

Lead contamination of an agricultural soil in the vicinity of a shooting range

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Abstract In this study, coupled Pb concentration/Pb isotope data were used to evaluate the effect of a shooting range (operational for over 30 years) on Pb contamination of adjacent agricultural soils and the associated environmental risks. Lead was mainly concentrated in the arable layer of the contaminated agricultural soils at total concentrations ranging from 573 to 694 mg kg⁻¹. Isotopic analyses (²⁰⁶Pb/²⁰⁷Pb) proved that Pb originated predominantly from the currently used pellets. Chemical fractionation analyses showed that Pb was mainly associated with the reducible

fraction of the contaminated soil, which is in accordance with its predominant soil phases (PbO, PbCO₃). The 0.05 M EDTA extraction showed that up to 62% of total Pb from the contaminated site is potentially mobilizable. Furthermore, Pb concentrations obtained from the synthetic precipitation leaching procedure extraction exceeded the regulatory limit set by the United States Environmental Protection Agency for drinking water. Ion exchange resin bags showed to be inefficient for determining the vertical distribution of free Pb²⁺ throughout the soil profile. Increased Pb concentrations were found in the biomass of spring barley (*Hordeum vulgare* L.) sampled at the studied site and two possible pathways of Pb uptake have been identified: (1) through passive diffusion-driven uptake by roots and (2) especially through atmospheric deposition, which was also proved by analyses of a bioindicator species (bryophyte *Hypnum cupressiforme* Hedw.). This study showed that shooting ranges can present an important source of Pb contamination of agricultural soils located in their close vicinity.

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Introduction

Shooting ranges present very important point sources of lead (Pb) contamination. In 2006, the

amount of Pb used in the USA for ammunition production, including shots and bullets, exceeded 70,000 t (USGS 2007). In Sweden, Denmark, and Finland, more than 500 t Pb year⁻¹ was produced in each of these countries for shotgun ammunition (Lin et al. 1995). A large portion of Pb originating from Pb shot accumulates in soils of the shooting ranges and in soils in their close vicinity. Lead concentrations in shooting range soils often exceed 1,000 mg kg⁻¹ (Lin et al. 1995; Cao et al. 2003a). There have even been evidences of concentrations well above 20,000 mg kg⁻¹ (Lin 1996; Stansley and Roscoe 1996; Dermatas et al. 2006). Therefore, the contamination of soils from the close vicinity of shooting ranges presents a serious environmental concern due to the risks associated with groundwater and surface water pollution (Craig et al. 1999; Knechtenhofer et al. 2003) and contamination of plants growing in the vicinity (Cao et al. 2003b; Robinson et al. 2008). Furthermore, it was found that increased Pb concentrations originating from Pb shot had an adverse effect on soil microbial populations and soil fauna (Rantalainen et al. 2006).

Lead shots and pellets contain mainly Pb (>90%) and other accessory elements such as Sb and As. When the Pb pellet enters the soil, weathering processes start and elemental Pb is transformed through oxidation, carbonation, and hydration into dissolved and particulate Pb species. The newly formed Pb oxidized phases include mainly cerussite (PbCO₃), hydrocerussite (Pb₃(CO₃)₂(OH)₂), possibly anglesite (PbSO₄), and massicot/plattnerite (PbO) (Lin et al. 1995; Cao et al. 2003b). The transformation of metallic Pb from pellets in soils can be described as: Pb → PbO → PbCO₃/Pb₃(CO₃)₂(OH)₂ (Ma et al. 2007); the formed Pb carbonates create a protective layer preventing further weathering of the pellets. The weathering rate of Pb is higher in organic soils compared to soils with low organic C contents (even calcite-rich soils) (Dermatas et al. 2006) and the transformation of Pb into oxidized species is associated with an increase of soil pH. This is mainly attributed to (1) the consumption of H⁺ ions during Pb corrosion (Pb⁰ → Pb²⁺), (2) the production of OH⁻ ions during Pb carbonate formation, and (3) the subsequent H⁺ consumption during the dissolution of Pb carbonates (Ma et al.

2007; Rooney et al. 2007). All these pH-dependent processes control the dissolution kinetics of Pb from pellets.

Several techniques have been proposed for the evaluation of metal availability and mobility in contaminated soils, including sequential extraction and 0.05 M EDTA extraction procedures (both proposed by the Commission of the European Communities Bureau of Reference, BCR programme followed by the Standards, Measurement and Testing Programme) (Quevauviller 1998; Rauret et al. 2000; Chrastný et al. 2008). The SPLP extraction procedure (synthetic precipitation leaching procedure; USEPA method 1312, 1994) has been proposed as a suitable method for shooting range soils (Cao et al. 2003a; Hardison et al. 2004). This extraction simulates, to some extent, precipitation water with a set pH (4.2 or 5.0). The use of Pb isotopes proved to be an efficient tool for tracing the degrees and sources of Pb contamination (Komárek et al. 2008). The method is based on differences in isotopic composition (e.g., in ²⁰⁶Pb/²⁰⁷Pb) between different Pb sources (e.g., anthropogenic Pb vs. background Pb derived from weathering bedrocks).

To our best knowledge, a vast majority of studies dealing with Pb contamination originating from Pb shot are focused mainly on soils directly from the shooting ranges. Therefore, the aim of this study was to evaluate (1) the influence of a shooting range on the immediate contamination of an agricultural soil located in the close vicinity using coupled Pb concentration/isotope data, (2) the risks associated with Pb contamination of these soils through the SPLP and 0.05 M EDTA extractions and analyses of crops growing at the studied sites, and (3) the comparison of standard methods (0.05 M EDTA, SPLP, and sequential extraction procedure) with method based on ion exchange resin bags for predicting the actual mobility of Pb in soils.

Materials and methods

Study area

Samples of agricultural soil were taken from an area in the close vicinity of a shooting range (N

48° 58.279'; E 14° 26.053') near the town of České Budějovice, Czech Republic. The shooting range has been operational for more than 30 years and serves as a training facility mainly for trapshooting using Pb pellets as ammunition. The soil is periodically ploughed, fertilized with mineral fertilizers, and sown (with spring barley, *Hordeum vulgare* L., at the time of the experiment). The studied area has been divided into two parts. The first part is situated in the close vicinity of the shooting range (10 m from the shooting range mound; 100–150 m from the shooters' position); therefore, it represents an area greatly exposed to Pb pellets (which were clearly visible on the ground). The second part is located further (~330 m) and thus serves as a control sampling site with no Pb shot deposited, however, with similar physico-chemical soil characteristics.

Sampling and sample preparation

At both the contaminated and control sites, soil samples were collected using a soil probe GeoSampler (Fisher Scientific, Czech Republic). The first three soil samples were collected from depths of 0–5, 5–15, and 15–30 cm, respectively. These samples represent the surface, subsurface, and the deeper arable layer, respectively. The deepest soil sample (30– x cm) represents the sub-arable layer. Soil samples were collected in triplicate, air dried to constant weight, and passed through a 2-mm stainless sieve so that no pellets were present in the sieved soil. Soil pH was measured in suspension using a ratio of 1:2.5 (w/v) (soil and deionized water). Total organic carbon (TOC) content was determined by catalytic oxidation (ELTRA CS 530 Elemental Analyzer, Neuss, Germany). Oxalate extraction (0.2 M ammonium oxalate/oxalate acid at pH 3) was performed in order to determine the approximate amount of amorphous and poorly crystalline Fe and Mn (hydr)oxides (McCarty et al. 1998). Cation exchange capacity (CEC) was determined as the sum of basic cations and Al extracted with 0.1 M $BaCl_2$ (Kalra and Maynard 1994). Clay content was determined using the hydrometer method.

Approximately 30 samples of spring barley growing at the studied locality (both at the contaminated and the control sites) were collected

during seed ripeness. Furthermore, samples of the bryophyte *Hypnum cupressiforme* Hedw., which is commonly used as a bioindicator of atmospheric metal contamination (Szczepaniak and Biziuk 2003), were sampled in the close vicinity of the contaminated and the control sites. Samples were dried at 105°C with barley roots, stems, leaves, and spikes carefully separated and homogenized to obtain a composite sample and decomposed in concentrated HNO_3 using microwave digestion (MARS 5, CEM, Matthews, USA).

Extraction/dissolution procedures

Soil samples were digested using a mixture of concentrated acids ($HF/HNO_3/HClO_4$) and analyzed for total metal concentrations. In order to obtain information about the chemical fractionation of Pb in the soils, the modified BCR sequential extraction procedure proposed by Rauret et al. (2000) was used. This scheme defines: (1) fraction A—exchangeable and acid extractable (0.11 M CH_3COOH); (2) fraction B—reducible (0.5 M $NH_2OH \cdot HCl$); (3) fraction C—oxidizable (8.8 M $H_2O_2/1$ M CH_3COONH_4); fraction D—residual fraction (total digestion of the residue). In order to determine the “potentially available” fraction of Pb at both studied localities, the 0.05 M EDTA extraction procedure by Quevauviller (1998) was used. Furthermore, the synthetic precipitation leaching procedure (SPLP) was carried out to evaluate the mobility of Pb in the contaminated soil. An amount of 100 g of the soil sample without Pb pellets was extracted using 2,000 g of solution prepared from deionized water with pH adjusted to 4.2 (simulation of acid rains) using an acid mixture of H_2SO_4/HNO_3 (60:40 w/w). The pH value of the SPLP extraction solution was chosen according to data about the pH values of precipitation in the area obtained from the Czech Hydrometeorological Institute. The samples were placed for 18 h at an end-over-end shaker. Lead concentrations were determined in filtered samples. The chemical composition of the pellets was determined using an XRF portable alloy analyzer NITON XLt 800 (Thermo Electron Corporation, USA). For Pb isotope analyses, ten unoxidized pellets were collected from the soil surface and dissolved using 50% HNO_3 (v/v) in an ultrasonic

laboratory device. Samples were filtered after dissolution and diluted to appropriate Pb concentrations. All the extraction solutions used were prepared using chemicals of analytical grade (Analytica, Prague, Czech Republic and Merck, Germany) and deionized water (MILLI-Q Element, Millipore, France).

Ion exchange resin bags

Ion exchange resin bags were used to estimate the relative concentration and isotopic composition of available Pb^{2+} throughout the sampled soil profiles. One gram of the resin beads (gel polystyrene sulfonate cation exchange resin, type C 100E, PUROLITE) was sealed into polyester mesh bags (150 μm mesh), saturated with Na^+ using 1 M NaCl solution and washed thoroughly with distilled water. In the beginning of the barley growth season (April 2007), resin bags in duplicate were inserted at 2, 10, 20, and 40 cm below the soil surface in two dug pits (corresponding to soil sampling depths). Three sites were established in the shooting radius (100–150 m from the shooters' position) and the results obtained were averaged. A single site out of the shooting radius (~ 330 m) was established as the control site. The resin bags were incubated in the soil for 110 days and collected a week before barley was harvested for grain. In the laboratory, the resin bags were carefully washed in distilled water to remove soil particles and adsorbed Pb^{2+} was eluted using 2% (v/v) HNO_3 . The sorption/desorption efficiency of resin bags was tested prior to use in the scheme of a laboratory model experiment (based on testing sorption/desorption equilibrium in Pb solution). The obtained recovery of desorbed to sorbed Pb amount was higher than 95%.

Metal determinations and QA/QC procedures

All Pb measurements (concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$) presented here were performed using an inductively coupled plasma mass spectrometer (PQ ExCell, VG Elemental, Winsford, UK). Concentrations of Fe, Mn, Ca, and Al were determined using a flame atomic absorption spectrophotometer (SpectrAA-640, Varian, Australia).

Results obtained from the sequential extraction procedure, as expressed by the sum of all fractions (A–D), were compared to the total Pb concentrations. The relative standard error expressed as a difference between the sum of all fractions and total concentrations did not exceed 10%. The total digestion procedure was evaluated by the certified reference material Light Sandy Soil 7002 (Analytica, Prague, Czech Republic). The concentrations of Pb determined in barley and bryophyte samples were evaluated using the standard reference material NIST 1515, Apple Leaves (NIST, Gaithersburg, USA). The accuracy of measurements was $<5\%$ RSD.

Results from Pb isotope analyses were corrected for mass bias against the standard reference material NIST 981, Common Lead (NIST). The standard error for $^{206}\text{Pb}/^{207}\text{Pb}$ measurements did not exceed 0.4% RSD based on ten replicates of each measurement. The accuracy of the Pb isotope measurements was evaluated using the isotopic standard AGV-2 (USGS, USA).

Results

Basic physico-chemical soil characteristics

Soil samples from the two studied sites reflect similar physico-chemical characteristics. Nevertheless, important differences can be found, especially in the pH value and TOC content. The contaminated site shows a higher pH (by 0.8–1.5 units) compared to the control site and a lower TOC content (by 1.1–2.0%). Cation exchange capacity, clay content, and oxalate-extractable Fe and Mn concentrations were similar at both localities (Table 1).

Lead concentrations in the studied soils

The XRF analyses showed that the Pb pellets currently used are composed mainly of Pb ($97.7 \pm 0.4\%$; $^{206}\text{Pb}/^{207}\text{Pb} = 1.156 \pm 0.003$) with trace amounts of Sb ($0.81 \pm 0.20\%$) and other metals at lower concentrations (e.g., Ag). As expected, total Pb concentrations in the arable layers (0–30 cm) of soils from the exposed site yielded values ~ 15 -fold higher compared to the control

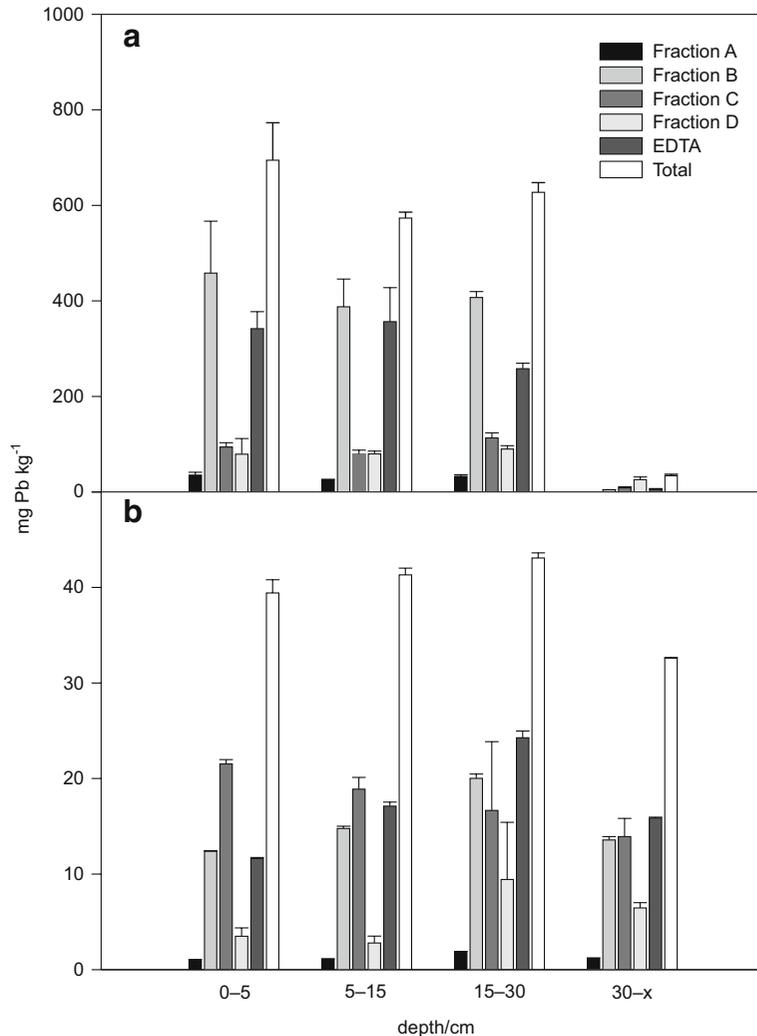
Table 1 Basic physico-chemical characteristics of the studied soil samples

| Depth | pH | CEC (cmol _c kg ⁻¹) | TOC (%) | Clay (%) | Oxalate-extractable | |
|-------------------|------|---|---------|----------|--------------------------|--------------------------|
| | | | | | Fe (g kg ⁻¹) | Mn (g kg ⁻¹) |
| Contaminated site | | | | | | |
| 0–5 cm | 5.86 | 6.74 | 0.94 | 7.40 | 3.17 | 0.36 |
| 5–15 cm | 5.96 | 7.52 | 1.02 | 7.52 | 3.02 | 0.30 |
| 15–30 cm | 5.82 | 7.05 | 0.99 | 8.23 | 3.07 | 0.34 |
| 30–x cm | 5.86 | 7.15 | 0.39 | 10.3 | 1.27 | 0.02 |
| Control site | | | | | | |
| 0–5 cm | 5.02 | 7.21 | 2.98 | 6.99 | 2.72 | 0.31 |
| 5–15 cm | 4.80 | 7.91 | 2.91 | 7.23 | 3.09 | 0.29 |
| 15–30 cm | 4.30 | 8.23 | 2.44 | 7.98 | 2.91 | 0.36 |
| 30–x cm | 4.42 | 7.29 | 1.49 | 10.5 | 1.05 | 0.02 |

site located ~330 m away (Fig. 1). The maximum value of 694 ± 79 mg Pb kg⁻¹ was observed in the superficial soil layer (0–5 cm) which sig-

nificantly exceeds the critical limit (300 mg Pb kg⁻¹) set for agricultural soils by the EC Council Directive 86/278/EC (1986). A steep drop of Pb

Fig. 1 Total concentrations, 0.05 M EDTA-extractable concentrations, and fractionation of Pb in the studied soils from the **a** contaminated and **b** control area



concentration down the profile is evident from the deepest soil sample. All these results indicate that the shooting range has had an immediate impact on the agricultural soil located in the close vicinity.

Data from the sequential extraction (Fig. 1) showed that Pb originating from pellets was mainly concentrated in the reducible fraction B (56–66%) of the contaminated arable layer, whereas at the control site, Pb was associated with other fractions as well, especially with the oxidizable fraction C. This is corresponding with the higher TOC content of the control soil. The concentration of Pb in the most available fraction A is very low, suggesting its low mobility in soils. Furthermore, the 0.05 M EDTA extraction, which represents a potentially mobilizable pool of Pb (Chrastný et al. 2008), showed that EDTA-extractable Pb in the contaminated arable layer reaches 41–62% from the total concentration. On the other hand, the EDTA-extractable/total Pb ratio below the contaminated arable layer (30–x cm) was only 16%.

Lead concentrations obtained from the SPLP extraction of the soil from the arable layer at the exposed site ($21.3\text{--}24.0\ \mu\text{g L}^{-1}$) exceeded the USEPA SPLP regulatory limit of $15\ \mu\text{g L}^{-1}$ set for drinking water. However, Pb concentrations were well below this limit in deeper soil horizons and in all soil samples from the control site (Table 2). Lead concentrations obtained from resin bags analyses did not follow any concentration trend and Pb was more or less evenly distributed at both sites. Significantly higher Pb concentrations were

obtained, as expected, at the contaminated site (Table 2).

$^{206}\text{Pb}/^{207}\text{Pb}$ analyses of the studied soils

Statistical analyses of $^{206}\text{Pb}/^{207}\text{Pb}$ Pb data proved the predominant influence of the shooting range on the contamination of the studied agricultural soil. While all the $^{206}\text{Pb}/^{207}\text{Pb}$ values of samples from the arable layer (0–30 cm) obtained from the total digestion, SPLP extraction, EDTA extraction, and fractions A, B, and C were statistically similar to the isotopic signature of the sampled pellets (according to the Duncan test, $P < 0.05$), samples originating from below the arable layer and Pb in the residual fraction D reflected a statistically different value (Table 3). Lead isotopic analyses of the resin bags showed no statistical difference throughout the soil profile and the $^{206}\text{Pb}/^{207}\text{Pb}$ values obtained were statistically identical to the isotopic signature of the pellets. The isotopic composition of soil samples from the control site revealed that no Pb present in these soils originated from recent pellets (Table 3) and that the contamination is restricted to the close vicinity of the shooting range.

Lead concentrations in barley and bryophyte samples

The concentration of Pb in samples of spring barley and the bryophyte *H. cupressiforme* are summarized in Table 4. Significantly higher concentrations of Pb were observed in samples of barley and bryophyte growing at the contaminated site and in its close vicinity, respectively. The largest difference in Pb pollution between the contaminated and the control site was observed from the bryophyte analyses where a ~40-fold increase in Pb concentrations was observed (Table 4). In the case of barley, Pb was mainly concentrated in roots ($138\ \text{mg Pb kg}^{-1}$); nevertheless, increased Pb concentrations were determined in above-ground parts as well, especially in leaves.

Discussion

This study confirmed that the shooting range has had an immediate impact on Pb contamination

Table 2 Lead concentrations obtained from the SPLP extraction procedure and resin bags analyses

| Depth | SPLP ($\mu\text{g L}^{-1}$) | Resin bags ($\mu\text{g L}^{-1}$) ^a |
|-------------------|-------------------------------|--|
| Contaminated site | | |
| 0–5 cm | 21.3 ± 2.1 | 261 ± 140 |
| 5–15 cm | 22.8 ± 3.3 | 213 ± 57 |
| 15–30 cm | 24.0 ± 0.5 | 320 ± 190 |
| 30–x cm | 0.67 ± 0.32 | 236 ± 88 |
| Control site | | |
| 0–5 cm | 0.59 ± 0.10 | 7.70 ± 2.33 |
| 5–15 cm | 0.26 ± 0.04 | 9.85 ± 0.23 |
| 15–30 cm | 0.55 ± 0.17 | 6.65 ± 1.04 |
| 30–x cm | 0.20 ± 0.04 | 8.40 ± 3.14 |

Data shown are means \pm SD ($n = 3$)

^aPb concentrations determined in eluates

Table 3 Isotopic composition of Pb (²⁰⁶Pb/²⁰⁷Pb) in different soil extracts/digests and resin bags

| Depth | Fraction A | Fraction B | Fraction C | Fraction D | EDTA | SPLP | Resin bags | Total |
|--|------------------------------------|-------------------------------------|-------------------------------------|----------------------------------|----------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| Contaminated site (²⁰⁶ Pb/ ²⁰⁷ Pb of pellets = 1.156 ± 0.003 ^{abc}) | | | | | | | | |
| 0–5 cm | 1.161 ± 0.003 ^{abcdef} | 1.165 ± 0.004 ^{abcdefg} | 1.164 ± 0.007 ^{abcdefg} | 1.172 ± 0.003 ^{fghi} | 1.153 ± 0.003 ^a | 1.166 ± 0.001 ^{bcdefg} | 1.168 ± 0.004 ^{cdefgh} | 1.166 ± 0.002 ^{bcdefg} |
| 5–15 cm | 1.161 ± 0.004 ^{abcdef} | 1.165 ± 0.007 ^{abcdefg} | 1.170 ± 0.006 ^{defgh} | 1.177 ± 0.005 ^{hij} | 1.154 ± 0.002 ^{ab} | 1.167 ± 0.001 ^{cdefgh} | 1.161 ± 0.006 ^{abcdef} | 1.154 ± 0.004 ^{ab} |
| 15–30 cm | 1.167 ± 0.006 ^{cdefgh} | 1.167 ± 0.004 ^{cdefgh} | 1.158 ± 0.006 ^{abcd} | 1.174 ± 0.001 ^{ghi} | 1.156 ± 0.002 ^{abc} | 1.165 ± 0.001 ^{abcdefg} | 1.159 ± 0.002 ^{abcde} | 1.165 ± 0.005 ^{abcdefg} |
| 30–x cm | 1.183 ± 0.003 ^{ijk} | 1.194 ± 0.005 ^l | 1.189 ± 0.021 ^{kl} | 1.194 ± 0.010 ^l | 1.170 ± 0.009 ^{efgh} | 1.189 ± 0.004 ^{kl} | 1.160 ± 0.001 ^{abcde} | 1.187 ± 0.002 ^{ijkl} |
| Control site (²⁰⁶ Pb/ ²⁰⁷ Pb of pellets = 1.156 ± 0.003 ^A) | | | | | | | | |
| 0–5 cm | 1.178 ± 0.002 ^{CDEF} | 1.176 ± 0.001 ^C | 1.175 ± 0.001 ^C | 1.188 ± 0.005 ^{EFG} | 1.177 ± 0.002 ^C | 1.172 ± 0.003 ^{BC} | 1.178 ± 0.006 ^{CDE} | 1.181 ± 0.000 ^{CDEF} |
| 5–15 cm | 1.177 ± 0.000 ^{CDE} | 1.173 ± 0.001 ^{BC} | 1.174 ± 0.001 ^C | 1.191 ± 0.002 ^G | 1.174 ± 0.001 ^C | 1.177 ± 0.007 ^{CD} | 1.168 ± 0.006 ^{AB} | 1.181 ± 0.002 ^{CDEF} |
| 15–30 cm | 1.176 ± 0.002 ^C | 1.173 ± 0.001 ^{BC} | 1.174 ± 0.004 ^C | 1.180 ± 0.002 ^{CDEF} | 1.175 ± 0.001 ^C | 1.179 ± 0.003 ^{CDEF} | 1.175 ± 0.010 ^C | 1.178 ± 0.001 ^{CDEF} |
| 30–x cm | 1.179 ± 0.001 ^{CDEF} | 1.178 ± 0.000 ^{CDEF} | 1.179 ± 0.001 ^{CDEF} | 1.188 ± 0.000 ^{DEFG} | 1.177 ± 0.000 ^{CDE} | 1.176 ± 0.001 ^C | 1.179 ± 0.010 ^{CDEF} | 1.188 ± 0.002 ^{FG} |

Data with the same letter represent statistically identical values ($P < 0.05$). Data shown are means ± SD ($n = 3$). Statistical analyses were performed separately for both sites

Table 4 Lead concentrations (mg kg^{-1}) in barley and bryophyte samples ($n = 3$)

| | Spring barley | | | | Bryophyte |
|-------------------|----------------|-----------------|-----------------|-----------------|-----------------|
| | Roots | Stems | Leaves | Spikes | |
| Contaminated site | 138 ± 9 | 4.24 ± 0.32 | 16.4 ± 0.4 | 2.37 ± 0.10 | 250 ± 20 |
| Control site | 11.0 ± 0.4 | 1.61 ± 0.10 | 1.09 ± 0.07 | 1.23 ± 0.22 | 6.33 ± 0.59 |

of the agricultural soil located in its close vicinity. This fact was proved by coupled Pb concentration/Pb isotope analyses. Lead was evenly distributed in the arable layer, suggesting that tillage plays a very important role in the redistribution of the metal in the soil profile. Isotopic analyses proved that Pb originating from Pb pellets was associated with the non-residual fractions A, B, and C of the contaminated soil and that Pb present in the residual fraction D must have had a different source. The sample below the arable layer reflected a completely different $^{206}\text{Pb}/^{207}\text{Pb}$ value (Table 3), suggesting that Pb originating from pellets have not yet migrated downward. The significantly higher pH of the contaminated soil is mainly attributed to the transformation of metallic Pb into oxidized species which is associated with an increase of soil pH due to the consumption of H^+ ions (Chen and Daroub 2002; Ma et al. 2007; Rooney et al. 2007). Moreover, the higher TOC content at the control site could have, to some extent, influenced the pH value as well (which alters mobility of metals).

Due to the fact that oxidized Pb originating from Pb shot is present mainly in the form of (hydro)cerussite or Pb oxide in soils (Lin et al. 1995; Cao et al. 2003b; Rooney et al. 2007; Dermatas et al. 2008), these are unstable under reducing acidic conditions of the hydroxylamine hydrochloric extraction (fraction B). For this reason, Pb at the contaminated site was mainly associated with the reducible soil fraction. However, it is needed to point out that the “reducible” fraction does not necessarily represent only Pb associated with Fe, Mn, and Al-(hydr)oxides but rather its chemical form in the soil (Bacon and Davidson 2008). A significant portion of Pb (up to 62%) is “potentially mobilizable” (EDTA extractable). The SPLP extraction further revealed that acidic precipitation is able to leach significant amounts of Pb from these soils and can thus pose a risk for (ground)water quality. The possible negative

influence of Pb pollution of shooting range soils on surface water and groundwater quality has been already described (e.g., Craig et al. 1999; Knechtenhofer et al. 2003). Coupled analyses of Pb concentrations in total digests, EDTA and SPLP extracts, Pb fractionation, and isotopic composition proved the different origins of Pb and the extent of its migration through the studied soils (Fig. 1; Tables 2 and 3).

The results obtained from the analyses of spring barley sampled at the studied sites suggest that a relatively large amount of Pb can be taken up by plants. Due to its low mobility and physiological nature (non-essential element), Pb was mainly concentrated in barley roots and the increased Pb concentrations observed in the above-ground parts can also be attributed to atmospheric deposition of dust particles containing Pb (even though the plant samples were carefully washed with deionized water). This observation was proved by the analyses of the bryophyte *H. cupressiforme*, a species commonly used as a bioindicator of atmospheric metal pollution (Szczepaniak and Biziuk 2003), thus indicating two major pathways of Pb uptake into agricultural crops. Atmospheric Pb can originate from different sources, as in other urban areas, such as coal combustion, waste incineration, and alternatively from the former use of leaded gasoline (Komárek et al. 2006).

There has been evidence from the literature that ion exchange resins can be successfully used for determining free metal ion (e.g., Cd^{2+}) concentrations in soils (Sakurai et al. 2007). The highly variable and low Pb concentrations obtained from resin bags analyses are results of low concentrations of free Pb^{2+} which is unevenly distributed in soils. The statistically similar $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (throughout the soil profile and compared to the pellets) shows that free Pb^{2+} sorbed to the resin bags originates solely from Pb pellets. However, due to the fact that resin bags were placed into dug pits, increased leaching influenced the redistribution of mobile Pb^{2+}

throughout the soil profile. For this reason, resin bags are not practical for evaluating the vertical distribution of mobile Pb in soils.

Although the total Pb concentrations in agricultural soils in the vicinity of the shooting range observed in our study are not as high as data published on soils directly from shooting ranges (e.g., Lin et al. 1995; Cao et al. 2003a, b; Dermatas et al. 2006), the contamination of agricultural land with Pb shot can present a significant danger for a safe agricultural production, especially when crops are grown on such soils. Lead isotope analyses coupled with Pb concentration analyses of soils (including sequential extractions) and plants proved to be an efficient tool for determining the intensity of Pb contamination of soils originating from the use of Pb shot at shooting ranges.

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