Available online at www.sciencedirect.com
ScienceDirect
Environmental Pollution 153 (2008) 668–676
ENVIRONMENTAL POLLUTION
www.elsevier.com/locate/envpol

Plant uptake of trace elements on a Swiss military shooting range: Uptake pathways and land management implications

Brett H. Robinson*, Simone Bischofberger, Andreas Stoll, Dirk Schroer, Gerhard Furrer, Stéphanie Roulier, Anna Gruenwald, Werner Attinger, Rainer Schulin

Swiss Federal Institute of Technology (ETH), Universitätstrasse 16, CH-8092 Zürich, Switzerland

Received 6 June 2007; received in revised form 24 August 2007; accepted 31 August 2007

Establishment of a complete vegetation cover on shooting ranges would reduce the contamination of plant leaves by toxic trace elements.

Abstract

Over 400 tons of Pb enters Swiss soils annually at some 2000 military shooting ranges (MSRs). We measured elements in the leaves of 10 plant species and associated rhizospheric soil on the stop butt of a disused MSR. The geometric mean concentrations of Pb, Sb, Cu, Ni in rhizospheric soils were 10,171 mg/kg, 5067 mg/kg, 4125 mg/kg and 917 mg/kg. Some species contained Pb, Cu and Ni, above concentrations (30 mg/kg, 25 mg/kg and 50 mg/kg) shown to be toxic to livestock. Most contaminants in leaves resulted from surface deposition. However, at soil Pb concentrations >60,000 mg/kg, *Equisetum arvense* and *Tussilago farfara* took up >1000 mg/kg Pb into the leaves. These plants are not hyperaccumulators, having <100 mg/kg Pb in leaves at lower soil concentrations. Removal of soil with more than 30,000 Pb, from which one could smelt this metal to offset remediation costs, followed by revegetation, would minimise dust and hence leaf-borne contaminants.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Lead; Antimony; Surface deposition; Phytoremediation; Phytomanagement

1. Introduction

1.1. Trace elements in military shooting ranges

Lead (Pb) and to a lesser extent antimony (Sb) are common contaminants in areas adjacent to the stop butts of military shooting ranges (MSRs). On an average, new bullets and pellets consist of over 90% Pb, 1–7% Sb, <2% arsenic (As) and <0.5% nickel (Ni) (Rooney et al., 1999). Low-quality Pb, from which bullets are made, may also contain bismuth (Bi) and silver (Ag) (Johnson et al., 2005). Zinc (Zn) and copper (Cu) covers improve the ballistic properties of high velocity rounds. Tracer and incendiary bullets contain strontium (Sr), barium (Ba) and Zn (Batelle Corporation, 1997).

Once in the soil, the bullets and the bullet fragments gradually oxidise through the weathering actions of air, water, organic acids and microbial activity (Lin et al., 1995; Johnson et al., 2005). The most important factor governing the rate of bullet oxidation is the soil's pH (Labare et al., 2004).

Switzerland is a highly militarised nation with an annual defence budget of US$ 2.5 billion (CIA, 2006). Military training, combined with recreational shooting, result in the annual deposition of >400 t of Pb into Swiss soils at some 2000 MSRs scattered throughout the country (Johnson et al., 2005).

1.2. Environmental risks of trace elements in MSRs

Lee et al. (2002) reported a reduction in the enzymatic activity in shooting range soils. Tuomela et al. (2005) and

* Corresponding author. Tel.: +41 44 633 6073; fax: +41 44 633 1123.
E-mail address: brett.robinson@env.ethz.ch (B.H. Robinson).

0269-7491/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envpol.2007.08.034

Rantalainen et al. (2006) demonstrated the negative effect of Pb on litter decomposers in Finnish forests.

The migration of toxic trace elements to the food chain or to the drinking water can reduce ecosystem functioning on a large scale and may present a human health risk. Craig et al. (1999) and Sorvari et al. (2006) reported that Pb from shooting range stop butts might leach and contaminate receiving waters (ground- and surface-waters). Wersin et al. (2002) measured elevated Sb concentrations in receiving waters near a Swiss MSR. Migliorini et al. (2003) reported the bioaccumulation of Pb by invertebrates on shooting ranges.

Although trace element phases with a low solubility may migrate from shooting ranges with surface runoff and erosion (Craig et al., 1999), soluble phases have the greatest mobility and present the largest environmental risk.

1.3. Plant interactions with trace elements on shooting ranges

Most studies investigating plants on shooting ranges have dealt with Pb, because this trace element occurs at the highest concentration in the soil. Rooney et al. (1999) clearly demonstrated the poor translocation of Pb from plant roots into the shoots. They showed that in a lead-shot contaminated soil containing nearly 6000 mg/kg of EDTA extractable Pb, the root concentrations of Barley, Lettuce, Ryegrass, Radish and Clover were about 60 times higher that the shoot Pb concentrations, which were, in all cases, less than 100 mg/kg.

Zellmer and Schneider (1993) measured some metal concentrations in leaves from assorted species on shooting ranges from Grafenwöhr, Germany. They found that the concentrations of most metals fell within the normal range for plants (Baker and Chesnin, 1975). They attributed the occasional high Pb concentration to surface contamination. Ma et al. (2002) measured Pb in Bermuda grass (*Cynodon dactylon*). They found up to 806 mg/kg Pb in the shoot tissue. Labare et al. (2004) found shoot concentrations up to 152 mg/kg Pb for various species growing at an active shooting range at West Point, New York. The Pb in plant tissue may have arisen from air-borne Pb generated by shooting as well as soil-bound Pb. Mozafar et al. (2002) reported that, when grown in shooting range soils under greenhouse conditions, Leeks (*Allium porrum* L.) accumulated Pb to over 1000 mg/kg in the aboveground portions.

Antimony has only recently become the focus of environmental concerns about trace element inputs into shooting range soils. Johnson et al. (2005) reported that Sb was the most soluble and mobile of all the trace element contaminants in Swiss MSRs.

1.4. Vegetation and the management of disused MSRs

There are limited remediation options for disused MSRs. One can remove the stop butts and reprocess the soil to recover the valuable Pb. However, it is impractical to remove all the contaminated soil, or cap entire MSRs with non-contaminated material. Nor is there any technology that would permit the safe in situ decontamination of such sites (Sorvari et al., 2006).

Vegetation and soil conditioners may reduce the mobility of the contaminating trace elements, thereby reducing the exposure pathways to humans and ecosystems. Since vegetation will eventually cover most disused MSRs, land managers could select plants that do not accumulate toxic metals in their aboveground portions, yet have a high transpiration rate, thus reducing the leaching of these metals into receiving waters (Robinson et al., 2003).

It is important to distinguish between trace elements in the aerial portions of plants that have arisen from surface deposition and those taken up by the roots and subsequently translocated to the shoots. When the site is entirely vegetated, the stabilising effect of plant roots will mitigate the generation of wind-borne dust and rain-induced redistribution of contaminated solid material from soil. Thus, uptake from the soil will play an overriding role in controlling the total aboveground trace element concentration, and hence the potential exposure to herbivores. Conversely, in a sparsely vegetated site, a large proportion of the trace elements in the aerial tissues may come from surface deposition. These trace elements, may nevertheless present an ecological or human health risk if consumed.

1.5. Aims

We aimed to determine the accumulation of trace elements by vegetation growing on the stop butt of a disused MSR in Switzerland, with a view to identifying plant species that may be useful for trace element immobilisation. In particular, we sought to distinguish between physiological trace element uptake by plants and trace elements in the shoots arising from aerial surface deposition.

2. Materials and methods

Sampling occurred on the stop butt (15 m × 100 m) of a 300 m military shooting range (MSR) at the Allmend (47°01′42.85″ N, 8°18′36.8″ E), near the city of Lucerne, Switzerland. The MSR has been disused for five years. The concentration of Pb in the soil of the stop butt ranged from 0.7% to 15%, while the soil Pb burden in the remainder of the MSR ranged from 0.01% to 1%. The average annual rainfall is 1171 mm, with an average annual temperature of 8.8 °C, as measured at a nearby meteorological station in Luzern. The soil pH was 6.9. The median sand, silt, and clay fractions were 59%, 26% and 15%, and the median organic carbon content was 7.3%.

On the 2nd of September 2005 (sunny, dry weather), we sampled leaves from 10 of the most commonly occurring plant species. For each plant sample, we took ca. 150 g of fresh shoot material at least 50 mm above the soil. We did not sample roots due to the impossibility of adequately removing the surrounding soil, which contained up to 15% Pb. For each plant, we also sampled soil from the root zone. After removing any surface litter, approximately 500 g of soil was sampled from a depth of 20–100 mm. In total, we sampled 70 individual plants and soils. Table 1 lists the plant species that were sampled, along with the number of samples taken.

Vegetative material was thoroughly washed for 18 h after sampling with distilled water, and then dried at 40 °C until a constant weight was obtained. Soils were similarly dried and then sieved to <2 mm using a nylon sieve. We found no bullet fragments in the soil, either in the <2 mm fraction or in the ≥2 mm fraction.

Table 1
Plant species sampled from a military shooting range, Luzern Allmend, Switzerland

Species	Botanical reference	Family	Number of samples
Equisetum arvense	L.	Equisetaceae	21
Dryopteris affinis	Lowe	Dryopteridaceae	5
Salix purpuria	L.	Salicaceae	5
Salix cinerea	L.	Salicaceae	5
Salix alba	L.	Salicaceae	5
Populus alba	L.	Salicaceae	3
Tussilago farfara	L.	Asteraceae	10
Silene vulgaris	Moench	Caryophyllaceae	5
Arrhenatherum elatius	L.	Poaceae	5
Molinia arundinacea	Schrank	Poaceae	5

2.1. Elemental determination

Soil samples were ground using a Retsch RS1 grinder with a tungsten carbide ball and ring. Plant samples were ground using a Retsch ZM200 titanium mill. Ground material (4 g) was mixed with 0.9 g of wax and pressed into tablets under a pressure of 15 t. The total element concentrations (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Hf, Ta, W, Hg, Tl, Pb, Bi, Th, U) of the tablets were determined using a Spectro X-lab 2000 X-Ray Fluorescence (XRF) spectrometer. Here, we only report elements that were above detection limits (0.1–5 mg/kg for all elements except Na (100 mg/kg) and Al (20 mg/kg) in both plant and soil samples) in >50% of the samples.

For quality assurance, we analysed 4 Wageningen soil standards, 958, 998, 989, and 951 (Wageningen, 2006) as well as a certified plant reference material (poplar leaves NCS DC73350, China National Analysis Center for Iron and Steel, Beijing, China). The average recoveries for soils were: Ca 113%, Cu 117%, Fe 106%, Pb 115%, K 100%, Mg 89%, Mn 112%, Ni 125%, Sb 121%, and Zn 101%. For the plant standard, the recoveries were: Ca 96%, Cu 101%, Fe 98%, K 97%, Mg 67%, Mn 126%, Ni 89%, and Zn 99%. In the plant reference, Pb and Sb were below the detection limits of our method for plant samples (<2 mg/kg).

In a second test of analytical quality, we sent 10 soil samples and 10 plant samples to an external laboratory (Niutec AG, Winterthur) for acid digestion and analyses with ICP-MS for Pb, Sb, Bi, Tl, Ga, and Hg. The recoveries of Pb and Sb, in this case the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) results as a percentage of the XRF results, were 114% and 127%. The correlation coefficients (r) between our XRF analyses and those of the external laboratory were 0.98 for both Pb and Sb. The recoveries (ICP-MS/XRF) were <3% for Bi, Tl and Hg, and <10% for Ga. Therefore, we do not report data for these elements. The high concentrations measured on the XRF were probably the result of interference from inordinately high Pb concentrations with Bi, Tl and Hg.

2.2. Calculating the fraction of trace elements in the leaves originating from surface deposition

Even careful washing does not remove all surface-deposited dust, which may incorporate particles into the waxy layers or entrap them in leaf hairs. Therefore, some fraction of a plant sample may actually consist of soil particles. To determine the mass of soil contamination on leaf samples, one can measure an indicator element that is indicative of the level of soil contamination on the leaves (Hinton et al., 1995). The indicator element should not be of interest in the study and should occur at high concentrations in the soil. Its physiological uptake by the plant should be either low or maintained at a constant tissue concentration over a wide range of soil concentrations. It is advantageous if it correlates with the elements of interest. This is because the calculation uses the indicator element concentration in the soil where the plant is growing; however, wind may have deposited soil from some distance onto the plant leaves. Titanium, Ba, and Cr make good indicator elements, since the plants do not take up significant concentrations of these elements (Brooks, 1998). Therefore, the measured concentrations are directly proportional to surface-deposited dust. Unfortunately, these elements were unsuitable as indicator elements in this study. The plant mill contained Ti, thus leading to elevated Ti concentrations in the plant samples. Barium and Cr occurred at relatively low concentrations in the soil (277 mg/kg and 126 mg/kg) and in any case were not positively correlated with Pb ($r = -0.46$ and $r = 0.10$), the principle element of interest. By contrast, Fe occurred at 65,766 mg/kg in the soil, and was strongly correlated with Pb ($r = 0.85$). However, Fe is an essential nutrient that plants take up to concentrations of around 112 mg/kg (Marschner, 1995). Therefore, when using Fe to calculate surface deposition, one must first subtract a baseline value, i.e. the Fe that the plants have accumulated through root uptake. The mass fraction of soil on the plant sample, M_{soil} (kg/kg) is therefore:

$$M_{\text{soil}} = \frac{T_{\text{plant}} - R_{\text{plant}}}{T_{\text{soil}}}$$

where T_{plant} is the measured indicator element concentration in the plant tissue (mg/kg), R_{plant} is the baseline concentration of the indicator element that the plant has accumulated through the roots and translocated to the shoots (mg/kg), and T_{soil} is the concentration of the indicator element in the soil (mg/kg). The corrected plant concentration of the target element, $C_{\text{plant}}*$ (mg/kg), is:

$$C^{*}_{\text{plant}} = C_{\text{plant}} - M_{\text{soil}}C_{\text{soil}}$$

where C_{plant} and C_{soil} are the measured concentrations (mg/kg) of the target element in the plant and soil.

For each target element, we separated plant uptake from surface deposition using Fe as an indicator element. We took the baseline concentration of Fe in the plant, i.e. R_{plant} for Fe, of 27.3 mg/kg, the lowest measured Fe concentration in any of our plant samples. To validate the amount of surface-deposited dust calculated with Fe, we repeated the calculation using Cu (baseline value = 2.3 mg/kg) and Al (baseline value = 22 mg/kg). The mass of surface-deposited material that we calculated with Cu and Al were in reasonable agreement ($r = 0.96$ and $r = 0.92$) with the values calculated using Fe.

Errors will arise in the corrected values calculated using Fe as an indicator element when the amount of Fe that the plant has taken up through the roots differs from the baseline value used in the calculation. Similarly, surface-deposited dust from soil that is chemically distinct from the plant's rhizospheric soil will result in errors.

2.3. Statistical treatment of data

Data that were log-normally distributed were log-transformed for statistical analyses. Data were considered lognormal when the geometric mean was closer to the median than the arithmetic mean. For lognormal data, we report geometric means and standard deviation ranges rather than means and standard deviations. With lognormal data, the geometric mean is a better measure of central tendency than the arithmetic mean. Use of geometric means reduces distortions caused by a few anomalous values and produces a value of better centrality.

3. Results

3.1. Elemental composition of soils

Fig. 1a shows the concentrations of selected elements in the soil samples taken from the plant rhizospheres. Lead, after Si, occurred at the highest concentration in the soil, some 160 times higher than the Dutch Intervention Value (DIV) of 530 mg/kg. Antimony, Cu and Ni concentrations also exceeded the DIVs, which are 15 mg/kg, 190 mg/kg, and 210 mg/kg (Heinrich, 2006). Lead was significantly ($p < 0.05$) and positively correlated with (in increasing order of p) Sb, Ni, Cu, Rb, Fe, Sm,

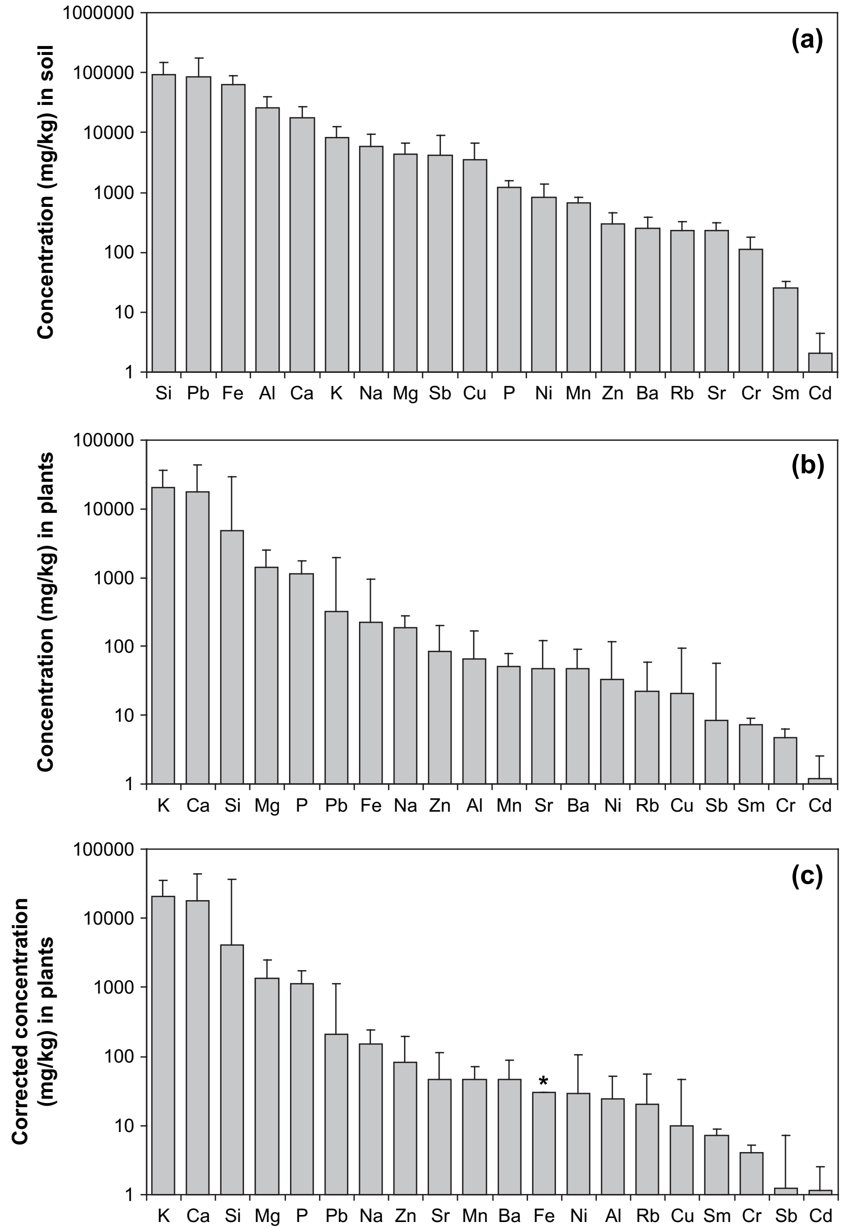

Fig. 1. Geometric mean trace element concentrations (mg/kg), with positive standard deviation ranges, in rhizospheric soil (a) and leaves (b) of all plant species sampled from the stop butt of a military shooting range near the city of Lucerne, Switzerland. The corrected plant concentrations (c) were calculated using Fe as an indicator element to determine surface deposition. *Fe, the indicator element, has been normalised to 27 mg/kg in the dry plant tissue.

Na, Cd, Sr and P, and significantly and negatively correlated with Ca, Al, K, Si, Ba, and Mg. Elements that are positively correlated with Pb are probably constituents of the bullets, while the remainder are probably the major components of the native soil.

3.2. Elemental composition of plants

Fig. 1b shows the geometric means of the uncorrected trace element concentrations in all 70 plant samples. As expected, the essential plant macronutrients occur at the highest concentrations. The geometric mean concentrations of Pb, Ni and Cu were manifold higher than the values (2–5 mg/kg, 0.1–5 mg/kg, and 3–20 mg/kg) that Chaney (1989) considered "normal levels" in the shoots of plant species growing in non-contaminated soil. The geometric mean Pb concentration was above 30 mg/kg, a threshold concentration in fodder (Chaney, 1989), above which livestock (cattle, sheep, swine, poultry) may show toxicity symptoms. Leaf Cu concentrations exceeded threshold levels for sheep (25 mg/kg) but not for other livestock. The geometric mean Ni concentration in leaves was below the threshold for livestock (50 mg/kg) given by Chaney (1989).

Upon correction of the plant concentrations using Fe as an indicator element, the concentrations of the plant macronutrients, namely K, Ca, Mg and P, stayed within 98% of their original value (Fig. 1c). However, the concentrations of Pb, Sb, and Cu, the major soil contaminants, dropped to 45%, <20% and 50% of their original values. The corrected Ni concentration was still 95% of its original value. These results indicate that, with the exception of Ni, surface deposition, rather than plant uptake, is responsible for most of the contaminants present in the plant leaves. Nevertheless, the levels of Pb remain far above levels that Chaney (1989) reported as normal for plant tissue.

Table 2 shows the Pb, Sb, Cu and Ni concentrations in the leaves of 10 sampled plant species, along with their concentrations in the rhizospheric soil and bioaccumulation coefficients (plant/soil concentration quotient). For *Dryopteris affinis*, *Salix* spp., and *Populis alba* the corrected leaf Pb concentrations were within the normal range for plants. *Silene vulgaris*, *Arrhenatherum elatius*, and *Molina arundinacea* contained elevated concentrations (20–70 mg/kg), while *E. arvense* and *T. farfara* contained Pb at concentrations (both corrected and uncorrected) 10 to 50 times higher than those shown to be toxic to livestock (30 mg/kg).

Across all species, the leaf concentrations of Pb, Cu, Ni, Sr and Sm were significantly and positively correlated with the concentrations of these elements in the soil. Fig. 2 shows these

Table 2
Geometric mean Pb, Sb, Cu and Ni concentrations (mg/kg), along with standard deviation ranges, in leaves and rhizospheric soil of plants sampled from the stop butt of a military shooting range near the city of Lucerne, Switzerland

	Soil	Plant	Plant (corrected)	BAF
Pb				
Equisetum arvense	96,100 (49,700–185,900)	855 (194–3760)	346 (102–1180)	0.004
Dryopteris affinis	95,700 (52,200–175,000)	113 (75–171)	4 (1–24)	0.001
Salix purpuria	85,700 (44,800–164,000)	145 (40–523)	5 (1–29)	0.001
Salix cinerea	87,800 (67,200–115,000)	169 (57–497)	4 (1–26)	0.002
Salix alba	100,000 (81,800–128,000)	50 (20–133)	3 (<1–9)	<0.001
Populus alba	156,000 (64,900–250,000)	92 (41–208)	<2	<0.001
Tussilago farfara	132,000 (111,000–158,000)	4640 (3130–6880)	1580 (1100–2280)	0.012
Silene vulgaris	56,000 (25,000–109,000)	86 (46–142)	24 (8–56)	<0.001
Arrhenatherum elatius	14,000 (9590–20,400)	69 (50–97)	56 (41–77)	0.004
Molinia arundinacea	90,600 (72,900–113,000)	87 (73–104)	67 (52–85)	0.001
Sb				
Equisetum arvense	4760 (2470–9160)	20 (3–116)	<2	<0.001
Dryopteris affinis	4580 (2590–8100)	1 (1–2)	<2	<0.001
Salix purpuria	4550 (2540–8140)	4 (2–11)	<2	<0.001
Salix cinerea	4420 (3310–5900)	4 (1–12)	<2	<0.001
Salix alba	4920 (4140–6100)	2 (1–3)	<2	<0.001
Populus alba	8230 (3300–13500)	4 (2–5)	<2	<0.001
Tussilago farfara	6420 (5550–7440)	143 (92–222)	10 (4–25)	0.002
Silene vulgaris	2930 (1280–5830)	2 (1–4)	<2	<0.001
Arrhenatherum elatius	629 (395–1000)	2 (1–2)	<2	<0.001
Molinia arundinacea	4750 (3870–5830)	2 (1–2)	<2	<0.001
Cu				
Equisetum arvense	4120 (2170–7810)	34 (8–150)	13 (4–46)	0.003
Dryopteris affinis	2340 (1380–3970)	7 (5–9)	3 (3–4)	0.001
Salix purpuria	3250 (1830–5790)	13 (8–21)	4 (2–10)	0.001
Salix cinerea	4030 (3880–4190)	13 (7–22)	3 (1–7)	0.001
Salix alba	4300 (3300–5590)	11 (8–16)	4 (1–10)	0.001
Populus alba	6200 (3090–10500)	10 (7–15)	2 (1–3)	<0.001
Tussilago farfara	4890 (3940–6080)	249 (155–402)	136 (82–228)	0.028
Silene vulgaris	2750 (1370–4830)	9 (6–13)	6 (5–7)	0.002
Arrhenatherum elatius	996 (670–1480)	7 (6–8)	6 (6–7)	0.006
Molinia arundinacea	4180 (3360–5200)	3 (2–4)	2 (1–3)	0.001
Ni				
Equisetum arvense	902 (521–1560)	79 (36–175)	72 (34–151)	0.080
Dryopteris affinis	581 (364–928)	16 (11–23)	15 (10–22)	0.025
Salix purpuria	783 (515–1190)	29 (17–47)	26 (14–47)	0.033
Salix cinerea	879 (745–1040)	39 (25–61)	36 (23–57)	0.042
Salix alba	985 (880–1140)	9 (4–16)	7 (3–15)	0.007
Populus alba	1490 (733–2440)	57 (25–88)	55 (25–85)	0.037
Tussilago farfara	1040 (881–1230)	111 (52–239)	85 (34–208)	0.081
Silene vulgaris	685 (360–1150)	27 (17–39)	26 (16–38)	0.038
Arrhenatherum elatius	265 (186–378)	4 (2–6)	3 (2–6)	0.013
Molinia arundinacea	979 (767–1250)	5 (4–5)	5 (4–5)	0.005

The corrected plant values were calculated using Fe as an indicator element to determine surface deposition. BAF is the bioaccumulation coefficient, defined here as the plant (corrected)/soil concentration quotient.

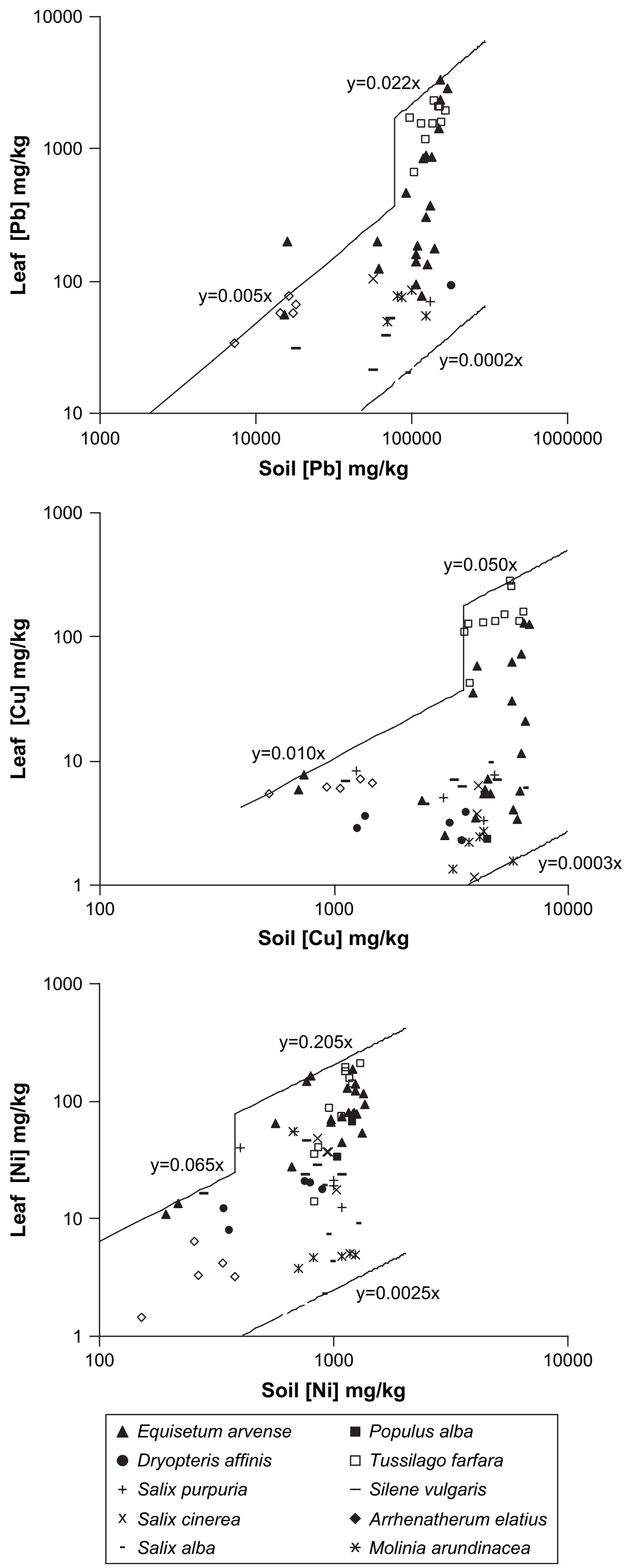

Fig. 2. Corrected leaf metal (mg/kg dry matter) for all species as a function of soil metal concentration (mg/kg). The corrected plant values were calculated using Fe as an indicator element to determine surface deposition. The regression lines represent the minimum and maximum plant concentration at a given soil concentration.

relationships for Pb, Cu and Ni along with the minimum and maximum bioaccumulation coefficients (plant/soil concentration quotient). The maximum bioaccumulation coefficient for these elements increased at higher soil metal concentrations, represented in Fig. 2 in a two-step equation. The threshold soil concentrations, above which plant metal concentrations sharply increased, were 60,000 mg/kg for Pb, 3600 mg/kg for Cu, and 400 mg/kg for Ni. These results show that the risk of these metals entering the food chain via plant uptake is disproportionately higher above these threshold concentrations. In a single species, *E. arvense*, for which we had 21 samples, Pb uptake followed a similar trend of increased bioaccumulation at higher soil Pb concentrations (Fig. 3). This species follows an accumulation pattern similar to that proposed by Baker (1981) for a metal-excluder species.

The corrected Sb concentrations in the leaves of all species except *T. farfara* were below detection limits (2 mg/kg). The bioaccumulation coefficients of all species were below 0.002. In leaf tissue, Sb was significantly and positively correlated with Fe ($r = 0.97$, $p < 0.001$), which we used as an indicator element (Fig. 4). This indicates that virtually all measured Sb in the plants arose from surface deposition, and little was translocated from the roots to the shoots.

The corrected Cu concentrations in the leaves of all species except *T. farfara* were in the range 3–20 mg/kg that Chaney (1989) considered normal for plant tissue. *T. farfara* had leaf concentrations above those reported to be phytotoxic (10–70 mg/kg) by Gupta and Gupta (1998). There was no significant correlation between the leaf and rhizospheric soil Cu concentration in *E. arvense*.

Except for *A. elatius*, the corrected Ni concentrations in all plants were above the normal range (0.1–5 mg/kg) in plants given by Chaney (1989). Nickel had the highest bioaccumulation factor of the 4 major contaminants. There was little difference between the uncorrected and corrected values, indicating that most of the Ni present in the leaves was taken up by the plant through the roots, and not surface-deposited. Nevertheless, the

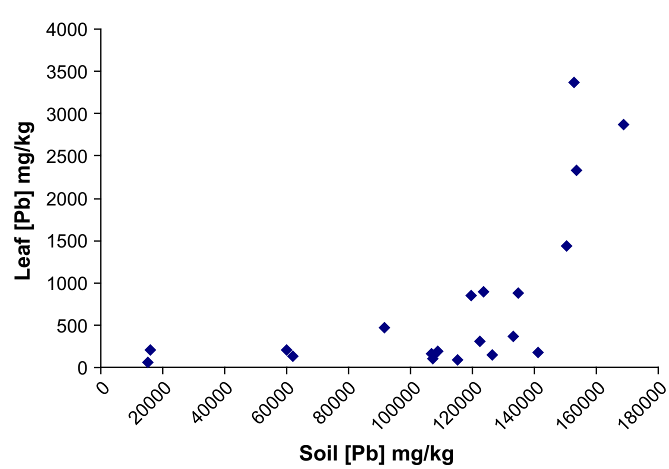

Fig. 3. Corrected Leaf Pb concentration (mg/kg dry matter) in *Equisetum arvense* as a function of soil Pb concentration (mg/kg). The corrected plant values were calculated using Fe as an indicator element to determine surface deposition.

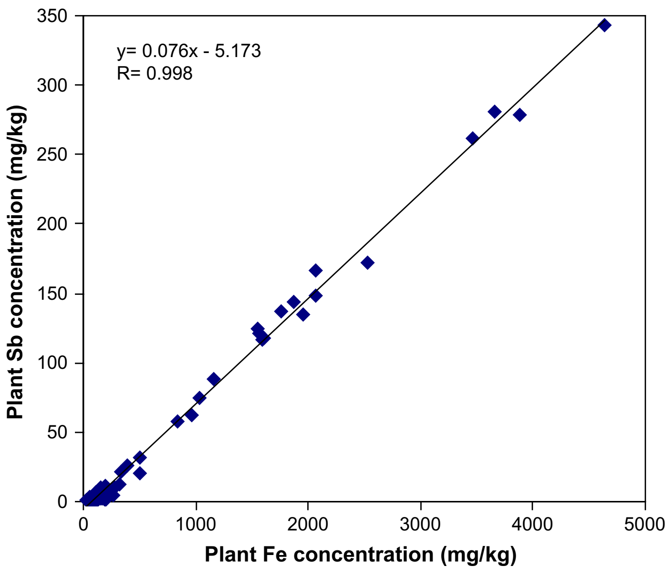

Fig. 4. Leaf Sb concentration vs leaf Fe concentration (mg/kg) in 10 plant species from the stop butt of a military shooting range near the city of Lucerne, Switzerland.

concentrations in the sampled plants were within the range found within non-hyperaccumulator plants growing on Ni-rich ultramafic (serpentine) soils (Brooks, 1987). There was a highly significant and positive correlation between the Ni concentration in the shoots of *E. arvense* and the soil Ni concentration.

4. Discussion

The high metal burden in the stop butt of the MSR may explain the sparse vegetation, even though more than five years have elapsed since the last shot was fired. The high pH (6.9) and high organic matter contents in the stop butt no doubt reduce the phytotoxicity of metals that may otherwise inhibit the establishment of vegetation. Unlike cationic elements, Sb is more soluble at high soil pH (Nakamaru et al., 2006) and thus more available to interact with plant roots. We did not quantify the trace element concentrations in soil solution.

After washing, the leaf Pb, Sb, Cu, and Ni concentrations of all species were above the normal range for plants and in the range reported by Chaney (1989) to be toxic to livestock. Presumably, unwashed plant material, which herbivores would consume, would have even higher concentrations of these toxic elements. Separating the trace elements that were deposited on the leaf surface from those that the plant has taken up from through the roots revealed that for most species, the metal uptake fell into the normal range for plants. The exceptions were *E. arvense* and *T. farfara*. Both these species were found on the most highly contaminated soil, which was devoid of other species. The physiological metal uptake in these plants may have been higher, because they were growing in soil with a relatively high trace element burden. High soluble trace element concentrations (which we did not quantify) can damage plant roots, allowing the direct entry of soil solution into the xylem, thus enhancing plant metal uptake. These phenomena may explain the sharp increase in Pb uptake by *E. arvense* at high soil Pb concentrations (Fig. 3).

The low physiological plant uptake of Sb found in this study is surprising, since Johnson et al. (2005) reported that Sb is the most soluble element in shooting range soils. Although we did not quantify soluble Sb in this study, one would expect Sb to be relatively soluble at the neutral pH in our soils. The large size of the $Sb(OH)_6^-$ anion, the predominant form in well aerated soils (Scheinost et al., 2006), may prohibit its passage through the root endodermis into the xylem, thus limiting its translocation to the aerial portions of the plant.

The plants in this study, which were all sampled in late summer, represent a snapshot of leaf trace element concentrations at only one time. Poplars and willows have the highest foliar concentrations of many trace elements at this time (Robinson et al., 2005). By contrast, Deram et al. (2006) found that Pb, Cd, and Zn concentrations in the leaves of *A. elatius* were highest at the beginning of the growing season.

4.1. Management implications

Unless the most highly contaminated soils were removed, Pb uptake by species such as *E. arvense* and *T. farfara* may still be above 30 mg/kg, a concentration that is toxic to livestock (Chaney, 1989). Lead immobilisation agents, such as hydroxyapatite or Zeolite minerals may also reduce plant Pb uptake (Chen et al., 2007).

Given that the Pb concentration in most rhizospheric soils of the stop butt are above those of many Pb ores (Mucha and Szuwarzynski, 2004), this soil could be removed, and the Pb extracted to recover the cost of the operation. The establishment of vegetation, using soil conditioners and metal-tolerant species, on the remainder of the MSR would greatly reduce the concentrations of toxic elements associated with plant leaves, because this would eliminate wind-borne and rain-splash soil particles, the main contributor to the plant's trace element burden. In the case of Sb, the most abundant contaminant after Pb, plant tissue concentrations could be reduced to <1 mg/kg. Without surface deposition, the reduced concentrations of Cu and Ni would be unlikely to present a risk to terrestrial ecosystems.

Intuitively, planting deep-rooted tree species to reduce leaching may seem like a logical choice, since they would maximise evapotranspiration from the site, thus minimising drainage. However, the roots of such trees may create preferential flow pathways that actually exacerbate contaminant leaching. Knechtenhofer et al. (2003) showed that preferential flow was the main mechanism for the downward mobility of otherwise immobile elements in another Swiss MSR. Vegetation with a high biomass production may also enhance trace element mobility through the generation of organic compounds, which Wang and Benoit (1996) demonstrated as important factors in the Pb flux in a contaminated forest.

Similar to other polluted sites, contaminants in MSRs occur heterogeneously. The interactions of roots with hotspots are of overriding importance on the contaminant fate. Root avoidance of hotspots will reduce contaminant mobility because of reduced plant uptake. Conversely, when roots penetrate a hotspot, the plant may accumulate higher amounts of the contaminant and the contaminants may have a preferential flow conduit into receiving waters (Roulier et al., in press).

The remediation of disused MSRs would be most effective by combining soil removal, soil conditioners, revegetation and perhaps reactive barriers to capture Pb, Sb, Cu and Ni that leach beyond the root zone. Since any remediation-technology is sensitive to climatic and edaphic conditions, the design of such systems requires mechanistic modelling. These models should incorporate variation in microtopography that may cause crusting (Roulier et al., 2002). This could increase run-off and erosion from Swiss MSRs, many of which are on steep slopes in the Alps.

5. Conclusions

The major soil contaminants Pb, Sb, Cu, and Ni occurred at high concentrations in the aerial portions of the sampled plants, primarily because of the surface deposition of wind-borne dust from the sparsely vegetated soil. At high soil Pb concentrations (>60,000 mg/kg) the physiological uptake of Pb by plant may present an exposure pathway for this toxic element to enter food chains. Revegetating the site, using metal-tolerant species, soil conditioners and possibly capping with uncontaminated topsoil, would reduce the upward mobility of these contaminants into plant tissues. Vegetation would also reduce, via evapotranspiration, the downward mobility of these contaminants into receiving waters. An important and as-yet unanswered question is whether deep-rooted tree species generate macropores that enhance contaminant leaching via preferential flow.

Acknowledgements

We gratefully acknowledge Niutec Laboratories AG, who conducted the independent analyses. We would like to thank Stefan Herfort at Umwelt und Energie Luzern for help with the plant identification.

References

Baker, A.J.M., 1981. Accumulators and excluders – strategies in the response of plants to heavy metals. Journal of Plant Nutrition 3, 643–654.

Baker, D.E., Chesnin, L., 1975. Chemical monitoring for environmental quality and animal and human health. Advances in Agronomy 27, 305–374.

Batelle Corporation, 1997. Implementation Guidance Handbook: Physical Separation and Acid Leaching to Process Small-arms Range Soils. Naval Facilities Engineering Service Center. Available from: http://enviro.nfesc.navy.mil/erb/erb_a/restoration/technologies/remed/uxo_remed/rpt-sar-imple.pdf (accessed 03.08.06).

Brooks, R.R., 1987. Serpentine and Its Vegetation. Discorides Press, Portland.

Brooks, R.R., 1998. Plants That Hyperaccumulate Heavy Metals: Their Role in Archaeology, Microbiology, Mineral Exploration, Phytomining and Phytoremediation. CAB International, Wallingford.

Chaney, R.L., 1989. Toxic element accumulation in soils and crops: protecting soil fertility and agricultural food chains. In: Bar-Yosef, B., Barrow, N.J., Goldshmid, J. (Eds.), Inorganic Contaminants in the Vadose Zone. Springer, Berlin, pp. 140–158.

Chen, S.B., Xu, M.G., Ma, Y.B., Yang, J.C., 2007. Evaluation of different phosphate amendments on availability of metals in contaminated soil. Ecotoxicology and Environmental Safety 67 (2), 278–285.

CIA, 2006. The CIA World Fact Book. Available from: https://www.cia.gov/cia/publications/factbook/geos/sz.html (accessed 04.08.06).

Craig, J.R., Rimstidt, J.D., Bonnaffon, C.A., Collins, T.K., Scanlon, P.F., 1999. Surface water transport of lead at a shooting range. Bulletin of Environmental Contamination and Toxicology 63, 312–319.

Deram, A., Denayer, F., Petit, D., Van Haluwyn, C., 2006. Seasonal variations of cadmium and zinc in *Arrhenatherum elatius*, a perennial grass species from highly contaminated soils. Environmental Pollution 140, 62–70.

Gupta, U.C., Gupta, S.C., 1998. Trace element toxicity relationships to crop production and livestock and human health: implications for management. Communications in Soil Science and Plant Analysis 29 (11–14), 1491–1522.

Heinrich, A., 2006. Comparison of soil clean-up standards for trace elements between countries: why do they differ? Journal of Soils and Sediments 6 (3), 173–181.

Hinton, T.G., Kopp, P., Ibrahim, S., Bubryak, I., Syomov, A., Tobler, L., Bell, C., 1995. A comparison of techniques used to estimate the amount of resuspended soil on plant surfaces. Health Physics 68, 523–531.

Johnson, C.A., Moench, H., Wersin, P., Kugler, P., Wenger, P., 2005. Solubility of antimony and other elements in samples taken from shooting ranges. Journal of Environmental Quality 34, 248–254.

Knechtenhofer, L.A., Xifra, I.O., Scheinost, A.C., Flühler, H., Kretzschmar, R., 2003. Fate of heavy metals in a strongly acidic shooting-range soil: small-scale metal distribution and its relation to preferential flow. Journal of Plant Nutrition and Soil Science 166, 84–92.

Labare, M.P., Butkus, M.A., Riegner, D., Schommer, N., Atkinson, J., 2004. Evaluation of lead movement from the abiotic to the biotic at a small-arms firing range. Environmental Geology 46, 750–754.

Lee, I.S., Kim, O.K., Chang, Y.Y., Bae, B., Kim, H.H., Baek, K.H., 2002. Heavy metal concentrations and enzyme activities in soil from a contaminated Korean shooting range. Journal of Bioscience and Bioengineering 94 (5), 406–411.

Lin, Z., Comet, B., Qvarfort, U., Herbert, R., 1995. The chemical and mineralogical behaviour of Pb in shooting range soils from central Sweden. Environmental Pollution 89 (3), 303–309.

Ma, L.Q., Cao, R.X., Hardison, D., Chen, M., Harris, W.G., Sartain, J., 2002. Environmental Impacts of Lead Pellets at Shooting Ranges and Arsenical Herbicides on Golf Courses in Florida. Report No. 02-01. Florida Center for Solid and Hazardous Waste Management. Available from: http://lqma.ifas.ufl.edu/Publication/MA-00-R.pdf (accessed 03.08.06).

Marschner, H., 1995. Mineral Nutrition of Higher Plants. Academic Press, London, UK, p. 65.

Migliorini, M., Pigino, G., Bianchi, N., Bernini, F., Leonzio, C., 2003. The effects of metal contamination on the soil arthropod community of a shooting range. Environmental Pollution 129 (2), 331–340.

Mozafar, A., Ruh, R., Klingel, P., Gamper, H., Egli, S., Frossard, E., 2002. Effect of heavy metal contaminated shooting range soils on mycorrhizal colonization of roots and metal uptake by leek. Environmental Monitoring and Assessment 79, 177–191.

Mucha, J., Szuwarzynski, M., 2004. Sampling errors and their influence on accuracy of zinc and lead content evaluation in ore from the Trzebionka mine (Silesian–Cracow Zn–Pb ore district, Poland). Chemometrics and Intelligent Laboratory Systems 74 (1), 165–170.

Nakamaru, Y., Tagami, K., Uchida, S., 2006. Antimony mobility in Japanese agricultural soils and the factors affecting antimony sorption behavior. Environmental Pollution 141, 321–326.

Rantalainen, M.L., Torkkeli, M., Strömmer, R., Setälä, H., 2006. Lead contamination of an old shooting range affecting the local ecosystem – a case study with a holistic approach. Science of the Total Environment 369, 99–108.

Robinson, B.H., Green, S.R., Mills, T.M., Clothier, B.E., van der Velde, M., Laplane, R., Fung, L., Deurer, M., Hurst, S., Thayalakumaran, T., van den Dijssel, C., 2003. Phytoremediation: using plants as biopumps to improve degraded environments. Australian Journal of Soil Research 41 (3), 599–611.

Robinson, B.H., Mills, T.M., Green, S.R., Chancerel, B., Clothier, B.E., Fung, L., Hurst, S., McIvor, I., 2005. Trace element accumulation by pop-

lars and willows used for stock fodder. New Zealand Journal of Agricultural Research 48, 489–497.
Rooney, C.P., McLaren, R.G., Cresswell, R.J., 1999. Distribution and phytoavailability of lead in a soil contaminated with lead shot. Water, Air and Soil Pollution 116, 535–548.
Roulier, S., Angulo-Jaramillo, R., Bresson, L.M., Auzet, A.V., Gaudet, J.P., Bariac, T., 2002. Water transfer and mobile water content measurement in a cultivated crusted soil. Soil Science 167 (3), 201–210.
Roulier, S., Robinson, B., Kuster, E., Schulin, R. Analysing the preferential transport of lead in a road-side soil under vegetation. European Journal of Soil Science, in press. doi:10.1111/j.1365-2389.2007.00954.x.
Scheinost, A.C., Rossberg, A., Vantelon, D., Xifra, I., Kretzschmar, R., Leuz, A.K., Funke, H., Johnson, C.A., 2006. Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy. Geochimica et Cosmochimica Acta 70, 3299–3312.
Sorvari, J., Antikainen, R., Pyy, O., 2006. Environmental contamination at Finnish shooting ranges – the scope of the problem and management options. Science of the Total Environment 366, 21–31.
Tuomela, M., Steffen, K.T., Kerko, E., Hartikainen, H., Hofrichter, M., Hatakka, A., 2005. Influence of Pb contamination in boreal forest soil on the growth and ligninolytic activity of litter-decomposing fungi. FEMS Microbiology Ecology 53, 179–186.
Wageningen, 2006. International Soil-analytical Exchange. Quarterly report 2006.1. WEPAL, Wageningen, Netherlands.
Wang, E.X., Benoit, G., 1996. Mechanisms controlling the mobility of lead in the spodosols of a northern hardward forest ecosystem. Environmental Science and Technology 30, 2211–2219.
Wersin, P., Johnson, C.A., Furrer, G., 2002. Antimony contamination in soil and groundwater by shooting range activities. Geochimica et Cosmochimica Acta 66, A829.
Zellmer, S.D., Schneider, J.F., 1993. Heavy-metal Contamination on Training Ranges at the Grafenwöhr Training Area, Germany. Prepared by Argonne National Laboratory, Argonne, IL, for the Department of the Army, U.S. Army Seventh Army Training Center, Grafenwöhr, Germany. ANL/ESD/TM-59. Available from: http://www.osti.gov/energycitations/servlets/purl/10132677-qRHg8M/native/ (accessed 02.08.06).