Impact of Aggregate-scale Heterogeneity of Transport and Biogeochemical Processes on Selenium Mobility in Soil

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Project Objectives

The overarching objective of this project is to determine how the combined effects of local variation in mass transfer and biogeochemical processes that operate from micron to cm scales govern the fate and transport of selenium (Se) in soils. To reach this goal, biogeochemical processes and physical complexity of soils at the aggregate scale will be integrated to quantify reaction rates and identify rate-controlling processes. The specific objectives that have been addressed so far are: 1) to determine the aggregate-scale physical and biogeochemical processes controlling the fate and transport of Se within soils; and 2) to identify diffusional constraints on biogeochemical reactions of Se and associated mobility within soils.

In line with recent publications demonstrating abiotic reduction of selenite by ferrous iron (Charlet et al. 2007; Scheinost and Charlet 2008) and after discussion with one of their authors (L. Charlet), the scope of our study was refined in order to explore further the decoupling between biotic and abiotic processes when affected by mass transfer limitations. Abiotic reduction of Se by iron (Fe) as well as Se sorption to Fe-oxides are now investigated in artificial soil aggregates in the present project for comparison with biotic cases.

Approach and Procedures

Following the review panel’s advice, the field component of the project has been eliminated, and the current research is focusing on characterizing model aggregate systems in terms of bacterial processes, transport, redox processes, and speciation. Well-controlled synthetic systems have the advantage that more advanced interpretations of important processes can be made, which can then be extrapolated to field settings and incorporated into future field experiments. Our experimental device consists of a single artificial aggregate (made of sand or Fe-coated sand and inoculated with a Se-reducing bacterium) that is placed at the center of a flow-through reactor cell. The flow rate and the composition of the input solution are controlled, and reaction rates can be measured at quasi-steady-state. Both solution and solid phase data are acquired by 1) analyzing liquid samples that are regularly collected at the reactor outflow throughout each experiment; and 2) determining the intra-aggregate spatial distribution of Se speciation. A series of preliminary batch experiments have been performed in order to test the effect of a range of environmental parameters on the Se reduction rates by Enterobacter cloacae SLD1a-1. Those results will be used to design the optimal conditions under which to run the artificial aggregate experiments.

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Results and Discussion

The first year of our project has been devoted to setup in our new lab the techniques necessary to run the project successfully, including the flow-through reactor setups and the analytical techniques to measure Se speciation, and to improve and finalize the reactive transport model for Fe-coated sand aggregates. So far, only a first-year graduate student has been involved in the project, limiting the amount of results that could be obtained. However, another graduate student, a part-time postdoctoral fellow, and two undergraduate students have joined our research group and are now all working on the present research project. Consequently, we are confident that enough results will be obtained in the second year of funding to finalize the project. Some experiments have been run and samples acquired but no quantitative results are available yet. In fact, we are waiting for beamtime access to analyze our solid phase samples (micro-XAS [X-ray absorption spectroscopy] and fluorescence mapping), and we are still currently working on improving the quality of the liquid samples analyses for Se speciation in presence of organic compounds (using hydride generation/ICP-OES). Research progress during the first year of funding can be summarized in the four points listed below:

1) Our proposal was involving the use of *Thauera selenatis*, a facultative anaerobe that reduces $\text{SeO}_4^{2-}$ only while growing anaerobically (Macy et al. 1993). However, our study has been initiated by using another bacterium, *Enterobacter cloacae* SLD1a-1, that has the ability to grow under aerobic conditions and can use $\text{SeO}_4^{2-}$ as an alternate electron acceptor in microaerophilic environments. Both bacterial strains are perfect candidates for our study at the aggregate scale in which redox gradients are known to occur. Since the artificial aggregate experiments are time-consuming and difficult to setup, we ran preliminary batch experiments to characterize the reduction potential of the model bacteria in response to various environmental factors, which would help us decide on the experimental conditions to use for the aggregate experiments. For that purpose, batch experiments have been run to test the effect of selenate concentrations, pyruvate concentrations, temperature, bacterial density, presence or absence of Fe(II), and presence or absence of oxygen on selenium reduction rates.

2) We optimized the experimental setup to run flow-through experiments using artificial aggregates under both aerobic and anaerobic conditions and a first set of experiments have been run, covering eight different conditions. Those first-run aggregates were made of sand/agarose and *E. cloacae*, but did not contain iron. The purpose was to look at the diffusion effects and mass transfer limitations on Se reduction and speciation. Future steps will include incorporation of the Fe component, using Fe-coated sand aggregates to test abiotic Se reduction but also abiotic competitive adsorption. From the experiments ran so far, thin sections have been prepared. We tested making non-resin impregnated thin sections from our artificial soil aggregates, but they were too thick to get satisfying results with micro-XAS and fluorescence mapping. Consequently, we are now working with resin-embedded aggregate thin sections. The resin used is EPO-TEK 301-2FL from Epoxy Technologies, Inc., that has been shown to preserve the oxidation states through the embedding, thin sectioning and microbeam measurement, as observed for Fe, U and As (C. Fuller and Y. Masue personal communications). An important part of our project progress is the submission of a proposal to the Advanced Light Source (ALS) in order to get beamtime on line 10-3-2 to analyze the thin section samples.
An important component of our proposed research was the use of a reactive transport model of the aggregate system. In addition to the experimental work he did, the graduate student involved in the project has been working on improving and finalizing the reactive transport model for our Fe-aggregate system. This resulted in a presentation at the American Geophysical Union Fall Meeting (Kausch et al. 2008) and a manuscript is in preparation. The model will now be adapted to include Se transformations.

During the first year of funding, we have also worked on setting up a method to measure Se speciation with hydride generation-ICP-OES in our lab. In order to obtain values for both selenite and selenate content, it is necessary to measure an aliquot of each sample directly and a second after quantitatively reducing all selenate to selenite (Bye and Lund 1988). A series of reduction conditions with different temperature and reduction times was tested in order to determine the optimal conditions to yield adequate Se recoveries. This method optimization was successful and allows for low-detection limits, but some recent problems have been identified when measuring Se in presence of organic compounds, and we are currently working on adapting the analytical method to samples containing organics.

References:


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