Quantitative antimony speciation in Swiss shooting range soils

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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