Lead forms in urban turfgrass and forest soils as related to organic matter content and pH

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Abstract Soil pH may influence speciation and extractability of Pb, depending on type of vegetation in urban soil environments. We investigated the relationship between soil pH and Pb extractability at forest and turf grass sites in Baltimore, Maryland. Our two hypotheses were: (1) due to lower pH values in forest soils, more Pb will be in exchangeable forms in forested than in turfgrass soils and (2) due to the greater lability of exchangeable Pb in equilibrium with soil solution in forest soils, concentrations of this form will increase with depth more so than in the turfgrass soils, as related to organic matter content and pH. Soil samples were collected from three forested and three turfgrass sites to depths of 20 cm. Lead forms were determined using a sequential extraction technique. Soils under turfgrass and forest vegetation differed in the extractability of soil Pb ($P<$ 0.01) for the Mn(III, IV)- and Fe(III)(hydr) oxide fraction. A greater Pb concentration was bound to this fraction under turfgrass (211 mg kg^{-1}, 69% of total Pb) than forested soils (67 mg kg^{-1}, 61% of total Pb), perhaps due to soil pH differences of 5.9 and 5.0, respectively. In the forested soils, as depth increased, the ratio of exchangeable-to-total Pb increased and the ratio of organically bound Pb-to-total Pb decreased. The results suggest changes in pH and organic matter content with depth affect the extractability of Pb, and these soil properties are affected differentially by grass versus tree vegetation in the urban soils investigated.

Keywords Fractionation · Metals · Lead · Sequential extraction · Urban soils

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Introduction

Lead is a toxic metal of social concern that is routinely found in high concentrations in urban soils (Mielke 1999). The primary sources of Pb in urban ecosystems are lead-based paint and leaded gasoline once used in internal combustion engines.

The soil Pb concentration patterns are closely related to existing roads in Baltimore City and therefore statistically suggest the major source of soil Pb is from automobiles (Mielke et al. 1983). Lead-contaminated soils that are spatially removed from the potential impact of deteriorated lead painted houses, suggest further contamination from the deposition of lead from gasoline fumes. The use of leaded gasoline

reached its peak in the 1970s and then declined until Congress banned it in 1986. It is estimated that the use of 5.9 million metric tons of Pb in gasoline left a residue of 4 to 5 million metric tons in the environment of the US (Mielke 1999). Soil Pb signatures should persist due to the long residence times of Pb in urban soils (Mielke 1999). As traffic increases toward the center of the city, roadside Pb concentrations also increase. It is well known that roadside soil Pb levels are directly related to annual average daily traffic (Lau and Wong 1982) and traffic density (Ward et al. 1977). Mielke et al. (1983) measured Pb concentrations in garden soils of Baltimore and found a relationship between the older "inner" city of Baltimore and elevated Pb concentrations.

The chemical changes that occur during transport of Pb-rich particles from motor vehicles to soils have been studied in some detail and are briefly outlined by the following four steps. (1) Lead was used as an antiknock additive which contains any or all of Pb $(CH_3)_4$, $Pb(CH_3)_3(C_2H_5)$, $Pb(CH_3)_2(C_2H_5)_2$, $Pb(CH_3)$ $(C_2H_5)_3$, and $Pb(C_2H_5)_4$. (2) Exhaust particles from internal combustion engines using primarily tetraethyl Pb consist mainly of Pb halides: $PbBr_2$, $PbBrCl$, Pb $(OH)Br$, $(PbO)_2PbBr_2$ and $(PbO)_2PbBrCl$ and as the double salts with ammonium halides (e.g., $2PbBrCl·NH_4Cl$; USEPA 1986). Robbins and Snitz (1972) reported that up to 75% of the bromine is lost from fresh automobile exhaust in the first 20 min after emission. (3) These lead halides transform to lead carbonates, oxides, and sulfates due to photochemically induced reactions during atmospheric transport (Olson and Skogerboe 1975; USEPA 1986). (4) These compounds are then deposited on the soil surface. Lead sulfate was the most frequently observed Pb compound in street dusts (Olson and Skogerboe 1975; Biggins and Harrison 1980).

Lead also is deposited and distributed in the environment from sources such as abraded tire material; coal, plastic, and rubber factories; insecticides; fertilizers and car batteries (Adriano 1986). Once in the soil, Pb is assumed to be relatively stable and immobile compared to other metals. However, changes in soil chemical conditions, such as aeration status, organic matter content, or acidity, may slowly convert immobile forms of Pb to more biologically available forms that are toxic to humans, especially over long periods of time after deposition. Increased exposure to Pb is particularly harmful to developing

nervous systems of young children and infants (Ratcliffe 1981). According to the Centers for Disease Control and Prevention, Pb is the most dangerous environmental health hazard affecting children in the USA (CDC 1991).

In urban areas, Pb is found in elevated levels (Mielke et al. 1983; Kaminski and Landsberger 2000; Madrid et al. 2002; Li et al. 2004) well above the average concentration of uncontaminated soils of 18 mg kg^{-1} (Nriagu 1978). In the Baltimore, Maryland metropolitan area, background concentrations of Pb range from 22 to 29 mg kg^{-1} for eastern and central Maryland, respectively (Maryland Department of the Environment 2001). The contemporary, median concentration is 227 mg kg^{-1}, and the maximum measured is 5,391 mg kg^{-1} (Pouyat et al. 2007). Moreover, the spatial pattern of soil Pb contamination is correlated with proximity to major roads, suggesting that historic automobile emissions may have been the major source of soil Pb in Baltimore urban soils (Mielke et al. 1983).

Once deposited from the atmosphere, Pb usually remains in the surface 5 cm of the soil profile (Page and Ganje 1970; Milberg et al. 1980). Lead moves slowly in soil because of its tendency to bind to soil mineral coatings, such as Mn(III, IV)- and Fe(III) (hydr) oxide phase and to the soil organic fraction, and to form insoluble precipitates or chemisorbed forms. The Pb found in the Mn(III, IV)- and Fe(III) (hydr) oxide phases will mostly be specifically or chemisorbed. The Pb found in the organic fraction will mostly be complexed by organic ligands. All of these reactions are regulated by organic matter concentrations, pH, cation exchange capacity, and sesqui (hydr)oxide contents. The binding of Pb in each of these fractions is regulated by the master variable, pH.

Xian and Shokohifard (1989), Elsokkary (1992), Elsokkary et al. (1995), Gupta et al. (1995) and Shuman (1998) showed that Pb was bound primarily to the organic phase (excluding the residual phase) using Tessier's (or a modification thereof) sequential extractions. Similarly, Xian and Shokohifard (1989), Elsokkary (1992), and Elsokkary et al. (1995) showed the strong tendency of Pb to form stable complexes with organic matter and sulfide minerals. Other studies have shown that Pb binds to phases other than the organic phase. Both Ramos et al. (1994) and Yarlagadda et al. (1995) showed that Pb was most

strongly associated with carbonate minerals and Mn (III, IV)- and Fe(III)(hydr) oxide phases. The latter study investigated three soils with CO_3–C percent by weight of 7.1, 1.8, and 5.4 that were from three industrial sites.

The discrepancy between these studies may be the result of the effect of different soil characteristics on the binding mechanisms of Pb. For example, soil pH varies widely among soils and with depth, and may affect concentrations of exchangeable Pb forms. Sauve et al. (1998) showed that the solubility of Pb decreased linearly from pH 3 to 6.5 in soils amended with organic matter, but it was independent of concentrations of soil organic matter in this pH range. By contrast, for pH values >6.5, the formation and dissolution of organo-Pb complexes were promoted, thereby increasing the solubility of Pb. Sauve et al. (1998) concluded that higher organic matter content resulted in higher concentrations of dissolved and labile Pb for this pH range.

To determine the influence of soil pH on the binding mechanism of Pb urban soils and how pH differences with depth and between vegetation type might explain the spatial variation of Pb contamination in urban areas, we compared the forms of Pb in soils collected from forest (deciduous mixed hardwoods, mostly *Quercus rubra*, *Liriodendron tulipifera*, *Carya tomentosa*, *Fraxinus americana*, *Fagus grandifolia*) and turf grass (mostly tall fescue, *Festuca arundinacea* L., and Kentucky blue, *Poa pratensis* L.) soils in Baltimore, MD. These vegetation types were chosen because they are the predominant cover types in Baltimore City, and they delineate vegetation patterns and soil–plant interactions in this urban area.

We hypothesized that differences in soil pH between forest and grass sites would be associated with different forms of Pb in the soil, operationally defined by a sequential extraction procedure, and thus potentially with its bioavailability and mobility in the soil profile. The average pH of parkland soils, transportation land use areas, and forest soils (0 to 10 cm) in Baltimore are 6.5±0.20 (n=10), 6.8±0.29 (n=7), and 5.7±0.16 (n=26; Kruskal–Wallis Test; Pr>chi-Square 0.0022), respectively (Pouyat et al. 2007). The more acidic soil conditions under forest vegetation suggest that concentrations of exchangeable forms of Pb will be greater in forest soils than under turfgrass. Chlopecka et al. (1996) found that soil samples with pH values <5.6 contained a higher

percentage of exchangeable metals than soil samples with pH>5.6, supporting the hypothesis that non-exchangeable metal sorption may increase with increasing pH (Puls et al. 1991). Specifically, we hypothesized that due to lower soil pH's in unmanaged forest soils (typical of Baltimore forested sites), more of the Pb is in exchangeable forms than in soils under turfgrass. Due to the greater expected lability between exchangeable and soluble Pb in forest soils, concentrations of this form should increase with depth to 20 cm in proportion to the other Pb forms in the forest soils. High organic matter contents and the accumulation of humic and fulvic acids in forest soil organic horizons also would be expected to enhance organic complexation of Pb^{2+} cations, thereby solubilizing exchangeable Pb forested surface horizons.

Material and methods

Study design

In a previous study, 202 circular plots (each 0.04 ha in area) were selected randomly and stratified by land use throughout Baltimore to measure vegetation and soil properties in order to create an urban forestry effects model (UFORE; Nowak et al. 2004; Pouyat et al. 2007). From these sites, we selected three grass and three forest plots for the current research. These sites were managed lawns and unmanaged forests surrounded by neighborhoods and streets which were chosen because concentrations of total Pb in the surface 10 cm of soil were high relative to other forest or grass plots in the study (Table 1). The depth of 0–10 cm was used in the earlier study for the purpose of examining soil characteristics and not exclusively metals. The forest sites were the Northern Parkway (FOR-NPF), Cross Keys (FOR-CK), and Gwynns Falls Park (FOR-GF). The grass sites were the Northern Parkway (GRA-NPM), Mount Olivet Lane (GRA-MtO), and Patterson Park (GRA-PP). At each site, three parallel transects to the road were established 20 m apart perpendicular to the nearest road if a road existed near the site. The samples were collected at each of the six locations using a shovel to cut a square, a 15- by 15-cm hole to 15 cm depth, so that the horizons were easy to view, and a knife was used to separate the horizons. A bulk sample was taken from each horizon at each transect. The FOR-

Table 1 Soil test results for study sites

Plot name	Cover	Bulk density[a] (g cm^{-3})	Texture[b]	P[c] (mg kg^{-1})	Ca[c]
Gwynns Falls Park (FOR-GF)	Forest	1.4	Loam	160	1,975
Cross Keys (FOR-CK)	Forest	0.9	Loam	197	406
Northern Parkway (FOR-NPF)	Forest	0.9	Loam	298	1,838
Patterson Park (GRA-PP)	Grass	1.2	Sandy L.	545	3,093
Mt. Olivet Lane (GRA-MtO)	Grass	1.2	Sandy L.	571	3,398
Median of N. Parkway (GRA-NPM)	Grass	1.1	Loam	775	5,552

The samples were composited using a 2.5 cm-wide soil probe to collect approximately 10 cores in an area of 0.04 ha to a depth of 10 cm

[a] Determined by the ring method (Blake and Hartge 1986)

[b] Texture done by the feel method

[c] Nitric acid digestion using a modified protocol of USEPA Method SW-846 3050 (USEPA 1996)

NPF, GRA-MtO, and GRA-PP sites were sampled at 10, 30, and 50 m from the road. These distances were chosen due to the expected trajectory of Pb from exhaust. As traffic increases toward the center of the city, roadside Pb concentrations also increase. Roadside soil Pb levels are directly related to annual average daily traffic (Lau and Wong 1982) and traffic density (Ward et al. 1977). The rate of deposition decreases rapidly with distance from the road (Jaradat and Momani 1999). Rodriguez-Flores and Rodriguez-Castellon (1982) showed that background levels were not restored until approximately 60 m from the road. For one site in this Puerto Rico study, which had a traffic density of 13,680 vehicles per day, the soil Pb concentration in the top 5 cm was 522 mg kg^{-1} at 3 m, 10.1 mg kg^{-1} at 10 m, 9.4 mg kg^{-1} at 20 m, and 5.5 mg kg^{-1} at 33 m. GRA-NPM, FOR-GF, and FOR-CK were sampled differently. For example, GRA-NPM, a road median strip about 7 m wide with two eastbound lanes and two westbound lanes, was sampled at three 15 m intervals. FOR-GF, an area in the middle of a 486-ha patch of urban woodland which is land covered with trees (mostly *Quercus* spp.) and shrubs (mostly *Viburnum* spp. and *Lindera*

spp.) in an urban setting, was sampled and composited according to slope position of an approximately 5% slope, i.e., top, middle, and bottom of the hill. The nearest road was approximately 300 m away. FOR-CK, a forest area on a hilltop, was sampled at 80, 90, and 100 m from the road. The reason for the discrepancies in sampling distances was because we wanted to overlap with established UFORE plots to investigate relationships between the soils and vegetation.

In this paper, horizons are referred to as the first, second, and third with increasing depth because traditional horizon descriptive units such as A, AB, and B could not be confidently established in this urban environment where there appeared to be evidence of filling and cutting activities for the grass sites: GRA-NPM, GRA-PP, GRA-MtO. The taxonomic subgroups for the plots FOR-GF, FOR-CK, FOR-NPF, GRA-NPM, GRA-PP, and GRA-MtO were Typic Hapludalfs Relay silt loam, Ultic Hapludalfs Urban land-Udorthents complex, Aquic Hapludalfs Jackland silt loam, Aquic Hapludalfs Jackland-Urban land complex, Typic Hapludults Sunnyside fine sandy loam, and Ultic Hapludalfs Legore-Urban land complex respectively (NRCS 1998). Horizons were determined by differences in color, texture, and rock fragment for 42 horizons (not including the O horizons). The O horizons of the forest soils were extremely decomposed to non-existent and were incorporated into the first horizons mainly by earthworms as evidenced by earthworm casts on the surface of the soil. There was very little formation of an Oa or Oe horizon, indicating that the flux of organic C into the surface mineral horizons was high on an annual basis under deciduous trees. The horizons were delineated, collected, and then the average depths and standard errors were determined. The first horizon was 0 to 8.6±0.72 cm for all the horizons of forest and grass, the second was 8.6±0.72 to 17.4±0.92 cm, and the third was 17.4±0.92 to 25±1.9 cm.

Soil samples were immediately stored in zip-lock bags and kept in a cooler filled with ice packs at 4°C to minimize the development of anaerobic conditions. Field-moist samples (approximately −10 kPa water potential) were used in the laboratory extraction to prevent acidification and changes in the concentration of soluble organic matter due to air-drying (Bartlett and James 1980). Whole samples, before subsampling for extraction, were passed through a 3-mm plastic sieve with a wooden implement to facilitate sieving. The samples were then weighed out for the speciation

sequential extraction (SSE) methodology and placed into centrifuge tubes and returned to the refrigerator set at 4°C until processing. Samples were processed as quickly as possible; however, some samples were processed a couple of weeks after the first batch due to logistical limitations.

Soil analyses

Three replicates per soil sample were used for soil pH (1:2 soil-to-0.01 M CaCl$_2$ ratio). Measurements were made with an Orion® model 520A pH meter. The soil and solution were stirred in a glass beaker for 15 s and allowed to sit for 20 min until the particles settled. A reading was taken after 2 min in the supernatant liquid. Moisture content was determined gravimetrically (105°C for 24 h). The oven-dried soil was then ashed in a Thermolyne Type 48000® furnace for 4 h at 450°C to determine organic matter content operationally as loss-on-ignition (Davies 1974). Organic carbon was determined at the University of Maryland Soil Testing Lab with a Leco CHN 2000 Analyzer® with the assumption there were no carbonates present.

Speciation sequential extraction method

We used the speciation sequential extraction (SSE) method of Tessier et al. (1979) as modified by Rauret et al. (1989). With this protocol, chemical extractants (in parentheses) are used to define operationally four fractions of Pb in the soil samples: exchangeable (1 M MgCl$_2$), bound to carbonates (1 M NaOAc–HOAc), bound to Mn(III, IV)- and Fe(III)(hydr) oxides (0.04 M NH$_2$OH · HCl in (v/v) 25% HOAc), and bound to organic matter (acidified H$_2$O$_2$).

Rauret et al. (1989) proposed multiple extraction repetitions for a given step extraction until certain conditions are met, e.g., the change in solubilized Fe and Mn remains constant in the NH$_2$OH · HCl step or the change in Eh is <25 mV for the H$_2$O$_2$ step. Rauret's procedure addresses two problems encountered with selective extraction: redistribution and readsorption of trace elements to different soil phases and the inability of a chemical extractant to release metals in soils with high concentrations of metals. Ramos et al. (1994) showed that two successive extractions were sufficient to characterize each fraction of three differently textured soils: sand, silt and clay. Of the extractions, the NH$_2$OH · HCl (for the Mn (III, IV)- and Fe(III)(hydr) oxide fraction) and 30% acidified H$_2$O$_2$ (for organic matter-bound metals) were the only steps carried out twice. The literature shows that the organic fraction (Shuman 1998; Elsokkary 1992; Elsokkary et al. 1995, Xian and Shokohifard 1989; Gupta et al. 1995) and the Mn(III, IV)- and Fe(III)(hydr) oxide fraction (Yarlagadda et al. 1995; Ramos et al. 1994; Dawson and Macklin 1998; and Tra and Egashira 1999) contain the highest concentrations of Pb compared to other fractions. All extractions were centrifuged using polycarbonate centrifuge tubes at 11,100×g for 10 min at 25°C. The supernatant liquid was decanted into plastic scintillation vials. The scintillation vials were immediately refrigerated at 4°C. All extraction steps followed the same centrifuging and decanting protocol. The extractants were analyzed using flame atomic absorption spectrometry. The standards for Pb, Mn, and Fe were prepared in the background chemical reagents of each individual extraction step. The limit of detection for Pb was 0.19 mg l^{-1} for this method.

All extractions were replicated three times. The moist equivalent mass of 1.0 g oven-dry soil was used to account for different moisture contents, e.g., 1.14 g of moist soil equals 1.0 g of oven-dry soil. To ensure the accuracy of moisture percentages, all sampled soils were weighed immediately, placed in polycarbonate centrifuge tubes to prevent drying of the soils within the plastic bags, and stored at 4°C for a period of a day to up to 2 weeks. Methodology details such as shaking times and temperatures can be found in Tessier et al. (1979).

Sequential extraction caveats

Critical reviews have exposed the limitations of SSE methods for soils, but also their value in operationally defining how metals are bound in soils. Since the extraction sequence of Tessier et al. (1979) is utilized in more studies than any other method, it has been the focus of many reviews. Some problems include readsorption of metals following extraction (Gilmore et al. 2001), reprecipitation (Calmano et al. 2001), non-selectivity of chemical reagents, and soil/solution ratio effects. Other problems may involve the sequence of the individual steps, specific "matrix effects" such as cross-contamination of the metal, and heterogeneity as well as physical associations (e.g.

Table 2 Soil metal concentrations and parameters for all sites

Plot	Top[a]	Bottom[b]	Depth[c]	Cover[d]	Horizon[e]	Extraction 1[f]	Extraction 2[g]	Extraction 3[h]	Extraction 4[i]	Total Pb[j]	Moisture[k]	Organic matter[l]	Carbon[m]	Sand[n]	Silt[n]	Clay[n]	pH[o]	Mn[p]	Fe[q]	Matrix color[r] (moist)
CK	O	O		F	O	1	22	94	56	173	52	37	228				5.2	1,225	2,094	10YR 2/2
CK	0	5	5	F	1	26	45	125	22	218	37	15	78	36	42	22	4.2	334	3,529	10YR 3/2
CK	5	10	5	F	2	47	54	89	8	198	26	9	40	36	41	23	4.2	150	4,616	10YR 4/4
CK	10	20	10	F	3	18	12	24	2	55	18	4	11				4	99	4,314	10YR 4/4
CK	O	O		F	O	5	28	130	35	197	43	25	177				5.4	640	2,401	10YR 2/2
CK	0	6	6	F	1	35	41	126	12	214	26	9	94	48	40	12	5.2	254	3,528	10YR 2/2
CK	6	15	10	F	2	58	64	215	14	350	26	8	46	46	44	10	4.7	375	3,797	10YR 3/2
CK	15	21	6	F	3	84	62	131	9	286	21	5	24				4.2	260	3,582	10YR 4/4
CK	O	O		F	O	5	11	41	28	84	59	38	229				6.1	455	2,756	10YR 2/2
CK	0	6	6	F	1	2	23	73	15	113	34	15	56	45	40	15	5.6	686	3,363	10YR 3/2
CK	6	18	12	F	2	4	18	76	6	104	22	6	27	45	39	16	5.9	367	3,876	10YR 4/4
GF	0	13	13	F	1	1	4	25	4	34	21	6	27	47	37	16	5.2	216	2,492	10 YR 3/3
GF	13	18	5	F	2	2	4	16	1	22	15	3	11	46	38	16	4.9	214	2,333	10 YR 4/4
GF	0	10	10	F	1	5	4	18	2	29	19	5	25	45	38	17	5.1	157	2,400	10YR 3/4
GF	10	18	8	F	2	3	5	13	0	21	17	4	12	46	38	16	4.8	142	2,252	10YR 4/4
GF	O	O		F	O	5	9	23	10	47	39	20	67				5.1	217	1,999	10 YR 3/2
GF	0	8	8	F	1	8	8	26	5	46	26	8	36	44	39	17	4.6	158	2,290	10 YR 3/2
GF	8	23	15	F	2	5	8	15	1	29	18	4	10				4.5	120	2,440	10 YR 4/4
NPF	O	O		F	O	2	18	82	22	123	36	19	110				5.9	359	3,587	10YR 2/2
NPF	0	13	13	F	1	10	17	79	9	114	24	11	47	40	46	14	5.3	267	4,655	10YR 2/2
NPF	O	O		F	O	2	6	46	11	64	39	15	71				5.6	414	4,305	10YR 2/2
NPF	0	10	10	F	1	5	6	53	9	72	32	12	47	43	35	22	5.5	573	4,715	10YR 2/2

NPF	10	20	10	F	2	10	6	32	5	25	52	7	21	48	31	21	4.6	544	4,500	10YR 3/3
NPF	O	O	O	F	O	4	9	61	17	44	89	24	118				5.4	1,686	4,729	10YR 2/2
NPF	0	10	10	F	1	4	10	71	13	31	98	12	46	35	43	22	4.8	1,623	4,742	10YR 2/2
NPF	10	16	6	F	2	14	13	89	9	26	125	8	28				4.5	591	5,920	10YR 3/3
NPF	16	28	12	F	3	6	5	33	1	21	45	6	16	30	40	30	4.2	1,292	5,983	10YR 3/4
NPM	0	8	8	G	1	3	121	469	48	21	641	12	60	43	40	17	6.6	901	3,577	10YR 3/2
NPM	8	15	7	G	2	2	41	283	17	18	343	7	24	35	40	25	6.6	1,459	5,043	5YR 3/4
NPM	0	6	6	G	1	7	128	668	44	22	847	11	57	43	38	19	6.4	1,093	4,201	10YR 3/2
NPM	6	16	10	G	2	3	40	198	17	18	257	7	23	34	40	26	6.3	1,236	4,311	5YR 3/4
NPM	0	6	6	G	1	5	126	555	64	22	750	13	75	42	38	20	6.6	853	3,072	10YR 3/2
NPM	6	13	7	G	2	2	70	343	22	17	438	7	28	45	33	22	6.2	1,104	5,057	5YR 3/4
MtO	0	3	3	G	1	10	39	80	11	26	140	11	51	58	26	16	5.5	144	2,115	10YR 4/6
MtO	3	8	5	G	2	11	13	37	4	17	66	6	11	54	21	25	5.1	129	4,699	10YR 4/6
MtO	8	20	12	G	3	9	86	230	16	16	341	7	34	61	23	16	5.7	272	3,930	10YR 4/6
MtO	0	9	9	G	1	5	30	127	10	19	171	7	32	59	23	18	5.6	296	4,119	10YR 4/6
MtO	9	21	12	G	2	0	41	117	9	0	167	6	36	57	26	17	6.2	316	4,504	10YR 3/2
MtO	0	8	8	G	1	5	22	115	16	22	159	9	46	52	27	21	5.4	337	4,672	10YR 3/2
MtO	8	20	12	G	2	4	41	135	14	18	194	7	23	49	26	25	5.9	460	5,453	10YR 3/2
PP	0	13	13	G	1	12	19	91	8	23	130	9	60	54	32	14	5.2	251	3,020	10YR 3/2
PP	13	20	7	G	2	7	25	97	10	19	139	7	28	57	26	17	5.1	133	3,454	10YR 3/3
PP	20	35	15	G	3	4	17	36	1	13	58	3	7	55	26	19	5.7	60	4,072	10YR 4/6
PP	0	13	13	G	1	27	50	235	20	21	332	8	67	62	25	13	5.4	163	2,456	10YR 3/2
PP	13	20	7	G	2	14	44	169	6	18	233	8	128	60	27	13	5.6	126	1,642	10YR 3/3
PP	20	28	8	G	3	17	91	149	15	16	271	5	61	63	23	14	5.8	117	2,178	10YR 4/6
PP	0	13	13	G	1	8	30	149	18	22	205	8	101	62	25	13	5.3	123	2,276	10YR 3/3

Table 2 (continued)

Plot	Top[a]	Bottom[b]	Depth[c]	Cover[d]	Horizon[e]	Extraction 1[f]	Extraction 2[g]	Extraction 3[h]	Extraction 4[i]	Total Pb[j]	Moisture[k]	Organic matter[l]	Carbon[m]	Sand[n]	Silt[n]	Clay[n]	pH[o]	Mn[p]	Fe[q]	Matrix color[r] (moist)
PP	13	23	10	G	2	2	18	158	14	192	19	6	88	60	26	14	5.9	128	2,555	10YR 3/3
PP	23	28	5	G	3	5	53	199	22	279	17	6	141	61	25	14	6.2	111	2,033	10YR 4/3

NPF Northern Parkway forest site; *CK* Cross Keys forest site; *GF* Gwynns Falls forest site; *NPM* Northern Parkway median grass site; *NPF* Northern Parkway forest site; *MtO* Mt. Olivet Lane grass site

[a] Top of horizon (cm)

[b] Bottom of horizon (cm)

[c] Depth of horizon (cm)

[d] Cover is divided in to two categories: forest (f) and grass (g). In this study grass is an expanse of ground, such as a lawn, covered with grass, which are the members of the grass family, Gramineae. A forest is a dense growth of plants, trees, and underbrush covering a large area

[e] The order of the horizons. "O" is the O horizon. The first horizon was 0 to 8.6±0.72 cm, the second was 8.6±0.72 cm to 17.4±0.92 cm, and the third 17.4±0.92 to 25±1.9 cm

[f] Extraction 1 is the exchangeable fraction operationally defined by the amount of Pb (mg kg^{-1}) solubilized using 1 M MgCl$_2$

[g] Extraction 2 is the Pb bound to carbonates operationally defined by the amount of Pb (mg kg^{-1}) solubilized using 1 M NaOAc–HOAc adjusted to pH 5.0

[h] Extraction 3 is the Pb bound to the Mn(III, IV)- and Fe(III)(hydr) oxides operationally defined by the amount of Pb (mg kg^{-1}) solubilized using 0.04 M NH$_2$OH · HCl in (v/v) 25% HOAc

[i] Extraction 4 is the organically bound Pb operationally defined by the amount of Pb (mg kg^{-1}) solubilized using 30% H$_2$O$_2$ (pH 2 with HNO$_3$)

[j] Total Pb (mg kg^{-1}) is the sum of the total amount of Pb extracted by all the extractants

[k] Moisture content (%) was determined gravimetrically (105°C for 24 h)

[l] Organic matter (%)was determined by the loss on ignition method (4 h at 450°C)

[m] Organic carbon (%) was determined with a Leco CHN 2000 Analyzer® with the assumption there were no carbonates present

[n] Particle size (%) was measured by the hydrometer method (Wilde et al. 1972)

[o] Soil pH was measured using 1:2 soil/0.01 M CaCl$_2$ ratio (i.e. the moist equivalent of 5 g oven-dry soil and 10 g of 0.01 M CaCl$_2$)

[p] Soluble Mn^{2+} (mg kg^{-1}) solubilized using 0.04 M NH$_2$OH · HCl in (v/v) 25% HOAc

[q] Soluble Fe^{2+} (mg kg^{-1}) solubilized using 0.04 M NH$_2$OH · HCl in (v/v) 25% HOAc

[r] Matrix color was determined in the field

coatings) of the various solid fractions (Kersten and Forstner 1989).

Lack of geochemical specificity was reported in experiments where Kheboian and Bauer (1987) studied metal spike recovery from calcite, iron hydroxides, and iron sulfides (mackinawite (FeS), greigite (Fe_3S_4)) created in the lab. Examining the Pb spiked into calcite, measurements of extracts by atomic absorption and inductively coupled plasma indicated that Pb was not recovered in the 1 M NaOAc (pH 5) phase. Most of the Pb (about 56%) was recovered in the Mn(III, IV)- and Fe(III)(hydr) oxide phase with about 3% in the carbonate phase. This may be explained by the solubilization of Pb in the 1 M NaOAc (pH 5) phase along with calcite and the readsorption of Pb to the remaining phases.

Phosphorus can have an effect on the partitioning of Pb within a soil. X-ray absorption spectroscopy has shown that the addition of 1,000 mg kg^{-1} P of calcium phosphate ($CaHPO_4 \cdot 2H_2O$) amendment causes a significant shift of extractable Pb to the residual phase (Scheckel et al. 2003). Other studies have used 5,000–32,000 mg P kg^{-1} of soil to investigate the formation of pyromorphite ($Pb_5(PO_4)_3Cl$) in Pb-contaminated soils as a remediation method. The phosphorus concentrations of the soils in our study are well below these concentrations (Table 1). It has been shown that the residual phase may contain up to 37% of the total Pb concentration for soils such as Haplorthods and Haplumbrepts (Chlopecka et al. 1996) and fluvisols (Tra and Egashira 1999). The residual phase was not analyzed in this study because it was not considered an environmentally available Pb form. This fraction should contain mainly silicates and primary and secondary minerals. Although, relative to the available fractions it may not be environmentally significant, it may become environmentally available and mobilized in certain circumstances. Furthermore, it may provide useful information for comparison to bulk analysis. Nevertheless, despite the inherent technique limitations related to the SSE method, recovery of metals in this procedure provides a potentially useful tool to operationally define the solid forms of metals and their potential for release into the soluble forms that could leach to groundwater or be bioavailable due to soil chemical changes. They also allow a more realistic assessment and simulation of plant and microbe-induced releases of metals. To maximize the SSE's potential to extract Pb, we must understand the chemical reactions between the reagents and soil components, (e.g. effects of pH, colloidal surfaces, and hydrous oxides), during extraction, and choose standard procedures to ensure we are generating comparable results for different soils. For the purposes of this study, the extraction methods are appropriate operational ways of making Pb form comparisons between forest and turf grass soils.

Statistical analysis

We analyzed the data as a doubly repeated measures ANOVA to avoid pseudo-replication for testing the differences between cover types. A doubly repeated measure was used because extraction was nested within depth (horizon); and depth (horizon) was nested within distance and distance is nested within replication (plot). With a nested design the sampling order cannot randomize, (i.e. the horizons cannot be randomized in the experimental design), the first horizon will always come before the second horizon. We used the *MIXED* procedure of the SAS System (SAS 1999) with the *REPEATED* option and its first-order autoregressive covariance structure for data analysis. The response variable modeled individually was the concentration of Pb quantified from a particular extraction. Since our models included vegetation cover type, extraction method, and depth as explanatory variables, we first examine the significance of the three- and two-way interactions and then we report and discuss the results of the main or simple effects, accordingly. Spearman correlations were run on Pb concentration (milligram per kilogram) and other variables such as pH and organic matter (SAS 1999).

Results and discussion

Vegetation cover type

For the purpose of accurate representation of the extraction results, from this point on, the chemical extractions will be referred to as the $MgCl_2$, HOAc, NH_2OH, and H_2O_2 for which the majority of the Pb released will be associated with the exchangeable (1 M $MgCl_2$), bound to carbonates (1 M NaOAc–HOAc), bound to Mn(III, IV)- and Fe(III)(hydr) oxides (0.04 M $NH_2OH \cdot HCl$ in (v/v) 25% HOAc),

and bound to organic matter (acidified H_2O_2). The soil metal concentration data and other parameters are given in Table 2.

Grass soils had 2.6-fold more Pb than did forest soils. Soils from forest and turfgrass sites differed significantly ($P<0.05$) in the fraction of Pb bound to the NH_2OH-extractable phase. Lead concentrations were higher in the NH_2OH fraction in turfgrass soils (210 ± 35 mg kg^{-1}) than in forest soils (67 ± 9.2 mg kg^{-1}). However, concentrations of Mn (496 ± 86 and 446 ± 94 mg kg^{-1} for forest and grass soils, respectively) and Fe ($3,600\pm224$ and $3,570\pm244$ mg kg^{-1} for forest and grass soils) did not differ significantly over all horizons or for the surface horizons.

The interaction between vegetative cover and NH_2OH extractable Pb was significant ($P<0.01$). A significant interaction shows that concentrations of Pb in the NH_2OH fractions are higher under grass than in forest soils compared to the difference in Pb concentration for the other three extractions (Fig. 1). These results support our hypothesis that lower pH in forest soils than in grass soils may inhibit binding of Pb by Mn(III,IV)(hydr)oxides. For example, forest soils had lower pH ($P=0.001$), but they did not have more Pb in the $MgCl_2$ form than in grass soils. However, grass soils with a higher pH had significantly more Pb associated with NH_2OH phases than forest soils (Fig. 1). While these results suggest a relationship between soil pH and NH_2OH extractable Pb, a more direct analysis of the relationship between soil pH and Pb form may be warranted. Ettler et al. (2005) found that in conventionally tilled agricultural soils with pH
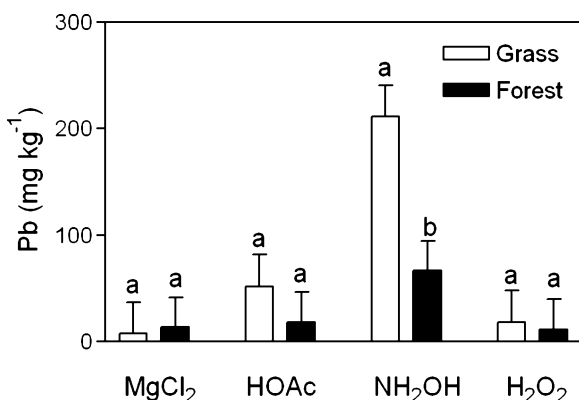

Fig. 1 The concentration of Pb (mg kg^{-1}) for forest and grass sites versus extraction steps averaged for all horizons and plots. Different *letters on the top of bars* indicate significant differences according to LSD ($P<0.05$). *Bars* indicate one SEM (standard error of the mean)

values in the range of 4.5–5.6, there was a greater percentage of Pb found in the NH_2OH phase using the Tessier sequential extraction procedure. However, in forest soils with pH values of approximately 3.5 under a spruce canopy, there was a greater percentage of Pb found in the $MgCl_2$ phase. Lead sulfate ($PbSO_4$) was found in these contaminated forest soils (concentrations up to 35,300 mg kg^{-1}) by X-ray powder diffraction. Also, Nguyen and Manning (2003) used X-ray absorption spectroscopy on a predominantly inorganic, mineral soil (fine-loamy, thermic, Typic Haploxeralf, Fallbrook series) and determined that the adsorption of Pb is strongly pH dependent. Lead removal mechanisms from solution included adsorption primarily on inorganic mineral surfaces and probably precipitation of $Pb(OH)_2$ at pH>5.5.

It is possible that the Mn(III, IV)- and Fe(III)(hydr) oxides in the grass soils is where the additional Pb is bound, and this may be related to precipitation, chemisorption, or complexation. For example, if the forest soils had equivalent levels of total lead, they could conceivably store the Pb in the same oxide forms. However, it doesn't negate a possible pH-dependent charge effect on the Mn(III, IV)- and Fe(III)(hydr) oxides (McBride 1994).

Soil pH effects

Combining the results of the three forest and three grass sites, the Pb in each soil fraction was significantly correlated ($P<0.01$) with pH (Table 3). Combining the results of forest and grass is done to examine the effect of pH and other soil characteristics regardless of cover type. Soil pH can be considered a master variable that controls complexation reactions, ion exchange, reduction/oxidation, dissolution/precipitation, and adsorption reactions in soils (McBride 1994). In turn, these variables affect pH-dependent charge, which influences the exchange capacity of Mn (III, IV)- and Fe(III)(hydr) oxide and thus soil retention mechanisms for Pb.

There was a significant correlation of NH_2OH extractable Pb and organic C. The correlation was low at 0.39 even though it was highly significant. Possible mechanisms for explaining the association between organic C and NH_2OH extractable Pb are that mixed carbon–Mn(III, IV)–Fe(III)(hydr) oxides may exist in the soils. Mn(III, IV) oxides may cause oxidation and polymerization of simple phenolic acids as they

Table 3 Correlation coefficients (r) and respective p values for Pb concentrations of given extraction related to pH, organic C, and Mn(III, IV)- and Fe(III)(hydr) oxides for combined grass and forest sites ($n=49$)

Pb fractions	pH	Organic carbon	Mn (III, IV) (hydr) oxides[a]	Fe (III) (hydr) oxides[a]
Mg$_2$Cl	−0.51***	0.02	−0.35**	−0.04
HOAc	0.44***	0.32**	0.07	−0.02
NH$_2$OH	0.57***	0.39***	0.24*	0.06
H$_2$O$_2$	0.60***	0.68***	0.47***	−0.03

*$P<0.1$

**$P<0.05$

***$P<0.01$

[a] Quantity of Mn^{2+} and Fe^{2+} solubilized by 0.04 M $NH_2OH \cdot HCl$ were used to quantify the easily reducible portion of the Mn(III, IV)- and Fe(III)(hydr) oxide concentrations

become fulvic and humic acids, and as a result, the Mn(III, IV) oxides, Fe(III)(hydr) oxides, and carbon are mixed coatings on other soil particles. It must be noted that for the purpose of looking for important relations between variables, an r value of >0.75 is usually used by scientists as a critical value. Even though the P values may be significant, it does not tell you whether the relation, however strong, is causal. Significant r values, however, do help to distinguish important explanatory variables for further consideration and discussion.

The oxides and hydroxides of Al, Fe(II,III) and Mn (III, IV) have little or no permanent surface charge but produce cation- and anion-exchange capacity (CEC and AEC) from the adsorption of protons and hydroxyl ions as inner sphere species in which hydration shell H_2O molecules are displaced in the binding process (McBride 1994). This adsorption allows the binding of metal cations through chemisorption or specific adsorption (McBride 2000).

Soil pH was positively correlated with NH_2OH extractable Pb concentrations ($r=0.57$; Table 3), suggesting that the Pb extracted from the NH_2OH fraction might be related to variable charge. Supporting this explanation, Yong and Galvez-Cloutier (1993) showed that as pH increases, the amount of Pb retained increases (using a modification of the Tessier procedure introduced by Belize et al. 1989). Their study revealed that an increase in pH from 5 to 6 increased the amount of Pb retained by the NH_2OH phases of a montmorillinitic soil from ~20% of the total amount of Pb (~0.20 cmol kg^{-1} soil) to ~35%

(~0.35 cmol kg^{-1}). Figure 2a depicts a similar relationship of pH and the concentration of Pb released by the NH_2OH solution.

The importance of the NH_2OH extractable Pb in this study warrants further investigation into the mechanisms controlling the binding of Pb, particularly the differential effects of Mn and Fe. Mn(III, IV)(hydr) oxide concentrations were significantly correlated ($P<0.05$) with extractable Pb in the MgCl$_2$ ($r=−0.35$), NH_2OH ($r=0.24$), and H$_2O_2$ fractions ($r=0.47$; Table 3). By contrast, the Fe(III)(hydr) oxide concentrations were not significantly correlated ($P<0.05$) with extractable Pb for any of the four phases.

Because correlation values were higher for soluble Mn than for soluble Fe, it would seem that Mn(III, IV)(hydr) oxides play a more important role than Fe (III)(hydr) oxides in binding Pb^{2+}. The mechanism responsible for the strong affinity of Mn(III, IV)(hydr) oxides for Pb might be related to their low point of

a

b
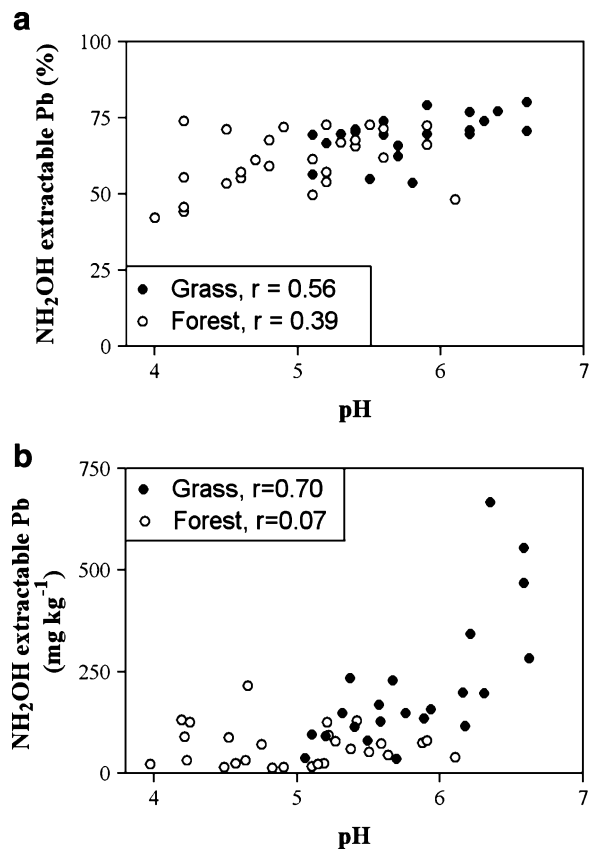
Fig. 2 **a** *X–Y* scatter plots of pH and Pb percentages for the NH_2OH extraction step by cover type. **b** *X–Y* scatter plots of pH and Pb concentrations (mg kg^{-1}) for the NH_2OH extraction step by cover type

zero charge (PZC). A low PZC results in a surface charge that is strongly negative for the pH range for most soils. For Mn(III, IV)(hydr) oxides, the PZC in soils is at pH 2 to 4, compared to 5 to 7 for Fe(III)(hydr) oxides. Another possible explanation for the affinity of Pb^{2+} for Mn(III, IV)(hydr) oxides is the oxidation of Pb^{2+} by Mn(III, IV) to Pb(IV), an insoluble oxide, e.g., PbO_2, (McBride 1994) forming a separate PbO_2 phase or binding Pb(IV) into oxide structure. The negative correlation between Mn(III, IV)(hydr) oxide concentrations and $MgCl_2$ extractable Pb^{2+} implies that as the concentration of Mn(III, IV)(hydr) oxides increases, the amount of $MgCl_2$ extractable Pb^{2+} decreases. Chorover and Sposito (1995) found out of the all the soils tested for surface charge characteristics of kaolinitc tropical soils, one soil high in Mn oxides showed points of zero net charge well below those of the other three soils, i.e. 2.3 compared to 3.0 to 3.5 at 0.01 mol kg^{-1} background electrolyte concentration.

Examining forest and grass soils separately, the pH is not well correlated with NH_2OH extractable Pb ($r= 0.07$) on forest sites (pH of 5.0±0.11). However, for grass sites with an average pH of 5.8±0.11, pH is well correlated with NH_2OH extractable Pb ($r=0.70$; Table 4, Fig. 2b). The pH was significantly different between cover types ($P=0.001$). This may suggest that the variable charge for Mn(III, IV)(hydr) oxides is becoming increasingly negative with an increase in pH. Indeed, Mn (III, IV)(hydr) oxides have a strong affinity for metal ions (McKenzie 1989). Dong et al. (2000) concluded that Mn(III, IV)(hydr) oxide and not Fe(III)(hydr) oxide dominated the adsorption of

Pb at pH 6.0. Furthermore, there is a strong relationship between the H_2O_2 extractable fraction and Mn(III, IV)(hydr) oxide concentration. This maybe an indication of the non-specificity of the extraction procedure and that a proportion of NH_2OH extractable Pb is readsorbed to be extracted using H_2O_2 in the next step. Furthermore, it is known that hydrogen peroxide dissolves Mn oxides especially at low pH (Neaman et al. 2004).

Organic carbon

Soil organic carbon (SOC) is significantly correlated with every phase of Pb except the $MgCl_2$ phase, though SOC concentrations did not differ significantly between cover types. The strongest association between SOC and extracted Pb was in the H_2O_2 phase ($P<0.01$, $r=0.68$; Table 3). Extracted Pb from the HOAc phase ($r=0.32$) and from the NH_2OH phase ($r=0.39$) also are significantly correlated with SOC. In forest soils, SOC is strongly correlated with H_2O_2 extractable Pb ($P<0.01$, $r=0.92$; Table 4). The decrease in SOC from 140±29 g kg^{-1} in the O horizon to 17±3.9 g kg^{-1} in the third horizon corresponds to a decrease in H_2O_2 extractable Pb from 25.3±6.1 mg kg^{-1} in the O horizon to 4.0±2.3 mg kg^{-1} in the third horizon. However, in grass soils SOC is weakly correlated with H_2O_2 extractable Pb ($r=0.37$; Table 4).

These results suggest that in forest soils SOC is more important for binding Pb in the H_2O_2 phase than it is in grass soils. A possible mechanism that binds Pb with SOC is proton displacement from acidic functional groups (ligands), e.g., phenolic, carboxylic,

Table 4 Correlation coefficients (r) and respective p values for Pb concentrations of given extraction related to pH, organic matter, organic carbon, and Mn(III, IV)- and Fe(III)(hydr) oxides for separate grass and forest sites

Pb fractions	Forest				Grass			
	pH	Organic carbon	Mn (III,IV) (hydr) oxides[a]	Fe(III) (hydr) oxides[a]	pH	Organic carbon	Mn (III,IV) (hydr) oxides[a]	Fe(III) (hydr) oxides[a]
Mg_2Cl	−0.64***	−0.21	−0.28	0.30	−0.65***	0.37*	−0.47**	−0.57***
HOAc	−0.05	0.43**	0.15	0.11	0.62***	0.37*	0.36*	−0.12
NH_2OH	0.07	0.54***	0.43**	0.29	0.70***	0.35	0.52**	0.01
H_2O_2	0.45**	0.92***	0.57***	0.05	0.60***	0.37*	0.51**	−0.06

*$P<0.1$

**$P<0.05$

***$P<0.01$

[a] Quantity of Mn^{2+} and Fe^{2+} solubilized by 0.04 M $NH_2OH \cdot HCl$ were used to quantify the easily reducible portion of the Mn(III, IV)- and Fe(III)(hydr) oxide concentrations

sulfhydryl, and other ligands (McBride 2000). The CEC of humic substances depends on the dissociation of H from –COOH and –OH groups (Oades 1989), which creates a negatively charged surface to bind cations such as Pb. Strawn and Sparks (2000) used X-ray absorption fine structure and theoretical models to show how soils without organic matter bound Pb using oxygen and silicon (sodium-hypochlorite-treated Typic Hapludult, Matapeake silt loam). However, the soils with organic matter (Typic Hapludult, Matapeake silt loam) bound Pb using oxygen and carbon. Baltimore City soils contain average organic matter concentrations of 61 g kg^{-1} (n=26) for forest, 51 g kg^{-1} (n=33) for grass (medium-density residential areas) and 57 g kg^{-1} (n=10) for park using the loss-on-ignition method for soil samples to a depth of 10 cm (Baltimore Ecosystem Study unpublished data).

Lead levels with depth and distance

No significant differences were found for Pb concentration with relation to distance from road. Furthermore, total soil Pb concentrations did not consistently increase or decrease with depth in the forest or grass plots. This may be related to historic anthropogenic mixing of the urban soils due to land grading, building, and other human land disturbances (Table 5). Lead concentration on the FOR-GF site decreased gradually as depth increased (Table 5). The FOR-NPF site showed a decrease in Pb concentration only after 20 cm.

Lead in the GRA-MtO site increased from 157 to 234 mg kg^{-1} from the first to the second horizon (Table 5), likely due to mixing of enriched-Pb surface horizons with deeper horizons as evidenced by human artifacts at GRA-MtO, e.g., pieces of brick grout and cement (urbic material), in the third horizon. Total Pb in GRA-PP soils did not change as a function of depth as expected, which also may be related to human activity and mixing of soil horizons as evidenced by disintegrated oyster shells in the third horizon of one of the replications. By contrast, on the GRA-NPM site, the Pb concentration fell sharply from 750 to 350 mg kg^{-1} from the first to second horizon (Table 5).

Unlike the inconsistent relationship between depth and total Pb concentrations, the ratio of H_2O_2 extractable Pb and $MgCl_2$ extractable Pb-to-total Pb exhibited a relationship with depth (Fig. 3) where H_2O_2 extractable Pb decreased with depth and $MgCl_2$

Table 5 Total Pb concentrations (mg kg^{-1}) for each horizon at each site

Site	Horizon depth (cm)	Total Pb (±SEM; mg kg^{-1})
FOR-GF[a]	O (3–0)	47
	0–10	36±5.1
	10–19	24±2.4
FOR-CK[b]	O (3–0)	150±35
	0–6	180±34
	6–13	220±72
	13–21	170±120
FOR-NPF[c]	O (3–0)	90±17
	0–10	100±12
	10–16	90±37
	16–28	45
GRA-PP	0–13	220±59
	13–21	190±27
	21–30	200±72
GRA-MtO[d]	0–6	157±9.2
	3–8	66
	8–20	234±54
GRA-NPM	0–7	750±60
	7–14	350±52

[a] Horizon O (0–3 cm) only had one replication

[b] Horizon 6–13 cm is a combination of 5–10 and 6–15 cm horizons; Horizon 13–21 cm is a combination of horizons 10–20, 15–21, and 6–18 cm
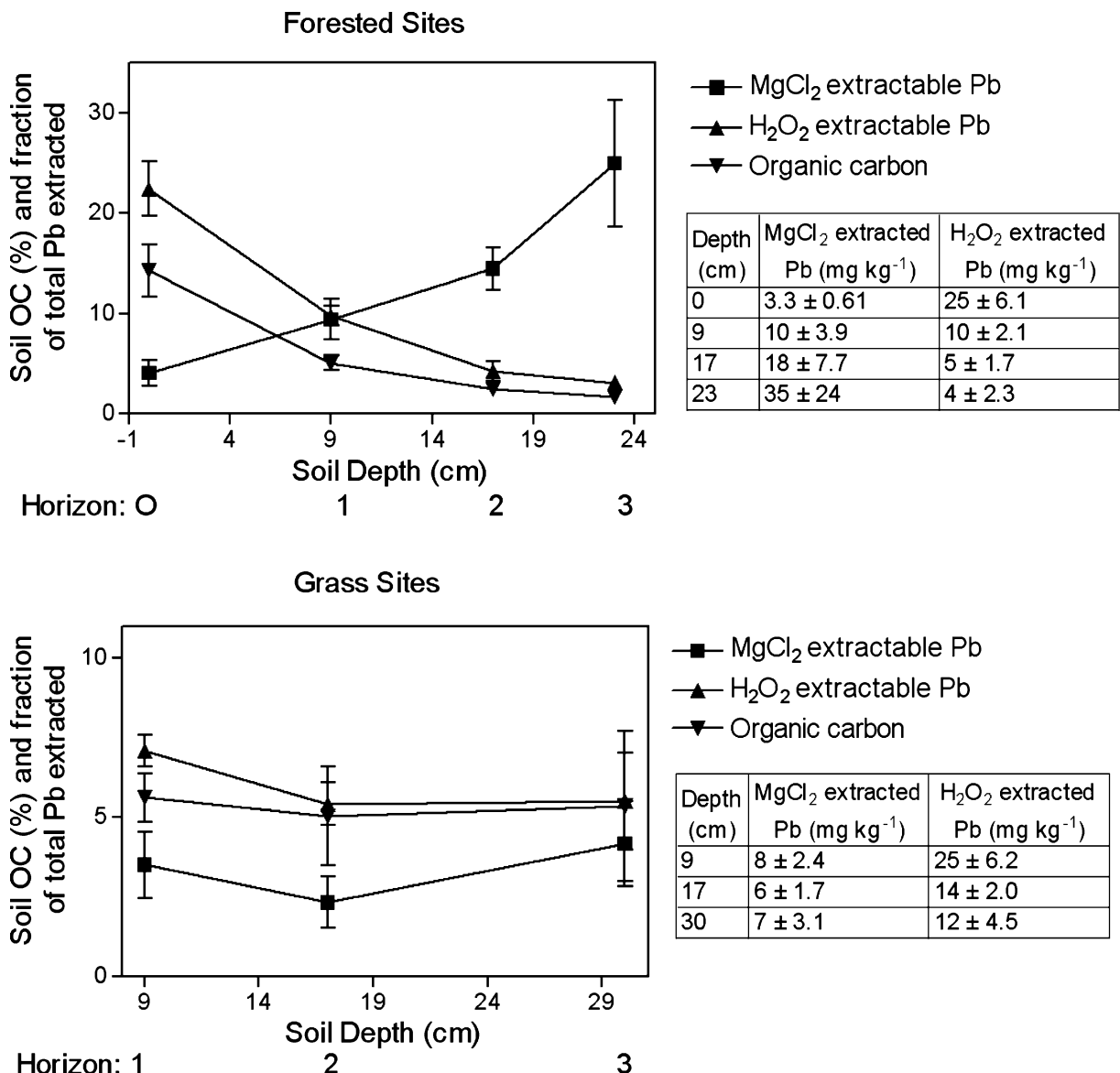
[c] Horizon 16–28 cm only had one replication

[d] Horizon 3–8 cm is an inclusion; Horizon 0–6 is a combination of horizons 0–3, 0–9, and 0–8 cm

extractable Pb-to-total Pb increased with depth for forest soils; however, this pattern was not expressed for grass soils. It should be noted that the fraction of total Pb dissolved by a given extractant (i.e., $MgCl_2$) is divided by the total Pb extracted, which is the sum of the all extractions, excluding the residual. Using the fraction-of-total Pb variable to compare vegetation cover types normalizes the data. For example, grass soils had an average of 211 mg kg^{-1} of Pb in the Mn (III, IV)- and Fe(III)(hydr) oxide fraction across depths versus only 67 mg kg^{-1} of Pb for forest soils. However, the fraction-to-total Pb is 68 and 61% for grass and forest soils, respectively.

There were significant differences between forest and grass soils in the ratio of $MgCl_2$ extractable Pb-to-total Pb in the second and third horizons (P=0.01), though differences were not significant in the first horizon. For forest soils, the ratio of $MgCl_2$ extractable Pb-to-total Pb increases with depth from the first

Forested Sites

Depth (cm)	MgCl$_2$ extracted Pb (mg kg^{-1})	H$_2$O$_2$ extracted Pb (mg kg^{-1})
0	3.3 ± 0.61	25 ± 6.1
9	10 ± 3.9	10 ± 2.1
17	18 ± 7.7	5 ± 1.7
23	35 ± 24	4 ± 2.3

Grass Sites

Depth (cm)	MgCl$_2$ extracted Pb (mg kg^{-1})	H$_2$O$_2$ extracted Pb (mg kg^{-1})
9	8 ± 2.4	25 ± 6.2
17	6 ± 1.7	14 ± 2.0
30	7 ± 3.1	12 ± 4.5

Fig. 3 Evaluation of soil organic C (%) and Pb (mg kg^{-1}) partitioning between H$_2$O$_2$ extracted Pb (organic C bound Pb) and MgCl$_2$ extracted Pb (exchangeable Pb); Data points are means±1 SEM (standard error of the mean)

to third horizon, likely due to a decrease in pH from 5.0 to 4.1 (Fig. 3). For grass, no change in the ratio of MgCl$_2$ extractable Pb-to-total Pb was observed; this result also may be related to pH, i.e., it remained constant at 5.8 with depth from the first to third horizon, with a slight increase (5.9) in the second horizon which may be related to the assumption that lawns were mixed and disturbed more that forest.

Many studies have shown that soluble Pb^{2+} or exchangeable Pb is strongly related to soil pH (Tsadilas et al. 1995; Sauve et al. 1997, 1998; Ge

et al. 2000). Chlopecka et al. (1996) found that soil samples with pH<5.6 contained a higher percentage of exchangeable metals than soil samples with pH> 5.6; this suggests that metal sorption may increase, thus becoming nonexchangeable, with increasing pH (Puls et al. 1991; Yoo and James 2002). The actual sorption mechanism responsible for the change from exchangeable to nonexchangeable forms of Pb could be the binding to, and surface-induced hydrolysis of Pb on Mn(III, IV)- and Fe(III)(hydr) oxides and organic matter. Yoo and James (2002) showed that

these sorption mechanisms may have increased non-exchangeable Zn at pH>5.8 due to the enhancement of surface-induced hydrolysis.

In forest soil, the ratio of H_2O_2 extractable Pb-to-total Pb decreases with depth. Under grass, the fraction of H_2O_2 extractable Pb-to-total Pb remains the same as depth increases (Fig. 3). This uniformity with depth may be the result of site history rather than the effect of grass cover. This uniform SOC concentration with depth is not typical of native, undisturbed soils of the Mid-Atlantic region. These grass soil profiles are similar to a plowed agriculture field in which the topsoil is mixed with the underlying soil to create a homogenized horizon in the plow layer to a depth of 10 to 20 cm. This suggests the importance of human modifications of the upper soil horizons.

Conclusions

Our results indicate that differences in forest and grass cover affected the amount of NH_2OH extractable Pb in the Baltimore soils studied. Soil Pb concentrations were not significantly different in the $MgCl_2$, HOAc, and H_2O_2 fractions between forest and grass soils. A possible explanation is the pH-dependent charge of the Mn(III, IV)- and Fe(III)(hydr) oxides. Differences in soil pH between forest and grass soils were used to investigate the possible influence of pH-dependent variable charge of Mn(III, IV)- and Fe(III)(hydr) oxides in the binding of Pb. Manganese(III, IV)(hydr) oxides should be more effective at binding Pb than Fe(III)(hydr) oxides because its PZC is lower than that in the latter.

Our results relating changes in Pb forms with depth did not show conclusively that Pb decreases with increased depth. However, when ratios ($MgCl_2$ extractable Pb-to-total Pb) rather than concentrations were analyzed, forest soils had a larger fraction of total Pb in the $MgCl_2$ phase for the second and third horizons than the grass sites. Both SOC and pH decreased with depth, resulting in an increase in the fraction of $MgCl_2$ extractable Pb to total Pb and a decrease in the fraction of H_2O_2 extractable Pb to total Pb.

Our results suggest that characteristics of an individual soil, such as pH and concentrations of Mn(III, IV)- and Fe(III)(hydr) oxides, can be important in determining the form of Pb in soil and thus its potential bioavailability to organisms and humans, and that human exposure to Pb can be reduced by manipulating soil pH and the status of Mn(III, IV)- and Fe(III)(hydr) oxides in the soil. For example, creating wetlands could increase the solubilization of Mn(III, IV)- and Fe(III)(hydr) oxides under anaerobic conditions and thus increase the solubility of Pb. Another example is the liming of soils, which raises soil pH. In this study, Pb began accumulating in the NH_2OH fraction at the expense of other fractions as soil pH increased. Finally, soils contaminated with Pb in an oxidized environment might be remediated by adding amendments that are rich in Mn(III, IV)- and Fe(III)(hydr) oxides to immobilize Pb, and thus reduce its potential bioavailability.

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