

## ASSESSMENT OF HEAVY METALS IN THE SEDIMENTS OF ANTHROPOGENICALLY DISTURBED PATALGANGA ESTUARY, INDIA

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### ABSTRACT

The present study aims to evaluate the effect of industrialization on the heavy metal accumulation in sediments of the Patalganga Estuary. The contamination level of the Patalganga estuary is evaluated based on the enrichment factor and geo-accumulation index of heavy metals in sediment. The results depicted the minimal enrichment and contamination of Cr, Mn, Fe, Co, Ni, Cu, Zn, and Hg in the core 1, core 2 and core 3. In core 4, minimal enrichment of Cr, Mn, Fe, Co, Ni, Cu, Zn, and Hg was observed. Whereas, Cr, Co, and Cu were moderately contaminated and other selected metals viz. Mn, Fe, Ni, Zn, and Hg were uncontaminated in core 4. Low to moderate contamination of selected metals viz. Cr, Mn, Fe, Co, Ni, Cu, Zn, and Hg was observed in all the selected cores, i.e. Core 1, core 2, core 2, core 3, and core 4. Significant correlation of selected metals with silt, clay and organic carbon inferred that they are concentrated in fine-grained particles and are released from a common source. The heavy metals are likely to be introduced to the system through industrial effluents as organometal complexes through anthropogenic activities. The texture of at cores 2 and core 3 were sandy-silt that increased to surface, whereas core 4 was mainly silty that increased to surface. Organic carbon levels in all the cores showed an increasing trend from bottom to surface. Overall results indicated moderate contamination of Patalganga sediment with anthropogenic sources it may be due to the industrial waste from multiple industries in the region.

**KEY WORDS :** Patalganga Estuary, Sediment, Heavy Metals, Enrichment factor, Contamination factor, Organic Carbon

### INTRODUCTION

Sediments are important repositories of metals in aquatic environment (Chatterjee *et al.*, 2007), whereas the varying texture and geochemistry influence their binding efficiency in sediments (Shea 1988). Metals are generally released to the aquatic environment by both natural and anthropogenic sources. Natural pathways are weathering of rocks, aeolian and volcanic activities, whereas anthropogenic sources include discharge of agricultural, municipal, and industrial wastes (Clark, 2001). Some metals like Fe, Zn, Mn, Co are essential to living organisms but becomes highly toxic at higher concentrations, whereas others (Pb, Ni, Cr), generally not required for metabolic

activities, are toxic even at very low concentrations (Forstner and Wittmann, 2012; Meria, 1991). Metals have great ecological significance because of their toxicity, persistence and bioaccumulation (Klavins *et al.*, 2000; Tam and Wong, 2000), as they tend to accumulate on the food-chain posing serious threat to the environment and human being (Marchand *et al.*, 2006).

The estuarine and coastal waters are highly complex areas owing to the varying terrestrial input, tidal activity and waves (Morris *et al.*, 1995). The estuaries are the vital sites of biological production and habitats of numerous species (Bricker *et al.* 2008). This study regions are also constantly influenced by anthropogenic activities (wastes from agriculture, domestic sectors, industries, mining,

port etc.). Among the various types of pollutants released, heavy metals are one of the most serious pollutants owing to their toxicity, persistence and bioaccumulation (MacFarlane *et al.*, 2003; Lindsey *et al.*, 2006; Vane *et al.*, 2009; Lal Shah, 2010).

Heavy metals, which includes Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb, Cd, Hg, Ti and V enter the ocean as a result of natural processes and human activities via river, land runoff, dumping, atmospheric and settle on the seabed. In such areas of intense activities, these metals occur at elevated concentrations in water and sediments (Attrill and Thomes, 1995, Gupta and Karuppiah, 1996, Balls *et al.*, 1997). Coastal sediments are therefore, an important repository for metals, as they are transported in association with particulate matter, which ultimately is deposited on sediments in harbours, estuaries and coastal regions (Bothner *et al.*, 1998; Miller *et al.*, 2000; Chen *et al.*, 2001; Feng *et al.*, 2004).

Heavy metals are one of the worldwide investigated environmental pollutant, and many monitoring reports has arisen in particular for coastal and estuarine ecosystems (Ghorbanzadeh Zaferani *et al.*, 2016). The accumulation of PBTs in marine sediment is a complex process, detailed investigation about distribution of heavy metals is necessary for better understanding of mechanisms controlling the geochemistry of metals in a particular environment. The accumulation of persistent bio-accumulative and toxics in marine sediment is a complex process. It is therefore necessary to characterize the distribution of heavy metals for better understanding of the mechanisms controlling the geochemistry of metals in an environment. Although there are several studies conducted related to environmental impact assessment and monitoring in the area like Amba Estuary, Ulhas Estuary and Thane Creek, published information is scarce (Yadav *et al.*, 2015; Zingde and Desai, 1981; Ram *et al.*, 2003; 2009; Rokade, 2009). The present study aims to evaluate the effect of industrialization and other anthropogenic activities on the biogeochemical characteristics and heavy metal distribution in the sediments of the important estuaries on the western coast of India. With the rampant pollution of areas in and adjoining the Patalganga industrial zone due to heavy industrial and anthropogenic activities, it is important to monitor the biogeochemistry of the sediments in the area.

## MATERIALS AND METHODS

### Study Area

Patalganga River is a tributary of Alaknanda River originating in Kunwarikhil catchment. It rises in the steep western scarps of the Matheran uplands where it branches off from the main ridge near Khopoli and maintains a general westward flow till it joins the Dharamtar Creek with a wide estuary. The tail-waters of the Khopoli power project are let into the river near Khopoli in Maharashtra. The river has its source in the Khandala portion of the Sahyadri scarp. In its meandering north-westward reach of about 25 miles, several streams on either side drain the land that is highly eroded and marked by remnant hill features, the more prominent of them being the Prabal heights (2,318 ft.) and the Kamala fort range. Many industries had been established in the vicinity of the said river. The river became not only main source of water supply to these industries but also for the drinking water supply to nearby villages. The climate of the district is typical of that on the west coast of India, with plentiful, regular and seasonal rainfall during the monsoon season. The area receives an average rainfall of more than 300 cm. Nearly 95 per cent of the annual rainfall is received during July-September. The tidal range in the estuary is 4.5 m at a distance of 35 km from mouth, which decrease to 1.2 to 1.7 m at a distance of 43 km from the mouth (CSIR-NIO, 2016). Tidal current varies from 0.70 to 1.5 m/s in the estuary. There are several urbanized zones along the banks of the Patalganga Estuary which release domestic  $H^{2.0} \times 10^4 \text{ m}^3/\text{d}$  sewage directly or indirectly to the estuary often without treatment and similar quantity of treated industrial effluent through Maharashtra Industrial Development Corporation (MIDC) (CSIR-NIO, 2016). This has significantly lowered the quality of the estuarine and adjacent water and ecological environment creating threat to the area. This study was aimed to find the deposition of heavy metals at different stages in the sediment and explain the anthropogenic impact.

### Sampling of core sediments

In the present study, four sampling stations on the Patalganga River were selected to study the biogeochemical characteristics and pollution levels. The four stations were; S1, S2, S3 and S4 as depicted in Figure 1. The first sampling station S1

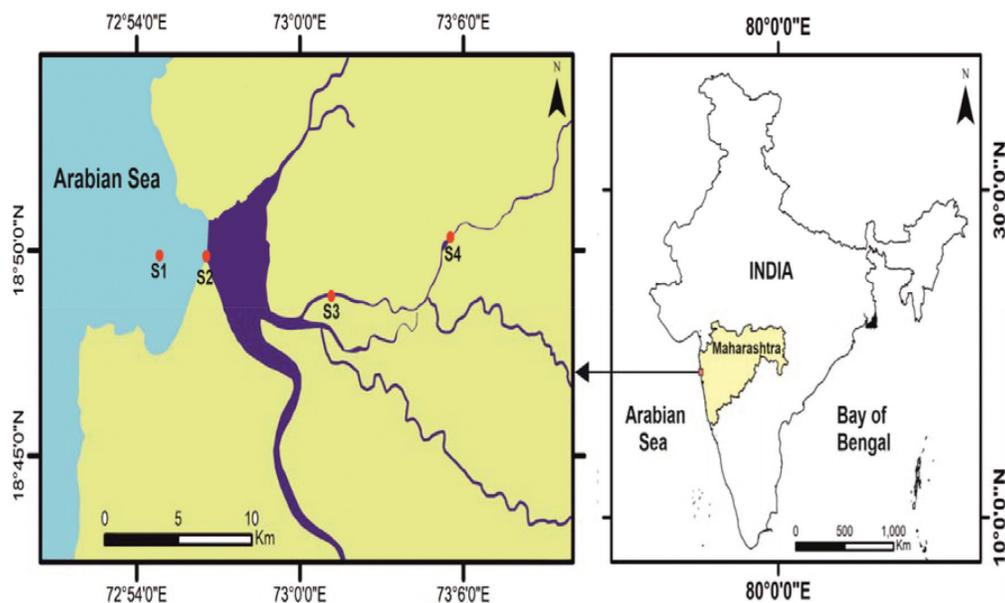


Fig. 1. Map showing the four stations selected around Patalganga industrial area for the study.

( $18^{\circ}49'52.87''\text{N}$ ,  $72^{\circ}54'50.26''\text{E}$ ) was in the coastal water of the Arabian Sea. The second sampling station S2 ( $18^{\circ}49'51.80''\text{N}$ ,  $72^{\circ}56'33.20''\text{E}$ ) was at the Revas beach near the amalgamation of the creek with the Arabian Sea. The third sampling station S3 ( $18^{\circ}48'53.80''\text{N}$ ,  $73^{\circ}01'08.98''\text{E}$ ) was near the Vasheni bridge and the final sampling station S4 ( $18^{\circ}50'19.20''\text{N}$ ,  $73^{\circ}05'31.40''\text{E}$ ) was near the Patalganga river bridge and which is very close to industrial effluent discharge point. Sediment core samples from the study area were collected using a gravity corer. A 1.8 m long, pre-cleaned acrylic liner (inner dia 5.5 cm) was inserted in the corer. Sufficient weight was added to pull the corer in the sediment. A catcher attached in the core barrel, just above the cutter will get closed due to weight action of sediment contained in the core liner when the corer was hauled up. The liner was removed from the corer and its lower end was closed with a plastic cap. The top portion was cut at the water-sediment interface and sealed with a plastic cap. Utmost care was taken throughout the operation from retrieval of the corer till the sealing of the top end, not to disturb the sediment in the liner. After sealing, the cores were transferred to the laboratory. Therefore, the sediment samples from the sampling sites S1, S2, S3 and S4 are here after referred to as Core 1, Core 2, Core 3 and Core 4 respectively.

#### Preservation

In the laboratory, sediment was carefully removed

from the acrylic liner on a clean glass sheet by holding the bottom end of the liner and carefully inserting a closely fitting acrylic plunger. As the plunger pushed the sediment came out on the glass sheet, the liner was pulled in the other direction till the sediment 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 2cm interval using a clean non-metallic cutter. The sliced sub-samples were immediately transferred to pre-cleaned wide mouth polypropylene containers. All the surface sediments and core sub-samples were oven dried at  $55^{\circ}\text{C}$  to constant weight. Dried samples were powdered using an agate pestle and mortar and were stored in air-tight pre-cleaned plastic containers for further analysis.

#### Metal analysis of sediments

Powdered and homogenized sediment samples were acid digested using  $\text{HF-HClO}_4\text{-HNO}_3\text{-HCl}$  added sequentially after drying earlier acid in Teflon beakers (Loring and Rantala, 1992). Suprapure (Merck Germany) grade chemicals, acids and high purity Milli-Q water were used during all digestion and analyses processes. Metal analysis was performed on the resultant digests using ICP-OES (Optima 7300DV, Perkin Elmer) for Al, Cr, Mn, Fe, Co, Ni, Cu and Zn. Mercury (Hg) was analyzed in triplicates with a Flow Injection Mercury System (FIMS-400, Perkin Elmer,) after digestion with aqua

regia and oxidation with  $KMnO_4$ . Standard Reference Materials (SRM) of sediment (PACS-2) obtained from the National Research Council, Canada, were analyzed with each set of sample to authenticate results of analysis. The results of SRM were found to be within  $\pm 5\%$  of the certified value. The blank samples were also processed in triplicate and analyzed along with the samples to check any loss or cross contamination. All metal concentrations were expressed in  $\mu g/g$  on a dry-weight basis except Al and Fe, which were expressed in percentage (%).

**Grain size analysis**

Grain size analysis of sediment was carried out on sub-samples from the 4 cores. About 1.5 g of dried sediment was dispersed with distilled water and treated with 1N HCl and 30%  $H_2O_2$  to remove carbonates and organic matter, respectively. Thereafter the sediments were washed thoroughly with de ionized water until the pH became neutral. The sediments were then dispersed with 0.5 mL of 1% sodium hexa-meta phosphate solution and wet sieved, using ISTM 230 mesh sieve to separate sand fraction (63  $\mu m$ ) from clay and silt. The sand fraction retained in the sieve was collected, dried and weighed. The sediment fraction < 63  $\mu m$  was used for measuring size fractions of silt and clay, using Malvern Laser Particle size analyzer (Master sizer 2000). Thereafter the percentages of sand (63  $\mu m$ ), silt (4  $\mu m$ ) and clay (< 4  $\mu m$ ) were calculated in each sample (Folk, 1968).

**Determination of organic carbon**

The organic carbon (OC) content was determined by the wet oxidation method (El Wakeel and Riley 1957).

**Determination of Enrichment factor (EF)**

Sediment metal enrichment factor (EF) was calculated based on the standardization of a tested element against a reference element Al using the formula given by Buat-Menard and Chesselet, (1979) and Kumar and Edward (2009) as given below:

$$EF = \frac{C_n(\text{Sample}) / C_{ref}(\text{Sample})}{B_n(\text{Background}) / B_{ref}(\text{Background})}$$

Where:

$C_n$  – Content of examined element in sample;  $C_{ref}$

– Content of examined element in selected reference;  $B_n$  – Content of the reference element in the examined environment;  $B_{ref}$  – Content of the reference element in the reference environment. Back ground reported by Ram *et al.*, (2009) and Rokade, (2009) by analyzing sediment core of the area and bottom section, which represent pre-industrialized year was used to calculate the EF. Thus background values used are: Al: 7.0%, Cr: 102  $\mu g g^{-1}$ , Mn: 817  $\mu g g^{-1}$ , Fe: 7.2%, Co: 38  $\mu g g^{-1}$ , Ni: 70  $\mu g g^{-1}$ , Cu: 86  $\mu g g^{-1}$ , Zn: 84  $\mu g g^{-1}$  and Hg: 0.10  $\mu g g^{-1}$ .

Level of contamination in the estuary based on the enrichment factor (Kumar and Edward, 2009).

- EF<2 Deficiency to minimal enrichment
- EF=2-5 Moderate enrichment
- EF=5-20 Significant enrichment
- EF=20-40 Very high enrichment
- EF>40 Extremely high enrichment

**Contamination Factor**

The level of sediment contamination by a metal is often expressed in terms of a contamination factor calculated as Contamination Factor (CF) = Metal content in the sediment / Background value of metal. According to Hakanson (1980) classification, CF < 1 refers to low contamination, 1 ≤ CF ≤ 3 means moderate contamination, 3 ≤ CF ≤ 6 indicates considerable contamination and CF > 6 indicates very high contamination.

**Pollution Load Index (PLI)**

PLI has been calculated by using the method proposed by Tomilson *et al.* (1980). This parameter is expressed as:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

Where “n” is the number of metals (eight in the present study) and CF is the contamination factor.

PLI is a potent tool in heavy metal pollution evaluation. According to Chakravarty and Patgiri (2009) and Harikumar *et al.* (2009) the PLI value > 1 indicates pollution whereas PLI value < 1 indicates no pollution.

**Determination of Geo-accumulation index ( $I_{geo}$ )**

The index of geo-accumulation ( $I_{geo}$ ) was computed using equation (Muller and Suess, 1979; Loska *et al.* 2004; Kumar and Edward, 2009).

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

Where  $C_n$  is the measured concentration of the element in the sediment fraction and  $B_n$  is the

geochemical background value. The constant 1.5 is used to compensate for possible variations with respect to background due to lithogenic variations. Six classes of geo-accumulation indices were distinguished (Muller and Suess, 1979).

Class	Value	Sediment Quality
0	$I_{geo} < 0$	Practically uncontaminated
1	$I_{geo} 0-1$	Uncontaminated to moderately contaminated
2	$I_{geo} 1-2$	Moderately contaminated
3	$I_{geo} 2-3$	Moderately to heavily contaminated
4	$I_{geo} 3-4$	Heavily contaminated
5	$I_{geo} 4-5$	Heavily to extremely contaminated
6	$I_{geo} 5-6$	Extremely contaminated

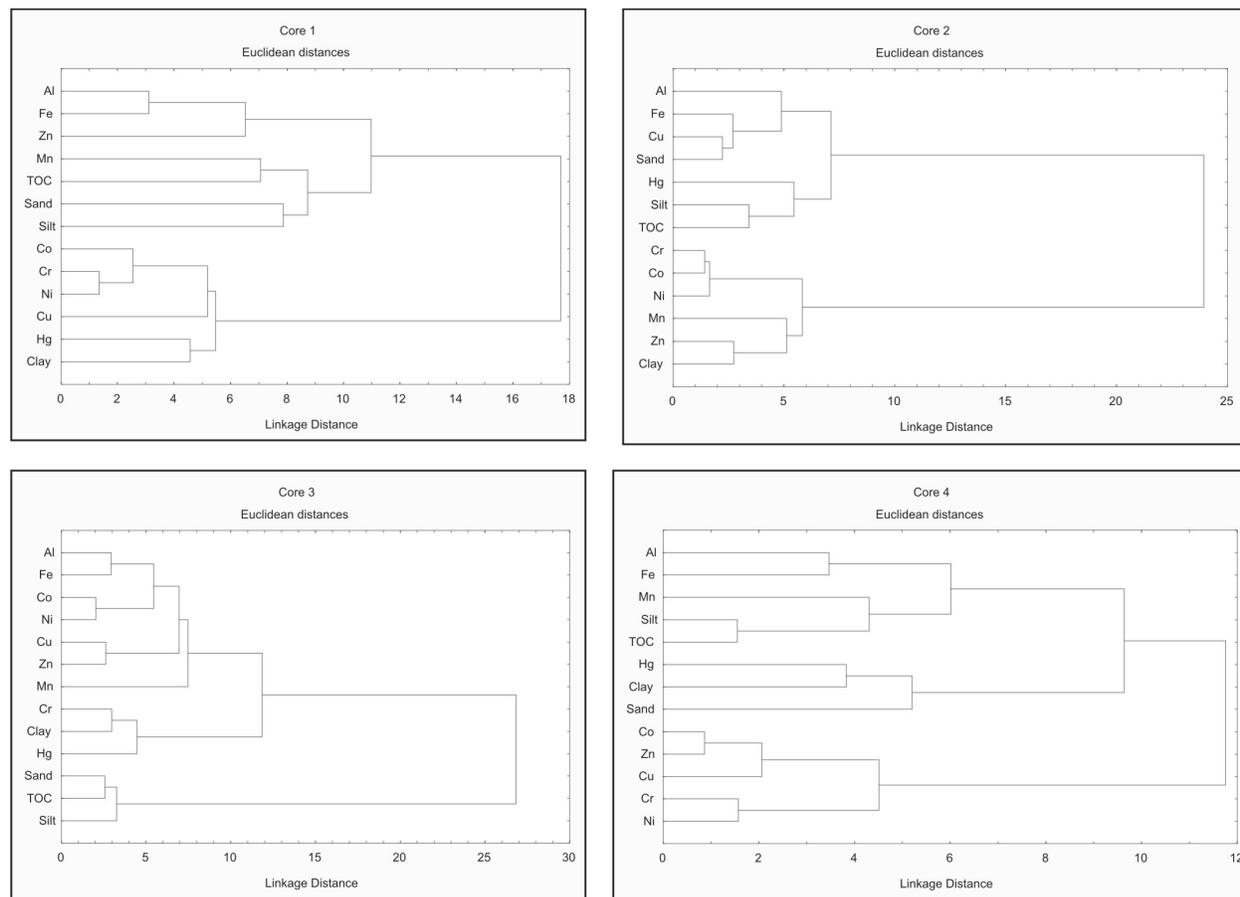
**Statistical analysis**

Statistical analyses including Pearson’s correlations and Cluster analysis was carried out using the STATISTICA 7.0 software (Statsoft, U.S., 1999). Graphs were plotted using Grapher 10.0 (Golden Software).

**RESULTS**

**Down core distribution of heavy metals**

The range and average values of all Cores depicted in Table 1. Core 4 showed highest concentration of all metals except Al and Hg. Hg was highest in Core 3. Down Core profile for Al, Cr, Co, Cu and Zn is consistent trend for Core 1, 2 and 3 whereas Core 4 showed increasing trend from surface to 18 cm depth bottom. There was no particular trend in variation of Fe, but decreased towards bottom in core 2 and increase in intermediate sections of core 4. Hg showed increasing trend towards bottom in all the Cores and highest concentration was observed in Core 3 at...cm. Core 1, which represents Mumbai harbour was dominated by sand in upper sections, but decreased towards bottom. The texture of cores 2 and 3 were sandy-silt that increased to surface, whereas core 4 was mainly silty that increased towards surface. Organic carbon levels in all the cores showed an increasing trend from bottom to surface (Figs. 3, 4 and 5).



**Fig. 2.** Diagrammatic representation of results obtained by Hierarchical Cluster Analysis (dendrogram) that shows relationships among various elements, sand, silt, clay and TOC Within the study are

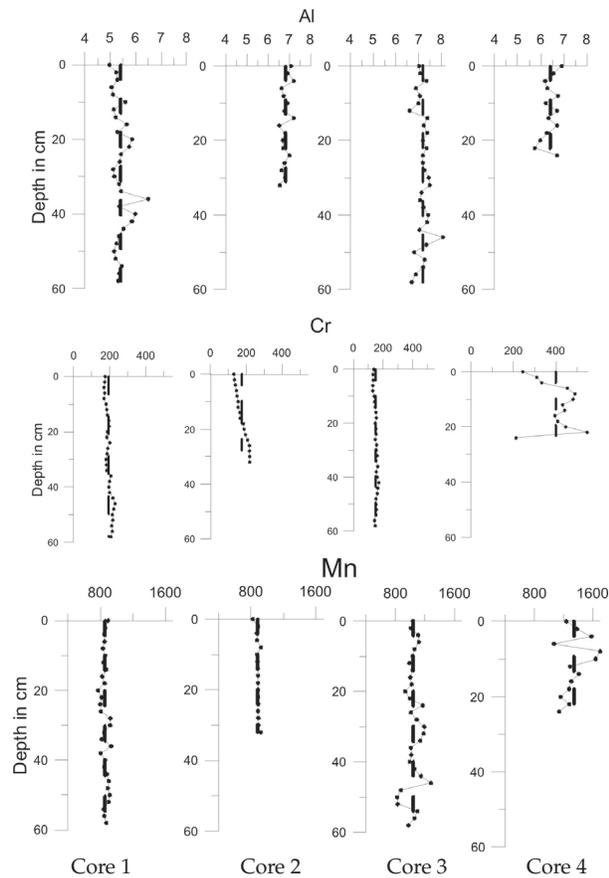
**Table 1.** Pearson’s correlation between different parameters (red colour indicates,  $p < 0.05$ ) in Core 1.

	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg	Sand	Silt	Clay	TOC
Al	1.00												
Cr	0.21	1.00											
Mn	-0.13	0.29	1.00										
Fe	0.83	0.50	-0.03	1.00									
Co	0.09	0.94	0.23	0.46	1.00								
Ni	0.26	0.97	0.29	0.49	0.88	1.00							
Cu	0.55	0.74	0.28	0.58	0.58	0.79	1.00						
Zn	0.54	0.09	0.01	0.34	-0.05	0.08	0.44	1.00					
Hg	0.28	0.70	-0.02	0.39	0.63	0.72	0.61	0.03	1.00				
Sand	-0.33	-0.77	-0.15	-0.47	-0.70	-0.83	-0.64	0.05	-0.67	1.00			
Silt	0.31	-0.22	-0.20	0.07	-0.23	-0.21	0.13	0.16	-0.16	-0.07	1.00		
Clay	0.06	0.75	0.25	0.33	0.71	0.80	0.43	-0.15	0.64	-0.75	-0.61	1.00	
TOC	0.04	-0.20	0.14	-0.17	-0.33	-0.06	0.01	-0.11	-0.04	-0.16	-0.02	0.14	1.00

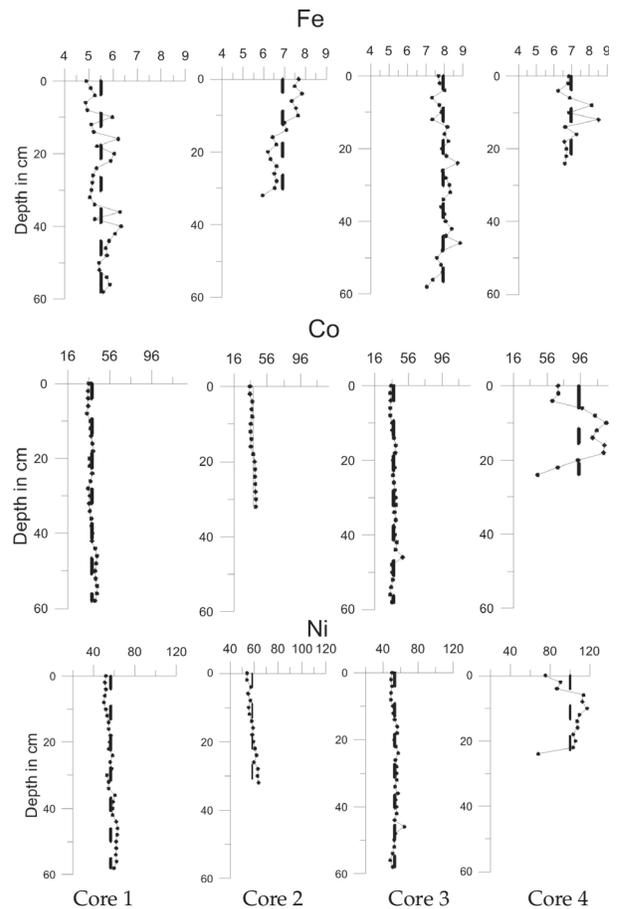
In Core 1 TOC ranged from 0.58 % to 2.3 % and sand ranged from 0.56 % to 44.8 %, silt from 33.4 % to 69.7 % and clay from 10.2 % to 64.5 %. In the case of elemental distribution in core 1, ranges of the metals were 5 – 6.5 % for Al, 168.9–229  $\mu\text{g/g}$  for Cr, 772–935  $\mu\text{g/g}$  for Mn, 4.9–6.3 % for Fe, 34.41 –44  $\mu\text{g/g}$  for Co 49.89–63  $\mu\text{g/g}$  for Ni 84, 67–104  $\mu\text{g/g}$

for Cu, 93.39–124  $\mu\text{g/g}$  for Zn, and 0.04 –0.19  $\mu\text{g/g}$  for Hg.

In Core 2 TOC ranged from 0.64 % to 2.0 % and sand ranged from 3.1 % to 24.2 %, silt from 22.4 % to 77.6 % and clay from 2.3% to 68.1 %. In the case of elemental distribution, ranges of the metals were 6.5



**Fig. 3.** Depth wise variation in Al (%), Cr and Mn ( $\mu\text{g.g}^{-1}$ ) in sediments of Patalganga



**Fig. 4.** Depth wise variation in Fe (%), Co and Ni ( $\mu\text{g.g}^{-1}$ ) in sediments of Patalganga

– 7.2 % for Al, 131–219  $\mu\text{g/g}$  for Cr, 824–925  $\mu\text{g/g}$  for Mn, 5.95–7.8 % for Fe, 35.4 – 42.5  $\mu\text{g/g}$  for Co 79.01–101.2  $\mu\text{g/g}$  for Ni, 53.7–63.5  $\mu\text{g/g}$  for Cu, 95.5–117.6  $\mu\text{g/g}$  for Zn, and 0.01 – 0.2  $\mu\text{g/g}$  for Hg.

In Core 3 TOC ranged from 0.18 % to 1.9 % and sand ranged from 1.7% to 17.5 %, silt from 33.7 % to

73.6% and clay from 9.2% to 60.5 %. In the case of elemental distribution, ranges of the metals were 6.6 – 8.1 % for Al, 130–171.2  $\mu\text{g/g}$  for Cr, 824.2–1282  $\mu\text{g/g}$  for Mn, 7.03–8.8 % for Fe, 33.9 – 48.9  $\mu\text{g/g}$  for Co 48.3–64.3  $\mu\text{g/g}$  for Ni, 93.6–114.5  $\mu\text{g/g}$  for Cu, 79–104.6  $\mu\text{g/g}$  for Zn, and 0.1 – 0.5  $\mu\text{g/g}$  for Hg. In core 3 Al, Fe and Hg showed the highest concentration compared to other three cores.

In Core 4 sand varied from 0.45 to 1.9%, silt 63.2 to 92.3 %, clay 7.18 to 34.9 % and TOC 0.54 to 2.3%. In the case of elemental distribution, ranges of the metals were 5.74 – 6.9 % for Al, 210–535.9  $\mu\text{g/g}$  for Cr, 1068–1699  $\mu\text{g/g}$  for Mn, 6.2–8.5 % for Fe, 44.82 – 126.8  $\mu\text{g/g}$  for Co 68.04–117.4  $\mu\text{g/g}$  for Ni, 115.2–601.2  $\mu\text{g/g}$  for Cu, 111.5–207.2  $\mu\text{g/g}$  for Zn, and 0.05 – 0.2  $\mu\text{g/g}$  for Hg. Core 4 showed highest concentration for Cr, Mn, Co Ni, Cu and Zn. This core was collected from the vicinity of industrial waste discharge; hence, the elevated concentration of above metals may be due to industrial waste.

#### Pearson's correlation analysis

Pearson's correlation coefficient of the sediment texture, organic carbon and metals in cores 1, 2, 3, and 4 is presented in the Tables 1, 2, 3, and 4 respectively. Pearson's correlation was used to identify the factors influencing the bonding among the elements and with sediments. For the core 1, Al was positively correlated with Fe, Cu and Zn, indicating their similar source. Clay was positively correlated with Cr, Co, Ni, Cu and Hg. Such significant correlation represents attachment of these elements with fine particle.

In core 2, sand and silt were significantly positively correlated with Fe and Cu, and negatively correlated with Cr, Co, Ni and Zn. Clay was

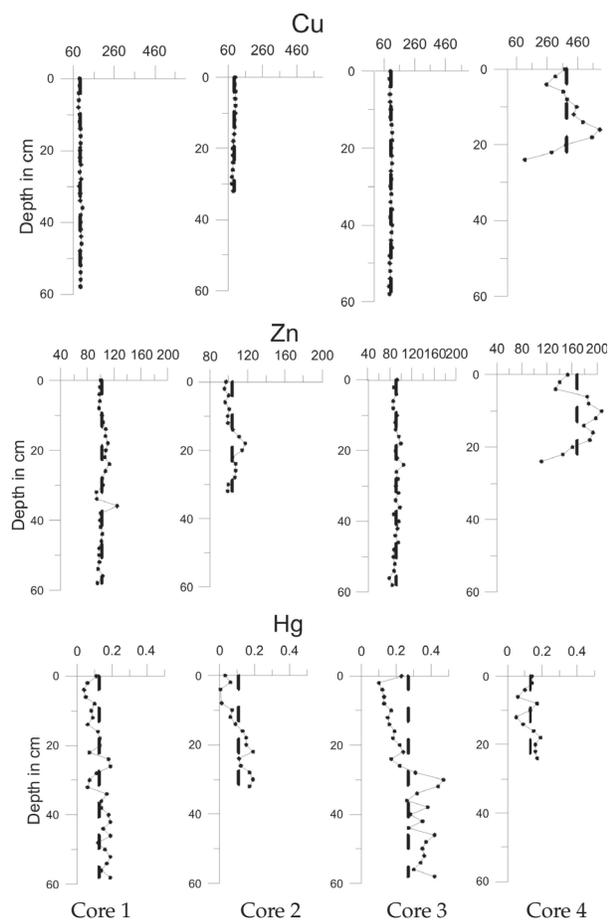


Fig. 5. Depth wise variation in Cu, Zn and Hg ( $\mu\text{g.g}^{-1}$ ) in sediments of Patalganga

Table 2. Pearson's correlation between different parameters (red colour indicates,  $p < 0.05$ ) in Core 2

	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg	Sand	Silt	Clay	TOC
Al	1.00												
Cr	-0.41	1.00											
Mn	-0.50	0.47	1.00										
Fe	0.62	-0.84	-0.47	1.00									
Co	-0.38	0.94	0.49	-0.76	1.00								
Ni	-0.38	0.93	0.54	-0.80	0.90	1.00							
Cu	0.41	-0.92	-0.27	0.83	-0.84	-0.82	1.00						
Zn	-0.21	0.43	0.16	-0.57	0.36	0.39	-0.49	1.00					
Hg	-0.23	-0.24	-0.15	0.19	-0.15	-0.29	0.25	-0.30	1.00				
Sand	0.39	-0.88	-0.44	0.75	-0.89	-0.83	0.84	-0.55	0.13	1.00			
Silt	0.43	-0.66	-0.49	0.77	-0.49	-0.61	0.61	-0.75	0.37	0.54	1.00		
Clay	-0.46	0.79	0.53	-0.84	0.66	0.75	-0.74	0.77	-0.33	-0.74	-0.97	1.00	
TOC	0.25	0.00	-0.43	0.26	0.08	-0.10	-0.09	-0.49	0.09	-0.07	0.63	-0.49	1.00

positively correlated with Cr, Mn, Co Ni & Zn and negatively correlated with Fe and Cu. In core3, negative correlation was found between sand and selected metals *viz.* Al, Cr, Fe, Co, Ni and Hg. Silt was negatively correlated with Cr, Fe, Co, Ni and Hg. Clay was positively correlated with the selected metals *viz.* Al, Cr, Fe, Co, Ni, and Hg. Whereas, Organic matter was negatively correlated with Cr, Co, Ni, Hg and Clay. Similarly, in core 4, sand was negatively correlated with Co, Cu and Zn. There was no significant correlation of any fraction of sediment with elements in this core indicating non-lithogenic concentration of these elements in this region.

Organic carbon showed significant negative correlation with Zn in core 2 and with Cr Co, Ni and Hg in core 4. There was no significant correlation of organic carbon in other cores and with other elements. Such behaviour indicates that source of organic carbon and metals are different in the entire area.

#### Enrichment factor (EF), Contamination factor (CF) and Geo-accumulation index ( $I_{geo}$ )

The results of enrichment factor (EF), contamination factor (CF) and Geo-accumulation index ( $I_{geo}$ ) index of core 1, core 2, core 3, and core 4 is presented in Table 5. The results depicted that the sediments of cores 1-3 have minimal enrichment, whereas the  $I_{geo}$  indicates uncontaminated sediment with respect to selected metals *viz.* Cr, Mn, Fe, Co, Ni, Cu, Zn, and Hg. The core 4 sediment showed minimal enrichment of selected metals *viz.* Cr, Mn, Fe, Co, Ni, Cu, Zn, and Hg. Whereas, moderate contamination of Cr, Co, and Cu were observed and other selected metals *viz.* Mn, Fe, Ni, Zn, and Hg showed no contamination in core 4. It was evident from results of contamination factor that the sediment of core 1 was moderately contaminated with Co, Cu, Zn and Hg. In core 2 sediment was moderately contaminated with Mn, Co, Cu, Zn and Hg. Similarly sediment of cores 3 was moderately

**Table 3.** Pearson's correlation between different parameters (red colour indicates,  $p < 0.05$ ) in Core 3.

	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg	Sand	Silt	Clay	TOC
Al	1.00												
Cr	0.46	1.00											
Mn	0.42	0.10	1.00										
Fe	0.85	0.57	0.52	1.00									
Co	0.71	0.76	0.41	0.71	1.00								
Ni	0.72	0.74	0.32	0.77	0.93	1.00							
Cu	0.54	0.57	0.26	0.68	0.72	0.75	1.00						
Zn	0.46	0.47	0.30	0.70	0.54	0.69	0.88	1.00					
Hg	0.32	0.62	0.09	0.19	0.45	0.43	-0.10	-0.12	1.00				
Sand	-0.41	-0.80	-0.07	-0.38	-0.53	-0.55	-0.14	-0.07	-0.77	1.00			
Silt	-0.35	-0.83	-0.10	-0.37	-0.58	-0.57	-0.26	-0.19	-0.77	0.84	1.00		
Clay	0.38	0.85	0.09	0.38	0.58	0.58	0.23	0.16	0.79	-0.91	-0.99	1.00	
TOC	-0.24	-0.76	0.06	-0.24	-0.45	-0.48	-0.12	-0.03	-0.78	0.89	0.83	-0.88	1.00

**Table 4.** Pearson's correlation between different parameters (red colour indicates,  $p < 0.05$ ) in Core 4.

	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg	Sand	Silt	Clay	TOC
Al	1.00												
Cr	-0.58	1.00											
Mn	0.06	0.26	1.00										
Fe	0.50	0.29	0.18	1.00									
Co	0.04	0.60	0.28	0.46	1.00								
Ni	-0.34	0.90	0.27	0.41	0.84	1.00							
Cu	0.08	0.42	0.14	0.27	0.89	0.65	1.00						
Zn	0.06	0.62	0.25	0.52	0.97	0.85	0.84	1.00					
Hg	-0.05	-0.12	0.07	-0.26	-0.12	-0.27	-0.04	-0.26	1.00				
Sand	-0.27	-0.32	-0.24	-0.32	-0.77	-0.52	-0.85	-0.70	-0.09	1.00			
Silt	0.14	0.10	0.49	0.20	0.11	0.22	0.05	0.25	-0.38	-0.16	1.00		
Clay	-0.13	-0.08	-0.48	-0.19	-0.08	-0.19	-0.01	-0.21	0.39	0.12	-1.00	1.00	
TOC	0.36	-0.10	0.42	0.30	-0.07	0.01	-0.11	0.08	-0.49	-0.07	0.90	-0.90	1.00

**Table 5.** Enrichment factor, Geoaccumulation Index, Contamination factor, degree of contamination and Pollution Load Index at Patalgangain different cores (S1, S2, S3, S4).

Metals		Core 1					
		Enrichment Factor		Geoaccumulation index		Contamination Factor	
Cr	1.21	Minimal	0.52	Uncontaminated	0.93	Low	
Mn	1.27	Minimal	-0.57	Uncontaminated	0.97	Low	
Fe	0.88	Minimal	-0.37	Uncontaminated	0.68	Low	
Co	1.33	Minimal	0.44	Uncontaminated	1.02	Moderate	
Ni	1.05	Minimal	-0.85	Uncontaminated	0.81	Low	
Cu	1.45	Minimal	0.48	Uncontaminated	1.12	Moderate	
Zn	1.47	Minimal	-0.48	Uncontaminated	1.13	Moderate	
Hg	1.63	Minimal	-2.38	Uncontaminated	1.26	Moderate	
		Degree of Contamination:	7.93	Very high Contamination			
		Pollution Load index:	1.00	indicates pollution			
Metals		Core 2					
		Enrichment factor		Geoaccumulation index		Contamination Factor	
Cr	0.86	minimal	0.35	uncontaminated	0.83	low	
Mn	1.03	minimal	-0.52	uncontaminated	1.00	moderate	
Fe	1.05	minimal	-0.04	uncontaminated	0.87	low	
Co	0.87	minimal	0.45	uncontaminated	1.02	moderate	
Ni	1.11	minimal	-0.81	uncontaminated	0.88	low	
Cu	0.86	minimal	0.43	uncontaminated	1.00	moderate	
Zn	1.18	minimal	-0.46	uncontaminated	1.15	moderate	
Hg	1.06	minimal	-2.97	uncontaminated	1.07	moderate	
		Degree of Contamination:	7.82	Very high Contamination			
		Pollution load Index:	1.00	indicates pollution			
Metals		Core 3					
		Enrichment Factor		Geoaccumulation index		Contamintion Factor	
Cr	0.68	minimal	0.15	uncontaminated	0.74	low	
Mn	0.91	minimal	-0.30	uncontaminated	1.00	moderate	
Fe	0.93	minimal	0.16	uncontaminated	1.02	moderate	
Co	0.92	minimal	0.42	uncontaminated	1.00	moderate	
Ni	0.76	minimal	-0.93	uncontaminated	0.82	low	
Cu	1.03	minimal	0.63	uncontaminated	1.12	moderate	
Zn	0.87	minimal	-0.65	uncontaminated	0.95	low	
Hg	2.46	moderate	-1.28	uncontaminated	2.68	moderate	
		Degree of Contamination:	9.33	Very High Contamination			
		Pollution Load index:	1.07	indicates Pollution			
Metal		Core 4					
		Enrichment factor		Geoaccumulation index		Contamintion Factor	
Cr	1.92	minimal	1.51	moderately contaminated	1.35	moderate	
Mn	1.61	minimal	0.06	uncontaminated	1.14	moderate	
Fe	1.09	minimal	-0.03	uncontaminated	0.78	low	
Co	1.47	minimal	1.65	moderately contaminated	1.04	moderate	
Ni	0.77	minimal	-0.04	uncontaminated	0.55	low	
Cu	0.89	minimal	2.42	moderately contaminated	0.63	low	
Zn	1.75	minimal	0.21	uncontaminated	1.24	moderate	
Hg	1.85	minimal	-2.29	uncontaminated	1.30	moderate	
		Degree of Contamination:	8.03	Very High Contamination			
		Pollution load Index:	1.00	indicates pollution			

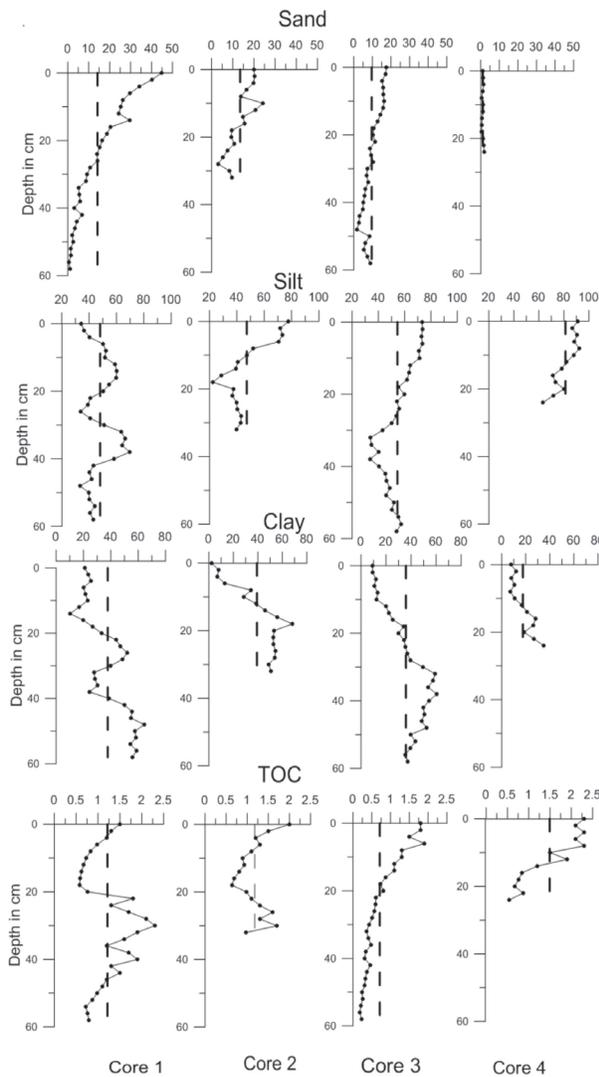


Fig. 6. Depth wise variation in Texture and Total Organic carbon (%) in sediments of Patalganga.

Table 6. Sediment components of Patalganga of all the Cores.

Variables	Core 1		Core 2		Core 3		Core4	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Al (%)	5.4	5–6.5	6.8	6.52–7.2	7.2	6.6–8.1	6.4	5.74–6.9
Cr (µg/g)	194.3	168.9–229	175.3	131–219	149.8	130.5–171.2	398.6	210.9–545.9
Mn (µg/g)	858.9	772.9–935	887.1	824–925	1042.0	824.2–1282	1340.8	1068–1699
Fe (%)	5.5	4.9–6.3	6.9	5.95–7.8	7.9	7.03–8.8	7.0	6.2–8.5
Co (µg/g)	38.8	34.41–44	38.9	35.4–42.5	38.1	33.9–48.9	93.8	44.82–126.8
Ni (µg/g)	56.6	49.89–63	90.9	79.01–101.2	53.5	48.3–64.3	100.2	68.04–117.4
Cu (µg/g)	94.0	84.67–104	58.3	53.7–63.5	104.4	93.6–114.5	385.5	115.2–601.2
Zn (µg/g)	102.1	93.39–124	103.5	95.5–117.6	91.1	79–104.6	167.8	111.5–207.2
Hg (µg/g)	0.1	0.04–0.19	0.1	0.01–0.2	0.3	0.1–0.5	0.1	0.05–0.2
Sand (%)	14.2	0.56–44.8	13.5	3.1–24.2	9.7	1.7–17.5	1.1	0.45–1.9
Silt (%)	48.1	33.4–69.7	47.2	22.4–77.6	54.5	33.7–73.6	81.3	63.2–92.3
Clay (%)	37.7	10.2–64.5	39.3	2.3–68.1	35.9	9.2–60.5	17.6	7.18–34.9
TOC (%)	1.2	0.58–2.3	1.2	0.64–2.0	0.7	0.18–1.9	1.5	0.54–2.3

contaminated with Mn, Fe, Co, Cu and Hg. In core 4 moderate contamination of Cr, Mn, Co, Zn and Hg was recorded. As it is evident from the result moderate contamination of Co and Hg is common in all the cores. Since, the Patalganga estuary receives effluent of chemical based industries in the Patalganga industrial zone such contamination are expected. The results of core sediments indicated that Hg was in higher concentration mostly in deeper sections and decreased towards surface regions. This is because the Hg based industries have been scrapped prior to year 2000 (Ram *et al.*, 2003; 2009).

### DISCUSSION

Human intervention of coastal cities all over the world have increased rapidly in recent years increasing the amount of contaminants introduced through rivers and estuaries (Ravichandran and Manickam, 2012). Alternately, the estuarine regions, the interface between terrestrial and marine environments, have become a repository of increased heavy metal input (Huang *et al.*, 2004; Unnikrishnan and Nair, 2004; Bianchi and Allison, 2009). Hence, the present study was designed to evaluate the status of heavy metal pollution in sediments of the Patalganga Estuary.

The role of organic matter and sediment grain size in relation to the accumulation of heavy metals in sediment has often been emphasised (Davies *et al.*, 1991). The significant correlations for most of the metals with organic carbon suggests that they have a common source and that these metals are introduced to the system attached to organic matter as organometal complexes (Brumsack, 2006).

However, in present study either there was no correlation or negative correlation between organic carbon and metals indicating that the source of organic matter and metals are different. Correlation of metals with clay fraction was also random, indicating no particular binding of metal with clay. In earlier study variation of Hg has been reported in the range of 0.05 -2.66 µg/g and the profiles of its variation indicated Patalganga Estuary that opens in the Amba Estuary is a major source of anthropogenic metal to the estuary, and enrichment factors support Hg contamination of the estuarine sediment to a varying degree (Balachandran *et al.*, 2005; Ram *et al.*, 2009). However, in the present study, the concentration of Hg is much lower compare to earlier data. Such decrease in the concentration of Hg is due restriction of Hg based industries (Fig. 4). Variation in Fe and Mn concentrations in different section of the core is an indication of oxic and suboxic interface (Santschi *et al.*, 1990). In steady state condition, metals in oxygenated water get bound to Fe-Mn oxyhydroxides and precipitated to the bottom sediment. Down the depth in the sediment, reduction of Fe-Mn oxyhydroxides takes place, thus releasing the bound elements. With diagenetic processes taking place in the sediment, free elements in anoxic sediment move upward and reprecipitate in oxic zone, thus there concentration increase at oxidation-reduction boundary. However, in the anthropogenically disturbed area, variation of metals in sediment depends upon their source and time of accumulation. The present study represents the area influenced by anthropogenic activities; hence, irregular distribution of metals was recorded in almost all the cores. Thus, the industrial effluents discharged through rivers may be responsible for the heavy metal accumulation in sediments (Lu and Chen, 1977).

According to Sundarayat *et al.* (2011) for Cu, organic matter is a major scavenger, as reflected in the high organic accumulation in polluted river sediments. Zhai *et al.* suggested that agrochemical (especially phosphorite fertilizers) and domestic wastes are the major source of Cu (Zhai *et al.*, 2003). Ayyamperumal *et al.* reported moderate levels of pollution due to heavy metals (Cr, Cu, Ni, Co, Pb, Zn and Cd) released from anthropogenic activities (Ayyamperumal *et al.*, 2006). Moderate enrichment of Cu in core 4 sediment could be due to the industrial effluent from Patalganga industrial zone in the region (CSIR-NIO, 2019).

Unique distribution pattern of heavy minerals

(Cr, Cu, Fe, Mn, Co, Ni and Zn) indicates that the major source of these metals to Patalganga estuarine sediment is the prevalent anthropogenic activities. A reduction in the concentrations of some metals down core could be due to their scavenging by Fe and Mn oxyhydroxides and re-deposition as metal sulphides at different sources (Prohic and Kniewald, 1987).

Very high concentration of Cr (210.9-545.9 µg/g) in sediment of core 4 is indicative of anthropogenic source, mainly industrial in the region. Vertical profiles of Cu, Ni and Co infer a moderate removal in the suboxic layer. The pattern of distribution of Ni and Co are similar to that of Fe and Mn, suggesting that they are also cycled along with Fe-Mn oxides in the redox boundaries and get precipitated along with iron sulphides (Klinkhammer, 1980). An enrichment of Cr, Co and Cu especially in core 4 is indicative of anthropogenic input of these elements (Alagarsamy, 2006). A relatively high enrichment of Zn in middle portion of S4 compared to other locations indicated an elevated level of pollution in this location caused by sewage and industrial wastes.

## CONCLUSION

This preliminary study on the status and distribution pattern of heavy metals in the Patalganga Estuary reveals the following information:

Low to moderate contamination of selected metals viz. Cr, Mn, Fe, Co, Ni, Cu, Zn and Hg was observed in all the selected cores. Clay and Al showed significant positive correlation between with Cr, Mn, Fe, Co, Ni, Cu, Zn and Hg indicating anthropogenic origin of these elements. There was either negative correlation or no correlation between organic carbon and heavy metal, indicating different sources of these elements. Down core profiles depicted that the main source of heavy metals in to Patalganga estuary was anthropogenic activities. Cores 1, 2 and 3 have a combination of metal-metal and metal-sediment (it may be either clay, silt or sand). But the fourth core is different, as it shows no correlation with sand, silt, clay or organic carbon. This is the reason why we have relative contamination in Core 4. It can be concluded that all 3 locations from the coast to the (Core 1, core 2 and core 3) estuary have normal distribution of metals owing to their geochemical normalization. However, S4 (core 4) located upstream is a hotspot

as it is very close to industrial discharge point. Due to the continuous discharge of effluents, geochemical normalization does not take place. Instead, these locations are increasingly favouring inorganic precipitation of metals, which may easily become bioavailable. This study provides a complete database on distribution of metals and its pollution indices. It may be a baseline for future studies.

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**Data Availability:** All data generated or analysed during this study are included in this manuscript

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