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Speciation of Co, Ni and Cu in the coastal and estuarine sediments: Some fundamental characteristics

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Abstract

Kinetic and sequential extraction methods were used to investigate chemical speciation and distribution of Co, Ni, and Cu in the estuarine and coastal sediments collected from the central east coast of India. The kinetic (single) extraction study provided a chemically significant description of the kinetics of metals-sediment interactions and correctly predicted the influences of ligand field stabilization energy (LFSE) and water exchange rate (k_w) on the dissociation rate constants of metals-sediments complexes in the natural systems. The results consistently demonstrate that the fast (k_{d1}) and medium fast (k_{d2}) dissociation rate constants of the 3d transition metals complexes in the estuarine and coastal sediments follow the trend as predicted from the LFSE's (weak field) ($k_{d1,2,Co(II)} > k_{d1,2,Ni(II)} > k_{d1,2,Cu(II)}$). However, a higher rate coefficient of water exchange (k_w) of Cu (II) helps them to form more strong inert complexes than predicted from its LFSE alone. Sequential extraction method was used to fractionate these metals depending upon their association with different phases in the studied sediments. The comparison and statistical analysis of the fractionation data obtained by two independent methods indicate that the transition metals formed strong complexes with the organic matter present in the sediments. However, Cu undergoes strong complexation reaction with organic matter within the sediments followed by Ni and Co. This study suggests that the non-residual fractions (obtained from sequential extraction study) may overestimate the bioavailable fraction of metals in a system.

Key words: Kinetic fractionation, sequential extraction, Trace metal speciation, Co speciation, Ni speciation, Cu speciation

1. Introduction

The interactions of trace metals with natural ligands (which are ubiquitous in freshwater and marine sediments) play an important role in their transport, fate, and bioavailability in natural systems (Buffle, 1988; Stumm and Morgan, 1988). The chemistry of trace metals and their interaction with natural ligands (such as, dissolved organic matter) are well studied in aquatic system as reflected by the large numbers of publications available in the literature (Groschner and Appriou, 1994; Achterberg and Braungardt, 1999; Guthrie et al. 2005; Bayen et al. 2006; Chakraborty and Chakrabarti, 2006; Chakraborty et al. 2006; Chakraborty et al 2007; Chakraborty and Chakrabarti 2008; Nicolau et al. 2008; Gopalapillai et al. 2008; Chakraborty et al. 2009; Chakraborty, 2010). However, the knowledge of speciation of trace metals and their interactions with heterogeneous binding sites present in sediments are not well understood.

Various experimental methods/techniques are being used to determine speciation of trace metals in soils and sediments. The approaches include batch techniques (Carski and Sparks, 1987; Langford and Gutzman, 1992; Yu and Klarup, 1994; Bermond et al. 1998; Ghestem and Bermond, 1999; Fabre et al. 2001; Bermond and Varrault, 2004;), flow techniques (Davison et al. 2000; Beauchemin et al. 2002; Jimoh et al. 2004), kinetic extraction methods (Chakraborty et al. 2006; Chakraborty et al. 2011; Chakraborty et al 2012a; Chakraborty et al. 2012b), as well as *in situ* techniques such as Diffusive Gradients in Thin Films (DGT) (Bermond et al. 1998; Fangueiro et al. 2002, Town et al 2009; Van der veeken et al. 2010). However, the kinetic extraction method is found to be cheaper, simpler and sensitive compared to the other techniques. It is capable of providing information on kinetically distinguishable metal complexes (in soil/sediment) and their corresponding dissociation rate constants in natural systems. This method helps us understand the distribution of trace metals in soil/sediment environment by providing information about the lability of various trace metal species in the systems (Yu and Klarup, 1994; Fabre et al. 2001; Bermond and Varrault, 2004;).

In the kinetic extraction method, trace metals are quantified in an extract (containing a suitable chelating agent) as a function of time until equilibrium is reached. This time dependent metal extraction study from sediments can be useful in understanding the transport, fate, and bioavailability of trace metals (Sparks, 1989; Yu and Klarup, 1994) in sediments. The kinetic (single) extraction method has been successfully applied to predict uptake rate of metals by plants or other living organism in natural systems (Pinheiro and Van Leeuwen, 2001; Van Leeuwen et al. 2005; Feng et al. 2005). This method has been widely used to ascertain the potential availability and

mobility of the pollutants and their migration in a soil /sediment profile in polluted or naturally contaminated soils/sediments (Zhimang et al. 2001; Fangueiro et al. 2002; Margare et al. 2003).

However, the association of metals in different phases of sediments can not be understood by kinetic extraction method. Sequential extraction method is able to fractionate metals depending upon their association with different phases in sediments, such as: water soluble, exchangeable, bound to carbonates, bound to Fe/Mn-oxides, associated with organic matter, bound to sulfides, and residuals.

This method has been widely used for the fractionation study of metals in sediments from different sources, such as rivers, estuaries or marine sediments (Tessier et al. 1979; Belzunce-Segarra et al. 1997; Singh et al. 1998; Tsai et al. 1998). It is well known that binding sites present in sediment are more complex and heterogeneous compared to the heterogeneity and complexity of dissolved organic matter present in aquatic system.

To provide a better understanding of metal-sediment interactions, metals distribution and the influence of transition metal chemistry of three biologically important metals (Co, Ni and Cu) on their speciation in sediments, kinetic (single) extraction and sequential extraction methods were applied in this study.

The objective of this study was to test the hypotheses that the distribution and speciation of the three important transition metals in sediments are influenced by (i) metal-to-Total organic carbon (TOC) ratio, (ii) ligand field stabilization energy (LFSE). This study also aimed to show that use of two independent methods (with different analytical windows) can provide a better physicochemical picture of metal speciation in sediments than either one of the method can do alone.

2. Experimental:

2.1 Study area and sampling

The sediment samples were collected from the three different environmentally significant sites of the central east coast of India. 1) Kalingapatnam (KGP): The Kalingapatnam site is located in north of Andhra Pradesh. This city is not industrially developed but an important minor port is located close to the sampling station. The approximate population of this area is 10000.

Estuarine sediment samples were collected from (2) the Goutami Godavari estuary (GGE) (A 100 square kilometer area around Gautami Godavari River has an aproximate population of 560000) and (3) the Vasishtha Godavari estuary (VGE). Being the largest part of the rich Godavari delta,

agriculture and aquaculture are major economy for these areas (Gautami and Vasistha Godavari estuary areas). With the recent findings of sources for oil and natural gas has increased the pace of the industrial sector. There are few major fertilizer factories and few gas based power plants and oil refineries. The general description, geographic location of the sampling sites, the distance from the shore, and the depth from where the sediment samples were collected are shown in Figure 1.

A Van Veen stainless steel grab (with an area of 0.02 m²) was used to collect sediment; without emptying the grab, a sample was taken from the centre with a polyethylene spoon (acid washed) to avoid contamination by the metallic parts of the grab. Multiple sampling was done at each station.

2.1.1 Sediment sample preparation

The sediment samples were stored at -20°C for 15 days, and then dried at 60 °C in a forced air oven (Kadavil Electro Mechanical Industry Pvt Ltd India, Model No. KOMS. 6FD). The sediment samples were stored at 4°C until needed. The texture analysis of the studied sediments suggests that the sediment samples were a mixture of silt, sand and clay. The percentage of sand was high followed by silt and clay (of similar percentage).

2.2 Leaching procedure and Reagents

All the reagents which were used in the following procedure were of analytical grade or better (ultrapure). All the extraction processes were performed in Teflon containers.

2.2.1 Sequential extraction procedure

A series of batch extractions were performed on sediment samples, following a modified Tessier protocol (Tessier et al. 1979). The flow chart of the modified protocol is presented in Fig. 2. In this investigation, water soluble metal fraction (Fr. 1); Exchangeable fraction (Fr. 2); Carbonates fraction (Fr. 3) Reducible fraction i.e., fraction of metal associated with Fe and Mn oxides (Fr. 4); fraction of metal bound to organic matter (Fr. 5) and Residual fraction (Fr. 6) were determined. The extracted liquid samples (containing metals) in each fractions (5.0 mL) were acid digested (with a mixture of H₂O₂ (1.5 mL), HNO₃ (1.5mL) and HClO₄ (1.5mL) in Teflon vessels) on a hot plate to dryness. The residues were redissolved in 2% ultrapure HNO₃ and analyzed by ICP-MS to obtain the distribution of metals in different phases of the sediments. Three replicates of each sample were analysed.

It is important to note that validation of sequential extraction data is necessary to obtain quality results by using certified reference materials (CRM). Unfortunately, CRM was not used in this study to validate the results obtained by sequential extraction method.

2.2.2 Kinetic extraction procedure

Kinetic extraction experiments were conducted for homogenized sediments. EDTA was chosen as the extracting reagent, as it is a well-characterized, strong chelating agent that allows good control of experimental variables. Most EDTA-metal chelate complexes are formed rapidly and are extremely stable. The use of EDTA as a complexing agent avoids difficulties associated with other complexants in that a single 1:1 complex species is formed rather than a stepwise formation of complexes, which helps to simplify calculations and interpretation of results. EDTA is a non-specific complexing agent, and is reported to remove metals held in carbonates, oxides, sulphate minerals, as well as from organic and exchangeable sediment-phases. Because it is a non-selective reagent, extracted trace metals cannot be localized *a priori* within a particular sediment component, as the concentration of metal extracted is not related to classical sediment species.

Two grams of sediments were added to 200 mL of 0.05 M EDTA solution (at pH 6.0) (Merck Pvt Ltd) in a 400 mL Teflon beaker and the mixture was continually stirred with a Teflon-coated magnetic stirring bar throughout the experiment.

The pH of the coastal sediments was 7.5 or higher. However, the pH used for the kinetic extraction study was 6.0. The optimization of pH was done and the optimal pH was chosen to be pH 6.0 due to the fact that this value is acidic enough to prevent precipitation of metal hydroxides, and was demonstrated to be alkaline enough to minimize competitive extraction by H^+ .

The ratio of the mass of sediment to the volume of EDTA solution (mass/volume) was set at 0.01, as this ratio provided sufficiently high metal concentrations in the extract to be accurately quantified, while requiring a minimum amount of sediment. A special effort was made to maintain a homogeneous suspension in order to avoid changing the mass/volume ratio during sampling. Larger mass/volume ratios would be undesirable, as they could cause problems with filtration. At set time intervals, 2 mL of the suspension were filtered through a 0.2 μm syringe filter (Millex, Millipore). Sample aliquots were collected over a 36 h period. The initial time for the kinetic measurement (i.e. $t = 0$) was taken as the time just before the sediment was added to the EDTA solution. The filtrate samples (1.0 mL) were then acid digested (with a mixture of H_2O_2 (0.5mL), HNO_3 (0.5mL) and $HClO_4$ (0.5mL) in Teflon vessels) on a hot plate to dryness. The residues were then redissolved in

2% ultrapure HNO₃ and analyzed by ICP-MS to monitor the change in concentrations of metals in the extracted solution as a function of time.

The total metals concentrations in the sediments were determined by digesting 0.1 gm of sediment samples with 10.0 mL of acid mixtures of HF, HNO₃ and HClO₄ (in 7:2:1 ratio) on hot plate. The sediments were digested and evaporated to dryness. The residues were redissolved in 2% HNO₃ and analyzed by inductively coupled plasma mass spectrometry (ICPMS).

2.3 Inductively coupled plasma mass spectrometry (ICPMS)

An ICPMS (Thermo FISCHER ICP-MS, X series 2, Germany) was used for the determination of the total metals concentrations. The radio-frequency power was set at 1400W. Plasma gas, auxiliary gas and carrier gas flows were 13, 0.7 and 0.87 l.min⁻¹, respectively. The vivid description of operating condition of ICP-MS has been provided in our recent study (Chakraborty et al 2011).

2.4 Determination of Total Organic Carbon (TOC)

The Walkley-Black method (Walkley and Black, 1934) was used in this study for the determination of TOC in the sediments. This method has been widely used for the determination of TOC in soil and sediments. The detailed procedure of this method has been discussed elsewhere in the literature (Schumacher, 2002). The Walkley-Black procedure is widely used because it is simple, rapid, and has minimal equipment needs (Nelson and Sommers, 1996). However, this procedure has been shown to lead to the incomplete oxidation of organic C and is particularly poor for digesting elemental C forms. Studies have shown that the recovery of organic C using the Walkley-Black procedure ranges from 60 to 86% with a mean recovery being 76%.

2.5 QA/QC

Each sample was analyzed three times to demonstrate that the ICP-MS readings were reproducible, and the kinetic experiments were performed in triplicate for all samples to ensure repeatability of results. To account for sensitivity of the ICP-MS instrument was monitored throughout each experiment by analyzing marine sediment reference material (HISS-1, MESS-3, PACS-2 from National Research Council of Canada) followed by a reagent blank between every 10 samples. If the sensitivity changed more than 5 % during an experiment, a correction factor was used to correct for the drift.

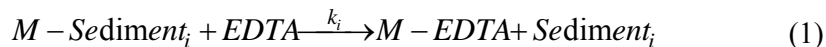
Validation of the sequential extraction method was done by comparing the total metal concentration (determined by ICP-MS) with the sum of the concentrations of metal fractions obtained by following the sequential extraction protocols. The comparable (close to 100% recovery) values of total metal concentration support the reliability and validity of the sequential extraction method. The data presented in this study are average of three replicates. Errors are indicated along with the average values. All the data are presented with 95.5% confidence interval. Relationships between concentrations of metals in the sediments were evaluated with Pearson's correlation coefficient.

3. Theory

3.1 The Kinetic Model

The kinetic model proposed by Olson and Shuman (Olson and Shuman, 1985) was adapted (Chakrabarti et al. 1994; Mandal et al. 1999) to investigate the kinetic fractionation of Co, Ni and Cu in the coastal sediments of Bay of Bengal. Consider sediment samples of n different components, in which each component, M -Sediment $_i$, exists in equilibrium with its dissociation products: the free metal ion or extractable metal complexes, M , and a naturally occurring, heterogeneous complexant, sediment $_i$, such as humic acid adsorbed on sediment and binding sites on sediments surfaces (charges have been omitted for simplicity). The subscript, i , represents different binding sites on the naturally-occurring heterogeneous complexant.

The extraction of metals from the sediment using EDTA is represented by the following reactions (charges are omitted for simplicity):



where $M - \text{sediment}_i$ and $M - \text{EDTA}$ represent a metal ion, M , bound to a sediment binding site, sediment_i , and EDTA , respectively. If EDTA is added in large excess, the metal is extracted from the original sediment binding site with a rate constant k_i , and the change in concentration of $M - \text{sediment}_i$ with time is given by the following pseudo first-order rate law.

$$-\frac{dc_{M - \text{sediment}_i}}{dt} = k_i c_{M - \text{sediment}_i} \quad (2)$$

The integrated rate law derived from equation 2, expressed in terms of the concentration of $M - \text{EDTA}$, shows that the concentration of metal extracted, $c_{M - \text{EDTA}}$, rises exponentially over time to

a limiting value, as shown in equation 3. Unfortunately, there is no way to study the individual binding sites separately or to *a priori* know the number of discrete binding sites, and there may be a nearly continuous distribution of sediment binding sites. Hence, equation 3 is written as a summation of exponentials.

$$c_{M-EDTA}(t) = \sum_{i=1}^n c_{M-sediment_i} (1 - e^{-k_i t}) \quad (3)$$

This system described by equation 3 can be approximated by a two or three-component first-order reaction model.

$$c_{M-EDTA}(t) = c_1(1 - e^{-k_1 t}) + c_2(1 - e^{-k_2 t}) + c_3(1 - e^{-k_3 t}) \quad (4)$$

Where, $c_{M-EDTA}(t)$ is the concentration of metal extracted by EDTA at time t , c_1, c_2 and c_3 are the concentrations of EDTA-extractable metal initially bound to labile (quickly extracted), slowly-labile (slowly extracted) and inert (with respect to the time scale of measurement) sediment binding sites, respectively, and k_1, k_2 and k_3 are the corresponding dissociation rate constants. The use of three kinetic components (labile and slowly-labile and inert) to describe similar systems is well reported in the literature.

The model assumes that 1) the reactions are first-order or pseudo-first-order; 2) reaction between M and EDTA is much faster than reaction the dissociation of M-sediment complexes, so that the dissociation reaction is the rate-determining step, and the measured kinetics represent the kinetics of the dissociation of the metal complex, M-sediment i , 3) M-sediment does not directly (i.e. without pre dissociation) react with the EDTA, and 4) the ratio between the concentrations of complexed metal and free metal is much larger than unity (i.e. $c_{M-Sediment} / c_M \gg 1$).

4. Result and Discussions

4.1 Total metals content in the sediments:

The average concentrations of trace metals (Sc, V, Cr, Co, Ni, Cu, Zn, Pb, Cd, and Sn) in the coastal and estuarine sediments collected at the three environmentally significant sites in the central east coast of India are presented in Table 1. Evidently, the general levels of trace metals concentrations were relatively high in both the estuarine sediments compared to the coastal

sediments. The correlation matrix and regression analysis suggest that a strong positive correlation exist between Co, Ni and Cu metals in the sediments (Table 2). These three metals were chosen to perform the sequential and kinetic extraction study to understand their fractionation and the chemistry of these metals in the sediments. The variations in the total metal contents are presented in Figure 3 a. It shows that the total Co contents were the same in all the three sediments. However, the estuarine sediments were found to have higher concentrations of Cu and Ni compared to their concentrations in the coastal sediments.

4.2 Kinetic fractionation of Co, Ni and Cu in the sediments

The simultaneous (by single extraction kinetic method) dissociation kinetics of Co (II), Ni (II), and Cu (II) complexes in the sediments was studied by using EDTA as an extracting competing ligand. The changes in concentrations of these metals in the solutions were determined by ICPMS.

Under the experimental conditions used in this work, metal complexes with $k_d > 10^{-2} \text{ s}^{-1}$ cannot be experimentally resolved from the metal aqua complex. This represents the upper limit of the rate constants that can be experimentally determined within the experimental time scale of the method. The lower limit is simply defined by the time taken to complete the kinetic run. Metal species with $k_d < 10^{-5}$ (i.e., k_{ft} and $k_{dt} \ll 1$) are defined as inert (van Leeuwen, 2001).

The extraction curves from the kinetic experiments of these three metals, presented in Figure 3 (b, c, and d), show the changes in concentrations of extracted Co, Ni and Cu in EDTA solution as a function of time. The concentrations of metals extracted, c_{M-EDTA} , rise exponentially over time to a limiting value, as shown in each curve. The curved solid lines represent the fitted line obtained from the non-linear regression analysis, and the corresponding numerical results that describe the fitted data are presented in Table 3. The extraction curves show that the concentrations of extracted metals in most of the sediments reached dynamic equilibrium after 36 h under the experimental conditions.

The experimental data from the kinetic extraction study were fit to a three component model because it was the simplest model (i.e. minimum number of components) that gave an adequate statistical and visual fit to the data (i.e. good representation of the system). Although use of more components in the model often statistically fit the data better, the additional components were often of negligible concentration or had a high degree of uncertainty. The three components model has been widely used by soil chemists (Jardine and Sparks, 1984; Brusseau and Rao, 1989; Comans et al. 1992; Langford and Gutzman, 1992; Gutzman and Langford, 1993; Yu and Klarup, 1994; Sparks, 1998). This three-component system should not be considered to assume that there are only three discrete sediment

binding sites for these three metals, but that it allows for diversity among sites, where the calculated parameters can be thought of as representing average values over a distribution of similar sites with closely-spaced rate constants (Yu and Klarup, 1994).

Each curves in Fig 3 (b, c, and d), show three distinguishable features: a quickly rising section that represents the rapid dissociation rate (k_{d1}) of weak metal-sediment complexes ($c_1\%$), and a slowly rising section which corresponds to relatively stronger metal-sediment complexes ($c_2\%$) with slower dissociation rate constant (k_{d2}) and the last part of the curve that lies almost parallel to x-axis, which can be attributed to slow dissociation (k_{d3}) of strong (inert) metal-sediment complexes ($c_3\%$).

Kinetic fractionation of Co in coastal and estuarine sediments

The changes in extractable Co concentrations (in the EDTA solutions from the sediments) as a function of time are presented in Fig. 3b. The first part of all the curves are almost indistinguishable from one another, suggesting that they represent dissociation of one type of Co-sediment complexes having very similar fast dissociation rate constants with low stability. These complexes can be considered as dynamic (within the time scale of the measurement) in nature. The dissociation rate constants of Co-sediment complexes are presented in Table 3.

The concentrations of readily extractable weak Co-sediment complexes ($c_1\%$) with low thermodynamic stability was high in one of the estuarine sediments collected at Vasishta Godavari estuary (22.9% of the total Co content) with k_{d1} value of $2.7 \times 10^{-3} \text{ s}^{-1}$, followed by Kalingapatnam (17.2% of the total Co content) with k_{d1} value of $4.2 \times 10^{-3} \text{ s}^{-1}$, and Goutami Godavari estuary (14.2% of the total Co content) with k_{d1} value of $8.3 \times 10^{-3} \text{ s}^{-1}$ (Table 3).

The middle part of all curves in Fig. 3b are easily distinguishable from one another, suggesting that they represent dissociation of different types of Co-sediment complexes ($c_2\%$) having different dissociation rate constants (k_{d2}); The dissociation rate constants of the second component of Co-sediment complexes are presented in Table 3 shows that the k_{d2} of Co-sediment complexes are relatively slow and differ from one sediment to the other.

Slow dissociating Co-sediment complexes ($c_2\%$) was high in the estuarine sediments collected at Vasishta Godavari estuary (47.8% of the total Co content) with k_{d2} value of $3.5 \times 10^{-5} \text{ s}^{-1}$, followed by Goutami Godavari estuary (35.6% of the total Co content) with k_{d2} value of $9.8 \times 10^{-5} \text{ s}^{-1}$, and Kalingapatnam (9.4% of the total Co content) with k_{d2} value of $8.5 \times 10^{-5} \text{ s}^{-1}$.

The last part of the curves, lies almost parallel to x-axis, can be attributed to slow dissociation of thermodynamically stable Co-sediment complexes (represented by $c_3\%$) with very slow dissociation rate constants (k_{d3}). Table 3 shows that 73.6% of the total Co was found to be inert in the sediment collected at Kalingapatnam with k_{d3} value of $< 1 \times 10^{-6} \text{ s}^{-1}$. Sediment samples collected at Vasishtha and Goutami Godavari estuary were found to have 29.3 and 50.2% of inert Co-sediment complexes respectively with very slow dissociation rate. It is interesting to note that the total Co content in all the sediments were very similar (Table 1).

Kinetic fractionation of Ni in coastal and estuarine sediments

Figure 3 c shows the kinetic extraction curves for Ni. It is evident from Fig 3c that three distinguishable types of Ni complexes were present in the sediments. Figure 3c shows that the three sediments contained similar type of fast dissociating Ni-sediment complexes with very similar fast dissociation rate constants and low stability. A fraction of these fast dissociating complexes of Ni can be an indicator of bioavailable Ni species in the systems.

Leaching of weak Ni-sediment complexes ($c_1\%$) with low stability was found to be high in one of the estuarine sediments collected at Vasishtha Godavari estuary (47.4% of the total Ni content) with k_{d1} value of $1.3 \times 10^{-3} \text{ s}^{-1}$, followed by Kalingapatnam (28.6% of the total Ni content) with k_{d1} value of $2.7 \times 10^{-3} \text{ s}^{-1}$, and Goutami Godavari estuary (8.9 % of the total Ni content) with k_{d1} value of $7.2 \times 10^{-3} \text{ s}^{-1}$ (Table 3).

The middle part of all the curves in Fig. 3c represents dissociation of different types of Ni-sediment complexes ($c_2\%$) having different dissociation rate constants (k_{d2}). The dissociation rate constants of the second component of Ni-sediment complexes are presented in Table 3.

Slow dissociating Ni-sediment complexes ($c_2\%$) was high in the estuarine sediments collected at Goutami Godavari estuary (41.5% of the total Ni content) with k_{d2} value of $3.9 \times 10^{-5} \text{ s}^{-1}$, followed by Kalingapatnam (22.9% of the total Ni content) with k_{d2} value of $3.8 \times 10^{-5} \text{ s}^{-1}$, and Vasishtha Godavari estuary (9.4% of the total Ni content) with k_{d2} value of $8.5 \times 10^{-5} \text{ s}^{-1}$.

The last part of the curves, lie almost parallel to x-axis, can be attributed to slow dissociation of thermodynamically stable Ni-sediment complexes (represented by $c_3\%$) are presented in Table 3 with very slow dissociation rate constants (k_{d3}). It was found that approximately 50% of the total Ni content in all the sediments was inert in nature. These inert (with respect to the timescale of the measurement) Ni-sediment complexes were found to have very slow dissociation rate constants.

Kinetic fractionation of Cu in coastal and estuarine sediments

Figure 3d shows the kinetic extraction curves for Cu. Each kinetically-distinguishable component of Cu-sediment complexes is presented in Table 3. The plot of changes in the extracted Cu concentrations in the EDTA solutions from the sediments as a function of time (s) show that there were three distinguishable types of Cu complexes (as found for other two metals) present in the sediments.

Cu-sediment complexes ($c_1\%$) with low thermodynamic stability was found to be high in one of the estuarine sediments collected at Vasishta Godavari estuary (25.6% of the total Cu content) with k_{d1} value of $2.0 \times 10^{-4} \text{ s}^{-1}$, followed by Kalingapatnam (19.8% of the total Cu content) with k_{d1} value of $1.8 \times 10^{-3} \text{ s}^{-1}$, and Goutami Godavari estuary (13.6% of the total Cu content) with k_{d1} value of $1.1 \times 10^{-3} \text{ s}^{-1}$ (Table 3).

Slow dissociating Cu-sediment complexes ($c_2\%$) was found to be highest of 25.4% of the total Cu content in the sediment collected at Kalingapatnam. The sediments collected at Goutami Godavari and Vashista Godavari estuaries were found to have 21 and 6.3% of the total Cu contents respectively with corresponding k_{d2} values of 2.9×10^{-5} and $1.1 \times 10^{-5} \text{ s}^{-1}$.

Major parts of the total Cu contents in all the sediments were found to be inert. These observations suggest that Cu interacts much more strongly with the strong complexing sites present in the sediments than Co and Ni.

4.3 Sequential extractions for Co, Ni and Cu fractionation in coastal and estuarine sediments

Modified classical sequential extraction method (Tessier et al. 1979) was applied to understand the distribution and speciation of Co, Ni and Cu in the coastal and estuarine sediments. Figure 4 shows the variation in percentage of these metals, associated with different phases of the sediments collected at three different sites.

Fractionation of Co in the estuarine and coastal sediments:

The fractionation data for Co are presented in Table 4 and the distribution is depicted in Fig 4a. The water soluble (Fr. 1) complexes of Co in all the sediments were found to be within the range of 4.5-14.5% of the total Co content within the sediments. High percentages of water soluble Co complexes (10.6 and 14.4% of the total Co) were present in the sediments collected at Goutami and Vasishta Godavari estuaries. The exchangeable (Fr.2) fraction of Co was found to be minor

contributors in all the sediments. Carbonate and bicarbonate fraction (Fr. 3) of Co in all the sediments was found to be within the range of ~7-10% of the total Co (Table 4).

The association of Co with Fe and Mn oxides has already been reported (30) showing that Co adsorption on these oxides within a sediment has high stability constants. This investigation suggests that relatively higher percentage of Co associated with Fe and Mn-oxide (Fr. 4) compared to Fr. 1, 2 and 3. Co associated with Fe, Mn-oxides were within the range of 20 to 35% of the total Co present in the sediments. Co was primarily present in the residual fraction (Fr. 6) (~38-50%). Co associated with organic fraction was in the range of (Fr.5) (~9-11%).

It important to mention that residual fraction could be considered as an inert phase corresponding to the part of the Co which cannot be mobilized. The experimental data suggest that appreciable amounts of Co were found in non-residual form in all the sediments (Table 4).

Fractionation of Ni in the estuarine and coastal sediments:

Table 4 and Fig 4b represents the fractionation data for Ni in the sediments. The water soluble (Fr. 1) complexes of Ni in all the sediments were found to be within the range of 6.7 -26% of the total Ni content within the sediments. High percentages of water soluble Ni complexes (26% of the total Ni) were present in the sediment collected at Vasistha Godavari estuary. The exchangeable (Fr.2) fraction of Ni and the fraction in the form of carbonate and bicarbonate (Fr 3) were found to be minor contributors in all the sediments. Ni was primarily present in the residual fraction (Fr. 6) (~48-60%) followed by organic fraction (Fr 4). Ni associated with organic fraction was in the range of (Fr.5) (~8-20%).

Fractionation of Cu in the estuarine and coastal sediments:

The distributions of Cu in the coastal and estuarine sediments are presented in Figure 4c. Cu was equally distributed between Fr 5 and Fr 6. The percentages of Cu in the residual fractions (Fr 6) in the sediments were in the range of 41-45%. The range (~30-45%) of the total Cu was found to associate with the organic fractions of the sediments (Fr 5). Highest concentration of Cu was found to associate with the organic carbon compared to the other transition metals in the sediments. This finding suggests that Cu probably interact very strongly than the other transition metals with organic carbon present in sediments. However, the concentration of water soluble complexes of Cu in the sediments were also found to be high compared to the other metals.

4.4 Metal-to-TOC Ratio and extractable metals species

The percentage of dissociable metal fractions ($c_1 + c_2$) obtained from kinetic (single) extraction method for the three metals in the sediment samples showed that the relative percentage of the dissociable components (c_1+c_2) of these metals did not increase with the increasing metal-to-TOC ratio except for Co.

Figure 5 showed that the readily extractable metal fractions of Co linearly increased with the increasing Co-to-TOC ratio. This observation indicates that at low Co loading, Co preferred to undergo strong complexation reactions with the strong binding sites available in the sediments (to form inert complexes) and Co moved to the available weaker binding sites (after occupying all the strong sites) for complexation with the increasing Co loading in the sediments and thus the dynamic extractable Co species increased. However, the concentrations of dynamic metal complexes of other two metals (Ni and Cu) did not increase with the increasing metal-to-TOC ratio.

It is always expected (in aquatic environment, dissolved phase) that the fast components (c_1) of metals should increase with the increasing metal-to-DOC ratio (if all strong binding sites are occupied) due to the progressive increase in complexation of metals with the weaker binding sites of the heterogeneous natural ligands (humics) present in the system. However, in this study the extractable concentrations of Ni and Cu complexes remain almost constant (Figure 5) with the increasing metal-to-TOC ratio. This observation suggests that probably more strong binding sites were available for Cu and Ni to undergo strong complexation reactions in the studied sediments.

However, the nature of binding sites present in sediment are more heterogeneous (associated with different phases of sediments) and complex in nature than the heterogeneity and complexity of dissolved organic carbon in freshwater.

The kinetic extraction method is unable to fractionate metals on the basis of their association with different phases in the sediments and thus, the kinetic (single) extraction method was unable to correctly predict the influence of the metal-to-TOC ratio on the distribution and fractionation of Ni and Cu in the sediments.

Data obtained from sequential extraction method (Table 4, Figure 6a) suggest that concentration of water soluble (Fr 1) Co-complexes increased (from 4.4 to 14.4%) with the increasing $[Co]_T/TOC$ ratio in the sediments. Table 4 shows that the percentage of Co (with respect

to the total Co content) associated with the other phases of the sediments (Fr. 2, Fr 3, Fr 4) decreased with the increasing $[\text{Co}]_{\text{T}}/\text{TOC}$ ratio in the sediments.

The kinetic extraction study also suggests that dynamic complexes of Co gradually increased with the increasing $[\text{Co}]_{\text{T}}/\text{TOC}$ ratio. The combination of both the data set suggests that the water soluble complexes of Co present in the sediments were dynamic in nature. Sequential extraction study suggests that the concentrations of non residual complexes of Ni and Cu gradually decreased with the increasing $[\text{metal}]_{\text{T}}/\text{TOC}$ ratio in the sediments (Figure 6b and c). This finding is in agreement with the kinetic data. Both the data set suggest that more strong binding sites were available for Cu and Ni to undergo strong complexation reactions in the studied sediments.

4.4 Effects of ligand field stabilization energy (LFSE) and water exchange rate (k_{w}) on fractionation of Co, Ni and Cu in the sediments.

The effects of ligand field stabilization energy (LFSE) are usually significant in the chemistry of the first-row transition metals. Ligand field stabilization energy (LFSE) (Butler and Harrod, 1989; Morel and Hering, 1993) is known to influence the rate of octahedral ligand substitution reactions of 3d transition metal complexes. It is well known that the maximum LFSE contributions to the activation energy give more stability to the complex with slow dissociation kinetics. Inert complexes are those with large LFSEs.

Results for the dissociation rate coefficients of the metal complexes of different concentrations of Co (II) d^7 , Ni (II) d^8 , and Cu (II) d^9 in the estuarine and coastal sediments are presented in Table 3. The influence of the d electron configuration on the dissociation rate constants (k_{d1} and k_{d2}) of Co (II) d^7 , Ni (II) d^8 , Cu (II) d^9 , in the sediments are presented in Figure 7 (a and b).

The results consistently demonstrate that the dissociation kinetics (k_{d1} and k_{d2}) of the 3d transition metal complexes in the estuarine and coastal sediments follow the trend as predicted from the LFSEs (weak field, high spin complexes) ($k_{\text{d},\text{Co(II)} d^7} > k_{\text{d},\text{Ni(II)} d^8} > k_{\text{d},\text{Cu(II)} d^9}$).

The apparently contradictory behaviour of Cu(II), is found to form thermodynamically stable metal complexes, and yet has a rapid rate constant of water exchange, $k_{\text{w}} = 1 \times 10^9 \text{ s}^{-1}$ (Morel and Hering, 1993, Langford, 1971), This can be attributed to the Jahn-Teller effect (Douglas et al. 1994), The Jahn Teller effect is responsible for the distorted octahedral structure of copper (II) aqua complex. This effect makes the axial Cu-H₂O bonds elongated and kinetically labile, and the equatorial bonds shortened and kinetically inert (Figure 3d and Table 3).

Hence, Cu (II) simultaneously both forms stronger bonds (equatorial ligands) and weak bonds (axial ligands) than predicted from its LFSE alone.

The kinetic single extraction method provided a chemically significant description of the kinetics of metal-sediment interactions and correctly predicted the influence of LFSE and k_w on the dissociation rate constants of metal-sediment complexes in the natural system.

The concentrations of residual fractions (Fr. 6) (assumed to be biologically unavailable stable complexes) of these metals in the sediments (obtained from sequential extraction study) must follow the same trend as predicted by their LFSE and Jahn Teller distortion effects. However, it is interesting to note that the sum of the concentrations of these metals in Fr. 6 and Fr. 5 (metal fraction associated with organics) follow the same trend as predicted by LFSE and Jahn Teller distortion effects. This suggests that these metals formed stable complexes (kinetically inert) with the organic matter in the studied sediments. Highest percentage of Cu was found to associate with organic carbon of the sediments followed by Ni and Co. This finding suggests that Cu undergoes strong complexation reaction with TOC of the sediments followed by Ni and Co. The data obtained from sequential extraction method are in very good agreement with the data obtained by kinetic extraction method.

4.5 Comparison of non residual fraction of Co, Ni and Cu obtained from sequential extraction method with their dynamic metal fractions obtained from kinetic extraction method in the coastal and estuarine sediments.

Total non-residual and residual metals complexes obtained from sequential extraction method and dynamic and inert complexes of these metals obtained from kinetic extraction method are compared. The statistical correlation study among the dynamic and inert complexes (obtained from kinetic extraction study) with the different combination of non residual and residual metal fractions of each metal were performed and presented in Table 5.

A strong correlation was found between the dynamic fractions, (c1+c2) (obtained by kinetic extraction study) of Co with its non-residual fractions (Fr 1+Fr 2+ Fr 3) (obtained by sequential extraction study). A similar strong correlation was found between the inert complexes (c3) of Co (obtained from kinetic extraction study) with the combine concentrations of Co complexes associated with Fe/Mn oxide, organic matter and residual Co complexes (Fr 4 + Fr. 5+ Fr. 6). This statistical analysis suggests that a fraction of non residual Co complexes (Co associated with Fe/Mn-oxide and

organic matter in the sediments) probably acted as inert complexes during the kinetic extraction study (under the experimental condition).

Table 5 shows a strong correlation between the dynamic fractions, (c_1+c_2) of Ni with its non-residual fractions (Fr 1+Fr 2+ Fr 3 + Fr 4). A similar strong correlation was found between the inert complexes (c_3) of Ni with the combine concentrations of Ni complexes associated with organic matter and residual Ni complexes (Fr. 5+ Fr. 6). This observation also suggests that a major part of the Ni-TOC complexes acted as inert complexes during the kinetic extraction study (under the experimental condition).

A good correlation was present in between the dynamic fractions, (c_1+c_2) of Cu with its non-residual fractions (Fr 1+Fr 2+ Fr 3 + Fr 4). The inert complexes (c_3) of Cu were found to have strong correlation with the combine concentrations of Cu complexes associated with organic matter and residual Cu complexes (Fr. 5+ Fr. 6). This observation indicates that a Cu formed inert complexes with the organic matter present in the sediments.

The comparison and statistical analysis of the fractionation data obtained by two independent methods suggest that the transition metals formed strong complexes with the organic matter present in the sediments and probably behaved as inert complexes during the single kinetic extraction study.

This experimental observation suggests that the non-residual fractions (obtained from sequential extraction study) may overestimate the bioavailable fraction of metals in a system.

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Table 1: The average concentrations (three replicates) (moles. kg⁻¹) of the trace metals in the coastal and estuarine sediments

Chemical Constituents	Sampling Stations		
	KGP	GGE	VGE
TOC (%)	3.7	2.0	1.4
Sc	$(3.4 \pm 0.1) \times 10^{-4}$	$(3.5 \pm 0.1) \times 10^{-4}$	$(3.0 \pm 0.1) \times 10^{-4}$
V	$(2.7 \pm 0.2) \times 10^{-3}$	$(4.1 \pm 0.1) \times 10^{-3}$	$(2.9 \pm 0.2) \times 10^{-3}$
Cr	$(1.6 \pm 0.2) \times 10^{-3}$	$(1.6 \pm 0.2) \times 10^{-3}$	$(1.4 \pm 0.3) \times 10^{-3}$
Co	$(4.4 \pm 0.2) \times 10^{-4}$	$(4.3 \pm 0.4) \times 10^{-4}$	$(4.3 \pm 0.2) \times 10^{-4}$
Ni	$(7.1 \pm 0.1) \times 10^{-4}$	$(9.4 \pm 0.1) \times 10^{-4}$	$(1.1 \pm 0.1) \times 10^{-3}$
Cu	$(1.0 \pm 0.1) \times 10^{-3}$	$(1.7 \pm 0.2) \times 10^{-3}$	$(1.6 \pm 0.2) \times 10^{-3}$
Zn	$(7.9 \pm 0.9) \times 10^{-3}$	$(7.8 \pm 0.9) \times 10^{-3}$	$(5.9 \pm 0.7) \times 10^{-2}$
Pb	$(1.1 \pm 0.1) \times 10^{-3}$	$(1.6 \pm 0.1) \times 10^{-3}$	$(2.0 \pm 0.1) \times 10^{-3}$
Cd	$(1.9 \pm 0.1) \times 10^{-4}$	$(2.1 \pm 0.1) \times 10^{-4}$	$(2.2 \pm 0.1) \times 10^{-4}$
Sn	$(4.0 \pm 0.1) \times 10^{-4}$	$(3.6 \pm 0.1) \times 10^{-4}$	$(3.6 \pm 0.1) \times 10^{-4}$

Table 2: Correlation coefficient matrix (r) for trace metals in surface sediments of coastal and estuarine sediments collected from the central east coast of India (Adj R² > 0.6, p < 0.05, Bold figures are significant)

	<i>Cu</i>	<i>Ni</i>	<i>V</i>	<i>Cr</i>	<i>Co</i>	<i>Zn</i>	<i>Cd</i>	<i>Sn</i>	<i>Pb</i>	<i>Bi</i>
Cu	1.00									
Ni	0.94	1.00								
V	0.38	0.53	1.00							
Cr	0.65	0.76	0.77	1.00						
Co	0.82	0.89	0.60	0.95	1.00					
Zn	0.49	0.69	0.13	0.26	0.43	1.00				
Cd	0.95	0.85	0.13	0.56	0.78	0.43	1.00			
Sn	-0.21	-0.10	0.60	0.57	0.30	-0.45	-0.28	1.00		
Pb	0.30	0.58	0.71	0.48	0.43	0.70	0.07	0.11	1.00	
Bi	-0.41	-0.32	0.27	0.36	0.12	-0.54	-0.38	0.93	-0.16	1.00

Table 3: Kinetically distinguishable components of CO, Ni and Cu complexes in the estuarine and coastal sediments obtained by kinetic extraction study using EDTA as a competing ligand

Element	Sampling sites	c ₁ (%)	k _{d1} (s ⁻¹)	c ₂ (%)	k _{d2} (s ⁻¹)	c ₃ (%)	k _{d3} (s ⁻¹)
Co	KGP	17.2 ± 0.9	(4.2 ± 0.2) × 10 ⁻³	9.4 ± 0.5	(8.5 ± 0.2) × 10 ⁻⁵	73.6 ± 2.9	<1 × 10 ⁻⁶
	GGE	14.1 ± 0.7	(8.3 ± 0.4) × 10 ⁻³	35.6 ± 0.8	(9.8 ± 0.2) × 10 ⁻⁵	50.2 ± 2.0	<1 × 10 ⁻⁶
	VGE	22.9 ± 1.1	(2.7 ± 0.1) × 10 ⁻³	47.8 ± 0.9	(3.5 ± 0.2) × 10 ⁻⁵	29.3 ± 1.2	<1 × 10 ⁻⁶
Ni	KGP	28.6 ± 1.4	(2.7 ± 0.1) × 10 ⁻³	22.9 ± 1.1	(3.8 ± 0.2) × 10 ⁻⁵	48.3 ± 1.9	<1 × 10 ⁻⁶
	GGE	8.9 ± 0.4	(7.2 ± 0.4) × 10 ⁻³	41.5 ± 0.9	(3.9 ± 0.2) × 10 ⁻⁵	49.7 ± 2.0	<1 × 10 ⁻⁶
	VGE	44.4 ± 2.4	(1.3 ± 0.1) × 10 ⁻³	3.0 ± 0.1	(2.0 ± 0.2) × 10 ⁻⁵	52.5 ± 2.1	<1 × 10 ⁻⁶
Cu	KGP	19.8 ± 1.0	(1.8 ± 0.1) × 10 ⁻³	25.4 ± 1.9	(3.5 ± 0.2) × 10 ⁻⁵	54.7 ± 2.2	<1 × 10 ⁻⁶
	GGE	13.6 ± 0.7	(1.1 ± 0.1) × 10 ⁻³	21.4 ± 1.1	(2.9 ± 0.2) × 10 ⁻⁵	64.8 ± 2.6	<1 × 10 ⁻⁶
	VGE	25.6 ± 1.3	(2.0 ± 0.1) × 10 ⁻⁴	6.3 ± 0.3	(1.1 ± 0.2) × 10 ⁻⁵	68.4 ± 2.7	<1 × 10 ⁻⁶

Values presented as the Average ± 2 × standard deviation, n = 3, All the data are presented with 95.5% confidence interval

Table 4: Distributions of Co, Ni and Cu (relative % of the total metal content) in different phases of the estuarine and coastal sediments determined by sequential extraction method. Different fractions of metals associated with different phases are presented as: water soluble metal fraction (Fr. 1); Exchangeable fraction (Fr. 2); Carbonates fraction (Fr. 3) Reducible fraction i.e., fraction of metal associated with Fe and Mn oxides (Fr. 4): fraction of metal bound to organic matter (Fr. 5) and Residual fraction (Fr. 6).

Metals	Sampling Stations	Fr. 1 (%)	Fr. 2 (%)	Fr. 3 (%)	Fr. 4 (%)	Fr. 5 (%)	Fr. 6 (%)
Co	KGP	4.4 ± 0.5	3.5 ± 0.5	10.6 ± 1.0	34.2 ± 0.5	9.0 ± 1.5	38.3 ± 1.0
	GGE	10.6 ± 2.8	1.4 ± 0.4	7.2 ± 0.5	21.0 ± 0.6	10.4 ± 2.9	49.4 ± 1.3
	VGE	14.4 ± 2.8	1.4 ± 0.4	10.1 ± 0.5	20.2 ± 0.6	9.7 ± 2.9	44.3 ± 1.3
Ni	KGP	6.6 ± 1.5	5.2 ± 0.1	6.6 ± 0.6	15.0 ± 0.5	19.3 ± 1.5	47.3 ± 1.3
	GGE	9.2 ± 1.5	3.1 ± 0.5	6.2 ± 1.0	9.7 ± 0.5	9.7 ± 1.5	62.0 ± 1.0
	VGE	6.8 ± 3.0	2.5 ± 0.4	6.7 ± 1.0	8.0 ± 0.5	7.4 ± 1.4	68.6 ± 2.5
Cu	KGP	9.6 ± 1.0	12.4 ± 1.5	1.8 ± 0.5	1.8 ± 0.2	30.1 ± 2.0	44.3 ± 1.5
	GGE	9.1 ± 1.5	14.5 ± 0.5	1.1 ± 0.5	2.2 ± 0.2	31.6 ± 1.5	41.4 ± 2.5
	VGE	5.8 ± 1.0	2.5 ± 0.5	1.4 ± 0.2	3.1 ± 1.0	45.3 ± 3.5	41.9 ± 4.5

Values presented as the Average ± 2 × standard deviation, n = 3, All the data are presented with 95.5% confidence interval

Table 5. Correlation coefficient matrix (r) for dynamic and inert fractions (obtained from kinetic extraction) and sequentially extracted different fractions of Co, Ni, and Cu in the surface of coastal and estuarine sediments collected from the central east coast of India (Adj $R^2 > 0.9$, all are significant)

Co	c_1+c_2	c_3	Fr. 1+Fr. 2 + Fr. 3	Fr. 4 + Fr. 5 + Fr. 6
c_1+c_2	1.0			
c_3	-1.0	1.0		
Fr. 1+Fr. 2 + Fr. 3	0.9	-0.9	1.0	
Fr. 4 + Fr. 5 + Fr. 6	-0.9	0.9	-1.0	1.0

Ni	c_1+c_2	c_3	Fr. 1+Fr. 2 + Fr.3+ Fr. 4	Fr. 5 + Fr. 6
c_1+c_2	1.0			
c_3	-1.0	1.0		
Fr.1+Fr.2 + Fr.3+ Fr.4	0.9	-1.0	1.0	
Fr. 5 + Fr. 6	-1.0	1.0	-1.0	1.0

Cu	c_1+c_2	c_3	Fr. 1+Fr. 2 + Fr.3+ Fr. 4	Fr. 5 + Fr. 6
c_1+c_2	1.0			
c_3	-1.0	1.0		
Fr.1+Fr.2 + Fr.3+ Fr.4	0.6	-0.7	1.0	
Fr. 5 + Fr. 6	-0.6	0.7	-1.0	1.0

Caption and Legends

Figure 1: Map of the sampling areas along the central east coast (Andhra Pradesh region) of India, The filled circles is the locations of the five environmentally significant sites.

Figure 2. Modified Tessier's sequential extraction scheme

Figure 3: a) Distribution of Co, Ni, and Cu in the sediments collected from three significant locations. b) Dynamic (extractable) Co species from the sediments as a function of time. c) Dynamic (extractable) Ni species from the sediments as a function of time. . d) Dynamic (extractable) Cu species from the sediments as a function of time. All the extraction process was carried out in presence of 0.05M EDTA at pH 6. (O); Kalingapatnam, (□); Vasistha Godavari estuary, (◇); Goutami Godavari.

Figure 4: Chemical fractionation of Co (a), Ni (b) and Cu (c) in three different sediment samples collected at three environmentally significant sites; KGP-Kalingapatnam; GGE- Goutami Godavari Estuary; VGE-Vasistha Godavari Estuary

Figure 5: Variation of dissociable metal complexes ($c_1 + c_2$) of Co (O), Ni (□) and Cu (◇) as a function of M /TOC ratio.

Figure 6: Variation in concentration of different fraction Co (a), Ni (b) and Cu (c) with the varying M/TOC ratio in three different sediment samples collected at three environmentally significant sites; KGP-Kalingapatnam; GGE- Goutami Godavari Estuary; VGE-Vasistha Godavari Estuary, water soluble (●), exchangeable (○), bound to carbonates (▼), bound to Mn- Fe-oxides (Δ), bound to organic matter (■), and residuals (□).

Figure 7: Variation in fastest (k_{d1}) and medium (k_{d2}) dissociation rate coefficients of Co(II), Ni(II), and Cu(II), complexes in the sediments collected from (O); Kalingapatnam, (□); Vasistha Godavari estuary, (◇); Goutami Godavari.

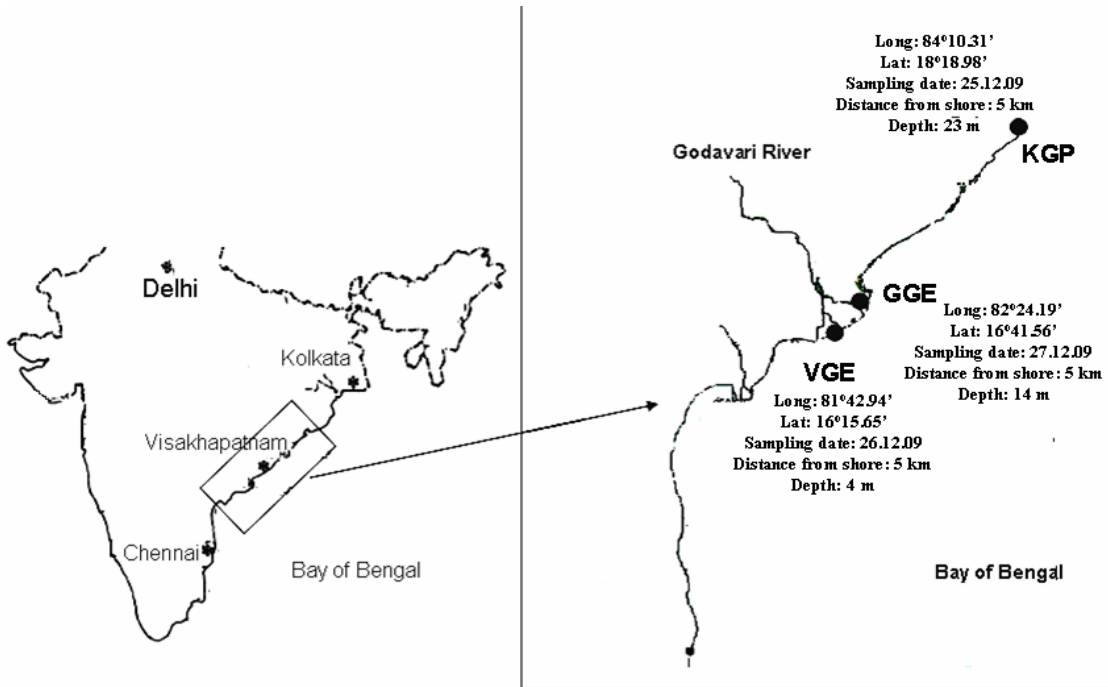
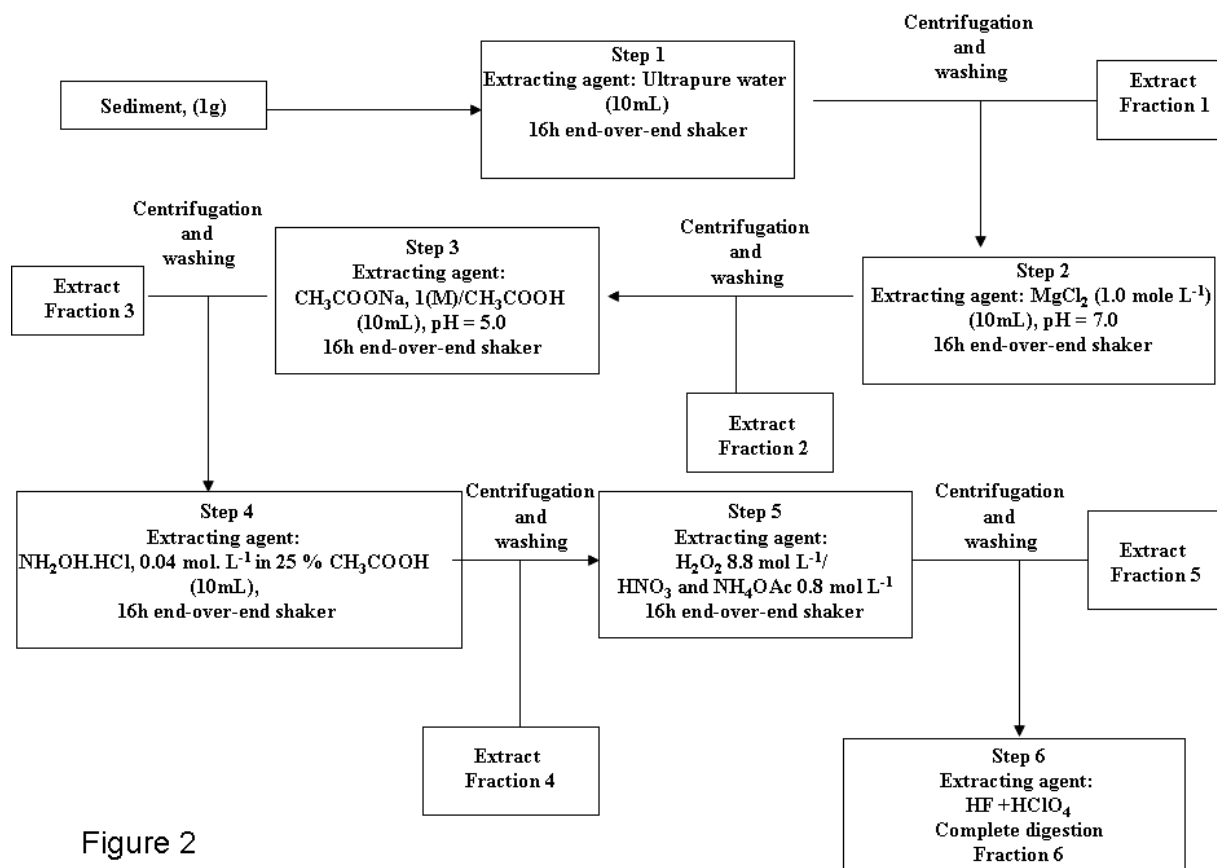


Figure 1



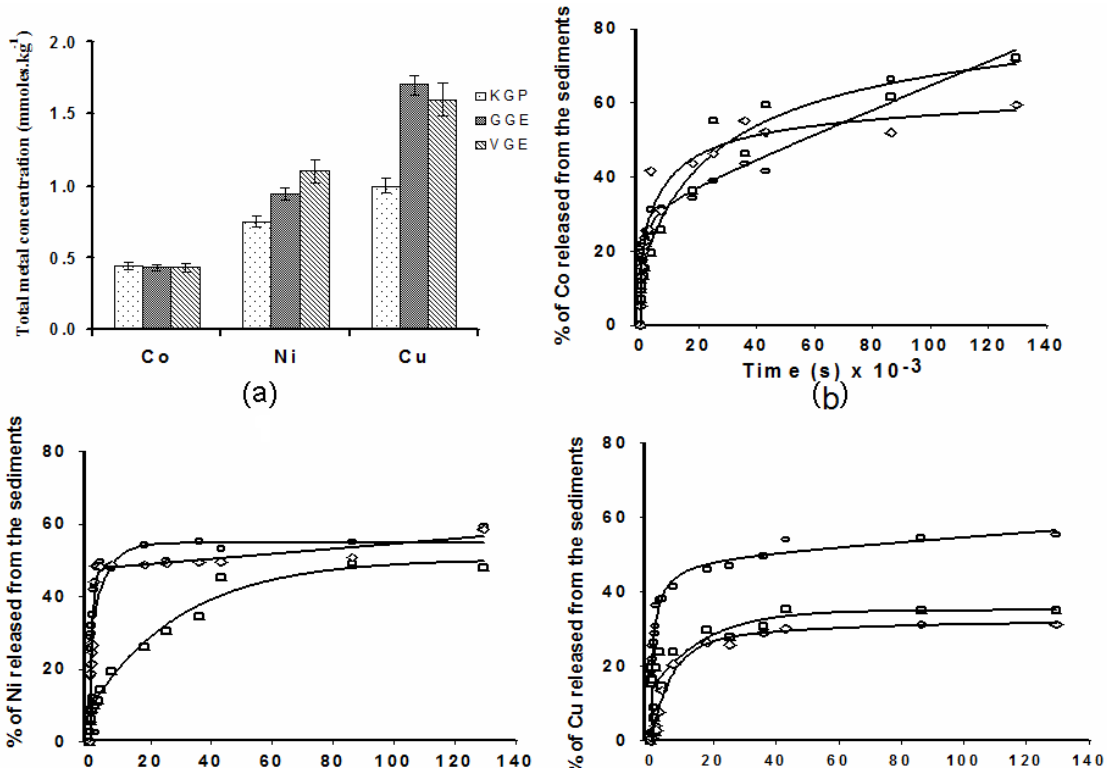


Figure 3

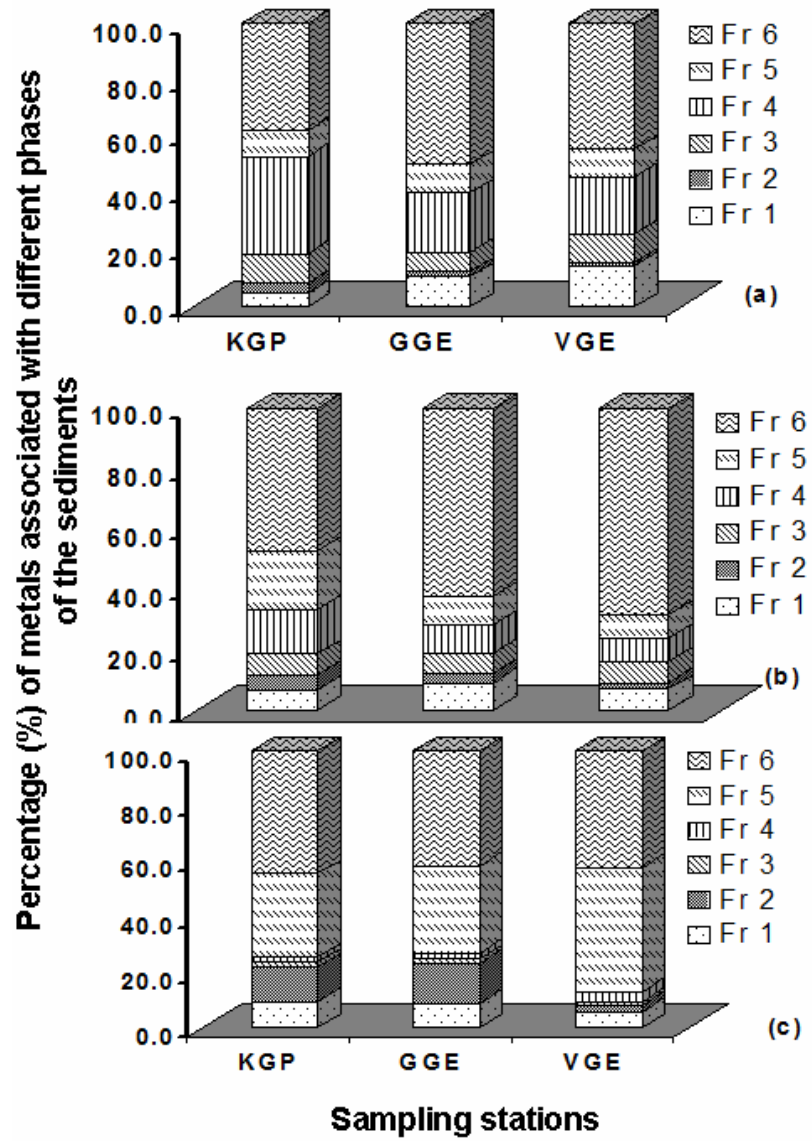


Figure 4

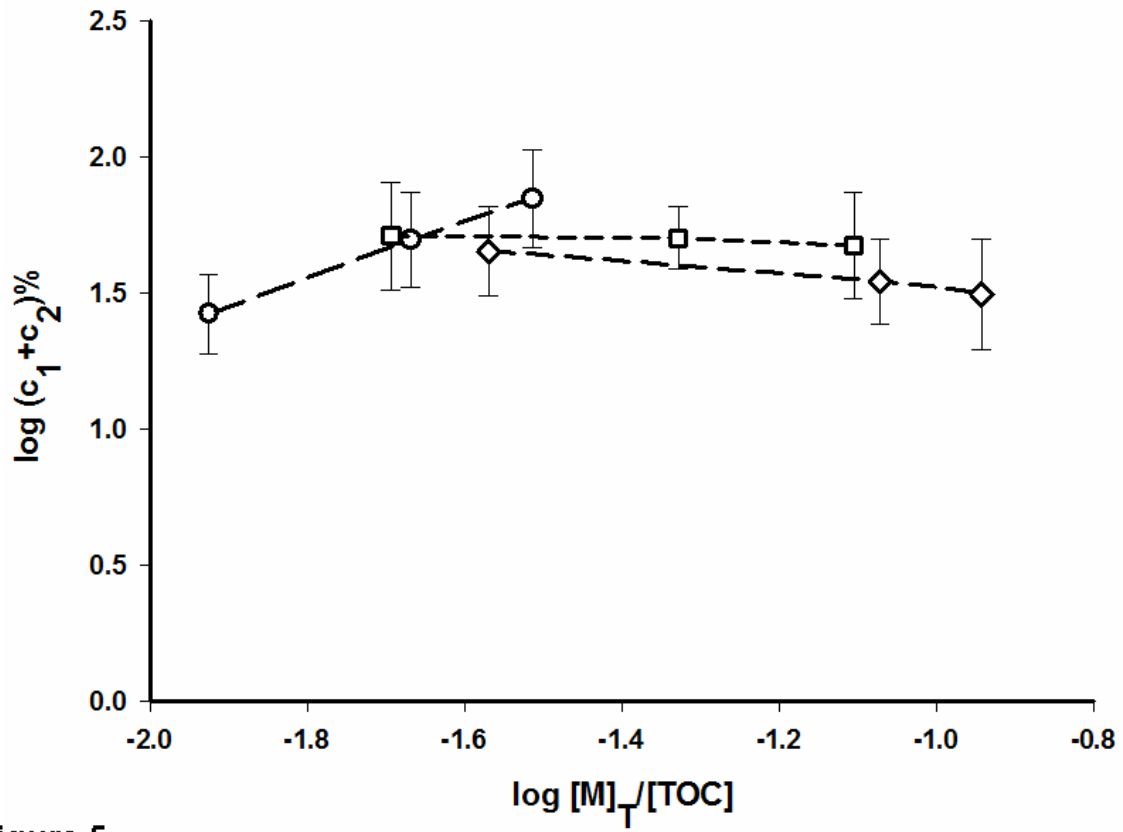
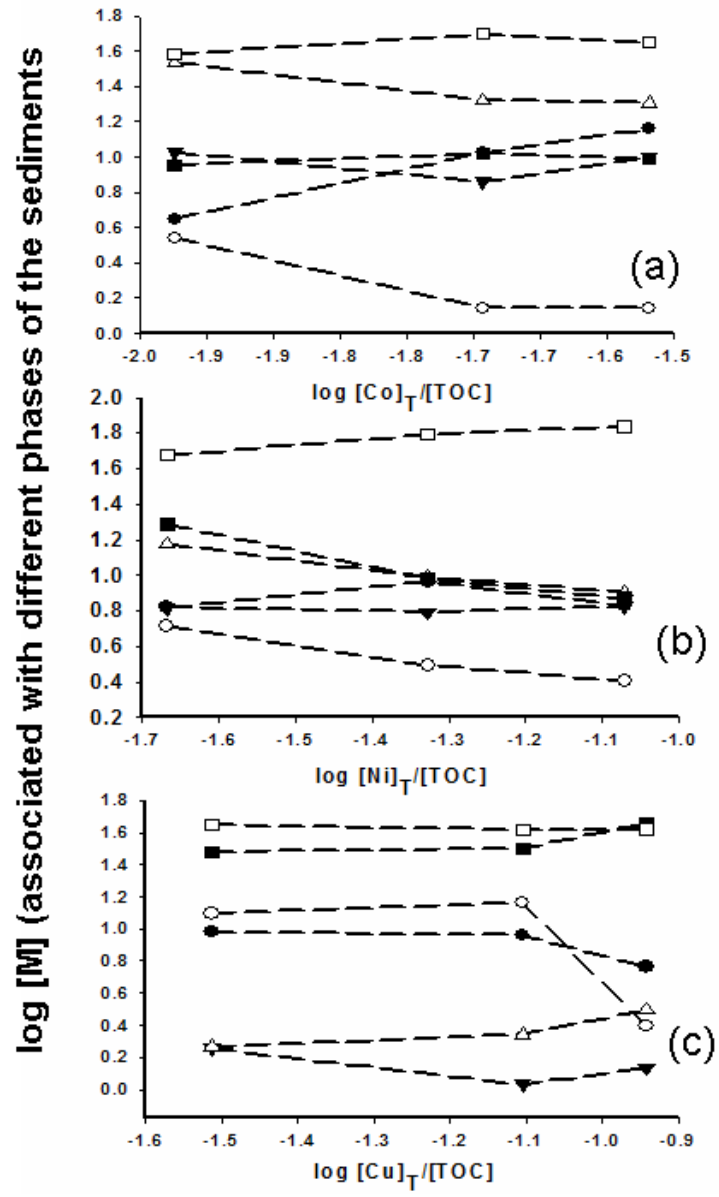
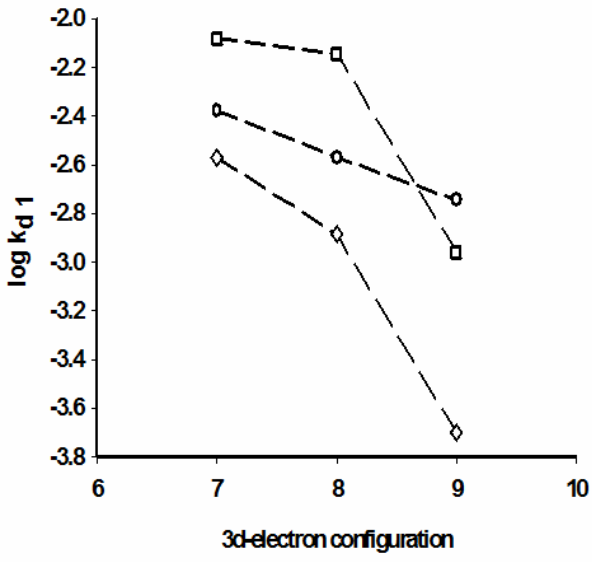
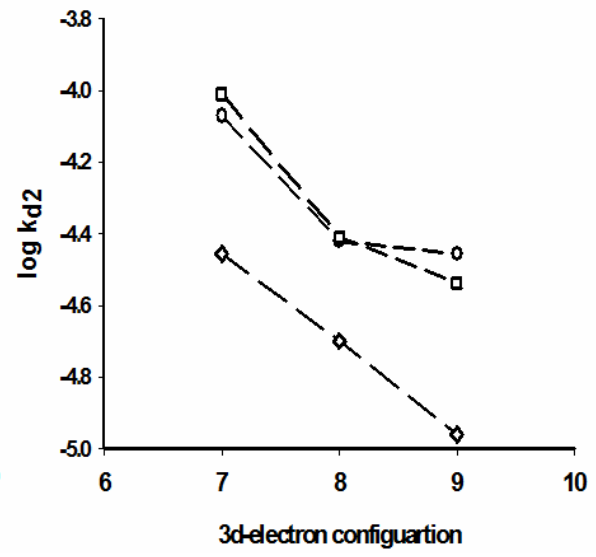


Figure 5





a



b

Figure 7