A study of lead and cadmium speciation in some estuarine and coastal sediments

Parthasarathi Chakraborty*, P. V. Raghunadh Babu, and V. V. Sarma

*National Institute of Oceanography (CSIR), India, 176 Lawsons Bay Colony, Visakhapatnam, 530017, Andhra Pradesh, India
E-mail: pchak@nio.org, Ph: 91-891-2509169, Fax-91-891-2543595

Abstract

Chemical speciation of lead (Pb) and cadmium (Cd) in the coastal and estuarine sediments along the central east coast of India was studied by applying sequential and kinetic extraction methods. The results of this study suggest that concentrations of non-residual and dynamic complexes (which are good indicators of bioavailability) of these toxic metals gradually increase with increasing total metal loading in sediments.

Increase in bioavailability of these toxic metals with increasing total metal loading in sediments can be a potential threat to benthic organisms and aquatic biota in the system. This study shows that total organic carbon (TOC) is one of the key factors which play a crucial role in controlling speciation of these toxic metals in sediments. However, distribution and speciation of these metals are influenced by their total metal loading and trace metal competitions rather than only TOC content in sediments.

An attempt was made to identify the key factors which control the speciation of these two toxic metals in natural system and provides a better understanding to predict and control pollution of Pb and Cd in coastal and estuarine sediments

Key words: Sequential extraction method; Kinetic extraction method; Pb speciation; Cd speciation; Coastal sediments; estuarine sediments;
1. **Introduction:**

Estuarine and coastal sediments are generally considered as a sink for metals and metalloids (Feng et al. 2004; Yao et al. 2007; Mishra et al. 2008). It is well understood that total metal content in sediments can not predict the bioavailability and toxicity of that metal (Forstner and Salomons, 1980; Luoma and Davies, 1983; Di Toro et al. 1990; Arjonilla et al. 1994; Pagnanelli et al. 2004; Clozer et al. 2006). It is in fact the physicochemical forms of the metal that determine its potential bioavailability and toxicity. Thus, the speciation and distribution study of metals in sediments has become one of the most important areas of environmental research. The distribution and speciation studies of metals in sediments not only provide an indication of the current quality of the overlaying waters (Zhang et al. 2006; Laing et al. 2007) but also provide important information on the transportation and fate of pollutants (Gupta and Sinha, 2007; Zhang et al. 2008; Cheng et al., 2009; Zhao et al. 2009).

Cadmium (Cd) and lead (Pb), known to be the toxic metals (Kumar et al. 2008; Lim et al. 2008; Weng et al. 2008) with very little (Lane et al. 2005; Xu et al. 2008) or no nutrient values, are abundant almost everywhere in the nature. Pollution of soils, sediments and waters with Pb and Cd cause their incorporation into the food chain, which could result in wide variety of adverse effects in animals and humans, since it is a cumulative contaminant (Sanborn et al. 2002; IARC Monograph, 2006; Loghman-Adham, 1997; Jacobson and Turner, 1980; Stohs and Bagchi, 1995; Waalkes, 2000). Thus, it is essential to control Pb and Cd pollution in environment.

In order to understand the mobility and potential ecological risks of Pb and Cd, particular attention was given to identify the key factors which control distribution and speciation of these two toxic metals in the coastal and estuarine sediments of the central east coast of India.

The sequential extraction method (Tessier et al. 1979; Martin et al. 1987; Usero et al. 1998; Koretsky et al. 2008; Gonzalvez et al 2009; Issaro et al. 2009; Rao et al. 2010) which can provide information about the distribution of metal associated with different specific solid phases in sediments (Arain et al. 2007) was applied in this study to understand the distribution, mobility and bioavailability of Pb and Cd in the estuarine and coastal sediments (It is well reported that non-residual metal complexes determined by sequential extraction method are reliable indicators of bioavailability). The most widely used sequential extraction protocols are those recommended by Tessier et al.(1979), Kersten and Förstner (1986) and the Community Bureau of Reference (BCR) (Quevauviller et al. 1993). The wide application of the sequential extraction protocols proposed by
Tessier for metal speciation in river, marine, estuarine and stream sediments provided the confidence to apply this method for this study.

Kinetic extraction study (Fangueiro et al. 2002; Fangueiro et al. 2005; Chakraborty and Chakrabarti, 2006; Chakraborty et al. 2006; Vanthvune and Maes, 2006; Reyhanitabar and Gilkes, 2010; Chakraborty et al. 2011) was also performed to understand the nature of Pb and Cd-sediment complexes (dynamic or inert) and determine their dissociation rate constants in the sediments (dynamic metal complexes and their dissociation rate constants determined by single kinetic extraction method are also considered as a good predictor of bioavailability of metals).

It has been reported (Gismera et al. 2004, Chakraborty et al. 2009; Chakraborty 2010 and Chakraborty et al. 2011) that the combination of two or more methods having complementary analytical capabilities can provide a better physicochemical picture of metal speciation in natural systems than either one of the analytical methods can do alone. Sequential and kinetic extraction methods have been widely used (individually) for metal speciation study in natural systems (sediments and soils). However, the combined use of these two methods for metal speciation study in natural systems is scarce in literature.

The thrust of this study was to provide better understanding of Pb and Cd speciation in estuarine and coastal sediments. An attempt was made to identify the key factors which regulate speciation and bioavailability of these toxic metals in coastal and estuarine sediments.

2. Materials and methods:

2.1 Sampling location and collection

Sediment samples were collected from five different environmentally significant sites off the central east coast of India as shown in Figure 1. Coastal sediment samples were collected from (1) Kalingapatnam, (2) Vishakhapatnam, and (3) Machilipatnam. 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. Vishakhapatnam is the second largest city in the state of Andhra Pradesh and the third largest city (after Kolkata and Chennai) in the east coast of India. Visakhapatnam has become a hub for many heavy industries. The Visakhapatnam port, the largest in the country, is the ideal gateway contributing to the development of petroleum, steel and fertilizer industries. The approximate population of Visakhapatnam city is 2,000,000. Machilipatnam is home to approximately 200,000 residents. Agriculture is the main occupation in Machilipatnam. Union Defence Ministry, of the
Government of India, operates a manufacturing unit to manufacture electronic equipment in Machilipatnam. The sampling station at Machilipatnam was very close to Krishna River estuary.

Estuarine sediment samples were collected from (4) the Goutami Godavari estuary (A 100 square kilometer area around Gautami Godavari River has an approximate population of 560000) and (5) the Vasishtha Godavari estuary. 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 Table 1.

A Van Veen stainless steel grab (with an area of 0.02 m²) was used to collect the sediments. 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 dredge. Multiple sampling was done at each station. The 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). Sediments were subsequently stored at 4°C until needed. The sediments were characterized (percentage of sandy, silt and clay content) and the data are presented as supporting documents (Table 1SD)

2.2 Leaching procedure and Reagents

All the extraction processes were performed in Teflon containers. The reagents used in this study were of analytical grade or better (ultrapure)

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). In this investigation, the 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 procedure and protocols has been elaborated elsewhere (Tessier et al. 1979).

The extracted liquid samples (containing metals) in each fractions (5.0 mL) were acid digested to dryness (with a mixture of H₂O₂ (1.5 mL), HNO₃ (1.5mL) and HClO₄ (1.5mL) in Teflon vessels) on a hot plate. 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.

2.2.2 Kinetic extraction procedure

Kinetic extraction experiments were conducted for sediments. 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 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 (0 min, 2 min, 4 min, 6 min, 8 min, 10 min, 15 min, 20 min, 25 min, 30 min, 45 min, 1 h, 2h, 5 h, 7h, 10 h, 24 h, 36 h), 2 mL aliquots of the suspension were filtered through a 0.2 μm syringe filter (Millex, Millipore). 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 to dryness (with a mixture of H\(_2\)O\(_2\) (0.5mL), HNO\(_3\) (0.5mL) and HClO\(_4\) (0.5mL) in Teflon vessels) on a hot plate. The residues were then redissolved in 2% ultrapure HNO\(_3\) and analyzed by ICP-MS to monitor the change in concentrations of metals in the extracted solution as a function of time. The kinetic experiments were performed in triplicate for all samples to ensure repeatability of results.

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, HNO\(_3\) and HClO\(_4\) (in 7:2:1 ratio) on hot plate. The sediments were digested and evaporated to dryness. The residues were redissolved in 2% HNO\(_3\) and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Each sediment samples were analyzed in triplicates.

2.3 Inductively coupled plasma mass spectrometry (ICP-MS)

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 operating condition of ICP-MS has been reported in our previous study (Chakraborty et al 2011). To account for sensitivity of the ICP-MS instrument was monitored throughout each experiment by analyzing marine sediment reference material (HISS-1, MESS-3, and PACS-2 from the National
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.

2.4 Statistical Analysis

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. Relationship between concentrations of metals associated with different solid phases in the sediments (obtained from sequential extraction study) and dynamic metal complexes (obtained from kinetic extraction study) were evaluated with Pearson’s correlation coefficient.

3. Theory

3.1 The Kinetic Model

The kinetic model proposed by Olson and Shuman (1985) was adapted (Lu et al. 1994; Mandal et al. 1999; Chakraborty and Chakrabarti, 2006; Chakraborty et al 2006; Chakraborty et al. 2011a; Chakraborty et al. 2011b) to investigate the kinetic speciation of Pb and Cd in the coastal and estuarine sediments of Bay of Bengal. Consider sediments 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.

\[
M_{-Sediment_i} \stackrel{k_{d,if}}{\rightleftharpoons} M + \text{Se dim ent}_i \quad \text{(slow)} \quad \text{(i)}
\]

\[
M + \text{EDTA} \rightarrow M - \text{EDTA} \quad \text{(fast)} \quad \text{(ii)}
\]

where the formation and dissociation rate constants, \( k_{f,if} \) and \( k_{d,if} \), are coupled by the stability constant, \( K = k_{f,ij}/k_{d,ij} \), through the principle of microscopic reversibility.

If each complex, \( M_{-Sediment_i} \), dissociates simultaneously and independently (at a rate that depends on the nature of the functional group, its position on the macromolecule, and the residual charge), the concentration of the free metal ion, \( c_M \), or extractable metal complexes and the total concentration of all complexes, \( c_{M_{-Sediment}} \), at any time, \( t \), is given by a summation of exponentials as shown in equations 3.

\[
c_{M_{-Sediment}}(t) = \sum_{i=1}^{n} c_{M_{-Sediment_i}} \cdot \exp(-k_{d,if} \cdot t) \quad \text{(iii)}
\]
where $c_{M\text{-Sediment}_i}^{0}$ is the initial concentration of M-Sediment $i$ and $c_{M\text{-Sediment}_i}(t)$ is the concentration of M-Sediment $i$ at any time, $t$.

The model assumes that a) the reactions are first-order and pseudo-first-order; b) reaction (ii) is much faster than reaction (i), so that reaction (i) is the rate-determining step, and the measured kinetics then represent the kinetics of the dissociation of the metal complex, M-Sediment $i$; c) M-Sediment does not directly (i.e. without predissociation) react with the EDTA, and 4) the ratio between the concentrations of complexed metal and free metal is much larger than unity (i.e. $c_{M\text{-Sediment}_i} / c_M >> 1$).

3.2 Non-linear regression analysis for kinetic measurement

Analyzing experimental data to obtain physical parameters is a crucial point in the kinetic extraction method. In this paper, data was fitted to the kinetic model by non-linear regression analysis using the Marquadt-Levenberg algorithm. The minimum number of parameters required to accurately fit the data was determined by finding the number of components in which the sum of square of the weighted residuals shown below achieved a minimum value.

Sum of squares of the weighted residuals = \[ \sum \left( \frac{C(t) - C_T(t)}{C(t)^{1/2}} \right)^2 \]

where, $C(t)$ is the experimental value and $C_T(t)$ is the calculated value using the parameters obtained from the regression analysis.

For a polyfunctional, complexant such as sediment, the number of components is not a simple issue. The small number of components with specific rate constants may not accurately describe the chemistry of the binding sites of sediment. A binding site may have a range of binding energy because of the heterogeneous nature. This in turn will lead to a distribution of values for the dissociation rate constants for the complexes. Nevertheless, the specific rate constants may represent an average value for a group of complexes on a particular site.

4. Results and discussions:

4.1 Accumulation of heavy metals in sediments

The average values of trace metals (Sc, V, Cr, Co, Ni, Cu, Zn, Pb, Cd, and Sn) concentrations in the coastal and estuarine sediments collected at five environmentally significant sites in the central east coast of India are presented in Table 2.
It is evident that the concentrations of Zn (ranging from 254 to 3876 mg.kg\(^{-1}\)) were high in all the studied sediments followed by V (ranging from 59 to 205 mg.kg\(^{-1}\)) and Cr (ranging from 24 to 83 mg.kg\(^{-1}\)). The concentrations of Pb (ranging from 147 to 424 mg.kg\(^{-1}\)) and Cd (ranging from 17 to 37 mg.kg\(^{-1}\)) were also found to be high in the sediments.

The pollution load index (PLI), proposed by Tomilson et al (1980) was used in this study to understand the quality (with respect to metals concentrations) of the estuarine and coastal sediments. The PLI values of the studied sediments varied from one site to another. The PLI value shows an increasing trend from Kalingapatnam (KGP) to Machilipatnam (MCP) (Table 2). The calculation of contamination factor and PLI are provided as supporting document (Table 2SD and 3SD). The lowest PLI was found in the sediment collected at Visakhapatnam (PLI = 1.8), followed by KGP (PLI = 3.0), GGE (PLI = 4.0), VGE (PLI = 5.5) and MCP (PLI = 5.4). The high values of PLI for the sediments collected at GGE, VGE and MCP were probably because of the contribution of metal pollutants from the Godavari and Krishna rivers. It was found that Pb, Cd, Zn were the major pollutants contributing towards the high PLI (relatively) in the coastal and estuarine sediments.

However, the total metal content in the sediments can not predict the bioavailability and toxicity of the pollutant. Thus, systematic investigations were performed in the sediments to understand the chemical distribution and speciation of Pb and Cd.

4.2 Chemical fractionations of Pb and Cd in coastal and estuarine sediments by sequential extraction method:

A modified sequential extraction protocol proposed by Tessier (1979) was applied to understand the chemical distributions and speciation of Pb and Cd in the coastal and estuarine sediments.

Figure 2 suggests that Pb had different affinities for the different solid-phases of the studied sediments. The concentrations of water soluble Pb complexes (Fr. 1) were found to be high in all the sediments. These water soluble Pb complexes is expected to leach out easily from the sediments and can increase the mobility and bioavailability of Pb in the overlaying water columns (data obtained from sequential extraction method are presented as a supporting document, Table 4SD).

The lowest concentrations of Pb were found in the exchangeable form (Fr. 2) in the studied sediments (Figure 2). A similar observation has also been reported in the literature (Ramos et al. 1994; Van Benschoten et al. 1994; Chen et al. 1995; Yarlaggada et al. 1995; Chlopecka et al. 1996; Heil et al. 1996).

The concentrations of Pb as carbonate and bicarbonate (Fr.3) were found to be in the range of 3.3-12.3 % of the total Pb content of the sediments (Figure 2) and depend upon the concentrations of...
carbonate and bicarbonate within the sediment. Yarlagadda et al. (1995) found the distribution of Pb from a waste site soil to contain mostly carbonate (60-70%) fractions. Similar observation was also reported by Urija and Branica (1995). Low concentrations of Pb in the carbonate form can also be obtained depending upon the carbonate content of sediment as found in this study. The association of Pb with Fe-Mn oxide (Fr. 4) in the sediments were in the range of ~4-15% of the total Pb content in the studied sediments.

The concentrations of water soluble Pb complexes (Fr. 1) were highest followed by the concentration of Pb complexed with organic matter (Fr. 5) in all the studied sediments. It was found that ~15-46% of the total Pb was complexed with organic matter present in the sediments to form thermodynamically stable complexes.

Organic matter in the sediments was probably playing a key role in controlling Pb speciation in the sediments under oxic condition. It is necessary to mention that Pb had specific binding sites in the different solid phases within the sediments. However, the increasing Pb loading in the sediments increased the water soluble Pb complexes (Fr 1) (which are usually thermodynamically less stable) in the studied sediments. This study suggests that Pb prefers to undergo complexation reaction with strong binding sites (probably present in organic matter in sediments) at low Pb loading. However, this toxic metal starts to occupy weaker binding sites (after saturating relatively stronger binding sites) with increasing concentration of Pb.

It must be kept in mind that the metals first form complexes that are kinetically favourable. Subsequent reequilibration requires a metal and ligand double-exchange reaction, that is, both a ligand exchange in which the ligand having stronger binding sites replaces the ligand having weaker binding sites, and a metal exchange in which the stronger-binding metal replaces the weaker-binding metal, to form a strong metal–ligand complex at chemical equilibrium.

It is interesting to note that the concentration of Pb as residual component (Fr 6) (expected as inert complexes) in the studied sediments were close to the concentrations of Pb as reported in the upper continental crust (UCC) and post archean Australian Shale (PACS). Thus, one could suggest that the high concentrations of Pb as non residual complexes (Fr 1+ Fr 2+Fr 3+Fr 4+ Fr 5) in the studied sediments were probably due to human activities.

Figure 3, shows the chemical distributions of Cd in the different phases of the sediments. The concentrations of water soluble Cd content (Fr. 1) varied from ~9 to 57% of the total Cd content in the sediments. Approximately ~18-38% of the total Cd was associated with organic matter. Figure 3 indicates that the concentrations of Cd associated with rest of the solid phases (Fr 2, Fr 3, Fr 4) were
evenly distributed in all the sediments. The residual fractions (Fr. 6) of Pb and Cd in the studied sediments were less than 10% of the total metal content. The fractionation data obtained from the sequential extraction method are provided as supporting documents.

The data obtained from sequential extraction method suggest that Cd also prefers to form complexes with organic matter in the sediments. The apparent stability and lability of Cd-organic complexes in the sediments is found to be dependent on Cd loading. Cd found to have specific binding sites on the different phases of the sediments (Fr 2 , Fr 3, Fr 4). It is suggested that Cd prefers to form thermodynamically strong complexes (probably with organic matter) at low Cd loading. However, the concentration of thermodynamically weak complexes (water soluble complexes of Cd) gradually increases with the increasing concentration of Cd in the sediments.

The total amounts of Cd associated with the organic matter (ranging from 5.6 to 6.9 mg.kg\(^{-1}\)) were lower than the amounts of Pb associated with the same organic matter (ranging from 42.1 to 53.2 mg.kg\(^{-1}\)) in the studied sediments (the data are presented as supporting documents, see Table 5SD). This is probably because of the fact that Pb forms thermodynamically more stable complexes with organic matter than Cd. It has been reported in the literature that Pb forms thermodynamically more stable complexes than Cd (Pinheiro et al. 1994; Grzybowski, 2000; Chang chien et al. 2006; Chakraborty et al 2007). Thus it is expected to have more accumulation of Pb in the organic phases than Cd in the sediments.

It is interesting to note that the accumulation of Pb and Cd in the organic phases (Fr. 5) did not increase with the increasing total organic carbon (TOC) concentrations in the sediments. This signifies that the accumulations of Pb and Cd in the organic fraction was probably influenced by other different factors, such as total metal loading and trace metal competitions (Chakraborty and Chakrabarti, 2008) rather than only organic matter content within the sediments.

It is important to note that validation of data obtained from the sequential extraction method is required by using certified reference materials (CRM). Unfortunately, a CRM was not used in this study. 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 are provided as a supporting document (Table 5SD).

Sequential extraction procedures (equilibrium based) for trace metal fractionation are actually directed to operationally defined fractionation (Templeton et al 2000) which may not represent the
dynamic natural systems. In order to have more precise information on Pb and Cd speciation in sediments, the competing ligand exchange method (CLEM) was applied using EDTA as the competing ligand, to determine the percentage of dynamic metal complexes and their dissociation rate coefficients in the sediments.

4.3 Kinetic speciation of Pb and Cd in sediments

The extraction curves obtained from the kinetic speciation experiments, given in Figures 4 and 5, show the changes in concentrations of extracted Pb and Cd as a function of time. Each curve displayed an exponential increase in the metal concentration in the extracting EDTA solution with respect to time. The curved solid lines represent the results from the non-linear regression analysis, and the corresponding numerical results that describe the fitted data are presented in Table 3.

Each kinetically-distinguishable component is expressed as a fraction of the total metal (Pb or Cd) concentrations in the sediments (i.e. as a percentage of the total Pb or Cd concentrations).

4.3.1 Kinetic speciation of Pb

The experimental data from the kinetic extraction curves were fitted to a three component model because it was the simplest model that gave an adequate statistical and visual fit to the data (i.e. good representation of the system) (Gutzman and Langford, 1993). 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-component system should not be considered to assume that there are only three discrete sediment binding sites, 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 (Gutzman and Langford, 1993).

Each curve (except for the sediments collected at Visakhapatnam) in Fig 4 shows three distinguishable features: a quickly rising section that represents the rapid dissociation rate ($k_{d1}$) of weak Pb-sediment complexes ($c_1$), and a slowly rising section which corresponds to relatively stronger Pb 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 Pb-sediment complexes ($c_3$).

The first part of all the curves in Fig. 4 are almost indistinguishable from one another, suggesting that they represent dissociation of one or more Pb complexes having very similar fast dissociation rate constants ($k_{d1}$); probably, they are all of Pb complexes with low thermodynamic stability and are
dynamic (within the time scale of the measurement) in nature. The dissociation rate constants of Pb-sediment complexes are presented in Table 3 shows that the $k_{d1}$ of Pb-sediment complexes are fast and almost very similar in all the sediments collected at five different stations.

The percentage of weak Pb-sediment complexes ($c_1$) with low thermodynamic stability were found to be similar in three different sediments collected at Visakhapatnam, Goutami Godavari estuary and Machilipatnam (~47.5% of the total Pb present in the sediments were easily extractable) with $k_{d1}$ value of $\sim 1.0 \times 10^{-3}$ s$^{-1}$. The lowest concentration of dynamic Pb complexes was found in the sediment collected at Kalingapatnam (13.9% of the total Pb present in the sediment) with $k_{d1}$ value of $1.1 \times 10^{-3}$ s$^{-1}$ (Table 3).

The middle parts of all the curves in Fig. 4 are easily distinguishable from one another, suggesting that they represent dissociation of different Pb complexes ($c_2$) having different dissociation rate constants ($k_{d2}$); they are all of Pb complexes with higher thermodynamic stability compared to the fast component. The dissociation rate constants ($k_{d2}$) of the second component of Pb-sediment complexes are presented in Table 3.

The percentage of slowly dissociating Pb complexes ($c_2$) were found to be high in the sediment collected at Kalingapatnam (56.5 % of the total Pb present in the sediment) with $k_{d2}$ value of $2.7 \times 10^{-5}$ s$^{-1}$), followed by Vasistha Godavari estuary, Goutami Godavari estuary and Machilipatnam (32.6, 28.6 and 27.5% of the total Pb present in the sediments) with $k_{d2}$ value of $1.4 \times 10^{-5}$ s$^{-1}$, $4.3 \times 10^{-4}$ s$^{-1}$ and $1.8 \times 10^{-5}$ s$^{-1}$ respectively. The sediment collected at Visakhapatnam station was found to have negligible concentration of $c_2$ component under the experimental conditions.

The last part of the curve that lies almost parallel to x-axis, which can be attributed to slow dissociation of strong Pb-sediment complexes (represented by $c_3$) are presented in Table 3 with very slow dissociation rate constants ($k_{d3}$). 52.1 % of the total Pb was found to be inert in the sediment collected at Visakhapatnam with $k_{d3}$ value of less than $1 \times 10^{-6}$ s$^{-1}$. Sediment samples collected at Kalingapatnam, Goutami Godavari estuary, Vasistha Godavari estuary and Machilipatnam were found to have 29.6, 22.8, 33.8 and 24.9% of inert Pb-sediment complexes respectively with very slow dissociation rate constants.

4.3. 2 Kinetic speciation of Cd

The experimental data from the kinetic extraction curves were fitted to a two component model for Cd metal. Each curve in Fig 5 shows two distinguishable features: a quickly rising section that represents the rapid dissociation rate ($k_{d1}$) of weak Cd-Sediment complexes ($c_1$), and the last part of
the curve that lies almost parallel to x-axis, which can be attributed to slow dissociation \((k_{d2})\) of strong Cd-sediment complexes \((c_2)\).

The first part of all curves in Fig. 5 are almost indistinguishable from one another, suggesting that they represent dissociation of one or more Cd complexes having very similar fast dissociation rate constants; probably, they are all of Cd complexes with low thermodynamic stability and are dynamic (within the time scale of the measurement). The dissociation rate constants and dynamic fractions of Cd-sediment complexes are presented in Table 3, shows that the \(k_{d1}\) of Cd-sediment complexes are fast and almost very similar in all the sediments collected at five different stations.

Leaching of weak Cd-sediment complexes \((c_1)\) with low thermodynamic stability was found to be similar in two different sediments collected at Kalingapatnam and Visakhapatnam (~57 % and 54% of the total Cd present in the sediments) with \(k_{d1}\) value of \(\sim 8 \times 10^{-4}\) and \(2 \times 10^{-3}\) s\(^{-1}\) respectively. The highest fraction of dynamic Cd complexes was found in the sediments collected at Machilipatnam (~83% of the total Cd present in the sediment) with \(k_{d1}\) value of \(\sim 2.0 \times 10^{-3}\) s\(^{-1}\) (Table 3).

Slow dissociating Cd complexes \((c_2)\) were found to be high in the sediment collected at Kalingapatnam (46.2% of the total Cd present in the sediment) with very slow \(k_{d2}\) value (with respect to the time scale of measurement), followed by Visakhapatnam, Goutami Godavari estuary and Vasistha Godavari estuary (43.2%, 34.7% and 32.4% of the total Cd present in the sediments respectively).

5. Comparison of non residual fraction of Pb and Cd obtained from sequential extraction method with the dynamic metal fraction obtained from kinetic extraction method.

It is well known that sediments contain a continuous distribution of metal binding sites with different binding energies. Progress in determination of reliable physicochemical parameters to describe metal complexation by sediment is hindered by the inherent physicochemical complexity of sediments. Combination of two or more appropriate methods and techniques, with their associated measurement timescales and detection windows, may provide better information of metal speciation in natural systems (Chakraborty, 2010; Chakraborty et al., 2009). It is of clear interest in this section to understand the dynamic behaviour of Pb and Cd in the coastal and estuarine sediments by combining the data obtained by two different extraction methods.

Total non-residual fractions \((Fr. 1 + Fr. 2 + Fr. 3 + Fr. 4 + Fr. 5)\) of Pb and Cd obtained from sequential extraction method and dynamic fractions of Pb \((c_1+c_2)\) and Cd \((c_1)\) obtained from kinetic extraction method are compared. The results are presented in Table 4. The inert complexes of Pb and Cd (i.e. \(c_3\) and \(c_2\) component of Pb and Cd respectively) obtained from kinetic extraction study were
assumed to be residual component of these metals in the sediments and not compared with the non-residual fraction of these two metals obtained from sequential extraction study.

It should be noted that the total non residual fractions (Fr. 1+ Fr. 2+Fr. 3+ Fr. 4 + Fr. 5) obtained by sequential extraction method for both the metals were higher than the dynamic metal fractions obtained by kinetic extraction method in all the studied sediments (Table 4).

It is interesting to note that the total percentage of non residual fraction of both the metals excluding Fr 5 (metals associated with organics in the sediments) were lower than the percentage of dynamic complexes obtained from kinetic extraction method. This probably suggest that both the metals formed strong (inert) and weak (dynamic) complexes with the different binding sites present in the organic matter within the studied sediments.

It can be assumed that the metals complexes in Fr 1, Fr 2, Fr 3 and Fr 4 (obtained from sequential extraction study) were probably dynamic in nature and having lower thermodynamic stability than their EDTA complexes. Thus, one could infer (by comparing the non-residual and dynamic concentrations of these metals) that a fraction of metal–organic complexes was dynamic in nature (within the time scale of measurement in the kinetic extraction study). However, a major part of metal-organic complexes were found to be inert (having higher stability than Pd or Cd-EDTA complexes, within the time scale of measurement).

The physical and chemical heterogeneity of organic matters make metal–organic complexes polydisperse and different in thermodynamic stability within the sediments. The data obtained from sequential and kinetic extraction methods provide the evidence of the dynamic behaviour of heavy metals in aqueous sediment suspensions.

A very good correlation was obtained between the residual fraction (excluding metal fraction associated with organic matter) and the dynamic fraction (kinetic extraction study) of both the metals.

The statistical correlation study among the dynamic fractions (obtained from kinetic extraction study) and the different combination of non residual metal fractions (Fr 1, Fr1+ Fr 2, Fr1+ Fr2+ Fr3, Fr1+ Fr2+ Fr3+Fr4, Fr1+ Fr2+ Fr3+Fr4+ Fr5) of each metal were performed and provided as supporting documents (Tables 5SD and 6SD). A very strong correlation was obtained between the dynamic fractions (kinetic extraction study) of Cd with its different non-residual fractions (sequential extraction study). However, a very strong correlation was found between the dynamic fraction and water soluble fraction of Pb. The statistical analysis suggests that both dynamic and non residual
fraction corresponds to the same metal fraction (except the inert complexes of metal-organic matter) which may be bioavailable.

The concentrations of total non residual fractions (excluding Fr 5) (obtained by sequential extraction method) and dynamic fractions of Pb and Cd (obtained by kinetic extraction method) linearly increased with the increasing concentration of total Cd and Pb in the sediments. Figure 6 shows that the water soluble fractions (% Fr. 1) of both the metals increased linearly with the increasing total metals content within the sediments. It is interesting to note that the other fractions (Fr 2, Fr 3, Fr4 and Fr 5) decreased with the increasing concentrations of Pb and Cd in the sediments (Table 5SD). This observation indicates that any further increase in Pb and Cd loading may increase the water soluble fraction of these metals within the system, which can be easily leached out from the sediments to the overlaying water column and can become bioavailable.

Combination of both the methods suggest that increase in further loading of Pb and Cd in the system may increase the water soluble or dynamic fraction of these toxic metals which can be bioavailable.

Significance

This study reveals that the concentrations of non-residual or dynamic complexes of Pb and Cd (which are good indicators of their bioavailability in a system) in coastal and estuarine sediments may increase with the increasing Pb and Cd loading in sediments. These non-residual or dynamic complexes of Pb and Cd can be easily leached out to the overlaying water column to alter the delicate balance between the speciation, bioavailability and toxicity of these metals which is essential to sustain life in the sediments and their overlaying water column. This study shows that total organic carbon (TOC) is one of the key factors which play a crucial role in controlling speciation of these toxic metals in sediments. However, the distribution and speciation of these metals are influenced by their total metal loading and trace metal competitions rather than only TOC content within the sediments. Combination of sequential and kinetic extraction methods, with their associated measurement timescales and detection windows, provides evidence of the dynamic behaviour of heavy metals in aqueous sediment suspensions.

Acknowledgement

Authors are thankful to the Director, NIO, Goa for his encouragement and support. Unconditional help and support from Dr J.N. Pattan and Dr G. Parthiban from NIO, Goa for providing ICPMS facility are gratefully acknowledged. This work is a part of the Council of Scientific and Industrial Research (CSIR) supported Supra Institutional Project (SIP 1308). This article bears NIO contribution Number XXXX
References:


Arjonilla, M., Forja, J. M., Goez-Parra, A., 1994, Sediment analysis does not provide a good measure of heavy metal bioavailability to Cerastoderma glaucum in confine coastal ecosystem. Bull Environ Contam Toxicol. 52, 810-817.


Chakraborty, P., Zhao, J., Chakrabarti, C.L., 2009, Copper and nickel speciation in mine effluents by combination of two independent techniques, Anal Chim Acta, 636, 70-76


Chang Chien, S. W., Wang, M. C., Huang, C. C., 2006, Reactions of compost-derived humic substances with lead, copper, cadmium, and zinc, Chemosphere, 64, 1353-1361.


Zhao, X., Dong, D., Hua, X., Dong, S., 2009, Investigation of the transport and fate of Pb, Cd, Cr(VI) and As(V) in soil zones derived from moderately contaminated farmland in Northeast, China, J Hazard Mater, 170 () 570-577.

Caption and Legends for figures

Figure 1. Map of the sampling areas along the East coast (Andhra Pradesh region) of India. The filled circles are the locations of the five environmentally significant sites.  
1) Kalingapatnam (KGP) 2) Vishakhapatnam (VSP) 3) Machilipatnam (MCP). Estuarine sediment samples were collected from 4) Goutami Godavari estuary (GGE) and 5) Vasishtha Godavari estuary (VGE).

Figure 2. Chemical fractionation of Pb in five different sediment samples collected at five different environmentally significant sites; KGP-Kalingapatnam; VSP-Visakhapatnam; GGE- Goutami Godavari Estuary; VGE-Vasistha Godavari Estuary and MCP-Machilipatnam.

Figure 3. Chemical fractionation of Cd in five different sediment samples collected at five different environmentally significant sites; KGP-Kalingapatnam; VSP-Visakhapatnam; GGE- Goutami Godavari Estuary; VGE-Vasistha Godavari Estuary and MCP-Machilipatnam.

Figure 4. Release of extractable non-residual Pb species from sediments as a function of time in presence of 0.05M EDTA at pH 6. , (□); Visakhapatnam, (O); Kalingapatnam, (Δ); Vasistha Godavari estuary, (◊); Goutami Godavari, (◊); Machilipatnam

Figure 5. Release of extractable non-residual Cd species from sediments as a function of time in presence of 0.05M EDTA at pH 6. , (Δ); Visakhapatnam, (O); Kalingapatnam, (◊); Vasistha Godavari estuary, (◊); Goutami Godavari, (□); Machilipatnam

Figure 6.: (a) Variation of water soluble fraction, non-residual and dynamic fractions of Cd with varying concentration of total Cd, (b) Variation of water soluble fraction, non-residual and dynamic fractions of Pb with varying concentrations of total Pb
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Table 1: Geographical locations of sampling sites, the distance from the shore and depth from where the sediment samples were collected

<table>
<thead>
<tr>
<th>Station</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Sampling Date</th>
<th>Distance from Shore (km)</th>
<th>Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kalingapatnam (KGP)</td>
<td>84°10.31’</td>
<td>18°18.98’</td>
<td>25.12.09</td>
<td>5</td>
<td>23</td>
</tr>
<tr>
<td>Visakhapatnam (VSP)</td>
<td>83°19.07’</td>
<td>17°38.96’</td>
<td>25.12.09</td>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>Goutami Godavari Estuary (GGE)</td>
<td>82°24.19’</td>
<td>16°41.56’</td>
<td>27.12.09</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>Vasistha Godavari Estuary (VGE)</td>
<td>81°42.94’</td>
<td>16°15.65’</td>
<td>26.12.09</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Machilipatnam (MCP)</td>
<td>81°16.32’</td>
<td>16°11.51’</td>
<td>26.12.09</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>
Table 2: The average concentrations (three replicates) (mg. kg⁻¹) of the trace metals in the studied (coastal and estuarine) sediments are presented along with the composition of worldwide shale and continental crust.

<table>
<thead>
<tr>
<th>Chemical Constituents</th>
<th>Sampling Stations</th>
<th>Worldwide Shale</th>
<th>Continental crust</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KGP</td>
<td>VSP</td>
<td>GGE</td>
</tr>
<tr>
<td>TOC (%)</td>
<td>3.7</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Sc</td>
<td>15.1 ± 0.5</td>
<td>5.6 ± 0.5</td>
<td>15.7 ± 0.5</td>
</tr>
<tr>
<td>V</td>
<td>137.9 ± 10.1</td>
<td>59.3 ± 5.0</td>
<td>205.3 ± 5.0</td>
</tr>
<tr>
<td>Cr</td>
<td>82.7 ± 10.3</td>
<td>23.9 ± 5.2</td>
<td>82.9 ± 10.3</td>
</tr>
<tr>
<td>Co</td>
<td>25.7 ± 1.1</td>
<td>8.6 ± 0.5</td>
<td>25.6 ± 2.2</td>
</tr>
<tr>
<td>Ni</td>
<td>41.8 ± 0.6</td>
<td>23.5 ± 0.6</td>
<td>55.1 ± 1.2</td>
</tr>
<tr>
<td>Cu</td>
<td>64.4 ± 4.3</td>
<td>43.3 ± 0.5</td>
<td>107.4 ± 6.3</td>
</tr>
<tr>
<td>Zn</td>
<td>513.8 ± 5.8</td>
<td>254.4 ± 7.9</td>
<td>507.3 ± 15.8</td>
</tr>
<tr>
<td>Pb</td>
<td>229.0 ± 20.2</td>
<td>147.1 ± 2.1</td>
<td>327.1 ± 20.0</td>
</tr>
<tr>
<td>Cd</td>
<td>21.0 ± 1.1</td>
<td>17.2 ± 1.1</td>
<td>23.9 ± 1.1</td>
</tr>
<tr>
<td>Sn</td>
<td>47.7 ± 1.2</td>
<td>29.4 ± 1.2</td>
<td>42.5 ± 1.2</td>
</tr>
<tr>
<td>PLI (w.r.t. worldwide shale vale)</td>
<td>3.3</td>
<td>1.7</td>
<td>4.0</td>
</tr>
<tr>
<td>PLI (w.r.t. continental crust)</td>
<td>3.6</td>
<td>1.9</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Values presented as the Average ± 2 × standard deviation, n = 3
All the data are presented with 95.5% confidence interval
Table 3: Kinetically distinguishable components (c1, c2, c3 etc) of Cd and Pb and their dissociation rate constants (kd1, kd2, kd3 etc) in the estuarine and coastal sediments obtained by kinetic extraction study using EDTA as a competing ligand.

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>Total Cd (mg. kg⁻¹)</th>
<th>c1 (%)</th>
<th>kd1 (s⁻¹)</th>
<th>C2 (%)</th>
<th>kd2 (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGP</td>
<td>21.0 ± 1.1</td>
<td>56.8 ± 0.5</td>
<td>7.7×10⁻⁴</td>
<td>46.2 ± 0.5</td>
<td>&lt;1×10⁻⁶</td>
</tr>
<tr>
<td>VSP</td>
<td>17.2± 1.1</td>
<td>53.9 ± 0.7</td>
<td>1.9×10⁻³</td>
<td>43.2 ± 1.5</td>
<td>&lt;1×10⁻⁶</td>
</tr>
<tr>
<td>GGE</td>
<td>23.9 ± 1.1</td>
<td>65.4 ± 1.5</td>
<td>1.1×10⁻³</td>
<td>34.7 ± 0.6</td>
<td>&lt;1×10⁻⁶</td>
</tr>
<tr>
<td>VGE</td>
<td>24.8 ± 1.1</td>
<td>67.6 ± 0.9</td>
<td>1.6 ×10⁻³</td>
<td>32.4 ± 0.5</td>
<td>&lt;1×10⁻⁶</td>
</tr>
<tr>
<td>MCP</td>
<td>37.2 ± 1.1</td>
<td>83.2 ± 2.3</td>
<td>2.1×10⁻³</td>
<td>16.8 ± 0.4</td>
<td>&lt;1×10⁻⁶</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>Total Pb (mg. kg⁻¹)</th>
<th>c1 (%)</th>
<th>kd1 (s⁻¹)</th>
<th>c2 (%)</th>
<th>kd2 (s⁻¹)</th>
<th>c3 (%)</th>
<th>kd3 (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGP</td>
<td>229.0 ± 20.2</td>
<td>13.9± 0.5</td>
<td>1.1×10⁻³</td>
<td>56.5± 0.5</td>
<td>2.7×10⁻⁵</td>
<td>29.6± 0.3</td>
<td>&lt;1×10⁻⁶</td>
</tr>
<tr>
<td>VSP</td>
<td>147.1 ± 2.1</td>
<td>47.9± 0.5</td>
<td>1.2×10⁻³</td>
<td>--</td>
<td>--</td>
<td>52.1± 0.8</td>
<td>&lt;1×10⁻⁶</td>
</tr>
<tr>
<td>GGE</td>
<td>327.1 ± 20.0</td>
<td>48.6± 0.5</td>
<td>2.0×10⁻³</td>
<td>28.6± 1.5</td>
<td>4.3×10⁻⁴</td>
<td>22.8± 0.7</td>
<td>&lt;1×10⁻⁶</td>
</tr>
<tr>
<td>VGE</td>
<td>424.0 ± 20.2</td>
<td>33.6± 0.5</td>
<td>9.8×10⁻⁴</td>
<td>32.6± 0.7</td>
<td>1.4×10⁻⁵</td>
<td>33.8± 0.8</td>
<td>&lt;1×10⁻⁶</td>
</tr>
<tr>
<td>MCP</td>
<td>203.2 ± 20.2</td>
<td>47.6± 0.5</td>
<td>8.1×10⁻⁴</td>
<td>27.5± 0.8</td>
<td>1.8×10⁻⁵</td>
<td>24.9± 0.8</td>
<td>&lt;1×10⁻⁶</td>
</tr>
</tbody>
</table>

Values presented as the mean ± 2 × standard deviation, n = 3
All the data are presented with 95.5% confidence interval.
Table 4: Comparison of the sequentially extracted non-residual fractions of metals (Pb or Cd) with the kinetically extracted dynamic metal fractions of Pb ($c_1+c_2$) and Cd ($c_1$) in the coastal and estuarine sediments. Both the fractions are presented as the percentage of the total metal content.

<table>
<thead>
<tr>
<th>Sampling station</th>
<th>Metal</th>
<th>Sequentially extracted non residual fractions ($F_{r.1}+F_{r.2}+F_{r.3}+F_{r.4}+F_{r.5}$) %</th>
<th>Kinetically extracted dynamic metal fractions, $c_1$ or ($c_1+c_2$)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGP</td>
<td>Cd</td>
<td>90.4± 7.8</td>
<td>56.8 ± 1.0</td>
</tr>
<tr>
<td>VSP</td>
<td></td>
<td>90.4± 6.9</td>
<td>53.9 ± 2.2</td>
</tr>
<tr>
<td>GGE</td>
<td></td>
<td>92.3± 5.7</td>
<td>65.4 ± 2.1</td>
</tr>
<tr>
<td>VGE</td>
<td></td>
<td>93.4± 10.0</td>
<td>67.6 ± 1.4</td>
</tr>
<tr>
<td>MCP</td>
<td></td>
<td>97.1± 6.9</td>
<td>83.2 ± 2.7</td>
</tr>
<tr>
<td>KGP</td>
<td>Pb</td>
<td>89.9 ± 5.6</td>
<td>70.4 ± 0.8</td>
</tr>
<tr>
<td>VSP</td>
<td></td>
<td>88.2± 6.6</td>
<td>47.9 ± 1.3</td>
</tr>
<tr>
<td>GGE</td>
<td></td>
<td>93.1 ± 7.2</td>
<td>77.2 ± 1.2</td>
</tr>
<tr>
<td>VGE</td>
<td></td>
<td>95.1 ± 6.7</td>
<td>66.2 ± 1.3</td>
</tr>
<tr>
<td>MCP</td>
<td></td>
<td>91.8± 5.1</td>
<td>75.1 ± 1.3</td>
</tr>
</tbody>
</table>

Values presented as the mean ± 2 × standard deviation, n = 3