Mechanisms controlling lead distribution in continental margin sediments of India

A Thesis submitted to the Goa University for the award of
Doctor of Philosophy

In

Marine Sciences

by
Sucharita Chakraborty (Kar)

Under the guidance of
Dr. B. Nagender Nath

Goa University
Taleigao, Goa
2016

Dedicated to maa and baba

Statement

As required under the University ordinance **OB-9.9 (v-vi),** I state that the present thesis entitled "***Mechanisms controlling lead distribution in continental margin sediments of India***" is an innovative research work that has been carried out by me for the mentioned study area. I am sure that this work has not been previously submitted and is not concurrently submitted for any other degree at Goa University or at any other institutions.

The literature related to the problem investigated has been cited. Due acknowledgements have been made wherever facilities and suggestions have been availed of**.**

21st September, 2016

Sucharita Chakraborty
Geological Oceanographic Division
National Institute of Oceanography
Dona Paula, Goa, 403004

Certificate

This is to certify that the thesis entitled *"**Mechanisms controlling lead distribution in continental margin sediments of India**"* submitted by Sucharita Chakraborty to the Goa University for the degree of Doctor of Philosophy, is based on her original research work carried out by her under my guidance. The thesis or any part there of has not been previously submitted for any other degree or diploma in any university or institution.

21st September, 2016

Dr. B. Nagender Nath
Geological Oceanographic Division
National Institute of Oceanography
Dona Paula, Goa, 403004

Acknowledgement

I would like to express my sincere gratitude to my supervisor Dr. B.Nagender Nath for suggesting this topic and suggesting to focus on the geochemistry of a single element, his continuous support and encouragement throughout my research work. He has given me the opportunity to restart my academic career after a long gap of 7 years. Dr. Nath has always motivated me to work hard and always bestowed his knowledge whenever I needed during my research work.

I express my sincere appreciation to Dr. Parthasarathi Chakraborty for giving me the opportunity to work with him in “Metal Speciation Laboratory”. My research work has been enriched with his innovative ideas and valuable suggestions. I am grateful to him for teaching me, how to express scientific findings in black and white.

My sincere gratitude also goes to Vice Chancellor’s nominee Dr.M.Dilip Kumar for his invaluable suggestions during FRC meetings. I am grateful to Prof. C.U. Rivonkar, H.O.D, Marine Sciences, Goa University, Prof. Malapati K. Janarthanam, Dean of Faculty of Life Sciences and Environment, Goa University and Mr.Yeshwant Naik for their help and support.

I am thankful to my fellow lab mates, Arindam Sarkar, Kartheek Chennuri, Krishna Vudamala, Saranya Jayachandra, Linsy P., Darwin Ramteke, Armoury Kazip, Anita Garg and Simontini Sensharma for helping me in every possible way throughout my stay at NIO.

My sincere gratitude goes to the former and present Directors, Dr.S.W.A, Naqvi (former director) and Dr.Prasanna Kumar (present director) of CSIR-NIO for providing all the research facilities to carry out my doctoral research work. I also express my sincere thanks to the Head, HRM CSIR-NIO for his help and support. I sincerely appreciate the help and supports provided by Drs. M. B. L. Mascarenhas Pereira, J. N. Pattan, G. Parthiban, C. Prakash Babu, V. Ramaswamy, B. Chakraborty, V. K. Banakar and K. A. Kamesh Raju during my Ph.D. research at CSIR-NIO. Lead isotopes was measured in collaboration with Dr. Ed Hathorne at the GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany

I gratefully acknowledge, Council of Scientific and Industrial Research (CSIR)-supported GEOSINKS (PSC0106) project for the fellowship to carry out this doctoral

research work. My sincere thanks to all the Chief Scientists and shipboard participants of GEOSINKS cruises who have painstakingly collected the sediment cores which have been used for this study, This is a contribution to this CSIR networked Project.

Finally, my heartfelt gratitude goes to my caring, loving and supportive family; my mother (maa), brother (dadabhai), sister-in-law, mother in-law, father in-law, niece Rishita, son Shubhayu and beloved husband Dr. Parthasarathi Chakraborty.

21st September, 2016

Sucharita Chakraborty
Geological Oceanographic Division
National Institute of Oceanography
Dona Paula, Goa, 403004

Preface

A comprehensive study of Pb geochemistry in continental margin sediments of India is presented in this thesis. The study comprises of deciphering the regional distribution of Pb in sediments around India, assessing the natural and anthropogenic Pb deposition in sediments, patterns of Pb accumulation in geochemically separable phases, the stability of Pb-hosting phases, response of Pb and its binding phases to varying bottom water oxygenation conditions, role of chemical properties (ionic potential etc.) in controlling Pb geochemistry in relation to other trace elements in aquatic sediments. An effort has been made to reconstruct the anthropogenic Pb depositional history for the last 100 years. The study is based on about 150 core tops and two sediment cores from both the continental shelves of India, 10 core tops from two transects cutting across the oxygen minimum zone in the Arabian Sea, 10 surface sediments from a coastal lagoonal/estuarine system. Five/four chemically separable fractions were studied in 64 sediments. Sedimentation rates were determined in two sediment cores (30 and 22 cm long); one representing each shelf, and the subsurface sediments (1cm sections) of these two cores were also studied for bulk chemistry, chemical fractionation and Pb isotopes.

While the geology of drainage areas in Indian sub-continent was found to be the principal source to the sedimentary Pb content in the shelf areas around India, anthropogenic influences are also seen in few locations, Fe/Mn oxyhydroxide has been identified as the major hosting phase for naturally or anthropogenically mobilised Pb in the sediments along the major parts of the Indian shelves. The high affinity of Pb for Fe/Mn oxyhydroxide phase in the sediment is due to the site availability for Pb^{2+} ion on Fe-oxyhydroxide phase and the less ability of Pb (compared to other trace metals viz. Cu,Ni) to form complexes with sedimentary organic carbon (C_{org}). However, C_{org} has been found to act as major host for sedimentary Pb in few sporadic locations of Indian shelf.

This thesis also presents chemically significant description of metal-ligand interactions in different binding phases of sediments. The role of ionic potential; water exchange rate (k_{-w}) of metals, ligand field stabilisation energy (LFSE) and Jahn-Teller effect on Pb-ligand interactions in different binding phases of sediments has been discussed in this thesis.The average stability and lability of Pb-sediment complexes in the eastern shelf sediments is compared to the western part in this thesis. Terrestrial nature of sedimentary C_{org} in the eastern shelf provides stronger binding sites for Pb compared to the less terrestrial C_{org} in the western shelf sediments. Thus, Pb forms more labile sedimentary Pb complexes with C_{org} from marine sources in the western shelf sediment and thermodynamically more stable Pb-C_{org} complexes from the terrestrial sources in the eastern shelf. This thesis also elucidates the impact of varying dissolved oxygen concentration in overlying bottom water on geochemical fractionation and lability of Pb complexes in the sediments across the OMZ, in the eastern Arabian Sea. This study suggests that association of Pb with Fe/Mn oxyhydroxide phase gradually decreases with decreasing DO concentration of the overlying bottom water (due to dissolution of Fe (III)/Mn oxyhydroxide phase). Pb prefers to associate with sedimentary organic matter under the low oxygen environment. The lability of Pb-sediment complexes gradually increases with decreasing dissolved oxygen concentrations of bottom water. This finding has an implication as the expansion of reduced oxygen levels in oceans (human-induced changes) may have dramatic consequences on the mobility and bioavailability of Pb in the coastal areas around India. Increasing flux of anthropogenic Pb during the last century has also been recorded in both the shelf areas of India. Two distinct isotopic signatures of stable Pb are seen in the sediments from either side of Indian continental shelf (eastern and western) indicates the influence of two different anthropogenic sources. The heavy industrial activities (mining, smelter and waste incineration) in India are identified as the major source of anthropogenic Pb in the western shelf sediments. The isotopic signature indicates that the Pb emission from Chinese coal burning can be a possible source of anthropogenic Pb in the eastern shelf sediment.

Contents

3. Patterns of lead distribution and the processes that control its speciation in the continental shelf sediments around India 44

List of Publications

Appendix

List of Tables

Page

List of Figures

Chapter 1

Introduction

Understanding the processes that control the distribution of lead (Pb) in marine environment is of great importance because of its toxic nature. Continental margins are the major depocenters of material transported from land and are key transition zones acting as interface between land and deep-sea. Therefore, geochemistry of Pb in continental margin sediments is controlled by the nature of the source rock, biogeochemical processes operating during the deposition, and anthropogenic activity on land. It has been reported that the anthropogenic flux of lead (Pb) in the surface environment (4309 ± 72 Gg/yr) is almost an order of magnitude higher than its corresponding natural flux (Sen and Peucker-Ehrenbrink, 2012).

Traditionally, Pb mining, industrial activities (which involve Pb) and coal combustion (another source of Pb) have been the major sources of anthropogenic contribution. Lee et al. (2014) have estimated that the emission of Pb from coal combustion has increased by 15 times in India from year 1970 to 2010. Increased leaded petrol usage since nineteen seventies in India made it another major source of anthropogenic Pb until it was phased out in the year 2000 (UNEP, 2007). Therefore, it is expected that different natural reservoirs are prone to enhanced Pb accumulation. However, the recently carried out review of sedimentary Pb (Chakraborty et al., 2015 and the references therein) has shown that the coastal sediments of India are relatively pristine with respect to total Pb content. The variation in sedimentary Pb concentration along the coast is found to be influenced by diverse geology of the Indian continent. Traditionally, the total Pb content is used for evaluating the relative role of natural and anthropogenic processes on its deposition. However, the total concentration of Pb cannot completely provide the information about the natural processes which control its distribution, speciation, pathways of deposition and fate in sediment. The knowledge of the association of Pb with different chemical phases in sediments will help to understand the natural geochemical processes.

Lead is quickly scavenged by negatively charged solid surfaces like clays, carbonates, oxides and hydroxides of Fe, Mn as well as by organic carbon (C_{org}) in the water column before becoming an integral part of sediment. Sedimentary Pb has been reported to have the highest binding strength for adsorption onto hydrous oxides compared to other trace metals (Benjamin and Lecke, 1981; Schindler, 1981: Leckie et al., 1981). In many studies, oxides and hydroxides of Fe/Mn have been reported to be a major scavenger of Pb in marine environment (e.g., O'Reilly & Hochella, 2003; Nelson et al., 2002). However, the stability of these complexes may vary with varying oxygen concentration in marine environment. The efficiency of sedimentary organic carbon (C_{org}) in scavenging Pb is debatable. Both poor and significant association of Pb with C_{org} has been reported in literature (Chakraborty et al.2012; Krupadam et al.2007; Abaychi and Douabul, 1986). It is not clearly known whether the quality and quantity of C_{org} will play any role in determining Pb association with C_{org}. Carbonate can be an important absorbent for Pb when C_{org} and Fe/Mn oxyhydroxides are less abundant in a given deposition environment (Lopez-Sanchezet al., 1996; Izquierdoet al., 1997).

It is a challenge to understand the geochemical processes that control Pb distribution, speciation and fate of Pb in the marine sediments around India owing to the diverse geology, climatic variability, varying physical processes of littoral, alongshore and overall circulation patterns, and anthropogenic activities.

To assess the gaps in our understanding and to define the scope of the work embarked in this study, the literature on geochemical distribution of lead (Pb) in coastal and estuarine sediments around India is reviewed by compiling the published data from the literature.

1.1. Background study of Pb geochemistry in the coastal sediments around India

The aim of this review is to provide the current understanding about the factors that control Pb distribution in coastal sediments around India. Since the source rocks are one of the major controls on Pb content in marine sediment, the diverse geology of the adjacent mass and the lithology around the coastal India are described below.

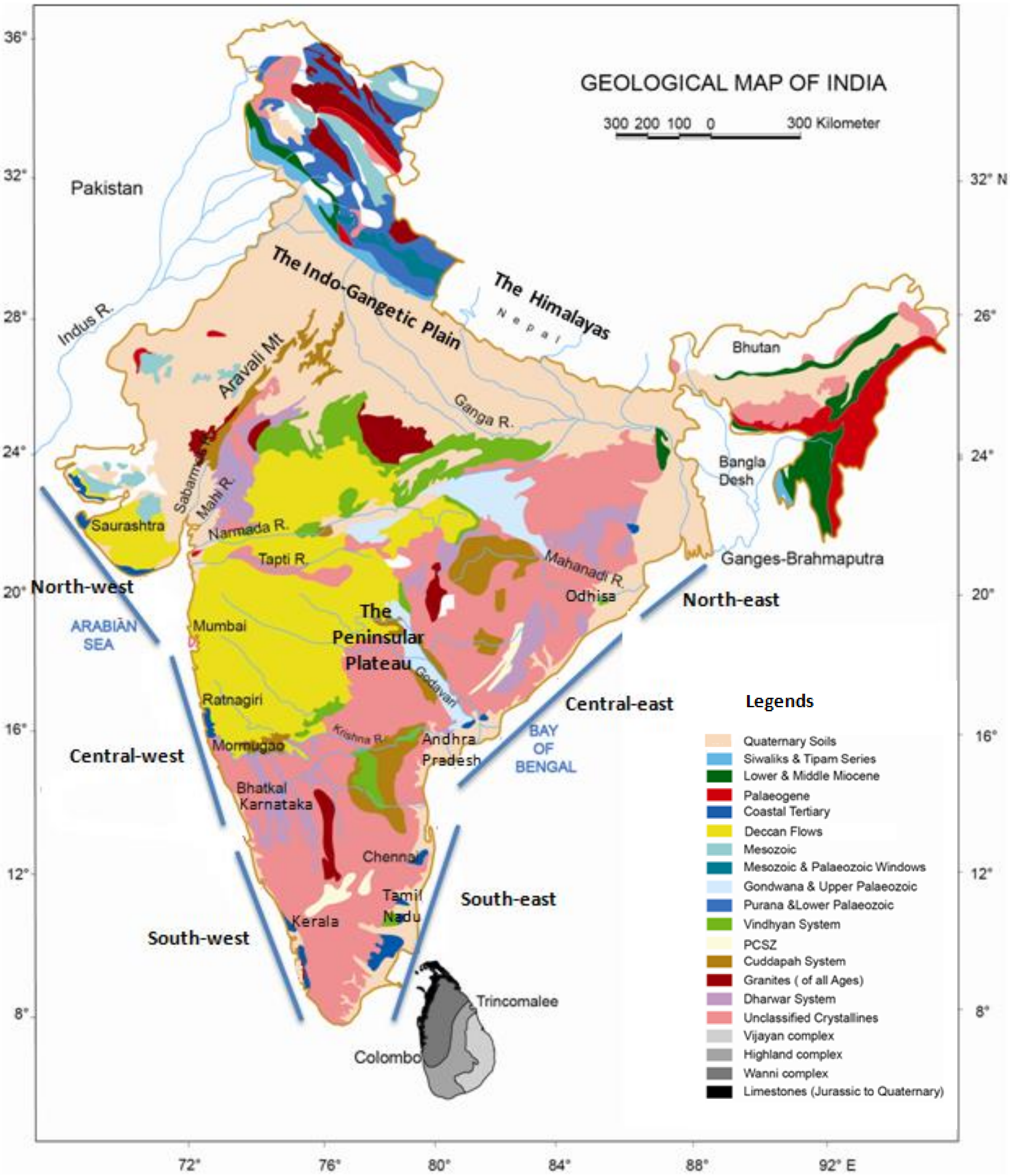


Figure 1.1 Geological map of India (source: Kessarkar et al., 2003 and Kessarkar et al., 2005). The reviewed/compiled Pb geochemical data has been divided area-wise and the solid lines represent different regions.

1.1.1 Geological setting of India:

India’s geological map is shown in Figure 1.1. The diverse geological setting of India has been described in three physiographic units viz. (i) the peninsula, (ii) the Indo-Gangetic alluvial plain and (iii) the extra peninsular of India.(i) The Indian peninsula is primarily composed of Deccan Traps of Cretaceous to Eocene period and metamorphic rocks of Archean and Pre-cambrian age. The north western part (one third) of Indian peninsula is covered by Deccan trap basalt, it is believed that the Deccan Traps were formed as a result of sub-aerial volcanic activity associated with the continental deviation in this part of the Earth during the Mesozoic Era. The rocks are in general fine grained, non-porphyritic doleritic or basaltic (tholeitic type) in composition. A major part of Maharashtra, a part of coastal Gujarat, Karnataka, Madhya Pradesh and Andhra Pradesh (partially) are made up by this type of rocks. The rest of the peninsular shield (Bihar, a marginal part of West Bengal, Orissa ,Tamilnadu, Karnataka, Kerala and Goa also fall under the same physiographic unit) is mainly composed of Precambrian rocks, principally the Dharwars, Peninsular granitic gneiss, charnockites and the Closepet Granite (Krishnan, 1968). The Dharwar metamorphic rocks comprise of phyllites, slates, schists with chlorite, biotite, garnet, staurolite, kyanite, silllimanite and hornblende (Srinivasan and Sreenivas, 1977; Krishnan, 1968; Naqvi et al., 1978; Naqvi et al., 1974); (ii) The Indo-Gangetic alluvial plains is the second major physiographic unit of India which belongs to the Quaternary era. The alluvial deposits were formed by the erosion of the Himalayan rocks by rivers and monsoon. Parts of Rajasthan, Punjab, Haryana, Uttar Pradesh, Bihar, Assam and West Bengal come under this second physiographic part; (iii) the third physiographic unit of India is the extra peninsula -the Himalayas and their eastern extensions including Andaman and Nicobar Islands. Most of the northern and north eastern states of India such as Jammu and Kashmir, Himachal Pradesh, Uttarakhand, Sikkim, Arunachal Pradesh, Manipur and Mizoram belong to this extra peninsula region.These part of India are primarily comprised of igneous plutonic rocks and sedimentary rocks. Specific igneous plutonic rock types in these zones include granite, diorite, gabbro, tonalite, and pegmatite. Types of sedimentary rocks found in this region include marl, dolomite, greywacke, siltstone, shale and limestone (Yin and Harrison, 2000).

As the river dominated environment prevails, the sediment contributed by rivers becomes the most predominant in the Bay of Bengal and Arabian Sea. Thus, diverse geological setting of India controls the concentrations of geogenic Pb around India.

1.1.2 Contributing source rocks to coastal sediment around India:

The composition and relative abundance of clay minerals in coastal sediments are controlled by their source rocks and weathering conditions.

The potential sources of Indian coastal and marginal sediments were described in the past using different proxies (Goldberg and Griffin, 1970; Nair et al., 1982; Rao and Rao, 1995; Kessarkar et al., 2003; Kurian et.al 2013). Mineralogical, studies on the coastal sediments (collected from the east coast of India) have indicated a geographical zoning related to the adjacent crustal rocks, soils and to the weathering processes occurring there.

The sediments deposited by the Himalayan rivers (Ganges, Brahmaputra, Gandak and Yamuna) are characterized by large amounts of illite, equal quantities of kaolinite and chlorite, and little or no mixed-layer clays and montmorillonite (Subba Rao, 1963; Goldberg and Griffin, 1970; Rao et al., 1988; Rao, 1991).The presence of these minerals in the sediments collected from the north-eastern coastal region (coastal areas of West Bengal and a part of Orissa) indicates that are mainly derived from the weathering of Himalayan rocks. The concentration of Pb in the contributing rocks granite, shale, greywacke, limestone, basalt and gabbros in the Himalayan region range between 3.5 and 32 mg.kg^{-1} (Wedehpohl, 1978). Not considering the volume, the average works out to ~ 15.0 mg.kg^{-1}. Sediments from the central and southern part of the eastern continental margin are mainly derived from Mahanadi, Godavari, Krishna and Cauvery. These coastal sediments are characterized by the absence of chlorite, presence of high concentrations of montmorillonite (or smectite), trace quantities of mixed-layer clays, and small quantities of illite (Subramanian, 1980). The Deccan Trap basalts have been reported to be one of the major sources of detrital solids for the shelf sediments in this region and mean concentration of Pb in these rocks are ~3.5 mg.kg^{-1} (Table 1.1).

Mineralogy of sediments from the west coast of India suggest a geographical zoning related to the adjacent rocks and soils (Gourbunova, 1966).

Three distinct clay mineral assemblages have been reported in literature. (i) illite-chlorite-rich sediment - supplied by Indus River which traverses Himalayan rock.

Table 1.1 Concentration of Pb in different lithologies (Taken from Wedepohl, 1978)

Lithology	Concentration of Pb (mg.kg^{-1})
Continental crust	15
Oceanic crust	0.9
Basalts,gabbros	3.5
Granites	32
Limestones	5.0
Granulites	9.8
Greywackes	14
Gneisses, mica schists	16
Shale	22

derived by Indus River, (ii) smectite-rich sediment from Deccan Traps derived by Narmada Tapti and (iii) kaolinite-smectite-rich sediment from the Gneissic province (Mattait et al. 1973; Nair et al. 1982a; Rao and Rao, 1995)

The illite and chlorite-rich assemblage derived from the Indus River (Indus Province) is predominant in continental margin sediments to the north of the Gulf of Kachchh. The average concentration of Pb in the source rocks of this region is ~ 15 mg.kg^{-1} (Himalayan rock).

An assemblage of smectite with minor kaolinite, illite and chlorite, mostly derived from the Deccan Trap basalts (Deccan Trap Province), occurs all along the inner shelf from Saurashtra to Goa (Northern to central part of the west coast of India). Illiite, however, dominates smectite in the outer shelf of Saurashtra (coastal areas of Gujarat) and on the continental slope from Saurashtra to Goa. The concentration of Pb in the source rock of this region ranges between 3.5 and 15 mg.kg^{-1}.

A smectite and kaolinite-rich assemblage with minor illite, chlorite and gibbsite derived from the Gneissic Province occurs both on the shelf and slope between Goa and Cochin (central to southern part of west coast of India). Geochemical study by Kurian et al. (2013) along the western continental shelf of India has shown distinct north-south provinciality with the source signatures, pointing at the Deccan basalt for sediments in the north (from coastal Gujarat to Goa) and gneisses and granulites in south (from Goa to southernmost part of Kerala). The average concentration of Pb in the source rocks of the southern part of west coast region has been found to vary between 9.8 and16 mg.kg^{-1}.

In addition to natural sources, anthropogenic activities can contribute substantially to the Pb found in the coastal sediments. The geochemical forms, bioavailability of Pb and fate of Pb-complexes in coastal sediments can be a function of site specific sediment chemistry. However, understanding the geological setting of India and contributing source rock to the coastal sediment are discussed to understand the impact of geological setting on Pb distribution in coastal sediments around India.

The baseline data distributions/speciation and geochemistry of Pb in different natural reservoirs in India is limited. In this review, we attempted to understand the distribution of Pb and interpreted the factors that can control Pb distribution in coastal sediments around India. Enrichment Factor (EF), was used (calculated on the basis of the available data in literature) to understand the extent of Pb accumulation and pollution in coastal sediments around India.

1.1.3 Enrichment Factor (EF) of Pb

Enrichment factor has been widely used to distinguish the contribution from anthropogenic and natural sources of heavy metals (Adamo et al., 2005; Darvish et al., 2012) in sediment. This index is calculated using a normalizing element (such as Fe or Al) which moderates the variation produced by natural heterogeneous sedimentation (Landsberger et al., 1982; Loring, 1991) and allows detection of anthropogenic metal contribution (if any) and its quantification.

The EF is calculated by using the following equation:

$$\mathbf{EF} = \frac{\mathbf{C_a} \times \mathbf{N_b}}{\mathbf{C_b} \times \mathbf{N_a}}$$

where, $\mathbf{C_a}$ and $\mathbf{C_b}$ are the examined metal content in sediment and background reference sample, respectively; $\mathbf{N_a}$ and $\mathbf{N_b}$ are the normalizing element content in the sediment and the background reference sample, respectively.

Fe and Al (depending upon the availability of data) were used as normalizing elements to calculate EF of Pb in the coastal sediments. Remobilization and precipitation can lead to changes in the Pb/Fe ratio in anoxic sediments (Schiff and Weissberg, 1999), which is unlikely in the coastal and estuarine sediment. The average concentrations of Pb (20 mg.kg^{-1}); Al (81 gm.kg^{-1}) and Fe (47 gm.kg^{-1}) in shale (Turekian and Wedepohl, 1961) were used as the background values.

Based on the Enrichment Factor (EF), Pb contamination can beclassified as follows : 1) $EF \leq 1$: noenrichment; 2) $1 < EF \leq 3$: minor enrichment; 3) $3 < EF \leq 5$: moderate enrichment; 4) $5 < EF \leq 10$: moderatelysevere enrichment; 5) $10 < EF \leq 25$: severe enrichment; 6) $25 < EF \leq 50$: very severe enrichment; 7) $EF > 50$:extremely severe enrichment (Belgica et al., 2010).

In order to understand and identify the factors that control Pb distribution in coastal sediment around India, the data set were further analyzed by correlation matrix and regression analysis.

1.1.4 Pb geochemistry in the coastal areas of India:

In this review, the east and west coasts of India were further divided into the following six coastal regions to provide a better understanding of regional variation of Pb-geochemistry around India (Figure 1.1).

East coast of India: East coast of India is divided into three parts:

- North-east coast-This part includes the coastal parts of West Bengal and Odisha states. There are two major estuaries in this region (namely the Ganges and Mahanadi estuaries)
- Central-east coast-This part includes the coastal region of Andhra Pradesh. There are two major estuaries in this region (namely Godavari and Krishna estuaries)
- South-east coast- This part includes the coastal region of Tamil Nadu. There is one major estuary in this region (namely Cauvery estuary).

West coast of India: West coast of India is divided into three parts:

- North-west coast- This part includes the coastal region of Gujarat. There are two major estuaries in this region (namely Narmada and Tapti estuaries).
- Central-west coast-This part includes the coastal region of Maharashtra Goa and northern part of Karnataka. There are three major estuaries in this region (namely Ulhas, Mandovi and Zuari estuaries).
- South-west coast-This part includes the coastal region of Kerala and there is one major estuary in this region (namely Cochin estuary).

The median value of Pb content was estimated from the compiled literature values for each region is presented in Table 1.2. The lithology of drainage area of each of these regions is also presented in the same table**.**

North-east coast

Coastal part of West Bengal and Odisha belongs to this region. A good amount of data (on Pb concentrations in sediments) is available in literature on the Ganges/Hooghly and Mahanadi estuarine regions (estuaries) (Subramanian, 1993; Subramanian et al., 1988; Sarkar et al., 2004; Chatterjee et al., 2007; Banerjee et al., 2012; Mukherjee and Kumar, 2012;Saha et al., 2001;Ramesh et al., 1999**;** Sundaray et al., 2012;Raj et al., 2013**).** However, data from the coastal areas are scarce.

Table 1.2 The average concentration of sedimentary Pb and contributing source rock of the different coastal parts of India

Coastal areas of India	Source rocks in the region	Median value of Pb (mg.kg^{-1}) in the sediment
North east coast	Igneous plutonic (granite, diorite, gabbro, tonalite, monazite and pegmatite) , sedimentary rocks (marl, dolomite, greywacke, siltstone, shale and limestone), (Yin and Harrison; 2000) khondalites, charnockites,leptynites granites, gneisses. (Chakrapani and Subramanian; 1993)	24.3 (n=105)
Central east coast	Basalt,Granite and sedimentary rock. (Krishnan, 1966)	12.7 (n=62)
South east coast	Charnockites and intermediate granites. (Chattopadhyay and Sarkar, 1999)	16.0 (n=335)
North west coast	Basalt (majorly) and Himalayan rocks (Igneuos plutonic and sedimentary rock)	58.3 (n=186)
Central west woast	Granites, gneisses, schists and charnockite. (Krishnan, 1968; Rao and Rao, 1995)	10.6 (n=41)
South west Coast	Charnockites, khondalities, granite gneisses and hornblende gneisses. (Nath et al., 2000)	33.3 (n=161)

The concentration of Pb in the surface sediments from this area varied from 6.8-214.4 mg. kg^{-1} with a median value of 24.3 $mg.kg^{-1}$ (Table 1.2). Much high concentration of Pb has been reported (Sundaray et al., 2012) in Mahanadi estuarine region (ranging from ~105-214 $mg.kg^{-1}$) compared to the Ganges/Hoogly estuary. The primary sources of sediments deposited in the Hoogly estuary and nearby coastal areas are principally due to the erosion of the Himalayan rocks which are drained by Ganges–Brahmaputra river system.However, the erosion of Precambrian rocks of Indian peninsula is the primary source of sediments deposited in the Mahanadi estuary and its nearby coastal areas. Sediments of this region are composed of the minerals eroded from the major rock types such as khondalites, charnockites, leptynites, granites, gneisses. The drainage basin chiefly erodes rocks of acidic composition and probably contributes high Pb content to the sediments of North eastern coastal region. The average concentration of Pb in the source rocks of this area ranges between 5 and 32 $mg.kg^{-1}$. The higher sedimentary Pb content in the Mahanadi estuary compared to the Ganges/Hooghly estuary may be due to the presence of the richest mineral belt of the subcontinent (consisting of Fe ore, coal, lime-stone, dolomite, bauxite, Pb and Cu deposits) which fall within the Mahanadi basin (Chakrapani and Subramanian, 1993). It has been documented that there are 15 large industries in the Mahanadi basin (Jena, 2008) and industrial effluent from these industries get released into the Mahanadi River (Jena, 2008). Several medium and small industries on the Mahanadi basin discharge 1, 00,000 m^3 of waste water every day; 12 coal mines discharge 14,000 m^3 mine water daily during non-monsoon months. These anthropogenic activities can be a reason for the high Pb content in the Mahanadi estuarine sediments

The Pearson correlation and statistical regression analysis (based on the available literature data from this region) show a significant positive correlation between Pb and Fe/Mn in the sediment (Table 1.3), but with a weak correlation between Pb and organic carbon (C_{org}) (Table 1.3). This is in very good agreement with the findings of Subramanian et al, (1988) and Banerjee et al., (2012) that C_{org} does not control metal distribution in the sediments of this region. The poor correlation can be due to low C_{org} content in the sediment. It has been reported that high microbial activity in this region is mainly responsible for low C_{org} content in the sediment (Canuel and Martens, 1993; Chatterjee et al., 2007). It is well known that oxides and hydroxides of Fe, Mn are the good scavengers of Pb, significant positive correlation and the good regression among them suggest that Fe/Mn oxy-hydroxide might be the major controlling factor for Pb distribution in the sediments of this region (Figure 1.2(a,b)). The poor regression between Pb with Al (Table 1.3) indicates that the anthropogenic sources dominate over geogenic sources for Pb in the sediments of this region, which has a support from moderately high EF values of Pb (Figure 1.3).

Central-east coast:

Geochemical information of Pb in coastal sediments from this region is limited. The Pb concentrations in estuarine and coastal sediments of this area range between 10–14 $mg.kg^{-1}$ except few elevated concentrations of Pb reported in in the estuarine sediments with a median concentration of 12.7 $mg.kg^{-1}$(Table 1.2) (Satyanarayana et al., 1994; Krupadam et al., 2007, 2003; Ray et al., 2006; Chakraborty et al., 2012a,b,c; Ramesh et al., 1999). High concentration of Pb was found in the coastal sediments adjacent to harbor region (Satyanarayana et al., 1994). The natural sources of Pb in the coastal and estuarine sediment of this region can be from the adjacent land mass/drainage area of Godavari and Krishna rivers with major geological formations such as the Tertiary Deccan Traps, Archean granites, Precambrian and Gondwana sedimentary rocks and recent alluvials (Krishnan, 1968). However, the mineralogical studies indicate that majority of the sediments are eroded from basaltic rocks (Subramanian, 1980) (depleted in Pb). The geochemical fractionation studies of Pb also indicate the same (Krupadam et al., 2007; Chakraborty et al., 2012a, b, c). The geogenic contribution of Pb in the total Pb of sediment in this region was found to be relatively small.High concentrations of Pb in the sediments from this region has been reported (Satyanarayana et al., 1994; Chakraborty et al.,2012b) in the literature and indicate that anthropogenic input of Pb in the sediments were higher than geogenic sources. The EF of Pb also indicates an anthropogenic input to the coastal sediments (Figure 1.3). It was not possible to determine the predominant geochemical carrier of Pb in these sediments due to the lack of data. However, C_{org} has been reported to play a key role in controlling Pb distribution and speciation in estuarine sediments from this region (Krupadam et al., 2007; Chakraborty et al., 2012 a, b, and c).

South-east coast:

The Pb concentrationsof this region vary widely between 0.1 and 130 $mg.kg^{-1}$ (Raju et al., 2011;Veerasingam et al., 2012; Ravichandran and Manickam, 2012; Raj and Jayaprakash, 2007; Achyuthan et al., 2002; Selvaraj, 1999; Satpathy et al., 2010; Dhanakumar et al., 2013; Ramesh et al., 1999; Kumar and Edward, 2009; Magesh et al., 2013, 2011; Venkatramanan et al., 2014; Subramanian and Mohanachandran, 1990; Anithamary et al., 2012; Jonathan et al., 2004; Sundararajan and Srinivasalu, 2010; Palanichamy and Rajendran, 2000) with the median Pb concentration working out to be 16 $mg.kg^{-1}$ for this region (Table 1.2). Charnockites, acidic to intermediate composition associated with granites (Chattopadhyay and Sarkar, 1999) are the major natural sources of Pb in the coastal and estuarine sediments of this region. Achyuthan et al. (2002) reported that coastal sediments of Tamil Nadu are depleted in Pb. The concentration of Pb in some of the places of south-east coast of India are found to be much lower than the average values found in Earth‘s crust (13 $mg.kg^{-1}$) or shale (20 $mg.kg^{-1}$) (Turekian and Wedepohl 1961). On the other hand, in few places, some of the estuarine as well as the coastal sediments have been reported to be moderately enriched with Pb. The EF values are found to vary from 0.18 to 8.43. However the calculated EF for the compiled data (Figure 1.3) in most of the areas in this region shows minor enrichment of Pb (EF value is 1 to 3). The Pearson correlation and regression analysis on the available literature data indicate a strong positive correlation between Pb and Al(Figure 1.4, Table 1.4) and suggest that most of the Pb in this region are probably from the crustal sources.

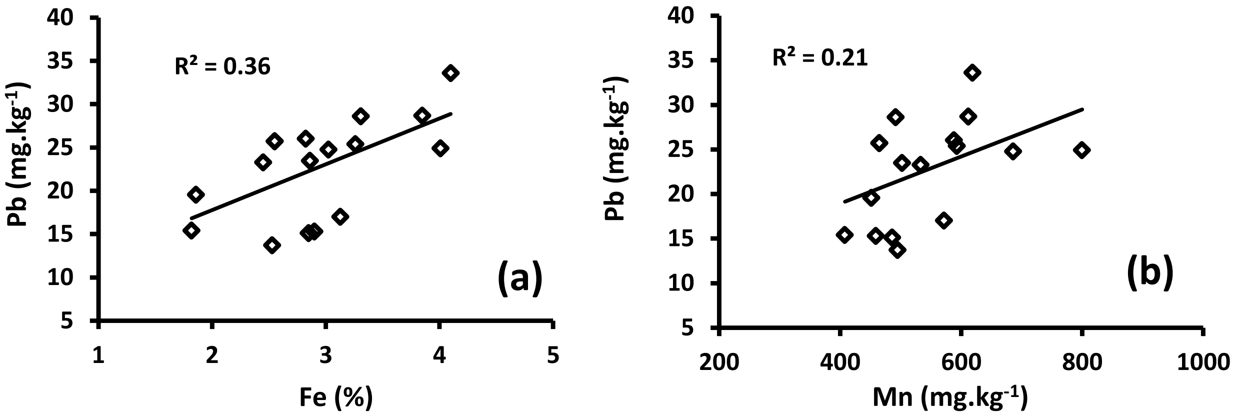


Figure 1.2 Variation of total Pb concentrations with varying concentrations of (a) Fe and (b) Mn in the sediment from of the north-east coast

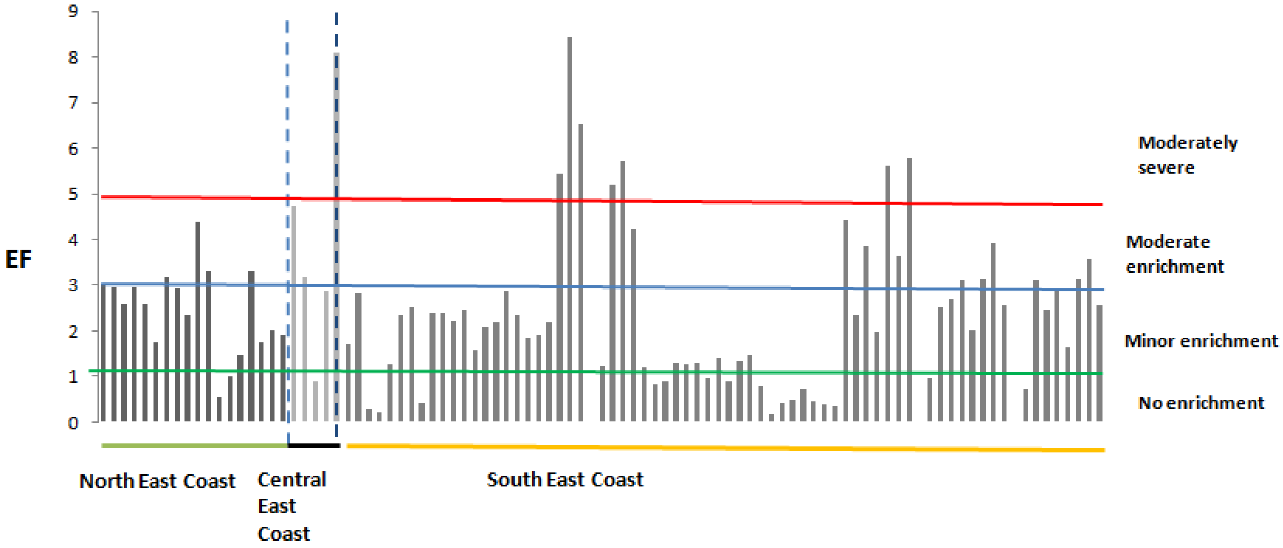


Figure 1.3 Distribution of Enrichment Factor (EF) along the east coast

Table 1.3 Correlation coefficient matrix of Pb, Fe, Mn, Al, C_{org}, Sand, Silt and Clay in the coastal and estuarine sediments from the North-east Coast of India.

	Pb	**Fe**	**Mn**	**Al**	**C_{org}**	**Sand**	**Silt**	**Clay**
Pb	1							
Fe	**0.82**	1.00						
Mn	**0.78**	0.86	1.00					
Al	0.23	-0.46	-0.29	1.00				
C_{org}	0.24	0.83	0.45	-0.05	1.00			
Sand	-0.01	-0.61	-0.52	0.20	0.41	1.00		
Silt	0.01	0.65	0.65	-0.29	-0.28	-0.86	1.00	
Clay	0.05	0.02	-0.16	0.25	-0.42	-0.54	0.06	1

Correlation is significant at the 0.01 level (2-tailed).

Table 1.4 Correlation coefficient matrix of Pb, Fe, Mn, Al, $CaCO_3$ and C_{org} in coastal and estuarine sediments from the South-east Coast of India

	Pb	**Fe**	**Mn**	**Al**	**C_{org}**	**$CaCO_3$**	**Sand**	**Silt**	**Clay**
Pb	1								
Fe	-0.83	1.00							
Mn	**0.82**	-0.54	1.00						
Al	**0.73**	-0.41	0.81	1.00					
C_{org}	0.24	-0.49	0.07	0.70	1.00				
$CaCO_3$	-0.66	0.51	-0.75	-0.78	-0.45	1.00			
Sand	-0.79	0.48	-0.66	-0.81	-0.51	0.65	1.00		
Silt	**0.66**	-0.36	0.58	0.72	0.40	-0.56	-0.94	1.00	
Clay	**0.82**	-0.61	0.68	0.81	0.63	-0.67	-0.85	0.64	1.00

Correlation is significant at the 0.01 level (2-tailed)

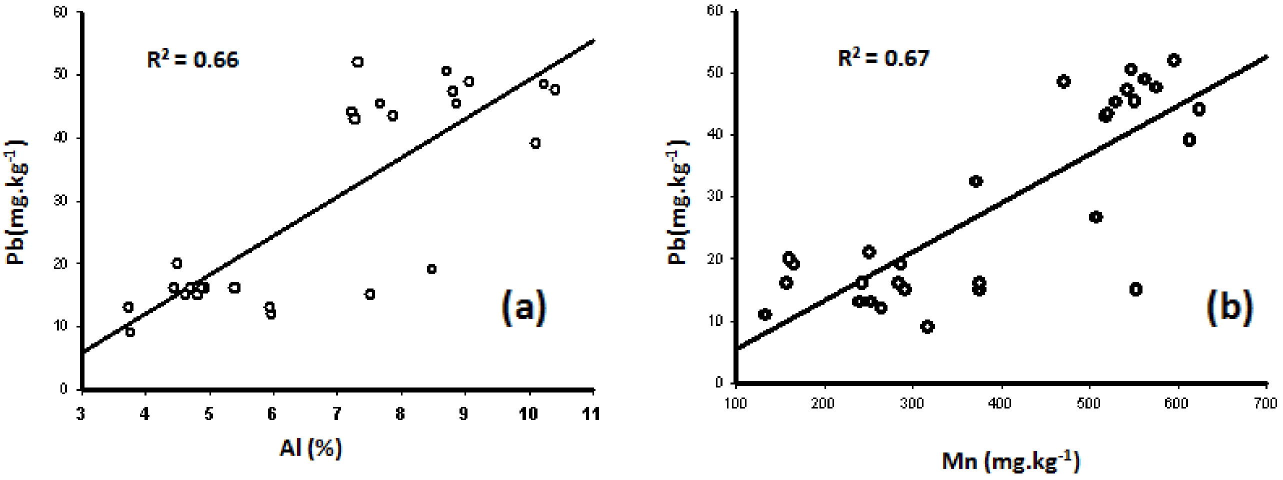


Figure 1.4 Variation of total Pb concentration with (a) Al, and (b) Mn concentrations in sediments from the south-east coast.

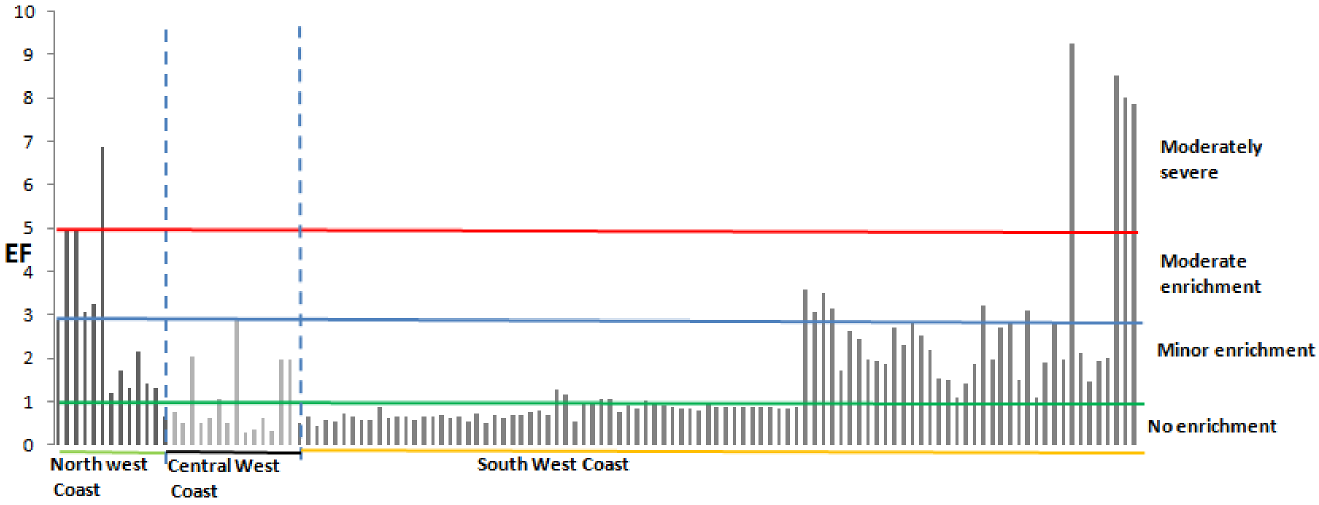


Figure 1.5 Distribution of Enrichment Factor (EF) along the west coast.

North-west coast:

The available literature data for this region covering the coastal parts of Gujarat and northern Maharashtra indicate that the Pb concentrations in the region varies from 8.9 to 220 mg.kg^{-1} (Rokade, 2009; Reddy et al., 2004; Tewari et al., 2001;Sahu and Bhosale, 1991; Fernandes et al., 2012, 2011; Fernandes and Nayak, 2014; Patel et al., 1985; Dilli, 1986; Zingde et al.,1988).The median concentration of Pb in this region (58.3 mg.kg^{-1}; Table 1.2) is found to be higher compared to the rest of the coastal areas of India. The concentrations of Pb in the estuarine sediments in general are higher than in the coastal sediments.

The natural sources of Pb in the coastal sediment from this region can be from the Himalayan rocks eroded by Indus River and the Deccan basalts drained by Narmada and Tapti Rivers. The main source rocks for the study areas off Maharashtra would be basalts from the Deccan Trap terrane. The average Pb content in basaltic rocks is 3.5 mg.kg^{-1} (Karl, 1991). Thus, the geogenic contribution of Pb is very less to the coastal sediment.The high value of EF in sediment indicates that heavy industrialization of Gujarat and Maharashtra was probably responsible for this enriched concentration of Pb in the coastal sediment of this region (Figure 1.5). Pearson correlation and regression analysis shows significant positive correlations between Pb, and Fe/Mn (Figure 1.6, Table 1.5). Concentrations of C_{org} in coastal sediments from this region has been reported to be relatively low compared to the rest of the west coast of India (Paropkari et al., 1993, 1992).

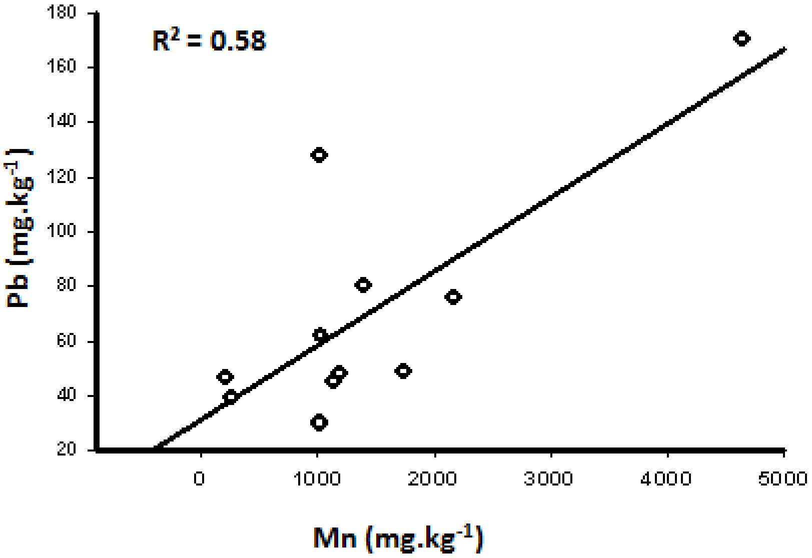


Figure 1.6 Variation of total Pb concentration with Mn concentration in the sediments from the north-west coast.

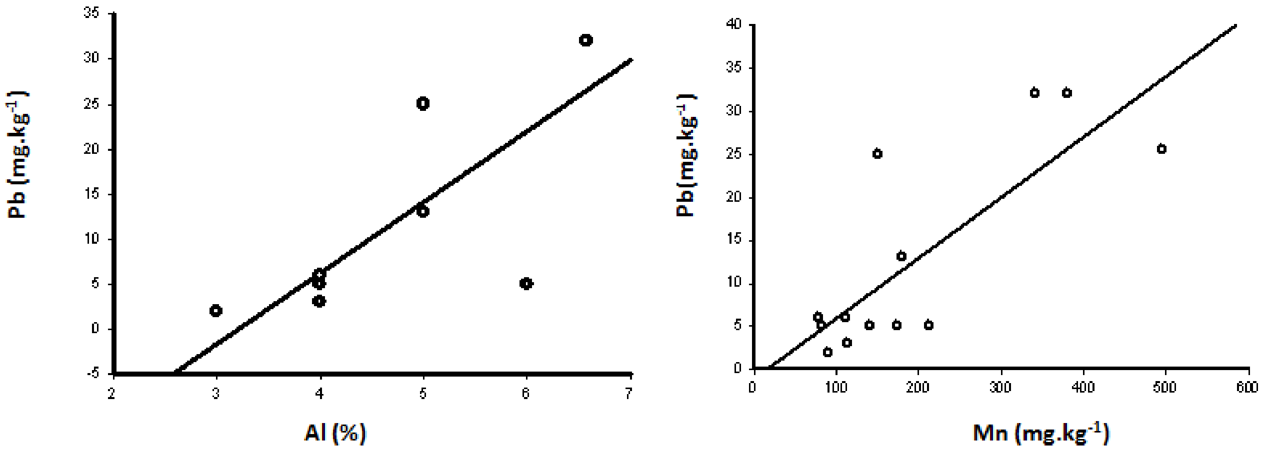
Table 1.5 Correlation coefficient matrix of Pb, Fe, Mn, and C_{org} in coastal and estuarine sediments from the North-west Coast of India

	Pb	Fe	Mn	C_{org}
Pb	1			
Fe	0.43	1.00		
Mn	**0.50**	0.62	1.00	
C_{org}	-0.32	0.29	-0.14	1.00

* Correlation is significant at the 0.05 level (2-tailed).

Central-west Coast:

Coastal parts of southern Maharashtra, Goa and Mangalore belong to this region. The Pb content in the region varies between 4.5 and 46.5 mg.kg^{-1} (Alagarsamy, 2006; Karbassi and Shankar, 2005; Rokade, 2009; Pandarinath and Narayana, 1992**;** Krishnakumar et al., 1998**)** and the computed median concentration of Pb for this region works out to 10.60 mg.kg^{1} (Table 1.2)**.** The source rocks in this area are the Precambrian granites, gneisses, schists and charnockites (Krishnan,1969; Rao and Rao, 1995). Pb concentrations in estuarine sediments were higher than those held in marine sediments of the region. Pb shows better association with Al and Mn when compared to C_{org} and Fe. The strong positive relation with Al indicates the abundance of Pb in sediment is principally from crustal sources (Figure 1.7, Table 1.6). The low average values of EF support the fact that there is no (or little) anthropogenic input of Pb in this region (Figure 1.5**).**



(a) **(b)**

Figure 1.7 Variation of total Pb concentration with (a) Al, and (b) Mn concentrations in sediments from the central-west coast.

Table 1.6 Correlation coefficient matrix of Pb, Fe, Mn, Al and C_{org} in coastal and estuarine sediments from the Central-west Coast of India

	Pb	Fe	Mn	Al	C_{org}
Pb	1.00				
Fe	0.35	1.00			
Mn	**0.63***	0.78	1.00		
Al	**0.72****	**0.82**	**0.89**	1.00	
C_{org}	0.38	0.70	0.52	0.82	1.00

* Correlation is significant at the 0.02 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

South-west coast:

The Pb content in the region covering the coastal parts of Kerala vary between 0.2 and176.8 mg.kg^{-1} (Balachandran et al., 2006; Sengupta et al., 2012; Kumar and Edward, 2009; Sudhanandh et al., 2011; Martin et al., 2012;Nair and Ramachandran, 2002; Dipu and Kumar, 2013**;** Selvam et al., 2012**)**, with the median concentration for this region being 33.3mg.kg^{-1} (Table 1.8). The highest value of Pb concentrations has been found in Manakudy estuary (Kumar and Edward, 2009) and the lowest concentration of Pb in sediment (Nair and Sujatha, 2012) is reported from the coastal part of this region .The source rocks of this region are composed mainly of charnockites, khondalities, granite gneisses and hornblende gneisses which are felsic (enriched in Pb) in nature (Nath et al., 2000) and probably contribute more natural Pb to the estuarine or marine sediment. However, very high enrichment of Pb (EF~9) in few sampling stations of estuarine sediment has been attributed to the point sources (anthropogenic influence). Sediments belong to this area is mostly rich in organic carbon (Balachandran et al., 2006; Kumar and Edward, 2009; Sudhanandh et al., 2011; ; Martin et al., 2012; Nair and Ramachandran, 2002) and the suboxic environment of the overlying water column specially in the continental shelf preserves the carbon content in the sediment (Martin et Balachandran et al., 2006 and reference there in). Therefore, in this region Pb shows strong affinity towards C_{org} within the sediments [Figure 1.8(a), Table 1.7]. However, Pb shows similar affinity for Fe/Mn oxy hydroxide phases [Figure 1.8(b), and Table.1.7]. It has been reported that Fe/Mn oxy-hydroxide phase is relatively low in marine sediment (sub-oxic condition) in this region compared to the estuarine sediment (oxic condition). Therefore, association of Pb was found to be higher with organic carbon in coastal sediment from this region.

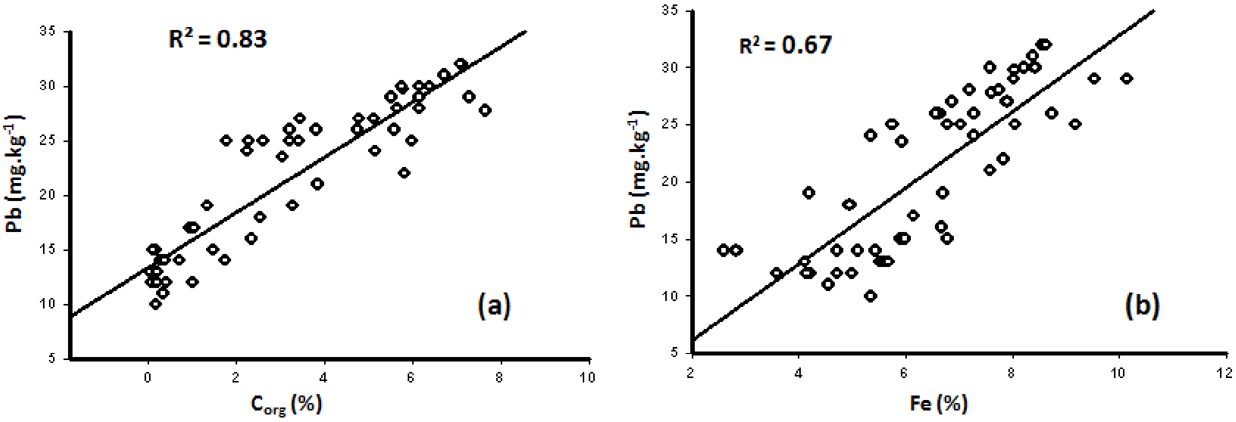


Figure 1.8 Variation of total Pb concentrations with the varying (a) C_{org} content and (b) Fe concentrations in the sediments of South-west coast.

Table 1.7 Correlation coefficient matrix of Pb, Fe, Mn, Al, C_{org} , $CaCO_3$, Sand, Silt and Clay in coastal and estuarine sediments from the South-west Coast of India

	Pb	**Fe**	**Mn**	**Al**	**C_{org}**	**$CaCO_3$**	**Sand**	**Silt**	**Clay**
Pb	1								
Fe	**0.78**	1.00							
Mn	0.01	0.32	1.00						
Al	0.72	0.61	0.04	1.00					
C_{org}	**0.88**	0.82	0.01	0.68	1.00				
$CaCO_3$	0.12	-0.02	-0.22	0.07	0.11	1.00			
Sand	-0.95	-0.76	0.04	-0.68	-0.91	-0.18	1.00		
Silt	**0.88**	0.67	-0.02	0.60	0.80	0.27	-0.93	1.00	
Clay	**0.81**	0.72	-0.07	0.59	0.84	-0.04	-0.83	0.60	1

Correlation is significant at the 0.01 level (2-tailed)

1.1.5 Quality of coastal sediments of India in terms of Pb :

To assess the quality of coastal and estuarine sediments of India in terms of Pb pollution, the concentrations of Pb in sediments from six different coastal regions of India (discussed above) is compared with the coastal and estuarine sediment from the different parts of the world. The effect range low (ERL)/effect range median (ERM) values proposed by Long et al. (1995) are also used to assess the quality of the coastal sediments around India (Table 1.8). It is found that the concentrations of Pb in most of the coastal and estuarine sediments around India are lower than the ERL values (Table 1.8) Furthermore the enrichment factor (EF) values also show that there was “no to minor enrichment” of Pb in the coastal areas around India. This study suggests that the coastal and estuarine sediments around India are not contaminated by Pb.

Table 1.8 Comparison of the concentration of Pb in the coastal sediments of India with the other parts of world. ERL, ERM values of Pb are also given

	Concentration of Pb (mg.kg^{-1}) in sediment	References
Pearl river estuary and surrounding coastal area, China	21.7-47.9	Ip et.al (2007)
Tees estuary, England	37-680	Jones & Turki (1997)
South west coast of Spain	20-197	Morillo, Usero, & Gracia (2004)
Suez Gulf, Egypt	70.4-93.7	el-Nemr et.al (2006)
Mangrove sediments along the coastline of French Guiana.	6.6-14.8	Marchand et al (2006)
Swartkops River Estuary, Port Elizabeth South Africa.	9.6-90.7	Binning and Baird (2001)
Mangrove and Lagoonal Sediments from south east Gulf of California,Mexico	14-100	Soto-Jiménez and Páez-Osuna (2001)
Continental Shelf of the North-western Black Sea, Romania	0.5-50.3	Secrieru and Secrieru (2002)
North east coast of India	6.8-214.4 Av=35.8 Med=24.3	This study
central east coast of India	5.7-95 Av=26 Med=12.7	This study
South east coast of India	1.01-74.2 Av=22.7 Med=16	This study
North west coast of India	8.83-130 Av=57.5 Med=58.3	This study
central west coast of India	2-46.5 Av=14.9 Med=10.6	This study
South west coast of India	0.10-163.3 Av=45.0 Med=33.3	This study
Effect range low value (ERL)	46.7	US NOAA's sediment quality guidelines
Effect range median (ERM)	218	US NOAA's sediment quality guidelines

Av=average,Med=median

1.2 The knowledge gap and the objectives of this study

The literature review provided an understanding on Pb distribution and predicted the probable controlling factors in coastal sediments around India. The emphasis of published Pb data of sediments around India is mainly centered on pollution.However; knowledge on the processes controlling Pb geochemistry is limited. The compiled data were not systematic in terms of time and area of sampling. Most of the sedimentary Pb data were from estuarine system whereas Pb data from marine environment were less. Pb has been usually studied along with a set of other elements and thus lacked a rigorous study to understand its geochemistry. As Pb is particle reactive, it can participate in biogeochemical reactions and can switch between the labile phases within the sediments depending upon the physicochemical factors prevailing in the depositional environment. Some Pb can be mobilized near the sediment surface during the aerobic degradation of organic matter and also may be associated with the redox-controlled cycles of Fe diagenesis (Gobeiel and Silverberg, 1989). Little is known on the behaviour of Pb in response to varying bottom water oxygenation conditions. Varying oxygenation conditions can lead to changes in organic matter preservation patterns which in turn may control the organic matter bound metals (one such metal could be Pb).The literature reveals that very little is known about Pb speciation in geochemically separable phases in sediments around India. Also there is complete lack of information on Pb isotopes in this area. In view of large gaps in our understanding of Pb geochemistry, and its importance in fields of Environmental and Marine Geochemistry, a comprehensive study of Pb geochemistry of continental margin sediments of India has been undertaken in this work. While a regional sedimentary Pb distribution map is a major output, new approaches have been used to understand the binding of Pb to various geochemical phases, and kinetic speciation studies were undertaken to assess the stability of Pb-binding geochemical complexes. In addition, the fractionation study of Pb in response to varying bottom water oxygenation conditions in the perennial oxygen minimum zone of the Arabian Sea has been carried out. For the first time for Indian shelves, a Pb isotopic study has been presented. The Pb geochemical study has been undertaken on ~150 core tops, few cores and chemically separable fractions from both the continental margins of India with the **following objectives:**

(i) to assess the regional distribution pattern of Pb in continental shelf sediments around India and to understand the contribution of natural and anthropogenic processes in accumulating Pb to marine sediments

(ii) to understand the distribution of Pb in different geochemical phases and to identify the factors that control Pb speciation in continental shelf sediments

(iii) to identify the sources and quantification of natural and anthropogenic Pb content using radiogenic Pb isotopic ratio as a tracer

(iv) to reconstruct the Pb accumulation history of few locations using fractionation studies and radiogenic isotopes

1.3 Outline of the thesis

The entire work has been presented in seven chapters and a brief outline of each of these chapters is presented below.

Chapter 1 presents an overall introduction for the whole thesis and a review on geochemical distribution of lead (Pb) in coastal and estuarine sediments around India by compiling the published data from the literature and defines the scope of this work in relation to the existing knowledge gaps.

Chapter 2 describes the study area and the materials and methods employed for the fulfillment of the research objectives. This chapter also describes the detailed analytical procedures those were used in this study.

Chapter 3 describes the regional distribution pattern of Pb content and its speciation in the continental shelf sediments around India. The regional distribution maps are based on analyses of 153 surficial sediments (81 from Bay of Bengal and 72 from the Arabian Sea). The chemical fractionation studies were performed on 64 surficial sediments (28 from Bay of Bengal and 36 from the Arabian Sea).

Chapter 4 presents the relative stability and lability of Pb-sediment complexes in the shelf sediments around India. Kinetic fractionation studies were performed on 21 surficial sediments (11 from Bay of Bengal and 10 from the Arabian Sea).

Chapter 5 describes influence of chemistry of other trace metals (such as Cu and Ni) on Pb speciation in marine/estuarine sediments. This chapter presentsthe influences of ligand field stabilization energy (LFSE), Jahn-Teller effect and water exchange rate (k_{-w}) on metal distribution in different binding phases of estuarine/marine sediments. This study also describes the influence of nature of sedimentary organic matter (terrestrial and marine derived OC) in controlling the metal distribution and speciation in estuarine sediment.

Chapter 6 describes the Pb-speciation in sediments of two transects, starting from depths with oxygenated bottom water, through the intense oxygen minimum zone (OMZ) and beyond the OMZ, off Gujarat and Goa in the eastern Arabian Sea to understand the impact of varying bottom water oxygenation conditions on sedimentary Pb speciation.

Chapter 7 presents the historical changes of Pb deposition in the shelf sediment of India. Two dated sediment cores of 30 cm (dating back to 129 years BP) and 22 cm long (118 years BP) representing the eastern and western shelves of India were studied to understand the historical changes of Pb deposition.Total Pb content, enrichment factor (EF) and Pb isotopes were used to assess the Pb deposition in coastal sediments of India during the past century.

Chapter 8 summarizes the results and major conclusions of the thesis.

Chapter 2

Materials and Methods

2.1 Study area and sampling

Two major depositional types and areas chosen for this study were, 1) the continental margins of India and, 2) the Vembanad lake, an estuarine system. The description of these areas are presented below.

2.1.1 Continental margins around India

Continental margins of India comprising of eastern margin in the western Bay of Bengal and the western margin in the eastern Arabian Sea are studied here. Both the Bay of Bengal and the Arabian Sea are enclosed by land in the north and encounter seasonally reversing monsoonal winds. However, the Arabian Sea undergoes stronger water mass mixing due to stronger monsoonal winds and weaker stratified water mass compared to the Bay of Bengal (Kumar et al., 2002). Thus, organic matter production is higher in the nutrient enriched surface water of Arabian Sea compared to the Bay of Bengal where surface water is depleted in nutrients (Kumar et al., 2002). Higher productivity in Arabian Sea leads to higher consumption of dissolved oxygen (DO) by the accumulated organic matter which subsequently leads to the near-total depletion of oxygen at depths from 150 to 1000 m in the north western Indian Ocean (e.g., Banse et al., 2014; Morrison et al., 1998). The western continental slope of India encircles the second-most intense perennial oxygen minimum zone (OMZ) in the world tropical ocean (e.g., Kamykowski and Zentara, 1990). The residence time of OMZ water is believed to be less than a decade (Banse et al., 2014 and references therein). The upper few hundred meters of this zone has been reported to be nearly anoxic but non-sulfidic (Banse et al 2014). Naqvi et al., (1991) have also reported that this zone is predominantly suboxic ($\lesssim 5$ µmol O_2/kg) nature.

The shelf of western continental margin of India is wider than the eastern shelf. The width of western shelf varies from 345 km off Daman in the north to 120 km off Goa (central part) and narrows down to 60 km off Kochi in the south (Faruque et al., 2014). In the eastern part, the width of the shelf varies from 35 km off Tamil Nadu (southern part) to 60 km off north Andhra Pradesh (central part) and 120 km off West Bengal (northern part) (Faruque et al., 2014). It has been well documented that both the shelves receive huge amount of terrigenous input from large number of rivers flowing through diverse geological formations of Indian sub-continent. However, the eastern shelf receives more riverine input compared to the western part. The areas of the shelves are further subdivided into six regions on the basis of their geology of the adjacent land mass:

(i) **North-East**: The shelf sediments of this region are derived from the erosion of acidic Himalayan rocks mainly drained by the rivers Ganga and Brahmaputra (G-B) (Goldberg and Griffin, 1970).

(ii) **Central–East**:Sediments of this region are mainly derived by Mahanadi, Godavari, Krishna rivers which flow through major geological formations of India such as the Tertiary Deccan Traps, Archean granites, Precambrian and Gondwana sedimentary rocks and recent alluvials (Krishnan,1968)

(iii) **South–East**: Major contributor of sediments is Cauvery River which largely drains Precambrian gneiss and schists of intermediate to acidic rocks (Chattopadhyay and Sarkar, 1999).

(iv) **North-West:** Indus derived Himalayan rocks are the major source of sediment of this region (Rao and Rao,1995; Kesserkar et al., 2003, Ramaswamy et.al., 2008; Kurian et.al., 2013).

(v) **Central-west:** The geology of the adjacent landmass of this region is Deccan Trap Basalt which is drained by rivers such as Narmada, Tapti, Sabarmati, and Mahi to the eastern Arabian Sea (Rao and Rao, 1995; Kurian et al., 2013).

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

Around 150 surface sediment samples (core tops) and two sediment cores, SSK35/SPC32 (30 cm long) and SSK40/SPC69 (22 cm long) were collected from the shelf regions covering the eastern Arabian Sea (off shore areas Gujarat to Kerala) and western Bay of Bengal (off shore areas from Bengal to Tamil Nadu) (Figure 2.1). Sediment samples from continental shelf were collected by using a spade corer (at the water depth of ~15 to ~440 m) during 35th, 40th and 50th expeditions (June 2012 to May, 2013) of CSIR-NIO's research vessel *Sindhu Sankalp* for CSIR XII Plan Project GEOSINKS.The details of the sampling locations are given in Table 2.1 and Table 2.2 . In addition to these, sediment samples from ten stations were collected along two E-W transects (cruises SSK71 and SSK 80) from the continental margin off Gujarat and off Karwar, west coast of India (across the perennial OMZ) during 8th-21st November 2014 and 26th-30th March 2015 respectively (Figure 2.2). The sediment samples were collected in such a way (along the transect) to ensure that there were distinct variations in the dissolved oxygen (DO) concentration of the overlying bottom waters.The sediment samples were also collected from the outer shelves (Stations # SSK71/SPC15, SSK71/SPC16, SSK80/SPC2), the upper slopes (stations # SSK71/SPC17, SSK80/SPC4, SSK80/SPC5), the middle slopes (stations # SSK71/SPC20, SSK80/SPC6) and the deeper region of the slopes (Stations # SSK71/SPC21, SSK80/SPC7).

2.1.2 Vembanad Lake

In addition to marginal sediments, the Vembanad Lake in the South-west coast of India was chosen to represent an estuarine sedimentary environment which acts as an interface between the land and the ocean. The 90 km long Vembanad Lake is the longest and largest brackish-water lake of India. The northern part of the lake is connected to Arabian Sea through two openings (at Kochi and Azhikode) whereas southern part of the lake receives freshwater discharge from the rivers. However, the northern part of the lake is separated from its southern part by 1.5 km long Thanneermukom bund which was constructed to prevent the sea water intrusion to the southern part of the lake (Figure 2.1). Consequently, northern and southern parts of the lake show two different sub-environments as the northern part is brackish and southern part of the lake is freshwater dominated (Nath et al., 2000). Eight stations, four from north and four from the southern part of the lake were selected for our study (Figure 2.1). The sampling was carried out when the Thanneermukom bund was closed during pre-monsoon time, March-April of 2012. Sediments were collected by Van Veen Grab. All the collected surface sediment samples were sub sectioned and two sediment cores (SSK35/SPC32 and SSK40/SPC69) were cut into 1 cm thin slices. The sediments were preserved in frozen condition on collection. The samples were then freeze dried and part of it was ground. The sediments were then subsequently stored at −4°C until needed.

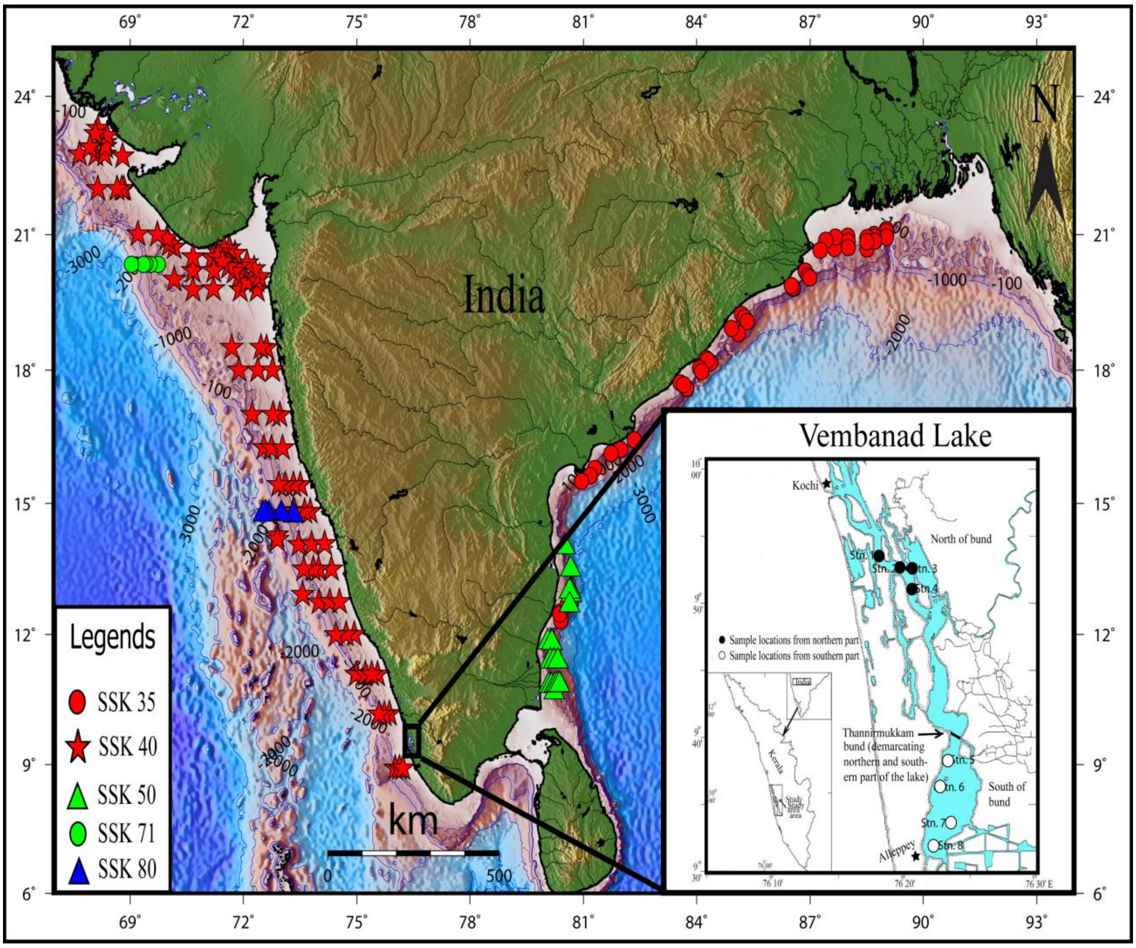


Figure 2.1 Sampling locations in the continental margins around India and Vembanad Lake in South-west coast of India. Two transects off Gujarat (green circles) and off Karwar (blue triangles) in the Eastern Arabian Sea cut across the perennial OMZ

Table 2.1 Longitude, latitude, and the water depth of the sediment samples collected from the eastern continental shelf of India

Station ID	Longitude (°E)	Latitude (°N)	Depth (m)	Station ID	Longitude (°E)	Latitude (°N)	Depth (m)
SSK35/ SPC-1	89.02	21.11	31	SSK35/SPC-35	83.52	17.84	31
SSK35/SPC-2	89.02	21.06	49	SSK35/SPC-36	82.34	16.48	145
SSK35/ SPC-3	89.02	20.94	104	SSK35/SPC-37	81.99	16.26	44
SSK35/ SPC-4	88.70	21.00	29	SSK35/SPC-38	81.73	16.17	52
SSK35/SPC-5	88.69	20.94	44	SSK35/SPC-39	81.26	15.83	62
SSK35/SPC-6	88.50	20.93	36	SSK35/SPC-40	81.08	15.71	53
SSK35/SPC-7	88.50	20.68	120	SSK35/SPC-41	80.86	15.59	69
SSK35/ SPC-8	88.70	20.85	94	SSK35/SPC-42	80.31	12.35	56
SSK35/ SPC-9	88.50	20.84	77	SSK35/SPC-43	80.38	12.52	52
SSK35/ SPC-10	88.00	20.96	31	SSK35/SPC-44	80.24	12.52	33
SSK35/SPC-11	88.00	20.85	59	SSK35/SPC-45	80.57	12.68	107
SSK35/SPC-12	88.00	20.71	83	SSK35/SPC-46	80.67	12.72	190
SSK35/ SPC-13	87.64	20.69	54	SSK50/SPC-05S	80.67	13.00	269
SSK35/ SPC-14	87.67	20.94	41.5	SSK50/SPC-06	80.67	12.92	238
SSK35/ SPC-15	87.41	20.87	36	SSK50/SPC-07	80.6	12.99	202
SSK35/SPC-16	87.27	20.65	28	SSK50/SPC-08	80.6	13.08	199
SSK35/SPC-17	86.87	20.20	34	SSK50/SPC-09	80.6	12.68	148
SSK35/SPC-18	86.95	20.10	54	SSK50/SPC-10	80.5	12.70	77.8
SSK35/SPC-19	86.99	20.05	96	SSK50/SPC-11	79.9	11.82	25.7
SSK35/SPC-20	86.55	19.81	107	SSK50/SPC-12	79.9	11.82	56.6
SSK35/SPC-21	86.51	19.87	47	SSK50/SPC-13	79.9	11.39	56.6
SSK35/SPC-22	86.47	19.91	36	SSK50/SPC-14	80.0	11.39	81.9
SSK35/SPC-23	85.09	19.32	34	SSK50/SPC-15	79.9	11.39	35
SSK35/SPC-24	85.13	19.29	55	SSK50/SPC-16	80.1	10.83	51.5
SSK35/SPC-25	85.25	19.16	106	SSK50/SPC-17	80.0	10.83	31.6
SSK35/SPC-26	85.01	18.85	122	SSK50/SPC-18	80.11	10.33	25.8
SSK35/SPC-27	84.83	19.01	55	SSK50/SPC-19	80.2	10.33	52.9
SSK35/SPC-28	84.37	18.16	99.5	SSK50/SPC-20	80.2	10.68	182
SSK35/SPC-29	84.25	18.25	54	SSK50/SPC-21	80.2	10.84	197
SSK35/SPC-30	84.20	18.30	36	SSK50/SPC-22	80.3	10.85	345
SSK35/ SPC-31	83.99	18.13	33.3	SSK35/SPC-23	80.4	10.85	522
SSK35/SPC-32	84.04	18.05	55	SSK35/SPC-24	80.4	13.50	51.6
SSK35/SPC-33	83.73	17.59	114	SSK35/SPC-25	80.5	13.50	76.6
SSK35/SPC-34	83.57	17.75	54	SSK35/SPC-26	80.4	14.01	61

Table 2.2 Longitude, latitude, and the water depth of the sediment samples collected from the western continental shelf of India

Station ID	Longitude (°E)	Latitude (°N)	Depth (m)	Station ID	Longitude (°E)	Latitude (°N)	Depth (m)
SSK40/SPC1	72.68	14.77	350	SSK40/SPC43	71.21	20.20	75
SSK40/SPC2	72.88	14.27	420	SSK40/SPC44	70.67	20.20	33
SSK40/SPC3	72.89	14.18	440	SSK40/SPC45	70.16	20.01	54
SSK40/SPC4	73.56	12.92	279	SSK40/SPC46	70.67	20.63	34
SSK40/SPC5	73.31	14.83	108	SSK40/SPC47	70.17	20.72	33
SSK40/SPC6	73.63	15.42	33.64	SSK40/SPC48	70.17	20.91	53.7
SSK40/SPC7	73.50	15.42	54	SSK40/SPC49	70.06	21.00	104.5
SSK40/SPC8	73.11	15.42	103	SSK40/SPC50	69.72	21.00	32.1
SSK40/SPC9	73.11	15.42	98.3	SSK40/SPC51	69.20	21.01	53
SSK40/SPC10	72.71	16.26	53.59	SSK40/SPC54	68.88	22.75	55
SSK40/SPC11	73.14	16.25	33	SSK40/SPC55	68.14	22.75	34.1
SSK40/SPC12	73.30	16.25	34	SSK40/SPC56	67.65	22.75	30
SSK40/SPC13	73.14	16.99	54	SSK40/SPC57	68.09	22.75	15
SSK40/SPC14	73.00	17.00	101	SSK40/SPC58	68.33	23.00	23
SSK40/SPC15	72.23	17.00	95.5	SSK40/SPC59	68.84	22.92	16
SSK40/SPC16	71.88	18.00	50	SSK40/SPC60	68.34	23.15	18.3
SSK40/SPC17	72.37	18.00	35	SSK40/SPC61	68.35	23.31	24
SSK40/SPC18	72.77	18.00	34	SSK40/SPC62	68.38	23.19	32.2
SSK40/SPC19	72.61	18.50	54	SSK40/SPC63	68.14	22.91	32
SSK40/SPC20	72.46	18.50	85	SSK40/SPC64	68.08	14.81	52.8
SSK40/SPC21	71.69	18.51	84	SSK40/SPC65	67.93	14.82	104.6
SSK40/SPC22	70.66	19.78	57	SSK40/SPC66	73.94	14.81	99.5
SSK40/SPC23	71.20	19.80	34.5	SSK40/SPC67	73.80	14.06	53.3
SSK40/SPC24	71.91	19.78	27.52	SSK40/SPC68	73.35	14.07	33
SSK40/SPC25	72.45	19.78	32	SSK40/SPC69	73.56	14.08	31
SSK40/SPC26	71.89	20.08	34.3	SSK40/SPC70	74.11	13.50	49.2
SSK40/SPC27	72.08	19.95	34	SSK40/SPC71	74.33	13.50	94
SSK40/SPC28	72.35	19.98	33.4	SSK40/SPC72	74.50	13.50	104.9
SSK40/SPC29	72.51	20.08	37	SSK40/SPC73	74.16	12.75	52.7
SSK40/SPC30	72.28	20.24	25.5	SSK40/SPC74	74.15	12.75	31
SSK40/SPC31	72.09	20.37	28	SSK40/SPC75	74.22	12.75	33
SSK40/SPC32	72.09	20.38	31	SSK40/SPC76	74.55	12.00	54
SSK40/SPC33	71.88	20.30	31	SSK40/SPC77	74.72	12.00	114.3
SSK40/SPC34	71.75	20.19	26	SSK40/SPC78	75.07	12.00	114.2

SSK40/SPC35	71.61	20.29	20	SSK40/SPC79	74.93	11.08	53
SSK40/SPC36	71.78	20.58	19.7	SSK40/SPC80	74.58	11.08	33
SSK40/SPC37	71.63	20.70	22.5	SSK40/SPC81	75.12	11.08	32
SSK40/SPC38	71.49	20.80	26	SSK40/SPC82	75.40	10.18	52.8
SSK40/SPC39	71.33	20.70	27	SSK40/SPC83	75.64	10.17	98
SSK40/SPC40	71.17	20.61	27.7	SSK40/SPC84	76.00	8.55	113.2
SSK40/SPC41	71.31	20.50	38.9	SSK40/SPC85	76.15	8.54	53.9
SSK40/SPC42	71.44	20.40	83.72	SSK40/SPC86	76. 26	8.55	32.7

Table 2.3 Longitude, latitude, and the water depth of the sediment samples collected from two transects from the western continental margin sediment of India

Station ID	Longitude (°E)	Latitude (°N)	Depth (m)
Off Gujarat			
SSK71/SPC15	69.7423	20.34	80
SSK71/SPC16	69. 3171	20. 2056	98
SSK71/SPC17	69. 2448	20. 2098	195
SSK71/SPC20	69. 1506	20. 2056	791
SSK71/SPC21	69. 2052	20. 2064	1544
Off Karwar			
SSK80/SPC2	73. 316	14. 729	110
SSK80/SPC4	73. 003	14. 759	304
SSK80/SPC5	72. 674	14. 761	307
SSK80/SPC6	72. 590	14. 780	475
SSK80/SPC7	72. 521	14. 752	1638

Table 2.4 Longitude, latitude and water depth of the sediment samples collected from the Vembalad Lake, West coast of India

Sample	Longitude (°E)	Latitude (°N)	Depth (m)
North of Thanneermukom Bund			
Stn-1	76.3010	9.9140	5
Stn-2	76.3022	9.8920	2
Stn-3	76.3320	9.8790	4
Stn-4	76.3395	9.8810	2
South of Thanneermukom Bund			
Stn-5	76.3816	9.6400	2
Stn-6	76.3765	9.6066	3
Stn-7	76.3895	9.5622	1.5
Stn-8	76.3648	9.5636	3

2.2 Analysis of total carbon (TC), total inorganic carbon (TIC), and total nitrogen (TN) in sediment*:*

Ground sediment samples were analyzed for total carbon (TC), total inorganic carbon (TIC), and total nitrogen (TN) contents. The TC and TN contents in sediments were determined using a Flash 2000 CHN elemental analyzer (Thermo Fisher Scientific Incorporation). The precision of the analysis was within ± 5%. The soil NC content (0.37% N and 3.5% C) was used as the certified reference material. TIC was determined by coulometry (UIC Coulometrics). Calcium carbonate (12% C) was used as a standard material. The relative standard deviation of the analysis was within ± 2%. The total organic carbon (C_{org}) content was derived by deducting TIC from TC. $CaCO_3$ content in sediment was calculated assuming that the majority of inorganic carbon (or carbonate) is associated with Ca.

2.3 Determination of the dissolved oxygen (DO) and pH in the overlying bottom water

Dissolved oxygen concentrations in the overlying bottom seawater were determined by Winkler method. The detailed description of the method is given in literature (Broenkow and Cline, 1969; Bryan et al., 1976). The procedure of DO measurement is briefly given in Appendix 1.2. The pH of the water samples were determined by pH meter (LabIndia, Mumbai, India). Salinity data obtained from conductivity sensor of CTD system (Sea-Bird, USA) was used.

2.4 Sediment texture

Texture of the dry sediment (in < 63μm) was analyzed by Particle Size Analyzer (LPSA from Malvern Mastersizer 2000, Worcestershire, UK.). The detailed procedure has been described in the literature by Ramaswamy and Rao (2006). The procedure is briefly given in Appendix 1.3.The sand data (sieved) is presented in weight percentage (wt %) and the silt and clay in vol (%) in this study.

2.5 Analysis of total metals (Pb, Cu, Ni, Ti, Mn and Fe) in sediment

Concentration of Pb and other trace and major elements in sediments were analysed by digesting the sediment sample with 10.0 mL of acid mixtures of HF, HNO_3 and $HClO_4$ (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 re-dissolved in 2% HNO_3 and analyzed by a graphite furnace, flame atomic absorption spectrometer (GFAAS) (Model: PinAAcle 900T, Perkin-Elmer) and ICP-MS (Thermo FISCHER ICP-MS, X series 2, Germany) at CSIR-National Institute of Oceanography (CSIR-NIO). MAG-1 (obtained from USGS), 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). The recoveries of the metals in CRM of all experiments were 95 to 98 %.The reproducibility of the analysis was less than 1% of all the metals.

2.6 Sequential extraction study

The modified BCR sequential extraction protocol (proposed by Ure et al., 1993), modified by Sahuquillo et al (1994), Quevauvillier et al (1997) and finally by Rauret et al., 1999) was further slightly modified (Chakraborty et al., 2015) and used in this study to understand the geochemical fractionation (operational speciation) of Pb and other elements in the sediments. 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. This modified BCR protocol allows us to separate and determine the concentrations of 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.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 experimental procedure is schematically presented in Figure 2.2. The concentrations of the metals in each extracted solution and in residual fraction were determined by electrothermal atomic absorption spectrometer (GFAAS). 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, Fr1 and Fr.2 (determined by the modified method) were added and compared with the certified reported values. Validation of the sequential extraction method was also done by comparing the total metal concentrations (determined by GFAAS) with the sum of the concentrations of 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 sequential extraction method. The recovery of certified Pb and other metals in different geochemical fraction from BCR-701 were very good and well within the acceptable range (±3% of the reported value). Replicate samples were used to measure overall analytical precision. The reproducibility of each measurement (n=3) was <1% for all elements.

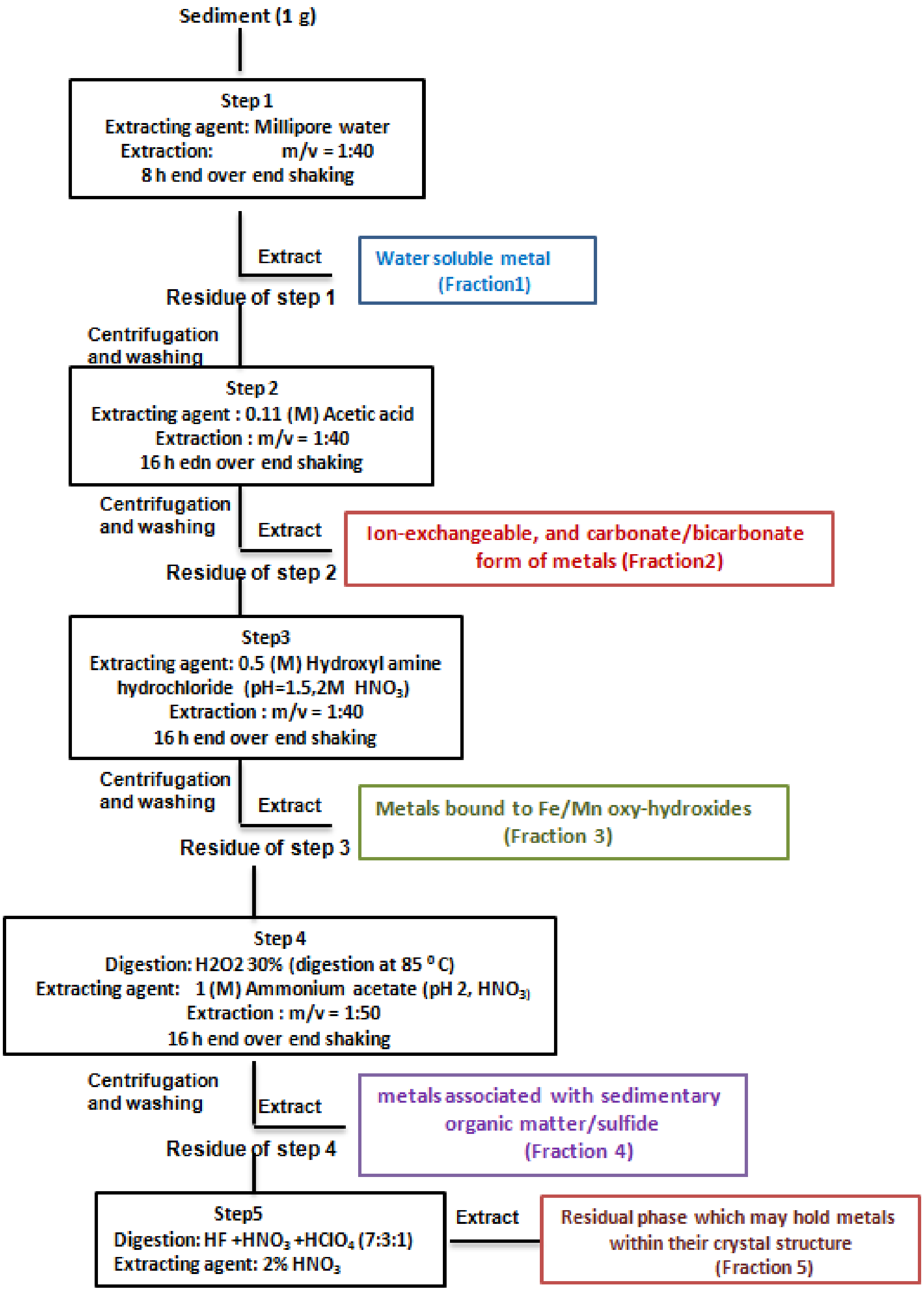


Figure 2.2 Schematic presentation of modified BCR sequential extraction procedure

2.7 Kinetic extraction study

To understand the stability of sedimentary metal complexes, kinetically distinguishable forms of metals in the sediments were studied by using kinetic model proposed by Olson and Shuman (1985).In this study ethylenediaminetetraacetate (EDTA)-extractable trace metal concentrations (from the sediments) as a function of time was investigated.

Experimental Procedure

Two grams (2.0 gm) of sediment was added to 200 cm^3 of 0.05 M EDTA (Merck Pvt. Ltd.) solution (at pH 6.0) in a Teflon beaker (400 cm^3) and the mixture was continually stirred with a Teflon-coated magnetic stirring bar throughout the experiment. The ratio of the mass of sediment to the volume of EDTA solution (mass/volume) was set at 0.01, as this ratio provided sufficiently high metal concentrations in the extract to be accurately quantified, while requiring a minimum amount of sediment. A homogeneous suspension was maintained with a constant mass/volume ratio during sampling. Larger mass/volume ratio is undesirable, as they can cause problems with filtration. At set time intervals (0 min, 5 min, 10 min, 30 min, 45min, 60 min, 2 hr, 6 hr, 12 hr, 24 hr, 48hr, 72 hr), 2 cm^3 aliquots of the suspension were filtered through a 0.2 ml syringe filter (Millex, Millipore). The initial time for the kinetic measurement (i.e.t = 0 s) was taken as the time just before the sediment was added to the EDTA solution. The filtrate samples (1.0 cm^3) were then (in 2% ultrapure HNO3) analyzed by GFAAS to monitor the change in concentrations of metals in the extracted solution as a function of time. The kinetic extraction experiments were performed in triplicate for all the samples to ensure repeatability of the results.The pictorial presentation of experimental set up is provided in Appendix 1.1.

EDTA was chosen as the extracting reagent, as it is a well-characterized, strong chelating agent that allows good control of experimental variables. Most EDTA-metal chelate complexes are formed rapidly and are extremely stable (Welcher 1958). The use of EDTA as a complexing agent avoids difficulties associated with other complexants in that a single 1:1 complex species is formed rather than a stepwise formation of complexes, which helps to simplify calculations and interpretation of results (Welcher 1958). As a hexaprotic acid, it has an inherently large pH buffering capacity. In addition, it forms negatively charged metal complexes at most pH values, helping to keep extracted metals in solution by minimizing readsorption of extracted metals to the sediment. The kinetic extraction experiments were performed in triplicate for all the samples to ensure repeatability of results.

Theory of kinetic speciation study

Kinetically distinguishable forms of metals in the sediments and their stability were studied by using kinetic model proposed by Olson and Shuman (1985). It is based on the assumption that each sediment sample consists of *n* different components, in which each component, M-sediment$_i$, exists in equilibrium with its dissociation products: M^{2+} or extractable M complexes, and naturally occurring heterogeneous complexant, sediment$_i$. The subscript, i, represents different binding sites of the naturally-occurring heterogeneous complexant.

The extraction of metals from sediment using EDTA (as an extractant) is represented by the following reactions (charges are omitted for simplicity):

$$M - sediment_i + EDTA \xrightarrow{k_i} M - EDTA + sediment_i \qquad (1)$$

Where $M - sediment_i$ and $M - EDTA$ represent the metal ion M, bound to a sediment binding site, sediment$_i$, and EDTA, respectively. If EDTA is added in large excess, the M is extracted from the original sediment binding site with a rate constant k_i. The change in concentration of $M - sediment_i$with time is given by the following pseudo first-order rate law.

$$-\frac{dc_{M-sediment_i}}{dt} = k_i c_{M-sediment_i} \qquad (2)$$

The integrated rate law derived from equation 2, expressed in terms of the concentration of M-EDTA, shows that the concentration of metal extracted in solution, $c_{\text{M-EDTA}}$, and rises exponentially over time to a limiting value, as shown in Eq. 3. Unfortunately, it is impossible to study the individual binding sites separately, or to a prioriknow the number of discrete binding sites, and there may be a nearly continuous distribution of sediment binding sites. Hence, Eq. 3 is written as a summation of exponentials.

$$C_{M-EDTA}(t) = \sum_{i=1}^{n} C_{M-sediment_i}(1 - e^{-k_i t}) \qquad (3)$$

This system described by equation 3 can be approximated by a two-component first-order reaction model

$$c_{M-EDTA}(t) = c_1(1 - e^{k_1 t}) + c_2(1 - e^{k_2 t}) \qquad (4)$$

Where, $c_{M-EDTA}(t)$ is the concentration of M (metal) extracted by EDTA at time t,C_1,C_2 are the concentrations of EDTA-extractable M initially bound to labile (quickly extracted), or stable (with respect to the time scale of measurement) sediment binding sites, respectively, and K_1 ,K_2 are the corresponding dissociation rate constants.

Non-linear regression analysis for kinetic measurements

In kinetic speciation method the experimental data (concentration of EDTA extractable Pb or other metal against time) was fitted to the kinetic model by non-linear regression analysis using the Marquadt–Levenberg algorithm. The number of the component was found by the minimum number of parameters required to accurately fit the data was determined by finding the number of components in which the sum of square of the weighted residuals shown below achieved a minimum value.

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

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 poly functional, 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.

The lability criteria in kinetic speciation study

The concept of *lability* describes the ability of complexes to maintain equilibrium with the free metal ion, M, within the context of an ongoing interfacial process in which a particular species, usually M, is consumed. Consider sediment of *n* components, in which each component, designated M-sediment$_i$, exists in equilibrium with its dissociation products:

$$\mathrm{M\text{-}sediment}_i \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{M} + sediment_i \qquad \text{(slow)} \qquad (1)$$

Where, where $k_1$and k_{-1} is the rate constants for complex association and dissociation respectively and the thermodynamic stability constant, K, equals k_1/k_{-1}.

Under conditions of sufficient excess ligand (L) over metal (M), the association reaction is quasi-monomolecular with rate constant $k'_1 = k_1 c_L$. On time scales, t, much larger than the characteristic lifetimes of M ($1/k'_1$) and M-sediment$_i$ ($1/k_{-1}$), a given metal ion undergoes frequent interchange between M and M-sediment$_i$. The complex system is then sufficiently dynamic to maintain bulk equilibrium and obeys the double condition (Gaabass et al., 2009)

$$k'_1 t,\ k_{-1} t >> 1 \qquad (2)$$

In the usual situation of practical interest, K' $(=K\ c_{\mathrm{sediment}})$ $k'_1/k_{-1}) > 1$, so Eq. 2 reduces to $k_{-1}t >> 1$. Thus, metal complexes in sediment will be called labile if their $k_1 t >> 1$.

2.8 Chronology of sediment core

Chronology of the cores was constructured using excess ^{210}Pb activity method determined by Gamma Spectroscopy in Radiochronology Laboratory, Laval University, Canada.

The age for each depth of the sediment cores were estimated by estimating the sedimentation rate. The activities of $^{210}\mathrm{Pb}_{\mathrm{exc}}$ were plotted logarithmically against the sedimentation depth. Sedimentation rates were calculated from this plot by following the constant initial concentration (CIC) model (Rooth and Cornwell, 2003; Koide et al., 1972). Assuming the top most layer of the core represent the year of collection, each sediment sections was dated (calendar year) by dividing the mean depth of the sediment interval by sedimentation rate.

2.9 Isotopic analysis:

2.9.1. Determination of stable Pb isotopes in sediment samples

For identification and quantification of sources of anthropogenic Pb, stable isotopes of Pb (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) were analysed in the authigenic component of the sediment.However, the anthropogenic component extracted from bulk sediment is an operationally defined phase and therefore it does not mean that the leached fraction only contain anthropogenic Pb but, there is a possibility that natural Pb can also leach out during the extraction process. Nevertheless, the leached fraction can be considered as dominated by anthropogenic Pb.

The experimental procedure for Pb isotope analysis is described below

Sediment leaching

An approximate amount of 300 mg of sediment samples were taken in Teflon containers and washed with deionized water prior to the leaching. Authigenic Pb was extracted by shaking 20 ml of freshly prepared hydroxyl amine hydrochloride (HH) solution (containing $NH_2OH.HCl$ +CH3COOH+NaOH) adjusted at pH 3.5 to 4 pH) with the washed sediment samples in an orbital shaker for 1 hr at 125 rpm. These leachates were then separated from the sediments by centrifugation for 30 min at 4500 r.p.m. The supernatant clear leachates were then transferred to Teflon containers and consecutively digested with conc HNO_3 and 6 M HCl on hotplate at 100^0 C.The digested leachates were then extracted in 1M HCl solution. The solution was then used for cation column separation.

Chemical separation and mass spectrometry

To avoid isobaric interference during isotopic measurement, Pb was chemically separated by using HBr-HCl chemistry and passing through a column containing AG1-X8 cation exchange resin.

The stable Pb isotopic ratios (^{206}Pb/ ^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb, ^{208}Pb/^{206}Pb, ^{206}Pb/^{207}Pb) were then measured by Nu Plasma MC-ICP-MS at GEOMAR, Helmholtz Centre for Ocean Research, Germany. Iinstrument drift and matrix effects during measurement were corrected by using an internal standard of Tl. The reproducibility and accuracy of the measurements were checked by using USGS marine sediment MAG 1. Reproducibility of Pb isotope ratios for MAG-1 was within 0.1% of the mean value. The internal precision (2se) of each Pb isotope analyses was within 0.05%.

2.9.2 Determination of $\delta^{13}C_{oc}$ in sediment samples by Isotope Ratio Mass spectrometer (IRMS):

Sources of the total sedimentary organic carbon (C_{org}) were identified by analyzing **δ** $^{13}C_{oc}$ in sediment samples by using Isotope Ratio Mass spectrometer (IRMS) at CSIR-

NIO, Goa. Subsamples of sediments for **δ**$^{13}C_{oc}$ contents were acidified with HCl (10%) to remove carbonates. Traces of HCl were removed by washing the sediments several times with distilled water. The sediments were then used for **δ**$^{13}C_{oc}$ analysis. Calibration was carried out using 2, 5-Bis-(5-tetrabutyl-benzoxazol-2-yl) thiopen (BBOT) as a standard. **δ**$^{13}C_{oc}$ of C_{org} was determined with the Thermo Finnigan Flash 1112 elemental analyzer, linked with a Thermo Finnigan Delta V plus IRMS. The overall analytical precision for replicate samples was within ±1.6% for C_{org} and ±0.2‰ for **δ**$^{13}C_{oc}$. All isotopic compositions are reported as, per-mil (‰) relative to variation (**δ**) from the PDB standard.

$$\partial^{13}C_{oc} = \left\{ \left({}^{13}C / {}^{12}C \right)_{Sample} / \left({}^{13}C / {}^{12}C \right)_{PDB} - 1 \right\} \times 1000$$

Chapter 3

Patterns of lead distribution and the processes that control its speciation in the continental shelf sediments around India

3.1 Introduction

Understanding of distribution and chemical speciation of lead (Pb) in marine environment is of great importance because of its toxic nature. Continental shelf sediments act as a major sink for heavy metals (including Pb). The Pb concentration in the continental shelves may reflect different geochemical and anthropogenic processes that occur in the adjacent landmass. The literature review (discussed in Chapter 1) has shown that the coastal environment of India is relatively pristine with respect to total Pb content and it's variation along the coast is mainly due to the diverse geology and varying anthropogenic activities in some sporadic locations along the Indian coastline. However, the compiled literature data were not systematic in terms of time and area of sampling. Most of the sedimentary Pb data are from estuarine areas whereas the data from marine environment are limited. In addition, the chemical phases hosting Pb are not well defined in the literature. However, the solid-phase geochemical speciation of sedimentary Pb is required for understanding the processes which control the Pb distribution and speciation in the coastal sediments around India.

The diverse geology, the long coastline (7000 km), climatic variability, oceanographic settings, and anthropogenic activities along the coastline of India can control the distribution pattern and speciation of Pb in estuarine and continental margin sediments around India. The objectives of this study were to (i) assess the regional distribution pattern of Pb to evaluate the relative contribution of natural and anthropogenic processes in accumulating Pb to the continental shelf sediments of India (ii) asses the distribution of Pb in different geochemical phases of the marine sediments around India and to (iii) identify the factors that control Pb speciation in coastal sediment.

To understand the regional distribution pattern of lead content in the continental shelf sediments around India, 153 surficial sediment (core top) samples (81 from Bay of Bengal and 72 from the Arabian Sea) were collected along the shelves of India. The chemical fractionation studies were performed on 64 sediments (28 from Bay of Bengal and 36 from the Arabian Sea) (Figure 3.1).

It has been well documented that both the shelves receive huge amount of terrigenous input from large number of rivers flowing through diverse geological formations of Indian sub-continent (Goldberg and Griffin, 1970; Goodbred and Kuehl, 2000).To facilitate an easy evaluation of the data, the long continental shelves of India (study area) were further subdivided into six regions on the basis of their geology of the adjacent land mass:

(i) **North-East**: The shelf sediment of this region is derived from the erosion of acidic Himalayan rocks mainly drained by the rivers Ganga and Brahmaputra (G-B) (Goldberg and Griffin, 1970).

(ii) **Central–East**: Sediment of this region is mainly derived by Mahanadi, Godavari, Krishna rivers which flow through major geological formations of India such as the Tertiary Deccan Traps, Archean granites, Precambrian and Gondwana sedimentary rocks and recent alluvial sediments (Krishnan, 1968).

(iii) **South–East**: Cauvery River largely drains Precambrian gneiss and schists of intermediate to acidic rocks to the shelf of this region (Chattopadhyay and Sarkar, 1999).

(iv) **North-West:** Indus derived Himalayan rocks are the major source of sediment of this region (Rao and Rao, 1995; Kesserkar et al., 2003, Kurian et al., 2013; Ramaswamy et.al., 2008).

(v) **Central-west:** The geology of the adjacent landmass of this region is Deccan Trap Basalt which is drained by rivers such as Narmada, Tapti, Sabarmati, and Mahi to the eastern Arabian Sea (Rao and Rao,1995; Kurian et al.;2013).

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

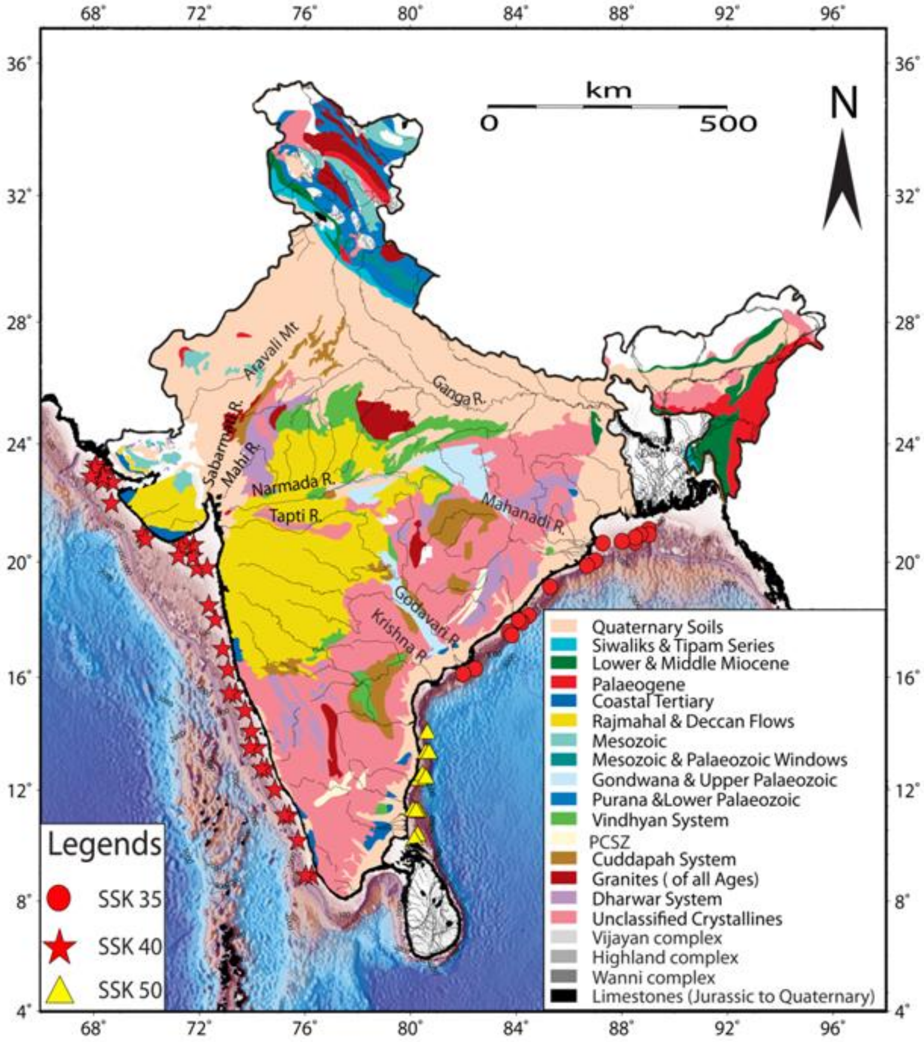


Figure 3.1 Geology of India with the sampling sites located in the eastern (red circles and yellow triangles) and western (red stars) continental shelves of India

3.2 Results:

3.2.1 Distribution of total Pb content and other geochemical parameters in the continental shelf sediments around India

The total Pb content in the continental shelf sediments of India determined for this study is presented in Figure 3.2. The concentration of sedimentary Pb was found to vary between 1.5 mg.kg^{-1} (in the western shelf) and 36.7 mg.kg^{-1} (in the eastern shelf). Region-wise comparison in the sedimentary Pb content showed that sediments from north-east region had the highest median/average concentration of sedimentary Pb (median: 26.3, mean: 25.9, SD: 3.9 mg.kg^{-1}) followed by central–east (median: 24.2, mean: 24.91, SD: 7.4mg.kg^{-1}) > north-west (median: 21.2, mean: 22, SD: 3.8 mg.kg^{-1}) >south-east (median: 16.1, mean: 16.4, SD: 6.9 mg.kg^{-1}) > south-west (median: 12.6, mean: 12.1, SD: 3.4 mg.kg^{-1}) > central-west (median: 11.2, mean: 11.6, SD:5.5 mg.kg^{-1}) region.

Total Pb content and the concentrations of important geochemical parameters that can control trace elements such as $CaCO_{3,}$ total organic carbon (C_{org}) and Fe in selected sediments are presented in Table 3.1. The highest median concentration of $CaCO_3$ was found in the shelf sediments collected from the south-east coast (~15.9 %) followed by north-west (~15 %) > south-west (10.9 %) > central-west (9.9 %) > central-east (3.6 %) > north-east (~2.5 %) region of India.

Regional variation was also observed in the concentration of sedimentary organic matter (presented as C_{org}) along the coastal areas of India. Low C_{org} content (<1%) was observed in most of the sediments from eastern shelf. In the western shelf except for the northern region, C_{org} content was comparatively higher than the other regions. The highest TOC content was found in the shelf sediments of south-west region (~2.2 %) followed by central-west (~1.1%) > central-east (~1.0%) > south–east (~0.8%)> north-east (~0.7%) > north-west (~0.6%) region.Low TOC content in the Indian shelf sediments especially the eastern shelf and the outer shelf of western part of the continent has also been reported in the literature (Paropkari et al.,1992; Paropkari et al.,1993; Sarkar et al.,2004; Banerjee et al.,2012,Kurian et al.,2013; Krishna et al.,2013).

Concentration of Fe in most of the shelf sediments was found to be higher than the average crustal abundance (3.5%, McLennan; 2001). This finding is consistent with the concentrations reported earlier (Mascarenhas et al., 1985; Paropkari et al., 1990; Rokade, 2009; Ray et al., 2005; Dhanakumar et al., 2012; Kurian et al.; 2013; Sundaray et al., 2011; Chakraborty et al.2015a). The highest median Fe content 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%) region of India.

The mobility and bioavailability of sedimentary metals depend strongly on their chemical speciation in the system. Chemical speciation of metals and determination of different natural ligands in sediment system always helps in understanding different geochemical processes which is responsible for remobilisation of metals in the systems(Gleyzes et.al., 2002 and references therein). Therefore, further geochemical fractionation (operational speciation) studies were carried out to provide better understanding of different geochemical processes that control Pb distribution and its fractionation in continental shelf sediments around India.

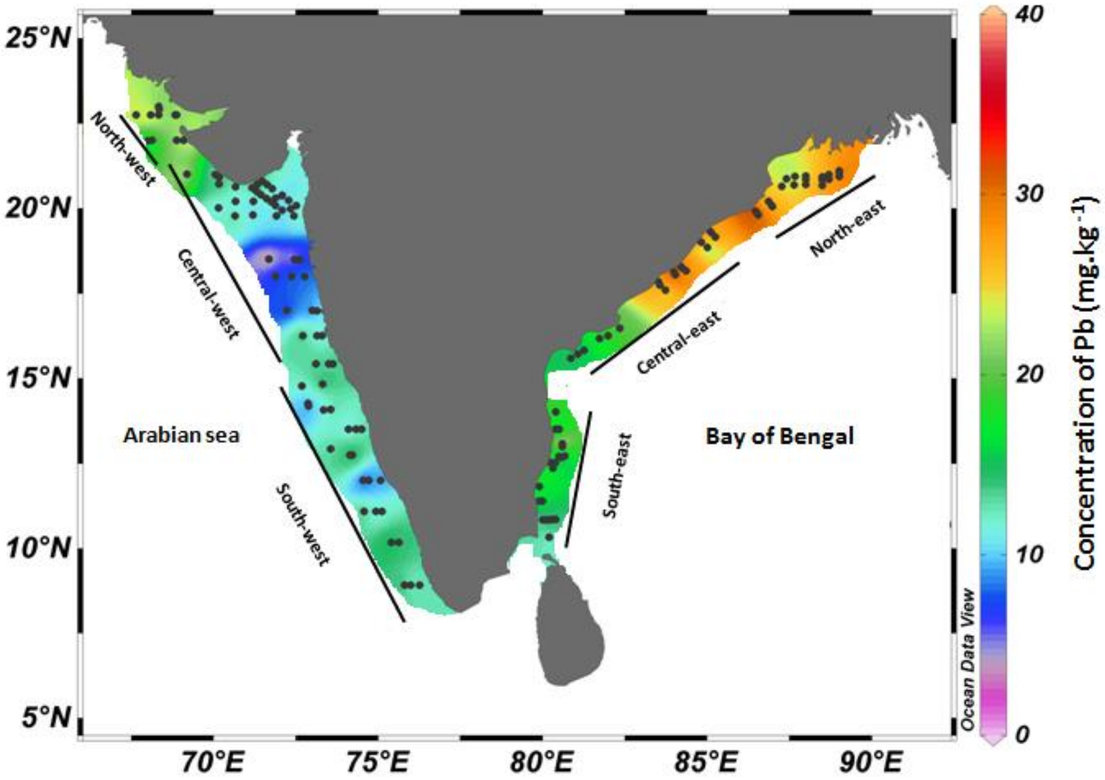


Figure 3.2 Distribution pattern of total Pb content (mg.kg $^{-1}$) in the continental shelf sediments around India.

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

The concentrations of chemically separated Pb (mg.kg^{-1}) from different geochemical hosting phases of continental shelf sediments from the different geographical locations around India are presented in Table 3.2 and described below.

Geochemical fractionation of sedimentary Pb in the north-eastern continental shelf region (Ganga-Bramhaputra derived sediment):

Figure 3.3(a) shows the distribution of Pb in different geochemical binding phases of shelf sediments from the north-eastern continental region of India. The concentrations of water soluble (Fr.1), exchangeable, and carbonate/bicarbonate Pb-complexes (Fr.2) were found to vary from ~2.8 to 8.3% (average~5%) of the total Pb content in the studied sediments. Lowest concentration of Pb was found in these geochemical forms (Fr.1 and Fr.2). A major fraction (33.7-57.2 %, with an average of ~40%) of the total sedimentary Pb was found to be associated with Fe/Mn oxyhydroxide phase (Fr.3) in the sediments [Figure 3.3(a)]. A fraction (4.2 to 13.3 %, with an average ~14 %) of the total Pb was associated with the sedimentary organic carbon phase [Figure 3.2(a)]. Another major fraction (32.6 to 56.9 %, with an average ~47 %) of the total sedimentary Pb content was present within the residual phase of the sediment. This residual Pb represents inert or immobile Pb present in the primary or secondary mineral structure of the sediment and comes from weathered source rocks of the sediment. The variation in the total concentration of Pb in the residual phase varied from ~9.5 to 13 mg.kg^{-1}.

Table 3.1 Concentration of Pb (mg.kg $^{-1}$), $CaCO_3$ (%), Fe (%) and C_{org} (%) in the sediments from six continental shelf regions of India

Area	Station	Pb (mg.kg^{-1})	$CaCO_3$(%)	Fe (%)	C_{org} (%)
North-east	SSK35/SPC1	29.0±0.5	2.6	7.3 ±0.1	0.49
	SSK35/SPC3	30.4±0.2	1.9	5.6±0.1	0.54
	SSK35/SPC5	26.3±0.2	2.9	5.8±0.5	0.58
	SSK35/SPC7	28.9±0.6	2.5	6.0±0.3	0.65
	SSK35/SPC9	26.2±0.3	2.5	6.2±0.6	0.72
	SSK35/SPC12	26.7±0.4	4.1	5.7±0.7	0.68
	SSK35/SPC16	25.6±0.9	1.6	6.9±1.1	0.69
	SSK35/SPC19	26.1±1.1	2.4	7.7±0.2	0.82
		Med=26.5	**Med=2.5**	**Med=6.1**	**Med=0.66**
Central-east	SSK35/SPC22	36.7±0.4	1.8	8.1±0.5	0.27
	SSK35/SPC24	31.1±1.7	2.1	9.1±0.8	1.03
	SSK35/SPC26	13.3±0.5	59.3	7.8±1.3	0.97
	SSK35/SPC28	24.4±0.5	56.8	11.0±0.5	1.73
	SSK35/SPC31	35.3±0.3	1.9	5.2±0.1	0.71
	SSK35/SPC33	19.9±0.3	74.8	11.8±0.6	0.74
	SSK35/SPC35	20.9±0.3	3.1	3.2±0.07	2.36
	SSK35/SPC36	20.3±0.2	2.9	8.2±0.1	0.99
	SSK35/SPC37	18.1±0.2	4.0	8.3±0.5	0.38
	SSK50/SPC26	18.4±0.1	9.0	1.3±0.5	0.99
		Med=20.57	**Med=3.6**	**Med=8.1**	**Med=0.98**
South east	SSK50/SPC24	15.9±0.3	13.7	0.3±0.03	0.44
	SSK50/SPC25	11.6±0.6	42.4	8.8±0.3	2.09
	SSK35/SPC42	18.9±0.4	18.1	0.6±0.1	0.49
	SSK35/SPC44	28.7±0.4	12.1	3.5±0.8	0.88
	SSK50/SPC10	10.9±0.1	61.8	0.7±0.6	1.30
	SSK50/SPC11	10.1±0.1	11.1	6.7±0.07	0.24
	SSK50/SPC13	16.5±0.5	6.1	0.2±0.1	0.68
	SSK50/SPC15	17.4±0.7	5.1	2.0±0.07	1.57
	SSK50/SPC17	5.9±0.2	24.7	5.6±0.3	0.45
	SSK50/SPC19	10.6±0.4	78.9	6.1±0.09	1.23
		Med=13.4	**Med=15.9**	**Med=2.7**	**Med=0.78**
North-west	SSK40/SPC59	30.4±0.1	11.8	5.2±1.1	0.49
	SSK40/SPC57	21.6±0.3	6.8	5.5±1.0	0.51
	SSK40/SPC60	22.7±0.8	7.9	4.0±0.8	0.47
	SSK40/SPC55	25.1±1.1	26.3	5.6±0.4	0.66
North-west	SSK40/SPC56	20.5±0.4	25.9	5.5±0.6	0.58
	SSK40/SPC58	21.2±1.0	7.4	5.9±0.16	0.62
	SSK40/SPC61	18.3±0.5	18.2	5.6±0.9	0.50
	SSK40/SPC62	20.3±0.5	19.2	5.6±1.2	0.66
		Med=21.4	**15.0**	**5.5**	**0.55**
Central-west	SSK40/SPC47	14.6±0.5	8.2	7.6±1.2	1.18
	SSK40/SPC51	23.4±0.3	41.5	6.4±0.6	1.36
	SSK40/SPC32	6.3±0.3	6.5	9.0±0.8	0.90
	SSK40/SPC34	12.9±0.3	7.5	8.6±2.1	0.29
	SSK40/SPC36	15.1±0.4	15.5	9.0±1.0	0.86
	SSK40/SPC39	24.2±0.7	7.5	7.6±0.1	0.31
	SSK40/SPC41	19.1±0.8	6.9	7.3±0.03	0.43
	SSK40/SPC46	12.1±0.1	6.8	7.5±0.4	1.02
	SSK40/SPC23	10.8±0.3	79.5	6.9±0.8	0.93
	SSK40/SPC24	10.5±0.3	7.2	6.3±0.1	1.00
	SSK40/SPC17	8.6±0.3	78.3	6.2±2.1	1.44
	SSK40/SPC19	8.78±0.8	25.2	4.9±1.1	1.61
	SSK40/SPC11	12.0±0.6	81.3	7.4±1.3	2.63
	SSK40/SPC12	10.7±0.4	11.5	7.5±2.1	2.13
	SSK40/SPC6	13.9±0.5	77.2	12.9±0.8	2.89
	SSK40/SPC7	12.8±0.2	3.9	6.1±0.3	2.89
		Med=12.5	**9.9**	**7.4**	**1.10**
South-west	SSK40/SPC63	16.5±0.1	11.2	5.3±0.1	3.06
	SSK40/SPC68	9.4±0.5	15.7	3.5±0.4	2.91
	SSK40/SPC69	14.6±0.7	13.1	4.5±0.1	2.65
	SSK40/SPC70	8.9±0.2	14.9	2.0±0.1	1.51
	SSK40/SPC73	8.1±0.5	4.9	2.4±0.1	2.24
	SSK40/SPC74	17.6±0.5	4.6	5.7±0.1	3.01
	SSK40/SPC75	19.1±0.3	6.6	4.8±0.4	3.03
	SSK40/SPC79	9.3±0.2	12.8	4.4±0.9	1.61
	SSK40/SPC80	14.8±0.8	6.3	3.4±2.1	0.79
	SSK40/SPC81	12.8±1.2	8.5	1.6±2.0	0.61
	SSK40/SPC85	6.5±1.5	10.7	0.9±0.1	0.43
	SSK40/SPC86	16.2±1.7	12.8	3.4±0.1	2.12
		Med=13.7	**10.9**	**3.5**	**2.18**

Table 3.2 Concentration of Pb (mg.kg^{-1}) in, water soluble fraction (Fr.1); ion-exchangeable and carbonate/bicarbonate fraction (Fr. 2); Fe/Mn oxyhydroxides i.e., reducible fraction (Fr. 3); sedimentary organic matter and sulfide fraction, i.e., oxidizable fraction (Fr. 4) and residual fraction (Fr. 5) in the studied sediments

Area	Station	Fr.1 (mg.kg^{-1})	Fr.2 (mg.kg^{-1})	Fr.3 (mg.kg^{-1})	Fr.4 (mg.kg^{-1})	Fr.5 (mg.kg^{-1})
North-east	SSK35/SPC1	0.5	1.2	16.6	1.2	9.5
	SSK35/SPC3	0.4	0.8	13.4	1.4	14.4
	SSK35/SPC5	0.8	1.4	9.3	3.1	11.8
	SSK35/SPC7	0.5	0.8	10.8	3.8	13.0
	SSK35/SPC9	0.2	0.7	9.3	1.6	14.4
	SSK35/SPC12	0.6	0.8	11.6	1.4	12.3
	SSK35/SPC16	0.3	0.4	8.9	1.4	14.5
	SSK35/SPC19	0.7	0.9	8.8	2.6	13.1
	Median	**0.5**	**0.8**	**10.1**	**1.5**	**13.0**
Central-east	SSK35/SPC22	0.7	0.7	15.5	4.0	15.9
	SSK35/SPC24	0.7	2.5	8.8	2.9	16.1
	SSK35/SPC26	0.4	0.2	0.9	4.0	7.8
	SSK35/SPC28	0.0	0.3	0.7	7.0	16.5
	SSK35/SPC31	0.9	0.4	11.2	1.3	21.5
	SSK35/SPC33	0.4	0.0	2.2	5.0	12.4
	SSK35/SPC35	0.0	0.7	2.2	1.4	16.5
	SSK35/SPC36	0.6	0.6	7.5	1.4	10.2
	SSK35/SPC37	0.7	1.5	5.9	2.0	7.8
	SSK50/SPC26	0.1	3.6	5.7	1.6	7.4
	Median	**0.5**	**0.8**	**8.9**	**1.6**	**13.0**
South east	SSK50/SPC24	0.3	0.7	5.6	0.7	8.6
	SSK50/SPC25	0.2	0.6	0.4	2.2	8.2
	SSK35/SPC42	0.6	0.2	2.2	0.5	15.4
	SSK35/SPC44	0.2	1.2	3.5	0.9	22.9
	SSK50/SPC10	0.1	0.1	0.5	2.8	7.3
	SSK50/SPC11	0.1	0.3	1.6	2.0	6.1
	SSK50/SPC13	0.2	1.9	3.3	2.0	9.2
	SSK50/SPC15	0.1	1.6	5.6	1.3	8.7
	SSK50/SPC17	0.4	0.1	1.5	0.1	3.9
	SSK50/SPC19	0.2	0.5	0.2	1.0	8.6
	Median	**0.2**	**0.6**	**1.9**	**1.2**	**8.6**
North-west	SSK40/SPC59	0.5	1.3	9.2	9.5	10.0
	SSK40/SPC57	0.0	0.7	6.7	3.5	10.7
	SSK40/SPC60	0.4	1.1	8.2	0.7	12.4
	SSK40/SPC55	0.1	0.8	13.4	1.0	9.8
North-west	SSK40/SPC56	0.0	0.5	10.0	0.6	9.4
	SSK40/SPC58	0.0	0.7	9.9	0.6	10.1
	SSK40/SPC61	0.0	0.7	5.7	0.5	11.4
	SSK40/SPC62	0.0	1.0	8.1	0.5	10.6
	Median	**0.0**	**0.8**	**8.7**	**0.7**	**10.3**
Central-west	SSK40/SPC47	0.0	0.2	6.4	2.3	5.7
	SSK40/SPC51	5.6	8.9	6.7	2.3	5.3
	SSK40/SPC32	0.5	1.2	2.7	1.9	5.2
	SSK40/SPC34	0.3	1.2	2.4	3.5	5.5
	SSK40/SPC36	0.8	1.6	3.9	5.2	3.6
	SSK40/SPC39	7.3	5.7	3.5	3.5	4.7
	SSK40/SPC41	2.7	2.1	3.2	5.4	5.8
	SSK40/SPC46	0.9	0.6	3.7	1.6	5.4
	SSK40/SPC23	0.1	0.2	2.7	2.2	5.7
	SSK40/SPC24	0.1	0.1	3.0	2.5	4.9
	SSK40/SPC17	0.2	0.1	0.3	2.6	5.5
	SSK40/SPC19	0.1	0.6	0.2	2.2	5.7
	SSK40/SPC11	0.0	0.2	2.7	2.6	6.5
	SSK40/SPC12	0.0	0.1	2.9	2.7	5.0
	SSK40/SPC6	0.1	0.2	4.5	2.8	6.4
	SSK40/SPC7	0.3	0.1	3.7	2.9	5.9
	Median	**0.2**	**0.4**	**3.0**	**2.6**	**5.5**
South-west	SSK40/SPC63	0.2	0.1	7.1	2.6	6.5
	SSK40/SPC68	0.1	0.2	1.7	1.8	5.6
	SSK40/SPC69	0.2	0.2	6.9	1.5	5.8
	SSK40/SPC70	0.7	0.2	0.3	1.5	6.2
	SSK40/SPC73	1.0	0.2	0.5	2.6	3.8
	SSK40/SPC74	0.2	0.3	8.4	0.6	8.1
	SSK40/SPC75	0.3	0.6	8.2	2.0	8.1
	SSK40/SPC79	0.2	0.3	0.2	2.1	6.5
	SSK40/SPC80	0.2	0.3	2.9	0.6	10.9
	SSK40/SPC81	0.5	0.2	2.0	0.6	9.5
	SSK40/SPC85	0.7	0.5	1.2	0.6	3.5
	SSK40/SPC86	0.1	0.4	9.8	0.6	5.3
	Median	**0.2**	**0.3**	**2.4**	**1.5**	**6.3**

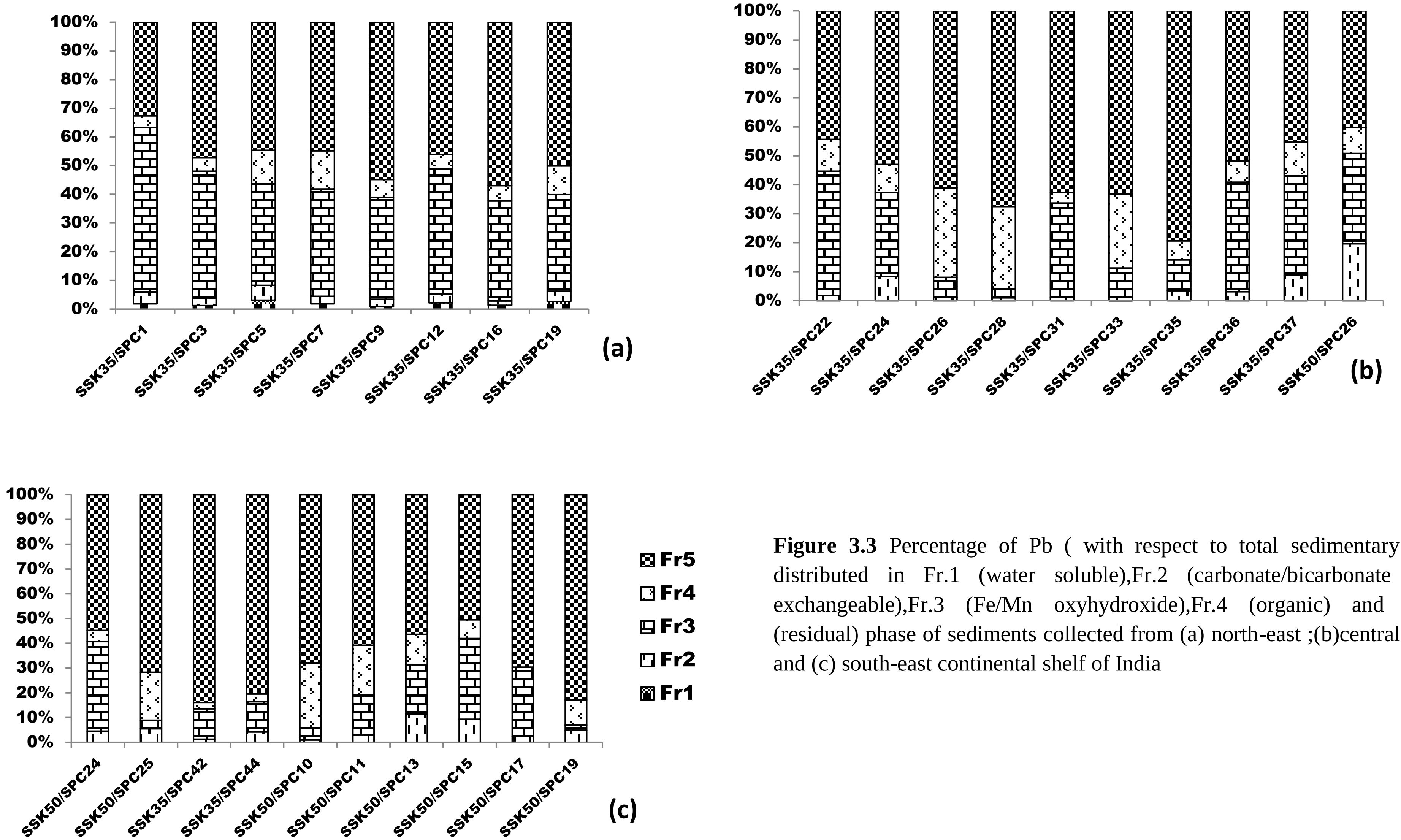


Figure 3.3 Percentage of Pb (with respect to total sedimentary Pb) distributed in Fr.1 (water soluble),Fr.2 (carbonate/bicarbonate and exchangeable),Fr.3 (Fe/Mn oxyhydroxide),Fr.4 (organic) and Fr.5 (residual) phase of sediments collected from (a) north-east ;(b)central-east and (c) south-east continental shelf of India

Geochemical fractionation of sedimentary Pb in the central-eastern continental shelf region (Mahanadi-Godavari rivers derived sediment):

Distribution of Pb in different geochemical phases of the sediments collected from the central-eastern continental shelf region is presented in Figure 3.3b. The concentration of Pb as water soluble (Fr.1), exchangeable, and carbonate/bicarbonate complexes (Fr.2) forms in the studied sediments varied from ~1.2 to 20.2 % (with an average value of ~7%) of the total Pb content in the sediments. The concentrations of these weak Pb complexes (Fr.1+Fr.2) were low in this region.

A major fraction (~3 to 42.2 % with an average value of ~23 %) of the total sedimentary Pb was found to associate with Fe/Mn oxyhydroxide phase (Fr.3). In some of the sediments, sedimentary organic carbon binding phase was an important host for Pb (as shown in Figure 3.2b). About40 to 79 % (ave. ~57%) of total Pb was found to associate with residual phase of the sediments. The absolute concentration of Pb in residual phases of the sediments varied from ~7.4 to 21.5 mg.kg$^{-1.}$

Geochemical fractionation of sedimentary Pb in south-eastern continental shelf area (Granulitic terrain and Cauvery derived sediment):

The distribution pattern of Pb in different binding phases of sediments collected from the south eastern continental shelf of India is presented in Figure 3.3c. The lowest concentration of non-residual Pb (~ 2.1 to 12.2% with an average of ~6.8% of the total Pb) was present as water soluble, exchangeable and carbonate/bicarbonate Pb complexes (Fr.1 and Fr.2) in the sediments. The concentrations of Pb associated with Fe/Mn oxyhydroxide binding phase (~2 to 34 %, with an average ~16% of the total Pb) in the sediments (Figure 3.2c) were comparatively lower than the other two regions of the eastern continental shelf. Association of Pb with sedimentary organic carbon binding phase was found to vary from ~1.4 to 25.6 % (with an average ~11%) of the total Pb content of the sediments. The highest fraction (~54 to 81%, with an average of ~67%) of the total Pb was found to be present in the mineral structure (residual phase) of the sediments which is in average higher than the northern shelf regions (Table 3.2) of east coast of India. Large variation was observed in the concentration of Pb (~6 to 23 mg.kg^{-1}) in residual phase of the sediments.

Geochemical fractionation of sedimentary Pb in north-western continental shelf area (Indus derived sediment):

Distribution of sedimentary Pb in different binding phases of the sediment collected from this region is presented in Figure 3.4a. A very similar geochemical distribution pattern of Pb was observed in the sediments collected from the north-east continental shelf region (Figure 3.3a).

Low concentrations of Pb (~ 2.5 to 5%, ave. ~4% of total Pb) were present as water soluble, exchangeable and carbonate forms (Fr1and Fr2) in the sediments. The major fraction of the total Pb (~30 to 54 %) was associated with Fe/Mn oxyhydroxide phase in the sediments. Low concentration of Pb was found to associate with organic phase in the sediments (~2.4 to 31 % of the total Pb). In majority, the amount of Pb associated with organic carbon was less than 3 % of the total sedimentary Pb. A major fraction of total Pb (~33 to 63 %, ave. ~44%) was present in the residual phase. The absolute Pb content in residual phases of the sediments varied from 9.8 to 12.4 mg.kg^{-1} which was found to have similar variation as the north-eastern region.

Geochemical fractionation of sedimentary Pb in central-western continental shelf (Narmada-Tapti–Mahi derived sediment):

Distribution of Pb in different geochemical phases of the shelf sediments from the central-west coast of India is shown in Figure 3.4b. Relatively higher concentration of Pb (~1.4 to 53 %, ave. ~14% of total Pb) was present as water soluble, exchangeable and carbonates forms (Fr.1andFr.2).The fraction of total Pb associated with Fe/Mn oxyhydroxide (Fr.3) (2 to 44 % with an average of ~ 23% of the total Pb) and organic phase (Fr.4) (8 to 35% with an average of ~22% of the total Pb) was found to be similar. An approximate 19 to 64 % (with an average of ~ 43 %) of the total Pb was in the residual phase of the sediment. The absolute concentration of Pb in the residual phase was relatively lower (3.5 to 6 mg.kg $^{-1}$) than the other regions.

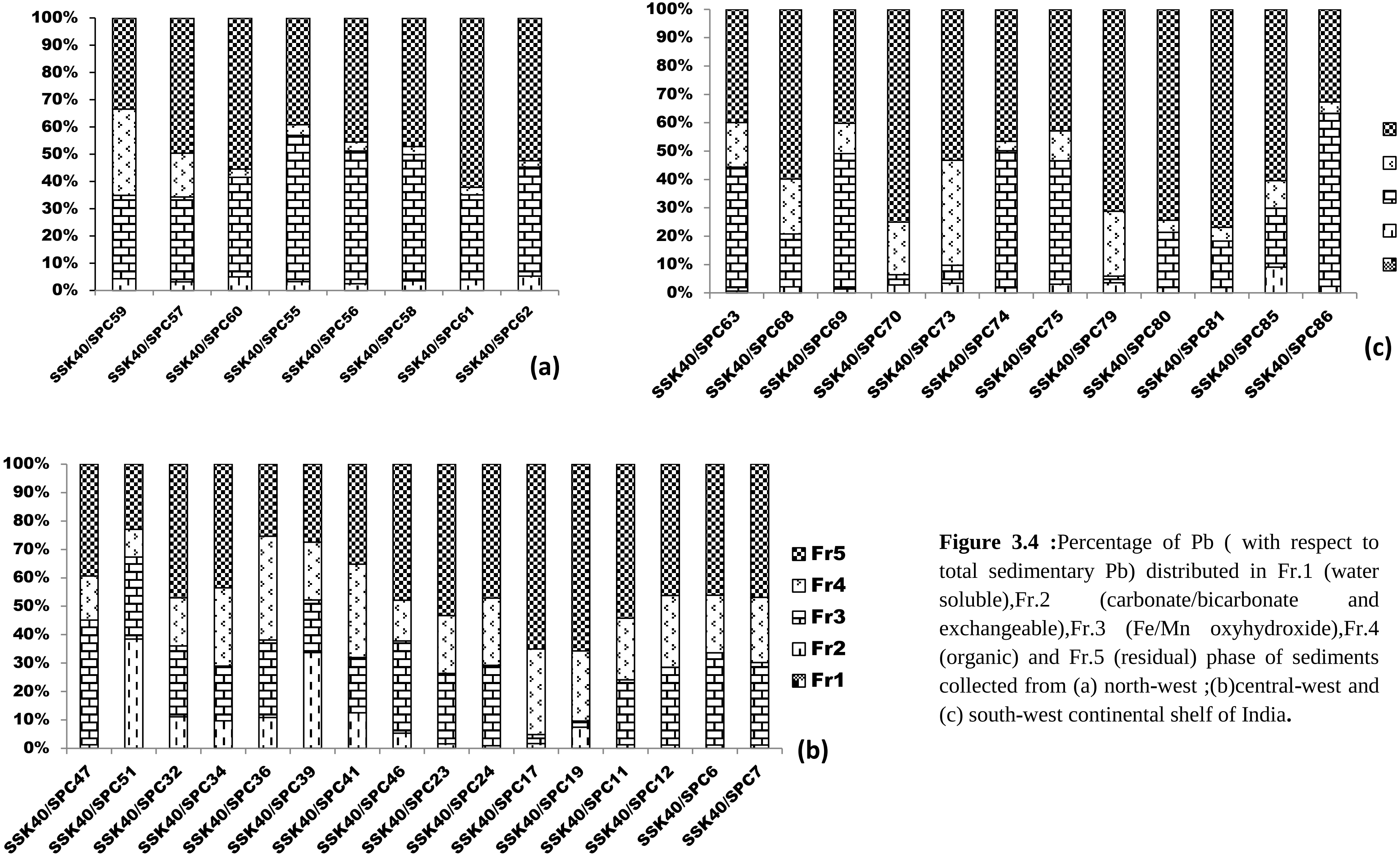


Figure 3.4 : Percentage of Pb (with respect to total sedimentary Pb) distributed in Fr.1 (water soluble),Fr.2 (carbonate/bicarbonate and exchangeable),Fr.3 (Fe/Mn oxyhydroxide),Fr.4 (organic) and Fr.5 (residual) phase of sediments collected from (a) north-west ;(b)central-west and (c) south-west continental shelf of India**.**

Geochemical fractionation of sedimentary Pb in south-west continental shelf (sediments derived from granulitic terrain):

Sedimentary Pb distribution in the different binding phases of the sediments from this region is presented in Figure 3.4c. It shows that ~ 2 to 15 %, (ave.~ 6.3%) of the total Pb was present as water soluble, exchangeable and carbonate/bicarbonate complexes (Fr.1and Fr.2). A major fraction (~2 to 62 %, average ~27 %) of the total Pb was associated with Fe/Mn oxyhydroxide phase. Significant association of Pb (~ 3 to 33 % of the total Pb) was also found with the sedimentary organic matter from this region. Percentage of Pb in the residual phase was comparatively higher than that of the other two regions of the west coast. Approximately 32 to 74 % (with an average of ~54%) of total sedimentary Pb was found to be in the mineral or residual phase.

The geochemical fractionation study in the shelf sediments from the different regions of India revealed that Fe-Mn oxyhydroxide was the major non-residual hosting phase for sedimentary Pb. The association of non-residual Pb with organic phase was found to be less. As Fe/Mn oxyhydroxide phase was found to be major non-residual hosting phase, fractionation studies of Fe was also carried out in order to assess which of the Fe hosting phase is a predominant host of Pb.

3.2.3 Geochemical fractionation of Fe in the continental shelf sediments of India

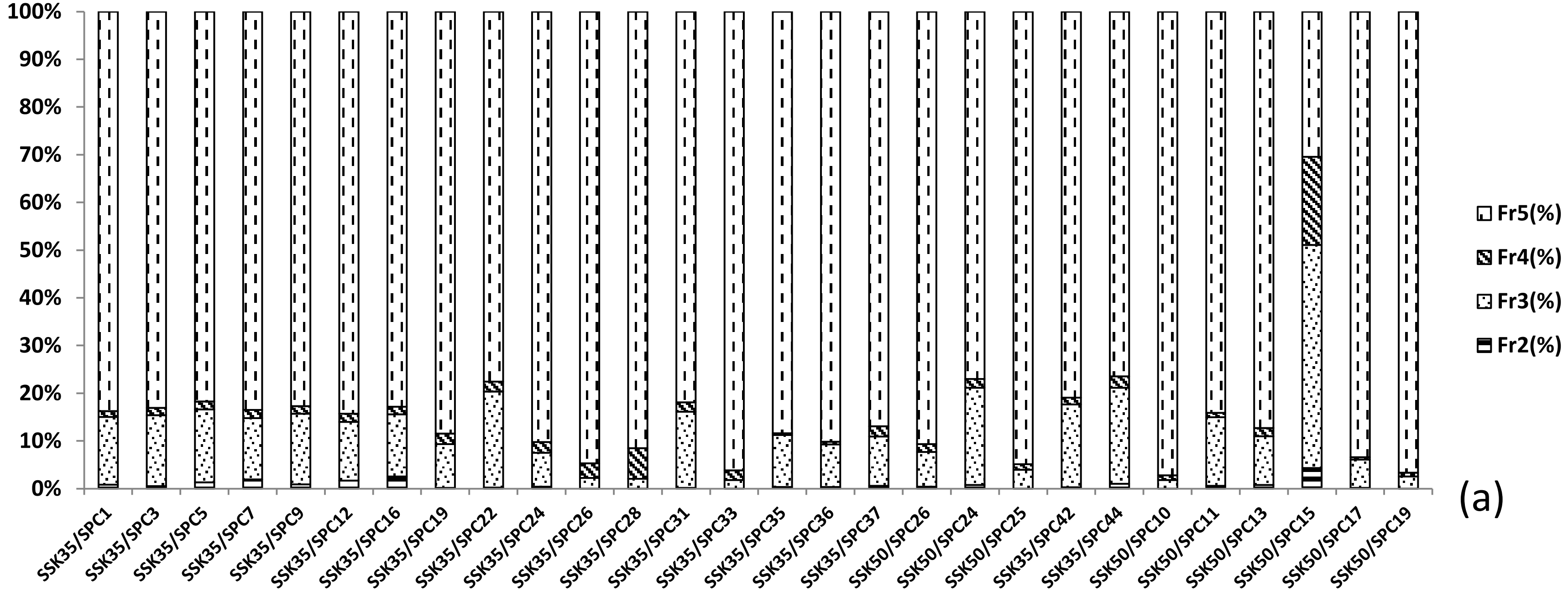
Fe content ($mg.kg^{-1}$) in different geochemical phases of the shelf sediments is given in Table 3.3 and the relative percentage of total Fe distributed in different geochemical phases of the sediments from the eastern and western continental shelves are given in Figures 3.5 (a) and (b) respectively. Fe was present mainly in the residual phase (Fr.5) (~70 to 90%) of the sediments. The oxyhydroxide form of Fe (Fr.3) was found to be ~2 to 47 % of the total Fe content in the sediments. Regional distribution shows that, the highest median concentration of Fe in oxyhydroxide form was in the sediments collected from the north-west (~16% of the total Fe content) followed by north-east (~14%) > south-east (~12%) > central-east (~8%) > north-west (~7%) and > central-west (~6%) continental shelf of India. Approximately 0.4 to 22 % of the total Fe was found to be associated with organic phase of the sediments.

The variation in median concentration of Fe associated with sedimentary organic phase in different shelf regions around India is given below. Highest percentage of total Fe

(~10%) was associated with sedimentary organic matter in the sediments from south–west region, followed by central-west (~5%) > central-east (~2.8 %) > north-east (~1.6%) > north-west (~1.4 %) > south-east (~1.3%) region.

Table 3.3 Concentration of Fe (mg.kg^{-1}) in, water soluble fraction (Fr.1); ion-exchangeable and carbonate/bicarbonate fraction (Fr. 2); Fe/Mn oxyhydroxides i.e., reducible fraction (Fr. 3); sedimentary organic matter and sulfide fraction, i.e., oxidizable fraction (Fr. 4) and residual fraction (Fr. 5) in the studied sediments

Area	Station	Fr.1 (mg.kg^{-1})	Fr.2 (mg.kg^{-1})	Fr.3 (mg.kg^{-1})	Fr.4 (mg.kg^{-1})	Fr.5 (mg.kg^{-1})
North-east	SSK35/SPC1	6.0	596	10310	906	60800
	SSK35/SPC3	6.1	298	8310	869	46500
	SSK35/SPC5	15.1	738	8793	974	47000
	SSK35/SPC7	27.6	1143	7718	1053	50200
	SSK35/SPC9	66.5	509	9353	953	52500
	SSK35/SPC12	52.7	903	6946	949	47600
	SSK35/SPC16	43.8	1720	8985	1092	57100
	SSK35/SPC19	48.4	95	7058	1696	68280.
	Median	**35.7**	**667**	**8552**	**963**	**51350**
Central-east	SSK35/SPC22	69.2	94	16292	1651	62680.
	SSK35/SPC24	71.0	325	6465	2089	82400
	SSK35/SPC26	36.0	48	1639	1533	74860
	SSK35/SPC28	47.5	62	2158	7061	100600
	SSK35/SPC31	53.2	44	8263	1010	42500
	SSK35/SPC33	74.2	71	2123	6834	115400
	SSK35/SPC35	64.2	52	3473	134	28300
	SSK35/SPC36	70.4	234	7426	1744	73920
	SSK35/SPC37	121.0	354	8593	1804	72220
	SSK50/SPC26	19.5	210	4414	1015	54860
	Median	**66.7**	**83.0**	**5439**	**1697**	**73070**
South east	SSK50/SPC24	13.2	187	5100	454	19280
	SSK50/SPC25	17.5	40	2172	651	53520
	SSK35/SPC42	31.8	5	2256	187	10520
	SSK35/SPC44	12.9	135	2960	348	11230
	SSK50/SPC10	28.1	62	1525	843	85600
	SSK50/SPC11	18.7	197	5151	343	30200
	SSK50/SPC13	32.2	232	3567	591	30460
	SSK50/SPC15	29.3	413	4763	1888	3100
	SSK50/SPC17	37.2	53	4006	310	62700
	SSK50/SPC19	28.7	47	1533	490	61000
	Median	**28.4**	**99**	**3263**	**472**	**30330**
North-west	SSK40/SPC59	52.0	473	3149	768	47657
	SSK40/SPC57	73.1	529	3846	537	50340
	SSK40/SPC60	32.6	583.	2695	566	36302
	SSK40/SPC55	73.3	381	5137	1279	48855
North-west	SSK40/SPC56	70	432	5378	890	47895
	SSK40/SPC58	69	539	5549	1187	51235
	SSK40/SPC61	55	449	4758	870	49768
	SSK40/SPC62	50	549	4389	1265	49854
	Median	**69**	**474**	**4758**	**880**	**49312**
Central-west	SSK40/SPC47	137	132	3472	3660	68899
	SSK40/SPC51	98	86	3751	3104	56486
	SSK40/SPC32	204	85	5554	1232	82851
	SSK40/SPC34	72	81	3917	255	82125
	SSK40/SPC36	420	83	6361	1429	81431
	SSK40/SPC39	329	178	4024	674	70720
	SSK40/SPC41	767	205	3731	787	67985
	SSK40/SPC46	315	116	3568	3102	68075
	SSK40/SPC23	112	159	4516	5939	58155
	SSK40/SPC24	991	45.2	5257	1548	55219
	SSK40/SPC17	112	26.3	1838	4966	54798
	SSK40/SPC19	61	88.3	518	8379	39974
	SSK40/SPC11	60	130	5335	9947	58299
	SSK40/SPC12	55	436	7864	4707	62149
	SSK40/SPC6	68	317	9506	21874	97733
	SSK40/SPC7	382	58	6178	9798	44935
	Median	**124**	**88**	**4270**	**3382**	**65067**
South-west	SSK40/SPC63	1694	388	7973	11581	31794
	SSK40/SPC68	159	145	5735	6353	22439
	SSK40/SPC69	51	115	6641	7169	31265
	SSK40/SPC70	191	26	263	664	18535
	SSK40/SPC73	19	24	632	1990	21555
	SSK40/SPC74	24.2	246	9820	6894	40076
	SSK40/SPC75	30.3	206	9287	6821	31637
	SSK40/SPC79	46.3	29.8	256	965	43062
	SSK40/SPC80	46.8	964	13555	1359	17654
	SSK40/SPC81	43.6	213	3708	725	11480
	SSK40/SPC85	36	83.0	1205	162	7351
	SSK40/SPC86	37.5	85	8861	4072	21324
	Median	**45**	**130**	**6188**	**3031**	**21997**


100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
SSK35/SPC1
SSK35/SPC3
SSK35/SPC5
SSK35/SPC7
SSK35/SPC9
SSK35/SPC12
SSK35/SPC16
SSK35/SPC19
SSK35/SPC22
SSK35/SPC24
SSK35/SPC26
SSK35/SPC28
SSK35/SPC31
SSK35/SPC33
SSK35/SPC35
SSK35/SPC36
SSK35/SPC37
SSK50/SPC26
SSK50/SPC24
SSK50/SPC25
SSK35/SPC42
SSK35/SPC44
SSK50/SPC10
SSK50/SPC11
SSK50/SPC13
SSK50/SPC15
SSK50/SPC17
SSK50/SPC19
Fr5(%)
Fr4(%)
Fr3(%)
Fr2(%)
(a)

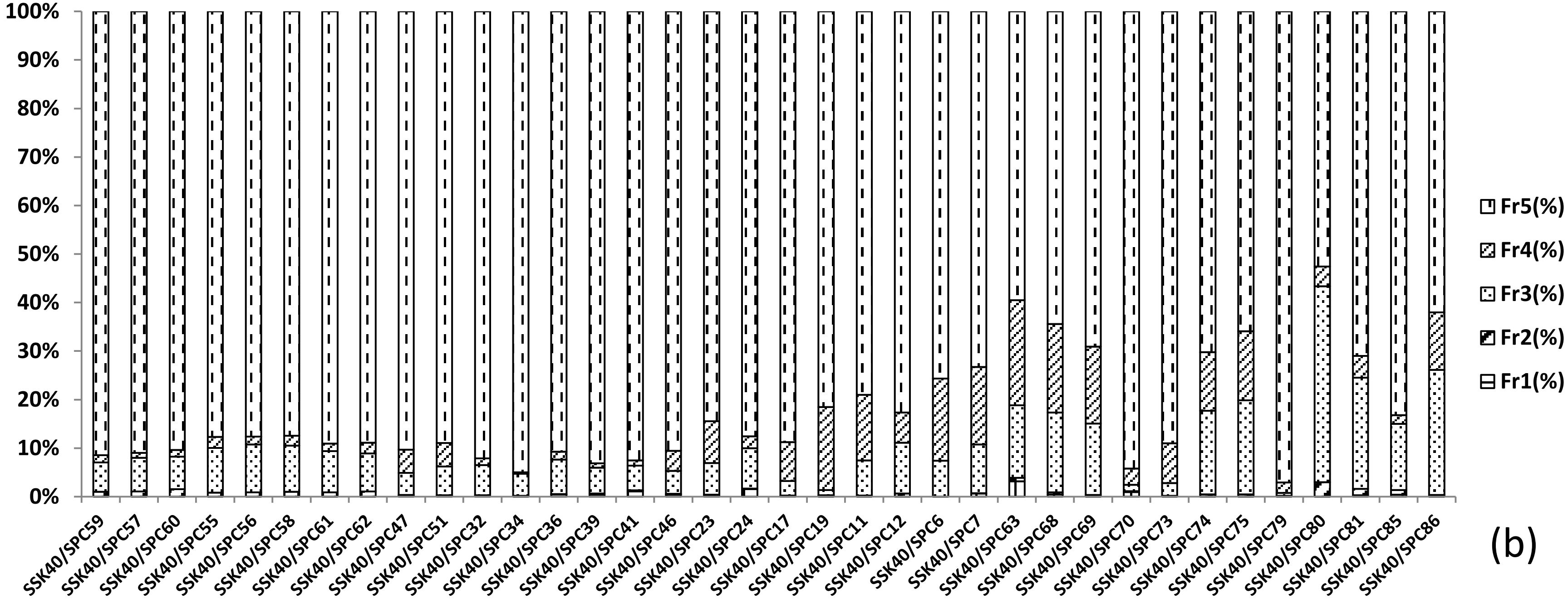


Figure 3.5 Percentage of Fe (with respect to total sedimentary Fe) distributed in Fr.1 (water soluble),Fr.2 (carbonate/bicarbonate and exchangeable),Fr.3 (Fe/Mn oxyhydroxide),Fr.4 (organic) and Fr.5 (residual) phase of sediments collected from (a) eastern and (b) western continental shelf of India.

3.3 Discussion

3.3.1 Diverse geology of India and its impact on total Pb distribution in the continental shelf sediments around India

Distribution of total Pb content (varying from 1.5±0.1 to 36.7±0.4 $mg.kg^{-1}$) in the shelf sediments around India was found to vary regionally. The diverse geology of Indian continent (Krishnan, 1968; Naqvi, 2005) is one of the reasons for this regional variation in sedimentary Pb content in the continental shelves areas (e.g., Chakraborty et al., 2015). Sediments derived from Himalayan rocks transported by Ganga-Brahmaputra and Indus rivers in the northern part of continental shelves (north-east and north-west coast region of India respectively) was found to have relatively higher concentration of sedimentary Pb (26-29 $mg.kg^{-1}$ in the north-east and 18-30 $mg.kg^{-1}$ in the north-west).

Concentration of sedimentary Pb in the central eastern shelf was found to vary from ~13 to 36.7 $mg.kg^{-1}$.However, the geology of adjacent land mass has been reported to consist of different types of rocks (basalt, metamorphosed granite and sedimentary rocks) (Krishnan, 1968;Chakrapani and Subramanian,1999). It was extremely difficult to pin point the source rocks of these sediment samples by relating the sedimentary Pb content possibly because of large variation and diverse geology. The central region of the western shelf was found to have the lowest sedimentary Pb content among the other five regions. This low concentration can be attributed mainly to the mafic nature of the source rocks (Krishnan, 1968; Rao and Rao, 1995; Kurian et.al., 2013) in the adjacent land mass which is known as 'Deccan Trap Basalt' of peninsular India. However, the concentration (6 -24 $mg.kg^{-1}$) of total sedimentary Pb in this region was higher compared to the Pb content reported in the mafic rocks. This enriched concentration of Pb was either due to the mixing of felsic component or the contribution from anthropogenic activities to the shelf sediment. Mixed sources of Deccan basalts and South Indian granulites were reported for shelf sediments off Karnataka (Kurian et al., 2013). The sources of sedimentary Pb in this region are discussed later.

The median concentrations of Pb in the sediments from the southern part of both the shelves (16.1 and 12.6 $mg.kg^{-1}$ in the eastern and western region respectively) was close to the Pb content found in the probable source rocks of the adjacent land in this region [granulites (9.8 $mg.kg^{-1}$) to gneisses,schists (16 $mg.kg^{-1}$) (Wedepohl, 1978)]. The granulitic terrain of southern India was probably the major contributor of sediments to the shelves of southern India (e.g., Nath et al., 2000; Kurian et al., 2013).

In addition to the source rock contribution, Pb can be contributed from other geochemical (atmosphere, water column etc.) and also the anthropogenic sources which is difficult to be assessed from total Pb data. Thus, a geochemical fractionation study of Pb in these sediments was performed and the data are discussed below.

3.3.2 Major hosting phases of Pb and identifying the factors controlling Pb distribution in shelf sediments

North-eastern and north-western shelf:

The northern regions of eastern and western continental shelves of India receive sediments from similar source (Himalayan rocks) and the geochemical distribution pattern of Pb in different binding phases also showed the similarities (Figure 3.3(a) and 3.4(a)). The concentration of Pb as water soluble, exchangeable and carbonate/bicarbonate complexes (Fr.1and Fr.2) did not increase with the increasing total Pb loading in the sediment from the north-eastern continental shelf (Table 3.4).This indicates that other Pb-binding ligands were available to form thermodynamically more stable Pb complexes in the sediments. However, in the north-western shelf, an increase in concentration of Pb in Fr.1 and Fr.2 (0.5 to 1.8 mg.kg $^{-1}$) with increasing Pb loading in the sediment (Table 3.7, $r^2=0.77$ and 0.70, $p<0.01$) was observed. This is probably due to the high carbonate content (~15%) of the sediment which provided enough binding sites to host Pb. Conversely, in the north-eastern shelf, $CaCO_3$ content was relatively low (~2.5%) and thus the concentration of Pb did not increase in Fr1 and Fr2 with the increasing total Pb loading in the sediments. Association of Pb with Fe/Mn oxyhydroxide phase gradually increased with the increasing total Pb content in the sediments from both the regions (Tables 3.4 and 3.5). This indicates that Fe/Mn oxyhydroxide was the major binding phase for Pb in the sediments, which is probably due to the high Pb adsorption efficiency on Fe/Mn oxyhydroxide in the sediment Pb in Fe/Mn oxyhydroxide. It has been reported that Fe-based nano particles are promising adsorbent for Pb. Goethite (α-FeOOH) and lepidocrocite (γ-FeOOH), two different phases of Fe oxyhydroxide nano-particles has been reported to have high adsorption capacity of Pb in aqueous solution (McKenzie et al., 1980; Babel et al., 2003; Liu et al., 2008). Co-precipitation of Fe/Mn oxyhydroxides in water column along with Pb and adsorption of Pb on their surface also probably increased Pb concentration in Fe/Mn oxyhydroxide phase of the sediments in this region.

However, Pb showed weak affinity towards the sedimentary organic carbon binding phases in the studied samples. Less amount of total Pb was found to be associated with organic carbon (C_{org}) phase in these sediments [Figure 3.3a and 3.4a]. The association of Pb with C_{org} (Fr. 4) did not increase with the increasing total Pb loading in the sediments from the north-eastern shelf region (Table 3.4). This is in agreement with the findings of Chakraborty et.al (2015a) that sedimentary organic carbon does not control the mobility of Pb in this region. However, association of Pb with Fr.4 was found to be increased with increasing Pb/C_{org} (Pb/C_{org} represents the normalised concentration of Pb with respect to sedimentary organic carbon content) inthe north-western shelf sediments (Table 3.5). Nevertheless, it is important to note that the concentration of C_{org} was low in this region and thus the association of Pb with this phase was low. Fe/Mn oxyhydroxide was also found to control Pb speciation in both the regions. The concentration of Pb in the residual phase in the north-eastern shelf varied from ~9.5 to 13 mg.kg^{-1} and very close to that in western region (varied from ~9.4 to 12.4 mg.kg^{-1}). The concentration of Pb in residual phases indicate the acidic nature of source rock and the similarity in sedimentary residual Pb of both these regions implies that the source rocks of the sediments of both the regions were similar in nature (from Himalaya). This is interesting since, the Indus River which would have contributed most of the sediments to the northwestern shelf, has been reported to carry a significant portion of Karakoram derived material in addition to that from Higher Himalayas (Clift et.al.,2002) while the major source of north-eastern shelf would be Ganges-Brahmaputra rivers. The Ganga Plain sediments were found to be derived gneiss and Cambro-Ordovician granites of High Himalayan Crystalline series IHHCS) (Galy and France-Lanord, 2001; Singh 2009). Homogenization and thorough mixing of lithologic and chemical diversity in the denudation regime (e.g., Dutta and Subramanian, 1998) may be responsible for the similar composition of residual portion of sediments from north-western and north-eastern shelves. A significant difference in concentration between the total sedimentary Pb content and the residual Pb content

Table 3.4 Correlation coefficient matrix of five geochemical phases (Fr.1, Fr.2, Fr.3, Fr.4, and Fr.5) of Pb (mg.kg $^{-1}$), total Pb (mg.kg $^{-1}$),Pb/C_{org} and $CaCO_3$ in the sediments from North-eastern continental shelf of India

	Pb-Fr.1	**Pb-Fr.2**	**Pb-Fr.3**	**Pb-Fr.4**	**Pb-Fr.5**	**TM(Pb)**	**Pb(T)/C_{org}**	**CaCO3**
Pb-Fr.1	1.00							
Pb-Fr.2	0.73	1.00						
Pb-Fr.3	-0.06	0.36	1.00					
Pb-Fr.4	0.51	0.26	-0.41	1.00				
Pb-Fr.5	-0.58	-0.78	-0.62	-0.03	1.00			
TM(Pb)	-0.12	0.21	**0.77**	0.00	-0.22	1.00		
Pb(T)/C_{org}	0.03	-0.43	-0.83	0.15	0.46	-0.82	1.00	
CaCO3	0.46	0.39	0.09	0.03	-0.47	-0.17	0.08	1.00

Correlation is significant at the 0.01 level (2-tailed). Bold numbers represent statistical significant correlation

Table 3.5 Correlation coefficient matrix of five geochemical phases (Fr.1, Fr.2, Fr.3, Fr.4, and Fr.5) of Pb (mg.kg $^{-1}$), total Pb (mg.kg $^{-1}$),Pb/C_{org} and $CaCO_3$ in the sediments from North-western continental shelf of India

	Pb-Fr.1	**Pb-Fr.2**	**Pb-Fr.3**	**Pb-Fr.4**	**Pb-Fr.5**	**TM(Pb)**	**Pb(T)/C_{org}**	***CaCO3***
Pb-Fr.1	1.00							
Pb-Fr.2	0.83	1.00						
Pb-Fr.3	0.07	0.01	1.00					
Pb-Fr.4	0.63	0.59	-0.03	1.00				
Pb-Fr.5	0.34	0.33	-0.62	-0.21	1.00			
TM(Pb)	**0.77****	**0.70****	0.44	**0.84***	-0.27	1.00		
Pb(T)/C_{org}	0.91	0.70	0.02	**0.86***	0.10	0.85	1.00	
CaCO3	-0.36	0.33	0.49	-0.30	-0.49	-0.12	-0.36	1.00

*Correlation is significant at the 0.01 level (2-tailed).

** Correlation is significant at the 0.02 level (2-tailed). Bold numbers represent statistical significant in the studied sediment may be due to significant anthropogenic input of Pb (fluvial and atmospheric) to these shelves (Table 3.2).

Central-eastern shelf:

Geochemical fractionation study of sedimentary Pb in this region suggests that, except for few sporadic locations, Fe/Mn oxyhydroxide phase was the major hosting phase for Pb (~3 to 42.2 % of the total Pb). The increasing concentration of total sedimentary Pb was found to correlate with increased Pb association in Fe/Mn oxyhydroxide hosting phase (Table 3.6, $r^2=0.88$, $p<0.01$).This probably suggests that there were enough Pb-binding sites in the Fe/Mn oxyhydroxide phase of the studied sediments. However, the sedimentary organic carbon content played an important role in controlling Pb distribution in some of the sediment samples. It was found that the sediments having higher concentration of C_{org} (≥ 1%, Table3.1) showed the significant association of Pb with organic binding phases in the sediments.A weak correlation between Pb/ C_{org} ratio and the Pb bound to organic phase (Fr 4) (Table 3.6) suggest that C_{org} was not the key factor controlling the sedimentary Pb speciation in this region.

The concentration of Pb content in the residual phase (~40 to 79 %, average ~57%) was found to increase with increasing concentration of total sedimentary Pb (~7.4 to 21.5 $mg.kg^{-1}$) (Table 3.6, $r^2=0.81$, $p<0.01$). The large variation in concentration of sedimentary Pb in the residual phase (see Table 3.2) was indicative of the presence of mixed sources of mafic and felsic composition in the sediments from this region. It has already been reported that marine sediments from this region receives sediment from Mahanadi, Godavari and Krishna river which flow through both mafic and felsic geological formations (Chakraborty et al., 2015 and references therein) and hence, the residual phase of sedimentary Pb showed the signature of mixed sources.

Central-western shelf:

The geochemical distribution pattern of sedimentary Pb was found to be different in this region from the other shelf regions. Association of Pb with Fr.1 and Fr.2 phases was found to increase with the increasing total Pb loading (Table 3.7, $r^2=0.86$ and 0.90, $p<0.01$) in the sediments from this region. The presence of high carbonate content (Table 3.1) in the sediment increased the concentration of Pb in Fr1+Fr2 forms. Concentrations of Pb associated with Fe/Mn oxyhydroxide and organic phases of the sediments were very similar (Table 3.2) in this region. It was found that association of

Pb gradually increased in both the phases with increasing Pb loading in the sediment (Table 3.7, $r^2=0.74$ and 0.64 ($p<0.01$) respectively). This indicates that sufficient uncomplexed Pb-binding sites were available in the sediments. Concentrations of sedimentary Fe and C_{org} content in the sediments were high in this region and thus, there was almost uniform distribution of sedimentary Pb in these two binding phases (Figure 3.4 b). The variation in concentration of Pb (3.6 to 6.5 $mg.kg^{-1}$) in the residual phase of the sediment was not dependent on the total Pb content of the sediments from this region (Table 3.7). The concentration of Pb in residual phase of the sediments in this region was relatively low (3.6 to 6.5 $mg.kg^{-1}$) compared to the residual Pb concentration in the other shelf sediments. The Pb content in the residual phase of the studied samples 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).

Table 3.6 Correlation coefficient matrix of five geochemical phases (Fr.1, Fr.2, Fr.3, Fr.4, and Fr.5) of Pb (mg.kg $^{-1}$), total Pb (mg.kg $^{-1}$), Pb/C$_{org}$ and CaCO3 in the sediments from Central-eastern continental shelf of India

	Pb-Fr.1	**Pb-Fr.2**	**Pb-Fr.3**	**Pb-Fr.4**	**Pb-Fr.5**	**TM(Pb)**	**Pb(T)/C$_{org}$**	**CaCO3**
Pb-Fr.1	1.00							
Pb-Fr.2	-0.06	1.00						
Pb-Fr.3	0.60	0.11	1.00					
Pb-Fr.4	-0.33	-0.41	-0.11	1.00				
Pb-Fr.5	0.18	-0.32	0.51	0.08	1.00			
TM(Pb)	0.47	-0.03	**0.88**	0.00	**0.81**	1.00		
Pb(T)/C$_{org}$	-0.80	-0.11	-0.73	0.03	-0.08	-0.55	1.00	
CaCO3	-0.38	-0.49	-0.63	0.78	-0.19	-0.44	0.24	1.00

Correlation is significant at the 0.01 level (2-tailed). Bold numbers represent statistical significant correlations.

Table 3.7 Correlation coefficient matrix of five geochemical phases (Fr.1, Fr.2, Fr.3, Fr.4, and Fr.5) of Pb (mg.kg $^{-1}$), total Pb (mg.kg $^{-1}$), Pb/C$_{org}$ and CaCO3 in the sediments from Central-western continental shelf of India

	Pb-Fr.1	Pb-Fr.2	Pb-Fr.3	Pb-Fr.4	Pb-Fr.5	TM(Pb)	Pb(T)/C$_{org}$	CaCO3
Pb-Fr.1	1.00							
Pb-Fr.2	0.91	1.00						
Pb-Fr.3	0.50	0.51	1.00					
Pb-Fr.4	0.36	0.43	0.12	1.00				
Pb-Fr.5	-0.29	-0.29	-0.05	-0.38	1.00			
TM(Pb)	0.86	0.90	0.74	0.64	-0.18	1.00		
Pb(T)/C$_{org}$	0.57	0.47	0.34	0.81	-0.13	0.68	1.00	
CaCO3	-0.18	-0.11	-0.18	-0.21	0.49	-0.16	-0.32	1.00

Correlation is significant at the 0.01 level (2-tailed). Bold numbers represent statistical significant correlations

Southern parts of eastern and western shelf:

Sediments collected from the southern parts of both the shelves were found to have similar concentration of total sedimentary Pb. This probably indicates the possible similar source rocks. It has been reported that Precambrian gneiss and schist are the major source rocks in this region. Thus, a very similar geochemical distribution pattern of Pb in the different binding phases of the sediments along the shelf of eastern and western part was also observed (Figure 3.3c and Figure 3.4c respectively).

Due to the presence of high carbonate content in both the regions, a considerable percentage of total Pb was found to be present as carbonate/bicarbonate complexes (as indicated by high Pb in Fr1+ Fr2). Formation of labile and weak Pb-sediment complexes increased with increasing Pb loading in the sediment collected from the eastern shelf. However, formation of weak Pb complexes (Fr1+Fr2) did not increase with the increasing total Pb loading in the sediments from the south-western shelf region. This clearly indicates that suitable binding sites in other geochemical phases of the sediment were available for hosting Pb in the sediments collected from the western shelf. However, association of Pb with the organic phase did not increase with the increasing Pb loading in the sediments from both the shelves (Tables 3.8 and 3.9). The poor correlation between Pb/C_{org} ratio and the total Pb loading (Tables 3.8 and 3.9) clearly indicates that sedimentary organic matter were not available for hosting Pb. Association of Pb with Fe/Mn oxyhydroxide phase in the sediments from both the shelves was increased with increasing Pb loading in the sediments (Tables 3.8 and 3.9).

It is interesting to note that association of Pb with sedimentary organic matter (with ~1.1%) was more than its association with Fe/Mn oxyhydroxide (Fe_T = 7.4%) phase in the sediment collected from the central west coast of India. However, sediments from south-western region where Fe content (~3.5%) was lower and C_{org} content (2.18 %) was relatively higher than the central west coast region showed an opposite trend and probably suggest that the concentration of sedimentary Fe in oxyhydroxide form is more important than the total sedimentary Fe content to adsorb Pb.

Percentage of Pb in the residual phase was comparatively higher in the southern part of both the shelves than their respective northern regions. Approximately ~54 to 81% of total Pb (with an average of ~67%) in the south-eastern shelf and 32 to 74 % of total Pb (with an average of ~54%) in the south-western shelf was found to be in the mineral or residual phase of the sediment. A significant increase in Pb concentration

Table 3.8 Correlation coefficient matrix of five geochemical phases (Fr.1, Fr.2, Fr.3, Fr.4, and Fr.5) of Pb ($mg.kg^{-1}$), total Pb ($mg.kg^{-1}$), Pb/C_{org} and CaCO3 in the sediments from South-eastern continental shelf of India

	Pb-Fr.1	**Pb-Fr.2**	**Pb-Fr.3**	**Pb-Fr.4**	**Pb-Fr.5**	**TM(Pb)**	**Pb(T)/C_{org}**	**CaCO3**
Pb-Fr.1	1.00							
Pb-Fr.2	-0.41	1.00						
Pb-Fr.3	-0.15	0.62	1.00					
Pb-Fr.4	-0.64	0.10	-0.32	1.00				
Pb-Fr.5	0.15	0.30	0.24	-0.24	1.00			
TM(Pb)	-0.03	**0.56****	**0.54****	-0.17	**0.93***	1.00		
Pb(T)/C_{org}	-0.25	-0.16	-0.54	0.44	-0.36	-0.44	1.00	
CaCO3	-0.05	**0.50****	-0.74	0.25	-0.24	-0.45	0.68	1.00

*Correlation is significant at the 0.01 level (2-tailed).

** Correlation is significant at the 0.1 level (2-tailed). Bold numbers represent statistical significant

Table 3.9 Correlation coefficient matrix of five geochemical phases (Fr.1, Fr.2, Fr.3, Fr.4, and Fr.5) of Pb ($mg.kg^{-1}$), total Pb ($mg.kg^{-1}$), Pb/C_{org} and CaCO3 in the sediments from South-western continental shelf of India

	Pb-Fr.1	**Pb-Fr.2**	**Pb-Fr.3**	**Pb-Fr.4**	**Pb-Fr.5**	**TM(Pb)**	**Pb(T)/C_{org}**	**CaCO3**
Pb-Fr.1	1.00							
Pb-Fr.2	0.09	1.00						
Pb-Fr.3	-0.57	0.17	1.00					
Pb-Fr.4	0.16	-0.32	-0.16	1.00				
Pb-Fr.5	-0.44	-0.07	0.16	-0.34	1.00			
TM(Pb)	-0.62	0.09	**0.89***	-0.13	**0.56****	1.00		
Pb(T)/C_{org}	-0.33	-0.51	0.73	0.44	0.04	0.63	1.00	
CaCO3	-0.12	-0.03	-0.07	0.16	-0.29	-0.22	0.19	1.00

*Correlation is significant at the 0.01 level (2-tailed).

** Correlation is significant at the 0.05 level (2-tailed). Bold numbers represent statistical significant in the residual phase was found with increasing total Pb loading in the sediments from both the southern regions (Table 3.8, $r^2=0.93$, $p<0.01$ and Table 3.9, $r^2=0.54$, $p<0.05$ respectively). However, unlike the total Pb content, residual Pb from these two regions showed dissimilarity. In the south-eastern region residual Pb varied from ~6 to 23 $mg.kg^{-1}$ whereas in the western part residual Pb varied from 3.5 to 10.9 $mg.kg^{-1}$. However, while assessing the residual Pb in each sediment samples, it was found that a considerable number of sediments contain similar residual Pb content in both the shelves and it was close to the concentration of Pb reported in granulites (9.8 $mg.kg^{-1}$) (Wedepohl,1978). This is consistent with the interpretations drawn from clay mineral studies (Chauhan and Gujar, 1996) from the shelf in the southern tip of India. They found that the sediments in these areas were derived from chemical weathering of the granulitic rocks in the catchment area of the Karmana, Neyyar and Tambraparni Rivers. Rest of the samples in both the regions had different residual Pb content. In the eastern shelf, the concentration of residual Pb in rest of the samples was higher than the granulitic concentration. However in the western shelf, residual Pb content in rest of the samples were of mafic signature (Table 3.2) .This probably is due to the coastal currents which would have transported sediments from northern regions to the south.

The geochemical fractionation study of Pb in the shelf sediments around India revealed the following:

(a) Fe/Mn oxyhydroxide was the major non-residual hosting phase followed by sedimentary organic binding phase for Pb.

(b) Total sedimentary Fe and organic carbon content did not control Pb speciation in the continental shelf sediments.

(c) The concentration of labile and mobile Pb complexes in sediment was found to depend on sedimentary carbonate content.

In order to understand the geochemical processes that control the distribution and speciation of Pb with different binding phases of the sediment, geochemical fractionation of Fe was carried out.

3.3.3 Effect of Fe fractionation on geochemical association of Pb in sediments

Distribution of Fe in different binding phases of the sediments is shown in Figure 3.4 (Table 3.3). The concentration of Fe in Fr.3 represents the amorphous Fe-oxyhydroxide form which was the major binding phases for Pb. While, the Pb bound to

Fe-oxyhydroxide did not show a positive correlation with the total Fe content, but a positive correlation was seen between the concentration of Pb associated with Fe/Mn oxyhydroxide phase and the concentration of Fe in oxyhydroxide form (Table 3.10) in the sediments.

Table 3.10 Correlation coefficient matrix of five geochemical phases (Fr.1, Fr.2, Fr.3, Fr.4, and Fr.5) of Fe (mg.kg $^{-1}$),C_{org} (%)and two geochemical phases (Fr.3 and Fr.4) of Pb (mg.kg $^{-1}$) in the eastern continental shelf sediments of India

	Fe-Fr.1	**Fe-Fr.2**	**Fe-Fr.3**	**Fe-Fr.4**	**Fe-Fr.5**	**C_{org}**	**Pb-Fr.3**	**Pb-Fr.4**
Fe-Fr.1	1.00							
Fe-Fr.2	-0.08	1.00						
Fe-Fr.3	0.11	0.46	1.00					
Fe-Fr.4	0.16	-0.22	0.40	1.00				
Fe-Fr.5	0.09	-0.14	0.06	0.20	1.00			
C_{org}	0.13	-0.30	0.39	**0.77**	-0.18	1.00		
Pb-Fr.3	0.02	0.61	**0.64**	0.05	0.03	0.07	1.00	
Pb-Fr.4	0.22	-0.12	-0.15	0.01	0.39	-0.09	-0.34	1.00

Correlation is significant at the 0.01 level (2-tailed).
Bold numbers represent statistical significant correlatio

This finding clearly suggests that association of Pb with Fe/Mn oxyhydroxide phase depend not on the total sedimentary Fe content but on the concentration of Fe in oxyhydroxide form. It was observed in this study that in spite of having lower total sedimentary Fe content in the sediments, high association of Pb with Fe/Mn oxyhydroxide phase was seen in the sediments from the north-east compared to central-east and the south-west compared to central west regions (Table 3.1). It was found that higher concentration of Fe as oxyhydroxide form in the sediments collected from the north-east and south west coast (Table 3.3) is responsible for the higher association of Pb with Fe/Mn oxyhydroxide phase compared to the central-east and central-west (where total Fe content was higher but its oxyhydroxide form was less than the southern part) respectively. A part of sedimentary Fe was also found to be associated with organic phase of sediment (Table 3.9) and the association was found to be increased with increasing concentration of C_{org} in the shelf sediments (Table 3.10).

3.4 Conclusions

This study suggests that, geogenic (residual Pb) sources of Pb controlled total sedimentary Pb concentration specifically in the central-east, south-east and south-west coast regions of India. However, significant anthropogenic Pb (non-residual Pb) input was observed in the other continental shelve areas (such as north-east, north-west and central-west coast of India). Total sedimentary Fe and organic carbon content did not control Pb speciation in continental shelf sediments. The concentration of sedimentary Fe/Mn in oxyhydroxide forms and quantity and quality of sedimentary organic matter determined the distribution and speciation of Pb in the continental shelf sediments. Fe/Mn oxyhydroxide phase was the major hosting phase for sedimentary Pb. However, sedimentary organic matter also acted as host for Pb in some sediment. The distribution and speciation of Pb in the sediment was found to depend on the relative abundance of the above two binding phases in the sediment. Concentration of Pb in residual phase was found to carry signature of the source rocks of the sediments.

3.5 Global Implication

This study reveals that Fe(III)-oxyhydroxide phase is the major hosting phase for non-residual Pb in the continental shelf sediments around India. It is well known that Pb association with Fe/Mnoxyhydroxide phases 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). 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 the coastal areas around India in future.

Chapter 4

Stability and lability of sedimentary Pb complexes: A kinetic fractionation study

4.1 Introduction

Geochemical fractionation (or operational speciation) of sedimentary Pb, discussed in the previous chapter provided the knowledge of major hosting phases of Pb and the factors which control the distribution and speciation of Pb in the shelf sediments around India. However, the knowledge of geochemical fractionation of Pb in sediment is not sufficient enough to understand the stability or lability of Pb complexes in a given system. Hence, in addition to geochemical fractionation, kinetic fractionation study was carried out to understand the nature of the Pb-sediment complexes (labile or inert) and their corresponding dissociation rate constants (k_d).

It has been well documented that sedimentary organic matter and Fe-oxyhydroxide are the major hosting phases of Pb in marine sediment (Tessier and Campbell, 1987; Coston et al., 1995; Takahasi et al., 2007; Chakraborty et al., 2012 and Chapter 3 of this thesis) Therefore, 21 sediment samples were selected (on the basis of their varying sedimentary organic carbon and Fe-oxyhydroxide content) around India for kinetic fractionation study. The results of kinetic fractionation study of Pb-sediment complexes are further combined with the outcome of the geochemical fractionation study (presented in the previous chapter) to identify the labile Pb-complexes and the key factors that control stability and lability of Pb-complexes in marine sediments.

4.2 Results

4.2.1 Concentration of total sedimentary organic carbon (C_{org}), $\delta^{13}C_{org,}$, $CaCO_3$ (%) ,total Fe (%) and its oxyhydroxide form ($mg.kg^{-1}$),total sedimentary Pb and Pb in different geochemical phases in the sediments

The concentrations of total Pb ($mg.kg^{-1}$) and its important binding phases sedimentary organic carbon (C_{org}) (%), total Fe (%) and its oxyhydroxide phase ($mg.kg^{-1}$) in the selected sediments from eastern and western continental shelves are presented in Tables 4.1 and 4.2 respectively. Percentage of total sedimentary Pb distributed in different geochemical phases of the sediments from eastern and western shelf is also presented in Tables 4.3 and 4.4 respectively. These data (presented in Tables 4.1, 4.2, 4.3 and 4.4) except the $\delta^{13}C_{org}$ values have already been presented and discussed in the previous chapter (Chapter 3). However, for the sake of convenience, these data of selected sediment samples are again presented with the new data in this chapter.

The concentration of C_{org} in the sediments collected from the eastern continental shelf ranged from 0.49 to 2.36 % (Table 4.1). The sediments from this region were found to have lower C_{org} content (<1%) except in few sediment samples.$\delta^{13}C_{org}$values (presented in Table 4.1) in these sediments ranged from -19.61 to -25.08‰. $CaCO_3$ content was low in most of the locations and found to vary from 1.8 to 74 % in the sediments (see Table 4.1).The Fe concentration showed large variations (0.3 to 11.8 %). The oxyhydroxide form of Fe (a major binding phase for Pb) was found to vary from 2123 to 10310 $mg.kg^{-1}$. The concentration of Pb varied from 15.9±0.3 to 36.7±0.4 $mg.kg^{-1}$ in the sediments (Table 4.1).

The concentration of C_{org} in the sediments from the western continental shelf ranged from 3.03 to 0.49 % (Table 4.2). Sediments from the northern part of the shelf were found to have lower C_{org} content (<1 %) compared to the southern part, where, on an average, C_{org} content was more than 2.5 % in the sediments. $\delta^{13}C_{org}$ values varied from -21.33 to -20.23 ‰ in the sediments along the shelf (shown in Table 4.2).The north–south variability was found to be seen in isotopic composition as well, where the $\delta^{13}C_{org}$ values in the sediments from northern part were seen to be heavier compared to the southern part.Concentration of $CaCO_3$ was found to vary from 3.9 to 81.3 % in the sediments and the average $CaCO_3$ content was higher that the eastern shelf. The concentrations of Fe and Fe-oxyhydroxide in the sediments from this region were found to vary from 4.5 to 12.9 % and 3149 to 9506 $mg.kg^{-1}$ respectively. The concentration of sedimentary Pb was found to vary from 12.0±0.6 to 30.4±0.1 $mg.kg^{-1}$ in the sediments from the western shelf of India (Table 4.2).

Table 4.1 Concentration of Pb (mg.kg $^{-1}$) and total organic carbon (C_{org}) (%), $C:N_{molar}$,$\delta^{13}C_{org}$ (‰)in the eastern continental shelf of India

Station	Conc.of Pb (mg.kg^{-1})	C_{org} (%)	Fe (%)	Fe/Mn oxy-Hydroxide (mg.kg^{-1})	$CaCO_3$ (%)	$C:N_{molar}$	$\delta^{13}C_{org}$ (‰)
SSK35/SPC1	29.0±0.5	0.49	7.3 ±0.1	10310	2.6	8.79	-22.58
SSK35/SPC5	26.3±0.2	0.58	5.8±0.5	8793	2.9	10.05	-23.38
SSK35/SPC7	28.9±0.6	0.65	6.0±0.3	7718	2.5	8.79	-21.89
SSK35/SPC19	26.1±1.1	0.82	7.7±0.2	7058	2.4	10.48	-22.18
SSK35/SPC22	36.7±0.4	1.03	8.1±0.5	16292	1.8	12.39	-23.86
SSK35/SPC33	19.9±0.3	0.74	11.8±0.6	2123	74.8	74.91	-23.95
SSK35/SPC35	20.9±0.3	2.36	3.2±0.07	3473	3.1	38.48	-25.08
SSK50/SPC26	18.4±0.1	0.99	1.3±0.5	4414	9.0	9.31	-19.61
SSK50/SPC24	15.9±0.3	0.44	0.3±0.03	5100	13.7	13.44	-21.19
SSK50/SPC15	17.4±0.7	1.57	2.0±0.07	4006	5.1	11.40	-20.89
SSK50/SPC17	5.9±0.2	0.45	5.6±0.3	4763	24.7	16.47	-24.18

Table 4.2 Concentration of Pb (mg.kg $^{-1}$) and total organic carbon (C_{org}) (%), C:N_{molar} ,$\delta^{13}C_{org}$ (‰)in the western continental shelf of India

Station	**Conc.of Pb (mg.kg^{-1})**	**C_{org} (%)**	**Fe (%)**	**Fe/Mn oxy-Hydroxide (mg.kg^{-1})**	**$CaCO_3$ (%)**	**C:N_{molar}**	**$\delta^{13}C_{org}$ (‰)**
SSK40/SPC59	30.4±0.1	0.49	5.2±1.1	3149	11.8	13.16	-20.23
SSK40/SPC57	21.6±0.3	0.51	5.5±1.0	3846	6.8	10.34	-20.33
SSK40/SPC55	25.1±1.1	0.66	5.6±0.4	5137	26.3	12.61	-20.73
SSK40/SPC39	24.2±0.7	0.31	7.6±0.1	4024	7.5	10.3	-20.66
SSK40/SPC11	12.0±0.6	2.63	7.4±1.3	5335	81.3	13	-22.04
SSK40/SPC6	13.9±0.5	2.89	12.9±0.8	9506	77.2	12.21	-20.94
SSK40/SPC7	12.8±0.2	2.89	6.1±0.3	6178	3.9	11.3	-20.44
SSK40/SPC69	14.6±0.7	2.65	4.5±0.1	6641	13.1	13.22	-21.35
SSK40/SPC74	17.6±0.5	3.01	5.7±0.1	9820	4.6	12.41	-21.33
SSK40/SPC75	19.1±0.3	3.03	4.8±0.4	9287	6.6	12.53	-21.09

The percentage of total Pb associated with different geochemical phases (Fr.1, Fr.2, Fr.3, Fr.4 and Fr.5) of the eastern and western continental shelf sediment is given in Table 4.3 and 4.4 respectively. The percentage of total Pb in the non-residual binding phases were found to vary from 35 to 67 % in the eastern continental shelf sediment, a major part of the non-residual Pb was found to associate with Fe/Mn oxyhydroxide phase (Fr.3) (10.6 to 57.2 % of total Pb) followed by organic (Fr.4) (1.4 to 25.1 % of total Pb), exchangeable/carbonate (Fr.2) (0.1 to 19.3 % of total Pb) and water soluble phase (0 to 6.9 % of total Pb) of the eastern continental shelf sediments. In the western continental shelf, the association of Pb with different non-residual sedimentary phases followed the same order as it was in the eastern shelf. The highest association of Pb was found with Fe/Mn oxyhydroxide phase (Fr.3) (13.0 to 53.5 % of total Pb) followed by organic phase (Fr.4) (3.3 to 31.1 % of total Pb), exchangeable/carbonate (Fr.2) (1.1 to 27.1 % of total Pb) and water soluble phase (0.2 to 34.4 % of total Pb). The non-residual fraction of total Pb was found to vary from 46 to 67% in the western continental shelf sediments.

It is important to note that geochemical fractionation study does not provide any information about the stability of the metal complexes (associated with different binding phases) in the sediments. In order to know the stability and lability of Pb-sediment complexes in the shelf sediments, further experiments were carried out by using competing ligand exchange method.

4.2.2 Kinetic fractionation of Pb-sediment complexes

The change in concentration of Pb released from Pb-sediment complexes in presence of EDTA was monitored against time. The kinetic extraction curves of Pb from Pb-sediment complexes from the eastern and western continental shelves are presented in Figures 4.1 and 4.2 respectively. Each curve shows an exponential increase of Pb concentration in EDTA solution as a function of time. There is a distinct feature in each curve (a sharply rising part followed by a slow or unchanged part). The non-linear regression analysis was carried out and the experimental data were fitted with two component model system. The sharply rising part of each curve represent the labile Pb-sediment complexes (C_1) with rapid dissociation rate constant (k_{d1}) and the second part parallel to x axis represent inert Pb-sediment complexes (C_2) of very slow dissociation rate constant (k_{d2}).

Table 4.3 Percentage of total Pb associated with water soluble (Fr.1), exchangeable and carbonate/bicarbonate (Fr.2), Fe/Mn oxyhydroxyde (Fr.3),organic (Fr.4) and residual (Fr.5) phase of the eastern continental shelf sediments

Station	Fr1(%)	Fr2(%)	Fr3(%)	Fr4(%)	Fr5(%)
SSK35/SPC1	1.8	4.2	57.2	4.2	32.6
SSK35/SPC5	3.1	5.2	35.5	11.6	44.6
SSK35/SPC7	1.8	2.7	37.4	13.3	44.8
SSK35/SPC19	2.7	3.5	33.7	10.0	50.0
SSK35/SPC22	1.6	1.8	42.2	10.9	43.5
SSK35/SPC33	1.8	0.1	11.0	25.1	62.0
SSK35/SPC35	0.0	3.5	10.6	6.6	79.3
SSK50/SPC26	0.6	19.6	31.0	9.0	39.9
SSK50/SPC24	1.6	4.5	35.6	4.4	54.0
SSK50/SPC15	0.4	9.3	32.5	7.6	50.2
SSK50/SPC17	6.9	2.3	24.5	1.4	64.9

Table 4.4 Percentage of total Pb associated with water soluble (Fr.1), exchangeable and carbonate/bicarbonate (Fr.2), Fe/Mn oxyhydroxyde (Fr.3), organic (Fr.4) and residual (Fr.5) phase of the western continental shelf sediments

Station	Fr1(%)	Fr2(%)	Fr3(%)	Fr4(%)	Fr5(%)
SSK40/SPC59	1.6	4.2	30.2	31.1	32.9
SSK40/SPC57	0.2	3.2	31.1	16.1	49.4
SSK40/SPC55	0.5	3.3	53.5	3.9	39.0
SSK40/SPC39	34.4	27.1	13.0	14.3	19.2
SSK40/SPC11	0.4	1.2	22.8	21.6	54.0
SSK40/SPC6	0.4	1.2	32.2	20.2	45.9
SSK40/SPC7	2.0	1.1	28.5	22.5	45.9
SSK40/SPC69	1.6	1.4	47.0	10.5	39.5
SSK40/SPC74	0.9	1.8	47.9	3.3	46.1
SSK40/SPC75	1.5	3.0	43.0	10.3	42.2

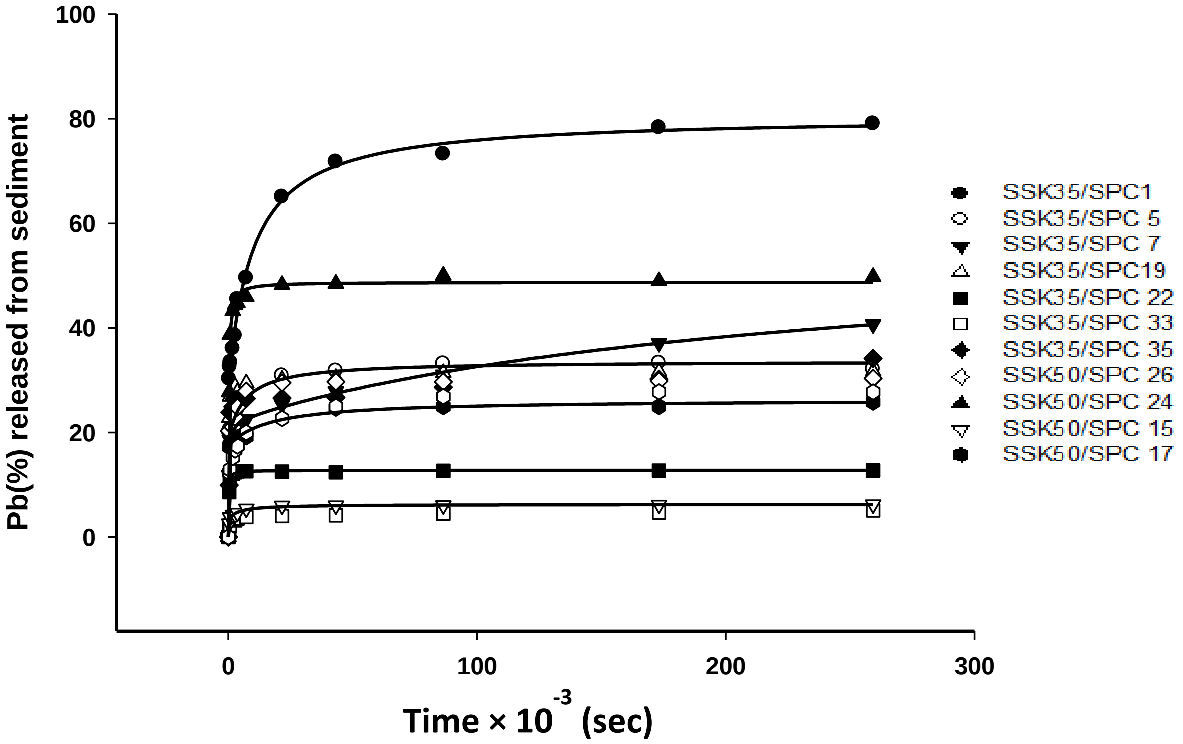


Figure 4.1 Release of labile Pb species from sediments of eastern continental shelf as a function of time in presence of 0.05M EDTA at pH 6

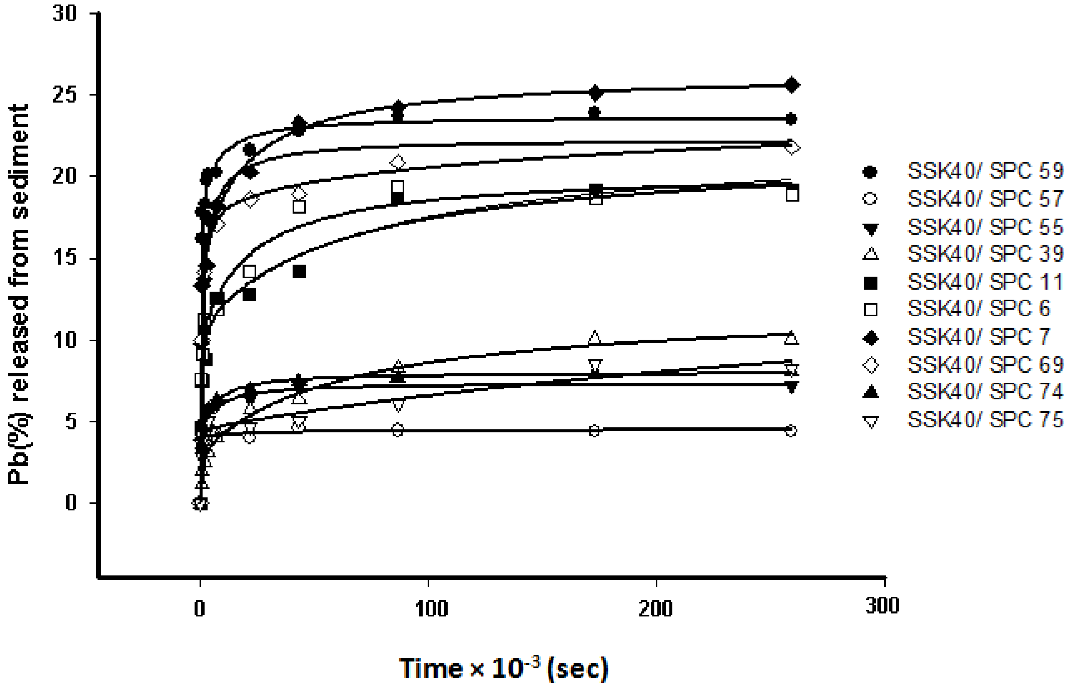


Figure 4.2 Release of labile Pb species from sediments of western continental shelf as a function of time in presence of 0.05M EDTA at pH 6

It should not be considered that there were two discrete binding sites for Pb present in the sediments. It is well known that determination of different types of metal-binding sites in a polyfunctional, complexant such as sediment is not a simple issue **(**Langford and Gutzman, 1992; Chakraborty, 2007; Chakraborty et al., 2011; Chakraborty et al., 2012)**.**Metal binding sites in sediments may have range of binding energies because of the heterogeneous nature. Thus, two discrete types of binding sites with specific dissociation rate constants of Pb-sediment complexes may not accurately describe the chemistry of the binding sites of the sediment. The specific dissociation rate constants, presented in this study, may represent anaverage value for a group of complexes on a particular site. The numerical data that describe the fitted line i.e, the percentage of kinetically distinguishable Pb-complexes (labile (c_1) and inert (c_2)) and their corresponding dissociation rate constant (k_{d1} and k_{d2} respectively) in the sediments of eastern and western continental shelf are given in Tables 4.5 and Table 4.6 respectively.

The percentage of weak Pb-sediment complexes (c_1) in the eastern shelf sediment samples ranged from ~3 to 46 % (with an average of ~ 27%) of the total sedimentary Pb complexes with the dissociation rate constant ranging from 1.2×10^{-3} to 6.4×10^{-3} S^{-1} (presented in Table 4.5). The percentage of dynamic sedimentary Pb complexes (a good representative of labile complexes) was found to be lower in the eastern part and it varied from 4 to 20 % (av. ~11 %) of the total sedimentary Pb. The dissociation rate constant of these complexes was found to vary from 1.6×10^{-3} to 4.8×10^{-3} S^{-1} (shown in Table 4.6). The percentage of inert Pb complexes (C_2) and their corresponding dissociation rate constants (k_{d2}) in the eastern and western shelf sediments are provided in Tables 4.5 and 4.6 respectively.

4.2.3 Kinetically distinguishable forms of Pb-sediment complexes and their dissociation rate constants

Kinetic fractionation experiment showed that sedimentary Pb complexes from both the continental shelves comprised of two kinetically distinguishable components. The exponential curves for all the sediment samples showed similar rising pattern (Figures 4.1 and 4.2). The initial section of the steeply rising parts of the curves was almost indistinguishable from each other, indicating dynamic Pb-sediment complexes with fast dissociation rate constants. However, the overall steep section for each curves were different from each other. The difference was found to be shown (Tables 4.5 and 4.6) in calculated dissociation rate constant (K_{d1}) for the labile complexes of the sediments

Table 4.5 Percentage of labile (C_1) and inert (C_2) complexes and their corresponding dissociation rate constants (K_{d1}) (S^{-1}) and (K_{d2})(S^{-1}) respectively in the eastern continental shelf of India

Station	C_1(%)	$K_{d1}(S^{-1})$	C_2(%)	$K_{d2}(S^{-1})$
SSK35/SPC1	45.5	6.4×10^{-3}	54.5	$< 10^{-6}$
SSK35/SPC5	25.6	5.1×10^{-3}	74.4	$< 10^{-6}$
SSK35/SPC7	21.6	4.1×10^{-3}	78.4	$< 10^{-6}$
SSK35/SPC19	28.8	2.4×10^{-3}	71.2	$< 10^{-6}$
SSK35/SPC22	12.4	3.1×10^{-3}	87.6	$< 10^{-6}$
SSK35/SPC33	3.1	1.2×10^{-3}	96.9	$< 10^{-6}$
SSK35/SPC35	26.0	5.2×10^{-3}	74.0	$< 10^{-6}$
SSK50/SPC26	25.7	2.4×10^{-3}	74.3	$< 10^{-6}$
SSK50/SPC24	45.8	3.9×10^{-3}	54.2	$< 10^{-6}$
SSK50/SPC15	19.7	2.2×10^{-3}	80.3	$< 10^{-6}$
SSK50/SPC17	19.2	2.7×10^{-3}	80.8	$< 10^{-6}$

Table 4.6 Percentage of labile (C_1) and inert (C_2) complexes and their corresponding dissociation rate constants (K_{d1}) (S^{-1}) and (K_{d2})(S^{-1}) respectively in the western continental shelf of India

Station	C_1(%)	$k_{d1}(S^{-1})$	C_2(%)	$k_{d2}(S^{-1})$
SSK40/SPC59	20.3	4.8×10^{-3}	79.7	$< 10^{-6}$
SSK40/SPC57	4.2	4.4×10^{-3}	95.8	$< 10^{-6}$
SSK40/SPC55	5.2	4.2×10^{-3}	94.8	$< 10^{-6}$
SSK40/SPC39	8.2	5.0×10^{-3}	91.9	$< 10^{-6}$
SSK40/SPC11	11.4	1.6×10^{-3}	88.6	$< 10^{-6}$
SSK40/SPC6	13.2	2.2×10^{-3}	86.8	$< 10^{-6}$
SSK40/SPC7	17.1	2.6×10^{-3}	82.9	$< 10^{-6}$
SSK40/SPC69	18.0	1.0×10^{-3}	82.0	$< 10^{-6}$
SSK40/SPC74	5.3	3×10^{-3}	94.7	$< 10^{-6}$
SSK40/SPC75	7.3	2.9×10^{-3}	92.7	$< 10^{-6}$

from both the shelves. The variation was also observed in the height of the steep section of each curve (Figures 4.1 and 4.2), suggesting the concentration of labile Pb-sediment complexes in the sediments varied along the shelves.The average concentration of labile Pb-sediment complexes (presented in percentage of the total sedimentary Pb) was found to be higher in the eastern shelf (~27 %) compared to the western shelf (~11%).

A major part of the sedimentary Pb-sediment complexes in both shelves were inert (c_2) in nature with very slow dissociation rate constant ($<1x10^{-6}$ s^{-1}) (see Tables 4.5 and 4.6).

4.3 Discussion

4.3.1 Influences of Pb/ [C_{org}] and [Pb]/[$Fe_{oxyhydroxide}$] ratios on the stabilities of Pb-sediment complexes

The stability of Pb-sediment complexes in shelf sediments depends on total sedimentary Pb loading and quantity and quality of sedimentary binding phases (Szarek-Gwiazda and Mazurkiewicz-Boron, 2006; Chakraborty et al., 2011; Chakraborty et al., 2012). It has been discussed in the previous section that C_{org} and Fe-oxyhydroxide were the major Pb-binding phases in the sediments. Thus, the influences of Pb/ [C_{org}] and [Pb]/[$Fe_{oxyhydroxide}$] ratios on the stabilities of Pb-sediment complexes are discussed below.

The dissociation of Pb-sediment complexes was found to depend on Pb/ [C_{org}] ratio. The dissociation rate constant of the labile complexes (k_{d1}) of Pb was found to increase with increasing Pb/C_{org} ratio in both the eastern and western shelf sediments (Figures 4.3(a) and 4.3(b) respectively).

A steady increase in dissociation rate constant (k_{d1}) was observed with the increasing Pb/ [C_{org}] ratio in the eastern shelf sediment. However, the increasing trend of k_{d1} against Pb/C_{org} was found to be different in the western shelf sediment. Variation in concentration of the total sedimentary organic matter (C_{org}) in the northern and southern part of the western continental shelf influenced the stability of Pb-sediment complexes. Sediment samples containing low C_{org} (<1 %) from the northern part of the western continental shelf showed slow increase in dissociation rate constant of Pb-sediment complexes with increasing Pb loading compared to the Pb-sediment complexes from the southern part of the western continental shelf sediment, where C_{org}

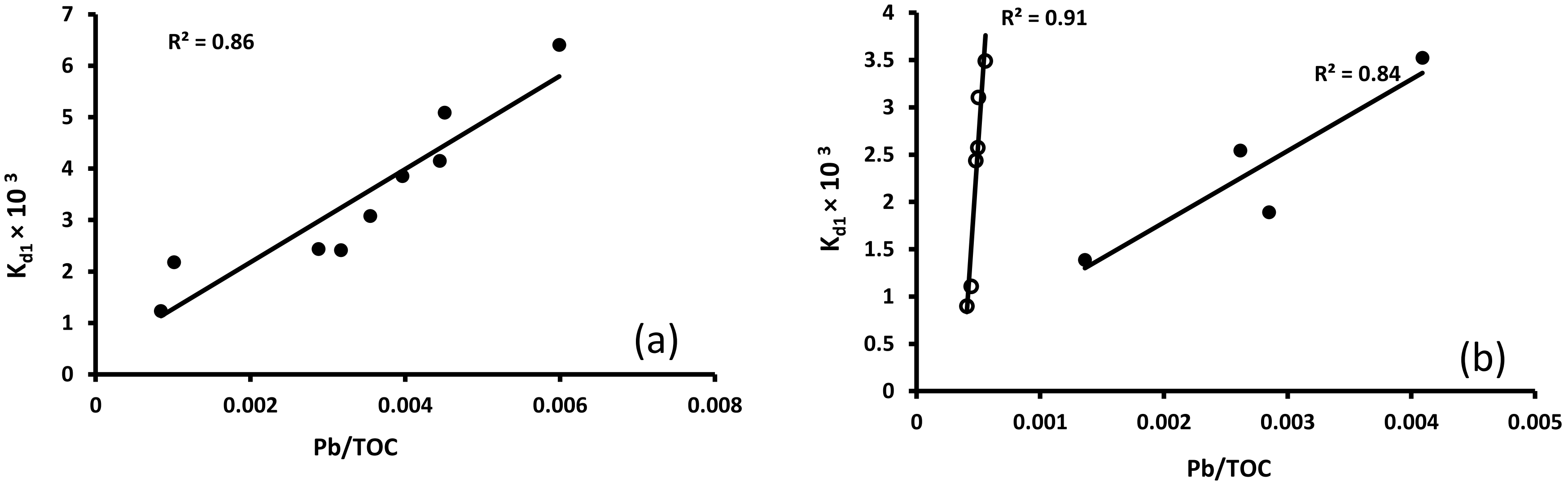


Figure 4.3 Increase of dissociation rate constant of labile Pb-sediment complexes (k_{d1}) with increasing Pb/ C_{org} ratio in the sediments from (a) eastern and (b) western (white circles and black circles indicates sediments with higher C_{org} from the southern part and lower C_{org} from the northern part respectively) continental shelf of India.

concentration was higher (<2.5%) (Figure 4.3.(b)).

The increase in dissociation rate constant (k_{d1}) of Pb-sediment complexes with increasing Pb/ [C_{org}] ratio suggests that there was progressive association of Pb with the weaker sites of the sediments. Thermodynamically more stable Pb complexes formed at lower Pb/[C_{org}] ratio in the sediments.

At lower Pb/[C_{org}] ratio, Pb undergoes more stable complex formation with available stronger binding sites of the sedimentary organic carbon. Thus, with increasing Pb loading, for a given concentration of C_{org} (with limited stronger binding sites for Pb), the formation of thermodynamically weaker complexes would probably increase. However, the findings in the western shelf sediment contradict the above explanation. It is necessary to consider several other factors (such as nature of the sedimentary binding sites, trace metal competition for a specific binding site) which may control the Pb-sediment complexation.

The variations in concentration of sedimentary Pb-labile complexes with the changing concentration of Fe-oxyhydroxide in the sediments were not statistically significant. Concentrations of labile Pb-sediment complexes were mainly controlled by the quality and quantity of C_{org} than Fe-oxyhydroxide binding phase in the sediments.

4.3.2 Geochemical phases of sedimentary Pb and its kinetically distinguishable forms

In kinetic fractionation study, a non-specific complexing agent (in this study EDTA) removes metals associated with carbonates, oxides, sulphate minerals, organic and exchangeable sedimentary phases (Chakraborty et al.,2011, Ure, 1991; Kennedy et al.,1997) depending upon their stability. However, in geochemical fractionation study specific reagents are used to extract metals by dissolving specific geochemical phases of sediments. Therefore, the results obtained from these two studies were compared in this section to provide a better understanding about the stability or lability of specific metal-sediment complexes. It has been reported that, naturally or anthropogenically mobile metals get associated with the sedimentary phases such as, carbonate, exchangeable, Fe/Mn oxyhydroxide and organic (Goldberg, 1954; Tessier et al., 1979; Chakraborty et al., 2015). Since, these metals are susceptible to remobilise under

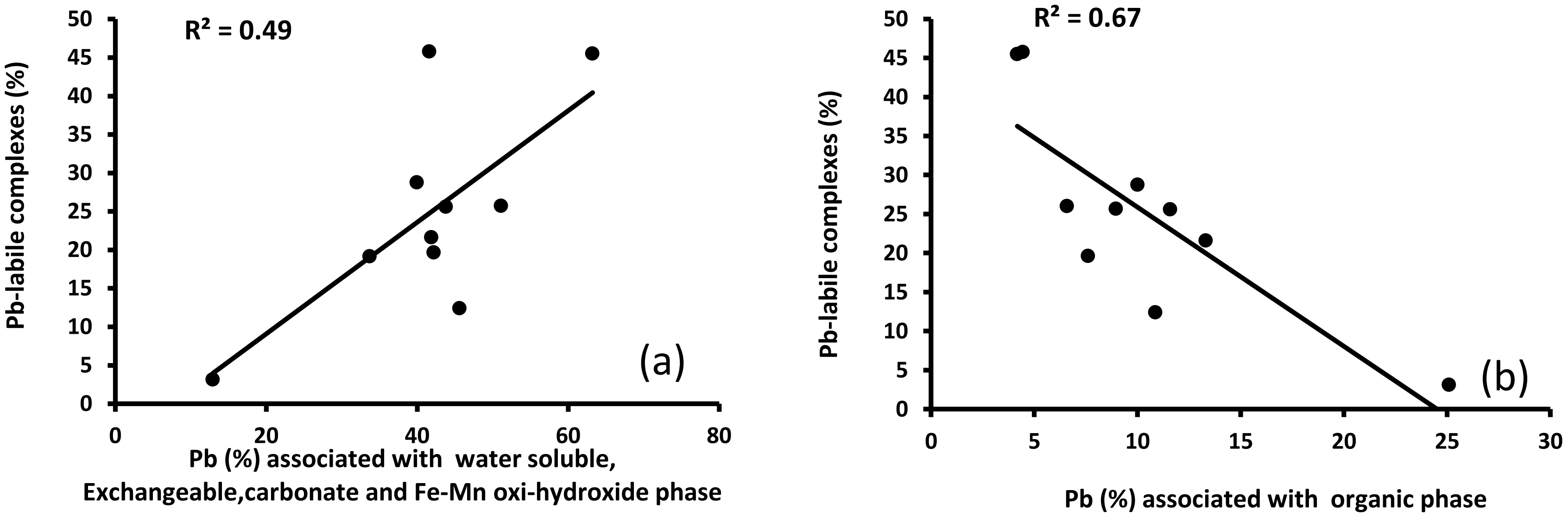


Figure 4.4 Increase in the concentration of labile complexes (C_1) of Pb with (a) increasing association of Pb with water soluble (Fr.1), exchangeable, carbonate/bicarbonate (Fr.2) and Fe/Mn oxyhydroxide phase (Fr.3) of the sediments (b) decreasing association with organic phase of the sediments from eastern continental shelf

different environmental conditions they are most likely labile in nature. Whereas, metals remained in the residual phase of sediments are inert in nature (Chakroborty et al., 2011). Therefore, in this study, labile complexes of Pb (C_1), separated in kinetic fractionation were compared with the different non-residual phases (Fr.1, Fr.2, Fr.3 and Fr.4) of the sediments.

The concentration of labile complexes of Pb in the sediments from eastern shelf was found to be increased with increasing association of Pb with water soluble (Fr.1), exchangeable, carbonate/bicarbonate (Fr.2) and Fe/Mn oxyhydroxide phase (Fr.3) of the sediments (Figure 4.3(a)). However, the lability of Pb complexes was found to be decreased with increasing association of Pb with organic phase (Figure 4.3(b). This probably indicates that Pb associated with Fr.1, Fr.2 and Fr.3 phases occupied weaker binding sites and hence formed labile complexes. However, it should be mentioned that, sum of the concentration of Pb in Fr.1, Fr.2 and Fr.3 phases was found to be greater than the concentration of labile Pb complexes and therefore it could be inferred that all the Pb associated with Fr.1, Fr.2 and Fr.3 were not labile in nature. On the other hand, though concentration of C_{org} was low in the entire eastern shelf sediments, Pb was found to form strong complexes (occupied stronger binding sites) and therefore with the increasing association of Pb with organic phase, the overall stability of sedimentary Pb complexes was increased.

In the western shelf sediments, the nature of Pb-sediment complexes was different from the eastern continental shelf region. It was found that increasing concentration of exchangeable and carbonate forms of Pb and association of Pb with Fe/Mn-oxyhydroxide decreased the lability of sedimentary Pb complexes (Figure 4.5(a)). However, increasing association of Pb with sedimentary organic phase (Fr.4) increased the lability of sedimentary Pb complexes (Figure 4.5 (b)). This indicates that sedimentary Pb associated with carbonate and Fe/Mn oxyhydroxide phase formed thermodynamically stable complexes whereas, water soluble and Pb-organic complexes were found to be thermodynamically labile in nature.

Total non-residual sedimentary Pb complexes separated in geochemical fractionation study was compared with the labile fraction of Pb found in kinetic fractionation study. It was interesting to note that the percentage of non–residual Pb was found to be higher than the percentage of labile complexes of Pb in the entire shelf

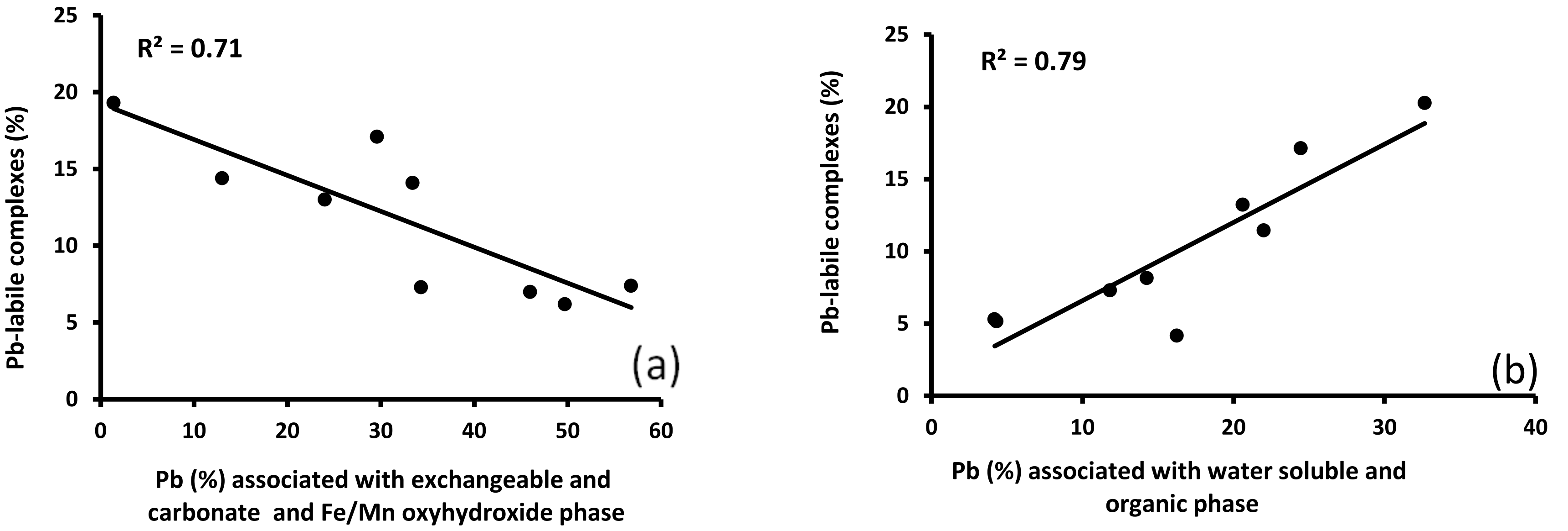


Figure 4.5 Increase in the concentration of labile complexes (C_1) of Pb with (a) decreasing association of Pb with exchangeable, carbonate/bicarbonate (Fr.2) and Fe/Mn oxyhydroxide phase (Fr.3) of the sediments (b) increasing association with water soluble (Fr.1), and organic phase of the sediments from western continental shelf

sediments. Therefore, it could be inferred that all the non-residual Pb (determined in geochemical fraction study) complexes were not kinetically labile in nature.

Contrast behaviour of Pb-sediment complexes was observed in the two different shelves. It is well known that, Pb complexes extracted in Fr.2 by BCR sequential extraction method were the sum of exchangeable and carbonate forms in the sediments. In the eastern shelf sediments, Pb was mainly in the exchangeable forms (as the $CaCO_3$ content was low, Table 4.1). These exchangeable forms of Pb were found to be labile in nature. Conversely, with higher $CaCO_3$ content (compared to the eastern shelf) (see Tables 4.1 and 4.2) in the western shelf sediments, Pb formed thermodynamically more stable complexes with sedimentary carbonate phase.

It was interesting to note that, Pb formed labile complexes with C_{org} in the western shelf sediment. However, Pb-C_{org} complexes were found to be thermodynamically more stable in the eastern shelf sediments. This observation was independent of C_{org} concentrations. It is suggested that the nature of C_{org} probably played an important role in controlling Pb-fractionation in the continental shelf sediments.

The nature of C_{org} from both the shelves were investigated and discussed below.

4.3.3 Nature of organic carbon and the stability of sedimentary Pb complexes

Organic matters derived from terrestrial origin are usually bigger molecules and more complex in nature compared to the marine derived organic matter (Hedges et al., 1997; Baldock et al.2004). Marine derived organic matter contains more of nitrogen containing binding ligands (Prahl et al., 1994; Baldock et al.2004; Müller et al., 1977). However, the bigger organic molecules derived from terrestrial origin has been reported to contain higher number of metal binding ligands (such as –OH (hydroxyl) and –COOH (carboxyl), phenolic-OH, etc) **(**Boggs et al., 1985; Christman and Gjessing; 1987 and references therein).

Larger surface area and greater number of binding ligands of terrestrial derived organic matters usually forms stable complexes with metals compared to marine derived organic matter. Thus, one could expect that the source of organic matter in sediments may play important role on the stability of Pb-organic complexes in sediment. Therefore the source of C_{org} in both the shelves was investigated to understand the dissimilar behaviour of Pb-C_{org} complexes in the two different shelves.

C/N molar ratio and $\delta^{13}C$ values of sediments were used to identify the sources of C_{org} in the sediments, which are widely used in the literature (Meyers and Ishiwatari, 1993; Meyers, 1997; Zhang et al., 2009). The freshly deposited marine produced organic matter has been reported to have $C:N_{molar}$ ratio in between 6-9 (Bordovskiy, 1965; Prahl et al., 1994, 1980) and $\delta^{13}C_{org}$ of -20.5‰. The vascular terrestrial C3 plant produced OM has been reported to have $C:N_{molar}$ ratio in between 12-14 or more (Hedges et al., 1986; Prahl et al., 1994, 1980) and $\delta^{13}C_{org}$ of -30 to -23 ‰ (Smith and Epstein, 1971; Pancost and Boot, 2004). However, the values in between may indicate mixture of both marine and terrestrial organic matter.

Except for few sporadic locations in the eastern shelf, C/N molar ratios in the sediments from both eastern and western shelves (Table 4.1 and 4.2 respectively) show the signature of terrestrial derived organic carbon (C/N ratio >11). However, in marine environment, the bacterial consumption of organic nitrogen (during deposition/post deposition) leads to the elevation of C/N ratio in sedimentary organic matter. Thus C/N ratio sometimes mislead in identifying the actual sources of organic matter (Ishiwatari and Uzaki 1987; Raymo et al., 1996). Therefore $\delta^{13}C$ was assessed to characterize the sedimentary organic carbon source.

$\delta^{13}C$ values, a robust indicator of C_{org} sources, showed two distinct features in the sedimentary organic matter from both the shelves. $\delta^{13}C$ values in the eastern shelf sediments (-19.61 to -25.08 ‰) was found to be lighter compared to the western shelf sediments (-20.23 –21.35 ‰). This indicates that the eastern continental shelf of India receives more terrestrial organic matter compared to the western shelf. This finding is consistent with the earlier studies reported in literature (Kirshna et al., 2013; Agnihotri et al.,2003; Cowie et al.,2009). The high riverine input in the eastern shelf was probably responsible for the accumulation of more terrestrial organic matter in the shelf sediments than the western shelf where riverine contribution is limited.

Formation of relatively more labile sedimentary Pb complexes with C_{org} (mainly derived from marine sources) in the western shelf sediment and thermodynamically more stable Pb-C_{org} complexes (with terrestrial derived C_{org}) in the eastern shelf sediments suggest that nature and sources of C_{org} played an important role in determining the stability and lability of Pb-sediment complexes in the shelf sediments around India.

4.4 Conclusions

Sedimentary Pb complexes in the continental shelf around India were comprised of two kinetically distinguishable forms (labile and inert Pb complexes). The inert Pb complexes were the major part of the total sedimentary Pb in the continental shelf sediments around India. The average percentage of total labile Pb-sediment complexes was more in the eastern shelf sediments compared to the western part.

It was found that Pb formed weaker complexes with water soluble, exchangeable, carbonate and Fe/Mn oxyhydroxide phases and stronger complexes with organic phase of the sediment from the eastern continental shelf. However, in the western shelf sediments, Pb formed weaker organic complexes.

Terrestrial nature of organic carbon in the eastern shelf provides stronger binding sites for Pb compared to the less terrestrial organic carbon in the western shelf sediments. Thus, Pb formed more labile sedimentary Pb complexes with C_{org} (from marine sources) in the western shelf sediment and thermodynamically more stable Pb-C_{org} complexes (from the terrestrial sources) in the eastern shelf.

Chapter 5

Influence of chemistry of other trace metals on Pb speciation

5.1 Introduction

Geochemical and kinetic fractionation study on Pb discussed in the previous chapters has revealed that the quality of binding phases i.e. the presence of specific binding ligands/sites in geochemical phases predominantly control the Pb speciation in marine sediments. However, the availability of binding sites will depend on the concentration of major binding phases (e.g. concentration of oxides/hydroxides of Fe and Mn, organic carbon etc) and the other trace metals which can compete with Pb for the complexation for same binding site.

It has also been documented that the rate of complex formation and stability of the formed complex determine the speciation of the metals in aquatic environment. If the rate of complex formation of a metal (M) with natural ligand (L) is faster and the stability of the formed complex (M-L) is higher (compared to the other metals in a given environment) then the metal (M) will be more associated with the ligands (L) than the other metals present in the system. A metal with faster kinetics of complex formation with high stability of the metal complex may out-compete other metals from complex formation with the same ligands in marine environments.

However, there are only few studies that have attempted to understand the influences of metal chemistry on metal-heterogeneous binding ligand interactions in marine sediments. There are several studies available in literature that have vividly discussed about the influences of metal chemistry on metal speciation in aquatic environment (Tessier and Turner, 1995; Florence et al., 1992). Three factors have been identified (Sekaly et al., 1999; Fasfous et al., 2006; Chakraborty and Chakrabarti, 2008; Chakraborty et al., 2012b) to influence trace metal speciation in freshwater environment: (1) metal to ligand mole ratio, (2) ionic potential (z^2/r), and (3) Ligand Field Stabilization Energy (LFSE) of metals. However, the influences of these basic chemical characteristics of metals on their speciation in marine sediments are not known.

In this study,we tried to compare the speciation of Cu, Ni and Pb in the light of their chemical characteristics (ionic potential (z^2/r),LFSE and water exchange rate (K_w) to understand the influence of other trace metal (Cu and Ni) chemistry on the speciation of Pb.Since the type of sedimentary organic matter (terrestrial and marine organic matter (OM) from in situ biological production) was also found to play an important role in Pb-organic complexation (in Chapter 4), the speciation of these metals are also compared in the sediments containing different nature of organic carbon.

Vembanad Lake in Kerala, west coast of India was chosen as the study area (Figure 5.1**)** (described in Chapter 2) because northern and southern part of the lake exhibit two different sub-environments. The northern part is brackish and southern part of the lake is freshwater dominated (Nath et al., 2000) and thus organic carbon in the collected sediments across the lake was different in nature (Sarkar et.al., 2016). Different geochemical parameters were analysed and geochemical fractionation of Cu, Ni and Pb was carried out in eight sediment samples collected from both the parts of the lake.

5.2 Results

5.2.1 Distributions of sand, silt, clay, C_{org}, TN and total metals in sediment along the lake:

The sediment texture is reported to be highly variable in estuaries including this Lake (Renjith and Chandrmohankumar 2007). Finer sediments were found in both north and southern side of the lake with a distinct coarsening on either side of the bund. This variation in texture may be result of variation in detrital sediment settlement from influence of mixing in the depositional environment. Sediments, collected at the middle of the lake (both side of the bund) was dominated by coarser particles. The average concentrations of sand, silt, clay) in the studied sediments are presented in Table 5.1.

The concentration of C_{org} in the sediments was varying from 0.9-3.8%. The concentration of sedimentary TN was in the range of 0.1-0.4%. Significant positive correlation coefficient was found between the C_{org}, TN and the finer particles (silt + clay) content in the sediments (Sarkar et al., 2016). This indicates that C_{org} and TN had high affinity for the fine-grained sediment and strongly adsorb towards large surfaces of fine-grained sediments. The concentration of trace metals (Ni, Cu, and Pb) in the studied sediment varied from northern to the southern part of the lake (Table 5.1).These metal concentrations were within the range reported from the other coastal sediments around India (Table 5.2). The average concentrations of Ni and Pb, in the sediments were higher in the southern part of the lake (Ni ranging from ~19.4 to 45.9 mg.kg^{-1}with an average concentration of 36.5 mg.kg^{-1}and and Pb concentrations ranging from ~22.0 to 45.3 mg/kg, with an average Pb concentration of 32.4 mg/kg) than the northern part of the lake (Ni ranging from ~21.1 to 36.1 mg.kg^{-1}, with an average concentration of 28.5 mg.kg^{-1} and the concentrations of Pb ranging from ~24.4 to 34.0 mg.kg^{-1}, with an average Pb concentration of 30.9 mg.kg^{-1}). However, the average concentrations of Cu in the sediments were relatively higher in the northern part (Cu ranging from ~22.2 to 82.2 mg.kg^{-1}, with an average concentration of 45.5 mg/kg) than the southern part of the lake (Cu concentrations ranging from ~23.5 to 51.5 mg.kg^{-1}, with an average Cu concentration of 34.3 mg/kg). Distribution and speciation of these metals in the lake sediments were further determined by following BCR sequential extraction protocol.

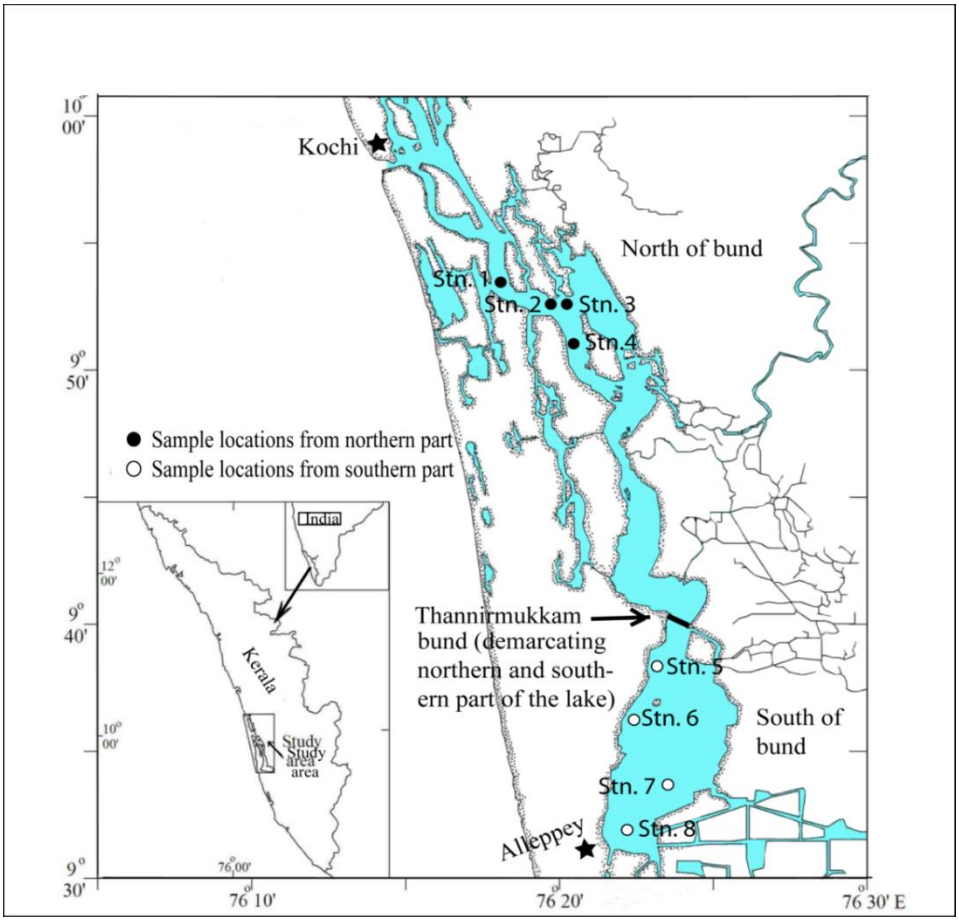


Figure 5.1 Study area and the sampling locations from the Vembanad Lake in Kerala, west coast of India

5.2.2 Chemical fractionations (operational speciation) of Ni, Cu and Pb in the sediments by using sequential extraction method

Distribution and speciation of Ni, Cu and Pb in different binding phases of the sediments are described below. Four geochemical phases of sedimentary metals viz. sum of water soluble, exchangeable and carbonate/bicarbonate (Fr.1), Fe/Mn-oxyhydroxide (Fr.2), organic (Fr. 3) and residual (Fr.4) were separated in this study.

Ni speciation:

Distribution of Ni in different binding phases of the studied sediments is presented in Figure 5.2a. It shows that lowest fraction of total concentration of Ni (vary from ~ 0.8 to 3.0% of the total Ni) were present as water soluble, exchangeable and carbonate/bicarbonate-Ni complexes (Fr.1) in the sediments. However, the absolute concentration of Ni (~ 0.12 to 0.57 $mg.kg^{-1}$) in Fr.1 gradually increased with the increasing total Ni concentrations in the sediments (Figure 5.2b).

Association of Ni with Fe/Mn-oxyhydroxide binding phases (Fr.2) in the sediments were higher (4 to 15% of the total Ni) (Figure 5.2a) than the Fr1. The concentration of Ni associated with Fe/Mn oxyhydroxide binding phase gradually increased (~0.9 to 5.0 $mg.kg^{-1}$) with the increasing Ni loading in the sediments (R^2=0.70) (Figure 5.2c) This indicates that Fe/Mn oxyhydroxide phase in the sediments acted as one of the important binding phases for Ni. The highest fractions of non-residual Ni (~ 22.0 to 27.0% of the Total Ni) were found to associate with organic binding phases in the sediments (Fr 3) (Figure 5.2d). The concentration of Ni in Fr.3 (associated with organic binding phases) gradually increased (~4.0 to 8.0 $mg.kg^{-1}$) with the increasing Ni loading in the sediments (R^2=0.93) (Figure 5.2d). Major fractions of the total Ni (~9.5 to 22.0 $mg.kg^{-1}$) were present within the structure of the sediments (Fr.4). Figure 5.2e shows the variation of residual fraction with changing total Ni content in the sediments. The range of Ni concentrations in residual fraction of the sediment is consistent with the lithology of the source rock (granulitic terrain) (Nath et al. 2000).

Figure 5.2f shows that the concentrations of Ni associated with organic phases (Fr. 3) gradually increased with the Ni-to-C_{org} ratio; the results indicate a progressive increase in association of Ni with organic binding phase with the increasing Ni loading. The relative affinity of Ni for the different non-residual binding phases in the sediments was in the following order; C_{org} binding phase> Fe/Mn-oxyhydroxide phase> exchangeable, carbonate/bicarbonate phases.

Table 5.1 Sampling location, sediment texture, C_{org}, TN and Ni, Cu, and Pb content in the surface sediments of Vembanad Lake

Sample	Longitude (°E)	Latitude (°E)	Depth (m)	C_{org} (%)	TN(%)	Sulfide (mg.kg^{-1})	C:N_{molar}	Clay + Silt (%)	Ni (mg. kg^{-1})	Cu (mg. kg^{-1})	Pb (mg. kg^{-1})
North of Thanneermukkom Bund											
Stn-1	76.3022	9.8920	2	2.58	0.22		13.52	71.3	24.0 ± 0.7	82.2 ± 2.8	32.5 ± 0.8
Stn-2	76.3320	9.8790	4	1.61	0.14	613.5	13.07	22.6	32.9 ± 1.2	29.0 ± 0.5	24.4 ± 0.7
Stn-3	76.3395	9.8810	2	3.55	0.33		12.55	99.4	36.1 ± 1.8	48.7 ± 1.2	32.6 ± 1.4
Stn-4	76.3453	9.8410	2.5	0.96	0.08	687.8	13.48	29.1	21.1 ± 0.5	22.2 ± 0.4	34.0 ± 1.2
South of Thanneermukkom Bund											
Stn-5	76.3816	9.6400	2	1.53	0.13	763.0	13.37	37.1	19.4 ± 0.5	26.5 ± 0.7	30.4 ± 1.2
Stn-6	76.3765	9.6066	3	0.93	0.08	668.9	14.48	21.9	33.7 ± 1.8	23.5 ± 0.6	22.0 ± 2.2
Stn-7	76.3895	9.5622	3	3.67	0.31	149.4	13.85	95.2	47.0 ± 1.9	51.5 ± 1.8	31.9 ± 0.7
Stn-8	76.3648	9.5636	2	2.60	0.20	500.1	14.93	77.2	45.9 ± 2.5	35.5 ± 1.2	45.3 ± 2.3

.

Table 5.2 Concentration in the estuarine sediments of India and the ISGQ, PEL, ERL and ERM values of Ni, Cu and Pb

	Ni (mg. Kg^{-1})	Cu (mg. Kg^{-1})	Pb (mg. Kg^{-1})	References
Ganges Estuary	33.9	21.6	23.4	Banerjee et al.(2012)
Godavari Estuary	25.1	25.8	14.4	Krupadam et al.(2007)
Cauvery estuary	13.5	29.5	8.5	Dhanakumar et al.(2013)
Narmada Estuary	200	188.3	13.9	Sharma and Subramanian (2010)
Mandovi Estuary	64.0	46.9	18.7	Chakraborty et al.(2014b)
Cochin Estuary	57	43.4	39.8	Martin et al.(2012)
Vembanad Lake (North)	28.5	45.5	30.9	This Study
Vembanad Lake (South)	42.2	34.2	32.4	This Study
ISGQ	NA	18.7	30.2	Long et al., 1995
PEL	NA	108	112	Long et al., 1995
ERL	20.9	34	46.7	SQG (NOAA)
ERM	51.6	270	218	SQG (NOAA)

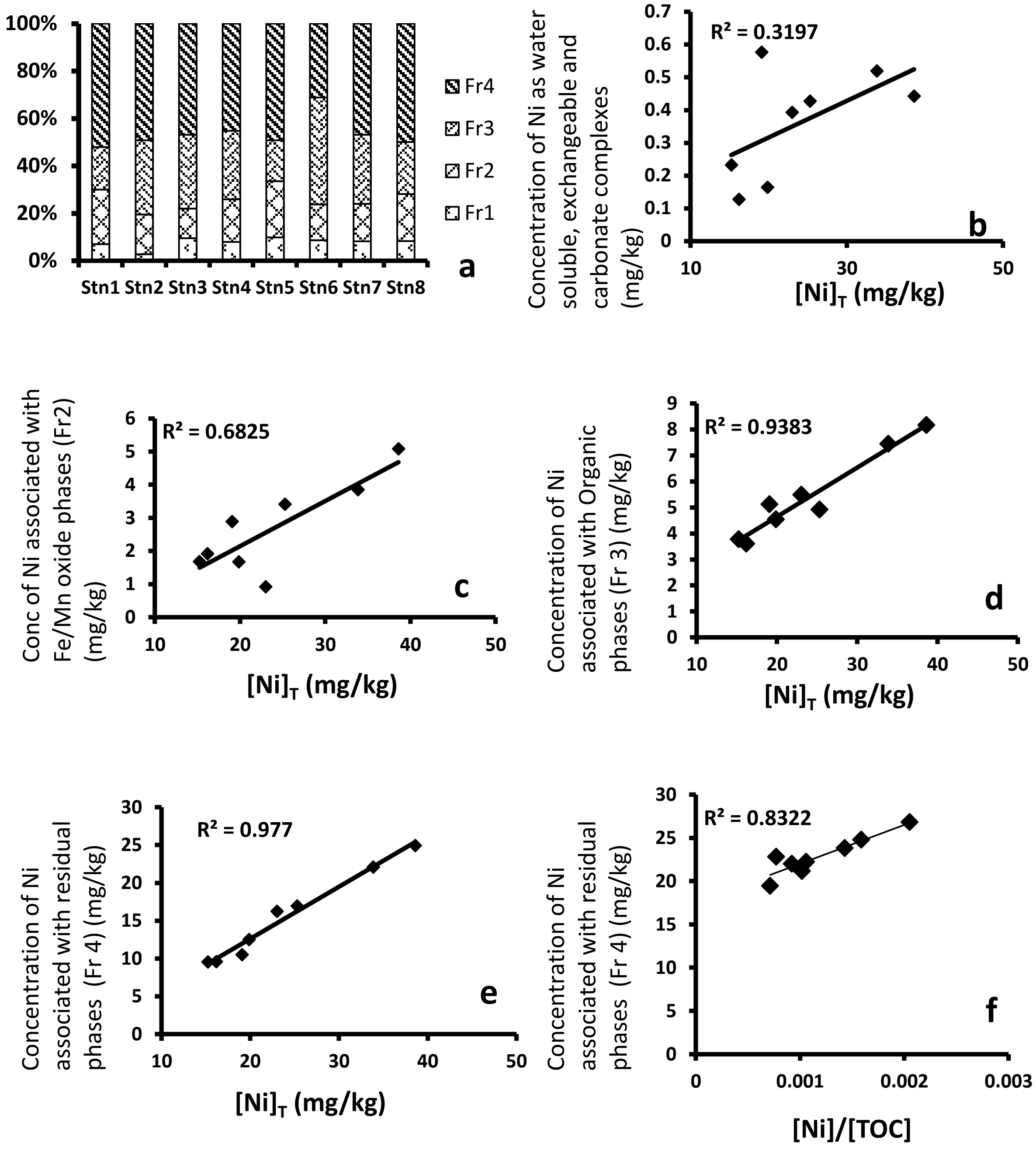


Figure 5.2 Ni speciation: **a)** distribution of Ni (%) as Fr1, Fr2,Fr3, and Fr4 in the sediments, **b)** variation of Ni in Fr1 (mg kg−1), **c)** variation of Ni in Fr2 (mg kg−1), **d)** variation of Ni in Fr3 (mg kg−1),and **e)** variation of Ni in Fr4 (mg kg−1) with total concentration of Ni (mg kg−1) in sediments. **f)** Variation of Ni (%) associated with organic phases (Fr3) with the Ni-to-C_{org} ratio

Cu speciation:

Distribution and speciation of Cu in the studied sediments are shown in Figure 5.3. Relative proportion of Cu content in different binding phases is shown in Figure 5.3a. Concentration of Cu as water soluble, exchangeable and carbonate/bicarbonate complexes (Fr. 1) were low and found to vary from ~0.3 to 3.0 % of the total Cu in the sediments (Figure 5.3b). Figure 5.3b shows that the absolute concentration of Cu (~0.1 to 0.9 mg.kg^{-1}) in Fr.1 did not gradually increase with the increasing Cu loading in the sediments (unlike Ni) (R^2=0.14). This indicates that enough binding sites were probably available for Cu to form thermodynamically stable complexes in the sediments. This statement is based upon the assumption that Cu forms thermodynamically weaker complexes in Fr. 1 than other binding phases.

The fraction of total Cu associated with Fe/Mn oxyhydroxide binding phase (Fr 2) was found to vary from ~ 3.5 to 26.0%. Figure 5.3c shows that the concentration of Cu in Fr.2 gradually decreased (~6.2 to 3.0 mg.kg^{-1}) with the increasing Cu loading in the sediments (R^2=0.50) (Figure 5.3c). The highest factions of non-residual Cu were found to associate with organic binding phases in the sediments (Fr 3) and probably the preemient binding phase for Cu in the studied sediments. The fraction of the total Cu associated with organic binding phase in the studied sediment was found to vary from ~ 15.0 to 32.0%. The concentration of Cu associated with organic phases of the sediments gradually increased (~4.0 to 8.0 mg.kg^{-1}) with the increasing Cu loading in the sediments (R^2=0.75) (Figure 5.3d).

Geochemical fractionation study suggested that major part of the total Cu in the sediments was present within the structure of the sediments (Fr.4) (~12.0 - 58.0 mg.kg^{-1}) and suggests that these sediments were mainly derived from the crustal sources with more felsic composition. Figure 5.3e shows that the concentrations of Cu in the residual fraction gradually increased with the increasing total Cu loading.

Figure 5.3f shows that the concentrations of Cu associated with organic phases (Fr 3) gradually increased with the increasing Cu/C_{org} ratio in the sediments. The results indicate a progressive increase in complexation of Cu with different binding sites present in the organic phase with the increasing Cu/C_{org} ratio. The relative affinity of Cu for different non-residual binding phases in the sediments were in the following order; C_{org}binding phase> Fe/Mn-oxyhydroxide phase> exchangeable, Carbonate/bicarbonate phases.

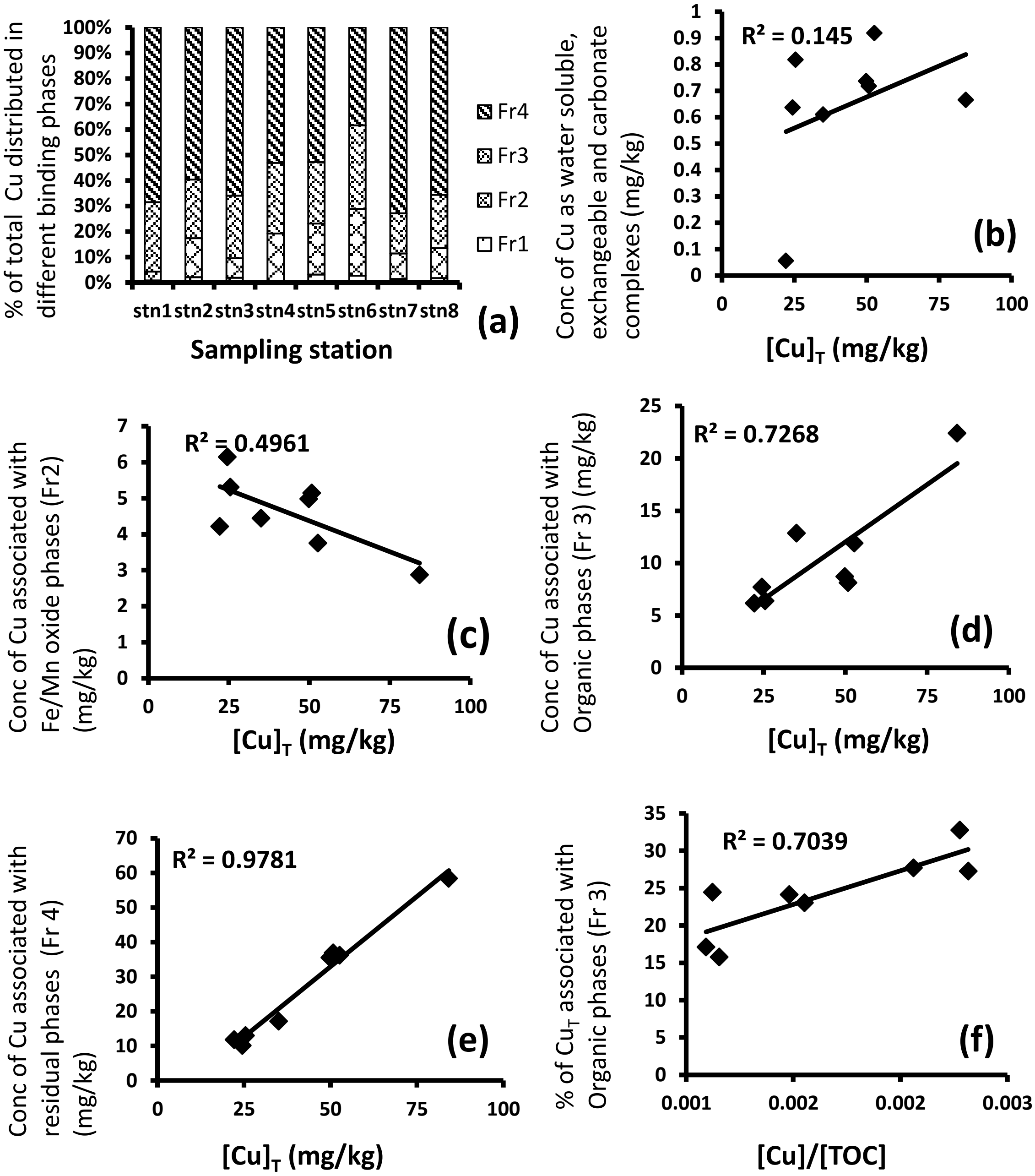


Figure 5.3 Cu speciation: **a)** distribution of Cu (%) as Fr1, Fr2,Fr3, and Fr4 in the sediments, **b)** variation of Cu in Fr1 ($mg.kg^{-1}$), **c)** variation of Cu in Fr2 ($mg.kg^{-1}$), **d)** variation of Cu in Fr3 (mg kg−1),and **e**) variation of Cu in Fr4 ($mg.kg^{-1}$) with total concentration of Cu ($mg.kg^{-1}$) in sediments. **f)** Variation of Cu (%) associated with organic phases (Fr3) with the Cu-to-C_{org} ratio

Pb speciation:

Distribution of Pb in different binding phases of the sediments is shown in Figure 5.4a. The concentrations of water soluble, exchangeable and carbonate/bicarbonate complexes of Pb (Fr. 1) were low and found to vary from ~0.3 to 2 % of the total Pb content in the studied sediments. Pb concentration in Fr 1 (~0.1 to 2.0 mg/kg) were found to increase slowly with the increasing total Pb content in the sediments (R^2=0.16) (Figure 5.4b). This indicates that there were other Pb-binding ligands available to form thermodynamically stable Pb- complexes in the sediments.

The highest fraction of the non-residual Pb (~ 20.0 to 48.0% of the total Pb) was found to associate with Fe/Mn oxyhydroxide (Fr. 2) binding phase. Absolute Pb concentration associated with Fe/Mn oxyhydroxide in the sediment gradually increased (~2.0 to 7.0 mg/kg) with the increasing total Pb loading in the sediments (R^2=0.92) (Figure 5.4c).

The second highest faction of non-residual Pb (~ 7.0 to 30.0% of the total Pb) was found to associate with the organic binding phase in the sediments (Fr.3). The concentration of Pb associated with organic binding phases did not gradually increase (~4.0 to 8.0 mg/kg) with the increasing Pb loading in the sediments (R^2=0.12) (as shown in Figure 5.4d). Unlike the other two elements considered here, this experimental data suggest that Pb preferred to associate with Fe/Mn oxyhydroxide binding phase than organic binding phases in the sediments.

Pb was primarily present in the residual fraction (Fr. 4) (~11.0 to 22.0 mg.kg^{-1}) of the studied sediments. The concentration of Pb (in the residual fraction) gradually increased with the total Pb concentrations of the sediments (Figure 5.4e).

Like other two elements (Ni and Cu), the concentrations range of Pb in the residual fraction also support that these sediments were mainly derived from felsic sources and consistent with earlier study (Nath et al., 2000). Figure 5.4f shows that there was no progressive increase in association of Pb with organic binding phases of the sediments against the increasing Pb/C_{org} ratio. This indicates that Pb preferred to associate with Fe/Mn-oxyhydroxide binding phase than organic binding phases in the sediments.The relative affinity of Pb for different non-residual binding phases in the sediments was in the order of; Fe/Mn-oxyhydroxide phase >C_{org} binding phase > exchangeable, Carbonate/bicarbonate phases.This study suggests that Cu had highestaffinity (as reflected by its concentrations in Fr. 3) for organic binding phases in the sediments followed by Ni and Pb, while, Pb had highest association with Fe/Mn-oxyhydroxide phases. These differences in distribution of these metals in different binding phases can be attributed to their metal chemistry and several other factors which are discussed below.

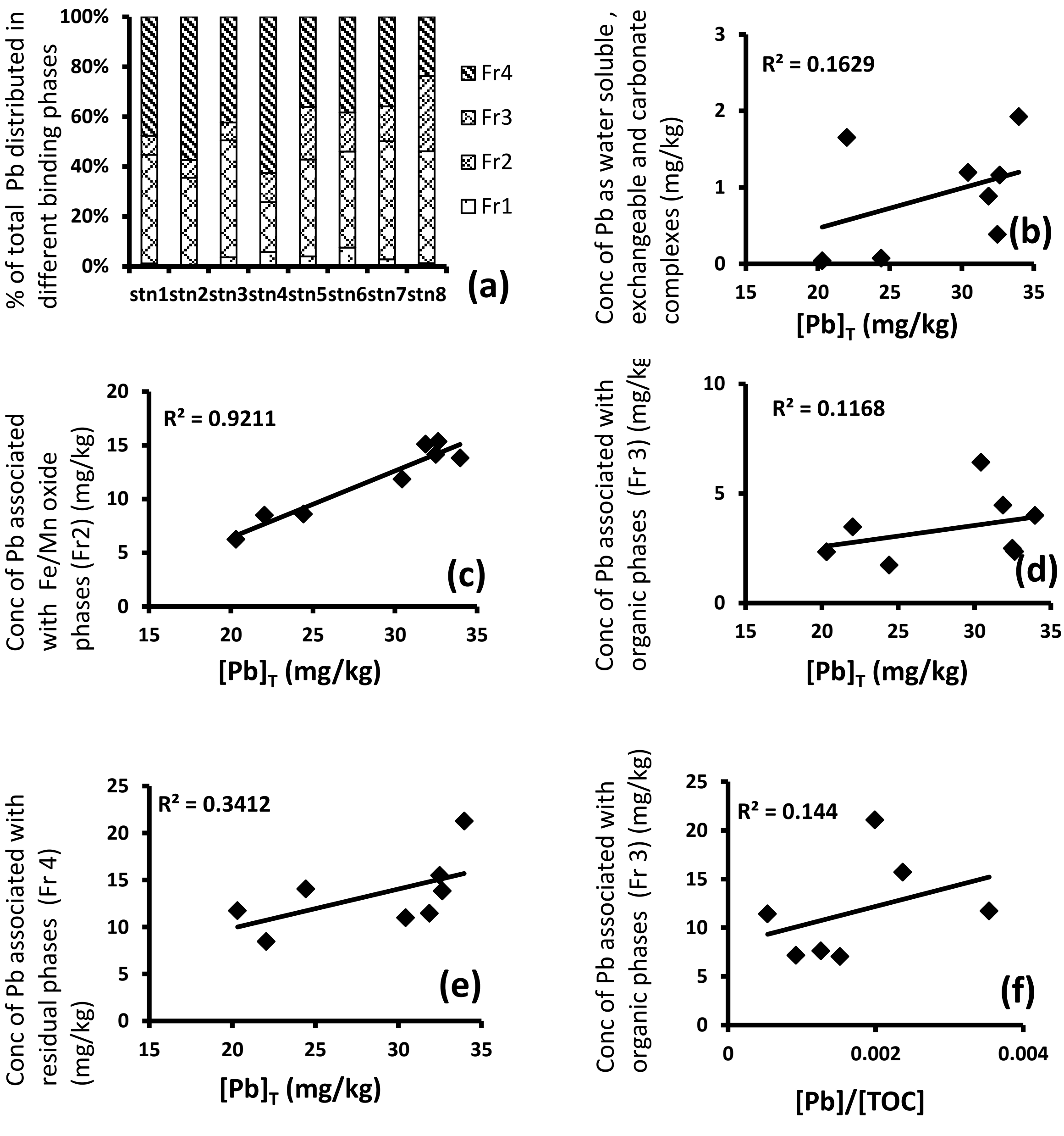


Figure 5.4 Pb speciation: **a)** distribution of Pb (%) as Fr1, Fr2,Fr3, and Fr4 in the sediments, **b)** variation of Pb in Fr1 (mg.kg^{-1}), **c)** variation of Pb in Fr2 (mg.kg^{-1}), **d)** variation of Pb in Fr3 (mg.kg^{-1}),and **e**) variation of Pb in Fr4 (mg.kg^{-1}) with total concentration of Pb (mg.kg^{-1}) in sediments. **f)** Variation of Pb (%) associated with organic phases (Fr3) with the Pb-to-C_{org} ratio

5.3 Discussion

Total concentrations of Ni, Cu and Pb in the studied sediments (Table 5.1) were found to be similar to the concentrations reported in other coastal sediments around India (Table 5.2).

According to the Canadian sediment quality guidelines for the protection of aquatic life, the interim sediment quality (ISQGs) and probable effect levels (PELs) for these metals are presented in Table 5.2. The United States environmental protection agency has also suggested that effects range low (ERL) and effects range median (ERM) values for these metals in coastal sediment. The studied sediments were found to be of good quality (in terms of Pb concentration). However, the concentrations of Ni and Cu were found to be in between the ERL and ERM concentrations (20.9-51.6 $mg.kg^{-1}$ for Ni and 34-270 $mg.kg^{-1}$ for Cu).

A significant positive correlation coefficient between the C_{org}, TN and the finer particle (silt + clay) content in the bulk sediments indicates that there was high sorption and affinity of C_{org} and TN on the surface of finer particles in the studied sediments. The similar observation has been reported in literature (Chakraborty et al., 2014b, 2015c).

Sequential extraction study determined the distribution of Ni, Cu and Pb in different binding phases of the sediments. It was found that these metals had different affinities for different binding phases in the sediments. It is hypothesised that the distribution of metals (Ni, Cu and Pb) in different binding phases of the studied sediments must provide chemically significant description of metals-ligand interactions in the sediments. It was found that Cu showed highest affinity for organic binding phases followed by Ni and Pb in the studied sediments. However, Pb had highest association with Fe/Mn-oxyhydroxide binding phases followed by Ni and Cu. Different factors are discussed below to understand their influences on metals distribution in different binding phases of the studied sediments.

5.3.1 Effect of metal/C_{org} ratio in geochemical fractionation of metals in the sediments

Total metal loading, quantity and quality of binding ligands in estuarine sediments play important role in controlling metal speciation and their distribution in sediment. Figure 5.5 shows the effects of metal/ C_{org} ratio in geochemical fractionation of metals in the sediments.Figure 5.5a shows that increasing [Ni]/ C_{org} ratio increased the accumulation of Ni in the organic phases of the studied sediments (across the lake sediments). It was found that enough uncomplexed Ni binding ligands were present in the organic binding phases of the sediments. Figure 5.5b and 5.5c shows the variation of accumulation of Ni in the organic phases against the varying [Ni]/ C_{org} ratio in the sediments from the northern and southern part of the lake. Organic phases in the sediments collected from the southern part of the lake were found to have better Ni complexing capacity.

Figure 5.5d shows the effect of varying [Cu]/ C_{org} ratio on Cu accumulation in organic phases of the studied sediments (across the lake sediments). It was found that the accumulation of Cu gradually increased with the increasing [Cu]/ C_{org} ratio. This study indicates that enough uncomplexed Cu binding ligands were present in the organic binding phases of the sediments. Figure 5.5e and 5.5f show the variation of accumulation of Cu in the organic phases of the sediments against the varying [Cu]/ C_{org} ratio in the sediments collected from the northern and southern part of the lake. Comparison of both the figures suggests that organic phases in the sediments collected from the southern part of the lake had better Cu complexing capacity.

However, a poor relation was observed between Pb accumulations in organic phases of the studied sediments (across the lake sediments) against [Pb]/ C_{org} ratio. Accumulation of Pb in organic phases did increase with the increasing [Pb]/ C_{org} ratio (Figure 5.5 g, h, and i) in the sediments. Organic phase in the sediment collected from the southern part of the lake was found to have better complexing capacity for Pb than the northern part of the lake. Figure 5.5 clearly shows that there was a distinct difference in the metal complexing capacity of the sedimentary organic phases in the southern and northern part of the lake. A systematic study was performed to understand if there is any difference in the nature of organic matter and its impact on metal speciation in the sediment.

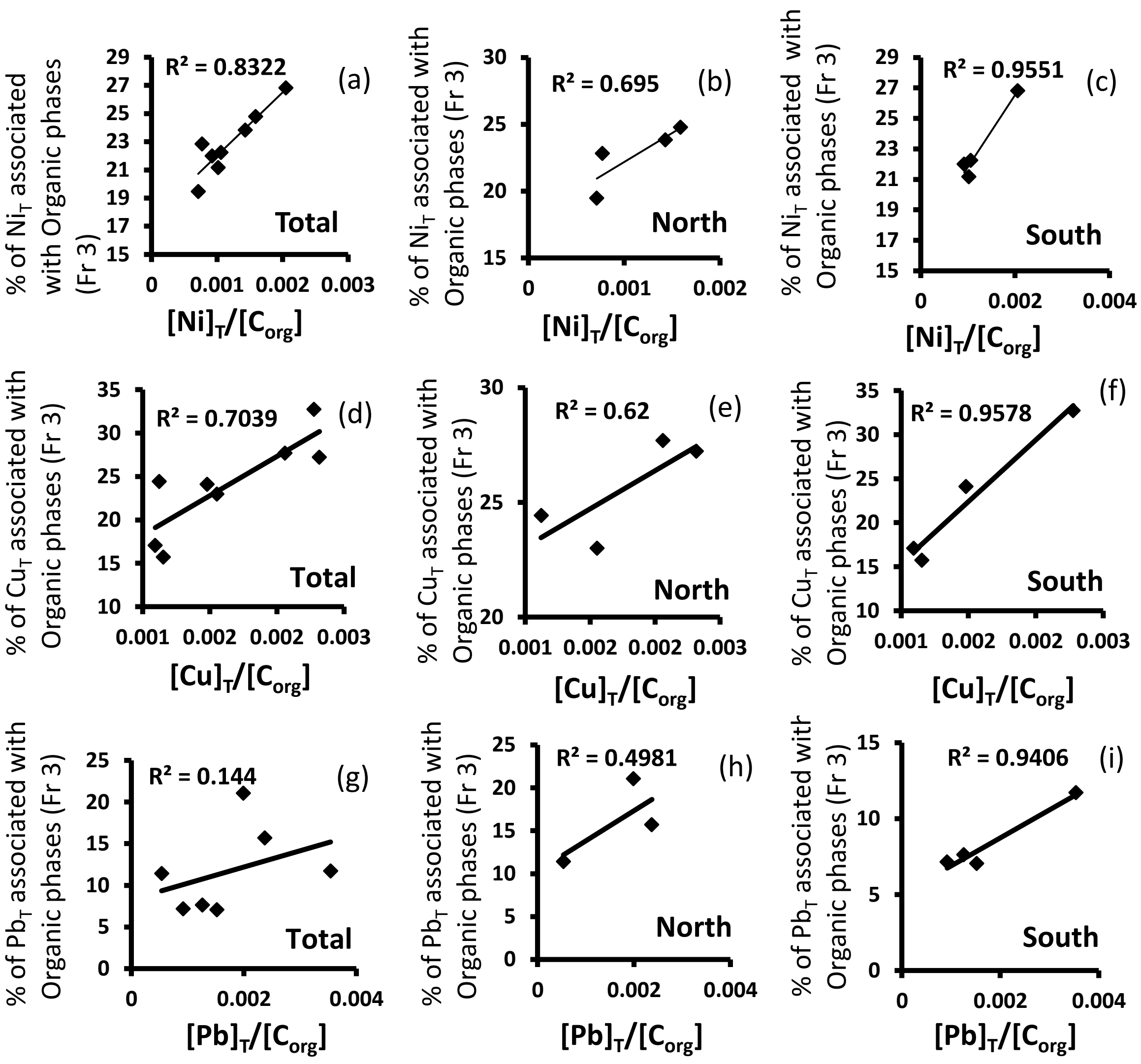


Figure 5.5 Association of Ni (%) with organic phase (Fr3) as a function of [Ni]/C$_{org}$ ratio in the studied sediments: a) across the lake sediments and b) northern part and c) southern part of the lake sediments. Association of Cu (%) with organic phase (Fr3) as a function of [Cu]/C$_{org}$ ratio of the studied sediments: d) across the lake sediments and e) northern part and f) southern part of the lake sediments. Association of Pb (%) with organic phase (Fr3) as a function of [Pb]/C$_{org}$ ratio of the studied sediments: g) across the lake sediments and h) northern part and
i) Southern part of the lake sediments

5.3.2 Sources of organic matter and its impact on geochemical fractionation of metals in the sediments

C:N_{molar} ratio and $\delta^{13}C_{org}$ were used to investigate the source of OM in the studied sediments from the Vembanad Lake. Both of these parameters have been widely used Meyers and Ishiwatari, 1993; Meyers, 1997; Zhang et al., 2009) to understand the sources of OM in sediments. However their utility and efficacy is based on the end-member (viz. fresh terrigenous OM and in-situ phytoplankton produced OM) shows distinct elemental and isotopic ratio from each other and these signatures does not get altered preferentially in sediments. The freshly deposited marine produced OM has C:N_{molar} ratio of 6-9 (Bordovskiy, 1965; Prahl et al., 1994, 1980) and $\delta^{13}C_{org}$ of -20.5‰. The vascular terrestrial C3 plant produced OM has C:N_{molar} ratio of 12-14 or more (Hedges et al., 1986; Prahl et al., 1994, 1980) and $\delta^{13}C_{org}$ of -30 to -23 ‰ (Smith and Epstein, 1971; Pancost and Boot, 2004). The values in between may indicate mixture of both marine and terrestrial OM. However the terrestrial C4 plant produced OM is richer in $\delta^{13}C_{org}$ (~ -17 to -9 ‰, (Smith and Epstein, 1971; Pancost and Boot, 2004;). But we did not consider C4 plants to be potential source in this area, as most of the vegetation in its watershed area is of C3 type.

The Figure 5.6a shows the latitudinal variation of C:N_{molar} ratio and $\delta^{13}C_{org}$ in the studied sediment along the lake. There was a drop in C:N_{molar} ratio in the northern part of the lake sediment compared to the C:N_{molar}ratio found in the sediment from southern part of the lake. This decreasing C:N_{molar} ratio indicates that the sedimentary C_{org} in from the northern part of the Vembanad Lake was mainly influenced by marine OM derived from in situ biological production and decreasing contribution from terrestrial OM. Further determination of stable isotopic ratio of C_{org} ($\delta^{13}C_{org}$) in the sediments confirms the increasing influence of marine C_{org} towards the northern part of the lake. Figure 5.6b shows that the $\delta^{13}C_{org}$ in sediments from north varied from -23.93‰ near Thannirmukkam Bund to -21.29 ‰ at northern most station. This clearly indicates increasing dominance of marine influence towards north. Similar observation has also been reported by Gireeshkumar et al. (2013) from sediments north of Thannirmukkam Bund. The $\delta^{13}C_{org}$ in the sediments from the southern part of the lake varied from -25.57 ‰ to -27.19‰ without any significant trend. Thus, sediments from the southern part receive OM from terrestrial origin. Similar observation has been reported by Verma and Subramanian (2002). It can be inferred that OM with terrestrial origin (in the southern part of the lake sediment) had more metal (Ni, Cu and Pb) complexing capacity than marine derived OM in the northern part of the lake.

5.3.3 Effect of ionic potential on geochemical fractionation of metals in the sediments

The intention of this section is to understand the influence of ionic potential of the studied metals on their geochemical fractionation in the major binding phase (organic phase) of the sediments**.** Ionic potential is a measure of density of charge of the ion. It is presented by charge/radius ratio of an ion. Ionic potential gives a sense of how strongly or weakly the ion will be electrostatically attracted to ions of opposite charge. High ionic potential of metal (high z^2/r) increases the covalency of metal-ligand bond (assuming the ligand is same). Thus, distribution of three different metals in the major binding phase (organic phase) of the studied sediment is interpreted by using their varying ionic potential (ionic potential (z^2/r): Ni (0.048), Cu (0.055), and Pb (0.034)).
Figure 5.7 shows the variation of metal association in the organic binding phases of the sediment from the different sampling sites of the lake. It shows that the association (as a result of complexation of metals) of metals gradually increased with the increasing ionic potential. It is assumed that the increasing covalency of Cu-ligand bond increased the thermodynamic stability of the Cu-ligand complexes in the sediments and highest concentrations of Cu was found to associate with organic phase followed by Ni and Pb. Figures 5.7a, b, c represent the variation of metal association in the organic phases of the sediments collected from the northern part of the lake. Figures 5.7d, e, f represent the sediments collected from the southern part of the lake. This study clearly indicates that ionic potential is an important parameter that can be used to understand the interactions of metals with organic binding phases of sediments.

5.3.4 Effect of metal chemistry on their distribution in different binding phases of the sediments

The geochemical distributions of a metal in different binding phases of marine sediments are influenced by the metal chemistry and the nature of ligands present in the sediment.

Association of a metal with different binding phases in sediment depends on the rate of complex formation by the metal and the stability of the formed complex.

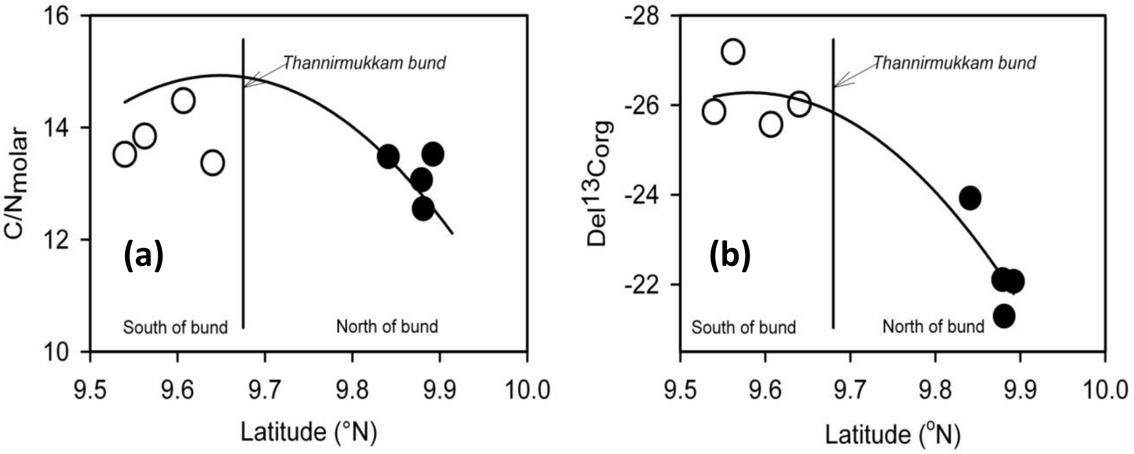


Figure 5.6 The latitudinal variation of a) C/Nmolar ratio and b) δ13Corg in the studied sediment along the lake

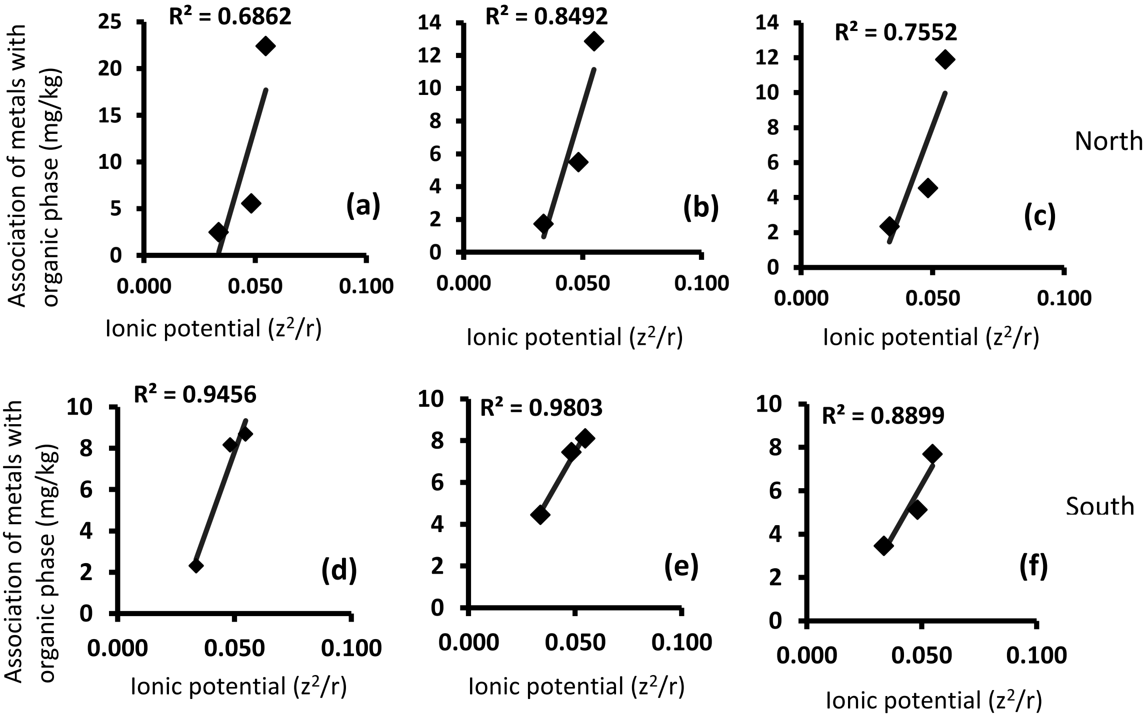


Figure 5.7 Variation of Ni (%) (a, d), Cu (%) (b, e), and Pb (%) (c, f) associated with organic phases (Fr3) of the sediments with the ionic potential (z^2/r) of the respective metals in the northern and southern parts of the lake sediments, respectively

Rate of complex formation (k_f) of a metal with different ligands (in any binding phases in sediment) depend on the water exchange rate of the metal ion (k_{-w}) and the stability of the outer-sphere complex (K_{OS}) of the metal with a particular ligand. The relation is given by: $k_f=K_{OS}.k_{-w}$

Thus, the distribution of Ni, Cu and Pb in organic and Fe/Mn oxyhydroxide phases of the studied sediments should be controlled by their K_{OS} and k_{-w}.

K_{OS} is primarily dependent on the charge of the reacting metal and ionic strength of the medium. In this study, Ni, Cu and Pb were considered as dipositive. It is assumed that the depositional environments (particularly ionic strength of the medium) were same for all the metals (during complexation) and thus, the rate of complex formation (k_f) with different ligands in the sediment were dependent only on the water exchange rates of the metal ions (k_{-w}).

Sequential extraction study suggests that highest concentration of Cu was associated with organic phases of the sediments followed by Ni and Pb.

The k_{-w} of Ni, and Cu are 3×10^4 (s^{-1}), 1×10^9 (s^{-1}) respectively. This clearly suggests that the faster water exchange rate helps Cu to undergo faster complex formation with the ligands in the binding phases of the sediment than Ni.

The Irving-Williams Series suggest that the stability constant for the formation of a high-spin complexes by Cu(II) is higher than Ni(II) complexes.

The smaller ionic radii and higher crystal field stabilization energy (CFSE) of Ni^{2+} is expected to increase the stability of Ni-sediment complexes than Cu-sediment complexes but octahedral Cu (II) complexes are subject to the Jahn-Teller effect, which affords Cu-sediment complex extra stability. Thus, a major part of the total Cu was associated with organic phases than Ni.

Faster water exchange rate of Cu (II) increased the rate of complex formation of Cu^{2+} ion with the ligand in the organic phases of the sediment. The Cu- ligand (from organic phase) complexes gain extra stability by the Jahn-Teller effect. The combined effects of these two phenomenons and high ionic potential increased the concentrations of Cu in the organic phases of the sediments than Ni and Pb. The second highest concentration of metal associated with organic phases in the studied sediment was Ni. The higher ionic potential of Ni^{2+} (0.048) than Pb^{2+} (0.034) increase the stability of Ni-ligand complexes in the organic phase of the sediments. In addition to that high CFSE of Ni (II) (compared to Pb^{2+} ions) make Ni-organic complexes increasingly stable than

Pb. High k-w (7×10^9 s^{-1}) of Pb did not help to associate with organic phases in the sediments.

However, maximum concentration of Pb was found to associate with Fe/Mn oxide phases of the sediment followed by Ni and Cu. Similar observation has also been reported in literature. Lion et al (1982) have reported that more than 70% of the extractable Pb from estuarine sediments can be associated with Fe and Mn oxides. Luoma and Bryan (1981) have also reported that iron is an important binding phase for Pb. Fe/Mn-oxyhydroxides has been reported to occur widely in surficial and subsurface geological environments and they are efficient scavengers of trace metals including Pb. The high concentration of Pb in Fe/Mn-oxyhydroxide in the sediments was probably due to co-precipitation of Pb^{2+} and Fe^{3+}. High surface area or site availability for Pb^{2+} ion on Fe-oxyhydroxide phase (Nelson et al., 1999; Lu et al., 2011) and greater binding strength over simple precipitate surface (Manceau et al.2002) was probably responsible for the high concentration of Pb in Fe/Mn oxyhydroxide phase.

The decreasing concentrations of Cu in Fe/Mn–oxyhydroxide phases with the increasing Cu loading in the sediment suggest that Cu did not prefer to associate with Fe/Mn oxyhydroxide phases. Increasing concentrations of Cu in organic phases with the increasing Cu-loading suggest that enough binding sites were available for Cu in the organic binding phases of the sediments.

5.4 Conclusions

This study provides chemically significant description of metals-ligand interactions in different binding phases of sediments. It was found that Cu showed highest affinity for organic binding phases followed by Ni and Pb in the studied sediments. However, Pb had highest association with Fe/Mn-oxide phases followed by Ni and Cu. Nature of sedimentary C_{org} (terrestrial and marine derived C_{org}) was found to play an important role in controlling metal distribution and speciation in marine sediments. Metals were found to have more affinity for terrestrial C_{org} than the marine derived C_{org} in the sediments. This study also suggests that ionic potential of the metal is an important parameter that can be used to understand the interactions of metals with organic binding phases of sediments. Faster k_{-w} of Cu (II) (1×10^9 s^{-1}) increased the rate of complex formation of Cu^{2+} ion with the ligand in the organic phases of the sediments. The Cu-ligand (from organic phase) complexes gain extra stability by the Jahn-Teller effect.

The combined effects of these two phenomena and high ionic potential increased the association of Cu in the organic phases of the sediments than Ni and Pb. The smaller ionic radii of Ni^{2+} (0.72 A) than Pb^{2+} (1.20 A) increase the stability of Ni-ligand complexes in the organic phase of the sediments. In addition to that high CFSE of Ni (II) (compared to Pb^{2+} ions) make Ni-organic complexes increasingly stable than Pb. The high concentration of Pb in the Fe/Mn-oxyhydroxide binding phase was probably due to co-precipitation of Pb^{2+} and Fe^{3+}. High surface area or site availability for Pb^{2+} ion on Fe-oxyhydroxide phase and greater binding strength over simple precipitate surface was probably responsible for the high concentration of Pb in Fe/Mn oxyhydroxide phase.

Chapter 6

Effects of bottom water dissolved oxygen variability and trace metal (Cu) competition on lead fractionation in the sediments across the oxygen minimum zone, Western Continental margin of India

6.1 Introduction

Changes in concentrations of dissolved oxygen in bottom water can modify metal speciation in the bottom sediments (Calmano et al., 1993; Middleburg and Levin, 2009). Different fractions of metals (operational speciation) in sediment can be classified based upon their association with different binding phases in the sediments: acid soluble forms (water soluble, exchangeable and carbonate/bicarbonate forms); reducible forms (metal associated with Fe, Mn-oxyhydroxide binding phases); oxidizable forms (metal associated with sedimentary organic carbon binding phases); and residual forms (metals within the structure of sediment). The first three forms of metals (acid soluble, reducible and oxidizable) are considered as bioavailable forms of metals (non-residual) in sediment. The residual fraction of metal is considered as inert and non-bioavailable pool of metals (Alvarez et al., 2002; Kwon, and Lee, 2001; Chakraborty et al., 2012; 2014).

Sedimentary organic matter and Fe/Mn oxyhydroxide have been reported to be the major metal binding phases in oxic sediments (Luoma and Bryan 1981; Tack and Verloo, 1995). Reduction of Fe(III), and Mn(IV) (from Fe/Mn-oxyhydroxide) predominates under hypoxic or anoxic condition (Greatz et al, 1973). However, preservation of sedimentary organic matter has been reported under the same condition (Jahnke et al., 1982; Henrichs and Reeburgh 1987; Lovely, 1987; Pedersen and Calvert, 1990; Paropkari et.al., 1993; Nath et.al., 1997; Middelburg and Levin, 2009). Thus, a change in dissolved oxygen concentration (from oxic to hypoxic and then close to suboxic) in overlying water can modify Fe(III)/Mn-oxyhydroxide and sedimentary organic binding phases of the bottom sediments. Thus, changes in bottom water oxygen levels may alter the distribution and speciation of metals associated with these two major metal binding phases

Copper (Cu) has been reported to have significant affinity towards organic phases in marine sediments (Chakraborty et al., 2015a; Chakraborty et al., 2016; Flemming and Trevors, 1989; Hanson and Quinn 1983). Major fractions of non-residual Cu has been reported to associate with sedimentary organic matter (oxidazable form). However, lead (Pb) has been reported to show strongest affinity for Fe/Mn-oxyhydroxide phase in sediments (reducible phase) (Chakraborty et al., 2015a; Chakraborty et al., 2015b; Belzile et al., 1989). Thus, distinct effects of varying bottom water oxygen concentration are expected to impact Cu and Pb speciation (as Fe/Mn-oxyhydroxide and sedimentary organic matter are the major hosting phases for these two metals) in the bottom sediments.

The Arabian Sea hosts the second-most intense perennial oxygen minimum zone (OMZ) in the world tropical ocean (Kamykowski and Zentara, 1990), with near-total depletion of oxygen at depths from 150 to 1000 m (Banse etal., 2014; Morrison et al., 1998). It is of global biogeochemical significance because of denitrification in the upper part leading to N_2 and N_2O production (Naqvi and Noronha, 1991). The residence time of OMZ water is believed to be less than a decade (Banse et al., 2014). The upper few hundred meters of this zone has been reported to be nearly anoxic but non-sulfidic (Banse et al 2014). Naqvi and Noronha (1991) have also reported that this zone is predominantly suboxic ($\lesssim 5$ µmol O_2/kg) in nature. The changing redox condition of overlying bottom water from this region is expected to have tremendous impact on Cu and Pb speciation in the bottom sediments and their stability across the OMZ, and thus, this study was undertaken, across the two transects of the OMZ in the eastern Arabian Sea.As Fe is the redox sensitive element and act as the major bonding phase (specially the oxyhydroxide form of Fe) of trace metals, total sedimentary Fe and its different geochemical forms were also studied in the sediments.

Sediment samples were collected in two transects passing through the perennial OMZ from the western continental margin of India. Off Karwar, in the southern part of the shelf ,where the existence of upwelling-favourable conditions has been reported and off Gujarat ,the northern part of the shelf, where the upwelling has been reported to be less conspicuous (Muraleedharan and Kumar 1996) (Figure 6.1).

The sediment samples were collected in such a way to ensure that there were distinct variations in the dissolved oxygen (DO) concentration of the overlying bottom waters. The definitions of various stages of oxygen deficiency in seawater are described in Table 6.1 Table 6.2 presents the details of the sediment sampling locations and the variation in, temperature salinity, dissolved oxygen concentration and redox state of the overlying bottom water.

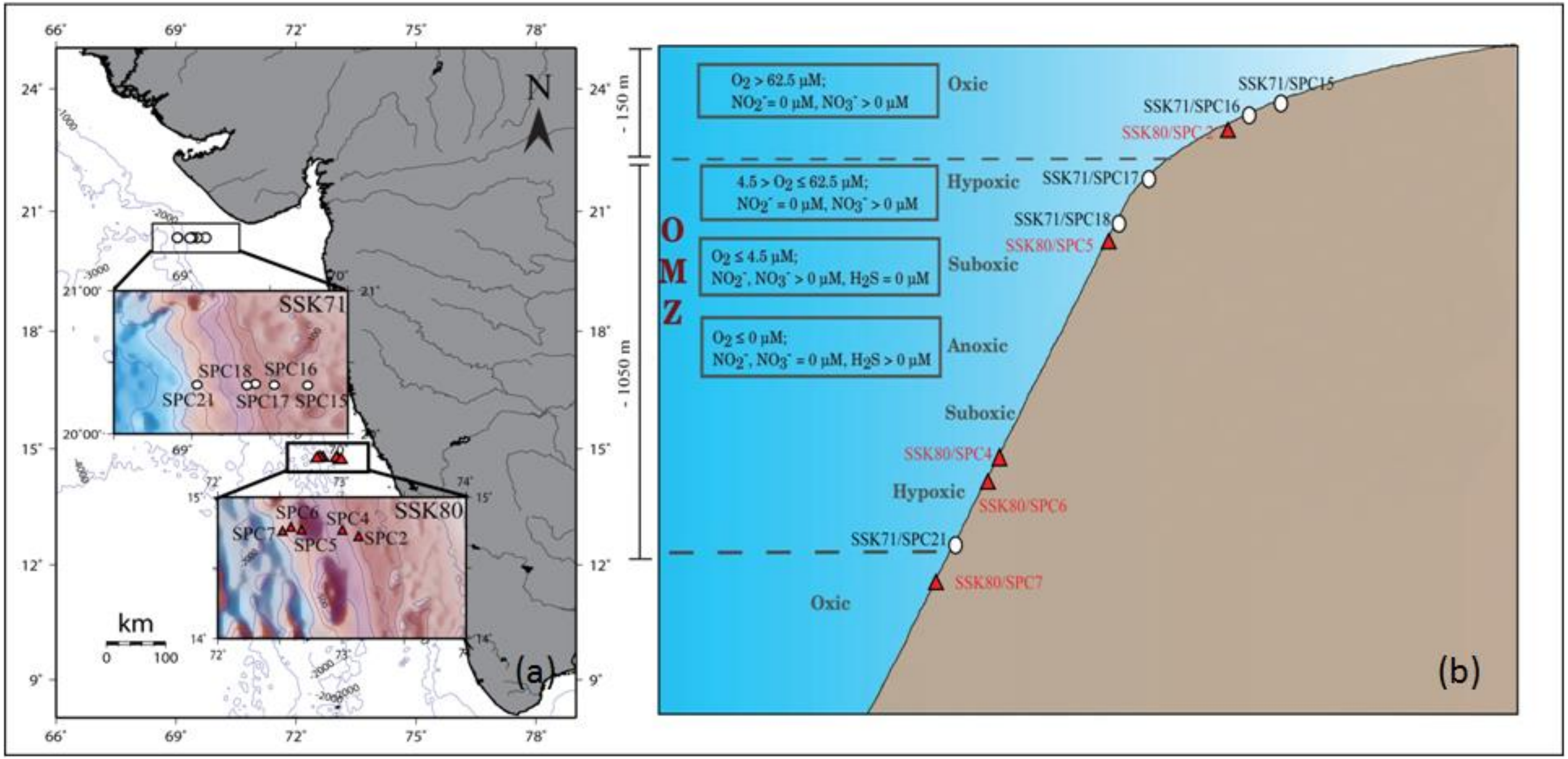


Figure 6.1 Study area: Sediment samples were collected from (a) the continental margin off Karwar (SSK#80) and off Gujarat (SSK#71), west coast of India; (b) Schematic diagram of sampling locations with respect to depth and oxygen concentrations

Table 6.1 The description of oxic, hypoxic, suboxic and anoxic conditions are defined below

Stage	Criteria
Oxic	O_2>62.49 μM*; NO^-_2 = 0 μM, NO_3^->0 μM
Hypoxia	4.46<O_2 ≤62.49 μM; NO^-_2 = 0 μM, NO_3^->0 μM
Suboxia	O_2 ≤ 4.46 μM, NO^-_2 , NO^-_3>0 μM; H_2S=0μM
Anoxia	O_2=0 μM , NO^-_2 , NO^-_3 =0 μM, H_2S>0μM

*1 ml l^{-1}=1.43 mg l^{-1}=44.6 μM (Naqvi et al 2010)

Table 6.2 Geographical locations of sampling sites, temperature, salinity, Dissolved oxygen (DO) (µM), redox state of the overlying bottom water, depth (m) from where the sediment samples were collected, concentration of C_{org} (%), texture (sand,silt+clay) (%), total Pb, Cu and Fe (mg.kg^{-1}) in the studied sediment

Station	**LAT (°N)**	**LONG (°E)**	**Depth (m)**	**Temp. (^{0}C)**	**Salinity (PSU)**	**DO (µM)**	**Redox state**	C_{org} **(%)**	**Particle size**		**Pb**	**Cu**	**Fe**
									Sand (%)	**Silt+Clay (%)**	**(mg.kg^{-1})**	**(mg.kg^{-1})**	**(mg.kg^{-1})**
SSK71/SPC15	20 20.44	69 44.54	80	23.6	36.4	81.1	Oxic	1.1	77	23	9.6±0.4	35.0±1.3	74158
SSK71/SPC16	20 20.56	69 31.71	98	22.9	36.4	67.5	Oxic	1.1	92	8	8.0±0.6	27.2±0.8	65856
SSK71/SPC17	20 20.98	69 24.48	195	19.9	35.9	32.0	Hypoxic	2.5	58	42	11.3±0.9	36.2±1.3	54891
SSK71/SPC18	20 20.40	69 21.19	297	14.8	35.8	7.4	Hypoxic	3.8	45	55	8.8±0.1	39.7±0.4	73446
SSK71/SPC21	20 20.64	69 02.052	1544	5.3	35.1	47.3	Hypoxic	3.4	4	96	9.8±1.4	50.3±1.4	63151
SSK80/SPC 2	14 43.72	73 18.93	110	26.8	39.2	150.5	Oxic	1.0	59	41	12.8±0.1	19.4±0.1	33210
SSK80/SPC4	14 45.52	73 00.19	563	10.9	37.2	8.2	Hypoxic	6.5	5	95	12.1±1.3	41.7±0.1	30940
SSK80/SPC5	14 45.65	72 40.45	329	12.7	37.1	4.7	Close to suboxic	8.0	14	86	11.5±0.4	35.4±1.8	31050
SSK80/SPC6	14 46.79	72 35.42	682	11.3	38.1	14.9	Hypoxic	6.8	24	76	11.9±0.3	31.7±1.8	22260
SSK80/SPC7	14 45.15	72 31.24	1711	4.1	37.9	84.6	Oxic	1.7	6	94	10.0±1.1	39.6±0.2	36760

The concentrations of Pb and Cu are expressed as mean ± standard deviation (n=3)

6.2 Results

6.2.1 Variability of dissolved oxygen (DO) concentrations (in bottom water), texture and sedimentary organic carbon content (in sediments) across the OMZ

The various stages of oxygen deficiency in the overlying bottom water (in the study areas) are described in Table 6.2. The sediment samples were purposely collected across the OMZ where the condition of the overlying bottom water changed from oxic to hypoxic and close to suboxic. The distributions of particle size in the sediments are presented in Table 6.2. Coarser particles (sand) (ranging from ~4 to 92%) dominated at the edge of the continental shelf but finer particles (silt+clay) subjugated (ranging from ~8 to 96%) in the sediment collected from the continental slope areas. The sedimentary organic matter (presented as total organic carbon, C_{org}) content was found to vary from ~1.1 to 8.0 %. A significant positive correlation coefficient was found between the finer sized particles (silt + clay) and C_{org} ($r = 0.62$ $p < 0.05$, $n = 10$) (Table 6.3) content in the sediments. This indicates that there was high sorption and affinity of C_{org} on the finer particles in the studied sediments. A similar observation has been reported in the literature (Hedges and Keil, 1995; Paropkari et al., 1987; Chakraborty et al., 2015c). Significant negative correlation was observed between the C_{org} content in the sediments and the dissolved oxygen (DO) of the overlying bottom water (Table 6.4, Figure 6.2). It was found that less amount of sedimentary organic matter (represented by C_{org}) was associated with the finer particles of the sediments under oxic environment. However, preservation of organic matter in the sediment was found to be more under the low oxygen environment. It has been reported that hypoxia of the overlying bottom water may increase organic matter (of higher quality, i.e. less degraded) accumulation and burial in the underneath sediment (Middelburg and Levin, 2009; Nath et al., 1997).

6.2.2 Distribution of total metals (Cu and Pb) in the surface sediments across the OMZ

The Cu and Pb content in the surface sediments across the OMZ were found to vary from 19.4±0.1 to 53.1±0.2 $mg.kg^{-1}$ and 8.0±0.6 to 12.8±0.1 $mg.kg^{-1}$ respectively (Table 6.2). Apparently it seems that varying concentration DO of the overlying bottom water

Table 6.3 Pearson correlation coefficient between the finer particles (silt + clay) and C_{org}

	sand%	Silt%	clay%	Silt+clay	C_{org}
sand%	1				
Silt%	-0.93	1			
clay%	-0.95	0.77	1		
Silt+clay	-1	0.93	0.95	1	
C_{org}	-0.62	**0.68**	**0.50**	**0.62**	1

Correlation is significant at the 0.05 level (2 tailed)(n=10)

Table 6.4 Pearson correlation of dissolved oxygen (DO) in overlying bottom water, total organic carbon (C_{org}), Cu, Pb, and Fe associated with Fe/Mn-oxyhydroxide (Fr.3), and the organic binding phase (Fr.4) in the sediments

	DO(μM)	**C_{org}(%)**	**Cu.Fr.3**	**Cu.Fr.4**	**Pb.Fr.3**	**Pb.Fr.4**	**Fe.Fr.3**	**Fe.Fr.4**
DO(μM)	1.00							
C_{org}(%)	**-0.78**	1.00						
Cu.Fr3	0.40	-0.38	1.00					
Cu.Fr4	**-0.82**	**0.82**	-0.21	1.00				
Pb.Fr3	0.64	-0.12	0.20	-0.28	1.00			
Pb.Fr4	-0.48	0.40	-0.46	0.55	-0.38	1.00		
Fe.Fr3	**0.89**	-0.46	0.36	-0.58	**0.91**	-0.46	1.00	
Fe.Fr4	-0.02	0.48	-0.37	0.39	0.60	0.09	0.34	1.00

Correlation is significant at the 0.01 level (2 tailed)(n=10) across the OMZ had little effect on the total Cu and Pb content distribution in the studied sediments. However, positive statistical correlation was observed between the C_{org} content, finer particle (silt+clay) content, and distance from the shore with the total Cu and Pb concentrations in the sediments. It is important to mention that total metal concentration in the sediment does not provide useful information about their specific chemical forms and their stability in the sediments. Thus, geochemical fractionation and kinetic fractionation studies of Cu and Pb were carried out to understand different geochemical processes that would take place in the sediment under the changing DO concentration of the overlying water across the OMZ in the Arabian Sea.

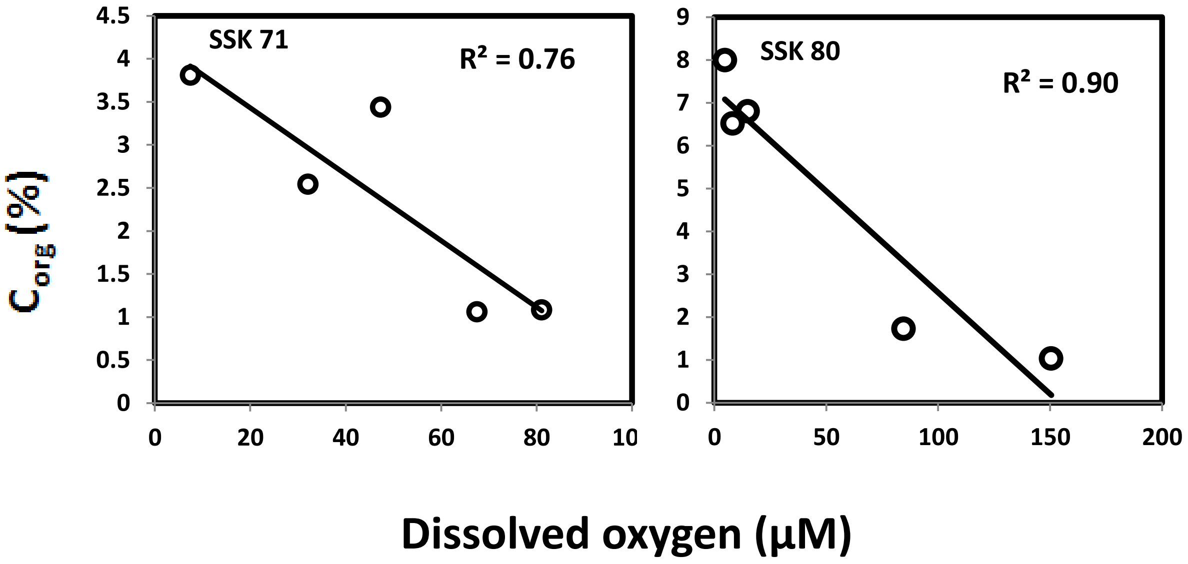


Figure 6.2 Variation of total organic carbon (C_{org}) (%) with varying bottom water oxygen concentration (DO) (µM) in the northern (shown on left) and the southern (right) transects of Eastern Arabian Sea

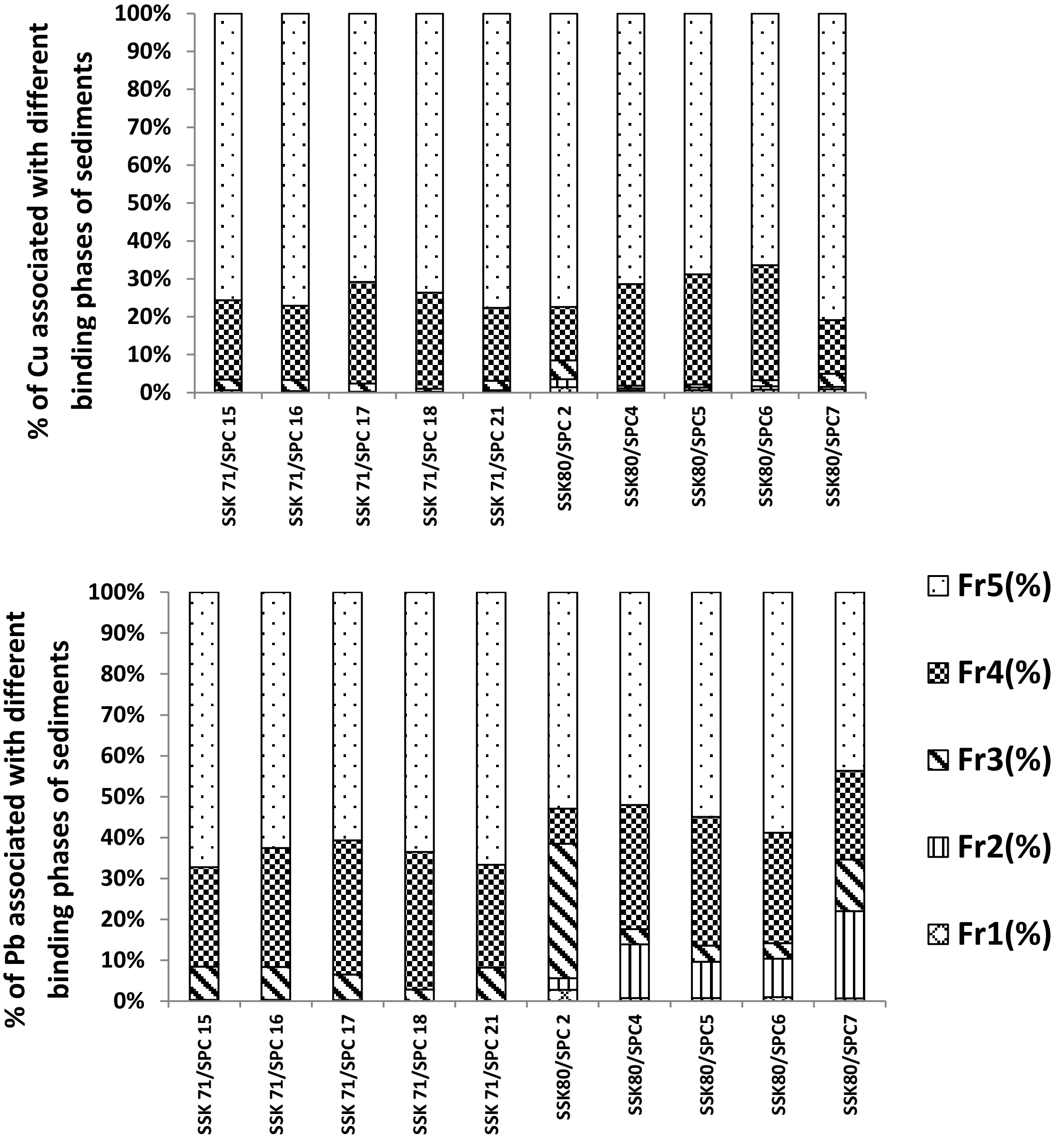


Figure 6.3 Distributions of Cu (a) and Pb (b) in different binding phases of the surficial sediments across the OMZ, SPC71 and SPC80 representing northern and southern transects

6.2.3 Geochemical fractionation of Cu and Pb in the surface sediments across the OMZ

Distributions of Cu and Pb in the different binding phases of the studied sediments are shown in Figure 6.3a and 6.3b and the data (in percentage) are presented in Table 6.5. The lowest fraction of the total concentration of both the metals (vary from 0.1 - 0.9% of the total Cu and ~ 0.0 - 2.7% of the total Pb) in the sediments were present as water soluble complexes.

The fraction of exchangeable and carbonate/bicarbonate forms of Pb and Cu (Fr.2) in the sediments were found to vary from ~0.1 - 2.1% and 0.0 - 21.3% of the total Cu and Pb concentrations in the sediments respectively. Concentrations of Cu and Pb associated with Fe/Mn-oxyhydroxide binding phases (Fr.3) in the sediments were higher than their concentrations in the Fr1 and Fr.2. Scavenging property of Pb by Fe/Mn oxyhydroxide phase in water column and sediment has been identified as an important process in controlling speciation and geochemistry of Pb in marine system (Jones and Turki, 1997; Tessier et al., 1979; Chakraborty et al., 2015a). However, the Fr.2 of Pb was occasionally higher than the Fr.3 in the underneath sediments (off Karwar) where DO concentration of the overlying bottom water was low (Table 6.5). The fraction of total Pb associated with Fe/Mn oxyhydroxide binding phase gradually increased (~2.8 to 32.9% of the total Pb across the two transects) with the increasing DO level of the overlying bottom water (Figure 6.4). The variations of Pb content (in terms of percentage of the total Pb) in the Fe/Mn oxyhydroxide binding phase against the varying DO level of the overlying bottom water from the two transects are shown separately in the inset (Figure 6.4).

Compared to Pb, less Cu was bound to Fe/Mn oxyhydroxide (0.7 to 5.0% of the total Cu across the two transects). This indicates that Fe/Mn oxyhydroxide phase in the studied sediments acted as one of the important hosting phases for Pb but not for Cu. Major fractions of the total non residual metal (8.6 – 33.6% of the total Pb and 14.1 to 30.3% of the total Cu) were associated with sedimentary organic matter and sulphides (Fr 4). It was found that Cu had more affinity towards the organic binding phases (including sulphides) than Fe/Mn oxyhydroxide binding phases in the sediments. Strong affinity of Cu for organic binding ligands has already been reported in the literature (Chakraborty et al 2007)**.** Major fractions of the total Pb (~43.7 – 67.3% of the total Pb) and Cu (66.4 – 80.9 % of the total Cu) were present within the structure of the sediments (Fr.5).

As Fe is the redox sensitive element and act as the major bonding phase (specially the oxyhydroxide form of Fe) of trace metals, geochemical fractionation study of Fe was performed to understand the changes in concentration of Fe-oxyhydroxide binding phase in the studied sediments.

6.2.4 Geochemical fractionation of Fe in the surface sediments across the OMZ

The Fe content in the surface sediments across the OMZ were found to vary from 22260 to 74158 mg.kg^{-1} (Table 6.2).Distributions of different geochemical forms of Fe in the studied sediments (across the OMZ) are presented in Table 6.5. The highest fraction of the total Fe was present in the residual phase (i.e. within the structure of the sediment) in all the sediments. The second highest fraction of the total Fe was associated with organic phase or present as Fe-sulphide. It has been reported that organic matter can trap Fe in marine environment. It was also found that the concentrations of Fe associated with organic binding phase increased with increasing sulphide concentrations in the sediments. Thus, one could expect that sedimentary organic matter were the major binding phases for Fe in the sediments. The concentration of Fe(III)-oxyhydroxide (one of the major hosting phases for Pb and Cu) was found to be the third highest fraction of the total Fe in all the sediment.

Table 6.5 Percentage of total Cu and Pb and the concentration of Fe in different binding phases of the studied sediments across the OMZ

	Station	**DO (µM)**	Fr1(%)	Fr2(%)	Fr3(%)	Fr4(%)	Fr5(%)
Cu	**SSK71/SPC15**	81.1	0.0	0.5	2.9	20.9	75.6
	SSK71/SPC16	67.5	0.0	0.3	3.0	19.5	77.1
	SSK71/SPC17	32.0	0.1	0.1	2.2	26.8	70.8
	SSK71/SPC18	7.4	0.1	0.1	0.8	25.3	73.7
	SSK71/SPC 21	47.3	0.5	0.1	2.6	19.2	77.7
	SSK80/SPC 2	150.5	1.5	2.1	5.0	14.1	77.4
	SSK80/SPC4	8.2	0.5	0.6	0.7	26.8	71.4
	SSK80/SPC5	4.7	0.6	0.7	0.8	29.1	68.8
	SSK80/SPC6	14.9	0.8	0.9	1.7	30.3	66.4
	SSK80/SPC7	84.6	0.9	0.7	3.4	14.1	80.9
Pb	**SSK71/SPC15**	81.1	0.2	0.1	8.1	24.3	67.3
	SSK71/SPC16	67.5	0.0	0.3	8.0	29.1	62.6
	SSK71/SPC17	32.0	0.0	0.2	6.2	32.9	60.7
	SSK71/SPC18	7.4	0.0	0.1	2.8	33.6	63.5
	SSK71/SPC 21	47.3	0.0	0.0	8.2	25.1	66.7
	SSK80/SPC 2	150.5	2.7	2.9	32.9	8.6	52.9
	SSK80/SPC4	8.2	0.7	13.1	3.8	30.4	52.0
	SSK80/SPC5	4.7	0.8	8.8	4.0	31.5	54.9
	SSK80/SPC6	14.9	1.0	9.4	3.8	27.0	58.8
	SSK80/SPC7	84.6	0.7	21.3	12.6	21.7	43.7
Fe	**Station**	**DO (µM)**	Fr1(mg.kg^{-1})	Fr2(mg.kg^{-1})	Fr3(mg.kg^{-1})	Fr4(mg.kg^{-1})	Fr5(mg.kg^{-1})
	SSK71/SPC15	81.1	2.1	37.4	329.9	278.2	73510
	SSK71/SPC16	67.5	3.7	10.9	370.9	180.8	65290
	SSK71/SPC17	32.0	13.4	13.7	192.2	541.1	54130
	SSK71/SPC18	7.4	3.9	16.3	128.4	1237.8	72060
	SSK71/SPC 21	47.3	11.9	16.3	269.2	1083.8	61770
	SSK80/SPC 2	150.5	0.0	41.6	1166.6	1927.3	30074
	SSK80/SPC4	8.2	0.0	12.3	267.8	1267.6	29392
	SSK80/SPC5	4.7	0.0	20.3	197.0	1552.2	29280
	SSK80/SPC6	14.9	0.0	23.3	356.4	1080.4	20799
	SSK80/SPC7	84.6	0.0	14.6	588.0	397.5	35759

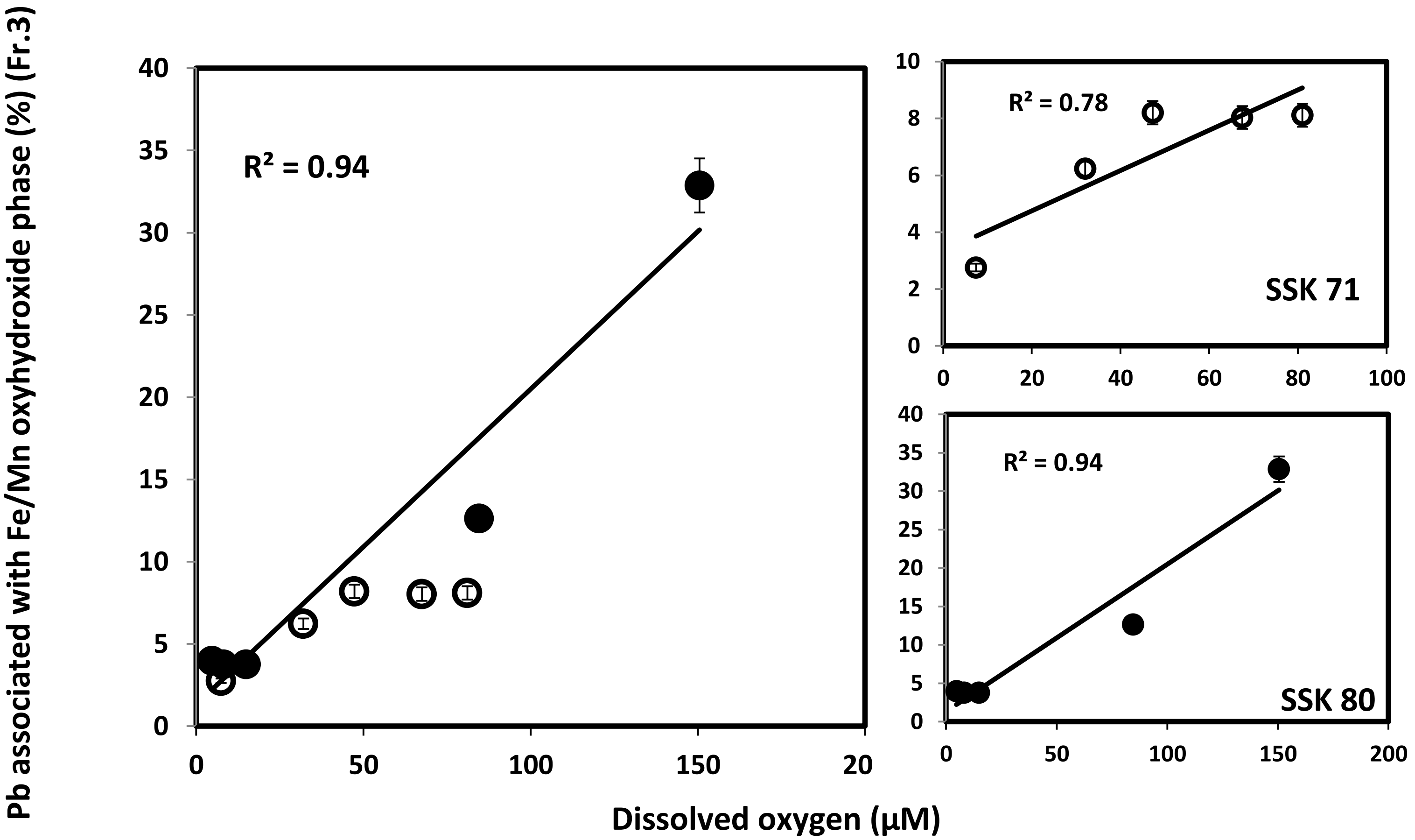


Figure 6.4 Variation of Pb (%) in Fe-Mn oxy-hydroxide phase in the studied sediment with varying bottom water oxygen concentration (DO)(µM) (together for both the transects on left and the individual transects on the right)

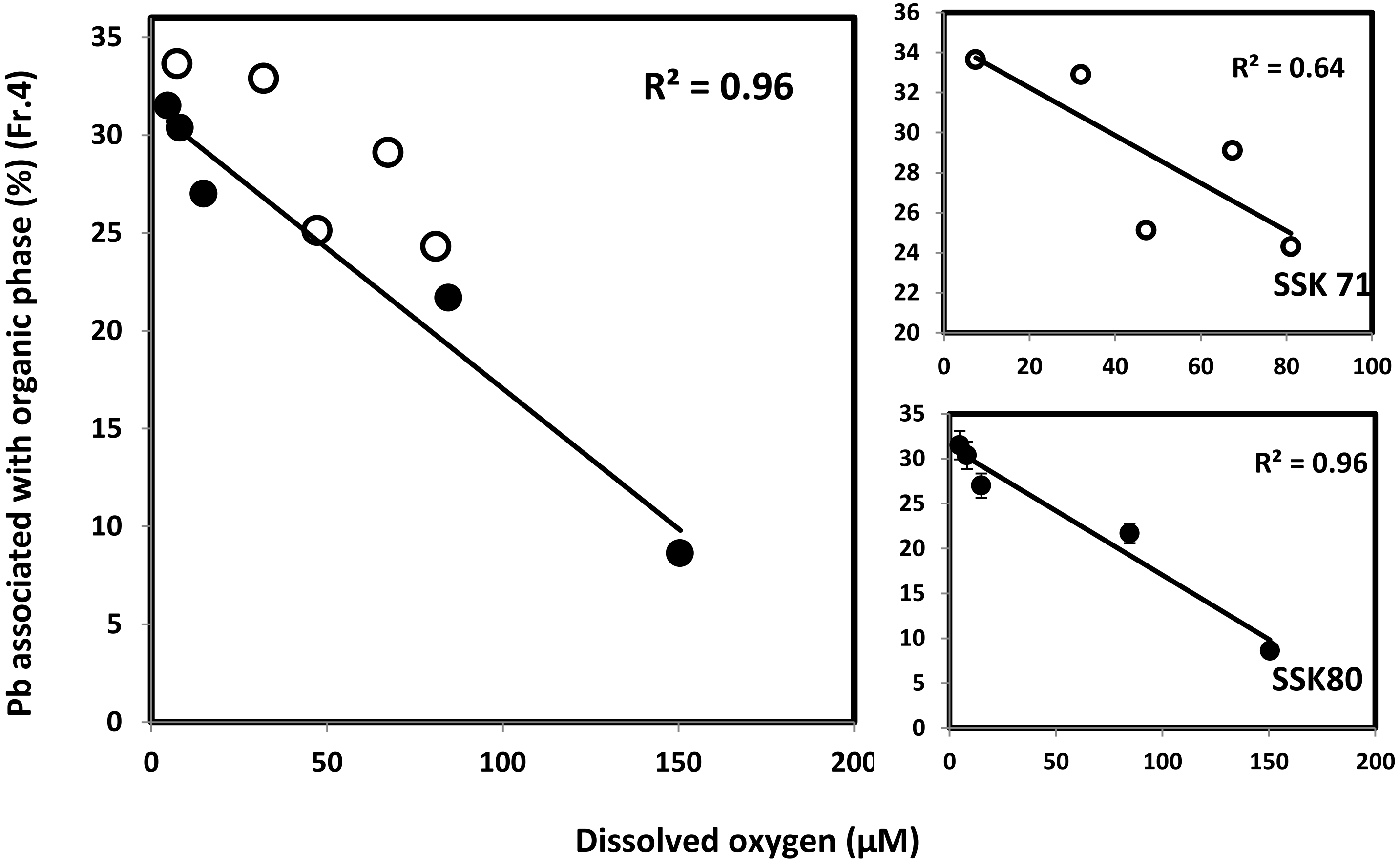


Figure 6.5 Variation of Pb (%) in organic phase in the studied sediment with varying bottom water oxygen concentration (DO) (µM) (togetherfor both the transects on left and the individual transects on the right)

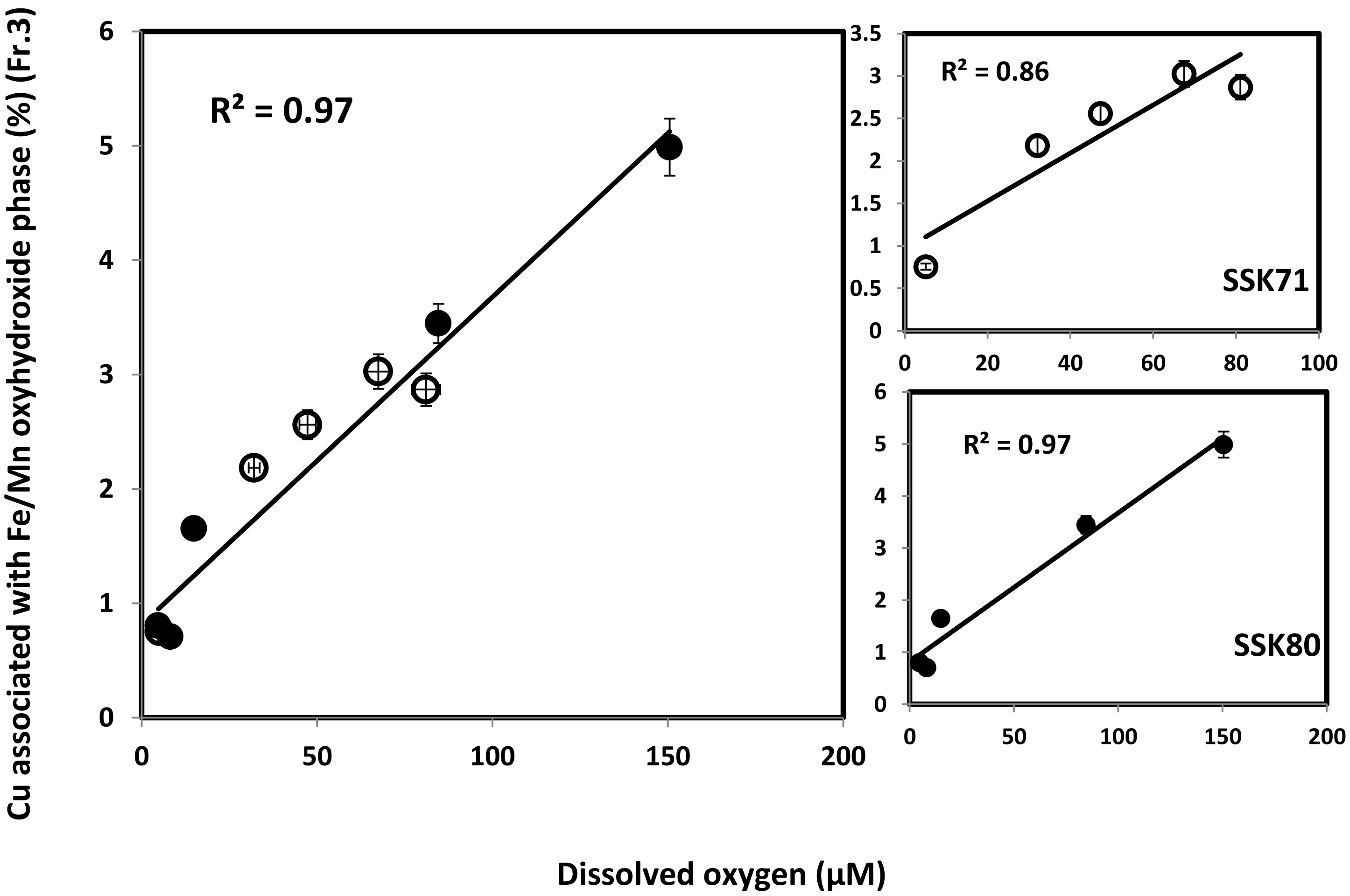


Figure 6.6 Variation of Cu (%) in Fe/Mn oxyhydroxide phase in the studied sediment with varying bottom water oxygen concentration (DO)(µM) (togetherfor both the transects on left and the individual transects on the right)

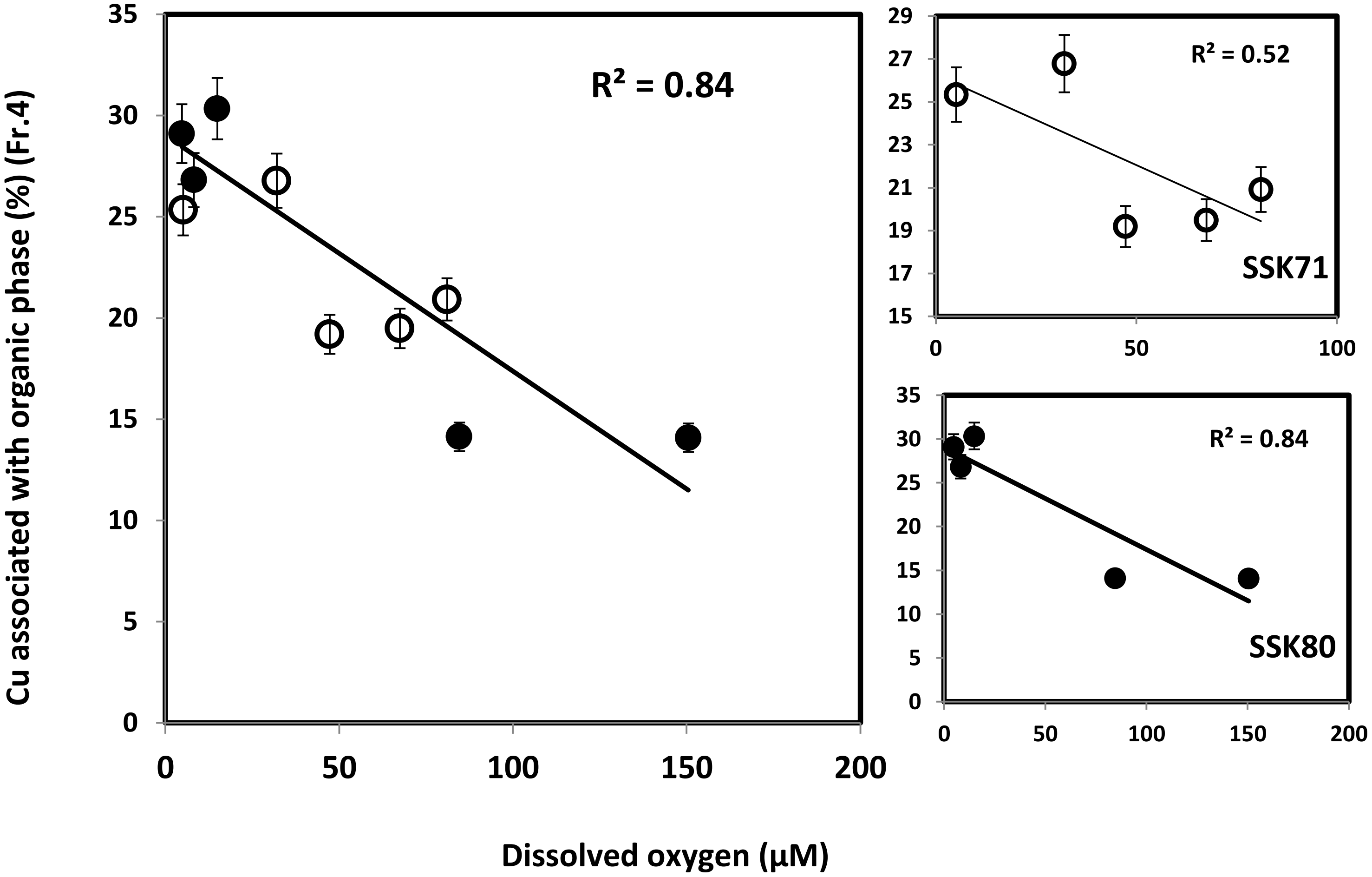


Figure 6.7 Variation of Cu (%) in organic phase in the studied sediment with varying bottom water oxygen concentration (DO) (µM)(togetherfor both the transects on left and the individual transects on the right)

6.3 Discussion

6.3.1 Impact of varying dissolved oxygen concentration in the bottom water on geochemical fractionation of Cu and Pb in the sediment

In this section, the impact of varying dissolved oxygen concentrationin the overlying bottom water on geochemical fractionation of Cu and Pb in the underneath sediments are discussed.

Table 6.4 indicates that there was a strong positive correlation ($r=0.70$, $p <0.05$, $n = 10$) between the Pb content associated with Fe/Mn-oxyhydroxide binding phase (Pb Fr.3) in the sediment and the dissolved oxygen concentrations of the overlying bottom water. There was a gradual decrease in Pb association (~8.2 to 2.8 % (SSK 71) and 32.9 to 3.8 % (ssk-80) of the total Pb) with Fe/Mn-oxyhydroxide binding phase in the sediment with the decreasing dissolved oxygen concentrations (from ~81.1 to 7.4 µM (SSK-71) and 150.5 to 8.2 µM (SSK-80)) of the overlying bottom water (Table 6.5 and Figure 6.4).

It is well known that reduction (Fe(III) to Fe(II)) and dissolution of Fe(III) takes place under hypoxic condition (Berner,1981; Lovely and Phillips,1988; Nealson and Saffarini ,1994; Sørensen,1982). Metals (trace/heavy) associated with Fe(III)-oxyhydroxides are expected to be released during dissolution of Fe(III) process under low oxygen environment. Thus, one could expect a gradual decrease of Pb association with Fe(III)-oxyhydroxide phase in the sediments with the decreasing dissolved oxygen level of the overlying bottom water. It is interesting to note that there was a strong negative correlation ($r = -0.57$, $p <0.05$, $n = 10$) (Table 6.4) seen between the Pb associated with the sedimentary organic phases (Pb Fr.4) and the dissolved oxygen concentration of the overlying bottom water. Increase in concentration of sedimentary organic matter with decreasing DO level was probably responsible for the increase in Pb association with organic binding phases in the sediments (as shown in Figure 6.5).

The concentration of Cu associated with Fe(III)-oxyhydroxide (Cu Fr.3) in the sediments was positively ($r = 0.97$, $p <0.05$, $n=10$) correlated with the DO concentration of the overlying bottom water (Figure 6.6). Association of Cu with Fe (III)-oxyhydroxide in the sediments decreased (~3.0 to 0.8 % (SSK 71) and 5.0 to 0.7 % (SSK-80) of the total Cu) with the decreasing DO concentrations (from ~81.1 to 7.4 µM (SSK-71) and 150.5 to 8.2 µM (SSK-80)) of the overlying bottom water as shown in Figure 6.6. Table 6.5 shows that there was increase in Cu association with the sedimentary organic matter (from ~19.2 to 26.8 % (SSK 71) and 14.1 to 30.3 % (ssk-80) of the total Cu) with the decreasing DO level (from ~81.1 to 7.4 µM (SSK-71) and 150.5 to 8.2 µM (SSK-80) of the overlying bottom water (Figure 6.7). Slow degradation of organic matter lead to increased preservation of sedimentary organic matter at low oxygen environment in this region.

The steady decrease in the Cu concentration associated with Fe/Mn oxyhydroxide is probably due to the reduction and dissolution of Fe(III)/Mn-oxyhydroxide binding phase in the sediment. Preservation of more organic matter in the sediments under low oxygen environment was also observed. It was found that Cu started accumulating more with the organic binding phases of the sediments with decreasing concentration of dissolved oxygen of the overlying bottom water. However, further geochemical fractionation study of Fe was performed to understand the changes in concentration of Fe-oxyhydroxide binding phase in the studied sediments.

6.3.2 Impact of varying dissolved oxygen concentration in the bottom water on geochemical fractionation of Fe in the surface sediments

It is important to note that there was no significant variation of the total sedimentary Fe concentration with varying DO concentrations of the overlying bottom water observed. However, a significant variation in the concentration of Fe (III)-oxyhydroxide was found with varying DO level of the overlying bottom water.Figure 6.8a and 6.8b shows that the concentration of Fe(III) oxyhydroxides in the surface sediments gradually decreased with the decreasing DO concentration of the overlying bottom water. This is due to increase in reduction of Fe(III) to Fe(II) (and dissolution of Fe(II) from the sediment to the overlying bottom water) with decreasing DO concentration of the bottom water. The similar variation was also found with the concentration of Cu and Pb associated with Fe/Mn oxyhydroxide binding phases (Fr.3) in the sediments with varying DO concentration of the overlying bottom water. The concentration of Pb and Cu associated with Fe/Mn oxyhydroxide binding phase gradually decreased with the decreasing DO concentration of the overlying bottom water.

Impact of varying dissolved oxygen concentration of the overlying bottom on trace/heavy metals speciation and their release from the underneath sediment in the Arabian Sea is poorly known. Thus, the impact of decreasing DO concentrations of the overlying bottom water on the stability and lability of Cu and Pb complexes in the underneath sediment were further studied.

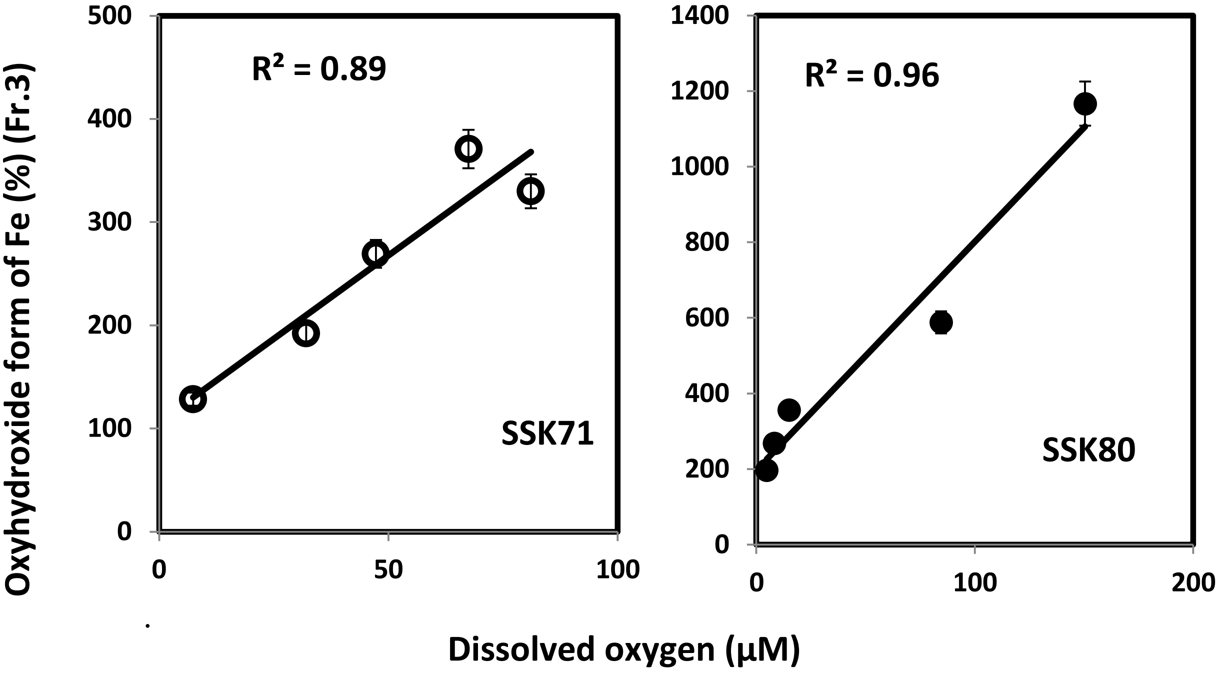


Figure 6.8 Variation of the concentration of oxyhydroxide form of Fe (mg.kg $^{-1}$) in the studied sediment with varying bottom water oxygen concentration (DO) (µM)

6.3.3 Impact of varying dissolved oxygen concentration in the overlying bottom water on the stability of Cu and Pb complexes in the underneath sediments

Kinetic fractionation study was performed to quantitatively estimate the stability and lability of the metal complexes in the underneath sediments across the OMZ. The kinetic extraction data are presented in Figure 6.9a and 6.9b. The data were fitted to the kinetic model by nonlinear regression analysis, as described elsewhere (Chakraborty et al. 2012; Chakraborty et al. 2011; Gaabass et al. 2009; Hassan et al. 2006; Mandal et al. 2002; Sekaly et al. 1999a; Sekaly et al. 1999b), to obtain the relative percentages of the kinetically distinguishable complexes and their associated dissociation rate constants. The percentage of labile and inert complexes of Cu and Pb and their corresponding dissociation rate coefficients are presented in Table 6.6.

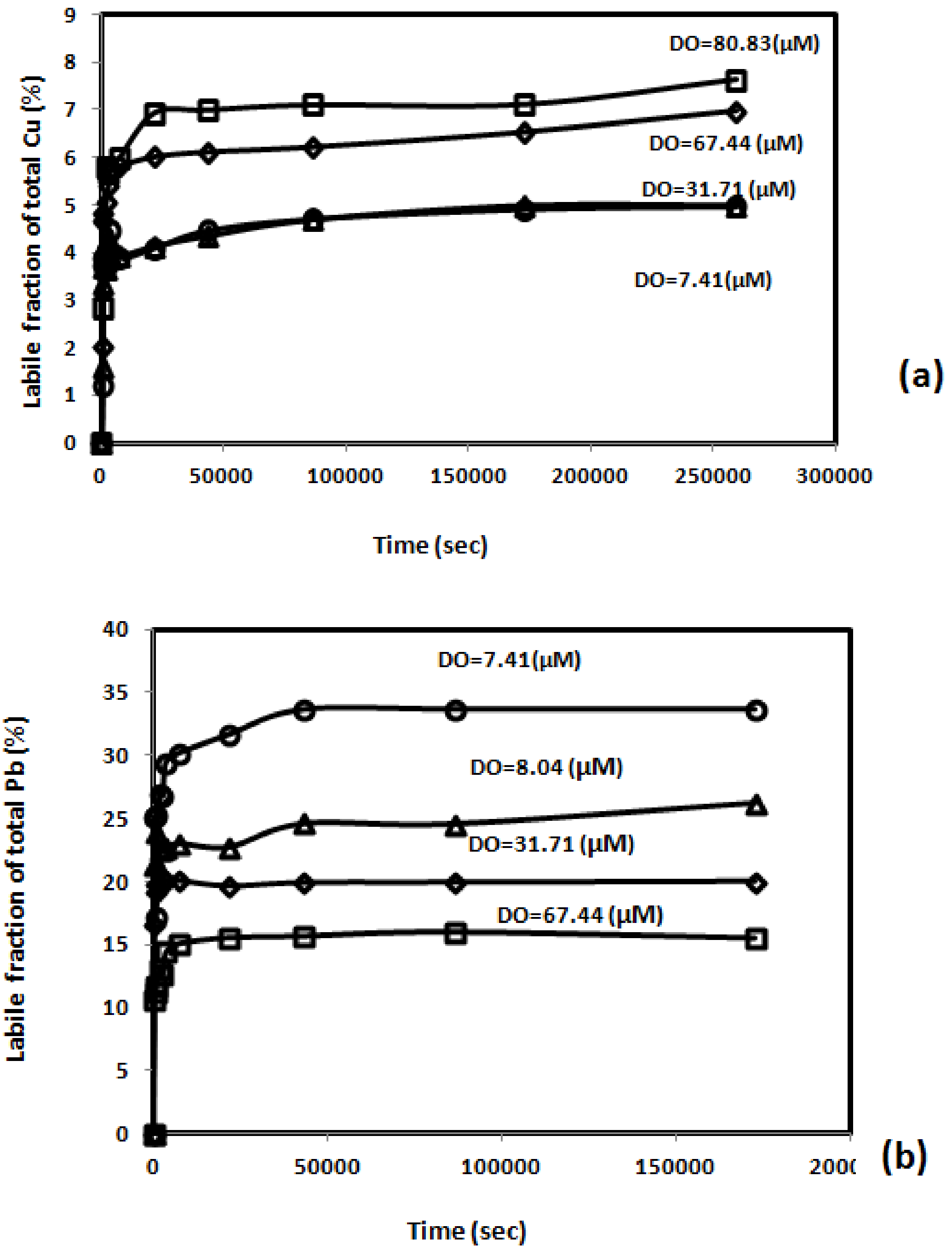


Figure 6.9 The percentage of total (a) Cu and (b) Pb released from the studies sediment with time (sec)

Table 6.6 The percentage of labile (C_1) and inert (C_2) complexes of Cu and Pb and their corresponding dissociation rate coefficients K_{d1} and K_{d2} respectively

	Station	**C_1 (%)**	**K_{d1} (S^{-1})**	**C_2 (%)**	**$K_{d2}\times10^7$(S^{-1})**
Cu	SSK71/SPC15	5.7	3.3×10^{-3}	94.3	$<10^{-6}$
	SSK71/SPC16	6.3	3.9×10^{-3}	93.7	$<10^{-6}$
	SSK71/SPC17	4.3	2.4×10^{-3}	95.7	$<10^{-6}$
	SSK71/SPC18	3.7	1.8×10^{-3}	96.3	$<10^{-6}$
Pb	SSK71/SPC16	13.9	3.6×10^{-3}	86.1	$<10^{-6}$
	SSK71/SPC17	19.8	5.9×10^{-3}	80.2	$<10^{-6}$
	SSK71/SPC18	27.0	7.8×10^{-3}	73.0	10^{-6}
	SSK80/SPC4	22.7	6.1×10^{-3}	77.3	$<10^{-6}$

Figure 6.10a and 6.10b show the variation in percentages of labile metal complexes and their dissociation rate constants (Figure 6.11c and 6.11d) in the sediments against the changing DO concentration of the overlying bottom water.

The kinetic fractionation study indicates that Cu-sediment complexes were stronger than the Pb-sediment complexes under low oxygen environment. The decrease in bottom water DO (from 81.1 to 7.4 µM) decreased the fractions of labile Cu-complexes from 6.3 to 3.7 % of the total Cu in the underneath sediments. The corresponding dissociation rate constant of the Cu-sediment complexes was found to change from 1.8×10^{-3} to 3.9×10^{-3} s^{-1}. This study indicates that the lability and dissociation rate constants of Cu-sediment complexes gradually decreased (i.e. stability of the Cu-sediment complexes steadily increased) with the decreasing DO concentration of the overlying bottom water.

It was found that the lability and dissociation rate constant of Pb-sediment complexes increased with the decreasing DO concentration in the overlying bottom water. The change in DO concentration from 7.6 to 81.1 µM increased the concentration of labile Pb-complexes from 19.8 to 27.0 % of the total Pb content in the sediment. The dissociation rate constant of the Pb-sediment complexes was found to increase from 5.9×10^{-3} to 7.9×10^{-3} s^{-1}. Although the results from the kinetic fractionation experiments are operationally defined, the observed trends in metal lability in sediment as a function DO concentration of the overlying water column elucidate the relative stability of metal-sediment complexes across the OMZ. This study suggests that low oxygen environment in the overlying bottom water may increase

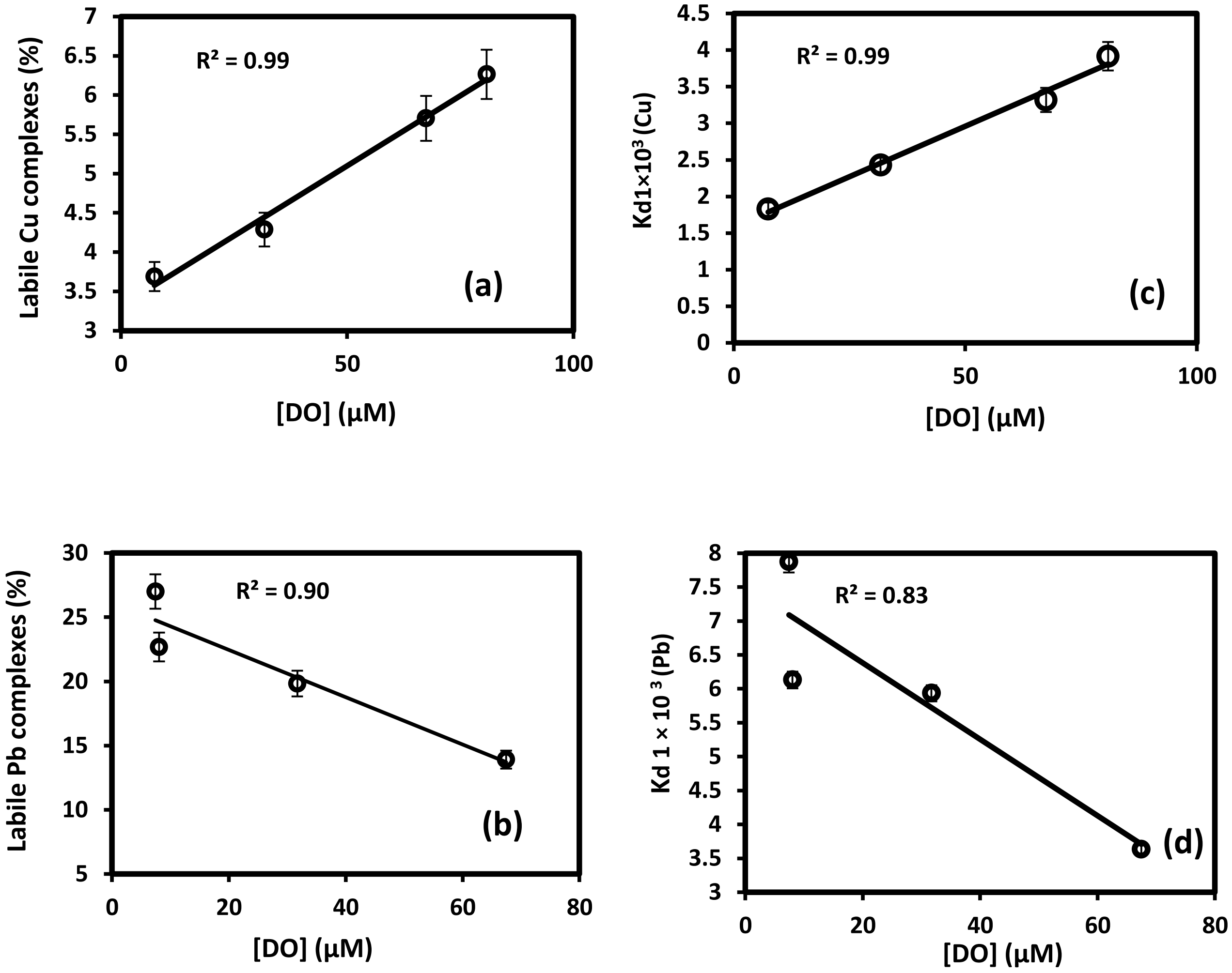


Figure 6.10 Variation in concentrations of labile complexes and their dissociation rate constants of (a and c) Cu and (b and d) Pb against the dissolved oxygen (DO) (µM) concentration of the overlying bottom water

lability of Pb-sediment complexes in the underneath sediment and may increase bioavailability of Pb in the system.

6.4 Conclusions:

This study provided useful information on the impact of varying dissolved oxygen concentration in overlying bottom water on geochemical fractionation of Cu and Pb complexes in the underneath sediments across the OMZ, in the eastern Arabian Sea. Increasing concentration of sedimentary organic matter (under low oxygen environment of the overlying bottom water) increased Cu complexation and association of Cu with the organic binding phases of the sediment. The average stability of Cu-sediment complexes was found to increase with decreasing dissolved oxygen concentrations of overlying bottom water. However, association of Pb with Fe/Mn-oxyhydroxide phase gradually decreased with decreasing dissolved oxygen concentration of the overlying bottom water. Pb was found to associate with sedimentary organic matter under the low oxygen environment. The lability of Pb-sediment complexes gradually increased with decreasing dissolved oxygen concentrations of bottom water. The labile Pb-sediment complexes may participate in exchange fluxes at the sediment-water interface at the low oxygen environment in the western continental margin of India.

Chapter 7

Signature of increasing anthropogenic Pb input in last century in the shelf sediments of India: A stable Pb isotopic and fractionation study

7.1 Introduction

As mentioned in the introductory chapter, that Pb flux in different natural environment has been increasing due to anthropogenic activities in many parts of the world and has already been reported to surpass the Pb flux from different natural processes (Sen and Peucker-Ehrenbrink, 2012). Combustion of leaded gasoline (in automobile), coal (thermal power plant) and other high temperature industries such as mining and smelting are the major sources of anthropogenic Pb in environment.

India is one of the most rapidly growing countries in terms of industrialization and urbanization. Emission of Pb from gasoline combustion reached maximum during mid 90’s in India. However, it has been reported that release of Pb from gasoline steadily declined (e.g., Lee et al., 2014), after the banning of leaded gasoline in 2000 (UNEP, 2007). However, other sources of Pb (coal, mining and smelters) are still active in a developing country like India where, the growth of industrialization and economic development are in full swing. One of the major requirements of this fast developing country is the energy and the requirement is majorly met by the coal fired power plants (one of the probable sources of Pb). It has been reported that around 116 coal based thermal power plants (situated all over the country) supply more than 51% of India's commercial energy demand (http://www.cea.nic.in). In addition to that, heavy industries in India also use significant amount of coal which may release considerable amount of Pb to the natural environment.

Lee et al. (2014) has shown that the amount of Pb emission from coal combustion in the recent years has crossed the highest Pb emission registered from gasoline combustion in the mid 90’s.

Stable isotopic signature of Pb study by Lee et al (2014) have suggested that combustion of leaded gasoline and burning of coal from India are the major sources of increasing dissolved Pb in the surface Indian Ocean.

Marine sediments are one of the best environmental archives to understand the historical evolution of anthropogenic Pb in the adjacent continent as it receives elemental flux in both atmospheric and fluvial pathways. Therefore, Pb emitted in Indian atmosphere or discharged in different rivers, marine sediments are thought to be the ultimate sink for these emissions. Thus, to understand the historical evolution of anthropogenic Pb in India, two well dated marine sediment cores, collected from central eastern continental shelf, off Nagavali river, (SSK35/SPC32) of 30 cm long and southern western continental shelf, off Sita Suvarna river (SSK40/SCP69) of 22 cm long were studied. The sampling sites of eastern and western continental shelf were ~20 km away from the coast of Andhra Pradesh and Karnataka (Figure 7.1).

Total Pb content, Enrichment Factor (EF), geochemical fractionation study and stable Pb isotopes has been widely used as powerful tools to understand historical input of anthropogenic Pb (if any) and its fate in marine sediments.

Stable Pb isotopes are the most effective tracer to identify the sources of Pb in the environment. Pb has four stable isotopes in nature, viz., ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb. Among these, ^{204}Pb is the only primordial isotope with no radioactive progenitor. The other three isotopes are the end members of U-Th radioactive decay series (^{238}U-^{206}Pb, ^{235}U-^{207}Pb and ^{232}Th-^{208}Pb) and are called radiogenic isotopes. Therefore, the concentration of primordial Pb is constant but, the concentration of ^{206}Pb, ^{207}Pb and ^{208}Pb has been increasing with time relative to ^{204}Pb.

Pb has distinct isotopic ratios in rocks and ore bodies. The stable isotopic ratios (e.g. ^{206}Pb/^{204} Pb, ^{207}Pb/^{204} Pb, ^{208}Pb /^{204} Pb, ^{208}Pb /^{206}Pb, ^{206}Pb /^{207}Pb) in rocks depend on the concentration of primordial Pb and parent U-Th in rocks and, the age of formation of the rock. On the other hand, the isotopic composition in ores depends on the age of ore formation. During formation of a Pb ore, Pb becomes isolated from its radioactive parent isotopes (U/Th) present in the rocks and therefore the isotopic compositions of Pb stops changing. These compositions are generally less radiogenic than the isotopic composition of Pb in rocks where Pb are still in contact with its parent isotopes (Bacon et al., 2005; Hansmann and Koppel, 2000; Sangster et al., 2000; Semlali et al., 2001). Therefore, anthropogenic Pb which is ultimately derived from ore, in general shows low isotopic ratios compared to the natural Pb. For example, ^{206}Pb/^{207}Pb ratio in

Australian ore (source of Pb used in petrol) is 1.06–1.09 (Monna et al., 1997) whereas, ^{206}Pb/^{207}Pb ratio typically found in geogenic Pb is 1.18–1.22. Thus, the presence of less radiogenic Pb in environmental samples is indicative of athropogenic sources.

In this study, an attempt was made to assess the anthropogenic contribution in the sediment cores by looking at the variation in the total sedimentary Pb content, Enrichment Factor (EF), Pb distribution in different sedimentary geochemical phases. Additionally, Pb isotopes were used to investigate the Pb sources.

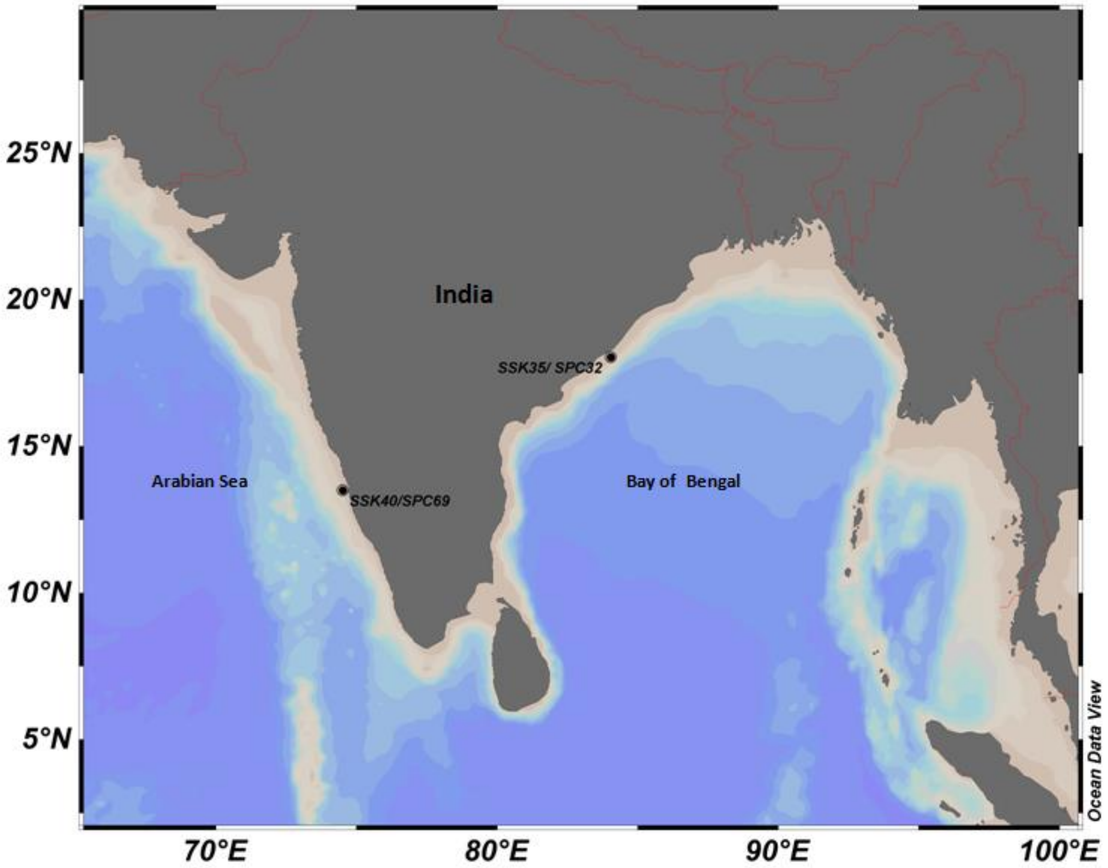


Figure 7.1 Study area: two sediment cores collected from eastern (SSK35/SPC32) (off Nagavali River, northern Andhra Pradesh) and western (SSK40/SPC69) (off SitaSuvarna River, Karnataka) continental shelves of India

7.2 Results

7.2.1 Downcore variation of Pb, Fe, Mn Ti content

Downcore variation in the concentration of Pb and other redox sensitive and refractory metals (Fe, Mn and Ti) in the sediment cores collected from the eastern (SSK35/SPC32) and western (SSK40/SPC69) continental shelves of India are presented in Tables 7.1 and 7.2. There was 1.5 to 2 times enrichment in the concentration of Pb observed on the core surface compared to the subsurface values. The concentration of Pb was found to range from ~21.9 ± 0.4 at the deepest layer (29-30 cm) studied here to 41.9 ±0.8 mg.kg $^{-1}$ at 5-6 cm depth of core representing a 2-fold increase in core collected from the eastern shelf. For the core collected from western shelf, Pb content varied from ~10.3 ± 0.2 at the deepest layer (21- 22 cm) to 15.6±0.3 mg.kg^{-1} at the surface of the core. There was very little/no variation was observed in sedimentary Pb content from the deepest layer to 14-15 cm in eastern shelf core. After that, a steady increase was observed in sedimentary Pb concentration up to 6-7 cm depth, followed by a decline in Pb content up to 1-2 cm depth. However, further enrichment in Pb concentration was observed in the surface layers. Periodic increase and decrease was observed in Pb concentration from the deepest layer (21-22 cm) to 9-10 cm depth of western shelf core. After that, there was a steady increase in Pb content up to the surface layer of the core.

The concentration of Fe, Mn and Ti in the sediment at different depth of the SSK35/SPC32 core was found to vary from 4.80±0.02 to 5.67±0.03%, 470 ±3 to 588±3 mg.kg^{-1} and 0.28 ±0.01 to 0.37±0.01 % respectively (Table 7.1). For SSK40/SPC69 core, the concentration of Fe, Mn and Ti varied from 3.90±0.02 to 5.68±0.03%, 286 ±2 to 408±2 mg.kg^{-1}, 0.40±0.01 to 0.43±0.01% respectively (Table 7.2).

7.2.2 Down-core variation of geochemical fractionation of Pb

Geochemical fractionation (or operational speciation) study was carried out in selected samples from both the cores to understand the changes of anthropogenic contribution and the fate of deposited Pb in the sediments with respect to time. The percentage of total sedimentary Pb and the absolute concentration of Pb (mg.kg^{-1}) distributed in different geochemical phases of the sediment layers of the cores

Table 7.1 Down core variation of Pb, Fe, Mn and Ti content in sediment core SSK35/SPC32. Corresponding calendar ages estimated from $^{210}Pb_{excess}$ dating are also given.

Depth	**Pb (mg.kg $^{-1}$)**	**Fe (%)**	**Mn (mg.kg $^{-1}$)**	**Ti (%)**	Calender Age(AD)
0-1	35.6±0.7	5.67±0.03	563±2.8	0.32±0.01	2012
1-2	28.3±0.6		525±2.6	0.31±0.01	2008
2-3	29.1±0.6	6.25±0.03	553±2.8	0.33±0.01	2005
4-5	32.9±0.7		544±2.7	0.31±0.01	1998
6-7	41.9±0.8	5.17±0.03	553±2.8	0.37±0.01	1992
8-9	24.9±0.5		508±2.5	0.28±0.01	1985
9-10	26.4±0.5		588±2.9	0.31±0.01	1981
12-13	24.5±0.5	5.24±0.03	529±2.6	0.28±0.01	1971
15-16	22.4±0.4		543±2.7	0.32±0.01	1964
17-18	22.6±0.5		533±2.7	0.30±0.01	1948
19-20	21.5±0.4	5.58±0.03	546±2.7	0.32±0.01	1941
21-22	22.6±0.5		505±2.5	0.31±0.01	1933
22-23	20.8±0.4	4.50±0.02	471±2.4	0.30±0.01	1929
23-24	21.7±0.4		535±2.7	0.33±0.01	1925
26-27	20.6±0.4	5.24±0.03	524±2.6	0.32±0.01	1912
27-28	21.4±0.4		470±2.4	0.29±0.01	1908
28-29	21.9±0.4	4.80±0.02	500±2.5	0.32±0.01	1898

Table 7.2 Down core variation of Pb, Fe, Mn and Ti content in sediment core SSK40/SPC69. Corresponding calendar ages estimated from $^{210}Pb_{excess}$ dating are also given.

Depth (cm)	**Pb (mg.kg $^{-1}$)**	**Fe (%)**	**Mn (mg.kg $^{-1}$)**	**Ti(%)**	**Calender Age (AD)**
0-1	15.6±0.3	5.39±0.03	403±2.0	0.43±0.01	2011
2-3	15.0±0.3	5.43±0.03	398±2.0	0.42±0.01	2001
5-6	14.3±0.3	5.68±0.03	402±2.0	0.42±0.01	1981
6-7	12.8±0.3	5.17±0.03	408±2.0	0.40±0.01	1975
9-10	11.8±0.2	5.46±0.03	403±2.0	0.42±0.01	1958
12-13	12.8±0.3	5.37±0.03	413±2.1	0.41±0.01	1940
14-15	10.6±0.2	5.33±0.03	408±2.0	0.42±0.01	1927
17-18	11.2±0.2	5.41±0.03	414±2.1	0.42±0.01	1899
21-22	10.3±0.2	3.90±0.02	286±1.4	0.41±0.01	1866

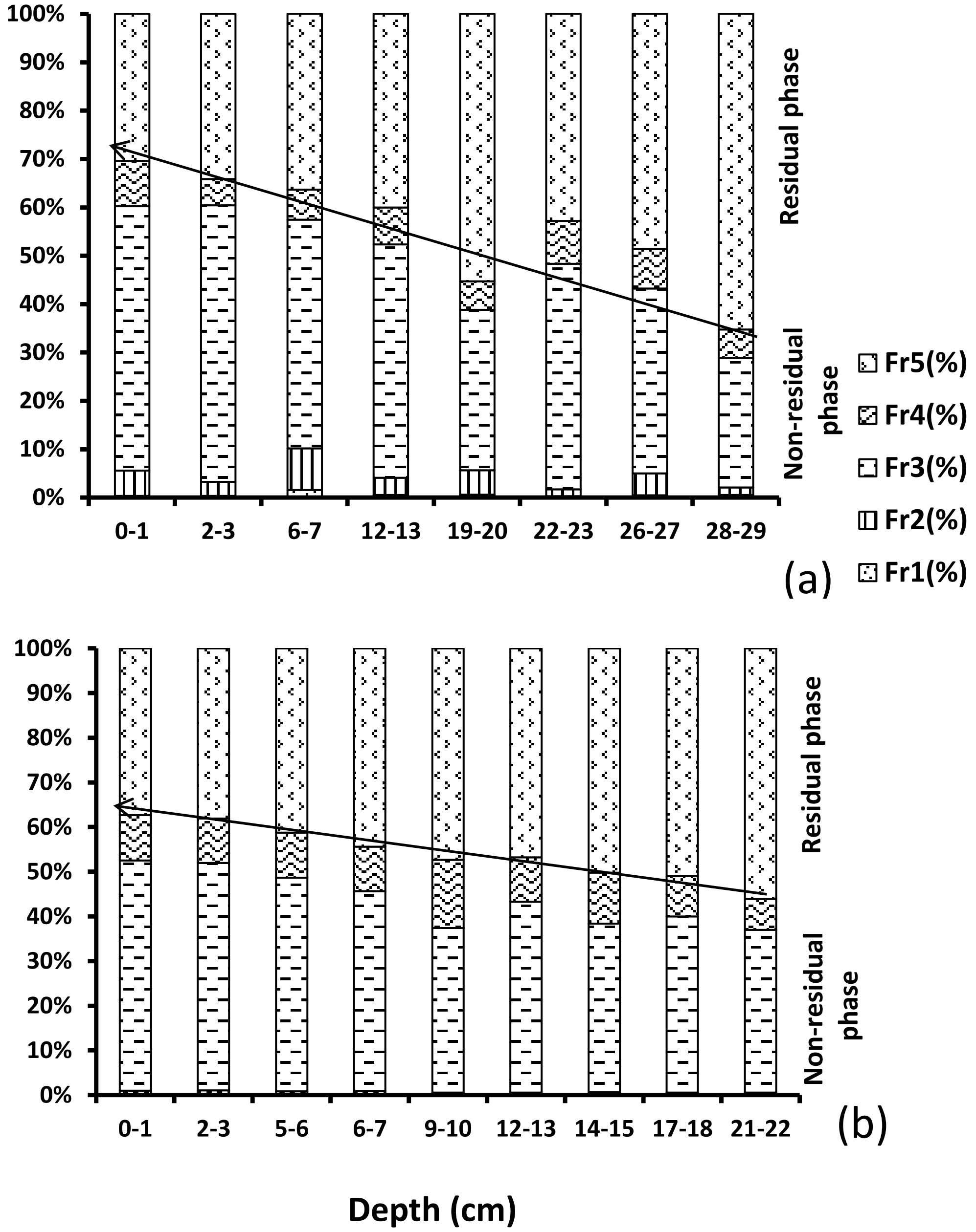


Figure 7.2 Percentage of total Pb associated with Fr.1 (water soluble),Fr.2 (carbonate/bicarbonate and exchangeable),Fr.3 (Fe/Mn oxyhydroxide), Fr.4 (organic) and Fr.5 (residual) phase in the sediment sections down the cores (a) SSK35/SPC 32 (Bay of Bengal) and (b) SSK40/SPC69 (Arabian Sea)

Table 7.3 Downcore variation of Pb content in different geochemical phases of sediment cores SSK35/SPC32 (Bay of Bengal) and SSK40/SPC69 (Arabian Sea)

	Depth (cm)	**Fr.1 (mg.kg^{-1})**	**Fr.2 (mg.kg^{-1})**	**Fr.3 (mg.kg^{-1})**	**Fr.4 (mg.kg^{-1})**	**Fr.5 (mg.kg^{-1})**
SSK35/SPC32	0-1	0.1	1.9	19.4	3.3	10.8
	2-3	0.1	0.8	16.6	1.6	9.9
	6-7	0.6	3.2	17.5	2.3	13.5
	12-13	0.1	0.9	11.8	1.9	9.8
	19-20	0.1	1.1	7.1	1.3	11.9
	22-23	0.1	0.3	9.7	1.8	8.9
	26-27	0.1	0.9	7.9	1.7	10.0
	28-29	0.1	0.3	5.9	1.3	14.3
	Depth (cm)	**Fr.1 (mg.kg^{-1})**	**Fr.2 (mg.kg^{-1})**	**Fr.3 (mg.kg^{-1})**	**Fr.4 (mg.kg^{-1})**	**Fr.5 (mg.kg^{-1})**
SSK40/SPC69	0-1	0.0	0.1	8.0	1.6	5.8
	2-3	0.0	0.1	7.6	1.5	5.7
	5-6	0.0	0.1	6.8	1.4	5.9
	6-7	0.0	0.1	5.7	1.3	5.7
	9-10	0.0	0.1	4.3	1.8	5.6
	12-13	0.0	0.1	5.5	1.3	6.0
	14-15	0.0	0.1	4.0	1.2	5.3
	17-18	0.0	0.1	4.4	1.0	5.7
	21-22	0.0	0.1	3.8	0.7	5.8

SSK35/SPC32 and SSK40/SPC69 are presented in Figure 7.2a, b and Table 5.3 respectively. The percentage of Pb in non-residual phase (sum of water soluble (Fr.1), carbonate and exchangeable (Fr.2), Fe/Mnoxyhydoxide (Fr.3) and organic (Fr.4) phase) was found to be increased upward the cores. On the other hand a steady decrease in the percentage of Pb in residual phase (Fr.5) towards the surface of the cores was observed. The concentration of water soluble Pb complexes (Fr.1) was negligible in both the cores. The concentration of soluble Pb complexes along the sediments layers of SSK35/SPC32 was found to be 0.1 mg.kg^{-1} with an exceptional increase to 0.6 mg.kg^{-1} at 6-7 cm depth. The concentration of water soluble Pb in the sediments of SSK40/SPC69 core was below the detection limit of the instrument. A periodic increase and decrease in the concentration of Pb associated with Fr.2 was observed upward the core, SSK35/SPC32. The concentration of Pb in Fr.2 varied from 0.3 mg.kg $^{-1}$at the bottom of the core (29-30 cm) to 3.2 mg.kg^{-1} at 6-7 cm depth of the core. Whereas, in SSK40/SPC69 core the concentration of Pb in Fr.2 was uniform and it was 0.1mg.kg^{-1} in different depths of the sediment core. In both the cores, major part of non-residual Pb (30.5 to 57.2 % of total Pb in the eastern shelf and 36.4 to 51.5 % of total Pb in the western shelf) in the sediments to associate with Fe/Mnoxyhydroxide phase (Fr.3) followed by the organic phase (Fr.4).There was increasing association of Pb with both these phases towards the surface of the core (Table 7.3).The concentration of Pb in Fe/Mn oxyhydroxide and organic phase gradually increased from 5.9 to 19.4 mg.kg $^{-1}$ and 1.3 to 3.3 mg.kg $^{-1}$ in SSK35/SPC32 and 3.8 to 8 mg.kg $^{-1}$ and 0.7 to 1.8 mg.kg^{-1} in SSK40/SPC69 core respectively. Concentration of Pb within the residual phase of the sediments varied from 8.9 to14.3 mg.kg^{-1} in SSK35/SPC32 core. However, there was no systematic trend in the core. On the other hand, residual Pb (Fr.5) in different depths of SSK40/SPC69 core was found to be nearly constant with little variation of 5.3 to 6.0 mg.kg$^{-1.}$

7.2.3 Sediment core chronology

The age for each depth of the sediment cores were estimated by using sedimentation rate (SR). The core collected from the eastern shelf showed one distinct change in SR from the depth of 15-16 cm of the core. The mean SR was estimated to be 0.298 cm/yr in the upper portion (15-16 cm to the surface layer of the core) and 0.249 cm/yr in the lower portion of the core (29-30 cm to 16-17 cm). The SR was also found to change twice in the core, collected from western shelf. The mean SR gradually decreased from 0.210 cm/yr in upper portion (4-5 to surface layer) to 0.170 cm/yr in the middle portion (14-15 to 5-6 cm) to 0.128 cm/yr in the lower portion (21-22 to 15-16 cm) of the core. The calculated calendar age for each depth of core collected from eastern shelf (SSK35/SPC32) and western self (SSK40/SPC69) are presented in Tables 7.1 and 7.2 respectively. The bottoms of both the cores represent pre-industrial age of India. The bottom layer of the sediment core (22 cm), collected from the western shelf represent older age (~ 145 yrs) compared to the core collected from the eastern shelf (~114 yrs).

7.2.4 Stable Pb isotopic variation

The historical evolution of anthropogenic Pb input in the marine sediment was further studied by using Pb isotopic composition. The Pb isotopic composition was determined in the non-residual phases (a good representative of anthropogenic Pb component) of the bulk sediment.

The variation in Pb isotopic ratios (^{206}Pb/^{204} Pb, ^{207}Pb/^{204} Pb, ^{208} Pb /^{204} Pb, ^{208} Pb /^{206}Pb, ^{206} Pb /^{207}Pb) in the sediment cores SSK35/SPC32 and SSK40/SPC69 are given in Table 7.4 and 7.5 respectively. A very similar changing trend in different isotopic profiles (^{206}Pb/^{204} Pb, ^{207}Pb/^{204} Pb, ^{208} Pb /^{204} Pb, and ^{206} Pb /^{207}Pb) was found in both the cores as shown in Figure 7.3a and b. In SSK35/SPC32 core, the overall decrease in ratios (^{206}Pb/^{204} Pb, ^{207}Pb/^{204} Pb, ^{208} Pb /^{204} Pb, and ^{206} Pb /^{207}Pb) was observed from 19.019, 15.843, 39.637 and 1.200 at the bottom sediment (depth 29 to 30 cm) to 18.575, 15.761, 38.978 and 1.179 at the surface sediment (0 to 1cm) of the core. A very similar observation was also made in the other core. A decrease in Pb isotopic ratios was seen in SSK40/SPC69 core, where the ratios were decreased from 18.470, 15.628, 38.805 and 1.182 at the bottom (21 to 22 cm) to 18.10, 15.618, 38.311 and 1.159 at the surface (0 to 1 cm). However, it is interesting to note that the upward decrease in isotopic ratios in both the cores were not linear as shown in Figure7.3a and b.

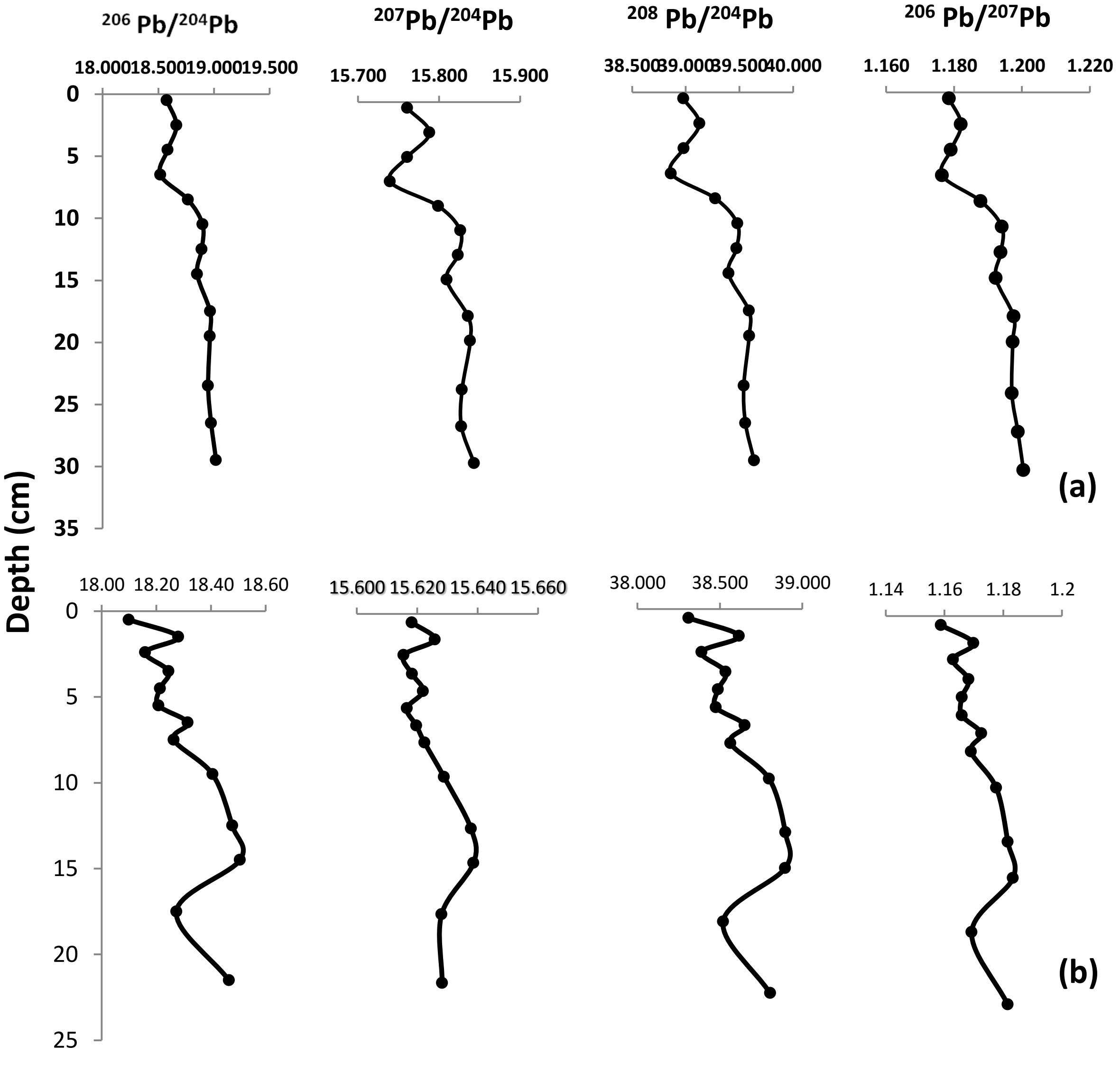


Figure 7.3 Variation of stable Pb isotopic ratios (^{206}Pb/^{204} Pb, ^{207}Pb/^{204} Pb, ^{208} Pb /^{204} Pb, and ^{206} Pb /^{207}Pb) along the sediment cores collected from (a) eastern (SSK35/SPC32) and (b) western (SSK40/SPC69) continental shelves of India

Table 7.4 Downcore Pb isotopic data of the sediment core, SSK35/SPC32 from the eastern shelf of India

Depth (cm)	**$^{206/204}$Pb**	**2se**	**$^{207/204}$Pb**	**2se**	**$^{208/204}$Pb**	**2 se**	**$^{208/206}$Pb**	**2 se**	**$^{206/207}$Pb**	**2 se**
0-1	18.575	0.001	15.761	0.002	38.978	0.005	2.098	0.0001	1.179	0.0000
2-3	18.663	0.001	15.788	0.002	39.127	0.005	2.097	0.0001	1.182	0.0000
4-5	18.583	0.001	15.761	0.001	38.980	0.004	2.098	0.0001	1.179	0.0000
6-7	18.518	0.001	15.740	0.002	38.863	0.005	2.099	0.0001	1.177	0.0000
8-9	18.767	0.001	15.799	0.001	39.276	0.004	2.093	0.0001	1.188	0.0000
10-11	18.897	0.001	15.826	0.001	39.480	0.004	2.089	0.0001	1.194	0.0000
12-13	18.890	0.001	15.823	0.002	39.473	0.005	2.090	0.0001	1.194	0.0000
14-15	18.849	0.001	15.809	0.002	39.398	0.005	2.090	0.0001	1.192	0.0000
17-18	18.965	0.002	15.836	0.002	39.589	0.005	2.088	0.0001	1.198	0.0000
19-20	18.963	0.001	15.839	0.001	39.591	0.004	2.088	0.0001	1.197	0.0000
23-24	18.947	0.001	15.828	0.001	39.541	0.004	2.087	0.0001	1.197	0.0000
26-27	18.974	0.001	15.828	0.001	39.556	0.005	2.085	0.0001	1.199	0.0000
29-30	19.019	0.002	15.843	0.002	39.637	0.006	2.084	0.0001	1.200	0.0000

Table 7.5 Down core Pb isotopic data of the sediment core SSK40/SPC69 from the western shelf of India

Depth (cm)	**$^{206/204}$Pb**	**2se**	**$^{207/204}$Pb**	**2se**	**$^{208/204}$Pb**	**2 se**	**$^{208/206}$Pb**	**2 se**	**$^{206/207}$Pb**	**2 se**
0-1	18.10	0.00146	15.618	0.001742	38.311	0.00516	2.117	0.000121	1.159	2.86E-05
1-2	18.28	0.001452	15.626	0.001592	38.616	0.00502	2.112	0.000128	1.170	0.000027
2-3	18.16	0.001318	15.616	0.00165	38.389	0.00504	2.114	0.000141	1.163	3.12E-05
3-4	18.25	0.001186	15.618	0.001416	38.535	0.00444	2.112	0.000122	1.168	2.64E-05
4-5	18.21	0.001326	15.622	0.001538	38.489	0.00462	2.113	0.000119	1.166	2.42E-05
5-6	18.21	0.001258	15.617	0.001576	38.476	0.00496	2.113	0.000139	1.166	0.00003
6-7	18.31	0.001804	15.620	0.00206	38.651	0.00628	2.110	0.000146	1.173	3.08E-05
7-8	18.26	0.001446	15.622	0.001806	38.565	0.00562	2.112	0.000147	1.169	3.44E-05
9-10	18.41	0.001284	15.629	0.001474	38.799	0.00456	2.108	0.000111	1.178	2.54E-05
12-13	18.48	0.001552	15.638	0.001782	38.896	0.00528	2.105	0.000126	1.182	0.000029
14-15	18.51	0.001572	15.639	0.001886	38.895	0.00578	2.102	0.000142	1.183	3.26E-05
17-18	18.27	0.001108	15.628	0.001412	38.519	0.00454	2.108	0.000128	1.169	0.000029
21-22	18.47	0.00134	15.628	0.001652	38.805	0.00518	2.101	0.000137	1.182	3.12E-05

7.3 Discussion

7.3.1 Increasing Pb input with respect to time in the shelf sediments of India

The down-core profile for total sedimentary Pb content in the cores from the eastern and the western shelf of India showed an overall increase in Pb accumulation in the last century. The increase in Pb accumulation in the marine sediments from eastern shelf (20.6 to 41.9 $mg.kg^{-1}$) was more compared to the western shelf (10.3 to 15.6 $mg.kg^{-1}$). The study areas, likely to get fluvial as well as atmospheric input, were probably affected by the anthropogenic activities occurring in the adjacent continent. Number of studies (Harikumar et al.2009; Lee et al., 2014; Chakraborty et al., 2016) on trace metal contamination in marine environment of India, supported the fact of increasing metal contamination with time. Nevertheless, the natural processes, such as, mineralogical/textural variation along the core and the redox mediated post depositional remobilisation also play an important role in controlling elemental distribution within the sediment cores (Zwolsman et al.,1993; Hornberger et al.,1999; Outridge et al.,2005). To understand the upward increase in Pb content in both the cores, the following studies were carried out.

Down-core variation in the enrichment factor (EF) of Pb: An indicator of anthropogenic input

Enrichment factor (EF) of Pb was calculated to normalize the sedimentary Pb content with respect to mineralogical or textural variation and estimate the anthropogenic contribution of Pb in the studied sediment. As described in Chapter 2, EF was calculated by taking the ratio of normalized Pb content of the sample to the background value of normalized Pb content. Ti was used as a reference material (Boes et al., 2011; Shotyk et al., 2001) to normalize the concentration of Pb in the sediments. The average concentrations of Pb and Ti of the deepest layer of the sediment cores were taken as the background concentrations in this study.

The variation in EF of Pb in both the cores (Figure 7.4a and b) was following the similar variation as found for the total Pb along the core. In both the cores, EF of Pb was found to enrich at the surface layers. The increasing EF in both the cores indicates that the variation in Pb content along the core was not due to the mineralogical variation of the depositing sediments in the last ~150 years.

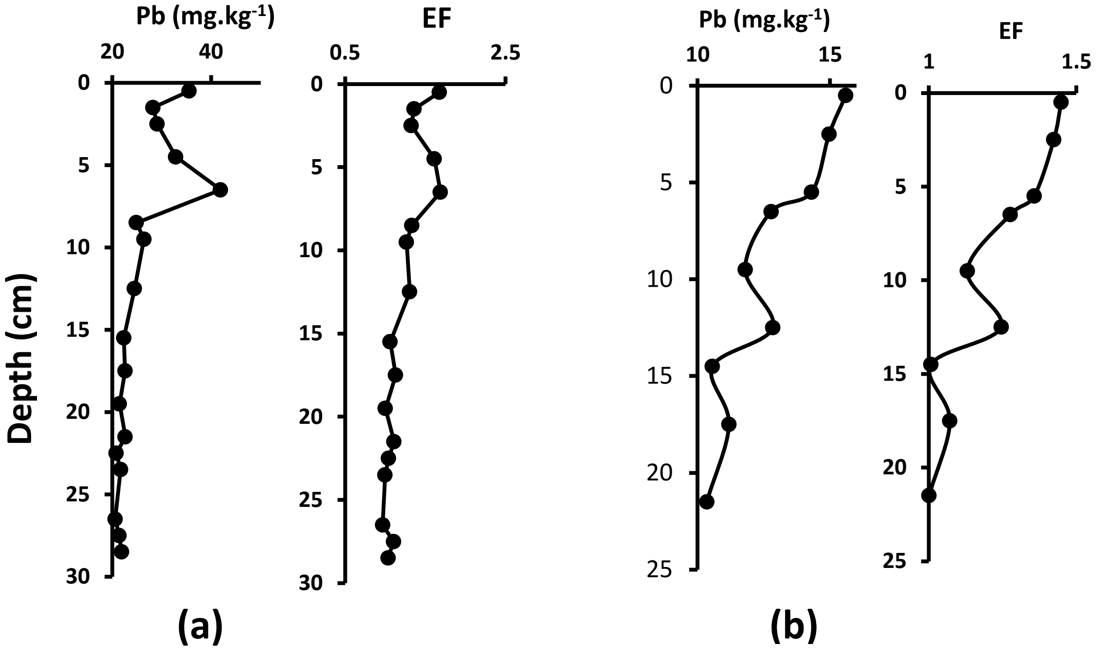


Figure 7.4 Downcore variation of Pb (mg.kg^{-1}) content and its EF in sediment cores from the eastern (a) and western (b) continental shelves of India

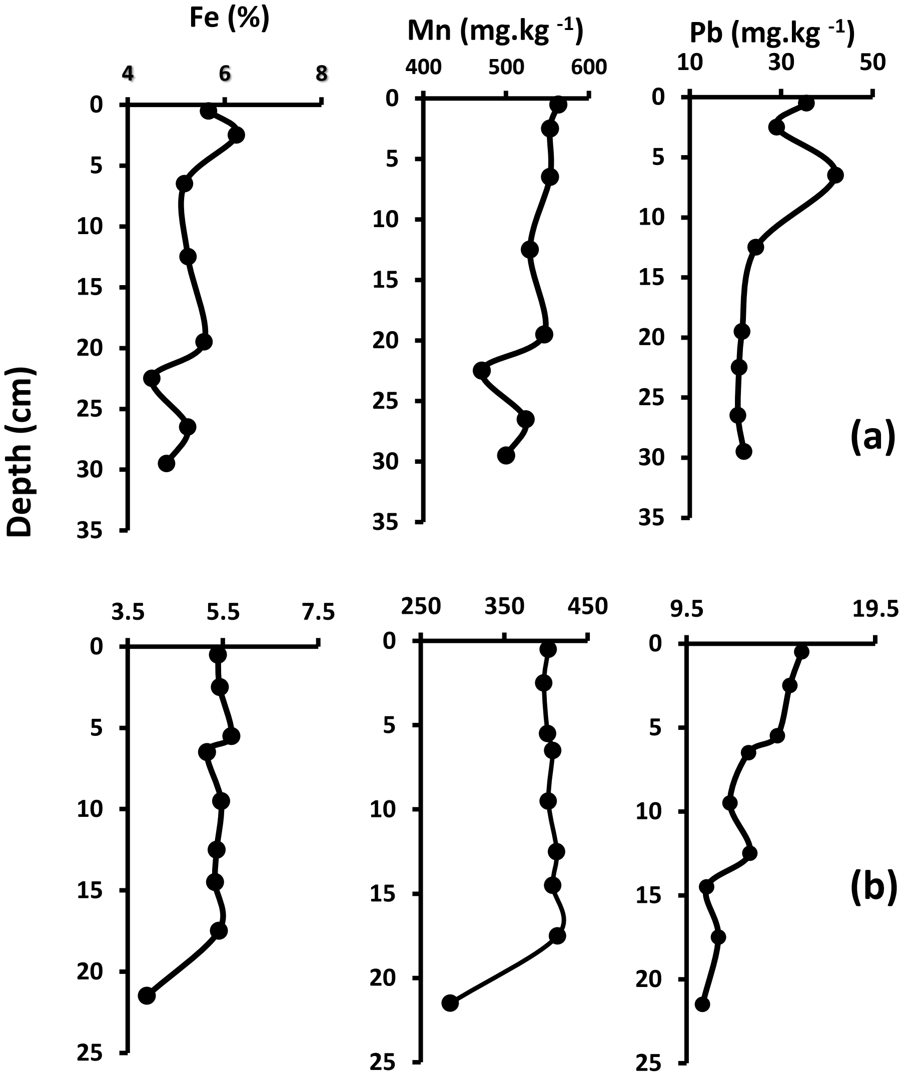


Figure 7.5 Down-core profile of Fe (%), Mn (mg.kg $^{-1}$) and Pb (mg.kg $^{-1}$) in the sediment of (a) eastern and (b) western continental shelf of India

Assessing redox mediated post depositional changes in the cores

It is well known that redox mediated remobilisation of sedimentary Pb can govern the upward increase of Pb content in the sediment cores. However, Pb is not known as the redox sensitive element whose solubility changes with changing redox environment. Nevertheless, a major part of sedimentary Pb was found to be associated with Fe (III)/Mn oxyhydroxide phase whose solubility changes with changing redox condition (as discussed in chapters 3, 5 and 6). Thus, the mobilisation of Fe and Mn under changing redox environment may increase mobility of Pb along the core. In reduced environment, Pb gets released from sediment to pore water due to the dissolution of particulate Fe(III)/Mn(IV) oxyhydroxide to soluble Fe(II)/Mn(II).The diffusion of soluble Pb from deeper layer and the re-precipitation at surface layer of sediment (at redox interface) increases Pb content upward the core. Therefore, similar kind of concentration profiles is expected for Fe, Mn and Pb, if the upward enrichment of Pb was due to the remobilisation of Fe and Mn. However, no similarity was observed between the down-core profile of Pb, Fe and Mn (Figure 7.5a and b). No significant surface enrichment was observed for both Fe and Mn in the studied cores. Thus, upward enrichment of Pb was not due to redox mediated post depositional mobilisations.

7.3.2 Upward increase in sedimentary non-residual Pb content: indication of increasing anthropogenic input

It is well known that, non-residual geochemical phases of sediment host metals which are mobilised by natural or anthropogenic process (Tessier et al., 1979; Badri and Aston, 1983; Schlinder, 1999; Chakraborty et al, 2012) and the residual phase hosts metals which are chemically inert and reside within the mineral structure of sediment. The geochemical fractionation study indicates that, association of Pb (presented as relative percentage with respect to their total Pb concentrations) with all the non residual binding phases increased upward the sediment core. This suggests the increasing concentration of mobilized Pb up the cores. As discussed in the in previous sections, natural processes were not responsible for the upward increase in Pb concentration in the cores. Thus, the increasing concentration of non-residual Pb (Figure 7.2a and b) indicates the increasing anthropogenic Pb contribution with time. Among the non-residual phases, Fe/Mn oxyhydroxide was the major hosting

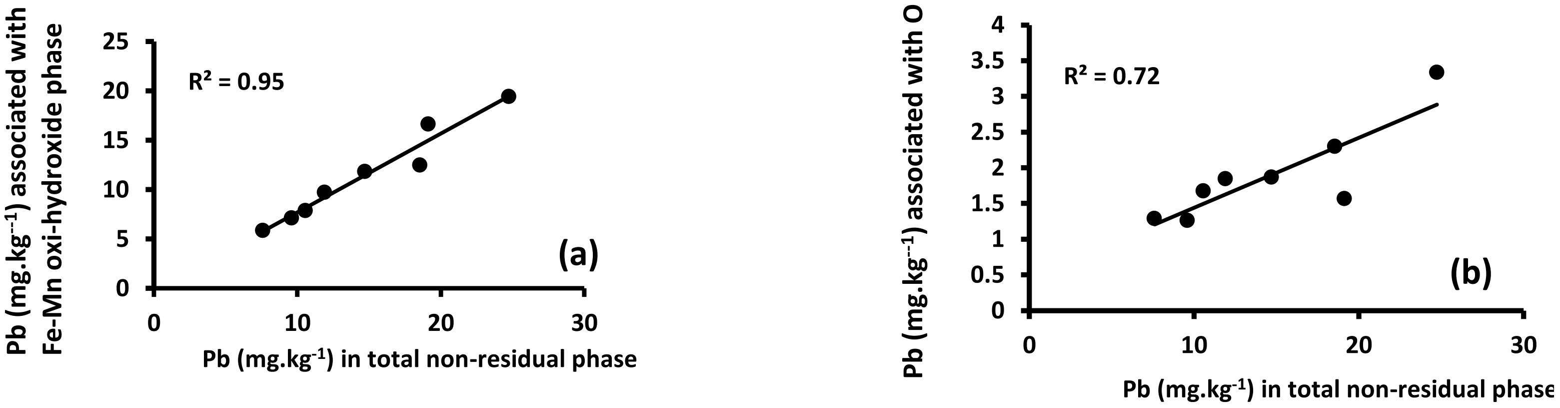


Figure 7.6 Variation of Pb (mg.kg^{-1}) associated with (a) Fe/Mn oxyhydroxide (b) organic phase of the sediment with varying non-residual Pb content along the sediment core (SSK35/SPC32)

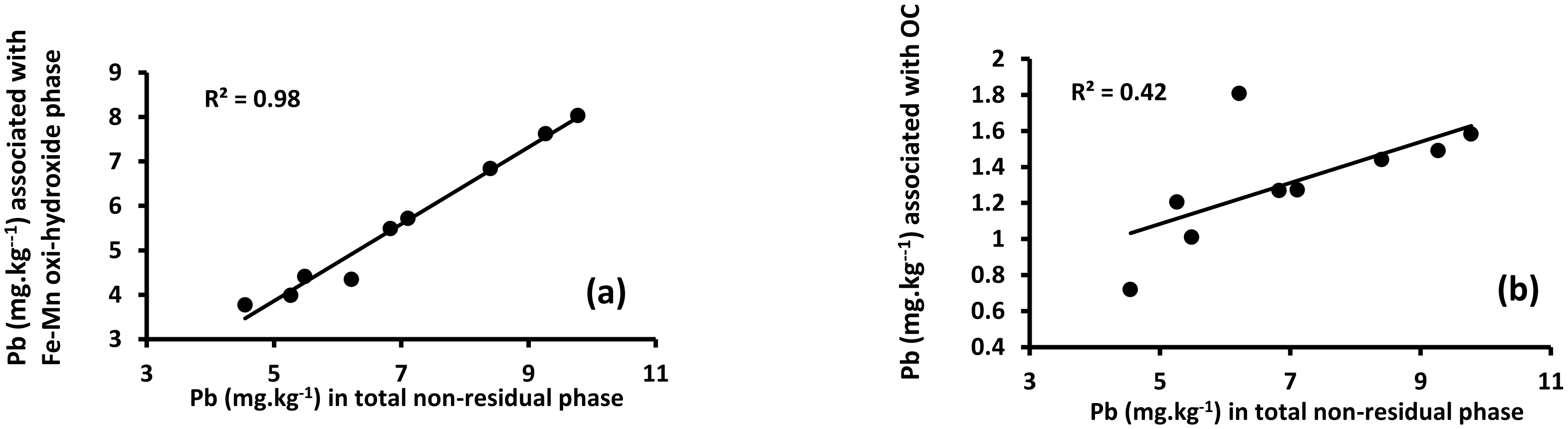


Figure 7.7 Variation of Pb (mg.kg^{-1}) associated with (a) Fe/Mn oxyhydroxide (b) organic phase of the sediment with varying non-residual Pb content along core from western continental shelf (SSK40/SPC69)

phase for anthropogenic Pb. A significant increase in association of Pb with Fe/Mn oxyhydroxide phases was observed with the increasing non-residual Pb (Figure 7.6a and 7.7 a) in both the cores. There was increase in association of Pb with sedimentary organic phase observed in the sediment cores (from the bottom to the surface). However, the percentage of total Pb associated with organic phase (Fr.4) was much lower than the relative percentage of Pb associated with Fe/Mn oxyhydroxide phase (Fr.3) (Figure 7.6b and 7.7b).

Therefore, down-core variation in total Pb, EF and geochemical fractionation of Pb suggest that there was increasing anthropogenic input upwards the core. However, further study was carried out to provide better understanding of anthropogenic Pb input in the shelf sediments of India and identify the probable sources of anthropogenic Pb in the sediments by using stable Pb isotope.

7.3.3 Assessing the historical anthropogenic Pb input:

The bottom of core SSK35/SPC32 from the eastern shelf was dated ~120 years back from the sampling time. This represent the pre-industrial period of India or the time when heavy industries were not started. The isotopic composition of the leachate from the sediment collected from the bottom most part (29-30 cm) of the core represents the isotopic composition found in natural rocks (^{206}Pb/^{207}Pb =1.20).This directly indicates that the major source of the sedimentary Pb was the source rocks and there were no/little anthropogenic influences. The upward decrease in the ^{206}Pb/^{207}Pb ratios in the core (with time) indicates the mixing of Pb from less radiogenic sources in the sediments. However, in the first 12 cm from the bottom of the core (see Table7.4 and Figure 7.8**)**, the isotopic variation was narrow and indicating the slow increase in the anthropogenic Pb input. The upward decreasing Pb isotopic ratio clearly indicates the increasing anthropogenic input in the sediments during the last century. A significant decrease in isotopic ratio was observed during the year 1948. This is consistent with the time when heavy chemical industries started in the early 40’s in India **(**Indian Industries: Historical Perspective of Indian Industries:http://www.yourarticlelibrary.com/industries/indian-industries-historical-perspective-of-indian-industries/19708/)**.** After that, periodic decrease and increase were observed upward the core suggesting varying anthropogenic input with time in the sediments.

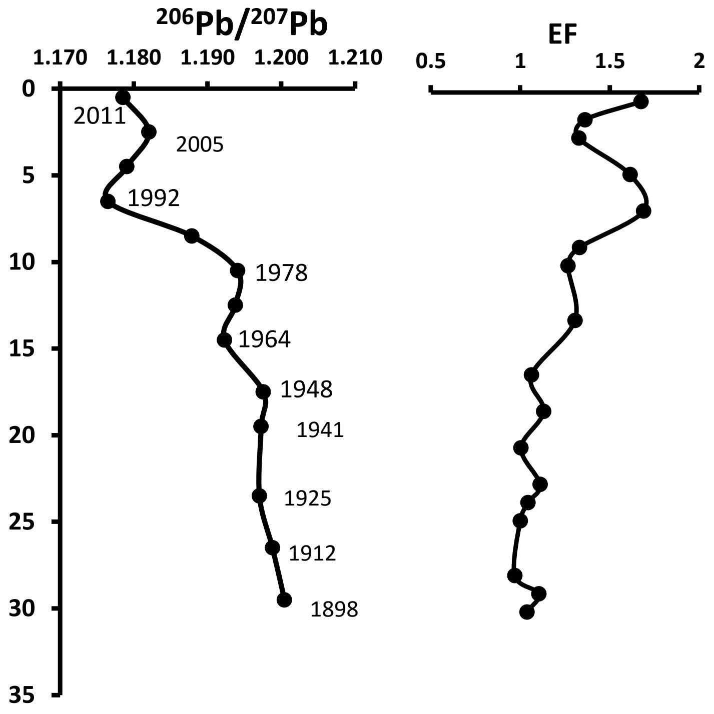


Figure 7.8 Historical changes in Pb isotopic (^{206}Pb/^{207}Pb) signature and EF in the core SSK35/SPC32 from the Eastern shelf

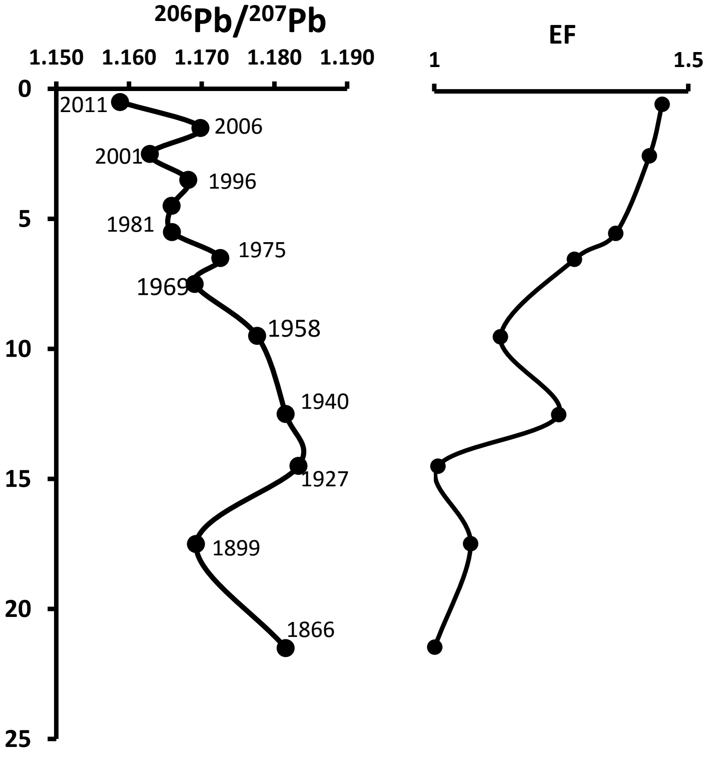


Figure 7.9 Historical changes in Pb isotopic (^{206}Pb/^{207}Pb) ratios and EF in sediment core SSK40/SPC69 from the western shelf.

This can also be possible that, there was no decrease in anthropogenic contribution in different interval but the relative contribution from multiple anthropogenic sources with different isotopic ratios. . Therefore, the increase in isotopic ratio might be due to the increase in the contribution from more radiogenic source of Pb and not for the relatively higher contribution from geogenic source. Moreover, the variation of ^{206}Pb/^{207}Pb was found to have a mirror image relation with variation in EF down the core. With the increase in EF, observed decrease in isotopic ratio (Figure 7.8) indicates the increased anthropogenic input to the sediments.

The lowest ^{206}Pb/^{207}Pb ratio, found in 1992 (Figure 7.8), was probably due to the highest emission of Pb from gasoline combustion during mid 90’s (Lee et.al, 2014). However, there was increase in ^{206}Pb/^{207}Pb ratio during 2005 was probably due to the phasing out leaded gasoline in 2000 from India. However, the decrease in isotopic ratio in the uppermost layer indicates that anthropogenic sources are still active and the phasing out of leaded gasoline could not reduce the anthropogenic emission of Pb in the Indian environment.

Stable Pb isotopic signature of the deepest layer of the core (SSK40/SPC69) collected from the western shelf of southern India (off Karnataka) was less radiogenic (^{206}Pb/^{207}Pb =1.182) than that found in the eastern shelf core (off Andhra Pradesh) and Pb isotopic composition study suggests that historical evolution of Pb in the core from the western shelf was different from the core collected from the eastern shelf of India.

This change in the isotopic ratio was due to the difference in geological heterogeneity of the sources of these two shelf sediments. We assumed that the deepest layer of the core was not contaminated by anthropogenic Pb as it was ~150 years older than the recent time of sampling. Sudden drop in ^{206}Pb/^{207}Pb ratio from 1.182 at the deepest layer to 1.169 at 17-18 cm depth (Table 7.2 and Figure 7.9) along with the increase in EF indicate that there was increase in anthropogenic Pb input in 1899 (Figure 7.9).

It has been reported in literature that the industrialisation started in Karnataka in 1884 (Chapter-II Industrial Development of Karnataka an Overview http://shodhganga.inflibnet.ac.in/bitstream/10603/62948/11/11_chapter%202.pdf). However, not much information is available about the type and the location of industry in Karnataka. Nevertheless, the decreased Pb isotopic ratio (along with the increased EF) indicates that Pb pollution occurred during that period.

Pb isotopic ratio reached the background value in the next layer i.e in 1927. A constant decrease was observed from the year 1940 to 1969. The increasing anthropogenic Pb input was consistent with the time of the growth in industrialisation in India as well as in Karnataka.

However, the emission of Pb in Indian environment due to the usage of leaded gasoline was not reflected in the isotopic profile of this core.

7.3.4 Identification of probable anthropogenic source

It is well known that, leaded gasoline combustion, coal combustion and Pb processing and smelting plants are the major anthropogenic Pb emitters in the environment (Monna et al., 1997; Pacyna and Pacyna, 2001; Bollhöfer and Rosman, 2000). In India, Pb emission is expected from all these three major sources.

To identify the source of anthropogenic Pb in the studied sediments, stable Pb isotopic composition of the above mentioned sources are discussed below.

The alkyl Pb used in gasoline was imported in India from two major suppliers' viz. Associated Octel and Ethyl Corporation in U.S.A (Bollhoffer and Roseman, 2001). The Pb used to synthesis alkyl Pb was extracted from Pb ores from the Broken Hill type deposit in Australia having the isotopic composition of 1.040 (^{206}Pb/^{207}Pb) and 2.224 (^{206}Pb/^{208}Pb) and Mississipi Valley type Pb deposit in USA having the isotopic composition of 1.406 (^{206}Pb/^{207}Pb) and 1.860 (^{206}Pb/^{208}Pb).Thus, it is expected that the isotopic composition of sediment similar to Broken Hill, Australia or Mississipi Valley, USA ore will indicate the gasoline source.

The isotopic composition of coal in general has more radiogenic signature compared to the Pb isotopic composition of gasoline. The ^{206}Pb/^{207}Pb ratio of major coal deposits worldwide ranges from 1.15 to 1.24 (D´iaz - Somoano et al; 2009; Farmar et al., 2012). The Pb isotopic composition of Indian coal is not known. However, to meet the coal consumption demand, India imports coal for power generation from Indonesia (^{206}Pb/^{207}Pb:1.180 to 1.188), South Africa (^{206}Pb/^{207}Pb:1.211 to 1.225) and Australia (^{206}Pb/^{207}Pb:1.253to1.257) (https://www.pwc.in/assets/pdfs/industries/power-mining/icc-coal-report.pdf).

There are active Pb processing and smelting plants present in different parts of India, e.g., Rajasthan (north-west), Mumbai (central-west), Kolkata (north-east), Bihar (north-east), Orissa (north-east) and Andhra Pradesh (central-east). The isotopic composition of Pb emitting from Pb smelters are actually the isotopic composition of

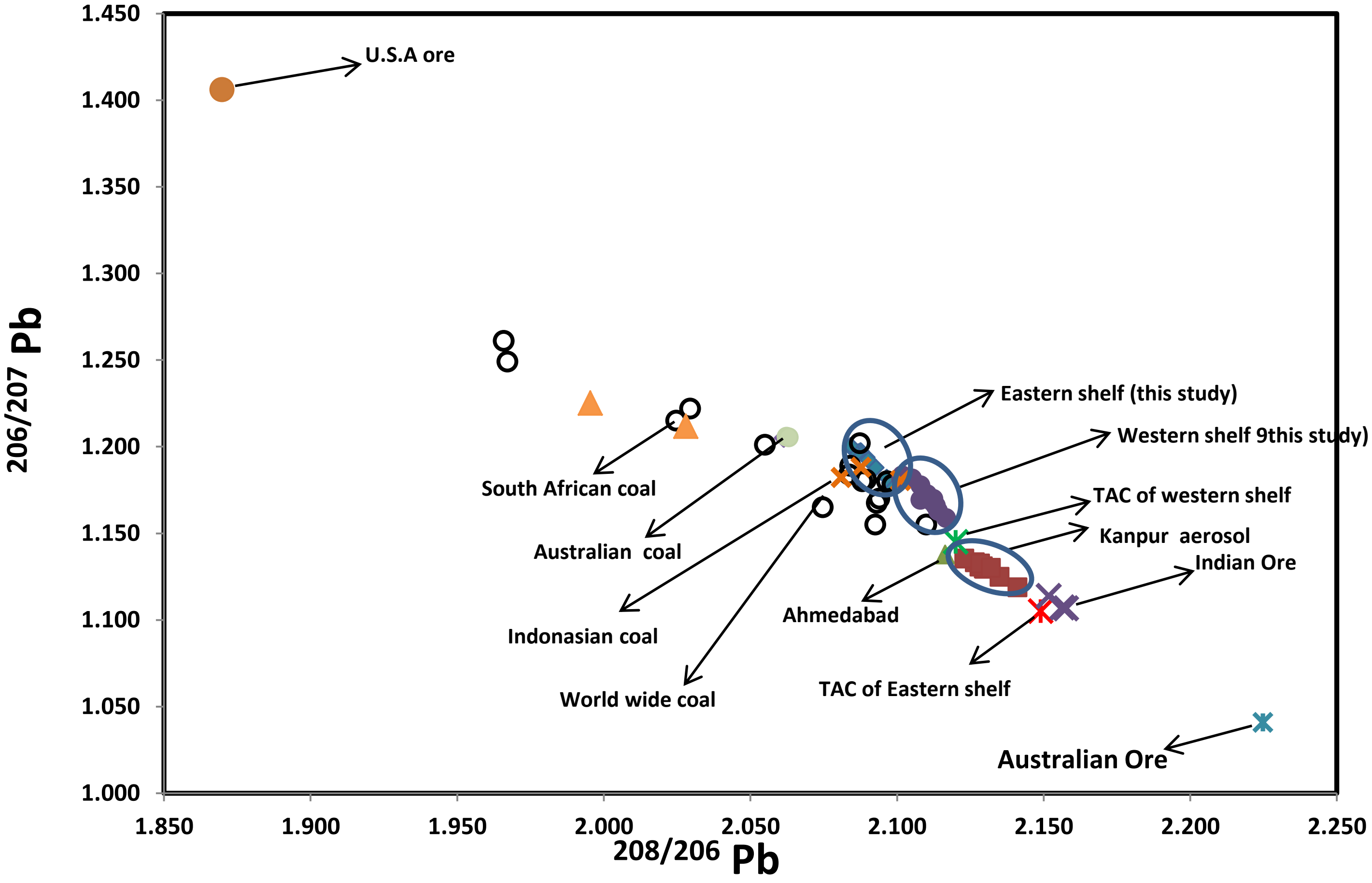


Figure 7.10 Co-isotopic plot (208Pb/206Pb vs 207Pb/206Pb) of the studied sediments in comparison to literature values for natural and anthropogenic end members :continental crust (Millot et al., 2004).;coal (Farmer et al.,1999; Díaz-Somoano et al., 2009; Álvarez-Iglesias et al.,2012 and references therein); aerosol from Kanpur city (Sen et al.,2016) and Ahmedabad city (Bollhöfer, and Rosman, 2001);ore from U.S.A ,Australia (Sangster et al., 2000) and India (Deb et al., 1989) and anthropogenic isotopic composition in the studied sediment.

Pb ore extracted in smelting plants. Thus it is expected that the composition of Pb coming from smelting plant might have the isotopic signature of Indian ores. The isotopic composition of Indian ore ranges from 1.106 to 1.114 (^{206}Pb/^{207}Pb) and 2.152 to 2.157 (^{206}Pb/^{208}Pb) (Deb et al., 1989). In addition to that, India imports Pb ore from China with isotopic composition of 1.1716 (^{206}Pb/^{207}Pb) and 2.068 (^{206}Pb/^{208}Pb) (Zhu, 1998), Korea (isotopic composition not found) and Australia with the isotopic composition varied from 1.043 to 1.204 (^{206}Pb/^{207}Pb) and 2.222 to 2.049 (^{206}Pb/^{208}Pb) (Sangster et al., 2000 and references therein) (http://ficci.in/spdocument/20317/mining-industry.pdf).

In order to identify the probable anthropogenic sources of Pb in the studied sediments, isotopic ratios (^{206}Pb/^{207}Pb vs ^{206}Pb/^{208}Pb) of the samples and the other probable sources (mentioned above) were plotted in a triple isotopic plot (Figure 7.10).The isotopic composition of the leachates of the eastern and western continental shelf sediments falls closer to the Indonesian and European coal (Figure 7.10). However, it was discussed earlier that the sediment leachates contain both anthropogenic and natural Pb and thus, the isotopic composition of the leachates were the resultant mixture of anthropogenic and natural isotopic signature. To know the isotopic signature of total anthropogenic component of the sediments a binary mixing model proposed by Ferrand et al. (1999) was applied. The equation of the binary mixing model is shown below.

$$\left(\frac{Pb^{206}}{Pb^{207}}\right)_{mean} = \left(\left(\frac{Pb^{206}}{Pb^{207}}\right)_{natural} - \left(\frac{Pb^{206}}{Pb^{207}}\right)_{anthrop}\right) \times \frac{[Pb]_{natural}}{[Pb]_{mean}} + \left(\frac{Pb^{206}}{Pb^{207}}\right)_{anthrop}$$

The isotopic composition of the anthropogenic component was calculated by plotting all the isotopic ratios (^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{206}Pb/^{204}Pb and ^{206}Pb/^{207}Pb) one by one against the inverse of corresponding Pb concentration (1/[Pb]), calculating the regression line, and then extrapolating the value of isotopic ratio at 1/[Pb] =0. Thus, the Pb isotopic ratio of the samples at 1/[Pb]=0, signified the isotopic ratio of anthropogenic component (Figure 7.11).

The anthropogenic isotopic ratios (Table 7.5) of sediments from both the regions indicate that the eastern and western shelf of India receives anthropogenic Pb from different sources. The anthropogenic composition of the western shelf sediment (^{206}Pb/ ^{207}Pb: 1.105; ^{206}Pb/^{208}Pb: 2.149) was found to be less radiogenic compared to the

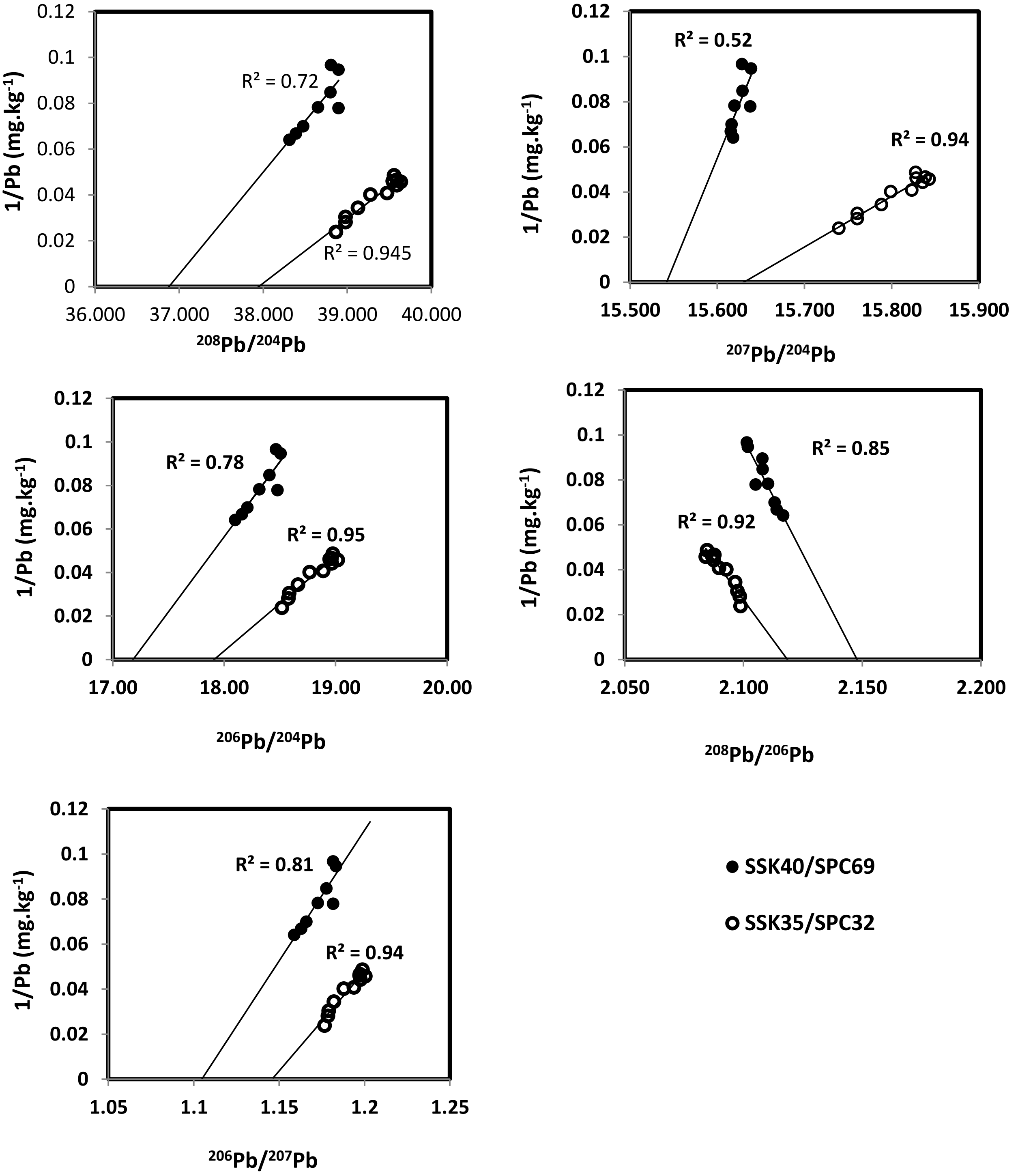


Figure 7.11 Dispersion plots for isotope ratios ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{206}Pb/^{204}Pb, ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb vs. 1/[Pb]: SSK35/SPC32 (eastern continental shelf) (N=13, r^2=0.95, r^2=0.94, r^2=0.95, r^2=0.92 and r^2=0.94, respectively) and SSK40/SPC69 core from western shelf (N=11, r^2=0.72, r^2=0.52, r^2=0.80, r^2=0.85 and r^2=0.81, respectively)

eastern shelf isotopic composition (^{206}Pb/^{207}Pb: 1.145; ^{206}Pb/^{208}Pb:2.120). The anthropogenic isotopic ratio of the sediments from western shelf had the similar isotopic composition of Indian ore (Figure 7.11) which indicate that heavy industries were the major source of anthropogenic Pb to the western continental shelf. On the other hand, anthropogenic isotopic signature of eastern shelf did not match with the isotopic signature of the mentioned anthropogenic sources. Since the isotopic signature of Indian coal is unknown, there could be a possibility of Indian coal being the source of anthropogenic Pb in the eastern shelf. In addition to that isotopic signature of Chinese coal (^{206}Pb/^{207}Pb: 1.141 to 1.18 (D´iaz- Somoano et al.2009) was found to have the similarity with the anthropogenic signature of eastern shelf sediment. It has been reported that Bay of Bengal receives aerosols from china and south-east Asia (Moorthy et al.,2008; Saxena et al.,2014) and thus, Pb emitted from the Chinese coal combustion might be the source of anthropogenic Pb in the eastern shelf sediments. This study was further supported by the stable Pb isotopic study by Lee et al. (2015) in the water of Arabian Sea and Bay of Bengal, where it was reported that, due to the monsoonal wind pattern Bay of Bengal receives more aerosol from china and south-east Asia whereas Arabian Sea receives more continental atmospheric outflow from India. Thus, these two regions showed distinct anthropogenic Pb signature.

7.4 Conclusions:

Down-core variation of total Pb, its EF, geochemical fractionation and Pb isotopic ratios (^{206}Pb/^{204} Pb, ^{207}Pb/^{204} Pb, ^{208} Pb /^{204} Pb, and ^{206} Pb /^{207}Pb) in the sediment cores from the continental shelves of India suggests that there was increasing anthropogenic Pb input over the last century. Isotopic signature of Pb in the shelf sediments indicates that anthropogenic Pb sources in the eastern and western shelf of India were different and leaded gasoline was not the major source of anthropogenic Pb. The anthropogenic composition of the western shelf sediment (^{206}Pb/ ^{207}Pb: 1.105; ^{206}Pb/^{208}Pb: 2.149) was found to be less radiogenic compared to the eastern shelf isotopic composition (^{206}Pb/^{207}Pb: 1.145; ^{206}Pb/^{208}Pb:2.120). Analysis by binary mixing model suggests that Pb emitted from the heavy industries (e.g, ore mining, Pb processing and smelting plants) of India was the major sources of anthropogenic Pb to the western continental shelf. However, it was difficult to identify the anthropogenic Pb sources in the eastern shelf of India by using Pb isotope. The sources of anthropogenic Pb in the eastern shelf sediment were convoluted. Since the isotopic signature of Indian coal is unknown, there could be a possibility of Indian coal being the source of anthropogenic Pb in the eastern shelf. However, Pb isotopic signature suggests that Chinese coal could be one of the major sources of anthropogenic Pb found in the eastern shelf sediment of India.

Chapter 8

Summary and Conclusions

This thesis provides the first comprehensive account of Pb geochemistry of continental shelf sediments of India and assesses the geochemical processes controlling the Pb accumulation and fractionation into different host phases.It also deciphers the natural versus anthopogenic Pb input into these sediments. A new approach of kinetic fractionation has been employed to evaluate the stability of Pb hosting non-residual phases. The response of Pb-hosting phases to the changes in bottom water oxygenation and its impact on Pb fractionation in suboxic to anoxic sediments was studied. For the first time to my knowledge, Pb isotopes have been measured in the sediments of this part of the world. Dating of couple of sediment cores helped evaluate the historical changes in the human-induced Pb accumulation pattern for the last hundred years. Large variation in Pb content was observed in the shelf sediments around India. Ganga-Brahmaputra and Indus derived sediments in the northern part and Mahanadi-Godavari-Krishna derived sediments in the central-east part contain higher Pb compared to the central-west and southern regions of the continental shelf. In addition to whole-sediment analyses, chemically separable phases were sequentially extracted and assessed the Pb fractionation among these phases.The residual phase revealed that, the diverse geology of Indian land mass greatly influenced the variation observed in sedimentary Pb content of Indian shelves. The acidic rocks of Himalaya contributed higher geogenic Pb in the northern part whereas basaltic terrain influenced sediments of central west region contain the lowest concentration of geogenic Pb. In some places (sporadically) evidences of anthropogenic Pb were also observed. Fe/Mn oxyhydroxide was the major hosting phase of naturally/anthropogenically mobilized Pb in the shelf sediments around India. In addition, sedimentary organic carbon also played important role in binding Pb in few sporadic locations of central and southern west regions.

The extent of association of mobilized Pb in different binding phases of sediment was not dependent on the relative abundance of total Fe or organic carbon content in the sediment. Fe fractionation study revealed that the Fe in oxyhydroxide form controlled the association Pb with Fe-Mnoxyhydroxide phase and the other non-residual phases as well.

Kinetic fractionation study on selected sediment samples collected from shelf regions around India showed that Pb complexes in shelf sediments from either side of the India comprised of two kinetically distinguishable components. Major part of sedimentary Pb was kinetically inert in nature. The average percentage of total labile Pb-sediment complexes was more in the eastern shelf sediments compared to the western part. Stability of Pb-sediment complexes was found to depend on the Pb loading and the nature of the organic carbon in the sediments. Pb formed weaker complexes with water soluble, exchangeable, carbonate and Fe/Mn oxyhydroxide phases and stronger complexes with organic phase of the sediment from the eastern continental shelf. However, in the western shelf sediments, Pb formed weaker organic complexes.

Terrestrial nature of organic carbon in the eastern shelf seems to provide stronger binding sites for Pb compared to the less terrestrial organic carbon in the western shelf sediments**.** Thus, Pb formed more labile sedimentary Pb complexes with sedimentary organic carbon from marine sources in the western shelf sediment and thermodynamically more stable Pb-organic carbon complexes in Eastern shelf sediments with organic carbon predominantly from the terrestrial sources

This study also suggests that trace metal competition for specific binding sites play important role in the geochemical speciation of Pb in sediments. It was found that Cu showed highest affinity for organic binding phases followed by Ni and Pb in the studied sediments. However, Pb had highest association with Fe/Mn-oxyhydroxide phases followed by Ni and Cu. Ionic potential; water exchange rate (k_{-w}) of metal, ligand field stabilisation energy (LFSE) and Jahn-Teller effect control the metals-ligand interactions in different binding phases of sediments. Faster k_{-w} and higher ionic potential of Cu in combination with the extra stability of Cu-ligand (from organic phase) complexes due to the Jahn-Teller effect increased the association of Cu in the organic phases of the sediments than Ni and Pb. The smaller ionic radii of Ni^{2+} (0.72 A) than Pb^{2+} (1.20 A) increase the stability of Ni-ligand complexes in the organic phase of the sediments. In addition to that high CFSE of Ni (II) (compared to Pb^{2+} ions) make Ni-organic complexes increasingly stable than Pb. The high concentration of Pb in the Fe/Mn-oxyhydroxide binding phase was probably due to co-precipitation of Pb^{2+} and Fe^{3+}. High surface area or site availability for Pb^{2+} ion on Fe-oxyhydroxide phase and greater binding strength over simple precipitate surface was probably responsible for the high concentration of Pb in Fe/Mn oxyhydroxide phase.

Varying oxygen concentration in the overlying bottom water also control the Pb fractionation in sediment. The reduction and dissolution of Fe (III)/Mn-oxyhydroxide binding phase at low oxygen environment in the overlying bottom water increases the lability of Pb-sediment complexes in the underneath sediment and may increase bioavailability of Pb in the oceans.

This study describes the effect of varying bottom-water oxygen concentration and trace metal (Cu) competition on geochemical fractionation (operational speciation) of Pb in the surface sediments across the oxygen minimum zone (Arabian Sea) in the west coast of India. Both, Cu and Pb were redistributed among the different binding phases of the sediments with changing dissolved oxygen level (from oxic to hypoxic and close to suboxic) in the bottom water. The average lability of Cu-sediment complexes gradually decreased (i.e., stability increased) with the decreasing dissolved oxygen concentrations of the bottom water. Decreasing bottom-water oxygen concentration increased Cu association with sedimentary organic matter. However, Pb association with Fe(III)/Mn-oxyhydroxide phases in the sediments gradually decreased with the decreasing dissolved oxygen concentration of the overlying bottom water (due to dissolution of Fe (III)/Mn oxyhydoxide phase). The lability of Pb-sediment complexes increased with the decreasing bottom-water oxygen concentration. This study suggests that bottom-water oxygen concentration is one of the key factors governing stability and lability of Cu and Pb complexes in the underneath sediment. Sedimentary organic matter and Fe (III)/Mn oxyhydroxide binding phases were the major hosting phases for Cu and Pb respectively in the study area. Increasing lability of Pb- complexes in bottom sediments may lead to positive benthic fluxes of Pb at low oxygen environment.

Down-core variation in total Pb, EF and geochemical fractionation of Pb in the sediments collected from continental shelf of India suggested that, even after the banning of leaded gasoline between mid 90’s to 2000 in India, anthropogenic Pb input in the marine sediment of India is still increasing over the last century.

Isotopic signature of the shelf sediments showed that, leaded gasoline was not the major source of anthropogenic Pb in the shelf sediments of India. The eastern and western shelf of India receives anthropogenic Pb from two different sources. The anthropogenic composition of the western shelf sediment (^{206}Pb/ ^{207}Pb: 1.105; ^{206}Pb/^{208}Pb: 2.149) was found to be less radiogenic compared to the eastern shelf isotopic composition (^{206}Pb/^{207}Pb: 1.145; ^{206}Pb/^{208}Pb:2.120). Pb emitted from the heavy industries (e.g, ore mining, Pb processing and smelting plants) of India was the major source of anthropogenic Pb to the western continental shelf. However, the source of anthropogenic Pb in the eastern shelf sediment was not clear. Since the isotopic signature of Indian coal is unknown, there could be a possibility of Indian coal being the source of anthropogenic Pb in the eastern shelf. However, the similarities in isotopic signature of eastern shelf sediment with the Chinese coal suggest the deposition of aerosol containing Pb from Chinese coal combustion in the Bay of Bengal.

Geochemical fractionation study indicated that, Fe/Mnoxyhydroxide phase was the major hosting phase for anthropogenic Pb in the sediment.

Thus, it is expected that, climate change including the vertical/lateral expansion of oxygen minimum zone may increase the positive benthic flux of Pb to the overlying waters around India and may impact the benthic ecosystem.

Bibliography

Abaychi, J. K., & Douabul, A. A.,1986. Trace element geochemical associations in the Arabian Gulf. Marine pollution bulletin, 17(8), 353-356.

Acharya, S.S., Panigrahi, M.K., Gupta, A.K. and Tripathy, S., 2015. Response of trace metal redox proxies in continental shelf environment: The Eastern Arabian Sea scenario. Continental Shelf Research, 106, 70-84.

Achyuthan, H., Richardmohan, D., Srinivasalu, S., 2002a. Trace metals concentrations in the sediment cores of estuary and tidal zones between Chennai and Pondicherry , along the east coast of India. Indian journal of marine sciences. 31, 141–149.

Adamo, P., Nardi, G., Stanzione, D., Ii, F., Mezzocannone, V., 2005. Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. Chemosphere 61, 800–809.

Agnihotri, R., Bhattacharya, S.K., Sarin, M.M. and Somayajulu, B.L.K.., 2003. Changes in surface productivity and subsurface denitrification during the Holocene: a multiproxy study from the eastern Arabian Sea. The Holocene, 13(5),701-713.

Alagarsamy, R., 2006. Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. Estuarine, Coastal and Shelf Science, 67(1), 333-339.

Alvarez, E. A., Mochon, M. C., Sánchez, J. J., & Rodríguez, M. T., 2002. Heavy metal extractable forms in sludge from wastewater treatment plants. Chemosphere, 47(7), 765-775.

Álvarez-Iglesias, P., Rubio, B. and Millos, J., 2012. Isotopic identification of natural vs. anthropogenic lead sources in marine sediments from the inner Ría de Vigo (NW Spain). Science of the total environment, 43(7).22-35.

Anithamary, I., Ramkumar, T. and Venkatramanan, S., 2012. Distribution and accumulation of metals in the surface sediments of Coleroon river estuary, east coast of India. Bulletin of environmental contamination and toxicology, 88(3),413-417.

Bacon, J.R. and Dinev, N.S., 2005. Isotopic characterisation of lead in contaminated soils from the vicinity of a non-ferrous metal smelter near Plovdiv, Bulgaria. Environmental Pollution, 134(2),247-255.

Badri, M.A. and Aston, S.R., 1983. Observations on heavy metal geochemical associations in polluted and non-polluted estuarine sediments. Environmental Pollution Series B, Chemical and Physical, 6(3),181-193

Balachandran, K.K., Laluraj, C.M., Martin, G.D., Srinivas, K. and Venugopal, P., 2006. Environmental analysis of heavy metal deposition in a flow-restricted tropical estuary and its adjacent shelf. Environmental Forensics, 7(4), 345-351.

Baldock, J.A., Masiello, C.A., Gelinas, Y. and Hedges, J.I., 2004. Cycling and composition of organic matter in terrestrial and marine ecosystems. Marine Chemistry, 92(1),39-64.

Banerjee, K., Senthilkumar, B., Purvaja, R., & Ramesh, R.,2012. Sedimentation and trace metal distribution in selected locations of Sundarbans mangroves and Hooghly estuary, northeast coast of India. Environmental geochemistry and health, 34(1), 27-42.

Banse, K., Naqvi, S. W. A., Narvekar, P. V., Postel, J. R., & Jayakumar, D. A.,2014. Oxygen minimum zone of the open Arabian Sea: variability of oxygen and nitrite from daily to decadal timescales.Biogeosciences, 11, 2237–2261.

Bastami, K.D., Bagheri, H., Haghparast, S., Soltani, F., Hamzehpoor, A. and Bastami, M.D., 2012. Geochemical and geo-statistical assessment of selected heavy metals in the surface sediments of the Gorgan Bay, Iran. Marine pollution bulletin, 64(12), 2877-2884.

Benjamin, M. M., & Leckie, J. O.,1981a. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. Journal of Colloid and Interface Science, 79(1), 209-221.

Benjamin M. M. and Leckie J. O.,198lb. Competitive adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhvdroxide. Journal of Colloid and Interface Science. 83. 410-419.

Berner, R.A., 1981. A new geochemical classification of sedimentary environments. Journal of Sedimentary Research, 51(2) 359-365.

Binning, K. and Baird, D., 2001. Survey of heavy metals in the sediments of the Swartkops River Estuary, Port Elizabeth South Africa. Water Sa, 27(4), 461-466.

Boës, X., Rydberg, J., Martinez-Cortizas, A., Bindler, R. and Renberg, I., 2011. Evaluation of conservative lithogenic elements (Ti, Zr, Al, and Rb) to study anthropogenic element enrichments in lake sediments. Journal of paleolimnology, 46(1),75-87

Boggs, S., Livermore, D. and Seitz, M.G., 1985. Humic substances in natural waters and their complexation with trace metals and radionuclides: A review. Argonne National Laboratory.

Bollhöfer, A. and Rosman, K.J.R., 2000. Isotopic source signatures for atmospheric lead: the Southern Hemisphere. Geochimica et Cosmochimica Acta, 64(19),3251-3262.

Bollhöfer, A. and Rosman, K.J.R., 2001. Isotopic source signatures for atmospheric lead: the Northern Hemisphere. Geochimica et Cosmochimica Acta, 65(11),1727-1740.

Bordovskiy, O.K., 1965. Sources of organic matter in marine basins. Marine Geology, 3(1-2),5-31.

Broenkow, W.W. and Cline, J.D., 1969. Colorimetric determination of dissolved oxygen at low concentrations. Limnology and Oceanography, 14(3),450-454.

Bryan, J.R., Rlley, J.P. and Williams, P.L., 1976. A Winkler procedure for making precise measurements of oxygen concentration for productivity and related studies. Journal of Experimental Marine Biology and Ecology, 21(3),191-197.

Calmano, W., Hong, J. and Förstner, U., 1993. Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. Water science and technology, 28,.223-223.

Canuel, E.A. and Martens, C.S., 1993. Seasonal variations in the sources and alteration of organic matter associated with recently-deposited sediments. Organic Geochemistry, 20(5),563-577.

Chakraborty, P., Gopalapillai, Y., Murimboh, J., Fasfous, I.I. and Chakrabarti, C.L., 2006. Kinetic speciation of nickel in mining and municipal effluents. Analytical and Bioanalytical chemistry, 386(6),1803-1813.

Chakraborty, P., Fasfous, I.I., Murimboh, J. and Chakrabarti, C.L., 2007a. Simultaneous determination of speciation parameters of Cu, Pb, Cd and Zn in model solutions of Suwannee River fulvic acid by pseudopolarography. Analytical and Bioanalytical Chemistry, 388(2), 463-474.

Chakraborty, P., 2007b. Chemical heterogeneity of humic substances and its impact on metal complexation in natural waters (Doctoral dissertation, Carleton University Ottawa).

Chakraborty, P., & Chakrabarti, C. L.,2008. Competition from Cu (II), Zn (II) and Cd (II) in Pb (II) binding to Suwannee river fulvic acid. Water, air, and soil pollution, 195(1-4), 63-71.

Chakraborty, P., Babu, P.R. and Sarma, V.V., 2011. A multi-method approach for the study of lanthanum speciation in coastal and estuarine sediments. Journal of Geochemical Exploration, 110(2),225-231.

Chakraborty, P., Babu, P. R., & Sarma, V. V., 2012a. A study of lead and cadmium speciation in some estuarine and coastal sediments. Chemical Geology, 294, 217-225.

Chakraborty, P., 2012b. Speciation of Co, Ni and Cu in the coastal and estuarine sediments: Some fundamental characteristics. Journal of Geochemical Exploration, 115, 13-23.

Chakraborty, P., Babu, P.R., Vudamala, K., Ramteke, D. and Chennuri, K., 2014a. Mercury speciation in coastal sediments from the central east coast of India by modified BCR method. Marine Pollution Bulletin, 81(1), 282-288.

Chakraborty, P., Manek, A., Niyogi, S. and Hudson, J., 2014b. Determination of dynamic metal complexes and their diffusion coefficients in the presence of different humic substances by combining two analytical techniques. Analytical Letters, 47(7), 1224-1241.

Chakraborty, P., Chakraborty, S., Vudamala, K., Sarkar, A., & Nath, B. N.,2015b . Partitioning of metals in different binding phases of tropical estuarine sediments: importance of metal chemistry. Environmental Science and Pollution Research, 1-13.

Chakraborty, S., Chakraborty, P., & Nath, B. N. 2015a . Lead distribution in coastal and estuarine sediments around India. Marine pollution bulletin, 97(1), 36-46.

Chakraborty, P., Ramteke, D. and Chakraborty, S., 2015c. Geochemical partitioning of Cu and Ni in mangrove sediments: Relationships with their bioavailability. *Marine pollution bulletin*, *93*(1),194-201.

Chakraborty, P., Sarkar, A., Vudamala, K., Naik, R. and Nath, B.N., 2015 c. Organic matter—a key factor in controlling mercury distribution in estuarine sediment. Marine Chemistry, 173,302-309.

Chakraborty, P., Vudamala, K., Chennuri, K., Armoury, K., Linsy, P., Ramteke, D., Sebastian, T., Jayachandran, S., Naik, C., Naik, R. and Nath, B.N., 2016. Mercury profiles in sediment from the marginal high of Arabian Sea: an indicator of increasing anthropogenic Hg input. Environmental Science and Pollution Research, 23(9),8529-8538.

Chakrapani, G.J. and Subramanian, V., 1993. Rates of erosion and sedimentation in the Mahanadi river basin, India. Journal of hydrology, 149(1-4),39-48.

Chandrasekharam, D., Mahoney, J.J., Sheth, H.C. and Duncan, R.A., 1999. Elemental and Nd–Sr–Pb isotope geochemistry of flows and dikes from the Tapi rift, Deccan flood basalt province, India. Journal of Volcanology and Geothermal Research, 93(1),111-123.

Chauhan, O.S. and Gujar, A.R., 1996. Surficial clay mineral distribution on the southwestern continental margin of India: evidence of input from the Bay of Bengal. Continental Shelf Research, 16(3), 321-333.

Chatterjee, M.V.S.F.E., Silva Filho, E.V., Sarkar, S.K., Sella, S.M., Bhattacharya, A., Satpathy, K.K., Prasad, M.V.R., Chakraborty, S. and Bhattacharya, B.D., 2007. Distribution and possible source of trace elements in the sediment cores of a tropical macrotidal estuary and their ecotoxicological significance. Environment International, 33(3),346-356.

Chattopadhyay, P.K. and Sarkar, S.C., 1999. Sulfur Isotope Geothermometry from the High Grade Metamorphosed Sulfide Deposit at Mamandur, Tamil Nadu. Geological Society of India, 53(6),705-710.

Chen, J., Algeo, T.J., Zhao, L., Chen, Z.Q., Cao, L., Zhang, L. and Li, Y., 2015. Diagenetic uptake of rare earth elements by bioapatite, with an example from Lower Triassic conodonts of South China. Earth-Science Reviews, 149, 181-202.

Christman, R.F. and Gjessing, E.T. eds., 1983. Aquatic and terrestrial humic materials (pp. 1-538). Michigan: Ann Arbor Science.

Clift, P.D., Lee, J.I., Hildebrand, P., Shimizu, N., Layne, G.D., Blusztajn, J., Blum, J.D., Garzanti, E. and Khan, A.A., 2002. Nd and Pb isotope variability in the Indus River System: implications for sediment provenance and crustal heterogeneity in the Western Himalaya. *Earth and Planetary Science Letters*, *200*(1), pp.91-106.

Clozel, B., Ruban, V., Durand, C. and Conil, P., 2006. Origin and mobility of heavy metals in contaminated sediments from retention and infiltration ponds. Applied Geochemistry, 21(10),1781-1798.

Coston, J.A., Fuller, C.C. and Davis, J.A., 1995. Pb 2+ and Zn 2+ adsorption by a natural aluminum-and iron-bearing surface coating on an aquifer sand. Geochimica et Cosmochimica Acta, 59(17),3535-3547.

Cowie, G.L. and Levin, L.A., 2009. Benthic biological and biogeochemical patterns and processes across an oxygen minimum zone (Pakistan margin, NE Arabian Sea). Deep Sea Research Part II: Topical Studies in Oceanography, 56(6),261-270.

Crusius, J., Calvert, S., Pedersen, T. and Sage, D., 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. *Earth and Planetary Science Letters*, *145*(1), pp.65-78.

Datta, D.K. and Subramanian, V., 1998. Distribution and fractionation of heavy metals in the surface sediments of the Ganges-Brahmaputra-Meghna river system in the Bengal basin. *Environmental Geology*, *36*(1-2), pp.93-101.

de Boyer Montégut, C., Madec, G., Fischer, A. S., Lazar, A., & Iudicone, D.,2004. Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology. Journal of Geophysical Research: Oceans, 109(C12).

Deb, M., Thorpe, R.I., Cumming, G.L. and Wagner, P.A., 1989. Age, source and stratigraphic implications of Pb isotope data for conformable, sediment-hosted, base metal deposits in the Proterozoic Aravalli-Delhi orogenic belt, northwestern India. Precambrian Research, 43(1),1-22.

Development of Indian Mining Industry – The Way Forward. http://ficci.in/spdocument/20317/mining-industry.pdf

Dhanakumar, S., Murthy, K.R., Solaraj, G. and Mohanraj, R., 2013. Heavy-metal fractionation in surface sediments of the Cauvery River Estuarine Region, Southeastern coast of India. Archives of environmental contamination and toxicology, 65(1),14-23.

Díaz-Somoano, M., Kylander, M.E., López-Antón, M.A., Suárez-Ruiz, I., Martínez-Tarazona, M.R., Ferrat, M., Kober, B. and Weiss, D.J., 2009. Stable lead isotope compositions in selected coals from around the world and implications for present day aerosol source tracing. Environmental science & technology, 43(4),1078-1085.

Dilli, K., 1986. Geochronology and geochemistry of a sediment core from Bombay coast. Mahasagar, 19(2),87-95.

DineshKumar, P.K., Sankaranarayanan, V.N. and Devi, K.S., 1994. Cochin backwaters: an introduction to the system, prior studies, historical trends and future implication.

Dipu, S. and Kumar, A.A., 2013. Distribution of mercury and other trace metals in the sediments of Cochin estuary (a Ramsar site), Kerala, India. Environmental monitoring and assessment, 185(8),6333-6341.

Electricity sector in India**:**https://en.wikipedia.org/wiki/Electricity_sector_in_India

El Nemr, A., Khaled, A. and El Sikaily, A., 2006. Distribution and statistical analysis of leachable and total heavy metals in the sediments of the Suez Gulf. Environmental Monitoring and Assessment, 118(1-3),89-112.

Farmer, J.G., Eades, L.J. and Graham, M.C., 1999. The lead content and isotopic composition of British coals and their implications for past and present releases of lead to the UK environment. Environmental Geochemistry and Health, 21(3),257-272.

Faruque, B.M., Vaz, G.G. and Mohapatra, G.P., 2014a. The continental shelf of eastern India. Geological Society, London, Memoirs, 41(1), 221-229.

Faruque, B.M. and Ramachandran, K.V., 2014b. The continental shelf of western India. Geological Society, London, Memoirs, 41(1),213-220.

Fasfous, I. I., Chakrabarti, C. L., Murimboh, J., & Yapici, T.,2006. Complexation of lead in model solutions of humic acid: heterogeneity and effects of competition with copper, nickel, and zinc. Environmental Chemistry, 3(4), 276-285.

Fernandes, L., Nayak, G.N., Ilangovan, D., 2012. Geochemical Assessment of Metal Concentrations in Mangrove Sediments along Mumbai Coast , India. World Acad. Sci. Technol. 61, 258–263.

Fernandes, L., Nayak, G.N., Ilangovan, D. and Borole, D.V., 2011. Accumulation of sediment, organic matter and trace metals with space and time, in a creek along Mumbai coast, India. Estuarine, Coastal and Shelf Science, 91(3),388-399.

Fernandes, L.L., Nayak, G.N., 2014. Characterizing metal levels and their speciation in intertidal sediments along Mumbai coast, India. Marine Pollution Bulletin 79, 371–8.

Ferrand, J.L., Hamelin, B. and Monaco, A., 1999. Isotopic tracing of anthropogenic Pb inventories and sedimentary fluxes in the Gulf of Lions (NW Mediterranean sea). Continental Shelf Research, 19(1),23-47.

Florence, T. M., Morrison, G. M., & Stauber, J. L., 1992. Determination of trace element speciation and the role of speciation in aquatic toxicity. Science of the Total environment, 125, 1-13.

Flemming, C.A. and Trevors, J.T., 1989. Copper toxicity and chemistry in the environment: a review. Water, Air, & Soil Pollution, 44(1),143-158.

Florence, T. M., Morrison, G. M., & Stauber, J. L.,1992. Determination of trace element speciation and the role of speciation in aquatic toxicity. Science of the Total environment, 125, 1-13.

Förstner, U., & Stoffers, P., 1981. Chemical fractionation of transition elements in Pacific pelagic sediments. Geochimica et cosmochimica acta, 45(7), 1141-1146.

Fulghum, J. E., Bryan, S. R., Linton, R. W., Bauer, C. F., & Griffis, D. P. (1988). Discrimination between adsorption and coprecipitation in aquatic particle standards by surface analysis techniques: lead distributions in calcium carbonates. Environmental science & technology, 22(4), 463-467.

Gaabass, I., Murimboh, J.D. and Hassan, N.M., 2009. A study of diffusive gradients in thin films for the chemical speciation of Zn (II), Cd (II), Pb (II), and Cu (II): The role of kinetics. Water, air, and soil pollution, 202(1-4), 131-140.

Galy, A. and France-Lanord, C., 2001. Higher erosion rates in the Himalaya: Geochemical constraints on riverine fluxes. *Geology*, *29*(1), pp.23-26.

Gireeshkumar, T. R., Deepulal, P. M., & Chandramohanakumar, N., 2013. Distribution and sources of sedimentary organic matter in a tropical estuary, south west coast of India (Cochin estuary): A baseline study. Marine pollution bulletin, 66(1), 239-245.

Gleyzes, C., Tellier, S., & Astruc, M.,2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. TrAC Trends in Analytical Chemistry, 21(6), 451-467.

Goldberg, E.D., 1954. Marine geochemistry 1. Chemical scavengers of the sea. The Journal of Geology,249-265.

Goldberg, E.D. and Griffin, J.J., 1970. The sediments of the northern Indian Ocean. In *Deep Sea Research and Oceanographic Abstracts* (Vol. 17, No. 3, 513-537). Elsevier.

Goodbred, S.L. and Kuehl, S.A., 2000. Enormous Ganges-Brahmaputra sediment discharge during strengthened early Holocene monsoon. Geology, 28(12),1083-1086.

Gourbunova, Z.N., 1966. Clay mineral distribution in the Indian ocean sediments. Oceanologia 6, 267–275.

Graetz, D. A., Keeney, D. R., & Aspiras, R. B., 1973. Eh status of lake sediment-water systems in relation to nitrogen transformations1. Limnology and Oceanography, 18(6), 908-917.

Hansmann, W. and Köppel, V., 2000. Lead-isotopes as tracers of pollutants in soils. Chemical Geology, 17*1*(1),123-144.

Hanson Jr, A.K. and Quinn, J.G., 1983. The distribution of dissolved and organically complexed copper and nickel in the middle Atlantic Bight. Canadian Journal of Fisheries and Aquatic Sciences, 40(S2),s151-s161.

Harikumar, P. S., Nasiru P. and Mujeeburahmanm P.,2009. Distribution of heavy metals in the core sediments of a tropical wetland system. International journal of environmental science and technology, 6 (2), 225–232

Hassan, N.M., Murimboh, J.D., Sekaly, A.L., Mandal, R., Chakrabarti, C.L. and Grégoire, D.C., 2006. Cascade ultrafiltration and competing ligand exchange for kinetic speciation of aluminium, iron, and nickel in fresh water. Analytical and Bioanalytical chemistry, 384(7-8), 1558-1566.

Hedges, J.I., Keil, R.G. and Benner, R., 1997. What happens to terrestrial organic matter in the ocean?. *Organic geochemistry*, *27*(5),195-212.

Hedges, J.I., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H. and Santos, U.D.M., 1986. Compositions and fluxes of particulate organic material in the Amazon River. *Limnology and Oceanography*, *31*(4),717-738.

Heinrichs, H., Schulz-Dobrick, B. and Wedepohl, K.H., 1980. Terrestrial geochemistry of Cd, Bi, Tl, Pb, Zn and Rb. Geochimica et Cosmochimica Acta, 44(10), 1519-1533.

Henrichs, S.M. and Reeburgh, W.S., 1987. Anaerobic mineralization of marine sediment organic matter: rates and the role of anaerobic processes in the oceanic carbon economy. Geomicrobiology Journal, 5(3-4), 191-237.

Hornberger, M.I., Luoma, S.N., van Geen, A., Fuller, C. and Anima, R., 1999. Historical trends of metals in the sediments of San Francisco Bay, California. Marine Chemistry, 64(1),39-55.

http://www.cdc.gov/niosh/docs/2003-154/pdfs/7105.pdf

Huu Hieu, H.O., Swennen, R. and Van Damme, A., 2002. Distribution and contamination status of heavy metals in estuarine sediments near Cua Ong Harbor, Ha Long Bay, Vietnam. Geologica belgica, 2010, 37-47.

Independent Statistics and Analysis: U.S. Energy Information Administration. **http://www.eia.gov/todayinenergy/detail.cfm?id=17551**.

Ishiwatari, R. and Uzaki, M., 1987. Diagenetic changes of lignin compounds in a more than 0.6 million-year-old lacustrine sediment (Lake Biwa, Japan). Geochimica et Cosmochimica Acta, 51(2),321-328.

Jahnke, R.A., Emerson, S.R. and Murray, J.W., 1982. A model of oxygen reduction, denitrification, and organic matter mineralization in marine sediments1. Limnology and Oceanography, 27(4), 610-623.

Jena, M., 2008. Pollution in the Mahanadi: urban sewage, industrial effluents and biomedical waste. Economic and Political Weekly,88-93.

Jonathan, M.P., Ram-Mohan, V. and Srinivasalu, S., 2004. Geochemical variations of major and trace elements in recent sediments, off the Gulf of Mannar, the southeast coast of India. Environmental Geology, *45*(4),466-480.

Jones, B. and Manning, D.A., 1994. Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. Chemical Geology, 111(1),111-129.

Jones, B., & Turki, A., 1997. Distribution and speciation of heavy metals in surficial sediments from the Tees Estuary, north-east England. Marine Pollution Bulletin, 34(10), 768-779.

Kamykowski, D., & Zentara, S. J.,1990. Hypoxia in the world ocean as recorded in the historical data set. Deep Sea Research Part A. Oceanographic Research Papers, 37(12), 1861-1874.

Karbassi, A.R. and Shankar, R., 2005. Geochemistry of two sediment cores from the west coast of India. International Journal of Environmental Science & Technology, 1(4), 307-316.

Kersten, M., & Förstner, U.,1986. Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. Water Science & Technology, 18(4-5), 121-130.

Kessarkar, P. M., Rao, V. P., Ahmad, S. M., & Babu, G. A.,2003. Clay minerals and Sr–Nd isotopes of the sediments along the western margin of India and their implication for sediment provenance. Marine Geology, 202(1), 55-69.

Kessarkar, P.M., Rao, V.P., Ahmad, S.M., Patil, S.K., Kumar, A.A., Babu, G.A., Chakraborty, S. and Rajan, R.S., 2005. Changing sedimentary environment during the Late Quaternary: Sedimentological and isotopic evidence from the distal Bengal Fan. Deep Sea Research Part I: Oceanographic Research Papers, 52(9), 1591-1615.

Kennedy, V.H., Sanchez, A.L., Oughton, D.H. and Rowland, A.P., 1997. Use of single and sequential chemical extractants to assess radionuclide and heavy metal availability from soils for root uptake. Analyst, *122*(8),89R-100R.

Koide, M., Soutar, A. and Goldberg, E.D., 1972. Marine geochronology with 210 Pb. Earth and Planetary Science Letters, 14(3), 442-446.

Krishnakumar, P.K., Bhat, G.S., Vaidya, N.G. and Pillai, V.K., 1998. Heavy metal distribution in the biotic and abiotic matrices along Karnataka coast, west coast of India. Indian Journal of Marine Sciences, 27, 201-205.

Krishnan, M.S., 1966. Geology of India and Burma, Higgin-. Higginbothms, Madras.

Krishnan, M.S., 1968. Geology of India: Burma. Higginbothams, Madras.

Krishna, M.S., Naidu, S.A., Subbaiah, C.V., Sarma, V.V.S.S. and Reddy, N.P.C., 2013. Distribution and sources of organic matter in surface sediments of the eastern continental margin of India. Journal of Geophysical Research: Biogeosciences, 118(4), 1484-1494.

Krupadam, R. J., Ahuja, R., & Wate, S. R. ,2007. Heavy metal binding fractions in the sediments of the Godavari estuary, East Coast of India. Environmental Modeling & Assessment, 12(2), 145-155.

Krupadam, R.J., Sarin, R., Anjaneyulu, Y., 2003. Distribution of trace metals and organic matter in the coast of India. Water,Air, Soil Pollut. 150, 299–318.

Kumar, S.P. and Patterson Edward, J.K., 2009. Assessment of metal concentration in the sediment cores of Manakudy estuary, south west coast of India. Indian Journal of Marine Sciences, 38(2), 235.

Kurian, S., Nath, B.N., Kumar, N.C. and Nair, K.K.C., 2013. Geochemical and Isotopic signatures of surficial sediments from the western continental shelf of India: inferring provenance, weathering, and the nature of organic matter. Journal of Sedimentary Research, 83(6),427-442

Kwon, Y.T. and Lee, C.W., 2001. Ecological risk assessment of sediment in wastewater discharging area by means of metal speciation. Microchemical Journal, 70(3), 255-264.

Landsberger, S., Jervis, R.., Aufreiter, S., Van loon, J.., 1982. The determination of heavy metal (Al,Mn,Fe,Ni,Cu,Zn,Cd and Pb) in urban snow using an atomic absorption graphite furnace. Chemosphere 11, 234–237.

Langford, C.H. and Gutzman, D.W., 1992. Kinetic studies of metal ion speciation. Analytica chimica acta, 256(1), 183-201.

Leckie J. O., Benjamin M. M., Hayes K., Ilwfman G. and Altnann S.,1980.Adsorption/coprecipitation of trace elements from water with iron oxyhydroxide. Electric Power Research Institute Report CS-1513, Palo Alto, California

Lee, J.M., Boyle, E.A., Nurhati, I.S., Pfeiffer, M., Meltzner, A.J. and Suwargadi, B., 2014. Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century. Earth and Planetary Science Letters, 398, 37-47.

Lee, J.M., Boyle, E.A., Gamo, T., Obata, H., Norisuye, K. and Echegoyen, Y., 2015. Impact of anthropogenic Pb and ocean circulation on the recent distribution of Pb isotopes in the Indian Ocean. Geochimica et Cosmochimica Acta, 170,126-144.

Li, X., Shen, Z., Wai, O. W., & Li, Y. S., 2001. Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. Marine Pollution Bulletin, 42(3), 215-223.

Lion, L.W., Altmann, R.S. and Leckie, J.O., 1982. Trace-metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of iron/manganese oxide and organic surface coatings. Environmental Science & Technology, 16(10),660-666.

Long, E. R., MacDonald, D. D., Smith, S. L., & Calder, F. D.,1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental management, 19(1), 81-97.

Lopez-Sanchez, J.F., Rubio, R., Samitier, C. and Rauret, G., 1996. Trace metal partitioning in marine sediments and sludges deposited off the coast of Barcelona (Spain). Water Research, 30(1),153-159.

Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. ICES Journal of Marine Science:Journal du Conseil, 48(1), 101-115.

Lovley, D.R., 1987. Organic matter mineralization with the reduction of ferric iron: a review. Geomicrobiology Journal, *5*(3-4),375-399.

Lovley, D.R. and Phillips, E.J., 1988. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. Applied and environmental microbiology, 54(6), 1472-1480.

Luoma, S.N. and Bryan, G.W., 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. Science of the Total Environment, 17(2), 165-196.

Lu, P., Nuhfer, N.T., Kelly, S., Li, Q., Konishi, H., Elswick, E. and Zhu, C., 2011. Lead coprecipitation with iron oxyhydroxide nano-particles. Geochimica et Cosmochimica Acta, 75(16), 4547-4561.

Magesh, N.S., Chandrasekar, N. and Roy, D.V., 2011. Spatial analysis of trace element contamination in sediments of Tamiraparani estuary, southeast coast of India. Estuarine, Coastal and Shelf Science, 92(4),618-628.

Magesh, N.S., Chandrasekar, N., Kumar, S.K. and Glory, M., 2013. Trace element contamination in the estuarine sediments along Tuticorin coast–Gulf of Mannar, southeast coast of India. Marine pollution bulletin, 73(1),355-361.

Manceau, A., Marcus, M. A., & Tamura, N.,2002. Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. Reviews in Mineralogy and Geochemistry, 49(1), 341-428.

Mandal, R., Hassan, N. M., Murimboh, J., Chakrabarti, C. L., Back, M. H., Rahayu, U., & Lean, D. R.,2002. Chemical speciation and toxicity of nickel species in natural waters from the Sudbury area (Canada). Environmental science & technology, 36(7), 1477-1484.

Marchand, C., Lallier-Verges, E., Baltzer, F., Albéric, P., Cossa, D. and Baillif, P., 2006. Heavy metals distribution in mangrove sediments along the mobile coastline of French Guiana. Marine chemistry, *98*(1),1-17.

Martin, G.D., George, R., Shaiju, P., Muraleedharan, K.R., Nair, S.M. and Chandramohanakumar, N., 2012. Toxic metals enrichment in the surficial sediments of a eutrophic tropical estuary (Cochin Backwaters, Southwest Coast of India). The Scientific World Journal, 2012.

Mattait, B., Peters, J. and Eckhardt, F.J., 1973. Results of petrographic analysis on sediments from the Indian Pakistan continental margin (Arabian Sea)(German). Meteor’’Forschungsergebnisse, Reihe, 14,1-50.

McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochemistry, Geophysics, Geosystems, 2(4).

Meyers, P.A. and Ishiwatari, R., 1993. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. Organic geochemistry, 20(7),867-900.

Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Organic geochemistry, 27(5), 213-250

Middelburg, J. J., & Levin, L. A.,2009. Coastal hypoxia and sediment biogeochemistry. Biogeosciences, *6*.1273–1293

Monna, F., Lancelot, J., Croudace, I.W., Cundy, A.B. and Lewis, J.T., 1997. Pb isotopic composition of airborne particulate material from France and the southern United Kingdom: implications for Pb pollution sources in urban areas. Environmental Science & Technology, 31(8),2277-2286.

Moorthy, K.K., Satheesh, S.K., Babu, S.S. and Dutt, C.B.S., 2008. Integrated campaign for aerosols, gases and radiation budget (ICARB): an overview. Journal of Earth System Science, *117*(1),243-262.

Morrison, J.M., Codispoti, L.A., Smith, S.L., Wishner, K., Flagg, C., Gardner, W.D., Gaurin, S., Naqvi, S.W.A., Manghnani, V., Prosperie, L. and Gundersen, J.S., 1999. The oxygen minimum zone in the Arabian Sea during 1995. Deep Sea Research Part II: Topical Studies in Oceanography, 46(8),1903-1931.

Mukherjee, D.P. and Kumar, B., 2012. Evaluation of metal contamination in freshly deposited sediment of Hugli Estuary, India. Arch Appl Sci Res, 4(2),1155-1168.

Murty, P.S.N. and Veerayya, M., 1972. Studies on the sediments of Vembanad Lake. Kerala State: Part I—Distribution of Organic Matter: Indian Journal of Marine Sciences, 1,45-51.

Müller, P.J., 1977. CN ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochimica et Cosmochimica Acta, 41(6),765-776.

Muraleedharan, P. M., & Prasannakumar, S.,1996. Arabian Sea upwelling-A comparison between coastal and open ocean regions, Current Science, 70 (11), 842-846.

Nair, M.P. and Sujatha, C.H., 2012. Biogeochemical quality assessment of the sediments in Kerala coast. International Journal of Environmental Sciences, 3(1),707-719.

Nair, R.R., Hashimi, N.H. and Purnachandra, V., 1982. Distribution and dispersal of clay minerals on the western continental shelf of India. Marine Geology, 50(1), M1-M9.

Naqvi, S.M., Rao, V.D., Hussain, S.M., Narayana, B.L., Rogers, J.J. and Satyanarayana, K., 1978. The petrochemistry and geologic implications of conglomerates from Archaean geosynclinal piles of southern India. Canadian Journal of Earth Sciences, 15(7), 1085-1100.

Naqvi, S.M., Rao, V.D., Narain, H., 1974. The protocontinental growth of the Indian shield and the antiquity of its Rift Valleys. Precambrian Research. 1, 345–398.

Naqvi, S.W.A. and Noronha, R.J., 1991. Nitrous oxide in the Arabian Sea. Deep Sea Research Part A. Oceanographic Research Papers, 38(7), 871-890.

Nasir, U.P., 2012. Water quality assessment and isotope studies of Vembanad Wetland System.

Nath, B.N., Bau, M., Rao, B.R. and Rao, C.M., 1997. Trace and rare earth elemental variation in Arabian Sea sediments through a transect across the oxygen minimum zone. Geochimica et Cosmochimica Acta, 61(12),2375-2388.

Nath, B.N., Kunzendorf, H. and Plüger, W.L., 2000. Influence of provenance, weathering, and sedimentary processes on the elemental ratios of the fine-grained fraction of the bedload sediments from the Vembanad Lake and the adjoining continental shelf, southwest coast of India. Journal of Sedimentary Research, 70(5), 1081-1094.

Nealson, K.H. and Saffarini, D., 1994. Iron and manganese in anaerobic respiration: environmental significance, physiology, and regulation. Annual Reviews in Microbiology, 48(1), 311-343.

Nelson, Y. M., Lion, L. W., Shuler, M. L., & Ghiorse, W. C., 2002. Effect of oxide formation mechanisms on lead adsorption by biogenic manganese (hydr) oxides, iron (hydr) oxides, and their mixtures. Environmental science & technology, 36(3), 421-425

Olson, D.L. and Shuman, M.S., 1985. Copper dissociation from estuarine humic materials. Geochimica et Cosmochimica Acta, 49(6), 1371-1375.

O'Reilly, S. E., & Hochella, M. F., 2003. Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides. Geochimica et Cosmochimica Acta, 67(23), 4471-4487.

Outridge, P.M., Stern, G.A., Hamilton, P.B., Percival, J.B., McNeely, R. and Lockhart, W.L., 2005. Trace metal profiles in the varved sediment of an Arctic lake. Geochimica et Cosmochimica Acta, 69(20), 4881-4894.

Pacyna, J.M. and Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environmental Reviews, 9(4),269-298.

Palanichamy, S. and Rajendran, A., 2000. Heavy metal concentrations in seawater and sediments of Gulf of Mannar and Palk Bay, Southeast coast of India. Indian journal of marine sciences, 29(2),116-119.

Pancost, R.D. and Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. Marine Chemistry, 92(1), 239-261.

Pandarinath, K. and Narayana, A.C., 1992. Clay minerals and trace metal association in the Gangolli estuarine sediments, West Coast of India. Estuarine, Coastal and Shelf Science, 35(4),363-370.

Paropkari, A.L., Rao, C.M. and Murty, P.S.N., 1987. Environmental controls on the distribution of organic matter in recent sediments of the western continental margin of India. Petroleum geochemistry and exploration in Afro-Asian Region, 347-361.

Paropkari, A.L., Prakash Babu, C., Mascarenhas, A., 1992. A critical evaluation of depositional parameters controlling the variability of organic carbon in Arabian Sea sediments. Marine Geology 107, 213–226.

Paropkari, A.L., Prakash Babu, C., Mascarenhas, A., 1993. New evidence for enhanced preservation of organic carbon in contact with oxygen minimum zone on the western continental slope of India. Marine Geology, 111, 7–13.

Patel, B., Bangeria, V.S., Patel, S., Balani, M.., 1985. Heavy Metals in the Bombay Harbour Area. Marine Pollution Bulletin. 16, 22–28.

Pedersen, T.F. and Calvert, S.E., 1990. Anoxia vs. productivity: what controls the formation of organic-carbon-rich sediments and sedimentary Rocks?(1). AAPG Bulletin, 74(4), 454-466.

Prahl, F.G., Bennett, J.T. and Carpenter, R., 1980. The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. Geochimica et Cosmochimica Acta, 44(12),1967-1976.

Prahl, F.G., Ertel, J.R., Goni, M.A., Sparrow, M.A. and Eversmeyer, B., 1994. Terrestrial organic carbon contributions to sediments on the Washington margin. Geochimica et Cosmochimica Acta, 58(14),3035-3048.

Prasanna Kumar, S., Muraleedharan, P.M., Prasad, T.G., Gauns, M., Ramaiah, N., De Souza, S.N., Sardesai, S. and Madhupratap, M., 2002. Why is the Bay of Bengal less productive during summer monsoon compared to the Arabian Sea?. Geophysical Research Letters, 29(24).

Prasanna Kumar, S., Narvekar, J., Kumar, A., Shaji, C., Anand, P., Sabu, P., & Nair, K. K. C.,2004. Intrusion of the Bay of Bengal water into the Arabian Sea during winter monsoon and associated chemical and biological response. Geophysical Research Letters, 31(15).

Rao, V. P., & Rao, B. R. ,1995. Provenance and distribution of clay minerals in the sediments of the western continental shelf and slope of India. Continental Shelf Research, 15(14), 1757-1771.

Raj, S., Jee, P.K., Panda, C.R., 2013. Textural and heavy metal distribution in sediments of Mahanadi estuary , East coast of India 42, 370–374.

Raj, S.M. and Jayaprakash, M., 2008. Distribution and enrichment of trace metals in marine sediments of Bay of Bengal, off Ennore, south-east coast of India. Environmental Geology, 56(1), 207-217.

Raju, K., Vijayaraghavan, K., Seshachalam, S. and Muthumanickam, J., 2011. Impact of anthropogenic input on physicochemical parameters and trace metals in marine surface sediments of Bay of Bengal off Chennai, India. Environmental monitoring and assessment, 177(1-4), 95-114.

Ramesh, R., Ramanathan, A.L., James, R.A., Subramanian, V., Jacobsen, S.B., Holland, H.D., 1999. Rare earth elements and heavy metal distribution in estuarine sediments of east coast of India. Hydrobiologia 89–99.

Ramaswamy, V., & Rao, P. S.,2006. Grain size analysis of sediments from the northern Andaman Sea: comparison of laser diffraction and sieve-pipette techniques. Journal of Coastal Research, 1000–1009

Ramachandran, K.K., 2002. Textural and trace elemental distribution in sediments of the Beypore estuary (SW coast of India) and adjoining innershelf. IJMS, 31, p.4.

Rao, V.P., Rao, B.R., 1995. Provenance and distribution of clay minerals in the sediments of the western continental shelf and slope of India. Continental Shelf Reasearch 15, 1757–1771.

Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A. and Quevauviller, P., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. Journal of Environmental Monitoring, 1(1), 57-61.

Revichandran, C., K. Srinivas, K. R. Muraleedharan, M. Rafeeq, Shivaprasad Amaravayal, K. Vijayakumar, and K. V. Jayalakshmy., 2011. Environmental set-up and tidal propagation in a tropical estuary with dual connection to the sea (SW Coast of India). Environmental Earth Sciences 66: 1031–1042

Ravichandran, R., Manickam, S., 2012. Heavy metal disrtibution in the coastal sediment of chennai coast Ramanibai Ravichandran and Shanthi Manickam * IIOAB-India. IIOAB J. 3, 12–18.

Ray, A.K., Tripathy, S.C., Patra, S., Sarma, V. V, 2006. Assessment of Godavari estuarine mangrove ecosystem through trace metal studies. Environmental International, 32, 219–223.

Raymo, M.E., Grant, B., Horowitz, M. and Rau, G.H., 1996. Mid-Pliocene warmth: stronger greenhouse and stronger conveyor. Marine Micropaleontology, 27(1),313-326.

Reddy, M.S., Basha, S., Sravan Kumar, V.G., Joshi, H. V, Ramachandraiah, G., 2004. Distribution, enrichment and accumulation of heavy metals in coastal sediments of Alang-Sosiya ship scrapping yard, India. Mararine Pollution Bulleton, 48, 1055–9.

Renjith, K.R. and Chandramohanakumar, N., 2007. Geochemical characteristics of surficial sediments in a tropical estuary, south-west India. Chemistry and Ecology, 23(4), 337-343.

Rokade, M. A.,2009. Heavy metal burden in coastal marine sediments of north west coast of India in relation to pollution (Doctoral dissertation, National Institute of Oceanography).

Rooth, J.E. and Cornwell, J.C., 2003. Increased sediment accretion rates following invasion byPhragmites australis: The role of litter. Estuaries, 26(2), 475-483.

Saha, S.B., Mitra, A., Bhattacharyya, S.B. and Choudhury, A., 2001. Status of sediment with special reference to heavy metal pollution of a brackishwater tidal ecosystem in northern Sundarbans of West Bengal. Tropical Ecology, 42(1), 127-132.

Sahu, K.C. and Bhosale, U., 1991. Heavy metal pollution around the island city of Bombay, India. Part I: quantification of heavy metal pollution of aquatic sediments and recognition of environmental discriminants. Chemical geology, 90(3-4), 263-283.

Sahuquillo, A., Lopez-Sanchez, J.F., Rauret, G., Ure, A.M., Muntau, H. and Quevauviller, P., 2002. Sequential extraction procedures for sediment analysis (pp. 10-27). The Royal Society of Chemistry: Cambridge, UK.

Sarkar, S. K., Frančišković-Bilinski, S., Bhattacharya, A., Saha, M., & Bilinski, H., 2004. Levels of elements in the surficial estuarine sediments of the Hugli River, northeast India and their environmental implications. Environment International, 30(8), 1089-1098.

Sarkar, A., Chakraborty, P. and Nath, B.N., 2016. Distribution and nature of sedimentary organic matter in a tropical estuary: An indicator of human intervention on environment. Marine pollution bulletin, 102(1), 176-186.

Satpathy, K.K., Mohanty, A.K., Natesan, U., Prasad, M.V.R. and Sarkar, S.K., 2010. Seasonal variation in physicochemical properties of coastal waters of Kalpakkam, east coast of India with special emphasis on nutrients. Environmental monitoring and assessment, 164(1-4), 153-171.

Satyanarayana, D., Panigrahy, P.K. and Sahu, S.D., 1994. Metal pollution in harbour and coastal sediments of Visakhapatnam, east coast of India.Indian journal of marine sciences, 23(1), 52-54.

Saxena, M., Sharma, S.K., Mandal, T.K., Singh, S. and Saud, T., 2014. Source apportionment of particulates by receptor models over Bay of Bengal during ICARB campaign. Atmospheric Pollution Research, 5(4),729-740.

Schindler P. W., 1981. Surface complexes at oxide-water interfaces. In Adsorption of Inorganics at Solid-Liquid Interfaces (eds. M. A. ANDERSON and A. J. RUBIN). 1- 49. Ann Arbor Sciences Publishers Inc

Secrieru, D. and Secrieru, A., 2002. Heavy metal enrichment of man-made origin of superficial sediment on the continental shelf of the north-western Black Sea. Estuarine, Coastal and Shelf Science, 54(3), 513-526.

Sekaly, A.L., Mandal, R., Hassan, N.M., Murimboh, J., Chakrabarti, C.L., Back, M.H., Gregoire, D.C. and Schroeder, W.H., 1999a. Effect of metal/fulvic acid mole ratios on the binding of Ni (II), Pb (II), Cu (II), Cd (II), and Al (III) by two well-characterized fulvic acids in aqueous model solutions. Analytica Chimica Acta, 402(1), 211-221.

Sekaly, A.L., Chakrabarti, C.L., Back, M.H., Gregoire, D.C., Lu, J.Y. and Schroeder, W.H., 1999b. Stability of dissolved metals in environmental aqueous samples: Rideau River surface water, rain and snow. Analytica Chimica Acta, 402(1), 223-231.

Selvam, A.P., Priya, S.L., Banerjee, K., Hariharan, G., Purvaja, R. and Ramesh, R., 2012. Heavy metal assessment using geochemical and statistical tools in the surface sediments of Vembanad Lake, Southwest Coast of India. Environmental monitoring and assessment, 184(10), 5899-5915.

Semlali, R.M., van Oort, F., Denaix, L. and Loubet, M., 2001. Estimating distributions of endogenous and exogenous Pb in soils by using Pb isotopic ratios. Environmental science & technology, 35(21), 4180-4188.

Sen, I.S. and Peucker-Ehrenbrink, B., 2012. Anthropogenic disturbance of element cycles at the Earth's surface. Environmental science & technology, 46(16), 8601-8609.

Selvaraj, K., 1999. Total dissolvable copper and mercury concentrations in innershelf waters, off Kalpakkam. Current Science, 77, 494–497.

Shotyk, W., Weiss, D., Kramers, J.D., Frei, R., Cheburkin, A.K., Gloor, M. and Reese, S., 2001. Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 14 C yr BP. Geochimica et Cosmochimica Acta, 65(14), 2337-2360.

Shetye, S. R., Gouveia, A. D., & Shenoi, S. S. C.,1994. Circulation and water masses of the Arabian Sea. Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences, 103(2), 107-123.

Singh, P., 2009. Major, trace and REE geochemistry of the Ganga River sediments: influence of provenance and sedimentary processes. Chemical Geology, 266(3), 242-255.

Smith, B.N. and Epstein, S., 1971. Two categories of 13C/12C ratios for higher plants.
Plant physiology, 47(3), 380-384.

Sørensen, J., 1982. Reduction of ferric iron in anaerobic, marine sediment and interaction with reduction of nitrate and sulfate. Applied and Environmental Microbiology, 43(2),319-324.

Soto-Jiménez, M.F. and Páez-Osuna, F., 2001. Distribution and normalization of heavy metal concentrations in mangrove and lagoonal sediments from Mazatlan Harbor (SE Gulf of California). Estuarine, Coastal and Shelf Science, 53(3), 259-274.

Srinivasan, R. and Sreenivas, B.L., 1977. Some new geological features from the Landsat imagery of Karnataka. Geological Society of India, 18(11),589-597.

Stone, M. and Marsalek, J., 1996. Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. Water, Air, and Soil Pollution, 87(1-4), 149-169.

Subramanian, V., 1980. Mineralogical input of suspended matter by Indian rivers into the adjacent areas of the Indian Ocean. Marine Geology, 36(3-4), M29-M34.

Subramanian, V., 1993. Phosphorus, silicon, and some trace contaminants in the Ganges Estuary. Estuaries 16, 453–458.

Subramanian, V., Jha, P.K., Grieken, R.. V., 1988. Heavy Metals in the Ganges Estuary. Marine Pollution Bulletin 19, 290–293.

Subramanian, V. and Mohanachandran, G., 1990. Heavy metals distribution and enrichment in the sediments of southern east coast of India. Marine Pollution Bulletin, 21(7), 324-330.

Sudhanandh, V.S., Udayakumar, P., Ouseph, P.P., Amaldev, S. and Narendra Babu, K., 2011. Dispersion and accumulation trend of heavy metals in coastal and estuarine sediments and its textural characteristics, a case study in India. Journal of Human Ecology, 36(2), 85-90.

Sundararajan, M. and Srinivasalu, S., 2010. Geochemistry of core sediments from Gulf of Mannar, India. International Journal of Environmental Research, 4(4), 861-876.

Sundaray, S.K., Nayak, B.B., Kanungo, T.K. and Bhatta, D., 2012. Dynamics and quantification of dissolved heavy metals in the Mahanadi river estuarine system, India. Environmental monitoring and assessment, 184(2), 1157-1179.

Sujatha, C.H. and Manju, N.P., 2013, April. Environmental Geochemistry of Core Sediment in the Cochin Estuary (CE), India. International Science Congress Association.

Szarek-Gwiazda, E. and Mazurkiewicz-Boron, G., 2006. Influence of cadmium and lead partitioning in water and sediment on their deposition in the sediment of a eutrophic dam reservoir. Oceanol. Hydrobiol. Stud, *35*,141-157.

Tack, F.M.G. and Verloo, M.G., 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. International Journal of Environmental Analytical Chemistry, 59(2-4), 225-238.

Takahashi, Y., Manceau, A., Geoffroy, N., Marcus, M.A. and Usui, A., 2007. Chemical and structural control of the partitioning of Co, Ce, and Pb in marine ferromanganese oxides. Geochimica et Cosmochimica Acta, 71(4), 984-1008.

Tessier, A., Campbell, P. G., & Bisson, M.,1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical chemistry, 51(7), 844-851.

Tessier, A., Rapin, F., & Carignan, R.,1985. Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. Geochimica et Cosmochimica Acta, 49(1), 183-194.

Tewari, A., Joshi, H.V., Trivedi, R.H., Sravankumar, V.G., Raghunathan, C., Khambhaty, Y., Kotiwar, O.S. and Mandal, S.K., 2001. The effect of ship scrapping industry and its associated wastes on the biomass production and biodiversity of biota in in situ condition at Alang. Marine Pollution Bulletin, 42(6), 461-468.

Turekian, K.K. and Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. Geological Society of America Bulletin, 72(2), 175-192.

UNEP, 2007. The global campaign to eliminate leaded gasoline: progress as of January. Easiest access by. http://www.unep.org/transport/pcfv/pdf/leadreport. pdf.

Ure, A.M., 1991. Trace element speciation in soils, soil extracts and solutions. Microchimica Acta, 104(1-6), 49-57.

Ure, A. M., Quevauviller, P., Muntau, H., & Griepink, B.,1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. International journal of environmental analytical chemistry, 51(1-4), 135-151.

Venkatramanan, S., Ramkumar, T., Anithamary, I. and Vasudevan, S., 2014. Heavy metal distribution in surface sediments of the Tirumalairajan river estuary and the surrounding coastal area, east coast of India. Arabian Journal of Geosciences, *7*(1),123-130.

Verma, A., & Subramanian, V., 2002. Organic matter and amino acid concentrations in surface sediments of Vembanad Lake–a tropical estuary, west coast of India. Regional Environmental Change, 2(4), 143-149.

Vidal, P., Cocherie, A., & Le Fort, P., 1982. Geochemical investigations of the origin of the Manaslu leucogranite (Himalaya, Nepal). Geochimica et Cosmochimica Acta, 46(11), 2279-2292.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G., & Pigna, M.,2010. Mobility and bioavailability of heavy metals and metalloids in soil environments. Journal of soil science and plant nutrition, 10(3), 268-292.

Volvoikar, S. P., & Nayak, G. N.,2013. Depositional environment and geochemical response of mangrove sediments from creeks of northern Maharashtra coast, India. Marine Pollution Bulletin, 69(1), 223-227.

Wedepohl, K.H., 1978. Handbook of Geochemistry. Springer-Verlag ,Berline.Vols. 2–4.

Welcher F.J., The Analytical uses of Ethylenediaminetetraacetic Acid, D. Van Nostrand Company, Inc., Toronto, Canada, 1958, Chapter 1.

Yin, A., & Harrison, T. M., 2000. Geologic evolution of the Himalayan-Tibetan orogen. Annual Review of Earth and Planetary Sciences, 28(1), 211-280.

Yuan, C. G., Shi, J. B., He, B., Liu, J. F., Liang, L. N., & Jiang, G. B., 2004. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. Environment International, 30(6), 769-783.

Zhang, L., Yin, K., Wang, L., Chen, F., Zhang, D., & Yang, Y. , 2009. The sources and accumulation rate of sedimentary organic matter in the Pearl River Estuary and adjacent coastal area, Southern China. Estuarine, Coastal and Shelf Science, 85(2), 190-196.

Zwolsman, J.J., Berger, G.W. and Van Eck, G.T.M., 1993. Sediment accumulation rates, historical input, postdepositional mobility and retention of major elements and trace metals in salt marsh sediments of the Scheldt estuary, SW Netherlands. Marine Chemistry, 44(1), 73-94.

List of Publications

Publications from the thesis

- Chakraborty, P., **Chakraborty, S**., Vudamala, K., Sarkar, A. and Nath, B.N., 2016. Partitioning of metals in different binding phases of tropical estuarine sediments: importance of metal chemistry. Environmental Science and Pollution Research, 23(4), pp.3450-3462.

- **Chakraborty, S**., Chakraborty, P. and Nath, B.N., 2015. Lead distribution in coastal and estuarine sediments around India. Marine pollution bulletin, 97(1), pp.36-46.

- Chakraborty, P., **Chakraborty, S**., Jayachandran, S., Madan, R., Sarkar, A., Linsy, P. and Nath, B.N., 2016. Effects of bottom water dissolved oxygen variability on copper and lead fractionation in the sediments across the oxygen minimum zone, western continental margin of India. Science of the Total Environment, 2016, 566-567, 1052-1061.

Manuscript communicated

- **Sucharita Chakraborty**[1], Parthasarathi Chakraborty[*1], Arindam Sarkar[1] and B. Nagender Nath[1] .Lead distribution and its speciation in the continental shelf sediments around India: Influences of geogenic and anthrpogenic input.

Other Publications

- Chakraborty, P., Ramteke, D., **Chakraborty, S**. and Nath, B.N., 2014. Changes in metal contamination levels in estuarine sediments around India–an assessment. Marine pollution bulletin, 78(1), pp.15-25.

- Chakraborty, P., Ramteke, D. and **Chakraborty, S**., 2015. Geochemical partitioning of Cu and Ni in mangrove sediments: Relationships with their bioavailability. Marine pollution bulletin, 93(1), pp.194-201.

- Chakraborty, P., **Chakraborty, S**., Ramteke, D. and Chennuri, K., 2014. Kinetic speciation and bioavailability of copper and nickel in mangrove sediments. Marine pollution bulletin, 88(1), pp.224-230.

- Chakraborty, P., Ramteke, D., **Chakraborty, S**., Chennuri, K. and Bardhan, P., 2015. Relationship between the lability of sediment-bound Cd and its bioaccumulation in edible oyster. Marine Pollution Bulletin, 100(1), pp.344-351.

- Chakraborty, P., Mason, R.P., Jayachandran, S., Vudamala, K., Armoury, K., Sarkar, A., **Chakraborty, S**., Bardhan, P. and Naik, R., 2016. Effects of bottom water oxygen concentrations on mercury distribution and speciation in sediments below the oxygen minimum zone of the Arabian Sea. Marine Chemistry, 186, pp.24-32.

Appendix

In this section, the experimental set up of kinetic fractionation study, the measurement technique of dissolved oxygen in seawater and the method of texture determination of sediment are described.

1.1 Experimental set up for kinetic fractionation study

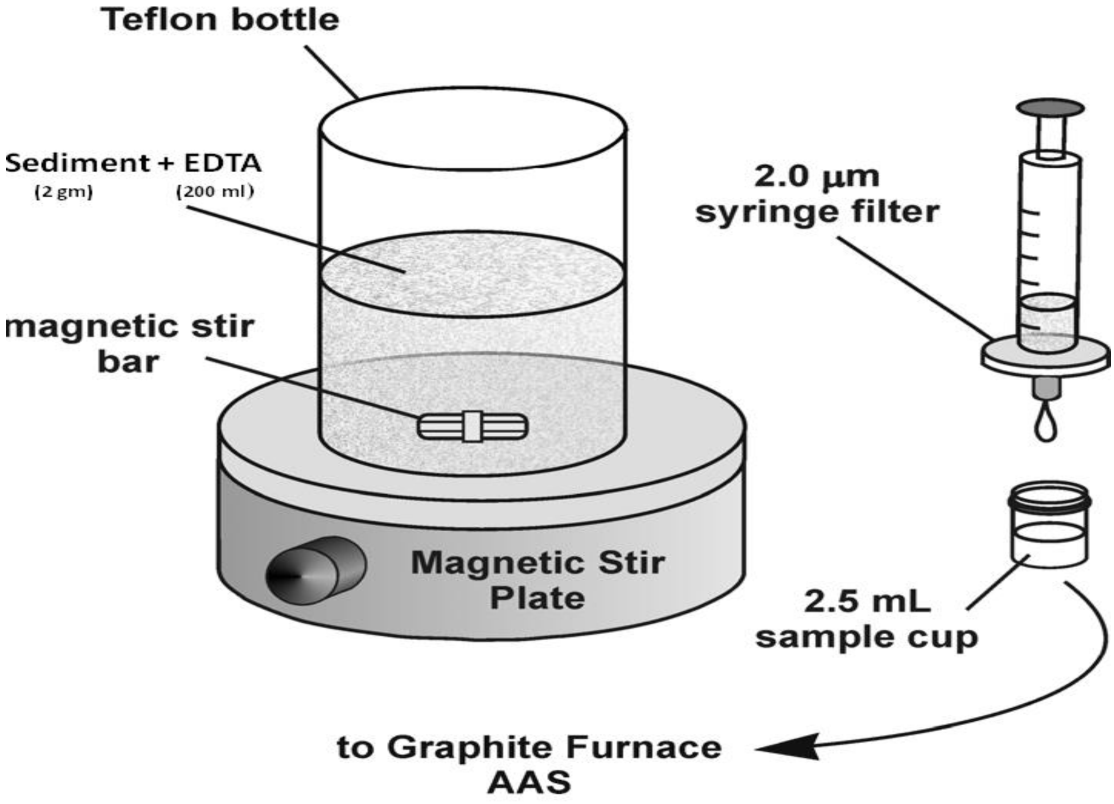


Figure: Experimental set up for kinetic fractionation study

1.2 Determination of Dissolved Oxygen by Winkler's Method

Principle:

Dissolved oxygen (DO) determination measures the amount of dissolved (or free) oxygen present in water. DO is determined by the titrimetric method developed by Winkler.

1. Dissolved molecular oxygen in water is not capable of reacting with KI, therefore an oxygen carrier such as manganese hydroxide is used. $Mn(OH)_2$ is produced by the action of KOH on $MnSO_4$.

2. $Mn(OH)_2$ so obtained reacts with dissolved molecular oxygen to form a brown precipitate of basic manganic oxide, $MnO(OH)_2$.

3. $MnO(OH)_2$ then reacts with concentrated sulphuric acid to liberate nascent oxygen.

4. Nascent oxygen results in oxidation of KI to I_2.

5. This liberated iodine is then titrated against standard sodium thiosulphate solution using starch as an indicator.

6. Thiosulphate reduces iodine to iodide ions and itself gets oxidized to tetrathionate ion. (Refer the reactions below.)

Reactions

$2NaOH + MnSO_4 \rightarrow Mn(OH)_2 + K_2SO_4$ ...(1)

$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2$ ...(2)

$MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + [O]$ ...(3)

$2KI + H_2SO_4 + [O] \rightarrow K_2SO_4 + H_2O + I_2$ ... (4)

$I_2 + I^- \rightarrow I_3^-$ ...(5)

$2S_2O_3^{2-} + I_3^- \rightarrow 3I^- + S_4O_6^{2-}$ ... (6)

Calculations

1000 mL of 1N $Na_2S_2O_3$ = 8 g oxygen

V mL of 0.025 N $Na_2S_2O_3$ = $V \times 0.025 \times 8/1000$ g oxygen per 100 mL water sample

= $V \times 0.025 \times 8$ mg oxygen per 100 mL water sample

= $V \times 0.025 \times 8 \times 10$ mg oxygen per 1000 mL water sample

Precautions

1. Do not allow air to trap while sampling water during DO analysis.

2. Dip the tip of the pipette just at the bottom of the DO bottle and gently release the reagents.

3. Take care that the chemicals do not flow out from the bottle while shaking/swirling.

4. Observe the colour changes during the DO reaction, if any.

1.3 Methodology for sediment texture analysis

This method is a combination of wet sieving of the fraction >63 μm and Laser Diffraction method on the <63 μm carbonate and organic carbon free fraction.

The salt content from the sedimentsamples were removed by washing repeatedly with deionized water. After that the sediment samples were dried at 45^0 C. Samples of 2 to 5g were disaggregated in deionized water and treated overnight with 30% H_2O_2 to remove the organic matter content. The samples were then sieved through 63 μm sieve to separate the sand from the silt+clay fraction. The material retained on the sieve represents the sand. Thesand fraction was dried and weighed to determine sand content.

The size distribution of the mud fraction (silt and clay) was measured with a Malvern laser particle size analyzer (Mastersizer 2000) which follows Laser Diffraction Method. This method is based on the principle that particles of a given size diffract light through a given angle, the angle increases with decreasing particle size. In this technique, a narrow beam of monochromatic light is passed through a sample cell containing an upward moving suspension of particles. The diffracted light is focused on to detectors, which sense the angular distribution of scattered light intensity from which the size distribution is calculated.

To measure the percentage of silt (<63 to >4 μm) and clay (<4 μm) content, a small aliquot of the mud fraction was diluted in 1 L of particle free water, and the size distribution was measured while the suspension was continuously pumped around. This ensures random orientation of most particles relative to the laser beam, and the equivalent spherical cross-sectional diameter is measured. Obscuration of the light beam by the mud solution was maintained between 8 and 20%. Pump and stirrer speeds were kept constant throughout the analysis. Calibration of the instrument was carried out using various Duke's latex and glass sphere standards in the range of 0.2 to 62μm. Prior to measurement, the samples were ultrasonicated for 1 to 2 min.The silt and clay data are presented in vol (%).