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Evaluation of arsenic sorption and mobility in stream sediment and hot spring deposit in three drainages of the Tibetan Plateau

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A B S T R A C T

Enrichment of arsenic (As) in sediment (12–227 mg/kg) in the upstream tributaries of the Indus and Brahmaputra Rivers originating from the Tibetan Plateau where hot springs were abundant has been found. Sandy sediment samples from the Nu-Salween River, Lantsang-Mekong River and Jinsha-Yangtze River also originating from the Tibetan Plateau were collected in July, 2012 and were found to contain 6.8 mg/kg to 30.5 mg/kg As (average17.3 $\pm$ 6.5 mg/kg, n = 12). Deposits collected within 1 m of two hot springs in Changdu, Tibet displayed significantly higher As levels: 263.7 mg/kg in LD-2 with 65% quartz and 101.8 mg/kg in NuD-1 with 82% calcite. To evaluate the valence states of As and also the phases responsible for sorption, X-Ray Absorption Spectroscopy (XAS) was employed to analyze the two hot spring deposits and three river sediment samples: coarse sand NuD-6 (As 14.6 mg/kg), fine sand NuD-4 (As 17.8 mg/kg), and silty sand LD-1 (As 30.5 mg/kg). The X-ray absorption near edge spectrum (XANES) data indicate that 70% of As from 3 samples in the Nu-Salween River drainage (NuD-1, NuD-4 and NuD-6) is As(V) or arsenate, with the rest being As(0) or As–Fe sulfides. The proportion of As(V) is 90% for 2 samples in the Lantsang-Mekong River drainage (LD-1 and LD-2). Linear combination fit of the iron extended X-ray fine structure spectrum (EXAFS) show that 3 samples from the Nu-Salween River contain 20% ferrihydrite and 10% goethite without any hematite being detected but 2 samples from the Lantsang-Mekong River contain <10% ferrihydrite, 20% goethite and with 30–60% of hematite. Concentrations of reductively leached As and Fe are correlated (Pearson correlation coefficient 0.673), with an average value of extracted As being 1.7 $\pm$ 0.6 mg/kg (n = 8) and 4.3 $\pm$ 2.0 mg/kg (n = 3) for the Nu-Salween and Lantsang-Mekong river, respectively. Parameters from the Langmuir isotherm fit to sorption experiments of As(III) and As(V) onto three river sediment samples were used to estimate "sorbed" As concentrations in river sediment in equilibrium with the average river water As concentrations. The "sorbed" As concentrations were 0.8 mg/kg and 2.8 mg/kg for the Nu-Salween and Lantsang-Mekong drainage, respectively. Taken together, the data suggest that this pool of "sorbed" As in river sand, likely to have a geothermal As component, remains largely particle-bound in the oxic and circumneutral riverine environment during transport; it is subject to mobilization once buried in the floodplain areas down gradient.

1. Introduction

Arsenic (As) has been known for its ubiquitous presence in the Earth's crust, with an upper crustal abundance of 5.7 mg/kg (Hu and Gao, 2008), recently revised from an earlier estimate of 4.8 mg/kg (Rudnick and Gao, 2003). This seemly minute amount of geogenic As has resulted in elevated levels of As in groundwater primarily under reducing conditions (Smedley and Kinniburgh,

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2002) impacting human health in many countries (Ravenscroft et al., 2009). The exposed population is the largest in Bangladesh (Flanagan et al., 2012); together with India and several countries of South and Southeast Asia, it has been estimated that >100 million people are at risk of drinking water with As concentrations above the guideline value of 10 μg/L recommended by the World Health Organization (WHO) (Chakraborti et al., 2002; Mukherjee et al., 2006). The major rivers that transported and deposited the sediment from which the As-rich groundwater is drawn in these affected countries include the Indus (BGS, 2001), Ganges (Chakraborti et al., 2003), Brahmaputra (Zheng et al., 2004), Meghna (Jung et al., 2012), Irrawaddy (van Geen et al., 2014) and Mekong (Berg et al., 2007). Although these rivers originate from the Tibetan Plateau, little is known regarding whether there is any regional geochemical anomaly of As in the Tibetan Plateau's upper crust, and if so, how it may have contributed to this wide spread groundwater As problem in these drainage basins. Several authors have proposed that the tectonic setting of the Tibetan Plateau lends itself to enrichment of As (Guillot and Charlet, 2007; Nordstrom, 2012; Saunders et al., 2005; Stanger, 2005; Zheng, 2007). Thus investigation of geochemical processes responsible for As cycling in geological materials in the headwater region of the Tibetan Plateau is a crucial first step toward understanding the role of tectonics in groundwater As occurrence in the down gradient areas.

Evidence is emerging for As enrichment in geological material in Tibetan Plateau. Concentrations of As in soil samples (N = 406) from a regional survey of all 205 representative pedons in the Tibetan Plateau averaged about 20 mg/kg for soils derived from sandstone, shale, limestone, glacial deposits, alluvial sediments and lake deposits with a lower average value of 14.7 mg/kg for soils derived from igneous rocks (Zhang et al., 2002). Compared to these Tibetan soils, soils (n = 73) and stream sediment (n = 77) from Singe Tsangpo (upstream of the Indus River) and Yarlung Tsangpo Rivers (upstream of the Brahmaputra River) have recently been reported to contain even more As, averaging 43.6 mg/kg, 30.1 mg/kg for soils and 32.5 mg/kg, 24.6 mg/kg for river sediments, respectively (Li et al., 2013). Li et al. (2013) suggests that these even higher average values of As in geological material along the Singe-Tsangpo (Indus) to Yarlung-Tsangpo (Brahmaputra) Suture Zone are probably influenced by superlative enrichment of As in Tibetan geothermal water. A study of 400 geothermal water samples collected between 1973 and 1976 immediately after eruptions of geyser reported a seemingly improbable maximum value of 125,000 μg/L As, although neither the location of the hot spring nor the analytical method were provided (Zhang et al., 1982). The same study also notes high-values of a suit of volatile elements found along both sides of Yarlung-Tsangpo River. Later studies confirm abundant hydrothermal activities with over 600 hot springs identified in the Suture Zone (Zhao et al., 2002; Zhou and Qin, 1991). At local spatial scale, discharge of water with 5700 μg/L As from Yangbajing geothermal power plant (Guo et al., 2007, 2008, 2009) has resulted in elevated As in downstream water (>20 μg/L). At regional spatial scale, elevated As in Singe-Tsangpo (average As = 58.4 μg/L) and Yarlung-Tsangpo river (average As = 10.8 μg/L) water can be found 350 and 830 km from the head water downstream (Li et al., 2013).

Simultaneous river water and stream sediment As enrichment in the Indus–Yarlung Tsangpo drainages suggest sorption of geothermal sourced As as a plausible mechanism for its removal from surface water environment. Although a few studies have investigated rapid oxidation of geothermal As(III) (Gihring and Banfield, 2001; Gihring et al., 2001; Nordstrom et al., 2005; Planer-Friedrich et al., 2007, 2009; Wilkie and Hering, 1998) followed by sorption to hot spring deposits and the associated Fe-mineralogy (Inskeep et al., 2004; Mitsunobu et al., 2013), the sorption phases for As in the river sediments further downstream have not been evaluated. Numerous studies have evaluated As sorption onto synthetic and natural minerals (Dixit and Hering, 2003, 2006; Waychunas et al., 1993) and to soil (Goldberg, 1986, 2002; Zhang and Selim, 2005). Recent studies suggest that characterization of As speciation and the mineral phases in aquifer sediment using synchrotron X-ray Absorption Spectroscopy (Kocar et al., 2006; O'Day et al., 2004) combined with sorption experiment (Jung et al., 2012) can provide molecular level information of the sorption process to better understand the mobility of this sorbed As in the environment.

This study investigates the sorption process governing the partitioning of As between river water and sediment in drainage basins influenced by geothermal As input. The three rivers area of Nu(Salween)-Lantsang(Mekong)-Jinsha(Yangtze) flowing nearly in parallel to each other from north to south along the eastern edge of the Tibetan Plateau is chosen (Fig. 1). In addition to documented hydrothermal activities in this tectonically active region (Wang et al., 1990; Xu et al., 1997), floodplains in downstream sections of the Nu(Salween)-Lantsang(Mekong)-Jinsha(Yangtze) have elevated groundwater As occurrence (Berg et al., 2007; Duan et al., 2015). River and hot spring water, and river sediment and hot spring deposit samples were collected in July of 2012 and analyzed in the field and in the laboratory later to determine chemical and mineralogical compositions including selectively leached and bulk As concentrations. Sorption experiments of 2 stream sediment sample from the Nu-Salween and 1 stream sediment sample from the Lantsang-Mekong River were conducted to allow determination of partitioning coefficient of As between aqueous and solid phases. These sediment samples and two hot spring deposit samples, one each from the Nu-Salween and the Lantsang-Mekong drainage, were subject to X-ray Absorption Spectroscopy analysis for As speciation and Fe mineralogy to illuminate phases responsible for As sorption. The implication of the results on mobility of the sorbed As in stream sediment and cycling of As is discussed.

2. Materials and methods

2.1. Geological setting of the three rivers area

The three rivers area is composed of several blocks including the Lhasa Block, Qamdo-Simao Block and Songpan Garze Block which were originated in the Devonian to Late Triassic period (Hou et al., 2003; Noh et al., 2009; Wang and Burchfiel, 2000). The lithology has been divided to six parts: (1) Carbonate rocks such as limestone, chalk, dolomitic limestone and dolomite; (2) Complex lithology including sedimentary, volcano-sedimentary and volcanic rocks with some metamorphic and plutonic rocks; (3) Plutonic acidic rocks such as granite, granodiorite, quartz-diorite, and diorite; (4) Precambrian basement having medium to highly metamorphic and predominantly granodioritic-granitic character; (5) Mixed sedimentary rocks, typically with 30–70% carbonate; and (6) Silicic-clastic rocks with less than 10% carbonate consisting of clay, silt-stone, and mudstone.

The study area lies in the western part of Yunnan Province close to the collision zone with complex geological structure. As the result of recent tectonic events, geothermal activities are abundant. In total, more than 660 geothermal spring fields exist in western Yunnan, 30 of which are high-temperature hydrothermal systems with reservoir temperatures above 150 °C (Liao et al., 1986). For the three rivers study area, there are 193, 167 and 77 geothermal spring fields along the Tengchong-Gaoligongshan belt, the Changning-Lantsang-Mekong belt and east of the Jinsha-Yangtze River Fault in Northern Yunnan, respectively.

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