



International Journal of Science, Architecture, Technology and Environment

Metal Distribution and Fractionation Profile of Surface Sediment in the Specific Zones of CES

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DOI: <https://doi.org/10.63680/ijstate1125028.024>

Abstract

This research focuses on the geochemistry of metal in total and in fraction using sequential extraction procedure (SEP). Sediments from 17 prominent regions of Cochin estuarine system (CES) was analyzed for metals, their fractions, grain size, total organic carbon (TOC) and CHNS. Approaches of factor analysis (FA) and geochemical indexes (GCI) were used to differentiate the sources of metals. Environmental risk of metals evaluated using risk assessment code (RAC) and mobility factor (MF). The metal fractionation in sediment enable to derive the sediment quality criteria of the estuary. Exchangeable (EXC) and carbonate bound (CA) fractions were dominated in the fractionation profile pose threat to the estuary.

Keywords: Metal, Fractionation, Sediment, Risk assessment, Cochin Estuarine System

INTRODUCTION

The world population has increased almost thrice in the last 60 years and is estimated to increase from about six billion currently to 8.3 billion by 2025 (Bowen and Crumbly 1999). Nearly, 60% of the world population is recorded to live in coastal areas and the present population of the coastal areas exceeds the global population of just 50 years ago. Majority of the people worldwide rely on seafood as the main source of protein in their diet and the consumption continues to increase globally. These food sources were contaminated from point source of pollution. Overpopulation, rapid urbanization and industrial revolution had discarded tremendous amounts of toxic pollutants into the ecosystem. Many of these wastes were potential sources for metal contamination that have the prospective threat for the balance of the aquatic environment. Metals that enter these environments will settle and become incorporated into the sedimentary reservoir (Peng et al., 2009). Therefore, analysis of metal content in sediments can reflect the pollution level of the water body. Previous studies on assessment of metals in sediments from estuarine and coastal areas are useful to assess the varying pattern of pollution status in the marine environment (Bellucci et al. 2002; Pekey 2006; Buccolieri et al. 2006; Anithamary et al. 2012). Trace elements have the ability to concentrate in organism directly from the water,

then accumulate and finally lead to biomagnification in the food chains, causing higher trophic organisms in contamination with elevated levels of pollutants. Hence it is imperative to understand the geochemical distribution and transport of metals in the sediment stratum in order to develop pollution control strategies and adopt suitable approaches for water quality management in the estuarine area.

CES, one of the largest tropical estuaries of India, is facing gross pollution problems due to the untreated or partially treated effluents from industries and domestic sectors. A number of investigations in recent years in this estuarine system conducted (Shajan 2001; Balachandran et al. 2005, 2006; Renjith & Chandramohanakumar 2009; Ratheesh Kumar et al. 2010; Paneer Selvam et al. 2012; Deepulal et al.2012) and revealed the high significance of this estuarine system for pollution studies. A review on these geochemical researches on sediment was carried out so far disclose that considerable amount of work still remains to entangle with regard to the metal geochemistry. Metal pollution levels in sediments of CES showed an increase in metal concentrations over the past several decades. The estuary potentially attributed to an annual loading of effluents from approximately 250 chemical industries situated in the northern part (Shibu et al., 1995; Paneer Selvam et al.2012; Martin et al. 2012). Toxic elements released into the aquatic system are often clubbed to particulate matter, which eventually settles and incorporates into the sediments. However major portion of the sediment bound metals may remobilize and be released back to the water column with a change in environmental conditions, and pose adverse effects on living species. The reported high enrichment factors of metals place the study region CES as one among the impacted estuaries in the world (Balachandran et al., 2005). Similarly, Ratheesh et al. (2010) reported severe enrichment for Cd in the CES. Moreover, the geoaccumulation index of metals also showed very strong evidence for metal pollution condition in these estuarine sediments (Ratheesh et al., 2010; Deepulal et al., 2012). Most of the earlier studies in CES were based on one time or seasonal sampling during a year from these areas. Though in any area in which distribution of pollutants in sediments collected over a considerable time period can provide a clue for the change in the environment pattern and such studies are limited.

In this context, the present work attempted to highlight the first detailed monograph on biennial distribution and fractionation of metals in the surface sediments from selected prominent regions of CES. Thus, this primer is designed to acquaint the basic concentration of metal, their distribution and fractionation associated with the surface sediments collected from 17 stations situated in the CES. The link between geochemical indices and ecological risk assessment of these metals in the study area were also incorporated. These 17 surface sediment samples were grouped in to three zones – **south**, **middle** and **north** based on the environmental variability such as the physicochemical and sediment characteristics. The results discussed hither are on the basis of three zones.

MATERIALS AND METHODS

STUDY AREA

Cochin Estuarine System (CES), one of the largest tropical estuaries of India is facing gross pollution problems following the release of untreated effluents from industries and domestic sectors. The major polluting industries in the region include fertilizer plant, oil refinery, rare earth processing plant, minerals and rutilles plant, zinc smelter plant, insecticide manufacturing unit and organic chemical plant. Reclamations over the past several decades have resulted in considerable shrinkage (40%) of the CES(Gopalan et al. 1983).The

development activities in and around the CES have added all the complexities and environmental dilemmas in this coastal niche. Further, construction of hydraulic barriers on the northern and southern limbs of the estuary to prevent saline intrusion into the upstream agricultural fields has imposed severe flow restrictions and increased sedimentation in the estuary (Menon et al., 2000). The rapid growth in the region accompanied by very high population growth, housing shortages, haphazard industrial and commercial improvement along transportation corridors have greatly increased the problems of urban development.

The study area was situated in the CES divided into three zones viz south, middle, and north.

South Zone: The zone situated in the fresh water region, originated from the southern bough of the Moovattupuzha. Major source of pollution is from sewage and agricultural runoff. This zone is far from the industrial effluents. **Middle Zone:** This zone has a perennial connection with the Arabian Sea and experiences an irregular encroachment of saline water intrusion there by making cradle grounds for diverse types of flora and fauna. With the advent of ICTT (International Container Transshipment Terminal) project, this area has become the backbone of the economy of the State of Kerala. It focuses on the enhancement of containerization in India, resulting in the improvement of trade and economic growth. Widespread activities like dredging and piling, along with anthropogenic inputs are carried out frequently. This zone was well regulated by a bund (namely Thannirmukham) which was constructed in order to prevent the intrusion of salt water into the paddy fields. The bund remains open during the monsoon season. **North Zone:** This zone originates from the industrial locale of Periyar - the life line of Kerala. Large scale industries on the river bank discharge effluents directly into these waterways resulting in the accumulation of varying amounts of pollutants in the Periyar River.

SAMPLING AND METHODS

Surface sediments (Figure 2.1) (top 0-5 cm) were collected from seventeen locations of CES during November 2009 and 2011 (Post monsoon). This was performed using a stainless steel grab sampler used repeatedly (three to five times) at each station, followed by thorough mixing of collected sediment on an aluminum tray in order to obtain a more representative sediment sample. All samples were kept in ice chest boxes on board and during transportation. The pH (Thermo Orion 420A+ model) of the sub samples was immediately measured and then they were frozen at 4°C for further analysis. These subsamples were air dried, finely powdered and used for further chemical analysis. Texture was determined using pipette analysis by Lewis 1984. For metal analysis 0.5g samples were treated with 5:1 mixture of concentrated HNO₃ and HClO₄ (Loring and Rantala 1992), and metal concentration was analyzed by AAS (Perkin Elmer 3110). Physicochemical parameters were determined according to standard procedures. Total organic carbon (TOC), CHNS were determined using analysers. Fractionation of metal was carried out according to Tessier et al. 1979. Statistical analysis (SPSS, 15.0) was done to understand the interrelationship between the parameters were utilized to assess the biogeochemical characteristics of the study region.

RESULTS AND DISCUSSIONS

PHYSICOCHEMICAL AND SEDIMENTARY CHARACTERISTICS

General physicochemical properties of overlying water and sedimentary parameters were studied which could help to understand the metal flux in the estuary. Salinity was ranged between 0.81 PSU to 32.95 PSU. Dissolved oxygen varied between 1.96 mg/L to 6.95 mg/L in the middle and north zone respectively. Sedimentary parameters showed that the pH values varied from 5.4 to 8.7 and highest value was noted at the middle zone in the first sampling campaign (2009) and a minor variation exhibited during the second sampling (2011). Eh ranged between -109 mV to +286 mV. Texture analysis showed a progressive increase of fine fractions at southern (96%) and northern part (80%) of the estuary and coarse grains dominated at the middle part of the CES (80-95%) during 2009 and it was found a mixed nature with minor fluctuations during 2011 sampling periods. Percentage of TOC ranged from 0.34 to 6.25 and was significantly higher at southern and northern part of the estuary.

BIENNIAL METAL DISCREPANCY IN THE SURFACE SEDIMENTS OF CES

In recent years, CES has become one of the distinguished regions in India due to the vast industrial and urban development activities aroused in various sectors. As a part and parcel of this, a variety of chemicals in turn discharges enormous wastes thrown out into the aquatic system and contribute significant enhancement of metal levels.

Even though enough work has been carried out so far in this respect within the estuary (Shajan 2001; Balachandran et al. 2005, 2006; Renjith & Chandramohanakumar 2009; Ratheesh Kumar et al. 2010; Paneer Selvam et al. 2012), this research work also details the continuous monitoring of metal variations in a two year gap (2009-2011) period. The residual metal concentrations were given in Table 1.

Metal distribution in the first sampling campaign (2009) was detailed in the initial part of this section and the results were compared with the analysed concentration levels in the second sampling.

The concentration of Cd ranged from 0.25 mg/Kg to 3.24 mg/Kg in southern zone at stations 4 and 5 respectively. In middle zone, Cd content was varied between 1.34 mg/Kg (station no.11) to 11.53 mg/Kg (station no.10). Northern zone revealed as the minimum and maximum content of Cd at station no.15, 0.7 mg/Kg and at station no.14, 32.52 mg/Kg. 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. Similar observations were reported (Padmalal et al. 1997) and noticed a high concentration of Cd in the same vicinity of the estuary. Other studies on Cd in estuarine sediments have reported for polluted areas like Mezica valley (Slovenia), had Cd concentrations in the range of 20.5–130.0 mg/Kg (Svete et al. 2001; Tack and Verloo 1999), whereas in unpolluted areas, Arosa estuary NW Spain were within the range of 1.56–8.0 mg/Kg (Santamaria-Fernandez et al. 2005; Svete et al. 2001). On comparison with the earlier reports (Table 2) with in the CES and other impacted estuaries, Cd concentration was heavily magnified. Earlier results reported by Martin et al. 2012 also justify the above trend. These inferences of Cd distribution establishes severe contaminant load of Cd in the northern part of the estuary. These outcomes were strongly agrees with the previous published research reports (Ratheesh *et al.*, 2010; Martin *et al.*, 2011; Paneer Selvam *et al.*, 2012). Finally, the sediment samples investigated in the study area are considered as moderate to severely polluted by Cd.

Among the southern zone stations, concentration of Co was higher at station no.5 (21.06 mg/Kg) and BDL at

stations 3 and 6. Middle zone showed intensified value for Co at station no.10 (72.75 mg/Kg) and diminished at station no.8. In the north zone, Co content was high at station no.16 (91.34 mg/Kg) and BDL at station no.15. The concentration of Cobalt observed in the present study was above the permissible limit (2 mg/Kg) which resulted severe pollution in the northern part of the estuary and observed very high concentration as compared to the earlier reports of the same aquatic system (Ratheesh *et al.*, 2010; Martin *et al.*, 2011; Paneer Selvam *et al.*, 2012).

In south zone, Cr content showed from BDL (station no.3) to 132.41 mg/Kg (station no.4). Concentration of Cr in the middle zone ranged between BDL (station nos. 7,10) to 125.8 mg/Kg (station no.8) and it was found only at station no.15 (54.17 mg/Kg) in the northern region of the estuary. Cr content was high at central part of the estuary. On comparison with the different SQGs (Table 3), the content of Cr was above the permissible limit (25-75 mg/Kg). Cr was found to be of elevated values as compared with other estuaries (Table 2). Paneer Selvam *et al.* 2012 reported a higher concentration (200.9 mg/Kg) than the above trend.

Southern zone showed greater content of Cu at station no.1 (43.80 mg/Kg) and diminished content at station no.6 (11.85 mg/Kg). Cu content was high (55.49 mg/Kg) and low (8.78 mg/Kg) at station no. 10 and 11 respectively in middle zone. In the northern region of the estuary Cu concentration was dominant at station no.14 (151.54 mg/Kg) and decreased at station no.15 (10.44 mg/Kg). Greater concentration of Cu was observed at northern part of the estuary. The Copper concentration cited in this study was moderately above the permissible limit (16- 270 mg/Kg) as given by different SQGs listed in Table 3. It has been reported that the concentration of Cu in polluted areas ranges from 20.0 to 343.0 mg/Kg, while in unpolluted areas, it will be between 1.0 and 13.0 mg/Kg (Santamaria-Fernandez *et al.* 2005; Spencer and MacLeod 2002; Sullivan and Taylor 2003). Cu concentration in this study revealed moderate pollution. The amount of Cu was increased in this study except two, one within the system reported by Mahesh *et al.* 2012 (166.14 mg/Kg) and other was from Ganga by Purushothaman and Chakrapani 2007 (717.09 mg/Kg).

At station no.5 noted as high value for Fe (12372.75 mg/Kg) and low at station no.1 (286.46 mg/Kg) in the south zone of the estuary. In the middle region, increased Fe concentration was observed (10848.3 mg/Kg) and decreased the content as 3642.11 mg/Kg at station nos: 7 and 11 respectively. Northern zone exposed heavy Fe content (68544.57 mg/Kg) at station no.14 and less (2017.89 mg/Kg) at station no.15. Heavy load of Fe was found in the northern region of the estuary. Residual level of Fe was increased in the study area as compared to the previous reports (Table 2), but there are exceptions showing heavy concentration of these by Purushothaman and Chakrapani 2007 (152700 mg/Kg) and Mahesh *et al.* 2012 (115200 mg/Kg).

Concentration of Mg in the south zone was high at station no.1 (64.98 mg/Kg) and low at station no.3 (18.35 mg/Kg); middle zone ranged as 28.97 mg/Kg (station no.11) to 264.12 mg/Kg (station no.10) and in the northern region the concentration ranged between 27.73 mg/Kg (station no.15) and 306.94 mg/Kg (station no.13). These results showed that Mg was intensified in the north zone of the estuary. On comparison with Table 2, Mg showed a less amount for the present study than the previous report in CES by Ratheesh Kumar *et al.* 2010 (17200 mg/Kg).

Content of Mn in the southern zone showed lower (1.65 mg/Kg) at station no.6 and high (508.18 mg/Kg) at station no.1. In the middle zone, Mn content was dominant at station no.9 (127.04 mg/Kg) and lower at station no.11 (0.18 mg/Kg). In the northern part of the estuary, less concentration of Mn was found at station no.15 (1.07 mg/Kg) and greater was noted at station no. 16, 17 (9.93 mg/Kg). Mn content showed to be high in the southern part of the estuary. The Manganese concentration analysed in this study was moderately above the

permissible limit (30 - 3000 mg/Kg) as given by different SQGs listed in Table 3. Concentration of Mn was high in this study as compared within the system and the other reports listed in the Table 2.

The southern part of the estuary showed greater Ni content at station no.1 (55.56 mg/Kg) and less at station no.6 (39.87 mg/Kg). Middle zone revealed high content of Ni at station no.7 (38.65 mg/Kg) and diminished at station no.11 (35.56 mg/Kg). In the North zone, Ni ranged between 51.57 mg/Kg (station no.13) and 70.65 mg/Kg (station no.17). Thus Ni revealed a high concentration in the southern part of the estuary, which was accounted by heavy sewage and domestic runoff. The Nickel concentration cited in this study was moderately above the permissible limit (16- 315mg/Kg) given by different SQGs listed in Table 3. Concentration of Ni was enormous in this study as compared within the system and the other reports listed in the Table 2.

Pb concentration > 100 mg/Kg in most of the stations, south zone ranged from 104.17 mg/Kg (station no.3) to 135.23 mg/Kg (station no.2), middle zone ranged between 109.62 mg/Kg (station no.11) and 142.22 mg/Kg (station no.7), northern region, noted high concentration at station no.17 (131.21 mg/Kg) and low at station no.12 (79.70 mg/Kg). Earlier, high levels of Pb, 26–630 mg/Kg, were detected in the sediments of polluted areas (Aluoupi and Angelidis 2001; Leivuori 1998; Everrarts and Fischer 1992) and low levels of Pb, 0.5–60 mg/Kg, were found in the sediments of unpolluted regions (Leivuori 1998) reported elsewhere. The Lead concentration cited in this study was above the permissible limit (12.5- 400 mg/Kg) given by different SQGs listed in Table 3. The Pb concentration recorded in the current study were highly intensified at the central part of the estuary. The Pb content was greater in this study except two previous reports, one within the system reported by Mahesh et al. 2012 (221.31mg/kg) and other was from Ganga by Purushothaman and Chakrapani 2007 (466.32 mg/Kg).

The concentration of Zn varied from 4.55 mg/Kg to 5.47 mg/Kg in southern zone at stations 6 and 4 respectively. In the middle zone, Zn content was varied between 4.95 mg/Kg (station no.8) to 233.18 mg/Kg (station no.10). Northern zone revealed as a minimum content of Zn (station no.15, 5.47 mg/Kg) and maximum at station no.14 (269.57 mg/Kg). Northern and middle region were Zn enriched zones. Previous studies showed that Zn concentrations in the polluted sediments were up to 4,000 mg/Kg (Everrarts and Fischer 1992; Spencer and MacLeod 2002) and in unpolluted sites, it ranged from 9 to 162 mg/Kg (Ridgway et al. 2003). The Zinc concentration analysed was moderately above the permissible limit (70-820 mg/Kg) given by different SQGs listed in Table 3 and will lead to generate moderate pollution in the study area.

On comparing the concentration of metal obtained in the first sampling periods (2009) with that of second (2011) revealed that similar trend was observed for Cd, Co, Cu, Fe, Mn and Pb; but for Ni and Zn, there is a slight deviation in the distribution pattern. Ni had high value; whereas Zn had lower than that of the first sampling campaign (2009). The result obtained in biennial evaluation of metal concentration values in the present study with the earlier research reports in the estuary and the other recognized polluted area are given in Table 2. Comparison of metal concentration with the maximum values reported worldwide generate most of the inference that metals were of the same magnitude or even higher than those information for other polluted estuaries, placing the region as one among the impacted estuaries around the world.

Major enrichment for the metal concentration was observed in the northern and middle zone in both the sampling (2009 and 2011) periods. These are in close agreement with previous report as levels of Fe, Mn, Ni, Zn, Cd, Co, Cr, Cu and Pb in the surficial sediments of the estuary which rendered significantly high concentration in the northern parts of the estuary (Nair *et al.* 1990; Balachandran *et al.* 2005; Martin *et al.* 2012). Cr and Mn in the sediments of the first sampling showed exceptions, as they were intensified in the

southern zone.

Metals such as Fe, Mn, Ni, Zn, Cd, Co, Cr, Cu and Pb generally exhibited higher levels in the northern and central regions of the estuary. This is due to the dynamic nature, whereas the northern and southern zone showed flow restrictions and hence showed more sensitive to the accumulation of contaminants (Balachandran 2008). 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 were detected towards the central estuary as 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 were characterized in the southern estuary, which receives agricultural wastes from Kuttanad Paddy fields.

The observed results showed high organic matter content and metal concentrations in the northern part of the estuary revealing fine particle dependence of these parameters. Generally, $\text{TOC} > 5\%$ indicate the polluted nature of the estuary. The poor dependence between organic carbon and the metals indicates that metal enrichment in the estuary may be initiated by inorganic processes, such as precipitation and scavenging by hydroxides of Fe and Mn. Fe and Mn in the estuary were accumulated and spatially segregated, as a consequence of their different flocculation properties. Furthermore, both the increased Eh and low pH values in the southern and northern part of the study region also favour the sorption of metals in the sediment. $\text{TOC}:\text{TS}$ ratio also well supports these results. The possible enrichment mechanism appears to be estuarine coagulation and flocculation of elements as colloids in association with hydrous iron oxides under fluctuating salinity in the entire study area. Inadequate flushing of pollutants released in the flow restricted water bodies could promote coagulation or co-precipitation of metals under the prevailing ionic (salinity) condition (Cobelo-Garcia and Prego, 2004). These processes could be critical in the study area, CES revealing fluctuating salinity between 0.81 PSU and 32.95 PSU which are characterized the intensification of metal content.

EVALUATION OF SEDIMENT POLLUTION WITH SEDIMENT QUALITY GUIDELINES (SQG)

The level of pollution in the aquatic system can be simply assessed by different worldwide used SQGs. Detailed distribution were given in Table 3. The ranges of metals in their comparative assessment are given in Table 4.

In most of the stations, all the metals identified had found to be of elevated concentration as compared to different SQGs. The US National Oceanic and Atmospheric Administration (NOAA) guidelines were used as interim measures to assess whether the concentrations of metals in sediments could have adverse biological impacts. Long et al 1995 suggested two guideline values, namely, the ERL (effective range: limit) and ERM (effective range: medium) delineating three concentration ranges of a particular metal. If a metal occurs in concentrations below ERL value, effects on the biota would rarely be observed. At concentrations $\geq$ ERL but $<$ ERM, the biota could "occasionally" be affected by the pollutant, whereas at concentrations $\geq$ ERM, effects would be expected to occur "frequently". Concentration of Cd in both the periods of study was higher than ERM indicating the frequent chance of adverse effect to biota. The values of Cu and Pb exhibit between ERL and ERM limit generating an occasional effect to the biota. For Ni, showed in between ERL and ERM and also greater than ERM, created occasional and frequent effect to aquatic biota. Zn concentrations were less than ERL and in between ERL to ERM which generate rare and occasional pollutant effect to the aquatic biota. Zonal comparison of the adverse effect to biota gave the order as North Zone $>$ Middle Zone $>$ South Zone.

GEOCHEMICAL CHEMICAL INDICES (GCI)

Majority of studies on the sediment contamination with metals come down to the determination of their content in samples without considering the specificity of their random and systematic variations. A good indicator of environmental pollution of sediments by metals can be assessed by measuring geochemical indices (GCI). The different GCI used in this study are enrichment factor (EF), contamination factor (CF), geoaccumulation index (*I_{geo}*) and pollution load index (PLI).

1. Enrichment Factor (EF)

Enrichment factor was attempted to differentiate between the metals originating from human activity and those from natural weathering processes. It is a powerful tool for the regional comparison of metal content in sediments and can be applied to determine enrichment of the studied metals with respect to crustal average (Nolting *et al.* 1999). Since Al, Fe, and grain size all tend to co-vary, the use of a single normaliser can often represent several underlying geochemical relationships. In this work, EFs were computed by normalizing with Fe (Blomqvist *et al.* 1992). Iron is a conservative element during diagenesis (Berner, 1980) and its geochemistry is similar to that of many metals both in oxic and anoxic environments. Natural concentrations of Fe in sediments are more uniform than Al and beyond the influence of humans which justify its use as a normaliser (Daskalakis and O'Connor, 1995).

Mg has minimal enrichment ($EF < 3$) in all the studied zones in the first sampling period, 2009. Mn had high enrichment ($EF > 50$) in the stations, sampled from south zone and minimal enrichment ($EF < 3$) in the middle and north zone. An exceedingly high enrichment ($EF > 50$) for Ni was noticed in south zone. In the middle-north region it had moderate to significant enrichment ($EF = 3-30$). Zn had significant enrichment ($EF = 1-9$) in the south zone and in the remaining zones revealed a minimal enrichment ($EF < 3$). Cd, Co, Cr, Cu and Pb had out of due proportion of enrichment ($EF > 50$) in the southern zone. Middle and northern zone had significant enrichment ($EF = 1-10$) for Co, Cr and Cu. Both Cd and Pb terrify by its magnitude of their enrichment ($EF > 50$), Co and Cu had moderate enrichment ($EF = 3-5$) and Cr had significant enrichment ($EF = 2-16$).

In the second set (2011) Mg, Mn and Zn were showed minimal improvement ($EF < 3$) where Ni had significant observation ($EF = 1-11$). For Cd showed rich in enrichment ($EF > 50$) was noticed in both the southern-northern region whereas very high enrichment ($EF = 25-50$) was noted in the middle zone. Co had moderate embellishment ($EF = 3-5$) in the southern zone and significant enrichment ($EF = 2-18$) in middle and north zone. In all the zones, Cr specifically showed minimal enrichment ($EF < 3$). For Cu the study inferred high enrichment ($EF > 50$) in the south zone and significant in middle- north region. Pb showed significant enrichment ($EF = 2-11$) in south- middle sites and extreme enrichment ($EF > 50$) at the north zone. To unveil, the northern and southern part of the estuary was magnified with all the toxic metals and it had a close agreement with the previous reported EF in the estuarine system (Ratheesh *et al.* 2010. Martin *et al.* 2012). This may be inferred due to the weak flow and the huge input of industrial effluents, which were the real picture in the northern estuary and earlier reports by Thomson 2002 also support these results. An EF value less than 1.5 suggests that, the metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002 and Feng *et al.* 2004). However, an EF value greater than 1.5 suggests that a significant portion of the metal is delivered from non-crustal materials, or non natural weathering processes (Feng *et al.*, 2004). In both the sampling period, most of the metals (Mn, Ni, Zn, Cd, Co, Cr, Cu and Pb) had $EF > 1.5$ indicating the exogenic input of these metals.

2. Contamination Factor (CF)

The level of sediment contamination by a metal is often expressed in terms of a contamination factor calculated as: Contamination Factor (CF) = Metal content in the sediment/ Background level of metal, where $CF < 1$ refers to low contamination, $1 \geq CF \geq 3$ means moderate contamination, $3 \geq CF \geq 6$ indicates considerable contamination, and $CF > 6$ indicates very high contamination. Metals in the study area exposed moderate contamination ($CF=1-3$) for Ni and low contamination ($CF < 1$) for Mg, Mn and Zn in both the sampling period. Contamination factor was high ($CF > 6$) for Cd, moderate ($CF = 1-3$) for Co and Cu, low ($CF < 1$) for Cr and $CF = 3-6$ for Pb in the study area during first sampling (2009). However, the sediment collected in the next set (2011) showed low ($CF < 1$) contamination for Cr; but all the other metals had very high ($CF > 6$) contamination factor. On comparison between the zones, the northern region of the estuary was vulnerable for severe metal contamination especially for Cd and was supported by the earlier reports by Ratheesh et al. 2010, Martin et al. 2011 and Paneer Selvam et al. 2012.

3. Geoaccumulation Index (Igeo)

The geoaccumulation index, Igeo values were calculated for different metals as introduced by Muller (1969) is as follows: $I_{geo} = \log_2 (C_n / 1.5 * B_n)$ Where C_n is the measured concentration of element 'n' in the sediment sample and B_n is the geochemical background for the element n. The factor 1.5 is introduced to include possible variation of the background values that are due to lithogenic variations. Igeo studies in sediments collected in first sampling campaign (2009) revealed uncontamination ($I_{geo} < 0$) for Fe, Mg, and Mn in all the zones of the estuary. But Ni and Zn showed moderate to high ($I_{geo} = 1-3$) pollution load in north and middle zone of the estuary. South zone is uncontaminated ($I_{geo} < 0$) for Ni and Zn. Moderate to high ($I_{geo} = 1-3$) contamination for Cd, moderate ($I_{geo} = 1-2$) with Pb, and uncontaminated to moderate ($I_{geo} = 0-2$) contamination for Cr, Co and Cu were observed at the south zone. Middle zone opened heavily to extremely contaminated ($I_{geo} = 3-6$) with Cd, moderately to heavily ($I_{geo} = 1-5$) contaminated with Pb and moderate ($I_{geo} = 1-2$) contamination for Co, Cr and Cu. North zone showed extreme contamination for Cd. For Co, Cr and Cu moderate ($I_{geo} = 1-2$) contamination were observed. Pb revealed as moderate to heavy ($I_{geo} = 1-5$) contamination. For sediments in the second sampling campaign (2011), Cd showed extreme contamination and all the other metals showed moderate contamination in the entire zones. Igeo studies confirm the contamination of the study area for Cd, Co, Cr, Cu, Pb and Zn. This was in agreement with results reported by Paneer Selvam *et al.*, (2012).

4. Pollution Load Index (PLI)

The extent of pollution by metals has been assessed by employing the method based on Pollution Load Index (PLI). $PLI = n\sqrt{\text{Product of } n \text{ number of CF values}}$, Where CF = contamination factor and n= number of metals. PLI provides a simple, comparative means for assessing a site or estuarine quality: a value of zero indicates perfection, a value of 1 indicates only baseline levels of pollutants present and values > 1 would indicate progressive deterioration of the site and estuarine quality. The sampling period, 2009 sediment PLI exposed low contamination ($PLI < 1$) in the study area for major metals (Fe, Mg, Mn, Ni, Zn) and severe load ($PLI > 1$) for minor metals (Cd, Co, Cr, Cu, Pb). But for the next set, PLI was high ($PLI > 1$) revealing greater pollution load for all the metals. This also confirms the polluted nature of the estuary.

Thus GCI results establishes metal enrichment in the study area and support it as a seriously impacted estuary.

STATISTICAL ANALYSIS

Correlation analysis revealed a strong positive interrelationships among all the metals in sediments which indicate that the northern, central, and southern parts of CES are influenced by direct point sources of contaminants and earlier published research works also support these facts (Thomson, 2002; Martin et al. 2011). Metals have not shown any significant correlation with sediment texture. This is well supported by Selvam et al. (2011) who found that Zn and Cd were not controlled by any size fraction. The same results have also been observed by Padmalal et al. (1997). This shows that the lithogenic component is not a controlling factor for metals in sediments and the high concentrations were affected by anthropogenic discharges. The absence of any significant correlation of the metals with texture, TOC, total C and total N in the estuarine sediments also reflects that the input is not through the natural weathering processes. Most of the metals showed a significant increase in the estuarine sediments and justifies the point sources contamination. In both the sampling period (2009 and 2011) observed insignificant granulometric, organic matter and elemental dependence for the metals which confirmed their anthropogenic origin. Hence, the absence of a significant correlation between metals and any of the sediment is physico-chemical parameters might be owed to the high influx of contaminants from the industries, which forms organic complexes through flocculation (Zourarah et al. 2007). Previous works do not find any strong associations of metals with organic carbon in the sediments of the Cochin estuary, and thus it is still a matter of controversy that whether metal distributions result from grain size or organic matter content (Nair et al. 1990; CPCB 1996).

Principal component analysis (PCA) was widely used as multivariate statistical tool to assess the origin of metals in sediment. PCA was performed on the entire data set, in order to identify the major estuarine process that leads to the trace metal enrichment. PCA for the first set (2009) of 10 metal distribution reduced to 4 factors (Table 3.4) in which first factor contribute to 40.196% had strong positive loading of Cd, Co, Cu, Fe, Mg, Ni and Zn and negative loading for Cr, Pb, Mn and S. This reflects that the redox process controlling the metal distribution. Second factor positively loaded by Cd, clay, silt, Mn, TOC and C and negative for sand with a variance of 17.959%. This could be attributed to the flocculation and sedimentation of organic matter and granulometric dependence of these metals. Mn found to be made the third factor of variance 16.340% and was negatively loaded for Pb, C, H, N and S. The remaining factor, factor 4 has less importance on the total variance was accounted. The second set (2011), principal component analysis of 10 metal distribution reduced to 4 factors (Table 3.5), in which first factor contribute to 33.78% and is laden up of Cd, Co, Cu, Mn and Ni. Second factor burdened by Cr, Pb and Mg and had a variance of 16.192%. The third factor of variance, 13.876% found to be made of Cd and Cu. The remaining factor had less importance on the total variance was accounted.

The overall results of metal distribution in the surface sediment of CES were concluded as:

- On comparing with the metal concentration in both sampling (2009 and 2011) periods showed major enrichment in the northern and middle zone.
- Similar trend was observed for Cd, Co, Cu, Fe, Mn and Pb in both the sampling periods; but for Ni and Zn there is a slight deviation in pattern. Ni had high value; where as Zn had low value than that of the first sampling campaign (2009).

METAL FRACTIONATION

The first part of the study conveyed on the distribution of metal along the CES that demonstrate heavy rate of pollution in the studied estuarine system. GCI and statistical results established that CES is facing serious environmental pollution threat. Even though environmental protection measures are improving, the development rate of the Cochin city suggests that industrial, domestic, and agricultural pollutant sources are likely to increase enormously and cause serious health problems. The system contamination in detail can be confirmed by studying the chemical forms of metals in the sediment. As these different metal forms generally exhibit different chemical entities, the measurement of the total concentration of a particular metal provides little information regarding the potential interactions with the abiotic or biotic components present in the environment. The partitioning of sediment-bound metals could provide significant insight into the factors influencing the bioavailability of metals. Therefore adopting the selective sequential extraction procedure would help to assess the partitioning of sediment associated metal and their accumulation mechanisms in sediment which lead to the metal mobility, biological availability and chemical behaviour. The extent of pollution hazard and to understand the metal dynamics in the CES, the intensities of different chemical fractions in the sediment have to be looked further. Therefore, this section describes the geochemical distribution of metal fractions in the sediments of CES. Chemical fractionation of metals viz- exchangeable (EXC), bound to carbonate (CA), organic matter bound (oxidisable) (OM), iron and manganese bound (reducible) (FMO) and residual (RES) (Tessier et al. 1979; Salomons et al. 1988) forms were encountered and were depicted in Figure 2.

Metal found in each fraction had specific and special features, in which exchangeable and carbonate fractions are considered to be weakly bound and are equilibrium with the aqueous phase and become readily available to the biological systems. Some amounts of metals are strongly bound to Fe and Mn oxides and organic matter, acting as internal reservoirs. On the other hand, the metals in the residual fraction are not available under normal conditions.

EXC fraction of metals can be easily released back to the water column which may cause secondary pollution and subsequent health risk to the sediment dwelling consumers in the aquatic niche. The amount of metals in this phase indicated the environmental conditions of the overlying water bodies. Metals in this fraction are the most mobile and readily available for biological uptake in the environment (Singh et al., 2005; Zakir et al., 2008). The exchangeable fraction recovered in the sediments of 2009 sampling period revealed major metal (Fe, Mn, Ni and Zn) distribution and expressed in the order as south zone: $Fe > Mn > Zn > Ni$; middle zone: $Zn > Fe > Mn > Ni$ and north zone: $Mn > Zn > Fe > Ni$. Comparing the zones, samples in the first sampling campaign (2009) showed that the north zone is enriched with exchangeable fraction and identifies the threat to the environment. In this study, Cd is intensified in northern part of the estuary. Co had greater content in all the zones of the study area. Cr had increased values in the southern and northern zone of the estuary than the middle zone. Cu was analysed in greater content in north zone, then to the middle zone and finally to the south zone. In the northern region of the estuary, Pb was found in higher amount. In the next set (2011) middle and north region of the estuary had same variation as that of major metal as: $Mn > Fe > Zn > Ni$, but the southern zone, the dynamics showed as: $Fe > Mn > Zn > Ni$. Minor metal concentration in all the zones of the estuary was in the order $Cd > Co > Cu > Pb > Cr$.

CA fraction is initially present as metal salts in sediment and readily available following a slight lowering of pH (Turner and Olsen (2000)). Association of metals with this fraction is probably the best example of human-induced influence in the sediments of the study area. Sediment in the first sampling campaign (2009), Fe and

Zn content in CA fraction was high at north zone, followed by middle and ends to the south zone. Mn content was higher in the middle zone and lower in the south and least in the north zone of the estuary. Ni in this fraction was found BDL. Cd and Cu content in this fraction was intensified at north zone, smaller to the middle and least to the south zone of the estuary. Co and Pb content was higher in the all regions of the estuary. Concentration of Cr in this fraction was BDL. All zones of the estuary in the second sampling (2011), the major metal distribution order is as: Fe > Mn > Zn > Ni; minor metals Cd, Co, Pb were BDL in many of the stations of the estuary and found only in few stations of the northern region. Similarly Cu and Cr were also intensified in the northern part of the estuary.

Metal adsorbed in sediments are found in FMO fraction. These oxides become unstable by reduction or acidic transformation of sediments. Sediments in first (2009) sampling, Fe, Mn, Zn fractions were intensified in all the zones of the estuary. Ni in this fraction was BDL. Present study revealed that Cd, Co, Cu and Pb fractions were highest in the three zones of the estuary and Cr fraction was BDL. In the next set (2011), the major metal varied as Fe > Mn > Zn > Ni in all the zones of the estuary and strengthen in the northern region. All the minor metals were abundant in northern region of the estuary and showed as Cr > Co > Cu > Pb > Cd.

The affinity of metals for organic substances and their decomposition products are of great importance for the release of the metals into the water column. Metal bound to this fraction is in chelated form assumed to reflect strong association with sediment organic material and can be immobilized in both oxidizing and reducing condition. During the first sampling period (2009), Fe, Mn and Zn fractions showed similar enrichment in the three zones of the estuary. Ni was BDL in this fraction. The present effort showed that Cd and Co had less content compared to Cu and Pb in this fraction. But Cr was BDL in this fraction. Sediments collected in 2011 sampling period revealed major metal distribution as Fe > Zn > Mn > Ni, for minor metal, Cd was BDL and others are in the order as Cr > Cu > Co > Pb.

The metal present in the residual fraction were in the form of metal precipitates which could be used as a baseline data for the assessment of the degree of contamination of the system. The association between metals and the residual fraction of uncontaminated sediments are so strong that metal association with non-residual fraction has been used as an indicator of anthropogenic enrichment (Sutherland et al., 2000; Zakir, 2008). The residual fraction is increased in all the three zones of the estuary. Residual fraction showed major metal abundance and was in the order as: Fe > Mn > Ni > Zn and that for minor metal the pattern of distribution was: Cr > Cu > Pb > Co > Cd. In the next sampling period (2011), all the metals heap on in this fraction. The major and minor metal variation illustrate as Fe > Mn > Ni > Zn and Cr > Pb > Cu > Cd respectively.

Comparison of sediment in two year gap revealed greater concentration of Cd and Mn in the exchangeable fraction for the sediment samples in 2011 sampling. Whereas Co, Cr, Cu, Fe, Ni and Pb were abundant in the residual fraction. On comparing the metal concentration between the sampling periods, greater concentration was found in the exchangeable fraction which revealed extensive pollution in the aquatic realm. Metal fractions were high in the residual form of the fraction during both years of study and proved mainly as anthropogenic enrichment component. All the fractions concludes greater content in the year 2009 than 2011. These revealed greater availability of the metals in the ecosystem, and in turn concentrate by the aquatic biota and finally create damage to the ecosystem.

BIENNIAL METAL FRACTIONATION PROFILE

The chemical partitioning trend was found to be different for each metal and discussed separately.

1. Cadmium:

The distribution of cadmium fractions biennially follows as:

Exchangeable fraction > Bound to carbonate fraction > Bound to Fe and Mn oxide > Residual fraction > Fraction bound to organic matters [2009].

Exchangeable fraction > Bound to Fe and Mn oxide > Residual fraction > Bound to carbonate fraction > Fraction bound to organic matters [2011].

High enrichment of Cd in the mobile fractions indicating its high mobilization potential in the study area. According to Muniz et al. (2004), the changing pH and redox conditions were of primary importance for the potential release of metals from sediment. Therefore, a great percentage of this metal can be mobilized from sediment to water with a decline in pH (from carbonate fraction) or a decrease of redox potential (from oxide fractions), due to the input of organic matter or the depletion of dissolved oxygen content (1.96 mg/L). In the present study, the northern and southern zones are vulnerable for this mechanism which in turn results release of Cadmium. Low organic and residual fractions of Cd in the entire study area illustrates the authigenic association with riverine sandy sediments (Nair et al. 1991). High Cd content in the exchangeable fraction was also found in the river sediments by Morillo et al. (2002) and marine sediments by Guevara-Riba et al. (2004) and Cuong and Obbard (2006). Changes in the ionic composition, influencing adsorption-desorption reactions, or lowering of pH could cause remobilization of metals from this fraction (Marin et al. 1997). Previous studies have shown that Cd has a good capacity to form soluble Cd-Cl complexes (CdCl^+ , $\text{CdCl}(\text{aq})$, CdCl_3^- , CdCl_4^{2-}) with Cl^- even at low Cl^- concentrations, which could promote Cd desorption from sediment particles (Doner 1987; Rasa et al. 2006) and enhance the extraction of the acid-soluble fractions (Makino et al. 2007). Therefore, it was assumed that the formation of Cd-Cl complexes in the studied sediments in the CES, with high Cl^- concentrations in the middle zone (32.95 psu), might induce Cd desorption from the sediments and hence result the Cd percentage increase in the exchangeable fraction.

2. Cobalt:

The relative distribution of different fractions of cobalt in the biennial sampling was in the order as:

Exchangeable fraction > Residual fraction > Bound to carbonate fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters [2009].

Residual fraction > Exchangeable fraction > Bound to Fe and Mn oxide > Bound to carbonate fraction > Fraction bound to organic matters [2011].

Exchangeable and residual fraction were intensified in the study area resulting the anthropogenic effect with geogenic origin of these metal. Fractions bound to organic matter had minimum concentration in both years of the sampling sites. Low organic fractions in both periods of study indicate the authigenic association with riverine sandy sediments (Nair et al. 1991) and this had close agreement with the results of the middle region of the estuary which constitute the coarse texture and less organic carbon.

3. Chromium:

Chromium fraction distribution was following the order as

Residual fraction > Exchangeable fraction > Bound to carbonate fraction = Bound to Fe and Mn oxide = Fraction bound to organic matters [2009].

Residual fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters > Bound to carbonate fraction > Exchangeable fraction [2011].

Cr was mostly concentrated in the residual fraction. Other studies carried out in Spain, in Singapore and in China (Martin et al. 1998; Morillo et al. 2004; Guevara-Riba et al. 2004; Cuong and Obbard 2006; Yuan et al. 2004) also showed that Cr was found mainly in the residual fraction in all the samples. These results indicate that Cr has the strongest association with the crystalline structures of sediments. Biennial comparison of Cr fractions revealed a decline in the bioavailable fraction in the second sampling campaign (2011) which may be due to the absence of its carbonate fraction in the natural environment (Förstner and Wittmann 1983). This establishes the inference as the bioavailable form of Cr in the system which is removed generating threat to the CES by biomagnification.

4. Copper:

Biennial variation of Copper was in the order as

Residual fraction > Fraction bound to organic matters > Bound to Fe and Mn oxide > Bound to carbonate fraction > Exchangeable fraction [2009].

Residual fraction > Fraction bound to organic matters > Bound to carbonate fraction > Exchangeable fraction > Bound to Fe and Mn oxide [2011].

The residual fraction and bound to organic matter were the dominant fractions in the entire study area. Residual fraction abundance generate less toxic behaviour of this metal. A significant amount of Cu is associated with the reducible fractions either by co-precipitation or by sorption onto pre existing coatings under physicochemical conditions (Panda *et al.*, 1995). Ho (2000) suggested that the high affinity of organic ligands create Cu in sediments more stable, leading to the suppression of diffusion and dispersion of Cu. In addition, organic compounds under the reduced condition may be more active to bind with Cu by complexation rather than by ion exchange (Balasoiu, 2001). This strong effect can also be attributed to the fact that copper easily forms complexes with the organic matter due to high stability constant of organic Cu compounds (Kotoky, 2004). Organic matter exhibits a high degree of selectivity for divalent ions and hence the organic bound Cu fraction is an important fraction in the sediments and is not available to the biological activity. Hence, the organic matter plays an important role in the immobilization of Cu, but mineralization of the host organic material under oxidizing conditions will release Cu into the overlying water column (Jain et al. 2007). Significantly high Cu concentration in organic and sulfide fraction in the sediments of Periyar River and Cochin estuary can be attributed to the high stability constant of organic-Cu compounds and the earlier studies of Lasheen and Ammar 2008 establishes the same.

5. Lead :

The biennial variation in the partitioning pattern of Pb was different and the order is given as:

Exchangeable fraction > Residual fraction > Fraction bound to organic matters > Bound to carbonate fraction > Bound to Fe and Mn oxide [2009].

Residual fraction > Bound to carbonate fraction > Bound to Fe and Mn oxide > Exchangeable fraction > Fraction bound to organic matters [2011].

Residual and bio available fractions were intensified in the entire study area. The high concentration of Pb in residual fractions might be due to the incorporation of Pb in alumino- silicate minerals (Yuan et al. 2004). Greater content of Pb in the bioavailable fraction generate severe threat to the aquatic system. The significant concentrations of Pb in Mn-Fe-oxides are due to the formation of a stable complex (LopezSanchez *et al.*, 1996; Jones and Turkie, 1997). The exchangeable lead content was intensified in the northern and southern zones of the estuary revealing the granulometric dependence of these fractions.

6. Iron:

Biennial variation of iron was in the order as

Residual fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters > Bound to carbonate fraction > Exchangeable fraction [2009 and 2011].

Fraction of Fe accounts for greater metal content in the residual form and this level is toxicologically insignificant to cause any adverse effect on biota. This result was in good agreement with data reported by several research work carried out in other marine systems (Usero et al. 1998; Martin et al. 1998; Yuan et al. 2004; Takarina et al. 2004). Large amounts of Fe accumulate in the residual phase probably because it is basically of natural origin (it is the most common element in the earth's crust) and can exists as crystalline iron peroxides (goethite, limonite, magnetite, etc.). The major part of the remaining Fe is associated with the reducible phase. Singh and Subramaniam (1984) explained that Mn-Fe oxides act as efficient scavengers for Fe which supports the occurrence of it as second most abundant fraction in the present study.

7. Manganese :

Manganese vary biennially as:

Bound to carbonate fraction > Exchangeable fraction> Residual fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters [2009].

Exchangeable fraction> Residual fraction > Bound to carbonate fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters [2011].

Bioavailable and residual fractions were strengthened in the entire study area. Mn content was mostly present in the labile phase. This is probably because of the known intimate association of Mn with carbonates as endorsed by Dassenakis et al. 2003 and also by other earlier workers (Kiratli and Ergin 1996; Morillo et al. 2004). In this phase, weakly sorbed Mn retained on sediment surface by relatively weak electrostatic interactions which may be released by ion exchange processes and dissociation of Mn-carbonate phase (Tessier et al. 1979).

8. Nickel :

Biennial variation of Ni fractions was in the order as

Residual fraction > Exchangeable fraction > Bound to carbonate fraction = Bound to Fe and Mn oxide = Fraction bound to organic matters [2009].

Residual fraction > Fraction bound to organic matters > Exchangeable fraction > Bound to carbonate fraction = Bound to Fe and Mn oxide [2011].

In the aquatic sediment, Ni is present predominantly in the residual fractions. The dominant proportion of Ni in the residual phase in this study is in agreement with the results of other studies (Martin et al. 1998; Mester et al. 1998). This also infers the less toxicity of this metal to the study area.

9. Zinc :

Zinc fraction partitioned as follows

Bound to Fe and Mn oxide > Residual fraction > Fraction bound to organic matters > Exchangeable fraction > Bound to carbonate fraction [2009].

Bound to carbonate fraction > Exchangeable fraction > Residual fraction > Bound to Fe and Mn oxide > Fraction bound to organic matters [2011].

A major part of Zn is associated with Fe-Mn oxide phase, because of the high stability constant of Zn oxides. Fe oxides adsorb considerable quantities of Zn and these oxides may also occlude with Zn in the lattice structures (Banerjee 2003). Singh and Subramaniam (1984) explained that Mn-Fe oxides act as efficient scavengers for Zn. Relatively higher concentration of Zn associated with this fraction is caused by the adsorption of these elements by the colloids of Mn and Fe (Jenne, 1968). The sorption of zinc with iron in the sediment may strongly hinder their mobility in the aquatic environment. In the present study minor amount of Zn is associated with carbonate and exchangeable fractions. Besides, Calcium carbonate forms complexes with zinc as a double salt ($\text{CaCO}_3 \cdot \text{ZnCO}_3$) in the sediment (Li *et al.*, 2000). The association of the metals with the carbonate phase is less in first sampling campaign (2009) which may be due to the low carbonate in the sediment. Low concentration in exchangeable fractions indicates low bio-availability of Zn.

The results of the sequential extraction revealed that Cd, Cr, Cu, Fe, Mn and Ni had similar pattern as for the dominant content in both years of sampling. Cd and Mn were found in the bioavailable fraction (EXC, CA). Greater availability of these metals in the ecosystem, and in turn enters in to the aquatic biota and cause biomagnification through food chain and finally create damage to the ecosystem. Cr, Cu, Fe and Ni in these fractionation profiles intensified with residual fraction. Co and Pb showed high concentration in EXC and RES in first and second sampling periods respectively.

RISK ASSESSMENT CODE (RAC) AND MOBILITY FACTOR (MF)

The results of sediment fractionation expose the presence of metals in various fractions and facilitate to determine the mobility of the metals by evaluating the percentage of metals in the weakly bound fractions with the total metal content.

In this study, the Risk Assessment Code (RAC) which accounts the mobility of the metal was evaluated in order to identify the extent of risk associated with the percentage of metals present in the sediments. From RAC and MF, Fe showed as low risk in the sediment of the first sampling period (2009), but revealed to be of medium

risk in the second sampling period (2011). Mn had very high risk effect in both the sampling period. Ni revealed high toxic nature in the sediment for the first set (2009) and in the next (2011), it had low toxic effect. Zn showed to be very high toxic nature in both the study periods. Sediment had very high risk with Cd and Co. Cr and Cu revealed as medium risk for the 2009 samples and no toxic effect for 2011. Pb showed high risk in the first set (2009) and medium risk for the next sampling year (2011). RAC and MF also confirmed as moderate to severe pollution behaviour in the estuary.

NON-RESIDUAL FRACTIONS ENRICHMENT FACTOR (KNRF)

In order to quantify the anthropogenic contamination of the metals, for the fractionation compositions, the KNRF approach is adopted and presented herewith. KNRF studies indicate extreme contamination in the surface sediment of the study area especially in the northern region of the estuary which revealed heavy anthropogenic pollution in these regions.

CONCLUSION

The cycling, mobility and biological effect of metals in the aquatic environment can be revealed from the knowledge of metal fractionation. Therefore, the study highlights the analysis of total metal content and its fractions to generate the quality of the sediment. Results showed that the distribution of metals in the sediment was not uniform over the whole study area and revealed extreme metal contamination in CES. In general, the northern region of the study area showed higher values as compared to the southern region. The sediment quality guideline and previous literature comparison resulted drastic pollution in CES. Geochemical indices also support these outcomes. The factor analysis and geochemical index effectively differentiate the natural anthropogenic sources of metals. Fractionation profile showed intensified content of metal in non residual fraction, creating severe threat to the aquatic system. EXC and CA fractions dominated in the fractionation profile in most of the metals which gain attention due to their bioavailable nature and susceptibility to release back to the water column in the entire zones of the estuary. RAC and MF revealed that certain pockets of the three zones of the estuary are polluted by metal either from human activities and industrial wastes or sewage disposal influences. EF and KNRF revealed extreme contamination in these surface sediments. The high concentration and bioavailability of metals indicate that there is urgent need to conduct more detailed and continuous monitoring studies in this region and to take necessary steps to reduce the sources of pollution. Further, deterioration of geochemical parameters may enhance the bioavailability of metals and will adversely affect the aquatic system and health of human, as they are depend on the system for their livelihood. Hence, the findings in this study will indicate the need for proper industrial planning and the safe disposal of industrial and urban waste, which would otherwise lead high levels of pollutants into the coastal ecosystem of Kerala, and would greatly invite socioeconomic disaster.

Declaration of Conflicting Interests

The authors declare no potential conflicts of interest with respect to the research, authorship and publication of this article.

Funding

The author received no financial support for the research, authorship and publication of this article.

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