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# Quantitative Antimony Speciation in Shooting-Range Soils by EXAFS Spectroscopy and Iterative Transformation Factor Analysis

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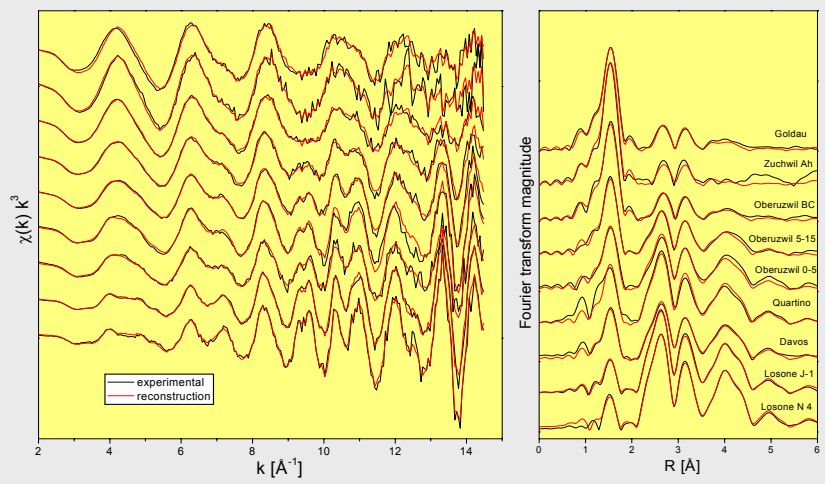
## Introduction

- Ca. 100,000 tons Sb mined annually.
- Toxicity similar to As, with Sb(III) 10x more toxic than Sb(V).
- Sb is used to harden the Pb cores of bullets (1-2% Sb). Since ca. 100,000 tons of bullets are deposited in the soils of shooting ranges each year, 1,000-2,000 tons of Sb reach the environment via this path.
- Very little is known on the geochemical behavior of Sb in the environment.
- For the first time, we were able to determine the chemical species of Sb and their distribution in soils, using EXAFS spectroscopy combined with a statistical approach (ITFA), a technique particularly suited for quantitative speciation in complex systems like soils (Scheinost et al. 2004).

## Materials & Methods

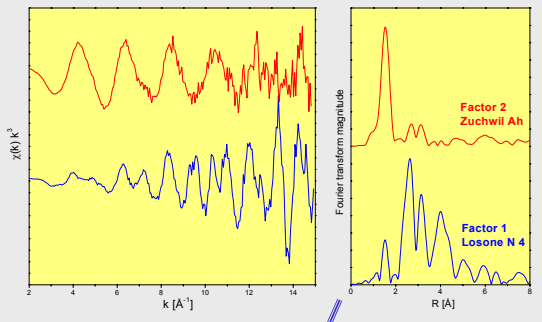
- Soil samples from 6 Swiss shooting ranges
- pH: 3.1 – 7.5
- Sb: 1000 – 17000 mg/kg
- EXAFS measurements at ROBL
- Sb K-edge: 30,491 eV
- Fluorescence with 4-element Ge detector
- Cryostat at 20 K to reduce thermal vibrations
- Iterative Transformation Factor Analysis (ITFA) as in Rossberg et al. (2003)

## Sb K-edge EXAFS spectra of soil samples



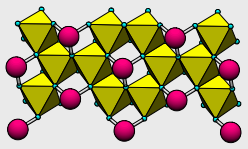

- All spectra can be reconstructed with two spectral components, indicating that only two species are present

## Identification of Sb species



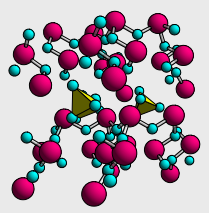

**Species 2:**
**Sb(V) polynuclear IS sorption complex on Fe (or Mn) oxides**

| CN | R / Å | σ / Å² |
|---|---|---|
| 5.9 O | 1.97 | 0.0030 |
| 1.2 Fe | 3.09 | 0.0024 |
| 1.8 Sb | 3.33 | 0.0056 |

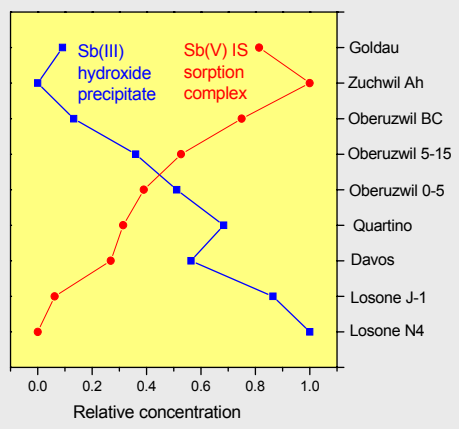


**Species 1:**
**Sb(III) hydroxide**

| CN | R / Å | σ / Å² |
|---|---|---|
| 1.2 O | 1.98 | 0.0019 |
| 2.1 Sb | 2.91 | 0.0016 |
| 2.7 Sb | 3.35 | 0.0037 |
| 7.5 Sb | 4.30 | 0.0063 |
| 4.2 Sb | 4.52 | 0.0024 |



## Quantification of Sb species




- **Species 1** prevails in acidic (pH 3), organic matter-rich soil (Losone)
- **Species 2** prevails in slightly acidic soil (Zuchwil)
- Species **1 and 2** are both present in calcareous soils (all others)

## Conclusions

- Inspite of a wide range of chemical conditions (pH, mineral composition, organic matter, etc.) present in the investigated soils, only two species could be detected: a Sb(III) hydroxide phase and Sb(V) sorbed to Fe (or Mn) oxides.
- The biogeochemical factors influencing distribution of Sb among the two species are unclear.
- Since the solubility of Sb(III) hydroxides is low, the more toxic Sb(III) is efficiently immobilized.
- Sb(V) is also tightly bound by formation of an IS sorption complex.
- **Our results suggest a low mobility and relatively small environmental risk of Sb in shooting range soils.**

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**References:**
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Scheinost, A. C.; Rossberg, A.; Marcus, M.; Pfister, S.; Kretzschmar, R. *Physica Scripta* **2004**, in press.