Impact of ferrihydrite coating and aeration conditions on microbial selenium (Se) reduction and retention in artificial soil aggregates

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Soils display large variations with respect to their physical, geochemical and biological characteristics at scales ranging from nanometers to kilometers. The impact of this heterogeneity on biogeochemical processes is as of yet poorly understood. In structured soils, the aggregate scale (mm-cm) is of particular interest due to the sharp transition in pore size at the surface of aggregates. Small intra-aggregate pores limit advective transport thus facilitating the formation of chemical concentration gradients that promote spatial variation in biogeochemical processes. One such process is the microbial reduction of selenium (Se), both an essential micronutrient and a toxicant. A mechanistic understanding of Se reduction within soil aggregates may lead to improved prediction of its transport and attenuation in soils of contaminated areas.

In order to investigate the coupling of physical and biogeochemical processes controlling Se reduction at the aggregate scale, we used artificial aggregates in flow-through reactor cells, mimicking the interface between soil micropores and macropores. Aggregates were constructed using either uncoated sand or ferrihydrite-coated sand homogenously inoculated with Se-reducing bacteria (*Thauera selenatis* and *Enterobacter cloacae* SLD1a-1 were compared). Saturated flow of aerobic or anaerobic artificial groundwater medium containing selenate and an electron donor, was initiated. Concentrations of selenite and total Se were measured in the outflow solution and in concentric sections of the aggregates' air dried solid phase.

Selenite export rates from aggregates increased by a factor of 600 between aerobic *T. selenatis* reactors with low selenate and acetate input and anaerobic *E. cloacae* reactors with high selenate and pyruvate input. Aerobic input solution significantly decreased Se reduction, however, the presence of a selenite signal indicates the occurrence of anaerobic/microaerobic microzones within aggregates. Solid phase selenite concentrations increased from the exterior to the core under aerobic as well as anaerobic conditions within both sand and ferrihydrite-coated sand aggregates. This is an indication that soil structure can impact Se retention in soils under a diverse set of conditions and that consideration of aggregate scale reactive transport may be essential for a complete understanding of field dynamics.

Metal mobility in clay formations – From batch experiments with mineral suspensions to column setup with compacted clay

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Nowadays, there is a broad consensus on the technical merits of the disposal of high-level nuclear waste (HLW) in deep and stable geological clay formations. For the long-term disposal of radioactive waste, detailed information about geochemical behaviour of radioactive and toxic metal ions under environmental conditions is necessary.

In our project europium, gadolinium (homologues of americium and curium) and uranium were used and their sorption and desorption behaviour onto Opalinus clay was studied [1]. Natural organic matter (NOM) can play an important role in the immobilisation or mobilisation of metal ions due to complexation and colloid formation. This complexation could interfere the sorption of metal ions onto clay. In addition to humic acid (HA) we used other natural appearing organics in Opalinus clay like lactate, formiate or propionate [2]. Therefore, we investigated the complexation behaviour of the metals with NOM as well as the influence of present NOM on the metal sorption onto clay [3].

Capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry (CE-ICP-MS) has been used to study the complexation behaviour of Eu (III), Gd (III) and U (VI) with HA. The influences of metal concentration as well as the presence of competing cations from clay dissolution as well as cations from clay porewater on the complexation behaviour was analysed [4]. For the sorption/desorption behaviour common batch experiments with mineral suspensions are performed, and in comparison a miniaturised column setup with compressed clay was used to study the influence of NOM on the metal mobility in compact Opalinus clay.

The authors thank the BMWi for financial support (grant no. 02E9683 and 02E10196).

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