

## **Behaviour Of Trace Metals In The Anoxic Environment Of Veraval Harbour, India**

**Divya Majithiya, Ajay Yadav, Anirudh Ram\***

Regional Centre, CSIR-National Institute of Oceanography, Mumbai, India

\*Corresponding author:e-mail: anirudhram@nio.org

Phone No.: +912226359605,Fax No.:+912226364627

### **Abstract**

The purpose of the present study is to investigate the behaviour of trace metals in anoxic environment. Water column of the harbour was found to be anoxic ( $\text{DO} < 0.2 \text{ mg l}^{-1}$ ) with high concentration of  $\text{NH}_4^+\text{-N}$  (av.  $459 \pm 21 \text{ } \mu\text{mol l}^{-1}$ ) and  $\text{H}_2\text{S}$  (av.  $73 \pm 2.5 \text{ } \mu\text{mol l}^{-1}$ ) irrespective of season and tide. High concentrations of Fe, Mn in bottom water indicated that Fe, Mn were diagenetically mobilized under the anoxic conditions prevailing in the harbour. In harbour sediments significant correlation of metals with TOC and TS indicated their diagenetic immobilization in anoxic environment. Fe was positively correlated with TS suggesting FeS formation in anoxic condition. TOC/TN ratio of sediments was higher ( $16 \pm 5.2$ ) than the normal marine planktonic sediments suggesting an increased burden of terrestrial carbon in the harbour. A sediment core collected 10 km away from the shore indicated build-up of trace metals in recent years, showing diagenetically upward movement of metals.

**Keywords:** trace metals, anoxic environment, diagenesis, C/N ratio

## 1. Introduction

Due to advective impact, diagenetically mobilized elements travel to the surface of the sediment and in the presence of oxygen get oxidised and again precipitate, giving rise to their higher concentrations in the surficial sediments (Berner, 1980). However, when overlying water is anoxic, the reduced elements may escape to the water column and remain in dissolved form, giving rise to their higher concentrations in the overlying waters (Berner, 1980; Sakata, 1985; Lukawska-Matuszewska and Kielczewska, 2016). Substantial amount of work have been published on the behaviour of trace metals in surficial sediment as well as in core sediment beneath the oxic waters (Yuan et al., 2012; Gang Xu et al., 2015; Ming et al., 2016). However, there is scarce work done on the sediment metal chemistry in the water body, which remains anoxic for all 365 days. Fishing harbours are widely distributed in coastlines of several countries. Fishing harbours also contain a special water area with high density of human activities, and thus the wastewater and oil, solid and house garbage from the fishing boats/ships are discharged into the harbours (Iduk and Samson, 2015). Harbours are also the recipients of contaminants from ship traffic, loading, repairs and dredging as well as rain water runoff, effluent discharge, dust, etc. (Schiff, 1997; Joksas et al., 2003; Garcia and Gomez, 2005). In addition, most are built in semi-enclosed coastal regions which are likely to decrease the seawater exchange ability (Owen and Sandhu 2000; Dassenakis et al., 2003; Aly et al., 2013). As a result, the contaminants can dramatically increase in the harbour sediment (Lin et al., 2009; Xu et al., 2012). Out of these contaminants, pollution by trace metals in coastal environment has become a global phenomenon because of its toxicity, persistence for several decades in the environment, bioaccumulation and biomagnifications in the food chain (Chinnaraja et al., 2011).

Sediments function as a sink for metals in aquatic ecosystems; they also act as a source of metals when environmental conditions change (pH, Eh, redox, humic acids) (Guo et al., 1997; Burton, 2002; Woods et al., 2012; Chapman et al., 2013). Mn, Fe and Al play a crucial role in the removal of metal ions from sea water as well as their behaviour in sediments. The oxyhydroxides of Mn and Fe have a high adsorption capacity and large surface area and can adsorb cations such as  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  (Forstner, 1979; Williams et al., 1994; Schulz and Zabel, 2005; Gasparatos, 2012).

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 (Middelburg and Levin, 2009; Chakraborty et al., 2016). Three types of processes namely oxic diagenesis, suboxic diagenesis and anoxic diagenesis occur in sediments. When dissolved oxygen

(DO) is present in the sediment porewaters, oxic diagenesis takes place and Mn concentrations in the pore waters remains extremely low (about  $2 \mu\text{g l}^{-1}$ ). When DO in porewater depletes to very low level, suboxic diagenesis dominates with a reduction of  $\text{NO}_3^-$ -N followed by reduction of Fe and Mn oxyhydroxides. When this occurs, the concentration of dissolved Mn increases by several orders of magnitude ( $>1000 \mu\text{g l}^{-1}$ ) compared to the ocean bottom water (about  $0.2 \mu\text{g l}^{-1}$ ) (Schulz and Zabel, 2005). In the sediment of oxic water, at a depth where oxygen diminishes, Fe and Mn oxyhydroxides are reduced to Fe (II) and Mn (II) ions and get dissolved in porewater along with other metals bound to Fe and Mn oxyhydroxides (Wijsman et al., 2001; Konovalov et al., 2007; Middelburg and Levin, 2009). Fe and Mn however, can migrate under redox gradients in sediments (Forstner, 1979; Soetaert et al., 2002). These metal ions migrate upward through the porewater 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).

In the present work, dissolved oxygen (DO), biochemical oxygen demand (BOD), ammonia ( $\text{NH}_4^+$ -N), inorganic phosphate ( $\text{PO}_4^{3-}$ -P), hydrogen sulphide ( $\text{H}_2\text{S}$ ) and dissolved metals such as Fe, Mn, Cr, Co, Ni, Cu, Zn, Cd, Hg, Pb were studied in overlying water to understand their variability and control on geochemistry of sediment in anoxic condition of the harbour. Sediment cores from polluted harbour as well as relatively clean offshore region were studied to find diagenetic behaviour of trace metals in different environment. Hence, the present study is a unique attempt to understand geochemical behaviour of trace metals in the sediment of Veraval harbour, the area where water remains anoxic throughout the year (NIO, 2014; 2015). The present work also helps in understanding the role of Fe, Mn, C, and S in vertical mobilization of toxic trace metals in anoxic waters. The ecological risk assessment of trace metal accumulation in sediments of Veraval Harbour was carried out by Sundararajan et al., 2017 which showed the contamination levels of surface sediments of the harbour during the year 2006. In the present research, effort has been made to find the depth wise variation of trace metals and their behaviour with elements such as C, N and S in sediment core of Veraval harbour, which remains anoxic throughout the year (NIO, 2014; 2015).

## **2. Materials and Methods**

### **2.1 Study area**

Veraval, located ( $20^\circ 53' \text{ N } 70^\circ 26' \text{ E}$ ) on north-west coast of India (Fig. 1), is home to many textiles, chemicals and food processing industries and is the largest fishing harbour in Asia. The maximum temperature in the Veraval region varies between  $30$  and  $39^\circ\text{C}$ . Being the coastal area, the humidity will not be below  $55\%$ . The annual rainfall in the area is around  $729 \text{ mm}$ . The maximum

rainfall occurs during July-August and tapers off by the end of November. The winds are light to moderate with some increase in speed during southwest monsoon season. The main activities at Veraval include fish processing and export that provides significant economic source to its residents.

The harbour receives around 20,000 m<sup>3</sup> d<sup>-1</sup> of anthropogenic waste from fish processing industries and about 24,000 m<sup>3</sup> d<sup>-1</sup> of sewage from Veraval City (CPCB, 2009-10). The harbour has the stagnant water condition, due to siltation at the mouth, lack of turbulence, wind action and tidal effect in and around the jetty because of the abrupt designing of it, making dilution an impossible task for tides coming towards the jetty. Due to fishing industries as well as domestic effluent discharge, and poor flushing, build-up of organic load has taken such an extent that Veraval harbour water has become anoxic giving rise to the high NH<sub>4</sub><sup>+</sup>-N (>1000 μmol l<sup>-1</sup>) concentration (NIO, 2014; 2015). Current direction of Veraval is parallel to the coast, hence water of Veraval harbour moves along the coast during low tide. Thus immediate rise of nutrient concentration in the water of Veraval is not noticed. As expected, the pH of coastal water varies in a narrow range (7.9 - 8.2) though lower values (7.3-7.8) are recorded in Veraval harbour due to environmental stress associated with the release of effluents from various sources in the harbour basin (NIO, 2014; 2015).

## 2.2 Sampling and analyses

For the present study, the samples were collected from three locations as shown in Fig. 2, during postmonsoon season of the year 2013. Overlying bottom water samples were collected using Niskin water sampler for the analysis of DO, BOD, NH<sub>4</sub><sup>+</sup>-N, PO<sub>4</sub><sup>3-</sup>-P, H<sub>2</sub>S and dissolved metals. Two sediment cores (core 1 & 2) were collected from Veraval harbour using hand operated corer (OD 6.5 cm and ID 5.5 cm). A core (Core 3) of 63 cm length was collected using a gravity corer at the water depth of 30 m from a distance of 10 km off Veraval. Soon after the collection, sediment cores were sectioned at 1 cm interval with the help of a plastic knife. The subsamples were sealed in clean plastic bags, labelled, and kept in the ice box. Subsamples were then oven-dried at 60°C, powdered and homogenized with the help of an agate mortar and pestle.

Analysis of DO, NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P was performed by using methods given by Grasshoff et al., (1983). BOD was analyzed by seeded method (APHA, 2005) with 3 days incubation at 27°C. H<sub>2</sub>S was analyzed by methylene blue method (Cline, 1969). Sample collected for dissolved metals were filtered through acid washed membrane paper (pore size 0.45 μm), pre-concentrated following solvent extraction method (Bruland et al., 1979) and analyzed using Graphite Furnace AAS (AAAnalyst 600, Perkin Elmer). Hg was analysed by cold vapour generation technique on Flow Injection Mercury System (FIMS-400, Perkin Elmer) coupled with gold amalgamation system for

on-line pre-concentration following method of Bloom and Cerecelius (1983). Certified standard reference seawater (NASS-6) was analyzed along with each set of dissolved metal following same procedure as that of sample. Analytical precision (checked with international reference standard NASS-6) was better than 5%.

Dried and powdered sediment subsamples were digested following Loring & Rantala (1992) method using concentrated HF, HClO<sub>4</sub>, HCl and HNO<sub>3</sub> added sequentially. All the chemicals and acids used were of Suprapur grade (Merck, Germany). After digestion, samples were diluted to constant volume with Milli-Q water and stored in acid cleaned plastic bottles for metal analysis. Metal analysis was performed immediately on the resultant digests using ICP-OES (Optima 7300DV, Perkin Elmer) for Fe, Mn, Cr, Co, Ni, Cu and Zn and Graphite furnace AAS (AAAnalyst 600, Perkin Elmer) for Pb and Cd. For Hg analysis (US EPA, 1979) sediments were digested with aqua regia followed by oxidization with KMnO<sub>4</sub>. The oxidized samples were decolourised with hydroxyl ammonium chloride and further reduced using alkaline sodium borohydride. Analysis of Hg was carried out using cold vapour generation technique on Flow Injection Mercury System (FIMS-400, Perkin Elmer) coupled with amalgamation system for on-line pre-concentration.

All metal concentrations in sediment were expressed in  $\mu\text{g g}^{-1}$  on a dry-weight basis. Dried and powdered sediments were directly used without any pre-treatment for total carbon (TC), total inorganic carbon (TIC), total nitrogen (TN) and total sulphur (TS) analysis using CHNS analyzer (Vario EL CUBE, Elementar) with TIC kit. Total organic carbon (TOC) was calculated as the difference between TC and TIC. TOC, TIC, TN and TS concentrations were expressed in %.

Standard Reference Materials (SRM) of sediment; (PACS-2) and (MESS-3), obtained from the National Research Council, Canada were analysed along with each set of sediments to ascertain the analytical accuracy. MAG-1 was used to validate the analysis of TC, TN and TS. All samples were run (in triplicate) in batches, that included known standards, reagent blanks, and SRM digested and processed same as samples. The precision/accuracy was better than  $\pm 5\%$  for all metals. Statistical analyses were carried out using the STATISTICA 7.0 software (Statsoft 1999).

### **2.3 Normalization of metals**

In order to account for geochemical variations, normalization by a conservative element is carried out, as geochemical normalization can compensate for both the granulometric and mineralogical variability of metal concentration in sediments (Liu et al., 2003). Consequently, in order to assess the possible anthropogenic impact, several authors (Datta and Subramanian, 1998; Ram et al., 2003; Badr et al., 2009; Milacic et al., 2010) have successfully used Al to normalize the

metal contaminants. In this study, we have also used Al as a conservative element to differentiate natural from anthropogenic components as Al is abundant in the earth's crust and is scarcely influenced by anthropogenic inputs (Ram et al., 2003).

Due to industrial and anthropogenic inputs, it is difficult to get background values for the metal concentrations. In some instances, researchers use shale value as background value (Gibbs, 1993; Rubio et al., 2000). However, concentration of some elements is reportedly high in shale samples (Gibbs, 1993; Rubio et al., 2000). Hence, the most appropriate method to use local background values found in the bottom sections of sediment cores, which represent pre-industrialised values (Angelidis & Aloupi, 1995). In the present study, the background values for studied metals were obtained by averaging concentrations of metals of last 5 cm of 63 cm core collected about 10 km away from the shore at water depth of 30 m. Background concentrations were: Al: 5.3 %; Cr: 54  $\mu\text{g g}^{-1}$ ; Mn: 638  $\mu\text{g g}^{-1}$ ; Fe: 6.2 %; Co: 30  $\mu\text{g g}^{-1}$ ; Ni: 25  $\mu\text{g g}^{-1}$ ; Cu: 53  $\mu\text{g g}^{-1}$ ; Zn: 71  $\mu\text{g g}^{-1}$ ; Cd: 0.2  $\mu\text{g g}^{-1}$ ; Pb: 12.5  $\mu\text{g g}^{-1}$ ; Hg: 0.1  $\mu\text{g g}^{-1}$ .

### Enrichment Factor

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 & Chesselet (1979); Kumar & Edward (2009).

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

Five contamination categories are recognized on the basis of the enrichment factor (Sutherland, 2000; 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        |

## Index of Geoaccumulation

The index of geoaccumulation ( $I_{geo}$ ) was computed using equation (Muller, 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 in the earth's crust. The constant 1.5 is used to compensate for possible variations with respect to background due to lithogenic variations. Practically uncontaminated sediments show Index of geoaccumulation less than 0. Six classes of geoaccumulation index (Muller, 1979; Kumar and Edward, 2009) have been distinguished.

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

## Contamination Factor

The assessment of metal contamination was also carried out using the contamination factor (CF).

$$CF = C_{\text{metal}} / C_{\text{background}}$$

Where  $C_{\text{metal}}$ , is mean concentration of metal in sediment and  $C_{\text{background}}$ , is background concentrations. The classifications (Szefer, 1998) according to CF results are as follows:

| Contamination Factor | Classification |
|----------------------|----------------|
| $CF < 1$             | Low            |
| $1 \leq CF < 3$      | Moderate       |
| $3 \leq CF < 6$      | Considerable   |
| $CF \geq 6$          | Very high      |

The degree of contamination (DC) of one determined area is the sum of all CFs:  $DC = \sum CF$ .

The areas are classified according to DC as follows:

| Degree of Contamination | Classification |
|-------------------------|----------------|
| DC<1                    | Low            |
| 1≤DC<3                  | Moderate       |
| 3≤DC<6                  | Considerable   |
| DC≥6                    | Very high      |

### Pollution Load Index (PLI)

The pollution level of trace metal was calculated by the method based on pollution load index (Nair et al., 1993).

$$CF = C_{\text{metal}} / C_{\text{background}}$$

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

Where, CF = Contamination factor; n = number of metals; C<sub>metal</sub> = metal contamination in polluted sediment; C<sub>background</sub> = background value of that metal.

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.

## 3. Results and Discussion

### 3.1 Water Quality

Water quality (Table 1) of the Veraval Harbour (Station 1 and 2) was found to be considerably degraded with low DO (<0.2 mg l<sup>-1</sup>) irrespective of tide and season. Anoxic oxidation of organic material resulted in elevated concentration of NH<sub>4</sub><sup>+</sup>-N (459±21 μmol l<sup>-1</sup>), PO<sub>4</sub><sup>3-</sup>-P (16.9±8.4 μmol l<sup>-1</sup>), H<sub>2</sub>S (53.5±29 μmol l<sup>-1</sup>) and BOD (158.4±30 mg l<sup>-1</sup>). The high values of NH<sub>4</sub><sup>+</sup>-N, PO<sub>4</sub><sup>3-</sup>-P and BOD were associated with the anthropogenic discharges like sewage, waste from fishing crafts, fish processing industries and poor flushing of the harbour water. In the anoxic conditions, the decomposition of organic matter by microbial sulphate reduction leads to the production of H<sub>2</sub>S (Lukawska-Matuszewska and Kielczewska, 2016). This justifies the high levels of H<sub>2</sub>S present in the water column of the Veraval harbour. Part of the H<sub>2</sub>S generated then may react with iron and organic matter and may be buried as FeS (Lukawska-Matuszewska and Kielczewska, 2016) and organosulphur compounds (Ferdelman et al., 1991; Bruchert, 1998; Werne et al., 2008). Concentration of dissolved Fe and Mn were found to be 41±0.4 μg.l<sup>-1</sup> and 40.9 ±0.7 μg.l<sup>-1</sup> respectively. These concentrations are higher than that reported for eastern Arabian Sea by George



(2005). However, concentrations of Cu ( $1.70 \pm 0.68 \mu\text{g.l}^{-1}$ ), Cd ( $0.15 \pm 0.1 \mu\text{g.l}^{-1}$ ), Pb ( $1.2 \pm 0.80 \mu\text{g.l}^{-1}$ ), Cr ( $0.2 \pm 0.14 \mu\text{g.l}^{-1}$ ), Ni ( $0.7 \pm 0.55 \mu\text{g.l}^{-1}$ ), Zn ( $24 \pm 2.5 \mu\text{g.l}^{-1}$ ), and Hg ( $0.2 \pm 0.01 \mu\text{g.l}^{-1}$ ) were lower than that reported in northern Indian Ocean by Sengupta and Qasim (2001). Co was below detection limit ( $<0.1 \mu\text{g.l}^{-1}$ ). Such results indicate diagenetic immobilization of these metals in anoxic sediment, which are associated with carbon and sulfides (Ram et al., 2009; Holmström et al., 1999 and Müller et al., 2002).

### 3.2 Sediment Quality

Depth wise variation of heavy metal concentrations, TOC, TIC, TN and TS at station 1 and 2 are shown along with the background values in Fig. 3. It clearly indicates that in harbour sediments, Al, Mn, Fe and Co are well below the background concentrations whereas Cr, Ni, Cu, Zn, Cd, Pb and Hg were found to be in higher concentrations than the background concentrations with intermittent irregularities throughout the length of sediment cores collected from harbour. These values suggest the impact of anthropogenic load on the sediment of Veraval harbour. To confirm this, various indices (Table 2) were calculated. Core sediments at station 1 showed extremely high enrichment of Cd (EF= $171 \pm 51$ ), followed by significant enrichment of Cr (EF= $7.86 \pm 1.5$ ), Hg (EF= $5.7 \pm 1.5$ ) and Pb (EF= $5.9 \pm 0.8$ ) and moderate enrichment of Ni (EF= $4.45 \pm 0.09$ ), Zn (EF= $4.5 \pm 0.7$ ) and Cu (EF= $2.8 \pm 0.5$ ). However at station 2, Cd and Cr were significantly enriched (EF= $8.8 \pm 3.2$  and  $5.43 \pm 0.18$  respectively), Ni and Pb were moderately enriched (EF= $3.39 \pm 0.07$  and  $3.0 \pm 0.8$  respectively) whereas enrichment of Hg, Zn and Cu were minimum (EF= $1.5 \pm 0.8$ ;  $1.0 \pm 0.1$  and  $0.7 \pm 0.2$  respectively). Similar trend of degree of contamination in the order of Cd>Cr>Pb>Hg>Zn>Ni>Cu>Co was observed from the Geoaccumulation index (Table 2). Considering the metals including Cr, Cd, Pb, Hg, Cu and Zn, Contamination factor (CF), Degree of Contamination (DC) and Pollution load Index (PLI) were calculated which are presented in Table 2. The study area showed very high degree of contamination with very high Pollution load Index.

To understand the relationships between the studied parameters and hence the geochemistry in the anoxic water, Pearson's correlation coefficients were calculated and the results are presented in Table 3(a) and 3(b). It is clearly evident from Table 3(a) and 3(b) that Cd, Pb, Hg, Cr, Co, Ni, Cu and Zn had significant positive correlation with TOC, TS and Fe suggesting that these metals are controlled by iron and organo-sulfur compounds. TIC was negatively correlated with all the studied elements except Mn, suggesting that it has no role in mobilization of trace metals during diagenesis (Jara-Marini et al., 2013). Factor analysis was carried out for the same data set. Two factors, accounting for 89.8% of cumulative percentage, were identified as controlling factors for geochemistry of trace metals with organic carbon, nitrogen and sulphur. Factor 1 accounted for

70.3% of total variance with an Eigen value of 7.7 and indicated significant positive loadings of Cu, Cr, Co, Ni, Cd, Hg, Pb along with TOC and TN. Factor 2 accounted for 19.5% of total variance with an Eigen value of 2.1. Positive loadings are found with Al, Fe, Zn and TS. The same relations were observed in the cluster analysis (Fig. 4) where Hg, Cd, Pb and Cu were associated with TOC and TN whereas Zn was associated with TS, Fe and Al.

### **3.3 Geochemical behaviour of metals**

At station 1 and 2, Mn showed increase in concentration with the increase in depth. This may perhaps be due to increase in organic pollutant loads that lowered the dissolved oxygen content of water decreasing flocculation intensity of MnO from the water column. Under reducing conditions prevailing in the harbour, the precipitated manganese oxides are reduced and mobilized as Mn (II). The reduced manganese diffuses upwards through interstitial water. As redox boundary is missing in the harbour sediment, the mobilized manganese escapes in the water column instead of precipitating at the water sediment interface, increasing the concentration of dissolved manganese in overlying water. In the anoxic conditions, reduction of Fe also takes place. However Fe showed significant positive correlation with TS suggesting that Fe might be re-precipitated as FeS (Berner, 1980; Lukawska-Matuszewska and Kielczewska, 2016). Cr, Co, Ni, Cd, Pb, Hg, Cu and Zn were positively correlated to TOC and TS suggesting that these metals were bound to organosulphur compounds. These organosulphur bound metals were immobilised in the sediments and were not found in dissolved forms. These metals also showed positive correlation with Fe and TS suggesting their relation with Fe and TS which indirectly confirms the presence of Fe in the sediments as FeS and not Fe-Mn oxyhydroxides (Astrom, 1998; Kumar and Edward, 2009).

Depth wise variation (Fig. 5) of all the parameters including trace metals, TOC, TIC, TN and TS were studied at station 3. Fig. 5 clearly indicates the systematic increase of Mn, Fe, Co, Ni, Cu, Zn and Pb with Fe and Mn in the upper 20 cm of the core. The significant positive correlation (Table 4) was observed between the above mentioned metal concentrations with Fe and Mn. It indicates that these metals are diagenetically mobilised along the redox gradient and settled in the first 20 cm section of the core (Kumar and Edward, 2009). These metals were also correlated with Al indicating their association with the finer fraction of the sediments (Alagarsamy and Zhang, 2010).

### **3.4 TOC/TN and TOC/TS ratio**

At station 1, the variability of TOC, TN and TS content along the sediment profile was irregular. The TOC: TN ratio in the analyzed sediments ranged from 10.3 to 16.5 whereas TOC: TS

ratio ranged from 3.1 to 5.8. The irregularities observed at station 1 were due to the disturbances caused by the fishing trawlers.

At station 2, TOC and TN content gradually decreased with increasing sediment depth (Fig. 3). At the same time, an increase in the molar ratio of TOC:TN along the sediment profile was noted (Fig. 3). In contrast to TOC and TN, content of TS increased with increasing sediment depth (Fig. 3). Increasing TS concentration was accompanied by a decreasing molar ratio of TOC to TS (TOC:TS) (Fig. 3). The TOC:TS ratio in all analyzed sediment samples at station 2 ranged from 1.9-3.2. TS concentration in sediments mainly depends on sulfide formation and its removal via re-oxidation during diagenesis. In the case of sediments located in the harbour, where the oxygen deficit or anoxic conditions prevail all year long, high TS concentrations results most likely from the organic matter sulfurization and sulfide formation in the entire sediment core (Lukawska-Matuszewska and Kielczewska, 2016).

TOC/TN ratios have been widely used to distinguish between the algal and land plant origins of sedimentary organic matter in lacustrine or coastal environments (Hatcher et al., 1982; Prahl et al., 1994; Yamamuro, 2000; Goni et al., 2003; Smittenberg et al., 2004; Xiao et al., 2008; Zhu et al., 2009; Tue et al., 2011). Fresh organic matter from aquatic algae, which are protein-rich and cellulose-poor, commonly have molar TOC/TN values between 4 and 10, whereas vascular land plants, which are protein-poor and cellulose-rich, usually create organic matter with TOC/TN ratios of 20 and greater (Meyers, 1994). The proportions of sediment organic matter that originate from these two general sources can consequently be distinguished by their characteristic TOC/TN ratios. Researchers generally conclude the following for TOC/TN ratios of sediment organic matter: 1) TOC/TN ratios ranging from 4 to 10 indicate that most of the organic matter in lacustrine or coastal sediment comes from aquatic phytoplankton; 2) TOC/TN ratios with values of 20 and greater imply that land plants provide essentially all of the organic content in the sediment; and 3) TOC/TN ratios varying from 10 to 20 suggest that lacustrine or coastal organic matter results from a mixture of aquatic and land plants, but is dominated by vegetation with terrestrial origins (Meyers, 1994). TOC/TN ratio of the harbour sediments varied from 10.3 to 29.8 with an average of  $16 \pm 5.2$  which indicated that the organic matter in the harbour sediments were influenced by terrestrial organic matter.

#### **4. Conclusion**

Water of Veraval Harbour remains anoxic irrespective of season and tide. Release of sewage and waste from fish processing industries and poor flushing are the main reasons for the anoxic

condition of the harbour. TOC: TN ratios suggest the source of terrestrial input of organic matter into the harbour. In the prevailing anoxic condition of Veraval harbour reduction of  $\text{SO}_4^{2-}$  has resulted in release of  $\text{H}_2\text{S}$ . Trace metals such as Cr, Co, Ni, Cu, Zn, Cd, Pb and Hg are controlled by organic carbon and organosulphur compounds in the sediment of present study. During diagenetic processes in the harbour sediment cores, reduction of Fe (III) and Mn (IV) occurs due to anoxic condition, which leads to formation of Fe (II) and Mn (II) that cross sediment-water boundary, increasing their concentration in overlying water. Metals released during this diagenesis escape to sediment-water interface due to prevailing anoxic condition, get adsorbed to the floating organosulphur moieties and settle down to the sediment surface. The elevated concentrations of metals recorded in the surficial sediment of a core, collected 10 km away from the shore were due to early diagenetic processes and resettling of metals to the surficial sediments along with Fe-Mn oxyhydroxides formed in the oxic overlying water.

### **Acknowledgement**

The authors are thankful to the Director, CSIR-National Institute of Oceanography and Scientist-in-Charge, Regional Centre, CSIR-National Institute of Oceanography, Mumbai, for providing the facility to carry out the work. We express our gratitude towards the Ministry of Earth Sciences (MoES) for providing financial support to carry the present study.

### **References**

- Alagarsamy R. and Zhang J., Geochemical characterization of major and trace elements in the coastal sediments of India. *Environmental Monitoring and Assessment*, February 2010, Volume 161, Issue 1–4, pp 161–176
- Aly, W., Williams, I.D. & Hudson, M.D. Metal contamination in water, sediment and biota from a semi-enclosed coastal area. *Environ Monit Assess* (2013) 185: 3879. doi:10.1007/s10661-012-2837-0
- Angelidis, M.O. & Aloupi, M. (1995). Metals in sediments of Rhodes Harbour, Greece. *Marine Pollution Bulletin*, Vol. 31, pp. 273-276.
- APHA (2005) Standard methods for the examination of water and waste water (21<sup>st</sup> edition) Washington, DC; American public Health Association
- Astrom M, Partitioning of transition metals in oxidised and reduced zones of sulphide-bearing fine-grained sediments. *Appl Geochem*, 5 (1998) 607-617.
- Badr N B E, El-Fiky A A, Mostafa AR, Al-Mur B A (2009). Metal pollution records in core sediments of some Red Sea coastal areas, Kingdom of Saudi Arabia. *Environ. Monit. Assess.* 155: 509-526.

- Berner, R.A. 1980. Early diagenesis - A theoretical approach. Princeton University Press, Princeton N.J. 241.
- Bloom, N.S., Crecelius, E.A., 1983. Determination of mercury in seawater at sub- nanogram per liter levels. *Marine Chemistry* 14, 49–59.
- Brannon, J. M. and Patrick, W. H. Jr. 1987. Fixation, transformation and mobilization of arsenic in sediments. *Environment Science & Technology*. 21: 450 - 459.
- Bruchert, V.: Early diagenesis of sulfur in estuarine sediments: The role of sedimentary humic and fulvic acids, *Geochim. Cosmo chim. Ac.*, 62, 1567–1586, 1998
- Bruland K. W., Franks R. P., Knauer G. A. and Martin J.H.. Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water, *analytica chimica acta*, 105 (1979) 233-245
- Buat-Menard, P., Chesselet, R., 1979. Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth Planet. Sci. Lett.* 42, 398–411.
- Burton, J.G.A., 2002. Sediment quality criteria in use around the world. *Limnology* 3, 65–76
- Chakraborty P., Mason R. P., Jayachandran S., Vudamala K., Armoury K., Sarkar A., Chakraborty S., Bardhan P., Naik R., 2016. Effects of bottom water oxygen concentrations on mercury distribution and speciation in sediments below the oxygen minimum zone of the Arabian Sea. *Mar. Chem.*: 186; 2016; 24-32.
- Chakravarty, I. M. and Patgiri, A. D. (2009). Metal Pollution Assessment in Sediments of the Dikrong River, N.E. India. *J Hum Ecol*, 27(1):63-67
- Chapman, P.M., Wang, F., Caeiro, S.S., 2013. Assessing and managing sediment contamination in transitional waters. *Environ. Int.* 55, 71–91
- Chinnaraja V1, Santhanam1 P, Balaji prasath B.1, Dinesh kumar S.1 and Jothiraj K., 2011. An Investigation on Heavy Metals Accumulation in Water, Sediment and Small Marine Food Chain (Plankton and Fish) from Coromandel Coast, Southeast Coast of India. *Indian Journal Of Natural Sciences*, Vol 2 (8) Oct-2011
- Cline J. D. (1969) Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14, 454-458
- CPCB (2009-10). Status of water supply, wastewater generation and treatment in class I cities and class II towns of India. Control of urban pollution series: CUPS/70/2009-10
- Dassenakis, M., Andrianos, H., Depiazi, G., Konstantas, A., Karabela, M., Sakellari, A., et al. (2003). The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece. *Applied Geochemistry*, 18(6), 781–794.
- Datta D K and Subramanian V (1998). Distribution and fractionation of heavy metals in the surface sediments of the Ganges-Brahmaputra-Meghna river system in the Bengal basin. *Environ. Geol.*, 36(1-2): 93-101.

- Ferdelman, T. G., Church, T. M., and Luther, G. W.: Sulfur enrichment of humic-substances in a Delaware saltmarsh sediment core, *Geochim. Cosmochim. Ac.*, 55, 979–988, 1991.
- Fernex, F.E. Span, D., Flatau, G.N. and Renard, D. 1984. Behaviour of some metals in surficial sediments of Northwest Mediterranean Continental Shelf. In: Sly P. G. (eds), *Sediment and water interactions*. Springer Verlag Pub., 353–370.
- Forstner U. 1979a. Chapter D: Metal pollution assessment from sediment analysis. In: *Metal pollution in the aquatic environment*, (Forstner U. and Wittmann G.T. eds), Springer-Verlag, Berlin Heidelberg, New York, 197-269.
- Gang Xu a,b,†, Jian Liu Shaofeng Pei Xianghuai Kong Gang Hu Distribution and source of heavy metals in the surface sediments from the near-shore area, north Jiangsu Province, China *Marine Pollution Bulletin* 83 (2014) 275–281
- Gasparatos D., 2012. Fe–Mn Concretions and Nodules to Sequester Heavy Metals in Soils. *Environmental Chemistry for a Sustainable World: Volume 2: Remediation of Air and Water Pollution*, DOI 10.1007/978-94-007-2439-6\_11
- George, Rejo Mon. Biogeochemistry of trace metals in the Indian EEZ of the Arabian Sea and Bay of Bengal. Diss. National Institute of Oceanography, 2005.
- Gibbs, R. J. (1993). Metals of the bottom muds in townsville harbour, Australia. *Environmental pollution* 81, 297-300.
- Goni M.A., Teixeira M.J., Perkey, D.W., 2003. Sources and distribution of organicmatter in a river-dominated estuary (Winyah Bay, SC, USA). *Estuar. Coast. Shelf Sci.* 57, 1023–1048.
- Grasshoff, K., Ehrhardt, M., Kremling, K., 1983. *Methods of Seawater Analysis*. Second revised and extended. Weinheim' Verlag Chemie.
- Guerra-Garcia J.M., Garcia-Gomez J.C. Assessing pollution levels in sediments of a harbour with two opposing entrances. *Environmental implications*. *J. Environ. Manage.* 77, 1, 2005.
- Guo, T.Z., DeLaune, R.D., Patrick, W.H., 1997. The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in estuarine sediment. *Environ. Int.* 23, 305–316
- Harikumar P. S., Nasir U. P and Mujeebu Rahma M. P. Distribution of heavy metals in the core sediments of a tropical wetland system, *International Journal. Environmental Science Technology*, Vol. 6, No. 2, 2009, pp.225-232
- Hatcher, P.G., Simoneit, B.R., Mackenzie, F.T., Neumann, A.C., Thorstenson, D.C., Gerchakov, S.M., 1982. Organic geochemistry and pore water chemistry of sediments from Mangrove Lake, Bermuda. *Org. Geochem.* 4, 93–112.
- Holmström H., Ljungberg J., Ekström M., Öhlander B. (1999) Secondary copper enrichment in tailings at the Laver min, northern Sweden. *Environ. Geol.* 38, 327 – 342.
- Iduk U. and Samson N. (2015) Effects and Solutions of Marine Pollution from Ships in Nigerian Waterways. *International Journal of Scientific & Engineering Research*, Volume 6, Issue 9, September-2015

- Jara-Marini M. E.; Tapia-Alcaraz J. N.; Dumer-Gutiérrez J. A.; García-Rico L.; García-Hernández J. and Páez-Osuna F., 2013. Comparative bioaccumulation of trace metals using six filter feeder organisms in a coastal lagoon ecosystem (of the central-east Gulf of California). *Environ Monit Assess* (2013) 185:1071–1085. DOI 10.1007/s10661-012-2615-z
- Jokšas K., Galkus A., Stakenienė R. The Only Lithuanian Seaport and its Environment. Institute of Geology and Geography: Vilnius, pp. 314, 2003.
- Katarzyna Lukawska-Matuszewska, Joanna Kielczewska. Effects of near-bottom water oxygen concentration on biogeochemical cycling of C, N and S in sediments of the Gulf of Gdansk (southern Baltic, Continental Shelf). *Research* 117(2016)30–42
- Konovalov, S. K., Luther, G. W., and Yucel, M.: Porewater redox species and processes in the Black Sea sediments, *Chem. Geol.*, 245, 254–274, 2007.
- Kumar, S.P., Edward, P., 2009. Assessment of metal concentration in the sediment cores of Manakudi estuary, south west coast of India. *Indian J. Mar. Sci.* 38 (2), 235–248.
- Lin, T., Hu, Z.H., Zhang, G., Li, X.D., Xu, W.H., Tang, J.H., Li, J., 2009. Levels and Mass Burden of DDTs in Sediments from Fishing Harbors: The Importance of DDT-Containing Antifouling Paint to the Coastal Environment of China. *Environ. Sci. Technol.* 43(21), 8033–8038
- Liu, W. X., Li, X. D., Shen, Z. G., Wang, D. C., Wai, O. W. H., & Li, Y. S. (2003). Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environmental Pollution*, 121, 377–388.
- Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth Sci. Rev.* 32, 235–283.
- Loska K, Wiechula D & Korus I, Metal contamination of farming soils affected by industry. *Environmental International*, 30 (2004) 159-165.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* 114, 289–302.
- Middelburg J. J. and Levin L. A., 2009. Coastal hypoxia and sediment biogeochemistry. *Biogeosciences*, 6, 1273–1293, 2009
- Milacic R, Scancar J, Murko S, Kocman D, Horvat M (2010). A complex investigation of the extent of pollution in sediments of the Sava River. Part 1: Selected elements. *Environ. Monit. Assess.*, 163: 263-275.
- Ming L., Dejiang F., Yongjie L., Bin C., Zuosheng Y. (2016). Heavy metals in surficial sediments of the central Bohai Sea: their distribution, speciation and sources. *Acta Oceanol. Sin.*, 2016, 35 (9) 98–110. DOI: 10.1007/s13131-016-0926-6
- Müller B., Axelsson M.D., Öhlander, B. (2002) Adsorption of trace elements on pyrite surfaces in sulfidic mine tailings from Kristineberg (Sweden) a few years after remediation. *Sci. Tot. Environ.* 298, 1–16.
- Muller G, Die Schwermetallbelastung der sedimenten des Neckars and Seiner. Nebenflusse. *Chemiker – Zeitung*, 6 (1981) 157-164.

- Muller G, Schwermetalle in den sedimenten des Rheins –Veränderungen Seit. 1971. Umschau, 79 (1979) 778-783.
- Nair C K, Balachand A N & Jacob Chacko, Sediment Characteristics in relation to changing hydrography of Cochin estuary. Indian J Mar Sci, 22 (1993) 33-36.
- NIO, 2014. Report on Monitoring of Environmental Quality off Veraval (2014).
- NIO, 2015. Report on Monitoring of Environmental Quality off Veraval (2015).
- Owen, R., & Sandhu, N. (2000). Heavy metal accumulation and anthropogenic impacts on Tolo Harbour, Hong Kong. Marine Pollution Bulletin, 40(2), 174–180.
- Prahl, F.G., Ertel, J.R., Goñi, M.A., Sparrow, M.A., Eversmeyer, B., 1994. Terrestrial organic carbon contributions to sediments on the Washington margin. Geochim. Cosmochim. Acta 58, 3035–3048.
- Ram A., Rokade M. A., Zingade M. D., (2003). Mercury in sediments of Ulhas estuary. Mar. Pollut. Bull. 46, 846-857.
- Ram, A., Rokade, M.A., Zingde, M.D., Borole, D.V., 2009. Post-depositional memory record of mercury in sediment near the effluent disposal site of a chlor-alkali plant in Thane Creek-Mumbai Harbour, India. Environ. Technol. 30 (8), 765–783.
- Rubio B., Nombela M. A. and Vilas F., 2000. Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): An assessment of metal pollution. Mar. Pollut. Bull. 40 (11), 968-980 (2000)
- Sakata M. Diagenetic remobilization of manganese, Iron. Copper and lead in anoxic sediment of a freshwater pond. Water Res. Vol. 19. No. 8, pp. 1033-1038. 1985
- Schiff K., Review of existing stormwater monitoring programs for estimating bight-wide mass emissions from urban runoff. In: S. Weisberg, C. Francisco, & D. Hallock (Eds.) Southern California coastal water research project annual report 1995-1996, Westminster, CA, pp. 44-55, 1997.
- Schulz H. D. and Zabel M., 2005. Marine geochemistry, second revised updated and extended edition, Springer-Verlag, 2005
- Sengupta R. and Qasim, S.Z., 2001. Chapter 8. Health of the Indian Ocean. In: The Indian Ocean-a perspective. Volume 1 Ed: R. Sengupta and Ehrlich Desa. 327-371.
- Smittenberg, R.H., Pancost, R.D., Hopmans, E.C., Paetzel, M., Sinninghe Damsté, J.S., 2004. A 400-year record of environmental change in an euxinic fjord as revealed by the sedimentary biomarker record. Palaeogeogr. Palaeoclimatol. Palaeoecol. 202, 331–351.
- Soetaert, K., Middelburg, J., Wijsman, J., Herman, P. and Heip, C. 2002. Ocean margin early diagenetic processes and models. In: Wefer G., Billett, D.
- Sundararajan S., Khadanga M.K., Kumar J., Raghuraman S., Vijaya R., Basanta Kumar Jena, 2017. Ecological risk assessment of trace metal accumulation in sediments of Veraval Harbor, Gujarat, Arabian Sea. Marine Pollution Bulletin 114 (2017) 592–601



- Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream Oahu, Hawaii. *Environ. Geol.* 39, 611–627.
- Szefer P, Glasby G P, Kusak A, Szefer K, Jankowska H, Wolowicz M & Ali A A, Evaluation of anthropogenic flux of metallic pollutants into Puck Bay, Southern Baltic. *Appl Geochem*, 13 (1998) 293-304.
- Tue, N.T., Hamaoka, H., Sogabe, A., Quy, T.D., Nhuan, M.T., Omori, K., 2011. The application of  $\delta^{13}\text{C}$  and C/N ratios as indicators of organic carbon sources and paleoenvironmental change of the mangrove ecosystem from Ba Lat Estuary, Red River, Vietnam. *Environ. Earth Sci.* 64, 1475–1486.
- US EPA, 1979. Methods for chemical analysis of water and wastes. EPA – 600/4-79-020, 294 pp.
- Werne, J. P., Lyons, T. W., Hollander, D. J., Schouten, S., Hopmans, E. C., and Damste, J. S. S.: Investigating pathways of diagenetic organic matter sulfurization using compound-specific sulfur isotope analysis. *Geochim. Cosmochim. Ac.*, 72, 3489–3502, 2008.
- Wijsman, J. W. M., Middelburg, J. J., and Heip, C. H. R.: Reactive iron in Black Sea Sediments: implications for iron cycling, *Mar. Geol.*, 172, 167–180, 2001.
- Williams T.P., Bubb J.M. and Lester J.N. 1994. Metal accumulation within marsh environments; a review. *Marine Pollution Bulletin.* 28: 277-290.
- Woods, A.M., Lloyd, J.M., Zong, Y.Q., Brodie, C.R., 2012. Spatial mapping of Pearl River Estuary surface sediment geochemistry: influence of data analysis on environmental interpretation. *Estuar. Coast. Shelf Sci.* 115, 218–233
- Xiao, J.L., Si, B., Zhai, D.Y., Itoh, S., Lomtatidze, Z., 2008. Hydrology of Dali lake in centraleastern Inner Mongolia and Holocene East Asian monsoon variability. *J. Paleolimnol.* 40, 519–528.
- Xu Weihai, Tian Lin, Zhaohui Hu & Wen Yan (2012) Environmental exposure and ecological risk of heavy metals in fishing harbors of the Pearl River Delta, South China, *Aquatic Ecosystem Health & Management*, 15:2, 192-199
- Yamamuro, M., 2000. Chemical tracers of sediment organic matter origins in two coastal lagoons. *J. Mar. Syst.* 26, 127–134.
- Yuan, H., Song, J., Li, X., Li, N., Duan, L., 2012. Distribution and contamination of heavy metals in surface sediments of the South Yellow Sea. *Mar. Pollut. Bull.* 64, 2151–2159.
- Zhu, L.P., Zhen, X.L., Wang, J.B., Lü, H.Y., Xie, M.P., Kitagawa, H., Possnert, G., 2009. A ~30,000-year record of environmental changes inferred from Lake Chen Co, Southern Tibet. *J. Paleolimnol.* 42, 343–358.

**Legend to figures:**

Fig. 1: Map showing study area

Fig. 2: Sampling locations

Fig. 3: Depth wise variations in trace metals ( $\mu\text{g g}^{-1}$ , except Al and Fe, which are in %), TOC, TIC, TN, TS, TOC: TN and TOC: TS in sediments of Veraval harbour

Fig. 4: Diagrammatic representation of results obtained by Hierarchical Cluster Analysis (dendrogram) that shows relationships among various trace elements, TOC, TN and TS within the study area

Fig. 5: Depth wise variations in trace metals ( $\mu\text{g g}^{-1}$ , except Al and Fe, which are in %), TOC, TIC, TN, TS, TOC: TN and TOC: TS in sediments at station 3

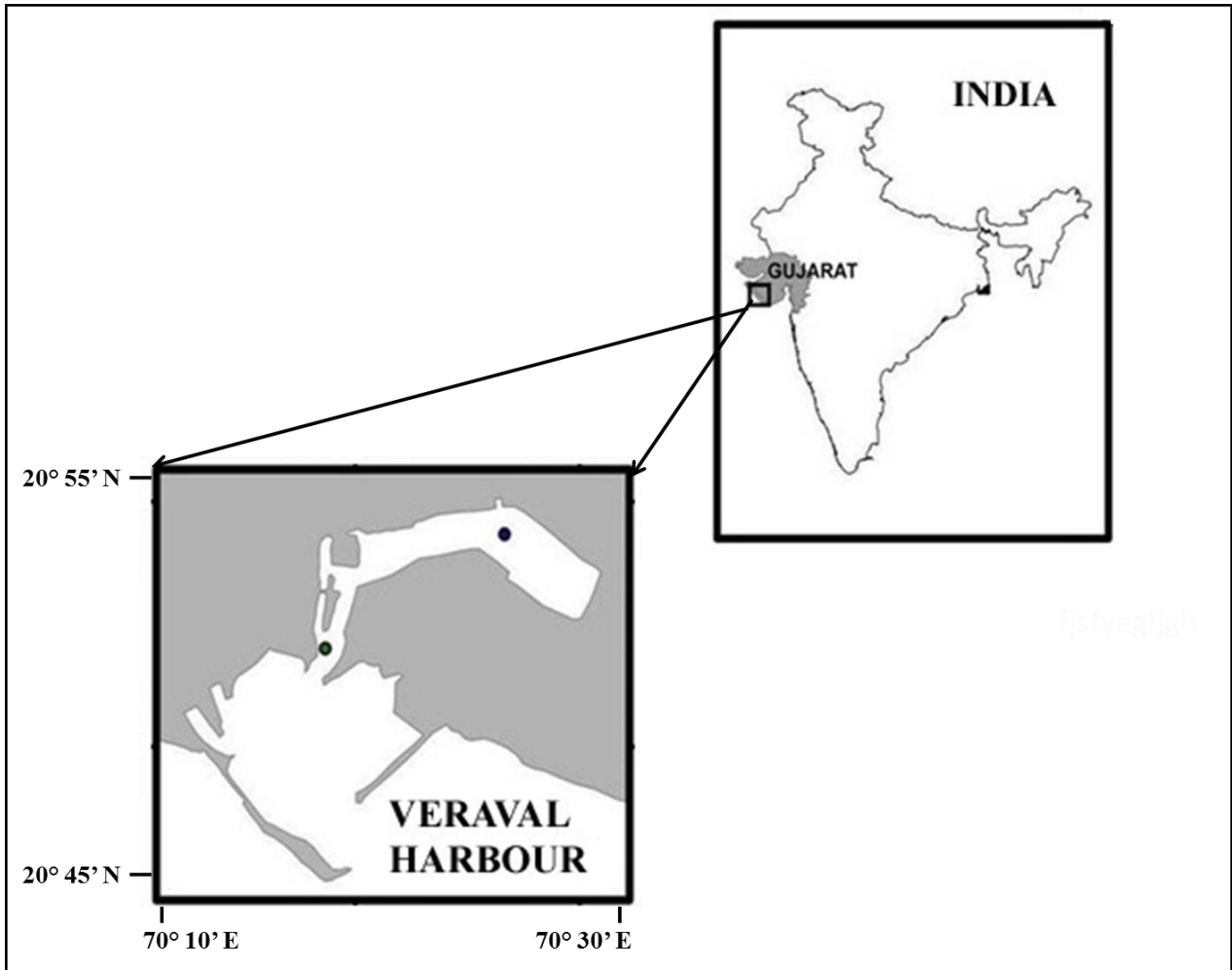
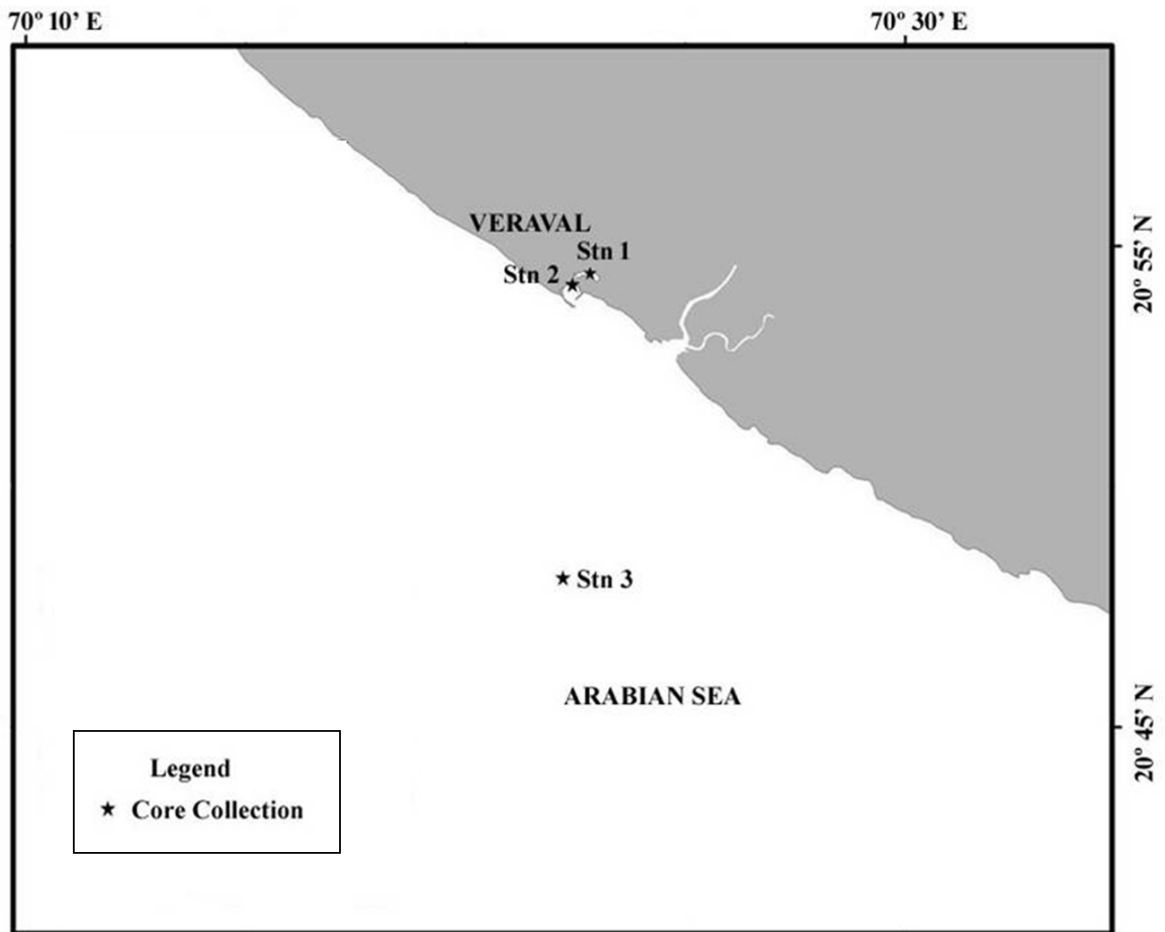


Fig. 1



**Fig. 2**

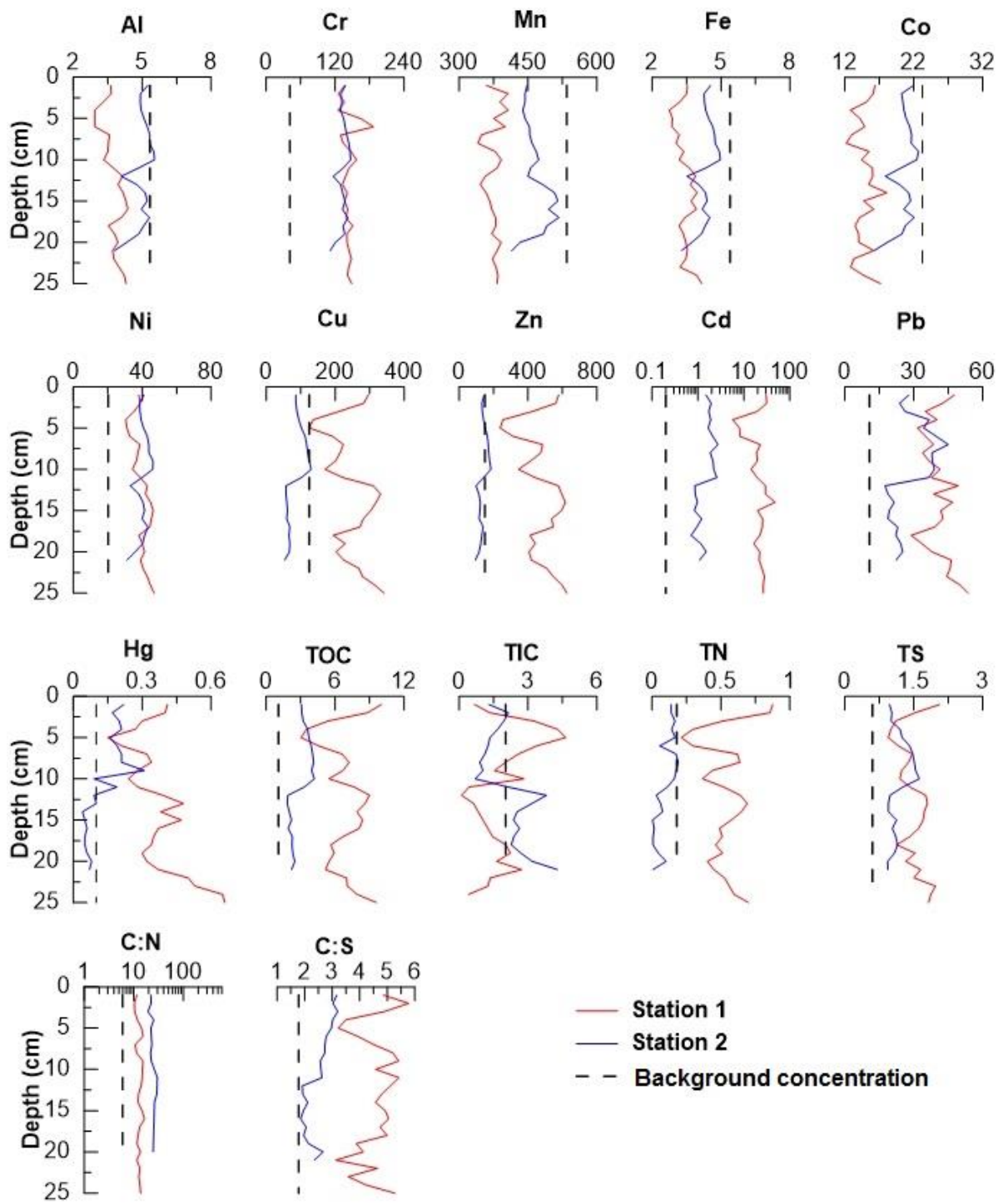


Fig. 3

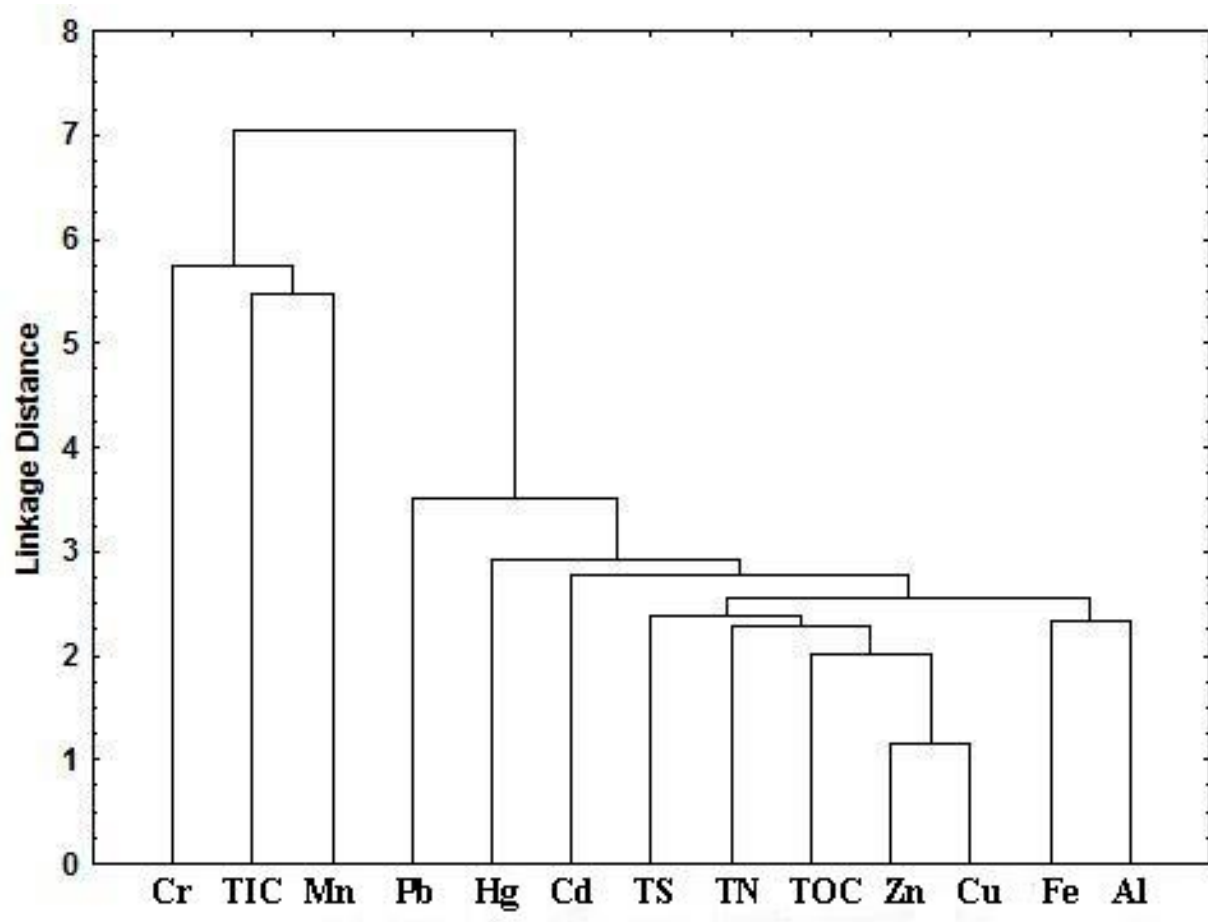
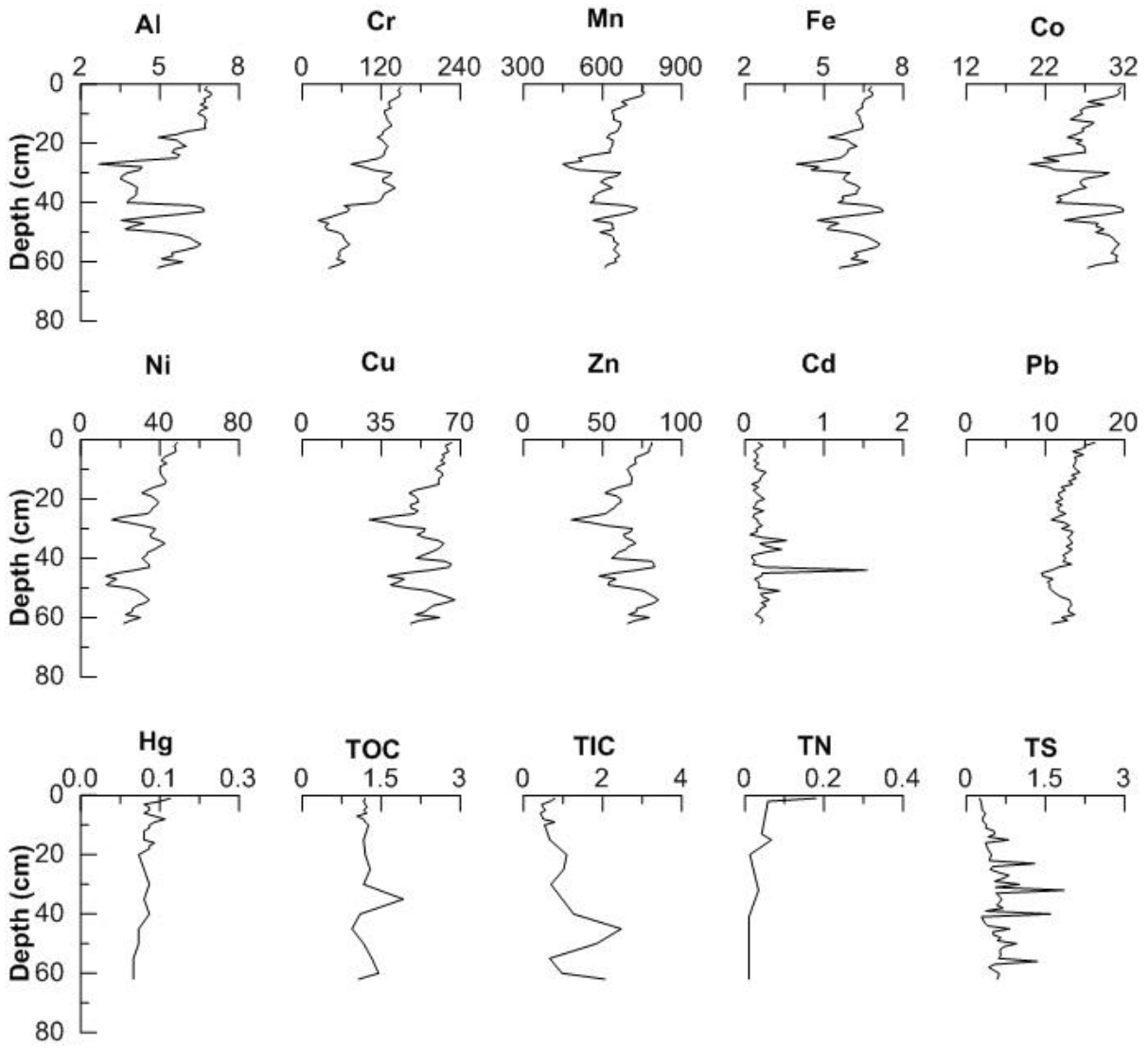


Fig. 4



**Fig. 5**

**Table 1: Water quality of Veraval Harbour**

| <b>Parameter</b>                                       | <b>Concentration</b> | <b>Unit</b>          |
|--|----------------------|----------------------|
| Dissolved Oxygen (DO)                                  | <0.2                 | mg l <sup>-1</sup>   |
| Biochemical Oxygen Demand (BOD)                        | 158.4±30             | mg l <sup>-1</sup>   |
| Ammonia Nitrogen (NH <sub>4</sub> <sup>+</sup> -N)     | 459±21               | µmol l <sup>-1</sup> |
| Inorganic Phosphate (PO <sub>4</sub> <sup>3-</sup> -P) | 16.9±8.4             | µmol l <sup>-1</sup> |
| Hydrogen Sulphide (H <sub>2</sub> S)                   | 53.5±29              | µmol l <sup>-1</sup> |
| Iron (Fe)  | 41±0.4               | µg l <sup>-1</sup>   |
| Manganese (Mn)   | 40.9±0.7             | µg l <sup>-1</sup>   |
| Cobalt (Co)  | BDL*                 | µg l <sup>-1</sup>   |
| Chromium (Cr)  | 0.2±0.14             | µg l <sup>-1</sup>   |
| Nickel (Ni)  | 0.7±0.55             | µg l <sup>-1</sup>   |
| Copper (Cu)  | 1.7±0.68             | µg l <sup>-1</sup>   |
| *BDL: Below Detection limit (0.1 µg l <sup>-1</sup> )  |                      |                      |
| Zinc (Zn)  | 24±2.5               | µg l <sup>-1</sup>   |
| Cadmium (Cd)   | 0.15±0.1             | µg l <sup>-1</sup>   |
| Lead (Pb)  | 1.2±0.8              | µg l <sup>-1</sup>   |
| Mercury (Hg)   | 0.2±0.01             | µg l <sup>-1</sup>   |

\*Below detection limit (0.1)



**Table 2: Enrichment Factor, Geoaccumulation Index, Contamination Factor, Degree of Contamination and Pollution Load Index at Veraval Harbour**

| Metals                        | Station 1         |                |                       |                |                      |                              | Station 2         |             |                       |                |                      |              |
|-------------------------------|-------------------|----------------|-----------------------|----------------|----------------------|------------------------------|-------------------|-------------|-----------------------|----------------|----------------------|--------------|
|                               | Enrichment factor |                | Geoaccumulation Index |                | Contamination Factor |                              | Enrichment factor |             | Geoaccumulation Index |                | Contamination Factor |              |
| Cr                            | 7.9               | Significant    | 1.2                   | Moderate       | 3.5                  | Considerable                 | 5.4               | Significant | 1.1                   | Moderate       | 3.5                  | Considerable |
| Co                            | 0.9               | Minimal        | -1.2                  | Uncontaminated | 0.7                  | Low                          | 1.0               | Minimal     | -0.7                  | Uncontaminated | 0.6                  | Low          |
| Ni                            | 2.8               | Moderate       | 0.4                   | Uncontaminated | 1.9                  | Moderate                     | 2.1               | Moderate    | 0.4                   | Uncontaminated | 2.0                  | Moderate     |
| Cu                            | 2.8               | Moderate       | 0.4                   | Uncontaminated | 1.9                  | Moderate                     | 0.7               | Minimal     | -1.2                  | Uncontaminated | 0.7                  | Low          |
| Zn                            | 4.5               | Moderate       | 1.0                   | Moderate       | 3.2                  | Considerable                 | 1.0               | Minimal     | -0.7                  | Uncontaminated | 0.9                  | Low          |
| Cd                            | 171               | Extremely High | 6.1                   | Extremely High | 113                  | Very High                    | 8.8               | Significant | 2.3                   | Moderate       | 7.7                  | Very High    |
| Pb                            | 5.9               | Significant    | 1.3                   | Moderate       | 3.8                  | Considerable                 | 3.0               | Moderate    | 0.8                   | Uncontaminated | 2.7                  | Moderate     |
| Hg                            | 5.7               | Significant    | 1.2                   | Moderate       | 3.7                  | Considerable                 | 1.5               | Minimal     | -0.5                  | Uncontaminated | 1.3                  | Moderate     |
| Degree of Contamination : 132 |                   |                |                       |                |                      | Degree of Contamination : 19 |                   |             |                       |                |                      |              |
| Very high contamination       |                   |                |                       |                |                      | Very high contamination      |                   |             |                       |                |                      |              |
| Pollution Load Index: 5675    |                   |                |                       |                |                      | Pollution Load Index: 9.2    |                   |             |                       |                |                      |              |
| Indicates Pollution           |                   |                |                       |                |                      | Indicates Pollution          |                   |             |                       |                |                      |              |

**Table 3 (a): Correlation matrices for studied elements (a: p<0.01; b: p<0.05) at Station 1**

| Element | Al                       | Cr                       | Mn                       | Fe                       | Co                       | Ni                       | Cu                       | Zn                       | Cd                       | Pb                       | Hg                       | TOC                      | TIC                      | TN                      | TS |
|---------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|----|
| Al      | 1                        |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Cr      | -0.35                    | 1                        |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Mn      | -0.36                    | 0.27                     | 1                        |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Fe      | <b>0.89<sup>a</sup></b>  | -0.25                    | -0.26                    | 1                        |                          |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Co      | 0.39                     | 0.05                     | 0.01                     | <b>0.71<sup>a</sup></b>  | 1                        |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Ni      | <b>0.99<sup>a</sup></b>  | -0.30                    | -0.35                    | <b>0.86<sup>a</sup></b>  | 0.36                     | 1                        |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Cu      | <b>0.85<sup>a</sup></b>  | -0.32                    | -0.39                    | <b>0.85<sup>a</sup></b>  | <b>0.52<sup>a</sup></b>  | <b>0.87<sup>a</sup></b>  | 1                        |                          |                          |                          |                          |                          |                          |                         |    |
| Zn      | <b>0.86<sup>a</sup></b>  | <b>-0.44<sup>b</sup></b> | <b>-0.46<sup>b</sup></b> | <b>0.82<sup>a</sup></b>  | <b>0.43<sup>b</sup></b>  | <b>0.88<sup>a</sup></b>  | <b>0.97<sup>a</sup></b>  | 1                        |                          |                          |                          |                          |                          |                         |    |
| Cd      | <b>0.70<sup>a</sup></b>  | -0.39                    | <b>-0.40<sup>b</sup></b> | <b>0.72<sup>a</sup></b>  | <b>0.54<sup>a</sup></b>  | <b>0.71<sup>a</sup></b>  | <b>0.80<sup>a</sup></b>  | <b>0.84<sup>a</sup></b>  | 1                        |                          |                          |                          |                          |                         |    |
| Pb      | <b>0.59<sup>a</sup></b>  | -0.21                    | -0.03                    | <b>0.71<sup>a</sup></b>  | <b>0.51<sup>a</sup></b>  | <b>0.57<sup>a</sup></b>  | <b>0.70<sup>a</sup></b>  | <b>0.64<sup>a</sup></b>  | <b>0.55<sup>a</sup></b>  | 1                        |                          |                          |                          |                         |    |
| Hg      | <b>0.72<sup>a</sup></b>  | -0.30                    | -0.17                    | <b>0.68<sup>a</sup></b>  | 0.20                     | <b>0.75<sup>a</sup></b>  | <b>0.82<sup>a</sup></b>  | <b>0.80<sup>a</sup></b>  | <b>0.56<sup>a</sup></b>  | <b>0.72<sup>a</sup></b>  | 1                        |                          |                          |                         |    |
| TOC     | <b>0.73<sup>a</sup></b>  | -0.40                    | <b>-0.43<sup>b</sup></b> | <b>0.78<sup>a</sup></b>  | <b>0.51<sup>a</sup></b>  | <b>0.72<sup>a</sup></b>  | <b>0.89<sup>a</sup></b>  | <b>0.92<sup>a</sup></b>  | <b>0.73<sup>a</sup></b>  | <b>0.62<sup>a</sup></b>  | <b>0.69<sup>a</sup></b>  | 1                        |                          |                         |    |
| TIC     | <b>-0.87<sup>a</sup></b> | 0.31                     | <b>0.38<sup>b</sup></b>  | <b>-0.85<sup>a</sup></b> | <b>-0.46<sup>b</sup></b> | <b>-0.84<sup>a</sup></b> | <b>-0.86<sup>a</sup></b> | <b>-0.88<sup>a</sup></b> | <b>-0.73<sup>a</sup></b> | <b>-0.56<sup>a</sup></b> | <b>-0.68<sup>a</sup></b> | <b>-0.91<sup>a</sup></b> | 1                        |                         |    |
| TN      | <b>0.53<sup>a</sup></b>  | <b>-0.57<sup>a</sup></b> | <b>-0.42<sup>b</sup></b> | <b>0.57<sup>a</sup></b>  | <b>0.38<sup>b</sup></b>  | <b>0.54<sup>a</sup></b>  | <b>0.79<sup>a</sup></b>  | <b>0.84<sup>a</sup></b>  | <b>0.74<sup>a</sup></b>  | <b>0.50<sup>b</sup></b>  | <b>0.61<sup>a</sup></b>  | <b>0.89<sup>a</sup></b>  | <b>-0.70<sup>a</sup></b> | 1                       |    |
| TS      | <b>0.76<sup>a</sup></b>  | -0.32                    | <b>-0.42<sup>b</sup></b> | <b>0.72<sup>a</sup></b>  | <b>0.40<sup>b</sup></b>  | <b>0.75<sup>a</sup></b>  | <b>0.88<sup>a</sup></b>  | <b>0.86<sup>a</sup></b>  | <b>0.71<sup>a</sup></b>  | <b>0.74<sup>a</sup></b>  | <b>0.78<sup>a</sup></b>  | <b>0.82<sup>a</sup></b>  | <b>-0.79<sup>a</sup></b> | <b>0.75<sup>a</sup></b> | 1  |

**Table 3 (b): Correlation matrices for studied elements (a: p<0.01; b: p<0.05) at Station 2**

| Element | Al                       | Cr                      | Mn    | Fe                       | Co                      | Ni                       | Cu                       | Zn                       | Cd                       | Pb                       | Hg                       | TOC                      | TIC                      | TN                      | TS |
|---------|--------------------------|-------------------------|-------|--------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|----|
| Al      | 1                        |                         |       |                          |                         |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Cr      | <b>0.96<sup>a</sup></b>  | 1                       |       |                          |                         |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Mn      | 0.36                     | 0.33                    | 1     |                          |                         |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Fe      | <b>0.97<sup>a</sup></b>  | <b>0.98<sup>a</sup></b> | 0.23  | 1                        |                         |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Co      | <b>0.99<sup>a</sup></b>  | <b>0.94<sup>a</sup></b> | 0.38  | <b>0.95<sup>a</sup></b>  | 1                       |                          |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Ni      | <b>0.94<sup>a</sup></b>  | <b>0.97<sup>a</sup></b> | 0.33  | <b>0.97<sup>a</sup></b>  | <b>0.91<sup>a</sup></b> | 1                        |                          |                          |                          |                          |                          |                          |                          |                         |    |
| Cu      | <b>0.73<sup>a</sup></b>  | <b>0.82<sup>a</sup></b> | -0.17 | <b>0.86<sup>a</sup></b>  | <b>0.67<sup>b</sup></b> | <b>0.84<sup>a</sup></b>  | 1                        |                          |                          |                          |                          |                          |                          |                         |    |
| Zn      | <b>0.86<sup>a</sup></b>  | <b>0.92<sup>a</sup></b> | 0.01  | <b>0.95<sup>a</sup></b>  | <b>0.81<sup>a</sup></b> | <b>0.94<sup>a</sup></b>  | <b>0.97<sup>a</sup></b>  | 1                        |                          |                          |                          |                          |                          |                         |    |
| Cd      | 0.37                     | 0.44                    | -0.37 | 0.52                     | 0.30                    | 0.49                     | <b>0.79<sup>a</sup></b>  | <b>0.66<sup>b</sup></b>  | 1                        |                          |                          |                          |                          |                         |    |
| Pb      | <b>0.59<sup>b</sup></b>  | <b>0.65<sup>b</sup></b> | -0.22 | <b>0.72<sup>a</sup></b>  | 0.53                    | <b>0.72<sup>a</sup></b>  | <b>0.90<sup>a</sup></b>  | <b>0.86<sup>a</sup></b>  | <b>0.85<sup>a</sup></b>  | 1                        |                          |                          |                          |                         |    |
| Hg      | 0.41                     | 0.43                    | -0.41 | 0.49                     | 0.44                    | 0.41                     | <b>0.58<sup>b</sup></b>  | 0.51                     | 0.53                     | 0.54                     | 1                        |                          |                          |                         |    |
| TOC     | <b>0.65<sup>b</sup></b>  | <b>0.71<sup>a</sup></b> | -0.35 | <b>0.79<sup>a</sup></b>  | <b>0.59<sup>b</sup></b> | <b>0.73<sup>a</sup></b>  | <b>0.97<sup>a</sup></b>  | <b>0.91<sup>a</sup></b>  | <b>0.79<sup>a</sup></b>  | <b>0.91<sup>a</sup></b>  | <b>0.61<sup>b</sup></b>  | 1                        |                          |                         |    |
| TIC     | <b>-0.43<sup>b</sup></b> | -0.34                   | 0.08  | <b>-0.55<sup>a</sup></b> | -0.35                   | <b>-0.46<sup>b</sup></b> | <b>-0.88<sup>a</sup></b> | <b>-0.85<sup>a</sup></b> | <b>-0.67<sup>a</sup></b> | <b>-0.79<sup>a</sup></b> | <b>-0.64<sup>a</sup></b> | <b>-0.85<sup>a</sup></b> | 1                        |                         |    |
| TN      | <b>0.61<sup>b</sup></b>  | <b>0.63<sup>b</sup></b> | -0.43 | <b>0.71<sup>a</sup></b>  | <b>0.56<sup>b</sup></b> | <b>0.63<sup>b</sup></b>  | <b>0.85<sup>a</sup></b>  | <b>0.81<sup>a</sup></b>  | <b>0.62<sup>b</sup></b>  | <b>0.74<sup>a</sup></b>  | <b>0.67<sup>b</sup></b>  | <b>0.92<sup>a</sup></b>  | <b>-0.72<sup>a</sup></b> | 1                       |    |
| TS      | <b>0.74<sup>a</sup></b>  | <b>0.83<sup>a</sup></b> | 0.06  | <b>0.85<sup>a</sup></b>  | <b>0.67<sup>b</sup></b> | <b>0.89<sup>a</sup></b>  | <b>0.95<sup>a</sup></b>  | <b>0.95<sup>a</sup></b>  | <b>0.70<sup>a</sup></b>  | <b>0.89<sup>a</sup></b>  | 0.42                     | <b>0.87<sup>a</sup></b>  | <b>-0.80<sup>a</sup></b> | <b>0.70<sup>a</sup></b> | 1  |

**Table 4: Correlation matrices for studied elements (a: p<0.01; b: p<0.05) at Station 3**

| Element | Al                       | Cr                       | Mn                       | Fe                       | Co                      | Ni                       | Cu                       | Zn                       | Cd    | Pb                       | Hg                      | TOC                      | TIC                     | TN    | TS |
|---------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------|--------------------------|--------------------------|-------|--------------------------|-------------------------|--------------------------|-------------------------|-------|----|
| Al      | 1                        |                          |                          |                          |                         |                          |                          |                          |       |                          |                         |                          |                         |       |    |
| Cr      | 0.23                     | 1                        |                          |                          |                         |                          |                          |                          |       |                          |                         |                          |                         |       |    |
| Mn      | <b>0.68<sup>a</sup></b>  | 0.17                     | 1                        |                          |                         |                          |                          |                          |       |                          |                         |                          |                         |       |    |
| Fe      | <b>0.76<sup>a</sup></b>  | 0.18                     | <b>0.80<sup>a</sup></b>  | 1                        |                         |                          |                          |                          |       |                          |                         |                          |                         |       |    |
| Co      | <b>0.51<sup>a</sup></b>  | -0.24                    | <b>0.85<sup>a</sup></b>  | <b>0.75<sup>a</sup></b>  | 1                       |                          |                          |                          |       |                          |                         |                          |                         |       |    |
| Ni      | <b>0.59<sup>a</sup></b>  | <b>0.87<sup>a</sup></b>  | <b>0.52<sup>a</sup></b>  | <b>0.61<sup>a</sup></b>  | 0.17                    | 1                        |                          |                          |       |                          |                         |                          |                         |       |    |
| Cu      | <b>0.70<sup>a</sup></b>  | <b>0.38<sup>a</sup></b>  | <b>0.73<sup>a</sup></b>  | <b>0.93<sup>a</sup></b>  | <b>0.58<sup>a</sup></b> | <b>0.75<sup>a</sup></b>  | 1                        |                          |       |                          |                         |                          |                         |       |    |
| Zn      | <b>0.66<sup>a</sup></b>  | 0.04                     | <b>0.80<sup>a</sup></b>  | <b>0.94<sup>a</sup></b>  | <b>0.85<sup>a</sup></b> | <b>0.50<sup>a</sup></b>  | <b>0.89<sup>a</sup></b>  | 1                        |       |                          |                         |                          |                         |       |    |
| Cd      | 0.01                     | -0.18                    | 0.05                     | 0.14                     | 0.10                    | -0.07                    | 0.12                     | 0.15                     | 1     |                          |                         |                          |                         |       |    |
| Pb      | <b>0.47<sup>a</sup></b>  | <b>0.65<sup>a</sup></b>  | <b>0.44<sup>a</sup></b>  | <b>0.49<sup>a</sup></b>  | 0.23                    | <b>0.76<sup>a</sup></b>  | <b>0.65<sup>a</sup></b>  | <b>0.47<sup>a</sup></b>  | -0.16 | 1                        |                         |                          |                         |       |    |
| Hg      | 0.31                     | <b>0.68<sup>a</sup></b>  | <b>0.44<sup>b</sup></b>  | 0.18                     | 0.08                    | <b>0.62<sup>a</sup></b>  | <b>0.40<sup>b</sup></b>  | 0.11                     | -0.31 | <b>0.59<sup>a</sup></b>  | 1                       |                          |                         |       |    |
| TOC     | -0.14                    | 0.19                     | -0.04                    | 0.30                     | 0.04                    | 0.23                     | 0.35                     | 0.23                     | 0.15  | 0.18                     | -0.15                   | 1                        |                         |       |    |
| TIC     | <b>-0.67<sup>a</sup></b> | <b>-0.82<sup>a</sup></b> | <b>-0.54<sup>b</sup></b> | <b>-0.75<sup>a</sup></b> | -0.30                   | <b>-0.88<sup>a</sup></b> | <b>-0.85<sup>a</sup></b> | <b>-0.54<sup>b</sup></b> | 0.32  | <b>-0.82<sup>a</sup></b> | -0.45                   | <b>-0.57<sup>b</sup></b> | 1                       |       |    |
| TN      | 0.44                     | <b>0.60<sup>b</sup></b>  | <b>0.70<sup>b</sup></b>  | 0.47                     | 0.33                    | <b>0.66<sup>b</sup></b>  | 0.55                     | 0.43                     | -0.13 | <b>0.85<sup>a</sup></b>  | <b>0.88<sup>a</sup></b> | -0.12                    | -0.41                   | 1     |    |
| TS      | <b>-0.45<sup>a</sup></b> | -0.13                    | <b>-0.35<sup>a</sup></b> | -0.25                    | -0.17                   | <b>-0.26<sup>b</sup></b> | <b>-0.30<sup>b</sup></b> | -0.21                    | -0.11 | -0.23                    | -0.34                   | -0.09                    | <b>0.47<sup>b</sup></b> | -0.21 | 1  |