



Antimony retention and release from drained and waterlogged shooting range soil under field conditions



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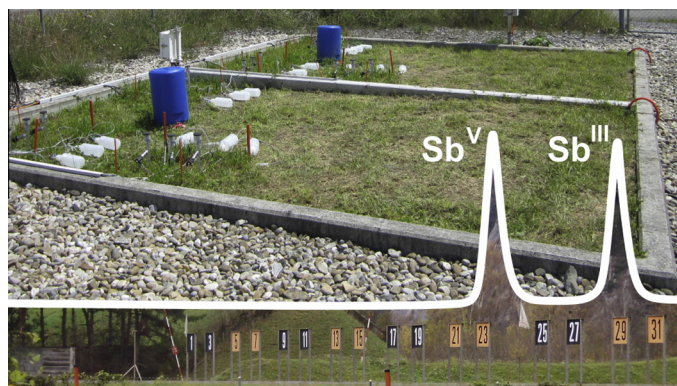
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HIGHLIGHTS

- Sb in leachate from drained and waterlogged lysimeters was monitored for >2.5 years.
- Sb concentrations under drained conditions showed a strong seasonal fluctuation.
- With the onset of waterlogging, Sb(V) was reduced to Sb(III).
- This caused Sb in leachate to decrease from $\sim 80 \mu\text{g L}^{-1}$ to $<5 \mu\text{g L}^{-1}$.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 July 2014

Received in revised form 14 November 2014

Accepted 2 December 2014

Available online 12 January 2015

Handling Editor: X. Cao

Keywords:

Sb speciation
Redox potential
Microbial reduction
Sb leaching
Transport
Eh

ABSTRACT

Many soils polluted by antimony (Sb) are subject to fluctuating waterlogging conditions; yet, little is known about how these affect the mobility of this toxic element under field conditions. Here, we compared Sb leaching from a calcareous shooting range soil under drained and waterlogged conditions using four large outdoor lysimeters. After monitoring the leachate samples taken at bi-weekly intervals for >1.5 years under drained conditions, two of the lysimeters were subjected to waterlogging with a water table fluctuating according to natural rainfall water infiltration. Antimony leachate concentrations under drained conditions showed a strong seasonal fluctuation between $110 \mu\text{g L}^{-1}$ in summer and $<40 \mu\text{g L}^{-1}$ in winter, which closely correlated with fluctuations in dissolved organic carbon (DOC) concentrations. With the development of anaerobic conditions upon waterlogging, Sb in leachate decreased to $2\text{--}5 \mu\text{g L}^{-1}$ Sb and remained stable at this level. Antimony speciation measurements in soil solution indicated that this decrease in Sb(V) concentrations was attributable to the reduction of Sb(V) to Sb(III) and the stronger sorption affinity of the latter to iron (Fe) (hydr)oxide phases. Our results demonstrate the importance of considering seasonal and waterlogging effects in the assessment of the risks from Sb-contaminated sites.

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1. Introduction

In the recent past, human activities have led to highly elevated Sb concentrations in many soils and consequently to increased exposure of biota to this toxic and potentially carcinogenic element (Hockmann and Schulin, 2013). A significant input of Sb into the environment occurs at shooting ranges, because lead ammunition contains 2–5% Sb as a hardener (Johnson et al., 2005). Although confined to locally rather small areas, this contamination poses a major environmental problem due the large number of shooting ranges. In Switzerland, for example, up to 25 tons of Sb enter the pedosphere every year on more than 2000 shooting ranges (Mathys et al., 2007). The United States has about 3000 military and 9000 civilian shooting ranges with an estimated annual Sb deposition of 1900 tons (Wan et al., 2013a). Shooting ranges have recently come into the focus of public concern also in other countries, notably Finland (Sorvari et al., 2006; Sorvari, 2007), Norway (Stromseng et al., 2009), and Canada (Laporte-Saumure et al., 2011). Antimony concentrations in ground (Wersin et al., 2002) and stream water samples (Stromseng et al., 2009; Heier et al., 2010) in the vicinity of shooting ranges have been found to exceed background concentrations by a factor of more than 20 in some studies, indicating a potential risk of uncontrolled Sb release from such sites.

A key factor of Sb mobility and thus its potential migration into the environment is the redox state, which depends on soil aeration and hence on the soil water regime. Based on thermodynamic equilibrium calculations, the pentavalent Sb(V), which is typically present as the oxyanion $\text{Sb}(\text{OH})_6^-$ (antimonate), is the stable Sb redox species in aerated soil solution (Filella et al., 2002). It has been suggested that its high affinity to Fe and manganese (Mn) (hydr)oxides (Leuz et al., 2006; Scheinost et al., 2006; Mitsunobu et al., 2010) and the solubility of calcium (Ca) antimonates are critical factors controlling the retention of Sb in soils under oxic conditions (Johnson et al., 2005; Okkenhaug et al., 2011, 2012). However, Sb K-edge X-ray absorption spectroscopy (XAS) measurements on highly calcareous shooting range soils (Scheinost et al., 2006; Hockmann et al., 2014) did not indicate the presence of Ca antimonates, rendering their role in the mobility of Sb in shooting range soils uncertain. Furthermore, competition by dissolved organic carbon (Hockmann and Schulin, 2013) and anions (Biver et al., 2011) (e.g. bicarbonate) for sorption sites has been proposed to enhance Sb mobility, but studies investigating this effect in soils are lacking.

Under reducing conditions, as commonly found in poorly drained and flooded soils (Reddy and DeLaune, 2004), Sb(III) is expected to predominate in form of the neutral species $\text{Sb}(\text{OH})_3$ (antimonite) (Filella et al., 2002). Because $\text{Sb}(\text{OH})_3$ sorbs more extensively to Fe (hydr)oxides at circumneutral pH than its oxidized counterpart antimonate (Leuz et al., 2006; Hockmann and Schulin, 2013), it has been concluded that reducing conditions would generally decrease the mobility of Sb (Mitsunobu et al., 2006; Okkenhaug et al., 2012; Wan et al., 2013b). In contrast to this view, a recent incubation study on shooting range soil demonstrated that reducing conditions can actually increase the mobility of Sb due to reductive dissolution of Fe (hydr)oxides and release of previously bound Sb(III) (Hockmann et al., 2014). It is, however, not clear how important these processes are in the field and how they play out in combination with other processes involved in Sb leaching.

This lack of understanding of Sb behavior in soils subject to strong variations in redox conditions hinders a confident risk assessment and thus the derivation of appropriate remediation strategies as well as the setting of clean-up values for Sb-contaminated sites. The goal of this study therefore was to investigate how

waterlogging affects Sb leaching from a contaminated soil under field conditions, with a special focus on the relationship between soil redox conditions and Sb speciation. In an outdoor experiment with calcareous shooting range soil, lysimeters subjected to waterlogging were compared to lysimeters with the same soil left to drain freely. In addition to the leachate samples, also soil solution was sampled and analyzed for Sb speciation in order to link Sb leaching to the chemical processes occurring in the soil. To our knowledge, this is the first study investigating Sb leaching from waterlogged contaminated soil under field conditions.

2. Materials and methods

2.1. Soil characteristics

The soil used in the lysimeter experiment was taken from the upper horizon (0–30 cm) of a floodplain soil (Fluvisol) on a military shooting range close to the River Rhine in Eastern Switzerland (46°51'19"N and 9°30'11"E). After the removal of plant residues and large stones, the excavated soil was mixed once on site and again after transport using a dredger bucket, before it was filled on top of a quartz sand drainage layer (average thickness 28 cm) into the lysimeters. The fine earth material (80% w/w of the total soil) had a silt loam texture (US soil taxonomy, Soil Survey Division Staff, 1993), contained 20% CaCO_3 , 0.9% organic carbon and had a pH in water of 8.5. Total metal(oid) concentrations measured by energy-dispersive X-ray fluorescence spectroscopy (XRF; X-Lab 2000, Spectro) in the fine material were 21 mg kg^{-1} Sb, 29500 mg kg^{-1} Fe, 820 mg kg^{-1} Mn, and 520 mg kg^{-1} Pb. Having a Pb concentration within the range of 250–2000 mg Pb kg^{-1} (EMD and BUWAL, 1997), the soil been classified as “moderately contaminated”, for which cost-efficient remediation strategies as an alternative to soil removal and landfilling are currently investigated (Evangelou et al., 2012). Spatial heterogeneity in soil properties (pH, carbonates, organic carbon and total element concentrations) at the beginning of the experiment was low (Supplementary material Fig. S1). According to a previous Sb K-edge X-ray absorption near edge structure (XANES) analysis on the <2 mm fraction of this soil (Hockmann et al., 2014), Sb(V) was with 88% the dominant Sb redox species in the solid phase, most likely bound to Fe (hydr)oxide phases.

2.2. Lysimeter experiment

The experiment was carried out at the lysimeter facility in Horw in central Switzerland (47°00'03"N, 8°18'02"E, 441 m above sea level). The mean annual temperature in this area is 8.8°C and total annual precipitation amounts to 1171 mm (Evangelou et al., 2012). Four lysimeter basins with a surface area of 17.5 m^2 each filled with the study soil to a soil depth of 0.7 m were used for this study. A standard meadow grass-clover seed mixture (Semences UFA 444 AR, Switzerland) was sown into the lysimeters soil, but no nutrients were applied. During the growing season, which lasts from approximately mid-March to end-September at the lysimeter site, the meadow vegetation was cut every six weeks and removed.

The seepage water from each lysimeter was drained through slotted plastic tubes embedded in the quartz sand drainage layer and collected by an automatic sampler (Teledyne ISCO 3700) in fractions equivalent to 3 mm of discharge. The redox potential was monitored in situ (Mansfeldt, 2003; Reiser et al., 2012) at 10 cm, 20 cm, 37 cm, and 54 cm below the soil surface using customized platinum glass electrodes purchased from an electrode manufacturer (Willi Möller AG, Zurich, Switzerland). Three electrodes were installed at each depth. The redox potential was

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