	-	-	-	-	-	-	-	-	-	-	-										
KL5	3.1	31	428	2.4	17	21	51	72	0.1	18	2110										
KL6	-	-	-	-	-	-	-	-	-	-	-										
KL7	7.9	76	757	6.2	35	60	37	77	0	17	782										
KL8	5.5	28	532	3.4	23	32	19	50	0.1	13	558										
KL9	1.7	26	492	1.2	16	9	6	12	0.3	15	424										

Table 6.2.6 : Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%), dry wt) in surficial sediment off Mundra																						
during different sampling events.																						
station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn		P	station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
1998 (July) (subtidal)											2005 (May) (Intertidal)											
MR1	6.4	80	752	4.3	33	53	33	71		1344	MRA	5.7	52	857	4.2	13	51	25	26	-	24	814
MR2	6.7	61	832	4.7	34	59	39	79		1337	MRB	4	31	417	1.8	6	29	12	49	0.9	17	609
MR3	6.4	54	758	4.4	33	54	34	73		1402	MRC	5.6	43	545	2.6	7	41	14	100	0.5	16	788
MR4	6	50	718	4.2	31	49	28	71		715	MRD	3.8	43	562	2.3	6	29	13	53	1.1	17	707
MR5	2.5	18	361	1.5	11	15	3	13		337	MRE	6.2	62	778	4.7	14	69	32	127	0.1	14	787
1999 (February) (subtidal)											2006 (April) (subtidal)											
MR1	9.3	172	886	4.8	43	68	47	106			MRF	2.7	48	478	1.8	4	22	10	22	0.5	16	454
MR2	9.2	171	900	5	42	66	47	98		807	MRG	2.7	45	526	1.7	5	20	10	20	1	12	522
MR3	7.9	136	823	4.4	37	53	38	84		882	MRH	7.2	72	493	4.4	16	68	32	106	0.4	16	762
MR4	7.6	139	847	4.4	37	56	38	85		827	MRI	1.9	16	339	1	5	19	8	173	0.4	18	626
MR5	6.5	117	702	4	34	47	37	75		788	MRJ	0	0	422	1.1	4	18	7	84	0.3	9.9	396
MR6	5.3	175	711	3.9	33	43	34	60		733												
MR7	6.7	90	706	3.7	32	42	25	71		547	MR1	3.9	34	702	2.7	11	32	9	213			350
MR8	4.7	91	643	3	27	33	22	56		663	MR2	1	5	731	1.3	5	29	4	199			188
MR9	2.5	60	533	1.8	70	10	11	27		719	MR3	4.4	58	677	3.7	16	40	22	222			502
MR10	0.5	7	431	1.1	16		6	14		416	MR4	5	67	1255	3.7	16	42	19	224			580
MR11	0.6	9	446	1.2	15	2	8	15		341	MR5	6.8	66	1329	5	18	46	26	226			631
1999 (February) (Intertidal)											2006 (April) (Intertidal)											
MRA	5.2	83	672	3.7	30	34	28	58		345	MR6	1.6	9	685	1.5	4	13	4	162			194
MRB	6.6	140	765	4	38	47	37	76			MR7	3.7	60	678	3.6	10	19	16	240			495
MRC	7.1	149	819	4.4	39	52	38	87		861	MR8	5.9	66	1566	4.6	13	23	26	242			549
MRD	6.5	146	763	4.3	38	52	35	82		774	MR9	7.7	86	302	4.7	17	20	25	132			694
MRE	7	154	759	4.5	40	56	42	84		802	MR10	1	6	769	1.4	0	0	2	122			249
MRF	6.8	163	923	4.5	42	55	42	87		756	MR11	6.4	76	378	4.8	16	9	21	116			589
MRG	6.4	107	790	4.2	38	47	36	87		848												
MRH	4.1	74	523	3	29	32	24	58		833	MRA	5.1	54	1094	3.5	10	7	10	144			434
MRI	6.9	127	676	4	39	33	33	92		782	MRB	3.2	35	505	2.3	58	2	11	124			310
MRJ	1.9	39	352	1.2	15	6	9	20		608	MRC	2.4	35	649	2.8	11	ND	6	164			270
MRK	4.9	111	706	3.6	36	41	31	72		706	MRD	2.6	30	293	2.5	6	61	7	141			259
											2006 (April) (Intertidal)											
											MRJ											
											MRE											
											MRF											
											MRG											

Table 6.2.6 (Continued...)																								
station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn		P		
2005 (May) (subtidal)												2007 (October) (subtidal)												
MR1	7.1	92	807	4.9	22	80	40	77	0.09	#	906	MR1	7.9	102	811	4.1	-	82	47	101	-	-	717	
MR2	7.2	90	820	4.4	22	87	42	85	0.54	#	956	MR2	7.6	84	767	3.4	-	69	35	85			683	
MR3	6.6	75	780	4.7	20	73	38	88	1.32	#	872	MR3	6.6	58	614	2.5		53	23	56			580	
MR4	6	61	701	3.9	19	57	29	69	0.45	#	805	MR4	-	-	-	-	-	-	-	-			-	
MR5	4.3	39	631	2.7	14	38	18	13	0.57	#	857	MR5	-	-	-	-	-	-	-	-			-	
MR6	-	-	-	-	-	-	-	-	-	-	-	MR6	2.7	23	313	0.2	-	16	5	10			335	
MR8	6.2	60	584	3.9	14	60	29	100	0.92	#	693	MR7	6.3	65	622	2.5	-	48	23	54			613	
MR9	1.9	19	274	1	4	16	8	29	2.46	#	901	MR8	5.6	51	617	2.1	-	46	23	47			609	
MR10	6	73	730	4.2	16	64	31	77	1.02	#	474	MR9	1.8	15	280	0.2	-	13	4	7			285	
												MR10	1.9	24	315	0.1	-	13	4	14			312	
												2007 (October) (Intertidal)												
												MRA	-	-	-	-	-	-	-	-	-			-
												MRB	-	-	-	-	-	-	-	-	-			-
												MRC	4.2	45	523	1.2	-	26	13	33			349	
												MRD	3	47	576	0.9	-	20	8	33			346	
												MRE	3.9	76	728	1.7	-	27	12	27			259	
												MRF	2.7	23	345	0.3	-	17	6	20			330	
												MRG	3	50	409	0.3	-	18	6	22			195	

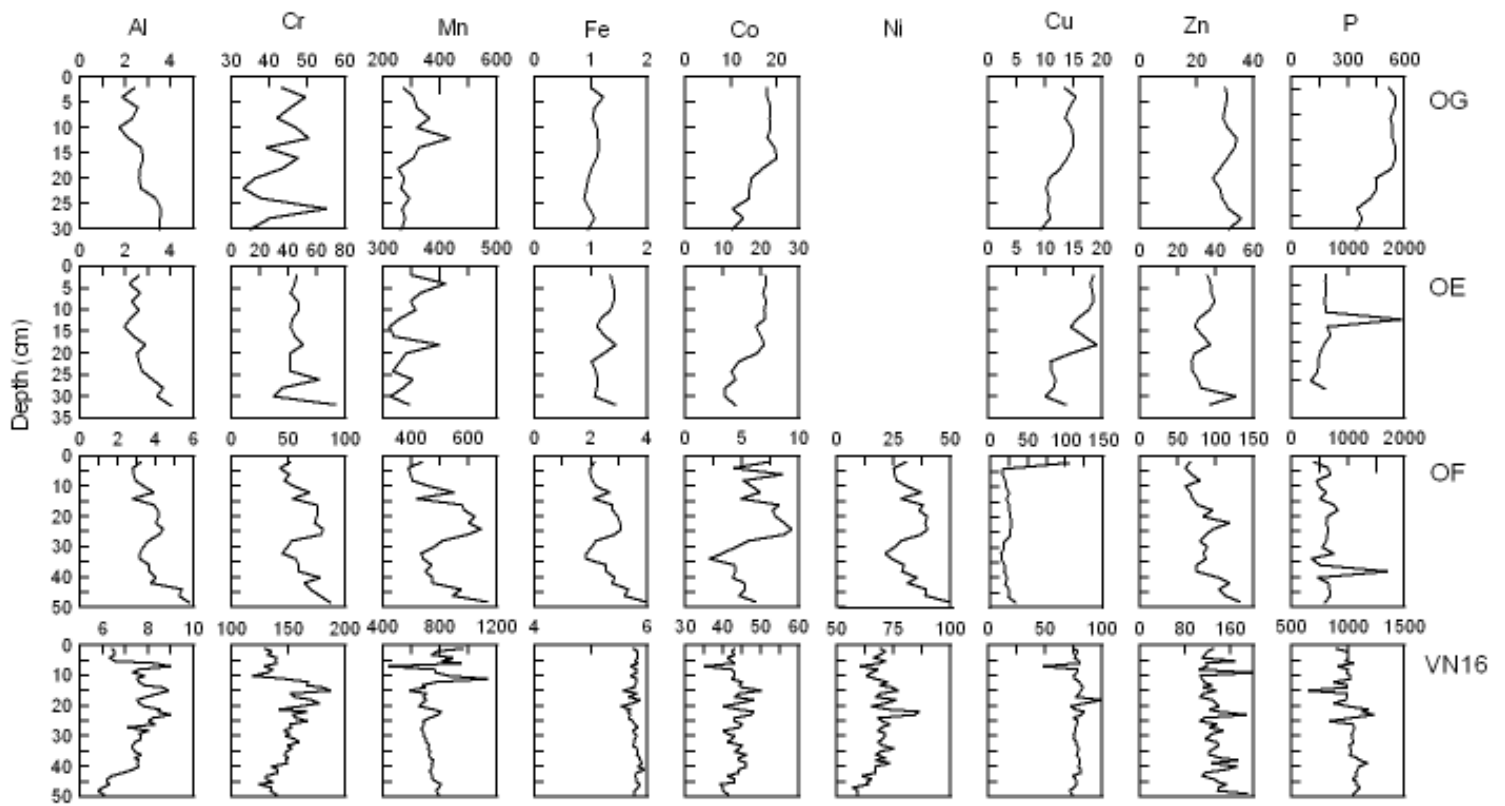


Figure 6.2.1: Depthwise variation of selected metals and P [$\mu\text{g/g}$, except Al and Fe in (%), dry wt] in core sediment of Gulf of Kachchh

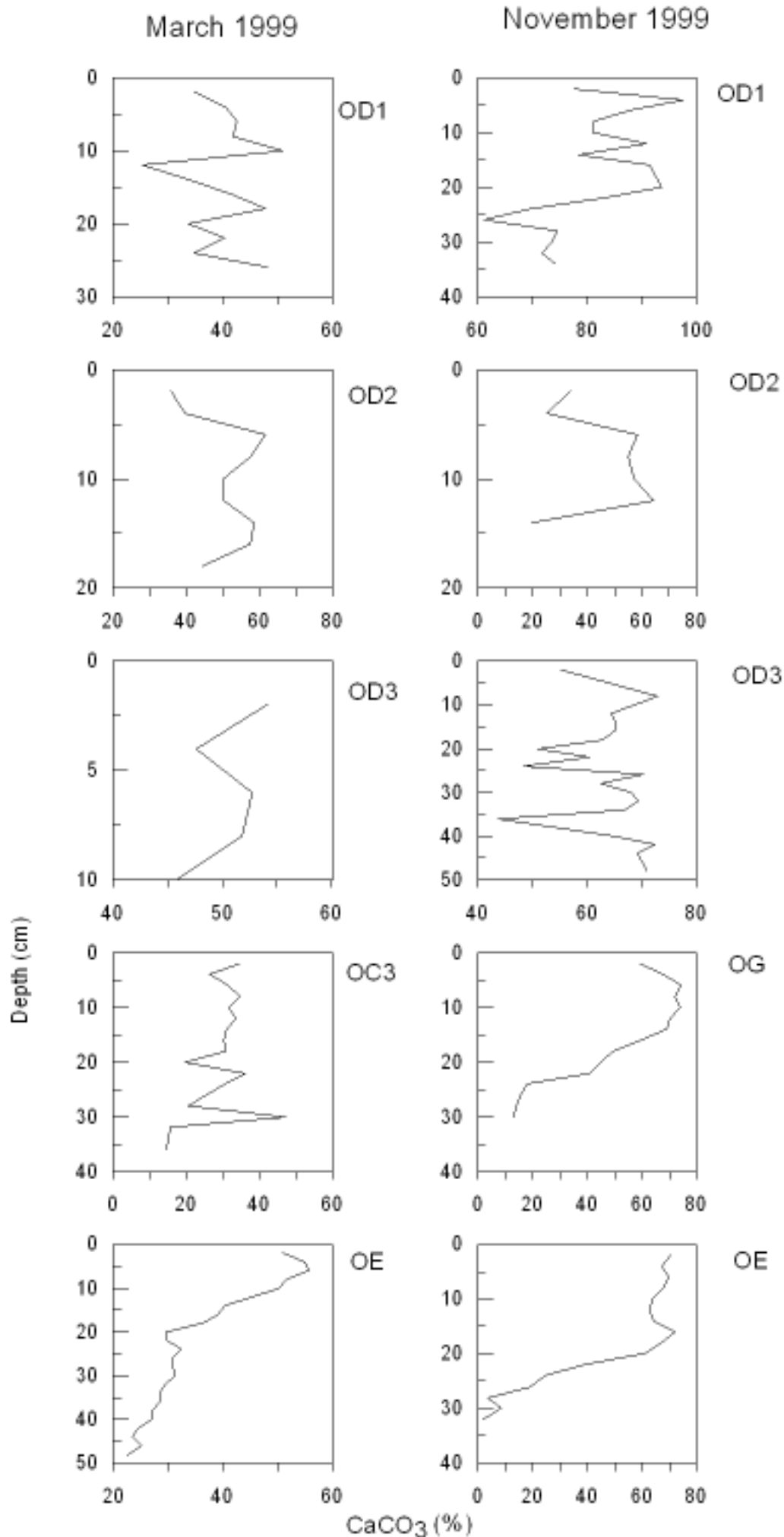


Figure 6.2.2: Depthwise variation of CaCO_3 (%) in core sediments of Gulf of Kachchh

CHAPTER 7

SUMMARY AND CONCLUSIONS

Human activities in the marine zone of India are mainly confined to the inner shelf where water depths are <50 m. Considering the vastness of the coastal area, the data on contaminants including metals in seawater, marine sediments and biota is scanty. Of these, Mumbai-Bassein region that houses more than 8 % of the Country's industries has received relatively greater attention though exhaustive studies in recent years are missing. With this background the research scheme for the Thesis was planned (i) to establish the baseline concentrations of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in the sediment of the drainage basin of the Mumbai region, (ii) to assess the present load of sewage-associated trace metals and P to the marine environment of Mumbai, (iii) to evaluate seasonal changes in the sediment metals and P of the Bay in relation to high monsoon-derived lithogenic flux, (iv) to investigate spatial heterogeneity of distribution of the metals if any, in the sediment of Docks and Bunders, of the Mumbai Port, (v) to examine whether the Bay is a passive link between the anthropogenic metals and the coastal Arabian Sea or a sink for trace metals, (vi) to quantify anthropogenic fraction of trace metals and P in marine sediments of the Mumbai region based on EF and I_{geo} , (vii) to assess the quantum of bioavailable Cr, Mn, Fe, Cu and Zn in a selected surface and core sediments of the Bay, (viii) to identify trends in distribution of metals and P in nearshore sediments of the northwest coast of India between Porbandar and Ratnagiri, and (ix) to establish levels of metals and P in the sediments of the fast-industrializing biorich Gulf.

7.1 Metals in Thane Creek-Mumbai Harbour

7.1.1 Anthropogenic sources of metals

The Bay receives anthropogenic metals from domestic as well as industrial sources. The data collected from various treatment plants and pumping stations during the present study reveals that out of the total sewage generated in the Mumbai city and surrounding area (3.16×10^6 m³/d), the Bay, Mahim Creek and the Versova Creek receive 1.16×10^6 , 8.3×10^5 and 4.4×10^5 m³/d respectively; the balance (7.3×10^5 m³/d) being released directly in the openshore area including the sea off Worli. At the Malad pumping station the concentration of Cr is high on most occasions, while, that of Ni, Pb and Cd is high in several instances. The average concentrations of Al, Cr, Fe, and Ni are relatively low at Ghatkopar, Bhandup and Versova treatment plants which can be due to treatment in aerated lagoons and retention in settling tanks prior to release, at these sites. The concentration of Pb in sewage has distinctly decreased (0-19.8 µg/l) in recent years which can be due to changeover to unleaded petrol. Though the concentrations of metals are relatively low in sewage, considering the volume generated in the city, the fluxes to the marine environment are fairly high. When all the values are pulled (n=76) good positive correlations are evident for the pairs Al:P, Cr:NI, Fe:Pb, Fe:P, Co: Cd, Ni:Cu, Ni:Zn, Ni:Pb, Ni:P, Cu:Zn, Cu:Pb and Zn:Pb.

Nearly 8 % of industries in the country located around Mumbai have been releasing their effluents-largely untreated in the past, in the Bay, Ulhas, Patalganga and Amba estuaries. Reliable data on the industrial effluents and fluxes of contaminants entering the creeks however are not available.

7.1.2 Lithogenic background of metals

In order to establish the concentrations of metals and P in sediments of the drainage basin, several soil and rock samples from the catchment of the Bay and Ulhas estuary were analysed. The results indicate wide variations in the concentrations. The highest concentration

of Al (55.3 %) in a soil sample from Lonavala is also associated with the highest concentrations of Mn (12469 µg/g), Co (342 µg/g), Cu (1586 µg/g), Zn (907 µg/g), Cd (1.1 µg/g) and P (4874 µg/g). This sample however sustains the lowest concentration of Fe (11.3 %). Correlation coefficients of 0.62-0.95 and the high level of significance (<0.001) of Mn, Co, Ni, Cu, Zn, Cd and P with Al indicate their preferential association with Al rather than Fe.

7.1.3 Metals in surface sediment

The variations in concentrations of trace metals in the Bay sediments can be partly due to changing concentrations of Al and Fe which vary over wide ranges in these sediments. Increase in the concentration of Al from 7.4-7.7 % in April 1996 to 8.4-10.0 % in October 2000 indicates an enhancement in the flux of clay material to the Bay over the years. The trend also indicates a rise in the Fe content of the sediment as compared to the April 1996 results but the increase is less well defined than in the case of Al.

Among trace metals, Cr burden in the surficial sediment seems to have increased with the passage of time. The concentration profiles of Cu, Zn and Ni also reveal a similar trend. Comparison of average concentrations of metals in the catchment soil and sediment at station B25 which is 25 km from the coast reveals a marked depletion in concentrations of most metals in marine sediments of the region. This decrease is particularly prominent for Cr, Mn, Fe, Ni and Cu. Thus though several workers have used trace metal contents of the catchment to assess anthropogenic fractions in marine sediments, such an approach would be flawed in the present case.

Considering the developmental history of Mumbai, sediment that might have been deposited off the coast about 100 years in the past can be a good source of the baseline. With this view the bottom sections of the dated cores B23, B24, B25, U34, U35, and U37 from the coastal area of Mumbai-Bassein and core R5 retrieved off Ratnagiri are utilized to

establish the baseline for metals for Bassein-Ratnagiri region in the present study.

A marked decrease in the concentrations of Al, Mn, Fe and P in the subtidal as well as the intertidal sediment in postmonsoon as compared to the premonsoon appears to be due to the influence of the particulate load associated with the runoff during monsoon. The fine-grained sediment transported to the Bay is largely of terrestrial origin which would have relatively high levels of metals. Under the dynamic Bay environment the native bed sediment disturbed by turbulence mixes with the load delivered through the land runoff. Hence, relative high concentrations of Al, Mn, Fe and P are recorded in the sediment during postmonsoon. With the withdrawal of monsoon the lithogenic flux of high metal content to the Bay nearly ceases and results in relative low concentrations of these elements in the surficial sediment of the Bay in premonsoon period.

7.1.4 Metals in sediment cores

The distribution of metals in cores from the Bay is neither uniform nor any definite trends common to all the cores are discernible.

a) Sedimentation rate

Core B2 was subjected to ^{210}Pb dating to introduce the timeframe on the metal profiles. The ^{210}Pb activity decreased with depth up to 10 cm in this core followed by the bottom segment of more or less constant and low activity. The sediment is therefore relatively undisturbed in the vertical. The clay accumulation rate of 0.92 cm/y calculated for core B2 compares well with the rate reported earlier for the same area.

b) Distribution of major metals

The trend of depth-wise variation of Al in the cores of the inner Bay indicates local changes in the depositional regime of the metal which can be probably due to changes in the hydrodynamics as a consequence of construction of structures such as bridges, reclamation, port development etc. The Al profiles in cores B23 and B24 do not reveal marked changes

in the depositional history of Al unlike in core B25 which indicates a distinct and systematic increase in the Al content in the upward direction. Based on the sedimentation rate of 1.4 cm/y the core B25 represents the history of deposition of about 114 years. The sharp fall in Al content at 60-62 cm which pertains to the year 1954 is probably an episodic event which is also reflected in the profiles of Cr, Mn, Fe, Co, Ni, Cu and Zn. The Core R5 represents the depositional history of 460 years based on the sedimentation rate of 0.21 cm/y. The minimum at 41-42 cm in the Al profile which probably occurred some 190 years in the past is unlikely to be associated with man-made modifications in the catchment. The intermediate peak around 48-50 cm in the Al profile coincides with similar peaks in the depth profiles of Cr, Fe, Ni and Cu suggesting their common source.

As in the case of Al, Fe is present in high concentration in these sediments and its concentrations are unlikely to be influenced by anthropogenic additions. The trend of concentration of Fe increasing with depth is similar to the Al profile in cores B2 and B3. The Fe profile in core B23 indicates a distinct increase in the concentration subsequent to the year 1954. In cores B25 and R5 the Fe concentration has increased with the deposition of sediment and its profile resembles that of Al in these cores. Fe and Al seem to co-vary in the area with significant correlations in cores B1, B2, B3, B4, B5, B25 and R5.

c) Distribution of minor elements

The concentration of Cr in the cores varies considerably in some instances from surface to bottom while in others the changes in vertical distribution is not marked thereby making the assessment of anthropogenic component of the metal a difficult task.

The concentration profiles of Cr in cores B1, B3, B4, B6, B23, B24 and B25 do not seem to support anthropogenic accumulation of Cr in the sediment. The uniformly high concentration of Cr over the depositional history of 50 years in core B2 suggests a point source of anthropogenic

Cr in the vicinity. The upward increase in Cr concentration in core B25 can be due to increase in the concentrations of Al and Fe. Sharp peaks of abnormally high concentrations of Cr (1423-3308 µg/g), Mn (6522-15264 µg/g), Co (1727-1990 µg/g), Ni (1928-2833 µg/g) and Zn (3537-5510 µg/g) at 1, 10, 18, 19, 21, 22, 24, 25, and 27 cm in core B5 indicate sporadic input of anthropogenic material rich in these metals. Considering that high percentage of Al coincides with these peaks it is probable that the sediment at this site has been intermittently enriched with metallic particles such as Al-Si alloys which are mainly used in castings. In cores B1, B5, B6, B23 and B25, Cr concentration directly varies with that of Al, while, the concentrations of Cr and Fe co-vary in cores B1, B2, B9 and B25.

Considering similarity in profiles of Mn, Al and Fe in core B1 and their excellent direct variations it is possible that Mn is associated with these major elements in this core. In core B3, Mn seems to be associated with Fe with which it has a good positive relationship. The nature of profile in core B23 suggests that Mn reduced in the sediment under anoxic environment and diffusing through the porewater is precipitated in the top section under oxic conditions.

The concentration of Co in core B1 is comparable throughout the core length with direct variation with Al, Mn, Cu and Ni. Its profile of increase in concentration with depth in cores B2 and B3 is in line with the variations of Al and Fe in these cores. A small increase in the concentration of Co from the bottom to the surface in cores B6 and B25 is in agreement with the decrease in Al content into the sediment. With the exception of core B5 the concentration of Ni in cores is generally low as compared to its concentration in the catchment soil suggesting its removal during the transport and deposition in the marine zone of Mumbai. Ni profile of increase in concentration with depth in core B2 is in line with the variation of Al and Fe with which it has direct relationship. The concentration of Ni in core B4 directly varies with that of Cr, Cu and Zn, while, in core B6 its concentration is positively correlated with that of Al

and Cu. The depth profile of Ni in core B25 is similar to that of Al and Fe. Ni also varies directly with Cr, Mn, Co, Cu and Zn in this core.

Considering the range 27-101 $\mu\text{g/g}$ observed in the bottom sections of the cores B23 to B25 as the background, the levels of Cu in cores from the Bay are consistently high suggesting anthropogenic addition. As in the case of Ni, its profile in core B2 which is inverse of that of Al and Fe, indicates incremental increase of anthropogenic Cu in the sediment with maximum (147 $\mu\text{g/g}$) concentration at 19 cm – the sediment deposited around 1978-1981. Similarly, though the concentration of Cu in core B3 varies considerably with depth, the trend suggests definite increase in concentration in the sediment deposited subsequent to 1963. Because of this incremental increase, the concentration of Cu is inversely related with that of Al in this core.

The concentration of Zn in core B1 has doubled or even tripled in several sections compared to the expected baseline and varies directly with the concentrations of Al, Fe, Cr, Ni and Cu. Because of its anthropogenic addition and the trend of increasing concentrations of Al and Co into the sediment, it is inversely correlated with Al and Co in core B2. Zn profile in core B3 is typical of incremental anthropogenic accumulation of the metal with the bottom (87 $\mu\text{g/g}$) concentration considerably lower than at the surface (138 $\mu\text{g/g}$). The Zn profile in core B4 suggests accumulation of Zn throughout the core length with values as high as 300-400 $\mu\text{g/g}$ in the mid-segment. Its concentration is higher than the expected baseline in core B6 with episodic additions of the metal represented by sharp peaks in its depth profile. Its concentration in core B23 seems to vary with that of Cr and their high concentrations in the surface sediment which coincide with that of Mn seems to be due to their mobilization along with Mn. The Zn profile in core B25 with concentration decreasing into the sediment is similar to that of Al and Fe with significant correlations.

Concentration of Cd has increased upto 20 times than the expected baseline (0.3 µg/g) during the period 1975-1989 in core B1. The average profile of Cd concentration in core B3 also indicates an increase in concentration from the year 1950 to 1972 followed by a decrease. The signature of anthropogenic Cd entering the Bay is seen even in core B24 – 25 km off the Bay mouth. The lithogenic baseline of Cd in core R5 appears to be high (0.55 µg/g) as compared to the baseline (0.3 µg/g) considered for the Mumbai region.

The Pb profile of core B2 is similar to that of core B1 with baseline concentration in sediment deposited prior to the year 1957. The subsequent increase in concentration upto the year 1982 (318 µg/g) indicates high anthropogenic additions of Pb to the Bay in that period. The concentration of Pb in core B3 is variable, but, is in the vicinity of the background. The relative high concentration of Pb in the top 3 cm sediment of core B23 (31.4-69.2 µg/g) is probably due to mobilized Pb along with Mn. The background concentration of Pb in core R5 seems to be around 8 µg/g and hence lower than considered for the Mumbai region.

The concentrations of about 1500 µg/g appears to be the baseline for P in sediments of the coastal region of Mumbai based on the levels in the bottom section of core B24. The average P profile in cores B1, B2 and B3 indicates concentration decreasing with depth and suggests accumulation with time. The high concentrations of P with value generally exceeding 1800 µg/g in most instances in core R5 is a natural occurrence and is supported by published literature.

d) EF and I_{geo}

The EF is as high as 30-40 in core B5 for Cr, Co, Ni and Zn as well as between 2 and 40 for Cd in core B2. I_{geo} of 1-4 in the inner Bay is suggestive of moderate to high level of Cd accumulation in the sediment of this zone. I_{geo} in the core B2 in the Bay is in class 1-5 indicating moderate to strong pollution with respect to Pb.

7.1.5 Sequential extraction of metals

Surface sediment from stations B1, B2, B5, B6 and B12 and selected sections of core B2 were subjected to sequential leaching to assess occurrence of metals in different phases in the sediment. Except for Mn the percentage of metals in the exchangeable fraction is extremely low and barely exceeds 2 % of the respective total metal content thereby suggesting that the sediment bound metals in the Bay may not be easily bioavailable. Even in the case of Mn this value is low and varies in the range 1-6 %.

Association of Cr with carbonates in the Bay sediments is also extremely low (0-2 %) followed by Cu (3-7 %), Zn (6-31 %) and Mn (29-64 %). The percentage of carbonate-associated Mn increases from 47 % at station B1 to 64 % at station B6 probably because of improved DO and pH in the seaward direction. About (5-15 %) of Cr is associated with Fe-Mn oxide phase in the sediments of the Bay without any spatial trends. The Zn profile of the carbonate phase mimics its bulk concentration in the sediment with decrease down the core length. The association of Mn, Cu and Zn with the Fe-Mn oxide phase which varies from 4 to 45 % indicates a trend of concentration increasing from station B1 to B6. The surface sediment in the Bay is likely to be oxic though the area receives large volume of sewage and these trace metals may not be released under the prevailing environmental conditions in the Bay. Only a small amount of Cr, Mn, Cu and Zn (2-11 %) is bound to organic matter though the Bay receives a variety of organic substances. A considerable fraction of Cr (36-94 %), Mn (22-30 %), Cu (49-60 %) and Zn (25-84 %) is associated with the residual phase and hence not easily available to biota except when consumed directly as sediment particles with food.

7.2 Metals in Ulhas estuary

Kalyan-Ulhasnagar belt is heavily industrialized and consists of chemical, metallurgical, pharmaceutical, textile and rayon industries which release their effluents in the Ulhas estuary and its tributaries. The human

settlements, which have grown multifold around the industrial belt also dispose domestic wastewater in the estuary, often untreated.

7.2.1 Metals in surface sediments

The profiles of distribution of Cr, Co, Ni, Cu, Zn, and P in surface sediment along the length of the estuary indicate high concentrations of most metals just below the weir which is the innermost limit of the estuary. The concentrations of metals and P in sediment upstream of the weir (river segment) are largely lithogenic. Variations in concentrations of metals and P from collection to collection appear to be due to the disturbance and redistribution of sediment. Under high tidal excursion the SPM enriched in metals in the Kalyan segment of the estuary would be transported in the inner estuarine segment of the Bhatsai and Kalu Rivers during flood tide where it probably settles during dry season. The contaminated SPM transported downstream during ebb tide gets diluted by naturally occurring high SPM in the outer estuary and distributed over a large area thereby explaining significantly lower and decreasing levels of metals in the outer estuary. The high concentration of Cr in the estuary and its decrease in the seaward direction suggests a significant source of Cr to the inner estuary subsequent to April 1996. Similar to Cr, distinctly high concentrations of Cu, Zn and P occur at station U4 with a trend of decrease in the seaward direction. With all the values taken together significant direct correlations occur among the pairs Al: Cd, Al: Pb, Al: P, Fe: Cd, Fe: P, Mn: Cr, Mn: Co, Mn: Ni, Mn: Zn, Mn: Cd, Cr: Cd, Cr: Pb, Ni: Co, Ni: Zn and Zn: P.

7.2.2 Metals in sediment cores

a) Distribution of major metals

The Al content in cores from the river segment varies in the range 8.7-9.3 % and the profiles are devoid of any definite features indicating a more or less uniform depositional regime. The deposition of Al in the sediment of the estuary as well as the coast varies in space and time. In core U23 the concentration of Al varies randomly but overall profile reveals a definite increase in concentration with depth in the sediment.

The trend is reverse in core U31. In coastal cores U31 and U37 the overall concentration of Al seems to have remained unaltered throughout the lengths unlike in core U35 which represents the history of deposition of about 50 year. In core U35 there is marginal but definite increase in concentration at the surface compared to the bottom section.

Fe occurs in relative high concentration in riverine cores (9.8-11.7 %) as compared to the core U4 (4.0-6.3 %) from the estuary head indicating that relatively heavy Fe-oxide particles are probably trapped in the reservoir upstream of the weir. Generally, the vertical profiles of Fe in other estuarine and coastal cores are devoid of any systematic features. Fe and Al co-vary in cores U23 and U35.

b) Distribution of minor elements

The cores U1 and U3 sustain high lithogenic concentration of Cr (450-602 µg/g) because of which it is difficult to conclude whether high concentrations observed in the inner estuary are natural or have anthropogenic component. Sharp intermediate peaks of abnormally high concentrations of Cr, Mn, Co, Ni and Zn in the profile of core U31 are probably due to enrichment with metallic particles such as Al-Si alloys as in the case of core B5. In cores U3, U31, U35 and U37, Cr concentration directly varies with that of Al with high correlation coefficient. Excellent positive correlations also occur between Cr and Fe in cores U1, U35 and U37. Cr and Co also vary linearly in cores U1, U4, U31 and U35.

The Mn profiles in cores U1 and U3 indicate its lithogenic concentration variable in the range 1224-2165 µg/g in sediment transported to the estuary. Mn is depleted in core U4 as compared to upstream and downstream cores. Mn directly varies with Fe in core U3; Ni and Pb in core B23; Co, Ni and Zn in core U31; Zn and Cd in core U34; Fe, Co and Cu in core U35; and Co in core U37.

Except for a few low values, the concentrations of Co are abnormally high in core U30 with peaks coinciding with those of Ni, Cu

and Zn. It is possible that this segment of the estuary receives very high input of these metals. The concentration of Co directly varies with that of Fe in core U1 and Zn in core U4. The profile of its concentration with depth in core U23 is in line with the variation of Fe and Ni with good linear relation. The concentration of Ni varies directly with that of Al and Zn in core U3; Cu and Zn in core U30 and core U31. The depth profiles of Cu are without any significant features in all cores from the Ulhas estuary. The concentration of Zn is high (603-833 $\mu\text{g/g}$) throughout the length in core U23 with a trend of decreasing concentration towards the surface. In this core the concentration of Zn varies directly with Al, Fe and Cu. Accumulation of Zn to high levels in certain sections is also evident in cores U30 and U31. The high concentration of Zn in the estuarine sediment is not reflected in elevated levels in the cores from the open coast.

The lithogenic baseline of Cd for the estuarine sediment is considered to be 0.3 $\mu\text{g/g}$. Its concentration in the sediment of the inner estuary has nearly doubled as compared to the baseline though the coastal cores seem to be free from anthropogenic Cd except for a few stray values. Similarly, the concentration of Pb in core U23 is about double that of the baseline. The depth profile of Pb in cores U34 and U35 also indicates increase in anthropogenic loading with the passage of time.

The concentration of P in cores U1 and U3, though variable, the average trend suggests the baseline concentration. The high concentrations of P in core U4 (average 5619 $\mu\text{g/g}$) indicates fast accumulation of P in only about 7 months from December to June in sediment at the estuary head.

c) EF and I_{geo}

The EF is as high as 30-40 for Cr, Co, Ni and Zn in core U30 while in cores U34, U35 and U37 the EF is below background level. I_{geo} for the cores reveals that the estuarine segment is moderately polluted, while, the sediment from the open-coast is unpolluted.

7.3 Metals in sediments off the northwest coast of India

The sediments at several transects upto a distance of 25 km from the shoreline along the northwest coast of India were studied for the distribution of metals and P. The silt-clay fraction constitutes more than 95 % of the surface sediment at all the stations.

7.3.1 Distribution of major metals

The concentration of Al at station 1 decreases from 9.2 % at station P1 attains minimum at station H1 (3.3 %) and subsequently increases down the coast with the value of 10.1 % off Ratnagiri. The profile of Al distribution at station 3 differs appreciably with respect to the one observed at station 1 with low concentration of the metal at station Du3 that increases southward attaining maximum (10.0 %) at station BY3. The high Al content of the nearshore and inner shelf sediments is probably associated with the fine-grained terrigenous material particularly clays. The overall trend of variation of Fe in coastal sediments indicates that the concentration increases southwards from Porbandar to Ratnagiri. When all the values are pulled (n=343) positive correlations at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Fe, Al:Ni, Al:Cu, Al:P, Fe:Cr, Fe:Ni, Fe:Cu, Fe:P, Mn:Cu, Cr:Ni, Cr:Cu, Cr:P, Ni:Cu, Ni:Zn, Ni:P, Cu:P, and Cd:P.

7.3.2 Distribution of minor elements

The average concentration of Cr seems to be uniform between Porbandar and Tarapur. Its relative average high concentrations at stations BS1, BY1, BS2 and BY2 may be due to high anthropogenic loading from industries and urban centres around Bassein-Mumbai. The distribution of Mn reveals a distinctive trend with concentrations increasing steadily southward upto about Bassein-Mumbai and then decreasing towards Ratnagiri. The concentration of Co varies in the range 17-88 µg/g in the sediment with the average concentration fairly uniform along the length. The trend of variation of the concentration of Ni in these sediments indicates a steady southerly increase. Baseline concentration

of Cu seems to be relatively low along the Gujarat coast and increases in the southerly direction. The average concentration of Zn is fairly uniform in the nearshore sediments of Gujarat and Maharashtra.

The Cd content of these sediments varies from 0.02 to 0.93 $\mu\text{g/g}$ and the overall trend indicates no abnormalities in its distribution. The Pb concentration in the west coast sediments is relative low and below 43 $\mu\text{g/g}$. This is by a factor of 5 lower than the concentrations which have been analysed in marine sediments from other coastal regions of the world. The distribution of P in sediments indicates a definite increase from north to south, as expected.

The overall trend of variation in concentrations of trace metals Cr, Co, Ni, Cu, Zn, Pb and Cd along the northwest coast of India indicates levels which can be explained based on the lithogenic component and there is no evidence for increase due to anthropogenic contributions.

7.4 Gulf of Kachchh

Because of its high biogeographical importance and rich flora and fauna, several areas along the southern Gulf are notified under MNP and MS. However, since nineties there is considerable industrial development along the Gulf with a potential to degrade marine ecology. Until the present studies, the published information on the distribution of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in the sediments of the Gulf was largely lacking.

The intertidal sediment of the Poshitra Bay is severely contaminated with SPM rich in carbonates, released through the effluent from a chemical industry at Mithapur. The concentration of CaCO_3 though variable, is uniformly high in cores (OD1, OD2, OD3) obtained from the area of effluent release indicating that the solids associated with the effluent have their signature upto the bottom of the cores. The cores OE and OG retrieved from the area away from the effluent channel clearly indicate a typical trend of low concentrations in the subsurface sections of

these cores. The distribution suggests that the effluent associated SPM is enriched with CaCO_3 as it is advected by the tidal currents due to preferential settling of constituents such as Fe_2O_3 , Al_2O_3 and SiO_2 which together constitute about 20-25 % of solids released through the effluent. From the distribution of excess CaCO_3 it is considered that the intertidal sediment atleast upto 5 km from the effluent channel is contaminated to a depth of 20-30 cm with effluent-associated SPM. Low concentrations of CaCO_3 in the subtidal sediment suggest minor transport of effluent associated SPM across the bay.

The concentrations of most metals are relatively low in cores from the intertidal area of the Positra bay as compared to their respective concentrations in core VN16 from Vadinar area due to dilution by CaCO_3 .

Sikka-Vadinar region is relatively industrialised and with the setting-up of refineries at Moti Khavdi and Vadinar, the developmental activities have accelerated in recent years. The concentrations of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in surficial sediment off Sikka and Vadinar are low even at the effluent release sites of the refineries. The trace metal content of surficial sediment off Bedi, Kandla Creek, off Mundra and Kori Creek is largely lithogenic with no evidence from anthropogenic accumulation.

Since, the sediment along the northern shores of the Gulf is sourced largely from the outflow of the Indus transported into the Gulf and as significant north-south transport is considered minor, it was interesting to investigate whether there were differences in the metal composition of sediments of the two shores of the Gulf. Data presented in this Thesis reveal the absence of marked difference in the concentrations of metals and P in sediments between the northern and the southern shores of the Gulf. This suggests that the source rocks from which the Gulf sediment is derived perhaps have comparable lithology.

7.5 Overall assessment

The concentrations of trace metals and P in the sediment of the Gulf probably represents the baseline and will be useful for future comparisons to assess anthropogenic influences. These concentrations compare well with the baseline established for the Mumbai-Bassein region based on dated cores.

When all the values are pulled (n=451) positive correlations at the level of significance of 0.001 are evident for the pairs Al:Cr, Al:Mn, Al:Fe, Al:Co, Al:Ni, Al:Cu, Al:Zn, Cr:Mn, Cr:Fe, Cr:Co, Cr:Ni, Cr:Cu, Cr:Zn, Mn:Fe, Mn:Ni, Mn:Cu, Mn:Zn, Fe:Co, Fe:Ni, Fe:Cu, Fe:Zn, Co:Cu, Co:Zn, Ni:Cu, Ni:Zn, Ni:Cd, Cu:Zn, and Zn:P.

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SYNOPSIS

Heavy metal burden in coastal marine sediments of northwest coast of India in relation to pollution

Human activities in the marine zone of India are mainly confined to the inner shelf where water depths are <50 m. Considering the vastness of the coastal area, the data on contaminants including metals in seawater, marine sediments and biota is scanty. Of these, Mumbai-Bassein region that is highly urbanized and industrialized has received relatively greater attention though exhaustive studies in recent years have been missing.

The research scheme for the Thesis was planned (i) to establish the baseline concentrations of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in sediments of the drainage basin of the Mumbai region, (ii) to assess the present load of sewage-associated trace metals and P to the marine environment of Mumbai, (iii) to evaluate seasonal changes in metals and P in the Thane Creek-Mumbai Harbour (Hereinafter referred as Bay) sediments in relation to high monsoon-derived lithogenic flux, (iv) to investigate spatial heterogeneity in distribution of the metals if any, in the sediment of Docks and Bunders, of the Mumbai Port, (v) to examine whether the Bay is a passive link between the anthropogenic metals and the coastal Arabian Sea or a sink for trace metals, (vi) to quantify anthropogenic fraction of trace metals and P in the sediments of the Bay and the Ulhas estuary based on Enrichment Factor (EF) and Index of Geoaccumulation (I_{geo}), (vii) to assess the fraction of bio-available Cr, Mn, Fe, Cu and Zn in selected surface and core sediments of the Bay, (viii) to identify trends in distribution of metals and P in nearshore sediments of the northwest coast of India between Porbandar and Ratnagiri, and (ix) to establish levels of metals and P in the sediments of the fast-industrializing biorich Gulf of Kachchh. The Thesis is presented in 8 Chapters as follows:

Chapter 1 briefly describes the general characteristics of metals and their distribution, behaviour and fate in different components of the marine environment with particular emphasis on the coastal region of India. The bases of selection of the topic of this Thesis and the research schemes undertaken during the course of the study are particularly addressed in this Chapter.

Chapter 2 includes the methods of collection, storage and analyses of surface and core sediment as well as sewage, and quality control of the emerging results. Analytical methods were critically assessed and precision and accuracy of these methods are recorded. The protocols followed for estimating the history of clay accumulation as preserved in sediment cores from Thane Creek and coastal Arabian Sea off Mumbai through ^{210}Pb technique, are listed. Sequential extraction method of Cr, Mn, Fe, Cu, and Zn in selected sediment samples aimed at identifying different phases in which these metals could exist in the sediment matrix is also included in this Chapter.

Chapter 3 is devoted for comprehensive discussion on metals and P in sediment of the Bay and adjacent coastal area to assess increase if any due to antropogenic additions. For this assessment concentrations of metals and P in rock and soil in the Mumbai catchment as well as those in marine sediments deposited prior to significant urbanization and industrialization of Mumbai are considered as a possible base for assessment in terms of EF and I_{geo} . Loads entering the marine zone of Mumbai through sewage to different water bodies and their influence on the metal content of sediments are examined. Seasonal changes in concentration of metals in surface sediments of the Bay are discussed in terms of the lithogenic flux associated with the monsoon runoff. Bioavailability of trace metals from sediments of the Bay is assessed based on their speciation in sediments derived through selective leaching experiments.

Chapter 4 is exclusively devoted to quantification of enrichment of trace metals and P in surface and core sediments from the polluted Ulhas estuary and adjacent Arabian Sea. The spatial and temporal distribution of metals in sediments is discussed in light of anthropogenic loadings in the inner estuary and the prevailing estuarine hydrography. EF and I_{geo} calculated based on dated sediment cores have been used to quantify the extent of sediment contamination by anthropogenic metals.

Chapter 5 addresses the temporal and spatial distribution of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in surface sediments along the northwest coast of India between Porbandar and Ratnagiri upto a distance of 25 km from the shoreline at several pre-decided transects. The emerging trends are discussed based on the available literature and lithogenic flux to the coastal area.

Chapter 6 assesses the concentrations of metals and P in marine segments adjacent to industrial and port developments along the coast of the Gulf of Kachchh – an area of high biodiversity and several protected marine zones. Metal distribution profiles in surface and column sediments of the intertidal area of the Positra Bay are examined in terms of the level of contamination of sediment by suspended load, rich in calcium carbonate, associated with the effluent of a chemical industry. Metal concentrations in sediments of the northern and southern shores of the gulf are discussed in light of the reported dynamic north – south barrier for sediment transport across the Gulf.

Chapter 7 summarizes the work presented in the Thesis and briefly discusses the findings emerging from the studies.

Chapter 8 compiles the bibliographic information for the literature referred in the Thesis.

Appendix-I (a) : Correlation coefficient (r) and level of significance (p) of metals and P in sewage (All values, n=76)																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Cr	0.08	>0.1																		
Mn	-0.01	>0.1	0.07	>0.1																
Fe	0.24	>0.05	0.23	>0.05	0.28	>0.01														
Co	0	-	-0.1	>0.1	0.01	>0.1	-0.1	>0.1												
Ni	0.15	>0.1	0.44	<0.001	-0	>0.1	0.22	>0.05	-0.1	>0.1										
Cu	0.08	>0.1	0.29	>0.01	-0	>0.1	0.16	>0.1	-0.1	>0.1	0.84	<0.001								
Zn	0.2	>0.05	0.27	>0.02	-0.1	>0.1	0.17	>0.1	-0	>0.1	0.52	<0.001	0.57	<0.001						
Cd	-0.18	>0.1	0.1	>0.1	0.23	>0.05	0.05	>0.1	0.64	<0.001	-0	>0.1	0.02	>0.1	-0.02	>0.1				
Pb	0.22	>0.05	0.26	>0.02	-0.1	>0.1	0.4	<0.001	-0.1	>0.1	0.8	<0.001	0.86	<0.001	0.56	<0.001	0.13	>0.1		
P	0.52	<0.001	0.25	>0.02	-0	>0.1	0.51	<0.001	-0.1	>0.1	0.32	>0.001	0.22	>0.05	0.25	>0.05	-0.05	>0.1	0.26	>0.02

Appendix-I (b): Correlation coefficient (r) and level of significance (p) of some metals in sewage of individual pumping station

Bhandup (n=8)																				
Cr	0.52	>0.1																		
Mn	0.03	>0.1	-0.2	>0.1																
Fe	0.34	>0.1	-0.4	>0.1	-0.1	>0.1														
Co	0.69	>0.02	0.9	<0.001	-0.1	>0.1	-0.4	>0.1												
Ni	0.65	>0.02	0.91	<0.001	0.16	>0.1	-0.3	>0.1	0.85	>0.001										
Cu	0.8	>0.001	0.79	>0.001	0.1	>0.1	0.04	>0.1	0.79	>0.001	0.85	>0.001								
Zn	0.86	>0.001	0.4	>0.1	0.35	>0.1	0.45	>0.1	0.44	>0.1	0.63	>0.02	0.79	>0.001						
Cd	0.8	>0.001	-0.5	>0.1	0.93	<0.001	0.92	<0.001	0.81	>0.001	-0.2	>0.1	0.79	>0.01	0.88	<0.001				
Pb	-0.67	>0.02	0.88	<0.001	-0.5	>0.1	-0.3	>0.1	0.81	>0.001	0.59	>0.05	0.48	>0.1	-0.4	>0.1	0.08	>0.1		
P	0.56	>0.05	-0.2	>0.1	0.15	>0.1	0.72	>0.01	0.06	>0.1	-0.1	>0.1	0.52	>0.1	0.52	>0.1	0.92	<0.001	-0.42	>0.1
Ghatkopar (n=10)																				
Cr	0.13	>0.1																		
Mn	0.14	>0.1	-0.3	>0.1																
Fe	0.41	>0.1	0.08	>0.1	-0.1	>0.1														
Co	-0.03	>0.1	0.09	>0.1	0.38	>0.1	-0.5	>0.05												
Ni	0.18	>0.1	0.7	>0.01	0.09	>0.1	0.44	>0.1	-0.1	>0.1										
Cu	0.28	>0.1	0.28	>0.1	-0.2	>0.1	0.96	<0.001	-0.5	>0.1	0.46	>0.1								
Zn	0.38	>0.1	0.42	>0.1	-0.1	>0.1	0.51	>0.05	-0.3	>0.1	0.7	>0.01	0.28	>0.1						
Cd	0.19	>0.1	0.8	>0.001	-0.2	>0.1	0.32	>0.1	0.86	<0.001	0.45	>0.1	0.59	>0.02	0.38	>0.1				
Pb	0.94	<0.001	-0.2	>0.1	0.18	>0.1	0.95	<0.001	0.25	>0.1	0.01	>0.1	0.42	>0.1	0.98	<0.001	0.43	>0.1		
P	0.53	>0.05	-0.1	>0.1	-0.1	>0.1	0.82	>0.001	-0.1	>0.1	0.08	>0.1	0.3	>0.1	0.3	>0.1	0.66	>0.01	0.93	<0.001
Colaba (n= 8)																				
Cr	0.16	>0.1																		
Mn	0.73	>0.01	0.03	>0.1																
Fe	0.18	>0.1	-0.4	>0.1	-0	>0.1														
Co	-0.05	>0.1	0.91	<0.001	-0.2	>0.1	-0.1	>0.1												
Ni	0.79	>0.001	0.04	>0.1	0.54	>0.1	0.06	>0.1	0.06	>0.1										
Cu	-0.6	>0.05	-0.3	>0.1	-0.6	>0.02	0.52	>0.1	0.45	>0.1	-0.5	>0.1								
Zn	-0.48	>0.1	-0.5	>0.1	-0.3	>0.1	-0.4	>0.1	-0.3	>0.1	-0.1	>0.1	0.08	>0.1						
Cd	-0.73	>0.01	-1	<0.001	-0.6	>0.05	-0.6	>0.05	-0.3	>0.1	-0.6	>0.05	0.49	>0.1	0.36	>0.1				
Pb	0.84	>0.001	1	<0.001	0.78	>0.001	0.83	>0.001	0	0	0.49	>0.1	-0.7	>0.02	-0.68	>0.02	-0.93	<0.001		

Appendix I-(b): (Contd..2)																				
Colaba (n= 8)																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
P	0.69	>0.02	0	0	0.51	>0.1	0.25	>0.1	0.16	>0.1	0.57	>0.05	-0.2	>0.1	-0.2	>0.1	-0.97	<0.001	0.98	<0.001
Colaba (n= 8)																				
Cr	-0.38	>0.1																		
Mn	-0.13	>0.1	0.25	>0.1																
Fe	-0.11	>0.1	0.38	>0.1	0.3	>0.1														
Co	0.19	>0.1	-0.4	>0.1	0.23	>0.1	0.6	>0.5												
Ni	-0.08	>0.1	0.38	>0.1	-0.1	>0.1	0.26	>0.1	-0.3	>0.1										
Cu	-0.32	>0.1	0.48	>0.1	-0.1	>0.1	0.56	>0.05	0.01	>0.1	0.73	>0.01								
Zn	0.07	>0.1	-0	>0.1	-0.3	>0.1	0.91	<0.001	0.67	>0.02	0.16	>0.1	0.44	>0.1						
Cd	-0.36	>0.1	0.24	>0.1	0.06	>0.1	0.87	>0.001	0.95	<0.001	0.28	>0.1	1	<0.001	0.95	<0.001				
Pb	0.7	>0.02	0.56	>0.05	0.94	<0.001	0.63	>0.05	0.56	>0.05	0.99	<0.001	0.46	>0.1	0.66	>0.02	0.4	>0.1		
P	0.71	>0.02	0.17	>0.1	0.02	>0.1	0.46	>0.1	0.23	>0.1	0.44	>0.1	0.42	>.1	0.42	>0.1	0.14	>0.1	0.96	<0.001
Dharavi (n=8)																				
Cr	0.03	>0.1																		
Mn	0.54	>0.05	-0.2	>0.1																
Fe	0.1	>0.1	-0.2	>0.1	0.87	>0.001														
Co	0.42	>0.1	0.84	>0.001	0.01	>0.1	-0.4	>0.1												
Ni	0.26	>0.1	-0.1	>0.1	0.66	>0.02	0.27	>0.1	0.17	>0.1										
Cu	-0.5	>0.1	0.04	>0.01	0.37	>0.1	0.61	>0.05	-0.4	>0.1	0.38	>0.1								
Zn	0.68	>0.02	0.42	>0.1	0.42	>0.1	-0.2	>0.1	0.52	>0.1	0.3	>0.1	-0	>0.1						
Cd	-0.07	>0.1	0.33	>0.1	-0.2	>0.1	-0.4	>0.1	0.3	>0.1	0.83	>0.001	-0.1	>0.1	-0.05	>0.1				
Pb	0.52	>0.1	0.4	>0.1	0.5	>0.1	0.57	>0.05	0.69	>0.02	0.49	>0.1	-0.5	>0.1	-0.51	>0.1	0.56	>0.05		
P	0.51	>0.1	0.13	>0.1	0.6	>0.05	0.54	>0.1	0.38	>0.1	0.31	>0.1	0.02	>0.1	0.02	>0.1	0.18	>0.1	0.91	<0.001
Worli (n=8)																				
Cr	-0.24	>0.1																		
Mn	0.52	>0.1	0.41	>0.1																
Fe	0.13	>0.1	0.72	>0.01	0.89	<0.001														
Co	0.21	>0.1	-0.2	>0.1	0.18	>0.1	0	0												
Ni	-0.33	>0.1	0.84	>0.001	0.43	>0.1	0.69	>0.02	-0.4	>0.1										
Cu	-0.48	>0.1	0.77	>0.001	0.32	>0.1	0.61	>0.05	-0.2	>0.1	0.81	>0.001								
Zn	0.12	>0.1	0.34	>0.1	0.75	>0.001	0.76	>0.01	0.59	>0.05	0.24	>0.1	0.27	>0.1						
Cd	-0.02	>0.1	0.77	>0.001	0.56	>0.05	0.78	>0.001	0.88	<0.001	0.04	>0.1	0.19	>0.1	0.96	<0.001				
Pb	0.97	<0.001	-0.3	>0.1	0.94	<0.001	0.79	>0.001	0.1	>0.1	0.79	>0.001	-0.5	>0.1	0.45	>0.1	0.24	>0.1		
P	0.32	>0.1	0.38	>0.1	0.76	>0.01	0.86	>0.001	0.18	>0.1	0.32	>0.1	0.51	>0.1	0.51	>0.1	0.44	>0.1	0.96	<0.001
Versova (n=8)																				
Cr	0.73	>0.01																		
Mn	0.59	>0.05	0.27	>0.1																
Fe	-0.27	>0.1	-0.2	>0.1	0.32	>0.1														
Co	0.85	>0.001	0.44	>0.1	0.65	>0.02	0.05	>0.1												
Ni	0.37	>0.1	0.13	>0.1	0.55	>0.05	0.16	>0.1	0.57	>0.05										
Cu	-0.08	>0.1	0.49	>0.1	0.13	>0.1	0.16	>0.1	-0.2	>0.1	-0	>0.1								
Zn	0.22	>0.1	0.71	>0.02	0.3	>0.1	0.06	>0.1	-0	>0.1	0.04	>0.1	0.94	<0.001						
Cd	0.5	>0.1	-0.6	>0.05	0.73	>0.01	0.61	>0.05	0.49	>0.1	0.89	<0.001	0.89	<0.001	0.66	>0.02				

Appendix-I (b): (Contd..3)																				
Versova (n=8)																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Pb	-0.55	>0.05	0.58	>0.05	-0.1	>0.1	0.47	>0.1	-0.7	>0.02	-0.3	>0.1	0	0	0.79	>0.001	0.06	>0.1		
P	0.55	>0.5	0.33	>0.1	0.84	>0.001	0.13	>0.1	0.36	>0.1	0.28	>0.1	0.34	>0.1	0.34	>0.1	0.7	>0.02	0.4	>0.1
Malad (n=7)																				
Cr	-0.07	>0.1																		
Mn	-0.18	>0.1	-0.8	>0.01																
Fe	-0.01	>0.1	0	0	-0.5	>0.1														
Co	-0.12	>0.1	-0.4	>0.1	0.65	>0.05	-0.7	>0.02												
Ni	0.29	>0.1	0.05	>0.1	-0.7	>0.05	0.91	<0.001	-0.6	>0.05										
Cu	0.58	>0.1	-0.3	>0.1	-0.4	>0.1	0.75	>0.01	-0.5	>0.1	0.89	>0.001								
Zn	0.04	>0.1	0.78	>0.01	-0.9	<0.001	0.56	>0.1	-0.7	>0.02	0.54	>0.1	0.22	>0.1						
Cd	-0.92	<0.001	0.91	<0.001	-0.9	<0.001	-0.3	>0.1	0.02	>0.1	-0.9	>0.001	-0.9	<0.001	0.95	<0.001				
Pb	-1	<0.001	1	<0.001	-1	<0.001	-0.7	>0.05	-0.3	>0.1	-1	<0.001	-1	<0.001	1	<0.001	0.94	<0.001		
P	0.73	>0.02	-0.4	>0.1	-0.2	<0.1	0.55	>0.1	-0.4	>0.1	0.74	>0.02	0.08	>0.1	0.08	>0.1	-0.96	<0.001	-1	<0.001

Appendix-I (c): (Contd..2)		February 2002 (n=8)																			
		Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
		r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Zn		-0.2	>0.1	0.2	>0.1	-0.4	>0.1	-0.3	>0.1	-0.5	>0.1	0.07	>0.1	-0.1	>0.1						
P		0.61	>0.05	-0.1	-	-0.7	-	0.59	>0.05	-0.9	-	0.52	>0.1	0.6	>0.05	0.26	>0.1				
May 2002 (n=8)																					
Cr		-0.41	>0.1																		
Mn		-0.24	>0.1	-0.7	>0.02																
Fe		0.93	<0.001	-0.6	>0.05	-0.2	>0.1														
Co		-0.2	>0.1	-	-	0.18	>0.1	-0.1	>0.1												
Ni		-0.48	>0.1	-0.6	>0.05	-0.1	>0.1	-0.3	>0.1	-											
Cu		0.63	>0.05	-1	<0.001	-0.2	>0.1	0.45	>0.1	-0.9	>0.001	0.84	>0.001								
Zn		0.88	<0.001	-1	<0.001	-0.3	>0.1	0.9	<0.001	0.13	>0.1	0.12	>0.1	0.65	>0.02						
P		0.52	>0.1	-1	<0.001	-0.2	>0.1	0.44	>0.1	-0.9	<0.001	0.19	>0.1	0.49	>0.1	0.68	>0.02				
February 2005 (n=11)																					
Cr		0.23	>0.1																		
Mn		-0.44	>0.1	-0.1	>0.1																
Fe		0.65	>0.01	0.34	>0.1	-0.3	>0.1														
Co		-0.28	>0.1	-0.3	>0.1	0.39	>0.1	-0.3	>0.1												
Ni		-0.07	>0.1	0.89	<0.001	-0.2	>0.1	0.09	>0.1	-0.2	>0.1										
Cu		-0.06	>0.1	0.89	<0.001	-0.2	>0.1	0.11	>0.1	-0.2	>0.1	1	<0.001								
Zn		0.1	>0.1	0.53	>0.05	0.12	>0.1	0.19	>0.1	-0.1	>0.1	0.58	>0.02	0.56	>0.02						
Cd		-0.3	>0.1	0.12	>0.1	0.32	>0.1	-0.4	>0.1	0.77	>0.001	0.18	>0.1	0.18	>0.1	-0.06	>0.1				
Pb		-0.07	>0.1	0.94	<0.001	-0.5	>0.1	0.08	>0.1	-0.3	>0.1	0.95	<0.001	0.95	<0.001	0.59	>0.02	0.04	>0.1		
P		0.84	<0.001	0.41	>0.1	-0.5	>0.1	0.72	>0.001	-0.5	>0.05	0.15	>0.1	0.17	>0.1	0.22	>0.1	-0.34	>0.1	0.18	>0.1
March 2005 (n=11)																					
Cr		0.38	>0.1																		
Mn		-0.66	>0.01	-0.2	>0.1																
Fe		0.95	<0.001	0.33	>0.1	-0.6	>0.02														
Co		-0.49	>0.05	-0.4	>0.1	0.39	>0.1	-0.4	>0.1												
Ni		0.3	>0.1	0.81	<0.001	-0.3	>0.1	0.36	>0.1	-0.3	>0.1										
Cu		0.17	>0.1	0.87	<0.001	-0.2	>0.1	0.21	>0.1	-0.2	>0.1	0.92	<0.001								
Zn		0.19	>0.1	0.62	>0.02	-0.2	>0.1	0.29	>0.1	-0.1	>0.1	0.82	<0.001	0.89	<0.001						
Cd		-0.51	>0.05	-0.2	>0.1	0.48	>>0.05	-0.4	>0.1	0.93	<0.001	-0.2	>0.1	-0.1	>0.1	-0.18	>0.1				
Pb		0.79	>0.001	-0.1	>0.1	-0.8	>0.001	0.77	>0.001	-0.9	<0.001	0.43	>0.1	-0.7	>0.001	-0.75	>0.001	0.31	>0.1		
P		0.9	<0.001	0.45	>0.1	-0.6	>0.02	0.82	<0.001	-0.5	>0.05	0.41	>0.1	0.18	>0.1	0.11	>0.1	-0.5	>0.05	0.28	>0.1
April 2005 (n=11)																					
Cr		0.61	>0.02																		
Mn		0.05	>0.1	0.22	>0.1																
Fe		0.8	>0.001	0.29	>0.1	-0.3	>0.1														
Co		0.08	>0.1	-0.3	>0.1	0.28	>0.1	0.14	>0.1												
Ni		0.54	>0.05	0.81	<0.001	0.28	>0.1	0.15	>0.1	-0.5	>0.05										
Cu		0.51	>0.1	0	0	-0.3	>0.1	0.79	>0.001	0.31	>0.1	-0.1	>0.1								
Zn		0.97	<0.001	0.61	>0.02	0.19	>0.1	0.77	>0.001	0.06	>0.1	0.61	>0.02	0.44	>0.1						
Cd		0.28	>0.1	0.11	>0.1	-0.1	>0.1	0.38	>0.1	0.26	>0.1	0.24	>0.1	0.57	>0.02	0.31	>0.1				
Pb		0.97	<0.001	0.52	>0.05	-0.1	>0.1	0.79	>0.001	0.32	>0.1	0.4	>0.1	0.57	>0.02	0.89	<0.001	0.49	>0.05		
P		0.49	>0.05	0.19	>0.1	-0.4	>0.1	0.51	>0.5	-0.2	>0.1	0.07	>0.1	0.25	<0.1	0.4	>0.1	-0.29	>0.1	0.43	>0.1

Appendix-II (a): Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%), dry wt) in subtidal sediment of the Bay during post- and pre-monsoon.																			
Station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	Station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
1996 (April)										1999 (March)									
B1	-	-	-	-	-	-	-	-	-	B1	6.7	403	1026	7.6	59	105	152	207	1672
B2	7.6	217	702	6.4	41	99	161	160	-	B2	-	-	-	-	-	-	-	-	-
B3	-	-	-	-	-	-	-	-	-	B3	-	-	-	-	-	-	-	-	-
B4	-	-	-	-	-	-	-	-	-	B4	-	-	-	-	-	-	-	-	-
B5	-	-	-	-	-	-	-	-	-	B5	7.9	312	939	7.8	59	96	133	150	1370
B6	7.7	96	789	6.4	40	80	105	76	-	B6	8.2	286	711	7.9	62	87	111	107	1013
B7	7.7	107	689	6	40	81	108	73	-	B9	6.9	255	956	7.8	58	82	116	118	1371
B23	7.5	115	660	5.8	40	80	104	75	-	B23	7.2	237	911	7.5	58	87	114	101	1207
B24	7.6	123	763	5.9	42	79	117	93	-	B24	-	-	-	-	-	-	-	-	-
B25	7.4	132	724	6.2	41	77	105	70	-	B25	-	-	-	-	-	-	-	-	-
1998 (April- May)										2000 (October)									
B1	7.3	127	1349	7.5	51	84	123	192	2244	B1	10	515	1095	8	57	-	171	321	1837
B2	7.3	121	758	7.3	48	83	122	232	1769	B2	-	-	-	-	-	-	-	-	-
B3	7.6	127	933	7.7	52	83	119	215	1636	B3	-	-	-	-	-	-	-	-	-
B4	7.6	149	907	7.7	54	92	126	279	1710	B4	-	-	-	-	-	-	-	-	-
B5	6.8	166	1183	7.3	53	90	122	178	1524	B5	10	335	1044	7	53	-	131	182	1486
B6	6.5	183	965	7.5	55	92	103	129	1023	B6	9	277	962	6	51	-	115	139	1431
B9	8.4	130	925	7.7	44	97	109	111	1312	B9	9	273	947	6	49	-	118	171	1816
B23	6.1	179	927	7.6	54	93	100	115	1189	B23	9	246	899	7	49	-	108	128	1409
B24	7.1	156	820	7.6	53	86	112	144	1102	B24	8.5	213	826	7.8	55	81	112	127	1083
B25	6.6	147	917	7.4	53	81	105	122	1088	B25	8.4	194	810	7.6	53	78	111	108	1084

Appendix-II (b): Concentration of selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%), dry wt) in subtidal sediments																			
of the Bay during Post- and Pre-monsoon																			
Station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	Station	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
1996 (November-December) (post-monsoon)										1997 (May- june) (pre-monsoon)									
B7	8.2	147	1090	7.7	44	93	109	117	1507	B7	81	205	773	-	56	83	105	170	771
B11	8	103	1050	7.8	44	92	104	111	1279	B11	8	201	955	-	55	80	110	128	455
B12	8.4	130	925	7.7	44	97	109	111	1312	B12	7.8	200	951	-	57	79	108	102	895
B13	7.4	141	990	7.6	45	96	105	117	1615	B13	7.9	162	823	-	52	79	105	115	509
B14	7.5	104	1019	7.7	43	92	105	110	1352	B14	8	151	858	-	52	74	102	107	818
B15	7.8	170	1075	7.9	47	96	95	119	1425	B15	8.3	183	799	-	54	87	143	217	1255
B16	9.7	187	1294	8.4	50	103	115	109	1330	B16	7.3	147	938	7.3	52	80	107	108	1006
B19	-	-	-	-	-	-	-	-	-	B19	7.1	151	920	7.1	52	75	107	120	922
B20	7.5	158	1231	7.5	44	84	113	92	1540	B20	7.9	196	1040	6.1	53	83	102	110	986
B21	-	-	-	-	-	-	-	-	-	B21	7.2	179	920	7.7	53	80	107	107	1380
B22	-	-	-	-	-	-	-	-	-	B22	7.3	185	988	7.4	52	76	107	100	1829
B23	-	-	-	-	-	-	-	-	-	B23	6.3	182	1291	6.2	51	68	85	76	842
B26	4.2	77	1126	4.1	32	51	49	90	1191	B26	4.4	142	1062	-	51	49	75	92	850

Appendix-II(c): (Contd..2)																
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
2000 (October) subtidal (n=7)																
Cu	0.79	>0.01	0.97	<0.001	0.82	>0.001	0.81	>0.001	0.68	>0.02	-	-				
Zn	0.8	>0.001	0.98	<0.001	0.84	>0.001	0.31	>0.1	0.57	>0.1	-	-	0.99	<0.001		
P	0.7	>0.02	0.75	<0.01	0.81	>0.001	-0.32	>0.1	-0.1	>0.1	-	-	0.65	>0.05	0.8	>0.01
1996 (November-December) subtidal (Post-monsoon) (n=9)																
Cr	0.73	>0.01														
Mn	0.12	>0.1	0.46	>0.1												
Fe	0.94	<0.001	0.69	>0.01	-0.01	>0.1										
Co	0.94	<0.001	0.83	>0.001	0.16	>0.1	0.96	<0.001								
Ni	0.94	<0.001	0.68	>0.02	-0.12	>0.1	0.98	<0.001	0.95	<0.001						
Cu	0.91	<0.001	0.64	>0.02	0.03	>0.1	0.95	<0.001	0.88	<0.001	0.9	<0.001				
Zn	0.6	>0.05	0.37	>0.1	-0.46	>0.1	0.68	>0.02	0.64	>0.02	0.77	>0.001	0.5	>0.1		
P	0.29	>0.1	0.54	>0.5	-0.01	>0.1	0.46	>0.1	0.45	>0.1	0.43	>0.1	0.54	>0.1	0.3	>0.1
1997 (May-June) subtidal (Pre-monsoon) (n=13)																
Cr	0.51	>0.05														
Mn	-0.61	>0.5	-0.02	>0.1												
Fe	0.09	>0.1	-0.44	>0.1	-0.75	>0.001										
Co	0.57	>0.2	0.75	>0.001	-0.44	>0.1	0.25	>0.1								
Ni	0.93	<0.001	0.54	>0.02	-0.54	>0.02	0.24	>0.1	0.55	>0.02						
Cu	0.77	<0.001	0.31	>0.1	-0.64	>0.1	0.73	>0.001	0.45	>0.05	0.81	<0.001				
Zn	0.5	>0.05	0.3	>0.1	-0.69	>0.001	0.41	>0.1	0.47	>0.05	0.56	>0.02	0.8	<0.001		
p	-0.03	>0.1	0.05	>0.1	0.05	>0.1	0.61	>0.01	-0.2	>0.1	0.11	>0.1	0.26	>0.1	0	>0.1
1996 (November-December) intertidal (Post-monsoon) (n=12)																
Cr	-0.3	>0.1														
Mn	-0.75	<0.001	0.48	>0.05												
Fe	-0.61	>0.02	-0.07	>0.1	0.31	>0.1										
Co	-0.76	<0.001	0.55	>0.02	0.85	<0.001	0.42	>0.1								
Ni	-0.42	>0.1	0.76	>0.001	0.51	>0.05	0.38	>0.1	0.55	>0.02						
Cu	0.63	>0.01	0.35	>0.1	-0.56	>0.02	-0.54	>0.02	-0.5	>0.05	0.17	>0.1				
Zn	0.72	<0.001	0.34	>0.1	-0.43	>0.1	-0.69	>0.001	-0.5	>0.05	0.14	>0.1	0.93	<0.001		
P	-0.24	>0.1	0.07	>0.1	0.28	>0.1	0.06	>0.1	0.08	>0.1	0.22	>0.1	0.04	>0.1	0	>0.1

Appendix-II(c): (Contd..3)																	
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	
1997 (May-June) intertidal(Pre-monsoon) (n=8)																	
Cr	0	-															
Mn	0.62	>0.05	0.18	>0.1													
Fe	0.5	>0.1	-0.02	>0.1	0.73	>0.01											
Co	0.12	>0.1	0.8	>0.001	-0.07	>0.1	-0.16	>0.1									
Ni	0	-	0.79	>0.001	-0.02	>0.1	-0.02	>0.1	0.57	>0.05							
Cu	0.4	>0.1	0.63	>0.05	0.51	>0.1	0.34	>0.1	0.24	>0.1	0.75	>0.01					
Zn	0.28	>0.1	0.06	>0.1	0.67	>0.02	0.65	>0.02	-0.5	>0.1	0.07	>0.1	0.62	>0.05			
p	0.44	>0.1	-0.16	>0.1	0.07	>0.1	-0.14	>0.1	-0.2	>0.1	0.28	>0.1	0.4	>0.1	0.2	>0.1	
1996 Docks (November-December) subtidal (Post-monsoon) (n=12)																	
Cr	-0.37	>0.1															
Mn	0.07	>0.1	-0.23	>0.1													
Fe	0.15	>0.1	-0.49	>0.1	0.49	>0.05											
Co	0.4	>0.1	-0.47	>0.1	0.51	>0.05	0.61	>0.02									
Ni	-0.6	>0.01	0.43	>0.1	0.23	>0.1	0.14	>0.1	-0.2	>0.1							
Cu	0.13	>0.1	0.25	>0.1	-0.23	>0.1	0.12	>0.1	0.14	>0.1	0.34	>0.1					
Zn	0.3	>0.1	-0.42	>0.1	-0.07	>0.1	0.55	>0.02	0.22	>0.1	-0.2	>0.1	0.03	>0.1			
P	-0.11	>0.1	0.09	>0.1	0.01	>0.1	0.1	>0.1	0.17	>0.1	0.46	>0.05	0.77	>0.001	-0.1	>0.1	
Docks 1997 (May-June) subtidal(Pre-monsoon) (n=12)																	
Cr	-0.01	>0.1															
Mn	0.01	>0.1	-0.73	>0.001													
Fe	0.38	>0.1	0.81	<0.001	-0.5	>0.05											
Co	0.16	>0.1	0.48	>0.05	-0.28	>0.1	0.6	>0.02									
Ni	-0.28	>0.1	-0.19	>0.1	0.2	>0.1	-0.03	>0.1	0.32	>0.1							
Cu	0.32	>0.1	0.02	>0.1	-0.06	>0.1	0.34	>0.1	0.62	>0.01	0.62	>0.01					
Zn	0.32	>0.1	0.35	>0.1	-0.66	>0.01	0.47	>0.05	0.58	>0.02	0.14	>0.1	0.6	>0.01			
p	0.2	>0.1	-0.24	>0.1	0.3	>0.1	0.16	>0.1	0.49	>0.05	0.84	<0.001	0.87	<0.001	0.3	>0.1	
Bunders 1996 (November-December) subtidal (Post-monsoon) (n=11)																	
Cr	0.55	>0.5															
Mn	0.08	>0.1	-0.43	>0.1													
Fe	0.5	>0.05	-0.14	>0.1	-0.2	>0.1											
Co	0.42	>0.1	0.42	>0.1	-0.12	>0.1	0.54	>0.05									
Ni	0.54	>0.05	0.21	>0.1	-0.42	>0.1	0.78	>0.001	0.68	>0.01							

Appendix-II(c): (Contd..4)																
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
	Bunders 1996 (November-December) subtidal (Post-monsoon) (n=11)															
Cu	-0.28	>0.1	0.43	>0.1	-0.12	>0.1	-0.31	>0.1	0.43	>0.1	0.08	>0.1				
Zn	-0.08	>0.1	0.49	>0.05	-0.21	>0.1	-0.02	>0.1	0.65	>0.01	0.37	>0.1	0.87	<0.001		
P	-0.07	>0.1	0.21	>0.1	0.14	>0.1	0.02	>0.1	0.21	>0.1	0.18	>0.1	0		-	0.4 >0.1
	1997 (May-June) subtidal(Pre-monsoon) (n=11)															
Cr	0.27	>0.1														
Mn	0.13	>0.1	-0.16	>0.1												
Fe	0.86	<0.001	0	>0.1	0.12	>0.1										
Co	-0.06	>0.1	-0.75	>0.001	-0.13	>0.1	-0.05	>0.1								
Ni	0.26	>0.1	-0.17	>0.1	-0.11	>0.1	0.17	>0.1	0.49	<0.1						
Cu	-0.06	>0.1	0.44	>0.1	-0.47	>0.1	-0.18	>0.1	-0.1	>0.1	-0.3	>0.1				
Zn	-0.07	>0.1	0.26	>0.1	-0.71	>0.001	-0.23	>0.1	0.29	>0.1	0.27	>0.1	0.69	>0.001		
p	-0.16	>0.1	0.19	>0.1	-0.57	>0.05	-0.51	>0.05	0.1	>0.1	-0.1	>0.1	0.23	>0.1	0.2	>0.1

Appendix-III-(a): (Contd..2)

Depth (cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Depth (cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
	Core B2												Core B24										
2	7.6	282	762	7.1	54	89	131	169	1.02	26.3	1210	5	6.2	179	1010	8.2	55	78	109	66	0.25	84.4	1581
3	7.9	313	747	7.5	55	93	135	188	-	-	1262	6	6.2	166	935	7.9	54	76	110	102	0.31	127	1573
4	8	307	772	7.7	55	96	136	185	0.89	72.7	1261	7	6.5	183	949	8.1	54	75	109	100	0.15	17.9	1492
5	7.7	291	904	7.2	53	93	134	175	0.85	95.7	1213	8	6.4	178	925	8.2	54	74	109	98	0.05	36.8	1537
6	7.9	312	871	7.7	55	98	137	164	0.61	135	1230	9	5.9	182	971	8.7	52	75	111	103	0.05	46.5	1560
7	8	346	902	7.8	56	95	138	160	0.58	137	1269	10	9.2	226	965	8.4	52	76	112	99	0.13	41.7	1590
8	8	293	912	7.6	54	95	135	146	0.24	112	1286	11	6.9	157	1058	8.1	52	77	112	86	0.15	129	1512
9	7.9	316	964	7.8	56	93	132	138	-	-	1295	12	7	184	1051	8.1	52	78	109	86	0.14	52.6	1530
10	8	293	870	7.7	55	88	130	137	0.19	159	1588	13	6.4	137	970	8	54	78	109	99	0.12	36.3	1756
11	8.1	267	939	7.6	53	92	131	160	0.26	160	1265	14	8	161	1020	8.3	54	78	110	111	0.05	19.8	1539
12	8	309	932	7.8	56	92	136	170	0.37	118	1289	15	6.2	211	1075	8.5	55	78	116	110	0.12	28.9	1496
13	7.9	313	926	7.6	56	95	142	198	0.69	133	1364	16	6	216	1153	8.6	58	79	129	148	0.27	44	1778
14	8	347	933	7.7	56	99	143	178	0.3	142	1311	17	6.3	163	1005	8.4	55	76	116	112	0.18	15.5	1550
15	7.8	302	917	7.5	55	96	140	181	0.28	318	1239	18	6.2	153	969	8.4	54	76	109	96	0.23	22.8	1563
16	8.1	350	906	8	58	103	145	218	0.28	156	1269	19	6.2	164	987	8.3	54	76	112	106	0.17	40.8	1649
17	8.3	341	837	8	59	103	147	200	0.38	192	1284	20	6.1	162	947	8.2	57	75	111	130	0.19	57.8	1602
18	8.3	348	853	8	58	104	144	192	0.29	170	1297	21	6.3	142	918	7.9	54	76	108	104	0.2	104	1662
19	8.2	354	858	8.2	58	104	147	197	0.45	166	1327	22	6.7	160	981	7.9	53	78	108	105	0.16	47.2	1522
20	7.9	326	958	7.8	56	96	144	156	0.37	171	1263	23	6.5	194	944	8	54	75	108	105	0.03	49.6	1536
21	8	315	910	7.6	56	98	137	166	0.11	139	1261	24	6.5	160	939	7.8	54	75	107	103	0.03	48.5	1517
22	8	325	949	7.7	56	98	141	157	0.27	158	1255	25	6.5	200	962	7.9	56	77	109	106	0.08	44.1	1575
23	8.4	332	975	8.1	56	100	137	170	0.51	142	1334	26	7.7	157	962	8	58	75	109	107	0.13	26.8	1618
24	8.4	340	926	8	57	101	140	162	0.32	131	1342	27	6.5	176	956	8.2	54	75	106	107	-	-	1503
25	8.4	335	952	7.8	57	96	137	138	0.07	128	1264	28	6.5	206	956	8	56	76	106	96	-	-	1527
26	8	328	904	7.7	56	99	138	134	0.04	137	1414	29	7	217	961	8	54	78	108	105	-	-	1550
27	8	318	896	7.6	57	99	135	140	0.22	57.8	1324	30	6.7	160	949	8.1	54	75	108	111	-	-	1499
28	8.6	341	786	7.9	58	97	131	119	0.31	22	1258	31	7	152	945	8	55	74	106	103	-	-	1552
29	8.7	349	777	8.2	58	100	134	117	0.2	107	1259	32	7.1	157	942	8.1	55	74	106	101	-	-	1953
30	8.6	326	804	7.8	57	95	129	117	0.24	18.8	1269	33	6.8	164	971	8	53	74	110	103	-	-	1739
31	8.8	339	721	8.1	59	108	136	112	0.19	113	1266	34	7.1	178	958	8.4	55	75	113	102	-	-	1666
32	8.8	340	718	8.1	60	109	137	133	-	-	1228	35	6.2	173	944	8.1	58	77	110	101	0.03	18.4	1761
33	8.9	331	729	8.1	59	111	135	128	0.09	130	1269	36	6.4	167	988	8.2	54	79	110	91	-	-	1563
34	8.7	335	772	8	58	106	129	116	0.25	18.3	1255	37	5.8	195	962	8.1	55	77	111	100	-	-	1678
35	7.9	344	794	7.6	58	99	124	116	0.23	16.8	1157	38	7.8	179	998	8.2	54	76	111	111	-	-	1626

Appendix-III-(a): (Contd..4)																								
Depth	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Depth	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P			
(cm)	Core B3											(cm)	Core B24											
19	8.2	181	797	7.2	54	86	112	108	0.31	17.7	1322	116	7.7	220	936	8.4	57	78	109	112	1486			
20	8.2	179	759	7.2	53	87	113	114	0.37	16.6	1337	118	8.6	213	960	8.1	57	76	109	114	1383			
21	8.3	165	838	7.5	53	82	113	116	0.32	17.6	1329	122	7.7	211	935	8.4	58	76	115	116	1480			
22	8.2	169	1022	7.6	53	87	110	119	0.06	-	1379	126	8.4	203	1011	8.5	57	82	114	119	1468			
23	7.3	176	1141	7.5	53	92	113	121	0.12	20.5	1329	130	8	195	994	8.9	54	76	110	115	1477			
24	7.7	178	964	7.6	53	92	115	120	0.6	21.4	1377	134	8	212	1038	8.3	55	74	109	122	1445			
25	7.9	173	845	7.5	55	87	112	118	0.19	26.5	1377	136	7	216	1143	8.1	56	66	110	120	1320			
26	8.2	180	887	7.7	53	90	118	126	0.41	23.1	1380	140	6.3	196	1102	7.5	54	61	96	109	1414			
27	8	254	914	7.6	53	87	111	114	0.28	30.5	1376	146	6.5	201	964	7.6	54	67	98	93	1330			
28	8.5	176	941	7.5	53	89	110	115	0.34	-	1348	148	7	189	1016	7.4	54	62	96	91	1177			
29	7.9	171	966	7.8	52	87	113	108	0.21	17.6	1375													
30	8.3	178	940	7.7	53	91	112	101	0.21	25.8	1358	1	9	166	878	7.2	54	71	47	79	-			
31	8.5	195	923	7.8	53	95	120	147	0.31	25.7	1369	2	8.9	170	876	7.3	54	73	43	101	-			
32	7.2	194	952	7.8	53	94	118	144	0.3	-	1364	3	8.9	167	912	7.4	53	74	47	80	-			
33	7.5	172	1031	7.6	53	91	112	99	0.23	18.7	1315	4	8.9	161	934	7.4	54	73	47	90	-			
34	8.3	164	1013	7.5	55	86	107	95	0.16	17.9	1307	5	8.7	169	911	7.4	57	71	48	105	--			
35	8.2	172	908	7.7	55	86	106	92	0.19	17.9	1373	6	9.1	159	854	7.5	58	68	49	88	-			
36	8.4	174	922	7.6	54	99	107	89	0.13	15.9	1231	7	8.8	173	839	7.7	59	70	49	87	-			
37	8.5	162	939	7.8	53	89	106	90	0.07	21.4	1442	8	9.1	165	828	7.8	59	72	48	92	-			
38	8.5	177	901	7.8	53	90	109	95	0.11	14.9	1242	9	9.2	160	799	7.6	58	71	47	98	-			
39	8.4	172	880	7.8	54	89	107	86	0.07	16.3	1179	10	8.7	177	872	8.1	59	73	51	88	-			
40	8	166	899	7.7	54	87	107	85	0.16	16.3	1113	11	7.9	230	1221	9.9	69	79	71	127	-			
41	8.1	202	908	7.9	55	91	109	92	0.11	14.8	1124	12	9.3	168	851	7.8	59	75	51	109	-			
42	8.5	184	864	7.8	55	88	108	95	0.17	7.7	1198	13	9.5	167	872	7.9	59	74	52	261	-			
43	8.6	183	930	7.8	53	89	112	87	0.18	18.1	1197	14	9	164	834	7.7	58	75	51	102	-			
44	8.5	190	908	7.8	58	91	111	87	0.1	21.4	1331	15	9.3	154	832	7.6	57	72	50	107	-			
45	8.5	211	931	8.1	55	92	112	88	0.14	21.9	1093	16	9.6	163	816	7.6	60	74	48	105	-			
46	8.5	181	913	7.7	55	89	109	88	0.11	18	1213	17	9.4	155	838	7.6	60	74	45	104	-			
47	8.3	164	905	7.8	56	86	106	86	0.08	17.9	1265	18	8.6	141	865	7.3	58	69	49	95	-			
48	7.8	153	828	7.5	58	86	105	115	0.2	20.5	1069	19	8.7	132	836	7.5	59	68	49	93	-			
49	8.7	166	904	7.7	56	86	105	91	0.12	17.7	1175	20	8.8	135	829	7.5	60	69	48	97	-			
50	8.8	162	976	7.7	55	89	107	84	0.12	15.4	1164	21	9.3	133	807	7.1	49	69	47	90	-			
51	8.6	174	919	7.7	53	87	105	80	0.11	18.9	1182	22	9.1	127	842	7	51	65	45	92	-			
52	8.7	171	926	7.7	54	85	104	77	0.12	23.5	1164	23	9.7	146	834	7.4	51	69	44	98	-			

Appendix-III-(a): (Contd..6)																						
Depth (cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	-	Depth (cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn			
Core B4											Core B25											
29	7.4	151	1126	8.4	71	113	135	222	1658		66	6.5	123	759	6.6	50	66	40	96			
30	8	152	1177	8.6	70	108	137	235	1663		68	7.2	120	765	6.3	50	62	39	91			
31	8.4	113	1196	8.8	68	95	126	196	1776		70	7.4	116	749	6.5	50	63	38	98			
32	7.6	140	1192	8.4	70	102	128	227	1632		72	8.6	116	737	6.6	50	66	36	82			
											74	8	125	796	6.6	52	65	44	76			
1	13.1	2683	11952	12.8	1727	2388	111	4555	2808		76	7.9	115	743	6.5	51	63	41	82			
2	9.8	125	724	11.7	173	86	121	167	2033		78	7.1	113	782	6.5	52	65	38	110			
3	6.5	65	499	7.3	59	57	81	102	1128		80	7.5	121	737	6.6	50	63	39	99			
4	9.1	84	655	11.2	67	75	113	139	2622		82	7.7	116	742	6.4	50	63	38	81			
5	9.5	104	698	11.3	66	81	128	168	1790		84	7.3	128	684	6.5	51	64	40	111			
6	8.9	92	634	10.6	63	76	118	159	1707		86	7.8	122	741	6.4	51	65	35	82			
7	9	126	657	10.3	66	67	109	139	1755		88	7.1	115	729	6	49	61	38	113			
8	9.5	139	732	11	66	71	118	150	2123		90	5.8	101	767	5.5	47	50	33	79			
9	10.1	139	641	11.5	65	75	117	146	1980		92	6.1	108	739	5.5	48	52	31	66			
10	14.8	3270	15264	12	1915	2777	120	5510	2119		94	6	108	698	5.6	46	51	33	96			
11	8.7	81	535	9.6	120	59	68	224	1607		96	4.9	86	695	4.8	43	42	29	48			
12	9.2	99	649	10.6	67	76	158	151	1717		98	6.8	129	770	6.1	50	59	34	69			
13	9	84	670	10.6	65	81	119	172	1782		100	6.8	135	769	6.2	51	61	34	77			
14	4.9	53	384	5.3	46	41	66	159	923		102	6.9	139	776	6.2	51	60	38	106			
15	9	91	695	10.1	67	76	116	165	1825		104	7.9	145	729	6.5	51	64	36	73			
16	8.6	92	629	9.7	65	71	113	158	1745		106	5.1	150	856	5.9	50	54	35	62			
17	9.9	123	698	10.6	70	77	124	169	1920		108	5.9	139	765	5.7	48	55	33	72			
18	11.2	3308	13906	9.4	1984	2833	120	5231	1702		110	6	136	774	5.7	48	56	33	97			
19	11	2972	14109	11.7	1883	2664	126	4697	2087		112	6.9	134	758	5.8	51	57	33	76			
20	10.8	130	688	12.8	278	81	132	197	2280		114	6.8	141	711	6.3	53	63	35	127			
21	13.3	2846	13217	12.6	1732	2463	115	4549	2359		116	6.5	122	806	5.9	48	58	34	75			
22	10	3093	12812	9.5	1886	2701	114	5005	1638		118	6.9	126	776	6.1	51	60	34	79			
23	9	160	688	10.3	82	72	111	172	1861		120	5.7	139	833	5.8	49	56	32	79			
24	11.3	1423	15219	9	1901	2742	106	5101	1618		122	5.1	85	644	4.4	44	38	25	82			
25	7.8	1436	6522	8.8	1858	1928	107	3537	1635		124	4	74	625	3.8	43	28	19	47			
26	8.8	120	661	10.3	133	83	113	163	1772		126	5.1	84	648	4.7	46	41	27	69			
27	8.4	2451	10244	9.4	1990	2530	117	4536	1841		128	4.2	78	563	4.1	42	35	23	74			
28	8.3	159	684	9.6	104	102	112	163	1747		130	4.3	85	613	4.6	44	41	26	90			
29	8.6	103	634	10.2	92	78	109	157	1801		132	4.5	87	600	4.2	45	33	23	45			

Appendix-III-(a): (Contd..7)

Depth (cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	-	Depth (cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
Core B5											Core B25											
30	8.7	116	653	10.2	75	73	107	163	1797		134	4.1	76	496	3.7	43	31	20	34	-	-	-
31	10	89	618	12	69	84	114	165	2132		136	3.3	62	523	3.1	40	23	18	38	-	-	-
32	8.5	88	635	9.9	71	79	118	170	1750		138	4.7	70	779	4.1	41	36	44	78	-	-	-
33	9	79	553	9.5	76	73	118	163	1626		140	4.3	67	777	4.2	42	35	28	53	-	-	-
34	8.9	86	631	10	74	80	121	179	1736		142	4.8	82	782	4.3	43	37	29	47	-	-	-
35	9.8	97	584	10.9	74	82	124	181	1901		144	5.2	83	709	4.2	43	37	26	61	-	-	-
36	9.5	88	602	10.2	72	69	118	169	1797		146	5.6	83	750	4.1	43	34	28	83	-	-	-
37	8.9	85	646	10.4	67	69	110	153	1873		148	6	81	755	4.2	42	33	26	47	-	-	-
38	5.8	56	382	6.5	56	41	73	177	1673		150	5.2	63	758	4.2	43	34	26	47	-	-	-
39	9.3	106	580	11.2	61	53	93	125	2349		152	5	71	727	4.3	43	35	27	72	-	-	-
40	8.9	85	656	11	68	74	119	171	1971		154	4.6	68	738	4.1	43	33	27	86	-	-	-
41	7.1	55	325	7.1	24	35	72	123	1261		156	5	83	737	4.1	46	37	30	43	-	-	-
42	11.2	91	686	11	46	71	121	170	1966		158	5	70	758	4.1	45	34	28	52	-	-	-
43	10.9	80	627	10.4	45	75	123	180	1789		160	4.7	87	746	4.2	44	38	27	79	-	-	-
44	6.3	63	386	6.3	27	42	82	283	1105		162	4.8	82	725	4.1	44	37	28	99	-	-	-
45	11.1	141	676	10.6	49	76	122	123	1945		Core R5											
46	13.1	147	701	12.2	51	81	127	130	2239		1	7.1	153	346	5.6	35	66	65	61	0.25	16.9	1812
Core B6											2	7	168	360	5.7	37	69	69	62	-	-	1937
1	6.6	163	658	6.1	35	115	114	142	1024		3	7.6	155	363	5.8	36	69	69	58	-	-	1902
2	7.1	160	680	6.2	37	126	124	156	1147		4	7.6	158	354	5.9	37	71	71	55	-	-	1901
3	7.1	179	705	6.1	44	127	125	152	1143		5	7.8	164	352	5.9	37	69	69	66	0.31	11.4	1867
4	7	176	693	6.2	43	109	124	153	1169		6	7.4	165	356	5.8	36	68	68	54	0.49	11.1	2105
5	7.2	183	1011	6.5	56	124	129	256	1284		7	7.3	160	357	5.6	37	67	64	57	-	-	2179
6	7	166	701	6.4	47	126	123	152	1165		8	7.1	156	359	5.6	36	67	65	166	0.38	15.3	1987
7	7.3	194	881	6.3	47	129	129	156	1224		9	6.9	155	367	5.7	37	68	64	59	0.36	10.7	1975
8	6.7	168	674	6.3	40	114	126	135	1225		10	7.1	164	378	5.7	38	68	66	58	0.39	11.6	1948
9	7	193	733	6.4	45	149	134	159	1261		11	7.2	159	364	5.7	54	70	66	57	0.38	12.3	1941
10	6.5	215	696	6.5	39	127	127	197	1193		12	7.2	153	370	5.8	58	70	67	59	0.52	11	1969
11	6.9	155	696	6.6	41	98	117	127	1251		13	7.1	156	359	5.7	38	71	66	60	0.79	11.2	1980
12	6.8	151	676	6.5	47	90	117	152	1329		14	7	161	360	5.7	38	70	67	61	0.63	15.9	2129
13	6.7	167	676	6.5	48	125	125	138	1238		15	7.1	163	380	5.7	38	73	66	59	0.4	13.6	2201
14	6.9	182	673	6.4	51	124	128	147	1255		16	7.1	160	376	5.7	38	71	67	53	0.57	10	2120
15	6.8	167	662	6.4	46	123	134	155	1208		17	7	159	367	5.7	38	68	66	59	-	-	2101
16	6.8	180	716	6.4	48	127	129	153	1333		18	7.1	165	373	5.7	39	70	67	56	0.49	15.2	2075

Appendix-III (b) (Contd..2)																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
B4(n=32)																				
Zn	-0.09	>0.1	0.6	<0.001	-0.72	<0.001	-0.17	>0.1	0.31	<0.1	0.79	<0.001	0.95	<0.001						
P	0.48	<0.01	0.14	>0.1	0.39	<0.05	0.75	>0.001	0.15	>0.1	0.11	>0.1	0.11	>0.1	0.3	>0.1	-	-	-	-
B5(n=47)																				
Cr	0.59	<0.001																		
Mn	0.6	<0.001	0.97	<0.001																
Fe	0.83	<0.001	0.26	>0.1	0.24	>0.1														
Co	0.52	<0.01	0.96	<0.001	0.97	<0.001	0.2	>0.1												
Ni	0.55	<0.01	0.97	<0.001	0.99	<0.001	0.2	>0.1	0.99	<0.001										
Cu	0.68	<0.001	0.26	>0.1	0.24	>0.1	0.77	<0.001	0.22	>0.1	0.23	>0.1								
Zn	0.56	<0.001	0.97	<0.001	0.99	<0.001	0.2	>0.1	0.99	<0.001	1	<0.001	0.22	>0.1						
P	0.77	<0.001	0.35	<0.05	0.32	>0.05	0.89	<0.001	0.29	>0.1	0.3	>0.02	0.62	<0.001	0.3	>0.02	-	-	-	-
B6(n=39)																				
Cr	0.6	<0.001																		
Mn	0.1	>0.1	0.4	<0.01																
Fe	-0.2	>0.1	0.1	>0.1	-0.01	>0.1														
Co	0.3	0	0.3	<0.1	0.3	>0.05	0.13	>0.1												
Ni	0.5	<0.001	0.3	>0.1	-0.36	>0.01	0.09	>0.12	0.17	>0.1										
Cu	0.2	>0.1	0.2	>0.1	-0.18	>0.1	0.1	>0.1	0.36	>0.01	0.56	>0.001								
Zn	0.2	>0.1	0.3	>0.05	0.31	>0.05	0	-	0.4	>0.001	0.13	>0.1	0.42	>0.001						
P	0.3	<0.1	0.3	>0.05	0.28	>0.05	0.01	>0.1	0.26	>0.05	-0.2	>0.1	-0.1	>0.1	0.18	>0.1	-	-	-	-
B23(n=65)																				
Cr	0.46	<0.001																		
Mn	-0.25	<0.05	0.19	<0.1																
Fe	-0.41	<0.001	-0.76	<0.001	0.12	>0.1														
Co	0.21	<0.1	0.29	<0.02	0.28	<0.02	0	-												
Ni	0.06	>0.1	0.15	>0.1	0.04	>0.1	0.01	>0.1	0.34	<0.01										
Cu	0.17	>0.1	-0.1	>0.1	-0.14	>0.1	0.34	<0.01	0.22	<0.1	0.19	>0.1								
Zn	0.24	<0.05	0.58	<0.001	0.24	<0.05	-0.6	<0.001	0.11	>0.1	0.06	>0.1	0.31	<0.01						
Cd	-0.15	>0.1	0.12	>0.1	0.33	>0.001	0.29	>0.02	0.22	>0.05	0.26	>0.05	0.06	>0.1	0.13	>0.1				
Pb	-0.35	>0.001	0.27	>0.02	0.72	<0.001	0.17	>0.1	0.36	>0.001	0.16	>0.1	-0.1	>0.1	0.45	<0.001	0.54	<0.001		
P	0.16	>0.1	0.53	<0.001	0	-	-0.44	<0.001	0.18	>0.1	0.04	>0.1	-0.1	>0.1	0.28	<0.02	-0.18	>0.1	-0.14	>0.1
B24(n=81)																				
Cr	0.19	<0.1																		
Mn	0.14	>0.1	0.3	<0.01																
Fe	-0.12	>0.1	0.03	>0.1	0.11	>0.1														
Co	-0.04	>0.1	0.17	>0.1	0.09	>0.1	0.23	<0.05												
Ni	-0.12	>0.1	0.01	>0.1	-0.14	.01	0.55	<0.001	0.23	<0.05										
Cu	-0.05	>0.1	0.3	<0.01	0.45	<0.001	0.49	<0.001	0.37	<0.001	0.61	<0.001								
Zn	0.38	<0.001	0.03	>0.1	0.16	>0.1	-0.09	>0.1	0.23	<0.05	-0.12	>0.1	0.17	<0.1						
Cd	-0.38	<0.001	-0.27	>0.01	0.08	>0.1	0.22	>0.02	0.1	>0.1	0.14	>0.1	0.17	>0.1	-0.1	>0.1				

Appendix-III (b): (Contd..3)																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
B24(n=81)																				
Pb	-0.13	>0.1	-0.13	>0.1	-0.04	>0.1	-0.19	>0.05	-0.22	>0.02	0.12	>0.1	-0.1	>0.1	-0.2	>0.02	0.33	>0.001		
P	0.02	>0.1	-0.06	>0.1	0.04	>0.1	0.31	>0.001	0.01	>0.1	0.33	<0.001	0.28	<0.01	-0.1	>0.1	0.17	>0.1	-0.04	>0.1
B25(n=106)																				
Cr	0.77	<0.001																		
Mn	0.48	<0.001	0.8	<0.001																
Fe	0.93	<0.001	0.94	<0.001	0.71	<0.001														
Co	0.61	<0.001	0.9	<0.001	0.85	<0.001	0.91	<0.001												
Ni	0.87	<0.001	0.93	<0.001	0.72	<0.001	0.98	<0.001	0.85	<0.001										
Cu	0.82	<0.001	0.92	<0.001	0.8	<0.001	0.94	<0.001	0.86	<0.001	0.92	<0.001								
Zn	0.54	<0.001	0.57	<0.001	0.59	<0.001	0.64	<0.001	0.7	<0.001	0.71	<0.001	0.7	<0.001						
P	0.19	>0.05	0.32	>0.001	0.49	<0.001	0.21	>0.02	0.36	<0.001	0.31	>0.001	0.35	<0.001	0.3	>0.001	-	-	-	-
R5(n=63)																				
Cr	0.19	>0.02																		
Mn	0.46	<0.001	0.05	>0.1																
Fe	0.84	<0.001	0.32	>0.02	0.46	<0.001														
Co	0.33	>0.2	0.08	>0.1	0.25	>0.02	0.18													
Ni	0.36	>0.001	0.68	<0.001	0.32	>0.02	0.61	<0.001	0.07	>0.1										
Cu	0.8	<0.001	0.04	>0.1	0.37	>0.001	0.86	<0.001	0.19	>0.1	0.4	>0.001								
Zn	0.33	>0.02	0.11	>0.1	0.11	>0.1	0.35	>0.001	0.03	>0.1	0.2	>0.1	0.3	>0.02						
Cd	-0.14	>0.1	-0.16	>0.1	0.08	>0.1	0.02	>0.1	-0.17	>0.1	0.18	>0.1	-0.1	>0.1	-0.2	>0.05				
Pb	0.43	<0.001	-0.04	>0.1	0.12	>0.1	0.42	<0.001	0.16	>0.1	0.22	>0.05	0.49	<0.001	0.46	<0.001	-0.22	>0.2		
P	0.31	>0.02	-0.06	>0.1	0.32	>0.02	0.43	>0.001	0.22	>0.1	0.35	>0.001	0.43	<0.001	0.25	>0.05	0.03	>0.1	0.35	>0.001

Appendix-IV: Concentration of Cr, Mn, Fe, Cu and Zn ($\mu\text{g/g}$, dry wt) in leachates of sediment core (B2) and percentage with respect to the total concentration in sediment.													
Depth (cm)	Leachate 1		Leachate 2		Leachate 3		Leachate 4		Leachate 5		F1+F2+F3	Bulk conc ($\mu\text{g/l}$)	% Recovery
	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)	(%)	Conc ($\mu\text{g/g}$)	(%)	+F4+F5= Conc ($\mu\text{g/g}$)		
Cr													
1	0.4	0	2	1	11	3	9	3	147	45	169	327	52
2	0.5	0	5	2	13	5	9	3	133	47	161	282	57
10	0.4	0	4	2	10	5	9	5	110	57	133	193	69
20	0.3	0	3	1	13	4	10	3	132	40	158	326	48
25	0.5	0	3	1	12	4	9	3	131	39	156	335	47
31	0.4	0	1	0	14	4	10	3	143	42	168	339	50
34	0.3	0	6	2	5	1	7	2	107	32	125	335	37
48	0.6	0	5	2	4	1	5	2	124	41	139	304	46
50	0.7	0	7	2	5	2	5	2	120	41	138	296	47
Mn													
1	52	6	375	42	136	15	51	6	302	34	916	899	102
2	38	5	335	44	126	17	47	6	272	36	818	762	107
10	44	5	374	43	165	19	55	6	276	32	914	870	105
20	94	10	279	29	144	15	57	6	282	29	856	958	89
25	69	7	385	40	173	18	57	6	283	30	967	952	102
31	75	10	213	30	137	19	48	7	301	42	774	721	107
34	58	8	226	29	114	15	48	6	266	34	712	772	92
48	25	3	279	35	125	16	47	6	361	46	837	789	106
50	25	3	355	44	119	15	45	6	347	43	891	812	110
Fe													
1	29	0	510	0.7	5259	7	4484	6	64357	86	74639	75000	99
2	11	0	655	0.9	6267	9	4371	6	67765	95	79069	71000	111
10	7	0	463	0.6	6261	8	4397	6	69072	90	80200	77000	104
20	15	0	319	0.4	5681	7	4392	6	73089	94	83496	78000	106
25	9	0	274	0.4	5902	8	4217	5	70755	91	81157	78000	104
31	16	0	273	0.3	6923	9	4111	5	74974	93	86297	81000	106
34	9	0	2976	3.7	3547	4	3550	4	74949	94	85031	80000	106
48	7	0	2930	3.7	3101	4	3261	4	71815	91	81114	79000	103
50	7	0	4325	5.5	3754	5	3342	4	71249	91	82677	78000	106

Appendix-IV: (Contd..2)													
Depth (cm)	Leachate 1		Leachate 2		Leachate 3		Leachate 4		Leachate 5		F1+F2+F3	Bulk conc (µg/)	% Recovery
	Conc (µg/g)	(%)	Conc (µg/g)	(%)	Conc (µg/g)	(%)	Conc (µg/g)	(%)	Conc (µg/g)	(%)	+F4+F5= Conc (µg/g)		
Cu													
1	1.1	1	7	5	13	10	7	5	88	65	116	135	86
2	0.9	1	8	6	17	13	9	7	88	67	123	131	94
10	0.7	1	5	4	15	12	9	7	86	66	116	130	89
20	1	1	6	4	19	13	11	8	91	63	128	144	89
25	0.8	1	5	4	16	12	9	7	89	65	120	137	88
31	0.5	0	4	3	19	14	8	6	87	64	119	136	88
34	0.4	0	6	5	9	7	6	5	77	60	98	129	76
48	0.3	0	6	5	5	4	5	4	73	62	89	118	75
50	0.2	0	8	7	7	6	5	4	74	62	93	119	78
Zn													
1	3	2	38	26	46	32	24	16	80	55	191	146	131
2	6	4	52	31	58	34	26	15	82	49	224	169	133
10	2	1	26	19	49	36	23	17	82	60	182	137	133
20	5	3	42	27	67	43	30	19	87	56	231	156	148
25	4	3	23	17	48	35	24	17	82	59	181	138	131
31	2	2	18	16	50	45	20	18	80	71	170	112	152
34	9	8	24	21	23	20	19	16	80	69	155	116	134
48	5	6	10	12	12	14	15	18		0		84	
50	7	9	16	21	16	21	14	18		0		78	

Appendix-V (b): Correlation coefficient (r) and levels of significance (p) of some metals and P in sediments from inshore areas of Ulhas estuary .																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
1996 (April) subtidal (n=10)																				
Cr	0.09	>0.1																		
Mn	0.07	>0.1	-0.63	>0.02																
Fe	-0.67	>0.02	0.23	>0.1	0.02	>0.1														
Co	0.26	>0.1	0.02	>0.1	0.66	>0.01	0.13	>0.1												
Ni	0.17	>0.1	-0.16	>0.1	0.8	>0.001	0.03	>0.1	0.93	<0.001										
Cu	-0.07	>0.1	0.73	>0.001	-0.92	>0.001	0.13	>0.1	-0.6	>0.2	-0.78	>0.001								
Zn	-0.03	>0.1	0.75	>0.001	-0.92	>0.001	0.13	>0.1	-0.55	>0.1	-0.75	>0.001	1	<0.001						
P	-0.06	>0.1	0.79	>0.001	-0.92	>0.001	0.15	>0.1	-0.51	>0.1	-0.71	>0.001	0.99	<0.001	1	<0.001				
1998 (April-May) subtidal (n=13)																				
Cr	0.19	>0.1																		
Mn	0	>0.1	0.08	>0.1																
Fe	0.7	>0.001	0.48	>0.05	0.2	>0.1														
Co	0.41	>0.1	0.22	>0.1	0.8	<0.001	0.68	>0.001												
Ni	0.33	>0.1	0.09	>0.1	0.75	>0.001	0.57	>0.02	0.93	<0.001										
Cu	-0.15	>0.1	0.68	>0.001	-0.51	>0.1	-0	>0.1	-0.5	>0.1	-0.55	>0.1								
Zn	-0.27	>0.1	0.67	>0.001	-0.41	>0.1	-0.1	>0.1	-0.43	>0.1	-0.5	>0.1	0.97	<0.001						
P	-0.31	>0.1	0.63	>0.01	-0.45	>0.1	-0.2	>0.1	-0.53	>0.1	-0.57	>0.1	0.98	<0.001	1	<0.001				
2000 (October) (n=11)																				
Cr	-0.35	>0.1																		
Mn	0.68	>0.001	0.18	>0.1																
Fe	-0.12	>0.1	0.27	>0.1	0.34	>0.1														
Co	-0.56	>0.02	0.56	>0.02	-0.14	>0.1	0.12	>0.1												
Ni	-0.9	>0.001	1	>0.1	-0.5	>0.05	-0.7	>0.001	1	<0.001										
Cu	0.42	>0.2	0.45	>0.1	0.9	<0.001	0.51	>0.05	0.2	>0.1	0.83	<0.001								
Zn	0.46	>0.1	0.37	>0.1	0.78	<0.001	0.2	>0.1	0.04	>0.1	0.96	<0.001	0.76	>0.001						
P	0.18	>0.1	0.59	>0.02	0.52	>0.02	0.43	>0.1	0.27	>0.1	-0.62	>0.02	0.67	>0.01	1	<0.001				

Appendix -VI (a) :Depthwise variation of some selected metals and P ($\mu\text{g/g}$, except Al and Fe in (%), dry wt) in core sediment of the Ulhas estuary.

Depth	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	Depth	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
(Cm)	Core U1									(Cm)	Core U34										
1	8.9	450	1530	10.4	76	122	122	121	837	36	9.3	189	514	7.4	56	118	111	155	-	-	973
2	8.7	564	1426	10.6	79	122	118	111	889	37	9.5	190	525	8.3	55	98	110	170	-	-	952
3	9	560	1362	10.3	80	126	121	121	854	38	9.1	191	500	7.4	56	104	110	136	-	-	992
4	9	499	1401	10.2	77	121	119	125	897	39	9.6	180	531	7.3	54	77	112	150	-	-	968
5	8.9	550	1414	10.5	80	120	121	124	893	40	9.7	173	526	7.3	55	70	109	148	0.1	13	964
6	9	556	1318	10.5	78	126	122	161	907	41	9.6	174	611	7.3	53	107	102	143	-	-	976
7	9.1	539	1217	10.4	77	125	122	128	957	42	9.5	160	554	7.2	53	105	105	137	-	-	975
8	9.1	561	1323	10.6	78	128	122	144	1197	43	9.7	189	527	7.4	56	104	108	139	-	-	948
9	8.9	575	1358	10.7	79	126	120	122	886	44	9.9	137	563	7.5	53	100	106	150	-	-	1058
10	8.9	593	1311	10.4	80	126	121	113	798	45	9.7	195	524	7.5	55	111	108	143	-	-	807
11	8.7	575	1348	10.4	79	125	120	117	779	46	9.1	167	576	7.3	53	97	105	137	-	-	1051
12	8.8	562	1367	10.4	80	126	120	117	807	47	9.5	192	636	7.3	54	110	108	157	-	-	950
13	8.7	564	1448	10.5	80	125	120	130	791	48	10.5	179	564	7.2	55	101	107	145	-	-	1005
14	8.7	466	1290	9.8	75	123	119	135	890	49	9.4	138	525	7.1	52	98	107	155	-	-	1156
15	8.9	538	1306	10.3	77	123	122	142	880	50	8.8	159	539	7.2	53	91	106	146	0.1	12	1016
16	8.8	591	1122	10.8	80	127	120	158	863	52	8.6	168	545	7.2	54	98	106	119	-	-	1017
17	9.2	535	1139	10.4	78	120	122	111	895	54	8.8	183	546	7.5	55	100	109	118	-	-	981
Core U3										56	8.8	211	534	7.1	56	109	112	126	-	-	618
1	8.7	602	1667	11.3	82	107	118	127	810	58	9.2	191	556	7.5	57	101	109	121	-	-	918
2	8.8	532	1728	11.2	80	108	119	132	847	60	8.9	191	570	7.3	58	103	110	113	-	9.8	965
3	9.3	591	1224	11.1	79	109	122	122	708	62	7.8	166	585	7.4	54	103	112	131	-	-	942
4	9.3	511	1469	11.2	81	106	124	144	791	64	9.5	154	514	7.5	55	96	110	114	-	-	1070
5	9.3	511	1680	11.3	85	107	120	142	686	66	8.9	184	556	7.9	55	104	112	117	-	-	934
6	9.2	522	2165	11.7	94	106	123	137	678	68	8.8	186	582	7.4	56	102	112	116	-	-	1004
7	9.2	518	2005	11.6	83	106	124	119	612	70	8.5	175	546	7.4	55	99	111	115	0.1	10	667
Core U4										72	9.6	200	562	7.3	58	98	111	116	-	-	962
1	4.6	362	474	5.9	29	59	171	2792	4558	74	8.7	202	517	8	57	104	111	125	-	-	985
2	5.6	540	714	4	33	70	224	3452	8460	76	8.9	184	472	7.6	55	105	107	118	-	-	945
3	5.3	544	619	6	37	67	231	3841	5797	78	9.2	181	480	7.2	56	92	106	117	-	-	958
4	5.2	608	541	6.3	37	69	255	3936	6050	80	8.7	200	486	7.4	56	93	106	120	0.1	9.4	994
5	5.3	509	606	6	37	67	239	4176	5379	82	9.1	189	472	7.3	57	100	107	114	-	-	985
6	5.3	535	544	5.7	36	79	239	4711	4500	84	9.1	198	483	7.2	56	110	108	115	-	-	927
7	5.9	639	592	6.3	39	79	219	4722	5128	86	9.1	205	516	7.2	56	99	107	124	-	-	1073

Appendix -VI (a): (Contd..2)

Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
	Core U4												Core U34										
8	5.4	638	614	6.2	38	73	205	3943	-	-	5081	88	8.8	168	467	7.4	56	92	106	116	-	-	919
	Core U23											90	9	202	503	7.3	55	100	105	119	-	-	976
1	6.1	293	1901	6.9	56	104	166	367	0.51	36.1	1118	92	9.4	225	571	7.6	57	106	105	143	-	-	991
2	7.1	329	1625	7.8	58	115	177	382	0.51	64.1	1093	94	9.3	188	530	7.6	57	104	108	126	-	-	926
3	7.2	313	1391	7.6	62	111	173	372	-	-	986	96	9.4	182	482	7.4	55	107	109	118	-	-	883
4	6.9	314	1535	7.4	56	110	169	366	0.57	23.9	817	98	8.7	171	533	6.8	52	97	100	105	-	-	863
5	7	312	1649	7.8	56	108	170	364	0.62	35.5	791	100	9.2	188	556	7.3	56	100	106	112	-	-	920
6	6.9	323	1671	7.7	61	111	179	407	0.62	71.2	927	102	9.1	199	502	7.5	56	99	108	109	-	-	931
7	6.9	336	1414	7.8	59	115	181	388	0.73	36.6	804	104	9.3	189	532	7.7	58	103	107	127	-	-	937
8	6.8	343	1561	8	60	119	182	429	0.71	46.1	906	106	9.5	185	543	7.3	56	107	109	113	-	-	964
9	6.6	330	1551	8	59	114	180	403	0.64	42.2	1144	108	9.8	208	532	7.5	57	115	110	120	-	-	880
10	6.9	340	1197	8.4	66	130	193	452	0.61	45.1	870	110	9.2	179	525	7.3	54	109	108	114	-	-	980
11	6.5	318	1072	8	66	137	210	441	0.54	151	768	112	9.4	181	520	7.4	55	96	107	113	-	-	916
12	6.8	329	1098	8.4	67	137	198	474	0.57	109	772	114	8.6	173	536	7.4	56	99	106	115	-	-	946
13	7.3	311	1021	8.8	67	129	187	420	0.28	27.9	819	116	9.6	215	529	7.6	59	112	109	118	-	-	920
14	6.8	311	1029	8.2	69	129	183	429	0.54	68.4	710	118	9.1	208	560	7.7	57	108	107	116	-	-	962
15	6.8	314	1105	8.2	60	131	184	407	0.39	73.4	662	120	8.8	217	539	7.3	60	109	111	185	-	-	853
	Core U35																						
16	6.5	361	1099	8.5	73	150	198	418	0.45	74.4	840												
17	6.9	366	1252	8.8	71	152	204	429	0.46	125	827	1	9.1	199	1102	7.3	57	83	113	177	0.15	39	950
18	7	372	1255	8.9	74	148	184	350	0.44	45.9	888	2	8.9	194	1057	7.3	57	69	114	155	0.09	20	910
19	6.6	408	1424	9.4	78	157	176	322	0.45	41.6	639	3	8.5	205	1064	7.4	58	67	118	169	0.12	27	485
20	7.2	293	1384	8.7	67	133	176	363	0.41	30	709	4	8.7	205	1040	7.4	56	69	116	198	0.1	16	570
21	7.1	272	1296	8.3	63	127	177	353	0.62	31.9	599	5	8.8	178	1022	7.2	56	67	114	147	0.14	15	910
22	7.9	315	1449	9.3	68	141	180	363	0.41	41.2	602	6	9.3	202	1044	7.2	56	67	114	139	0.14	18	929
23	7.5	353	1460	9.1	71	143	182	340	0.19	27.5	518	7	9.2	230	1059	7.2	56	81	114	147	0.12	19	853
24	8	313	1475	9.2	64	134	189	365	0.46	38.7	1008	8	9.4	179	1060	7.3	55	76	112	155	0.13	19	1021
25	7.4	343	1315	9	75	144	174	358	0.28	34.2	777	9	9.1	221	1035	6.9	57	70	117	146	-	20	317
26	7.7	340	1315	9	70	138	184	398	0.56	50.5	822	10	9.2	226	1126	7.1	56	73	118	139	0.1	29	540
27	7.4	366	1245	8.9	74	142	188	435	0.46	36	858	11	9.2	226	1050	7.9	55	74	113	150	-	-	945
28	7.5	362	1300	8.8	77	151	174	340	0.42	41.9	700	12	9.3	253	1084	7.7	57	73	117	157	-	-	952
29	7.4	354	1259	9	72	138	196	460	0.39	44.9	962	13	9.3	218	1094	7.7	56	61	116	144	-	-	930
30	7.5	355	1329	9.3	75	144	187	364	0.39	44.6	731	14	9.7	241	1105	7.4	58	63	118	148	-	-	872
31	6.7	344	1457	8.8	77	146	197	474	0.67	36.6	744	15	9.5	234	1100	7.7	55	73	114	160	-	-	1030

Appendix -VI (a): (Contd..3)

Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
	Core U23												Core U35										
32	6.9	376	1307	9	73	150	178	363	0.39	55.9	852	16	9.4	232	1151	7.2	56	66	120	151	-	-	393
33	7.3	378	1259	9	74	154	193	422	0.6	46.1	1073	17	9.1	224	1090	8	57	66	119	165	-	-	956
34	7.7	378	1318	9.1	72	152	197	453	0.66	47.2	1161	18	9.1	219	1054	7.6	56	64	118	157	-	-	1133
35	8	284	1350	9.7	66	126	213	603	0.39	38	788	19	9.4	223	1082	7.6	55	75	119	162	-	-	950
36	7.7	292	1281	9.6	66	117	209	602	0.48	71.2	722	20	9	224	1011	7.1	56	64	118	154	0.13	20	1016
37	7.8	319	1339	10.2	69	125	220	601	0.48	43.1	875	21	9.1	210	1144	7.5	56	64	118	183	-	-	988
38	7.6	322	1405	9.8	72	124	211	752	0.75	50	760	22	8.7	224	1183	8.1	56	64	118	164	-	-	1016
39	7.1	357	2559	10.9	74	119	163	541	0.56	35.1	773	23	9.2	270	1104	7.7	57	76	121	178	-	-	995
40	7.6	310	1784	10.4	73	119	168	542	0.49	36.3	818	24	9.1	286	1059	7.7	59	78	122	168	-	-	986
41	7.7	321	1687	10.5	73	114	174	567	0.43	40.6	881	25	9.1	205	1009	7.7	56	66	118	165	-	-	1119
42	7.5	298	1577	9.9	75	114	198	833	0.76	35.2	930	26	8.9	283	1067	7.4	59	77	119	155	-	-	457
43	7.6	268	1576	9.7	75	122	200	772	0.46	41.3	825	27	9	204	1118	7.6	59	65	117	154	-	-	916
44	7.5	257	1645	9.4	71	113	206	763	0.37	53	1070	28	8.7	262	1154	7.6	60	77	119	166	-	-	887
45	8	262	1607	9.7	70	110	216	802	0.53	47.7	922	29	9	252	1270	8.5	60	78	118	160	-	-	959
46	7.6	254	1472	9.3	68	118	203	682	0.72	40.7	761	30	9	227	1254	7.8	59	69	119	162	0.17	15	943
47	7.3	281	1399	9.5	73	121	210	632	0.58	41.1	848	31	8.7	196	1239	7.7	59	68	117	135	-	-	940
48	7.4	270	1334	9.2	73	115	234	709	0.81	46.4	664	32	9.1	253	1186	7.6	60	78	120	140	-	-	923
49	7.6	288	1770	9.7	71	109	192	525	0.59	34.1	1021	33	9.1	265	1216	7.7	59	78	121	137	-	-	834
	Core U30											34	9.2	229	1194	8.1	60	66	120	142	-	-	895
1	6.8	274	1408	7.7	1128	1751	2096	1740	0.38	26.6	1238	35	9.2	232	1213	7.7	58	80	122	145	-	-	942
2	6.7	280	1640	7.8	51	83	140	157	0.26	29.7	1343	36	9.2	228	1243	7.6	59	77	117	139	-	-	916
3	7.2	304	1444	8	1966	2932	3437	3090	0.31	32.5	1287	37	9	246	1192	7.6	60	80	120	156	-	-	880
4	7.4	294	1345	8.4	1167	1834	2108	2163	0.33	29.5	1379	38	8.9	230	1196	7.7	61	79	120	146	-	-	892
5	7.1	293	1201	8.3	821	1364	1556	1532	0.23	29.8	1309	39	9	238	1185	7.6	61	71	122	138	-	-	763
6	8.9	284	1167	8.5	349	502	616	874	0.28	26.1	1531	40	9.1	217	1187	7.5	60	72	124	145	0.11	14	723
7	8.9	288	1124	8.5	335	490	601	951	0.35	33.6	1465	41	9.4	229	1218	8.2	57	80	120	166	-	-	991
8	8.6	283	1021	8.3	52	88	132	154	0.19	22.1	1256	42	9.5	248	1246	7.3	58	70	123	148	-	-	194
9	8.8	254	933	8.4	1785	2687	3174	2915	0.24	22.9	1103	43	10.1	229	1293	7.7	58	70	122	148	-	-	925
10	8.7	245	978	8.3	1073	1688	1902	1835	0.2	34.5	1036	44	9.6	256	1237	7.7	58	82	122	158	-	-	839
11	8.4	226	972	8.1	1299	1944	2258	2040	0.17	21.2	1179	45	9.8	234	1231	7.3	59	75	126	152	-	-	188
12	8.2	230	937	8.2	52	88	127	278	0.25	22.4	1102	46	9.8	251	1257	7.5	60	84	122	175	-	-	940
13	8.5	208	1036	8.5	887	1366	1618	1844	0.25	26.3	1257	47	9.6	250	1200	7.7	59	73	122	192	-	-	992
14	8.4	213	968	8.4	1001	1464	1678	1727	0.65	25.3	1183	48	9.6	242	1198	8.1	58	71	115	159	-	-	966

Appendix -VI (a): (Contd..4)

Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
	Core U30												Core U35										
15	8.1	266	1019	8.8	54	91	137	249	0.32	36	1158	49	9.3	222	1031	8.1	56	71	99	153	-	-	782
16	8.2	280	1129	8.5	1873	2724	3115	2964	0.35	64.7	1209	50	9.8	203	1025	7.7	57	68	96	154	0.13	14	930
17	7.9	306	1143	8.4	53	96	154	208	0.4	79.8	1119	52	8.7	234	1106	7.5	56	75	112	145	-	-	884
18	8.1	255	1183	8.4	614	964	1086	1315	0.39	61.3	1195	54	8.6	183	1149	4.9	54	64	110	136	-	-	872
19	8.1	267	1273	9.1	1611	2403	2707	3008	0.27	39.5	1235	56	8.8	243	1076	7.5	55	72	110	141	-	-	968
20	6.3	227	2432	15	1277	1908	2211	2538	0.27	18.3	1415	58	9.1	211	1133	7.4	56	77	109	139	-	-	848
21	8.3	237	1063	9	1561	2278	2648	2431	0.25	274	1293	60	9	195	1088	7.6	54	67	110	135	0.14	9.8	889
22	8.7	239	1044	8.8	832	1275	1437	1470	0.3	94	1296	62	9.1	200	1064	7.4	54	69	112	134	-	-	782
23	7.5	268	1073	8.6	51	102	159	245	-	148	1230	64	8.7	216	1004	7.3	55	69	113	137	-	-	967
24	7.5	294	1313	8.9	53	104	148	290	0.43	354	1137	66	8.6	223	1272	7.6	58	82	109	148	-	-	885
	Core U31 (a)											68	9	208	1168	7.5	57	68	111	138	-	-	891
1	9.4	251	1472	8.2	63	88	120	149	-	-	1225	70	9.1	213	1350	7.5	59	70	110	143	0.08	9.9	924
2	9.4	224	1449	8.1	61	85	120	140	-	-	1245	72	8.8	221	1224	7.5	58	69	110	134	-	-	897
3	9.1	228	1361	8.1	63	86	118	134	-	-	1463	74	8.4	302	1508	8.8	63	77	111	159	-	-	661
4	9.1	223	1406	8	61	85	125	154	-	-	1095	76	8.7	197	1151	7.5	56	69	106	86	-	-	944
5	9.3	219	1325	7.7	59	85	126	163	-	-	889	78	8.9	155	1114	7.2	55	68	105	283	-	-	883
6	9.2	202	1297	8.2	58	82	124	182	-	-	1325	80	8.3	205	1093	7.2	57	77	107	169	0.15	10	890
7	9.1	195	1382	7.9	67	81	121	173	-	-	1259	82	8.5	161	1115	7.2	55	65	106	148	-	-	920
8	7.6	157	1081	7.1	48	66	101	113	-	-	1024	84	8.5	199	1152	7.2	57	79	106	227	-	-	891
9	9.4	191	1414	7.9	57	84	122	144	-	-	1348	86	8.3	183	1189	7.1	54	67	107	144	-	-	941
10	8.2	196	1425	7.7	58	82	122	137	-	-	1328	88	8.6	170	1132	7.2	56	72	107	178	-	-	893
11	10.8	2992	13046	8	1855	4543	122	5782	-	-	1188	90	8.8	184	1128	7.3	55	77	105	125	-	-	916
12	9.3	188	1359	8	75	118	119	235	-	-	1347	92	8.7	177	1169	7.2	55	67	106	150	-	-	948
13	9.2	184	1452	7.9	72	103	121	172	-	-	1296	94	8.8	195	1126	7.1	55	74	107	355	-	-	953
14	10.5	2926	12767	8.1	1822	4466	122	6937	-	-	1348	96	8.2	184	1041	6.8	50	73	99	131	-	-	922
15	9.6	225	1631	8.5	98	115	125	262	-	-	1355	98	8.5	189	1095	7.4	54	75	103	132	-	-	994
16	8.1	206	1399	7.9	76	101	131	176	-	-	1161	100	8.8	212	1096	7.2	54	76	106	186	-	-	952
17	8.1	2903	12561	8	1778	4408	128	8246	-	-	1210	102	8.7	191	1106	7.2	54	74	106	140	-	-	958
18	8.9	234	1586	8.2	124	128	124	312	-	-	1259	104	7.8	209	1014	6.8	52	74	101	177	-	-	938
19	9.1	177	1387	7.9	90	100	125	209	-	-	1246	106	8.9	199	1094	7.1	55	79	105	150	-	-	1013
20	8.2	2903	11066	7.9	1722	4010	124	6525	-	-	1244	108	8.5	212	1025	7.1	54	76	105	127	-	-	962
21	9.2	194	1128	8.1	57	88	124	162	-	-	1204	110	8.4	196	1030	7.2	54	80	106	127	-	-	941
22	8.6	195	1210	8.2	63	92	124	170	-	-	1185	112	7.7	210	1081	7.4	55	76	105	143	-	-	1186

Appendix -VI (a): (Contd..5)

Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P	Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
Core U31 (a)										Core U37									
23	9.8	3014	13136	8.2	1845	4597	136	9624	1401	1	7.7	97	1018	7.8	55	69	112	103	1001
24	9.3	2871	12686	8	1815	4450	122	7696	1148	2	7.2	93	925	7	54	67	110	96	657
25	10.5	3034	12882	7.9	1793	4474	124	9271	1328	3	7.5	114	982	7.5	57	71	115	97	914
26	10.1	2801	12126	7.8	1697	4182	124	8810	1170	4	7.5	109	1021	7.5	59	71	114	107	864
27	8.4	263	1497	7.7	88	93	122	337	1166	5	7.4	100	1004	6.9	57	71	114	94	364
28	8.5	245	1451	8.2	91	98	128	216	1220	6	8.3	93	1014	7.3	55	70	115	99	469
29	10	2857	12188	7.8		4217	127	7200	1377	7	8.1	99	1055	7.5	52	68	115	99	829
30	7.9	255	1540	8	100	106	125	229	1176	8	7.9	98	1019	7.4	55	66	115	97	819
31	8.4	166	1468	8.1	60	84	124	158	1305	9	7.6	101	1037	7.4	55	67	116	97	521
32	8.2	230	1427	8.2	60	88	130	197	1303	10	7.4	111	992	7.3	54	66	115	89	536
33	8	185	1513	8.1	61	91	123	144	1224	11	7.7	112	976	7	54	67	114	100	802
34	7.9	179	1424	8	59	88	123	157	1290	12	7.5	86	969	7.1	53	67	113	94	868
35	7.9	153	1494	7.8	58	89	125	167	1210	13	7.7	82	1061	7.1	54	66	114	97	642
36	7.9	178	1389	8.1	58	87	124	147	1239	14	7.3	81	980	7.2	52	66	113	94	0
37	8.2	226	1426	8.2	60	93	126	139	1203	15	4.9	83	1016	7.1	54	71	113	98	536
38	8.5	227	1455	8.4	59	87	125	160	1233	16	7.6	87	1004	7	53	68	113	94	686
39	7.7	245	1485	8.1	59	91	124	160	1266	17	7.8	79	1046	7.1	52	70	113	100	654
40	7.6	254	1569	7.6	59	91	126	166	1170	18	7.4	78	988	7.3	53	68	112	94	779
41	8.3	247	1490	7.6	59	88	125	151	1207	19	7	74	938	7	55	65	111	93	757
42	8.8	208	1647	8.1	58	91	128	180	1483	20	6.5	71	937	6.7	55	65	113	86	736
43	7.8	232	1453	8.1	58	88	125	149	1138	21	8.1	85	966	6.6	51	69	114	98	600
44	8	307	1615	8.8	61	90	126	156	1106	22	8.2	98	960	7.2	51	69	114	107	900
45	7.6	347	1625	8.3	64	99	122	174	1160	23	8.1	83	973	6.6	51	71	114	99	147
46	7.2	388	1583	7.9	63	95	112	160	1230	24	7.8	77	978	6.6	53	71	111	96	736
47	7.8	439	1622	8.1	61	96	125	167	1263	25	7.6	74	980	6.7	54	69	112	102	685
48	7.7	442	1501	8	59	92	124	180	1166	26	7.4	77	918	6.6	48	67	109	105	802
Core U31(b)										27	7.3	76	886	7.1	48	70	110	104	868
1	-	219	8003	-	70164	20633	102	54898	-	28	-	-	-	-	-	-	-	-	-
2	-	216	12598	-	115045	33101	104	83375	-	29	7.5	90	877	6.7	53	74	116	111	656
3	-	241	599	-	154	152	102	227	-	30	7.6	86	948	6.8	51	70	114	105	0
4	-	175	13330	-	124278	349701	107	88523	-	31	8	99	974	7.4	53	71	113	108	857
5	-	312	682	-	105	117	100	185	-	32	7.9	101	943	7.4	52	72	114	105	791
6	-	331	730	-	95	110	102	287	-	33	7.9	89	989	7.4	52	73	112	98	784

Appendix -VI (a): (Contd..6)

Depth (Cm)	Al	Cr	Mn	Co	Ni	Cu	Zn		Depth (Cm)	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	P
Core U31 (b)									Core U37									
7	-	206	476	70	88	111	348		34	7.5	79	948	7.2	52	73	114	94	633
8	-	219	473	63	84	115	183		35	7.5	77	949	7.4	50	74	113	99	579
9	-	231	461	58	82	114	192		36	7.8	82	1023	7.4	51	73	115	97	579
10	-	299	596	75	97	102	217		37	7.5	81	986	7.2	48	71	114	97	571
11	-	314	621	86	98	103	231		38	5.5	87	1012	7.2	51	72	112	110	613
12	-	343	645	129	113	100	233		39	8.1	82	957	7.1	51	73	112	100	636
13	-	241	12494	110360	33124	103	81610		40	7.7	90	954	7.4	51	69	114	97	875
14	-	266	966	2458	681	108	3184		41	8.5	105	1050	7.5	50	71	112	98	864
15	-	262	8312	70594	21205	102	57242		42	8.4	102	1034	7.4	52	72	112	106	809
16	-	386	666	124	118	102	239		43	7.9	105	927	7.5	50	75	113	102	796
17	-	349	684	86	102	96	269		44	8.1	118	943	7.5	52	75	112	104	854
18	-	376	769	77	105	92	228		45	7.9	71	868	7.2	45	67	110	102	394
19	-	300	732	71	102	88	184		46	8.1	90	857	7.2	48	72	108	94	764
20	-	265	574	80	95	107	198		47	7.8	102	889	7.3	50	72	111	103	588
21	-	216	507	130	107	110	231		48	7.9	88	839	7.2	47	71	110	100	95
22	-	211	6647	56031	16104	103	45117		49	8.2	109	844	7.5	50	71	113	97	840
23	-	255	1658	99	122	101	376		50	8.5	131	903	7.6	49	72	112	99	868
24	-	261	10139	89722	26708	104	61873		52	8.2	129	947	7.6	49	68	112	98	928
25	-	328	9246	82835	24012	103	64304		54	7.7	134	919	7.6	50	68	112	99	948
26	-	280	577	74	106	103	221		56	7.9	110	954	7.5	49	63	110	103	496
27	-	287	535	60	92	108	194		58	7.4	99	923	7.2	49	70	111	95	71
28	-	286	540	88	89	111	189		60	7.4	95	960	7.3	48	72	111	96	536
29	-	303	563	185	98	108	218		62	7.9	92	893	7.2	46	67	111	92	805
30	-	265	548	96	129	112	375		64	7.8	98	963	7.3	48	73	112	94	760
31	-	233	16913	162083	45346	110	110494		66	7.9	104	967	7.4	48	68	110	93	843
32	-	258	5586	45986	13485	103	38093		68	8	130	1016	7.4	49	73	112	97	824
33	-	227	23794	190379	54421	99	128591		70	8.9	130	1029	7.4	48	69	112	96	850
34	-	243	8757	74022	21858	98	58557		72	7.7	116	989	7.3	54	69	115	97	826
35	-	230	11969	110762	32617	106	82952		74	8	100	978	7.5	51	72	112	95	307
36	-	341	671	89	98	101	204		76	8	86	971	7.5	49	66	107	102	948
37	-	331	688	73	100	99	327		78	7.1	95	907	7.4	51	69	111	94	292
38	-	209	452	77	91	115	205		80	7.6	93	974	7.2	51	69	112	101	514
39	-	182	5504	48144	13883	110	39470		82	7.9	70	971	7.3	48	63	108	109	864

Appendix -VI (a): (Contd..8)

Depth (Cm)	U34										
	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
11	9.3	201	589	7.5	56	113	123	158	-	-	988
12	9.3	231	579	7.4	59	113	126	158	-	-	699
13	9	246	567	7.6	61	103	124	160	-	-	951
14	9.4	232	516	7.2	60	121	124	165	-	-	968
15	9.1	232	521	7.1	59	103	122	165	-	-	1182
16	8.8	229	465	7.1	57	121	119	162	-	-	1032
17	8.8	217	535	7.2	58	111	116	142	-	-	1006
18	8.8	202	532	7.1	58	112	112	149	-	-	950
19	8.5	217	520	7.1	52	118	115	131	-	-	926
20	8.9	205	466	7.6	59	121	116	131	0.12	14.8	802
21	8.6	184	500	7.5	59	99	111	129	-	-	977
22	8.9	204	546	7.5	59	105	111	136	-	-	1004
23	9.1	196	535	7.8	58	104	108	128	-	-	1120
24	9.1	192	500	7.4	60	109	108	130	-	-	1025
25	9.1	218	510	7.5	60	103	110	138	-	-	989
26	9.1	204	540	7.5	59	103	110	134	-	-	1018
27	9.2	198	484	7.3	60	101	109	127	-	-	990
28	9.3	189	512	7.4	58	82	109	136	-	-	1050
29	9.5	206	569	7.6	61	88	110	138	-	-	888
30	8.5	236	539	7.7	61	100	111	129	0.15	10.2	1048
31	9.4	190	592	7.5	54	99	109	133	-	-	974
32	9.5	186	584	7.4	54	105	109	144	-	-	1001
33	9.7	200	559	7.5	55	95	109	132	-	-	934
34	9.8	192	583	7.5	57	92	108	141	-	-	957
35	9.5	184	531	7.5	56	233	111	139	-	-	1229

Appendix-VI (b): Correlation coefficient (r) and levels of significance (p) of metals and P in core sediments of the Ulhas estuary and coastal area

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Core U1 (n=17)																				
Cr	-0.07	>0.1																		
Mn	-0.36	>0.1	-0.3	>0.1																
Fe	0.07	>0.1	0.67	>0.001	-0.08	>0.1														
Co	-0.18	>0.1	0.85	<0.001	0	0	0.62	>0.001												
Ni	-0.07	>0.1	0.56	>0.01	-0.2	>0.1	0.36	>0.1	0.35	>0.1										
Cu	0.7	<0.001	-0.04	>0.1	-0.22	>0.1	0.12	>0.1	-0.14	>0.1	0.12	>0.1								
Zn	0.06	>0.1	0.05	>0.1	-0.32	>0.1	0.16	>0.1	-0.17	>0.1	0.42	>0.1	0.26	>0.1						
P	0.55	>0.01	-0.06	>0.1	-0.2	>0.1	0.14	>0.1	-0.29	>0.1	0.19	>0.1	0.32	>0.1	0	>0.1				
Core U3 (n=7)																				
Cr	-0.47	>0.1																		
Mn	-0.13	>0.1	-0.47	>0.1																
Fe	0.11	>0.1	-0.4	>0.1	0.93	<0.001														
Co	0.2	>0.1	-0.38	>0.1	0.77	>0.01	0.82	>0.001												
Ni	-0.17	>0.1	0.61	>0.05	-0.67	>0.02	-0.7	>0.02	-0.57	>0.1										
Cu	0.77	>0.1	-0.5	>0.1	0.16	>0.1	0.39	>0.1	0.24	>0.1	-0.47	>0.1								
Zn	0.24	>0.1	-0.56	>0.1	0.02	>0.1	-0.1	>0.1	0.33	>0.1	-0.36	>0.1	0.02	>0.1						
P	-0.66	>0.05	0.3	>0.1	-0.39	>0.1	-0.6	>0.05	-0.44	>0.1	0.31	>0.1	-0.6	>0.05	0	>0.1				
Core U4 (n=8)																				
Cr	0.8	>0.001																		
Mn	0.7	>0.02	0.45	>0.1																
Fe	-0.16	>0.1	0.21	>0.1	-0.63	>0.05														
Co	0.71	>0.02	0.88	<0.001	0.3	>0.1	0.46	>0.1												
Ni	0.78	>0.001	0.74	>0.01	0.26	>0.1	0.06	>0.1	0.69	>0.02										
Cu	0.44	>0.1	0.54	>0.1	0.31	>0.1	0.02	>0.1	0.63	>0.05	0.44	>0.1								
Zn	0.69	>0.02	0.68	>0.02	0.13	>0.1	0.33	>0.1	0.83	>0.001	0.88	<0.001	0.62	>0.05						
P	0.37	>0.1	0.16	>0.1	0.79	>0.001	-0.8	>0.001	-0.11	>0.1	-0.08	>0.1	0.28	>0.1	0	>0.1				
Core U23 (n=49)																				
Cr	-0.3	<0.05																		
Mn	0.07	>0.1	-0.17	>0.1																
Fe	0.69	<0.001	-0.07	>0.1	0.28	<0.02														
Co	0.33	<0.02	0.3	>0.02	-0.08	>0.1	0.71	<0.001												
Ni	-0.06	>0.1	0.72	>0.001	-0.53	<0.001	0.1	>0.1	0.57	<0.001										
Cu	0.35	<0.01	-0.34	<0.02	-0.35	>0.01	0.33	<0.01	0.28	>0.02	0.01	>0.1								
Zn	0.46	<0.001	-0.6	>0.001	0.22	>0.1	0.57	<0.001	0.3	<0.02	-0.43	>0.001	0.67	<0.001						
Cd	-0.14	>0.1	-0.19	>0.1	0.17	>0.1	-0.1	>0.1	-0.19	>0.1	-0.38	>0.01	0.25	>0.05	0	>0.01				
Pb	-0.34	>0.01	0.11	>0.1	-0.38	>0.001	-0.2	>0.1	-0.06	>0.1	0.22	>0.1	0.32	>0.02	-0	>0.1	0.02	>0.1		
P	-0.02	>0.1	0.02	<0.1	0.24	<0.05	-0.2	>0.1	-0.22	<0.01	-0.27	<0.05	-0	>0.1	0	>0.1	0.02	>0.1	-0.2	>0.1

Appendix-VI (b): (Contd..2)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Core U30 (n=24)																				
Cr	-0.26	>0.1																		
Mn	-0.79	<0.001	0.11	>0.1																
Fe	-0.37	>0.05	-0.28	>0.1	0.75	<0.001														
Co	-0.02	>0.1	-0.19	>0.1	0.13	>0.1	0.14	>0.1												
Ni	-0.03	>0.1	-0.18	>0.1	0.13	>0.1	0.14	>0.1	1	<0.001										
Cu	-0.04	>0.1	-0.18	>0.1	0.13	>0.1	0.13	>0.1	1	<0.001	1	<0.001								
Zn	-0.02	>0.1	-0.21	>0.1	0.18	>0.1	0.23	>0.1	0.99	<0.001	0.99	<0.001	0.99	<0.001						
Cd	-0.06	>0.1	0.03	>0.1	-0.02	>0.1	-0.1	>0.1	-0.09	>0.1	-0.1	>0.1	-0.1	>0.1	-0	>0.1				
Pb	-0.05	>0.1	0.12	>0.1	-0.06	>0.1	0.02	>0.1	-0.14	>0.1	-0.15	>0.1	-0.2	>0.1	-0	>0.1	0.19	>0.1		
P	-0.17	>0.1	0.22	>0.1	0.46	>0.01	0.29	>0.1	-0.01	>0.1	-0.02	>0.1	-0	>0.1	0	>0.1	-0.08	>0.1	-0.15	>0.1
Core U31-i (n=48)																				
Cr	0.55	<0.001																		
Mn	0.57	<0.001	1	<0.001																
Fe	0.07	>0.1	-0.07	>0.1	-0.07	>0.1														
Co	0.54	<0.001	1	<0.001	1	<0.001	-0.1	>0.1												
Ni	0.57	<0.001	1	<0.001	1	<0.001	-0.1	>0.1	1	<0.001										
Cu	0.13	>0.1	0.19	>0.1	0.2	>0.1	0.44	>0.1	0.17	>0.1	0.19	>0.1								
Zn	0.55	<0.001	0.98	<0.001	0.99	<0.001	-0.1	>0.1	0.98	<0.001	0.99	<0.001	0.22	>0.1						
P	0.3	>0.02	0.14	>0.1	0.15	>0.1	0.26		0.09	>0.1	0.14	>0.1	0.19	>0.1	0	>0.1				
Core U31-ii (n=61)																				
Mn	-	-	0.04	>0.1																
Fe	--	-																		
Co	-	-	0.01	>0.1	1	<0.001														
Ni	-	-	0.17	>0.1	0.65	1	0.64	<0.001												
Cu	-	-	0.09	>0.1	0.07	>0.1	0.07	>0.1	0.18	>0.1										
Zn	-	-	-0.02	>0.1	0.99	<0.001	1	<0.001	0.62	<0.001	0.07	>0.1								
Core U34 (n=85)																				
Cr	-0.23	>0.02																		
Mn	0.21	>0.02	0.02	>0.1																
Fe	0.09	>0.1	0.07	>0.1	0.06	>0.1														
Co	-0.14	>0.1	0.69	<0.001	-0.11	>0.1	0.29	>0.001												
Ni	0.02	>0.1	0.19	>0.05	-0.01	>0.1	0.04	>0.1	0.09	>0.1										
Cu	-0.21	>0.1	0.7	<0.001	0.17	>0.1	0.01	>0.1	0.45	<0.001	0.24	>0.02								
Zn	0.3	>0.001	0.14	>0.1	0.33	>0.001	0.01	>0.1	0.11	>0.1	0.11	>0.1	0.29	>0.001						
Cd	0.14	>0.1	0.22	>0.02	0.5	<0.001	-0	>0.1	0.12	>0.1	0.19	>0.05	0.27	>0.01	1	<0.001				
Pb	0.06	>0.1	0.52	<0.001	0.09	>0.1	-0.2	>0.05	0.09	>0.1	0.34	>0.001	0.64	<0.001	-0	>0.1	0.24	>0.02		
P	0.11	>0.1	-0.08	>0.1	0.03	>0.1	-0	>0.1	-0.03	>0.1	0.2	>0.05	0.01	>0.1	0	>0.1	0.11	>0.1	0.2	>0.1

Appendix-VI (b): (Contd..3)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Core U35 (n=81)																				
Cr	0.36	<0.001																		
Mn	0.18	>0.1	0.38	<0.001																
Fe	0.3	>0.001	0.51	<0.001	0.38	<0.001														
Co	0.36	<0.001	0.64	<0.001	0.65	<0.001	0.53	<0.001												
Ni	-0.03	>0.1	0.35	>0.001	0.22	>0.02	0.14	>0.1	0.2	>0.05										
Cu	0.55	<0.001	0.6	<0.001	0.32	>0.001	0.31	>0.001	0.64	<0.001	0.02	>0.1								
Zn	0	0	-0.08	>0.1	-0.02	>0.1	-0	>0.1	-0.02	>0.1	0.06	>0.1	-0	>0.1						
Cd	-0.06	>0.1	0.2	>0.05	-0.08	>0.1	-0.2	>0.05	-0.1	>0.1	-0.05	>0.1	0.22	>0.02	0	>0.1				
Pb	0.05	>0.1	0.06	>0.05	-0.21	>0.05	-0.4	>0.001	-0.05	>0.1	0.41	<0.001	0.29	>0.001	0	>0.01	0.05	>0.1		
P	-0.18	>0.1	-0.21	>0.05	-0.15	>0.1	0.12	>0.1	-0.24	>0.02	0.03	>0.1	-0.3	>0.001	0	>0.1	-0.49	<0.001	-0.23	>0.02
Core U37 (n=87)																				
Cr	0.33	>0.001																		
Mn	-0.01	>0.1	0.05	>0.1																
Fe	0.25	>0.01	0.28	>0.001	0.08	>0.1														
Co	-0.27	>0.001	0.06	>0.1	0.46	<0.001	-0.2	>0.1												
Ni	0.02	>0.1	0.05	>0.1	-0.04	>0.1	0.19	>0.05	-0.04	>0.1										
Cu	0.01	>0.1	-0.2	>0.05	0.23	>0.02	0.29	>0.001	0.17	>0.1	0.34	<0.001								
Zn	0.07	>0.1	-0.06	>0.1	0.06	>0.1	0.16	>0.1	-0.05	>0.1	0.28	>0.001	0.32	>0.001						
P	0.31	>0.001	0.26	>0.01	-0.01	>0.1	0.32	>0.001	-0.04	>0.1	-0.15	>0.1	-0.1	>0.1	0	>0.1	-	-	-	-
All values (n=382)																				
Cr	0.1	>0.1																		
Mn	0.14	>0.1	0.58	<0.001																
Fe	-0.06	>0.1	0.12	>0.1	0.11	>0.1														
Co	0.04	>0.1	-0.04	>0.1	0.79	<0.001	0.12	>0.1												
Ni	0.11	>0.1	0	>0.1	0.45	<0.001	0.08	>0.1	0.57	<0.001										
Cu	-0.18	>0.1	-0.03	1	-0.04	>0.1	0.16	>0.1	-0.04	>0.1	-0.01	>0.1								
Zn	-0.12	>0.1	0.03	>0.1	0.8	<0.001	-0.1	>0.1	1	<0.001	0.57	<0.001	-0	>0.1						
Cd	-0.72	<0.001	0.69	<0.001	0.6	<0.001	0.45	<0.001	-0.1	>0.1	-0.09	>0.1	-0.1	>0.1	0	>0.1				
Pb	-0.3	>0.001	0.28	>0.001	0.14	>0.1	0.2	>0.02	0.11	>0.1	0.11	>0.1	0.12	>0.1	0	>0.1	0.28	>0.001		
P	-0.48	<0.001	0.12	>0.1	0	>0.1	-0.3	<0.001	0.04	>0.1	0.05	>0.1	0.07	>0.1	0	<0.001	-0.15	>0.1	0.12	>0.1

Appendix-VII (a): Concentration of selected metals and P [$\mu\text{g/g}$; except Al and Fe in (%), dry wt]																							
in surficial sediment along the northwest coast of India																							
Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
Station P1												Station DN2											
1997	7.8	95	748	6.1	53	77	56	90	-	-	542	1997	8.4	101	1230	8	68	70	118	105	-	-	456
2000	7.9	108	887	6.6	46	57	85	106	-	-	857	2000	8.9	120	1108	7.4	50	67	113	91	-	-	763
2001	9.2	168	609	5.9	26	89	73	109	-	-	902	2001	9.6	134	1234	7.9	35	72	137	117	-	-	812
2002	7.8	134	697	6.2	25	73	63	75	-	-	807	2002	7.9	118	1140	7.9	35	68	124	82	-	-	694
2003	5.9	141	853	4.2	37	46	51	232	-	-	439	2003	5	151	1291	5.2	32	55	123	147	-	-	195
Jan-04	7.4	-	675	5.7	-	-	-	-	0.28	16.4	-	Jan-04	7.8	-	1039	7.1	-	-	-	-	0.16	11.9	-
Oct-04	6.6	-	655	5.2	-	-	-	-	0.21	18	-	Oct-04	7.3	-	1102	6.6	-	-	-	-	0.37	17.2	-
Dec-05	8.6	-	774	7	-	-	-	-	0.16	16.2	-	Dec-05	8.9	-	1075	8.6	-	-	-	-	0.08	14.9	-
Mar-06	6.2	-	658	5.8	-	-	-	-	0.08	16.3	-	Mar-06	6.6	-	877	7.8	-	-	-	-	0.05	12.6	-
Station P2												Station DN3											
1997	6.7	67	713	6.7	55	70	68	80	-	-	509	1997	8.2	91	1195	8.4	68	70	120	100	-	-	454
2000	8.4	150	663	5.9	42	69	65	121	-	-	970	2000	8.4	136	1152	7.3	50	67	107	108	-	-	745
2001	9.1	174	742	6.4	27	87	81	96	-	-	949	2001	11	148	1446	7.9	36	74	143	114	-	-	841
2002	7	132	622	6.2	26	67	70	69	-	-	782	2002	8	118	1171	8	35	70	128	81	-	-	605
2003	8	159	639	4.4	24	48	66	100	-	-	436	2003	6.1	141	1071	5.4	33	54	119	111	-	-	559
Jan-04	7.6	-	640	5.9	-	-	-	-	0.19	13.5	-	Jan-04	7.7	-	1024	7.2	-	-	-	-	0.17	12.9	-
Oct-04	6.1	-	674	5.4	-	-	-	-	0.05	18.1	-	Oct-04	7	-	1062	6.9	-	-	-	-	0.26	13.9	-
Dec-05	8.4	-	1180	9.1	-	-	-	-	0.18	12.8	-	Dec-05	8.7	-	1165	8.6	-	-	-	-	0.16	15.6	-
Mar-06	6.4	-	591	6.1	-	-	-	-	0.12	14.7	-	Mar-06	6.5	-	902	7.7	-	-	-	-	0.02	12.9	-
Station P3												Station TP1											
2000	8.1	125	670	6.1	42	62	68	120	-	-	1004	1997	8.5	82	1077	8.2	71	75	122	108	-	-	482
2001	9	174	745	6.8	28	88	89	95	-	-	872	2000	9.2	145	1258	7.6	52	72	113	104	-	-	824
2002	7.3	132	627	7	26	71	78	75	-	-	761	2001	9.3	150	1219	9.1	35	75	140	113	-	-	869
2003	8.4	162	756	3.2	25	51	78	143	-	-	650	2002	8	132	1136	7.8	35	76	121	81	-	-	644
Jan-04	7.7	-	636	6.2	-	-	-	-	0.27	11.9	-	Dec-05	9.4	-	704	11	-	-	-	-	0.28	12.6	-
Oct-04	4.6	-	445	3.8	-	-	-	-	0.39	10.8	-	Station TP2											
Dec-05	8.4	-	715	7.3	-	-	-	-	0.24	19.6	-	1997	8.2	74	1093	8	68	71	119	103	-	-	471
Mar-06	6.4	-	588	6.2	-	-	-	-	0.26	11.7	-	2000	8.5	157	1172	7.4	53	71	115	116	-	-	798
Station V1												2002	8.3	134	1238	7.8	36	76	126	85	-	-	635
1997	8.7	110	1138	7.8	63	71	83	95	-	-	514	Dec-05	8.5	-	713	11	-	-	-	-	0.23	13.6	-
2000	9	148	781	6.4	44	72	75	126	-	-	876	Station TP3											
2001	8.9	181	1041	6.7	28	88	95	101	-	-	931	1997	8.1	112	1103	8	68	72	111	111	-	-	551
2002	6.3	107	817	6.8	32	56	83	76	-	-	733	2000	7.1	149	1082	7.8	53	72	118	114	-	-	846

Appendix-VII (a): (Contd..2)

Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
Station V1												Station TP3											
2003	8.1	173	774	5.7	24	52	80	100	-	-	644	2001	8.9	152	1402	8.8	32	73	131	153	-	-	1010
Jan-04	7.2	-	790	6.2	-	-	-	-	0.11	12.4	-	2002	8.3	136	1241	8.1	36	76	124	70	-	-	623
Oct-04	7.2	-	754	5.9	-	-	-	-	0.5	18.5	-	Dec-05	8.8	-	1264	9.4	-	-	-	-	0.12	16.8	-
Dec-05	7.4	-	768	5.6	-	-	-	-	0.09	17.8	-	Station BS1											
Mar-06	6.5	-	749	6.9	-	-	-	-	0.14	26.5	-	2000	9.3	171	1084	7.7	53	78	116	119	-	-	959
Station V2												2001	9.7	171	1191	9.2	33	77	132	119	-	-	1012
1997	6.7	84	928	6.9	62	49	70	88	-	-	472	2002	8	185	1374	8.1	39	84	125	105	-	-	828
2000	7.4	96	838	5.9	44	52	71	123	-	-	706	2003	6.5	189	1222	6.3	50	103	96	237	-	-	181
2001	8	145	1066	6.4	30	64	94	94	-	-	899	Jan-04	7.9	-	1125	7.6	-	-	-	-	0.08	17	-
2002	6.6	111	784	6.9	28	59	83	69	-	-	731	Oct-04	7.3	-	1084	7.3	-	-	-	-	0.15	17.5	-
2003	6.7	141	872	5	26	44	94	146	-	-	324	Apr-05	7.4	-	967	6.9	-	-	-	-	0.16	17.8	-
Jan-04	7.1	-	839	6.4	-	-	-	-	0.13	11	-	Mar-06	8.2	-	1308	8.4	-	-	-	-	0.24	4.9	-
Oct-04	6.7	-	858	6	-	-	-	-	0.07	13	-	Station BS2											
Dec-05	7.7	-	890	7.2	-	-	-	-	0.19	13.8	-	2000	8.2	216	1090	8	56	80	123	118	-	-	1022
Mar-06	6.2	-	757	6.8	-	-	-	-	0.08	9.7	-	2001	10	235	1361	9.5	36	76	136	119	-	-	980
Station V3												2002	8.3	152	1209	8	36	78	123	81	-	-	848
2000	7.5	131	711	5.3	88	66	54	107	-	-	840	2003	6.7	164	1169	7.7	51	98	94	129	-	-	199
2001	8.1	140	1013	6.5	30	67	99	90	-	-	815	Jan-04	7.9	-	1018	7.7	-	-	-	-	0.06	19.1	-
2002	7.4	139	798	6.5	33	73	81	77	-	-	771	Oct-04	7.5	-	1097	7.4	-	-	-	-	0.3	17.6	-
2003	7.8	136	938	5	27	38	93	89	-	-	235	Apr-05	7.5	-	1032	7.4	-	-	-	-	0.15	15.3	-
Jan-04	7	-	851	6.6	-	-	-	-	0.11	9.7	-	Mar-06	8	-	1016	7.7	-	-	-	-	0.12	13.7	-
Oct-04	6.6	-	874	6.4	-	-	-	-	0.21	12.7	-	Station BS3											
Dec-05	8.3	-	984	7.8	-	-	-	-	0.33	14.2	-	2000	8.8	166	1028	8	54	74	117	129	-	-	938
Mar-06	6.1	-	804	6.9	-	-	-	-	0.09	10.7	-	2001	9.2	236	1275	8.3	36	73	134	113	-	-	779
Station DU1												2002	8.2	149	1199	7.7	36	77	118	74	-	-	733
1997	7.4	77	1031	7.8	62	59	87	86	-	-	454	2003	6.3	150	1263	5.9	48	78	95	185	-	-	264
2000	8.5	122	948	7	48	64	96	117	-	-	765	Jan-04	8	-	1023	7.7	-	-	-	-	0.09	9.8	-
2001	8.8	141	1276	5.9	31	72	111	100	-	-	765	Oct-04	7.7	-	1208	7.2	-	-	-	-	0.07	14.8	-
2002	7	108	976	6.6	34	60	94	78	-	-	585	Apr-05	7.4	-	1006	9	-	-	-	-	0.2	11.9	-
2003	7.2	133	1043	5	29	43	93	160	-	-	255	Mar-06	8.2	-	1060	7.6	-	-	-	-	0.13	11.8	-
Jan-04	7	-	957	6.4	-	-	-	-	0.08	9.8	-	Station BY1											
Oct-04	6.8	-	1200	8.4	-	-	-	-	0.46	15.6	-	2000	5.7	145	1234	5.5	46	62	61	93	-	-	972
Dec-05	7.8	-	970	7.7	-	-	-	-	0.2	14.5	-	2001	9.1	215	1124	9.1	35	80	120	111	-	-	1151
Mar-06	6.2	-	874	6.8	-	-	-	-	0.03	15.5	-	2002	6.8	460	1528	8.3	50	128	86	82	-	-	918

Appendix-VII (a): (Contd..3)

Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
Station DU2												Station BY1											
1997	7.1	70	1048	7.7	63	64	93	98	-	-	429	2003	8	241	1070	5.9	35	83	141	134	-	-	529
2000	8.5	111	1001	7.1	48	62	97	115	-	-	741	Jan-04	7.7	-	1042	7.6	-	-	-	-	0.15	20	-
2001	8.8	134	1166	7.7	31	73	113	103	-	-	807	Oct-04	6.3	-	924	7.9	-	-	-	-	0.08	13.3	-
2002	7.2	116	954	7.8	32	67	114	81	-	-	767	Apr-05	7	-	941	6.7	-	-	-	-	0.22	15.7	-
2003	4	114	1033	6	29	37	85	126	-	-	556	Mar-06	7.5	-	989	7.7	-	-	-	-	0.12	14.1	-
Jan-04	7.3	-	963	6.7	-	-	-	-	0.1	10.4	-	Station BY2											
Oct-04	11.6	-	1974	13	-	-	-	-	-	27.7	-	2000	8.5	213	826	7.8	55	81	112	127	-	-	1083
Dec-05	7.8	-	1015	7.2	-	-	-	-	0.19	27	-	2001	9.2	170	1003	10	32	79	127	116	-	-	1198
Mar-06	6.1	-	826	7	-	-	-	-	0.08	12.6	-	2002	8.1	134	972	8	32	77	110	86	-	-	1064
Station DU3												2003	9.1	371	966	6.1	33	74	112	134	-	-	549
1997	6.7	62	1070	7.8	65	58	96	94	-	-	411	Jan-04	7.8	-	803	7.5	-	-	-	-	0.1	18.1	-
2000	8.1	114	1046	6.9	48	61	91	127	-	-	769	Oct-04	6.9	-	941	7.2	-	-	-	-	0.02	16	-
2001	8.1	142	1130	7.5	39	72	115	104	-	-	827	Apr-05	7.5	-	881	7.9	-	-	-	-	0.18	43	-
2002	6.8	111	1009	7.2	32	59	95	79	-	-	613	Mar-06	7.7	-	827	7.6	-	-	-	-	0.12	13.2	-
2003	6.5	125	1538	5	28	38	91	131	-	-	265	Station BY3											
Jan-04	7.1	-	966	6.6	-	-	-	-	0.08	11.7	-	2000	8.4	194	810	7.6	53	78	111	108	-	-	1084
Oct-04	6.5	-	1066	7	-	-	-	-	0.44	12.4	-	2001	8.7	173	928	10	32	72	121	114	-	-	1216
Dec-05	7.5	-	991	7.8	-	-	-	-	0.15	16	-	2002	8	136	924	7.8	34	76	105	87	-	-	1202
Mar-06	6.1	-	870	7	-	-	-	-	0.11	12.7	-	2003	10	183	1190	5	35	78	113	142	-	-	753
Station PJ1												Jan-04	8	-	808	7.7	-	-	-	-	0.1	17.4	-
1997	7.1	56	1170	7.7	63	57	101	97	-	-	418	Oct-04	6.9	-	869	7.6	-	-	-	-	0.12	15.1	-
2000	7.7	110	1272	6.8	48	61	102	116	-	-	701	Apr-05	6.8	-	782	6.5	-	-	-	-	0.16	14.4	-
2001	9.3	151	1393	7.6	33	89	146	110	-	-	832	Mar-06	7.6	-	822	7.1	-	-	-	-	0.16	12.3	-
2002	7.3	111	1047	8.2	31	67	119	84	-	-	731	Station M1											
2003	5.8	125	1290	5.4	29	52	110	100	-	-	298	1997	8.1	81	959	9.2	69	75	116	97	-	-	760
Jan-04	7.6	-	1115	7.2	-	-	-	-	0.06	10.1	-	2000	7.6	226	644	7.4	53	79	106	107	-	-	1065
Oct-04	6.4	-	1204	8.3	-	-	-	-	-	16.4	-	2001	8.4	197	1281	12	38	89	175	125	-	-	1245
Dec-05	8	-	1151	8.6	-	-	-	-	0.22	18.1	-	2002	7.9	154	871	8.1	35	79	116	72	-	-	791
Mar-06	6.2	-	950	7.3	-	-	-	-	0.06	12	-	2003	5.5	145	1070	5.8	46	90	96	118	-	-	331
Station PJ2												Jan-04	7.7	-	808	7.8	-	-	-	-	0.1	9.7	-
1997	7	66	1136	7.9	63	60	101	102	-	-	439	Oct-04	7.2	-	791	7.2	-	-	-	-	0.3	12.6	-
2000	7.6	102	1051	6.1	46	56	90	126	-	-	681	Apr-05	5.7	-	970	8.2	-	-	-	-	0.22	15.8	-
2001	8.9	152	1335	7.1	35	48	132	100	-	-	808	Mar-06	8.1	-	768	7.3	-	-	-	-	0.19	10.6	-
2002	7.7	113	1042	7.3	35	61	99	73	-	-	543												

Appendix-VII (a): (Contd..4)																								
Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	
	Station PJ2												Station M2											
2003	7.8	116	1078	6	28	47	106	105	-	-	502	1997	7.8	119	765	8.4	71	75	126	110	-	-	712	
Jan-04	7.4	-	989	6.7	-	-	-	-	0.1	10.9	-	2000	8.3	170	744	7.7	50	79	108	101	-	-	1152	
Oct-04	6.9	-	1046	5.5	-	-	-	-	0.03	12.3	-	2001	8.7	178	806	9.4	30	83	122	112	-	-	1243	
Dec-05	9	-	1128	8.2	-	-	-	-	0.21	17.7	-	2002	7.7	150	1076	8.3	35	76	117	68	-	-	1016	
Mar-06	6.1	-	911	7	-	-	-	-	0.1	12.4	-	2003	6.2	151	889	5.8	48	93	109	114	-	-	510	
	Station PJ3											Jan-04	8.1	-	742	7.9	-	-	-	-	0.11	11.1	-	
1997	8	77	1138	7.7	66	61	99	98	-	-	432	Oct-04	7.6	-	790	7.5	-	-	-	-	0.15	14.5	-	
2000	7.7	106	1053	6.1	48	58	91	126	-	-	698	Apr-05	6.5	-	732	6.9	-	-	-	-	0.39	14	-	
2001	8.4	121	1173	6.3	33	57	106	91	-	-	718	Mar-06	7.9	-	755	7.8	-	-	-	-	0.26	11.6	-	
2002	6.6	102	978	6.9	32	55	91	71	-	-	563		Station M3											
2003	7.8	128	1145	5	29	44	101	95	-	-	210	2000	8.8	205	732	7.3	52	79	105	100	-	-	1164	
Jan-04	7	-	998	6.9	-	-	-	-	0.08	10.1	-	2001	8.8	178	849	9.5	31	82	126	104	-	-	1248	
Oct-04	6.9	-	1051	6.2	-	-	-	-	0.24	14.5	-	2002	7.4	139	727	7.5	31	71	99	70	-	-	1086	
Dec-05	7	-	1028	7.3	-	-	-	-	0.1	10.9	-	2003	8	138	778	5.6	43	85	94	108	-	-	547	
Mar-06	6.4	-	873	7.6	-	-	-	-	0.07	11.2	-	Jan-04	8	-	717	7.7	-	-	-	-	0.3	14.2	-	
	Station H1											Oct-04	7.4	-	743	6.8	-	-	-	-	0.36	22.1	-	
1997	3.3	65	1817	4.9	59	35	56	74	-	-	448	Apr-05	7.2	-	661	6.4	-	-	-	-	0.52	12.4	-	
2002	7.6	106	960	6.8	33	58	101	68	-	-	666	Mar-06	7.9	-	678	7.2	-	-	-	-	0.1	10.8	-	
2003	8	115	1013	5	28	41	96	108	-	-	496		Station DL1											
Jan-04	7	-	1037	6.6	-	-	-	-	0.14	11.5	-	2001	8.8	178	703	9.4	28	86	122	103	-	-	1681	
Oct-04	7	-	1042	6.3	-	-	-	-	0.25	11.5	-	2003	6.5	166	887	5.9	45	101	82	153	-	-	367	
Dec-05	7.8	-	1039	7.8	-	-	-	-	0.12	16	-	Jan-04	8.3	-	701	8.1	-	-	-	-	0.14	7.2	-	
Mar-06	6.3	-	995	7.4	-	-	-	-	0.01	11.2	-	Oct-04	7.9	-	773	7.4	-	-	-	-	0.3	11.8	-	
	Station H2											Apr-05	7.5	-	648	7	-	-	-	-	0.49	11.2	-	
1997	5.3	47	1340	5.9	54	40	84	75	-	-	290		Station DL2											
2001	8.8	141	1382	8.9	33	70	141	105	-	-	828	2001	9	186	649	8.4	30	88	95	102	-	-	901	
2002	8.5	120	1087	7.3	34	67	120	71	-	-	560	2003	8.4	163	677	6	46	102	124	123	-	-	411	
2003	10.6	134	1103	5	29	52	116	75	-	-	256	Jan-04	7.8	-	575	7.3	-	-	-	-	0.14	9.4	-	
Jan-04	7.4	-	1056	6.9	-	-	-	-	0.08	8.9	-	Oct-04	6.9	-	567	7	-	-	-	-	0.25	14.3	-	
Oct-04	4.6	-	980	5.3	-	-	-	-	0.26	13.4	-	Apr-05	7.3	-	1050	6.7	-	-	-	-	0.93	14.8	-	
Dec-05	8.3	-	1220	9	-	-	-	-	0.11	17.3	-		Station DL3											
Mar-06	5.8	-	1362	7	-	-	-	-	0.12	10.4	-	2001	7.8	167	557	8	22	77	180	91	-	-	1312	
	Station H3											2003	6	143	608	4.9	37	88	62	140	-	-	325	
1997	7.3	83	1270	6.5	64	69	129	100	-	-	477	Jan-04	7.4	-	531	7.1	-	-	-	-	0.17	7.3	-	

Appendix-VII (a): (Contd..5)																							
Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	Year	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P
	Station H3												Station DL3										
2000	7.5	97	1014	6	46	55	89	134	-	-	656	Apr-05	7.4	-	1014	6.1	-	-	-	-	0.08	13.1	-
2001	8.7	138	1407	8.9	34	71	142	106	-	-	816		Station R1										
2002	7.6	119	1131	7.7	35	47	122	63	-	-	729	1997	9	125	797	9.5	72	89	151	111	-	-	884
2003	6.6	143	1310	6	54	85	127	152	-	-	228	2000	10	244	815	9.8	60	95	161	102	-	-	1398
Jan-04	7.3	-	1052	6.6	-	-	-	-	0.12	10.8	-	2001	9.5	198	867	13	33	105	122	126	-	-	1516
Oct-04	6.3	-	1104	6.1	-	-	-	-	0.05	15	-	Jan-04	8.6	-	1058	12	-	-	-	-	0.13	11.7	-
Mar-06	6.3	-	940	7.1	-	-	-	-	0.12	12.5	-	Apr-05	6.9	-	664	8.3	-	-	-	-	0.09	9.6	-
	Station DN1												Station R2										
1997	8.5	102	1101	8.7	71	72	123	112	-	-	470	1997	8.2	124	601	8.5	63	79	105	99	-	-	951
2000	9.1	135	1193	7.3	50	67	110	98	-	-	790	2000	9.6	233	554	8	49	88	115	92	-	-	1579
2001	9.1	149	1304	8.3	36	74	147	111	-	-	835	2001	8.7	192	565	13	24	91	88	106	-	-	1683
2002	8.1	118	999	7.7	35	67	117	79	-	-	723	Jan-04	8.3	-	479	8	-	-	-	-	0.22	12.2	-
2003	7.1	160	1054	8	33	56	123	139	-	-	584	Apr-05	7.9	-	611	8	-	-	-	-	0.41	11.1	-
Jan-04	7.6	-	1053	6.9	-	-	-	-	0.12	10.7	-		Station R3										
Oct-04	7	-	1277	6.9	-	-	-	-	0.34	13.5	-	1997	7	134	423	7.2	59	78	95	92	-	-	919
Dec-05	7.9	-	1136	8.4	-	-	-	-	0.23	15.5	-	2000	7.9	227	424	6.3	53	78	81	93	-	-	1718
Mar-06	6.7	-	1008	7.7	-	-	-	-	0.04	12.5	-	2001	7.8	175	423	14	17	79	213	95	-	-	1996
												Jan-04	7.4	-	396	6.9	-	-	-	-	0.35	10.8	-

Appendix-VII (b): Correlation coefficient (r) and level of significance (p) of selected metals and P in surface sediments of individual station along north west coast of India																		
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
P1 (n=9)																		
Cr	0.22	>0.1																
Mn	-0.16	>0.1	-0.56	>0.05														
Fe	0.73	>0.01	-0.38	>0.1	0.02	>0.1												
Co	-0.25	>0.1	-0.87	<0.001	0.60	>0.5	0.13	>0.1										
Ni	-0.25	>0.1	0.26	>0.1	-0.91	<0.001	0.53	>0.5	-0.30	>0.1								
Cu	0.62	>0.02	0.01	>0.1	0.04	>0.1	0.70	>0.01	-0.04	>0.1	0.18	>0.1						
Zn	-0.77	>0.001	0.28	>0.1	0.47	>0.1	-0.94	<0.001	0.02	>0.1	-0.71	>0.1	-0.46	>0.1				
Cd	0.28	>0.1	0.00	0	-0.07	>0.1	-0.28	>0.1	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	-0.42	>0.1	0.00	0	-0.49	>0.1	-0.70	>0.01	0.00	0	0.00	0	0.00	0	0.00	0	0.27	>0.1
P	0.82	>0.001	0.31	>0.1	-0.42	>0.1	0.73	>0.01	-0.46	>0.1	0.53	>0.5	0.85	<0.001	-0.65	>0.02	0.00	0
P2 (n=9)																		
Cr	0.86	<0.001																
Mn	0.41	>0.1	-0.10	>0.1														
Fe	0.25	>0.1	-0.48	>0.1	0.87	<0.001												
Co	-0.44	>0.1	-0.81	>0.001	0.38	>0.1	0.54	>0.05										
Ni	-0.44	>0.1	0.06	>0.1	0.75	>0.001	0.82	>0.001	0.17	>0.1								
Cu	0.50	>0.1	0.37	>0.1	0.67	>0.02	0.43	>0.1	-0.35	>0.1	0.78	>0.001						
Zn	0.70	>0.01	0.50	>0.1	0.10	>0.1	-0.37	>0.1	0.05	>0.1	-0.05	>0.1	-0.21	>0.1				
Cd	0.88	<0.001	0.00	0	0.42	>0.1	0.57	>0.05	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	-0.86	<0.001	0.00	0	-0.49	>0.1	-0.68	>0.02	0.00	0	0.00	0	0.00	0	0.00	0	-0.97	<0.001
P	0.58	>0.05	0.49	>0.1	0.23	>0.1	0.44	>0.1	-0.13	>0.1	0.72	>0.01	0.44	>0.1	0.35	>0.1	0.00	0
P3 (n=9)																		
Cr	0.86	<0.001																
Mn	0.95	<0.001	0.67	>0.02														
Fe	0.39	>0.1	-0.37	>0.1	0.28	>0.1												
Co	-0.44	>0.1	-0.78	>0.001	-0.14	>0.1	0.32	>0.1										
Ni	-0.44	>0.1	0.07	>0.1	-0.03	>0.1	0.81	>0.001	0.20	>0.1								
Cu	0.67	>0.02	0.91	<0.001	0.40	>0.1	0.00	0	-0.79	>0.001	0.37	>0.1						
Zn	0.50	>0.1	0.36	>0.1	0.58	>0.05	-0.90	<0.001	-0.22	>0.1	-0.76	>0.001	-0.05					
Cd	-0.90	<0.001	0.00	0	-0.94	<0.001	-0.98	<0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.78	>0.001	0.00	0	0.94	<0.001	1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0	-0.94	<0.001
P	0.45	>0.1	0.25	>0.1	-0.21	>0.1	0.22	>0.1	-0.34	>0.1	0.03	>0.1	0.26	>0.1	0.14	>0.1	0.00	0
V1 (n=9)																		
Cr	0.52	>0.1																
Mn	0.58	>0.05	-0.17	>0.1														
Fe	0.16	>0.1	-0.68	>0.02	0.73	>0.01												
Co	0.33	>0.1	-0.64	>0.02	0.57	>0.05	0.82	>0.001										
Ni	0.33	>0.1	0.32	>0.1	0.63	>0.02	0.39	>0.1	0.22	>0.1								
Cu	0.07	>0.1	0.32	>0.1	0.61	>0.02	0.24	>0.1	-0.27	>0.1	0.61	>0.2						
Zn	0.81	>0.001	0.49	>0.1	-0.18	>0.1	-0.29	>0.1	0.15	>0.1	0.39	>0.1	-0.37	>0.1				
Cd	0.11	>0.1	0.00	0	-0.46	>0.1	-0.20	>0.1	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	-0.81	>0.001	0.00	0	-0.88	<0.001	0.63	>0.02	0.00	0	0.00	0	0.00	0	0.00	0	0.04	>0.1
P	0.20	>0.1	0.55	>0.05	-0.27	>0.1	-0.38	>0.1	-0.50	>0.1	0.54	>0.05	0.30	>0.1	0.41	>0.1	0.00	0
V2 (n=9)																		
Cr	0.39	>0.1																
Mn	0.73	>0.01	0.43	>0.1														
Fe	0.07	>0.1	-0.51	>0.1	-0.05	>0.1												
Co	-0.14	>0.1	-0.84	>0.001	0.07	>0.1	0.43	>0.1										
Ni	-0.14	>0.1	0.25	>0.1	0.39	>0.1	0.58	>0.02	-0.29	>0.1								
Cu	0.25	>0.1	0.98	<0.001	0.37	>0.1	-0.44	>0.1	-0.85	<0.001	0.23	>0.1						
Zn	0.05	>0.1	0.32	>0.1	-0.03	>0.1	-0.97	<0.001	-0.19	>0.1	-0.67	>0.02	0.23					

Appendix-VII (b): (Conte..3)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
PJ1 (n=9)																		
Cu	0.72	>0.01	0.76	>0.001	0.44	>0.1	0.29	>0.1	-0.58	>0.05	0.92	<0.001						
Zn	0.42	>0.1	0.32	>0.01	0.83	>0.001	-0.36	>0.1	0.18	>0.1	0.23	>0.1	0.08	>0.1				
Cd	0.67	>0.02	0.00	0	0.64	>0.02	1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.19	>0.1	0.00	0	0.57	0.05	0.99	<0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.97	<0.001
P	0.87	<0.001	0.48	>0.1	0.09	>0.1	0.64	>0.02	-0.22	>0.1	0.83	<0.001	0.63	>0.02	0.22	>0.1	0.00	0
PJ2 (n=9)																		
Cr	0.97	<0.001																
Mn	0.75	>0.001	0.56	>0.05														
Fe	0.34	>0.1	-0.33	>0.1	0.27	>0.1												
Co	-0.65	>0.02	-0.80	>0.001	-0.04	>0.1	0.59	>0.05										
Ni	-0.65	>0.02	-0.68	>0.02	-0.50	>0.1	0.58	>0.05	0.63	>0.02								
Cu	0.84	>0.001	0.73	>0.01	0.93	<0.001	0.20	>0.1	-0.35	>0.1	-0.64	>0.02						
Zn	-0.08	>0.1	-0.15	>0.1	0.01	>0.1	-0.55	>0.05	0.26	>0.1	-0.33	>0.1	-0.20	>0.1				
Cd	0.78	>0.001	0.00	0	0.50	>0.1	0.98	<0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.79	>0.001	0.00	0	0.76	>0.001	0.75	>0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.83	>0.001
P	0.85	<0.001	0.78	>0.001	0.63	>0.02	-0.25	>0.1	-0.34	>0.1	-0.45	>0.1	0.56	>0.05	0.26	>0.1	0.00	0
PJ3 (n=9)																		
Cr	0.16	>0.1																
Mn	0.92	<0.001	0.23	>0.1														
Fe	-0.39	>0.1	-0.91	<0.001	-0.50	>0.1												
Co	0.25	>0.1	-0.88	<0.001	0.12	>0.1	0.70	>0.01										
Ni	0.25	>0.1	-0.75	>0.001	-0.12	>0.1	0.85	<0.001	0.71	>0.1								
Cu	0.79	>0.001	0.36	>0.1	0.92	<0.001	-0.19	>0.1	-0.15	>0.1	-0.19	>0.1						
Zn	0.46	>0.1	-0.04	>0.1	0.21	>0.1	-0.22	>0.1	0.44	>0.1	0.20	>0.1	-0.15	>0.1				
Cd	0.29	>0.1	0.00	0	0.64	>0.2	-0.89	<0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.00	0	0.00	0	0.40	>0.1	-0.74	>0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.96	<0.001
P	0.06	>0.1	-0.09	>0.1	-0.24	>0.1	0.32	>0.1	0.06	>0.1	0.70	>0.01	-0.18	>0.1	0.21	>0.1	0.00	0
H1 (n=7)																		
Cr	1.00	<0.001																
Mn	-0.93	<0.001	-0.97	<0.001														
Fe	0.45	>0.1	0.39	>0.1	-0.60	>0.5												
Co	-1.00	<0.001	-1.00	<0.001	0.98	<0.001	-0.41	>0.1										
Ni	-1.00	<0.001	0.57	>0.1	-0.74	>0.02	0.98	<0.001	-0.59	>0.05								
Cu	0.98	<0.001	0.96	<0.001	-1.00	<0.001	0.62	>0.05	-0.97	<0.001	0.77	>0.01						
Zn	0.44	>0.1	0.53	>0.1	-0.32	>0.1	-0.58	>0.1	-0.51	>0.1	-0.40	>0.1	0.28	>0.1				
Cd	0.42	>0.1	0.00	0	0.86	>0.001	-0.70	>0.02	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.87	>0.001	0.00	0	0.38	>0.1	0.70	>0.02	0.00	0	0.00	0	0.00	0	0.00	0	-0.01	>0.1
P	0.61	>0.05	0.54	>0.1	-0.71	>0.02	0.99	<0.001	-0.55	>0.1	1.00	<0.001	0.74	>0.02	-0.44	>0.1	0.00	0
H2 (n=8)																		
Cr	0.92	<0.001																
Mn	-0.04	>0.1	-0.33	>0.1														
Fe	0.26	>0.1	0.38	>0.1	0.47	>0.1												
Co	-0.97	<0.001	-0.98	<0.001	0.52	>0.1	-0.19	>0.1										
Ni	-0.97	<0.001	0.80	>0.001	-0.11	>0.1	0.79	>0.01	-0.71	>0.02								
Cu	0.70	>0.02	0.93	<0.001	-0.03	>0.1	0.69	>0.02	-0.83	>0.001	0.92	<0.001						
Zn	0.14	>0.1	0.43	>0.1	0.71	>0.2	0.76	>0.01	-0.23	>0.1	0.52	>0.1	0.68	>0.02				
Cd	-0.81	>0.001	0.00	0	-0.51	>0.1	-0.71	>0.02	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.28	>0.1	0.00	0	0.04	0.1	0.50	>0.1	0.00	0	0.00	0	0.00	0	0.00	0	0.25	>0.1
P	0.14	>0.1	0.53	>0.1	0.40	>0.1	0.99	<0.001	-0.34	>0.1	0.87	>0.001	0.80	>0.001	0.79	>0.01	0.00	0

Appendix-VII (b): (Contd.4)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	
H3 (n=8)																			
Cr	0.12	>0.1																	
Mn	0.53	>0.1	0.53	>0.1															
Fe	0.71	>0.02	0.40	>0.1	0.40	>0.1													
CO	-0.68	>0.02	-0.51	>0.1	0.04	>0.1	-0.74	>0.01											
Ni	-0.68	>0.02	0.44	>0.1	0.74	>0.01	-0.18	>0.1	0.47	>0.1									
Cu	0.30	>0.1	0.48	>0.1	0.93	<0.001	0.63	>0.05	-0.07	>0.1	0.49	>0.1							
Zn	-0.44	>0.1	0.22	>0.1	0.08	>0.1	-0.59	>0.05	0.41	>0.1	0.68	>0.02	-0.27	>0.1					
Cd	0.50	>0.1	0.00	0	-0.74	>0.01	0.87	>0.001	0.00	0	0.00	0	0.00	0	0.00	0			
Pb	-0.81	>0.001	0.00	0	0.41	>0.1	-0.59	>0.05	0.00	0	0.00	0	0.00	0	0.00	0	-0.92	<0.001	
P	0.90	<0.001	-0.08	>0.1	-0.15	>0.1	0.75	>0.01	-0.77	>0.001	-0.69	>0.02	-0.01	>0.1	-0.62	>0.02	0.00	0	
DN1 (n=9)																			
Cr	-0.27	>0.1																	
Mn	0.43	>0.1	0.33	>0.1															
Fe	0.34	>0.1	-0.27	>0.1	-0.04	>0.1													
CO	0.35	>0.1	-0.75	>0.001	0.03	>0.1	0.43	>0.1											
Ni	0.35	>0.1	-0.52	>0.1	0.57	>0.05	0.37	>0.1	0.45	>0.1									
Cu	0.21	>0.1	0.35	>0.1	0.62	>0.02	0.60	>0.05	-0.25	>0.1	0.43	>0.1							
Zn	-0.49	>0.1	0.57	>0.05	0.12	>0.1	0.41	>0.1	-0.04	>0.1	-0.49	>0.1	0.31						
Cd	0.22	>0.1	0.00	0	0.98	<0.001	-0.15	>0.1	0.00	0	0.00	0	0.00	0	0.00	0			
Pb	0.29	>0.1	0.00	0	0.46	>0.1	0.74	>0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.53	>0.05	
P	0.55	>0.5	0.42	>0.1	0.57	>0.05	-0.59	>0.05	-0.58	>0.05	0.26	>0.1	0.24	>0.1	-0.43	>0.1	0.00	0	
DN2 (n=9)																			
Cr	-0.58	>0.05																	
Mn	0.02	>0.1	0.50	>0.1															
Fe	0.78	>0.001	-0.79	>0.001	-0.36	>0.1													
CO	0.35	>0.1	-0.82	>0.001	-0.15	>0.1	0.44	>0.1											
Ni	0.35	>0.1	-0.69	>0.01	-0.45	>0.1	0.98	<0.001	0.40	>0.1									
Cu	0.18	>0.1	0.43	>0.1	0.44	>0.1	0.11	>0.1	-0.58	>0.05	0.23	>0.1							
Zn	-0.65	>0.02	0.75	>0.001	0.91	<0.001	-0.80	>0.001	-0.32	>0.1	-0.68	>0.02	0.31	>0.1					
Cd	-0.14	>0.1	0.00	0	0.65	>0.02	-0.82	>0.001	0.00	0	0.00	0	0.00	0	0.00	0			
Pb	0.17	>0.1	0.00	0	0.65	>0.02	-0.24	>0.1	0.00	0	0.00	0	0.00	0	0.00	0	0.72	>0.01	
P	0.90	<0.001	-0.35	>0.1	-0.71	>0.1	0.78	>0.001	-0.02	>0.1	0.81	>0.001	0.23	>0.1	-0.72	>0.01	0.00	0	
DN3 (n=9)																			
Cr	0.19	>0.1																	
Mn	0.89	<0.001	0.26	>0.1															
Fe	0.60	>0.05	-0.55	>0.05	0.34	>0.01													
CO	0.05	>0.1	-0.78	>0.001	-0.08	>0.01	0.51	>0.1											
Ni	0.05	>0.1	-0.24	>0.1	0.76	>0.001	0.94	<0.001	0.29	>0.1									
Cu	0.63	>0.02	0.23	>0.1	0.81	>0.001	0.31	>0.1	-0.42	>0.1	0.49	>0.1							
Zn	0.19	>0.1	0.57	>0.05	0.28	>0.1	-0.43	>0.1	-0.02	>0.1	-0.25	>0.1	0.01	>0.1					
Cd	0.32	>0.1	0.00	0	0.66	>0.02	-0.40	>0.1	0.00	0	0.00	0	0.00	0	0.00	0			
Pb	0.78	>0.001	0.00	0	0.88	<0.001	0.70	>0.01	0.00	0	0.00	0	0.00	0	0.00	0	0.34	>0.1	
P	0.70	>0.01	0.79	>0.001	0.66	>0.05	0.06	>0.1	-0.47	>0.1	0.38	>0.1	0.37	>0.1	0.42	>0.1	0.00	0	
TP1 (n=5)																			
Cr	0.49	>0.1																	
Mn	-0.24	>0.1	0.88	>0.001															
Fe	0.59	>0.1	0.13	>0.1	-0.85	>0.01													
CO	-0.04	>0.1	-0.83	>0.02	-0.47	>0.1	-0.26	>0.1											
Ni	-0.04	>0.1	-0.30	>0.1	-0.69	>0.05	0.39	>0.1	-0.27	>0.1									
Cu	0.31	>0.1	0.23	>0.1	0.04	>0.1	0.98	<0.001	-0.44	>0.1	0.51	>0.1							

Appendix-VII (b): (Contd.5)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
TP1 (n=5)																		
Zn	0.81	>0.02	-0.06	>0.1	0.25	>0.1	0.60	>0.1	0.38	>0.1	-0.38	>0.1	0.42	>0.1				
Cd	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
P	0.75	>0.05	0.94	0	0.95	>0.001	0.28	>0.1	-0.66	>0.1	-0.45	>0.1	0.32	>0.1	0.26	>0.1	0.00	0
TP2 (n=4)																		
Cr	0.90	>0.001																
Mn	-0.46	>0.1	0.74	>0.05														
Fe	0.41	>0.1	-0.90	>0.001	-0.97	<0.001												
Co	-0.29	>0.1	-0.67	>0.05	-1.00	<0.001	0.29	>0.1										
Ni	-0.29	>0.1	0.25	>0.1	0.84	>0.01	0.19	>0.1	-0.88	>0.001								
Cu	-0.53	>0.1	-0.12	>0.1	0.59	>0.1	0.53	0.1	-0.66	>0.1	0.93	>0.001						
Zn	0.58	>0.1	0.18	>0.1	-0.54	>0.1	-0.58	>0.1	0.61	>0.1	-0.91	>0.001	-1.00	<0.001				
Cd	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
Pb	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
P	0.98	<0.001	0.97	<0.001	0.55	>0.1	-0.98	<0.001	-0.47	>0.1	0.00	0	-0.36	>0.1	0.42	>0.1	0.00	0
TP3 (n=5)																		
Cr	0.00																	
Mn	0.85	>0.01	0.49	>0.1														
Fe	0.81	>0.01	0.39	>0.1	0.69	>0.05												
Co	-0.54	>0.1	-0.74	>0.05	-0.85	>0.01	-0.67	>0.05										
Ni	-0.54	>0.1	0.09	>0.1	0.39	>0.1	0.13	>0.1	-0.64	>0.1								
Cu	0.61	>0.1	0.78	>0.02	0.92	<0.001	0.80	>0.02	-0.97	<0.1	0.45	>0.1						
Zn	0.29	>0.1	0.38	>0.1	0.43	>0.1	0.64	>0.1	-0.10	>0.1	-0.66	>0.1	0.33	>0.1				
Cd	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
Pb	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
P	0.18	>0.1	0.88	>0.001	0.59	>0.1	0.62	>0.1	-0.59	>0.1	-0.24	>0.1	0.73	>0.5	0.77	>0.02	0.00	0
BS1 (n=8)																		
Cr	-0.96	<0.001																
Mn	0.06	>0.1	0.67	>0.02														
Fe	0.84	>0.001	-0.70	>0.02	0.41	>0.1												
Co	-0.39	>0.1	0.17	>0.1	-0.50	>0.1	-0.80	>0.001										
Ni	-0.39	>0.1	0.87	>0.001	0.25	>0.1	-0.87	>0.001	0.41	>0.1								
Cu	0.82	>0.001	-0.62	>0.05	0.16	>0.1	0.98	<0.001	-0.78	>0.001	-0.88	<0.001						
Zn	-0.81	>0.001	0.63	>0.05	-0.08	>0.1	-0.83	>0.001	0.46	>0.1	0.93	<0.001	-0.91	<0.001				
Cd	0.34	>0.1	0.00	0	0.54	>0.1	0.53	>0.1	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
Pb	-0.81	>0.001	0.00	0	-0.90	<0.001	-0.91	<0.001	0.00	0	0.00	0	0.00	0	0.00	0	-0.81	>0.001
P	0.95	<0.001	-0.83	0.001	-0.18	>0.1	0.89	<0.001	-0.45	>0.1	-1.00	<0.001	0.91	<0.001	-0.95	<0.001	0.00	0
BS2 (n=8)																		
Cr	0.71	>0.02																
Mn	0.64	>0.02	0.35	>0.1														
Fe	0.90	<0.001	0.75	>0.01	0.85	>0.001												
Co	-0.62	>0.05	0.06	>0.1	-0.83	>0.001	-0.60	>0.05										
Ni	-0.62	>0.05	-0.49	>0.1	-0.38	>0.1	-0.61	>0.05	0.53	>0.1								
Cu	0.95	<0.001	0.64	>0.02	0.51	>0.1	0.76	>0.01	-0.54	>0.1	-0.97	<0.001						
Zn	-0.19	>0.1	0.48	>0.1	-0.05	>0.1	0.11	>0.1	0.59	>0.05	0.53	>0.1	-0.36	>0.1				
Cd	-0.72	>0.01	0.00	0	0.96	<0.001	-0.76	>0.01	0.00	0	0.00	0	0.00	0	0.00	0	0.02	>0.1
Pb	-0.15	>0.1	0.00	0	0.30	>0.1	-0.01	>0.1	0.00	0	0.00	0	0.00	0	0.00	0	0.02	>0.1
P	0.80	>0.001	0.61	>0.05	0.19	>0.1	0.53	>0.1	-0.27	>0.1	-0.96	<0.001	0.94	<0.001	-0.38	>0.1	0.00	0

Appendix-VII (b): (Contd..6)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	
BS3 (n=8)																			
Cr	0.65	>0.02																	
Mn	-0.12	>0.1	0.33	>0.1															
Fe	0.60	>0.05	0.59	>0.05	-0.52	>0.1													
Co	-0.28	>0.1	-0.42	>0.1	-0.68	>0.02	-0.32	>0.1											
Ni	-0.28	>0.1	-0.82	>0.001	0.28	>0.1	-0.84	>0.001	0.05	>0.1									
Cu	0.95	<0.001	0.79	>0.001	-0.03	>0.1	0.94	<0.001	-0.54	>0.1	-0.84	>0.001							
Zn	-0.70	>0.02	-0.17	>0.1	0.14	>0.1	-0.76	>0.01	0.63	>0.05	0.30	>0.1	-0.71	>0.02					
Cd	-0.49	>0.1	0.00	0	-0.68	>0.02	0.94	<0.001	0.00	0	0.00	0	0.00	0	0.00	0			
Pb	-0.36	>0.1	0.00	0	0.88	<0.001	-0.32	>0.1	0.00	0	0.00	0	0.00	0	0.00	0	-0.24	>0.1	
P	0.93	<0.001	0.36	>0.1	-0.64	>0.02	0.94	<0.001	-0.04	>0.1	-0.77	>0.001	0.78	>0.001	-0.69	0.0	0.00	0	
BY1 (n=8)																			
Cr	-0.02	>0.1																	
Mn	-0.15	>0.1	0.80	>0.001															
Fe	0.49	>0.1	0.49	>0.1	0.12	>0.1													
Co	-0.82	>0.001	0.51	>0.1	0.91	<0.001	-0.05	>0.1											
Ni	-0.82	>0.001	1.00	<0.001	0.78	>0.001	0.53	>0.1	0.48	>0.1									
Cu	0.85	>0.001	0.00	0	-0.60	>0.05	0.19	>0.1	-0.84	>0.001	0.03	>0.1							
Zn	0.62	0.05	-0.44	>0.1	-0.87	>0.001	-0.26	>0.1	-0.91	<0.001	-0.42	>0.1	0.87	>0.001					
Cd	0.34	>0.1	0.00	0	0.08	>0.1	-0.96	<0.001	0.00	0	0.00	0	0.00	0	0.00	0			
Pb	0.69	0.02	0.00	0	0.82	>0.001	-0.18	>0.1	0.00	0	0.00	0	0.00	0	0.00	0	0.41	>0.1	
P	0.06	>0.1	-0.08	>0.1	0.24	>0.1	0.62	>0.05	0.21	>0.1	-0.06	>0.1	-0.47	>0.1	-0.59	>0.05	0.00	0	
BY2 (n=8)																			
Cr	0.54	>0.1																	
Mn	0.39	>0.1	-0.05	>0.1															
Fe	0.30	>0.1	-0.73	>0.01	0.28	>0.1													
Co	-0.27	>0.1	-0.02	>0.1	-0.98	<0.001	-0.14	>0.1											
Ni	-0.27	>0.1	-0.63	>0.05	-0.59	>0.05	0.60	>0.05	0.70	>0.02									
Cu	0.68	>0.02	-0.24	>0.1	0.46	>0.1	0.84	>0.001	-0.29	>0.1	0.29	>0.1							
Zn	0.70	>0.01	0.79	>0.001	-0.35	>0.1	-0.32	>0.1	0.38	>0.1	-0.05	>0.1	0.13	>0.1					
Cd	0.66	>0.02	0.00	0	-0.45	>0.1	1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0			
Pb	0.04	>0.1	0.00	0	0.18	>0.1	0.77	>0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.72	>0.01	
P	-0.30	>0.1	-0.93	<0.001	-0.09	>0.1	0.86	>0.001	0.21	>0.1	0.83	>0.001	0.47	>0.1	-0.50	>0.1	0.00	0	
BY3 (n=8)																			
Cr	0.51	>0.1																	
Mn	0.81	>0.001	0.04	>0.1															
Fe	-0.17	>0.1	-0.21	>0.1	-0.39	>0.1													
Co	-0.23	>0.1	0.59	>0.05	-0.55	>0.05	-0.14	>0.1											
Ni	-0.23	>0.1	0.29	>0.1	0.21	>0.1	-0.87	>0.001	0.58	>0.05									
Cu	0.37	>0.1	0.50	>0.1	0.11	>0.1	0.46	>0.1	-0.23	>0.1	-0.64	>0.02							
Zn	0.98	<0.001	0.67	>0.02	0.76	>0.01	-0.54	>0.1	-0.10	>0.1	0.23	>0.1	0.50	>0.1					
Cd	-0.46	>0.1	0.00	0	-0.37	>0.1	-0.88	<0.001	0.00	0	0.00	0	0.00	0	0.00	0			
Pb	0.32	>0.1	0.00	0	-0.03	>0.1	0.56	>0.05	0.00	0	0.00	0	0.00	0	0.00	0	-0.89	<0.001	
P	-0.91	<0.001	-0.48	>0.1	-0.81	>0.001	0.90	<0.001	-0.04	>0.1	-0.65	0.02	0.02	>0.1	-0.86	0.001	0.00	0	
M1 (n=9)																			
Cr	0.08	>0.1																	
Mn	-0.11	>0.1	-0.19	>0.1															
Fe	0.57	>0.05	0.09	>0.1	0.61	>0.02													
Co	0.05	>0.1	-0.53	>0.05	-0.30	>0.1	-0.13	>0.1											
Ni	0.05	>0.1	0.35	>0.1	0.69	>0.01	0.05	>0.1	-0.58	>0.05									
Cu	0.65	>0.02	0.26	>0.1	0.68	>0.02	0.95	<0.001	-0.36	>0.1	0.33	>0.1							
Zn	-0.27	>0.1	0.33	>0.1	0.52	>0.1	0.22	>0.1	0.04	>0.1	0.71	>0.01	0.37	>0.1					

Appendix-VII (b): (Contd..7)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
M1 (n=9)																		
Cd	-0.34	>0.1	0.00	0	0.07	>0.1	-0.39	>0.1	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	-0.95	<0.001	0.00	0	0.86	<0.001	0.53	>0.5	0.00	0	0.00	0	0.00	0	0.00	0	0.56	>0.05
P	0.83	>0.001	0.57	>0.5	0.02	>0.1	0.78	>0.001	-0.16	>0.1	-0.13	>0.1	0.74	>0.001	0.15	>0.1	0.00	0
M2 (n=9)																		
Cr	0.40	>0.1																
Mn	-0.15	>0.1	-0.06	>0.1														
Fe	0.88	<0.001	0.16	>0.1	0.02	>0.1												
Co	-0.24	>0.1	-0.79	>0.001	-0.50	>0.1	-0.25	>0.1										
Ni	-0.24	>0.1	0.32	>0.1	-0.01	>0.1	-0.69	>0.01	-0.24	>0.1								
Cu	0.42	>0.1	-0.44	>0.1	-0.08	>0.1	0.73	>0.01	0.19	>0.1	-0.53	>0.05						
Zn	-0.10	>0.1	0.02	>0.1	-0.80	>0.001	-0.19	>0.1	0.36	>0.1	0.52	>0.1	0.05	>0.1				
Cd	-0.85	<0.001	0.00	0	-0.52	>0.1	-0.80	>0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	-0.70	>0.01	0.00	0	0.42	>0.1	-0.77	>0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.35	>0.1
P	0.90	<0.001	0.70	>0.01	-0.09	>0.1	0.75	>0.001	-0.58	>0.05	-0.44	>0.1	0.10	>0.1	-0.29	>0.1	0.00	0
M3 (n=8)																		
Cr	0.87	>0.001																
Mn	0.61	>0.05	0.07	>0.1														
Fe	0.55	>0.05	0.44	>0.1	0.51	>0.1												
Co	0.41	>0.1	0.52	>0.1	-0.43	>0.1	-0.54	>0.1										
Ni	0.41	>0.1	0.14	>0.1	0.61	>0.5	-0.19	>0.1	0.35	>0.1								
Cu	0.68	>0.02	0.53	>0.1	0.76	>0.01	0.93	<0.001	-0.38	>0.1	0.17	>0.1						
Zn	0.73	>0.01	0.36	>0.1	0.58	>0.05	-0.09	>0.1	0.46	>0.1	0.97	<0.001	0.27	>0.1				
Cd	-0.81	>0.001	0.00	0	-0.08	>0.1	-0.64	>0.02	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	-0.34	>0.1	0.00	0	0.87	>0.001	-0.15	>0.1	0.00	0	0.00	0	0.00	0	0.00	0	0.27	>0.1
P	0.41	>0.1	0.64	>0.02	0.11	>0.1	0.87	>0.001	-0.24	>0.1	-0.47	>0.1	0.72	>0.01	-0.30	>0.1	0.00	0
DL1 (n=5)																		
Cr	1.00	<0.001																
Mn	-0.67	>0.0	-1.00	<0.001														
Fe	0.97	<0.001	1.00	<0.001	-0.60	>0.1												
Co	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001										
Ni	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001								
Cu	1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	-1.00	<0.001						
Zn	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001	1.00	<0.001	-1.00	<0.001				
Cd	-1.00	<0.001	0.00	>0.001	-0.47	>0.1	-0.98	<0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	-0.80	>0.01	0.00	0	0.21	>0.1	-0.88	>0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.77	>0.02
P	1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	>0.001	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	0.00	0
DL2 (n=5)																		
Cr	1.00	<0.001																
Mn	-0.20	>0.1	-1.00	<0.001														
Fe	0.40	>0.1	1.00	<0.001	-0.27	>0.1												
Co	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001										
Ni	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001								
Cu	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001	1.00	<0.001						
Zn	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001	1.00	<0.001	1.00	<0.001				
Cd	-0.19	>0.1	0.00	0	0.99	<0.001	-0.92	>0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	-0.86	>0.01	0.00	0	0.56	>0.1	-0.90	>0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.67	>0.05
P	1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	-1.00	<0.001	-1.00	<0.001	-1.00	<0.001	0.00	0

Appendix-VII (b): (Contd..8)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
DL3 (n=4)																		
Cr	1.00	<0.001																
Mn	0.09	>0.1	-1.00	<0.001														
Fe	0.91	>0.01	1.00	<0.001	-0.32	>0.1												
Co	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001										
Ni	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001								
Cu	1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	-1.00	<0.001						
Zn	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001	1.00	<0.001	-1.00	<0.001				
Cd	0.00	0	0.00	0	-1.00	<0.001	1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.00	0	0.00	0	1.00	<0.001	-1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0	-1.00	<0.001
P	1.00	<0.001	1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	-1.00	<0.001	1.00	<0.001	-1.00	<0.001	0.00	0
R1 (n=5)																		
Cr	0.92	>0.001																
Mn	0.44	>0.1	0.61	>0.1														
Fe	0.52	>0.1	0.45	>0.1	0.79	>0.02												
Co	-0.33	>0.1	-0.47	>0.1	-0.48	>0.1	-0.91	>0.001										
Ni	-0.33	>0.1	0.69	>0.05	0.92	<0.001	0.93	>0.001	-0.78	>0.02								
Cu	0.74	>0.05	0.49	>0.1	0.60	>0.1	-0.06	>0.1	0.35	>0.1	0.30	>0.1						
Zn	0.29	>0.1	0.15	>0.1	0.73	>0.05	0.93	<0.001	-0.75	>0.05	0.82	>0.02	-0.08	>0.1				
Cd	1.00	<0.001	0.00	0	1.00	<0.001	1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	1.00	<0.001	0.00	0	1.00	<0.001	1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0	1.00	<0.001
P	0.77	>0.02	0.88	>0.001	0.66	>0.1	0.78	>0.02	-0.83	>0.02	0.86	>0.01	0.14	>0.1	0.51	>0.1	0.00	0
R2 (n=5)																		
Cr	0.61	>0.1																
Mn	0.48	>0.1	-0.13	>0.1														
Fe	0.38	>0.1	-0.03	>0.1	0.49	>0.1												
Co	-0.44	>0.1	-0.44	>0.1	-0.26	>0.1	-0.85	>0.01										
Ni	-0.44	>0.1	0.46	>0.1	0.56	>0.1	0.79	>0.02	-0.86	>0.01								
Cu	0.54	>0.1	-0.09	>0.1	0.57	>0.1	-0.08	>0.1	0.31	>0.1	0.23	>0.1						
Zn	0.21	>0.1	-0.18	>0.1	0.61	>0.1	0.92	>0.001	-0.70	>0.05	0.55	>0.1	-0.25	>0.1				
Cd	-1.00	<0.001	0.00	0	1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	1.00	<0.001	0.00	0	-1.00	<0.001	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	-1.00	<0.001
P	0.57	>0.1	0.92	<0.001	-0.02	>0.1	0.27	>0.1	-0.69	>0.05	0.58	>0.1	-0.33	>0.1	0.18	>0.1	0.00	0
R3 (n=4)																		
Cr	0.88	>0.02																
Mn	0.22	>0.1	0.90	>0.001														
Fe	0.35	>0.1	-0.18	>0.1	0.29	>0.1												
Co	-0.53	>0.1	-0.06	>0.1	0.38	>0.1	-0.97	<0.001										
Ni	-0.53	>0.1	-0.07	>0.1	-0.50	>0.1	0.99	<0.001	-0.99	<0.001								
Cu	0.32	>0.1	-0.16	>0.1	-0.58	>0.1	1.00	<0.001	-0.97	<0.001	1.00	<0.001						
Zn	0.69	>0.1	0.26	>0.1	-0.19	>0.1	0.90	>0.001	-0.98	<0.001	0.94	>0.001	0.91	>0.01				
Cd	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0		
Pb	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	
P	0.94	>0.001	0.67	>0.1	0.27	>0.1	0.62	>0.1	-0.79	>0.05	0.70	>0.05	0.63	>0.1	0.89	>0.01	0.00	

Appendix-VII (c): Correlation coefficient (r) and level of significance (p) of selected metals and P in liments during different sampling events																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
1997																				
Cr	0.55	>0.001																		
Mn	-0.46	>0.01	-0.6	<0.001																
Fe	0.8	<0.001	0.39	>0.02	-0.32	>0.1														
Co	0.6	<0.001	0.28	>0.1	0.1	>0.1	0.81	<0.001												
Ni	0.82	<0.001	0.74	<0.001	-0.7	<0.001	0.62	<0.001	0.39	>0.05										
Cu	0.62	<0.001	0.3	>0.1	-0.03	>0.1	0.79	<0.001	0.86	<0.001	0.5	>0.001								
Zn	0.78	<0.001	0.47	>0.01	-0.16	>0.1	0.79	<0.001	0.86	<0.001	0.63	<0.001	0.84	<0.001						
P	0.35	>0.05	0.77	<0.001	-0.68	<0.001	0.43	>0.02	0.21	>0.1	0.66	<0.001	0.32	>0.1	0.29	>0.1				
1998																				
Cr	0.68	<0.001																		
Mn	-0.25	>0.1	-0.44	>0.01																
Fe	0.78	<0.001	0.48	>0.001	0.02	>0.1														
Co	0.58	<0.001	0.3	>0.05	0.31	>0.1	0.79	<0.001												
Ni	0.66	<0.001	0.78	<0.001	-0.58	<0.001	0.55	>0.001	0.33	>0.05										
Cu	0.71	<0.001	0.38	>0.02	0.21	>0.1	0.88	<0.001	0.87	<0.001	0.33	>0.05								
Zn	0.35	>0.02	0.26	>0.1	0.23	>0.1	0.39	>0.02	0.38	>0.02	0.43	>0.01	0.23	>0.1						
P	0.5	>0.001	0.6	<0.001	-0.47	>0.001	0.54	>0.001	0.21	>0.1	0.76	<0.001	0.3	>0.05	0.36	>0.02				
2000																				
Cr	0.44	>0.01																		
Mn	-0.19	>0.1	0.05	>0.1																
Fe	0.68	<0.001	0.25	>0.1	-0.15	>0.1														
Co	0.18	>0.1	0.54	>0.001	0.36	>0.02	-0.21	>0.1												
Ni	0.14	>0.1	0.93	<0.001	0.29	>0.1	0.14	>0.1	0.66	<0.001										
Cu	0.31	>0.05	0.7	<0.001	0.56	<0.001	0.41	>0.01	0.48	>0.001	0.81	<0.001								
Zn	-0.31	>0.05	0.26	>0.1	0.59	<0.001	-0.45	>0.001	0.49	>0.001	0.47	>0.001	0.44	>0.01						
P	0.09	>0.1	0.9	<0.001	-0.05	>0.1	0.06	>0.1	0.49	>0.001	0.86	<0.001	0.54	>0.001	0.25	>0.1				
2001																				
Cr	0.21	>0.1																		
Mn	0.41	>0.01	-0.26	>0.1																
Fe	-0.05	>0.1	0.45	>0.001	-0.27	>0.1														
Co	0.44	>0.001	-0.04	>0.1	0.82	<0.001	-0.15	>0.1												
Ni	0.19	>0.1	0.5	>0.001	-0.47	>0.001	0.41	>0.01	-0.29	>0.05										
Cu	-0.1	>0.1	0.04	>0.1	0.18	>0.1	0.37	>0.02	0.01	>0.1	-0.12	>0.1								
Zn	0.46	>0.001	0.25	>0.1	0.41	>0.01	0.37	>0.02	0.44	>0.001	0.21	>0.1	0.19	>0.1						
P	-0.27	>0.1	0.42	>0.001	-0.66	<0.001	0.8	<0.001	-0.57	<0.001	0.48	>0.001	0.32	>0.05	0.06	>0.1				
2002																				
Cr	-0.1	>0.1																		
Mn	0.37	>0.02	0.51	>0.001																
Fe	0.48	>0.001	0.36	>0.02	0.69	<0.001														
Co	0.2	>0.1	0.73	<0.001	0.89	<0.001	0.66	<0.001												
Ni	0.2	>0.1	0.9	<0.001	0.51	>0.001	0.5	>0.001	0.66	<0.001										
Cu	0.68	<0.001	-0.11	>0.1	0.65	<0.001	0.79	<0.001	0.47	>0.001	0.05	>0.1								
Zn	0.22	>0.1	0.23	>0.1	0.42	>0.01	0.4	>0.02	0.33	>0.05	0.41	>0.01	0.3	>0.05						
P	0.07	>0.1	0.32	>0.05	-0.14	>0.1	0.29	>0.1	0.05	>0.1	0.41	>0.01	-0.09	>0.1	0.21	>0.1				

Appendix-VII (c):(Contd..2)

Correlation coefficient (r) and level of significance (p) of selected metals and P in surface sediments during different sampling events																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
2003																				
Cr	0.44	>0.01																		
Mn	0.1	>0.1	0.11	>0.1																
Fe	0.23	>0.1	0.44	>0.01	0.6	<0.001														
Co	-0.12	>0.1	0.17	>0.1	0.3	>0.05	0.46	>0.001												
Ni	0.19	>0.1	0.4	>0.02	0.2	>0.1	0.46	>0.001	0.85	<0.001										
Cu	0.35	>0.02	0.45	>0.001	0.65	<0.001	0.74	<0.001	0.24	>0.1	0.25	>0.1								
Zn	0.06	>0.1	0.3	>0.05	0.47	>0.001	0.29	>0.1	0.42	>0.02	0.39	>0.02	0.07	>0.1						
Cd	0.04	>0.1	0	0	-0.48	>0.001	-0.25	>0.1	-0.05	>0.1	-0.01	>0.1	-0.17	>0.1	0.16	>0.1				
Pb	0.06	>0.1	0.12	>0.1	0.03	>0.1	-0.34	>0.05	-0.02	>0.1	0.09	>0.1	-0.42	>0.01	0.06	>0.1	0.04	>0.1		
P	0.14	>0.1	0.18	>0.1	0.41	>0.02	-0.11	>0.1	-0.28	>0.1	-0.13	>0.1	-0.01	>0.1	-0.25	>0.1	0.18	>0.1	0.38	>0.02
All values n= 343																				
Cr	0.42	<0.001																		
Mn	0.1	>0.1	0	>0.1																
Fe	0.48	<0.001	0.27	>0.001	0.21	>0.02														
Co	-0.09	>0.1	-0.25	>0.01	0.03	>0.1	0.09	>0.1												
Ni	0.31	>0.001	0.51	<0.001	-0.23	>0.02	0.44	<0.001	0.17	>0.05										
Cu	0.53	<0.001	0.3	>0.001	0.33	<0.001	0.7	<0.001	-0.04	>0.1	0.27	>0.001								
Zn	0.01	>0.1	0.18	>0.05	0.08	>0.1	-0.1	>0.1	0.11	>0.1	0.75	<0.001	-0.01	>0.1						
Cd	0.03	>0.1	0	>0.1	-0.22	>0.02	-0.07	>0.1	-0.05	>0.1	-0.01	>0.1	-0.17	>0.05	0.16	>0.1				
Pb	0.19	>0.05	0.12	>0.1	0	>0.1	-0.14	>0.1	-0.02	>0.1	0.09	>0.1	-0.42	<0.001	0.06	>0.1	0.07	>0.1		
P	0.3	>0.001	0.37	<0.001	-0.42	<0.001	0.55	<0.001	-0.09	>0.1	0.47	<0.001	0.29	>0.001	-0.07	>0.1	0.38	<0.001	0.18	>0.01

Appendix-VIII (a): Concentration of CO ₃ ²⁻ (%) in core sediment of Positra Bay.										
	Mar-99					Nov-99				
Depth (cm)	OD1	OD2	OD3	OC3	OF	OD1	OD2	OD3	OG	OE
2	34.8	35.7	54.1	34.4	51	77.6	33.7	55.2	59.2	70.6
4	40.6	39.8	47.6	26.4	55.1	97.6	25.4		67.6	67.2
6	42.6	61.8	52.7	31.3	55.7	87.9	58.3	94.9	74.1	69.7
8	41.9	57.5	51.8	34.6	51.6	81.2	54.9	72.8	71.9	67.7
10	51	50.1	45.8	31.5	50.3	80.9	57.1	85.1	73.7	63.9
12	25.4	50.3		33.7	45.6	90.9	64.1	64.3	70	62.7
14	34.1	58.6		31.1	40.3	78.4	19.7	65.2	69.2	64.2
16	41.6	57.4		30.3	39.1	91.3		65.1	59.8	71.9
18	47.7	44.4		30.8	36.4	-		62.9	49.3	66.9
20	33.7			19.6	29.6	93.7		50.9	44.9	61.3
22	40.3			36.1	29.7	82.4		60.4	40.7	38.8
24	34.7			30.7	32.3	69.8		48.3	18.3	24.3
26	48.2			25.5	30.6	61		70.2	15.6	19.1
28				20.5	30.8	74.5		62.4	13.9	3.7
30				47.1	31.3	73.5		68.1	12.8	8.6
32				15.5	29.4	71.7		69.4		1.7
34				15.2	28.4	74.1		66.9		
36				14.3	28.4			43.7		
38					27.1			95		
40					26.9			64.8		
42					24.5			72.4		
44					23.4			69.1		
46					25.2			82.5		
48					22.5			70.8		

Appendix-VIII (c) : Correlation coefficient (r) and coefficient of significance (p) of selected metals, P and CO ₃ ²⁻ -																		
in sediment core from inshore areas of Positra Bay and Vadinar																		
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		P	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
	station OG (n=15)																	
Cr	-0.28	>0.1																
Mn	-0.5	>0.02	0.38	>0.1														
Fe	-0.58	>0.01	0.54	>0.02	0.52	>0.02												
Co	-0.77	<0.001	0.27	>0.1	0.52	>0.02	0.64	>0.001										
Ni	-		-		-		-											
Cu	-0.8	<0.001	0.53	>0.02	0.65	>0.001	0.85	<0.001	0.91	<0.001	-	-						
Zn	0.16	>0.1	0.33	>0.1	0.41	>0.1	0.52	>0.02	0		-	-	0.26	>0.1				
P	-0.84	<0.001	0.29	>0.1	0.5	>0.02	0.66	>0.001	0.98	<0.001	-	-	0.91	<0.001	-0.06	>0.1		
CO ₃ ²⁻	-0.9	<0.001	0.31	>0.1	0.59	>0.01	0.65	>0.001	0.93	<0.001	-	-	0.9	<0.001	-0.06	>0.1	0.95	<0.001
	station OE (n=16)																	
Cr	0.35	>0.1																
Mn	-0.07	>0.1	0.3	>0.1														
Fe	-0.06	>0.1	0.45	>0.05	0.72	<0.001												
Co	-0.75	<0.001	0.03	>0.1	0.48	>0.05	0.65	>0.001										
Ni	-		-		-		-		-		-							
Cu	-0.5	>0.02	0.15	>0.1	0.63	>0.001	0.85	<0.001	0.93	<0.001	-	-						
Zn	0.31	>0.1	-0.13	>0.1	0.2	>0.1	0.36	>0.1	-0.02	>0.1	-	-	0.16	>0.1				
P	-0.48	>0.02	-0.02	>0.1	-0.19	>0.1	-0.07	>0.1	0.28	>0.1	-	-	0.16	>0.1	-0.29	>0.1		
CO ₃ ²⁻	-0.86	<0.001	-0.17	>0.1	0.35	>0.1	0.47	>0.05	0.96	<0.001	-	-	0.84	<0.001	-0.11	>0.1	0.35	>0.1
	station OF (n=24)																	
Cr	0.83	<0.001																
Mn	0.82	<0.001	0.88	<0.001														
Fe	0.94	<0.001	0.9	<0.001	0.85	<0.001												
Co	0.23	>0.1	0.49	>0.001	0.58	>0.001	0.39	>0.05										
Ni	0.88	<0.001	0.92	<0.001	0.9	<0.001	0.95	<0.001	0.55	>0.001								
Cu	0.05	>0.1	0.05	>0.1	0.06	>0.1	0.07	>0.1	0.32	>0.1	0.2	>0.1						
Zn	0.74	<0.001	0.66	<0.001	0.59	>0.001	0.73	<0.001	0.05	>0.1	0.6	<0.001	-0.07	>0.1				
P	0.32	>0.1	0.29	>0.1	0.4	>0.02	0.33	>0.05	0.37	>0.05	0.26	>0.1	-0.31	>0.1	0.19	>0.1		
CO ₃ ²⁻	-0.65	<0.001	-0.54	>0.001	-0.52	>0.001	-0.57	>0.001	0.21	>0.1	-0.4	>0.02	0.23	>0.1	-0.75	<0.001	-0.2	>0.1

Appendix-VIII (e) : Correlation coefficient (r) and coefficient of significance (p) for Al, Cr, Mn, Fe, Co, Ni, Cu, ZN and P																		
in sediment core from inshore areas of Vadinar																		
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		P	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
	station VN16 (n=49)																	
Cr	0.5	<0.001																
Mn	-0.4	>0.001	-0.4	>0.001														
Fe	-0.4	>0.001	-0.4	>0.001	0.3	>0.02												
Co	0.4	>0.001	0.6	<0.001	0.03	>0.1	-0.03	>0.1										
Ni	0.6	<0.001	0.6	<0.001	-0.05	>0.1	-0.2	>0.1	0.7	<0.001								
Cu	0.03	>0.1	0.5	<0.001	0.2	>0.1	0.3	>0.02	0.8	<0.001	0.6	<0.001						
Zn	-0.05	>0.1	0.2	>0.1	-0.1	>0.1	-0.03	>0.1	0.1	>0.1	0.1	>0.1	0.2	>0.1				
P	-0.2	>0.1	-0.4	>0.001	0.3	>0.02	0.3	>0.02	-0.1	>0.1	-0.01	>0.1	0.02	>0.1	-0.1	>0.1		

Appendix-VIII(f): Correlation coefficient (r) and coefficient of significance (p) for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, P and CO ₃ ²⁻																				
in surface sediment from inshore areas of Positra Bay																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Positra Bay March 1999 subtidal (n=6)																				
Cr	0.31	>0.1																		
Mn	-0.59	>0.05	-0.21	>0.1																
Fe	0.72	>0.02	0.56	>0.1	-0.64	>0.05														
Co	-0.08	>0.1	-0.22	>0.1	-0.41	>0.1	0.44	>0.1												
Ni	0.71	>0.02	-0.12	>0.1	-0.54	>0.1	0.24	>0.1	-0.18	>0.1										
Cu	0.19	>0.1	0.88	>0.001	-0.15	>0.1	0.57	>0.1	-0.02	>0.1	-0.07	>0.1								
Zn	0.7	>0.02	0.05	>0.1	-0.49	>0.1	0.84	>0.001	0.58	>0.001	0.36	>0.1	0.14	>0.1						
P	-0.71	>0.02	-0.15	>0.1	0.89	>0.001	-0.49	>0.1	-0.09	>0.1	-0.6	>0.05	0.09	>0.1	-0.38	>0.1	-	-	-	-
CO ₃ ²⁻	-0.93	<0.001	-0.53	>0.1	0.51	>0.1	-0.61	>0.1	0.36	>0.1	-0.64	>0.05	-0.32	>0.1	-0.43	>0.1	-	-	-	-
Positra Bay March 1999 intertidal (n=6)																				
Cr	0.76	>0.001																		
Mn	0.32	>0.1	0.59	>0.02																
Fe	0.25	>0.1	0.5	>0.05	0.8	<0.001														
Co	0.2	>0.1	0.3	>0.1	0.5	>0.05	0.64	>0.01												
Ni	0.39	>0.1	0.68	>0.001	0.89	<0.001	0.91	<0.001	0.67	>0.001										
Cu	0.29	>0.1	0.57	>0.02	0.75	>0.001	0.85	<0.001	0.82	<0.001	0.93	<0.001								
Zn	0.64	>0.01	0.87	<0.001	0.78	<0.001	0.75	>0.001	0.69	>0.001	0.88	<0.001	0.86	<0.001						
P	-0.09	>0.1	-0.39	>0.1	-0.36	>0.1	-0.06	>0.1	-0.16	>0.1	-0.35	>0.1	-0.25	>0.1	-0.29	>0.1	-	-	-	-
CO ₃ ²⁻	-0.17	>0.1	0.2	>0.1	0.32	>0.1	0.15	>0.1	-0.23	>0.1	0.15	>0.1	0.03	>0.1	0.06	>0.1	-	-	-	-
Positra Bay November 1999 subtidal (n=7)																				
Cr	0.99	<0.001																		
Mn	0.7	>0.02	0.83	>0.001																
Fe	0.78	>0.01	0.93	<0.001	0.54	>0.1														
Co	0.33	>0.1	0.3	>0.1	0.06	>0.1	0.49	>0.1												
Ni	0.62	>0.05	0.78	>0.01	0.28	>0.1	0.88	>0.001	0.61	>0.05										
Cu	0.64	>0.05	0.73	>0.02	0.21	>0.1	0.7	>0.02	0.85	>0.001	0.87	>0.001								
Zn	0.92	<0.001	1	<0.001	0.45	>0.1	0.88	>0.001	0.49	>0.1	0.76	>0.01	0.75	>0.01						
P	0.5	>0.1	0.54	>0.1	0.2	>0.1	0.59	>0.05	0.98	<0.001	0.64	>0.05	0.87	>0.011	0.63	>0.05	-	-	-	-
Positra Bay November 1999 Intertidal (n=9)																				
Cr	0.88	<0.001																		
Mn	0.88	<0.001	0.84																	
Fe	0.88	<0.001	0.91	<0.001	0.91	<0.001														
Co	0.19	>0.1	0.53	>0.1	0.4	>0.1	0.54	>0.05												
Ni	0.92	<0.001	0.94	<0.001	0.94	<0.001	0.96	<0.001	0.51	>0.1										
Cu	0.86	<0.001	0.97	<0.001	0.84	>0.001	0.9	<0.001	0.62	>0.02	0.95	<0.001								
Zn	0.89	<0.001	0.93	<0.001	0.92	<0.001	0.93	<0.001	0.39	>0.1	0.9	<0.001	0.86	<0.001						
P	0.01	>0.1	0.14	>0.1	0.36	>0.1	0.35	>0.1	0.67	>0.02	0.35	>0.1	0.28	>0.1	0.12	>0.1	-	-	-	-

Appendix-VIII(f) (Contd..2)																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Positra Bay December 2004 subtidal (n=7)																				
Cr	0.02	>0.1																		
Mn	0.84	>0.001	0.45	>0.1																
Fe	-0.53	>0.1	0.01	>0.1	-0.58	>0.1														
Co	-0.41	>0.1	-0.28	>0.1	-0.4	>0.1	-0.25	>0.1												
Ni	-0.59	>0.05	-0.18	>0.1	-0.67	>0.1	0.94	>0.001	-0.05	>0.1										
Cu	-0.22	>0.1	-0.45	>0.1	-0.42	>0.1	0.77	>0.01	-0.36	>0.1	0.82	>0.001								
Zn	-0.45	>0.1	-0.65	>0.05	-0.6	>0.05	0.51	>0.1	-0.03	>0.1	0.63	>0.05	0.84	>0.001						
Cd	0.57	>0.1	0.02	>0.1	0.46	>0.1	-0.35	>0.1	0.22	>0.1	0.26	>0.1	-0.19	>0.1	-0.26	>0.1				
Pb	-0.29	>0.1	0.25	>0.1	-0.12	>0.1	0.14	>0.1	0.66	>0.05	-0.21	>0.1	-0.28	>0.1	-0.54	>0.1	0.5	>0.1		
P	-0.54	>0.1	-0.53	>0.1	-0.58	>0.1	0.37	>0.1	0.48	>0.1	0.64	>0.05	0.56	>0.1	0.71	>0.02	0.4	>0.1	0	-
CO₃²⁻	-0.86	>0.01	-0.08	>0.1	-0.8	>0.001	0.85	>0.001	0.1	>0.1	0.91	<0.001	0.64	>0.05	0.64	>0.05	0.24	>0.1	-0.48	>0.1
Positra Bay All (n=102)																				
Cr	0.52	<0.001																		
Mn	0.26	>0.001	0.26	>0.001																
Fe	0.76	<0.001	0.39	<0.001	0.4	<0.001														
Co	-0.51	<0.001	-0.49	<0.001	-0.23	>0.01	-0.3	>0.001												
Ni	0.79	<0.001	0.31	>0.001	0.27	>0.001	0.96	<0.001	-0.32	>0.001										
Cu	0.24	>0.01	0.1	>0.1	0.19	>0.05	0.43	<0.001	-0.05	>0.1	0.43	<0.001								
Zn	0.65	<0.001	0.28	>0.001	0.27	>0.001	0.83	<0.001	-0.42	<0.001	0.84	<0.001	0.38	<0.001						
Cd	0.57	<0.001	0.02	>0.1	0.46	<0.001	-0.35	<0.001	0.22	>0.02	-0.21	>0.02	-0.28	>0.001	-0.54	<0.001				
Pb	0.76	<0.001	-0.4	<0.001	0.42	<0.001	0.91	<0.001	0.01	>0.1	0.92	<0.001	0.88	<0.001	-0.26	>0.001	0.5	<0.001		
P	0	-	0.04	>0.1	0.1	>0.1	0.14	>0.1	0.03	>0.1	0.06	>0.1	-0.01	>0.1	0.07	>0.1	0	-	-0.31	>0.001
CO₃²⁻	-0.41	>0.001	-0.16	>0.1	-0.11	>0.1	-0.16	>0.1	0.36	<0.001	0.03	>0.1	0	0	-0.03	0	0.69	>0.001	-0.03	>0.1

Appendix-VIII(h) (Contd..3)																				
(2006) November (subtidal) n=8																				
	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
Ni	0.68	>0.02	-0.5	>0.1	0.1	>0.1	0.64	>0.02	0.74	>0.01										
Cu	0.63	>0.05	-0.4	>0.1	-0.1	>0.1	0.74	>0.01	0.74	>0.01	0.61	>0.05								
Zn	0.64	>0.02	-0.4	>0.1	-0.2	>0.1	0.73	>0.01	0.76	>0.01	0.64	>0.02	0.79	>0.001						
P	-0.8	>0.01	0.76	>0.1	0.49	>0.1	-0.3	<0.01	-0.1	>0.1	-0.5	>0.1	-0.5	>0.1	-0.7	>0.02				
(2006 (November) (intertidal) n=5																				
Cr	1	<0.001																		
Mn	0.99	<0.001	0.99	<0.001																
Fe	0.98	<0.001	0.99	<0.001	0.96	<0.001														
Co	0.99	<0.001	0.99	<0.001	0.98	<0.001	1	<0.001												
Ni	0.99	<0.001	1	<0.001	0.99	<0.001	0.99	<0.001	1	<0.001										
Cu	1	<0.001	1	<0.001	0.99	<0.001	0.99	<0.001	0.99	<0.001	1	<0.001								
Zn	1	<0.001	1	<0.001	1	<0.001	1	<0.001	1	<0.001	1	<0.001	1	<0.001						
P	-0.8	>0.02	-0.8	>0.02	-0.7	>0.05	-0.8	>0.02	-0.8	>0.02	-0.8	>0.02	-0.8	>0.02	-1	<0.001				
Cr	0.78	>0.001																		
Mn	0.67	>0.02	0.88	<0.001																
Fe	0.72	>0.01	0.91	<0.001	0.85	>0.001														
Co	0.74	>0.01	0.91	<0.001	0.85	>0.001	0.99	<0.001												
Ni	-0.9	>0.001	-0.9	<0.001	-0.7	>0.02	-0.8	>0.001	-0.8	>0.001										
Cu	0.71	>0.02	0.85	<0.001	0.78	>0.001	0.98	<0.001	0.98	<0.001	-0.8	>0.001								
Zn	0.64	>0.02	0.82	<0.001	0.79	>0.001	0.71	>0.02	0.75	>0.01	-0.7	>0.02	0.71	>0.02						
P	0.45	>0.1	0.64	>0.02	0.67	>0.02	0.71	>0.02	0.63	>0.05	-0.6	>0.05	0.55	>0.05	0.25	>0.1				
(2007(April) (intertidal) n=5																				
Cr	0.46	>0.1																		
Mn	-0.2	>0.1	0.46	>0.1																
Fe	-0.1	>0.1	0.83	>0.02	0.68	>0.05														
Co	-0.6	>0.1	0.83	>0.02	0.62	>0.1	0.58	>0.1												
Ni	0.42	>0.1	0.85	>0.001	0.49	>0.1	0.59	>0.1	0.52	>0.1										
Cu	0.86	>0.01	0.8	>0.02	0.02	>0.1	-0.1	>0.1	-0.1	>0.1	0.77	>0.02								
Zn	-	-	-	-	-	-	-	-	-	-	-	-								
P	-0	>0.1	0.71	>0.05	0.78	>0.02	0.93	>0.001	0.41	>0.1	0.42	>0.1	0.22	>0.1						

Appendix-VIII(i): Correlation coefficient (r) and levels of significance (p)) for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in sediments from subtidal and Intertidal areas of Bedi.

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
1997 (February -March) (Subtidal) n=9																				
Cr	0.83	>0.001																		
Mn	0.05	>0.1	0.28	>0.1																
Fe	0.94	<0.001	0.84	>0.001	-0.17	>0.1														
Co	0.11	>0.1	-0.15	>0.1	0.05	>0.1	0.05	>0.1												
Ni	0.89	<0.001	0.76	>0.001	-0.27	>0.2	0.97	<0.001	-0.01	>0.1										
Cu	0.87	<0.001	0.88	<0.001	-0.17	>0.1	-0.05	>0.1	-0.05	>0.1	0.95	<0.001								
Zn	0.69	>0.01	0.49	>0.1	-0.17	>0.1	0.69	>0.1	-0.17	>0.1	0.75	>0.001	0.64	>0.02						
Cd	-0.26	>0.1	0.01	>0.1	-0.14	>0.1	-0.03	>0.1	0.11	>0.1	0.04	>0.1	0.09	>0.1	-0.39	>0.1				
Pb	0.53	>0.05	0.16	>0.1	-0.44	>0.1	0.52	>0.1	-0.03	>0.1	0.57	>0.05	0.4	>0.1	0.43	>0.1	-0.23	>0.1		
P	-0.12	>0.1	-0.26	>0.1	-0.8	>0.001	0.12	>0.1	0.1	>0.1	0.2	>0.1	0.12	>0.1	0.04	>0.1	0.34	>0.1	0.44	>0.1
1997 (November) (Subtidal) n=9																				
Cr	0.71	>0.01																		
Mn	0.58	>0.05	0.61	>0.02																
Fe	0.87	<0.001	0.85	<0.001	0.87	<0.001														
Co	0.75	>0.001	0.9	<0.001	0.88	<0.001	0.97	<0.001												
Ni	0.79	>0.001	0.85	<0.001	0.84	>0.001	0.92	<0.001	0.95	<0.001										
Cu	0.7	>0.01	0.84	>0.001	0.93	<0.001	0.95	<0.001	0.98	<0.001	0.92	<0.001								
Zn	0.86	<0.001	0.56	>0.05	0.7	>0.01	0.84	>0.001	0.73	>0.01	0.72	>0.01	0.73	>0.01						
P	0.5	>0.1	0.43	>0.1	0.32	>0.1	0.48	>0.1	0.41	>0.1	0.38	>0.1	0.34	>0.001	0.33	>0.1				

Appendix-VIII(j): Correlation coefficient (r) and levels of significance (p) for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in sediments from subtidal and Intertidal areas of Kandla.

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
1996 (October) (subtidal) n=5																				
Cr	0.96	<0.001																		
Mn	0.98	<0.001	0.91	>0.001																
Fe	0.97	<0.001	0.89	>0.001	0.95	>0.001														
Co	0.94	>0.001	0.93	>0.001	0.88	>0.001	0.98	<0.001												
Ni	0.99	<0.001	0.93	>0.001	0.96	<0.001	0.99	<0.001	0.98	<0.001										
Cu	0.95	>0.001	0.9	>0.001	0.9	>0.001	0.98	<0.001	1	<0.001	0.99	<0.001								
Zn	0.98	<0.001	0.89	>0.001	0.99	<0.001	0.98	<0.001	0.93	<0.001	0.98	<0.001	0.94	>0.001						
1998 (February) (subtidal) n=7																				
Cr	0.83	>0.001																		
Mn	0.85	>0.001	0.92	<0.001																
Fe	0.96	<0.001	0.9	<0.001	0.92	<0.001														
Co	0.95	<0.001	0.91	<0.001	0.95	<0.001	0.98	<0.001												
Ni	0.97	<0.001	0.91	<0.001	0.91	<0.001	1	<0.001	0.99	<0.001										
Cu	0.36	>0.1	0.44	>0.1	0.24	>0.1	0.36	>0.1	0.36	>0.1	0.47	>0.1								
Zn	0.73	>0.02	0.62	>0.05	0.44	>0.1	0.72	>0.01	0.61	>0.05	0.73	>0.02	0.8	>0.001						
Cd	0.45	>0.1	0.45	>0.1	0.42	>0.1	0.57	>0.1	0.52	>0.05	0.54	>0.1	0.51	>0.1	0.56	>0.1				
Pb	-0.4	>0.1	-0.3	>0.1	-0.2	>0.1	-0.3	>0.1	-0.3	>0.1	-0.4	>0.1	-0.6	>0.05	-0.53	>0.1	0.17	>0.1		
P	-0.3	>0.1	-0.1	>0.1	-0.4	>0.1	-0.2	>0.1	-0.3	>0.1	-0.2	>0.1	0.74	>0.02	0.44	>0.1	0.1	>0.1	-0.42	>0.1
2004 (December) (subtidal) n=6																				
Cr	0.99	<0.001																		
Mn	0.87	>0.001	0.83	>0.01																
Fe	0.69	>0.05	0.78	>0.02	0.35	>0.1														
Co	0.94	<0.001	0.6	>0.1	0.91	>0.001	0.79	>0.01												
Ni	0.95	<0.001	0.97	<0.001	0.83	>0.01	0.8	>0.01	0.69	>0.05										
Cu	0.89	>0.001	0.57	>0.1	0.65	>0.05	0.88	>0.001	0.88	>0.001	0.69	>0.05								
Zn	0.84	>0.001	0.9	>0.001	0.84	>0.02	0.82	>0.01	0.61	>0.1	0.95	<0.001	0.53	>0.1						
P	0.95	<0.001	0.26	>0.1	0.94	<0.001	0.6	>0.1	0.85	>0.001	0.3	>0.1	0.56	>0.1	0.16	>0.1				

Appendix-VIII(k) (Contd..2)

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
May 2005 (intertidal) n=10																				
Ni	0.64	>0.02	0.82	>0.001	0.7	>0.001	0.97	<0.001	0.92	<0.001										
Cu	0.49	>0.1	0.86	<0.001	0.8	>0.001	0.93	<0.001	0.93	<0.001	0.97	<0.001								
Zn	0.74	>0.001	0.17	>0.1	-0.18	>0.1	0.32	>0.1	0.35	>0.1	0.48	>0.1	0.3	>0.1						
Cd	-0.67	>0.02	-0.5	>0.05	-0.01	>0.1	-0.51	>0.05	-0.65	>0.02	-0.56	>0.05	-0.47	>0.1	-0.64	>0.02				
Pb	0.37	>0.1	-0.52	>0.05	-0.69	>0.1	-0.27	>0.1	-0.1	>0.1	-0.35	>0.1	-0.4	>0.1	0.1	>0.1	-0.26	>0.1		
P	0.51	>0.05	0.7	>0.01	0.71	>0.001	0.77	>0.001	0.84	<0.001	0.81	>0.001	0.78	>0.001	0.31	>0.1	-0.35	>0.1	-0.29	>0.1
April 2006 (subtidal) n=11																				
Cr	0.95	<0.001																		
Mn	0.11	>0.1	0.07	>0.1																
Fe	0.97	<0.001	0.96	<0.001	0.2	>0.1														
Co	0.92	<0.001	0.92	<0.001	0.14	>0.1	0.91	<0.001												
Ni	0.34	>0.1	0.31	>0.1	0.47	>0.1	0.34	>0.1	0.61	>0.02										
Cu	0.93	<0.001	0.94	<0.001	0.28	>.1	0.92	<0.001	0.92	<0.001	0.44	>0.1								
Zn	0.07	>0.1	0.15	>0.1	0.66	>0.001	0.18	>0.1	0.27	>0.1	0.73	>0.001	0.29	>0.1						
P	0.96	<0.001	0.98	<0.001	0.14	>0.1	0.97	<0.001	0.91	<0.001	0.35	>0.1	0.95	<0.001	0.13	>0.1				
April 2006 (intertidal) n=7																				
Cr	0.83	>0.001																		
Mn	0.68	>0.02	0.46	>0.1																
Fe	0.17	>0.1	0.25	>0.1	-0.01	>0.1														
Co	-0.05	>0.1	-0.12	>0.1	0.02	>0.1	-0.5	>0.1												
Ni	0.36	>0.1	0.6	>0.05	-0.09	>0.1	-0.26	>0.1	-0.26	>0.1										
Cu	0.6	>0.05	0.84	>0.001	-0.03	>.1	-0.01	>0.1	-0.01	>0.1	0.81	>0.001								
Zn	0.33	>0.1	0.53	>0.1	0.26	>0.1	-0.24	>.1	-0.38	>.1	0.93	<0.001	0.5	>0.1						
P	0.94	<0.001	0.85	<0.001	0.61	>0.05	-0.04	>0.1	-0.02	>0.1	0.6	>0.05	0.7	>0.02	0.58	>0.1				
October 2007 (subtidal) n=8																				
Cr	0.96	<0.001																		
Mn	0.99	<0.001	0.98	<0.001																
Fe	0.98	<0.001	0.99	<0.001	0.99	<0.001														
Co	-	-	-	-	-	-	-	-												
Ni	0.98	<0.001	0.99	<0.001	0.99	<0.001	1	<0.001	-	-										
Cu	0.95	<0.001	0.99	<0.001	0.97	<0.001	0.99	<0.001	-	-	0.99	<0.001								
Zn	0.96	<0.001	0.99	<0.001	0.98	<0.001	0.99	<0.001	-	-	0.99	<0.001	0.99	<0.001						
P	0.99	<0.001	0.95	<0.001	0.99	<0.001	0.98	<0.001	-	-	0.97	<0.001	0.95	<0.001	0.95	<0.001				
October 2007 (intertidal) n=5																				
Cr	0.59	>0.1																		
Mn	0.64	>0.1	0.88	>0.001																
Fe	0.83	>0.02	0.78	>0.02	0.94	>0.001														
Co	-	-	-	-	-	-														
Ni	0.96	<0.001	0.71	>0.05	0.82	>0.02	0.95	>0.001	-	-										
Cu	0.97	<0.001	0.57	>0.1	0.73	>0.05	0.99	<0.001	-	-	0.98	<0.001								
Zn	0.59	>0.1	0.31	>0.1	0.59	>0.1	0.62	>0.1	-	-	0.6	>0.1	0.67	>0.05						
P	0.12	>0.1	-0.45	>0.1	0.01	>0.1	0.16	>0.1	-	-	0.13	>0.1	0.28	>0.1	0.55	>0.1				

Appendix-VIII(l): Correlation coefficient (r) and levels of significance (p) for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and P in sediments from subtidal and Intertidal areas of Kori.

	Al		Cr		Mn		Fe		Co		Ni		Cu		Zn		Cd		Pb	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
February 1999 (subtidal) n=5																				
Cr	0.84	>0.01																		
Mn	0.55	>0.1	0.82	>0.02																
Fe	0.33	>0.1	0.75	>0.05	0.89	>0.001														
Co	0.96	<0.001	0.91	>0.001	0.74	>0.05	0.5	>0.1												
Ni	0.98	<0.001	0.91	>0.001	0.71	>0.05	0.48	>0.1	1	<0.001										
Cu	0.67	>0.05	0.84	>0.01	0.97	<0.001	0.76	>0.02	0.84	>0.001	0.81	>0.01								
Zn	0.94	>0.001	0.91	>0.001	0.77	>0.02	0.6	>0.1	0.96	<0.001	0.97	<0.001	0.81	>0.01						
P	0.91	>0.001	0.56	>0.1	0.19	>0.1	-0.06	>0.1	0.78	>0.02	0.82	>0.01	0.34	>0.1	0.75	>0.02				
February 2000 (subtidal, n=6)																				
Cr	0.94	>0.001																		
Mn	0.83	>0.05	0.95	>0.001																
Fe	0.95	>0.001	0.94	<0.001	0.93	>0.001														
Co	0.95	>0.001	0.95	<0.001	0.93	>0.001	0.99	>0.001												
Ni	0.99	<0.001	0.94	<0.001	0.87	>0.02	0.98	>0.001	0.97	<0.001										
Cu	0.96	<0.001	0.99	<0.001	0.94	>0.001	0.98	>0.001	0.98	<0.001	0.97	<0.001								
Zn	0.97	<0.001	0.92	<0.001	0.88	>0.01	0.99	>0.001	0.98	<0.001	0.99	<0.001	0.96	<0.001						
Cd	-0.81	>0.01	-0.83	>0.01	-0.81	>0.01	-0.82	>0.01	-0.78	>0.02	-0.82	>0.01	0.96	<0.001	-0.83	>0.01				
Pb	-0.28	>0.1	-0.24	>0.1	-0.1	>0.1	-0.09	>0.1	-0.05	>0.1	-0.21	>0.1	-0.14	>0.1	-0.16	>0.1	0.52	>0.1		
P	0.94	<0.001	0.78	>0.02	0.49	>0.1	0.78	>0.02	0.77	>0.02	0.9	>0.001	0.8	>0.01	-0.54	>0.1	-0.55	>0.1	-0.17	>0.1
February 2000 (Intertidal n=4)																				
Cr	0.98	<0.001																		
Mn	0.94	>0.001	0.97	>0.001																
Fe	0.1	>0.1	0.08	>0.1	-0.16	>0.1														
Co	0.87	>0.02	0.96	>0.001	0.94	>0.001	0.03	>0.1												
Ni	0.97	>0.001	0.99	<0.001	0.99	<0.001	-0.05	>0.1	0.95	>0.001										
Cu	0.92	>0.001	0.95	>0.001	1	<0.001	-0.25	>0.1	0.91	>0.01	0.98	<0.001								
Zn	0.98	<0.001	0.99	<0.001	0.99	<0.001	-0.02	>0.1	0.94	>0.001	1	<0.001	0.97	>0.001						
Cd	0.15	>0.1	0.32	>0.1	0.47	>0.1	-0.63	>0.1	0.53	>0.1	0.38	>0.1	0.97	>0.001	0.35	>0.1				
Pb	-0.85	>0.02	-0.72	>0.1	-0.67	>0.1	-0.17	>0.1	-0.49	>0.1	-0.72	>0.1	-0.66	>0.1	-0.74	>0.05	0.31	>0.1		
P	-0.14	>0.1	-0.35	>0.1	-0.36	>0.1	0.03	>0.1	-0.61	>0.1	-0.33	>0.1	-0.33	>0.1	-0.64	>0.1	-0.79	>0.05	-0.39	>0.1