Antimony mobility during prolonged waterlogging and reoxidation of shooting range soil: A field experiment

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HIGHLIGHTS

- Shooting range soil lysimeters were waterlogged for almost 3 years.
- Sb leachate and soil solution concentrations quickly decreased upon waterlogging.
- On reoxidation of the soil, Sb was remobilised.
- 1.5 years later Sb concentrations were still slightly lower in reoxidised lysimeters.

GRAPHICAL ABSTRACT
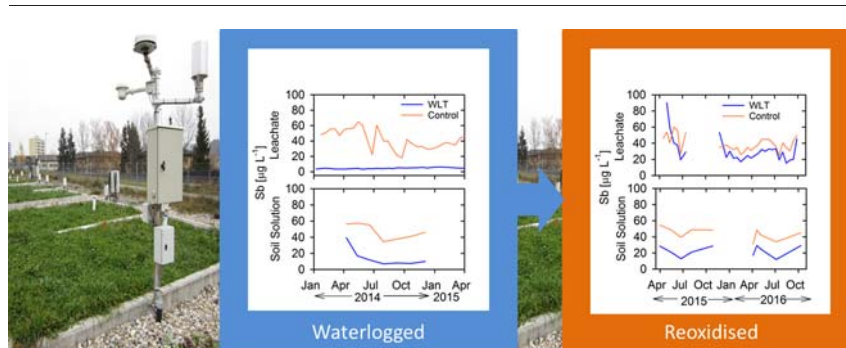
ARTICLE INFO

ABSTRACT

Due to its increasing anthropogenic use, antimony (Sb) soil pollution is of growing concern. Many soils experience fluctuating hydrological conditions, yet very little is known about how this affects the mobility of this toxic element under field conditions. In this study, we performed an outdoor lysimeter experiment to compare Sb leaching from a calcareous shooting range soil under drained and prolonged waterlogged conditions (1.5–2.75 years), followed by a 1.5-year period of soil reoxidation. Waterlogging reduced Sb leachate concentrations significantly compared to drained conditions and soil solution concentrations decreased with depth due to the increased reducing conditions. This was attributed to the reduction of Sb(V) to Sb(III) and the more effective sorption of the latter to metal (hydr)oxides. However, reductive dissolution of iron (hydr)oxides released Sb into solution, although Sb concentrations never exceeded those in the drained lysimeters. On reoxidation of the soil, Sb was remobilized, but even after 1.5 years under reoxidised conditions, Sb leachate and soil solution concentrations still remained below those of the drained lysimeters. Our results demonstrate that prolonged waterlogging may have an irreversible effect on Sb leachate and soil solution concentrations.

1. Introduction

Antimony (Sb), a priority pollutant in both the United States and the European Union, is becoming more and more prevalent in the environment due to human activity (Hockmann and Schulin, 2013). Sources of Sb release include abrasion from brake linings, use as flame retardants, the production of plastics, mining and shooting activities (He et al., 2012; Hjortenkrans et al., 2009; Hockmann and Schulin, 2013). In particular, mining soils and shooting ranges both have very high concentrations of Sb and are point sources of pollution. However, it has been shown in leaching tests that a larger percentage of the total Sb concentration may be mobilized from shooting range soil than from mining impacted soils (Lewińska et al., 2017). In several countries including the

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USA, Canada, Norway, Sweden, Finland and Switzerland, Sb migration from shooting ranges has become a major concern (Sanderson et al., 2015). In Switzerland between 10 and 25 t of Sb are deposited in shooting range soil each year (Mathys et al., 2007), while for the USA it is estimated to be 1900 t (Wan et al., 2013). Antimony also enters the soil from game and clay pigeon shooting and it is estimated that 100 t enter UK soils from this alone (Wan et al., 2013). Elevated concentrations of Sb have been found in both surface water (Heier et al., 2010; Mariussen et al., 2017; Martin et al., 2013) and groundwater (Martin et al., 2013; Wersin et al., 2002) in the vicinity of shooting ranges. It was also found that Sb groundwater concentrations could exceed those of streams (Martin et al., 2013). While most countries do not have guidelines for Sb in natural waters, those that do, such as Canada (Director Land Environment of the Department of National Defence, 2012) and Switzerland (The Swiss Federal Council, 2012), found these were exceeded in groundwater under small arms shooting ranges (Director Land Environment of the Department of National Defence, 2012) or in leachate from large lysimeters filled with shooting range soils (Hockmann et al., 2015).

Antimony is redox sensitive, and its mobility greatly depends on its oxidation state (Hockmann and Schulin, 2013), therefore the level of soil aeration and hence soil water content are important factors governing its behaviour in the environment. The most environmentally relevant oxidations states of Sb are $+V$ and $+III$ (Filella et al., 2002). In aqueous solutions under oxidising conditions the predominant species is $Sb(OH)_6^-$, the antimonate oxyanion, while under reduced conditions Sb(III) is predominant as the neutral antimonite species, $Sb(OH)_3$ (Hockmann and Schulin, 2013).

Manganese (Mn) and especially iron (Fe) (hydr)oxides are thought to be key constituents in most soils controlling Sb mobility (Belzile et al., 2001; Leuz et al., 2006; Liu et al., 2015; Okkenhaug et al., 2016). Under oxic conditions, the adsorption of $Sb(OH)_6^-$ to Fe (hydr)oxides is pH dependant, with adsorption to goethite, a major Fe mineral in temperate soils, becoming weaker at pH higher than six (Leuz et al., 2006). Calcareous shooting range soils may therefore represent an important source of Sb release into ground and surface waters.

Under anaerobic conditions, Sb is found as the reduced species $Sb(OH)_3$ (Hockmann and Schulin, 2013), which binds more effectively than $Sb(OH)_6^-$ to Fe (hydr)oxides over a wide range of pH (Leuz et al., 2006), resulting often in a decrease of Sb mobility under reducing conditions (Couture et al., 2015; Hockmann et al., 2014; Wan et al., 2013). However, under more strongly reducing conditions in batch and pot experiments, Sb has been found to be released again, as Fe (hydr)oxides become reductively dissolved (Frohne et al., 2014; Fu et al., 2016; Hockmann et al., 2014; Wan et al., 2013).

Large-scale leaching experiments of Sb, simulating oxic field conditions are rare in literature. Shangguan et al. (2016) recently investigated the leaching of Sb from a thin layer of mine-contaminated soil through four uncontaminated soils of different characteristics. Retention of Sb by the soils followed the trend alkaline sand < alkaline sandy loam < organic rich < iron rich. Okkenhaug et al. (2016) also investigated leaching of a silty sand shooting range soil in the field; they found a seasonal trend in porewater Sb concentrations which were highest in the summer. They attributed this to higher weathering rates of bullets at warmer temperatures along with seasonal differences in soil water content. They also showed that leaching remained high over four years (19–349 μg L^{-1}) and concluded that this was due to the metallic bullet fragments being a constant source of Sb. Hockmann et al. (2015) found a similar seasonal trend in Sb leaching under oxic conditions in large field lysimeters filled with alkaline silty loam shooting range soil, but explained it by increased dissolved organic carbon (DOC) production in the summer competing with Sb for binding sites. Irrespective of the underlying processes resulting in the observed seasonal Sb dynamics, these studies underpin the importance of long-term field studies to accurately understand Sb mobility in contaminated soils.

Knowledge of Sb behaviour in contaminated soil under reducing conditions in the field is particularly scarce, given that all available studies except one (Hockmann et al., 2015) have been either small scale batch (Couture et al., 2015; Frohne et al., 2014; Fu et al., 2016; Hockmann et al., 2014; Rouwane et al., 2016; Rouwane et al., 2016), column (Hockmann et al., 2014) or pot experiments (Wan et al., 2013). It is important to carry out field-scale studies in order to understand the interplay between environmental processes and their effect on Sb mobility to enable reliable risk assessments of Sb-contaminated sites. Only the preceding study to this has investigated leaching from contaminated waterlogged soil on a field scale, but this was for an initial phase of just over one year (Hockmann et al., 2015). In the pre-waterlogging phase of this experiment, leachate Sb concentrations followed a seasonal pattern with concentrations being highest in summer. Upon waterlogging, leaching of Sb decreased as the system became more reduced and total Sb in soil solution decreased with depth along with redox potential. There was some indication that Sb(III) in soil solution may be released again with the reduction of Fe phases, but the experimental evidence was not enough for a conclusive assessment.

As a lot of soils are often only intermittently waterlogged (Kirk, 2004), it is also important to investigate what occurs when a soil is re-drained or dries out after waterlogging or flooding, in particular considering that extreme hydrological events are likely to become more frequent due to climate change (Couture et al., 2015). Only two available studies to date investigated the effect of re-oxidation on Sb leaching behaviour in stirred microcosms at the laboratory scale (Couture et al., 2015; Hockmann et al., 2014). As both studies found an increase in Sb concentrations with reoxidation, drainage of reduced soil may be a critical process leading to the release of Sb in the environment.

This study investigates how waterlogging affects Sb leaching in the long term and assesses if reoxidation results in a remobilisation of Sb. Therefore, in an continuation of the outdoor lysimeter experiment from Hockmann et al. (2015), we compared leaching from long-term waterlogged calcareous soil (1.5–2.75 years) to freely drained soil. In a second phase of the experiment, the waterlogged lysimeters were drained and solute concentrations were monitored for 1.5 years after reoxidation. In addition to leachate samples, soil solution from different depths were analysed to complement leachate results with in-situ geochemical data.

2. Materials and methods

2.1. Soil characterization

The soil used in the lysimeter experiment was taken from a military shooting range on the floodplain (Fluvisol) (0–30 cm) of the River Rhine in Eastern Switzerland (46°51′19″N and 9°30′11″E). Plant material and large stones were removed and the soil was mixed thoroughly. The fine fraction of the soil had a silt loam texture following the US soil taxonomy (Soil Survey Division Staff, 1993), contained 20% $CaCO_3$, 0.9% organic carbon and had a pH of 8.5 (Hockmann et al., 2015). Total metal(loid) concentrations were 21 mg kg^{-1} Sb, 29,500 mg kg^{-1} Fe, 820 mg kg^{-1} Mn and 520 mg kg^{-1} lead (Pb), 53 mg kg^{-1} nickel (Ni), 109 mg kg^{-1} zinc (Zn) and 61 mg kg^{-1} copper (Cu) and the soil was considered to be moderately contaminated (Hockmann et al., 2015).

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). As described by Hockmann et al. (2015), four lysimeters with a surface area of 17.5 m^2 each were filled with the study soil to a soil depth of 0.7 m on top of a quartz sand drainage layer (average thickness 28 cm). A standard meadow grass-clover seed mixture was