

ZHANG Yinfeng, LI Shehong, WANG Hui, WANG Mingguo, ZHENG Baoshan, ZHENG Lirong, YANG Qiang and ZHENG Yan, 2013. Evaluation of Arsenic Speciation of Stream and Hot Spring Deposits through X-ray Absorption Spectroscopy and Sorption Experiment. *Acta Geologica Sinica* (English Edition), 87(supp.): 665-666.

Evaluation of Arsenic Speciation of Stream and Hot Spring Deposits through X-ray Absorption Spectroscopy and Sorption Experiment

ZHANG Yinfeng¹, LI Shehong¹, WANG Hui¹, WANG Mingguo¹, ZHENG Baoshan¹,
ZHENG Lirong², YANG Qiang^{3,4} and ZHENG Yan^{3,4,*}

1 State Key Lab of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

2 Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

3 Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA

4 School of Earth and Environmental Sciences, Queens College, City University of New York, Flushing, NY 11367, USA

Enrichment of arsenic (As) was found in the upstream tributaries to the Indus and Brahmaputra Rivers originating from the Tibetan Plateau where hot springs were abundant (Li et al, 2012), suggesting a hot spring influence of river water As enrichment. However, river water samples (n=18) collected from the Nu River, Lantsang River, Jinsha River and Red River in July 2012 were found to contain As concentrations < 6.51 µg/L except for several small stream segments, suggesting that the influence of As from the hot springs were limited in these drainage basins due to dilution of low-As river water from snow melt and precipitation, with an additional loss to sorption on the suspended sediments. That sorption enriches As in stream sediments is evidenced by elevated As levels in the sediments of these drainage basins, ranging from 14 mg/kg to 211 mg/kg with an average value of 50 ± 64 mg/kg (n=11, excluding 4 samples below detection limit of a handheld XRF instrument (Thermo Scientific XLT-3). The highest As concentration (211 mg/kg) was collected within 1 m of a brine well in Changdu area of Tibet (YTD-23). The second highest As concentration (83 mg/kg) was collected within 1 m of a hot spring from Tibet (YTD-33).

To illustrate that sorption is responsible for the enrichment of As in the river sediments and to ascertain how differently arsenite (As(III)) and arsenate (As(V)) behave during sorption, batch sorption experiments combined with X-Ray Absorption Spectroscopy (XAS) analysis at the Beijing Synchrotron Facility were carried out. Two river sediment samples, YTD-40 and YTD-46, were from different sections of the Nu River. YTD-40 was

a coarse sand sample composed of quartz, illite, anorthose and calcite with 14 mg/kg arsenic. YTD-46 was a fine sand sample composed of quartz, anorthose with 16 mg/kg arsenic. A third river sediment sample, YTD-27, was from the, Lantsang River, was silty sand composed of quartz and calcite with 31 mg/kg arsenic. The XANES (X-Ray Absorption Near Edge Spectrum) usually between the -20 to 50 eV part of XAS (X-Ray Absorption Spectrum) can be used to ascertain the valence state of As in the aforementioned river (YTD-40 and YTD-46) and hot spring sediments (YTD-23 and YTD-33) suggest that As occurs as As(0) and As(V), but As(V) is predominant and As(0) may occur as arsenopyrite (Fig. 1).

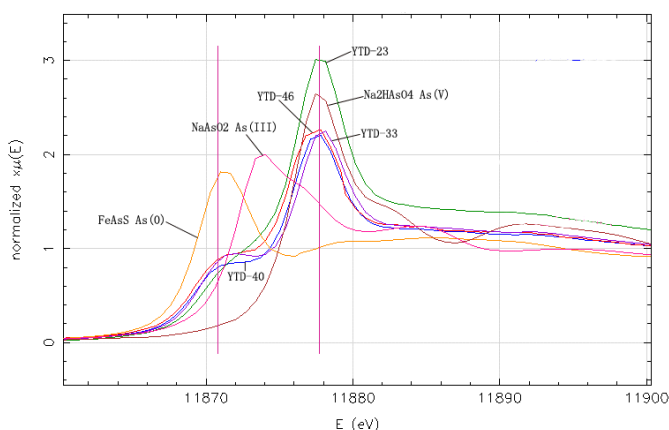


Fig. 1. XANES of river and hot spring sediments

In the sorption experiments, 1000 mg/kg NaAsO₂ and Na₂HAsO₄ standard solutions were added to approximately 3 g of sediment samples of YTD-40,

* Corresponding author. E-mail: yzheng@ldeo.columbia.edu

YTD-46、YTD-27 suspended in 20 ml of river water in a test tube (50mL) collected at the same location where the sediment samples were obtained, respectively. The sediment samples were kept wet after collection, with sorption experiments began approximately 60 days after sample collection. The initial added As(III) or As(V) concentration was from 0 mg/kg, 1 mg/kg, 2 mg/kg, 4 mg/kg, 5 mg/kg to 10 mg/kg. The test tubes had a screw top cover and were sealed by parafilm and left on a shaker for seven days. The final pH of the solutions ranged from 6.5 to 8.0, and did not change significantly from the initial pH. The sediment samples (n=3) with the highest amount of As spike in each of the sorption experiment sequence were subjected to XAS analysis. The sorption experiment results fitted well to Langmuir sorption isotherms with high correlation coefficients ($R^2 > 0.95$ Table1). A comparison of the binding coefficient (K) and sorption capacity (M) for the paired As(III) and As(V) sorption experiment for each sediment sample reveals that the difference is the smallest for YTD-46 and is the greatest for YTD-40 (Table 1). The similar Langmuir sorption isotherms for As(III) and As(V) for YTD-46, and to a lesser extent, YTD-27, are perhaps due to oxidation of As (III) to As(V) during the experiment. This is because XANES spectra of spiked YTD-46 and YTD-27 samples detected only AsV regardless whether As(III) or As(V) were added. For YTD-40, the XANES spectrum of As(V) spiked sediment detected As(V) only. However, the XANES spectrum of As(III) spiked sediment show mixed As(III) and As(V) species. For YTD-40, the binding coefficient for As(III) is higher than that for As(V). The reasons for this is not yet understood. But this may due to the solution composition, especially the pH, and compositions of sediments. (Suvasis Dixit et al, 2003)

Although we have not completed selected leaching of these samples, stream sediments enriched in As collected in Tibet (n=10) was subjected to reductive leaching with

hydroxylamine hydrochloride-acetic acid. Results showed that 24% of As in stream sediment is reductive leachable, with bulk As displaying a positive correlation with stream water As, suggesting sorption from stream water.

Table1 Langmuir parameters of adsorption experiments

Langmuir parameters	K(L/mg)	M(mg/kg)	R ²
YTD40 As(III)	7.88	33.68	0.9745
YTD40 As(V)	1.46	69.92	0.9555
YTD46 As(III)	6.67	77.55	0.9809
YTD46 As(V)	5.57	75.13	0.9641
YTD27 As(III)	4.97	134.29	0.9956
YTD27 As(V)	6.82	94.48	0.9844

Notes: K is binding coefficient, M is saturation adsorption capacity, R² is correlation factor.

In conclusion, sorption of As onto sediments in rivers influenced by As from hot spring sources has contributed to lack of large As anomaly in river waters, with As(III) and As(V) behaving similarly in sorption experiments, although this similarity may be due to oxidation occurred during the experiment. An improved understanding of the carrier phases of As in the sediment, including potential oxidation reactions with mineral phases in sediments, can shed light on whether sorbed As in sediment in turn controls riverine As level. Arsenic speciation in river sediments is predominantly As(V), with some As(0).

Key words: arsenic, sediment, Tibet, XAS, adsorption

References:

- Li S, Wang M, Yang Q, Wang H, Zhu J, Zheng B, Zheng Y (2013) Enrichment of arsenic in surface water, stream sediments and soils in Tibet. *Journal Of Geochemical Exploration*. <http://dx.doi.org/10.1016/j.gexplo.2012.08.020>
- Suvasis, D., and Janet, G.H., 2003. Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. *Environ. Sci. Technol.*, 37: 4182-4189.