

# Understanding of Chemical Speciation of Lead, Zinc and Copper in Vertical Profile of the Sediments of the Brahmaputra River, Assam, India

**Pallavi Das, Kali Prasad Sarma and Manish Kumar\***

Department of Environmental Science, Tezpur University, Napaam – 784028, Assam

✉ manish.env@gmail.com

*Received December 5, 2014; revised and accepted December 19, 2014*

**Abstract:** Lead (Pb), zinc (Zn) and copper (Cu) are ubiquitous in the environment as a result of anthropogenic and geogenic processes. The fate of these metals in the environment is largely governed by their speciation, which is influenced by sediment properties. Therefore present study focusses on the distribution of Pb, Zn and Cu in different chemical forms in core sediments. Four sediment cores were collected from upstream to downstream of the Brahmaputra river. Metal speciation study revealed that most of the heavy metals were associated with the residual fraction. Among non-residual fraction Zn and Pb were mainly associated with reducible fraction while Cu was associated with oxidisable fraction. The bioavailable fractions for Pb are found to be comparatively higher. Correlation analysis was carried out among different geochemical fractions of heavy metals and sediment properties. It was found that most of the non-residual fraction of heavy metals is significantly correlated with grain size, pH and organic matter. Significant correlation was found between metals (Pb, Cu and Zn) in oxidisable fraction and organic matter. The risk assessment code suggests low to medium risk for all heavy metals.

**Key words:** Heavy metal, speciation, core sediment, Brahmaputra river.

## Introduction

Heavy metal pollution is a serious concern due to its prevalence, toxicity and persistence in the environment (Bacon et al., 2006; Kumar et al., 2006). Its concentration in aquatic system is usually monitored by measuring its concentration in water, sediments and biota. In river system, precipitation, adsorption and chelation are the major processes by which sediments provide a major sink for various contaminants in the aquatic environment. Sediments are considered as ultimate sink for heavy metals and play an important role in assessing heavy metal pollution (Forstner et al., 1981). These sediment-bound metals can also be remobilized to water either by physical disturbances like floods or changes in geochemical parameters such

as pH and redox potential or by biological and chemical agents.

It is widely recognized that sequential extraction is a useful tool for determination of different chemical or binding form of heavy metals with sediment (Tessier et al., 1979; Iwegbue, 2011). Binding fraction of heavy metals has been identified as exchangeable carbonates, oxidizing organic matter and residual fractions (Tessier et al., 1979; Stephen et al., 2001; Egila et al., 2002). These metal fractions determine different mobility, bioavailability and chemical behaviours (Chakrapani et al., 2008; Li et al., 2001).

The Brahmaputra river, which is of interest in the present study, is one of the largest sand-bar braided rivers in the world due to high seasonal discharge and sediment. The river has been serving for years

\*Corresponding Author

as one of the most important freshwater resources for agriculture, irrigation, transportation, electricity and habitat for aquatic organism. The potential cause of degradation of sediment and water quality is due to increase in population, extensive agricultural practices, industrialization and urbanization along the river bank.

Considering the presence of numerous point and non-point sources of pollution as well as thick human settlements in the vicinity of the Brahmaputra river, it is imperative to understand heavy metal enrichment and its chemical behaviour. An effort has been made to understand the mobility and speciation of heavy metals in core sediments of the Brahmaputra river which will help to take necessary steps to control anthropogenic impact and maintain freshwater system. Overall objectives of the present study were (1) to determine the geo-chemical form of three heavy metals (Cu, Zn and Pb) in sediment profile and (2) to evaluate effect of sediment properties on concentration of heavy metals in the Brahmaputra river.

## Material and Methods

### Study Area

The Brahmaputra river is the fifth largest river in the world (Berner and Berner, 1996) with respect to discharge and second in terms of sediment transport per unit area (Milliman and Meade, 1983). The river has high seasonal variation, high sediment load, and is characterized by frequent changes in channel position (Thorne et al., 1993). The Brahmaputra river originates on the Angsi Glacier, located on the northern side of the Himalayas in Burang county of Tibet, at an elevation of 5300 m above mean sea level (Sarin et al., 1989).

The Brahmaputra river has a drainage area of 580,000 km<sup>2</sup> (50.5% in China, 33.6% in India, 8.1% in Bangladesh and 7.8% in Bhutan) and an annual mean discharge of 510 km<sup>3</sup> (Subramanian, 2004). The width of the river varies from 3 km to 18 km with an average of 10 km in the plains of Assam and Bangladesh. The Brahmaputra river is subjected to the Southeast Asian Monsoonal regime with a mean annual rainfall of 2300 mm. Approximately 90% of the rainfall occurs during the period from April to September. Because of abundant precipitation, erosion is at a maximum during this period. The geology of the Brahmaputra system on the Assam Plain consists of the Higher and Lesser Himalaya sequences that consists schists, marbles with amphibolites, and quartzites (Sarin et al., 1989). The Brahmaputra valley of Assam consists of older and newer alluvium deposits. Alluvium formed during the Pleistocene age (older alluvium) is found in slightly

undulating areas on both sides of the Brahmaputra river and the new alluvium soils near the river consist of alluvial materials washed down from the highland areas.

### Sediment Sampling and Chemical Analyses

The study covers the section of the Brahmaputra river flowing through Assam (India) from upstream to downstream. Four sediment core samples were collected from upstream to downstream along the river course namely C1 (Guijan, upstream), C2 (Tezpur, middle stream), C3 (Guwahati, downstream) and C9 (Dhubri, downstream) as shown in Figure 1. Core samples were collected by inserting a PVC pipe of length 100 cm at the drier part of the river channels. The pipes were then sealed and transferred to the laboratory where they were cut horizontally into 5 cm sections, stored at 4°C. Sediment pH was measured in a suspension of 1:5, sediment to water ratio using Multiparameter Analyser. Organic matter was determined using Walky and Black titration method. Grain size analysis was performed using dry sieving method. Heavy metals (Cu, Zn and Pb) were analyzed in ICP-OES (2100 DV Perkin Elmer). Statistical analysis was performed using SPSS version 18.

### Heavy Metal Fractionation

Extraction of heavy metals in core sediment samples were determined using sequential extraction method. The technique proposed by Tessier et al. (1979) was followed. The following four fractions were used for partitioning the heavy metals:

*Exchangeable fraction* (1M MgCl<sub>2</sub>, pH 7 with continuous agitation for one hour); *carbonate bound fraction* (1M NaOAc adjusted to pH 5.0 with acetic acid with continuous agitation for five hours); *Reducible fraction or Bound to Fe-Mn oxides* (0.04M NH<sub>2</sub>OH.HCl in 25% (v/v) acetic acid at 96°C refluxed for six hours; and *Oxidisable fraction or Bound to organic matter* (3 ml of 0.02M HNO<sub>3</sub> and 5% of 30% H<sub>2</sub>O<sub>2</sub> and pH adjusted to 2.0 with HNO<sub>3</sub>). The mixture was refluxed at 100°C for 2 h. A second 3 ml aliquot of 30% H<sub>2</sub>O<sub>2</sub> (pH 2 with HNO<sub>3</sub>) refluxed for 3 h, cooling, 5 ml of 3.2M ammonium acetate in 20% (v/v) HNO<sub>3</sub> was added, diluted to 100 ml and agitated continuously for 30 min.

### Residual Fraction

Total digestion with concentrated mixture of HF-HNO<sub>3</sub>-HCl. Four ml of concentrated HF was added to the sediment sample and allowed to react overnight at room temperature. 12 ml of aqua regia (HCl+ HNO<sub>3</sub>) was added to the sample and digested in Teflon Bomb at 130°C.

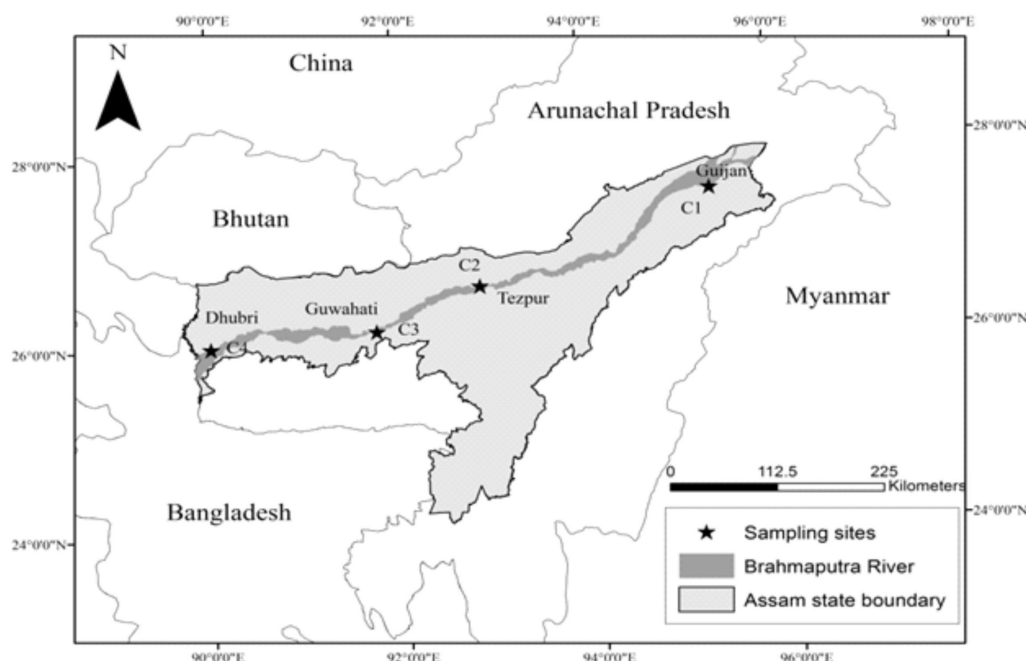


Figure 1: Map illustrating four sampling locations in the Assam stretch of the Brahmaputra river.

After each step the suspension was centrifuged for 30 minutes at 10,000 rpm and the supernatant was filtered through a filter paper; the filtrate was separated and the solid phase was added with the reagents for subsequent extraction. The concentration of heavy metals extracted in each fraction was determined using ICP-OES.

## Results and Discussion

### Physico-chemical Characteristics

Concentrations of organic matter, pH and particle size in four sediment core samples are shown in Figure 2. The pH of the sediment samples varied from 6.71 to 8.06 indicating alkaline nature of the sediments. Organic matter content in the sediment core samples range from 0.1 to 2.8%. Organic matter decreases with increase in depth due to natural decomposition process. A similar trend is observed in all samples.

### Sediment Texture

Sediment textures of core samples are shown in Figure 2 (c-f). Textural studies in the core samples (C1, C2, C3 and C4) showed that the percentage of sand, silt and clay differed markedly in relation to depth. The sediment of C1, C2, C3 and C4 of the Brahmaputra river is dominated by sand fraction. Sand % is higher in upstream (C1) and (silt+clay) fraction is higher in middle (C2) and downstream locations (C3 and C4) which indicate finer grain size available in downstream of the river.

### Total Metal Content

Table 1 presents average concentration of heavy metals in surface and underlying section of sediments. The order of abundance in sediment profiles are  $Zn < Cu < Pb$ . Metal enrichment for Cu, Zn and Pb is high at the surface layer than the bottom. It was found that concentration of these metals decreases with increase in depth. The average heavy metal concentration in the core sediments reveals that the concentrations of Zn at some locations are higher than respective shale value which attribute anthropogenic origin.

### Fractionation of Heavy Metal

The partitioning of heavy metals in the four sediment cores from the sequential extraction results are shown in Figure 3 (a-l). In Figure 3, major portion of copper (Cu) is associated with residual fraction. In core 2 (C2) 72% of total Cu was associated with residual fraction. Comparing average concentration of Cu in non-reducible fraction is in the order: oxidisable > reducible > carbonate > exchangeable.

Among non-residual fractions Cu is mainly associated with oxidisable fraction. Several workers reported that extractable Cu is mainly associated with oxidizable phase, where it forms complex with organic compound (Samanidou et al., 1987; Pardo et al., 1993; Marin et al., 1997). Cu has high affinity for humic substance which is present in organic matter and easily make complex with metal. Under oxic condition, copper which is present

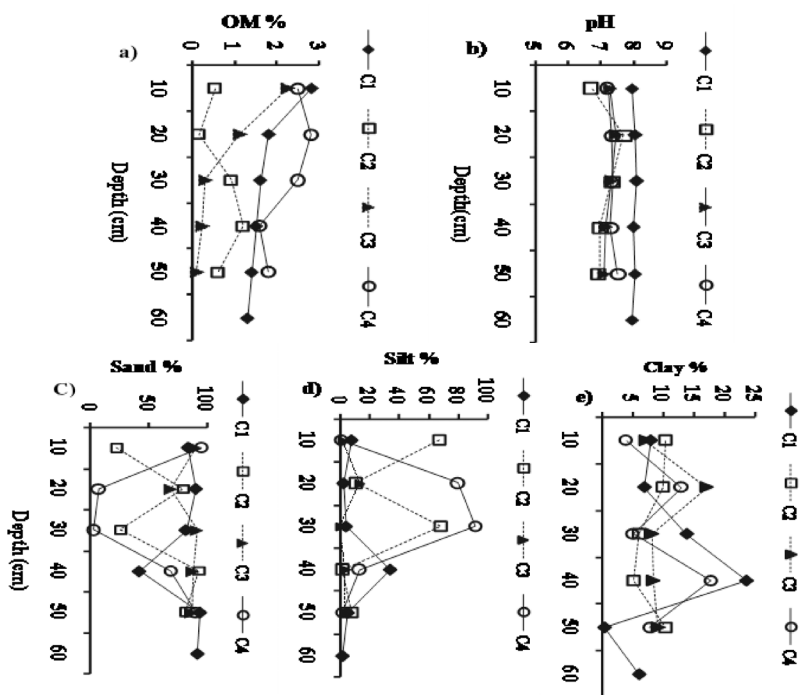


Figure 2: (a) Organic matter, (b) pH and (c-e) % composition of grain size variation in sediment core samples at Core 1 (C1), Core 2 (C2), Core 3 (C3) and Core 4 (C4).

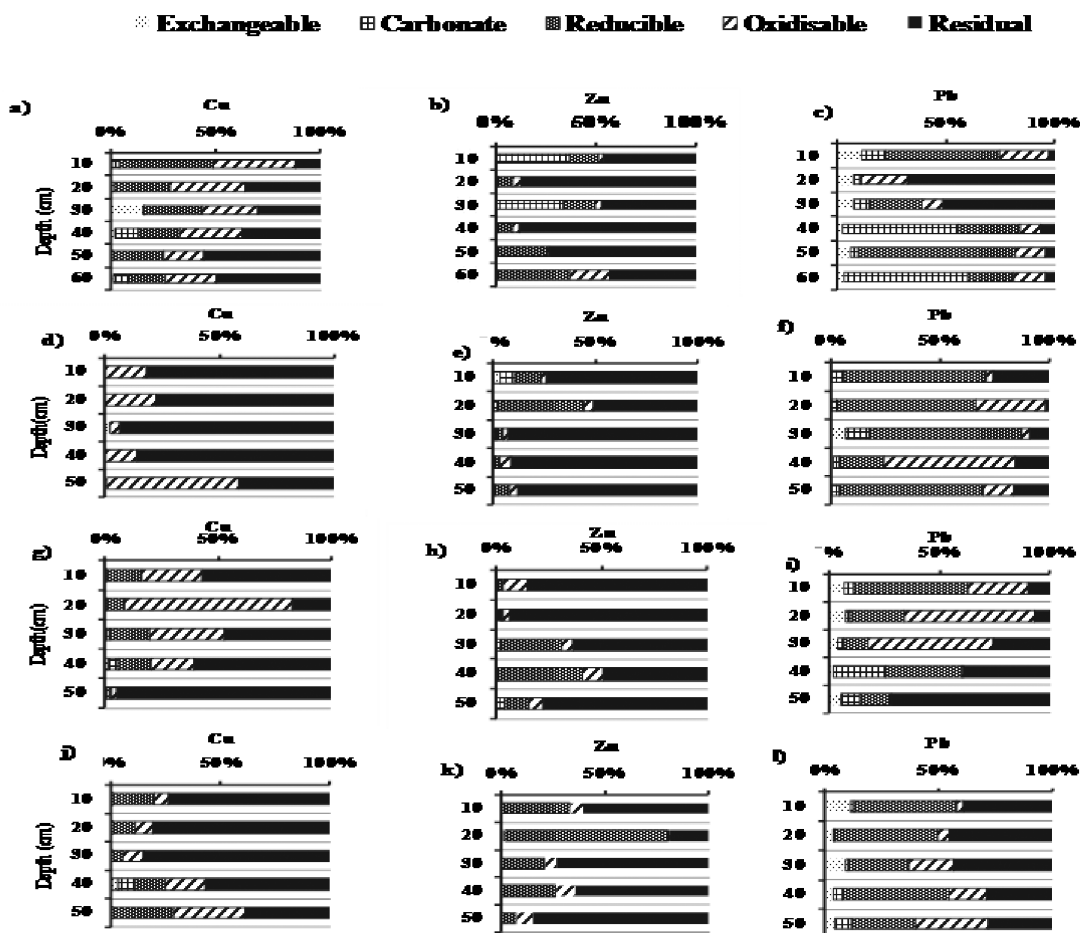


Figure 3: The variations of Cu, Zn and Pb concentrations in various fractions with depth in the sediment at Core 1 (a-c), Core 2 (d-f), Core 3 (g-i) and Core 4 (j-l).

**Table1: Total metal concentration of surface (<10 cm) and underlying (>50 cm) sediment samples of four locations along with their descriptive statistical summary**

	Surface			Underlying		
	Cu	Zn	Pb	Cu	Zn	Pb
Core 1	38.2	81.8	11.5	33.8	46.0	14.1
Core 2	13.8	32.0	23.0	33.2	26.9	12.0
Core 3	38.0	571	11.5	24.0	27.5	11.3
Core 4	46.0	25.1	12.0	32.0	44.8	9.8
Average	34.0	177	14.5	30.7	36.3	11.8
SD	14.0	263	5.70	4.6	10.5	1.8

Conc are in  $\mu\text{g g}^{-1}$ , SD represents standard deviation.

at the sediment surface, may come to the overlying water column by mineralization of organic matter. Cu concentration decreases in oxidisable fraction with depth in all sediment cores except at C4. At C2 some portion of carbonate fraction is associated with Cu which may be due to increase of pH with depth. Cu in most of the samples is enriched at 10-20 cm in organic fraction which may be due to presence of humic substance at the surface.

Zn is mostly associated with residual fraction followed by reducible and oxidisable fractions. The percentage of Zn associated with non-residual fraction is in the order: reducible > oxidisable > carbonate > exchangeable. Several studies reported that Zn is mostly associated with reducible fraction in sediment (Li et al., 2001; Korfali et al., 2004). In the present study, 33% of total Zn is associated with reducible fraction at C4. Higher percentage of Zn associated with Fe-Mn oxide fraction may be due to high constant stability of Zn oxide in soil (Li et al., 2001; Turki et al., 2007). Zn in reducible fraction decreases with depth at C2 and C3. The results suggest accumulation of Zn in surface layer due to precipitation and co-precipitation of Fe-Mn oxide.

Lead (Pb) is mostly bound with residual and reducible fraction. The percentage of Pb associated with among non-residual fraction is in the order: reducible > oxidisable > carbonate > exchangeable. Higher percentage of Pb associated with reducible fraction may be due to higher stability of Pb-oxides, and adsorption, flocculation and co-precipitation of Pb with the colloids of Fe and Mn oxyhydroxide (Rath et al., 2009). At C1, some portion of Pb is associated with carbonate

**Table 2: Pearson correlation coefficient for the relationship between percentage of metal partitioning in different fraction with the sediment properties at Core 1 (C1), Core 2 (C2), Core 3 (C3), Core 4 (C4)**

	<i>Metals fraction</i>	<i>Organic matter (OM)</i>				<i>pH</i>				<i>Clay</i>			
		<i>C1</i>	<i>C2</i>	<i>C3</i>	<i>C4</i>	<i>C1</i>	<i>C2</i>	<i>C3</i>	<i>C4</i>	<i>C1</i>	<i>C2</i>	<i>C3</i>	<i>C4</i>
Cu	Exc.	-	-.834	-	-.683	.703	-.632	.555	.565	.625	-	.625	.593
	Carb.	-	-	-	-.727	.411	-	.846	.656	-	-	-	.587
	Red.	.802	.537	.709	.425	-	.586	.587	.525	-	.584	-	-
	Oxid.	.472	-	-	-.771	-	.902*	-	.804	.509	-.885*	.509	-.773
	Resid	-.796	-	-.388	.902**	.403	-.751	-	-.677	-	-.406	-	-
Zn	Exc.	-	-	.467	.574	-.939**	.757	.467	.545	-.637	.632	-.637	-.480
	Carb.	-.475	-	-.686	.533	-.557	.617	-.686	-	-	.482	-	.786
	Red.	-.850*	-.653		.757	-.347	-	-	.656	-	-	-	.449
	Oxid.	.775	-.623		-.752	-.769	-	-	.573	-	.949*	-	.532
	Resid	-.515	.953*		-.465	.823*	-	-	.778	-	-.638	-	.432
Pb	Exc.	.615	.413	-.846	.633	-	.810	-	-.483	.848	.421	.848	-.771
	Carb.	-.422	-	.520	-.781	-.485	-.493	-	.764	-.888*	-	-.888	.589
	Red.	-	-	.832	.639	-	-	-	-.522	-.517	-	-.517	-.407
	Oxid.	.557	-	.845	-.483	-	.941*	-	.846	-	-	-	.698
	Resid	-	-.800	-	.925**	.683	.846	-	.656	-.732	-	-.732	-.455

Exc – Exchangeable, Carb – Carbonate, Oxid – Oxidisable, Resid – Residual

\*Correlation is significant at the 0.05 level (2-tailed). \*\* Correlation is significant at the 0.01 level (2-tailed).



fraction. A number of studies reported the Pb associated with carbonate fraction. Carbonate can be important absorbent for Pb when organic matter and Fe-Mn oxides are less abundant in the aquatic system (Li et al., 2001). The carbonate form is loosely bound phase and liable to change with the environmental condition.

It is evident from the results that major portions of the metals are bound in different forms with different strengths. Among the metals analyzed in the four sediment core samples, the metal showing the highest average percentage in the exchangeable and carbonate fraction is Pb. Higher percentage of Pb in exchangeable fraction indicates that the metals in the sediment are potentially available for uptake and release in the river system. In reducible fraction Zn and Pb show highest percentage at C3, C4 and Cu and Zn at C1, C2. Metals bound to reducible fraction act as scavenger for metal. In oxidisable fraction Cu shows highest percentage in all core sediments. It was reported that degradation of organic matter under oxidizing condition can lead to release of soluble metal (Chakrapani et al., 2008). Residual fraction is found to be high for all metals.

#### Risk Assessment Code

The risk assessment code (RAC) includes sum of exchangeable and carbonate bound fractions for assessing the availability of metals in sediments. These fractions are considered to be weakly bonded metals which may equilibrate with the aqueous phase and thus become more rapidly bioavailable (Baruah et al., 1996; Singh et al., 2005). According to RAC, for any metal, sediment which can release in exchangeable and carbonate fractions less than 1% of the total metal will be considered safe for the environment and with 11-30% carbonate and exchangeable fractions will be at medium risk to the environment. On the contrary, sediment releasing in the above fractions more than 50% of the total metal has been considered being highly dangerous, which can easily enter the food chain (Perin et al., 1985). The average risk assessment code as applied to the present study reveals that Cu (4.98%), Zn (4.81%) and Pb (15.2%) that exist in exchangeable and carbonate fractions come under low to medium risk. Cu and Zn come under low risk whereas Pb medium risk.

#### Mobility Factor

Mobility factors (MF) of metals provide an indication of the bio-availability or non-bioavailability of the metal (Osakwe et al., 2014). The mobility factor is calculated in percentage on the basis of following equation:

$$\frac{F1 + F2 + F3}{F1 + F2 + F3 + F4 + F5} \times 100$$

where F1 = exchangeable fraction, F2 = carbonate fraction, F3 = Fe-Mn oxide fraction, F4 = organic fraction and F5 = residual fraction. The MF index in core sediment is in the order of Pb (47.5%) < Zn (23.8%) < Cu (21.4%). The MF value indicates that there is a potential risk by Pb in the river system.

#### Statistical Analysis

##### Correlation

Significant correlation between percentage partitioning of Cu, Zn and Pb in the different geochemical fractions and sediment properties in Core 1, Core 2, Core 3 and Core 4 are presented in Table 2. Most of the non-residual fractions of Cu, Zn and Pb are negatively correlated with sand, silt and clay fractions which originate mainly from natural weathering of the Brahmaputra basin, whereas residual fraction of Zn is positively correlated with clay content. This indicated that sediment texture plays an important role in metal mobilization. Significant negative correlation of exchangeable fraction of Pb and Zn with pH indicates the mobility of these metals dependent on sediment pH. Significant positive correlations of residual fractions of Pb and Zn reflect that the lowering of pH can enhance the dissolution of these metals bound to the crystalline lattice of minerals. At some core Pb, Cu and Zn, in oxidisable fraction positively correlated with organic matter indicate that presence of humic substance in sediment is effective in metal binding behaviour.

#### Conclusion

In the present study, sequential extraction technique was used to determine partitioning of Cu, Zn and Pb in core sediment. The speciation pattern of heavy metals in core sediment show significant variation with depth. The dominant binding phases for Zn and Pb are residual and reducible whereas for Cu are oxidisable and residual fraction. The risk assessment code suggests low to medium risk for all heavy metals. The bioavailable fraction and metal mobility was found to be comparatively higher for Pb. This is extremely important because it represents the proportion of heavy metals that can be easily remobilized by changes in environmental conditions. Correlation analysis was carried out to understand major controlling factors in vertical distribution of metals in different fractions.

Results suggest that sediment grain size affect metal mobilization and act as major carrier. Metals in non-residual fraction are affected by increase or decrease in pH. Metal in oxidisable fraction is found to be significantly correlated with organic matter. Speciation study reveals that chemical form of heavy metals is useful in assessing their potential release in aquatic system.

### Acknowledgement

This study is supported financially by University Grant Commission (UGC) under Major Research Project Scheme. We wish to acknowledge the help received from Tezpur University through Seed Money Grant. First author thanks Rajiv Gandhi National Fellowship (RGNF) for junior research fellowship.

### References

- Bacon, R.J., Farmer, G.J., Dunn, M., Graham, C.M. and I.S. Vinogradoff (2006). Sequential extraction combined with isotope analysis as a tool for the investigation of lead mobilization in soils: Application to organic-rich soils in upland catchment in Scotland. *Environmental Pollution*, **141**: 469-481.
- Berner, E.K. and R.A. Berner (1996). Global Environment: Water, Air, and Geochemical Cycles. *Geochimica Cosmochimica Acta*, **60**: 5157-5158.
- Baruah, N. K., Kotoky, P., Battacharya, K.O. and O.C. Borah (1996). Metal speciation in Jhanji river sediments. *Science of the Total Environment*, **193**: 1-12.
- Chakrapani, G.J., Gupta, H. and C.K. Jain (2008). Enrichment and Fractionation of heavy metals in bed sediments of River Narmada, India. *Environmental Monitoring Assessment*, **141**: 35-47.
- Engila, J.N. and D.N. Nimyel (2002). Determination of Trace Metal Speciation in Sediments from Some Dams. *Journal of the Chemical Society of Nigeria*, **27**: 71-76.
- Forstner, U. and G.T.W. Wittmann (1981). Metal Pollution in the aquatic environment. Springer-verlag, Berlin Heidelberg New York.
- Iwegbue, C.M.A. (2011). Chemical fractionation of metals in core sediments of Orogodo River, south Nigeria. *Toxicological and Environmental Chemistry*, **93**: 1341-1358.
- Kumar, M., Ramanathan, A.L., Rao, M.S. and B. Kumar (2006). Identification and evaluation of hydrogeochemical processes in the groundwater environment of Delhi, India. *Environmental Geology*, **50**: 1025-1039.
- Kumar, M., Furumai, H., Kurisu, F. and I. Kasuga (2013). Tracing source and distribution of heavy metals in road dust, soil and soakaway sediment through speciation and isotopic fingerprinting. *Geoderma*, **212**: 8-17.
- Korfali, S.I. and B.E. Davies (2004). Speciation of metal in sediment and water in a river underline by limestone: role of carbonate species for purification capacity of rivers. *Advances in Environmental Research*, **8**: 599-612.
- Mihaljevic, M. (1999). Zinc. In: C.P. Marshall and R.W. Fairbridge (eds.), Encyclopedia of Geochemistry. Kluwer Academic Publisher, Dordrecht Germany.
- Ma, L.Q. and G.N. Rao (1997). Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. *Journal of Environmental Quality*, **26**: 259-264.
- Milliman, J.D. and R.H. Meade (1983). World-wide delivery of river sediment to the oceans. *Journal of Geology*, **91**: 1-21.
- Marin, B., Vallado, M., Polve, M. and A. Monaco (1997). Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta*, **342**: 91-112.
- Pardo, R., Barrado, E., Castrillejo, Y., Velasco, M.A. and M. Vega (1993). Study of the contents and speciation of heavy metals in River sediments by factor analysis. *Analytical Letters*, **26**: 1719-1739.
- Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanetta, M.L. and A.A. Oro (1985). Heavy metal speciation in the sediments of northern Adriatic Sea. A new approach for environmental toxicity determination. *Heavy Metals in the Environment*, **2**: 454-456.
- Rath, P., Panda, U.C., Bhatta, D. and K.C. Sahu (2009). Use of sequential leaching, mineralogy, morphology and multivariate statistical technique for quantifying metal pollution in highly polluted aquatic sediments--a case study: Brahmani and Nandira Rivers, India. *Journal of Hazardous Material*, **16**: 632-644.
- Sarin, M.M., Krishnaswami, S., Dilli, K., Somayajulu, B.L.K. and W.S. Moore (1989). Major ion chemistry of the Ganga-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal. *Geochimica Cosmochimica Acta*, **53**: 997-1009.
- Osakwe, S.A. (2010). Chemical Speciation and Mobility of Some Heavy Metals in Soils around Automobile Waste Dumpsites in Northern Part of Niger Delta, South Central Nigeria. *Journal of Applied Science and Environment Management*, **14**: 123-130.
- Samanidou, V. and K. Fytianos (1987). Partitioning of heavy metals into selective chemical fractions in sediments from rivers in northern Greece. *The Science of the Total Environment*, **67**: 279-285.
- Singh, K.P., Mohan, D., Singh, V.K. and A. Malik (2005).. Studies on distribution and fractionation of heavy metals in Gomti river sediments—A tributary of the Ganges, India. *Journal of Hydrology*, **312**: 14-27.
- Subramanian, V. (2004). Water Quality in South Asia. *Asian Journal of Water, Environment and Pollution*, **1-2**: 41-54.

- Tessier, A., Campbell, P.G.C. and M. Bisson (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, **51**: 844-850.
- Thorne, C.R., Russell, P.G. and M.K. Alam (1993). Planform pattern and channel evolution of the Brahmaputra River, Bangladesh. In: Best, J.L., Bristow, C.S. (eds.), Braided Rivers. *Geological Society London Special Publications*, **75**: 257-276.
- Turki, A.J. (2007). Metal Speciation (Cd, Cu, Pb and Zn) in Sediments from Al Shabab Lagoon, Jeddah, Saudi Arabia. *JKAU: Marine Science*, **18**: 191-210.
- Wedepohl, K.H. (1978). Handbook of Geochemistry. Springer Verlag, Berlin.
- Xiangdong, Li, Zhenguo, S., Wai, Onyx W.H. and Y.S. Li (2001). Chemical forms of Pb, Zn, Cu in the sediment profiles of the Pearl River Estuary. *Marine Pollution Bulletin*, **42**: 215-223.
- Yuang, C., Shi, J., He, B., Liu, J., Liang, L. and G. Jiang (2004). Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environmental International*, **30**: 769-783.