

Partitioning of metals in different binding phases of tropical estuarine sediments: Importance of metal chemistry

P. Chakraborty^{1*}, Sucharita Chakraborty¹, Krushna Vudamala¹,
Arindam Sarkar¹, B. Nagender Nath¹.

^{1*}Geological Oceanographic Division, CSIR-National Institute of Oceanography,
Dona Paula, Goa, India (403004), E-mail: pchak@nio.org

ABSTRACT

Distribution of metals in different binding phases of marine sediments provides chemically significant description of metal-sediment interactions. This study describes the influences of ligand field stabilization energy (LFSE), Jahn-Teller effect and water exchange rate (k_w) on metal distribution in different binding phases of estuarine sediments. It was found that Cu had highest affinity for organic binding phases in the studied sediments followed by Ni and Pb. However, Pb showed strong association with Fe/Mn-oxide phases followed by Ni and Cu. Faster k_w of Cu (II) ($1 \times 10^9 \text{ s}^{-1}$) increased the rate of complex formation of Cu^{2+} ion with ligand in the organic phases. The Cu-ligand (from organic phase) complexes gained extra stability by the Jahn-Teller effect. The combined effects of these two phenomena and high ionic potential increased the association of Cu with the organic phases of the sediments than Ni and Pb. The smaller ionic radii of Ni^{2+} (0.72 Å) than Pb^{2+} (1.20 Å) increase the stability of Ni-ligand complexes in the organic phase of the sediments. High LFSE of Ni (II) (compared to Pb^{2+} ions) also make Ni-organic complexes increasingly stable than Pb. High k_w ($7 \times 10^9 \text{ s}^{-1}$) of Pb did not help it to associate with organic phases in the sediments. The high concentration of Pb in the Fe/Mn-oxyhydroxide binding phase was probably due to co-precipitation of Pb^{2+} and Fe^{3+} . High surface area or site availability for Pb^{2+} ion on Fe-oxyhydroxide phase was probably responsible for the high concentration of Pb in Fe/Mn oxyhydroxide phase. Increasing concentrations of Cu in organic phases with the increasing Cu-loading suggest that enough binding sites were available for Cu in the organic binding phases of the sediments. This study also describes the influence of nature of sedimentary organic carbon (terrestrial and marine derived OC) in controlling these metal distribution and speciation in marine sediment.

Key words: ligand field stabilization energy (LFSE); Jahn-Teller effect; water exchange rate (k_w); sequential extraction, metal-sediment interactions; marine sediment

Introduction

Chemical interactions of metals with different ligands in estuarine sediment determine their physicochemical forms in the estuarine system. Mobility, bioavailability and toxicity of metals in sediment are controlled by their physicochemical forms in the sediments (Tack et al.,1995; Stone and Marsalek,1996; Clozel et al.,2006;Violante,et al.,2010; Chakraborty et al.,2015). Several sequential chemical extraction protocols have been proposed and widely used to quantify the distribution, speciation and bioavailability of metals in marine sediments (Tessier et al.,1979; Kersten and Förstner,1986; Gleyzes et al.,2002). Sequential extraction protocols are widely used to estimate bioavailable metal fractions associated in marine sediments (Chakraborty et al., 2012a; Chakraborty et al., 2014; Chakraborty et al.,2015a; Chakraborty et al 2015b;). Geochemists have used different sequential extraction protocols to quantify the fractions of total metals involved in authigenesis (removal from the dissolved to the particulate phase) and their remobilization during the early diagenesis or resuspension of deposited sediments. Sequential partitioning of transition elements in Pacific pelagic sediments has also been reported to predict the source rock of the sediments by looking at the residual metal percentages in the sediments (Forstner and Stoffers, 1981).

However, there are only few studies that have attempted to understand the influences of metal chemistry on metal- heterogeneous binding ligands interactions in marine sediments. .

There are several studies available in literature that have vividly discussed about the influences of metal chemistry on metal speciation in aquatic environment (Tessier and Turner,1995; Florence et al.,1992). Three factors have been identified (Sekaly et al., 1999; Fafous et al., 2006; Chakraborty and Chakrabarti, 2008; Chakraborty et al., 2012b) to influence trace metal speciation in freshwater environment: (1) metal to ligand mole ratio, (2) ionic potential (z^2/r), and (3) Ligand Field Stabilization Energy of metals. The importance of considering the valence-shell electron configuration in studying trace metal speciation in freshwater environment has also been projected.

It has also been documented that the rate of complex formation and stability of the formed complex determine the speciation of the metals in aquatic environment. If the rate of complex formation of a metal (M) with natural ligand (L) is faster and the stability of the formed complex (M-L) is higher (compared to the other metals in the system) then the metal (M) will be more associated with the ligands (L) than the other metals present in the system. A metal with fast kinetics of complex formation with high stability of the metal complex may out-compete other metals from complex formation with the same ligands in marine environments.

However, the influences of different factors such as (i) metal-ligand ratio (ii) ionic potential of metals (iii) water exchange rate (iv) ligand field stabilization energy (LFSE) on metal speciation in marine sediments are not known. This study is the first attempt to understand the influences of above factors on metal distribution and its complex formation with different binding phases of estuarine sediments.

This study also aimed to show the importance of type of sedimentary organic matter (terrestrial and marine organic matter (OM) from in situ biological production) in controlling metal speciation in estuarine sediments.

The objectives of this study were to test whether the factors such as (i) metal-ligand ratio (ii) ionic potential of metals (iii) water exchange rate (iv) ligand field stabilization energy (LFSE) and (v) nature of sedimentary organic carbon have any role in controlling the distribution and speciation of metals in estuarine sediments. In this study, modified BCR protocol was used to understand the distribution of nickel (Ni), copper (Cu) and lead (Pb) in different binding phases of tropical estuarine sediments.

Materials and Methods:

Study area:

The sediment samples were collected from the Vembanad Lake in Kerala, west coast of India. It is the longest (stretching about 90 km) and largest brackish-water lake of India. The Vembanad wetland system has formed an intricate network of estuaries, lagoons and canals. The lake is well connected to Arabian Sea through two openings (at Kochi and Azhikode). This lake is regularly influenced by mixed semidiurnal tides. However 1.5 km long Thannirmukam bund (dividing the whole lake in two parts, viz north and south) prevents intrusion of saline water to the southern part of the lake (**Figure 1**). Thus, northern and southern part of the lake exhibit two different sub-environments as the northern part is brackish and southern part of the lake is freshwater dominated (Nath et al., 2000). Salinity of surface water in the northern part of the lake varies from fresh-water condition (during S-W monsoon) to 34‰ (during inter-monsoon) at location near bar mouth (Verma and Subramanian, 2002). The average salinity of southern part of the lake reduced from 23 ‰ to 2.8 ‰ due to building of Thannirmukkam bund. Average value of dissolved oxygen (DO) at surface during pre-monsoon time remains high at ~ 5 mg/l and pH varies from 5.86 to 8.91 (Nasir 2010). Sediments undergo periodic anoxia ($E_h \approx -242$ to -160 mV) below an oxygenated water column (Gireeshkumar 2013). Very high concentration of Chlorophyll-a was reported due to additional input of nutrients due to anthropogenic activity. The fresh water discharge through the rivers is

maximum during monsoon ($1346 \text{ m}^3\text{s}^{-1}$) and totaling to $22.41 \times 10^3 \text{ Mm}^3 \text{ yr}^{-1}$ (Revichandran et al. 2011).

Water depth in most part of the lake varies between 1.5 to 6 m (Murty and Veerayya, 1973). It receives about 320 cm rainfall during S-W monsoon (Gireeshkumar et al., 2013). Major parts of the lake in the south are reclaimed for agricultural purpose. High sedimentation rates (0.5cm/yr) have been reported (Dinesh Kumar et al., 1994) in the Vembanad Lake. This high sedimentation rate is due to river discharge (south part) and the resulting tidal influx (north part). Eight stations were selected for our study covering most part of the lake (**Figure 1**). Sampling was done during pre-monsoon time, March-April of 2012. The Thannermukkaom bund was closed during the sampling period. Sediments were collected by Van Veen Grab. Top layer from the sediment-water interface were collected and transferred to plastic bags, sealed and preserved in frozen condition until further analysis.

Sediment texture:

The frozen sediment samples (bulk) were dried at 35°C in oven. Textural analysis of the silt and clay particles ($<63\mu\text{m}$) was carried out by particle size analyzer (LPSA, Malvern Mastersizer 2000). The detailed procedure has been described in the literature by Ramaswamy and Rao (2006). The data are presented as weight percentage (wt %) in this study.

Elemental analysis:

Both bulk sediment samples were analyzed for total carbon (TC), total inorganic carbon (TIC), total nitrogen (TN) content. TC and TN in sediments were determined by using Flash 2000 CHN-elemental analyzer (Thermo Fisher Scientific Incorporation). Precision of the analysis was within $\pm 5\%$. Soil NC was used as certified reference material. TIC was determined by coulometry (UIC coulometrics). Total organic carbon (TOC) was derived by subtracting TIC from TC.

Sequential extraction method for metal speciation

The sequential extraction protocols proposed by the European Community Bureau of Reference, usually called the BCR sequential extraction protocol (Ure et al., 1993) was used to understand the distribution of metals in the different binding phases of the studied sediments. This protocol allows us to determine the sum of ion-exchangeable, water soluble and carbonate/bicarbonate form of metals (Fr. 1); metals bound to Fe–Mn oxyhydroxides i.e., reducible fraction of metals (Fr. 2); concentrations of metals associated with organic matter and sulfide, i.e., oxidizable fraction of metals (Fr. 3) and residual metal fraction (Fr. 4) in sediment. All the extraction processes were performed in Teflon containers. The reagents used in this study were of analytical grade or better (suprapure). The

concentrations of Ni, Cu and Pb in each leach solution were directly measured by using graphite furnace-atomic absorption spectrometer (GFAAS) (Perkin Elmer PinAAcle 900T). The leaches were preserved in 2% HNO₃ solution prior to analysis. BCR 701 (Sigma Aldrich) was used as a certified reference material (CRM) for modified BCR protocol. Before each step, two procedural blanks were run and the metal concentrations were found below detection limit. The optimized condition of the GFAAS has been reported by Chakraborty et al (2015a). Three replicates of each sample were analysed. Two reagent blanks were analyzed for every extraction. In all cases blank results were below the detection limit of the analytical technique.

Results

Distributions of sand, silt, clay, TOC, TN and total metals in sediment along the lake:

The sediment texture is reported to be highly variable in estuaries including this Lake (Renjith and Chandrmohankumar 2007). Finer sediments were found in both north and southern side of the lake with a distinct coarsening on either side of the bund. This variation in texture may be result of variation in detrital sediment settlement from influence of mixing in the depositional environment. Sediments, collected at the middle of the lake (both side of the bund) was dominated by coarser particles. The average concentrations of sand, silt, clay) in the studied sediments are presented in Table 1.

The concentration of TOC in the sediments was varying from 0.9-3.8%. The concentration of sedimentary TN was in the range of 0.1-0.4%. Significant positive correlation coefficient was found between the TOC, TN and the finer particles (silt + clay) content in the sediments. This indicates that TOC and TN had high affinity for the fine-grained sediment and strongly adsorb towards large surfaces of fine-grained sediments. The concentration of trace metals (Ni, Cu, and Pb) in the studied sediment varied from the northern and southern part of the lake (Table 1). These metal concentrations were within the range reported from the other coastal sediments around India (Table 2).

The average concentrations of Ni, in the sediments were higher in the southern part of the lake (ranging from ~19.4 to 49.8 mg/kg with an average concentration of 37.2 mg/kg) than the northern part of the lake (ranging from ~21.1 to 36.1 mg/kg, with an average concentration of 28.1 mg/kg). However, the average concentrations of Cu and Pb, in the sediments were relatively higher in the northern part (Cu ranging from ~22.2 to 82.2 mg/kg, with an average concentration of 47.9 mg/kg and the concentrations of Pb ranging from ~24.4 to 34.2 mg/kg, with an average Pb concentration of 31.5 mg/kg) than the southern part of the lake (Cu concentrations ranging from ~26.5 to 51.5 mg/kg,

with an average Cu concentration of 37.9 mg/kg and Pb concentrations ranging from ~20.3 to 45.3 mg/kg, with an average Pb concentration of 29.0 mg/kg). Distribution and speciation of these metals in the lake sediments were further determined by following BCR sequential extraction protocol.

Chemical fractionations (speciation) of Ni, Cu and Pb in the sediments by using sequential extraction method

Distribution and speciation of Ni, Cu and Pb in different binding phases of the sediments are described below.

Ni speciation:

Distribution of Ni in different binding phases of the studied sediments is presented in **Figure 2a**. It shows that lowest fraction of total concentration of Ni (vary from ~ 0.8 to 3.0% of the total Ni) were present as water soluble, exchangeable and carbonate/bicarbonate-Ni complexes (Fr.1) in the sediments. However, the absolute concentration of Ni (~ 0.12 to 0.57 mg/kg) in Fr.1 gradually increased with the increasing total Ni concentrations in the sediments (**Figure 2b**).

Association of Ni with Fe/Mn-oxyhydroxide binding phases (Fr.2) in the sediments were higher (4 to 15% of the total Ni) (**Figure 2a**) than the Fr.1. The concentration of Ni associated with Fe/Mn oxyhydroxide binding phase gradually increased (~0.9 to 5.0 mg/kg) with the increasing Ni loading in the sediments ($R^2=0.70$) (**Figure 2c**). This indicates that Fe/Mn oxyhydroxide phase in the sediments acted as one of the important binding phases for Ni. The highest fractions of non-residual Ni (~ 22.0 to 27.0% of the total Ni) were found to associate with organic binding phases in the sediments (Fr 3) (**Figure 2d**). The concentration of Ni in Fr.3 (associated with organic binding phases) gradually increased (~4.0 to 8.0 mg/kg) with the increasing Ni loading in the sediments ($R^2=0.93$) (**Fig. 2d**).

Major fractions of the total Ni (~9.5 to 22.0 mg/gm) were present within the structure of the sediments (Fr.4). **Figure 2e** shows the variation of residual fraction with changing total Ni content in the sediments. The range of Ni concentrations in residual fraction of the sediment was in close correspondence with the geology of the adjacent source rock (granulitic terrain) (Nath et al. 2000).

Figure 2f shows that the concentrations of Ni associated with organic phases (Fr 3) gradually increased with the Ni-to-TOC ratio; the results indicate a progressive increase in association of Ni with organic binding phase with the increasing Ni loading. The relative affinity of Ni for the different non-residual binding phases in the sediments was in the following order; organic carbon binding phase > Fe/Mn-oxyhydroxide phase > exchangeable, Carbonate/bicarbonate phases.

Cu speciation:

Distribution and speciation of Cu in the studied sediments are shown in Figure 3. Association of Cu in different binding phases of the sediments is shown in **Figure 3a**. Concentration of Cu as water soluble, exchangeable and carbonate/bicarbonate complexes (Fr. 1) were low and found to vary from ~0.3 to 3.0 % of the total Cu in the sediments (**Figure 3b**). Figure 3b shows that the absolute concentration of Cu (~0.1 to 0.9 mg/kg) in Fr.1 did not gradually increase with the increasing Cu loading in the sediments (unlike Ni) ($R^2=0.14$). This indicates that enough binding sites were probably available for Cu to form thermodynamically stable complexes in the sediments. This statement is based upon the assumption that Cu forms thermodynamically weaker complexes in Fr. 1 than other binding phases.

The fraction of total Cu associated with Fe/Mn oxyhydroxide binding phase (Fr 2) was found to vary from ~ 3.5 to 26.0%. Figure 3c shows that the concentration of Cu in Fr.2 gradually decreased (~6.2 to 3.0 mg/kg) with the increasing Cu loading in the sediments ($R^2=0.50$) (**Figure 3c**). The highest fractions of non-residual Cu were found to associate with organic binding phases in the sediments (Fr 3) and probably the preminent binding phase for Cu in the studied sediments. The fraction of the total Cu associated with organic binding phase in the studied sediment was found to vary from ~ 15.0 to 32.0%. The concentration of Cu associated with organic phases of the sediments gradually increased (~4.0 to 8.0 mg/kg) with the increasing Cu loading in the sediments ($R^2=0.75$) (**Figure 3d**).

Geochemical fractionation study suggested that major part of the total Cu in the sediments was present within the structure of the sediments (Fr.4) (~12.0 - 58.0 mg/kg) and suggests that these sediments were mainly derived from the crustal sources with more felsic composition. **Figure 3e** shows that the concentrations of Cu in the residual fraction gradually increased with the increasing total Cu loading.

Figure 3f shows that the concentrations of Cu associated with organic phases (Fr 3) gradually increased with the increasing Cu/TOC ratio in the sediments. The results indicate a progressive increase in complexation of Cu with different binding sites present in the organic phase with the increasing Cu/TOC ratio. The relative affinity of Cu for different non-residual binding phases in the sediments were in the following order; organic carbon binding phase> Fe/Mn-oxyhydroxide phase> exchangeable, Carbonate/bicarbonate phases.

Pb speciation

Distribution of Pb in different binding phases of the sediments is shown in **Figure 4a**. The concentrations of water soluble, exchangeable and carbonate/bicarbonate complexes of Pb (Fr. 1) were low and found to vary from ~0.3 to 2 % of the total Pb content in the studied sediments. Pb concentration in Fr 1 (~0.1 to 2.0 mg/kg) were found to increase slowly with the increasing total Pb content in the sediments ($R^2=0.16$) (**Figure 4b**). This indicates that there were other Pb-binding ligands available to form thermodynamically stable Pb- complexes in the sediments.

The highest fraction of the non-residual Pb (~ 20.0 to 48.0% of the total Pb) was found to associate with Fe/Mn oxyhydroxide (Fr. 2) binding phase. Absolute Pb concentration associated with Fe/Mn oxyhydroxide in the sediment gradually increased (~2.0 to 7.0 mg/kg) with the increasing total Pb loading in the sediments ($R^2=0.92$) (**Figure 4c**).

The second highest fraction of non-residual Pb (~ 7.0 to 30.0% of the total Pb) was found to associate with the organic binding phase in the sediments (Fr 3). The concentration of Pb associated with organic binding phases did not gradually increase (~4.0 to 8.0 mg/kg) with the increasing Pb loading in the sediments ($R^2=0.12$) (as shown in **Figure 4d**). Unlike the other two elements considered here, this experimental data suggest that Pb preferred to associate with Fe/Mn oxyhydroxide binding phase than organic binding phases in the sediments.

Pb was primarily present in the residual fraction (Fr. 4) (~11.0 to 22.0 mg/gm) of the studied sediments. The concentration of Pb (in the residual fraction) gradually increased with the total Pb concentrations of the sediments (**Figure 4e**).

Like other two elements (Ni and Cu), the concentrations range of Pb in the residual fraction also support that these sediments were mainly derived from felsic sources and consistent with earlier study (Nath et al., 2000). **Figure 4f** shows that there was no progressive increase in association of Pb with organic binding phases of the sediments against the increasing Pb/TOC ratio. This indicates that Pb preferred to associate with Fe/Mn-oxyhydroxide binding phase than organic binding phases in the sediments.

The relative affinity of Pb for different non-residual binding phases in the sediments was in the order of; Fe/Mn-oxyhydroxide phase > organic carbon binding phase > exchangeable, Carbonate/bicarbonate phases.

This study suggests that Cu had highest affinity (as reflected by its concentrations in Fr. 3) for organic binding phases in the sediments followed by Ni and Pb, while, Pb had highest association with Fe/Mn-oxyhydroxide phases. These differences in distribution of these metals in different

binding phases can be attributed to their metal chemistry and several other factors which are discussed below.

Discussion

Total concentrations of Ni, Cu and Pb in the studied sediments (Table 1) were found to be similar to the concentrations reported in other coastal sediments around India (Table 2).

According to the Canadian sediment quality guidelines for the protection of aquatic life, the interim sediment quality (ISQGs) and probable effect levels (PELs) for these metals are presented in Table 2. The United States environmental protection agency has also suggested that effects range low (ERL) and effects range median (ERM) values for these metals in coastal sediment. The studied sediments were found to be of good quality (in terms of Pb concentration). However, the concentrations of Ni and Cu were found to be in between the ERL and ERM concentrations (20.9-51.6 mg/kg for Ni and 34-270 mg/kg for Cu).

A significant positive correlation coefficient between the TOC, TN and the finer particle (silt + clay) content in the bulk sediments indicates that there was high sorption and affinity of TOC and TN on the surface of finer particles in the studied sediments. The similar observation has been reported in literature (Chakraborty et al., 2014b, 2015c).

Sequential extraction study determined the distribution of Ni, Cu and Pb in different binding phases of the sediments. It was found that these metals had different affinities for different binding phases in the sediments. It is hypothesised that the distribution of metals (Ni, Cu and Pb) in different binding phases of the studied sediments must provide chemically significant description of metals-ligand interactions in the sediments. It was found that Cu showed highest affinity for organic binding phases followed by Ni and Pb in the studied sediments. However, Pb had highest association with Fe/Mn-oxyhydroxide binding phases followed by Ni and Cu. Different factors are discussed below to understand their influences on metals distribution in different binding phases of the studied sediments.

Effect of metal/TOC ratio in geochemical fractionation of metals in the sediments

Total metal loading, quantity and quality of binding ligands in estuarine sediments play important role in controlling metal speciation and their distribution in sediment. **Figure 5** shows the effects of metal/TOC ratio in geochemical fractionation of metals in the sediments. **Figures 5a** shows that increasing [Ni]/TOC ratio increased the accumulation of Ni in the organic phases of the studied sediments (across the lake sediments). It was found that enough uncomplexed Ni binding ligands were present in the organic binding phases of the sediments. **Figure 5b and 5c** shows the variation

of accumulation of Ni in the organic phases against the varying [Ni]/TOC ratio in the sediments from the northern and southern part of the lake. Organic phases in the sediments collected from the southern part of the lake were found to have better Ni complexing capacity.

Figure 5d shows the effect of varying [Cu]/TOC ratio on Cu accumulation in organic phases of the studied sediments (across the lake sediments). It was found that the accumulation of Cu gradually increased with the increasing [Cu]/TOC ratio. This study indicates that enough uncomplexed Cu binding ligands were present in the organic binding phases of the sediments. **Figures 5e and 5f** show the variation of accumulation of Cu in the organic phases of the sediments against the varying [Cu]/TOC ratio in the sediments collected from the northern and southern part of the lake. Comparison of both the figures suggests that organic phases in the sediments collected from the southern part of the lake had better Cu complexing capacity.

However, a poor relation was observed between Pb accumulation in organic phases of the studied sediments (across the lake sediments) against [Pb]/TOC ratio. Accumulation of Pb in organic phases did increase with the increasing [Pb]/TOC ratio (Figure 5g,h, and i) in the sediments. Organic phase in the sediment collected from the southern part of the lake was found to have better complexing capacity for Pb than the northern part of the lake. **Figure 5** clearly shows that there was a distinct difference in the metal complexing capacity of the sedimentary organic phases in the southern and northern part of the lake. A systematic study was performed to understand if there is any difference in the nature of organic matter and its impact on metal speciation in the sediment.

Sources of organic matter and its impact on geochemical fractionation of metals in the sediments

C:N_{molar} ratio and $\delta^{13}\text{C}_{\text{org}}$ were used to investigate the source of OM in the studied sediments from the Vembanad Lake. Both of these parameters have been widely used (Meyers and Ishiwatari, 1993; Meyers, 1997; Zhang et al., 2009) to understand the sources of OM in sediments. However their utility and efficacy is based on that our end-member (viz. fresh terrigenous OM and in-situ phytoplankton produced OM) shows distinct elemental and isotopic ratio from each other and these signatures does not get altered preferentially in sediments. The freshly deposited marine produced OM has C:N_{molar} ratio of 6-9 (Bordovskiy, 1965; Prahl et al., 1994, 1980) and $\delta^{13}\text{C}_{\text{org}}$ of -20.5‰. The vascular terrestrial C3 plant produced OM has C:N_{molar} ratio of 12-14 or more (Hedges et al., 1986; Prahl et al., 1994, 1980) and $\delta^{13}\text{C}_{\text{org}}$ of -30 to -23 ‰ (Smith and Epstein, 1971; Pancost and Boot, 2004). The values in between may indicate mixture of both marine and terrestrial OM. However the terrestrial C4 plant produced OM is richer in $\delta^{13}\text{C}_{\text{org}}$ (~ -17 to -9 ‰, (Smith and Epstein, 1971;

Pancost and Boot, 2004;). But we did not consider C4 plants to be potential source in this area, as most of the vegetation in its watershed area is of C3 type.

The **Figure 6a** shows the latitudinal variation of C:N_{molar} ratio and $\delta^{13}\text{C}_{\text{org}}$ in the studied sediment along the lake. There was a drop in C:N_{molar} ratio in the northern part of the lake sediment compared to the C:N_{molar} ratio found in the sediment from southern part of the lake. This decreasing C:N_{molar} ratio indicates that the sedimentary OC in from the northern part of the Vembanad Lake was mainly influenced by marine OM derived from in situ biological production and decreasing contribution from terrestrial OM. Further determination of stable isotopic ratio of OC ($\delta^{13}\text{C}_{\text{org}}$) in the sediments confirms the increasing influence of marine OM towards the northern part of the lake. Figure 6b shows that the $\delta^{13}\text{C}_{\text{org}}$ in sediments from north varied from -23.93‰ near Thannirmukkam Bund to -21.29‰ at northern most station. This clearly indicates increasing dominance of marine influence towards north. Similar observation has also been reported by Gireeshkumar et al. (2013) from sediments north of Thannirmukkam Bund. The $\delta^{13}\text{C}_{\text{org}}$ in the sediments from the southern part of the lake varied from -25.57 ‰ to -27.19‰ without any significant trend. Thus, sediments from the southern part receive OM from terrestrial origin. Similar observation has been reported by Verma and Subramanian (2002). It can be inferred that OM with terrestrial origin (in the southern part of the lake sediment) had more metal (Ni, Cu and Pb) complexing capacity than marine derived OM in the northern part of the lake.

Effect of ionic potential on geochemical fractionation of metals in the sediments

The intention of this section is to understand the influence of ionic potential of the studied metals on their geochemical fractionation in the major binding phase (organic phase) of the sediments. Ionic potential is a measure of density of charge of the ion. It is presented by charge/radius ratio of an ion. Ionic potential gives a sense of how strongly or weakly the ion will be electrostatically attracted to ions of opposite charge. High ionic potential of metal (high z^2/r) increases the covalency of metal-ligand bond (assuming the ligand is same). Thus, distribution of three different metals in the major binding phase (organic phase) of the studied sediment is interpreted by using their varying ionic potential (ionic potential (z^2/r): Ni (0.048), Cu (0.055), and Pb (0.034)).

Figure 7 shows the variation of metal association in the organic binding phases of the sediment from the different sampling sites of the lake. It shows that the association (as a result of complexation of metals) of metals gradually increased with the increasing ionic potential. It is assumed that the increasing covalency of Cu-ligand bond increased the thermodynamic stability of the Cu-ligand complexes in the sediments and highest concentrations of Cu was found to associate with organic

phase followed by Ni and Pb. **Figures 7a, b, c** represent the variation of metal association in the organic phases of the sediments collected from the northern part of the lake. **Figures 7d, e, f** represent the sediments collected from the southern part of the lake. This study clearly indicates that ionic potential is an important parameter that can be used to understand the interactions of metals with organic binding phases of sediments.

Effect of metal chemistry on their distribution in different binding phases of the sediments

The geochemical distributions of a metal in different binding phases of marine sediments are influenced by the metal chemistry and the nature of ligands present in the sediment.

Association of a metal with different binding phases in sediment depends on the rate of complex formation by the metal and the stability of the formed complex.

Rate of complex formation (k_f) of a metal with different ligands (in any binding phases in sediment) depend on the water exchange rate of the metal ion (k_w) and the stability of the outer-sphere complex (K_{OS}) of the metal with a particular ligand. The relation is given by: $k_f = K_{OS} \cdot k_w$

Thus, the distribution of Ni, Cu and Pb in organic and Fe/Mn oxyhydroxide phases of the studied sediments should be controlled by their K_{OS} and k_w .

K_{OS} is primarily dependent on the charge of the reacting metal and ionic strength of the medium. In this study, Ni, Cu and Pb were considered as dispositive. It is assumed that the depositional environments (particularly ionic strength of the medium) were same for all the metals (during complexation) and thus, the rate of complex formation (k_f) with different ligands in the sediment were dependent only on the water exchange rates of the metal ions (k_w).

Sequential extraction study suggests that highest concentration of Cu was associated with organic phases of the sediments followed by Ni and Pb.

The k_w of Ni, and Cu are 3×10^4 (s^{-1}), 1×10^9 (s^{-1}) respectively. This clearly suggests that the faster water exchange rate helps Cu to undergo faster complex formation with the ligands in the binding phases of the sediment than Ni.

The Irving-Williams Series suggest that the stability constant for the formation of a high-spin complexes by Cu(II) is higher than Ni(II) complexes.

The smaller ionic radii and higher crystal field stabilization energy (CFSE) of Ni^{2+} is expected to increase the stability of Ni-sediment complexes than Cu-sediment complexes but octahedral Cu (II) complexes are subject to the Jahn-Teller effect, which affords Cu-sediment complex extra stability. Thus, a major part of the total Cu was associated with organic phases than Ni.

Faster water exchange rate of Cu (II) increased the rate of complex formation of Cu^{2+} ion with the ligand in the organic phases of the sediment. The Cu- ligand (from organic phase) complexes gain extra stability by the Jahn-Teller effect. The combined effects of these two phenomenons and high ionic potential increased the concentrations of Cu in the organic phases of the sediments than Ni and Pb. The second highest concentration of metal associated with organic phases in the studied sediment was Ni. The higher ionic potential of Ni^{2+} (0.048) than Pb^{2+} (0.034) increase the stability of Ni-ligand complexes in the organic phase of the sediments. In addition to that high CFSE of Ni (II) (compared to Pb^{2+} ions) make Ni-organic complexes increasingly stable than Pb. High k_w ($7 \times 10^9 \text{ s}^{-1}$) of Pb did not help to associate with organic phases in the sediments.

However, maximum concentration of Pb was found to associate with Fe/Mn oxide phases of the sediment followed by Ni and Cu. Similar observation has also been reported in literature. Lion et al (1982) have reported that more than 70% of the extractable Pb from estuarine sediments can be associated with Fe and Mn oxides. Luoma and Bryan (1981) have also reported that iron is an important binding phase for Pb. Fe/Mn-oxyhydroxides has been reported to occur widely in surficial and subsurface geological environments and they are efficient scavengers of trace metals including Pb. The high concentration of Pb in Fe/Mn-oxyhydroxide in the sediments was probably due to co-precipitation of Pb^{2+} and Fe^{3+} . High surface area or site availability for Pb^{2+} ion on Fe-oxyhydroxide phase (Nelson et al., 1999; Lu et al., 2011) and greater binding strength over simple precipitate surface (Manceau et al. 2002) was probably responsible for the high concentration of Pb in Fe/Mn oxyhydroxide phase.

The decreasing concentrations of Cu in Fe/Mn–oxyhydroxide phases with the increasing Cu loading in the sediment suggest that Cu did not prefer to associate with Fe/Mn oxyhydroxide phases. Increasing concentrations of Cu in organic phases with the increasing Cu-loading suggest that enough binding sites were available for Cu in the organic binding phases of the sediments.

Conclusions

This study provides chemically significant description of metals-ligand interactions in different binding phases of sediments. It was found that Cu showed highest affinity for organic binding phases followed by Ni and Pb in the studied sediments. However, Pb had highest association with Fe/Mn-oxide phases followed by Ni and Cu. Nature of sedimentary organic carbon (terrestrial and marine derived OC) was found to play an important role in controlling metal distribution and speciation in marine sediments. Metals were found to have more affinity for terrestrial OC than the marine derived OC in the sediments. This study also suggests that ionic potential of the metal is an

important parameter that can be used to understand the interactions of metals with organic binding phases of sediments. Faster k_w of Cu (II) ($1 \times 10^9 \text{ s}^{-1}$) increased the rate of complex formation of Cu^{2+} ion with the ligand in the organic phases of the sediments. The Cu-ligand (from organic phase) complexes gain extra stability by the Jahn-Teller effect. The combined effects of these two phenomena and high ionic potential increased the association of Cu in the organic phases of the sediments than Ni and Pb. The smaller ionic radii of Ni^{2+} (0.72 Å) than Pb^{2+} (1.20 Å) increase the stability of Ni-ligand complexes in the organic phase of the sediments. In addition to that high CFSE of Ni (II) (compared to Pb^{2+} ions) make Ni-organic complexes increasingly stable than Pb. The high concentration of Pb in the Fe/Mn-oxyhydroxide binding phase was probably due to co-precipitation of Pb^{2+} and Fe^{3+} . High surface area or site availability for Pb^{2+} ion on Fe-oxyhydroxide phase and greater binding strength over simple precipitate surface was probably responsible for the high concentration of Pb in Fe/Mn oxyhydroxide phase.

Acknowledgements:

Authors are thankful to the Director, CSIR-NIO, Goa for his encouragement and support. This work is a part of the Council of Scientific and Industrial Research (CSIR) supported GEOSINKS (PSC0106) project. This article bears NIO contribution number XXXX.

References

- Banerjee K, Senthilkumar B, Purvaja R, & Ramesh R (2012). Sedimentation and trace metal distribution in selected locations of Sundarbans mangroves and Hooghly estuary, Northeast coast of India. *Environmental geochemistry and health*, 34(1): 27-42.
- Bordovskiy O K (1965). Sources of organic matter in marine basins. *Marine Geology*, 3(1): 5-31.
- Chakraborty, P., & Chakrabarti, C. L. (2008). Competition from Cu (II), Zn (II) and Cd (II) in Pb (II) binding to Suwannee river fulvic acid. *Water, air, and soil pollution*, 195(1-4), 63-71.
- Chakraborty P, Babu P R, & Sarma V V (2012a). A study of lead and cadmium speciation in some estuarine and coastal sediments. *Chemical Geology*, 294: 217-225.
- Chakraborty P (2012b). Speciation of Co, Ni and Cu in the coastal and estuarine sediments: Some fundamental characteristics. *Journal of Geochemical Exploration*, 115: 13-23.
- Chakraborty P, Chakraborty S, Ramteke D, & Chennuri K (2014a). Kinetic speciation and bioavailability of copper and nickel in mangrove sediments. *Marine pollution bulletin*, 88(1): 224-230.
- Chakraborty, P., Babu, P. R., Vudamala, K., Ramteke, D., & Chennuri, K. (2014b). Mercury speciation in coastal sediments from the central east coast of India by modified BCR method. *Marine pollution bulletin*, 81(1), 282-288.

- Chakraborty, P., Ramteke, D., & Chakraborty, S. (2015a). Geochemical partitioning of Cu and Ni in mangrove sediments: Relationships with their bioavailability. *Marine pollution bulletin*, 93(1), 194-201.
- Chakraborty, P., Ramteke, D., Chakraborty, S., Chennuri, K., & Bardhan, P. (2015b). Relationship between the lability of sediment-bound Cd and its bioaccumulation in edible oyster. *Marine Pollution Bulletin*, doi:10.1016/j.marpolbul.2015.08.027
- Chakraborty, P., Sarkar, A., Vudamala, K., Naik, R., & Nath, B. N. (2015c). Organic matter—a key factor in controlling mercury distribution in estuarine sediment. *Marine Chemistry*, 173, 302-309.
- Clozel, B., Ruban, V., Durand, C., & Conil, P. (2006). Origin and mobility of heavy metals in contaminated sediments from retention and infiltration ponds. *Applied Geochemistry*, 21(10), 1781-1798.
- Dhanakumar, S., Murthy, K. R., Solaraj, G., & Mohanraj, R. (2013). Heavy-metal fractionation in surface sediments of the Cauvery River Estuarine Region, southeastern coast of India. *Archives of environmental contamination and toxicology*, 65(1), 14-23.
- DineshKumar, P. K., Sankaranarayanan, V. N., & Devi, K. S. (1994). Cochin backwaters: An introduction to the system, prior studies, historical trends and future implication.
- Fasfous, I. I., Chakrabarti, C. L., Murimboh, J., & Yapici, T. (2006). Complexation of lead in model solutions of humic acid: heterogeneity and effects of competition with copper, nickel, and zinc. *Environmental Chemistry*, 3(4), 276-285.
- Florence, T. M., Morrison, G. M., & Stauber, J. L. (1992). Determination of trace element speciation and the role of speciation in aquatic toxicity. *Science of the Total environment*, 125, 1-13.
- Förstner, U., & Stoffers, P. (1981). Chemical fractionation of transition elements in Pacific pelagic sediments. *Geochimica et cosmochimica acta*, 45(7), 1141-1146.
- Gleyzes, C., Tellier, S., & Astruc, M. (2002). Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *TrAC Trends in Analytical Chemistry*, 21(6), 451-467.
- Gireeshkumar, T. R., Deepulal, P. M., & Chandramohanakumar, N. (2013). Distribution and sources of sedimentary organic matter in a tropical estuary, south west coast of India (Cochin estuary): A baseline study. *Marine pollution bulletin*, 66(1), 239-245.
- J.I. Hedges, W.A. Clark, P.D. Quay, J.E. Richey, A.H. Devol, U.de M. Santos. Composition and fluxes of particulate organic material in the Amazon River. *Limnol. Oceanogr.*, 31 (1986), pp. 717–738
- Kersten, M., & Förstner, U. (1986). Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. *Water Science & Technology*, 18(4-5), 121-130.
- Krupadam, R. J., Ahuja, R., Wate, S. R., & Anjaneyulu, Y. (2007). Forest bound estuaries are higher methane emitters than paddy fields: A case of Godavari estuary, East Coast of India. *Atmospheric Environment*, 41(23), 4819-4827.
- Lion, Leonard W., R. Scott Altmann, and James O. Leckie. "Trace-metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of iron/manganese oxide and organic surface coatings." *Environmental Science & Technology* 16.10 (1982): 660-666.

- Long, E. R., MacDonald, D. D., Smith, S. L., & Calder, F. D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental management*, 19(1), 81-97.
- Lu, P., Nuhfer, N. T., Kelly, S., Li, Q., Konishi, H., Elswick, E., & Zhu, C. (2011). Lead coprecipitation with iron oxyhydroxide nano-particles. *Geochimica et Cosmochimica Acta*, 75(16), 4547-4561.
- Luoma, S. N., & Bryan, G. W. (1981). A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *Science of the Total Environment*, 17(2), 165-196.
- Manceau, A., Marcus, M. A., & Tamura, N. (2002). Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. *Reviews in Mineralogy and Geochemistry*, 49(1), 341-428.
- Martin, G. D., George, R., Shaiju, P., Muraleedharan, K. R., Nair, S. M., & Chandramohanakumar, N. (2012). Toxic metals enrichment in the surficial sediments of a eutrophic tropical estuary (Cochin Backwaters, Southwest Coast of India). *The Scientific World Journal*, 2012.
- Meyers, P. A., & Ishiwatari, R. (1993). Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic geochemistry*, 20(7), 867-900.
- Meyers, P. A. (1997). Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic geochemistry*, 27(5), 213-250.
- Murthy, P. S. N., & Veerayya, M. (1972). Studies on the sediment of Vembanad Lake, Kerala State, Part-I Distribution of organic matter. *Indian J. Mar. Sci*, 1, 45-51.
- Nasir, U P. 2010. Water quality assessment and isotope studies of Vembanad Wetland System. Ph.D thesis. University of Calicut. <http://shodhganga.inflibnet.ac.in:8080/jspui/handle/10603/11474>.
- Nath, B. N., Kunzendorf, H., & Pluger, W. L. (2000). Influence of provenance, weathering, and sedimentary processes on the elemental ratios of the fine-grained fraction of the bedload sediments from the Vembanad Lake and the adjoining continental shelf, southwest coast of India. *Journal of Sedimentary Research*, 70(5).
- Nelson, Y. M., Lion, L. W., Shuler, M. L., & Ghiorse, W. C. (1999). Lead binding to metal oxide and organic phases of natural aquatic biofilms. *Limnology and Oceanography*, 44(7), 1715-1729.
- Pancost, R. D., & Boot, C. S. (2004). The palaeoclimatic utility of terrestrial biomarkers in marine sediments. *Marine Chemistry*, 92(1), 239-261.
- Prahl, F. G., Bennett, J. T., & Carpenter, R. (1980). The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. *Geochimica et Cosmochimica Acta*, 44(12), 1967-1976.
- Prahl, F. G., Ertel, J. R., Goni, M. A., Sparrow, M. A., & Eversmeyer, B. (1994). Terrestrial organic carbon contributions to sediments on the Washington margin. *Geochimica et Cosmochimica Acta*, 58(14), 3035-3048.
- Ramaswamy, V., & Rao, P. S. (2006). Grain size analysis of sediments from the northern Andaman Sea: comparison of laser diffraction and sieve-pipette techniques. *Journal of Coastal Research*, 1000-1009.

- Renjith, K. R., and N. Chandramohanakumar. 2007. Geochemical characteristics of surficial sediments in a tropical estuary, south-west India. *Chemistry and Ecology* 23: 337–343. doi:10.1080/02757540701497154.
- Revichandran, C., K. Srinivas, K. R. Muraleedharan, M. Rafeeq, Shivaprasad Amaravayal, K. Vijayakumar, and K. V. Jayalakshmy. 2011. Environmental set-up and tidal propagation in a tropical estuary with dual connection to the sea (SW Coast of India). *Environmental Earth Sciences* 66: 1031–1042. doi:10.1007/s12665-011-1309-0.
- Sekaly, A. L., Mandal, R., Hassan, N. M., Murimboh, J., Chakrabarti, C. L., Back, M. H., ... & Schroeder, W. H. (1999). Effect of metal/fulvic acid mole ratios on the binding of Ni (II), Pb (II), Cu (II), Cd (II), and Al (III) by two well-characterized fulvic acids in aqueous model solutions. *Analytica chimica acta*, 402(1), 211-221.
- Smith, B. N., & Epstein, S. (1971). Two categories of $^{13}\text{C}/^{12}\text{C}$ ratios for higher plants. *Plant physiology*, 47(3), 380-384.
- Stone, M., & Marsalek, J. (1996). Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. *Water, Air, and Soil Pollution*, 87(1-4), 149-169.
- Tack, F. M. G., & Verloo, M. G. (1995). Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *International Journal of Environmental Analytical Chemistry*, 59(2-4), 225-238.
- Tessier, A., Campbell, P. G., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical chemistry*, 51(7), 844-851.
- Tessier, A., & Turner, D. R. (Eds.). (1995). *Metal speciation and bioavailability in aquatic systems*. J. Wiley.
- Ure, A. M., Quevauviller, P., Muntau, H., & Griepink, B. (1993). Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International journal of environmental analytical chemistry*, 51(1-4), 135-151.
- Verma, A., & Subramanian, V. (2002). Organic matter and amino acid concentrations in surface sediments of Vembanad Lake—a tropical estuary, west coast of India. *Regional Environmental Change*, 2(4), 143-149.
- Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G., & Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of soil science and plant nutrition*, 10(3), 268-292.
- Zhang, L., Yin, K., Wang, L., Chen, F., Zhang, D., & Yang, Y. (2009). The sources and accumulation rate of sedimentary organic matter in the Pearl River Estuary and adjacent coastal area, Southern China. *Estuarine, Coastal and Shelf Science*, 85(2), 190-196.

Caption and legends

Figure 1. Study area: The sediment samples collected from the Vembanad Lake in Kerala, west coast of India

Figure 2. Ni speciation : (a) Distribution of Ni (%) as Fr1,Fr2,Fr3 and Fr4 in the sediments,(b)variation of Ni in Fr1 (mg.kg^{-1}),(c) variation of Ni in Fr2 (mg.kg^{-1}) ,(d) variation of Ni in Fr3 (mg.kg^{-1}),(e) variation of Ni in Fr4 (mg.kg^{-1}) with total concentration of Ni (mg.kg^{-1}) in sediments.(f) Variation of Ni(%) associated with organic phases (Fr 3) with the Ni-to-TOC ratio.

Figure 3. Cu speciation : (a) Distribution of Cu (%) as Fr1,Fr2,Fr3 and Fr4 in the sediments,(b)variation of Cu in Fr1 (mg.kg^{-1}),(c) variation of Cu in Fr2 (mg.kg^{-1}) ,(d) variation of Cu in Fr3 (mg.kg^{-1}),(e) variation of Cu in Fr4 (mg.kg^{-1}) with varying total concentrations of Cu (mg.kg^{-1}) in sediments.(f) Variation of Cu (%) associated with organic phases (Fr 3) with varying Cu-to-TOC ratio.

Figure 4. Pb speciation: (a) Distribution of Pb (%) as Fr1,Fr2,Fr3 and Fr4 in the sediments,(b)variation of Pb in Fr1 (mg.kg^{-1}),(c) variation of Pb in Fr2 (mg.kg^{-1}) ,(d) variation of Pb in Fr3 (mg.kg^{-1}),(e) variation of Pb in Fr4 (mg.kg^{-1}) with varying total concentration of Pb (mg.kg^{-1}) in sediments.(f) variation of Pb (%) associated with organic phases (Fr 3) with varying Pb-to-TOC ratio.

Figure 5. Association of Ni(%) with organic phase (Fr3) as a function of [Ni]/TOC ratio in the studied sediments (a) across the lake sediments (b) northern part (c) southern part of the lake sediments;

Association of Cu (%) with organic phase (Fr3) as a function of [Cu]/TOC ratio of the studied sediments (d) across the lake sediments (e) northern part (f) southern part of the lake sediments;

Association of Pb(%) with organic phase (Fr3) as a function of [Pb]/TOC ratio of the studied sediments (g) across the lake sediments (h) northern part (i) southern part of the lake sediments,

Figure 6.The latitudinal variation of (a) C:N_{molar} ratio and (b) $\delta^{13}\text{C}_{\text{org}}$ in the studied sediment along the lake.

Figure 7. Variation of Ni(%) (a) and(d);Cu(%) (b) and (e); Pb(%) (c) and (f) associated with organic phases (Fr3) of the sediments with the ionic potential (z^2/r) of the respective metals in the northern and southern part of the lake sediments respectively.

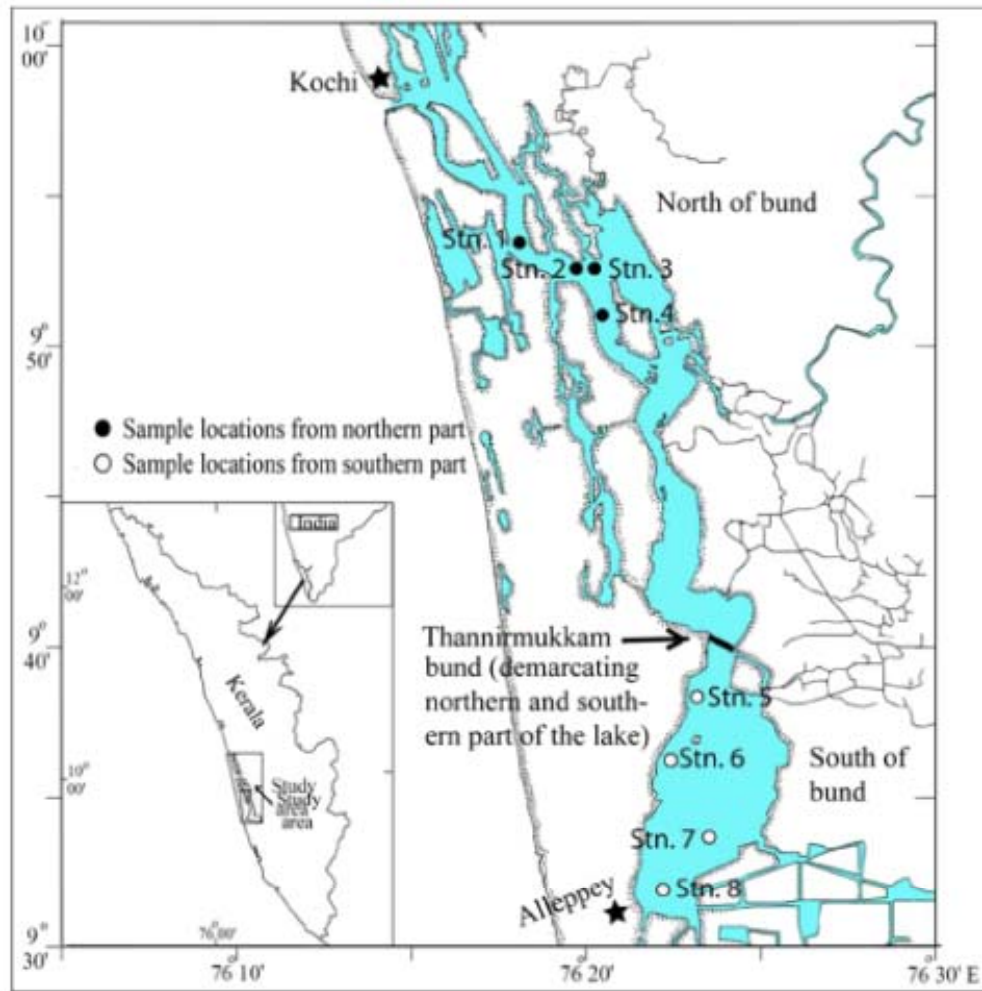


Figure 1

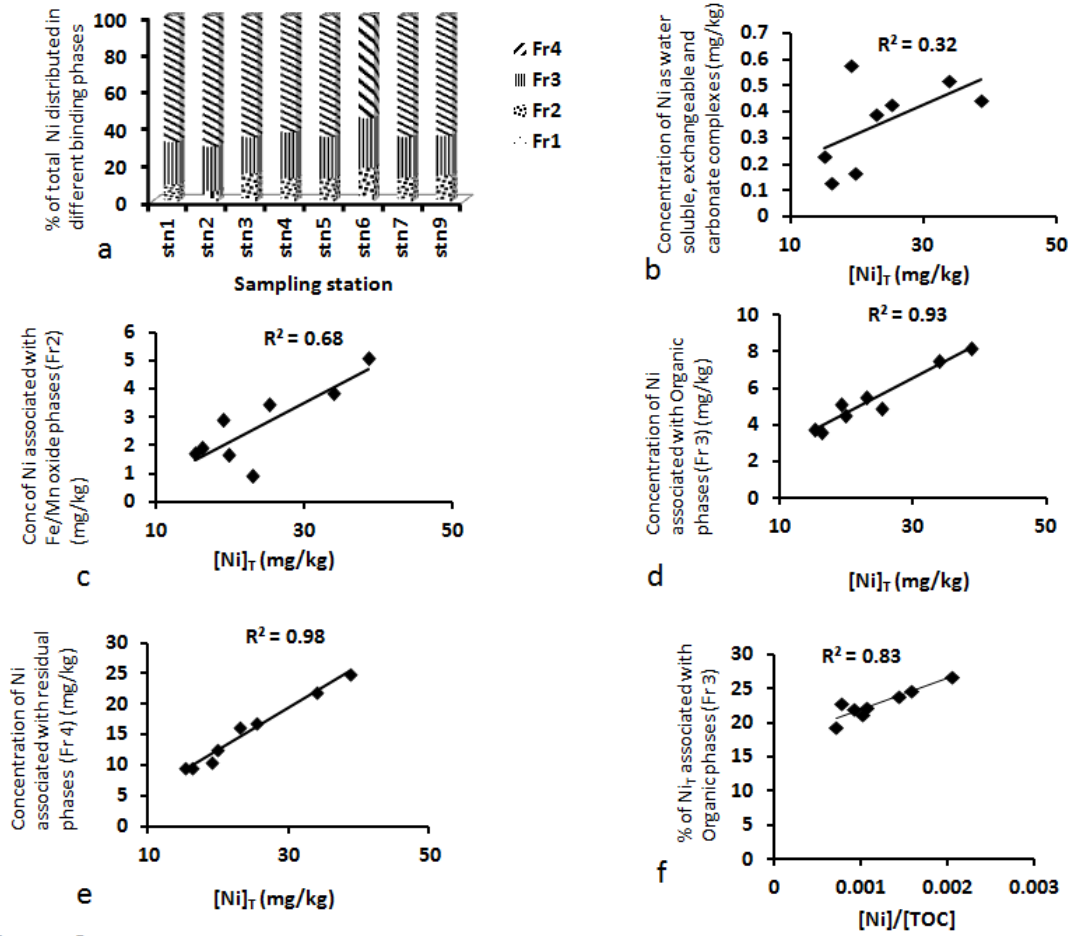


Figure 2

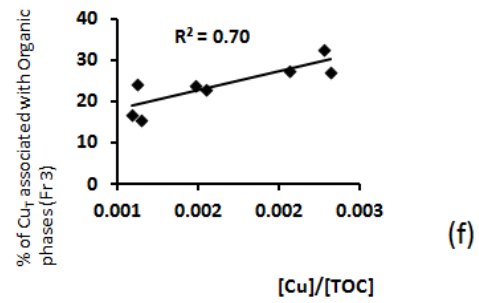
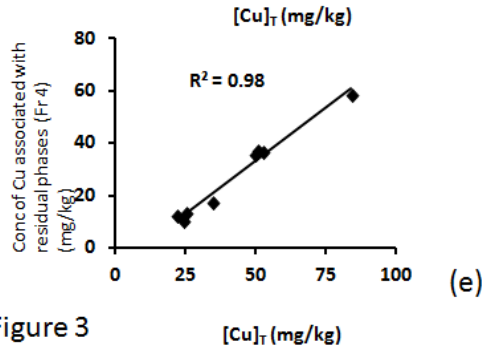
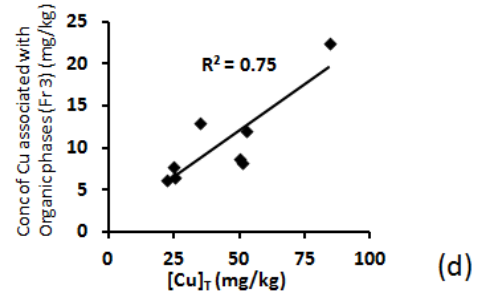
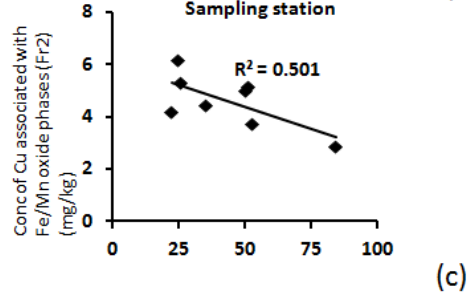
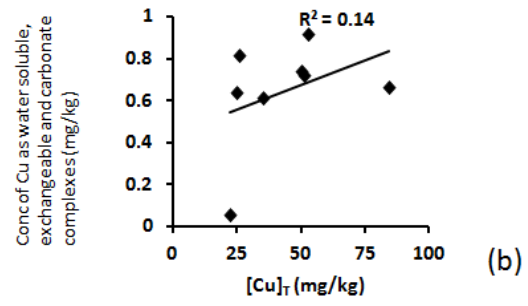
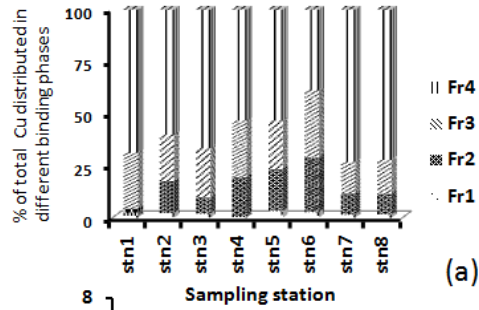


Figure 3

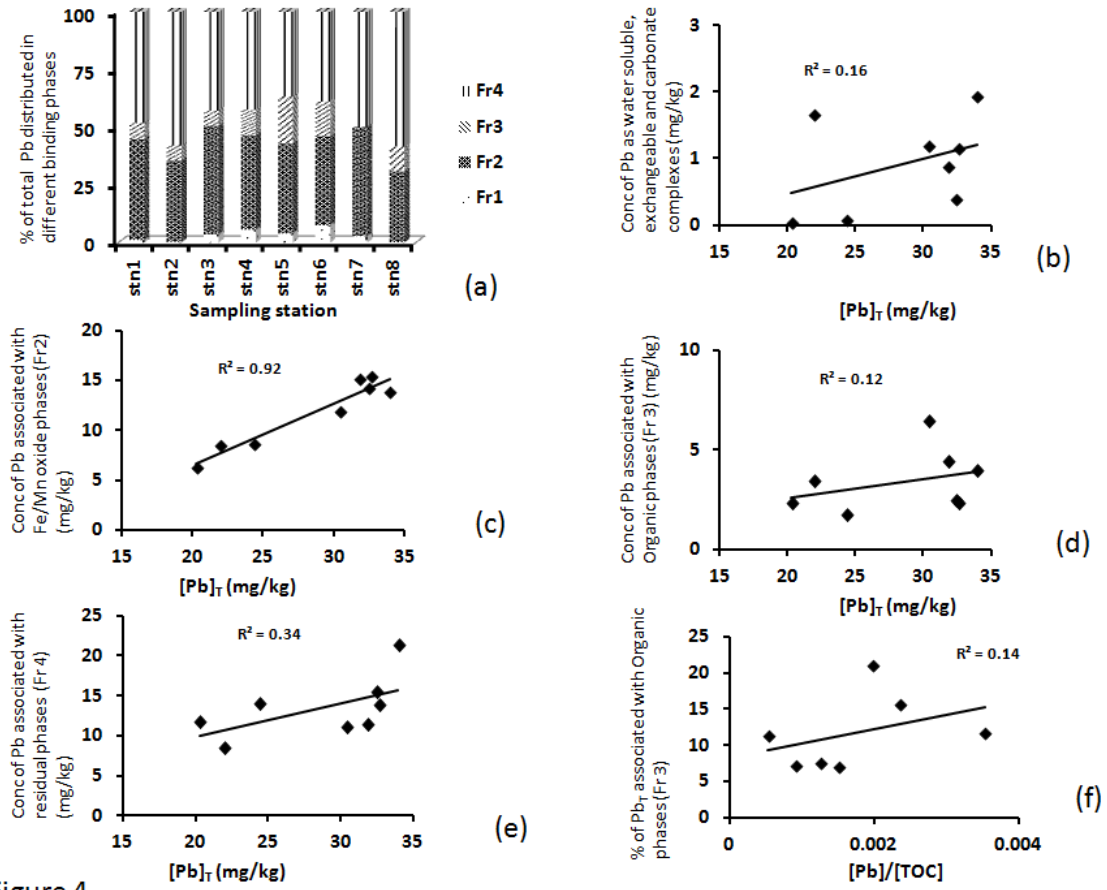


Figure 4

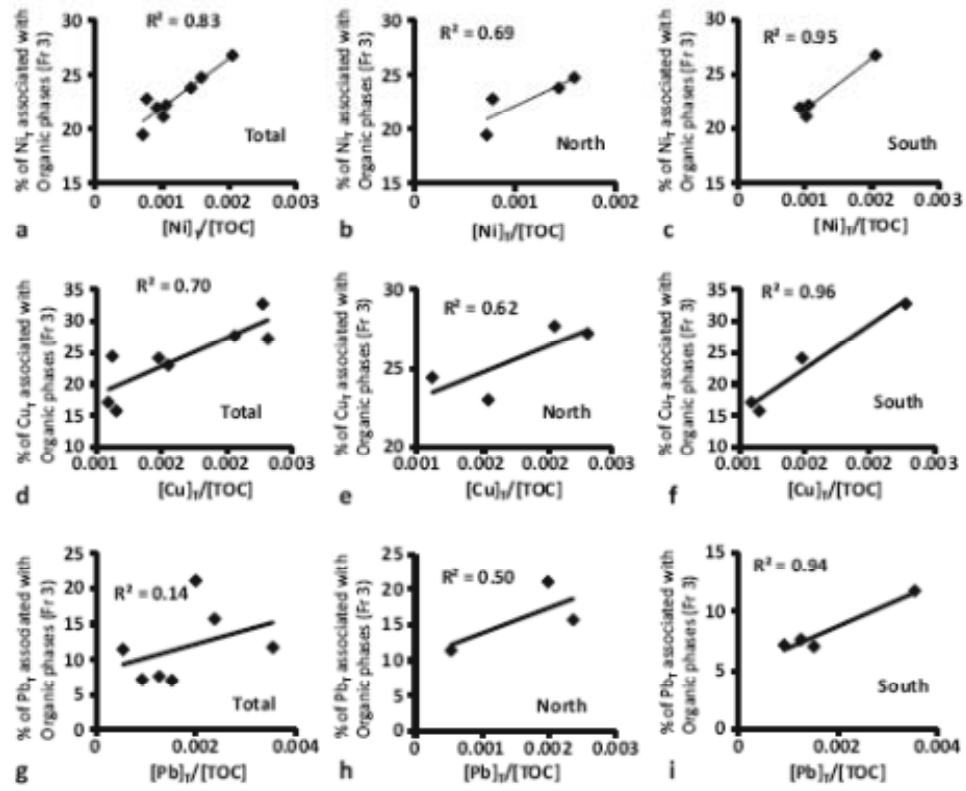


Figure 5

Table 1: Sampling location, sediment texture, TOC, TN and Ni, Cu, and Pb content in the surface sediments of Vembanad Lake

Sample	Longitude (°E)	Latitude (°E)	Depth (m)	TOC (%)	TN (%)	Sulfide (mg.kg ⁻¹)	C:N _{molar}	Clay + Silt (%)	Ni (mg. Kg ⁻¹)	Cu (mg. Kg ⁻¹)	Pb (mg. Kg ⁻¹)
North of Thannirmukkam Bund											
S-1	76.3010	9.9140	5	3.62	0.39	375.0	10.77	87.6	26.3 ± 0.8	57.6 ± 2.1	34.2 ± 1.6
S-2	76.3022	9.8920	2	2.58	0.22		13.52	71.3	24.0 ± 0.7	82.2 ± 2.8	32.5 ± 0.8
S-3	76.3320	9.8790	4	1.61	0.14	613.5	13.07	22.6	32.9 ± 1.2	29.0 ± 0.5	24.4 ± 0.7
S-4	76.3395	9.8810	2	3.55	0.33		12.55	99.4	36.1 ± 1.8	48.7 ± 1.2	32.6 ± 1.4
S-5	76.3453	9.8410	2.5	0.96	0.08	687.8	13.48	29.1	21.1 ± 0.5	22.2 ± 0.4	34.0 ± 1.2
South of Thannirmukkam Bund											
S-13	76.3816	9.6400	2	1.53	0.13	763.0	13.37	37.1	19.4 ± 0.5	26.5 ± 0.7	30.4 ± 1.2
S-18	76.3765	9.6066	3	0.93	0.08	668.9	14.48	21.9	33.7 ± 1.8	23.5 ± 0.6	22.0 ± 2.2
S-22	76.4119	9.5627	1.5	2.51	0.18	588.0	16.09	42.3	27.4 ± 1.3	39.8 ± 0.6	24.1 ± 0.6
S-23	76.3895	9.5622	3	3.67	0.31	149.4	13.85	95.2	47.0 ± 1.9	51.5 ± 1.8	31.9 ± 0.7
S-24	76.3648	9.5636	2	2.60	0.20	500.1	14.93	77.2	45.9 ± 2.5	35.5 ± 1.2	45.3 ± 2.3
S-25	76.3684	9.5396	2	3.79	0.33	489.6	13.52	91.1	49.8 ± 2.3	50.9 ± 1.8	20.3 ± 0.5

Table2: Concentration in the estuarine sediments of India and the ISGQ, PEL, ERL and EPL values of Ni, Cu and Pb

	Ni (mg. Kg ⁻¹)	Cu (mg. Kg ⁻¹)	Pb (mg. Kg ⁻¹)	References
Ganges E stuary	33.97	21.64	23.45	Banerjee et al.(2012)
Godavari E stuary	25.1	25.8	14.4	Krupadam et al.(2007)
Cauvery estuary	13.5	29.5	8.5	Dhanakumar et al.(2013)
Narmada E stuary	200	188.3	13.9	Sharma and Subramanian (2010)
Mandovi E stuary	64.02	46.96	18.74	Chakraborty et al.(2014b)
Cochin E stuary	57	43.4	39.8	Martin et al.(2012)
ISGQ	NA	18.7	30.2	Long et al., 1995
PEL	NA	108	112	Long et al., 1995
ERL	20.9	34	46.7	SQG (NOAA)
ERM	51.6	270	218	SQG (NOAA)