4.1 Introduction

Coastal and estuarine waters are sensitive zones acting as important sinks for many persistent pollutants and they accumulate in bottom sediments (Szefer et al. 1995). Among the varying contaminants, metals in aquatic systems could be transported rapidly into the sediments, where they could be released according to the changing environmental conditions, ultimately resulting to a secondary contamination source affecting the ecosystem. Sediment cores provide information about the events that occurred in preindustrial time and can be used as a tool to assess and monitor the pollution history encountered in changing climatic conditions (Karbassi and Amirnezhad. 2004), rate of sedimentation (Karbassi. 1996), weathering trend and the source of pollution etc of the aquatic system (Lopez and Lluch. 2000, Karbassi et al. 2005, Ahmad et al.2010; Mohamed. 2005). Over the last few decades intensive research has been carried out on sediment cores for establishing the effects of anthropogenic and natural processes on depositional environments. Changes in metal concentration
with depth in sediment cores can show long-term changes in the metal input trends and thereby imply pollution status. Vertical profiles of pollutant species in sediment cores have been commonly used as “pollution records” in the aquatic realm.

The geochemical research reviews on core sediment metal carried out so far on and off the west coast (Priju and Narayan. 2007; Harikumar et al. 2009; Harikumar and Nasir. 2010) reveals that considerable amount of work still remains to be done with regard to metal pollution. The sediment core analysis can be used as a gauge of the quality control in the CES and would provide a clear cut idea about the environmental dynamics of the studied site under consideration. This Chapter characterize the depth profile pattern of metals (Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Lead (Pb), Iron (Fe), Magnesium (Mg), Manganese (Mn), Nickel (Ni) and Zinc (Zn) in the core sediment collected from different hotspots in the CES. Anthropogenic Factor (AF), Contamination Factor (CF), Enrichment Factor (EF), Geoaccumulation Index (IGEO) and Pollution Load Index (PLI) were used to differentiate the typical metal sources. Statistical analyses were employed to understand the origin of metals in the core sediment samples.

4.2 Sediment Geochemistry

Estuaries are frequently conceptualized as large reactors of chemical wastes which are supplied, mixed, processed and transported along the salinity and suspended sediment gradient (Church. 1986). The fate of pollutant is a complex pattern, because estuaries are heterogeneous, chemically reactive and hydro dynamically variable and sedimentologically
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active. For getting an idea about the depth profile of pollutant behavior, geochemical analyses of metals in the sediment core were carried out in two year gap. In any environmental sampling, the water column depth and the respective core length of the same site may not be uniform; therefore the study cannot be related year wise. Therefore, this section only details the geochemistry of metal including the sedimentary characteristics, TOC and depth profile of metals in the two year gap (2009 and 2011) sampling period and discussed in separate sections as Part A and Part B.

4.2.1 Part A

This section describes the salient portrayal on the geochemical characteristics of six sediment cores collected during November 2009 from three specific zones of CES and are grouped as South, Middle and North. More details were discussed in Chapter 2. These core sediments are named as S₁, S₂, (South); M₁, M₂, (Middle); N₁ and N₂ (North).

4.2.1.1 General Sedimentary Characteristics

Colour, pH, Eh and texture for each core sediment are discussed as given below:

S₁: Varying colour combination in core sediment length was observed. Up to 10 cm it showed blackish brown, brownish black till 40 cm and then blackish brown. Values of pH ranged from 5.4 at 3 cm depth to 7.2 at 42 cm depth and it was found to exhibit an increasing trend with minor fluctuations from surface to bottom. Values of Eh ranged from -263 to -107 mV and it was highest negative value in the bottom portion of the core. Clay content
dominated in this core and showed a variation ranging from 3.2% to 97.8%. Along the core, as depth increases, clay fraction was noted both at the top and bottom portion of the core and in the middle section, sand content was dominated (48% to 70%).

\[ S_2: \] Uniform black colour up to 12 cm and mixed black and grey colour up to 30 cm was noted. pH ranged from 7.53 to 8.75 and it was found to exhibit an increasing trend towards the bottom portion of the core. Values of Eh ranged from +102 to +264 mV and it was high at the top portion of the core. Sand content dominated in this core, and it was observed a variation as 81.7% to 95.5% to the entire core.

\[ M_1: \] The whole core appeared blackish brown in colour. Values of pH ranged from 7 to 8. Values of Eh ranged from -324 to -263 mV and it was found highest negative value at bottom portion of the core. Sand content dominated (54.6% to 93.7%) in this core. Relative textural distribution was in the order; sand > clay > silt.

\[ M_2: \] Mixed black and grey colour at 0-36 cm and uniform black colour up to 63 cm were noted. Values of pH ranged from 7.9 at 63 cm depth to 8.7 at 9 cm depth and exhibited a decreasing trend with minor fluctuations from surface to bottom. Values of Eh ranged from -412 to -310 mV and it was found highest negative value at bottom portion of the core. Sand content was intensified in this core. The textural variation was in the order; sand > clay > silt.

\[ N_1: \] The entire core was blackish brown in colour. pH value ranged from 6.1 to 6.6 and it decreased towards the bottom. Values of Eh
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ranged from -376 to -252 mV and it was found highest negative value at middle to bottom portion of the core. Clay content varied between 1.9 % and 85.4 %. Increased sand content was observed at bottom portion of the core.

N2: Varying colour combination in core sediment was observed. Up to 18 cm, it showed uniform black colour, brownish black till 45 cm and then followed by mixed black and grey colour. Values of pH ranged from 5.6 to 7.54 and highest at bottom portions of the core. Values of Eh ranged from +172 to +286 mV and it was found highest at top portion of the core. Clay content dominated in this core and showed a variation ranging from 2.2 % to 88.9 %. Along the core, as depth increases, clay fraction was also decreased.

4.2.1.2 TOC and CHNS

In core S1, the percentage of TOC ranged from 2.7 to 3.8, showing the lowest and the highest at a depth of 27 cm and 12 cm respectively. Core S2 showed percentage of TOC ranging from 0.44 to 0.56 and almost equal in the entire portions of the core. Core M1 had TOC decreased from top (0.7%) to bottom (0.6%) of the core. Core M2 revealed the content of TOC as 0.7 to 1.2. The maximum was noted at 24 cm depth and minimum at 6 cm of the core. TOC values increased towards the bottom of the core. In the core N1, percentage of TOC ranged from 0.6 to 2.9. The maximum was noted at 12 cm depth and the minimum at 27 cm length of the core. Core N2, had percentage of TOC ranged from 0.75 to 4.01, showing the lowest at bottom and highest at the top portions of the core.
A number of important bulk sediment parameters are available for the evaluation of OM sources and its fate within the marine sediments, in which C/N ratios are often used to differentiate marine from terrestrial OM (Redfield et al. 1963; Atkinson and Smith. 1983; Perdue and Koprivnjak. 2007), although selective degradation of the different minerals in sediments can affect the C/N ratios of OM (Muller. 1997). C/N values are typically lower for aquatic OM than for terrestrial OM (Meyers and Lallier-verges. 1999) and it ranges were 6-9 for planktonic organisms and 20-100 for terrestrial plant tissue and soil (Tyson. 1995). In this research findings, C/N ratio varied from 18.5 to 25.23, averaging 22.75 for core (S1); from 15.3 to 25 averaging 20.4 for core (S2); from 11.9 to 14.2, averaging 12.9 for core (M1); from 20 to 22, averaging 21 for core (M2) and from 14.4 to 32.8, averaging 20.7 for core (N1); from 13.51 to 17.42 averaging 14.9 for core N2. Among the six cores, C/N ratio was > 20 in four cores (S1, S2, M2, & N1) ascertaining the input of terrestrial material into the area and justifying that the source of organic matter is allochthonous. It also suggests that less productive and terrestrial OM could be a dominant contributor in the study region. However, the succession of post depositional changes may also modify the environment niche drastically. Percentage of elemental distributions (CHNS) in all the four sediment cores were in the order: C> S> H> N.

The ratio of total organic carbon (TOC) % to total sulfur (TS) % (TOC: TS), in the studied core sediments was determined. Their values ranged as: core S1 (1.2 to 3.0), S2 (5 TO 6.38), M1 (0.7 to 3.0), M2 (0.46 to 1.22), N1 (1.2 to 3.0) and N2 (5.60 to 5.8) respectively. However, its ratio was highest at cores N2 and S2 indicating that the amount of metabolizable
organic matter were available to support sulphate reducing bacteria which increases with the total amount of organic matter arriving at the sediment water interface. As a consequence, the sedimentary pyrite sulphide content is positively correlated with the non metabolized (resistant and unused) organic matter content (TOC). Further, fresh water sediment have very high TOC/TS ratios because of the low sulphate concentrations in most fresh water bodies (Berner and Raiswell. 1983). In general, under anoxic conditions, dissolved sulfate is reduced to hydrogen sulfide gas, which reacts with iron minerals to form iron sulfides causing a qualitative redox status of the environment under deposition. Marine sediments undergoing sulfate reduction under euxinic/ inhospitable bottom conditions typically have TOC: TS ratios lower than 1.5 (Niffy Benny. 2009) and similar observation was found at bottom portions of the cores viz; S1, M1, M2 and N1. These sites were under the threat of anthropogenic waste materials and were associated with the dredging, and piling activities. This region endure sulfate reduction below an oxygenated water column exhibiting TOC: TS ratios in the range: 1.5 to 5 and these results were well corroborated with the earlier works by Berner and Raiswell. 1983. Thus sediments from these stations (S1, M1, M2 and N1) were characterized as under predominantly anoxic stipulation. Increased anoxia in the study area not only increases preservation of the pigments but also excludes the benthic animal community, thereby reducing ingestion and bioturbation, which has a significant effect on the degradation of sedimentary pigments. TOC/TS ratio > 5 in core S2 and N2 are considered as oxic sediment with oxygenated bottom water.
4.2.1.3 Depth Profile of Metals

$S_1$: Depth profile of metal was given in Figure 4.1. Cd content showed almost similar trend in the entire sections of the core. The content was diminished to 15-18 cm length of the core and increased towards the bottom. Concentration of Co was diminished in the top section of the core i.e up to 15 cm and increased towards the bottom section of the core. Cr showed a decline up to 15 cm length and intensified in mid and bottom section of the core. The top section of the core is concentrated with Cu and changes slightly from 15 cm to the bottom. Intensified Fe concentration was observed in the top (3-12 cm) and bottom section (24-33 cm) of the core. Pb showed high residual levels in the top and bottom section of the core. In the entire sections of the core, Mg had high content in top (12 cm) and bottom (33 cm). Mn revealed larger content in the top section (up to 15 cm) of the core and diminished in the bottom. Concentration of Ni was highest in the bottom section of the core. Zn also revealed greater content in the top and bottom section of the core and less in the middle part.

High content of Fe, Mn and Cu were present in the top section of the core and indicated bottom layer anoxia. The Eh and TOC: TS values also support the increased anoxia along the bottom portion of the core. All the metals analyzed revealed an increase in concentration at the top and bottom section of the core, clearly reveals the granulometric dependence as intensified by clay content in the top and bottom part of the core.
**S1:** Distribution of metal was given in Figure 4.2. Cd content showed prevailing trend in the top-bottom section and lessen in the mid portion. Depth increased Co content also reduced. Cr content declined as depth increased up to 6 cm and again intensified towards 27 cm and later diminished up to 33 cm. Cu showed somewhat similar pattern in all the sections of the core. Fe and Mg showed same pattern revealing a heavy load in the top and bottom section of
the core. Pb content was intensified in the top and bottom section of the core. Mn and Ni showed the same trend as metals were enriched in the top and bottom section. Zn content was diminished at the top and mid section of the core and intensified in the bottom region.

Cd, Cu, Fe, Mg, Mn, Pb and Ni content showed intensified concentration in the top and bottom section of the core. Cr and Zn had shown high concentration in the bottom section of the core. Sand content was dominant in the core and showing granulometric independence, revealing anthropogenic origin of these metals. Similarly Eh and pH value had no significant impact on the metal distribution in the core.
**Figure 4.2** Discrepancy of metals in core S₂ (2009)

\textbf{M₁}: Discrepancy of metal given in Figure 4.3. Cd, Co, Cr, Fe, Mg, Mn, Ni and Zn were directly related to depth where Cu and Pb were concentrated to the middle then decreased towards to the bottom.

Except Cu and Pb all the other metals were intensified in the bottom portion of the core. Eh value showed increased anoxia in the bottom portion of the core. High sand % revealed a textural independence of metal and showing its source as anthropogenic origin.

**Figure 4.3** Discrepancy of metals in core \textit{M₁} (2009)
**M₂**: Metal distribution was given in Figure 4.4. Cd, Co, Cr, Cu, Fe, Mg, Mn and Ni content was directly related to depth; but for Pb and Zn, concentration was increased towards the middle and decreased towards the bottom. Except Zn and Pb, all the other metals were intensified in the bottom portion of the core. Eh value showed increased anoxia in the bottom portion of the core. Dominant content of sand revealed textural independence of metal and clearly outweights its anthropogenic source.

![Figure 4.4 Discrepancy of metals in core M₂ (2009)]
**N1:** Metal allocation was given in Figure 4.5. Cd and Ni were high along the deeper length of the core. Cr content was improved to the mid portion and diminished to the bottom; concentration of Co, Cu, Fe, Mg, Mn, Pb and Zn were high in the top section of the core and reduced in the remaining sections of the core indicating a reduced metal layer below the bottom portion of the core. The Eh and TOC: TS values also support the increased anoxia along the bottom portion of the core. Most of the metals analyzed revealed increased concentration in the top section of the core which clearly revealed the granulometric dependence as intensified by clay content in the top portion of the core.

![Figure 4.5 Discrepancy of metals in core N1 (2009)](image.png)
**N2**: Distribution of metal was given in Figure 4.6. Fe, Mg and Pb were dominant in the top section of the core; Cd, Ni and Zn were directly related with depth; Co, Cr and Mn content was intensified to the middle and weaken towards the bottom and Cu was decreased to the middle and augmented towards the bottom. This core revealed fluctuated behavior of the different metals and had high concentration in the core due to high clay content and oxic nature of the sediment. Eh and TOC: TS values also support these results.

![Figure 4.6 Discrepancy of metals in core N2(2009)](image-url)
4.2.1. 4 Geochemical Normalisation Methods

1. Antropogenic Factor (AF)

A deviation in anthropogenic metal enrichment in different cores from the study area was observed for AF. In core S\textsubscript{1} showed Cd content anthropogenic enrichment was up to 12 cm depth, towards 18 cm depth it had no enrichment. In the depth 21, 24 and 30 cm had anthropogenic input, whereas at 27 cm depth had no enrichment. Co had anthropogenic pollution at 6, 15, 18, 27 and 30 cm depth. The remaining parts had no anthropogenic input. Up to 12 cm depth, Cr had anthropogenic enrichment; remaining part up to 24 cm has no enhancement. Again towards the bottom, it showed anthropogenic pollution. Cu and Zn revealed severe anthropogenic pollution in the entire core. Fe and Mg had anthropogenic origin only between 12-18 cm depth. Mn had no anthropogenic pollution in the entire core. Ni had exogenic pollution load up to 6 cm and the residual part had no such contamination. Pb generated anthropogenic pollution at 9, 18, 27 cm depth and no contamination at the rest. Except Mg and Zn, S\textsubscript{2} are showed for all the metal showed exogenic origin in the entire core. Top to mid section of the core Mg and Zn had wholly different origin. M\textsubscript{1} core had anthropogenic pollution for Cr, Cu and Pb. In M\textsubscript{2} core, most of the metals revealed AF > 1. Zn is excluded from this inference. In core N\textsubscript{1} and N\textsubscript{2}, all the metals displayed greater anthropogenic factor indicating the exotic origin.

2. Contamination Factor (CF)

Among the metals Cd and Mg had high contamination in core S\textsubscript{1}. Core S\textsubscript{2} had high contamination for Cd and Pb than other metals. M\textsubscript{1} core reported contamination for Cd and Cr. In M\textsubscript{2} core, high metal contamination
was found for Cd and Cr. Among the metals, Cd, Cu, Pb and Zn had high pollution for core N1. N2 core showed high toxicity only for Cd.

3. Enrichment Factor (EF)

In core S1, Cd content showed significant at 3cm depth, moderate to significant enrichment was found up to 12 cm. Very high enrichment towards 18 cm. At 21cm had moderate enrichment and thereafter up to 27 cm, a significant enrichment was observed. At 30 cm depth, it had moderate enrichment. Co showed minimal enrichment in all the sections of the core. Cr revealed moderate enrichment at 15 -24 cm depth and the rest minimal enrichment. Cu had significant enrichment at 3 cm depth and minimal enrichment in remaining depth. For Pb revealed a minimal enrichment. Mg had moderate enrichment. Mn content had extremely high enrichment at 6-12 cm; in the remaining, it had minimal enrichment. Entire core revealed minimal enrichment for Ni. Zn showed a moderate enrichment at 3cm depth and minimal enrichment in the remaining section. Core S2 showed Cd as moderate- significant enrichment in the entire core. Mg, Cr and Cu had moderate enrichment. Pb showed extremely high enrichment in this study. Mn showed minimal enrichment. Ni had significant enrichment. For Zn observed of moderate enrichment up to 18 cm, and also moderate up to 21 cm and significant to 30 cm length. In core M1, Cd had extremely high enrichment. Co had minimal enrichment. Cr had maximum enrichment at 3 cm then significant to very high enrichment in the remaining depth. Cu showed moderate to minimal enrichment. Pb had significant up to 18 cm depth and minimal for the rest. Mg showed moderate to minimal enrichment. Mn, Ni and Zn had minimum enrichment. Core M2 showed Cd
as significant, very and extremely high enrichment in the entire core. Co had minimum for the core. Cr had moderate enrichment up to 24 cm then significant enrichment in the remaining depth. Cu and Pb had minimal enrichment. Mg and Mn showed moderate enrichment. Ni showed moderate enrichment. Zn showed minimal enrichment in this core. In core N 1 Cd had extremely high enrichment. Co and Cr showed minimal enrichment. Cu showed moderate to minimal enrichment. Pb showed moderate to extremely enrichment. Mg and Mn showed moderate enrichment. Ni and Zn had minimal to extremely high enrichment. N 2 core revealed Cd as extremely high enrichment. Co showed significant enrichment. Cr had minimum enrichment. Cu showed moderate to low enrichment. Pb showed moderate to maximum enrichment. Mg and Mn showed moderate enrichment. Ni and Zn had minimal to highest enrichment.

4. **Geoaccumulation Index (IGEO)**

IGEO showed high accumulation rate for Cd in the entire sections of the cores in different zones of the estuary under investigation.

5. **Pollution Load Index (PLI)**

PLI revealed severe metal contamination for the two cores (N 1, N 2) in the northern region of the estuary.

In core S 1, GCI showed significant anthropogenic and enrichment factors were significant for all the metals. Contamination factor revealed that contamination exists for Cd and Mg. Geoaccumulation index suggests severe accumulation of Cd in the entire core. PLI resulted less contamination in the core.
Except Mg and Zn, all the other metal showed anthropogenic input in the entire section of the core $S_2$. Mg and Zn revealed anthropogenic origin only at mid section. Contamination factor gave enormous contamination for Cd and Pb. Except Co all the other metals showed enrichment in the study area. Geoaccumulation index suggest severe accumulation of Cd in the entire core. PLI resulted less contamination in the entire core.

Anthropogenic pollution was noted for Cr, Cu and Pb in core $M_1$. Contamination factor was reported for Cd and Cr. All the metals showed enrichment but Cd showed extreme enrichment, in the study area.

In core $M_2$, Except Zn most of the metals revealed $AF > 1$. Contamination factor was found for Cd and Cr. Except Cd all the other metal showed moderate to minimal enrichment. Cd had significant, very and extremely high enrichment in the entire core.

On comparison between the GCI of the cores collected from the north zone showed severe contamination for all the metals.

4.2.1. 5 Statistical Analysis

Statistical analysis showed no significant correlation between the components, revealing the anthropogenic input of these metals. Principal component analysis results the reduction of the components to four factors of variance > 8%.

In core $S_1$, five factors (Table 4.4 annexure) account for total variance 90.43%. The factor 1 corresponds to 31.03% variance revealing the granulometric dependence of the metals, Fe, Mg and Mn. Factor 2 had 23.49% of variance showed anthropogenic origin of Co and Pb and also
these metals had strong binding affinity with organic matter. Variance of factor 4, showed as 11.16% which generate exogenic input of Cd.

$S_2$ generate four factors (Table 4.5 annexure), accounts the total variance as 86.66%. The factor 1 corresponds to 31.03% variance revealing the granulometric dependence of the metals Fe, Mg and Mn. Factor 2 had 23.49% of variance, shows the anthropogenic origin of Co and Pb and also these metals had strong binding character with organic matter. Variance of factor 4 showed as 11.16% which generate exogenic input of Cd.

Four factors (Table 4.6 annexure) account for total variance 86.20 % for core $M_1$. The factor 1 corresponds to 37.63% variance, revealing the anthropogenic origin of Cd, Co, Cr, Cu, Fe, Mg, Mn and Ni. Factor 2 had 27.62% of variance showed granulometric dependence of Fe, Mg and Mn. Factor 3 and factor 4 demonstrate variance as 11.68% and 8.70 % respectively indicate the exogenic input of Cd.

Core $M_2$ had four factors (Table 4.7 annexure) which account for total variance 78.69%. The factor 1 corresponds to 56.21% variance, revealing the granulometric and organic matter dependence of anthropogenic origin of Cd, Co, Cr, Cu, Fe, Mg, and Mn. Factor 2 generate 18.90% of variance showed granulometric and organic matter dependence of Zn. Factor 3 had variance of 11.47% organic matter with the control over Cr. Variance of factor 4 showed as 10.69% generate exogenic input of metals.

Core $N_1$, create three factors (Table 4.8 annexure) which accounts for total variance 81.32 %. The factor 1 corresponds to 37.63% variance revealing the anthropogenic origin of Co, Cu, Fe, Mg, and Mn. Factor 2 and
factor 3 generate variance as 14.14% and 18.90% respectively showing exogenic input of Cr and Cd correspondingly.

In core N$_2$ five factors (Table 4.9 annexure) account for total variance 90.07%. The factor 1 corresponds to 32.99% variance revealing the allothonous input of the metals Co, Cr, Mg and Mn. Factor 2 had 24.19% of variance showed granulometric relation of Cd and Ni and also these metal had strong binding with organic matter. Variance of factor 3 showed as 16.144% which generate exogenic input of Cu and Pb. Factor 4 had variance of 10.342% organic matter with the control over Zn. Variance of factor 5 showed as 8.40% generate exogenic input of Cd.

4.2.2 Part B

This section details the relevant portraits on geochemical characteristics of six sediment cores collected from the specific zones (described same as in the first sampling period, 2009) of CES during November 2011. Most of the earlier published research contributions were based on one-time or seasonal sampling during a year. Present research approach based on the geochemical analysis of sediment cores collected over a considerable time period which could provide a definite change in the environment niche and such studies are limited.

4.2.2.1 General Sedimentary Characteristics

Colour, pH, Eh and texture for each core sediment are discussed here under.

S$_1$: Uniform black colour. pH ranged from 6.3 at 9-12 cm depth to 7.5 at 30-33 cm depth and it was found to exhibit an increasing trend with minor fluctuations from surface to bottom. Values of Eh ranged from -
101 to +218 mV and it was found highest negative value at bottom portion of the core. Sand content dominated in this core and showed a variation ranging from 28 % to 86.7 %. Along the core, as depth increases sand fraction also increases. Besides slight highest (35% to 49%) percentage of silt was observed at top (0-15 cm) portion of the core. Relative textural distribution was found in the order sand > silt.

**S2**: Greyish brown colour up to 6 cm and uniform black colour up to bottom. Values of pH ranged from 7.4 to 8 and it was found to exhibit an increasing trend with minor fluctuations towards bottom part of the core. Values of Eh ranged from -434 to -323 mV and it was found highest negative value at bottom portion of the core. Sand content dominated in this core, and it was found almost equal (83 % to 98 %) to the entire core. Relative textural distribution was in the order sand > clay > silt.

**M1**: Greyish black colour up to 9-12 cm and uniform black colour up to bottom were noted. Values of pH ranged from 7.3 to 8 and it was found to exhibit an increasing trend towards the bottom portion of the core. Values of Eh ranged from -216 to -108 mV and it was found highest negative value at bottom portion of the core. Sand content dominated in the middle to bottom portion of the core (41% to 81 %). Top portion of the core was slightly enriched with silt content (23% to 44%). Relative textural distribution was in the order: sand > clay > silt.
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M2: The whole core appeared black in colour. Values of pH ranged from 6.9 at 39-42 cm depth to 8.4 at 9-12 cm depth and it was found to exhibit a decreasing trend with minor fluctuations from surface to bottom. Values of Eh ranged from -211 to -97 mV and it was found highest negative value at the middle to bottom portion of the core. Sand content was intensified in this core (31% to 82%) and towards the bottom, silt and clay fraction were dominated (~57%). The textural variation was in the order: sand > silt > clay.

N1: Black colour up to 21-24 cm section and uniform greyish black colour towards bottom of the core were observed. Values of pH ranged from 6.3 to 7. The highest pH at 9-12 cm depth and lowest at 27-30 cm depth. Eh ranged from -86 to +376 mV, and it was found highest positive value at top portion of the core. Clay content varied between 35% and 94%. Along the core, as depth increases sand content also intensified. The textural variation was in the order: clay > silt > sand.

N2: The whole core appeared black in colour. Values of pH ranged from 5.2 to 8.1 and highest were highest at middle portions of the core. Eh ranged from +64 to +376 mV and it was found highest positive value at top portion of the core. Top portion of the core was dominated with silt content and showed a variation ranging from 43% to 89%. As depth increases, silt fraction was decreased and increased sand content was noted towards the bottom portion of the core. The textural variation was in the order: silt > clay > sand.
4.2.2.2 TOC and CHNS

In core S1, percentage of TOC ranged from 0.85 to 3, showing the lowest and the highest at a depth of 39-42 cm and 6-9 cm respectively. In S2 core, TOC ranged from 0.12 to 0.29 showing the lowest and the highest at a depth of 3-6 cm and 21-24 cm respectively.

Core M1 showed percentage of TOC as ranged from 0.39 to 0.88 showing the lowest and the highest at a depth of 51-54 cm and 33-66 cm respectively. For M2 core, percentage of TOC ranged from 1.12 to 1.95. The maximum was noted at 24-27 cm depth and minimum at 15-18 cm of the core. TOC values increased towards the bottom of the core. In Core N1 percentage of TOC ranged from 0.63 to 4.9. The maximum was noted at of 3-6 cm depth and the minimum at 39-42 cm of the core. In Core N2 the percentage of TOC ranged from 2.39 to 5.6, showing the lowest at bottom and highest at the middle portions of the core.

C/N ratio varied from 15.1 to 22.2, averaging 19.13 for core (S1); from 17.3 to 22.2 averaging 18.5 for core (S2); from 9.6 to 12.4, averaging 10.7 for core (M1); from 18 to 31.7, averaging 22.6 for core (M2) and from 13.1 to 42.2, averaging 23.6 for core (N1); from 12.3 to 13.1 averaging 12.8 for core N2. Among the six cores, C/N ratio was greater than 20 in four cores (S1, S2, M2, & N1) ascertaining the input of terrestrial material into the area, justifying that the source of organic matter is allochthonous also it clearly indicates the less productive and terrestrial OM could be a dominant contributor in the study region. However the succession of post depositional
changes may also modify the environment niche drastically. Percentage of elemental distributions (CHNS) in all the four sediment cores were in the order: C> S>H>N.

The ratio of total organic carbon (TOC) % to total sulfur (TS) percentages (TOC: TS), in the studied core sediments was determined. Their values ranged as: core S\(_1\) (3.35 to 5.7), S\(_2\) (0.28 to 0.84), M\(_1\) (0.98 to 1.77), M\(_2\) (0.25 to 1.21) and N\(_1\) (2.52 to 10.14) and N\(_2\) (4.78 to 15.5) respectively. Generally, under anoxic conditions dissolved sulfate is reduced to hydrogen sulfide gas, which reacts with iron minerals to form iron sulfides causing a qualitative redox status of the environment under deposition. Marine sediments undergoing sulfate reduction under euxinic/ inhosiptable bottom conditions typically have TOC: TS ratios lower than 1.5 (Niffy Benny, 2009) and similar observation was found in the cores (S\(_2\), M\(_1\), M\(_2\)). These sites were under the threat of anthropogenic inputs and were associated with dredging, and piling activities. This region endure sulfate reduction below an oxygenated water column exhibiting TOC: TS ratios were in the range 1.5 to 5 and well corroborated earlier by Berner and Raiswell, 1983. Sediments in the stations (S\(_1\), N\(_1\), N\(_2\)) were characterized as under predominantly anoxic stipulation in deeper portion of the core. Increased anoxia in the study area not only increases preservation of the pigments but also excludes the benthic animal community, thereby reducing ingestion and bioturbation, which has a significant effect on the degradation of sedimentary pigments. TOC/S ratio > 5 in the top to middle portions of the core N\(_2\) are considered as oxic sediment with oxygenated bottom water.
4.2.2.3 Depth Profile of Metals

$S_1$: Depth profile of metal was given in Figure 4.7. Cd content showed similar trend in the entire sections of the core. The content was diminished to 15-18 cm depth and increased to the bottom. Co was similar dominance in the whole sections of the core with slight decrease till 27 cm and increased to the bottom. Cr was BDL in the samples. The top section of the core is strengthen with Cu and dwindles slightly from 15 cm to the bottom. Fe revealed to be of great heaps in the mid portion (21-30 cm) of the core. Pb showed to be of heavy load in the top and bottom section of the core. Mg was shrinking towards the bottom segment. Mn revealed larger content in the top section (up to 15 cm) of the core and diminished the bottom. Ni was dominant in the top (15 cm) and bottom (39 cm) section of the core and diminished the mid portion Zn concentration was decreased with depth.

Cd, Co and Pb showed increased content in the bottom layer of the core revealed grain size independence to these metal distributions. But Zn and Mg were intensified to the top layer of the core supported by the grain size distribution in these sections. This was also supported by Eh and pH variation. Cr was spotted to be BDL in the samples.
Figure 4.7 Discrepancy of metals in core S1 (2011)

S2: Depth profile of metal was given in Figure 4.8. Cd content showed similar trend in the entire sections of the core as it prevailing in the top-bottom section and lessen in mid portion. Co revealed that as depth was directly related to metal content. Cr content was BDL. Cu showed a fluctuated metal content variation. Fe and Mg shows same pattern as concentrations diminished with increased depth. Pb content was directly related to metal content and was maximum at 48
cm depth. Mn and Ni had the same trend as depth increased metals were also amplified. Zn content showed trend as metal intensification in the top- mid section.

Co, Cu, Mn, Pb and Ni were intensified in the bottom portion of the core. Cd was high at top and bottom portion of the core. Cr content was BDL. Fe and Mg concentration were intensified at the top portion of the core. Zn had intensification towards the top mid section of the core. The high negative Eh and increased pH values also support these outcomes. Sandy texture of the sediment suggests anthropogenic origin of these metals.

Figure 4.8 Discrepancy of metals in core S2 (2011)
M1: Depth profile of metal was given in Figure 4.9. Concentration of Cd, Co, Cu, Fe, Mg, Pb and Zn were intensified to the middle and shrink to the bottom section of the core. High negative Eh and increased pH values responsible for this distribution. But content of Cr was BDL where as Mn and Ni augmented with improved depth. Coarse nature of the sediment account for the anthropogenic origin of these metals.

![Figure 4.9 Discrepancy of metals in core M1 (2011)](image)

M2: Depth profile of metal was given in Figure 4.10. Cd and Mn content were decline to the middle and amplified to the bottom; Co, Fe,
Metal Distribution in the Specific Core Sediments of Cochin Estuarine System (CES)

Mg, Pb and Ni were enlarged to the mid section then drop off to the bottom and Cu, Zn content enhanced with increase in depth. Co, Fe, Mg, Pb and Ni distribution was influenced by the Eh and pH variation. Textural distributions revealed dominant sand content suggesting the anthropogenic source of this metal.

![Graph showing metal distribution](image)

Figure 4.10 Discrepancy of metals in core M2 (2011)

Ni: Depth profile of metal was given in Figure 4.11. Cd, Cr, Cu, Pb, Mn and Zn content were inversely related with depth; Co, Fe, Mg and Ni were increased to the middle and lessen to the bottom. Highest pH and oxic nature of the sediment (high positive Eh) in the top section

Department of Chemical Oceanography
responsible for the metal abundance. Textural characteristics revealed the granulometric dependence of these metals.

![Graph of metal abundance vs depth](image_url)

**Figure 4.11** Discrepancy of metals in core N1 (2011)

**N2:** Depth profile of metal was given in Figure 4.12. Cd was lessen to the middle and augmented to the bottom; Cr was amplified to the middle and diminished to the bottom; Co, Cu, Fe, Mg, Pb, Ni and Zn were prevailing in the top section and lessened in the bottom section. Mn content was directly related to depth. Highest pH and oxic nature of
the sediment (high positive Eh) in the top section responsible for the metal abundance. Textural characteristics revealed the granulometric dependence of Co, Cu, Fe, Mg, Pb, Ni and Zn.

Figure 4.12 Discrepancy of metals in core N2 (2011)

4.2.2.4 Geochemical Normalisation Methods

1. Anthropogenic Factor (AF)
Chapter 4

AF revealed vast variation of anthropogenic metal enrichment in different cores from the study area.

The core $S_1$ revealed AF < 1 for Cr. But Cd, Co, Cu, Ni and Zn had exotic nature in the mid and bottom sections of the core. Fe, Mg and Pb showed extravagant input at the top and bottom sections of the core. Mn had anthropogenic origin only in the bottom section of the core. Core $S_2$ showed no anthropogenic origin for Cd, Cr, Ni and Zn. Exotic origin was observed at the top section of the core for metals Co, Cu and Fe. The entire section of the core enriched with Mg, Mn and Pb. Excluding Cr all the other metals displayed exotic toxicity for $M_1$ core. In core $M_2$ most of the metals revealed AF > 1. Cr is the exception for this inference. $N_1$ and $N_2$ cores displayed greater anthropogenic factor for all the metals indicating the exotic origin.

2. Contamination Factor (CF)

In core $S_1$ showed great contamination for Cd, Co and Pb. Among the metals $S_2$ exposed contagion only for Cd. In $M_1$ core metal contamination reported for Cd and Pb. Metal toxicity was found for Cd, Co and Pb in core $M_2$. $N_1$ core revealed amid the metals immense pollution opened for Cd, Co, Cr, Cu, Ni, Pb and Zn. Core $N_2$ had enormous toxicity was revealed for Cd, Co, Cu, Ni, Pb and Zn.

3. Enrichment Factor (EF)

In core $S_1$, all sections of the core showed extremely high enrichment for Cd. Co showed extremely high enrichment in the entire core. Cr was BDL. Cu at depth 6 cm, 21 cm and 45 cm showed extremely high enrichment and residual part had significant to very high enrichment. Pb
generated extremely high enrichment. Mg had minimal enrichment. Mn had minimal enrichment in the entire core. Ni showed extremely high enrichment. Zn was enriched at 6 cm, 21 cm, 27 cm and 45 cm depth had extremely high enrichment and the rest very high enrichment. S2 core Cd showed extremely high enrichment in the entire section. Cr and Cu had at 6 cm depth extremely high enrichment, very high enrichment at 30-33 cm and the residual section showed significant enrichment. Pb showed extremely high enrichment for the study. Mg showed minimal for the core. Mn showed minimal enrichment. Ni had extremely high enrichment. Zn showed shuffled significant, very high and extremely high enrichment. M1 core Cd had extremely high enrichment. Co had extremely high enrichment. Cr was BDL. Cu showed significant, very and extremely high enrichment in the entire core. Pb had extremely high enrichment at 30-33 cm and the residual section showed significant enrichment. Mg showed minimal enrichment. Mn had minimal enrichment Ni and Zn had extremely high enrichment. M2 showed Cd had extremely high enrichment. Co had extremely high enrichment. Concentration of Cr was BDL. Cu and Pb had extremely high enrichment. Mg and Mn showed moderate enrichment. Ni showed extremely high enrichment in the entire core. Zn showed very high enrichment in the entire core. N1 core Cd had extremely high enrichment. Co and Cr showed extremely high enrichment in the entire core. Cu showed extremely high enrichment in the entire core. Pb showed extremely high enrichment in the entire core. Mg and Mn showed moderate enrichment. Ni and Zn showed extremely high enrichment in the entire core. N2 core Cd had extremely high enrichment. Co showed extremely high enrichment in the entire core. Cr had extremely high enrichment in the entire core. Cu showed extremely high enrichment in the entire core. Pb showed extremely
high enrichment in the entire core. Mg and Mn showed moderate enrichment in the core. Ni and Zn had extremely high enrichment in the entire core.

4. Geoaccumulation Index (IGEO)

IGEO showed Cd had enormous accumulation in the entire sections of the cores in different zones of the estuary studied.

5. Pollution Load Index (PLI)

PLI revealed severe metal contamination for the two cores (N1 and N2) from the biennial collection in the northern region of the estuary.

In core S1, except for Cr all the metals showed anthropogenic origin. Contamination factor revealed contamination for the metals Cd, Co and Pb. Enrichment factor showed extreme enrichment for Cd, Co, Cu, Pb, Mg, Mn, Ni and Zn. Geoaccumulation index suggest severe accumulation of Cd in the entire core. PLI resulted less contamination in the core.

GCI studies for core S2 revealed no anthropogenic origin for Cd, Cr, Ni and Zn. In the top section of the core showed exotic origin for Co, Cu and Fe. The entire section of the core anthropogenically loaded with Mg, Mn and Pb. Contamination factor result high contamination only for Cd. Enrichment factor showed enrichment for Cd, Cr, Cu, Pb, Mg, Mn, Ni and Zn. Geoaccumulation index suggest severe accumulation of Cd in the entire core. PLI resulted less contamination in the core.

Except Cr all the other metal had high anthropogenic and enrichment factor for core M1. Greater contamination factor was reported for Cd and
Pb. Geoaccumulation index suggests severe accumulation of Cd in the entire core. PLI resulted less contamination in the core.

Except Cr, all the other metal had high anthropogenic and enrichment factor for core M2. Greater contamination factor was reported for Cd, Co and Pb. Geoaccumulation index suggest severe accumulation of Cd in the entire core. PLI resulted less contamination in the core. On comparison between the GCI of the cores the cores collected from the north zone (N1 and N2) showed severe contamination for all the metals except Cr.

4.2.2.5 Statistical Analysis

Statistical analysis showed no significant correlation between the components, revealing the anthropogenic input of these metals. Principal component analysis results the reduction of the components to four factors were variance > 7%.

In core S1, four factors (Table 4.10 annexure) account for total variance 82.10%. The factor 1 corresponds to 47.89 % variance revealing the granulometric and organic matter dependence of the metals Cd, Cu, Mn, Ni and Pb. Factor 2 had 15.08 % of variance showed anthropogenic origin of Cd and Mg. Variance of factor 3 and 4 showed as 10.65% and 8.48 % which corresponds to exogenic input of Co.

S2 generate five factors (Table 4.11 annexure), accounts the total variance as 84.22 %. The factor 1 corresponds to 24.04 % variance revealing the granulometric independence of all the metals. Factor 2 had 21.73% of variance, shows the anthropogenic origin of these metal.
Variance of factor 3 and 4 showed as 16.55 and 12.44% which also generate exogenic input of the metals.

Four factors (Table 4.12 annexure) account for total variance 76.71% for core M1. The factor 1 corresponds to 36.72% variance, revealing the granulometric and organic matter dependence of Cu, Fe, Ni and Zn. Factor 2 had 16.18% of variance showed granulometric dependence of Pb. Factor 3 and factor 4 demonstrate variance as 13.63% and 9.19 % respectively indicating the exogenic input of all the metals.

Core M2 had four factors (Table 4.13 annexure) which account for total variance 74.35%. The factor 1, 3 and 4 had variance corresponds to 32.77%, 11.88 % revealing the anthropogenic origin of the metals. Factors 2, generate 21.92% of variance showing the organic matter dependence of Cu, Mn and Ni.

Core N1 create two factors (Table 4.14 annexure) account for total variance 80.42%. The factor 1 corresponds to 67.11% variance revealing the granulometric relation of Cd, Co, Cu, Mg, Mn, Ni and Zn and also these metal had strong binding behavior with organic matter. Factor 2 generate variance as 13.31% showing exogenic input of all the metals.

In core N2 four factors (Table 4.15 annexure) account for total variance 83.50%. The factor 1 corresponds to 46.97% variance revealing granulometric relation of Cd, Co, Cu, Mg, Mn, Ni, Pb and Zn also these metal had strong binding with organic matter. The allothonous input of the metals Co, Cr, Mg and Mn. Factor 2 had 17.43% of variance showed granulometric relation of Cu and Cr. Variance of factor 3 showed as 11.77%
generate granulometric dependence of Mg. Factor 4 had variance of 7.33% showed exogenic input of these metals.

The two year gap variation of the depth profile of metals in the CES revealed greater metal content was found in the northern part of the estuary which was due to the high clay content present in the sediment. The sediment textural characteristics in terms of changing hydrography of the CES have been predominantly studied by Nair et al. 1993 revealed large areas of the estuary was covered by clay. Similar trend for textural behavior was observed in most of the sediments cores of the present study. The dependence of metal with organic matter and texture revealed a fluctuation in distribution due to dynamic nature of the estuary. Zonal comparison of the metal in cores gave the order as North Zone > Middle Zone > South Zone. Due to the weak flow and the huge input of industrial effluents, higher levels of metals were found in the northern estuary (Thomson. 2002). On the contrary, consistent with a strong flow, moderate levels of metals were found in the central estuary, which receives both domestic and industrial effluents. Decreasing trends in metal levels, detected towards the central estuary when compared with north may be due to strong rectilinear current, which maintains an effective flushing (Balachandran. 2008). Likewise, in relation with weak flow and minor inputs, lower levels of metals characterized in the southern estuary, which receives agricultural wastes from Kuttanad Paddy fields.

4.2.3 Sediment Quality Guideline Comparison

The major and minor metals in the core sediments from three prominent zones of CES were compared with different world wide used
guidelines (Table 2.2 in Chapter 2). The major and minor metal disparity were given in Table 4.1 and 4.2.

<table>
<thead>
<tr>
<th>ZONE</th>
<th>CORE CODE</th>
<th>YEAR</th>
<th>Cd (mg/Kg)</th>
<th>Co (mg/Kg)</th>
<th>Cr (mg/Kg)</th>
<th>Cu (mg/Kg)</th>
<th>Pb (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOUTH</td>
<td>S1</td>
<td>2009</td>
<td>0.67 - 2.98</td>
<td>0.54 - 11.62</td>
<td>3.57 - 105.67</td>
<td>20.44 - 134.06</td>
<td>1.22 - 22.95</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>2009</td>
<td>3.59 - 8.58</td>
<td>0.99 - 11.70</td>
<td>8.57 - 95.67</td>
<td>9.76 - 18.69</td>
<td>75.61 - 106.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2011</td>
<td>3.38 - 6.02</td>
<td>11.27 - 16.9</td>
<td>1.81 - 7.27</td>
<td>7.5 - 38.11</td>
<td></td>
</tr>
<tr>
<td>MIDDLE</td>
<td>M1</td>
<td>2009</td>
<td>2.31 - 3.78</td>
<td>1.65 - 8.91</td>
<td>293.33 - 582.51</td>
<td>13.05 - 16.35</td>
<td>1.11 - 24.63</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>2009</td>
<td>1.31 - 6.21</td>
<td>1.47 - 8.31</td>
<td>52.59 - 391.54</td>
<td>7.59 - 68.03</td>
<td>1.13 - 20.51</td>
</tr>
<tr>
<td>NORTH</td>
<td>N1</td>
<td>2009</td>
<td>1.38 - 6.31</td>
<td>5.11 - 21.51</td>
<td>26.33 - 122.51</td>
<td>28.32 - 134.39</td>
<td>7.81 - 74.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2011</td>
<td>5.65 - 35.2</td>
<td>10.7 - 37.32</td>
<td>0 - 171.34</td>
<td>1.55 - 49.33</td>
<td>22.91 - 211</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2011</td>
<td>1.33 - 6.05</td>
<td>11.95 - 60.4</td>
<td>0 - 21.63</td>
<td>35.82 - 210.28</td>
<td>36.53 - 114.66</td>
</tr>
</tbody>
</table>

Cadmium concentration of the core sediments in the south zone ranged as 0.67 - 8.79 mg/Kg, middle zone revealed the array as 1.31 - 6.81 mg/Kg and northern zone showed variation as 1.27 - 53.05 mg/Kg. In the study area Cd concentration was found to be maximum (53.05 mg/Kg) in core sampled from the northern region of the estuary and minimum (1.27 mg/Kg) was analyzed for the cores from the southern region. The cadmium concentration recorded in the present study was above the permissible limit (0.6- 10 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2.
Metal Distribution in the Specific Core Sediments of Cochin Estuarine System (CES)

Co content of the core sediments in the south zone ranged as 0.54 - 35.97 mg/Kg, middle zone showed as 1.47 - 21.32 mg/Kg and northern zone revealed discrepancy as 1.68 - 71.14 mg/Kg. In the study area Co was found to be maximum (71.14 mg/Kg) in core sampled from northern region of the estuary and minimum (1.68 mg/Kg) was noted for the cores obtained from the southern region. The concentration of Cobalt documented in the present study was above the permissible limit (2 mg/Kg).

Cr in the core sediments of the south zone sort as BDL - 105.67 mg/Kg, middle zone showed the range as BDL - 582.51mg/Kg and northern zone exposed divergence as BDL - 171.34 mg/Kg. In the study area Cr was found to be maximum (171.34 mg/Kg) in core sampled from northern region of the estuary and minimum (BDL) was found for the core sections obtained from the southern and middle region. On comparison, with the different SQGs (Table 2.2 in Chapter 2) the content of Cr was above the permissible limit (25-75 mg/Kg).

Concentration of Cu in the core sediments of the south zone arrange as 1.81-134.06 mg/Kg, middle zone ranged as 4.28 - 68.03 mg/Kg and in the northern zone open to the discrepancy as 1.55 - 210.28 mg/Kg. In the study area, Cu was established to be maximum (210.28 mg/Kg) in core obtained from northern region of the estuary and minimum (1.81 mg/Kg) was found for the core sections from the southern region. Copper concentration cited in this study was moderately above the permissible limit (16- 270 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2.

Pb in the core sediments of the south zone assembled as 1.22- 106.10 mg/Kg, middle zone ranged as 1.11 - 41.43 mg/Kg and northern zone
exposed divergence as 2.59 - 714.29 mg/Kg. In the study area Pb was maximum (714.29 mg/Kg) in the core from northern region of the estuary and minimum (1.11 mg/Kg) was observed for the core sections from the middle region. The Lead concentration cited in this study was above the permissible limit (12.5- 400 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2.
Iron concentration of the core sediments in the south zone ranged as 32.08-39311.59 mg/Kg, middle zone revealed the array as 100.58 -45373.13 mg/Kg and in the northern zone showed variation as 102.97-48878.74 mg/Kg. In the study area, Fe concentration was found to be maximum (48878.74 mg/Kg) in core sampled from northern region of the estuary and minimum (32.08 mg/Kg) was noted for the cores obtained from the southern region.

Mg content of the core sediments in the south zone ranged as 10.2 -63987.8 mg/Kg, middle zone had the assortment as 19.69 - 31741.29 mg/Kg and northern zone exposed divergence as 22.68 -411.47 mg/Kg. In the study area, Mg was found to be maximum (63987.8 mg/Kg) and minimum (10.2 mg/Kg) in the cores from the southern region.

Mn in the core sediments of the south zone sort as 4.66 - 63987.8 mg/Kg, middle zone showed the range as 3.48 - 31741.29 mg/Kg and northern zone exposed divergence as 4.27-411.47 mg/Kg. In the study area Mn was found to be maximum (63987.8 mg/Kg) in core obtained from southern region of the estuary and minimum (3.48) was for the core sections sampled from the middle region. The Manganese concentration generated in
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this study was moderately above the permissible limit (30 - 3000 mg/Kg) as given by different SQGs listed in Table 2.2 in Chapter 2.

Concentration of Ni in the core sediments of the south zone range as 9.15-74.91 mg/Kg, middle zone ranged as BDL - 53. 63 mg/Kg and northern zone observed as 8.25 - 87.50 mg/Kg. In the study area Ni was established to be maximum (87.50 mg/Kg) in core from northern region of the estuary and minimum (BDL) was noted for the core sections from the middle region. The Nickel concentration cited in this study was moderately above the permissible limit (16- 315mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2.

Zn in the core sediments of the south zone assembled as 2.31-137.61 mg/Kg, middle zone ranged as 0.12 - 135.47 mg/Kg and northern zone exposed divergence as 14.29 - 814.91 mg/Kg. In the study area Zn was maximum (814.91 mg/Kg) in the core sediment from the northern region of the estuary and minimum (0.12 mg/Kg) was found in the core sections from the middle region. The Zinc concentration cited in this study was moderately above the permissible limit (70-820 mg/Kg) given by different SQGs listed in Table 2.2 in Chapter 2 generate moderate pollution in the study area.

Most of the identified metal in the core revealed pollution load as concentration far higher than the guideline values. This revealed moderate to severe pollution of metals in the study area.

4.2.4 Previous Literature Comparison

Metal enrichment was found in the Cochin estuarine sediments, it would be worth to compare the metal concentration values with previously reported within the system and other large urban-coastal settings or recognized polluted areas (Table 4.3). In comparison to the ranges reported worldwide, the maximum values of metals were found in this study and
were similar order of magnitude or even higher than those reported for other polluted estuaries, placing the region as one among the impacted estuaries around the world.
### Table 4.3 Comparison metal concentration (mg/Kg) within the system and other large urban-coastal settings or recognized polluted areas

<table>
<thead>
<tr>
<th>Location</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CES</td>
<td>5.36</td>
<td>7.14</td>
<td>58.7</td>
<td>21.2</td>
<td>24.2</td>
<td>2.0</td>
<td>1.4</td>
<td>0.94</td>
<td>0.14</td>
<td>0.01</td>
<td>Present Study</td>
</tr>
<tr>
<td>Pearl River Estuary</td>
<td>1.55</td>
<td>22.9</td>
<td>13.8</td>
<td>1.05</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>68.5</td>
<td>234</td>
<td>Babu Liu et al. 2011</td>
</tr>
<tr>
<td>CES</td>
<td>29.4</td>
<td>NA</td>
<td>NA</td>
<td>16.6</td>
<td>NA</td>
<td>NA</td>
<td>15.9</td>
<td>72.3</td>
<td>98.9</td>
<td>2746</td>
<td>Harikumar and Harih 2018</td>
</tr>
<tr>
<td>CES</td>
<td>0.73</td>
<td>NA</td>
<td>NA</td>
<td>4.93</td>
<td>0.91</td>
<td>NA</td>
<td>86.9</td>
<td>44.0</td>
<td>54.8</td>
<td>211.39</td>
<td>Harikumar et al. 2009</td>
</tr>
<tr>
<td>Manekudy Estuary</td>
<td>3.168</td>
<td>6.052</td>
<td>482.1</td>
<td>138</td>
<td>45.867</td>
<td>480.3</td>
<td>627.6</td>
<td>528.4</td>
<td>358.216</td>
<td>58.912</td>
<td>176.877</td>
</tr>
<tr>
<td>CES</td>
<td>16.5</td>
<td>52.5</td>
<td>30.4</td>
<td>50.1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>11.8</td>
<td>NA</td>
<td>850</td>
<td>Pillu and Mursy, 2007</td>
</tr>
<tr>
<td>Gotland Basin, Baltic Sea</td>
<td>NA</td>
<td>19</td>
<td>1.17</td>
<td>71</td>
<td>52900</td>
<td>NA</td>
<td>419</td>
<td>46</td>
<td>83</td>
<td>210</td>
<td>Bolinno-Segers et al. 2007</td>
</tr>
<tr>
<td>Manjushwar and Sontoshwar</td>
<td>NA</td>
<td>20</td>
<td>NA</td>
<td>36</td>
<td>NA</td>
<td>NA</td>
<td>149</td>
<td>103</td>
<td>43</td>
<td>80</td>
<td>Karbassi and Shami, 2005</td>
</tr>
<tr>
<td>Bilbao, Spain</td>
<td>NA</td>
<td>NA</td>
<td>350</td>
<td>1949</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>2556</td>
<td>7867</td>
<td>Cuney et al. 2003</td>
</tr>
<tr>
<td>Tamki Estuary, New Zealand</td>
<td>1.49</td>
<td>NA</td>
<td>NA</td>
<td>60.35</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>200</td>
<td>365</td>
<td>Abraham and Parker 2002</td>
</tr>
<tr>
<td>Golden Horn, Turkey</td>
<td>0.6</td>
<td>24.5</td>
<td>390</td>
<td>194</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>510</td>
<td>890</td>
<td>Turner et al. 2001</td>
</tr>
</tbody>
</table>

NA-Not Available
On comparison with the previous reports (Table 4.3) within the CES and other polluted estuaries, Cd concentration was high in the study area. The heavy load of Cd can be justified in the light of local pollution due to dumping of sewage and industrial effluents. Co resulted severe pollution in the estuary and was very high as compared to the earlier reports of the same aquatic system and polluted estuaries. The heavy load of Co can be justified in the light of local pollution due to dumping of sewage and industrial effluents. Cr was found elevated values compared with other estuaries (Table 4.3). Sugirtha and Patterson. 2009 reported a similar concentration (482.138 mg/Kg) than the above trend. Cr establishes to be highly intensified in the study area due to the excess of industrial and municipal effluents. The previous reports (Table 4.3) within the CES and other impacted estuaries, Cu content heavily magnified in the study area. The source of copper includes industrial and municipal effluents. Fe was increased in the study area as compared to the previous reports (Table 4.3), but there are exception, showing heavy concentration of the metal reported earlier by Belzunce Segarra et al. 2007 (52000 mg/Kg) than the present study. On comparison with earlier studies in Table 4.3, Mg showed a greater amount for the present study than the previous report. The heavy load of Mg is due to the disposal of wastes, sewage and industrial effluents. Concentration of Mn was high in this study when compared within the system and the other reports listed in the Table 4.3. The Mn source includes industrial and municipal effluents. Concentration of Ni was very high in this study as compared within the system and the other reports listed in the Table 4.3. But there are exceptions showing heavy concentration of the metals by Karbassi and Shankar 2005. (103mg/Kg) and Priju and Narayana. 2007 (118 mg/Kg) than the present study. Ni ascertains to be highly intensified in the study area. The source of Ni includes industrial and municipal effluents. Content of Pb was
high in this study when compared within the system and the other reports listed in the Table 4.3. The effluent from chromium plating industries is one of the major sources of lead. Zn concentration was high in this study when compared within the system and the other reports listed in the Table 4.3. But there are exceptions showing heavy concentration of the metals by Harikumar and Nasir. 2010 (2246mg/Kg) and Cundy et al. 2003 (7687mg/Kg) than the present study. The effluent from industries is one of the major sources.

4.3 Conclusion

The distribution, movement and storage of contaminants in the hydrosphere have a substantial effect on various scientific aspects of ecology, environmental biogeochemistry and proper management of aquatic resources. Therefore, the study compiles the ecological risk of metals in the estuary with reference to biennial spatial and depth profile of core sediment in CES. Investigation on the influence of anthropogenic activities using GCI resulted in moderate to severe pollution for all the metals under investigation and specifically for Cd. The link between geoaccumulation and ecological risk has been examined to gain insight into the processes affecting the representation of pollution magnitude in terms of toxicity of metals. SQG comparison generate severe contamination for Cd, Co, Cr, Pb, Mn, Zn and moderate for Cr and Ni. Except elements Ni and Zn, all the metals showed enrichment in comparison with previous reports placing the region as one among the impacted estuaries around the world. This study generates an authority on metal distribution and their chemical control in the estuarine core sediments. An assessment has been made based on a sequential extraction procedure to understand the binding fractions and mobility of metals to the surrounding environment. These geochemical fractionation of metal in specific core sediment of CES is studied in detail and are given in Chapter 5.
### Annexure

#### Table 4.4 Component matrix of the core sediment S₁ (2009) using principle component analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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#### Table 4.5 Component matrix of the core sediment S₂ (2009) using principle component analysis

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## Chapter 4

### Table 4.10 Component matrix of the core sediment S₁ (2011) using principle component analysis

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### Table 4.11 Component matrix of the core sediment S₂ (2011) using principle component analysis

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### Table 4.12 Component matrix of the core sediment M₁ (2011) using principal component analysis

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<td>.443</td>
<td>.157</td>
</tr>
<tr>
<td>Clay</td>
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<td>-.679</td>
<td>-.365</td>
<td>-.174</td>
</tr>
<tr>
<td>Silt</td>
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<td>.733</td>
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<td>-.036</td>
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</table>

### Table 4.13 Component matrix of the core sediment M₂ (2011) using principal component analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
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<td>.205</td>
<td>.373</td>
<td>.459</td>
</tr>
<tr>
<td>Co</td>
<td>.816</td>
<td>.066</td>
<td>-.385</td>
<td>-.172</td>
</tr>
<tr>
<td>Cu</td>
<td>.631</td>
<td>.609</td>
<td>-.325</td>
<td>-.057</td>
</tr>
<tr>
<td>Fe</td>
<td>.766</td>
<td>.134</td>
<td>.216</td>
<td>.476</td>
</tr>
<tr>
<td>Mg</td>
<td>-.480</td>
<td>.106</td>
<td>-.365</td>
<td>.560</td>
</tr>
<tr>
<td>Mn</td>
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<td>.577</td>
<td>.349</td>
<td>.022</td>
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<tr>
<td>Ni</td>
<td>.587</td>
<td>.604</td>
<td>-.379</td>
<td>-.105</td>
</tr>
<tr>
<td>Pb</td>
<td>.811</td>
<td>-.205</td>
<td>.004</td>
<td>-.120</td>
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<tr>
<td>Zn</td>
<td>.596</td>
<td>-.371</td>
<td>.145</td>
<td>.135</td>
</tr>
<tr>
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<td>.371</td>
<td>.421</td>
<td>.144</td>
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<td>Sand</td>
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<td>-.822</td>
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<td>.077</td>
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<tr>
<td>Clay</td>
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<td>.570</td>
<td>-.476</td>
<td>.215</td>
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<tr>
<td>Silt</td>
<td>-.210</td>
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Table 4.14 Component matrix of the core sediment N1 (2011) using principle component analysis

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</tr>
<tr>
<td>Co</td>
<td>.777</td>
<td>.271</td>
</tr>
<tr>
<td>Cu</td>
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<td>.297</td>
</tr>
<tr>
<td>Fe</td>
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<td>.821</td>
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<tr>
<td>Mg</td>
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<tr>
<td>Mn</td>
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<tr>
<td>Ni</td>
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<td>Pb</td>
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<tr>
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<tr>
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Table 4.15 Component matrix of the core sediment N2 (2011) using principle component analysis

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<th>3</th>
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</tr>
</thead>
<tbody>
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<td>-.012</td>
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<tr>
<td>Cu</td>
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<tr>
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<td>.409</td>
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<tr>
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<td>.620</td>
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<tr>
<td>Mn</td>
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<td>-.657</td>
<td>.243</td>
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</tr>
<tr>
<td>Ni</td>
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<td>.025</td>
<td>-.004</td>
<td>.077</td>
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<tr>
<td>Pb</td>
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<td>-.465</td>
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<td>Zn</td>
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<td>.258</td>
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<tr>
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<td>.541</td>
<td>.239</td>
</tr>
<tr>
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<td>.881</td>
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<td>.202</td>
<td>-.165</td>
</tr>
<tr>
<td>Cr</td>
<td>.445</td>
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</tbody>
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**********