Lead in various chemical pools in soil depth profiles on two shooting ranges of different age

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We investigated the distribution of pellet-derived lead (Pb) in various chemical pools within soil depth profiles in a new and an old clay pigeon shooting range to assess its tendency for mobility. The results showed that the pellets weathered slowly: about 10% of metallic Pb had been released over 16–37 years. Nevertheless, the resulting Pb concentrations in the soil largely exceeded the upper guideline value defined as contaminated on grounds of ecological risk. The operational fractionation analysis produced a useful, although tentative, insight into the environmental fate of Pb. In the acid forest soil of the ranges studied, organic matter seemed to act as a primary sink for Pb but became a mobile carrier with increasing Pb load. Generally, the residual fraction (including oxide-bound Pb) predominated in the mineral soil layers. The estimated average migration rate was roughly 2–3 mm a year. The abnormally high Pb concentrations in the control area outside the shooting ranges suggest that environmental risks are not limited only to pellet-shot-fall areas.

Introduction

Indigenous lead (Pb) concentrations of soils are generally very low. Data compiled by Ewers and Schlipköter (1991) from various reviews reveals that the typical range of total Pb concentrations in surface soil layers in rural areas is 5–60 mg kg^{-1}, and in urban areas 50–300 mg kg^{-1}, but near smelters, the peak concentration may rise to 20 000 mg kg^{-1}. Owing to its superior ballistic properties, Pb is a common metal in shots and pellets, rendering ammunition an important source of Pb load. In Finland, the estimated number of open-air shooting ranges in operation is 2000–2500, and the total annual Pb load in them is about 530 tonnes (Mukherjee 1994).

Metallic Pb that has ended up in soil as spent pellets is unstable and undergoes various transformation processes controlled by soil characteristics (for reactions *see* Jörgensen and Willems 1987, Cao *et al*. 2003). In acid soils, the compounds formed on the surfaces of pellets such as massicot (PbO), cerussite (PbCO$_3$) and hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$) may be further subjected to solubilisation (Jörgensen and Willems 1987, Ma *et al*. 2007). Because the age of pellets in shooting range soils can vary greatly, these areas are very complex environments. The pellets differ in the degree of weathering and in the reaction products they produce, and the Pb released from the pellets may have reacted with a variety of soil constituents.

A general finding is that within a forest soil profile the main part of the Pb present is retained in the organic horizon (Heinrichs and Mayer 1980, Smith and Siccama 1981, Friedland *et al.* 1992). Depending on soil characteristics, the transport of Pb from the organic topsoil horizon to deeper soil layers may occur as soluble organic complexes or as organo-mineral complexes (Miller and Friedland 1994, Weng *et al.* 2001). However, humic substances, which are important reaction components of soil organic matter (SOM), are very complex by nature and, depending on the type of functional groups, form different complexes with metals. Buffle *et al.* (1990) classified carboxylate and phenolate groups of fulvic (FA) and humic acids (HA) as weak binding sites (major site type) and FA and HA groups containing sulphur and nitrogen as strong binding sites (minor site types).

In mineral soil horizons, Pb is retained on hydrated oxides of manganese (Mn), iron (Fe) and aluminium (Al) by a specific mechanism (McKenzie 1980, Aualiitia and Pickering 1987). A major factor is pH which dictates the dissociation of functional organic groups, the charge properties of oxides, and the occurrence of different Pb species differing in their sorption tendency (e.g. Hahne and Kroontje 1973). This means that Pb in soil may occur in many different forms differing in their ecological impact and potential risk to human health. That is why many workers have employed specific extractants to identify the chemical forms or solubility categories of Pb to describe its chemistry. Unfortunately, there is no consensus about the methodology, and opinions concerning which metal forms the different solutions extract are in conflict. In his thorough review on the extractants used for trace metals, Beckett (1989) showed that some discrepancies result merely from differences in terms, but others are fundamental. The ease of dissolution of a given metal compound is dependent on physical factors such as crystallinity and particle size. The extractability of metals retained by soil components, in turn, depends on the chemical species of the metals and on reactions they have undergone.

In shooting ranges, pellet loading is uneven and varies along the shooting sectors. Hot spots are likely to occur in areas where the shooting sectors overlap. We hypothesized that the degree of Pb pollution affects the distribution of this heavy metal between various chemical pools and, in the course of time, its transport to deeper soil horizons. In this survey, we compared the pellet load and the forms of pellet-derived Pb within the soil depth profiles of two clay pigeon shooting ranges. The ranges were located on the same soil formation but differed in the amount of time they had been in operation and, consequently, in the time spans during which the pellets had been subjected to chemical reactions and transport processes in the soil. We characterized the different Pb pools at various soil depths by using extractants in a sequence of increasing aggressiveness. The aim was to elucidate the concentration profile and, accordingly, the tendency for mobility of pellet-derived Pb in order to assess its ecological risks.

Materials and methods

Study area

The Hälvälä shooting range area in Hollola, southern Finland, is located on the distal part of the terminal moraine formation Salpausselkä deposited 12 250–12 050 years ago. The area is a typical sandy delta complex, i.e. the soil has a coarse and stony texture. According to the WRB system (FAO 2006), the soil is a Haplic Regosol (Humic, Dystric, Arenic), and according to Soil Taxonomy (Soil Survey Staff 2006) it is a Typic Cryorthent. The soil shows some features of podzolization, but these features are much too weak to meet the criteria for Podzols/Spodosols of the two classification systems.

There are two separate clay pigeon shooting ranges: the old one, used from 1967 to 1987, and the new one, which has been in use since 1987 (it had been in use for 16 years at the time of sampling). The shooting range area is located in a typical dry peaty forest with moss and lichen cover. According to the vegetation description published by Rantalainen *et al.* (2006), the forest in the control area and new range consisted mainly of Scots pine (*Pinus sylvestris*), but in the old area silver birch (*Betula pendula*) was also present. The ground layer was dominated by

a few species of grasses (mainly *Deschampsia flexuosa* and *Calamagrostis arundinacea)* and shrubs (*Vaccinium vitis-idaea* and *V. myrtillus*). The new range was a bit more grassy than the old range and the control area. The moss species were *Pleurozium schreberi* and *Dicranum scoparium*.

Soil sampling and sample preparation

We collected soil profile samples from five points representing sites of dissimilar pellet loading. At each range, one selected sampling point represented the least loaded sites (points 2 and 4 in the front areas of the shooting sectors) and another, the most heavily loaded sites (points 1 and 3 in the areas where two shooting sectors overlapped) (Table 1). One profile (point 5) that was located 200–300 m north behind the new range was used to sample control material. The soil formation features were so weak that it was impossible to take all samples according to horizons. At almost all sampling sites, only a thin eluvial horizon was seen. The ground cover was removed before sampling the organic layer, which was 0–7(or 8) cm thick. We dug a pit and sampled the mineral

soil as follows: the uppermost mineral soil layer sample taken immediately below the organic horizon was about 15 cm thick, and each subsequent sample representing the deeper soil layers was about 10 cm thick (Table 1). In two profiles, the total sampling depth was 50–60 cm; in the three others, stoniness and plant roots hindered digging that deep. To avoid contamination of the lower layer samples by material possibly dropped from the upper layer, we took the samples in terraces, i.e. the upper layer was sampled from a larger area than the sample beneath.

The soil samples were stored at 5 °C until passed through a 1-cm sieve. After removing the plant roots, stems and leaves, the material was homogenized. For laboratory analyses, a 0.2-kg portion of each sample was air-dried. Pellets were picked out of the soil, their degree of weathering was estimated visually, and their total mass was weighed. Finally, the soil samples were passed through a 4-mm sieve. For the particle size analysis, a small portion was further sieved through a 2-mm mesh.

In the shooting range soil profiles, lead pellets were found in all organic layer samples, but in the old range they were also found in the uppermost mineral soil layer (Table 1). The

Table 1. The physico-chemical properties of soil profiles, and the number and mass of pellets at various sampling points. CEC_{ef} = effective cation exchange capacity.

Sampling		Depth (cm)	Ignition loss (%)	pH	Oxalate soluble (mg kg^{-1})			CEC_{ef} (cmol(+) kg^{-1})	Particles 2–0.2 mm (%)	Pellets in 100 g of soil	
Site	Point				Al	Fe	Mn			Number	Mass (g)
New range	1	0–7	57.5	3.4	1400	1600	140	156		294	15.1
		7–22	8.8	4.5	5200	3600	14	17	61		
		22–32	5.7	5.1	7200	1500	3.5		58		
		32–42	3.1	5.6	4200	1100	2.1		54		
		42–52	1.9	6.0	2900	660	1.5		52		
		52–62	1.3	6.5	2600	580	1.8		53		
	2	0–5	76.4	3.9	2100	2100	85	255		80	6.0
		5–20	11.3	4.5	4600	6000	6.9	11	64		
		20–30	6.9	6.3	7200	2400	5		63		
Old range	3	0–8	56.3	4.9	1400	2000	420	130		530	40.6
		8–20	14.7	4.8	4300	7600	22	20	66	10	0.7
	4	0–7	48.7	4.7	1900	2100	280	137		263	21.0
		7–20	18.6	4.8	7900	5900	7.2	41	61	3	0.2
		20–30	9.7	5.1	11000	1900	1.4		49		
Control area	5	0–7	68.5	4.5	2000	2200	69	397		1	0.1
		7–22	12.4	4.6	4800	4900	1.8	30	66		
		22–42	13.3	5.2	12000	2800	1.3		63		
		42–52	5.5	5.6	8600	1600	1.1		56		

number and mass of the pellets were highest in the organic layer of sampling point 3, where the uppermost mineral soil layer also contained a rather high number of pellets. Surprisingly, one pellet was also found in the organic layer in the control area. The calculated mean mass of a single pellet ranged from 0.051 to 0.086 g. Visual examination revealed weathering: a brownish or white precipitate covered the pellets and their surfaces looked dull.

Soil properties

The soil texture of mineral layers, determined according to a pipette method (Elonen 1971) and by dry-sieving, was sand or gravel (Table 1). To define the chemical properties of the samples, organic matter was determined as an ignition loss (2 hours at 550 °C) and the pH was measured in 0.01 M $CaCl_2$ suspension (soil:solution ratio 1:2.5, w/v). Aluminium, Fe and Mn in oxides (Al_{ox}, Fe_{ox}, Mn_{ox}) were extracted with oxalate solution (0.029 M $(NH_4)_2C_2O_4$, 0.021 M $H_2C_2O_4$, pH 3.3) at a soil to solution ratio of 1:25 (w/v) according to Niskanen (1989), and determined by ICP-MS (Perkin Elmer SCIEX Elan6000). The effective cation exchange capacity (CEC_{ef}) in the two uppermost layers of each depth profile was determined as the sum of Ca, Mg, K and Na extracted from a 2-g soil sample with four portions 50 ml of 1 M NH_4Cl. Before extraction we washed the soil sample with 50 ml of MQ water to remove free Pb^{2+} cations. The exchangeable cations were analysed with ICP-MS.

Sequential fractionation of Pb

The total Pb (Pb_{tot}) was determined in five replicates by microwave digestion (Milestone Microwave Laboratory systems Etos 1600) according to the EPA 3051 protocol. NIST® 2711 Montana Soil served as a reference sample. Lead in soil was fractionated into various chemical pools with a sequential extraction procedure (in five replicates) as follows. A 2-g air-dried soil sample was shaken in a centrifuge tube for 2 h at 150 rpm with 50 ml of MQ water, and after 15-min centrifugation at 2500 G, the supernatant was filtered through Schleicher & Schuell 589/3 filter paper (Pb_w). Then the sample was extracted for 2 h with 50 ml of 1 M Ca-acetate (pH 7), which was assumed to represent mainly exchangeable Pb (Pb_{ex}). Thereafter, the sample was washed twice with 25 ml of MQ water. It was then extracted for 16 h with 50 ml of 0.5 M NaOH to solubilise Pb bound to the organic matter (Pb_{OM}). The oxide-bound Pb fraction was extracted with 0.03 M NH_4-oxalate (pH 3.3) after washing the sample with MQ water. The Ca-acetate and NaOH extracts were observed to be coloured by humic matter. To avoid the precipitation of humus during later analytical steps (including acid additions), the organic matter in the extracts was decomposed by acid digestion. All extracts were analysed for Pb by ICP-MS.

We noticed that pH in the oxalate extracts remained too high (7 ± 0.6) due to the preceding extraction with NaOH, and we discarded the results obtained in this fractionation step. Thus, in the present survey the sum of Pb_w, Pb_{ex} and Pb_{OM} represents the fractionated Pb ($\sum$ fractions). Accordingly, the residual fraction, which is the portion not recovered in the extraction steps ($Pb_{res} = Pb_{tot} - \sum$ fractions), is assumed to constitute Pb bound to the oxide surfaces in addition to metallic Pb in small pellet pieces, their weathering products, and Pb in the mineral matrix.

Statistics

We calculated the arithmetic means and standard deviations (MS Exel 9.0) of five replicates for Pb_{tot} and Pb fractions obtained in the sequential extraction procedure. The means were calculated separately for each soil depth at each sampling point. We also calculated the coefficients of Pearson's linear correlation between the various Pb pools to elucidate the dependence of Pb in the different chemical fractions on the pollution degree.

Results

The sampling sites differed markedly in Pb_{tot}, the concentrations being higher at the old range than at the new one (Table 2). As expected, the con-

trol area was lowest in Pb_{tot}. Within the soil depth profiles, the Pb_{tot} concentrations peaked in the organic layer and drastically decreased towards the deeper mineral soil layers. At the new range, the concentration drop between the two uppermost layers was 160–230-fold. In comparison, at the old range the concentrations were also rather high in the uppermost mineral soil layer, but the concentration difference between the organic and mineral layer was much smaller, 18–34-fold.

Despite some rather large standard deviations in the various Pb fractions, especially in some mineral soil samples low in Pb_{tot} (Table 2), the data show some trends within depth profiles.

For Pb recovered in the fractionation analysis, the predominant pool was Pb_{ex} followed by Pb_{OM}, for both of which peak concentrations were found in the organic soil layers of the old range. The amount of Pb_w remained extremely small. For distribution of Pb_{tot} between various fractions, the relative proportions given in Table 3 reveal that Pb_{ex} was still most abundant in the organic soil layers and constituted up to 53%–62% of Pb_{tot}.

In contrast, in the mineral soil layers, Pb_{res} (i.e. Pb not recovered in the fractionation steps)

was the most abundant pool (Table 2). The only exception was the old range where Pb_{ex} also predominated in the uppermost mineral layers. The relative proportion of Pb_{res} increased with increasing soil depth (Table 3). Even though the relative proportion of Pb_{res} increased to 88% in the deeper mineral soil layers (Table 3), the absolute peak values occurred in the uppermost mineral soil layers concomitantly with the peak values of Fe oxides (Tables 1 and 2). Surprisingly, the relative proportion of Pb_{OM} was lowest in the organic soil layer (3%–4%) and highest in the mineral layer beneath it (7%–13%). Each Pb fraction obtained in the sequential extraction procedure correlated closely with Pb_{tot} (r = 0.95–0.99, n = 18).

Discussion

As expected, the Pb concentrations at the sampling points revealed a marked variation in the degree of pollution within the ranges. However, in all soil profiles, including the control area, Pb_{tot} in the organic layer dramatically exceeded the upper guideline value for Pb (750 mg kg^{-1}),

Table 2. Total Pb (Pb_{tot}) and its distribution between operationally defined pools: water soluble (Pb_w), acetate soluble (Pb_{ex}), NaOH soluble (Pb_{OM}) and residual (Pb_{res}) fractions at various depths in the soil profiles (mg kg^{-1}). Σfractions = the sum of Pb_w, Pb_{ex} and Pb_{OM}. Pb_{res} = Pb_{tot} – Σfractions. n = 5.

Sampling Site	Point	Depth (cm)	Pb_{tot} (mean ± SD)	Pb_w (mean ± SD)	Pb_{ex} (mean ± SD)	Pb_{OM} (mean ± SD)	Σfractions (mean ± SD)	Pb_{res}
New range	1	0–7	15500 ± 541	20.5 ± 0.44	9570 ± 147	450 ± 84	10040 ± 231	5460
		7–22	68.2 ± 8.4	0.15 ± 0.02	19.6 ± 2	7.24 ± 1.1	27 ± 3	41
		22–32	14.1 ± 2.7	0.15 ± 0.05	2.65 ± 0.39	0.62 ± 0.11	3.4 ± 0.5	11
		32–42	7.60 ± 1.2	0.30 ± 0.06	1.03 ± 0.37	0.22 ± 0.07	1.6 ± 0.5	6
		42–52	3.70 ± 0.47	0.10 ± 0.03	0.58 ± 0.21	0.23 ± 0.08	0.9 ± 0.2	3
		52–62	3.52 ± 0.36	0.11 ± 0.02	0.40 ± 0.11	0.28 ± 0.09	0.8 ± 0.2	4
	2	0–5	6900 ± 321	4.53 ± 0.45	4250 ± 554	237 ± 54	4490 ± 564	2410
		5–20	42.8 ± 5.0	0.08 ± 0.01	9.56 ± 1.7	3.06 ± 0.43	12.7 ± 2.0	30
		20–30	9.52 ± 0.54	0.004 ± 0.00	0.72 ± 0.19	0.36 ± 0.19	1.1 ± 0.3	8
Old range	3	0–8	41800 ± 1580	42.2 ± 4.6	23840 ± 847	1290 ± 299	25170 ± 1019	16630
		8–20	2260 ± 407	3.71 ± 1.4	1054 ± 405	516 ± 507	1574 ± 887	686
	4	0–7	20400 ± 1050	25.5 ± 1.9	13120 ± 413	630 ± 206	13780 ± 582	6620
		7–20	603 ± 123	1.05 ± 0.18	323 ± 14	76.2 ± 6.2	400 ± 12	203
		20–30	64.5 ± 8.0	0.07 ± 0.01	20.7 ± 0.50	4.61 ± 0.50	25.4 ± 0.7	39
Control area	5	0–7	2010 ± 116	2.05 ± 0.40	1060 ± 337	70.5 ± 32	1130 ± 368	880
		7–22	132 ± 16	0.11 ± 0.01	48.1 ± 5.9	10.1 ± 1.4	58.3 ± 6.6	74
		22–42	19.4 ± 3.5	0.01 ± 0.00	4.21 ± 1.0	1.55 ± 0.32	5.8 ± 1.3	14
		42–52	8.30 ± 1.2	0.01 ± 0.00	1.34 ± 0.16	0.65 ± 0.10	2.0 ± 0.1	6

which identifies soils in industrial, storage and transport areas as contaminated on grounds of ecological risks (http://www.finlex.fi/en/laki/kaannokset/2007/en20070214.pdf). At the old range, the uppermost mineral layer (7(or 8)–20 cm) can also be classified as heavily polluted, the concentrations ranging from just under to significantly over the upper guideline value (Table 2).

If we assume that the pellets consist mainly of Pb, the amounts of metal removed as pellets from the organic soil layers of the new range were 150 000 mg kg^{-1} and 60 000 mg kg^{-1} at sampling points 1 and 2, respectively. At the old range, the corresponding figure for sampling point 3 was 406 000 mg kg^{-1} and for point 4 was 21 000 mg kg^{-1}. When comparing these amounts with the results of soil analyses (Table 2), we can roughly estimate that Pb_{tot} left in the soil corresponded to about 10% of the total Pb load removed with the pellets. In other words, the pellets had released 10% of their Pb during a period of 16–37 years.

The estimation of Pb release agrees with the results obtained by Lin *et al.* (1995) in Sweden: over 20–25 years, an average of 4.8% of the metallic Pb in pellets in soils was transformed into Pb carbonate or sulphate, but in a soil rela-

tively rich in humus the percentage increased to 15.6%. However, the estimation of the half-life time of Pb in the pellets is complicated because the dissolution of Pb to soil solution does not proceed linearly and is faster for old pellets than for new ones (Levonmäki *et al.* 2006). In the control area, we found only one pellet in the soil profile studied, but the amount of Pb in the pellet corresponded to about 50% of Pb_{tot} measured in the organic soil horizon. This proportion is five times higher than in the proper shooting-range soils. Actually, Pb_{tot} in the control area was abnormally high and markedly exceeded the normal range of 50–300 mg kg^{-1} reported for urban areas (Ewers and Schlipköter 1991) and also the upper guideline value (750 mg kg^{-1}) given by the Ministry of the Environment (http://www.finlex.fi/en/laki/kaannokset/2007/en20070214.pdf).

It is likely that the high Pb load in the control area largely originated from air-borne metal-containing dust rather than from a marked pellet load to the area. Hits on clay pigeons may have produced tiny metallic Pb particles transported via air to the control area. Furthermore, comparison of the vertical Pb distribution patterns suggests that the migration of Pb has been faster in the control area (profile 5) than at the new range (profile 1); at depths below 42 cm Pb_{tot} was much higher in profile 5, although the concentration in the organic layer was much lower than in the profile 1. Similarly, a higher Pb_{ex} in the uppermost mineral layer in profile 5 can be ascribed to the fact that dissolution of Pb is much faster from fine dust power than from pellets with their much lower surface area. We can assume that production of reactive species, being faster in the control area, also resulted in their faster translocation with seepage water to deeper soil layers. Because the sampling points did not significantly differ in soil characteristics (Table 1), these findings support our conclusion that the Pb load originated in air-borne dust rather than in stray pellets.

Of all soil profiles studied, the profile at sampling point 1 was the deepest one. Therein Pb_{tot} seemed to level out at a soil depth below 42 cm. This allows a rough estimate that during a period of 16 years the pellet-derived Pb migrated downwards at a rate of about 2.5 mm a year. This is within the range of 1–3 mm a year estimated by Miller and Friedland (1994) for labile Pb of

Table 3. The relative distribution (%) of Pb_{tot} between various chemical pools extracted in the sequential fractionation analysis.

Sampling		Depth (cm)	Pb_w	Pb_{ex}	Pb_{OM}	Pb_{res}
Site	Point					
New range	1	0–7	0.1	62	3	35
		7–22	0.2	29	11	60
		22–32	1.1	19	4	76
		32–42	3.9	14	3	79
		42–52	2.7	16	6	76
		52–62	3.1	11	8	77
	2	0–5	0.1	62	3	35
		5–20	0.2	22	7	70
		20–30	0.0	8	4	88
Old range	3	0–8	0.1	57	3	40
		8–20	0.2	47	23	30
	4	0–7	0.1	64	3	33
		7–20	0.2	54	13	34
		20–30	0.1	32	7	61
Control area	5	0–7	0.1	53	4	44
		7–22	0.1	36	8	56
		22–42	0.1	22	8	70
		42–52	0.1	16	8	76

atmospheric origin in the organic layers of forest soils in the north-eastern United States, but it is much below the range of 8–20 mm calculated for the mineral soil layers. For European forest soils, Dörr and Münnich (1991) reported that the migration velocity of atmospheric Pb in surface horizons ranged from 0.35 to 1.6 mm a year.

The concentration gradients, which have been normalized to take into account the source concentration of Pb by dividing the concentration in the organic soil layer by that of the mineral layer beneath, approximate the tendency for mobility of various Pb fractions. The gradient indices were decisively smaller for the old range than for the new one (Table 4). This outcome, showing that the downward movement of Pb was more marked on the old range, agrees with the longer reaction time of the pellets in soil. Similarly, the low indices for the control area confirm the conclusion about the extensive leaching of Pb.

Of the various Pb pools, the gradient indices for Pb_{OM} were smallest in all profiles, which shows the organically bound fraction to be the most mobile one. The high mobility of Pb_{OM} was also evident in the deep mineral soil layers where this fraction increased with increasing organic matter content (Tables 1 and 2). This finding supports the conclusion of previous studies that dissolved organic matter serves as a mobile carrier for Pb (Dörr and Münnich 1991, Miller and Friedland 1994, Sauvé *et al*. 1998).

It is likely that Pb_w was also to some extent present as organic complexes. Quantitatively, this fraction, assumed to represent the most bioavailable Pb pool, was low in all samples. However, the chemistry of organically bound Pb is complicated because both HA and FA are able to form soluble and insoluble complexes with polyvalent cations (Stevensson 1976, 1977). Furthermore, the stability of FA-metal complexes decreases when the metal saturation of high-energy binding sites increases, rendering the weak outer-sphere complexes dominant (Sekaly *et al*. 1999). This means that in the organic soil layer the proportion of exchangeable Pb^{2+} in FA must increase with increasing pollution. The exchangeable (non-specifically sorbed) Pb^{2+} cations, in turn, can be replaced by other cations to the solution phase and transported downwards with seepage water until they are retained on cation exchange

sites or, upon increase in soil pH, on the oxide surfaces through a specific sorption mechanism. Actually, the relative abundance of Pb_{ex} in the organic soil layers (53%–64% of Pb_{tot}) was of the same magnitude (47%–54%) as reported by Ettler *et al*. (2005) for forest soils heavily polluted by Pb metallurgy.

The residual fraction conventionally refers to Pb that is mainly present as silicates and is determined by complete dissolution of the residual sample from the fractionation procedure. Usually it is rather stable within soil profiles (*see* e.g. Ettler *et al*. 2005), but in our study Pb_{res} showed a sharply decreasing trend with increasing depth. Thus, in the upper layers this reserve can be taken to be mainly secondary in nature, i.e. to originate in the weathered pellets rather than in the mineral matrix. Because we removed the pellets from the samples before analyses, it is likely that Pb_{res} included secondary Pb bound to oxides, some metallic Pb in tiny pellet pieces and compounds possibly released from the weathered pellets. It is likely that the very small amounts of Pb_{res} at soil depths below 40 cm represented mainly naturally occurring reserves in the mineral matrix.

The Pb_{res} concentrations were highest in the organic topsoil layer followed by the uppermost mineral soil layer having the peak oxide concentrations (Table 2). However, Pb_{res} in these two upper layers did not entirely originate in oxide surfaces because a rather high pH is a prerequisite for the specific sorption of Pb as a hydroxy complex ($PbOH^+$) on oxide surfaces (*see* e.g. Saha *et al*. 2002). The pK_a value of exchangeable Pb^{2+} ions is 7.7 (Lindsay 1979: p. 331), which

Table 4. The indices for concentration gradients[1] for Pb in various pools in the soil profiles.

	Sampling point	Pb_{tot}	Pb_w	Pb_{ex}	Pb_{OM}	Pb_{res}
New range	1	227	136	488	61	134
	2	161	56	455	77	80
Old range	3	18	11	23	3	24
	4	34	24	41	8	32
Control	5	15	19	22	7	12

[1] The index is the Pb concentration in the organic layer divided by the concentration in the mineral layer beneath.

means that the formation of hydroxy complex species must have been negligible at the pH prevailing in the organic and the uppermost mineral soil layers (pH range 3.4–4.9 and 4.5–4.8, respectively). Thus, the abundance of Pb_{res} may be an artefact: Pb hydroxy complexes, possibly formed during the extraction step with NaOH, could have been transferred to the residual fraction through sorption onto oxide surfaces. The importance of pH in reactions of Pb with soil components was evident in the model experiment of Cruz-Guzmán *et al*. (2003) showing that in acid conditions (pH 3) the sorption of Pb^{2+} was high on HA, moderate on clay mineral (montmorillonite) and zero on poorly crystallized ferrihydrite. However, HA coatings on the clay mineral significantly enhanced Pb sorption, but did not on ferrihydrite because of blockage of the functional groups of HA. Furthermore, much of the Pb sorbed on mineral and organomineral model particles was in exchangeable form.

The concentration gradient indices were largest for Pb_{ex}, which is assumed to represent the exchangeable pool, indicating that this fraction was not very mobile. However, the marked decrease in the indices with prolonged reaction time, from 16 years on the new range up to 37 years on the old range, demonstrates that this fraction is potentially mobile. In fact, acetate or simple salt solutions at pH 7 are common extractants for "exchangeable" (e.g. Tessier *et al*. 1979, Margane 1992, Li *et al*. 2007) or for "exchangeable non-specific" or "bioavailable" trace metals (Rendell *et al*. 1980, Soon and Bates 1982). Nevertheless, it is possible that the high pH of the extractant for Pb_{ex} caused some transfer of Pb between different pools during the fractionation procedure. It is evident that it extracted some organically bound Pb (the extract was coloured by humus) and, consequently, diminished Pb_{OM}. On the other hand, as a response to the high pH, some exchangeable Pb might have been transformed to an oxide-bound form recovered in the Pb_{res} fraction.

Conclusions

The results show that the weathering of pellets is slow: during a period of 16–37 years about 10% of metallic Pb was released to more mobile secondary forms in the soil profile. Based on the vertical Pb distribution in the soil profiles we estimate that in the shooting ranges locating on coarse-textured formations, the average migration rate of pellet-derived Pb is roughly 2–3 mm a year. The operational fractionation analysis applied in this study produced a useful, albeit tentative, insight into the environmental fate of Pb in acid forest soil. Organic matter seems to have a dual role in Pb mobility. In the surface soil, it acts as a primary sink for Pb, leading to its accumulation. However, it is likely that with increasing Pb load as result of pellet weathering, the stability of organic Pb complexes diminishes and Pb becomes more prone to leaching. Low-molecular weight fulvic acids, in turn, contribute to the leaching of Pb. Increasing pH, together with high Mn, Fe, and Al oxide concentrations, may favour the specific sorption of Pb in the deeper mineral soil layers and, consequently, retard its downward migration. Furthermore, our results on the vertical Pb distribution in soil revealed that abnormally high Pb concentrations may occur also at some distance outside the proper clay pigeon shooting ranges, demonstrating that environmental risks are not limited to the pellet-shot-fall areas.

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