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## Marine Pollution Bulletin

journal homepage: [www.elsevier.com/locate/marpolbul](http://www.elsevier.com/locate/marpolbul)

## Kinetic and equilibrium based fractionation study of Pb in continental shelf sediment of India

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## ARTICLE INFO

## Keywords:

Pb fractionation  
Sedimentary Pb  
Kinetic fractionation  
Geochemical fractionation  
Pb geochemistry

## ABSTRACT

Two independent analytical methods (kinetic and sequential extraction protocols) were used to understand the distribution, stability, and lability of Pb-sediment complexes in Indian continental shelf. The concentrations of sedimentary Pb varied from  $12.0 \pm 0.6$  to  $30.4 \pm 0.1$   $\text{mg}\cdot\text{kg}^{-1}$  and  $15.9 \pm 0.3$  to  $36.7 \pm 0.4$   $\text{mg}\cdot\text{kg}^{-1}$  in the western and eastern shelf of India respectively. The kinetic extraction study showed that higher proportion of labile Pb-complexes were present in the eastern shelf sediments (~24% of total Pb) than the western shelf sediments (~14% of total Pb). The sedimentary organic matter was found to regulate lability of sedimentary Pb complexes. The sequential extraction study suggested that Fe/Mn oxyhydroxide were the primary hosting phase for labile Pb complexes. This study showed that water soluble, exchangeable, carbonate/bicarbonate-Pb complexes in the sediments was labile. This study provides a better physicochemical description of stability or lability of Pb complexes in the coastal sediment of India.

### 1. Introduction

Metal fractionation study in marine sediments not only provides useful information about metals bioavailability in sediment system (Sunda, 1975; Morel, 1983; Xue et al., 1988; Ge et al., 2000; Campbell et al., 2002; Slaveykova and Wilkinson, 2005) but also improves our understanding of different complex geochemical processes occurring within the sediment systems (Dang et al., 2002; Chakraborty et al., 2015a).

India has been mining and using lead (Pb), a widely used toxic heavy metal, for over a century. Unfortunately, the awareness of Pb pollution was only realized in India during the late 90s. Being a maritime country with a long coastline (~7000 km), coastal marine sediments around India is expected to act as a major sink for Pb. The main sources of Pb in coastal marine systems are either from natural sources (due to the erosion of rocks, soil, and dissolution of soluble Pb-salts) or from anthropogenic sources (industrial activities, domestic wastes containing Pb, etc.) (Chakraborty et al., 2015a; Vitousek et al., 1997). In industrialized coastal regions, anthropogenic activities are the primary sources of Pb pollution in the marine environment (Chakraborty et al., 2014a). The marine sediments have also been reported to serve as a source of toxic metals under different environmental conditions (e.g., at varying pH, Eh, etc.) (Tessier et al., 1979; Tessier and Campbell, 1987; Chakraborty et al., 2016). The concentration of different binding

phases in marine sediments has been reported to play vital roles in controlling Pb distribution, speciation in coastal marine sediments. The nature of sedimentary organic matter, the concentration of Fe-oxyhydroxide binding phase plays critical roles in controlling Pb fractionation in coastal marine sediment. These are the key variables in the shelf sediments (Chakraborty et al., 2016). The prediction of Pb-distribution pattern, its mobility, and bioavailability in Indian coastal region becomes difficult due to the diverse geology of India and different anthropogenic activities along the long coastline.

Therefore, knowledge of Pb-fractionation in sediments from the coastal areas around India is very much required to understand different geochemical processes that control sedimentary Pb distribution and bioavailability in the shelf sediments around India.

It has been reported that Pb shows different affinities toward different geochemical binding phases of marine sediment (Tessier et al., 1979; Abaychi and Douabul, 1986; Fulghum et al., 1988; Jones and Turki, 1997; Chakraborty et al., 2016). The distributions of Pb in different phases of marine sediments usually follow the following order: residual  $\gg$  Fe/Mn oxides occluded  $>$  organically complexed  $>$  exchangeable and specifically adsorbed (Li et al., 2001; Kabala and Singh, 2001; Morillo et al., 2004; Chakraborty, 2012; Chakraborty et al., 2015a). However, this sequence may change with a changing marine environment.

Lead associated with different binding phases in sediment has been

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<http://dx.doi.org/10.1016/j.marpolbul.2017.08.063>

Received 1 August 2017; Received in revised form 21 August 2017; Accepted 24 August 2017  
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reported to exhibit cation-exchange capacity with biological systems in marine environments (Jarvis and Leung, 2002; Sharma and Dubey, 2005). The reduction of Pb associated with Fe/Mn oxyhydroxide in sediment has been reported to increase bioavailability and mobility of Pb in a marine system (Environment Canada 1998, Chakraborty et al., 2016). The sedimentary organic matter has also been reported to show strong affinity to Pb (Abaychi and Douabul, 1986; Krupadam et al. 2007; Chakraborty et al., 2012). However, geochemical fractionation study does not provide any information on the stability, lability of Pb-sediment complexes in marine systems. The stability, lability, and mobility of Pb complexes in sediment can be reflected by its kinetics release from the sediments. Extraction of Pb from sediment over time can be very useful to distinguish sedimentary Pb complexes with different stabilities and provide information on their mobility. The release of Pb from sediments can be characterized by their distinctly separate dissociation rate constants and two metal pools: readily labile and less labile. Two independent analytical methods (kinetics and equilibrium-based methods) were applied to understand the geochemical distribution and stability of Pb-complexes in coastal marine sediment. This study was the first effort that aimed to (i) quantify sedimentary labile Pb complexes in shelf sediments. (ii) Identify sedimentary Pb complexes (based on its association with different binding phases) which resemble labile Pb complexes. (iii) Classify the factors that control geochemical distribution and fractionation of Pb in the continental shelf sediments around India.

## 2. Material and methods

### 2.1. Study area and sampling

The studied sediments include 21 sites on the eastern and western continental shelf of India (Fig. 1). The sediment samples were collected during GEOSINKS cruises SSK-35, 40 and 50 by using spade corer. The cruises were conducted by CSIR-NIO during May 2012 to March 2015. Short sediment cores were collected by inserting pre-cleaned PVC pipes in the spade corer of 30 cm × 15 cm × 50 cm dimension. The PVC pipes were then capped, sealed and kept immediately at −4 °C and brought back to the laboratory. The sediment samples were then sub-sectioned, freeze-dried and stored in airtight zip-lock bags at 4 °C. The surface sediment samples were only used to achieve the objective of this study. The sediment samples were found to retain their initial color after the sample processing time.

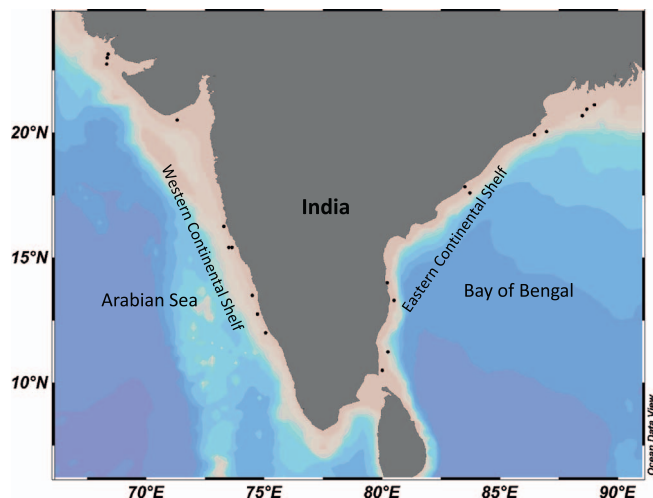


Fig. 1. Locations of sediment samples collected from continental shelf around India.

### 2.2. Total metal analysis

The concentration of total sedimentary Pb and Fe were analyzed by digesting 0.05 g of sediment sample with 10.0 mL of acid mixtures of HF, HNO<sub>3</sub>, and HClO<sub>4</sub> (in 7:3:1 ratio) on a hot plate at 180 to 200 °C. The sediments were digested and evaporated to dryness. The residues were extracted in 2% HNO<sub>3</sub> and analyzed by an electro-thermal atomic absorption spectrometer (ETAAS) (Pb), flame atomic absorption spectrometer (Model: PinAAcle 900T, Perkin-Elmer) (Fe) at CSIR-National Institute of Oceanography (CSIR-NIO). MAG-1, a fine grained gray–brown clay mud with low carbonate content, from the Wilkinson Basin of the Gulf of Maine, was used as a certified reference material (CRM) (obtained from USGS) ([http://crustal.usgs.gov/geochemical\\_reference\\_standards/pdfs/marine.pdf](http://crustal.usgs.gov/geochemical_reference_standards/pdfs/marine.pdf)). The recoveries of the metals in CRM of all experiments were 95 to 98%. The reproducibility of the analysis was < 1% of all the metals.

### 2.3. Elemental and isotopic analysis

Total carbon (TC), total inorganic carbon (TIC), total nitrogen (TN) content was analyzed in the freeze dried and homogenized sediment samples. TC and TN in the sediment samples were determined using Flash 2000 CHN elemental analyzer (Thermo Fisher Scientific Incorporation). The sensitivity of the instrument was checked by using Soil NC sample as certified reference material (Chakraborty et al., 2016). The quality of the data was also checked by random replicate measurement of few samples. The precision of the replicate analysis was within ± 5%. TIC content in the sediment samples was determined by a coulometer (UIC coulometric). Anhydrated calcium carbonate was used as a standard material. Relative standard deviation of the analysis was within ± 2%. Total organic carbon (C<sub>org</sub>) was derived from deducting TIC from TC.

The isotopic ratio of carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) was analyzed in decalcified sediment samples. Decalcification was done by treating the ground sediment samples with 10% HCl, followed by multiple washing with distilled water and drying.  $\delta^{13}\text{C}_{\text{org}}$  was then measured in the Thermo Finnigan Flash 1112 elemental analyzer, linked with a Thermo Finnigan Delta V plus IRMS. Calibration was carried out using 2, 5-Bis-(5-tetrabutyl-benzoxazol-2-yl) thiopen (BBOT) as a standard. The overall analytical precision for replicate samples was ± 0.2‰ for  $\delta^{13}\text{C}_{\text{org}}$ . All isotopic compositions are reported as, per-mil (‰) relative to variation ( $\delta$ ) from the PDB standard.

### 2.4. Geochemical fractionation study

#### 2.4.1. Sequential extraction of sedimentary geochemical phases

Different sedimentary phases of Pb and Fe were separated by following the improved BCR (initially proposed by the Community Bureau of Reference) three step sequential extraction protocol (as described by Rauret et al., 1999) which was slightly modified (as described in Chakraborty et al., 2015b) and used in this study. In this modified protocol, water-soluble metal complexes (a good indicator of bioavailability) in the sediments were separated. This step also helps to remove excess salt content from the marine sediments. The sedimentary phases of metal separated in this modified BCR protocol are water-soluble metal complexes (Fr. 1); ion-exchangeable, and carbonate/bicarbonate forms of metals (Fr. 2); metals bound to Fe/Mn oxyhydroxides i.e., reducible fraction of metals (Fr. 3); concentrations of metals associated with organic phases, i.e., oxidizable fraction of metals (Fr. 4) and residual metal fraction (Fr. 5) in sediment. The detail of the protocol is schematically presented in SM Fig. 1. All the extraction processes were performed in Teflon containers. The reagents used in this study were of Suprapur grade (of Merck) or better (ultrapure). The concentrations of Pb and Fe in each extracted solution and residual fraction were determined by ETAAS respectively. BCR-701 was used as certified sediment reference material (CRM) (produced by IRMM-Institute Reference

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