

Author version: *Mar. Pollut. Bull.*, vol.79(1-2); 2014; 342-347

Impact of Total Organic Carbon (in sediments) and Dissolved Organic Carbon (in overlying water column) on Hg sequestration by coastal sediments from the central east coast of India

Parthasarathi Chakraborty^{*1}, Brijmohan Sharma^{1,2}, P.V. Raghunath Babu¹, Koffi Marcellin Yao^{1,3}, Saranya Jaychandran^{1,4}

^{*1}National Institute of Oceanography (CSIR), India, 176 Lawsons Bay Colony, Visakhapatnam, 530017, Andhra Pradesh, India
Phone-91-891-2539180 (Ext 332); Fax: 91-891-2543595; e-mail: pchak@nio.org

²TERI University, 10, Institutional area, Vasant Kunj, New Delhi, India

³ Centre de Recherches Oceanologiques, BP V18 Abidjan, Cote d'Ivoire

⁴ Cochin University of Science and Technology, Cochin-682022, Kerala, India

Abstract:

Total organic carbon (TOC) (in sediment) and dissolved organic matter (DOM) (in water column) play important roles in controlling the mercury sequestration process by the sediments from the central east coast of India. This toxic metal prefers to associate with finer size particles (silt and clay) of sediments. Increasing concentrations of DOM in overlying water column may increase complexation/reduction processes of Hg²⁺ within the water column and decrease the process of Hg sequestration by sediments. However, high concentrations of DOM in water column may increase Hg sequestration process by sediments.

Keywords: Hg-Sediment interaction; Hg speciation; Hg-TOC complexes; Humic acid-Hg complexes

1.0 Introduction

Mercury (Hg) has received a worldwide attention due to its significant global adverse impact on both environment and human health (Boening, 2000; Ratcliffe et al., 1996; Wolfe et al., 2009). Due to its high toxicity, distributions of Hg compounds in coastal, estuarine and marine environments have been the subject of many researchers (Borja et al., 2000; Daskalakis and O'Connor, 1995; Gagnon et al., 1997; Hines et al., 2000; Horvat et al., 1999; Kannan and Falandysz, 1998; Kannan et al., 1998; Long et al., 1995; Valette-Silver, 1993). It is well known that sediment, an integral and inseparable part of aquatic system, plays an important role in controlling Hg pollution in aquatic systems (Bubb and Lester, 1996; Farmer, 1991; Liu et al., 2006; Tack and Verloo, 1995). Mercury accumulates in sediment globally from many physical, chemical, biological, geological and anthropogenic environmental processes. Thus, sediment can be a good indicator of water quality of a particular area (Bilotta and Brazier, 2008; Dai et al., 2007; Yu et al., 2008).

The toxicity and bioavailability of Hg is dependent on its chemical speciation rather than its total concentrations in sediments. In sediments, Hg can be associated with different binding phases. These forms, or species, are of key importance in understanding bioavailability, and the hazard and risk assessments of Hg in sediments (as well as in the overlying water column). However, determination of Hg associated with different binding phases is a very difficult task due to intrinsic complexity of binding sites in sediment (Chakraborty, 2012; Chakraborty et al., 2012a, 2012c, 2011).

In addition to that there are several factors (dissolved organic matter (DOM) in water column, adsorption capacity of sediments, different type of binding sites, pH of the water column, chloride ion concentrations, ionic strength, cation exchange capacity (CEC), oxidation-reduction potential (Eh)) may also influence the distribution and speciation of Hg in sediments (Chakraborty and Chakrabarti, 2008, 2006; Chakraborty, 2010; Chakraborty et al., 2012b, 2010; Gopalapillai et al., 2008). Sequential extraction procedures (SEP) are designed to determine metal contents associated to different solid phases present in sediments. These methods lead to obtain operationally defined fractions related to the mobility and potential toxicity of metals and rarely with specific individual species. Several operationally-defined sequential extraction procedures have been widely used to assess the bioavailable Hg fraction and their mobility in sediment. In this work a modified BCR (sequential extraction) method was used for the evaluation of the geochemistry of Hg and determines non-residual (bioavailable) Hg species and phases in the coastal sediment. The aims of this study was also to identify the factors which control Hg-sediment interaction and elucidate the impacts of DOM

(in this case humic acid in the overlying water column) on the sequestration processes of Hg by the coastal sediments from the central east coast of India.

2.0 Materials and methods

2.1 Study area and sampling

Sediment samples were collected from the four different environmentally significant sites of the central east coast of India as shown in the Fig 1. The coastal sediments were collected from 1) Bhimili 2) Visakhapatnam, 3) Gangavaram, and 4) Kakinada.

The Bhimili (BHI) is located in the north of Andhra Pradesh. This city is not industrially developed. The approximate population of this area is ~50,000. Vishakhapatnam (VSKP) is the second largest city in the state of Andhra Pradesh and the third largest city (after Kolkata and Chennai) in the east coast of India. VSKP has become a hub for many heavy industries. The VSKP port, the largest in the country, is the ideal gateway contributing to the development of petroleum, steel and fertilizer industries. The approximate population of VSKP city is 2,000,000.

Gangavaram (GVM) is located in VSKP. India's deepest port is situated in GVM. The Gangavaram Port Ltd. plans to build conveyors for taking imported raw materials directly to the Visakhapatnam Steel plant, in order to reduce the railway transportation costs. Kakinada is an industrially developing city, having an approximate population of 300,000. The general description, geographic location of the sampling sites, the distance from the shore, and the depth from where the sediment samples were collected are given as supporting document (Table 1SD).

A Van Veen stainless steel grab sampler with an area of 0.02 m² was used to collect the sediments; without emptying the grab, a sample was taken from the centre with a polyethylene spoon to avoid contamination by metallic parts of the dredge. The samples were stored at -20⁰C for 15 days, and then dried at 60⁰C in a forced air oven (Kadavil Electro Mechanical Industry Pvt. Ltd. India, Model No. KOMS.6FD). Sediments were subsequently stored at 4⁰C until needed.

2.2 Leaching procedure and Reagents

A series of batch extractions were performed on the coastal sediment, following BCR protocol (Quevauviller et al., 1993; Ure et al., 1993). This sequential extraction method allows us to determine the sum of ion-exchangeable, water soluble and carbonate/ bicarbonate form of Hg (Fr.1); Hg bound to Fe and Mn oxides i.e., reducible fraction of Hg (Fr 2); fraction of total Hg bound to organic matter (Fr.3) and residual Hg fraction (Fr. 4) in sediment.

1 gm of coastal sediment sample was processed by triplicate using the modified BCR protocol. Samples and reagents were placed in 50 mL falcon tubes and shaken with a mechanical end-over-end shaker (Tarson Rotospin) at a speed of 40 rpm to ensure continuous suspension of the mixture. After completion of the specific conditions of the stage, the mixture was centrifuged at 10,000 rpm for 30 min (Fischer Scientific, LabServ). The supernatant was transferred to a volumetric flask, acidified (HNO_3 , $\text{pH} < 2$) if necessary, and diluted to volume before analysis. The residue was washed by adding 5 mL of sub-boiling ultra pure water ($18.2 \text{ m}\Omega$), shaking for 10 min with the end-over-end shaker, and centrifuged for 20 min at 10,000 rpm. The supernatant was decanted and discarded. The residue was then treated with the next reagent. An acetic acid solution (0.11 mol L^{-1} of CH_3COOH) was used to extract exchangeable, water-soluble forms, and carbonates forms of Hg. The next extraction step was performed with hydroxylamine hydrochloride (0.5 mol L^{-1} of $\text{NH}_2\text{OH}\cdot\text{HCl}$ $\text{pH} = 1.5$, HNO_3) to dissolve the Hg bound to reducible oxides. The oxidizable organic/sulfide fraction was extracted with hydrogen peroxide (8.8 mol L^{-1} H_2O_2 ($\text{pH} = 1.5$ HNO_3) and 1 mol L^{-1} $\text{CH}_3\text{COONH}_4$ (at $\text{pH} = 2$, HNO_3) and ammonium acetate. Total Hg concentrations in the residual fraction of the studied sediments were determined directly by direct mercury analyzer. All extractions were performed in triplicate. Two reagent blanks were analyzed for every extraction. In all cases blank results were below the detection limit of the analytical technique (1.0 ng g^{-1}). Validation of the sequential extraction method was done by comparing the total Hg concentration in the sediment with the sum of the concentrations of Hg fractions obtained by following the sequential extraction protocols in the same sediment. The comparable (close to 100% recovery) values of total Hg concentration support the reliability and validity of the sequential extraction method.

2.3 Determination of Hg and TOC

Total Hg 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 Hg complexes in sediment and introduced into a quartz tube. A continuous flow of oxygen carries the decomposition products through a catalyst bed where interferences are trapped. All Hg species are reduced to elemental Hg and are then carried along to a gold amalgamator where the Hg is selectively trapped. The system is purged and the amalgamator is subsequently heated which releases all Hg vapors to the single beam, fixed wavelength atomic absorption spectrophotometer. Here, absorbance measured at 253.7 nm is proportional to Hg content in the sample. Operational conditions were established according to EPA method 7473 (EPA, 2007). The sensitivity and the accuracy of the DMA was monitored in each experiment by analyzing

certified reference material (Reference marine sediments (MESS-2, PACS-1) from Natural Resources of Canada) followed by a reagent blank between every 10 samples. Total Organic Carbon (TOC) in the studied sediments was determined by following the Walkley-Black method (Schumacher, 2002). This method has been widely used for the determination of total organic carbon in the soil and sediments.

3.0 Results and discussion

The general description and texture analysis of the studied sediments are presented in Table 1. The total Hg content in the coastal sediments was found to vary from 16.6 to 88.4 $\mu\text{g.kg}^{-1}$. The maximum concentration of Hg was found in the sediment collected at Kakinada (88.4 $\mu\text{g.kg}^{-1}$) followed by Gangavaram (59.4 $\mu\text{g.kg}^{-1}$), Visakhapatnam (28.9 $\mu\text{g.kg}^{-1}$) and Bhimli (16.6 $\mu\text{g.kg}^{-1}$). It is interesting to note that the total Hg content in the coastal sediments were found to increase from north to south of the central east coast of India. The concentrations of the finer size (sum of silt and clay contents) particles of the sediment influenced the accumulations of Hg in the studied sediments. A positive correlation ($R^2=0.96$) was found between the total Hg content and the finer particles fractions in the coastal sediments. Yoshida et al (2006) have also reported that finer particles in sediments strongly influence the distribution of Hg between sediment and the overlying water column.

TOC content in the studied sediment was found to increase with the increasing concentrations of finer particles and decrease with the increasing coarser fraction (sand) in the sediments. A strong correlation ($R^2=0.83$) was found between the total organic carbon (TOC) concentrations with the fraction of finer particles in the coastal sediments. Percival et al (2000) has reported that finer particles of sediment control organic carbon level in sediments. A strong correlation ($R^2=0.92$) between the total concentrations of Hg with the TOC content in the sediments (as shown in Table 2) indicates that TOC in the coastal sediments probably plays an important role in controlling Hg sequestration process by the sediment from the central east coast of India.

It has been reported that TOCs in sediment interact with Hg and change the speciation, transformation, and fate of Hg in sediment (Lambertsson and Nilsson, 2006; Ravichandran, 2004; Stein et al., 1996; Wallschläger et al., 1998). TOC (in sediment) has been reported to enhance Hg sorption on sediments by providing additional sorption sites (Bengtsson and Picado, 2008; Melamed et al., 1997). However, TOC may also cause reduction of Hg^{2+} to Hg^0 by intramolecular electron transfer (Barkay et al., 1997; Ravichandran, 2004). The strong correlation between total Hg and TOC in the studied sediment indicates that Hg had strong affinity for TOC associated with the finer

particles of the coastal sediments (under the environmental conditions, pH, Salinity etc.). Further investigation was carried out to understand the association of Hg with the different binding phases in the coastal sediments.

3.1 Fractionation of Hg in the coastal sediments by using BCR-sequential extraction protocol:

A modified sequential extraction protocol proposed by Community Bureau of Reference (BCR)(Quevauviller et al., 1993; Ure et al., 1993) was used to understand the chemical distributions and fractionations of Hg in the studied sediments.

Figure 2 shows the distributions of Hg associated with different binding phases in the coastal sediments. The concentrations of Fr. 1 of Hg (which include water soluble Hg complexes + Hg in exchangeable form + carbonate/bicarbonate complexes of Hg) were found to vary from ~ 2 to 23% of the total Hg content of the sediments.

The concentrations of Hg associated with Fe and Mn-oxides (Fr. 2) were found to vary along with the coastal sediments. The highest concentrations of Hg was associated with Fe and Mn-oxide phases in the sediments collected at Bhimli (up to 23% of the total Hg) followed by Visakhapatnam (13.0%), Gangavaram (11.9%) and Kakinada (6%).

A major fraction of Hg was associated with organics (Fr 3) in the studied sediments. Figure 2 shows that the concentrations of Hg associated with organic fraction gradually increased with the increasing TOC content in the studied sediments. The highest percentage of Hg was found to associate with organic carbon in sediments at Gangavaram (52.3% of the total Hg concentration) followed by Bhimli (44.1%) Visakhapatnam (29.4%), and Kakinada (21.7%). A positive correlation coefficient (R^2) value of 0.98 was found between the concentration of Hg associated with organics and the TOC content of the sediments. This observation suggests that TOC content in the sediments play a key role in controlling the distribution and speciation of Hg in the studied sediments. The residual Hg concentration (probably Hg complexes with sulfur containing group in the sediments) was found to vary from ~ 20 to 70% of the total concentrations of Hg in the studied sediments. The data are presented as supporting document (Table 2SD)

The distribution of Hg (obtained by BCR sequential extraction method) in the studied sediments indicate that TOC of the studied sediments played a key role in the sequestration of Hg from the water column. Further investigations were carried out to provide a better understanding of Hg-sediment interaction in the coastal sediments.

3.2 Sequestering process of Hg by the coastal sediments

Several equilibrium adsorption isotherms were used to understand the Hg sorption capacity of the studied sediments. It is important to note that these isotherms do not reflect microscopic mechanisms of Hg uptake at the sediment–water interface.

Kinetic uptake study of Hg (from water column) by the coastal sediments was performed to determine the time required for Hg (in water column) and the coastal sediments to reach equilibrium. Figure 3a shows that the dissolved concentrations of Hg (from the overlying water column) gradually decreased in the presence of the coastal sediments. This finding indicates that Hg interacted quite fast with the coastal sediments and the Hg-sediments system reached equilibrium within 2 hrs. An equilibrium time of 2 hrs was used through out this study to understand Hg adsorption isotherm by the coastal sediments.

The adsorption isotherms of Hg were constructed to compare Hg adsorption capacity among the four coastal sediments samples collected from the four environmentally significant sites. The adsorption of Hg by the sediment was found to decrease in the following order: Visakhapatnam > Kakinada > Bhimili > Gangavaram. Hg was found to adsorb completely by the studied sediments at low Hg loading. The adsorbed concentrations of Hg (by the sediments) were found to increase with the increasing Hg concentrations in the overlying water column. However, the adsorbed concentration of Hg in the sediments reached a plateau with the higher concentrations of Hg in the solution. This is because of the saturation of the adsorbing sites for Hg on the sediment. The isotherms of Hg adsorption on the sediments are presented in Fig. 3b. These isotherms are described by the simple Langmuir and Freundlich isotherms.

The Freundlich parameters, K_D and b_F , were used to measure the adsorption affinity and the intensity of adsorption of the sediments (Table 3SD). The value of b_F , between 0 and 1; confirm the heterogeneity of the adsorbent. The value of b_F for sediments collected at Bhimili was found to be 0.85, Visakhapatnam (0.95), Gangavaram (0.7) and Kakinada (0.85). The K_D values of Bhimili (0.11), Visakhapatnam (0.18), Gangavaram (0.33), and Kakinada (0.59), suggests that the order of adsorptive capacity of sediments collected from the different stations for Hg were Kakinada>Gangavaram>Visakhapatnam>Bhimili. It is important to note that the TOC content in the studied sediments collected from different stations were Kakinada>Gangavaram>Visakhapatnam>Bhimili. This finding again indicates that the adsorption affinity of Hg in sediments was influenced by TOC content of the sediments.

The monolayer maximum adsorption (Q_{\max}) values (from the Langmuir isotherm) were 0.22 mg g⁻¹ for Bhimili, 0.40 mg g⁻¹ for Visakhapatnam, 0.11 mg g⁻¹ for Gangavaram, and 0.26 mg g⁻¹ for Kakinada.

The “b” is a constant related to the binding energy and partly reflect adsorption energy level. Positive value of b indicates that adsorption reaction could spontaneously proceed at ordinary temperature. The larger the value of b is, the stronger the degree of spontaneous reaction. The “b” value was 0.05 for Bhimili, 0.04 for Visakhapatnam, 0.5 for Gangavaram, and 0.29 for Kakinada. This study indicates that TOC of sediment played a crucial role in controlling Hg distribution, speciation in the coastal sediment. However, the impact of DOM (humic acids) in water column in controlling sequestration of Hg by the studied sediments was further studied.

3.3 Effects of DOM in overlying water column on the adsorption of mercury by the coastal sediments:

DOM (in overlying water column) and TOC (within the sediments) can alter the speciation of Hg in a natural system. Further experiments were carried out to understand the impact of DOM in Hg partitioning among the gaseous (Hg⁰), aqueous (Hg complexes) and solid (Hg-sediment) phases in natural systems.

Figure 4 shows the adsorption isotherms of the coastal sediments for Hg in the presence of varying concentrations of humic acid (HA) (as a representative of DOM) in the overlying water columns. The data are presented as supporting documents (Table 4SD). The association of Hg was found to be highest in absence of HA (0.0 ppm), followed by 0.1 mg. dm⁻³, 1.0 mg. dm⁻³ and 10.0 mg. dm⁻³.

The maximum monolayer adsorption (Q_{\max}) of the coastal sediment collected from Bhimili was found to decrease from 0.22 mg g⁻¹ (0.0 mg. dm⁻³ of HA) to 0.11 mg g⁻¹ (0.1 mg. dm⁻³ of HA) 0.02 mg g⁻¹ (1.0 mg. dm⁻³ of HA) to 0.02 mg g⁻¹ (10.0 mg. dm⁻³ of HA).

The Q_{\max} of the coastal sediment collected from Visakhapatnam decreased from 0.4 mg g⁻¹ (0.0 mg. dm⁻³ of HA) to 0.35 mg g⁻¹ (0.1 mg. dm⁻³ of HA) to 0.25 mg g⁻¹ (1.0 mg. dm⁻³ of HA) to 0.12 mg g⁻¹ (10 mg. dm⁻³ of HA). The Q_{\max} of the sediment collected from Gangavaram was found to decrease from 0.11 mg g⁻¹ (0.0 mg. dm⁻³ of HA) to 0.08 mg g⁻¹ (0.1 mg. dm⁻³ of HA) to 0.06 mg g⁻¹ (1 mg. dm⁻³ of HA) to 0.05 mg g⁻¹ (10 mg. dm⁻³ of HA). The Q_{\max} of the sediment collected from Kakinada decrease from 0.26 mg g⁻¹ (0.0 mg. dm⁻³ of HA) to 0.19 mg g⁻¹ (0.1 mg. dm⁻³ of HA) to 0.09 mg g⁻¹ (1.0 mg. dm⁻³ of HA) to 0.08 mg g⁻¹ (10.0 mg. dm⁻³ of HA). The maximum adsorption capacity (Q_{\max}) of all the coastal sediments suggests that accumulation of Hg in the sediments gradually decreased with the increasing DOM concentrations in the water column.

Comparison of Q_{\max} values revealed that the reactivity of Hg with the sediments decreased with the increasing HA concentrations in the overlying water column for all the coastal sediments (Figure 5 a). The maximum amount of Hg was absorbed by the coastal sediments collected from Visakhapatnam followed by Kakinada, Bhimli and Gangavaram. The decrease in Q_{\max} was prominent when the concentrations of HA (in water column) varied from 0.0 to 1.0 $\text{mg}\cdot\text{dm}^{-3}$. The change in Q_{\max} was found to be insignificant with increasing concentration of HA from 1.0 to 10.0 $\text{mg}\cdot\text{dm}^{-3}$. This observation probably suggest that the complexation (binding sites) of dissolved HA in (1.0 $\text{mg}\cdot\text{dm}^{-3}$) the water column was sufficient enough to bind all the available Hg^{2+} ion in solution and thus, the change in Q_{\max} was found to be insignificant.

A steady decrease in adsorption affinity (K_D) of the coastal sediments for Hg was observed with the increasing HA concentrations in the overlying water column (Figure 5b). The decrease in K_D values was significant for all the studied sediments with changing HA concentration from 0 to 0.1 to 1.0 $\text{mg}\cdot\text{dm}^{-3}$. Interestingly, further increase in HA concentrations (to 10.0 $\text{mg}\cdot\text{dm}^{-3}$) increased the adsorption affinity of the studied sediments for Hg. This is probably because of the adsorption of HA on the surface of the sediments and by increasing the available binding sites for Hg on the costal sediments.

The intensity of adsorption (b_F) was also found to decrease with the increasing HA concentrations in the water column. The b_F of the coastal sediment collected from Bhimli was found to decrease from 0.85 (0.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.80 (0.1 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.76 (1.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.66 (10.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA). The b_F of the sediment collected from Visakhapatnam decrease from 0.95 (0.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.90 (0.1 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.80 (1.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.70 (10.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA).

The b_F of the sediment collected from Gangavaram was found to decrease from 0.7 (0.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.8 (0.1 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.6 (1.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA) to 0.5 (10.0 $\text{mg}\cdot\text{dm}^{-3}$ of HA).

Thus, this study suggests that DOM in overlying water column decrease Hg sequestration process by sediment. However, high concentrations of DOM in overlying water column may also increase adsorption of DOM on sediments and this may lead to increase Hg sequestration process. It is important to note that adsorption of DOM from water column to sediment is dependent on the texture of the sediments. However, further detail investigation is required to understand the interaction between Hg^{2+} , DOM (in water column) and TOC of sediments.

Acknowledgment:

Authors are thankful to the Director, NIO, Goa for his encouragement and support. This work is a part of the Council of Scientific and Industrial Research (CSIR) supported OLP 1201. S. Jayachandran and Brijmohan Sharma acknowledge the Summer Research Fellowship provided by the Indian Academy of Science. Kofi Marcellin Yao acknowledges Department of Science and Technology, India for providing CV Raman Postdoctoral Fellowship. This article bears NIO contribution number XXXX

References

Barkay, T., Gillman, M., Turner, R.R., 1997. Effects of dissolved organic carbon and salinity on bioavailability of mercury. *Applied and Environmental Microbiology*, 63, 4267–4271.

Bengtsson, G., Picado, F., 2008. Mercury sorption to sediments: Dependence on grain size, dissolved organic carbon, and suspended bacteria. *Chemosphere* 73, 526–531.

Bilotta, G.S., Brazier, R.E., 2008. Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research*, 42, 2849–2861.

Boening, D.W., 2000. Ecological effects, transport, and fate of mercury: a general review. *Chemosphere* 40, 1335–1351.

Borja, A., Franco, J., Pérez, V., 2000. A marine biotic index to establish the ecological quality of soft-bottom benthos within European estuarine and coastal environments. *Marine Pollution Bulletin*, 40, 1100–1114.

Bubb, I.M., Lester, J.N., 1996. Factors controlling the accumulation of metals within fluvial systems. *Environmental monitoring Assessment*, 41, 87–105.

Chakraborty, P., 2010. Study of cadmium–humic interactions and determination of stability constants of cadmium–humate complexes from their diffusion coefficients obtained by scanned stripping voltammetry and dynamic light scattering techniques. *Analytica Chimica Acta*, 659, 137–143.

Chakraborty, P., 2012. Speciation of Co, Ni and Cu in the coastal and estuarine sediments: Some fundamental characteristics. *Journal of Geochemical Exploration*.

Chakraborty, P., Babu, P.V., Sarma, V.V., 2011. A study of lead and cadmium speciation in some estuarine and coastal sediments. *Chemical Geology*.

Chakraborty, P., Babu, P.V.R., Sarma, V.V., 2012a. A new spectrofluorometric method for the determination of total arsenic in sediments and its application to kinetic speciation. *International Journal of Environmental Analytical Chemistry*, 92, 133–147.

Chakraborty, P., Boissel, M., Reuillon, A., Babu, P.V.R., Parthiban, G., 2012b. Ultrafiltration technique in conjunction with competing ligand exchange method for Ni-humics speciation in aquatic environment. *Microchemical Journal*.

- Chakraborty, P., Chakrabarti, C.L., 2006. Chemical speciation of Co, Ni, Cu, and Zn in mine effluents and effects of dilution of the effluent on release of the above metals from their metal-dissolved organic carbon (DOC) complexes. *Analytica Chimica Acta*, 571, 260–269.
- 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, 63–71.
- Chakraborty, P., Jayachandran, S., Babu, P.V., Karri, S., Tyadi, P., Yao, K.M., Sharma, B.M., 2012c. Intra-annual variations of arsenic totals and species in tropical estuary surface sediments. *Chemical Geology*.
- Chakraborty, P., Raghunadh Babu, P.V., Acharyya, T., Bandyopadhyay, D., 2010. Stress and toxicity of biologically important transition metals (Co, Ni, Cu and Zn) on phytoplankton in a tropical freshwater system: An investigation with pigment analysis by HPLC. *Chemosphere* 80, 548–553.
- Dai, J., Song, J., Li, X., Yuan, H., Li, N., Zheng, G., 2007. Environmental changes reflected by sedimentary geochemistry in recent hundred years of Jiaozhou Bay, North China. *Environmental Pollution* 145, 656–667.
- Daskalakis, K.D., O'Connor, T.P., 1995. Distribution of chemical concentrations in US coastal and estuarine sediment. *Marine Environmental Research* 40, 381–398.
- Farmer, J.G., 1991. The perturbation of historical pollution records in aquatic sediments. *Environmental Geochemistry and Health* 13, 76–83.
- Gagnon, C., Pelletier, É., Mucci, A., 1997. Behaviour of anthropogenic mercury in coastal marine sediments. *Marine Chemistry* 59, 159–176.
- Gopalapillai, Y., Fasfous, I.I., Murimboh, J.D., Yapici, T., Chakraborty, P., Chakrabarti, C.L., 2008. Determination of free nickel ion concentrations using the ion exchange technique: application to aqueous mining and municipal effluents. *Aquatic Geochemistry* 14, 99–116.
- Hines, M.E., Horvat, M., Faganeli, J., Bonzongo, J.C.J., Barkay, T., Major, E.B., Scott, K.J., Bailey, E.A., Warwick, J.J., Lyons, W.B., 2000. Mercury biogeochemistry in the Idrija River, Slovenia, from above the mine into the Gulf of Trieste. *Environmental Research* 83, 129–139.
- Horvat, M., Covelli, S., Faganeli, J., Logar, M., Mandić, V., Rajar, R., Sirca, A., Zagar, D., 1999. Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. *Science of the Total Environment*, 237, 43–56.
- Kannan, K., Falandysz, J., 1998. Speciation and concentrations of mercury in certain coastal marine sediments. *Water Air, and Soil Pollution*, 103, 129–136.
- Kannan, K., Smith, J., Lee, R.F., Windom, H.L., Heitmuller, P.T., Macauley, J.M., Summers, J.K., 1998. Distribution of total mercury and methyl mercury in water, sediment, and fish from south Florida estuaries. *Archive of Environmental Contamination Toxicology*, 34, 109–118.
- Lambertsson, L., Nilsson, M., 2006. Organic material: the primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments. *Environmental Science and Technology* 40, 1822–1829.
- Liu, L., Li, F., Xiong, D., Song, C., 2006. Heavy metal contamination and their distribution in different size fractions of the surficial sediment of Haihe River, China. *Environmental Geology* 50, 431–438.

- 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. *Journal of Environmental Management* 19, 81–97.
- Melamed, R., Villas Bôas, R.C., Goncalves, G.O., Paiva, E.C., 1997. Mechanisms of physico-chemical interaction of mercury with river sediments from a gold mining region in Brazil: Relative mobility of mercury species. *Journal of Geochemical Exploration* 58, 119–124.
- Percival, H.J., Parfitt, R.L., Scott, N.A., 2000. Factors Controlling Soil Carbon Levels in New Zealand Grasslands Is Clay Content Important? *Soil Science Society of America Journal* 64, 1623–1630.
- Quevauviller, P., Ure, A., Muntau, H., Griepink, B., 1993. Improvement of analytical measurements within the BCR-programme: single and sequential extraction procedures applied to soil and sediment analysis. *International Journal of environmental analytical chemistry* 51, 129–134.
- Ratcliffe, H.E., Swanson, G.M., Fischer, L.J., 1996. Human exposure to mercury: a critical assessment of the evidence of adverse health effects. *Journal of Toxicology and Environmental Health* 49, 221.
- Ravichandran, M., 2004. Interactions between mercury and dissolved organic matter—a review. *Chemosphere* 55, 319–331.
- Schumacher, B.A., 2002. Methods for the determination of total organic carbon (TOC) in soils and sediments. National ESD, ed.: EPA.
- Stein, E.D., Cohen, Y., Winer, A.M., 1996. Environmental distribution and transformation of mercury compounds. *Critical Reviews in Environmental Science and Technology*, 26, 1–43.
- Tack, F.M.G., Verloo, M.G., 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *Int J Environ Anal Chem* 59, 225–238.
- 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, 135–151.
- Valette-Silver, N.J., 1993. The use of sediment cores to reconstruct historical trends in contamination of estuarine and coastal sediments. *Estuaries and Coasts* 16, 577–588.
- Wallschläger, D., Desai, M.V.M., Spengler, M., Windmüller, C.C., Wilken, R.D., 1998. How humic substances dominate mercury geochemistry in contaminated floodplain soils and sediments. *Journal of Environmental quality* 27, 1044–1054.
- Wolfe, M.F., Schwarzbach, S., Sulaiman, R.A., 2009. Effects of mercury on wildlife: a comprehensive review. *Environmental Toxicology and Chemistry* 17, 146–160.
- Yoshida, M., Abderhaman, L., Slimani, B., 2006. Sediment and water contamination with mercury caused by industrial waste and wastewater in Oued El Harrach, Algeria, in: *The Proceedings of the 17th Annual Conference of the Japan Society of Waste Management Experts, International Session in Kitakyushi*.
- Yu, R., Yuan, X., Zhao, Y., HU, G., TU, X., 2008. Heavy metal pollution in intertidal sediments from Quanzhou Bay, China. *Journal of Environmental Science* 20, 664–669.

Table1: Percentages of silt, clay, sand, TOC, total Hg, in the coastal sediments.

Station	Sand (%)	Silt (%)	Clay (%)	TOC(%)	[Hg]_T($\mu\text{g}/\text{kg}$)
Bhimili	67.2	15.8	20.4	0.06	16.6
Visakhapatnam	58.2	39.3	2.5	0.12	28.9
Gangavaram	14.2	50.4	35.4	0.42	59.4
Kakinada	6.6	88	5.4	0.24	88.4

Table 2: Pearson correlations matrix between percentages of silt, clay, sand, TOC, and total Hg in the sediments.

	<i>Sand (%)</i>	<i>Silt (%)</i>	<i>Clay (%)</i>	<i>Fine</i>	<i>TOC(%)</i>	<i>[Hg]_T($\mu\text{g}/\text{kg}$)</i>
Sand (%)	1.00					
Silt (%)	-0.88	1.00				
Clay (%)	-0.20	-0.29	1.00			
Fine	-1.00	0.87	0.22	1.00		
TOC(%)	-0.83	0.51	0.60	0.83	1.00	
[Hg]_T($\mu\text{g}/\text{kg}$)	-0.96	0.97	-0.06	0.96	0.65	1.00

CAPTIONS AND LEGENDS FOR FIGURES

Figure 1. Location of sampling sites.

Figure 2. Distribution of Hg in different binding phases of the coastal sediments (by following BCR protocol)

Figure 3. (a) Adsorption of mercury (from solution) by sediment as a function of time (b) Isotherms of Hg adsorption in the four coastal sediments collected from the central east coast of India. (Δ) Kakinada; (\blacktriangledown) Gangavaram; (o) Visakhapatnam, (\bullet) Bhimili

Figure 4. Adsorption isotherms of Hg in the coastal sediments as a function of different concentrations of humic acid in the water column.

Figure 5. Variation of (a) maximum monolayer adsorption (Q_{\max}) and (b) adsorption affinity of the coastal sediments as a function of different concentrations of humic acid in the overlying water column.

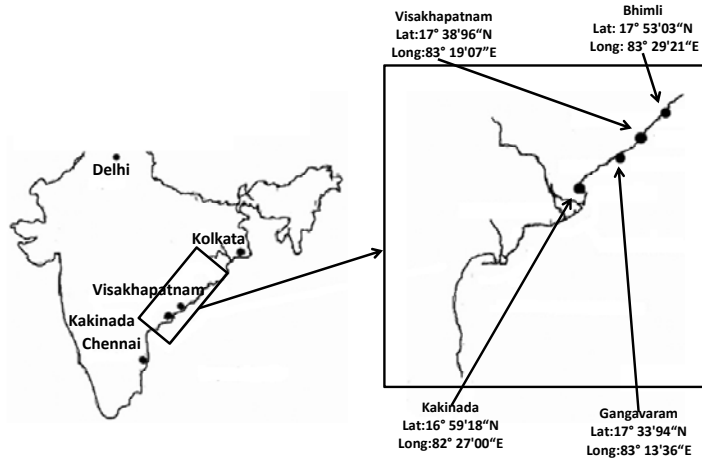


Figure 1

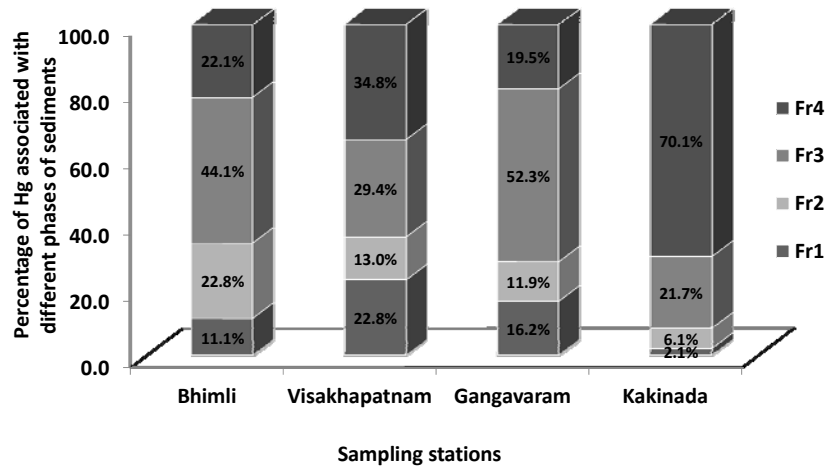


Figure 2

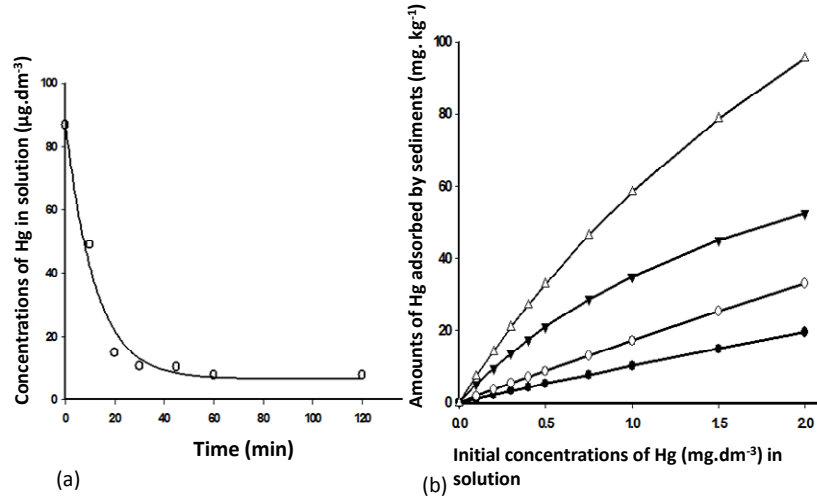


Figure 3

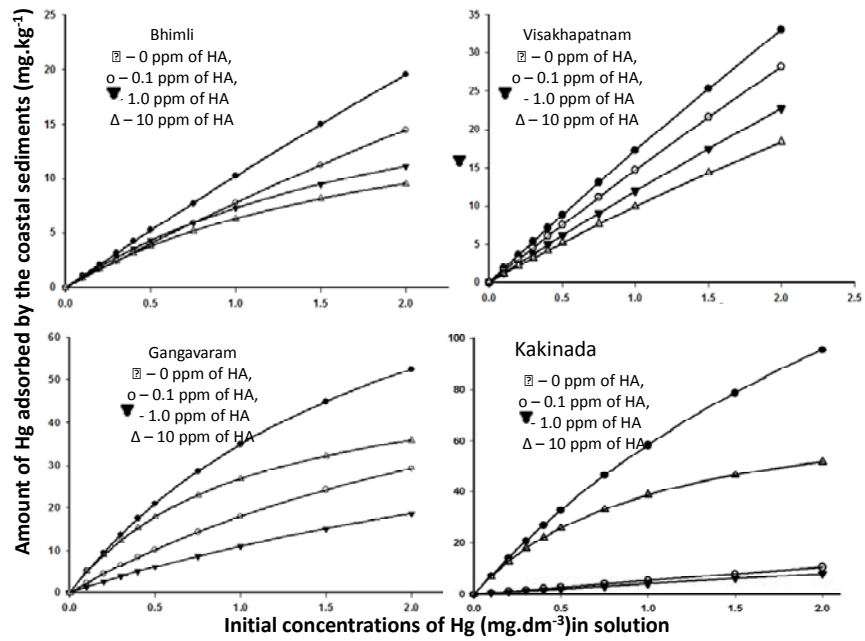


Figure 4

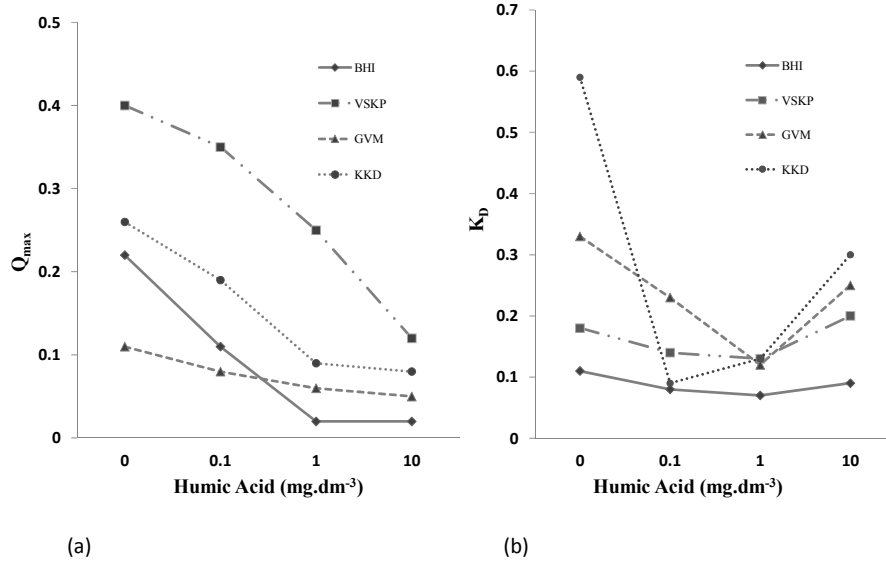


Figure 5

SUPPORTING DOCUMENTS**Table -1SD** Geographical Location of Sampling Sites

Station	Latitude (°North)	Longitude (°East)	Sampling Date	Distance	
				from Shore (Km)	Depth (m)
Bhimili	17° 53'03"	83° 29'21"	25/12/2009	5	19
Visakhapatnam	17° 38'96"	83° 19'07"	25/12/2009	5	35
Gangavaram	17° 33'94"	83° 13'36"	26/12/2009	5	14
Kakinada	16° 59'18"	82° 27'00"	27/12/2009	5	31

Table -2SD Mercury fractionation and speciation in the coastal sediments (by BCR sequential extraction protocol)

Sampling stations	Fr. 1	Fr. 2	Fr. 3	Fr. 4
Bhimli	11.1	22.8	44.1	22.1
Visakhapatnam	22.8	13.0	29.4	34.8
Gangavaram	16.2	11.9	52.3	19.5
Kakinada	2.1	6.1	21.7	70.1

Table 3SD: Isotherm characteristics of Hg adsorption on the coastal sediments collected from central east coast of India.

Metal	Sampling Station	Humic Acid Concentration	Freundlich		Langmuir	
			K_D $L^{b_F} \text{mmol}^{1-b_F} \text{g}^{-1}$	b_F	Q_{\max} mg g^{-1}	b $L \text{mg}^{-1}$
Hg	BHI	0	0.11	0.85	0.22	0.05
	VSKP	0	0.18	0.95	0.4	0.04
	GVM	0	0.33	0.7	0.11	0.5
	KKD	0	0.59	0.85	0.26	0.29

BHI – Bhimili, VSKP – Visakhapatnam, GVM – Gangavaram, KKD – Kakinada

Table 4SD Isotherm characteristics of Hg adsorption in presence of different concentrations of Humic Acid on the coastal sediments collected from central east coast of India.

Metal	Sampling Station	Humic Acid Concentration (mg.L ⁻¹)	Freundlich		Langmuir		
			L ^{b_F}	KD mmol ^{1-b_F} g ⁻¹	b _F	Q _{max} mg g ⁻¹	b L mg ⁻¹
Hg	BHI	0		0.11	0.85	0.22	0.05
		0.1		0.08	0.80	0.11	0.8
		1		0.07	0.76	0.02	0.45
		10		0.09	0.66	0.02	0.5
	VSKP	0		0.18	0.95	0.4	0.04
		0.1		0.14	0.90	0.35	0.04
		1		0.13	0.80	0.25	0.05
		10		0.2	0.70	0.12	0.09
	GVM	0		0.33	0.70	0.11	0.5
		0.1		0.23	0.80	0.08	0.3
		1		0.12	0.60	0.06	0.22
		10		0.25	0.50	0.05	0.99
	KKD	0		0.59	0.85	0.26	0.29
		0.1		0.09	0.99	0.19	0.03
		1		0.13	0.96	0.09	0.05
		10		0.3	0.30	0.08	0.99

BHI- Bhimili, VCI- Visakhapatnam, GVM- Gangavaram, KKD- Kakinada