Effect of microbial sulfate reduction on arsenic mobilization in aquifer sediments from the Jiangnan Plain, Central Yangtze River Basin

J. Gao¹, Y. Deng¹, T.I. Zheng¹ & H.C. Jiang²

¹Geological Survey, China University of Geosciences, Wuhan, China

²State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, China

ABSTRACT: The natural enrichment of arsenic (As) in the shallow groundwater of the Jiangnan Plain, central Yangtze River Basin, has been reported recently. However, the mechanism of As mobilization in the aquifer is not clearly understood yet. To evaluate the effect of microbial sulfate-reducing activities on As mobilization in the aquifer, the sediment samples were collected from 20.75 m at the typical As-rich depth of shallow aquifer. The results indicated that 3 mg kg⁻¹ As released from the sediment with acetate amended or without amendment. It was notable that, in the late cultural period, the Fe(II) was scavenged in the aqueous phase along with the decrease of sulfate, suggesting that the Fe-sulfide mineral may be generated in the incubation systems. Correspondingly, high abundance of sulfate-reducing bacteria *Desulfomicrobium* were observed, indicating the occurrence of bacteria sulfate reduction. Those results suggested that the As was mobilized under the sulfate reducing condition, and furthermore, the released As was not immobilized by the re-generation of Fe-sulfide minerals. These results can provide new insights for the mobilization mechanism of As in aquifer systems.

1 INTRODUCTION

Natural enrichment of arsenic (As) in groundwater has caused serious healthy and environmental crisis in many parts of the world. The microbially mediated reductive dissolution of iron oxide minerals is widely accepted as the main mechanism of As mobilization in subsurface aquifers (Fendorf *et al.*, 2010). However, recently, the sulfur redox cycle has been recognized with important influences on the As mobilization, in which indigenous microbes play crucial roles in facilitating As transformation in high As groundwater systems (Huang, 2014).

On one hand, microbial sulfate-reducing process is recognized as a mechanism for sequestering As via forming As-sulfide minerals directly or forming iron-sulfide minerals through co-precipitation and/or adsorption (Burton *et al.*, 2014); on the other hand, the sulfide produced by bacteria can reduce As-bearing iron oxides to release As and form sulfarsenate and sulfarsenite further to enhance As solubility (Sun *et al.*, 2016).

2 METHODS/EXPERIMENTAL

2.1 Experimental materials and methods

The experiment were conducted in an anaerobic glovebox under N₂ atmosphere. Sediments were homogenized before use and the microcosm slurries were generated by mixing 5 g of sediment with 50 mL artificial groundwater (10 mmol L⁻¹ PIPES,

7.9 mmol L⁻¹ NaCl, 2.7 mmol L⁻¹ KCl, 0.3 mmol L⁻¹ MgSO₄, 0.4 mmol L⁻¹ CaCl₂ · 2H₂O, pH = 7.1).

The microcosm batches were set up into three groups in duplicate: 1) the first group was supplemented with mol L⁻¹ acetate to stimulate the microbial activities; 2) the second group was not amended; 3) the third group was sterilized twice by autoclave at 121°C, 250 Kpa for 20 min. The aqueous subsamples were filtered through 0.22 μm syringe filters and then collected for the analysis of Fe(II), As(III), As(V), As(total), anions and cations. The remaining solids in the microcosms through centrifuging were collected and stored at -75°C for molecular biological analysis.

2.2 Sampling and analysis

The pH and Eh of solutions were measure by a portable gel-filled probe (HQ40D, HACH, Japan). Fe(II) was measured using a Spectronic 601 spectrophotometer (UV-1750, Shimadzu, Japan) with the ferrozine method at 562 nm wavelength. The total As was determined using an atomic fluorescence spectrophotometer (HG-AFS-930, Haiguang, China). The As speciation was measured by the liquid chromatography-hydride generation-atomic fluorescence spectrometry (LC-HG-AFS, Haiguang, China). The major cations were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES) (iCAP 6000 series, Thermo Fisher Scientific, USA). The anions including F⁻, Cl⁻, NO₃⁻, and SO₄²⁻ were determined using an ion chromatograph (ICS-2100, Thermo Fisher Scientific, USA).

Figure 1. Dissolved arsenic, arsenite, iron and sulfate concentrations during the incubation.

The microbial community dynamics were analyzed by the illumine high-throughput sequencing.

3 RESULTS AND DISCUSSION

3.1 The mobilization and retention of As and Fe(II) during incubation

The results indicated 3 mg kg^{-1} As is released from the sediment. From the first to tenth day, the As concentration increased correspondingly with the increase of Fe(II), during which sulfate was reduced completely. The As concentration decreased from the fourteenth day and then remained stable from the twenty-first day (Fig. 1).

In the late culture period, the Fe(II) was scavenged in the aqueous phase along with the decrease of sulfate. However, the As concentration remained stable. These results suggested that the Fe-sulfide mineral may be generated in the incubation systems. As was mobilized under the sulfate reducing condition, and furthermore, the released As was not immobilized by the re-generation of Fe-sulfide minerals.

3.2 The role of functional microbial groups involved in arsenic mobilization

According to the results of the illumina high-throughput sequencing, the sulfate-reducing bacteria, *Desulfomicrobium*, and the iron-reducing bacteria, *Geobacter*, were the predominant functional bacteria in the microbial community, which can affect the As variation (Fig. 2). In the late culture period, the methane producing bacteria became the main functional bacteria, which have competitive impact with the sulfate-reducing bacteria.

From the first to tenth day, the As concentration increased. Correspondingly, high abundance of sulfate-reducing bacteria *Desulfomicrobium* were observed, indicating the occurrence of bacterial sulfate reduction. These results can provide direct evidence and insights for the cause of As-rich groundwater in Jiangnan plain.

Figure 2. The variation of functional microbial groups involved in arsenic mobilization.

4 CONCLUSIONS

In this study, 3 mg kg^{-1} As was released from the sediment with acetate amended or without amendment. The microbial sulfate-reducing activities had important influences on the As mobilization, in which indigenous microbes, the sulfate-reducing bacteria, *Desulfomicrobium*, played crucial roles and the Fe-sulfide mineral may be generated in the incubation systems. The As was mobilized under the sulfate reducing condition.

ACKNOWLEDGEMENTS

This research was financially supported by the National Natural Science Foundation of China (Nos. 41572226 & 41521001), Program of China Geological Survey (Nos. 12120114069301 & 12120100100015 0121), and State Key Laboratory of Biogeology and Environmental Geology (No.128-GBL21711), China University of Geosciences.

REFERENCES

- Burton, E.D., Johnston, S.G. & Kocar, B.D. 2014. Arsenic mobility during flooding of contaminated soil: the effect of microbial sulfate reduction. *Environ Sci Technol.* 48(23): 13660–13667.
- Fendorf, S., Michael, H.A. & Geen, A.V. 2010. Spatial and Temporal Variations of Groundwater Arsenic in South and Southeast Asia. *Science* 328(5982): 1123–1127.
- Huang, J.H. 2014. Impact of microorganisms on arsenic Biogeochemistry: A Review. *Water, Air Soil Poll.* 225(2): 1848.
- Sun, J., Quicksall, A.N., Chillrud, S.N., Mailloux, B.J. & Bostick, B.C. 2016. Arsenic mobilization from sediments in microcosms under sulfate reduction. *Chemosphere* 153: 254–261.