4.65.41

Quantitative antimony speciation in Swiss shooting range soils

A.C. SCHEINOST[1], A. ROSSBERG[1], CH. HENNIG[1], D. VANTELON[2], R. KRETZSCHMAR[2] AND C.A. JOHNSON[3]

[1] Biogeochemistry Group, Forschungszentrum Rossendorf, D-01314 Dresden, Germany (scheinost@esrf.fr)
[2] Institute of Terrestrial Ecology, ETH Zurich, CH-8952 Schlieren, Switzerland
[3] Swiss Federal Institute for Environmental Science and Technology (EAWAG), CH-8600 Duebendorf

Antimony is used to harden the Pb cores of ammunition. Thus, between 4 and 10 tons of Sb are annually deposited on Swiss shooting ranges by bullets. Due to the relatively rapid weathering of the bullets, Sb is released into the soil, but little is known about its further fate. As part of investigations to determine the geochemical factors that control Sb mobility, we have determined the oxidation state and species of Sb in 6 shooting-range soils, using a combination of EXAFS (extended x-ray absorption fine structure) spectroscopy and ITFA (iterative transformation factor analysis), a technique particularly suited for quantitative speciation in complex matrices [1, 2].

Antimony concentrations varied between 1,000 and 17,000 mg/kg. In spite of a wide range of soil chemical conditions (pH, mineral and organic matter composition), we found only two Sb species. In the first species, Sb is surrounded by 6 O atoms at a distance of 1.97 Å, by 1 Fe atom at 3.09 Å, and by 2 Sb atoms at 3.33 Å. This arrangement suggests pentavalent Sb sorbed onto Fe or Mn oxides by forming a polynuclear inner-sphere sorption complex.

In the second species, Sb is surrounded by 2 O atoms at a distance of 1.98 Å, and by Sb atoms at 2.91 Å, 3.35 Å, 4.30 Å, and 4.52 Å. This structure is consistent with Sb(III) (hydr)oxide.

The (hydr)oxide species prevailed in a very acidic soil (pH 3.1), the sorption complex prevailed in a slightly acidic soil, and mixtures of both species occurred in calcareous soils (pH 7.5).

The results for Sb(V) are in agreement with previous findings suggesting that Sb is bound to Fe oxides. Antimony(III) solubility appears to be controlled by Sb(III) (hydr)oxide. Our results suggest that Sb remains tightly bound in soils, confirming our previous macroscopic observation that Sb is strongly enriched in the uppermost layer of a soil profile [3].

References

[1] Scheinost A. et al. (2003) *Physica Scripta*, in press.
[2] Rossberg A. et al. (2003) *Analyt. Bioanalyt. Chem*. **376**, 631-638
[3] Knechtenhofer L. A. et al. (2003) *J. Plant Nutr. Soil Sci.* **166**, 84-92.

4.65.42

Selenite mobility in soils: Implication of chemical and microbiological processes

L. FEVRIER AND A. MARTIN-GARIN

Institute for Radiological protection and Nuclear Safety, DEI/SECRE/LRE, Bldg 186, Cadarache, BP3, 13115 Saint Paul-lez-Durance Cedex, France (laureline.fevrier@irsn.fr)

Understanding the biogeochemical behaviour of selenium in the biosphere is of major concern in ecotoxicology [1] but also in radioecology due to its presence as a long-lived radionuclide (^{79}Se) in the nuclear wastes. In moderately oxidizing conditions like surface soils, selenium exists as selenite (Se(IV)) which can react with mineral particles [2] but also with microorganisms [3]. This study investigated the role of abiotic and biotic processes in the control of Se(IV) mobility in soils.

Selenite, radio-labelled with ^{75}Se, was used at an environmentally relevant concentration of 1.3 µmol/l. A 2 mm-sieved calcareous silty clay soil (from Bure, France) was studied. Selenite mobility was investigated by column experiments both for water saturated and non saturated soils. Microbiological processes were screened in a set of batch experiments with soils constrained to different microbial states (sterilized, raw or amended soil). Total Se concentration, Se(IV) concentration and amount of Se in the fraction > 0.22 µm were determined.

Percolation of selenite through soil columns revealed a strong retention of Se in the top layer of the soil linked to a very slow migration in depth, whatever the soil water saturation state. Se strong retention was due to a dual contribution of abiotic and microbiolological processes. The latter led to a kinetically-limited sorption correlated with the reduction of aqueous Se(IV). Adding glucose and nitrate as soil amendments increased Se retention in soil. In that case, the presence of a Se associated to a > 0.22 µm fraction suggested the existence of a direct and specific interaction between selenite and microorganisms. The consequences of these various processes on Se fate in soils will be discussed. This study was carried out in a joint program with Andra (Nuclear Waste Management French Agency)

References

[1] Haygarth P.M. (1994) *Selenium in the environment*, Marcel Dekker, New York, 1-7.
[2] Myneni S.C.B., Tokunaga T.K., and Brown Jr. G.E. (1997) *Science* **278,** 1106-1109.
[3] Garbisu C., Ishii T., Leighton T., and Buchanan B.B. (1996) *Chem. Geol.* **132,** 199-204.