Microbial mobilization / volatilization of selenium sorbed on soil minerals

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Selenium has major nutritional and biological function but the range between essential and toxic concentration is very small. The more toxic Se(IV) and Se(VI) are water soluble and hence bioavailable. The iron oxide and clay content of soils can affect the bioavailability through adsorption reactions, whereby Se(IV) is stronger adsorbed than Se(VI) [1]. The most reliable natural attenuation process of enriched Se in the environment is microbial methylation [2].

In order to investigate the alkylation / methylation process, *Alternaria alternata*, known as a Se resistant and active methylating saprophytic fungus [3], was used for incubation studies. First we observed the alkylation of dissolved inorganic selenium (SeO_3^{2-}, SeO_4^{2-}) and found different alkylated species over a wide pH range. Then, different selenium enriched materials, e.g. goethite enriched by SeO_3^{2-} or SeO_4^{2-} adsorption, were incubated with *A. alternata* inoculums to study the dependence of solid selenium binding on alkylation reactions. For Se speciation studies we used different analytical tools. Volatile selenium species were measured with a cryotrapping / cryofocussing gaschromatographic system coupled with ICP-MS. Beside the dominantly occuring dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe) we found also other alkylated species like diethyl selenide (DESe) and diethyl diselenide, especially in dissolved selenium experiments. In adsorption experiments the aqueous inorganic selenium species were measured by hydride generation – atomic absorption spectroscopy. In icubation experiments we used a hyphenated HPLC-ICP-MS to separate the dissolved selenium species.

In our incubation studies we found different patterns of alkylation of dissolved and adsorbed selenium. For dissolved Se, Se(IV) were alkylated in higher amounts and we found more volatile species than for Se(VI) caused by a lacking reduction step in the methylation mechanism [4]. In the opposite we found a higher methylation for Se(VI) than for Se(IV) adsorbed on soil minerals because of different kinds of adsorption [5].

References

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Speciation of Cd, Cu and Pb by DPASV in unpolluted soil solutions

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The mobility and the bioavailability of trace elements in soils are largely dependent upon their interactions with various organic and mineral ligands. These interactions control trace metal concentration and speciation in complex geochimical systems. The aim of this work is to determine the chemical speciation of cadmium, copper and lead in subsurface waters circulating in an unpolluted soil (Planosol). The study area is located on the Aigurande plateau in the northern part of the Massif Central (France). The substratum is composed of Paleozoic gneiss and intrusive granitic rocks. Soil solutions were collected in a gravely and concretion-rich horizon (Fe- and Mn- oxyhydroxides) from 2004 to 2006 during the soil saturation period.

Chemical speciation of Cd, Cu and Pb was obtained by titrating the filtered water samples using differential pulse anodic stripping voltammetry. Cd, Cu and Pb have been chosen principally because of their various behaviours in the soil solutions. The aim of these experiments is to determine the apparent stability constant K and the corresponding apparent ligand concentration (i.e. complexation capacity CC) using graphic method and the linear transformation method decribed by Ruzic (1982). A 1:1 complexing model was applied for result interpretation. Polarographic curves of Cd and Cu show significant peaks which may be associated with metal complexes. However, the copper titration curves underline different processes (complexation, adsorption and both processes) and provide evidence for “slow” kinetic reactions (in the experimental conditions). The cadmium titration curves show complexation processes and fast kinetic reactions. Results for measurement of complexation parameters are differently discussed for both metals. To evaluate the copper potential binding in all cases, potential distribution coefficients (Kd) are calculated based on (1) the estimation of K (complexation processes) and (2) the estimation of the number of sites available for metal association using potentiometry (adsorption processes). Potential Kd indicate that copper has a stronger affinity for complexation processes on organic compounds than adsorption processes. No significant seasonal variation pattern in the potential Kd parameter is observed. For cadmium, CC and K results show seasonal evolutions which can be linked to soil solution modifications and/or presence of various ligands. Pb experiments are actually in progress.

As a conclusion, voltammetry data give evidence about relationships between trace metals, organic matter and soil compounds.