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Contemporary distribution and impending mobility of arsenic, copper and zinc in a tropical (Brahmaputra) river bed sediments, Assam, India

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ABSTRACT

The present study develops a correlationship among different phases of metal for developing an understanding of metal distribution and speciation, which is seldom reported in many studies. Also, the study examines the effect of sediment texture, pH, CEC, organic content and conductivity to understand the metal distribution. Bed sediment (n = 8) samples were collected from Brahmaputra river by grab sampling method to understand the spatial distribution and speciation of Cu, As and Zn. X-ray Diffraction (XRD) analysis strongly indicated the presence of arsenopyrite in Dhansirimukh site (BRS-5) sample as a dominating As containing mineral. It was found that distribution of As was relatively higher in downstream side due to increase in clay content of the sediment. Partition coefficient (k_d) indicated higher mobility of Zn and Cu in comparison to As. The presence of organic matter and clay resulted in high metal content due to high CEC values, which is because of negative charge on clay and organic matter. The negative charge in clay and organic matter is due to isomorphous substitution and dissociation of organic acids, respectively. High clay content leads to Cu enrichment at BRS-4, while sandy nature of sediment at BRS-8 and absence highly active mineral leads to low Zn content. Sediment properties like organic matter and grain size were the main controlling parameters for metal concentration and its potential mobility as indicated by correlation and factor analysis. Factor analysis further revealed three probable processes governing metal enrichment and distribution viz. (i) Textural driven (ii) Metal solubility at sediment-water interface and (iii) Carbonate weathering. The study demonstrates that the textural assemblage governs metal mobility in the river sediments. Study developed a conceptual diagram for probable geochemical processes explaining the specific observations in this study, which is essential for environmental safety.

1. Introduction

Sediments are an important source and sink of contaminants, including metals, (Das et al., 2015) through the processes of precipitation, adsorption and chelation. Metal contamination in sediments has potential long-term implications for human and ecosystem health. Metal leaching from the river bed to groundwater depends on several factors like distribution of metals in particulate and dissolved phase, sediment grain size sorting, aquifer characteristics like porosity, conductivity and solid phase buffering of the metal in solution (Gogoi et al., 2016; Sauve et al., 2000).

Metals accumulate in environmental reservoirs and biomagnify through the food chain. Metal speciation in the river sediment is of great concern in the context of groundwater pollution in the alluvial settings (Kumar et al., 2009a, 2009b, 2013a, 2013b; Karezewska, 1996; Li and Thornton, 2001; Li et al., 2001). The behaviour of metals in natural water changes with the substrate and suspended sediment composition, as well as water chemistry and ions present (Osmond et al., 1995). Lu and Yu (2018) studied the relationship between human activities and spatial-temporal variations of metals in Songhua river (China) by multivariate statistical analysis. The effect of human activities on the spatial and temporal change was studied by comparing the metal concentration at different flow periods. Kerr and Cooke (2017) investigated the distribution of metal along the upstream and downstream in Red deer river (Alberta) due to erosion. The effect of anthropogenic activities as an attribute of metal in river Ganga and toxic effect of metal in the riverine environment was investigated by Paul (2017). Jaiswal and Pandey (2018) investigated the effect of metals on

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enzymatic activities of microbes in the river sediment of Ganga. Qu et al. (2018) carried out risk analysis of metal in the sediment of Wen-Rui tang river (China) to assess human health and ecological risk. Bhuyan et al. (2017) extensively studied the metal contamination by Atomic Absorption Spectrophotometer (AAS) on the surface water and sediments of river Meghna (Bangladesh). Arfaeinia et al. (2016) carried out AVS (Acid volatile sulphide) and SEM (Simultaneously extracted metals) analysis for determining the concentration of heavy metals in marine sediments along the stretches of harbour of Asaluyeh, and also evaluated the spatial distribution of heavy metals and their potential toxicity and ecological risk. Gogoi et al. (2016) studied the effect of ligands on metal speciation and metal transport in Brahmaputra River during monsoon season. Despite extensive studies on metal contamination and risk assessment along the river course, study related to the assessment of metal contamination, metal mobility by developing a correlation between phases i.e. particulate and dissolved form of metal to total metal, particulate form to dissolved form of metal is seldom reported.

The present study is carried out on Brahmaputra river, Assam (India) which is the lifeline of Assam and exhibited significant land use change owing to rapid population increase over last few decades. People utilize the river and discard the wastes generated by their activities into the river. Thus, the river has become a carrier of waste which is polluting the river water and sediments. As Brahmaputra river flows through Southern Tibet, it carries a pronounced high concentration of Arsenic (As) released from sediments of the Holocene period. Many contaminants and nutrients become bound to sediment particles and are transported and deposited along with the sediment. It is very important to understand the spatial and temporal distribution of contaminants like metals, their concentration level, leaching processes and mineralogy of sediments of the river for better understanding and management.

Under the light of above discussion, the present study develops a correlation and scenarios among different forms of metals for a better understanding of the implications of various physicochemical factors i.e., grain size, texture, conductivity, pH, organic content etc, on metal distribution, speciation and leaching from the river bed sediment to groundwater. The study further develops a conceptual diagram for probable geochemical processes explaining the specific observations in this study, which is essential for river ecotoxicity management and environmental safety.

2. Materials and methods

2.1. Study Area and site description

The Brahmaputra River originates at an elevation of 5150 m from the Kailash ranges in the Himalayas. With a total length of about 2900 km, the river flows through 2920 km of geographical area encompassing three countries i.e. China, India and Bangladesh. In Bangladesh, it merges with Ganga and forms Padma which joins with Meghna near Dhaka and finally flows out to the Bay of Bengal. In India, it flows for 916 km. Dibang and Lohit join the upper course of the Brahmaputra to form Siang and the combined flow travels through Assam for about 640 km. With around 3% share of the total world water discharge and drainage area of 1, 94,413 sq km in India (out of which 70,634 sq. km in Assam), the Brahmaputra river is one of the greatest sediment sources to the ocean from a tropical country (Berner and Berner, 1996).

A sub-tropical monsoon climate prevails in the Brahmaputra river basin with approximately 1500 mm of rainfall per year. About 85% of the precipitation in the basin occurs during monsoon months of May to October. The average daytime temperature in summer is~ 35 °C and in winter~ 25 °C with a night time temperature of around~ 10 °C (Mirza et al., 1998). Flooding is a common phenomenon in the river valley which sustains the agriculture of the region by replenishing the soil through annual fresh alluvial deposits.

2.2. Sampling

Eight surface sediment samples were collected by grab sampling method during the month of November 2012 along the Assam stretch of the Brahmaputra river from upstream to downstream (Supplementary Fig. 1). The sampling sites were Guijan (BRS-1), Raumeria (BRS-2), Dibrugarh (BRS-3), Nimatighat (BRS-4), Dhansirimukh (BRS-5), Tezpur (BRS-6), Guwahati (BRS-7) and Jogighopa (BRS-8). It may be argued that 8 samples across 480 km stretch of the river will vary greatly may not be sufficient. However, the number of the sediment samples and their locations were decided based on the preliminary survey of 30 water samples and the variation in their physico-chemical characteristics and metal concentration.

2.3. Elemental analyses

pH, Electrical conductivity (EC), total alkalinity, organic carbon and cation exchange capacity (CEC) were measured following standard procedures (APHA, 2005). Grain size analysis was performed using International Pipette Method. Inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 2100 DV) was used to analyze As (Arsenic), Cu (Copper) and Zn (Zinc). Stock multi-element metal solutions of 10 mgL^{-1} were prepared from multi-element standard metal solutions (CertiPUR-1.11355.0100). Further, the internal standards like Sc (Scandium), In (Indium) and Bi (Bismuth) were added to working standard as well as samples to reach a final concentration of 200 μL^{-1} (Gogoi et al., 2016). The coefficient of variation was found to be less than 10% as obtained after triplicate measurements of the samples (Deka et al., 2015).

Metal extraction is done by acid and water extraction procedures (Gogoi et al., 2015). The total metal content in the sediments was determined by wet extraction in which 1 g of sediment was put in a Teflon bomb with a 3:1 mixture of HNO_3 (65%)and $HClO_4$ (70%)in 3:1 ratio and left for 8 h in the microwave. After cooling, samples were diluted with 20–30 ml of Milli-Q water and filtered with 0.45 μm Whatman filter paper and then analyzed in ICP-OES. Standard reference material (SRM-8704, Buffalo river sediment) from the National Institute of Standards and Technology (NIST) were used to verify the results of As, Cu and Zn in the sediment samples. Recovery of the three metals was 80–110%. Water extraction was carried out for sediments of grain size 2 mm using Milli-Q water in a ratio of 1:20 (w/v). 1 g of dry sediment was shaken for 8 h at room temperature and then centrifuged at 1200 rpm for 15 min. Supernatant was filtered and analyzed by ICP-OES.

2.4. Mineral analyses

Mineralogy of the sediment samples was characterized by X-ray Diffraction (XRD) and scanning electron microscopy (SEM, Rigakuminiflex). All samples were ground to powder and mounted on a quartz plate' for analysis. XRD analysis was from 2.0 to 70.0 degree with a step size of 0.02 degree and applicable time for 4 s. Proper diffraction pattern comparisons were made with the available electronic database for reference standards to identify different mineral phases.

2.5. Calculation of partition coefficient

The partition coefficient (K_d) for metals in water-soluble extracts to sediments was obtained from the ratio between the dissolved and total metal concentration (Jung et al., 2005).

$$\mathbf{K_d = \log\ [Me_{(Sed)}/Me_{(W)}]},$$

Where, K_d = partition coefficient $M_{e(Sed)}$ = metal concentration in sediments and $M_{e(W)}$ = metal concentration in water extracts