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Plant uptake and availability of antimony, lead, copper and zinc in oxic and reduced shooting range soil☆

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ABSTRACT

Shooting ranges polluted by antimony (Sb), lead (Pb), copper (Cu) and zinc (Zn) are used for animal grazing, thus pose a risk of contaminants entering the food chain. Many of these sites are subject to waterlogging of poorly drained soils. Using field lysimeter experiments, we compared Sb, Pb, Cu and Zn uptake by four common pasture plant species (*Lolium perenne*, *Trifolium repens*, *Plantago lanceolata* and *Rumex obtusifolius*) growing on a calcareous shooting range soil under waterlogged and drained conditions. To monitor seasonal trends, the same plants were collected at three times over the growing season. Additionally, variations in soil solution concentrations were monitored at three depths over the experiment. Under reducing conditions, soluble Sb concentrations dropped from ~50 $\mu g\,L^{-1}$ to ~10 $\mu g\,L^{-1}$, which was attributed to the reduction of Sb(V) to Sb(III) and the higher retention of the trivalent species by the soil matrix. Shoot Sb concentrations differed by a factor of 60 between plant species, but remained at levels <0.3 $\mu g\,g^{-1}$. Despite the difference in soil solution concentrations between treatments, total Sb accumulation in shoots for plants collected on the waterlogged soil did not change, suggesting that Sb(III) was much more available for plant uptake than Sb(V), as only 10% of the total Sb was present as Sb(III). In contrast to Sb, Pb, Cu and Zn soil solution concentrations remained unaffected by waterlogging, and shoot concentrations were significantly higher in the drained treatment for many plant species. Although showing an increasing trend over the season, shoot metal concentrations generally remained below regulatory values for fodder plants (40 $\mu g\,g^{-1}$ Pb, 150 $\mu g\,g^{-1}$ Zn, 15–35 $\mu g\,g^{-1}$ Cu), indicating a low risk of contaminant transfer into the food chain under both oxic and anoxic conditions for the type of shooting range soil investigated in this study.

1. Introduction

Contamination of shooting range soils with hazardous metal(loid)s, such as antimony (Sb), lead (Pb), zinc (Zn) and copper (Cu), is an environmental issue of worldwide concern. Although confined to rather small areas, this contamination poses a major environmental problem due the large number of shooting ranges. For example, Switzerland has more than 2,000 shooting ranges with an annual deposition of up to 25 tons Sb and 500 tons Pb (Mathys et al., 2007). In the United States, 1,900 tons Sb (Wan et al., 2013) and 60,000 tons Pb (Bannon et al., 2009) enter the soil on around 12,000 shooting ranges. Also in other countries, notably Norway (Okkenhaug et al., 2016), Finland (Selonen and Setälä, 2015), Poland (Lewińska et al., 2017), Canada (Laporte-Saumure et al., 2011) and Australia (Seshadri et al., 2017), shooting ranges have come into the focus of public attention.

Bullets cores typically consist of >90% Pb, with 2–7% of Sb and minor amounts of Zn and Cu (Ahmad et al., 2012). Thus, Pb input into soil is usually the critical factor determining the need for remediation or the choice of managing practices for shooting ranges. However, Sb pore water concentrations have been reported to greatly exceed Pb concentrations under alkaline conditions, which was attributed to the predominant presence of Sb as an oxyanion in aqueous solutions (Hockmann et al., 2015). While the highest Pb concentrations in shooting range soils are usually found close to the stop butts (up to 97,600 mg Pb kg^{-1} in the study of Laporte-Saumure et al. (2011)), bullet fragments were also found to spread over larger areas around them (Okkenhaug et al., 2016). These areas, which are typically contaminated to a much lower

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degree (i.e. below the clean-up threshold concentration of 2,000 mg Pb kg^{-1} in Swiss legislation (BUWAL, 2005)), are often used as pasture for sheep and cattle during times of no shooting activity or when the site has been decommissioned (Evangelou et al., 2012; Tandy et al., 2017), although the risk of Sb or metal mobilization and transfer into the food chain is largely unknown.

Studies addressing Sb and metal transfer from shooting range soils into fodder plants are scarce. In a field experiment, Sb, Pb, Cu and Zn concentrations in above-ground biomass of various plant species growing on shooting range soils remained below the Swiss threshold value for fodder plants (Evangelou et al., 2012). Another study investigated the accumulation of metals by vegetation growing on a stop butt and found that for most of the ten plant species considered, metal uptake fell into the normal range for plants (Robinson et al., 2008). These studies were conducted on well-aerated soils. Many soils, however, are subject to reducing conditions caused by waterlogging of poorly drained soils or flooding (Reddy and DeLaune, 2004). Changes in redox conditions are coupled to a series of chemical reactions, including the reductive dissolution of mineral phases hosting Sb and toxic metals and may therefore result in an enhanced bioavailability (Borch et al., 2009). Furthermore, the solubility and plant uptake of redox-sensitive elements such as Sb, which exists as Sb(V) in oxic and as Sb(III) in reduced soil solutions, will be directly impacted by changes in Sb speciation (Ren et al., 2014). For example, Sb(III) was found to be rather immobile in soils (Hockmann et al., 2014a; Mitsunobu et al., 2006), suggesting a lower availability than Sb(V). On the other hand, Sb(III) was reported to be preferentially taken up in hydroponic and pot experiments (Cui et al., 2015; Ren et al., 2014; Wan et al., 2013). How these two counteracting relationships affect total Sb uptake by plants in natural environments remains poorly understood.

A pot experiment investigating redox speciation and uptake of Sb from shooting range soil by two pasture grass species showed that reducing conditions caused by waterlogging increased Sb shoot concentrations of *L. perenne* by ~10 fold (Wan et al., 2013). To our knowledge, no study exists addressing the effect of waterlogging on Sb and metal uptake by plants from waterlogged soil under field conditions. While pot experiments are well suited to investigate uptake mechanisms and the role of specific factors under well-controlled conditions, caution is needed in transferring their results in quantitative terms to field situations. For example, biomass production and thus metal(loid) accumulation in plants was found to be strongly affected by pot size and growing conditions in climate chambers (de Vries, 1980; Poorter et al., 2012).

As knowledge about plant metal uptake is a critical aspect for the safe management of both active and abandoned shooting ranges, we investigated Sb, Pb, Zn and Cu uptake by four different plant species growing on reduced and oxic shooting range soil under field conditions. The hypothesis was that reducing conditions induced by waterlogging would impact the availability of the above elements in soil, in particular that of the redox-sensitive metalloid Sb, and thus their uptake by plants. We used four large outdoor lysimeters, two of which were subjected to waterlogging conditions. In order to link Sb and metal shoot concentrations to soluble element concentrations, soil solution samples were extracted from three soil depths at regular intervals during the growing season. A particular feature of the study presented here is that we collected plant material every six weeks to monitor changes in metal(loid) uptake that are linked to variations in plant growth or redox potential. This study builds upon our recent study which examined the effect of waterlogging on Sb speciation and leaching using the same set of outdoor lysimeters (Hockmann et al., 2015). Here, we expand this lysimeter study to the investigation of the role of waterlogging on metal availability and the uptake of Sb, Pb, Zn, and Cu by pasture plants, as a basis for the assessment of potential risks associated with the use of such soils for fodder production, thus adding a new perspective to the project.

2. Materials and methods

2.1. Experimental setup and soil characteristics

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 is 1,171 mm (Evangelou et al., 2012). Four lysimeters with a surface area of 17.5 m^2 each and a depth of 1 m were filled with a homogenized, calcareous shooting range soil. The soil had been taken from the upper 30 cm of an alluvial floodplain soil on a military shooting range close to the River Rhine in Eastern Switzerland (46°51′19″N and 9°30′11″E). The silt loam soil (US soil taxonomy) contained 20% $CaCO_3$, 0.9% organic carbon and had a pH in water of 8.5 (Hockmann et al., 2015). Total metal(loid) concentrations in the <2 mm soil fraction were measured by energy-dispersive X-ray fluorescence spectroscopy (XRF; X-Lab, 2000; Spectro) in samples taken at five locations per lysimeter and three depths (Sb 21 ± 1; Pb 471 ± 13; Zn 108 ± 1; Cu 60 ± 1; Mn 809 ± 2; Fe 28,800 ± 100; in mg kg^{-1}; n = 60; mean ± standard error (Hockmann et al., 2015)).

To monitor the soil water content, each lysimeter was equipped with eight time domain reflectometry (TDR) probes (three each at 20 cm and 37 cm and two at 54 cm depth). Each probe consisted of a polyoxymethylene head connected to two stainless steel rods (15 cm long with 2.8 cm rod spacing).

A standard meadow grass-clover seed mixture (Semences UFA 444 AR, Switzerland) recommended for cultivation on poorly-drained pastures and containing *Lolium perenne* and *Trifolium repens* was sown into the lysimeters soil in March 2010. In addition, *Plantago lanceolata* and *Rumex obtusifolius* grew spontaneously. From mid-March to end-September, the entire vegetation of each lysimeter was cut every six weeks and removed to simulate the practice on Swiss farms of regular grazing or harvesting grasslands during the growing season. After three years of operation under drained conditions, two of the four lysimeters were subjected to a controlled waterlogging regime starting in July 2012. The drainage outlet was closed and the soil allowed to saturate through natural rainfall infiltration. When saturation was achieved, the water table was regulated using piezometers at reference points in the lysimeters and valves in the drainage outlet, causing the water table to fluctuate between a depth of 30 cm and ~50 cm below soil surface. Details on the setup of the lysimeter experiment are given by Hockmann et al. (2015).

2.2. Plant sampling

During the 2013 growing season, above-ground plant samples of *T. repens*, *L. perenne*, *P. lanceolata* and *R. obtusifolius* were collected approximately every six weeks (16 May, 26 June and 7 August 2013). Three to four plants per species and lysimeter were harvested by cutting shoots and leaves (but no flowers or seed heads) approximately 3–4 cm above the soil surface. Three to five shoots were cut from the stolon-forming species *L. perenne* and *T. repens* and all leaves were collected from *P. lanceolata* and *R. obtusifolius*. In total, three to four replicate samples per lysimeter and species were collected (with two exceptions: *R. obtusifolius* in the waterlogged treatment grew only at two to three locations per lysimeter in June and at one location per lysimeter in August). Approximately 400 mg to 2,000 mg (dry weight) per sample were harvested, depending on plant species and season. (The biomass production was similar in