

A multi-method approach for the study of lanthanum speciation in coastal and estuarine sediments

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Abstract:

Two independent analytical methods (sequential extraction and kinetic extraction methods) were applied in order to understand the distribution and speciation of La in the coastal and estuarine sediments collected from the central east coast of India. Data obtained from sequential extraction study revealed that La was primarily present as inert complexes (~ 50-60% of the total La) in all the sediments. Amounts of ~ 20-30% of the total La in all the sediments were found to associate with the total organic carbon (TOC) in the sediments. The dissociation rate constants of La-sediment complexes obtained from kinetic extraction studies revealed that the concentration of thermodynamically weak complexes of La gradually increased with the increasing La/ TOC ratio in the sediments.

The results of this investigation demonstrate that combination of two analytical methods having complementary analytical capabilities can provide a better physicochemical picture of La speciation than either one of the method can do alone. Combination of the data obtained from sequential extraction and kinetic extraction methods suggest that TOC is one of the key factors in controlling speciation and distribution of La in the sediments.

Key words: Lanthanum speciation; Sequential Extraction Method; Kinetic extraction method; Lanthanum-organic complexes; Rare earth speciation, sediments

1. Introduction:

The exponential growth of human population along the sea coast and estuarine areas around the world has deteriorated the environmental quality of the coastal and estuarine sediments. The increasing use of lanthanum (La) in different fields (agricultural field, water treatment technology, nuclear industry, glass industry and medicine manufacturing industry) (Guo, 1987; Zhang et al. 1988; Eisenbud and Paschoa, 1989; Tribe et al. 1990; Buckingham et al. 1995) is expected to increase the total concentration of La in estuarine and coastal sediments which may potentially results in associated environmental and health problems.

Effects of La on mammalian systems have been extensively studied. It has been reported that La can act as a biochemical probes. Lanthanum reacts with tissue components like nucleoproteins, amino acids, phospholipids, enzymes and intermediary metabolites and it can precipitate DNA in vitro and bind to serum proteins. Its action is mainly mediated through the displacement or replacement of calcium in different cell functions and also its high affinity for phosphate groups of biological macromolecules. La^{3+} ion usually prevents the influx of Ca^{2+} ion and competes for available binding sites (Das et al. 1988). In consequence, La may interact with many Ca-dependent biological systems, resulting in toxicity or impaired function.

It has also been reported (Lurning and Tolman, 2010) that increasing amounts of lanthanum, in the presence of phosphate, animals remained smaller, matured later, and reproduced less, resulting in lower population growth rates in aquatic system. Xin et al. (2002) reported that the damage increases in wheat seedlings with increasing concentrations of La in culture medium. It has been shown that lanthanide elements can accumulate in humans (Zhang et al. 2000) and other organisms (Weltje et al. 2002), and their toxicity has also been reviewed in literature (Hirano and Suzuki, 1998). Due to the potential threat posed to human health by the lanthanides, adsorption studies of trivalent metals at mineral/water interfaces has been carried out by Jordan et al. (2010) to assess their pollutant risk.

However, it is well known that the environmental ecotoxicity, mobility and bioavailability of a metal are strongly dependent upon its specific chemical forms. The toxic effects and biogeochemical pathways of a metal in a system can only be studied on the basis of their speciation.

The data available exclusively on speciation of La (Moermond et al. 2001; Shengqing et al. 2004; Sonke, 2006; Sonke and Salters, 2006) in natural systems are scarce compared to large numbers of toxicology data available for La in literature.

Thus, it is essential to provide fundamental information on distribution and speciation of La in coastal and estuarine sediments. It is also imperative to know those factors which control La speciation and bioavailability in sediments.

Sequential extraction method has been widely used to study trace metal partitioning in soil and sediments. The most widely used sequential extraction methods are those recommended by Tessier et al. (1979), Kersten and Förstner (1986) and the Community Bureau of Reference (BCR) (Quevauviller et al. 1993). However, all these methods suffer from the non selectivity of extractants used and redistribution of trace elements among the solid phases during the extraction processes (Shan and Chen, 1993; Howard and Van den Brink, 1999). In addition to all these limitations, sequential extraction scheme are widely used for soil and sediment studies to estimate the environmentally accessible metals, as reflected by the number of recently published papers dealing with their applications to various environmental studies (Martin et al. 1987; Usero et al. 1998; Koretsky et al. 2008; Issaro et al. 2009; Gonzalez et al. 2009; Rao et al. 2010). Sequential extraction method provides information about the distribution of metals associated with specific solid phases in sediments and was employed in this study to understand La speciation in sediments.

However, it is important to note that sequential extraction procedures for trace metal fractionation are actually directed to operationally defined fractionation (Templeton et al. 2000) which may not represent natural systems.

In order to have a more precise picture on La speciation in sediments, kinetic extraction study was also performed for a better understanding of dynamic and inert La-sediment complexes with their dissociation rate constants in sediments. The major aim of this paper is to provide a better understanding of La speciation and its distribution in coastal and estuarine sediments and identify the key factor which controls the speciation and bioavailability of La in sediments. The finding of this study is also important to extrapolate our understanding about the speciation and distribution of light lanthanide elements in sediments, as La is considered as a representative of light lanthanide elements.

2. Experimental:

2.1 Study area and sampling

Sediment samples were collected from the five different environmentally significant sites of the central east coast of India. The coastal sediment samples were collected from 1) Kalingapatnam (not an industrially developed city and an important minor port is present close to the sampling station); 2) Vishakhapatnam (an industrially developed city); 3) Machilipatnam (not an industrially developed city but Krishna River estuary is very close to the sampling sites). Estuarine sediment samples were collected from 4) Goutami Godavari estuary and 5) Vasistha Godavari estuary. The general description, geographic location of the 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 a large amount of sediment; without emptying the grab, a sample was taken from the center with a polyethylene spoon to avoid contamination by the metallic parts of the dredge. 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 ground in an agate mortar, homogenized and stored at 4°C until needed.

2.2 Leaching procedure and reagents

All the reagents used in this study were of analytical grade or better. 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). 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 procedure and protocols have been elaborated elsewhere (Tessier et al. 1979). 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 inductively coupled plasma mass spectrometry (ICP-MS) to obtain the

distribution of metals in different phases of the sediments. Three replicates of each sample were analyzed.

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. However, the data obtained by using sequential extraction method were compared with the data obtained from kinetic extraction method (these two methods are having two different analytical windows) to provide reliability of the data set.

2.2.2 Kinetic extraction procedure

Kinetic extraction experiments were conducted for homogenized 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 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 (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 of the suspension were filtered through a 0.2 μ m 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 HNO_3 and analyzed by ICP-MS to monitor the change in

concentrations of La 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 La 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 ICP-MS. Each sediment samples were analyzed in triplicates.

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

2.2.3 Inductively coupled plasma mass spectrometry (ICP-MS)

An ICP-MS (Thermo FISCHER ICP-MS, X series 2, Germany) was used for the determination of the total La 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 conditions of ICP-MS are presented in Table 2.

The sensitivity of the ICP-MS instrument was monitored throughout the experiments by analyzing marine sediment reference materials (HISS-1, MESS-3, and PACS-2 from National Research Council 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.

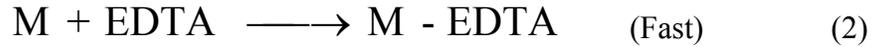
2.2.4 Determination of total organic carbon (TOC)

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 carbon and is particularly poor for digesting elemental C forms. Studies have shown that the recovery of organic carbon using the Walkley-Black procedure ranges from 60 to 86% with a mean recovery being 76%.

3. Theory

3.1 The kinetic model

The kinetic model proposed by Olson and Shuman (1985) was adapted to investigate the kinetic speciation of La in the coastal and estuarine sediments. The kinetic model has been extensively discussed in the literature (Lu et al. 1994; Mandal et al. 1999; Chakraborty et al. 2006; Chakraborty and Chakrabarti, 2006; Chakraborty et al. 2011). This model considers sediment sample 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 sites, sediment $_i$, (charges have been omitted for simplicity). The subscript i , represents different binding sites on the naturally-occurring heterogeneous complexant.



where the formation and dissociation rate constants, $k_{f,i}$ and $k_{d,i}$, are coupled by the stability constant, $K = k_f/k_d$, 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, $C_{\text{M-Sediment}}$, at any time, t , is given by a summation of exponentials as shown in equations 3.

$$C_{\text{M-Sediment}}(t) = \sum_{i=1}^n c_{\text{M-Sediment}_i}^{\circ} \cdot \exp(-k_{d,i} \cdot t) \quad (3)$$

where $c_{\text{M-Sediment}_i}^{\circ}$ is the initial concentration of M-Sediment $_i$ and $c_{\text{M-Sediment}_i}(t)$ is the concentration of $C_{\text{M-Sediment}_i}$, at any time, t .

The model assumes that 1) the reactions are first-order and pseudo-first-order; 2) reaction (2) is much faster than reaction (1), so that reaction (1) is the rate-determining step, and the measured kinetics then represent the kinetics of the dissociation of the metal complex, M-Sediment_i. (Chakrabarti et al. 1994, Lu et al. 1994a, 1994b, Lu et al. 1995), 3) 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. $c_{\text{M-Sediment}} / c_{\text{M}} > 1$).

3.2 Non-linear regression analysis for kinetic measurement

Analyzing experimental data to obtain physical parameters is a crucial point in the kinetic speciation 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.

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

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:

The total concentrations of La and TOC in the sediments are summarized in Table 1. The mean average concentrations of La in the unpolluted sediments (from Japan) and the average shale (worldwide) concentrations of La has been reported to be 22.3 and 92.0 $\mu\text{g. kg}^{-1}$ respectively (Turekian and Wedepohl, 1961; Gamo, 2007; Mohiuddin et al. 2010) and thus, the concentrations

of La in the studied sediments were within the range found in unpolluted sediments as reported in the literature.

4.1 Sequential extractions for La speciation in coastal and estuarine sediments

Modified classical sequential extraction method (Tessier et al. 1979) was applied to understand the distribution and speciation of La in the coastal and estuarine sediments. Figure 1 shows the variation in the percentage of La (with respect to the total La concentrations) associated with the different phases of the sediments collected at the five different sites.

The water soluble (Fr. 1) fraction of La (i.e. water soluble complexes of La) in all the sediments were found to be within the range of 1-11% of the total La. Highest percentage of water soluble La complexes (10-11%) were present in the sediments collected at estuaries (Goutami and Vasistha Godavari estuaries) and Machilipatnam.

The exchangeable (Fr.2) fraction of La (i.e. La complexes from where La can be exchanged by other metals) was found to be minor contributors in all the sediments.

Carbonate and bicarbonate fraction (Fr. 3) of La (i.e. carbonate and bicarbonate complexes of La) in all the sediments was found to be within the range of ~3-6% of the total La (Table 3).

This investigation suggests that relatively higher percentage of La was associated with Fe and Mn-oxide (Fr. 4) compared to Fr. 1, 2 and 3 in all the studied sediments. This is because of the higher stability constants of La associated with Fe-Mn oxides complexes in sediments as reported in the literature (Fendorf and Fendorf, 1996).

La associated with Fe, Mn-oxides were found to be within the range of 8.5 to 16% of the total La present in all the sediments. La was primarily present in the residual fraction (Fr. 6) (~ 50-60%) followed by organic fraction (Fr.5) (~20-30%) in all the studied sediments. These two fractions accounted for around 80% of the total La in all the sediments (Figure 1).

It is important to mention that the residual fraction of La in the sediment is considered as inert complexes of La and is expected not to be bioavailable. The experimental data suggested that appreciable amount of La were present as residual component in all the sediments (Table 3). It is expected that the light lanthanides (in this case La) should be present in the Earth's crust than the heavier one (which are expected in the Earth's mantle) (Masuda and Matsui, 1966).

4.2 Kinetic speciation of La in sediments

The extraction curves from the kinetic experiments, presented in Figure 2, show the changes in concentration of extracted La in EDTA solution as a function of time. Each curve displayed an exponential increase in La concentration in the extracting EDTA solution with respect to time. 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 4.

Each kinetically-distinguishable component is expressed as a fraction of the total non-residual La concentration in the sediments (i.e. as a percentage of the total non-residual La concentration). The extraction curves show that the concentration of extracted La in most of the samples reached equilibrium after 36 h.

The experimental data from the kinetic extraction curves were fitted to a three components model (except one set of data obtained from the sediment collected at Visakhapatnam) which is widely used by soil chemists (Jardine and Sparks, 1984; Brusseau and Rao, 1989; Sparks, 1989; Comans and Hockley, 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 La, 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 curve (except for the sediments collected at Visakhapatnam) in Figure 2 shows three distinguishable features: a quickly rising section that represents the rapid dissociation rate (k_{d1}) of weak La-sediment complexes ($c_1\%$), and a very slowly rising section which corresponds to relatively stronger La-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 La-sediment complexes ($c_3\%$).

The first part of all the curves (Figure 2) are almost indistinguishable from one another, suggesting that they represent dissociation of one type of La-sediment complexes having very similar fast dissociation rate constants with low thermodynamic stability. These complexes can be considered as dynamic (within the time scale of the measurement) in nature. The dissociation rate constants of La-sediment complexes are presented in Table 4,

Leaching of weak La-sediment complexes ($c_1\%$) with low thermodynamic stability was found to be high in the coastal sediment collected at Machilipatnam (59.9%) with k_{d1} value of $8.9 \times 10^{-3} \text{ s}^{-1}$, followed by Vasistha Godavari estuary (46.3%) with k_{d1} value of $9.9 \times 10^{-3} \text{ s}^{-1}$, and Goutami Godavari estuary (30.7%) with k_{d1} value of $1.0 \times 10^{-2} \text{ s}^{-1}$. The lowest fraction of dynamic La complexes was found in the sediments collected at Visakhapatnam (21.3%) with k_{d1} value of $2.7 \times 10^{-3} \text{ s}^{-1}$ (Table 4).

The middle part of all curves (except Visakhapatnam) in Figure 2 are readily distinguishable from one another, suggesting that they represent dissociation of different types of La-sediment complexes ($c_2\%$) having different dissociation rate constants (k_{d2}); these complexes are thermodynamically more stable than the fast component. The dissociation rate constants of the second component of La-sediment complexes are presented in Table 4, shows that the k_{d2} of La-sediment complexes are relatively low and differ from one sediment to another.

The concentrations of slow dissociating La-sediment complexes ($c_2\%$) was high in the estuarine sediment collected at Vasistha Godavari estuary (44.2%) with k_{d2} value of $3.0 \times 10^{-4} \text{ s}^{-1}$, followed by Goutami Godavari estuary (28.7%) with k_{d2} value of $1.1 \times 10^{-3} \text{ s}^{-1}$, and Kalingapatnam (27.1%) with k_{d2} value of $4.9 \times 10^{-5} \text{ s}^{-1}$. This second component of La complexes was negligible in the sediment collected at Visakhapatnam (Table 4).

The last part of each curve, lies almost parallel to x-axis, can be attributed to slow dissociation of thermodynamically stable La-sediment complexes (represented by $c_3\%$) are presented in Table 4 with very low dissociation rate constants (k_{d3}). 78.6% of the total La was found to be inert in the sediment collected at Visakhapatnam with k_{d3} value of $1.5 \times 10^{-6} \text{ s}^{-1}$. Sediment samples collected at Kalingapatnam and Goutami Godavari estuary were found to have 47 and 40.5% of inert La-sediment complexes respectively with very slow dissociation rate.

4.3 Dissociation rate constant and La/TOC ratio

The dissociation of La-sediment complexes was found to be dependent on La/TOC ratio. The dissociation rate constants of La-sediment complexes increased with the increasing La/TOC ratio within the sediments. The La/TOC ratio determine the formation of strong and weak La-TOC complexes.

Figure 3 shows that the dissociation rate constants (k_{d3} , dissociation rate constant of thermodynamically stable La-sediment complexes) increased with the increasing La/TOC ratio. This is because of the fact that at low La/TOC ratio, La tends to undergo strong complexation with the strong binding sites of TOC and form thermodynamically stable La-TOC complexes with slow dissociation rate constant. However, with the increasing La/TOC ratio, strong sites of TOC get occupied and La moves towards the weaker sites of TOC for complexation reaction to form thermodynamically weaker complexes with faster dissociation rate constant. This is clearly shown in Figure 3 that k_{d3} increases with the increasing La/TOC ratio.

The variation of k_{d1} (dissociation rate constant of thermodynamically unstable La-sediment complexes) with La/TOC ratio is not appreciable. It is important to note that k_{d1} represents the dissociation rate constant of weak La-sediment complexes (which includes La-inorganic complexes, La ion, La associated with Fe/Mn oxide and weak La-TOC complexes) present in the sediments. The insignificant change in the k_{d1} value with the varying La/TOC ratio suggests that the weaker binding sites probably had similar complexing strength for La complexation.

4.4 Factor controlling La speciation in estuarine and coastal 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 et al. 2009; Chakraborty, 2010). It is of clear interest in this section to identify the key factors which control La speciation in coastal and estuarine sediments by combining the data obtained by two different extraction methods.

Variation in non-residual La fractions (obtained from sequential extraction method) are plotted along with the variation in fast dynamic La-sediment complexes ($c_1\%$) (obtained from kinetic extraction method) against the varying La/TOC ratio in Figure 4. Total non-residual fraction and dynamic fraction of La were found to increase exponentially with the increasing La/TOC ratio. This observation suggests that there was a progressive binding of La with the weaker binding sites as the La loading within the sediment increased. These findings suggested that La was progressively complexing with the weaker binding sites (having very similar dissociation rate constant) of TOC and the concentrations of weak fast component ($c_1\%$) of La gradually increased with the increasing La/TOC ratio but k_{d1} value remained almost unchanged.

It is important to note that the non-residual fractions of La complexes excluding La-TOC fraction is almost constant at all the five sediment samples with the varying La/TOC ratio. Exponential increase in fast component ($c_1\%$) and total non-residual fraction of La with increasing La/TOC ratio suggest that TOC played a crucial role in controlling the concentration of non-residual and dynamic fraction of La in the sediments.

5. Conclusions

This study reveals that La was mainly present as residual component in all the sediments. However, La progressively binds to weaker binding sites of sediments as the La loading within the sediment increased. The weaker binding sites were found to have similar complexing strength for La complexation within the sediments. Combination of data obtained from sequential extraction and kinetic extraction methods were found to be very useful in identifying TOC as the key factor in controlling La speciation in sediments. This study is significantly important for providing the fundamental speciation parameters of La in coastal and estuarine sediments which are scarce in literature and identifying the key factor which controls La speciation in sediments. However, further study is required to understand the effect of trace metal competition and screening effect of major cations on La speciation in sediments.

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Table 1. Geographical locations of sampling sites and total La (mg kg^{-1}) concentration (determined by ICPMS) and Total Organic Carbon (TOC) concentrations in sediments in wt %.

Station	Longitude	Latitude	Sampling Date	Distance from Shore (km)	Depth (m)	La (mg.Kg^{-1})	TOC (%)	La/TOC
Kalingapatnam	84°10.31'	18°18.98'	25.12.09	5	23	40.7 ± 0.8	3.7	0.001
Visakhapatnam	83°19.07'	17°38.96'	25.12.09	5	35	33.7 ± 1.0	1.5	0.001
Goutami Godavari Estuary	82°24.19'	16°41.56'	27.12.09	5	14	37.1 ± 0.7	2.0	0.002
Vasistha Godavari Estuary	81°42.94'	16°15.65'	26.12.09	5	4	37.7± 0.8	1.4	0.003
Machilipatnam	81°16.32'	16°11.51'	26.12.09	5	9	23.9± 0.7	1.9	0.005

Table 2: ICP-MS-operating condition

RF Power (W)	1400
Sampling depth (mm)	145
Carrier gas flow rate (l.min ⁻¹)	0.86
Plasma gas flow rate (l.min ⁻¹)	1.3
Auxiliary gas flow rate (l.min ⁻¹)	0.7
Nebulizer	Glass concentric (Meinhard)
Spray chamber	Cyclonic-peltier cooled
Sampler	Ni, 1.1 mm orifice
Skimmer	Ni, 0.75 mm orifice
Sweeps per reading	100 sweeps, two readings
Scanning mode	Peak jumping
Dwell time (ms)	10000

Table 3 Partitioning of La in five different sediment samples collected at five different environmentally significant stations

Stations	Fr-1 (%)	Fr-2 (%)	Fr-3 (%)	Fr-4 (%)	Fr-5 (%)	Fr-6 (%)	La_{Total} (mg. Kg⁻¹)
Kalingapatnam	1.2	0.1	3.8	15.8	23.6	55.4	40.7 ± 0.8
Visakhapatnam	3.9	0.2	3.8	13.5	19.8	61.1	33.7 ± 1.0
Goutami Godavari Estuary	9.7	0.1	5.2	8.8	27.2	49.2	37.1 ± 0.7
Vasistha Godavari Estuary	10.7	0.0	5.7	7.9	23.9	51.8	37.7± 0.8
Machilipatnam	8.4	0.1	3.6	12.1	30.2	45.8	23.9 ± 0.7

Table 4 Kinetically distinguishable non-residual La species from sediments and their corresponding dissociation rate constants

Stations	c₁ (%)	k_{d1} × 10³ (s⁻¹)	c₂ (%)	k_{d2} × 10⁴ (s⁻¹)	c₃ (%)	k_{d3} × 10⁵ (s⁻¹)
Kalingapatnam	25.9 ± 0.8	9.9 ± 0.1	27.1 ± 0.8	0.5 ± 0.1	47.0 ± 1.4	0.1 ± 0.0
Visakhapatnam	21.3 ± 0.6	2.7 ± 0.2	-	-	78.6 ± 2.4	0.2 ± 0.0
Goutami Godavari Estuary	30.7 ± 0.9	9.8 ± 0.1	28.7 ± 0.9	11.0 ± 0.5	40.5 ± 1.2	5.4 ± 0.6
Vasistha Godavari Estuary	46.3 ± 1.4	9.5 ± 0.5	44.2 ± 1.3	3.0 ± 0.8	9.4 ± 0.3	0.5 ± 0.5
Machilipatnam	59.9 ± 1.8	8.9 ± 0.3	17.4 ± 0.5	1.1 ± 0.1	22.6 ± 0.7	1.1 ± 0.1

Captions 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.

Figure 2: Partitioning of La in five different sediment samples collected at five different environmentally significant sites 1) KGP-Kalingapatnam; 2) VSP-Visakhapatnam; 3) GGE Goutami Godavari Estuary; 4) VGE-Vasistha Godavari Estuary and 5) MCP-Machilipatnam

Figure 3 Release of dynamic (extractable non-residual) La species from sediments as a function of time in presence of 0.05M EDTA at pH 6. , (\square); Visakhapatnam (O); Kalingapatnam, (\blacktriangledown); Vasistha Godavari estuary, (Δ); Goutami Godavari, (\diamond);Machilipatnam

Figure 4 Variation of dissociation rate constants of thermodynamically weak (k_{d1}) and strong (k_{d3}) La-complexes with varying La/TOC ratio

Figure 5: Plot of residual, non-residual (obtained from sequential extraction method) and dynamic fractions (obtained from kinetic extraction method) of La-complexes with varying La/TOC ratio

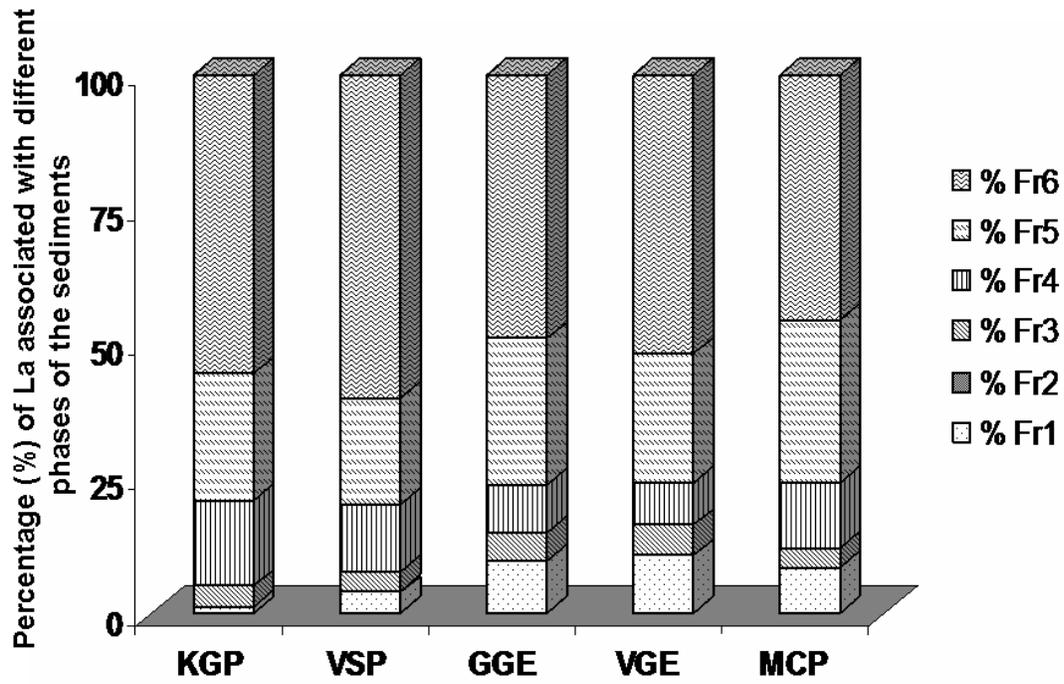


Figure 1

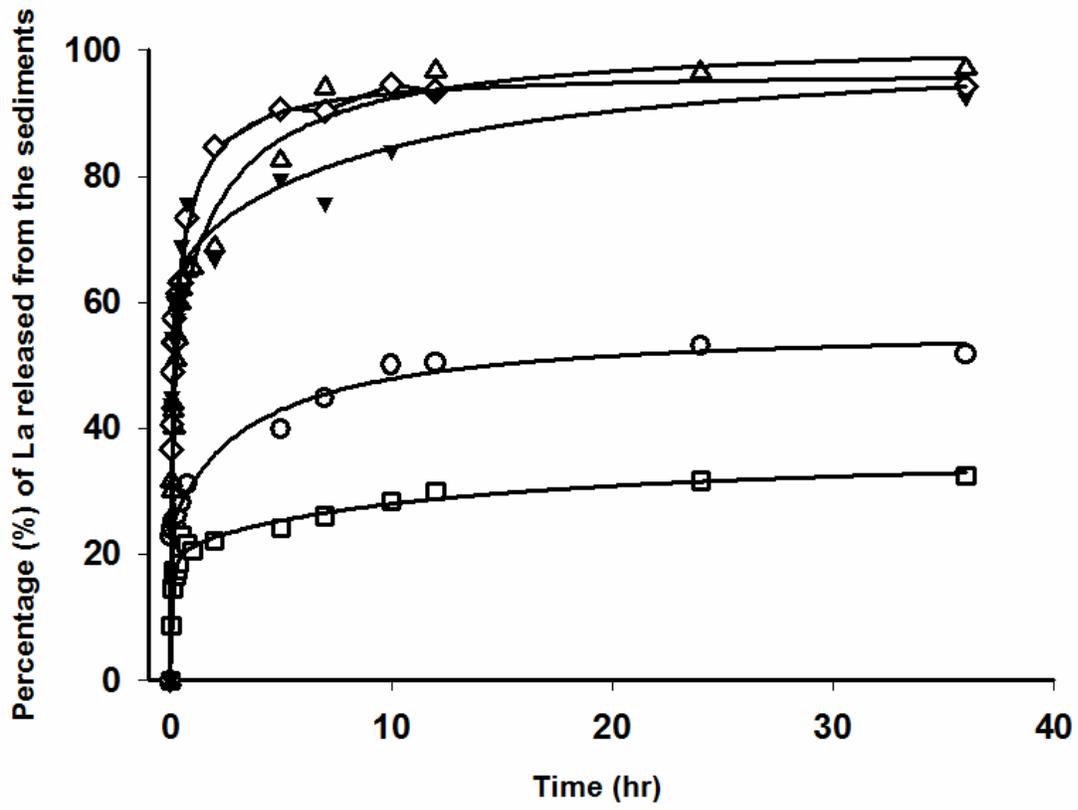


Figure 2

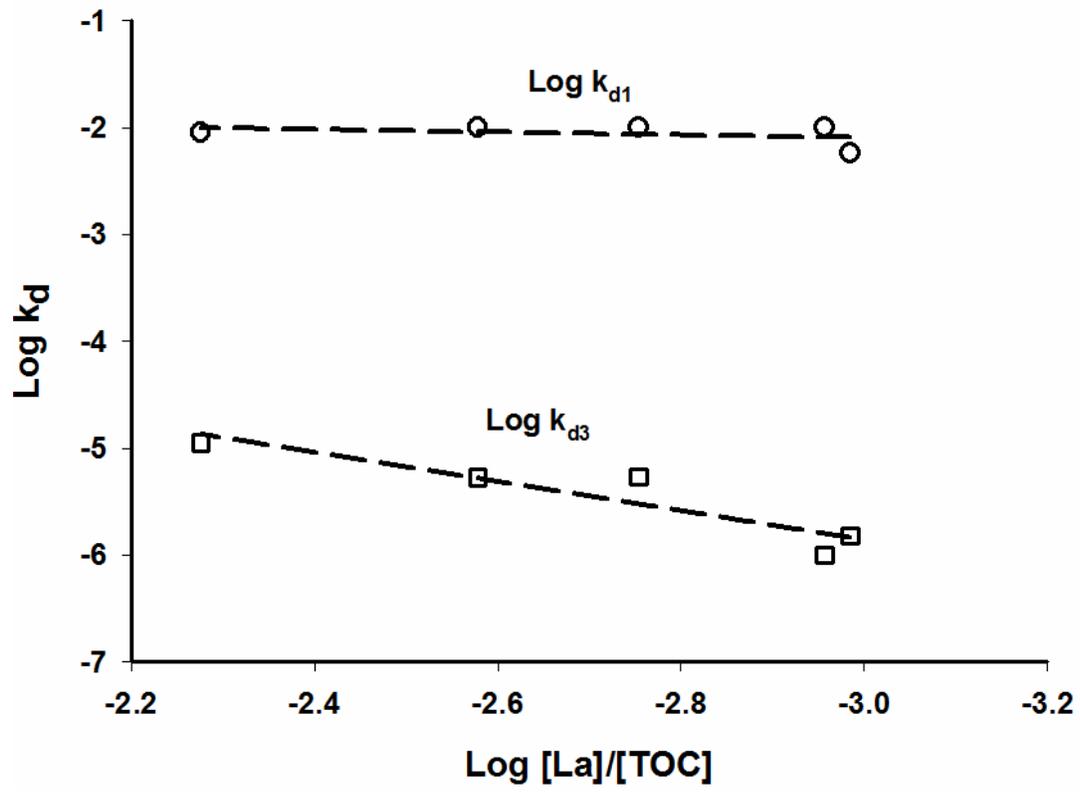


Figure 3

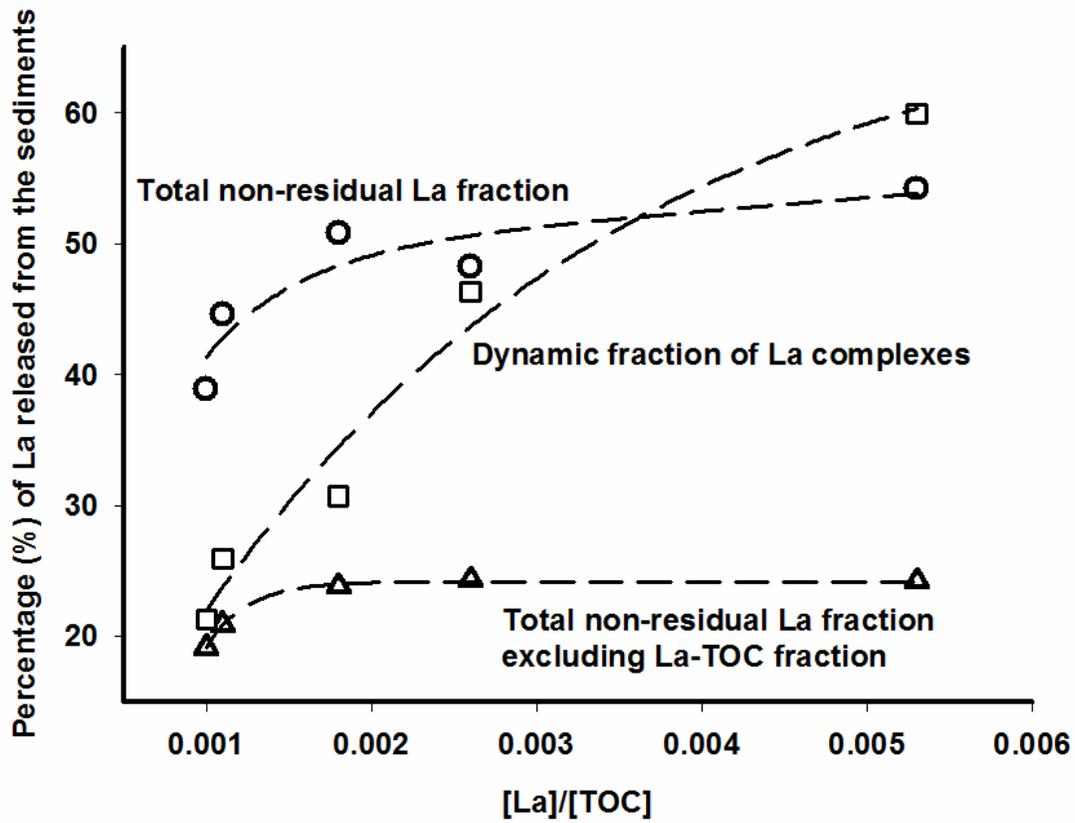


Figure 4