

^{210}Pb based trace element fluxes in the nearshore and estuarine sediments off Bombay, India

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Abstract

Seven sediment cores from the Thana creek–Bombay harbour complex (THC) have been studied for excess ^{210}Pb ($^{210}\text{Pb}_{\text{exc}}$, that portion of ^{210}Pb not supported by decay of ^{226}Ra in sediment), C_{org} , Mn, Fe, Co, Ni, Cu, Zn and Al. The sediment accumulation rates based on ^{210}Pb depth profiles decrease from 1.9 cm/yr, in the northern segment of the THC, to 0.4 cm/yr, in the southern segment. The calculated inventories of $^{210}\text{Pb}_{\text{exc}}$ increase from 16 dpm/cm², for the core from the southern area, to 187 dpm/cm², for the northernmost core, which was much higher compared to the atmospheric fallout inventory of 40–50 dpm/cm². The inner creek acted as a sink for ^{210}Pb while active winnowing prevailed in the southern segment.

Trace elements depth profiles in sediments did not exhibit signatures of significant environmental pollution. Variations in metal concentrations, metal/Al ratios and low excess metal inventories, suggested that the majority of the anthropogenic metals were either exported beyond the creek and nearshore region thus making the THC a passive link between the land and the sea for trace metals or largely removed prior to their entering the THC proper.

1. Introduction

Changes in the contemporary sedimentation and assessment of the degree of man made pollution of nearshore marine areas can best be understood through the knowledge of sedimentation records since several pollutants, including trace metals, on entering seawater are transferred to the bed by adsorption onto the suspended particulate matter (SPM) and subsequent sedimentation. The radionuclide ^{210}Pb has been frequently used as a tracer for reconstruction of sedimentation records over short time scales, of a century or so (Koide et al., 1972; Turekian et al., 1977; Krishnaswami and Lal, 1978; 1982; Robbin, 1978; Schell, 1982).

Introduction of such a time scale is of considerable significance since substantial environmental changes have occurred in recent years due to increased land use and industrial activities which have accelerated world wide over this century.

The inshore marine zones, particularly estuaries, creeks and bays, are the major sites of rapid accumulation of anthropogenic pollutants in their bed sediments. The geochronological investigations coupled with geochemistry are of considerable help in elucidating the history of local pollution of fast changing depositional environments of the inshore marine areas (Bruland et al., 1974; Thompson et al., 1975; Goldberg et al., 1979). The Thana creek–Bombay harbour

complex (THC) and adjoining marine areas are under considerable environmental stress due to the indiscriminate release of domestic as well as industrial wastewaters through several natural channels. The transport and distribution of heavy metals and radionuclides in water, suspended particles and surficial sediment of selected near-shore regions of Bombay have been studied in an attempt to elucidate the degree of metal contamination (Patel et al., 1975; 1985; Zingde and Desai, 1981; Bhosale and Sahu, 1991; Sahu and Bhosale, 1991).

In the study reported in this paper we have addressed the ^{210}Pb chronology and geochemistry of sediment cores from THC and adjacent coastal areas with the objective of constructing a metal pollution history of the region over a century and determining the fate of ^{210}Pb as well as other metals supplied to this sub-environment, by computing their inventories.

2. Description of the study area

The THC is a V-shaped semi-enclosed basin open to the Arabian Sea at its southwest approach and connected at its northern extremity to the Bassein creek through a narrow channel. The shallow tidal inlets of the Dharamtar, Nhava-Sheva and Panvel creeks are tributaries to the harbour, discharging into its eastern shore.

The THC is dominated by fairly strong semi-diurnal tides with mean spring and neap high waters of 4.42 and 3.30 m, respectively, near the entrance which renders the complex vertically well-mixed except during monsoon. The flood tidal front advances in the complex in the north-easterly direction and ebbs towards the southwest. It has been estimated that about one third of the THC water is renewed during each tidal cycle (Patel et al., 1985). The tidal currents set in a near ENE–WSW direction in the harbour area and attain peak speeds as high as 2 m/s. Pillai et al. (1989) recognised three sets of currents in the THC area, two of which flow northwards parallel to both the shores and transport sediments towards the head while the third one, in the mid-creek region, flows to the south.

The strong currents sweeping the complex disperse the fine grained and poorly sorted sediment from the bed and from extensive mud flats along the intertidal zone into the water column resulting in high suspended particulate matter (SPM) in the water which is largely inorganic in nature with an organic carbon (C_{org}) content of less than 6%. The load, though variable, is generally below 100 mg/l during the dry season and may exceed 200 mg/l during monsoon (Zingde, 1989). The sediment is dominated by montmorillonite, degraded chlorite, illite and to some extent silica (Sahu and Bhosale, 1991). The 10–15 m thick acoustically transparent clay beds as revealed through shallow seismic reflections (Almeida et al., 1989) indicate recent sedimentation. A yearly load of $0.84 \times 10^6 \text{ m}^3$ of fine grained sediment is estimated to be transported to the central reaches of THC via Thana, Panvel and Dharamtar creeks (CWPRS, 1963). The oscillating tidal movements probably spread this material fairly uniformly over the 240 km^2 area of the THC with a sedimentation rate of 4 mm/yr (Sastry, 1971). The complex exhibits hydrographic characteristics similar to estuarine environs with weak vertical salinity gradients during June–September, the period of heavy seasonal monsoon rainfall.

The domestic wastewater estimated to be around $2.6 \times 10^5 \text{ m}^3/\text{day}$ is released generally partly treated, through point discharges scattered along the western shore of the THC. In addition, the Thana creek receives around $1.8 \times 10^5 \text{ m}^3/\text{day}$ of industrial wastewater from a wide variety of industries established along its shores (MCGB, 1979). According to the available records, about 35 t of SPM and 1250, 35, 20, 10 and 10 kg of Zn, Cu, Hg, Pb and Cr, respectively, entered Ulhas river and other tributaries through industrial wastewaters (Mukherjee, 1981).

3. Materials and methods

Seven piston and gravity cores (THC-1–THC-7) were obtained from the complex during 1982, from locations (marked in Fig. 1) in areas which were well outside the dredging zone for the port operations. Core 2595 was collected during the 115th

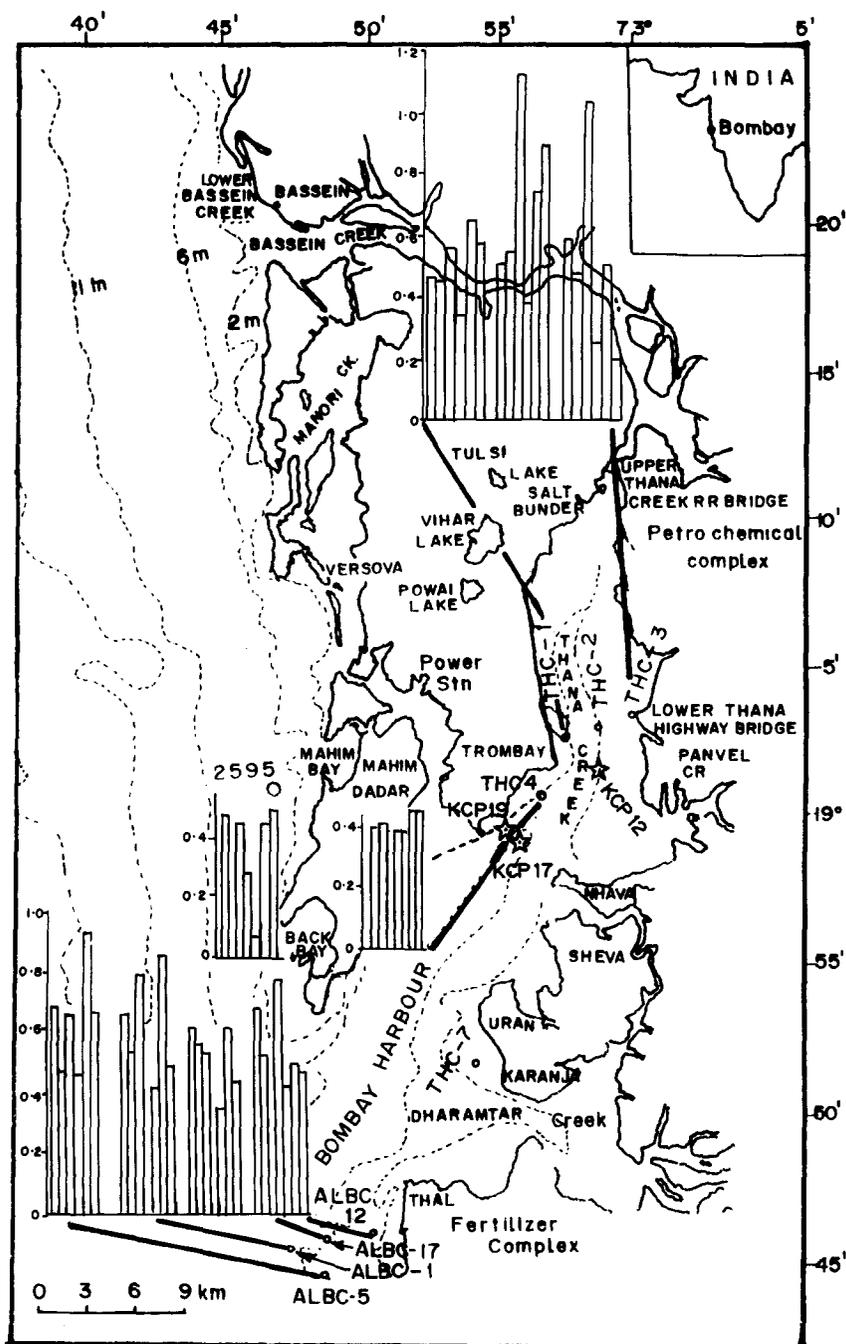


Fig. 1. Area of study indicating core locations. The six bars in each histogram represent molar ratios $Mn/Al \times 10^{-2}$, Fe/Al , $Ni/Al \times 10^{-3}$, $Co/Al \times 10^{-3}$, $Cu/Al \times 10^{-3}$ and $Zn/Al \times 10^{-3}$, from left to right.

Table 1
²¹⁰Pb concentration in the THC cores

Core	Interval (cm)	Al ^a (%)	²¹⁰ Pb _{total} (dpm/g)	²¹⁰ Pb _{excess} ^b (dpm/g)	
THC-1	0–2	9.3	4.40 ± 0.06	3.71 ± 0.11	
	30–32	9.2	2.97 ± 0.21	2.28 ± 0.23	
	50–52	8.0	1.96 ± 0.03	1.29 ± 0.09	
	70–72	6.2	1.63 ± 0.09	0.94 ± 0.13	
	90–92	7.9	1.19 ± 0.08	0.50 ± 0.12	
	110–112	7.5	1.01 ± 0.04	0.32 ± 0.10	
	120–122	7.3	0.93 ± 0.03	0.24 ± 0.09	
	136–139	7.8	0.69 ± 0.08	–	
THC-2	0–2	6.2	4.63 ± 0.17	3.98 ± 0.18	
	18–20	7.3	4.03 ± 0.22	3.38 ± 0.23	
	26–28	7.3	3.18 ± 0.14	2.53 ± 0.16	
	48–50	7.6	2.66 ± 0.13	2.01 ± 0.15	
	59–62	8.1	2.15 ± 0.25	1.50 ± 0.26	
	71–74	7.4	2.11 ± 0.13	1.46 ± 0.15	
	89–92	7.0	1.87 ± 0.18	1.22 ± 0.19	
	98–101	7.1	1.12 ± 0.09	0.47 ± 0.11	
	137–140	7.2	0.61 ± 0.1	–	
	THC-3	0–2	6.7	4.87 ± 0.20	4.21 ± 0.21
		4–7	6.8	5.13 ± 0.39	4.47 ± 0.40
13–16		7.4	3.32 ± 0.09	2.66 ± 0.11	
19–22		7.2	3.59 ± 0.21	2.93 ± 0.22	
28–31		8.2	3.35 ± 0.14	2.69 ± 0.16	
40–43		7.3	2.41 ± 0.14	1.75 ± 0.16	
52–55		8.3	3.53 ± 0.19	2.87 ± 0.20	
64–67		7.9	2.15 ± 0.09	1.49 ± 0.11	
70–73		8.3	1.69 ± 0.07	1.03 ± 0.10	
82–85		8.4	1.60 ± 0.10	0.94 ± 0.12	
88–91		7.9	2.62 ± 0.27	1.96 ± 0.28	
94–98		7.7	1.52 ± 0.18	0.86 ± 0.20	
THC-4		0–2	9.1	4.87 ± 0.92	4.10 ± 0.92
		6–8	8.4	4.72 ± 0.31	3.95 ± 0.32
	10–12	7.2	3.30 ± 0.27	2.64 ± 0.28	
	14–16	8.3	3.01 ± 0.14	2.24 ± 0.15	
	22–24	7.8	1.77 ± 0.04	1.00 ± 0.09	
	30–34	8.0	2.17 ± 0.09	1.40 ± 0.12	
	39–43	6.3	1.54 ± 0.05	0.77 ± 0.09	
	79–82	8.6	0.92 ± 0.10	0.15 ± 0.13	
THC-7	0–2		2.95 ± 0.27	2.36 ± 0.29	
	4–6		1.52 ± 0.12	0.93 ± 0.16	
	6–8		1.92 ± 0.14	1.33 ± 0.17	
	12–14		2.23 ± 0.22	1.64 ± 0.24	
	22–25		1.06 ± 0.19	0.47 ± 0.22	

^a Standard deviation for Al was ± 4%.

^b $^{210}\text{Pb}_{\text{excess}} = ^{210}\text{Pb}_{\text{total}} - ^{226}\text{Ra}$ (all in units of dpm/g).

An average ²²⁶Ra concentration (0.69 ± 0.09) and (0.65 ± 0.07) dpm/g measured in the core THC-1 and THC-2 were used to calculate ²¹⁰Pb_{excess} in all sections. For cores THC-3, THC-4 and THC-7 the measured ²²⁶Ra concentrations in the surface sections (0.66 ± 0.07), (0.77 ± 0.05) and (0.59 ± 0.10) dpm/g were used.

cruise of the RV *Gaveshani* while cores in ALBC series were piston cores obtained in 1983. Standard acrylic tubes of about 2 m length and an inner diameter of 6 cm were used as core liners. Soon after collection, the cores were sectioned at regular interval and these sections were frozen at –20°C. Subsamples of the core sections were used for radiodating and chemical analysis following the procedure of Krishnaswami et al. (1973).

The ²¹⁰Pb activity was beta-assayed via its daughter ²¹⁰Bi using low background gas flow type Geiger counters (Lal and Schink, 1960). ²²⁶Ra was measured by assaying Rn emanation (Bhat et al., 1974; Krishnaswami and Sarin, 1976). ²¹⁰Pb_{exc} was calculated (Table 1) by subtracting the measured ²²⁶Ra in the surface sections of the cores from the ²¹⁰Pb_{total} activity at each level. The support activity for selected samples of THC-1 and THC-2 was verified from the measured ²²⁶Ra in the bottom sections (137–140 cm and 131–134 cm, respectively). Organic carbon was determined to an accuracy of ± 0.01% following El Wakeel and Riley (1957).

The analytical method employed for the determination of metals has been described by Sarin et al. (1979). A mixture of HF–HClO₄–HNO₃ was used for complete dissolution of dry sediment samples in teflon vessels. Resulting solutions and reagent blanks were analysed for Mn, Fe, Co, Ni, Cu, Zn and Al by flame-AAS. The precision of analysis checked by analysing replicates of several samples was better than 4% for all elements, except Ni for which precision was ± 6%. The accuracy (± 12%) of analysis was confirmed by analysing USGS rock standard W-1.

Sediment accumulation rates were estimated from the profiles of ²¹⁰Pb_{exc} vs. depth (Fig. 2) and the inventories of ²¹⁰Pb_{exc} activity (Table 2) were calculated using the relation:

$$\Sigma \text{dpm/cm}^2 = \int_0^{\infty} \rho A(z) dz = A_0 \rho s \tau$$

where A_0 was the activity at the sediment–water interface, s was the sediment accumulation rate (cm/yr), τ was the radioactive mean life (33.3 yr) of ²¹⁰Pb and ρ was the in-situ bulk density (0.7 g/cm³). Although minor variations in

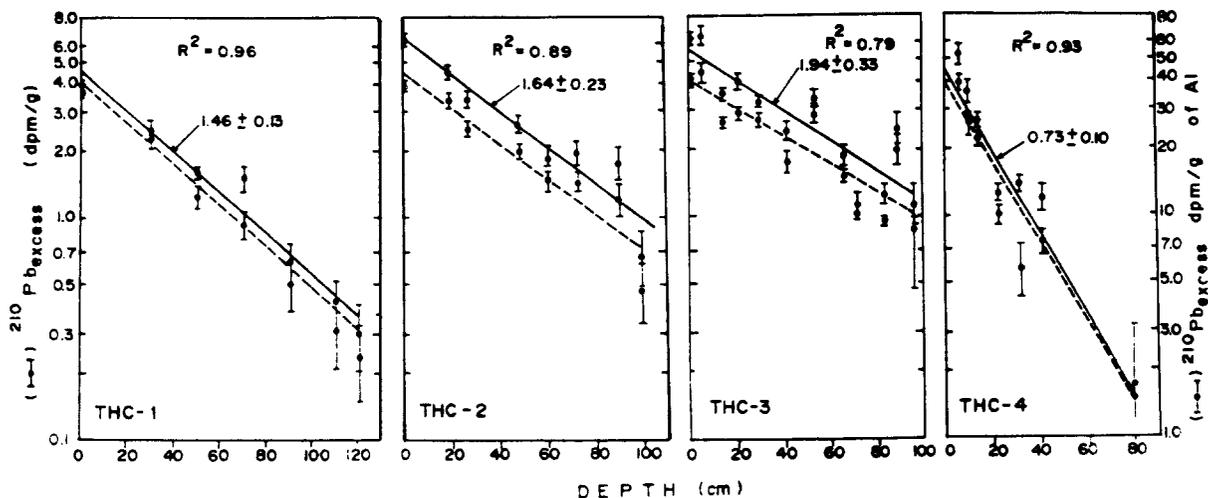


Fig. 2. $^{210}\text{Pb}_{\text{exc}}$ and $^{210}\text{Pb}_{\text{exc}}/\text{g of Al}$ as a function of depth for cores. Numbers across the best-fit lines indicate deposition rate (cm/yr).

density could occur down the core depending on porosity, in our cores the Al content was more or less uniform throughout the length in all cores indicating that drastic variations in density were unlikely.

Inventories of excess metal were computed from the relation

$$\Sigma \mu\text{g}/\text{cm}^2 = \Sigma C_i \cdot Z_i \cdot \rho$$

Table 2

Summary of sediment accumulation rates and integrated fluxes of ^{210}Pb in THC and western continental shelf sediments

Core ^a	Extrapolated to surface $^{210}\text{Pb}_{\text{excess}}$ activity (dpm/g) (A_0)	Accumulation rate (mm/yr)	$^{210}\text{Pb}_{\text{excess}}$ inventory in sediments ^b ($\Sigma \text{dpm}/\text{cm}^2$)	Reference
THC-1 (10; 1.4)	4.2	14.6 ± 1.3	142	This work
THC-2 (10; 1.4)	4.5	16.5 ± 2.3	173	
THC-3 (3; 0.97)	4.0	19.4 ± 3.3	181	
THC-4 (10; 1.1)	4.2	7.3 ± 1.0	72	
ALBC-1 (10; 0.7) 2595	3.4	6.2 ± 0.3	33.8	Borole (1988)
(20; 0.9)	4.8	5.5 ± 0.6	42.3	
2590 (36; 0.9)	4.1	7.2 ± 0.9	47.3	
KCP-12 (8; 0.9)	4.9	16.0	187	Pillai et al. (1989)
KCP-19 (4; 0.7)	2.6	3.2	20	
KCP-17	1.6	4.4	16	

^aNumbers in brackets indicate depth of water and core length in m.

^b $(\Sigma \text{dpm}/\text{cm}^2) = A_0 \cdot \rho \cdot s \cdot \tau$, where A_0 is the extrapolated activity at the surface (dpm/g), s is the accumulation rate (cm/yr), τ is radioactive mean life of ^{210}Pb (33.3 yr), and ρ is density ($0.7 \text{ g}/\text{cm}^3$).

Table 3
Regression equations for concentration profiles of C_{org} , Al and Mn

Core	Parameter		
	C_{org}	Al	Mn
THC-1	$Y = -0.0035X + 1.74$	$Y = -0.0036X + 3.19$	$Y = -0.00005X + 0.018$
THC-2	$Y = 0.00016X + 1.37$	$Y = -0.00028X + 2.69$	$Y = -0.00001X + 0.015$
THC-3	$Y = -0.00076X + 1.29$	$Y = 0.0062X + 2.56$	$Y = -0.00007X + 0.02$
THC-4	$Y = 0.0077X + 0.81$	$Y = -0.0015X + 3.17$	$Y = -0.00001X + 0.22$
2595	$Y = -0.00017X + 1.22$	$Y = -0.00077X + 3.05$	$Y = 0.00007X + 0.015$
ALBC-1	$Y = -0.00003X + 1.19$	$Y = -0.0002X + 2.95$	$Y = 0.00002X + 0.018$

C_{org} , Al and Mn concentrations expressed in mmol/g.

where C_i was the excess anthropogenic metal concentration defined as $C_i = [(X/Al)_i - (X/Al)_{\text{bkgd}}] \cdot Al_i$, where $(X/Al)_i$ is the metal to Al concentration ratio in the i th sampling layer, and $(X/Al)_{\text{bkgd}}$ is the same ratio in the uncontaminated sediment, which is defined in each core from the composition at depth where metal/Al ratio reached a minimum constant level; ρ is the in-situ density (0.7 g/cm^3) and Z_i was the mean depth interval in the core. Shale composition was used as a background for computing the inventories for the cores THC-4, ALBC-1 and 2595.

Regression equations for C_{org} , Al and Mn for selected cores are given in Table 3.

4. Results

The measured ^{226}Ra concentration for THC-1 for the surface (0–2 cm) section was $0.68 \pm 0.04 \text{ dpm/g}$ and for the bottom (137–140 cm) section $0.70 \pm 0.08 \text{ dpm/g}$. For THC-2, the surface (0–2 cm) and the bottom (131–134 cm) ^{226}Ra values were 0.63 ± 0.03 and $0.67 \pm 0.06 \text{ dpm/g}$,

Table 4
Downcore inventories of excess metals

Core	C_{org} (10^4)	Inventory of excess metals ($\mu\text{mol/cm}^2$) $\times 1000$				
		Mn	Co	Ni	Cu	Zn
THC-1	–12.0 (0.50)	6.36 (35.3)	0.67 (2.46)	1.64 (3.91)	0.97 (4.83)	4.39 (0.66)
THC-2	88.6 (0.37)	3.44 (45.0)	4.53 (3.03)	1.65 (9.07)	0.04 (6.95)	1.93 (6.24)
THC-3	29.1 (0.32)	1.23 (49.2)	0.16 (1.73)	0.40 (8.68)	0.18 (4.23)	0.11 (1.42)
THC-4	116.0 (0.18)	–5.15 (52.2)	1.19 (1.09)	0.27 (3.91)	0.85 (2.39)	–0.11 (4.9)
ALBC-1	4.75 (0.35)	0.93 (53.0)	0.16 (1.11)	0.31 (3.91)	0.47 (2.39)	–0.26 (4.9)
2595	17.8 (0.35)	–2.63 (53.0)	–0.16 (1.11)	–0.24 (3.91)	0.63 (2.39)	–0.036 (4.9)

Bracketed values indicate background metal/Al $\times 10^{-4}$ (molar ratio) values estimated from depth profiles. For ALBC-1 and 2595 values are from shale composition.

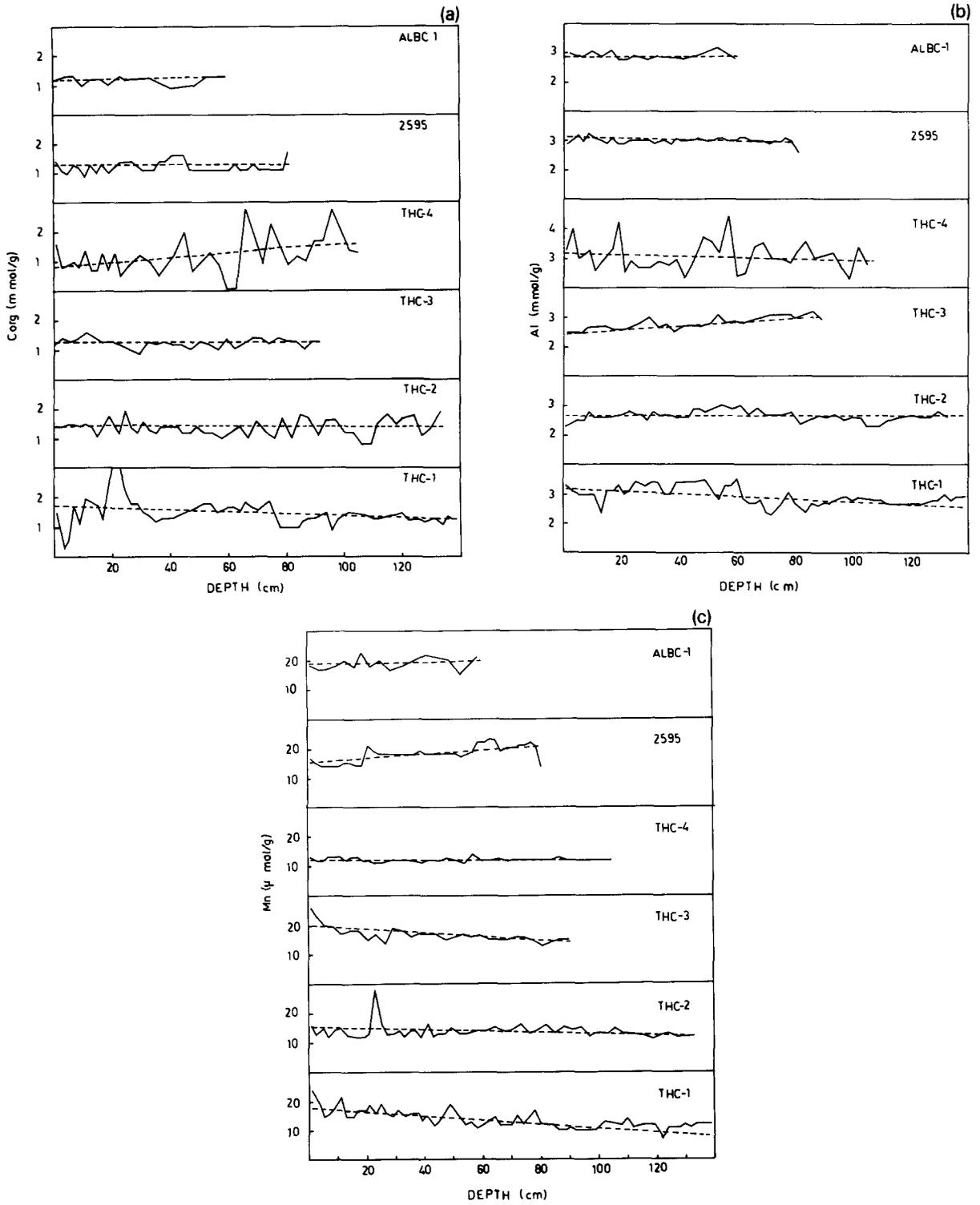


Fig. 3. Distribution of (a) C_{org} (b) Al, and (c) Mn concentrations in cores. General trends are indicated by dashes.

respectively. The concentrations of ^{226}Ra in the surface sections of THC-4 and THC-7 were 0.77 ± 0.05 and 0.59 ± 0.10 dpm/g, respectively. The average ^{226}Ra concentrations were used to calculate $^{210}\text{Pb}_{\text{exc}}$ in all core sections.

The excess ^{210}Pb content of the sediments decreased considerably with depth (Table 1 and Fig. 2) for all cores. The sediment accumulation rates determined from the slope in the excess ^{210}Pb profiles varied between 1.9 ± 0.33 and 0.73 ± 0.1 cm/yr and were comparable to those reported for the coastal regions of the western continental margins of India (Borole, 1988). The $^{210}\text{Pb}_{\text{exc}}$ activity extrapolated to the sediment–water interface (Table 2) varied from 4.0 to 4.9 dpm/g in the northern and the southern areas, and between 1.6 and 2.6 dpm/g in the central complex (harbour area). The $^{210}\text{Pb}_{\text{exc}}$ inventories which varied from 16 to 187 dpm/cm² revealed a

marked decrease from the inner creek to the outer harbour region.

The metal concentrations were normalised with Al to compensate for grain size effects and mineralogical variations (Windom et al., 1989). Examination of geochemical results illustrated in Figs. 3–7 indicated certain definite trends as given below:

- (1) Higher metal concentrations as well as metal/Al ratios in the surface 5 cm portions of most cores as compared to the sections below.
- (2) Absence of an inverse relationship between the transition metal concentration and C_{org} in the top 5 cm pertaining to 1975–1982, indicating dominance of anthropogenic influence over diagenesis at the sediment–water interface.
- (3) Inverse relationships between Mn and C_{org} (Fig. 3a and c) in the deeper portions of

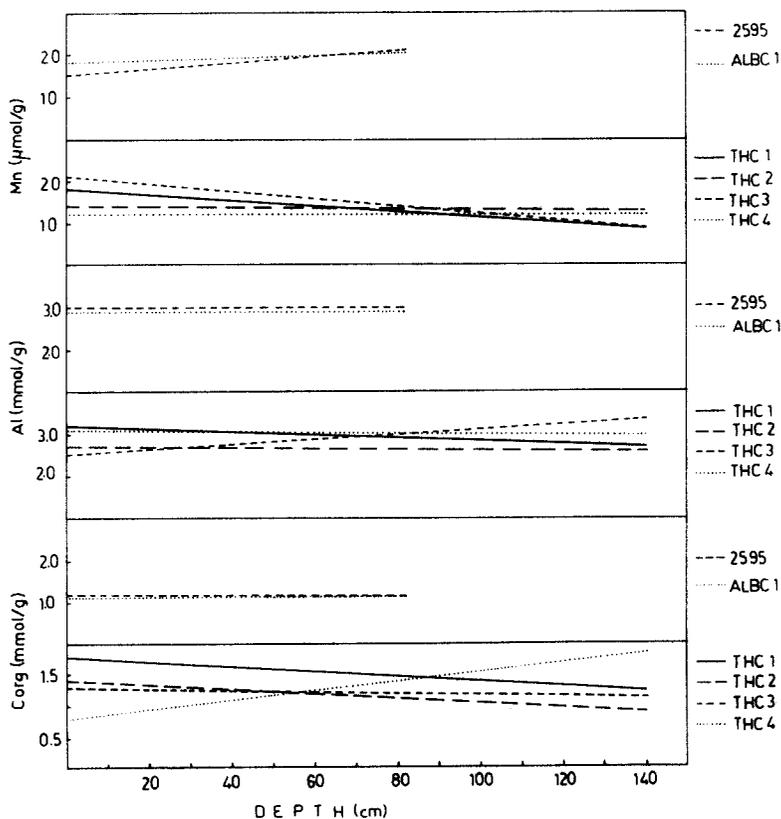


Fig. 4. Lines of regression for the concentrations of C_{org} , Al and Mn in cores.

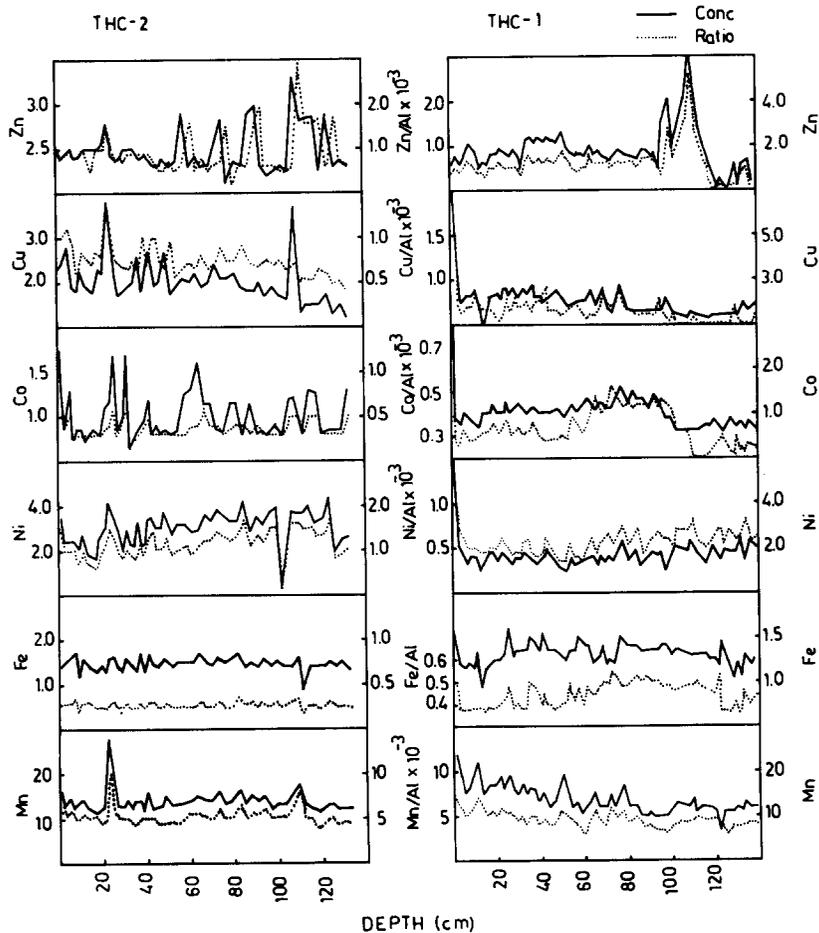


Fig. 5. Metal concentrations (Fe in mmol/g and remaining metals in $\mu\text{mol/g}$; solid lines) and metal/Al molar ratios (dotted lines) in THC-1 and THC-2.

cores THC-1, THC-2 and THC-4, due to the influence of diagenetic processes.

- (4) A prominent peak between 91 and 120 cm in THC-1 in the concentration of Zn as well as in the Zn/Al ratio (Fig. 5) reflecting an episodic event of Zn contamination in the period between 1900 and 1920, prior to any industrialization in the surrounding areas. A peak in the concentration of C_{org} was also evident in the core between 18 and 26 cm.
- (5) Markedly different trends in the profiles of Al, Mn and C_{org} in THC-1 to THC-4 as compared to those in ALBC-1 and 2595 (Fig. 3).
- (6) Several maxima in metal concentrations as well as metal/Al ratios in profiles of some

cores which were well clear of analytical uncertainties, perhaps due to the sporadic anthropogenic enrichments (Figs. 5 and 6).

- (7) Similar sediment depositional conditions in THC and nearby coastal areas as evident from histograms of metal/Al ratios illustrated in Fig. 1, except for THC-4 where the magnitude was marginally less.
- (8) Gradual but definite increase in Ni concentrations down the profiles in all cores (Figs. 5–7).
- (9) Significant spatial variations in calculated excess inventories for C_{org} , Mn, Co, Ni and Zn (Table 4).

The above observations and their implications

for the bed sediment as a source or sink for anthropogenic fluxes of metals are discussed below together with the pattern of distribution of attendant metal concentrations and their signatures in the form of environmental pollution.

5. Discussion

The sediment accumulation rates are controlled by redistribution and “bottom focussing”, or through preferential deposition of particulate matter by bottom currents (Bacon and Rosholt, 1982; Bacon, 1984) in the pelagic areas and similar processes are operative in the dynamic coastal

environments. The observed concentration gradients in the profiles of ^{210}Pb in a sediment core, in terms of Pb isotope, might be either due to the temporal variations in the source of ^{210}Pb particles accumulating in a given region, or due to real decay with time. In order to confirm which of these two processes was dominant, in the present study, $^{210}\text{Pb}/\text{Al}$ ratios (Table 1 and Fig. 2) were critically examined. As the normalisation of ^{210}Pb concentration against Al content in the sediment bypassed the problem of porosity changes with depth, estimation of clay accumulation rates became possible for near constant ^{210}Pb flux and rate of sediment accumulation. The average accumulation rates (Table 2) estimated from the slopes of the best-fit

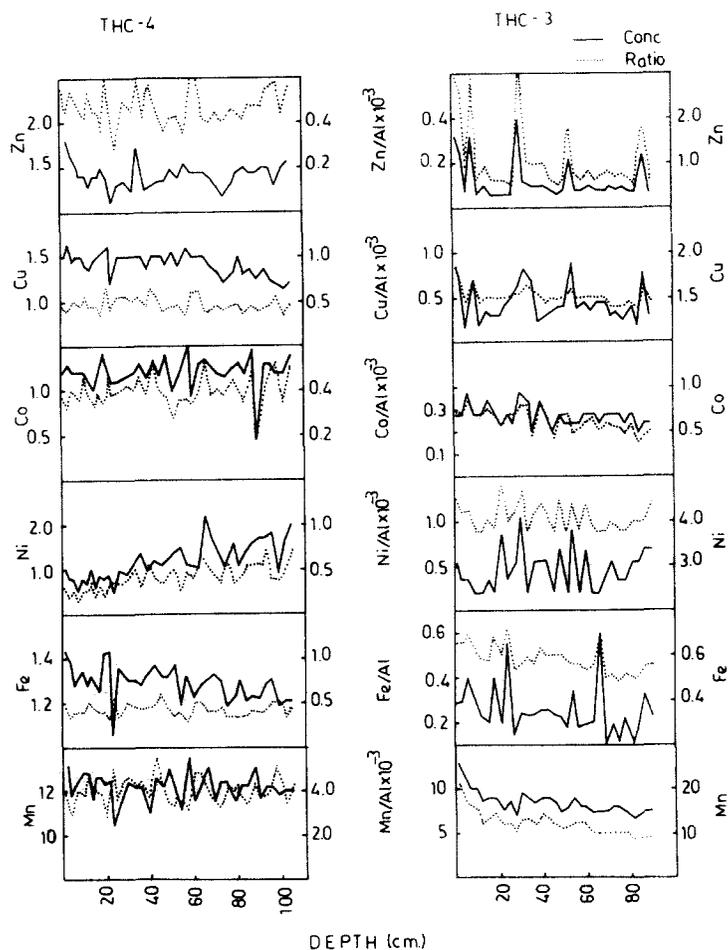


Fig. 6. Metal concentrations (Fe in mmol/g and remaining metals in $\mu\text{mol/g}$; solid lines) and metal/Al molar ratios (dotted lines) in THC-3 and THC-4.

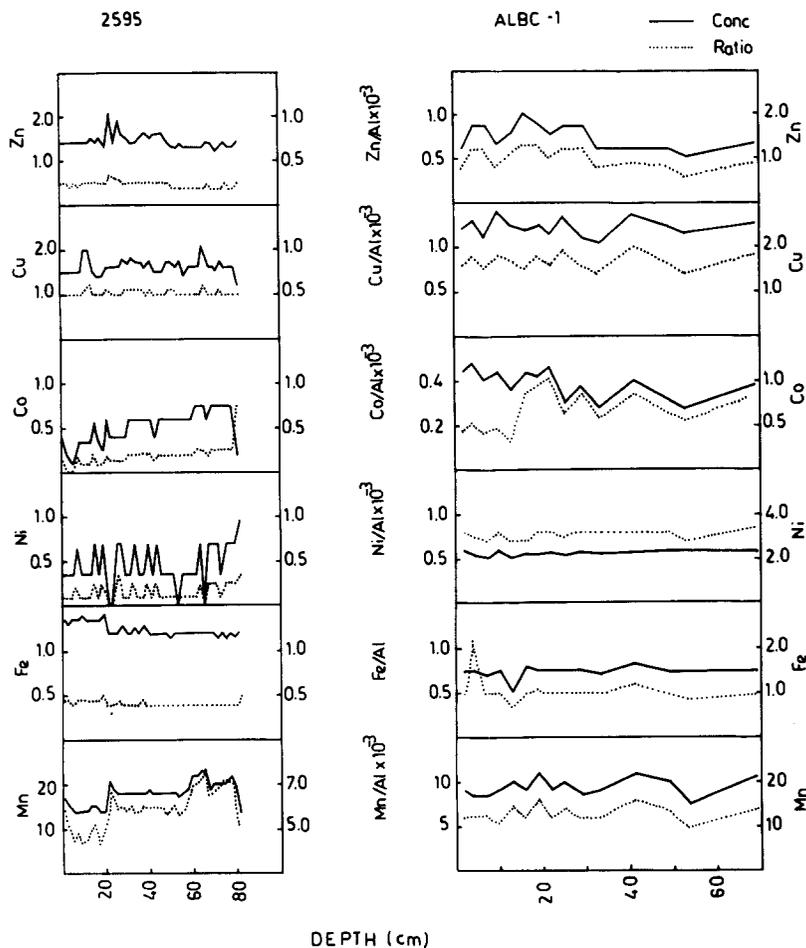


Fig. 7. Metal concentrations (Fe in mmol/g and remaining metals in $\mu\text{mol/g}$; solid lines) and metal/Al molar ratios (dotted lines) in ALBC-1 and 2595.

lines enabled to group the sediments of the THC into northern (zone of high sediment accumulation rate of 1.6–1.9 cm/yr), central (zone of winnowing by bottom currents with accumulation rate of 0.3–0.7 cm/yr), and southern (zone marked by intermediate deposition probably controlled by the coastal dynamics, with rate of accumulation of 0.6–0.7 cm/yr) segments.

A high degree of sediment accumulation in the northern segment could be due to the differential macro-tidal regimes and prevailing pattern of circulation within the complex. The considerable time lag in the occurrences of high and low tides between the Bombay harbour and Ulhas estuary facilitated the exchange of water between the two

creeks during part of a tide cycle (MCGB, 1979) which resulted in a low energy field in the northern segment that assisted sedimentation of SPM. During the dry season, much of the SPM which was derived from the scour of the bed and the intertidal mudflats, as the tidal front advanced through the Bombay harbour was advected in the northern segment where the currents were relatively weak (Zingde, 1989). High riverine flow with high concentrations of SPM into the Ulhas estuary during southwest monsoon (Zingde, 1989) enhanced the tidal flow from the Ulhas estuary into the THC due to the water level elevation of the estuary which also contributed to sedimentation in the northern segment. During this period, a

portion of the settled sediment was resuspended and transported to the lower regions due to increase in ebb current speeds associated with the increased flow of water in the creek via Ulhas estuary and also increased land runoff. Available literature (Sastry, 1971; Swamy et al., 1980; Swamy and Suryanarayana, 1984) also supported the view that the northern segment was the region of confluence of two opposing tidal currents resulting in a low flushing rate and high SPM. Similar conclusions have also been drawn in parts of the Wadden Sea and Jiangu (Postma, 1967; Zhang, 1992).

The lower rate of sedimentation around THC-4 could either be due to low levels of sediment supply (stagnant environs) or higher dynamic activity leading to the removal of fine grained material (active environs). It is quite likely that the supply of sediment associated with the ebb flow was highly restricted in this area as the location fell in the lee of the protruding shore.

The ^{210}Pb activity in sediments was expected to be influenced by the atmospheric component which could account for up to $1.5 \text{ dpm/cm}^2/\text{yr}$ (Krishnaswami and Lal, 1982) and by the in-situ component which, in a water column of 20 m, was $0.01 \text{ dpm/cm}^2/\text{yr}$, considering an average ^{226}Ra concentration of 0.15 dpm/l (Sarin et al., 1994). These two components together resulted in a steady state ^{210}Pb inventory of $\sim 50 \text{ dpm/cm}^2$ in sediments and constituted only about 25% of the measured inventory of $142\text{--}187 \text{ dpm/cm}^2$ (Table 2) suggesting that the inner THC was a "sink" for this radionuclide. Similar higher inventories have been reported for the coastal reaches of southern California (Bruland et al., 1974; Krishnaswami et al., 1975; Moore et al., 1981; Huh et al., 1987). Low ^{210}Pb inventories ($\sim 16 \text{ dpm/cm}^2$), which were lower by a factor of at least 2 compared to those of the overhead precipitation in the central segment, in contrast were probably associated with the scouring of sediments by strong tidal currents leading to low accumulation rates of $0.3\text{--}0.5 \text{ cm/yr}$ (Table 2). Nearly equal inventories of $34\text{--}47 \text{ dpm/cm}^2$ between the sediment and the overhead precipitation indicated material balance between the supply and deposition of ^{210}Pb in the sediments of the southern segment of the THC. In order to assess the mobilisation of metals

and its implications to the marine environmental quality, we examined factors most likely to produce these changes. Variations in the organic content could be caused by productivity changes in the surface waters, varying rates of terrestrial inputs and the degree of preservation. From these sources, the contribution from productivity would be low in the THC because of sunlight limitation on photosynthesis due to high turbidity (Zingde, 1989). Hence, the organic load would be dominantly terrestrial with substantial contribution from domestic and industrial sources. It has been estimated that around $8.7 \times 10^4 \text{ kg/d}$ of BOD entered the THC through domestic wastewater alone (Zingde, 1989) which would have considerable influence on the C_{org} content of the bed sediments, particularly in the northern segment where the sedimentation rate was high. In order to obtain information about the source of C_{org} , we attempted to correlate the concentrations of C_{org} with those of Al.

The concentrations of C_{org} in THC-1 and THC-4 (from sheltered/stagnant zone) presented opposing trends (Fig. 4) with a point of inflection at about 85 cm. The closeness of the parameters for the cores 2595 and ALBC-1 was also quite evident and indicated a near uniform or stable environment, similar to that of THC-2 and THC-3.

In the core THC-1, C_{org} and Al showed an overall similar trend (Fig. 4). The C_{org} surprisingly increased only marginally towards the surface despite the fact that the nearby areas were highly urbanised and industrialised and contributed voluminous anthropogenic fluxes of pollutants to the complex (Zingde, 1989). In contrast, opposing features in the C_{org} and Al profiles of THC-4 (Fig. 4) were perhaps due to the consequence of prevailing hydrodynamic conditions. The higher tidal flushing due to relatively stronger currents resulted in the retention of coarser terrigenous minerals in the region while C_{org} , being lighter, remained mobile getting flushed in and out during each tide cycle. Similarity in the regression trends of C_{org} and Al for THC-2 indicated that a terrestrial source dominated the sediments. Supply of sediment from the continental sources seemed to increase with age in THC-3 as evident from Al concentration which increased with depth, while

the C_{org} remained more or less uniform over the past 46 years or so, indicating that the anthropogenic influence was not dominant in this core. Similarity in the trends in variation in the concentrations of C_{org} and Al for cores 2595 and ALBC-1 indicated their terrestrial source and received further support from the higher C/N ratio (> 10) reported by Paropkari et al. (1987) in the sediments of the region.

To ascertain whether the variations in C_{org} had any relation with early diagenesis, the Mn profiles were investigated. Mn is a redox sensitive element and prone to be affected by diagenetic processes. THC-1 and THC-3 showed decreasing trends of Mn concentration (Fig. 4) with depth while in case of THC-2, the Mn content did not show any significant trend in variation, unlike Al and C_{org} concentrations at the mid-core level. The Mn–Al relation was better ($r = 0.47$) in THC-1 than Mn– C_{org} relation ($r = 0.30$) probably because the major portion of Mn could be of detrital origin and not from the diagenetic source. In THC-2, the maxima in the concentrations of Mn, Co, Ni, Cu and Zn at depths corresponding to 12 and 65 yr coincided with the C_{org} minima (Figs. 3a and 5) probably indicating the influence of local diagenesis during these periods.

In THC-3, the Mn concentration presented an increasing trend from the bottom to the surface, perhaps due to an increase in supply; it did not have any similarity with the trends in Al and C_{org} contents.

The concentration peaks of Mn matched closely with those of Cu, Zn and Co and with those of Al and C_{org} in the profiles of THC-4. As discussed above, the prevailing hydrodynamics did not favour deposition of lighter fractions of sediments due to which the heavy ferro-manganese minerals were retained and enriched in the area. Positive correlations between Mn and other elements like Cu, Zn and Co also support this view.

The effects of local diagenesis at few depths in THC-2 were discussed earlier. However, surface enrichment of metals occurred in several cores due to anthropogenic influences and there was no inverse relation between C_{org} and the transition metal. This would support the contention that diagenetic effects had no significant influence on surface enrichment of trace metals.

From the regression equations (Table 3) it was seen that for the coastal cores 2595 and ALBC-1, the concentration of Mn exhibited an opposite trend when compared with the cores from the THC. Incidentally, in these two cores, concentrations of Al and C_{org} were more or less uniform but, particularly in Core 2595, Mn behaved differently with a steady increase in concentration with depth attaining maxima at the bottom (150 yr or so from the present) suggesting that the Mn was not of anthropogenic origin. Hence, it was likely that Mn in these cores was largely authigenic, perhaps in the form of hydroxide floccule. Dissolved Mn, like dissolved Fe, when entering the sea, comes in contact with alkaline and oxidizing environments and tends to precipitate as insoluble, finely divided MnO. This process is very effective in nearshore regions (e.g. Krauskoff, 1965; Paropkari, 1990). It is evident from Fig. 7 that Mn shows a decreasing upward trend during the preceding 30 yr period from the present. This was perhaps due to decrease in the authigenic Mn precipitation due to increase in organic pollutants loads that lowered the dissolved oxygen content of water which decreased flocculation intensity of MnO from the water column. In acidic water, due to less effective scavenging, the metals remain in solution and are therefore carried away by the tidal currents.

It has been known that estuaries and tidal creeks are active reservoirs for sediments between land and ocean (Kennedy, 1984; Salomons and Foerster, 1984). In order to cross-check whether the THC was a filter for these metals, we examined the histograms depicting the metal/Al ratios (Fig. 1). We did not encounter any significant difference between the sediments of the THC and those from the coastal water. It therefore appeared that either the THC was a passive link and not an active trap for trace metals entering the complex or that the trace metals were largely scavenged under prevailing high SPM and sedimented prior to their transport to the THC proper from where the cores were collected. The latter possibility was more likely because the majority of wastewater discharges to the THC were through natural storm-water drains and narrow and shallow tidal tributaries permitting sufficient time for the metals

to be adsorbed by SPM and their removal by sedimentation either in the channel or around the confluence point thus considerably reducing the trace metal loading on the THC proper. Hence, study of cores from intertidal mudflats and tidal creeks would be required to settle the argument.

Interestingly, Ni concentrations in all cores exhibited gradual increase from the surface to the bottom. Detailed mineralogical and geochemical studies on these cores should throw more light on the weathering patterns and supply of resultant detrital material over time.

Based on excess metal inventories (Table 4) it appeared that elements potentially dangerous to the marine environment (Preston, 1989; Foerstner et al., 1990) had not attained alarming concentrations in this region.

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