Investigation of iron oxyhydroxides reduction and associated metals release in soils using an *in-situ* iron-coated support

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Iron oxyhydroxide dissolution and precipitation are important control of element such as metal and organic matter solubilization and immobilization in soil solution. Knowledge of iron biogeochemistry is thus essential to understand soil behaviour. Dissolution of iron oxyhydroxides under reductive conditions have been extensively studied in the laboratory, (i) either in simplified batch experiments that have synthetic iron oxide mixed with a chemical reducer (hydroxylamine, ascorbic acid) or (ii) by performing anaerobic incubation of natural soil samples. However, both approaches are faced with several problems. In the simplified systems, the role of other soil phases such as clays and/or organic matter is not taken into account. In soil incubation experiments, the chemistry and crystallography of the iron oxides is little known since it is difficult to separate them from the soil matrix. In the present study, a new and original in situ methodology is proposed. Several iron oxides -amorphous: ferrihydrite, mixed: lepidocrocite or well crystallized: goethite- spiked with metals (Cd, Pb, Cu and As) were fixed on an inert polymer support and directly inserted in a controlled way in selected soil profiles. They were then recovered after definite time intervals. Such conditions allow the whole mineral surface to be exposed and to interact with the surrounding soil solution and organic or mineral components. This technique allows the study of the iron oxide surface after a long-term in-situ exposure to natural soil without any difficulty to isolate the mineral from the matrix. The first experiment was set up in controlled conditions in the laboratory. The iron coated supports were mixed in batches with a suspension of an organic-rich soil recovered in a previously studied wetland. Reductive conditions were induced under anaerobic conditions, either by the autochthon biomass, or by chemical reducers. In the second experiment, iron coated supports were inserted directly in the field into lysimetric cases where reductive conditions are forced by imposed storage of stagnant water above the studied soil sequence. Water samples were collected under a nitrogen pressure to preserve the anaerobic conditions. Fe(II) and associated released trace-metal concentrations were controlled in the soil solution. Supports were collected under inert atmosphere to allow the analysis of the mineral phases. The iron oxides on the support were then analysed to: (i)study their alteration and development of new mineral phases using XRD and TEM and (ii) to allow the dynamics of the metals possibly associated to these secondary phases be constrained.

Microbially controlled selenate reduction in nutrient limited systems

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Introduction

The widespread contamination of aquatic ecosystems with selenium has led to growing concern regarding the factors that control the distribution, fate, and bioavailability of selenium in these settings. Of specific concern is the more mobile anionic species which have a relationship with mortality and teratogenic mutations in many aquatic species.

In this study we provide evidence that *Shewenella putrafaciens* mediates the reduction of selenate and selenite in experimental systems devoid of nutrients. Considering the ubiquity of microorganisms in near-surface geological environments and that many of these systems are considered nutrient poor this mechanism may have important implications for Se cycling and bioavailability in these settings.

Results and Discussion

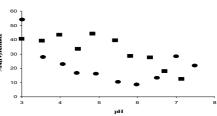


Figure 1: Reversibility of selenate removal as a function of pH. After 2 hours reaction time (squares) at pH 3 samples were readjusted to their final pH. Also presented here are the results of 2 hour adsorption experiment (circles).

Our preliminary results from batch kinetics, reversibility and adsorption experiments at multiple ionic strength and pH conditions indicate that *S. putrifaciens* irreversibly (Fig 1) removes some selenate from our reactors. Analysis of the reaction products via XANES techniques indicate that the irreversible Se fraction is reduced selenate in the form of elemental selenium associated with the cell wall of *S. putrifaciens*.

Conclusions

Results from this study indicate that *S. putrafaciens* is capable of both dissimilatory reduction of Se and reduction via other pathways which do not utilize a carbon substrate.