

The partitioning of Sb in contaminated soils after being immobilization by Fe-based amendments is more dynamic compared to Pb

Å.R. Almås^{a,*}, E. Pironin^{a,b}, G. Okkenhaug^{a,c}

^a Norwegian University of Life Sciences (NMBU), Faculty of Environmental Sciences and Natural Resource Management, P.O. Box 5003, NO-1432, Ås, Norway

^b Sorbonne Université, Faculté des Sciences et Ingénierie, 4 place Jussieu, 75005, Paris, France

^c Norwegian Geotechnical Institute (NGI), P.O. Box 3930, Ullevål Stadion, N-0806, Oslo, Norway

ARTICLE INFO

Editorial handling by Prof. M. Kersten

Keywords:

Antimony
Lead
Fe-oxide
Lability
Soil
DGT

ABSTRACT

Soils and sediments from shooting ranges can be heavily contaminated with metals and metalloids that can leach significant concentrations into the environment. To prevent trace element leaching, contaminated soils must be stabilized prior to deposition. Here, we present a geochemical study on the lability of Sb (oxyanion) and Pb (cation) in heavily contaminated shooting range soil after amendment with a Fe-rich slag in combination with either FeSO₄ or an acidic contaminated organic soil. The treatment effect on leaching potential and chemical lability with time was tested in a column leaching experiment and by a diffusive gradient in thin film technology (DGT) experiment, respectively. Both treatments substantially reduced the Sb and Pb leaching, but the slag&FeSO₄ was most effective. The DGT-lability of the slag&organic-soil treatment caused a 78% and 93% reduction in Sb_{DGT} and Pb_{DGT}, respectively. The slag&FeSO₄ reduced the Sb_{DGT} and Pb_{DGT} by 90% and 98.5%, respectively. Application of slag&FeSO₄ to the contaminated soil, increasingly immobilized Pb as time prevailed, leaving only an insignificant fraction geochemically labile. Antimony was comparably more labile with time. This outcome indicates that although the Sb leaching was effectively reduced, the Sb sorption to the amendments is weaker and that the sorbed Sb may remain geochemically labile beyond a few weeks of contact with the Fe-rich slag.

1. Introduction

Trace elements fill prominent roles in our society as essential nutrients for plants, animals, and human beings. However, they are also hazardous contaminants. Even if they are naturally present in the environment, they can become concentrated and contaminate largely through mining and processing of metal ores for their industrial applications (Okkenhaug et al., 2011; Almås and Manoko, 2012). Mineral oil and trace metals represent the largest source of soil contaminants (60%), and the cost of managing contaminated sites is estimated to amount to approximately 6 billion Euro (Panagos et al., 2013).

Bullet traps are normally well-defined constructions at shooting ranges heavily contaminated with metals and metalloids that can leach significant concentrations into the environment. Additionally, there are areas used for field shooting contaminated by scattered impacts of firearm residues and fractures posing similar risk. The primary contaminants are lead (Pb), copper (Cu), and antimony (Sb). This study is focuses on the geochemistry of antimony (Sb) and lead (Pb) in shooting range soils. Antimony and Pb contaminate a variety of soils, aquifers, and surface waters (Bargar et al., 1997; Okkenhaug et al., 2012). The

history of Pb contamination in shooting range soils is long, and management actions with respect to such soils are implemented with a strong focus on Pb (US-EPA, 2005). The acknowledgment of Sb contamination is of more recent date. It is, for instance, used as flame retardant, used as bullet hardener, and applied in semiconductors and alloys (Okkenhaug et al., 2015). Hence, the identification of Sb origin transport routes and environmental geochemistry have lately gained high priority (Filella et al., 2009; Okkenhaug et al., 2011, 2015; Tamas, 2016; Majzlan et al., 2018).

Although extensive pollution control programs have been introduced in most industrialized countries, environmental impacts and the fate of trace elements such as Pb and Sb still cause much concern (Dousova et al., 2015; Okkenhaug et al., 2015). This phenomenon is partly connected to the increased consumption and intercontinental trade of consumables and wastes. The US Environmental Protection Agency lists both elements as priority pollutants (US-EPA, 2014) due to their deleterious effects on humans and other organisms even at minimal exposure concentrations (Tamas, 2016).

Unlike organic contaminants (e.g., pesticides, petrol byproducts, polychlorinated biphenyls (PCB), and polycyclic aromatic

* Corresponding author.

E-mail address: asgeir.almås@nmbu.no (Å.R. Almås).

hydrocarbons (PAH)), trace elements are generally immutable and persistent in nature (Smolders et al., 2009). Depending on the geochemistry, the bioavailability of the trace elements in soils can pose a threat to living organisms such as plants, animals, and humans. To study the bioavailability and dynamic geochemistry of trace elements, different nondestructive techniques can be applied. One that has shown usefulness and frequent employment (Batley et al., 2004; Menegario et al., 2017) is the diffusive gradients in thin film technique, DGT (Davison and Zhang, 1994). The DGT technique has been applied to study the speciation of trace elements by separating free and labile species from geochemically inactive forms (Degryse et al., 2009a), as well as their kinetic response to shifts in equilibrium solution as DGTs are deployed in soils (Almås et al., 2017). Like uptake through plant roots, the accumulation of trace elements in the DGT lowers the concentrations in soil solution at the surface of the device. This lowering induces the resupply of trace elements from the geochemically active fractions in solid soil. Laboratory soil measurements by DGT have been demonstrated as robust predictors of cationic metal concentrations with respect to zinc (Zn) and cadmium (Cd) (Almås et al., 2006), and even for oxyanions such as As, selenium (Se) and Sb (Sogn et al., 2008; Luo et al., 2010; Williams et al., 2011).

To prevent trace element leaching, contaminated soils and wastes must be stabilized prior to landfilling to comply with leaching limits set by the European Waste Regulation (EU, 1999). The use of stabilizing materials for remediation of metals and metalloids in soils has been widely studied and is gaining broader acceptance as a remediation technology. In situ remediation technology makes use of organic residues, such as composted biosolid, peat, and coal (Adriano et al., 2004; O'Day and Vlassopoulos, 2010) in addition to inorganic materials, such as lime, phosphate, and iron compounds (Boisson et al., 1999; Adriano et al., 2004; Klitzke and Lang, 2009; Okkenhaug et al., 2013). Such amendments are abundant and inexpensive (O'Day and Vlassopoulos, 2010).

Here, we present a lability study of two geochemically contrasting elements (Pb, a cation and Sb, an oxyanion) following stabilization of a strongly contaminated soil making use of low cost Fe-based amendments. We hypothesized that (I): the addition of Fe-based and peat soil amendments to soil will immobilize both Pb and Sb. Following from this hypothesis, we further hypothesize (II) that the initial immobilization is rapid and that the partitioning between geochemically active and inactive forms of Pb and Sb remains stable with time.

To test these hypotheses, we designed a laboratory study using heavily contaminated shooting-range soils where an uncontaminated Fe-based waste material was added to the soil in combination with peat material. The rate of the Fe-based waste material added to the soil is high to make sure we get strong effects. Follow-up experiments have to be conducted for developing realistic application ranges for remediation purposes. A column leaching experiment and a DGT exposure test of the treated and untreated soils were carried out to test the efficiency of the amendments. The latter was the major part of our study where the impacts of treatments were investigated on geochemical lability of Pb and Sb.

2. Materials and methods

2.1. Contaminated soil

To study Sb and Pb immobilization, a mineral soil containing only 5% total organic carbon (TOC), was collected from bullet traps from Tittelsnes shooting ranges in Sveio municipality, in southwest Norway (59°43'22.4"N, 5°30'52.2"E, EU89). This soil is highly contaminated by Pb ($3633.3 \pm 57.7 \text{ mg kg}^{-1}$) and Sb ($72.7 \pm 2.1 \text{ mg kg}^{-1}$) and is hence classified as hazardous waste (Table S1). The pH of this soil is 7.7. Soil pH is measured in 15 g air-dried (40 °C during 30 min) subsamples of the mixtures in a 1:2.5 solid-water suspension (v/v) after 24 h of equilibration.

2.2. Amendments

We used two different amendments: a i) mixture of an Fe-oxide byproduct and an Fe-sulfate by product and ii) a contaminated organic rich topsoil (sampled from an O_A horizon).

i) The Fe-oxide is an industrial byproduct (slag) from the processing of titanium (Ti) and Fe. The mineral source for the process is ilmenite with the main chemical compound FeTiO₃. The ilmenite may be associated with magnetite, Fe₃O₄ and contains often hematite, Fe₂O₃, as well as various impurities (Mg, Mn, Si, Ca, Al, Cr, V) (Hagberg, 2016). The slag contains oxides of iron (0.04% of Fe), calcium (6%) and aluminum (0.8%), as well as sulfur (1.2%) (Table S1). The slag is classified as environmentally harmless, containing low concentrations of Pb and Sb (respectively, $4.43 \pm 0.2 \text{ mg kg}^{-1}$ and 0.7 mg kg^{-1}). The pH of the slag is 11.0.

The slag is strongly alkaline; hence, an Fe(II)-sulfate (FeSO₄) by-product (from titanium oxide production) was applied together with the slag to reduce pH for optimal Sb immobilization. The Fe-sulfate is acidic with a pH of 2.8 (1:10 solid-water ratio (w/v)), containing insignificant concentrations of Pb and Sb (Table S1). Under aerobic conditions, Fe(II) oxidizes to Fe(III) and further precipitates as Fe(OH)₃. Initial testing indicated that the best combination was 4 g dry Fe-sulfate to a 50/50 g soil/slag mixture (100 g in total), which produced an initial soil pH of 5.5 (Table S2).

ii) At the same shooting range area, a less contaminated soil collected from an O_A horizon (18% total organic carbon) containing $953 \pm 55 \text{ mg kg}^{-1}$ Pb and $7.8 \pm 0.6 \text{ mg kg}^{-1}$ Sb was used as an alternative amendment for our trials. The pH of this organic rich soil is 4.7. This soil is from now on referred to as "organic soil" for simplicity. This organic soil must be treated before deposition, and since the pH of this soil is < 5 we explored the potential applications of this soil in combination with the alkaline Fe-oxide product and the high-pH mineral soil to reach a lower, optimal, pH.

The soils and the slag were stored in a cold room (4–6 °C) in sealed polyethylene buckets prior to use, whereas the Fe-sulfate was stored in a clean plastic bag.

This means the amount of FeSO₄ being added was ~4%, and the amount of slag being added was ~50%. These are high treatment rates, not directly applicable to real contaminated soils in large scale. The situation is that heavily contaminated soils are required to be near 100% stabilized at landfills to prevent any leaching of harmful elements (EU, 1999). These experiments are thus conducted to investigate if a combined Pb and Sb stabilisation is realistic making use of low cost amendments. Follow up experiments, at laboratory- and large scale; have to be conducted to search finding practical treatment combinations making use of less treatment material.

2.3. Leaching column experiment

A parallel sample of the contaminated mineral soil was homogenized by sieving moist soil (no drying to minimize geochemical changes) through a < 2.8 mm steel sieve to reduce heterogeneity before filling the columns. Lead and Sb leaching from the treated and untreated mineral soil was studied by a water leaching column experiment at room temperature (22 °C). Four grams of dry FeSO₄ was applied to a 50/50 g soil/slag mixture with the initial soil pH at 6.5. The leaching column tests were conducted in triplicate, where: i) 50 g homogenized mineral soil was amended with 4 g Fe-sulfate and 50 g slag (slag&FeSO₄); ii) 45 g homogenized mineral soil was amended with 45 g peat soil and 10 g slag (slag&organic-soil) and iii) 100 g homogenized untreated mineral soil (untreated soil) was used.

Acid-washed polyethylene columns of 300 mm height and 22 mm

internal diameter were filled with 100 g of thoroughly mixed material. Acid-washed (in 10% HCl) inert plastic beads (5 mm diameter) were placed at the bottom of each column, over a membrane filter, to facilitate leaching. Experimental blanks (no soil) were also included. Each column (made of poly propylene) was saturated by adding 20–30 mL deionized water, depending on the treatment. Equilibrated water in all columns was displaced and collected by applying equal volumes of water as initially used to saturate the columns. For the slag&organic-soil treatment and the untreated soil, the leachates were collected after 24 h contact time, whereas leachates from the FeSO₄&slag treatment were collected after 24, 48, 168 and 336 h contact time. The leachates were immediately filtered through 0.45 µm polyethersulfone membrane filters (vwf, Oslo, Norway) before the determination of pH, dissolved organic carbon (DOC), inorganic anions (Cl⁻, NO₃⁻ and SO₄²⁻) and the concentrations of Ca, Fe, Pb and Sb.

2.4. Chemical lability estimations by DGT deployments

Two types of DGT disks, loaded with either Chelex or an Fe-oxide gel, were provided by DGT[®] Research (Lancaster, UK). The DGTs were stored at 4 °C to minimize the risk of drying pending exposure.

Using the same methods as for the column leaching experiment, a parallel sample of the contaminated mineral soil was homogenized by sieving moist soil through a < 2.8 mm steel sieve to reduce heterogeneity before DGT deployments. Unused clean plastic boxes (poly propylene) of 100 mL were filled with: 50 g homogenized mineral soil, 50 g slag and 4 g Fe-sulfate (slag&FeSO₄); 45 g homogenized mineral soil, 45 g organic soil and 10 g slag (slag&organic-soil), and homogenized mineral soil as a treatment blank (untreated soil). The prepared soil mixtures were moistened by deionized water application in several operations to obtain water saturation and (pseudo) equilibrium between the soil, iron oxide and sulfate at room temperature (22 °C) over 24 h before DGT deployment. Triplicate samples of both DGT types (Chelex and Fe-ox) were carefully pushed into the soils after 24 h, 48 h, 168 h (1 week) and 336 h (2 weeks) contact time between soils and amendments.

In addition to testing the effect of contact time between soil and treatment, the Sb and Pb partitioning between fast and slow reacting fractions was investigated. This investigation was conducted by exposing the DGTs for 6 and 48 h for each treatment contact-time interval (24 h - 2 weeks).

To maintain constant humidity, plastic films were wrapped around each plastic box. Each DGT-unit was removed according to the experimental plan and rinsed with deionized water before dismantling. The resins were eluted with 1.6 M ultra-pure (UP) HNO₃.

2.5. WHAM speciation of Pb

The speciation of Pb was conducted by supplying WHAM 7 (Lofts and Tipping, 2011) with input data from chemical analysis of the leaching column experiment. The concentrations of input parameters and major Pb-species calculated are shown in Table 1. We assumed dissolved organic matter (DOM) to have the ion-binding properties of default fulvic acid, FA and that the DOM is 50% carbon by weight. We assumed 50% of the acid groups of FA as active in proton/metal binding. Total dissolved Fe was assumed to be dominated by Fe(III). As in earlier experiments (Almås et al., 2006; Ivezic et al., 2012), partitioning 20% of leached Fe as Fe(II) elicited little effect on the predominant Pb species.

2.6. Chemical analysis

2.6.1. Inductively coupled plasma mass spectrometry (ICP-MS)

The elemental concentrations in all extracts were determined using an Agilent Technologies 8800 ICP-MS Triple Quadrupole mass spectrometer (CA, USA). DGT-blanks, internal standards and standard

reference materials were used for the determination of analytical quality parameters. Certified reference material for soil analysis was the CRM 2709 (NIST, 2003), whereas the CRM 1643e was used for water analysis (NIST, 2004).

2.6.2. Ion-exchange chromatography

A Zellweger Analytics Lachat IC5000 ion chromatograph equipped with XYZ Autosampler ASX-500 series was used for the determination of phosphate (PO₄³⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻) and chloride (Cl⁻) in leached samples. Total organic carbon was determined using a LECO CHN-1000 analyzer.

2.7. Statistics

Statistical tests were conducted using JMP v. 11 software (SAS-Institute, 2016). Outliers were determined in line with Dean and Dixon (1951): the difference between the suspected value and the nearest value (d1) is divided by the difference between max. and min. values (d2). For 3 observations (at 90% significance), the limit rate (d1/d2) is 0.94, whereas for 4 observations the limit is 0.76. Since the slag is added as particles, causing large geochemical heterogeneity in soil, we chose to be conservative before rejection, and all d1/d2-rates higher than 0.8 were accepted. The statistical significance is reported as significant or nonsignificant as defined by $\alpha = 0.05$.

3. Results and discussion

In this study, we investigated the effective immobilization of Pb and Sb in a contaminated shooting range soil after application of slag and an organic soil. Column leaching is a classic method for investigating potential environmental impacts from soil and waste material, whereas experiments using DGT exposure to metal contaminated soils have shown to be good indicators of their bioavailability (Almås et al., 2006; Williams et al., 2011) and kinetic parameters (Zhang and Davison, 2015; Almås et al., 2017).

3.1. Column leaching experiment

3.1.1. Treatment with slag&FeSO₄

Leached Sb (Sb_L) and (Pb_L) from the slag&FeSO₄ treated soil were significantly lower (≈ 1 and $20 \mu\text{g L}^{-1}$, respectively, $n = 3$, $\alpha = 0.05$) than from the untreated control soil (≈ 60 and $250 \mu\text{g L}^{-1}$, respectively). Leached Sb and Pb from all soil treatment combinations are shown in Fig. 1. After 24 h equilibration time, the pH was 7.0, and DOC concentration was 41 mg L^{-1} .

The Sb_L from treated and even untreated columns were very low, hence unlikely to cause hazardous impacts. Comparison with the EU landfill directive requires a strict protocol, which our experiment does not fulfill. However, the leached Sb_L concentrations are well below the $150 \mu\text{g L}^{-1}$ guideline value for environmentally safe material (EU, 1999). We also tested Sb leaching from slag&FeSO₄ treated soil with increasing equilibration time (Fig. 2). The leached Sb concentration was stably low ($0.82\text{--}1.77 \mu\text{g L}^{-1}$) for up to 336 h, with no significant variations ($\alpha = 0.05$). The low concentrations are probably caused by Sb sorption to Fe-oxides.

Antimony sorption to Fe-oxides is a rapid reaction (Okkenhaug et al., 2013), and aging effects add to the initial Sb retention by Fe-oxides. Leverett et al. (2012) showed that secondary Fe-Sb mineral tripuyite (FeSbO₄) is an important and ultimate sink for Sb in the supergene environment with very low solubility ($\log K_{so} = -13.41$). The Ca concentration in leachates from both treatments mixed with slag was in the range of 525 mg L^{-1} , and the Ca concentrations in leachates from the slag-&FeSO₄ treated soil did not vary much with time. Such high concentrations of Ca may precipitate Sb by formation of secondary Ca-Sb(V) precipitates (Okkenhaug et al., 2012). Supply of Ca, through liming, has been shown to form Ca(Sb(OH)₆)₂, which is suggested to

Table 1

The table shows input parameters and their concentrations used for the calculation of Pb species in the column leached water. The resulting fraction of Pb bound to colloidal Fa, concentrations of diffusively ($Pb_{FA-diff}$) and specifically ($Pb_{FA-spec}$) bound Pb to fulvic acid (FA) and the free ion activity (FIA) of Pb are shown in the lower part of the table.

Input parameters								
Treatment	pH	Pb	Fe	Ca	DOM	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
		µg/L			mg/L			
T1	7.4	25.3 ± 17.9	1700 ± 529	533 ± 28,9	40.3 ± 2.5	9108 ± 1613	29.3 ± 2.5	25.0 ± 6.1
T2	8.3	52.7 ± 10.4	0.7 ± 0.3	530 ± 34.6	47.4 ± 6.6	1389 ± 159	18.0 ± 4.3	25.0 ± 5.3
T3	8.1	250 ± 120	0.03 ± 0.01	104 ± 49.3	37.6 ± 2.1	421 ± 6.7	43.7 ± 0.6	107 ± 3.6

Major output Pb-species				
	Pb _{FA} /Pb _L ^a	Pb _{FA-diff}	Pb _{FA-spec}	FIA-Pb
		µg/L		
T1	1	4.92*10 ⁻⁶	2.03*10 ⁻¹²	7.83*10 ⁻¹⁰
T2	1	5.43*10 ⁻⁶	4.09*10 ⁻¹²	2.61*10 ⁻¹¹
T3	1	3.17*10 ⁻⁵	3.81*10 ⁻¹⁰	1.46*10 ⁻⁹

^a Pb_L is total Pb in the leachate, equal to the input value.

control Sb(V) solubility at high soluble Ca-concentrations (Klitzke and Lang, 2009).

The leached Pb_L from the slag&FeSO₄ treated and the untreated soils were well below the leaching limit (3000 µg L⁻¹) for ordinary waste landfills (EU, 1999), Fig. 1. The latter can most likely be explained by the high pH of this soil. Fig. 1 shows that the most effective treatment combination was mineral soil treated slag&FeSO₄, as it was for Sb. That treatment stably retained Pb at low levels during the entire experimental period of 336 h (Fig. 2). The trend intensified with time, which can be a combined effect of aging and increasing pH (Fig. S1). It is very difficult to separate pH effect from surface absorption or co-precipitation at a solid surface. The slag contains 6% Ca (probably in the form of CaO), and the increasing pH and increased Pb retention is likely

connected. Hence is the Pb retention likely a combined effect of increased Fe-oxide retention efficiency and a pH effect related to the high CaO content.

The leaching of Fe was higher from slag&FeSO₄ treated soil (1700 ± 432 mg L⁻¹) compared to the two others after 24 h contact time (0.76 and 0.02 mg L⁻¹ for slag&organic-soil and untreated soil, respectively). This increase in leached Fe was probably due to the addition of Fe-sulfate more than mobilization of reduced Fe (FeII) from the slag. The water saturation does not create appropriately reducing conditions for Fe- reduction to take place in a mineral soil with low organic matter content. This latter assumption is partly supported by the reduction of Fe-leaching from the slag&FeSO₄ column during the 2 weeks of experimental time. The value dropped from 1700 mg L⁻¹ to

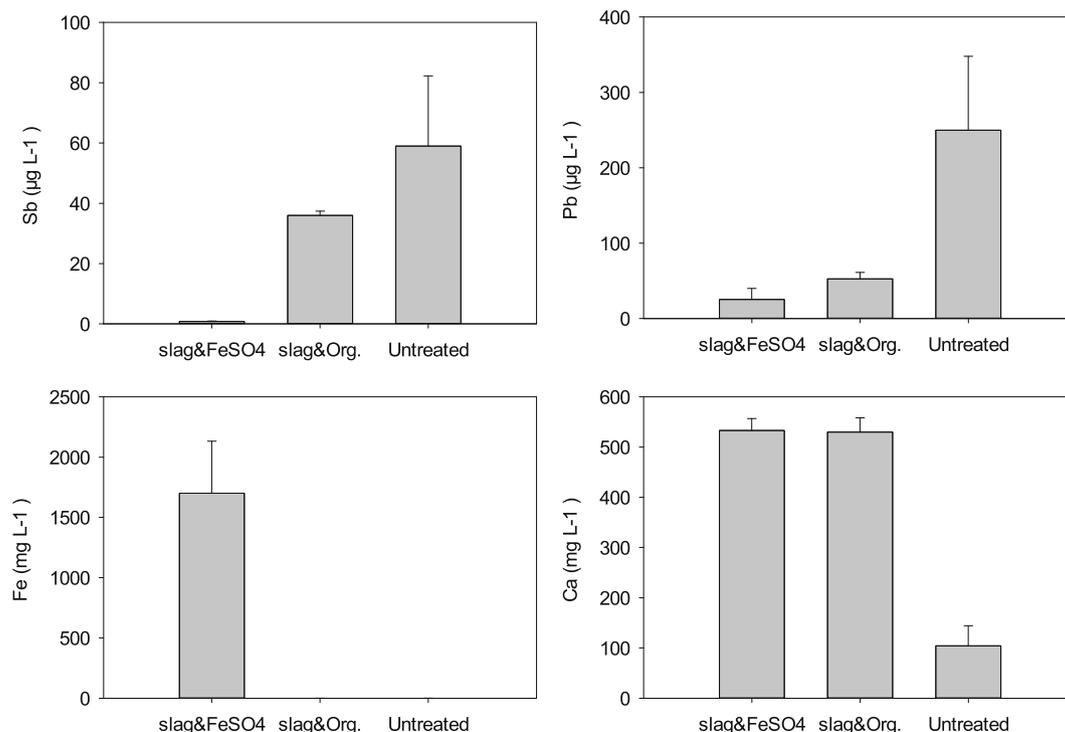


Fig. 1. The figure shows concentrations of Sb, Pb, Fe and Ca in leached samples 24 h after water saturation and treatments with slag&FeSO₄ (pH 7.0), slag&organic soil (pH 8.3) and the untreated soil (pH 8.0). Mean values and standard deviations are shown (n = 3).

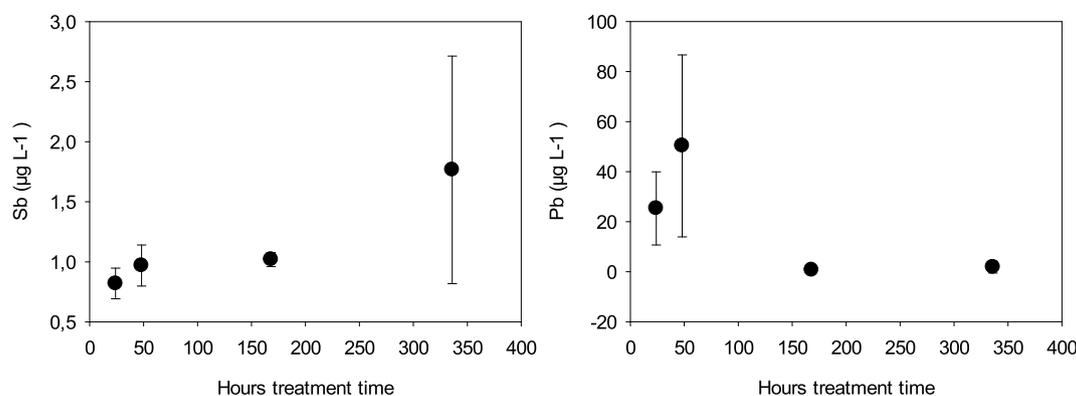


Fig. 2. The figure shows concentrations of Sb and Pb ($\mu\text{g L}^{-1}$) in leached water collected from columns containing soil treated with slag&FeSO₄ after increasing hours of water saturation and contact time between soil and the slag&FeSO₄. Mean values and standard deviations are shown ($n = 3$).

$77 \pm 16 \text{ mg L}^{-1}$ towards the end.

3.1.2. Treatment with slag&organic-soil

Antimony concentration was substantially lower in leachates from the slag&FeSO₄ treated soil, $0.82 \pm 0.13 \mu\text{g L}^{-1}$, in comparison with the slag&organic-soil treated soil, leaching $36 \pm 1 \mu\text{g L}^{-1}$ (Fig. 1). After 48 h, the pH was $8.25 (\pm 0.03)$ in leachates from the slag&organic-soil treated column and 8.0 in leachates from the nontreated. There was no clear trend in DOC solubility explaining the increased leaching of Sb from the slag&organic-soil treated soil compared to slag&FeSO₄ treated soil. The DOC leaching values were 41 (slag&FeSO₄), 47 (slag&organic-soil) and 38 (untreated soil) mg/L. Sorption of natural organic material to iron oxides is well known and has been thoroughly documented (Gu et al., 1994). Hence, the mixing of organic soil into the mineral soil likely reduced the effective sorption of Sb to the slag by organic acid competitive sorption to the reactive sorption sites. This effect has earlier been demonstrated by Redman et al. (2002), where As-sorption to hematite was greatly diminished as a result of natural organic matter competition for the same surface sites.

The leaching of Pb in columns treated with slag&organic-soil relative to those treated with slag&FeSO₄ was not increased significantly, as was the case with Sb. This outcome can possibly be related to the abovementioned organic acid competitive effect with Sb and partly because Sb in its oxyanion form is more labile in soil than the cationic Pb. Lead also demonstrates very high affinity for organic material (Degryse et al., 2009a; Zhang and Davison, 2015) in addition to the mineral phase.

3.2. Effect of amendments on chemical lability (DGT exposures)

The estimations of Pb and Sb lability in the contaminated mineral soil were conducted by exposing DGTs to the soils mixed with slag&FeSO₄, slag&organic-, and the untreated contaminated soil. First, we report the Sb and Pb recoveries in DGTs deployed for 48 h as affected by treatment time (24–336 h) between the soil and the different additives. Then, we report the treatment effects on fast (6 h deployment) and slow reacting (48 h deployment) Sb and Pb during the same experimental period. The hypothesis is that fast reacting Sb and Pb will be accumulated in the DGT during the first 6 h, whereas a sum of fast and slow reacting Sb and Pb fractions (replenished from exchangeable sites) will be accumulated after 48 h exposure (Almás et al., 2017).

The concentrations of Sb (Sb_{DGT}) and Pb (Pb_{DGT}) accumulated by the DGT (48 h deployment time), as affected by increasing equilibration between the two amendments and the soil, are shown in Fig. 3 compared with the control soil. We observed some changes in Sb_{DGT} and Pb_{DGT} during the experimental period of 336 h (2 weeks), but none of them were significant. These samples correspond to soil exposed to the slag&FeSO₄ and the slag&organic-soil treatments. The Sb_{DGT} and Pb_{DGT}

concentrations were also very low, and the variations observed were of little importance. The most important consideration is whether both treatment scenarios reduce the DGT-lability effectively in comparison to the untreated soil. The slag&organic-soil treatment caused 78% and 93% reduction of Sb_{DGT} and Pb_{DGT} , respectively, compared to the untreated soil. The slag&FeSO₄ was even more efficient, reducing Sb_{DGT} and Pb_{DGT} by, respectively, 90% and 98.5%.

3.2.1. Comparison of leached- and DGT-labile fractions after 48 h

Compared to the Sb_L and Pb_L , the Sb_{DGT} and Pb_{DGT} concentrations were mostly lower. The Sb_{DGT} and Pb_{DGT} articulate the lability or potential bioavailability of Sb and Pb in soil; implicitly, the sum of labile forms in soil solution and the geochemically active solid fractions. The Pb speciation, presented in Table 1, shows that nearly 100% of all Pb in solution is bound to DOM; in WHAM, DOM was defined as fulvic acid (FA). Lead and Cu have strong affinities for DOM (Almás et al., 2007), and we found that the fraction of Pb_{DGT} to $\text{Pb}_L \ll 0.01$ irrespective of soil treatment. We do not have estimations of Sb speciation, but the relative lability of Sb was much higher than for Pb: at 48 h equilibration time between soil and amendments, the rates of $\text{Sb}_{\text{DGT}}/\text{Sb}_L$ ranged from 1.8 (slag&FeSO₄) via 0.1 (slag&organic-soil) to 0.3 (untreated soil). The slag&FeSO₄ treatment reduced the leaching of Sb ($\sim 1 \mu\text{g L}^{-1}$) very effectively compared to the untreated sample ($\sim 60 \mu\text{g L}^{-1}$), Fig. 1. The slag-FeSO₄ treatment did not reduce the DGT-lability (Sb_{DGT}) to an equally effective extent. The slag&FeSO₄-treatment reduced the $\text{Sb}_{\text{DGT-48hr}}$ to only 1/20 of the $\text{Sb}_{\text{DGT-48hr}}$ in the untreated soil (Fig. 3).

3.2.2. Effect of treatments

The DGT experiments showed that the slag&FeSO₄ treatment retains Sb more strongly than does the slag&organic-soil treatment and, as seen before, the two treatments retain Sb and Pb much more strongly than the untreated soil.

The slightly higher Sb lability in soils treated with peat might be related to the indirect soil organic matter (SOM) mobilization of Sb by competition for the same binding sites at the slag. The OM-Sb complex is weak, and hence direct mobilization of Sb with DOM (dissolved organic matter) is probably not as important as competition. Antimony has a weak association to organic ligands at near neutral pH, but the affinity increases substantially at lower pH (Tella and Pokrovski, 2012). For Pb, there is no significant lability difference whether slag was applied to soil in combination with organic soil or the Fe-sulfate. Lead has high affinity for organic matter, and mobilization of Pb by DOM may take place. However, from the column experiment we found little evidence of higher DOM leaching from the organic soil-treated columns compared to those to which no extra organic matter was applied. If any DOM-Pb mobilization takes place, the lability of the Pb-DOM complex is slow.

The effect of equilibration time between soil and amendments on

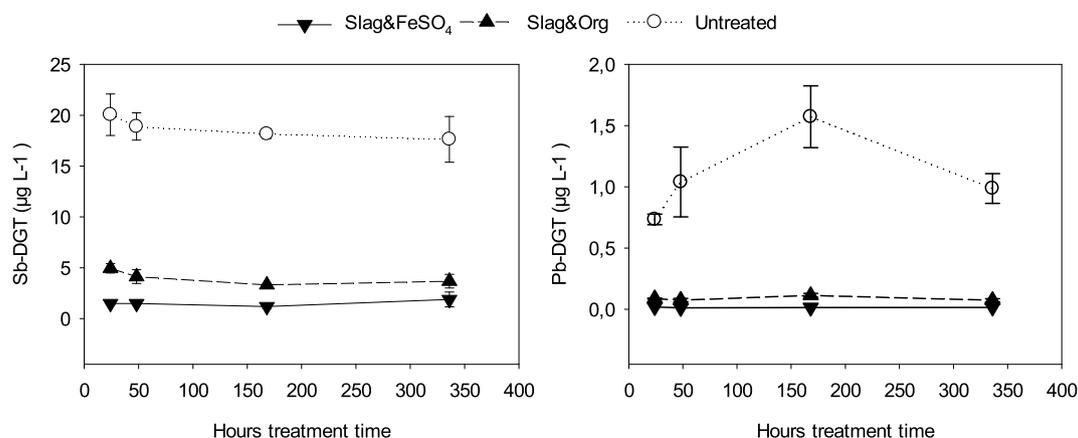


Fig. 3. The figure shows changes in the concentrations of Sb and Pb ($\mu\text{g L}^{-1}$) accumulated by the DGT (Sb_{DGT} and Pb_{DGT}) as affected by contact time between soil and two amendments. The DGT exposure time is 48 h. Mean values and standard deviations are shown ($n = 3$).

the Sb_{DGT} and Pb_{DGT} is not very different between the two elements. Antimony-DGT remains at the same concentration level for any treatments, whereas for Pb_{DGT} we noted a steady increase, but only in the untreated soil as saturation time increased (until 168 h). The concentrations are, however, low for Pb_{DGT} , and the changes are insignificant. The trend can, however, be worth investigating to determine whether it indicates differences in kinetic response to shifts in equilibrium solutions during DGT deployment.

3.2.3. Fast and slow reacting fractions

Discrimination of slowly reacting complexes from fast reacting ones can be investigated using thick and thin diffusive membranes (Zhang and Davison, 2015) in a DGT-device, or by changing the deployment time between soil and the DGT. Increasing deployment time allows slowly reacting complexes to dissociate at the DGT surface (Lehto et al., 2006). When comparing the 6- and 48-h deployment times, we present the accumulated mass of Sb and Pb – not concentrations, because the mass accumulation of Sb and Pb by the DGT is not linear with time when exposed to soil. The accumulation is gradually reduced with time as the soil is kinetically incapable of fully replacing the time integrated uptake of elements. Hence, a lowering of trace elements at the DGT surface develops (Harper et al., 2000). The $\text{Sb}_{48\text{hr}}/\text{Sb}_{6\text{hr}}$ and $\text{Pb}_{48\text{hr}}/\text{Pb}_{6\text{hr}}$ hourly mass rates of Sb and Pb accumulated in the DGT exposed to soil after treatments with slag- FeSO_4 or slag-organic-soil and the untreated soil are shown in Fig. 4.

The partitioning of fast reacting (6 h) compared to the sum of fast and more slowly reacting (48 h) Sb can be illustrated by calculating the

$\text{Sb}_{48\text{hr}}/\text{Sb}_{6\text{hr}}$ rates. For Sb, these rates were always > 1 . In the untreated soil, the rates are stable or even increasing towards the end of the trial period (increasing from 4.5 to 5). As deployment time increases (48 h), slowly labile complexes are allowed to dissociate (Figura and McDuffie, 1980; Warnken et al., 2007; Degryse et al., 2009b), making more Sb available to the DGT. In our soils, pH increased towards $\sim \text{pH } 8$ with time (Fig. S1), which should facilitate the dissociation of Sb. In this trial, the DGT deployment time and treatment equilibration time both indicate an initial reduction of labile Sb following treatment. During the first hours after mixing in the amendments, the longer deployment time (48 h) allows relatively higher DGT accumulation of Sb compared to 168 and 332 h treatment time. Towards the end of the observations, the rate of slow to fast labile Sb is fairly stable at 3 to 3.5. Examining the slag& FeSO_4 treatment, the $\text{Sb}_{6\text{hr}}$ accounts for approximately 25–30% of the $\text{Sb}_{48\text{hr}}$, whereas this fraction is much larger for Pb.

If the sorption is highly effective, the partitioning of slowly labile element to the fast labile fraction should be reduced substantially with treatment time. Moreover, if the rate is reduced to < 1 , the slowly labile stores are not replenishing elements removed from soil solution by the DGT-uptake sufficiently to be measured. This outcome appears to be the situation with Pb. After treating the soil with slag&organic-soil, the ratio is maintained at 1, indicating a stable kinetic situation. The slag& FeSO_4 treatment forces this ratio down to 0.1, indicating a near complete immobilization of fast reacting Pb. The Pb_{DGT} is already extremely low, and the small fraction diffusing into the DGT is insufficiently replaced from DOM - and even less so from solid soil.

The effect of treatment on Pb is generally the same as for Sb: slag&

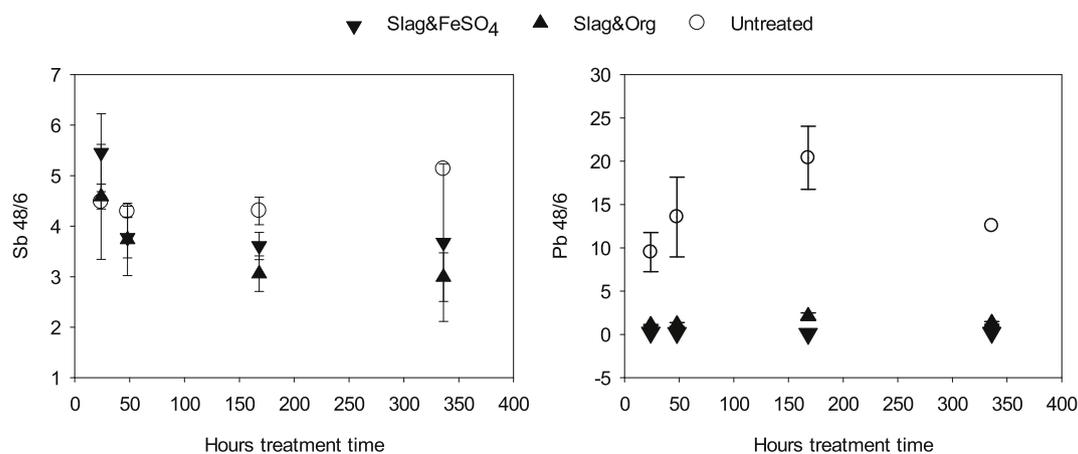


Fig. 4. The figure shows the mass ratios of Sb and Pb accumulated by the DGT exposed for 6 and 48 deployment hours in soil with increasing contact time between the soil and the two amendments. Mean values and standard deviations are shown ($n = 3$).

FeSO₄ treatment is more effective than slag&organic-soil treatment. Interestingly, the partitioning of Pb_{6hr} relative to Pb_{48hr} in the slag& organic-soil treated soil supports the earlier discussed possibility that some of the presumably organic bound Pb is made labile with increasing deployment time. Such a possibility does not exist in the slag& FeSO₄ treated soil. The slag&organic-soil treatment retains Pb effectively in soil, as very little was leached through in the column experiment, but the peat-treatments forced a small (but significant, $\alpha = 0.05$) part of soil Pb towards a more bioavailable form. Although this increase in lability is minimal compared to the untreated soil, it provides indications with respect to the concept of slow kinetics (Figura and McDuffie, 1980; Warnken et al., 2007; Degryse et al., 2009b) that can occur at the surface of a living cell, even in the case of Pb.

4. Conclusion

The hypotheses defined were related to the quantitative efficiency in reducing the lability of Pb and Sb following soil amendments with slag&FeSO₄ and slag&organic-soil. Both amendments reduced the leaching significantly in comparison to no treatment. The stability of the retained (co)precipitated elements were, however, different. The general result of treating the contaminated soil with slag&FeSO₄ is that Pb has been successfully immobilized, and more so as time after treatment prevails, leaving only an insignificant geochemically labile fraction responding to the flux of Pb from soil solution and exchangeable sites to the DGT-resin (difference between Pb_{6hr} and Pb_{48hr}). In contrast, Sb is comparably more geochemically labile, also increasing with time after treatment. There is no tendency for the two fractions to meet (Sb_{48hr}/Sb_{6hr} = 1), as with Pb. This indicates that the Sb sorption to the amendments is weaker and that the sorbed Sb may remain geochemically labile beyond the period of this experiment.

Acknowledgements

The authors are grateful to the waste treatment company Lindum AS (Drammen, Norway) for financing the study and for providing the amendments, soils used and related product quality sheets.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2019.104378>.

References

Adriano, D.C., Wenzel, W.W., Vangronsveld, J., Bolan, N.S., 2004. Role of assisted natural remediation in environmental cleanup. *Geoderma* 122, 121–142.

Almås, Å.R., Lofts, S., Tipping, E., Mulder, J., 2007. Solubility of major cations and Cu, Zn and Cd in soil extracts of some contaminated agricultural soils near a zinc smelter in Norway: modelling with a multisurface extension of WHAM. *Eur. J. Soil Sci.* 58, 1074–1086.

Almås, Å.R., Lombnæs, P., Sogn, T.A., Mulder, J., 2006. Speciation of Cd and Zn in contaminated soils determined by DGT-DIFS, and WHAM Model/VI in relation to uptake by spinach and ryegrass. *Chemosphere* 62, 1647–1655.

Almås, Å.R., Manoko, M.L.K., 2012. Trace element concentrations in soil, sediments, and waters in the vicinity of geita gold mines and North mara gold mines in Northwest Tanzania. *Soil Sediment Contam.* 21, 135–159.

Almås, Å.R., Sævarsson, T.H., Krogstad, T., 2017. The partitioning of P in soil determines the fluxes and deliveries of labile P in soil solution. *Geoderma* 306, 135.

Bargar, J.R., Brown, G.E., Parks, G.A., 1997. Surface complexation of Pb(II) at oxide-water interfaces. 1. XAFS and bond-valence determination of mononuclear and polynuclear Pb(II) sorption products on aluminum oxides. *Geochim. Cosmochim. Acta* 61, 2617–2637.

Batley, G.E., Apte, S.C., Stauber, J.L., 2004. Speciation and bioavailability of trace metals in water: progress since 1982. *Aust. J. Chem.* 57, 903–919.

Boisson, J., Mench, M., Vangronsveld, J., Ruttens, A., Kopponen, P., DeKoe, T., 1999. Immobilization of trace metals and arsenic by different soil additives: evaluation by means of chemical extractions. *Commun. Soil Sci. Plant Anal.* 30, 365–387.

Davison, W., Zhang, H., 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature* 367, 546–548.

Dean, R.B., Dixon, W.J., 1951. Simplified statistics for small numbers of observations. *Anal. Chem.* 23, 636–638.

Degryse, F., Smolders, E., Parker, D.R., 2009a. Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications - a review. *Eur. J. Soil Sci.* 60, 590–612.

Degryse, F., Smolders, E., Zhang, H., Davison, W., 2009b. Predicting availability of mineral elements to plants with the DGT technique: a review of experimental data and interpretation by modelling. *Environ. Chem.* 6, 198–218.

Dousova, B., Buzek, F., Herzogova, L., Machovic, V., Lhotka, M., 2015. Effect of organic matter on arsenic(V) and antimony(V) adsorption in soils. *Eur. J. Soil Sci.* 66, 74–82.

EU, 1999. Council directive 199/31/EC of 26 April 1999 on the landfill of waste. In: Union, E., OJ L 182, Brussel.

Figura, P., McDuffie, B., 1980. Determination of labilities of soluble trace-metal species in aqueous environmental-samples by anodic-stripping voltammetry and chelex column and batch methods. *Anal. Chem.* 52, 1433–1439.

Filella, M., Williams, P.A., Belzile, N., 2009. Antimony in the environment: knowns and unknowns. *Environ. Chem.* 6, 95–105.

Gu, B.H., Schmitt, J., Chen, Z.H., Liang, L.Y., McCarthy, J.F., 1994. Adsorption and desorption of natural organic-matter on iron-oxide - mechanisms and models. *Environ. Sci. Technol.* 28, 38–46.

Hagberg, R.S., 2016. Solidification of Titanium Slags and Influence on Post Processing. MSc. Thesis. Department of Materials Science and Engineering. Norwegian University of Science and Technology, Trondheim, Norway.

Harper, M.P., Davison, W., Tych, W., 2000. DIFS - a modelling and simulation tool for DGT induced trace metal remobilisation in sediments and soils. *Environ. Modell. Softw.* 15, 55–66.

Ivezic, V., Almås, Å.R., Singh, B.R., 2012. Predicting the solubility of Cd, Cu, Pb and Zn in uncontaminated Croatian soils under different land uses by applying established regression models. *Geoderma* 170, 89–95.

Klitzke, S., Lang, F., 2009. Mobilization of soluble and dispersible lead, arsenic, and antimony in a polluted, organic-rich soil - effects of pH increase and counterion valency. *J. Environ. Qual.* 38, 933–939.

Lehto, N.J., Davison, W., Zhang, H., Tych, W., 2006. Theoretical comparison of how soil processes affect uptake of metals by diffusive gradients in thinfilms and plants. *J. Environ. Qual.* 35, 1903–1913.

Leverett, P., Reynolds, J.K., Roper, A.J., Williams, P.A., 2012. Triphuyite and schafarzikite: two of the ultimate sinks for antimony in the natural environment. *Mineral. Mag.* 76, 891–902.

Lofts, S., Tipping, E., 2011. Assessing WHAM/Model VII against field measurements of free metal ion concentrations: model performance and the role of uncertainty in parameters and inputs. *Environ. Chem.* 8, 501–516.

Luo, J., Zhang, H., Santner, J., Davison, W., 2010. Performance characteristics of diffusive gradients in thin films equipped with a binding gel layer containing precipitated ferrihydrite for measuring arsenic(V), selenium(VI), vanadium(V), and antimony(V). *Anal. Chem.* 82, 8903–8909.

Majzlan, J., Kiefer, S., Herrmann, J., Stevko, M., Sejkora, J., Chovan, M., Lanczos, T., Lazarov, M., Gerdes, A., Langenhorst, F., Radkova, A.B., Jamieson, H., Milovsky, R., 2018. Synergies in elemental mobility during weathering of tetrahedrite (Cu, Fe, Zn) (12)(Sb, As) S-4(13) : field observations, electron microscopy, isotopes of Cu, C, O, radiometric dating, and water geochemistry. *Chem. Geol.* 488, 1–20.

Menegario, A.A., Yabuki, L.N.M., Luko, K.S., Williams, P.N., Blackburn, D.M., 2017. Use of diffusive gradient in thin films for in situ measurements: a review on the progress in chemical fractionation, speciation and bioavailability of metals in waters. *Anal. Chim. Acta* 983, 54–66.

NIST, 2003. National Institute of Standards & Technology, Certificate of Analysis. Standard Reference Material 2709. San Joaquin Soil. Baseline Trace Element Concentrations. Gaithersburg, USA MD 20899.

NIST, 2004. National Institute of Standards & Technology, Certificate of Analysis. Standard Reference Material 1643e. Trace Elements in Waters. Gaithersburg, USA MD 20899.

O'Day, P.A., Vlassopoulos, D., 2010. Mineral-based amendments for remediation. *Elements* 6, 375–381.

Okkenhaug, G., Almås, Å.R., Morin, N., Hale, S.E., Arp, H.P.H., 2015. The Presence and Leachability of Antimony in Different Wastes and Waste Handling Facilities in Norway. *Environmental Science: Processes & Impacts* 1861-1994.

Okkenhaug, G., Amstatter, K., Bue, H.L., Cornelissen, G., Breedveld, G.D., Henriksen, T., Mulder, J., 2013. Antimony (Sb) contaminated shooting range soil: Sb mobility and immobilization by soil amendments. *Environ. Sci. Technol.* 47, 6431–6439.

Okkenhaug, G., Zhu, Y.G., He, J.W., Li, X., Luo, L., Mulder, J., 2012. Antimony (Sb) and arsenic (As) in Sb mining impacted paddy soil from Xikuangshan, China: differences in mechanisms controlling soil sequestration and uptake in rice. *Environ. Sci. Technol.* 46, 3155–3162.

Okkenhaug, G., Zhu, Y.G., Luo, L., Lei, M., Li, X., Mulder, J., 2011. Distribution, speciation and availability of antimony (Sb) in soils and terrestrial plants from an active Sb mining area. *Environ. Pollut.* 159, 2427–2434.

Panagos, P., Van Liedekerke, M., Yigini, Y., Montanarella, L., 2013. Contaminated sites in Europe: review of the current situation based on data collected through a European network. *J. Environ. Publ. Health* 11.

Redman, A.D., Macalady, D.L., Ahmann, D., 2002. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* 36, 2889–2896.

SAS-Institute, 2016. JMP, Statistical Discovery Software v 13.0.0 SAS Institute, Inc., Cary, NC, USA.

Smolders, E., Oorts, K., van Sprang, P., Schoeters, I., Janssen, C.R., McGrath, S.P., McLaughlin, M.J., 2009. Toxicity of trace metals in soil as affected by soil type and aging after contamination: using calibrated bioavailability models to set ecological soil standards. *Environ. Toxicol. Chem.* 28, 1633–1642.

Sogn, T.A., Eich-Greatorex, S., Royset, O., Ogaard, A.F., Almås, Å.R., 2008. Use of diffusive gradients in thin films to predict potentially bioavailable selenium in soil.

- Commun. Soil Sci. Plant Anal. 39, 587–602.
- Tamas, M.J., 2016. Cellular and molecular mechanisms of antimony transport, toxicity and resistance. *Environ. Chem.* 13, 955–962.
- Tella, M., Pokrovski, G.S., 2012. Stability and structure of pentavalent antimony complexes with aqueous organic ligands. *Chem. Geol.* 292, 57–68.
- US-EPA, 2005. Best Management Practices for Lead at Outdoor Shooting Ranges. United States Environmental Protection Agency, New York, pp. 103.
- US-EPA, 2014. In: Agency, U.S.E.P. (Ed.), Priority Pollutant List. United States Environment Protection Agency.
- Warnken, K.W., Davison, W., Zhang, H., Galceran, J., Puy, J., 2007. In situ measurements of metal complex exchange kinetics in freshwater. *Environ. Sci. Technol.* 41, 3179–3185.
- Williams, P.N., Zhang, H., Davison, W., Meharg, A.A., Hossain, M., Norton, G.J., Brammer, H., Islam, M.R., 2011. Organic matter-solid phase interactions are critical for predicting arsenic release and plant uptake in Bangladesh paddy soils. *Environ. Sci. Technol.* 45, 6080–6087.
- Zhang, H., Davison, W., 2015. Use of diffusive gradients in thin-films for studies of chemical speciation and bioavailability. *Environ. Chem.* 12, 85–101.