Project Report on FIMIN travel grant: 3363

Biogeochemical link between iron and mercury cycling in field and laboratory systems

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Host: Prof. Ulf Skyllberg, SLU Umeå, Sweden
Date: Mai 31 – July 15, 2011 (6 weeks)

1. Purpose of visit

The purpose of the exchange visit to Umeå was twofold: (1) collection of field samples from forest clear-cut areas in the region of Umeå (Sweden), and (2) laboratory experiment with enriched isotope spikes investigating the sorption of mercury to goethite.

2. Field study on iron and mercury cycling in forestry soils

The clear-cutting of forest areas results in significant changes in the hydrology and the prevailing biogeochemical conditions in soils. The development of anoxic conditions (e.g., iron-reducing) can for instance stimulate the formation of toxic methyl mercury which can be leached from the site into surrounding ecosystems. The exact mechanisms which govern the rates of methylation and demethylation of Hg in nature are still largely unknown. In one part of my PhD project I plan to use natural Hg and Fe isotope signatures in soils as tracers to better understand the link between mercury and iron cycling in these forestry soils. This work is embedded in a broad collaboration led by Ulf Skyllberg and involves different methods such as speciation analysis, microbial characterization, and isotope analysis. Together with Rose-Marie Kronberg, a PhD student of Ulf Skyllberg, I performed a soil sampling campaign during my exchange stay in Umeå. We sampled 8 forest soils, wherefrom four have been harvested in 2009 and represent the clear-cut areas and four reference sites which are covered by over 80 years old spruce forests.
Figure 1 shows a podsol close to a creek of a reference stand close to Junsele. On each sampling site five composite samples were taken, representing a gradient from wet to dryer conditions. Each sample was further divided in Of and Oh horizon. In addition to the organic horizon samples, we sampled the bleached Ae-horizon and the underlying Bs horizon. All samples were brought to the lab, homogenized, sieved and split for different analyses. The subsamples for total elemental composition and isotope measurements were dried and are now being shipped to Switzerland. In the next weeks the samples will be analyzed for total elemental composition (CHNS organic analysis, XRF- spectroscopy, and combustion-AAS for total Hg analysis). Based on the elemental composition a subset of samples will be selected for analysis of its Hg and Fe isotopic composition.
Originally I planned to take large quantities of water samples which I wanted to process in the laboratory in Umeå. Unfortunately technical problems related to the clogging of filter membranes occurred during the processing of the first sample and I was not able to solve these problems during my stay. Another attempt to collect water samples from the sampling areas will be undertaken at a later time.

Figure 1: Soil profile (Podsol) in a reference stand close to Junsele, Sweden

3. Laboratory experiment on sorption of mercury to goethite

Mineral phases like iron(oxihydr)oxides are important sorbents for mercury and other heavy metals in mineral soils. As part of my PhD project I investigate the stable mercury isotope fractionation during sorption to goethite (α-FeOOH) under equilibrium conditions. The aim for this project is to quantify and understand the isotope fractionation mechanisms of such individual biogeochemical processes. Sorption of mercury to goethite causes isotope effects which are about 5 times higher than the analytical precision. Although we are able to resolve systematic trends by investigating the natural abundant isotopes, it is hard to judge, whether our experimental setup is equilibrium controlled. Therefore we decided to perform an experiment with monoisotopic enriched mercury spikes. Erik Björn, Lecturer in analytical chemistry at Umeå University, has a lot of experience with mercury isotope spike analytics and offered me his help and lab for the experiment. We spiked ^{198}Hg to goethite and let it equilibrate for 48 hours under continuous shaking. After this equilibration time the suspension was centrifuged and the concentration of the supernatant was measured. In a second step ^{201}Hg was added to the goethite at the same concentration as the removed ^{198}Hg. The goethite was resuspended and samples were taken between 1 and 48 hours with the aim to determine the rate of desorption under these equilibrium conditions. The concentrations of ^{198}Hg and ^{201}Hg were measure by quadrupole-ICP-MS. The experiment revealed that between 1 and 48 hours after spiking of the second isotope there is no detectable desorption taking place.

4. Projected publications and future collaboration

After the soil sampling campaign the sampled are now shipped to Switzerland. During the next months they will be analyzed. As unfortunately the water sampling campaign failed during my stay, I will probably go back to Umeå in 2012 to take water samples. In this context my stay in Umeå this summer was a first stage in a longer collaboration with Ulf Skyllberg and his group throughout my PhD. It is our goal to have as a final result a publication on the link between iron and mercury cycling in Swedish forestry soils investigated by natural Fe- and Hg- isotopes.

The results of the mercury spike experiments are currently being evaluated. Probably they will be incorporated in the work with the natural isotopes. A publication on Hg isotope fractionation during sorption of Hg(II) to goethite is planned to be submitted late 2011/ early 2012. I already presented some results of the lab experiments with enriched isotope spikes in an oral presentation at the 10th International Conference on Mercury as a Global Pollutant (Halifax, Canada, July 24-29th, 2011). In september 2011, I will present a poster at the 13th International Conference on Chemistry and the Environment (Zurich, Switzerland) on which I will also display some data which were collected during my exchange visit in Umeå.

5. Other comments

I had a wonderful time in Umeå. The new environment and especially the enthusiastic people who took care of me allowed me to learn a lot and to widen my view on the interaction of iron and mercury and on science in general. Therefore I would like to thank the FIMIN training network for the financial support and for giving me the chance to benefit from this exchange stay. I also would like to encourage other PhD students who work with iron in the environment to plan a stay at another university and to ask FIMIN for financial support.