

# Effects of waterlogging on the solubility and redox state of Sb in a shooting range soil and its uptake by grasses: a tank experiment

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## Abstract

**Aims** The effects of waterlogging on redox state and solubility of antimony (Sb) in a calcareous shooting range soil and its uptake by forage grass *Lolium perenne* L. and pasture weed *Holcus lanatus* L. were investigated.

**Methods** Grasses were grown on semi-waterlogged or waterlogged shooting range soil in a laboratory tank. The soil solution was sampled at various depths over time and analyzed for the concentrations of Sb(III), Sb(V) and total Sb, as well as other trace elements.

**Results** Although the reduction of Sb(V) to Sb(III) under increased waterlogging time decreased Sb solubility, it increased Sb uptake by *L. perenne* from 1.1 to 1.7 mgkg<sup>-1</sup> (and to a lesser extent *H. lanatus*), implying preferential uptake of Sb(III) by this grass. The tank showed considerable variation in redox conditions with depth and plant treatment. The soil root zone (30 cm for *L. perenne* and 15 cm for *H. lanatus*) instead of the water saturated bottom, showed the highest manganese (Mn) and iron (Fe) concentrations in solution, accompanied by a higher proportion of Sb(III) in solution than the bottom zone of the tank.

**Conclusions** Waterlogging can increase the risk of Sb entering the food chain from shooting range soil.

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## Introduction

Antimony (Sb) is ubiquitously present in the environment at low concentrations. The background value in soil is less than 1 mgkg<sup>-1</sup> (Filella et al. 2007). In the recent past, human activities have caused locally elevated concentrations of Sb in the environment. In mining areas Sb concentrations of up to 15,000 mgkg<sup>-1</sup> have been reported (Baroni et al. 2000). Shooting activities are another source of soil contamination with Sb. In Switzerland approximately 10–25 t of Sb enter soil as

a result of military shooting activities each year (Mathys et al. 2007). In Norway a similar quantity was deposited from small arms ranges in the year 2000 (Stømseng and Ljønes 2000). The USA has about 12,000 shooting ranges (Bannon et al. 2009), so the predicted amount of Sb entering the environment in the USA is very large. Input of Sb into the environment with shooting also occurs from lead shot used for game and clay pigeon shooting. Based on a 2 % Sb content of lead shot (Migliorini et al. 2004), the estimated annual deposition of Sb is 41 t in Canada (Cao et al. 2003) and about 100 t in the UK (Ives K, BASC, UK, personal communication).

Antimony compounds are considered pollutants of primary concern by the Environmental Protection Agency of the United States (1979) and the Council of the European Communities (1998). Excessive exposure to Sb through ingestion and inhalation can cause deleterious health effects in humans and animals (Elinder and Friberg 1986; Sundar and Chakravarty 2010). However, despite the wide distribution of Sb contamination and its well known toxicity, the chemical behavior of Sb in the environment and the risks associated with Sb contamination are poorly understood.

Similar to its sister element arsenic (As), Sb exists mainly in its trivalent (Sb(III)) and pentavalent (Sb(V)) redox states in the environment (Arai 2010). Under anoxic conditions, Sb(III) is the main form, whereas Sb(V) dominates under oxic conditions. Antimony(III) is present in soil solution primarily as antimonite ( $\text{Sb(OH)}_3$ ) and Sb(V) as antimonate ( $\text{Sb(OH)}_6^-$ ) (Cornelis et al. 2008). Antimonite is less soluble than antimonate and also adsorbs more strongly to Fe (hydr)oxides, the main Sb sorbents in soil, particularly at alkaline pH (Hammel et al. 2000; Mitsunobu et al. 2010). Antimony(III) is shown to have a higher toxicity than its pentavalent counterpart for both human beings and plants (Gebel 1997; He and Yang 1999).

The number of studies on the uptake of Sb by plants is still limited however and information on uptake mechanisms scarce. Sb(III) transporters belonging to the aquaglyceroporin subfamily have been identified in bacteria, yeast and mammals (Filella et al. 2007). Recently aquaglyceroporins contributing to Sb transport were identified in plant species *Arabidopsis thaliana* and *Oryza sativa* (Kamiya and Fujiwara 2009; Bienert et al. 2008), so it is postulated that this could be true for other plant species as well. Much less

information is available for Sb(V). It has been suggested that it is transported by a different route to that of Sb(III) but this has not yet been identified (Filella et al. 2007). Due to the influence on the potential environmental risks of Sb, redox transformations of Sb have received particular attention. Under aerobic conditions, Fe(III) and Mn(IV) (hydr)oxides can oxidize Sb(III) adsorbed to them and thus mobilize Sb (Leuz et al. 2006; Belzile et al. 2001). On the other hand, Sb(V) can be reduced to Sb(III) by Fe(II) in alkaline, anaerobic waters (Leuz et al. 2002). Fe(II) in the form of magnetite, mackinawite and green rust have also been reported to reduce Sb(V) (Kirsch et al. 2008; Mitsunobu et al. 2008).

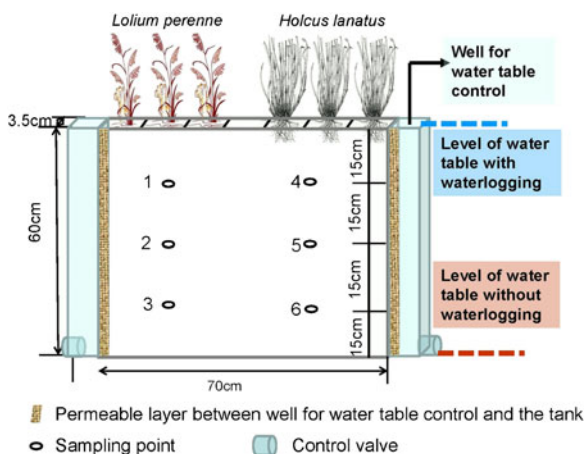
As it is assumed that Sb is stable in well-aerated soils primarily in the form of Sb(V) (Filella et al. 2009), the study of Sb(V) reduction and its possible impacts on the safe use of soil has received little attention so far. However, there are many soils that are temporarily subject to reducing conditions due to waterlogging. If such soils are contaminated with Sb, reductive dissolution of Fe or Mn (hydr)oxides can lead to the release of bound Sb, despite Sb reduction to less mobile Sb(III) (Scheinost et al. 2006). In a pot experiment with a calcareous shooting range soil we found that after imposing reducing conditions, the total Sb concentrations in soil solution at first decreased due to the reduction of Sb(V) to Sb(III), but then exhibited a significant increase with the further decrease in redox potential due to the dissolution of Fe and Mn (hydr)oxides (Wan et al. 2013). More importantly, the increased concentration in dissolved Sb(III) resulted in an apparent increase in the uptake of Sb by forage plants, thus posing a higher risk than well-aerated soil. However, pot experiments can mimic the conditions and dynamics of waterlogged soils only to a limited degree as the development and activity of roots is confined to a rather small volume of shallow soil (Ray and Sinclair 1998; Huang et al. 1996; Audet and Charest 2010).

In this study, we investigated how waterlogging affected the redox species and solubility of Sb in a relocated calcareous shooting range soil and how these effects translated into Sb uptake by forage grasses using a tank system. The tank system represented conditions that were much closer to a field situation with regards to rooting space, soil water regime and aeration than small pots, but were still relatively well controlled and enabled easy sampling.

## Materials and methods

**Experiment design** The Sb contaminated soil used in the experiment was the same as used by Wan et al. (2013). It was collected from a military shooting range located in an alluvial plain along the Rhine River, next to the city of Chur in Eastern Switzerland (9°30'11"E and 46°51'19"N). The soil was taken from the upper 30 cm depth of a field in the immediate vicinity of the stop butts. Sod and rooty materials were removed, and the remaining soil was homogenized on site and again in the laboratory. The soil was dried at 40 °C and sieved to 2 mm. The soil properties are given by Conesa et al. (2011). The soil was a silty loam (US soil taxonomy), composed of 45 % sand, 52 % silt and 3 % clay. The soil had a CaCO<sub>3</sub> content of 15 %, a pH in water of 8.2 and an organic carbon content of 0.9 %. The total Sb and lead (Pb) concentrations of the soil were approximately 21 and 500 mg kg<sup>-1</sup>, respectively. The percentage of Sb adsorbed to Fe and Mn hydr(oxide)s was ~70 % (Conesa et al. 2010).

Forty kilograms of soil were filled into a 70×5×60 cm plastic (polymethylmethacrylate) tank with water and air-tight walls and bottom. Two wells (2×3.5×60 cm) at the lateral sides of the tank each with a valve at the base allowed the regulation of the water table and the control of drainage (Fig. 1). To allow settling of the soil, the tank was slowly saturated from bottom up for 1 day by adding water through the wells, which were in hydraulic contact with the soil compartment through a porous screen, and then drained again by opening the valves for 3 days. This cycle was repeated three times, then the tank was drained for 1 week.



**Fig. 1** Experimental tank design

During this wetting-draining cycle, the particle loss from the soil was insignificant. After this period six sampling holes with a diameter of 3 mm were drilled into the sidewalls, into which six soil solution samplers (Rhizon flex, 4 cm porous material, pore size 0.2 μm, 2.5 mm outer diameter, and 12 cm PVC/PE tubing, Rhizosphere Research Products, Wageningen, Netherlands) were inserted as illustrated in Fig. 1. After installation, the interspaces between samplers and walls were sealed with silica gel (which did not release any Sb or Pb, as tested prior to the experiment). *Lolium perenne* L. and *Holcus lanatus* L. were selected as experimental grass species. The plants were germinated on the soil of the tank at a density of 10 gm<sup>-2</sup> after being soaked in 150 mg L<sup>-1</sup> gibberellic acid (Merck) for 48 h.

Each species was planted in three compartments (10×3.5 cm) with the middle compartment left free (Fig. 1). These seven compartments were separated in the surface layer (~5 cm) but not below. Therefore, samplers at each depth collected soil solution representative for the whole horizon for each plant species. The plants were grown under drained conditions for 5 weeks at first, and then the soil was waterlogged for 15 weeks. During the non-waterlogging period, the valves on both sides of the tank were kept open, enabling excessive irrigation water to drain out. To induce waterlogging, the valves were closed and water was added through the side wells (with a porous screen between the well and tank) to the level of the soil surface and kept constant during the waterlogging period (Fig. 1). During the whole experiment, 20 mL water was added to each small planted compartment every 2 days in order to compensate for evapotranspiration losses during both the non-waterlogged and waterlogged time.

During the first 5 weeks of waterlogging, the soil solution was sampled every week. After these 5 weeks, i.e. after a total growth time of 10 weeks, the shoots were harvested by cutting them to 0.5 cm above the soil surface. Thereafter, the plants were allowed to regrow without reseeded for another 10 weeks under waterlogged conditions, before their shoots were harvested again as above. During the second growth period, the soil solution was sampled every 2 weeks. Harvested plants were rinsed in deionized water, and dried at 60 °C until constant weight was reached. The experiments were performed in a climate chamber with a daily photoperiod of 16 h at a light intensity 13,000 lx and 22 °C and a night period of 8 h at 14 °C.

**Soil solution extraction and preservation** To prevent the oxidation of Sb(III) in the sampled soil solution, samples of 0.4 mL soil solution were extracted through the rhizon-flex samplers using a nitrogen-flushed syringe and immediately injected into a 1 mL plastic vial containing 0.4 mL argon-flushed 0.1 M EDTA solution. All Sb speciation analyses were completed within half an hour of solution extraction. After the sampling for Sb speciation analysis, another 10 mL soil solution was extracted through each sampling point, 3 mL of which was used to measure pH, while the rest was acidified using HNO<sub>3</sub> and preserved in a refrigerator at 4 °C for the later analysis of elemental concentrations. All elemental analyses were completed within 3 weeks of sampling.

**Sb redox state speciation analysis** Soil solution samples extracted for Sb redox speciation were analyzed by means of HPLC-ICP-MS (ICP-MS, ELAN DRC II, Perkin Elmer) using a strong anion exchange column (Hamilton PRP-X100, USA) and pump (880 PU, Jasco). The eluent contained 20 mM EDTA (Merck), 2 mM potassium hydrogen phthalate (Fluka), and 2 % methanol, at pH4. The flow rate was 1 mL min<sup>-1</sup>, and the injection volume was 50 µL. Chemicals were of analytical grade or higher purity. Mixed standard solutions of Sb(V) and Sb(III) prepared from an Sb(V) stock solution of 1,000 mgL<sup>-1</sup> Sb by dissolving KSb(OH)<sub>6</sub> (Merck) in ultrapure water and an Sb(III) stock solution of 1,000 mgL<sup>-1</sup> Sb (Sb<sub>2</sub>O<sub>3</sub> in 2 M HCl, Merck) were used to quantify the concentration of Sb(III) and Sb(V). The standard solutions were mixed with equal volumes of a 0.1 M EDTA solution under oxygen free conditions. The detection limit, determined as three times the standard deviation ( $\sigma$ ) on the measured blanks ( $n=10$ ) for the speciation analysis was 0.2 µgL<sup>-1</sup> for both species.

**Soil solution analysis** The pH was measured by means of a Metrohm713 pH meter. Acidified soil solution extracts (see above) were analyzed for total concentrations of trace elements by ICP-MS (ELAN DRC II, Perkin Elmer) and for Fe by ICP-OES (Varian, Vista-MPX CCS simultaneous). The detection limit ( $3\sigma$ ) was 0.2 µgL<sup>-1</sup> for Sb, Pb and Mn and 5 µgL<sup>-1</sup> for Fe.

**Plant sample analysis** Plant samples were finely ground using a ceramic ball mill (Retsch MM-200, RETSCH Schieritz und Hauenstein AG) and digested

in a Microwave (MLS-1200 MEGA ETHOS), using aliquots of 0.25 g plant material in 2 mL HNO<sub>3</sub> and 4 mL H<sub>2</sub>O<sub>2</sub>, and made to a final volume of 25 mL with ultrapure water. The digests were analyzed in the same way as the soil solution samples. Certified Reference Material (ERM-CD281 Rye Grass) for plants was digested along with the samples for quality control. The mean  $\pm$  standard error of our measurements was 0.046 $\pm$ 0.005 mgkg<sup>-1</sup> for Sb, 81 $\pm$ 2 mgkg<sup>-1</sup> for Mn, and 1.61 $\pm$ 0.12 mgkg<sup>-1</sup> for Pb, which agreed well with the certified values (0.042 $\pm$ 0.007 mgkg<sup>-1</sup>, 82 $\pm$ 4 mgkg<sup>-1</sup>, and 1.67 $\pm$ 0.11 mgkg<sup>-1</sup> for Sb, Mn and Pb, respectively) of these standards.

**Statistics** PASW statistics 18.0 was used for the statistical analysis of the data. ANOVA (LSD was used for multiple comparisons) was adopted to analyze elemental concentrations in plant samples. The significance level was set at an error probability of 0.05.

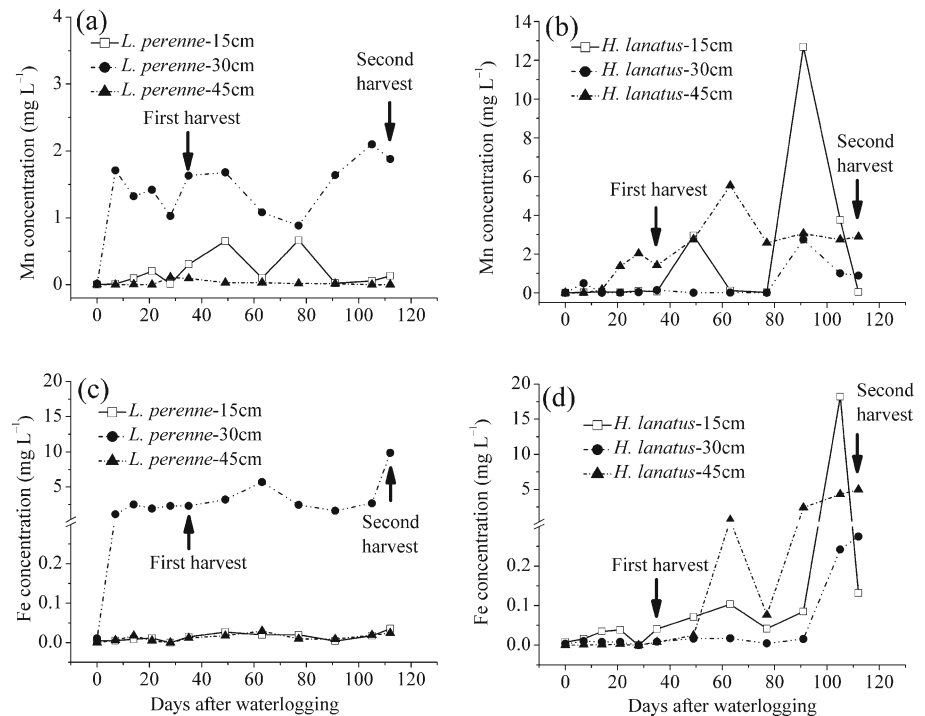
## Results

### Mn and Fe concentrations in soil solution

In the soil compartment below *L. perenne*, the concentrations of dissolved Mn and Fe both increased within 1 week of waterlogging at the sampling depth of 30 cm. In contrast, only low Mn concentrations and a much slower increase in Mn, with large fluctuations, was found at 15 cm depth and almost no increase in Fe at 15 cm depth or for both metals at 45 cm depth (Fig. 2). The dissolved Mn concentrations at 30 cm depth also showed fluctuations between 1 and 2 mgL<sup>-1</sup> after the initial increase, while the Fe concentrations were much more stable ( $\sim$ 2.5 mgL<sup>-1</sup>), implying a steady state. At the same time, the pH of the soil solution decreased, also with some fluctuations, from a pH close to 7.9 to values between 7.4 at 30 cm depth and 7.8 at 45 cm depth at the end of the experiment (Fig. 3).

Below *H. lanatus*, the change in Mn and Fe concentrations was quite different and less consistent than below *L. perenne* (Fig. 2). The dissolved Mn concentrations started to increase first after 3 weeks of waterlogging at the lowest sampling depth of 45 cm, and then reached concentrations that were much higher than below *L. perenne* ( $\sim$ 6 mgL<sup>-1</sup>). The Mn concentration at this depth remained highest compared to other depths except for a brief period shortly before the end of

**Fig. 2** Mn (a, b) and Fe concentration (c, d) in soil solution under waterlogged conditions



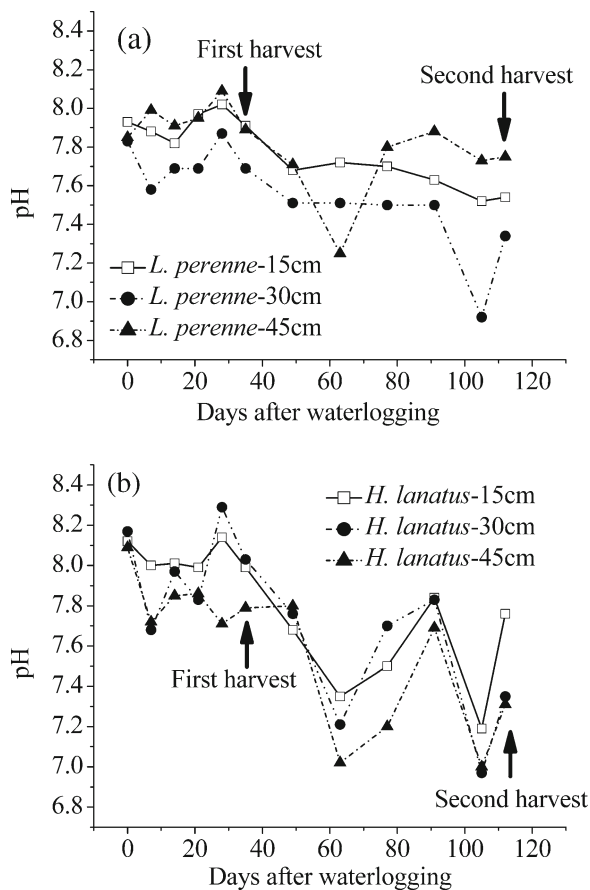
the experiment when a large peak of dissolved Mn at 15 cm depth reached  $12.7 \text{ mg L}^{-1}$  on day 91, followed by a drop back to  $0.04 \text{ mg L}^{-1}$  on day 112. The lowest Mn concentration was always detected at the depth of 30 cm throughout. The Fe concentrations showed a similar pattern (Fig. 2) with the main difference being that concentrations did not start to increase substantially at the depth of 45 cm within the first 7 weeks of waterlogging, while there was a small but gradual increase in dissolved Fe at the depth of 15 cm during this period. The Fe concentration at the depth of 30 cm was relatively consistent in the first 13 weeks and showed a gradual increase from day 91 until the end of the experiment. The highest dissolved Fe concentration below *H. lanatus* was recorded in the week before the final harvest at 15 cm depth with a singular peak that reached  $18 \text{ mg L}^{-1}$ , 2 weeks after the Mn peak. The overall decline in pH was stronger with larger fluctuations below *H. lanatus* than below *L. perenne* (Fig. 3).

#### Sb concentration and redox states in soil solution

Dissolved Sb concentrations (Fig. 4) showed much less variation between sampling depths than Mn and Fe concentrations. With increasing duration of waterlogging, the total Sb in solution gradually decreased at all three depths

from initial concentrations of  $50\text{--}90 \text{ } \mu\text{g L}^{-1}$  to constant concentrations of  $13\text{--}18 \text{ } \mu\text{g L}^{-1}$  after 8 to 10 weeks of waterlogging below the plants of both species. Antimony (III) concentrations increased from below the detection limit to a maximum value of  $\sim 2 \text{ } \mu\text{g L}^{-1}$  after around 5 weeks below *L. perenne* or a maximum of  $\sim 4 \text{ } \mu\text{g L}^{-1}$  after around 7 weeks followed by a sharp decrease below *H. lanatus* (Fig. 5).

With an opposing trend to total Sb, the relative abundance of Sb(III) (as a percentage of the sum of Sb(III) and Sb(V)) increased, before reaching a steady value or even showing a trend to decrease again, with the exception of the samples taken at 15 cm depth below *H. lanatus*. The Sb(III) percentages of the latter increased until the last week before the final harvest and then showed a sudden drop. Below *L. perenne*, Sb(III) percentages were similar at 15 cm and 30 cm depth, at which they reached a plateau between 15 % and 20 % after 35 days of waterlogging, whereas they remained much lower at the 45 cm depth with a maximum value of close to 5 %. In contrast, below *H. lanatus*, there was more variation in Sb(III) percentages between sampling depths, with lowest values at 30 cm depth and highest values at 15 cm depth and a strongly widening gap during the second half of the waterlogging period, until it dropped in the last week.

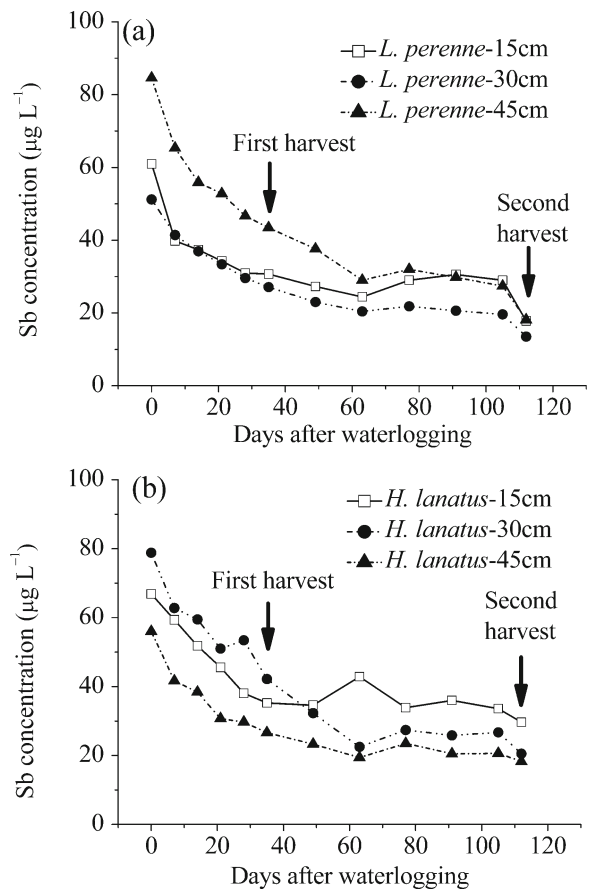


**Fig. 3** The pH of soil solution under waterlogged conditions in the presence of *L. perenne* (a) and *H. lanatus* (b)

Interestingly, the peak in Sb(III) at 15 cm depth below *H. lanatus* coincided with the Fe peak at this sampling location. Apart from the latter peak, Sb(III) concentrations did not vary with depth below *H. lanatus*, and were lower and decreased more strongly with the duration of waterlogging at 45 cm than compared to the upper two sampling depths below *L. perenne*.

At the beginning of the experiment, the total Sb concentration was higher at the depth of 45 cm than at the other two sampling depths below *L. perenne*. Since *L. perenne* was grown for 5 weeks before waterlogging, and the roots reached the depth of 30 cm, this initial difference among depths may have resulted from the uptake of Sb by *L. perenne* from the depths of 15 and 30 cm.

Comparing these two plant species, the Sb(III) percentages at 15 cm depth were higher below *L. perenne* than below *H. lanatus* during the first 9 weeks of waterlogging. In the 11th week, with an apparent increase in Sb(III) percentages below *H. lanatus*, the Sb(III)



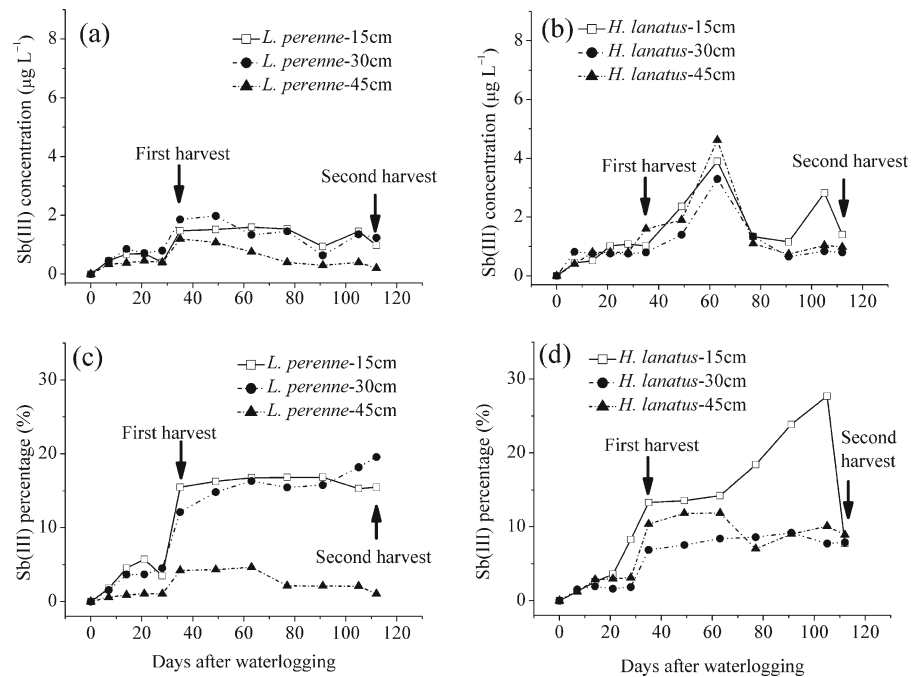
**Fig. 4** Sb concentration in soil solution under waterlogged conditions in the presence of *L. perenne* (a) and *H. lanatus* (b)

percentages at 15 cm below *H. lanatus* surpassed that below *L. perenne* but dropped at the final sampling point. The Sb(III) percentages at 30 cm depth were higher below *L. perenne* than below *H. lanatus* while the Sb(III) percentages at 45 cm depth were lower below *L. perenne* than below *H. lanatus* throughout the experiment.

#### Sb concentrations in plants

Both plant species adapted well to the waterlogged conditions. There was no difference in biomass between the first and the second growth of the shoots (supporting information, Fig. S1), although *H. lanatus* shoots looked less healthy than those of *L. perenne*. The second-growth shoots, which grew entirely under waterlogged conditions, tended to accumulate more Sb than the first shoots that grew under 'semi-waterlogged' conditions (i.e. only waterlogged for the second half of their growing period) (Fig. 6), although the difference was not significant ( $p >$

**Fig. 5** Sb (III) concentration (a, b) and Sb(III) percentage (c, d) in soil solution under waterlogged conditions

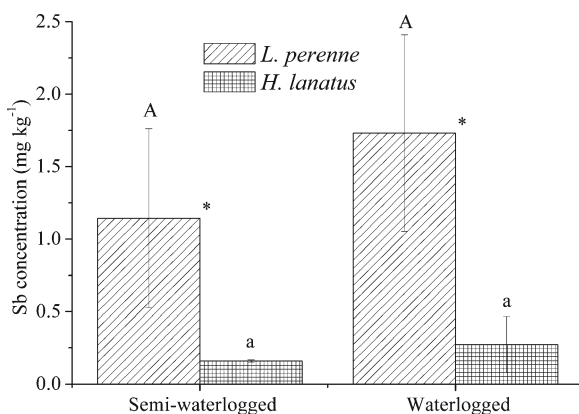


0.05). The *L. perenne* shoots did not only produce more biomass, but also accumulated higher Sb concentrations than *H. lanatus* in both stages of the experiment (Fig. 6).

#### Pb concentrations in soil solution and plants

The Pb concentration in soil solution below both species exhibited very similar behavior, i.e. a slight increase under waterlogged conditions from below the detection limit to  $\sim 1.3 \mu\text{g L}^{-1}$  followed by a fall to below the

detection limit again (supporting information, Fig. S2). However, the shoot Pb concentration showed apparent difference between these two plant species. The shoot Pb concentration of *L. perenne* under entirely waterlogged conditions ( $1.3 \pm 0.1 \text{ mg kg}^{-1}$ ) was 1/3 of that under semi-waterlogged conditions ( $4.9 \pm 2.3 \text{ mg kg}^{-1}$ ), (supporting information, Fig. S3). Oppositely, the waterlogged *H. lanatus* ( $5.8 \pm 1.0 \text{ mg kg}^{-1}$ ) took up 93 % more Pb than the semi-waterlogged ones ( $3.1 \pm 1.0 \text{ mg kg}^{-1}$ ).



**Fig. 6** Shoot Sb concentration of *L. perenne* and *H. lanatus* growing under different water regimes. The same letter indicates that the difference among treatments for each plant species was insignificant ( $p > 0.05$ ). Asterisks indicate significant difference between plant species in the same treatment ( $p < 0.05$ )

## Discussion

Waterlogging reduced Sb(V) to Sb(III) and increased its uptake by forage plants

Because redox potentials (Eh) at different depths in the tank system could not be measured due to technical restrictions, the concentrations of dissolved Fe and Mn were adopted as parameters reflecting the redox state of the soil. The increased Fe and Mn concentrations in the soil solution are evidence that the waterlogged treatment led to a strong reduction in the redox potential of the soil. According to the Eh-pH diagram of Mn and Fe solubility given by Cornelis et al. (2008), Mn and Fe (hydr)oxides are reduced and thus become soluble at Eh  $< 400 \text{ mV}$  and Eh  $< 100 \text{ mV}$ , respectively, at pH 7–8 and the reduction of Fe (hydr)oxides occurs after Mn. This

was in fact observed in our previous pot experiment using the same soil (Wan et al. 2013). Waterlogging in the tank experiment led to a decrease in redox potential, but apparently to a lesser extent than in the pot experiment, as evidenced by the difference in soluble Mn and Fe. This discrepancy may result from different increase extents of soil water content caused by waterlogging: an 80 % increase in the pot and a 33 % increase in the tank from non-waterlogged conditions. Another possible reason is the lower density of plant roots in the tank. The seed density at the beginning of the experiment in pots and tank was the same, but the tank had a larger volume.

The degree of reducing conditions in response to waterlogging is expected to increase with soil depth (Massmann et al. 2008), as oxygen diffusing into the soil from surface is gradually consumed. In fact, the Mn and Fe concentrations sampled below *H. lanatus* indicate that the redox potential here declined more quickly and more strongly at the bottom of the tank. However, the picture was very different below *L. perenne*. Here, the Mn and Fe concentrations revealed that the most reducing conditions occurred at medium depths, while only the slight increase in the concentrations of Sb(III) in soil solution at 45 cm depth showed also some decrease in redox potential at the lowest depth. Thomas et al. (2009) suggested that the degree of redox response to water table fluctuation decreased with an increase in soil depth due to the role of plants. As the two plant species had different rooting depths, the plants could indeed have affected the redox potential especially at depths of 15 and 30 cm. Although *H. lanatus* is regarded as being able to adapt well to different water regimes (Turkington and Harper 1979), it had a more restricted rooting depth as we observed. At the end of the experiment, roots of *L. perenne* reached 30 cm depth, while roots of *H. lanatus* only reached the depth of 15 cm. Given that plant root exudates can greatly affect soil chemistry through changing soil pH, supplying carbon source for microbes, and affecting the composition of soil organic matter (Bowen and Rovira 1991; Nardi et al. 2000; Hinsinger et al. 2003), this difference in rooting depth may be the main reason for the observed differences in redox conditions below *L. perenne* and *H. lanatus*. In addition, oxygen supplied with the irrigation water infiltrating laterally from the two wells at the sides of the tank may also have had some effect.

Furthermore, it has to be considered that redox conditions are generally not in thermodynamic equilibrium in

soils and often show large small-scale spatial and also short-term temporal variability in soils due to spatial heterogeneity and temporal fluctuations in the activity and growth of roots, microorganisms and other soil organisms (Yang et al. 2006). If soil is water-saturated, soil and root respiration can quickly deplete available oxygen and result in anaerobic soil conditions even at moderate rates of soil or root activities (Inglett et al. 2005), and result in a difference in redox potentials of several hundred mV within regions as small as 10 cm in diameter (Norrstrom 1994).

The strong variations in redox potential with time and position may also have been a major reason for the lack of strong correlations between the concentrations of Fe or Mn and the concentrations or percentages of Sb(III) in solution in our experiments ( $R^2=0.2-0.4$ ,  $p<0.05$ ). This poor correlation furthermore indicates that there was only a weak relationship between the processes of reductive Mn and Fe (hydr)oxide dissolution and Sb immobilization. The decrease in dissolved Sb concentrations with waterlogging can partly be attributed to a dilution effect, as the water content of the soil increased by approximately 33 %. However, a dilution effect alone cannot explain the 55–79 % decrease in the total concentration of Sb in solution. There are several other possible explanations: (1) stronger absorption of Sb(V) to Fe/Mn (hydr)oxides due to a decrease in pH (Fig. 3); (2) improved adsorption of Sb(V) to the re-precipitated less crystalline Fe (hydr)oxides, as suggested by Mitsunobu et al. (2006); and (3) reduction of Sb(V) to Sb(III), with the latter having a greater absorption affinity to Fe (hydr)oxides (Mitsunobu et al. 2010). For our study, the last explanation is most reasonable, as there was no correlation between the pH values and Sb (V) concentrations in solution, and no evidence was observed indicating the re-precipitation of Fe (hydr)oxides. Therefore, it is suggested that Sb was removed from the soil solution after reduction from Sb(V) to Sb(III) due the much stronger sorption strength of the latter to Fe and Mn (hydr)oxides (Leuz et al. 2006; Mitsunobu et al. 2010).

On the other hand, with the dissolution of Mn and Fe (hydr)oxides, sorbed Sb would also be released (Takahashi et al. 2010; Mitsunobu et al. 2006). The latter process apparently did not become dominant during this experiment, in contrast to the pot experiment (Wan et al. 2013). It was probably part of the interplay of processes resulting in the approximately constant total Sb solution concentration towards the end of the experiment. In line with the lower Mn and Fe concentrations found in soil



solution of the tank compared to the pot experiment, the concentrations and percentages of Sb(III) in soil solution were also lower in the tank than in the pots, again highlighting that conditions in the tank were less reducing.

In a similar pattern to the total Sb concentrations, the increase in soluble Pb in the waterlogged tank (Fig. S2) was less obvious than that in the pot, which may also result from the lower dissolution percentage of Mn and Fe (hydr)oxides caused by the less reducing conditions in the tank system (Miao et al. 2006; Phillips 1999).

Despite the decreased Sb concentration in soil solution, Sb accumulation by both grass species increased in the second part of the experiment. This result agrees with the findings of the pot experiment (Wan et al. 2013), where it has also been found that waterlogging decreased the solubility of Sb with the reduction of Sb(V) to Sb(III) but increased the Sb uptake by *L. perenne*. This may be a result of uptake of Sb(III) by aquaglyceroporins. Sb(III) transporters belonging to the aquaglyceroporin subfamily have been identified in plant species *Arabidopsis thaliana* and *Oryza sativa* (Kamiya and Fujiwara 2009; Bienert et al. 2008). This could be true for *L. perenne* as well, so there is preferential uptake of Sb(III). It was also shown however, that in mutant plants lacking this transport protein, 50 % of Sb(III) taken up by the non-mutant plants was still taken up, implying that an additional uptake mechanism may be in play (Kamiya and Fujiwara 2009). The bioaccumulation factor (ratio of shoot Sb concentration in  $\text{mg kg}^{-1}$  to Sb concentration in soil solution in  $\text{mg L}^{-1}$ ) for *L. perenne* was  $26 \pm 10$  under semi-waterlogged conditions and  $68 \pm 26$  under waterlogged conditions, much higher than for *H. lanatus*, which was  $3.3 \pm 0.2$  under semi-waterlogged conditions and  $8.1 \pm 4.0$  under waterlogged conditions. The increasing trend in Sb accumulation with increased exposure to waterlogging contrasted to the decreased total Sb concentration in the soil solution, but was in line with the increased concentration and percentage of dissolved Sb(III). This finding suggests that Sb was at least partially taken up from the pool of Sb(III) and explains why the bioaccumulation factor was roughly three times higher for both plant species in the second part of the experiment ( $p < 0.05$ ). Tschan et al. (2009b) reported literature data suggesting that the uptake of Sb by plants is in general approximately proportional to the soluble Sb concentration in soil. Our results here indicate that redox state can make an important difference and needs to be taken into account in determining the uptake of Sb by plants.

In contrast to the pot experiment where a decrease in shoot Sb uptake of *H. lanatus* occurred under waterlogged conditions (Wan et al. 2013), shoot Sb concentration of this species growing in the tank increased with increasing waterlogging time, but the differences were not significant. *H. lanatus* has been reported to be an As tolerant plant species, inducing As(III) efflux to the external medium under As stress conditions (Logoteta et al. 2009). Antimony(III) and As(III) have similar chemical structures (Bienert et al. 2008; Wysocki et al. 2001), and they displayed a similar uptake mechanism in yeast (Wysocki et al. 2001; Ramanathan et al. 1997) and plants (Kamiya and Fujiwara 2009). In a number of micro-organisms, it was furthermore shown that Sb(III) efflux from cells is often mediated by an As(III) efflux protein (Filella et al. 2007). Therefore, in contrast to *L. perenne*, it is not likely that the As excluding species *H. lanatus* prefer to take up Sb(III) to Sb(V). In healthy roots, apoplastic bypass to shoots is minimal, but increases if the plant is subjected to anaerobic stress or physical damage (Moon et al. 1986; Hanson et al. 1985). Although the biomass of *H. lanatus* did not significantly change with waterlogging, the plants appeared less healthy than those of *L. perenne*. It is proposed that with increased waterlogging time, the waterlogged *H. lanatus* in the tank system experienced increased apoplastic bypass, which enabled more Sb to be transferred from roots to the xylem. This increased apoplastic bypass may also partly explain the increase in Pb uptake by *H. lanatus* under waterlogging (Fig. S3). The slight increase in dissolved Pb from below the detection limit to  $\sim 1.3 \mu\text{g L}^{-1}$  may have also played a role (Fig. S2), although the pot experiment showed that an increase in Pb in soil solution from 5 to  $\sim 50 \mu\text{g L}^{-1}$  did not significantly change the shoot Pb concentration (Wan et al. 2013). In contrast to *H. lanatus*, *L. perenne* showed a decrease in shoot uptake of Pb (Fig. S3). A decrease in the uptake of Pb, As and potassium (K) by the regrowth of plants has been reported in several studies (Cheng and Wong 2008; Gonzaga et al. 2008; Everaarts and van Beusichem 1998). In the tank system, the 2nd harvested shoots also grew on existing roots; therefore, the decreased uptake of Pb by *L. perenne* may have resulted from this regrowth effect.

In general, the tank system showed less reducing conditions than the pot experiment, but a similar trend in both the change of soil chemical properties and the plant uptake characteristics. Because of its larger size and higher complexity, the tank allowed a study of the same

processes under conditions that were closer to the process in real soils. An associated trade-off was that conditions were much less controllable than in the pot and only one treatment with no true replicates of the tank and the soil solution samples could be run at a time. To ensure that the soil solution was drawn from only one treatment, samplers had to be a certain distance apart and an area without plants of 10 cm was left between the two plant species to make sure there was no interaction between them. As a consequence, it was not possible to have replicate soil solution samplers for a particular treatment and depth or gain a true assessment of variability in soil solution. The large standard deviations of shoot Sb and Pb concentration (Fig. S3 & Fig. 6) indeed imply differences between single compartments. Due to the lack of replicates and the increased complexity of the tank system, there still existed some issues that could not be easily interpreted, and which still require further investigation using a larger-scale and even more realistic system. Despite its limitations, this experiment provides information about the transport and transformation of Sb under different extents of plant activities and oxygen diffusion that are not possible from pot experiments alone and also reveals the heterogeneity of natural systems.

#### Practical implications

Shooting range soil contamination, mainly by Sb and Pb, has received increasing attention in recent years due to the large number of shooting ranges across the world (Sorvari 2007; Lin 1996; Johnson et al. 2005; Bannon et al. 2009; Griggs et al. 2011; Laporte-Saumure et al. 2011; Reid and Watson 2005; Stømseng and Ljønes 2000). The results of the pot experiment suggested that re-using moderately contaminated shooting range soils e.g. for pasture of cattle and sheep, as proposed by Tschan et al. (2009), should be feasible, but the risk of Sb entering food chains must be controlled and in particular the potential effects of variations in soil moisture have to be taken into account (Wan et al. 2013). However, solute accumulation rates are often quite different in pot experiments from that in the field. A tank system as used in this study represents field soil conditions better than pots, while still allowing much better control and monitoring of experimental conditions than a field site. Thus, the finding of similar Sb accumulation rates for *L. perenne* with both systems is important evidence demonstrating that, for some plants at least, there is indeed an

increased risk of Sb transfer into the food chain under waterlogged conditions.

By Swiss regulations, shooting range soils must be treated as hazardous waste if the concentration of Pb exceeds  $1,000 \text{ mg kg}^{-1}$  (The Swiss Federal Council 1998). Similar regulations apply in other countries. However, usually only small amounts of soil are so heavily contaminated as to require treatment as hazardous waste. Much larger amounts are only moderately contaminated and are still a valuable natural resource for plant production if adequate restrictions are imposed to control the risks. As disclosed by this study, the shoot Pb concentrations in both pot and tank experiments were far below the threshold concentration of  $40 \text{ mg kg}^{-1}$  for fodder in Switzerland (BUWAL 2005), which is in accordance with the reported low mobility of Pb in plants (Comino et al. 2011). Thus, the main concern currently is the potential risks that could arise from the accumulation of Sb.

The plant concentrations are compared with fodder concentrations for As because limits for Sb have not been established and Sb toxicity is believed to be comparable to that of As (Gebel 1997). The maximum allowed concentration of As in fodder is  $2 \text{ mg kg dry weight}^{-1}$  according to Swiss regulations (Baroni et al. 2000). The *L. perenne* growing in the waterlogged tank for 2 months had an average value close to that and one single value higher than that ( $2.5 \text{ mg kg dry weight}^{-1}$ ). If waterlogging lasted for a longer time or the plants were older, it is expected that the accumulation of Sb in the shoots of *L. perenne* would be even higher (Tighe et al. 2005). Therefore, Sb contamination of shooting range soils should remain the focus of attention (Johnson et al. 2005; Lewis et al. 2010), especially on lands temporarily or permanently under flooded conditions.

In summary, the results indicate that there is a potential risk of Sb transfer into the food chain in using Sb-contaminated shooting range soils for pasture or forage production if these soils are subject to waterlogging. Before the re-use of moderately contaminated shooting range soil, risk assessments must be performed that include addressing the risks that could arise from changing redox conditions.

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