

Mercury profiles in sediment from the marginal high of Arabian Sea: An indicator of increasing anthropogenic Hg input in Sea

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Abstract: Total Hg distributions and its speciation was determined in two sediment cores collected from the western continental marginal high of the Indian Ocean. Total Hg content in the sediment was found to gradually increase (by ~ 2 times) towards the surface of both the cores. It was found that Hg was preferentially bound to sulfide under anoxic condition. However, redox mediated reactions (Fe (II)/Fe (III) and Mn (IV)/Mn(VI) cycling) in the upper part of the core influenced the total Hg content in the sediment cores. This study suggests that probable increase in authigenic and allochthonous Hg deposition attributed to the increasing Hg concentration on the surface sediment in the study area.

Key words: mercury deposition; Hg speciation; anoxic sediment; redox cycling and mercury; mercury pollution

Introduction

The global cycle of Hg involves atmospheric transport, deposition to land and ocean, and revolatilization (Selin 2009). Mason & Sheu (Mason and Sheu 2002) calculated an overall lifetime of 10,000 years for Hg in the combined atmosphere-ocean-terrestrial system against transfer to the sediments. It has been claimed that majority of the Hg entering ocean is buried within the sediments of ocean (Wang et al. 2004; Hare et al. 2008) and remains essentially immobilized within the sediment column (Amos et al. 2014). Thus, the accumulating sediments preserve a record of the flux of mercury over time provided the sediments remain undisturbed by either natural or anthropogenic forces (Engstrom et al. 2007). However, it has also been suggested that early diagenesis in sediment column may increase mobility of Hg and can alter concentration profile of Hg in a sediment core (Han et al. 2008).

Down core profiles of Hg in sediment usually shows enrichments near the sediment surface. The debate about whether core profiles with Hg enrichments near the sediment surface reflect diagenesis (Rasmussen et al. 1998; Gobeil et al. 1999; Lockhart et al. 2000) or whether they reflect enhanced atmospheric fluxes during the past century due to human activities (Fitzgerald 1995) is still on. However, not much information is available in literature on distribution of Hg in marine sediment cores underneath oxygen minimum zones (OMZ). It is required to understand the distribution, speciation and subsurface variation of Hg in sediments under OMZ.

Thus, “careful scrutiny” is necessary to understand the impact of atmospheric deposition or redox mediated reaction on Hg profile in a sediment core. Limited information is available in relation to emissions from anthropogenic sources and mercury deposition in coastal sediment around India. The fate of Hg-complexes in coastal water and sediment from this region is not known.

Distribution of mercury in different binding phases (exchangeable, bound to carbonates, bound to manganese-oxides, bound to iron-oxides, and bound to organic matter) of sediment are well documented in literature (Chakraborty et al. 2012a; Chakraborty et al. 2012b; Chakraborty 2012) (. The major possible sinks for Hg in sediments have been reported to be; sulfide binding sites, Fe/Mn oxyhydroxide and organic carbon phases (Chakraborty et al. 2014c; Chakraborty et al. 2014a; Chakraborty et al. 2014b). Association of mercury with these different binding phases in sediment is dependent on several environmental factors. Redox cycling of iron and manganese has been reported to influence the mobility of Hg in sediment (Dehairq 1989; Gagnon and Mucci 1997; van der Zee and van Raaphorst 2004; Konovalov et al. 2007). Oxidation of sedimentary organic matter also appears to release significant amounts of mercury (associated with organic phase). It is

important to note that increasing concentration of sulfide in sediment under anoxic condition may influence Hg speciation and its mobility in the marine sediment.

In this study an effort was made to understand the distribution and speciation of Hg in two sediment cores collected from marginal high of the west coast of India. These two cores were consciously chosen to understand the impact of variable redox condition (on concentration profile of Hg in marine sediment core. The aim of this study was to understand the influences of redox mediated processes (Fe(II)/Fe(III) and Mn(IV)/Mn(VI) cycling) and sulfide content on down core variation of total Hg concentrations and its speciation in sediment cores. Impact of increasing concentration of dissolved Hg (after industrialization) in sea water was also assessed.

Materials and methods

Study area

Geological and geophysical investigations of the western continental margin of India have revealed the presence of several structures- bathymetric highs and lows, buried basement ridges, sediment filled grabens etc (Rao et al. 2010). The highs and lows have been reported to occur in 245 to 1600 m water depths of the southwest continental margin of India between the Mormugoa (~ 15°N) and Kochi (~ 11°N) coasts. In this study, the sediment cores were collected from two locations (14°46.1050 N, 72° 40.35440 E and 14°16.2597 N, 72° 52.45000 E) (**Fig 1**). Samples were collected during the 40th expedition of R V Sindhu Sankalp (#SSK 40) in October 2012 from an area which is ~150 km away from the shore. The sediment cores were collected by using spade corer of 30cm ×15cm ×50 cm, immediately sub sectioned, freeze dried and packed in air tight zip lock bag and stored. This study area was chosen to minimize anthropogenic input of Hg on surface sediments.

Textural analysis of sediments

Texture of the dry sediment was analyzed by (after sieving with 63µm sieve size) particle size analyzer (LPSA from Malvern Mastersizer 2000) was used for textural analysis. The detailed procedure has been described in the literature by (Ramaswamy and Rao 2006). The data were presented as weight percentage (wt %) in this study. AMS C¹⁴ dating of the sediment cores was done in NSF-Arizona AMS Laboratory.

Cleaning Procedures for Containers

All containers used were made of Teflon. After cleaning with ultrapure water, all the containers and quartz boats were filled to the top with 10% (v/v) nitric acid and allowed to stand at the room temperature for 1 week. They were then rinsed five times with ultrapure water, filled with ultrapure

water (daily), and allowed to stand until they were used. Quartz boats were heated to 800°C prior to Hg analysis by direct mercury analyzer.

Determination of Hg in sediments by Direct Mercury Analyzer

Mercury was analyzed by Direct Mercury Analyzer (Tri cell DMA-80) from Milestone, Italy. The DMA-80 combines the techniques of thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry. Controlled heating stages are implemented to first dry and then thermally decompose a sample introduced into a quartz tube. A continuous flow of oxygen (99.9% pure) carries the decomposition products through a catalyst bed where interferences are trapped. All mercury species are reduced to elemental Hg and are then carried along to a gold amalgamator where the mercury is selectively trapped. The system is purged and the amalgamator is subsequently heated which releases all mercury vapours to the single beam, fixed wavelength atomic absorption spectrophotometer. Here, absorbance measured at 253.7 nm is proportional to mercury content in the sample. Quality control and assurance measures were implemented in this study. In addition to blanks and replicates, certified reference materials (PACS-2 and MESS-3 Marine Sediment Reference Materials for Trace Metals) from National Research Council Canada was used for quality control of mercury determination in sediments.

Determination of sulfide in sediment samples

Sediment sample of ~0.2g was taken to a 3-neck round-bottom flask. A volume of 10 mL of dimethylformamide (DMF) was added. The mixture was thoroughly stirred with a magnetic stir bar to secure an efficient mechanical breakup of the sample. Whereas DMF enhances the reactivity of reduced sulfur species, it also allows oxidation to take place at an enhanced rate. To prevent oxidation prior to distillation, extended contact of the sediment- DMF slurry with air avoided. As soon as the sample was mixed with DMF, the reaction flask was connected to the gas line and flushed with N₂ for 10 min. Subsequently, 8 mL 5M HCl was injected through the chemical port followed by the addition of 16 mL 1M CrCl₂ solution. The sample is bubbled at a rate of 2 to 5 bubbles per second with N₂ for 2 h and the system was stirred continuously. Zinc acetate solution was used as sulfide trap. The liberated sulfide was trapped as zinc sulfide in 20 mL of 5% (w/v) ZnAc-solution. Zinc sulfide precipitate was dissolved by adding 2ml of 50% HCl and liberated sulfide was measured on a spectrophotometer at 670nm by Cline method.

Determination of total metal concentrations in the sediment by using Inductively coupled plasma mass spectrometry (ICP-MS)

An ICPMS (Thermo FISCHER ICP-MS, X series 2, Germany) was used for the determination of the total metals concentrations. The radio-frequency power was set at 1400 W. Plasma gas, auxiliary gas and carrier gas flows were 13, 0.7 and 0.87 l·min⁻¹, respectively. The operating condition of ICP-MS has been reported in our previous study (Chakraborty et al. 2012b; Chakraborty 2012; Chakraborty et al. 2012c). The sensitivity of the ICP-MS instrument was monitored throughout the measurements by analyzing marine sediment reference material (MAG-1 from the U.S. Geological Survey) followed by a reagent blank between every 10 samples. If the sensitivity changed more than 5% during an experiment, a correction factor was used to correct for the drift.

Determination of methylmercury concentration in sediments

Approximately 1.0–2.0 g of dry sediment (freeze dried) was weighed out in triplicate; each sample was placed in 50 mL screw-capped polypropylene tube and hydrolyzed with 6M HCl (10mL). The sample was shaken for 5 min using a mechanical vertical shaker, centrifuged at 2400 rpm for 10 min and the liquid phase was discarded (no significant MeHg concentration, <LOQ, was detected).

20mL toluene was added to the sediment residue. All the sediment samples were vigorously mixed for 20 min. After centrifugation (2400rpm for 20min) the supernatant, containing organomercury species, was collected in falcon tubes. The whole procedure was repeated and 15 mL of toluene was added again to tube containing sediment.

The combined organic extracts were subjected twice to back extraction with 6mL of 1% (v/w) L-cysteine aqueous solution to strip methylmercury from toluene. Then, an aliquot of L-cysteine extract was immediately analysed with mercury analyser (DMA-80). The procedure has been vividly described in literature ((Maggi et al. 2009). Certified reference material of methylmercury in sediment (SQC1238-50G) (from Sigma Aldrich) was used to validate analytical measurement methods.

Statistical analysis

The data presented in this study are the average of three replicates. Errors are indicated along with the average values. All the data are presented with 95.5% confidence interval. Relationship between concentrations of metals associated with different solid phases in the sediments (obtained from sequential extraction study) and dynamic metal complexes (obtained from kinetic extraction study) were evaluated with Pearson's correlation coefficient.

Results and Discussion

General physical and chemical characteristic of the sediment cores are presented in **Table 1**. There was distinct down core variation observed in the particle size distribution. Sediments composed largely of sands and silts in the lower part (from 20-28cm (SPC-1R) and 10-24 cm (SPC-2)) of the cores to sediments consisting primarily of silt and clay in the upper parts (0-20cm (SPC-1R) and 0-10cm (SPC-2)). Sandy section of the cores was probably biogenic and detritus materials. Total inorganic carbon (TIC) was found to be high and gradually increased down the cores and reach the maxima at the bottom of the cores. This probably suggests that the studied sediments (down the core) were dominated by calcareous materials. Thus, the variation in concentrations of Fe, Mn, Hg, U, Th (shown in **Table 1**) are presented on carbonate-free basis. The sedimentation rate in the study area was slow and it was ~ 3 cm/ky.

Evaluations of redox conditions of the sediment cores

U/Th ratio in the sediment was used as a proxy to understand the down core changes in redox conditions of the studied sediment. It is well known that oxic condition helps U to form water soluble complexes (as U^{6+}), with little or no changes in Th concentration. A low U/Th ratio in sediment indicates that there was an oxic depositional environment. Jones and Manning (Jones and Manning 1994) have quantitatively reported that the low U/Th ratio of 0.75 in sediments indicates an oxic depositional environment. However, in an anoxic environmental condition, the ratio of U/Th gradually increases with the increasing particle reactive reduced U form (U^{4+}). Jones and Manning [26] have reported that the ratio $U/Th > 1.25$ in sediment indicates completely anoxic depositional environments.

Fig 2 shows that the variation of U/Th ratio at different depth in the sediment cores. It was found that the upper part of the sediment core (0-5 cm) in SPC 1R was in suboxic state. The U/Th ratio in the sediments gradually increased down the core with a maxima at 17 -18 cm (depth) of the core (SPC-1R). The redox state was completely anoxic further down the core. However, the other core (SPC 2) was found to be in completely anoxic state from the top to the bottom.

Mercury profiles in the sediment cores

Down core variation of Hg concentration in two sediment cores are presented in **Fig 3**. The down core variations of Hg concentrations show a relatively smooth exponential-like decrease up to ~ 20 cm (in SPC-1R) and ~ 5 cm (in SPC-2). However, this decrease was interrupted by well-defined subsurface maximum further down the cores (~ 20 -27 cm and ~ 5 -22 cm in SPC 1R and SPC 2 cores respectively) (**Fig 3**). Surface enrichment factors in the sediment cores, defined as the Hg

concentration at the core top (surface sediment) divided by the average Hg concentration at depth from 10-15 cm depth, vary from 2.5 to 1.4 with an average of 1.9. The Hg enrichment factors seem consistent with a history of increasing Hg fluxes (Fitzgerald et al. 1998; Gobeil et al. 1999). Lamborg et al (REF) (Lamborg, Carl H., Chad R. Hammerschmid, Katlin L. Bowman, Gretchen J. Swarr, Kathleen M. Munson, Daniel C. Ohnemus, Phoebe J. Lam, Lars-Eric Heimbürger 2014) have reported that anthropogenic perturbations to the global mercury cycle have led to an approximately 150 per cent increase in the amount of mercury in thermocline waters and have tripled the mercury content of surface waters compared to pre-anthropogenic conditions.

The increasing authigenic and allochthonous Hg deposition can probably be attributed to the increasing Hg concentration on the surface sediment in an area not affected by bottom transport processes. The declining Hg concentrations down the sediment cores could be because of different types of processes, (i) textural changes in sedimenting particles or variations in natural Hg input occurring within the period spanned by the core could lead to a change in the concentration of Hg with depth; (ii) diagenesis, in particular redox mediated reactions, could redistribute Hg through a sequence of remobilization, diffusion, and scavenging processes; and (iii) formation of monomethyl mercury (MMHg) down the cores might have mobilized across the sediment-pore water interface to the top and (iv) authigenic and allochthonous Hg deposition processes. In this study, all the above processes were evaluated to understand the concentration profiles of Hg in sediment cores from the marginal high of Arabian Sea.

Textural changes in sedimenting particles down the sediment cores and Hg profiles

The down core variation of sand, silt and clay content in the sediments are presented in **Fig 4** (the data are presented in Table 1). In one of the cores (SPC 1R), the sand percentage ranges from 1.1% to 60.7%. Low percentage of coarser particle was found at the depth interval ~1cm to 10cm. The maximum percentage of coarser particle was present at 24cm to 28cm depth. The silt content was found to vary from 19% to 52% in SPC 1R core. The maximum percentage of silt was present in the surface and remained almost constant till 20cm. At 24cm to 28cm depth and low percentage of silt was present. The similar variation was found for the clay particles in this sediment core (SPC-1R). However, the abundance of coarser particle gradually increased with the depth in the other core (SPC 2). Finer particles were found to gradually decrease down the core (SPC-2).

Fig 4 shows that there was no (or little) change in the concentrations of total finer particles (silt and clay) in one core (SPC 1R) up to ~22 cm. However, there was a gradual decrease in abundance of finer particles (silt and clay) down the core in another core (SPC-2).

A significant positive correlation coefficient is usually found between total metal content and the finer particle (silt and clay) content in sediments and probably indicates that fine grained fraction of sediment, namely the silt – clay fraction, facilitates the uptake of metals more than any other grain size. However, there was no change (or little change) in the texture was observed down the core (SPC-1R) (up to ~22 cm). It suggests that the variations in the Hg content (down the core in SPC 1R) was not due to change in particle-size distribution in the studied core (SPC-1R). Very poor correlation was found between the total Hg content and the finer particles in the sediments collected at different depths down the sediment core (SPC-2). This indicates that the textural changes did not affect the concentration profiles of Hg in both the sediment cores.

It is interesting to note that there was a sudden increase in concentration of coarser particle at depth 20-28 cm in SPC 1R sediment core. Usually, poor negative correlation is expected between coarser grain size and increasing trace metal concentrations in sediments. However, increasing concentration of Hg with the increasing concentration of coarser grain size in this sediment core indicate that the presence of other binding sites of Hg in coarser particle (>63 μ M).

Diagenesis, in particular redox mediated reactions and Hg profiles

It has been well documented that diagenetic processes (particularly Fe(II)/Fe(III) and Mn(IV)/Mn(VI) cycling) may bring Hg up to the surface sediment from the bottom of a sediment core (if Hg associates with Fe/Mn-oxo hydroxide phases in the sediments).

Mercury usually come into pore water (during diagenetic processes) and can diffuse up and undergo several geochemical changes, followed by adsorption on different binding phases in the surface sediment on the top of the sediment core or re-precipitation on the water-sediment interface (depending upon redox condition of the boundary layer). These processes can enrich Hg concentration in sediment toward the surface.

Similar kind of concentration profiles for Fe, Mn, and Hg in sediment cores is usually expected if the enrichment of Hg on the surface of the sediment core is due to Fe(II)/Fe(III) and Mn(IV)/Mn(VI) cycling. A very similar concentration profiles of Fe, Mn and Hg was observed at the top (1-5 cm) of SPC 1R sediment (which was under suboxic depositional environment) (**Fig 5**). However, no relation or similarity between the concentrations of Fe, Mn and Hg in this sediment was found further down the core (i.e. from 6-28 cm depth) under anoxic depositional condition. There was no similarity between the concentration profiles of Fe, Mn and Hg was found in the other sediment core (SPC-2) (**Fig 6**) (under anoxic depositional environment). The use of U/Th ratio indicates that the upper 5 cm of one sediment core (SPC-1R) was in suboxic condition. However, further down the core (at 6-28 cm) and the other sediment core (SPC-2) was in anoxic state.

This findings probably suggest that Hg was associated with Fe/Mn binding phases in the upper part of the sediment core (0-5 cm) (where suboxic condition prevailed) and were involved in diagenetic processes. Thus, similar profile of Fe, Mn and Hg was observed in the sediment core (SPC 1R) in the upper 5 cm. Further down the core, under anoxic condition, Hg probably associated with sulfides and did not show the similar profile of Fe and Mn.

Fig 7 shows similar concentrations profiles of the total sulfide and Hg down the core (SPC 1R) at 6-28 cm depth (under anoxic condition). This clearly indicates that Hg prefers to associate with sulfides (in sediments) under anoxic conditions (SPC1R).

There was no similar profile of Fe, Mn and Hg was found in the other sediment core (which was collected from a completely anoxic condition) from the top to the bottom (SPC-2). However, a very similar concentration profiles were observed between Hg and sulfide in the sediment core. This clearly indicates that Hg prefers to associate with reduced sulphur than Fe/Mn oxyhydroxide binding phases in the studied sediments under anoxic condition.

This study indicates that Fe (II)/Fe(III) and Mn(IV)/Mn(VI) cycling had little effects on the concentration profile of Hg in both the sediment cores and sulfide concentration plays an important role in Hg mobility under anoxic condition.

Dissimilar concentration profiles of Hg along with other redox sensitive metals in the SPC-2 core clearly indicate that redox mediated reaction were not the main reasons for Hg enrichment on the top of the core. Further speciation study was carried out to understand the distribution of methylmercury (MeHg^+) down the cores. However, redox mediated reaction was found to play important role in Hg mobilization at the top 5 cm of SPC 1R core (under suboxic condition).

Formation of monomethyl mercury (MMHg) down the cores and Hg profiles

Down core variation of of MMHg concentration is shown in **Fig 8**. The concentration of MMHg decreased with the depth of both the cores from (2.5 to 1.4 ng. g⁻¹). However, the change in MMHg concentrations was not systematic down cores. There were sub- surface maxima of MMHg down the cores. However, it is interesting to note that the ratio of $[\text{Hg}]_T/\text{MMHg}$ is ~ 100 (at any depth) down the core.

It is proposed that the relatively consistent fraction of total Hg as MMHg may be related to proportional sediment-water partitioning and solid-phase retention of MMHg and Hg(II). Scavenging by sulfide ligand (in sediment) may also influence the sediment-water partitioning of Hg species. However, recent studies have shown that distribution coefficients of both Hg (II) and MMHg are correlated positively with the concentration of organic matter in sediments. This indicates

that there was probably no significant influence of MMHg formation (at the bottom of the sediment core) in the enrichment of Hg on the top of the core.

Increase in total Hg concentration in sea water and its impact on Hg profiles

The declining Hg concentrations down the sediment cores were scrutinized and different probable processes were evaluated. It was found that Fe(II)/Fe(III) and Mn(IV)/Mn(VI) cycling (most important redox mediated reactions) processes may not be an important factor to mobilize Hg in sediment under anoxic condition. Lamborg et al (Lamborg, Carl H , Chad R. Hammerschmid , Katlin L. Bowman , Gretchen J . Swarr , kathleen M.Munson , Daniel C . Ohnemus , Phoebe J. Lam , Lars-Eric Heimburger 2014) have suggested that anthropogenic perturbations to the global mercury cycle have led to an approximately 150 per cent increase in the amount of mercury in thermocline waters and have tripled the mercury content of surface waters compared to pre-anthropogenic conditions. It is suggested that higher deposition of Hg from water column was probably the main reason for the enrichment Hg concentrations in the surface sediment.

Industrialized nations have made important progress toward controlling atmospheric Hg pollution in recent decades, but air quality is much worse in many developing countries, and global circulation patterns can transport Hg rapidly around the world. The rapid increase in the concentrations of Hg on the surface sediment of the cores (by factors~2) probably indicates that anthropogenic activity was an important factor that attributed to the increasing Hg concentration on the surface sediment of the sediment cores, collected from the Ocean basins of marginal high on the west coast of India.

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Captions and Legends for Figs:

Fig 1: Location of the study area.

Fig 2 Variation of U/Th ratio at different depth in the sediment cores.

Fig 3: Concentration profile (depth) of Hg in the two sediment cores.

Fig 4: Sediment texture variation down the two sediment cores.

Fig 5: Profiles of Fe, Mn and Hg in SPC-1R sediment core.

Fig 6: Profiles of Fe, Mn and Hg in SPC-2 sediment core.

Fig 7: Concentration profiles of sulfide and Hg in the two sediment core.

Fig 8: Profile of MeHg concentration in two sediment core.

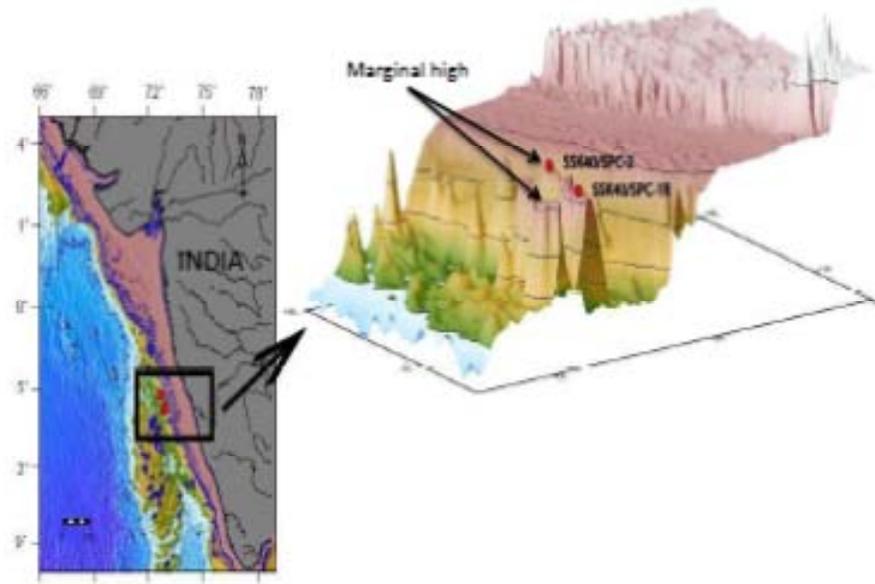


Fig. 1

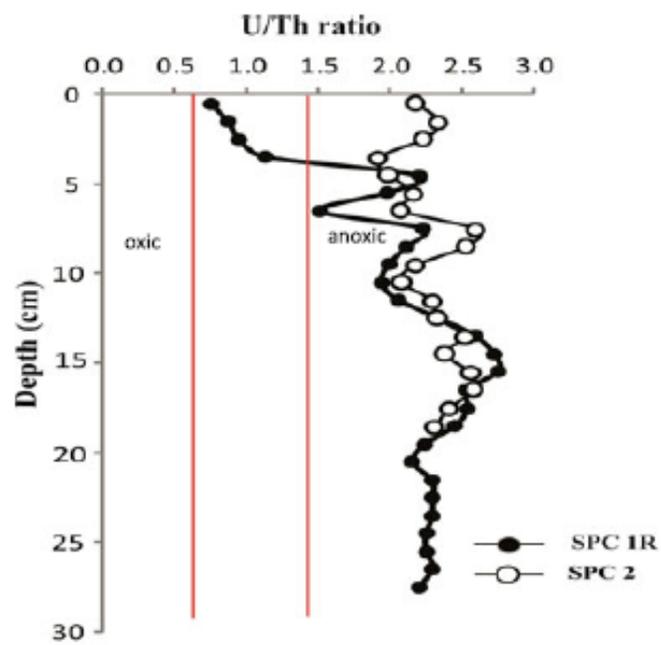


Fig. 2

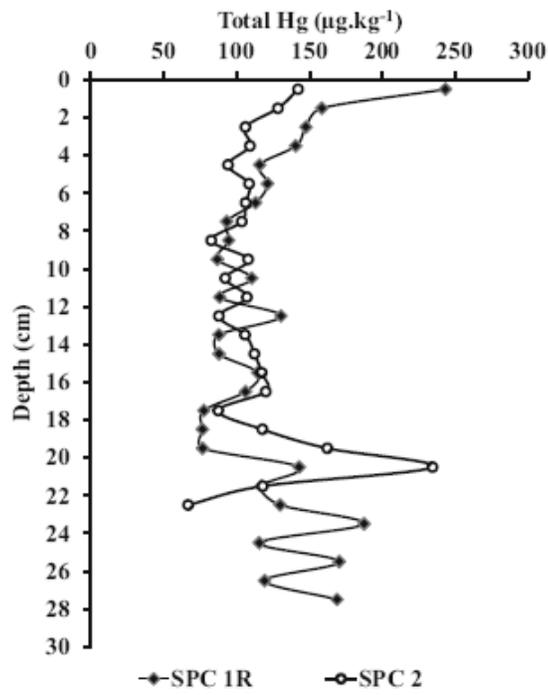


Fig. 3

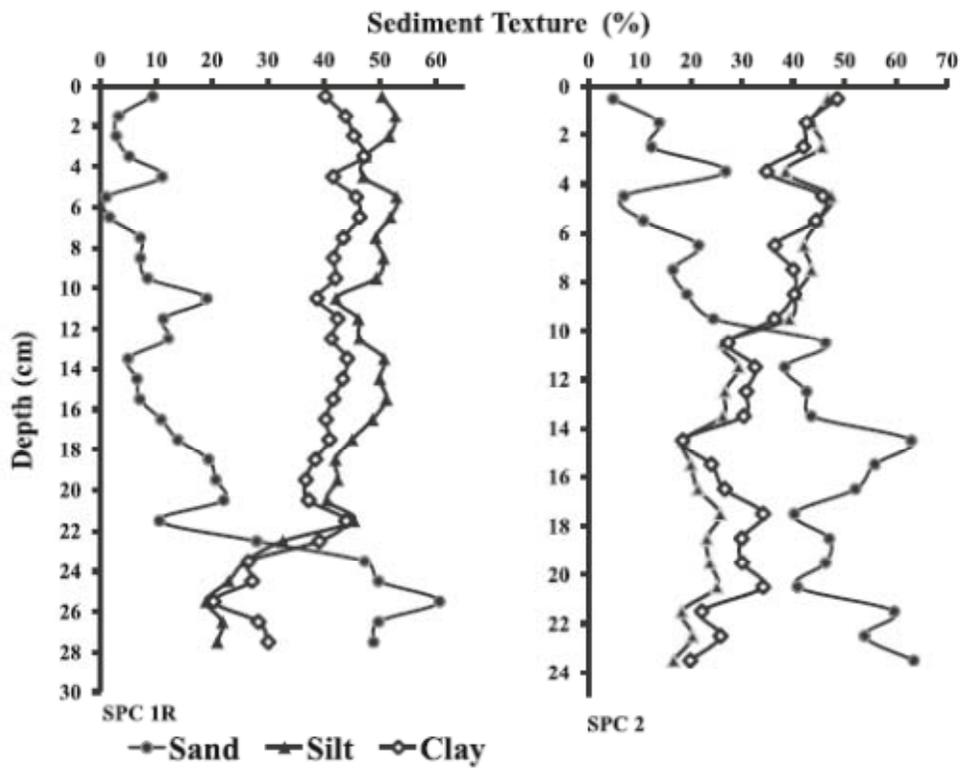


Fig. 4

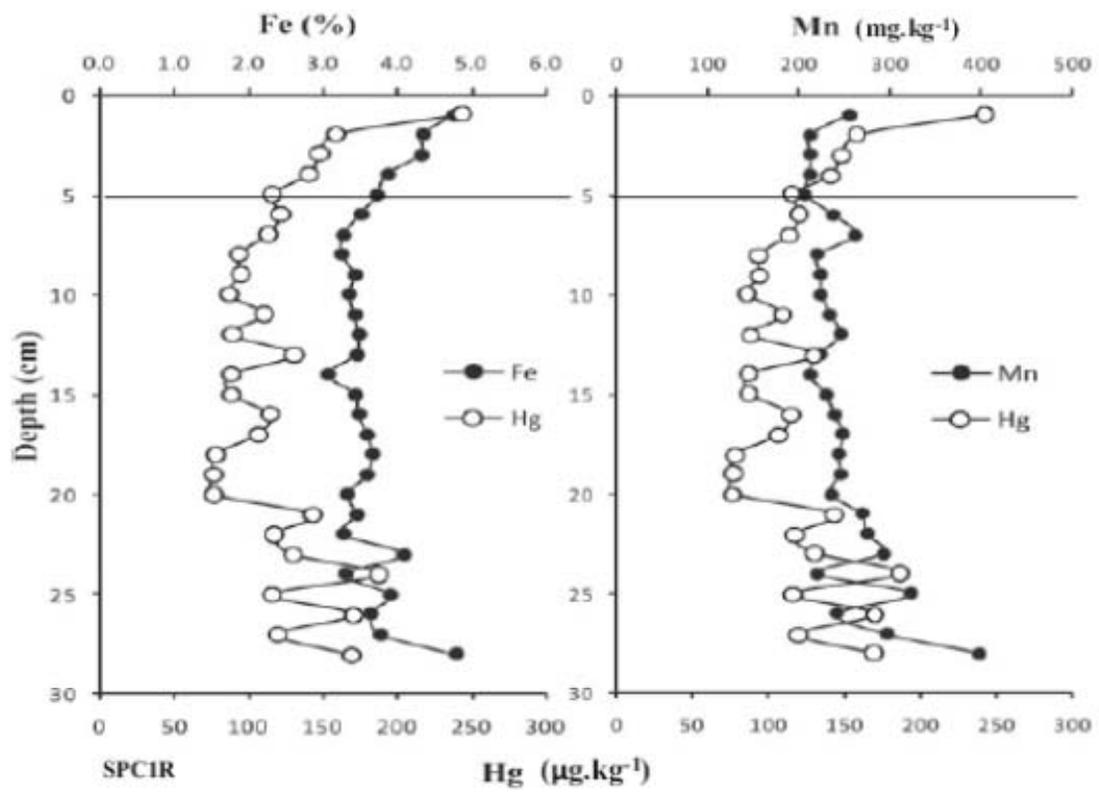


Fig. 5

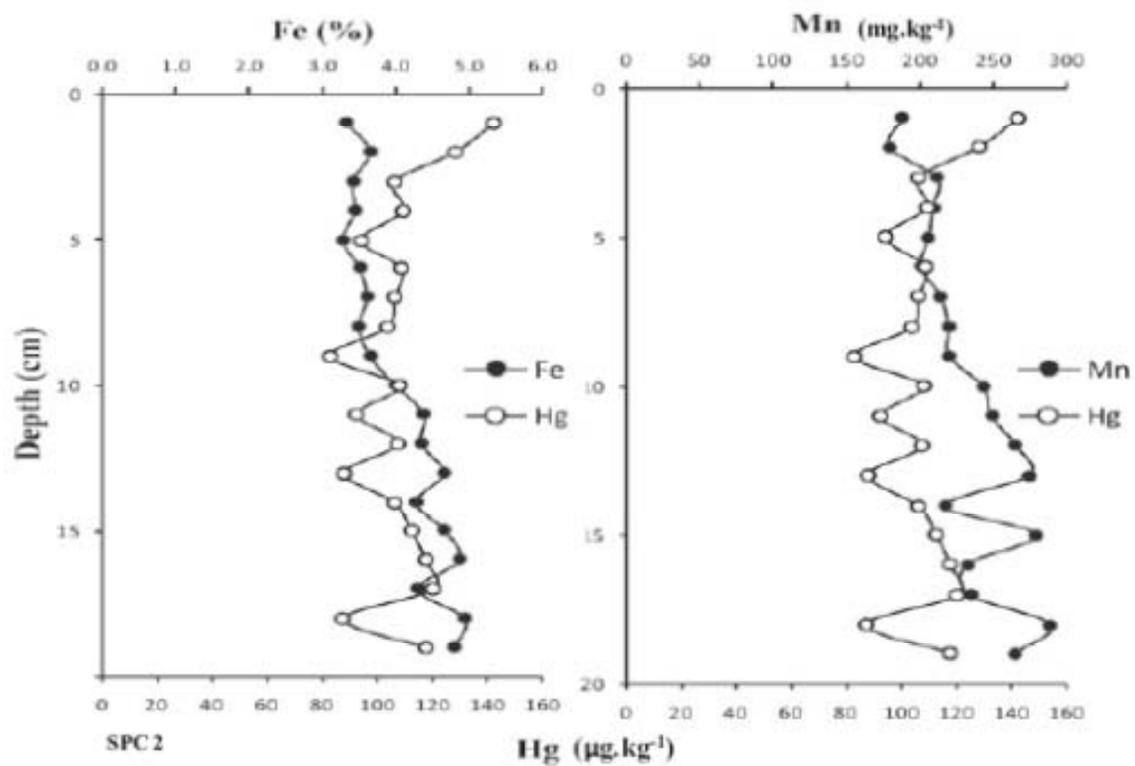


Fig. 6

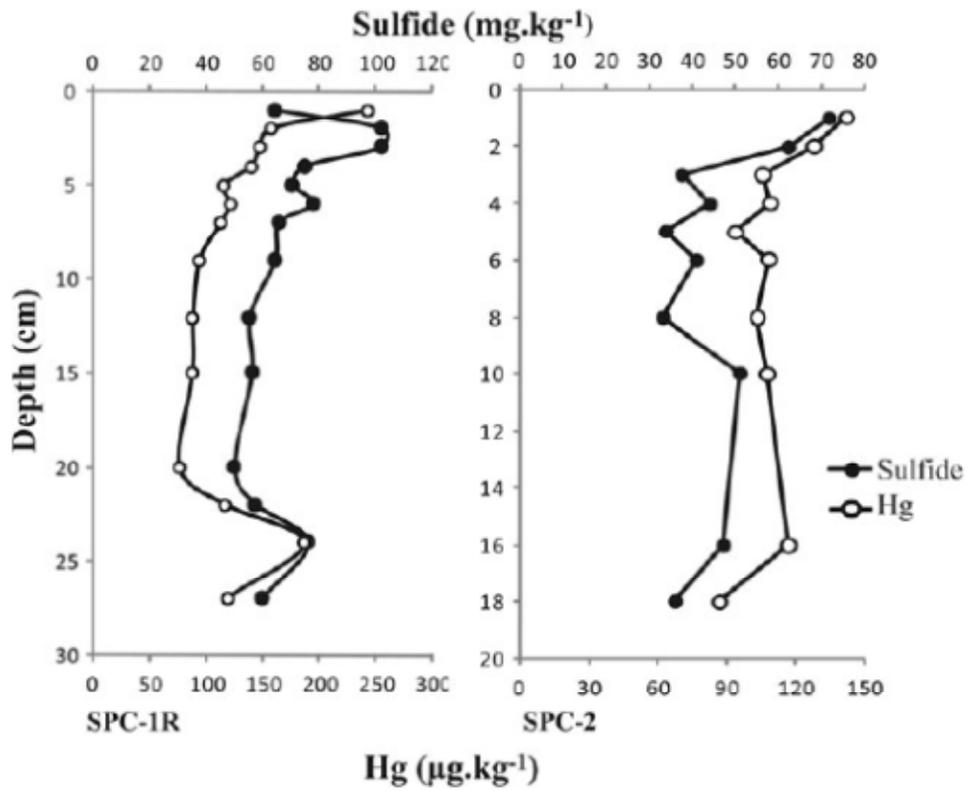


Fig. 7

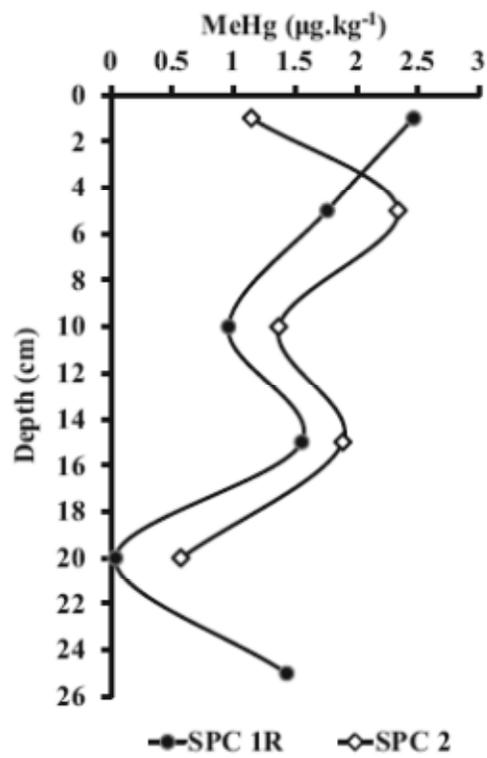


Fig. 8

