



Mobilization and co-reduction of arsenic(V) by dissimilatory iron(III)-reducing bacteria : a biogeochemical model approach

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The mobilization of arsenic into groundwater is a major health problem but the processes of this release are still not well known. During the 1990s, naturally occurring As was found to be widespread in groundwater particularly in South Asia (Bangladesh, West Bengal, Pakistan) where tens and possibly hundreds of millions of people consume groundwater containing levels of As that exceeds the 10 ug/l guideline value defined by the World Health Organization. The toxicity of arsenic depends on its oxidation state and bioavailability: As(III) is a highly toxic and soluble oxyanion, whereas As(V) is less mobile because it tends to sorb more strongly onto hydrous ferric oxides (HFO) in acidic conditions. We investigate quantitatively these mechanisms with synthetic As-rich ferrihydrite (adsorbed or coprecipitated) by using techniques of microbiology and molecular ecology in combination with aqueous and solid phase speciation analysis. We explore whether the solubilization rate of arsenic is congruent to the solubilization rate of iron and discuss biotic or abiotic causes for disparities.

Synthetic ferrihydrite with As/Fe molar ratio around 5.5 % were diluted to concentrations of 0.33 to 1.63 g/L with a growth medium and inoculated with a community of dissimilatory iron(III)-reducing bacteria. Experiments were carried out under anoxic controlled laboratory conditions during two months. At the start of incubations, 5% to 25% of the initially adsorbed As(V) exchanged with aqueous phosphates from the culture medium. During the first month of inoculation, bacterial reduction resulted in the release in the dissolved phase of only 3% to 8% of initial Fe(III). Conversely, after the last month, Fe(II) concentration remained constant or decreased whereas total quantity of As released accounted for 15% to 45% of initial As(V). At the end

of the incubations, aqueous arsenic was predominately in trivalent form As(III) while X-ray absorption analysis indicated an As(V) dominant solid phase (>70%) and X-ray diffraction the possible presence of vivianite and, to a lesser extent, magnetite. Other experiments were performed to check for the reduction of HFO and/or As(V) in solution by three pure strains isolated from the DIRB community. These three pure strains were identified by small-subunit ribosomal RNA (16S rRNA) complete sequence analysis. The comparative analyses of 16S rRNA gene sequences shown that two strains are closely related to the genus *Clostridium* and one strain is closely related to the genus *Sporolactobacillus*. The experiments indicated that, at least, one of them respire both solid Fe(III) and aqueous As(V).

Based on these results, a biogeochemical model [1] with two different redox kinetics has been developed to simulate that bacterial As(V) reduction took place after Fe(III) reduction, rather than occurring simultaneously. A sensitivity study of the model shows that the mobility of arsenic may be controlled by competitive adsorption of As(III) with bicarbonate onto the As(V)-ferrihydrite at the slightly acidic pH range for which the bacterial growth is maximum ($5 < \text{pH} < 7$).

The results provide significant insights on recent observations of the decoupling of As and Fe release after incubation of Bengal Delta sediments [2] [3].

References

- [1] Bethke C. M. (2002) *The Geochemist's Workbench. A user's guide to Rxn, Act2, Tact, React, and Gplot. Release 4.0.* University of Illinois, Urbana.
- [2] van Geen A., Rose J., Thorai S., Garnier J. M., Zheng Y. and Bottero J. Y. (2004) Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations. *Geochim. Cosmochim. Acta* 68, 3475-3486.
- [3] Islam F. S., Gault A. G., Boothman C., Polya D. A., Charnock J. M., Chatterjee D. and Lloyd J. R. (2004) Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature* 430, 68-71.