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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 from the central east coast of India. 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.

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) (Buckingham et al., 1995; Eisenbud and Paschoa, 1989; Guo, 1987; Tribe et al., 1990; Zhang et al., 1988) is expected to increase the 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 (Lürling 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, 1996). 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

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sequential extraction methods are those recommended by Tessier et al. (1979), Kersten and Forrstner (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 (Howard and Van den Brink, 1999; Shan and Chen, 1993). 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 (Gonzalvez et al., 2009; Issaro et al., 2009; Koretsky et al., 2008; Martin et al., 1987; Rao et al., 2010; Usero et al., 1998). 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 the sediments, kinetic extraction study was performed to determine dynamic and inert La-sediment complexes with their dissociation rate constants in the 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 m^2 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); Carbonate and bicarbonate 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 H_2O_2 (1.5 mL), HNO_3 (1.5 mL) and $HClO_4$ (1.5 mL) in Teflon vessels) on a hot plate to dryness. The residues were redissolved in 2% ultrapure HNO_3 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,

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	Longtitude	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