Geophysical Research Abstracts
Vol. 16, EGU2014-3283-2, 2014
EGU General Assembly 2014

Characterising microbial reduction of arsenate sorbed to ferrihydrite and its concurrence with iron reduction and the consequent impact on arsenic mobilisation

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Mobilisation of solid phase arsenic under reducing conditions involves a combination of microbial arsenate and iron reduction and is affected by secondary reactions of released products. A series of model anoxic incubations were performed to understand the concurrence between arsenate and ferrihydrite reduction by *Shewanella putrefaciens* strain CN-32 at different concentrations of arsenate, ferrihydrite and lactate, and with given ΔG_{rxn} for arsenate and ferrihydrite reduction in non-growth conditions at pH 7. The reduction kinetics of arsenate sorbed to ferrihydrite is predominately controlled by the availability of dissolved arsenate, which is measured by the integral of dissolved arsenate concentrations against incubation time and shown to correlate with the first order rate constants. Thus, the mobilisation of adsorbed As(V) can be regarded as the rate determining step of microbial reduction of As(V) sorbed to ferrihydrite. High lactate concentrations slightly slowed down the rate of arsenate reduction due to the competition with arsenate for microbial contact. Under all experimental conditions, simultaneous arsenate and ferrihydrite reduction occurred following addition of *S. putrefaciens* inoculums and suggested no apparent competition between these two enzymatic reductions. Ferrous ions released from iron reduction might retard microbial arsenate reduction at high arsenate and ferrihydrite concentrations due to formation of ferrous arsenate. At high arsenate to ferrihydrite ratios, reductive dissolution of ferrihydrite shifted arsenate from sorption to dissolution and hence accelerated arsenate reduction. Reductive dissolution of ferrihydrite may cause additional releases of adsorbed As(V) into solution, which is especially effective at high As(V) to ferrihydrite ratios. In comparison, formation of Fe(II) secondary minerals during microbial Fe(III) reduction were responsible for trapping solution As(V) in the systems with high ferrihydrite but low As(V) concentrations. In summary, the interaction between microbial arsenate and ferrihydrite reduction did not correlate with ΔG_{rxn}, but instead was governed by geochemical and microbial parameters, which may substantially influence the mobility of arsenic.