

Distribution and geochemical fractionation of lead in the continental shelf sediments around India

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Abstract

This study provides a first, preliminary data on geochemical distribution and fractionation of Pb in continental shelf sediments around India and identifies the factors that control geochemical fractionation processes of Pb in convoluted coastal marine sediments. For the sake of clarity, the long coastline (~7000 km) of India was divided into six coastal regions in this study. The total concentration of sedimentary Pb showed regional variation along the coast. The highest median concentration of Pb was found in the sediments collected from the North-east region (26.5 mg.kg⁻¹) followed by North-west (21.4 mg.kg⁻¹) > Central-east (20.6 mg.kg⁻¹) > South-west (13.7 mg.kg⁻¹) > South-east (13.3 mg.kg⁻¹) > Central-west (12.5 mg.kg⁻¹) region. Geochemical fractionation study suggested that the concentration of sedimentary Fe/Mn in oxyhydroxide form and the nature of sedimentary organic matters determined the geochemical distribution and fractionation of Pb in the shelf sediments. The major Pb hosting phases in the shelf sediments were Fe/Mn oxyhydroxide phase followed by the sedimentary organic matter binding phases. The concentration of labile and mobile Pb complexes in the shelf sediment was found to depend on the total sedimentary Pb loading. This study suggests that increase of anthropogenic Pb input and expansion of reduced oxygen levels in the coastal marine environment may have detrimental effects on the increasing mobility and bioavailability of Pb in the coastal areas around India.

Key Words: Geochemical fractionation of Pb; continental shelf sediment; geochemical fractionation; controlling factors; sediment binding phases

1. Introduction:

Geochemical fractionation study of heavy metals in marine sediments not only provides information on mobility, and bioavailability of the metals but also helps to describe different geochemical processes occurring within the system (Singh et al., 1998). Lead (Pb), a highly toxic heavy metal, has long environmental persistence. Lead toxicity has proven to be a major threat and there is several health risks associated with it (Breckle and Kahle, 1992; Harrison, 2001; Eriksson et al., 2007; Duruibe et al., 2007). Thus, understanding of geochemical distribution and fractionation of Pb in the coastal marine environment has received great importance in the recent times in India. While Pb mining has been carrying out for over a century in India, the awareness of Pb pollution was only realized in the late 90s. Leaded petroleum, one of the most important sources of anthropogenic Pb pollution in India, was banned in the year 2000 (UNEP, 2007). However, Pb-mining and industrial activities that involve Pb are continued to carry out in different parts of India for social and economic benefits. Thus, increasing concentration of Pb (well above the natural background level) in different natural environments of India is expected.

Continental shelf sediments act as a major sink for heavy metals (including Pb) (Meade, 1982; Hung and Hsu, 2004; Roussiez et al., 2006; Radakovitch et al., 2008). Therefore, variation in coastal sedimentary Pb concentration (from continental shelve areas) around India may reflect different geochemical and anthropogenic processes that occur in the adjacent landmass.

Chakraborty et al. (2015a) have reported that total Pb concentrations in coastal sediments around India are below the upper limit of the recommended concentration of Pb for Class I sediment (~60 mg.kg⁻¹). However, large spatial variability has also been observed across the coastal India (Chakraborty et al., 2015a). The reason for the spatial variability has been reported to be the diverse geology of the adjacent landmass and different anthropogenic activities along the long coastline (Chakraborty et al., 2015a).

It is necessary to mention that total sedimentary Pb concentration unable to provide any information about its mobility, bioavailability in a system. It is also impossible to differentiate geogenic and anthropogenic Pb contribution in coastal sediments only by looking at total sedimentary Pb concentration. Thus, a large number of studies have been reported in the literature on geochemical distribution and fractionation of Pb in shelf sediments in different parts of the world to provide a better understanding of different geochemical coastal processes (Kersten and Förstner, 1986; Ramos et al., 1994; Yap et al., 2002; Cuong and Obbard, 2006; Chakraborty et al., 2012). However, there is

not much information available on geochemical distribution and fractionation of Pb in the shelf sediment around India.

It has been reported that Pb has different affinities for different geochemical binding phases (such as, sedimentary organic matter, Fe/Mn oxyhydroxide) in sediment (Abaychi and Douabul, 1986; Tessier et al., 1979; Fulghum et al., 1988; Jones and Turki, 1997; Chakraborty et al., 2016a). Different environmental conditions (such as salinity, pH, Eh) along the continental shelf areas have reported to play important roles in controlling mobility and bioavailability of Pb in marine sediments. Lead has been reported to show high binding strength for sedimentary hydrous oxides compared to other trace metals (Benjamin and Lecke, 1981a; Benjamin and Lecke, 1981b; Schindler, 1981; Leckie et al., 1981; Tessier et al., 1985). Oxides and hydroxides of Fe-Mn have been reported as one of the major hosting phases for Pb in marine sediments (Sensarma et al., 2016; Chakraborty et al., 2016a; Takahashi et al., 2007; O'Reilly & Hochella, 2003; Nelson et al., 2002).

However, the efficiency of sedimentary organic carbon (C_{org}) in scavenging Pb is debatable. Both poor and significant association of Pb with the sedimentary organic matter have been reported in the literature (Chakraborty et al. 2012; Krupadam et al. 2007; Abaychi and Douabul, 1986). It has been reported that the quality and quantity of sedimentary organic matter determines the thermodynamic stability of Pb-sedimentary organic matter complexes in the sediments (Chakraborty et al., 2016 a; Chakraborty et al., 2012).

Sedimentary carbonate phase has also been reported to host Pb in marine sediments. Sedimentary carbonate phase controls geochemical fractionation of Pb when sedimentary organic matter and Fe/Mn oxyhydroxide phases are less abundant in a system (Lopez-Sanchez et al., 1996; Izquierdo et al., 1997).

It is well documented that concentrations of different binding phases in coastal sediments vary widely with changing sources (geological setting) of the sediments.

The poor understanding of different processes that control geochemical fractionations of Pb in the continental shelf sediments around India is probably due to the diverse geology, the long coastline (~7000 km), climatic variability, different oceanographic settings, and changing anthropogenic activities along the long coastline of India. To date, the systematic data on geochemical distribution and fractionation of Pb in continental shelf sediments around India are not available. The improved BCR (described by Rauret et al. 1999) was slightly modified (as described in Chakraborty et al., 2015 b) and used in this study to separate i) water soluble Pb complexes (Fr.1), ii) ion-exchangeable and carbonate/bicarbonate forms of Pb (Fr.2), iii) Pb associated with Fe/Mn oxy-hydroxides phase

(Fr.3), iv) Pb associated with organic matter/sulfides (Fr.4), and v) Pb within the structure of the sediments (residual phase) (Fr.5). This study provides a first, preliminary data on Pb distribution and its fractionation in continental shelf sediment and identify the factors that control geochemical fractionation of Pb in convoluted coastal marine sediments around India.

2. Materials and Methods

2.1 Study area and sample collection:

The sediment samples were collected from 120 sampling sites across the eastern (bordering the Bay of Bengal) and the western (bordering the Arabian Sea) continental shelf of India. The number of surface sediment samples (used in this study) was not sufficient enough to represent the long coastline (~7000 km) of India. However, this study was the first attempt to generate preliminary data on geochemical distribution and fractionation of Pb in the shelf sediments around India. For the sake of simplicity, the long continental shelf of India was divided into the following six regions (on the basis of the geology of the adjacent land mass):

- (i) **North-east continental shelf region:** The shelf sediments of this region derive from the erosion of acidic Himalayan rocks. The major rivers debouches in this region are Ganga and Brahmaputra (G-B) (Goldberg and Griffin, 1970).
- (ii) **Central –east continental shelf region:** The sediment of this region derives from the major geological formations of India (such as the Tertiary Deccan Traps, Archean granites, Precambrian rocks including Gondwana sedimentary rocks and recent alluvials) (Krishnan,1968). The major rivers that debouche in this region are Mahanadi, Godavari, and Krishna rivers.
- (iii) **South–east continental shelf region:** The shelf sediment in this region is derived mainly from the Precambrian, gneiss, and schists of intermediate to acidic rocks. Cauvery River is the major river that debouches in this region (Chattopadhyay and Sarkar, 1999).
- (iv) **North-west continental shelf region:** The shelf sediment of this region derives from the Himalayan rocks. The major river of this region that connects with Arabia sea is Indus (Rao and Rao, 1995; Kesserkar et al., 2003, Kurian et.al. 2013).
- (v) **Central-west continental shelf region:** The continental shelf sediment derives mainly from the Deccan Trap Basalt. The major rivers that debouche in this region are Narmada, Tapti, Sabarmati, and Mahi (Rao and Rao,1995; Kurian et al.;2013).

(vi) **South-west continental shelf region:** Precambrian gneiss and schist are the major geological formations contributing sediments to the south-west continental shelf of India (Krishnan, 1968; Rao and Rao, 1995)

Surface sediment samples were collected by using spade corer during GEOSINKS cruises (SSK-35, SSK-40, and SSK-50) (May 2012 to May 2013) conducted by CSIR-NIO. The depth and the distance of the sampling sites from the coast are presented in Table 1a and 1b. It is important to note that the surface sediment was collected from oxic environment (based on the bottom water dissolved oxygen concentrations). Short sediment cores were collected by inserting polyvinyl chloride (PVC) pipes in the spade corer of 30 cm × 15 cm × 50 cm. The PVC pipes were thoroughly cleaned with acid. 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 taken for this study. The sediment samples were found to retain their initial colour during sample processing. Sixty-four (64) sediment samples were selected for geochemical fractionation study of Pb from the six regions (mentioned above) for this study. The sampling locations are shown in Figure 1.

2.2 Texture analysis:

Texture of the shelf sediment (in < 63 μm) was analyzed by Particle Size Analyzer (LPSA from Malvern, Mastersizer 2000). The detailed procedure has been described in the literature by Ramaswamy and Rao (2006). The sand data are presented in weight percentage (Wt %) and the silt and clay in volume (%) in this study.

2.3 Analysis of total inorganic carbon (TIC) and total sedimentary organic carbon (C_{org}):

The surface sediment samples were analyzed for the determination of total carbon (TC), and total inorganic carbon (TIC) contents in the sediments. The TC content in the sediments was determined by using a Flash 2000 CHN elemental analyzer (Thermo Fisher Scientific Incorporation). The precision of the analysis was within ± 5%. The NC reference soil sample (containing 3.5% C) was used as the certified reference material (Chakraborty et al., 2016b; Halvorson et al., 2013). TIC was determined by coulometry (UIC Coulometrics, Illinois, USA). Calcium carbonate (12% C) was used as a standard material. The relative standard deviation of the analysis was within ± 2%. The total sedimentary organic carbon (C_{org}) content was derived by deducting TIC from TC. Calcium carbonate (CaCO₃) content in sediment was calculated by assuming that the majority of inorganic carbon was in carbonate form and associated with Ca.

2.4 Determination of total metals in the sediments:

The dried sediment samples (from each station) were homogenized and ground-milled. The total metal concentrations in the sediments were determined by digesting ~ 50.0 mg of sediments with 10.0 mL of acid mixtures of HF (Suprapure, Merck, Germany), HNO₃ (Suprapure, Merck, Germany) and HClO₄(GR, Merck, Germany) (in 7:3:1 ratio) on a hot plate at 200 °C. The sediments were digested (completely dissolved) and evaporated to dryness. The residues were re-dissolved in 2% HNO₃ (ultrapure) and analyzed by an Electrothermal and flame atomic absorption spectrometer (ETAAS and FAAS) (Model: PinAAcle 900T, Perkin-Elmer) at CSIR-National Institute of Oceanography (CSIR-NIO).

The concentrations of sedimentary Pb and Fe were determined by ETAAS and Flame AAS by using hollow cathode lamp (HCL) of Pb and Fe at 283.3 and 248.33 nm wavelengths respectively.

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). The recoveries of Pb and Fe from the CRM were more than 95 to 98 %.

2.5 Sequential extraction protocol for geochemical fractionation of sedimentary Pb:

The operationally defined BCR protocol (harmonized and standardized protocol by Rauret et al 1999) was used in this study with an additional leaching step at the beginning to remove water-soluble metal complexes (Fr.1) and excess salt (NaCl) content from the sediments. The detailed description of the slightly modified protocol (used in this study) is presented and compared with the protocol proposed by Rauret et al (1999) in the supporting document (SM Figure 1). This modified sequential extraction protocol has already been used in our previous studies (Chakraborty et al., 2015b; Chakraborty et al., 2016 a, b, c).

In this modified protocol, water-soluble metal complexes (Fr.1) (a good indicator of bioavailability) were extracted from the sediments by stirring with ultrapure water (with resistivity of 18.2 mΩ, from Merck Millipore synergy system, SYNS50001, USA). This step also helped to remove excess salt content from the shelf sediments at the beginning. Ion-exchangeable and carbonate/bicarbonate form of metals (Fr. 2) (extracted by 0.11M CH₃COOH, Suprapur glacial acetic acid (100%) from Merck Millipore, Germany); metals bound to Fe/Mn oxyhydroxides i.e., reducible fraction of metals (Fr. 3) (extracted by 0.5M NH₂OH.HCl at pH 1.5, 99.999% from Merck Millipore, Germany); metals associated with sedimentary organic matter and sulfide, i.e., oxidizable fraction of metals (Fr. 4) (extracted by 1.0M CH₃COONH₄ ((99.99%, Merck, Darmstadt, Germany)

after digestion with 30% H₂O₂ (30% GR, Merck, Darmstadt, Germany) and residual metal fraction (Fr. 5) (extracted by complete digestion with acid mixture (HF (Suprapure, Merck, Germany):HNO₃(Suprapure, Merck, Germany):HClO₄ (GR, Merck, Germany) =7:3:1) as described before. The detail description of the protocol has been described in Rauret et al (1999). The geochemical phases (Fr.1, Fr.2, Fr.3, and Fr.4) are considered as non-residual metal complexes. It is assumed that naturally or anthropogenically mobilised metals remain in the non-residual phases. The residual phase (Fr.5) mainly represents primary and secondary minerals, which may hold trace metals within their crystal structure.

The sequential extraction protocol was carried out in acid cleaned Teflon containers. The reagents used in this study were of ultrapure/suprapure grade. The extracted leach solutions (containing metals) of 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 then re-dissolved in 10 mL of 2% suprapure HNO₃ ((Suprapure, Merck, Germany)) and analyzed by ETAAS to obtain the concentrations of Pb in different binding phases of the sediments. Three replicates of each sample were analysed. Two reagent blanks were analyzed for every set of extraction. In all cases, blank results were below the detection limit of the analytical technique. BCR-701 was used as certified sediment reference material (CRM) (produced by IRMM- Institute Reference material and Measurements, Geel, Belgium and marketed by Sigma-Aldrich).

The BCR-701 certificate does not provide certified values for the water soluble fraction. Thus, the total concentrations of water-soluble, ion-exchangeable and carbonate/bicarbonate form of Pb (determined by the modified method) were added and compared with the certified reported value. The Recovery of certified Pb concentrations in different geochemical fractions from BCR-701 was in very good agreement with the certified reference concentrations ($\pm 3\%$ of the reported value). Validation of the sequential extraction method was further done by comparing the total metal concentrations (determined by ETAAS) with the sum of the concentrations of each metal fractions obtained by following the modified sequential extraction protocols. The comparable (close to 100% recovery) values of total metal concentrations support the reliability and validity of the modified sequential extraction protocol. Replicate samples were used to measure overall analytical precision. The reproducibility of each measurement (n=3) was <1% for Pb.

2.6 Statistical Analysis:

One-way analysis of variance (ANOVA) was used to compare the Pb concentrations in the shelf sediments from the six different regions around India. If statistically significant then Bunferroni

corrected post t-test was further carried out. This test was to check if sedimentary Pb concentrations in different regions were statistically different or not. Pearson's correlation coefficient (r) was used to understand the strength of association between the sedimentary Pb concentrations and sedimentary texture, sedimentary organic matter, Fe-oxyhydroxides in the studied sediments.

3. Results and discussion

3.1 Distribution of total concentration of Pb and other geochemical parameters in the continental shelf sediments around India

The variations in the grain size characteristics, CaCO_3 , organic matter, and total Fe contents in the continental shelf sediments are presented in Tables 1a and b. The latitudinal distributions of sand, silt and clay contents (in percentage) in the studied sediments suggest that the sediments from the northern part of both the shelves dominated by finer (silt and clay) particles. However, the sediments from the southern regions of both the shelves were dominated by the coarser particles. The highest (average/median??) amount of coarser particles (sand sized fraction, $> 63\mu\text{m}$) was found in the sediments from the south-east region (69.6 %) followed by the $>$ south-west (55.3%) $>$ central-east (36.4%) $>$ central-west (3.4%) $>$ north-west (2.8%) $>$ north-east (2.5%). The high content of coarser particles in shelf sediments from the southern part of both the coasts has also been reported in the literature (Hashimi et al., 1981; Selvaraj and Mohan, 2003). It has been argued by Hashimi and Nair (1986) that estuaries permit deposition of only fine-grained sediments on the inner shelf because coarse-grained sediments are trapped in the estuarine basin. Thus, in spite of heavy sediment discharge by G-B and Indus, the inner shelf of north-east and north-west regions contains a greater amount of finer particles.

The highest median concentration of CaCO_3 was found in the shelf sediments collected from the south-east coast ($\sim 15.9\%$) followed by the north-west ($\sim 15\%$) $>$ south-west (10.9) $>$ central-west (9.9 %) $>$ central-east (3.6%) $>$ north-east ($\sim 2.5\%$) regions of India. The order of variation of sedimentary CaCO_3 was found to be very similar to the variation of the coarser particles.

The concentrations of sedimentary organic matter (presented as C_{org}) also showed regional variation along the shelf area around India. The data are presented as wt. %. The highest C_{org} content was found in the shelf sediments collected from the south-west region ($\sim 2.2\%$) followed by the central-west ($\sim 1.1\%$) $>$ central-east ($\sim 1.0\%$) $>$ south-east ($\sim 0.8\%$) $>$ north-east ($\sim 0.7\%$) $>$ north-west ($\sim 0.6\%$) regions. Relatively higher C_{org} content ($> 1\%$) was found in the shelf sediments collected from the south-west and central-west regions of India. A similar observation has been reported in the literature (Paropkari et al., 1992; Paropkari et al., 1993; Sarkar et al., 2004; Banerjee et al., 2012).

There was no correlation observed between the finer particles (silt+clay), and the C_{org} (supporting materials, SM Figure 2) content in the studied sediment (both in the east and west coast of India). However, this finding is unusual. It is well documented that there is always high sorption of C_{org} on finer particles in sediments (Hedges and Keil, 1995; Paropkari et al., 1987). This inverse relationship was probably due to the change in nature of finer particles (due to diverse geology), and sedimentary organic matter.

The concentrations of total Fe (in wt. %) in most of the studied sediments were more than the average crustal abundance (3.5%, McLennan; 2001). High concentration of Fe in the continental shelf sediment around India has also been reported in the literature (Rokade, 2009; Reddy et al., 2004; Chakraborty et al., 2015a). The highest median concentrations of Fe was found in the sediment collected from the central-east (~8.1%) coast followed by Central-west (~7.4%) > North-east (~6.1) > North-west (~5.5%) > South-west (~3.5%) > South-east (~2.7%) regions of India.

Figure 2 shows the distribution of sedimentary Pb concentrations in the continental shelf areas around India. The total concentrations of sedimentary Pb showed regional variation and varied from 5.9 ± 0.2 to 36.7 ± 0.4 mg.kg⁻¹ (the data are presented as an average \pm standard deviation). The low concentrations of sedimentary Pb were found along shelf region of India. Region wise comparison in the sedimentary Pb content showed that the north-east region had the highest median concentration of sedimentary Pb (26.5 mg.kg⁻¹) followed by north-west (21.4 mg.kg⁻¹) > central-east (20.6 mg.kg⁻¹) > south-west (13.7 mg.kg⁻¹) > south-east (13.4 mg.kg⁻¹) > central west (12.5 mg.kg⁻¹) region. The condition (with reference to Pb pollution) of shelf sediments around India was evaluated by comparing the sedimentary Pb concentrations obtained from the six different coastal regions around India with sedimentary Pb concentrations from the different coastal area around the world (reported in Chakraborty et al., 2015a). The concentrations of sedimentary Pb around India were similar with the unpolluted coastal sediments from different parts of the world.

One-Way analysis of variance (ANOVA) was used to compare the statistical significance of the mean concentrations of sedimentary Pb from the six different shelf regions of India. Concentrations of sedimentary Pb in the continental shelf sediments from the north-east and central-east coast of India were not statistically different. However, the concentration of Pb in the sediments collected from the north-east coast was statistically different from the south-east coast region. Likewise, the total concentration of Pb in the sediments collected from the north-west coast differed from the central-west and south-west coast of India. The Bonferroni corrected post t-test indicates that sedimentary Pb concentration in North West region was significantly higher than central west and

south west region. The post t-test also indicates that sedimentary Pb concentration in south east is significantly higher than central east and North East region.

It is important to note that total sedimentary Pb concentration represents both detrital (i.e. geogenic sources) and authigenic Pb. Dilution of detrital minerals by authigenic phases is also likely to influence the total Pb concentrations in sediments. In fact, even if 100% of the Pb resides in detrital phases, total Pb concentrations can still be diluted by the accumulation authigenic phases devoid of Pb, lowering the total concentration. Therefore, the variation in total sedimentary Pb concentration from the different coastal regions is unable to provide any information on the geogenic and authigenic contribution on the total sedimentary Pb.

However, it would have been better to interpret the results based on more number of samples. Nevertheless, it is also necessary to realize the constraint of rigorous sampling within a given ship time and covering ~7000 km long coastline. The total concentrations of sedimentary Pb showed poor correlation with finer particles (silt+clay) in the shelf sediments (supporting materials, SM Figure 2) around India. A very similar poor correlation was also observed between the sedimentary organic matter and total Pb content (supporting materials, SM Figure 2) in the studied sediments. These observations suggest that the finer particles and sedimentary organic matter content in the shelf sediments were not responsible for the variation of sedimentary Pb concentrations along the coast around India. The variation in sedimentary Pb concentration was probably because of changing anthropogenic activities and the diverse geology of Indian continent (Krishnan, 1968; Naqvi, 2005; Chakraborty et al., 2015). Further geochemical fractionation studies were carried out to provide a better understanding of different geochemical processes that control Pb distribution and its fractionation in continental shelf sediments around India.

3.2 Geochemical fractionation study of Pb in the continental shelf sediments around India

The geochemical fractionations of Pb in continental shelf sediments (Table 2) from the six different regions around India are discussed below. It is important to mention that the sequential extraction protocol, used in this study, is an "operationally defined" method. Therefore, the importance of the analytical results is profoundly conditional upon the extraction protocol used. However, in most cases, the use of operationally defined extraction protocols is good enough to understand different geochemical processes in marine systems.

The geochemical fractionation study showed that the significant portion (33 to 81 %) (SM Figures 3a,b,c and 4a,b,c) of total sedimentary Pb was present in the non-residual fraction. This fraction represents geochemically active Pb. The lowest concentration of non-residual Pb was present as

water soluble Pb complexes (Fr.1) in the shelf sediments from all the regions. The concentration of water soluble sedimentary Pb varied from very low (below the detection limit, BDL) to 7.3 mg. kg⁻¹. The regional comparison in the median concentration of water soluble Pb complexes followed the order of North-east (0.5 mg.kg⁻¹) = Central-east (0.5 mg.kg⁻¹) < South-east = Central-west = South west (0.2 mg.kg⁻¹) < North-west (BDL). The levels of water soluble Pb-complexes (Fr.1) did not increase significantly with the increasing total Pb concentration in the sediments from all the regions except for the central-west region (SM Table 1 to 5). The insignificant increase in concentrations of water soluble Pb-complexes with the increasing Pb loading in the shelf sediments indicates that other Pb-binding ligands were available in the sediments to form thermodynamically stable Pb complexes in these regions. However, in the central-west region, the significant increase of water soluble complexes with increasing Pb content indicates the unavailability of stronger binding sites especially in few sporadic locations (SM Table 6) where the concentration of water soluble complexes was higher than the other non-residual phases of sediments. The Concentration of acid leachable (exchangeable and carbonate/bicarbonate) Pb-complexes (Fr.2) varied from 0.1 to 8.9 mg.kg⁻¹ in the studied sediments. The regional variation indicated that the sediments collected from the North-east, Central-east and North-west regions contained highest acid leachable Pb-complexes (Fr.2) (~0.8 mg.kg⁻¹) followed by South-east (0.6 mg.kg⁻¹) > Central-west (0.4 mg.kg⁻¹) > South-west (0.3 mg.kg⁻¹) regions.

A significant increase in the concentration of acid leachable Pb complexes (Fr.2) (SM Tables 3, 4, 5) was observed with the increasing total Pb content in the sediments from South-east, North-west and Central-west regions. The presence of high carbonate content in the sediments from these areas (Table 1a, b), probably helped to host sedimentary Pb as carbonate/bicarbonate form. The concentration of water soluble (Fr.1) and acid leachable Pb complexes (Fr.2) can be considered as labile and mobile Pb complexes in the shelf sediment. It was found that the concentration of water soluble (Fr.1) and acid leachable Pb complexes (Fr.2) in the studied sediments depend on the total sedimentary Pb loading. However, the availability of stronger binding sites in different sedimentary phases also played a significant role in controlling Pb concentration in the acid leachable fraction. The concentration of reducible (Fe/Mn oxyhydroxide) fraction of sedimentary Pb in the studied sediments varied from 0.7 to 16.6 mg.kg⁻¹. The highest median concentration of reducible Pb was present in the sediments collected from North-east region (10.1 mg.kg⁻¹) followed by Central-east (8.9 mg.kg⁻¹) > North-west (8.7 mg.kg⁻¹) > Central-west (3.0 mg.kg⁻¹) > South-west (2.4 mg.kg⁻¹) > South-east (1.9 mg.kg⁻¹) region.

Association of Pb with reducible phase significantly increased with the increasing concentrations of total Pb in the sediments (SM Tables 1 to 6). In most of the studied sediment, a major fraction of the total non-residual Pb was present in reducible phase (Fr.3).

This was probably due to the presence of Fe- based nanoparticles in the water column which have been reported to show promising adsorbing capacity for Pb (Zare et al., 2016). Goethite (α -FeOOH) and lepidocrocite (γ -FeOOH), two different phases of Fe oxyhydroxide nanoparticles (one of the major component of reducible phase) has been reported to have an excellent capability of hosting Pb in aqueous solution (Rahimi et al., 2015; Mahapatro and Anand 2010). Co-precipitation of Fe/Mn oxyhydroxides in water column along with Pb and adsorption of Pb on their surface may also increase Pb concentration in Fe/Mn oxyhydroxide phase of sediments. It has been well reported in the literature that Pb forms stable complexes with the binding sites present in Fe/Mn oxyhydroxides phase (Ramos et al., 1994, Lopez-Sanchez et al. 1996, Jones and Turki, 1997 and Li et al. 2001) in estuarine and coastal sediments. Their findings are in good agreement with the outcome of this research and infer that Fe-oxyhydroxide was probably the primary hosting phase for Pb in the shelf sediments.

The concentration of oxidizable Pb complexes (Fr.4) varied from 0.1 to 9.5 mg.kg⁻¹ in the studied sediments. The Regional variation in the median concentration of oxidizable Pb followed the order of Central-west (2.6 mg.kg⁻¹) > Central-east (1.6 mg.kg⁻¹) > South-west (1.5 mg.kg⁻¹) = North-east (1.5 mg.kg⁻¹) > South-east (1.2 mg.kg⁻¹) > North-west (0.7 mg.kg⁻¹). Sedimentary Pb showed weaker affinities towards the oxidizable binding phases (e.g., sedimentary organic matter and sulfide, etc.) compared to the reducible phases (Fe/Mn oxyhydroxide) in the studied sediments. It has been reported in our recently published paper that Pb forms weaker complexes (with fast dissociation rate constant) with sedimentary organic matter (Chakraborty et al., 2016b). However, the association of Pb with oxidizable and reducible phases were comparable in some of the sporadic locations from the Central-west and North-west coast of India. The association of Pb with sedimentary oxidisable phase (Fr. 4) was found to increase with the increasing concentration of total Pb in the studied sediments collected from the Central-west and North-west coast of India (as shown in SM Tables 1 to 6). Sedimentary organic carbon (C_{org}) was the primary oxidisable geochemical phase (Fr.4) in the studied (surface) sediment. The presence of sulfide phase in the surface shelf sediments under oxic condition was negligible. In general, statistically insignificant change in the concentration of Pb associated with sedimentary organic carbon binding phase (SM Tables 1 to 6) was observed with increasing C_{org} in the sediments.

The concentration of Pb within the mineral structure (Fr.5) of the shelf sediments varied of 3.6 to 22.9 mg.kg⁻¹. This phase, also known as residual phase, carried a significant part (22.1 to 81.1 %) of the total sedimentary Pb along the shelf. The regional variation in median concentration of residual Pb follows the order of North-east (13.0 mg.kg⁻¹) = Central-east (13 mg.kg⁻¹) > North-west (10.3 mg.kg⁻¹) > South-east (8.6 mg.kg⁻¹) > South-west (6.3 mg.kg⁻¹) > Central-west (5.5 mg.kg⁻¹). It is well known that the concentration of Pb in residual phase carries the signature of the source rocks (Tessier et.al, 1979; Lin et al., 1997; Ladigbolu et.al, 2014). Thus, an attempt was made to identify the source rocks by comparing the residual Pb concentrations from different shelf regions of India. There was a significant variation in the residual Pb content of the shelf sediments. However, it was not possible to identify the different source rocks by comparing the residual Pb content in different shelf regions except Central west coast of India. The low concentration of residual Pb in the self-sediments from the Central-west region (3.6 to 6.5 mg.kg⁻¹) (Table 2) was probably due to the weathering of mafic type source rocks (Krishnan, 1968; Rao and Rao, 1995; Kurian et.al., 2013). The Pb content in the residual phase of the studied sediments from this region are very similar to those of basaltic lava flows, dykes of Toranmal section (Pb concentration: 1.3 to 6.7 mg.kg⁻¹) and Tapi rift (Pb concentration: 2.1 to 5.9 mg.kg⁻¹) of Deccan volcanic province (Chandrashekharam et al., 1999).

3.2.7 Outcome of the geochemical fractionation study of Pb in the shelf sediments:

The major findings are given below:

- (a) Mobility and bioavailability of sedimentary Pb: The variation in concentrations of water soluble, exchangeable, and carbonate/bicarbonate forms of Pb complexes in the shelf sediments were in the following order. These complexes are good representatives of bioavailable Pb complexes with higher mobility.

North-east \approx Central-east > South-east \approx North-west > Central-west > South-west

- (b) Reducible phase was the major non-residual hosting phase for Pb followed by oxidisable binding phase in the shelf sediments.
- (c) The Pb content in the residual fraction of the shelf sediments were not good indicators of the source rocks except Central-west coast of India.

Further study was carried out to identify the factors that control the geochemical distributions and fractionations of Pb in reducible phase. Thus, geochemical fractionation study of sedimentary Fe was carried out.

3.3 Association of Pb with different geochemical fractionation of Fe in the continental shelf sediments of India

In order to understand the association of Pb with different geochemical phases of sedimentary Fe, further geochemical fractionation study of Fe was carried out in the studied sediments from the eastern and western continental shelves. It was found that major fraction of the total sedimentary Fe was present mainly in the residual phase (Fr.5) (~70 to 90% of the total sedimentary Fe content) (Table 3, SM Figure 4). The concentration of reducible (oxyhydroxide) form of Fe (Fr.3) in the continental shelf sediments showed regional variation.

Highest median concentration of Fe in oxyhydroxide (reducible) form was found in the sediments collected from the north-east (8552 mg.kg⁻¹) followed by South-west (6188 mg.kg⁻¹) > Central-east (5439 mg.kg⁻¹) > North-west (4758 mg.kg⁻¹) > Central-west (4270 mg.kg⁻¹) and > South-east (3263 mg.kg⁻¹) continental shelf region of India. The concentration of Fe-oxyhydroxide was not dependent on the total Fe content of the sediments (see Tables 1 and 3). The concentration of Pb in reducible phase (Fr.3) showed a strong positive correlation with reducible Fe (Fe-oxyhydroxide) concentration but not with the total Fe content (SM Table 7, $r^2=0.64$, $p < 0.01$, $n=64$) in the sediments. This observation suggests that the concentration of Fe-oxyhydroxide was the primary binding phase for Pb in the sediments.

A significant portion of Fe was also associated with the oxidizable (organic) phase of the sediments. Highest concentration of Fe (3382 mg.kg⁻¹) was found to associate with sedimentary organic matter from the Central–west coast of India, followed by South-west (3031 mg.kg⁻¹) > Central-east (1697 mg.kg⁻¹) > North-east (963 mg.kg⁻¹) > North-west (880 mg.kg⁻¹) > South-east (472 mg.kg⁻¹) region. Unlike Pb (SM Tables 1 to 6), there was a strong correlation between Fe associated with C_{org} and the C_{org} content of the sediments (SM Table 7). It is important to note that sedimentary organic binding phase is polyfunctional, polyelectrolyte and polydisperse in nature and contains a large number of binding sites (-COOH, -OH, etc.) to form strong complexes with metals. The weak association of Pb with the sedimentary organic matter in the studied sediment suggests that trace metal competition, quantity, and quality of sedimentary organic matter, availability of other Pb-complexing sites in the sediments probably played a key role in controlling Pb-sedimentary organic matter interaction in the shelf sediments. A strong correlation between the C_{org} and concentration of Fe associated with the organic phase in the studied sediments reflects the strong affinity of Fe(III) towards the sedimentary organic carbon (SM Table 7, $r^2=0.77$, $p < 0.01$, $n=64$). The strong affinity of Fe(III) for different binding ligands in sediment probably outcompeted Pb to get associated with the sedimentary organic binding phase. The weak association of Pb with the organic phase in spite of

high C_{org} abundance was observed in South-west region. The geochemical fractionation data of Pb in the shelf sediments from the south-west and central-west coast of India suggested that Pb had higher affinity towards C_{org} (even though the concentration of C_{org} was less; ~1.1%) in the sediment collected from the central west than the south-west (~ C_{org} ; ~2.2%) coast of India. This observation can be justified by considering the relative concentrations of sedimentary Fe-oxyhydroxide in these two regions. Less amount of Fe oxyhydroxide phase in the sediment from the central-west coast region forced Pb to associate with C_{org} (C_{org} was less; ~1.1%). The relatively higher concentration of Fe oxyhydroxide in the sediment from the south-west coast region provided enough binding sites to host Pb and thus, there was small association Pb with C_{org} (even though ~ C_{org} ~2.2%) in this region. The concentration of Pb associated with other geochemical fractions (water soluble Fe, ion-exchangeable and carbonate/bicarbonate forma of Fe, and residual phase of sedimentary Fe) was probably low. However, it was not possible to quantitatively estimate the concentration of Pb associated with other geochemical phases of Fe in the sediments.

This study suggests that Pb has high affinity towards Fe-oxyhydroxide phase. Fractionation study of sedimentary Fe revealed that the concentrations of Fe as oxyhydroxide form in the sediments played a key role in controlling geochemical fractionation of Pb in the sediment from the shelf region around India.

Overall conclusion

The present work is the first comprehensive study reporting geochemical distribution and fractionation of Pb in the shelf sediments around India. The total concentrations of sedimentary Pb showed regional variation. The variation in sedimentary Pb concentration was probably because of changing anthropogenic activities and the diverse geology of Indian continent. The geochemical fractionation study suggests that the concentration of sedimentary Fe/Mn oxyhydroxide form, quantity and quality of sedimentary organic matters determined the geochemical distribution and fractionation of Pb in the continental shelf sediments. Fe/Mn oxyhydroxide phase was the major hosting phase for sedimentary Pb in the continental shelf sediments around India. However, sedimentary organic matter also acted as host for Pb in some sediment. The distribution and fractionation of Pb in the shelf sediment was found to depend on the relative abundance of binding sites in the above two sedimentary binding phases. Future work has been planned to identify the source rocks of the shelf sediments (with extensive field sampling) by determining the concentrations of trace/heavy metals in residual phases of the sediments.

Global Implication

The outcome of this research summarizes that Fe (III)-oxyhydroxide phase was the major hosting phase for non-residual Pb in the continental shelf sediments around India. It is well known that Pb association with Fe/Mn-oxyhydroxide phase in the sediments gradually decreases with the decreasing dissolved oxygen concentration of the overlying bottom water (due to dissolution of Fe(III)/Mn oxyhydroxide phase) (Chakraborty et al.,2016 c; Audry et al.,2011; Middelburg and Levin, 2009; Graetz et al., 1973). Climate models have predicted declining oceanic dissolved oxygen due to global warming. This study suggests that expansion of reduced oxygen levels may have dramatic consequences on the mobility and bioavailability of Pb in coastal areas around India in future.

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Captions and legends for the figures:

Figure 1: Geology of Indian continent (source: Kessarkar et al., 2003 and Kessarkar et al., 2005) with the sampling sites located in the eastern (red circles and yellow triangles) and western (red stars) continental shelf of India

Figure 2 (a) Distribution pattern of total Pb content (mg.kg^{-1}) in the continental shelf sediments around India. (b) Variation in concentration of mean sedimentary Pb in different coastal region around India. ** One-way Anova was significant. Bunferroni corrected post t-test indicates that sedimentary Pb concentration in North-west region is significantly higher than Central west and South-west region. *Bunferroni corrected post t-test indicates that sedimentary Pb concentration in Central-west and South-west shelf regions are not statistically different. ## Anova was significant. Bunferroni corrected post t-test indicates that sedimentary Pb concentration in South-east is significantly higher than Central-east and North-east region. #Bunferroni corrected post t-test indicates that sedimentary Pb concentrations in North-east and Central-east shelf are not statistically different

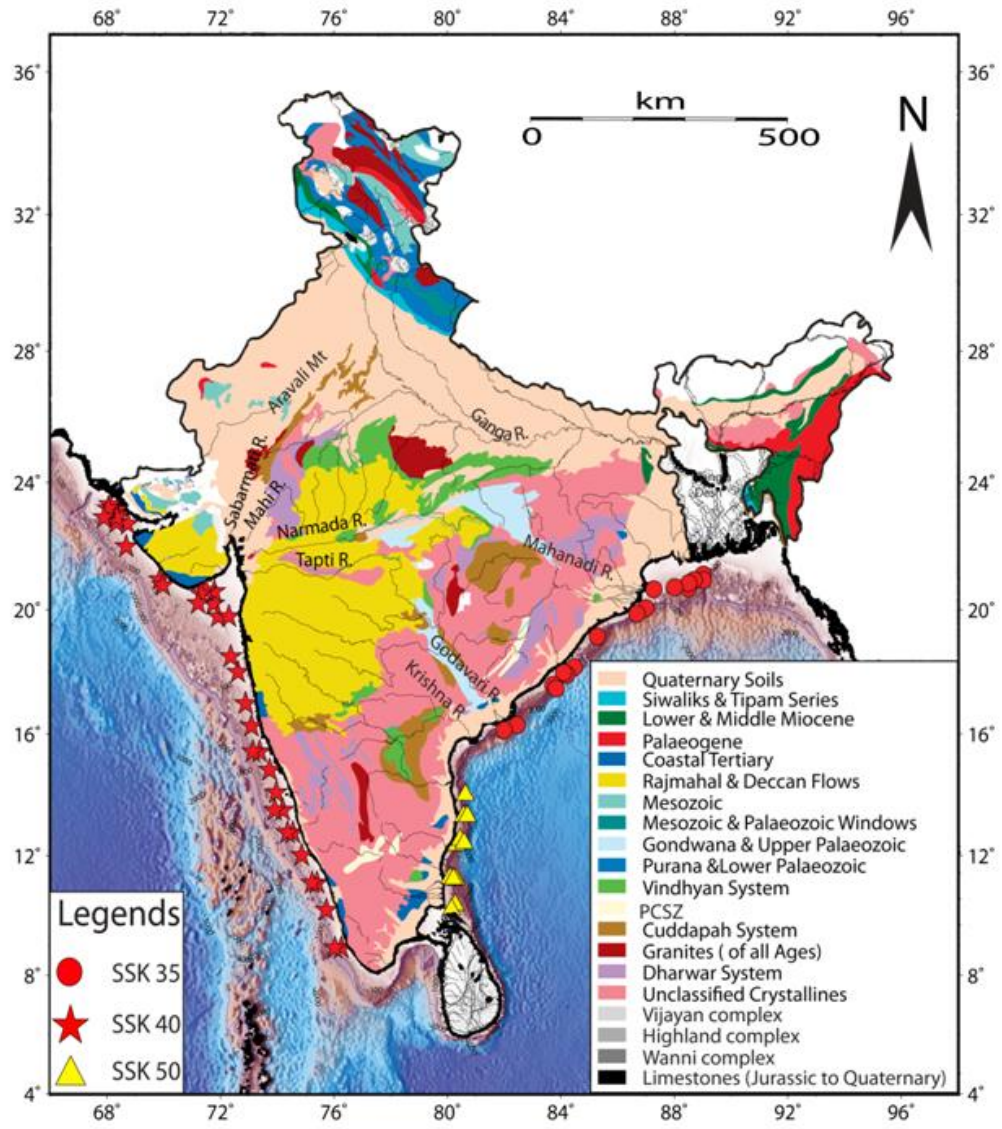


Figure 1

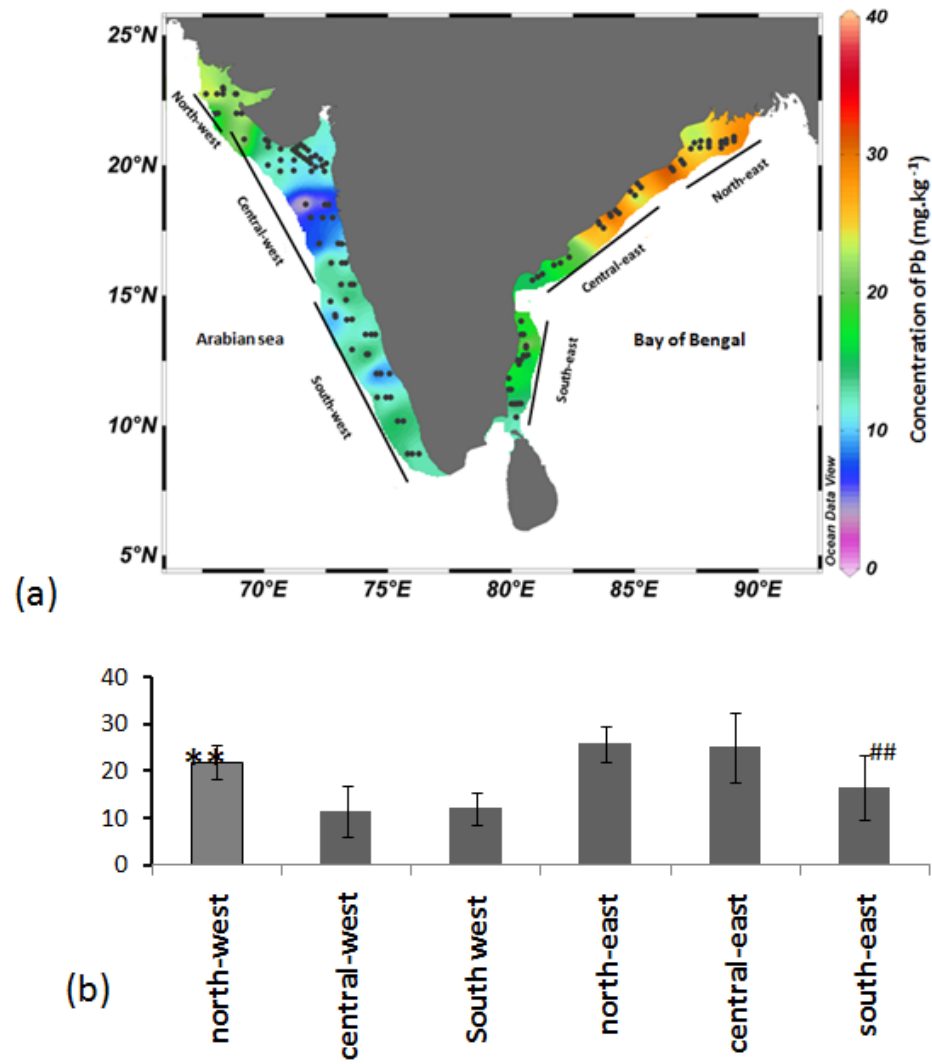


Figure 2