Weathering of Lead Bullets and Their Environmental Effects at Outdoor Shooting Ranges

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ABSTRACT

Lead contamination at shooting range soils is of great environmental concern. This study focused on weathering of lead bullets and its effect on the environment at five outdoor shooting ranges in Florida, USA. Soil, plant, and water samples were collected from the ranges and analyzed for total Pb and/or toxicity characteristic leaching procedure (TCLP) Pb. Selected bullet and berm soil samples were mineralogically analyzed with X-ray diffraction and scanning electron microscopy. Hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] was found in both the weathered crusts and berm soils in the shooting ranges with alkaline soil pH. For those shooting ranges with acidic soil pH, hydrocerussite, cerussite ($PbCO_3$), and small amount of massicot (PbO) were predominantly present in the weathered crusts, but no lead carbonate mineral was found in the soils. However, hydroxypyromorphite [$(Pb_{10}(PO_4)_6(OH)_2$] was formed in a P-rich acidic soil, indicating that hydroxypyromorphite can be a stable mineral in P-rich shooting range soil. Total Pb and TCLP Pb in the soils from all five shooting ranges were significantly elevated with the highest total Pb concentration of 1.27 to 4.84% (w/w) in berm soils. Lead concentrations in most sampled soils exceeded the USEPA's critical level of 400 mg Pb kg^{-1} soil. Lead was not detected in subsurface soils in most ranges except for one, where elevated Pb up to 522 mg kg^{-1} was observed in the subsurface, possibly due to enhanced solubilization of organic Pb complexes at alkaline soil pH. Elevated total Pb concentrations in bermudagrass [*Cynodon dactylon* (L.) Pers.] (up to 806 mg kg^{-1} in the aboveground parts) and in surface water (up to 289 μg L^{-1}) were observed in some ranges. Ranges with high P content or high cation exchange capacity showed lower Pb mobility. Our research clearly demonstrates the importance of properly managing shooting ranges to minimize adverse effects of Pb on the environment.

LEAD CONTAMINATION at shooting ranges from the use of lead shot and bullets (pellets) as ammunition is under increasing scrutiny as a potentially significant source of lead pollution. Lead pellets are mainly composed of lead, with lead shot containing 97% and lead bullets containing 90% of metallic lead (Scheuhammer and Norris, 1995). Previous investigations have shown that the annual flux of lead in shooting ranges is significant in some countries. Annual deposition of metallic lead of 200 to 6000 Mg was reported for the Netherlands, Denmark, Canada, and England (Jorgensen and Willems, 1987; Mellor and McCartney, 1994; Scheuhammer and Norris, 1995; VanBon and Boersema, 1988). In the USA, the total amount of lead expended as munitions in hunting and recreational shooting has exceeded 3 million Mg in the 20th century and is presently increasing at a rate of approximately 60 000 Mg per year (Craig et al., 1999).

When lead pellets come into contact with soil, they are subject to oxidation, carbonation, and hydration reactions, and ultimately could be transformed into dissolved and particulate species and enter the environment at a weathering rate of approximately 1% per year (Jorgensen and Willems, 1987). Jorgensen and Willems (1987) estimated that all of the metallic lead pellets deposited in the soil in Denmark would be transformed within 100 to 300 years. Lin et al. (1995) found that an average of 5% of metallic lead has been transformed to lead carbonate and lead sulfate in a period of 20 to 25 years in shooting range soils in central Sweden. These transformed products are composed of various lead compounds, predominantly cerussite ($PbCO_3$), hydrocerussite [$Pb(CO_3)_2(OH)_2$], and small amounts of anglesite ($PbSO_4$) (Lin, 1996).

As a result of Pb bullet weathering, heavily contaminated soils have been found at shooting ranges that have been in operation for many years. Murray et al. (1997) found that soil Pb concentrations at an outdoor shooting range in Michigan were 10 to 100 times greater than the background. Lead concentrations of 3400 to 5000 mg kg^{-1} in skeet shooting ranges in northern England and central Sweden were reported (Lin et al., 1995; Mellor and McCartney, 1994). Also, Murray et al. (1997) observed elevated Pb levels in subsurface soil where Pb concentrations in surface soil were high, indicating Pb mobilization through the soil profile. The primary cause of Pb mobilization in soils appears to be dissolution and oxidation of metallic Pb to form Pb carbonates or sulfate compounds. In addition to soil contamination, elevated Pb concentrations in surface water and in plants grown in shooting range soils were also found. The highest Pb concentration was found in plant roots, and it was positively correlated with soil EDTA-extractable Pb concentrations (Rooney et al., 1999). Mellor and McCartney (1994) reported reduced crop density of plants grown within a shot-fall zone at soil Pb concentrations of approximately 1500 to 10 500 mg kg^{-1}. Elevated Pb levels in water were reported by Stansley et al. (1992) in an investigation of eight target shooting ranges in the USA. They suggested that the weathering of lead pellets resulted in elevated concentrations of water-borne Pb (4.3–838 μg L^{-1} vs. 7.4 μg L^{-1} at the control sites). At a trap and skeet range located in Westchester County, New York, surface water lead concentration ranged from 60 to 2900 μg L^{-1} (USEPA, 1994).

The rate of lead oxidation and the resulting weathering products are highly variable and site specific. In gen-

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Abbreviations: CEC, cation exchange capacity; TCLP, toxicity characteristic leaching procedure.

eral, Pb is much more soluble under acidic (low pH) conditions than at neutral or alkaline (high pH) conditions. Some anion ligands, especially phosphate, carbonate, and sulfide, are particularly effective in controlling lead solubility due to the formation of less soluble Pb compounds, often resulting in low lead concentrations in water. Iron and Al (hydro) oxides, clay, and organic matter do not form chemical compounds with lead, but provide a large surface to sorb lead. Thus, lead mobility and leachability in soils with high amounts of these components or high cation exchange capacity (CEC) tend to be low.

In Florida, soils are generally low in clay (extremely sandy), organic matter, Fe and Al oxide, and CEC as well as showing low pH (Chen and Ma, 1998), which makes them more favorable for lead weathering and leaching. In addition, a subtropical and tropical environment (i.e., high humidity, high temperature, and high rainfall) enhances lead weathering, making Florida soils more vulnerable for lead contamination. For these reasons, lead-contaminated soils at shooting ranges should be of particular concern in Florida. However, little information is available about the effects of these Pb pellets on the soil, water, and vegetation in Florida shooting ranges.

The purpose of the present study was to (i) examine the weathering products of lead bullets in shooting ranges; (ii) determine lead concentrations in soil, surface water, and vegetation in shooting ranges; and (iii) investigate the effects of soil properties on the lead weathering and retention capacity.

MATERIALS AND METHODS

Sampling Procedure and Sample Characterization

The present study investigated five 100-yard (91.4-m) outdoor rifle shooting ranges in Florida. The shooting range locations and soil properties are provided in Fig. 1 and Table 1. For each range, a berm was built with soil excavated from the nearby site, sometimes creating a pond in the back of the berm. The predominant vegetation for ranges is bermudagrass. For each shooting range, three samples of surface soil (0–10 cm) were collected along a central transect at 1.5, 31.5, 61.5, and 91.5 m from the firing line. Composite berm soil samples were collected by mixing bottom, middle, and top berm surface samples. Selected weathered bullets were taken from the surface soil at the berm for mineralogical analysis. Profile soil samples (0–10, 10–30, 30–50, and 50–100 cm) were collected with a bucket auger of (2-cm diameter) at 91.5 m from the firing line (i.e., near the berm).

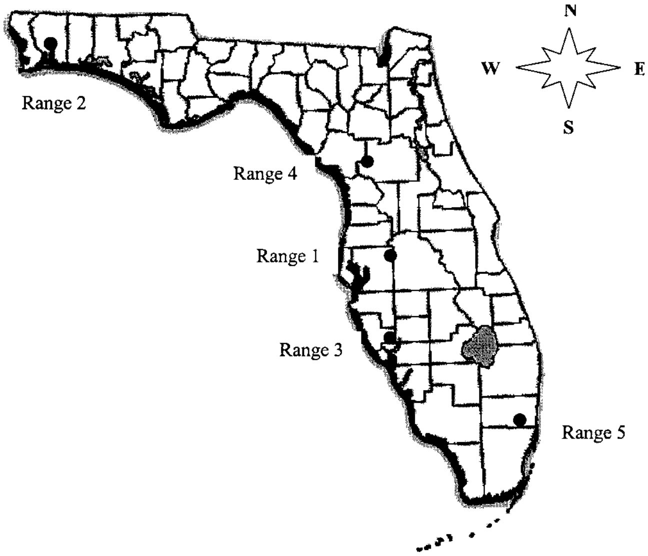

Fig. 1. Locations of the studied shooting ranges in Florida.

Soil samples were air-dried, sieved (2 mm), and digested with HNO_3 and H_2O_2 using the hot block digestion procedure (USEPA Method 3050A). Soil organic matter was determined with the Walkley–Black procedure (Nelson and Sommers, 1982). Soil dissolved organic carbon was extracted with the method of Zhou and Wong (2001), and determined with a carbon analyzer (TOC-5050A; Shimadzu, Kyoto, Japan). Cation exchange capacity (CEC) was determined with the method of Rhoades (1982). Total P was measured colorimetrically with a Shimadzu 160U spectrometer with the molybdate ascorbic acid method (Olsen and Sommers, 1982).

Plant samples, whenever available, were collected together with surface soil. They were first rinsed with deionized water to remove soil particles and then separated into roots and aboveground biomass. They were oven-dried at 65°C, ground into fine powder, digested with HNO_3 and H_2O_2 (USEPA Method 3050A), and analyzed for total Pb concentration. Surface water samples, whenever available, were collected, including retention ponds, shallow lakes, and background sam-

Table 1. Chemical properties of surface and berm soils from five shooting ranges.

Range	Age	pH	CEC†	OM‡	Total P	Total Al	Total Fe
	yr		cmol kg^{-1}	%	g kg^{-1}		
				Surface soil§			
1	2	5.66 ± 0.23	8.32 ± 0.97	1.08 ± 0.24	4.35 ± 1.20	1.65 ± 0.26	1.62 ± 0.31
2	7	5.00 ± 0.32	6.13 ± 0.41	1.37 ± 0.22	0.31 ± 0.21	6.82 ± 1.12	6.38 ± 0.89
3	12	6.32 ± 0.12	12.2 ± 1.14	1.72 ± 0.33	0.26 ± 0.13	1.52 ± 0.21	1.41 ± 0.33
4	15	5.97 ± 0.12	7.40 ± 0.83	4.12 ± 0.54	0.32 ± 0.11	2.69 ± 1.11	1.52 ± 0.51
5	16	7.03 ± 0.13	59.9 ± 4.72	13.5 ± 3.51	0.56 ± 0.21	2.93 ± 0.65	1.97 ± 0.35
				Berm soil¶			
1	2	5.82 ± 0.25	8.63 ± 0.67	1.72 ± 0.23	3.36 ± 1.10	1.15 ± 0.20	1.21 ± 0.21
2	7	5.32 ± 0.21	5.60 ± 0.23	1.04 ± 0.16	0.19 ± 0.11	2.82 ± 1.00	1.38 ± 0.62
3	12	7.12 ± 0.23	6.29 ± 0.12	2.07 ± 0.52	0.21 ± 0.12	1.22 ± 0.21	1.21 ± 0.36
4	15	7.23 ± 0.15	5.01 ± 0.21	1.03 ± 0.11	0.22 ± 0.10	2.09 ± 1.00	1.51 ± 0.51
5	16	7.45 ± 0.11	40.6 ± 1.23	21.3 ± 2.65	0.50 ± 0.20	2.11 ± 0.25	1.27 ± 0.12

† Cation exchange capacity.

‡ Organic matter.

§ Soil samples (n = 4) collected along a central transect at 1.5, 31.5, 61.5, and 91.5 m from the firing line.

¶ Soil samples (n = 3) collected from the top, middle, and bottom of the berm.

ples. The water samples were analyzed for pH and total Pb concentration before (total Pb) and after (dissolved Pb) filtration with a 0.45-μm membrane.

Mineralogical Analysis of Bullet Crusts and Berm Soils

Most of the collected lead bullets were visibly corroded and partially covered by a crust, which was removed via ultrasonication (Jorgensen and Willems, 1987). The bullet crusts as well as berm soils, which contained high Pb concentrations, were characterized with an X-ray diffractometer (Philips Electronic Instruments, Mahwah, NJ) with Cu Kα radiation at 35 kV and 20 mA. Measurements were made with continuous scanning techniques, and X-ray diffraction patterns were obtained from 2 to 60° at a rate of 2°θ per minute. Selected soil clay samples were further examined with a scanning electron microscope (JSM-6400/TN500; JEOL, Peabody, MA) equipped with energy dispersive X-ray elemental spectrometry.

Leaching Test

The toxicity characteristic leaching procedure (TCLP) uses a buffered mild acetic aqueous solution at a solid to liquid

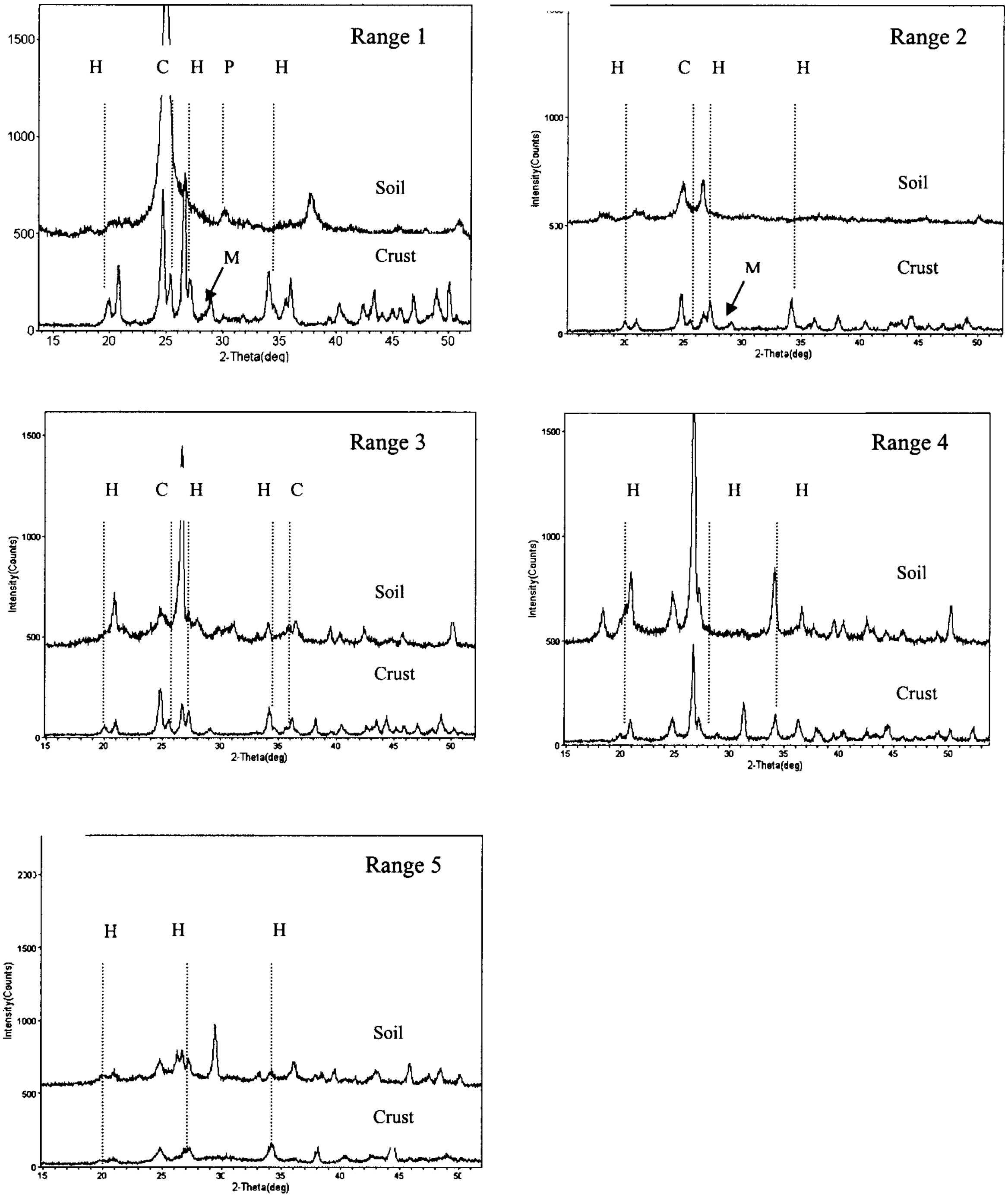

Fig. 2. X-ray diffraction patterns of lead compounds in weathered bullet crusts and berm soils of five shooting ranges in Florida. C, cerussite; H, hydrocerussite; M, massicot; and P, hydroxypyromorphite.

ratio of 1:20 (USEPA, 1990). In this study, TCLP Pb in the shooting range soils was extracted with Fluid no. 1 (pH = 4.93 ± 0.05) and determined following a modified procedure of USEPA Method 1311 (USEPA, 1990), which is a test used to determine the toxicity of the waste in an acid environment, such as a landfill.

Chemical Analysis

Lead concentrations of >1 mg L^{-1} were determined with inductively coupled plasma spectrometry (ICP–AES) (ICP 61-E; Thermo Jarrell Ash, Franklin, MA), and those of <1 mg L^{-1} were determined with graphite furnace atomic absorption spectrometry (GFAAS) (SIMAA 6000; PerkinElmer, Wellesley, MA). Quality control samples included standard reference materials of soil (2709 San Joaquin soil and 2710 Montana soil) and plant (1547 peach leaves) (National Institute of Standards and Technology, Gaithersburg, MD).

RESULTS AND DISCUSSIONS

Characteristics of Shooting Range Soils

Selected chemical properties of surface and berm soils from five shooting ranges are presented in Table 1. Among the five shooting range soils, Range 2 had the lowest pH (pH = 5.00) whereas Range 5 had the highest (pH = 7.03). Range 5 had the highest CEC and OM contents, whereas Range 1 had the highest P content. This is because Range 5 was built on a calcareous soil, while Range 1 was established on a P-rich soil. Range 2 had the highest total Al and Fe concentrations. Properties of berm soils generally were similar to the corresponding surface soils since they were excavated in close vicinity, with some exception (Table 1). Generally, pH values in berm soils were greater than those in surface soils, which may result from weathering of Pb bullets in the berm soil (Astrup et al., 1999; Chen et al., 2002)

Mineralogical Characterization of Bullet Crusts and Berm Soils

X-ray diffraction patterns in Fig. 2 showed that weathering products of lead bullets differed in shooting ranges. Hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], cerussite ($PbCO_3$), and trace amounts of massicot (PbO) were formed on the surface of weathered bullets collected from Ranges 1, 2, and 3, whereas only hydrocerussite was observed in those collected from Ranges 4 and 5 (Fig. 2). Lead carbonate was found in weathering crusts in all ranges, which agreed with the fact that when the lead bullets contact with soil, the lead will be readily transformed into oxidization species (Lin et al., 1995; Jorgensen and Willems, 1987). Composition of weathering products is dependent on soil properties, especially on soil pH. This could be best illustrated by the Eh–pH diagram (Fig. 3), which shows the stability of various lead species under different Eh and pH values for a lead–water system with a total Pb = 1 × 10^{-6} mol L^{-1} (modified slightly from EA Engineering, Science, and Technology, 1996). Note that metallic lead (Pb) is only stable in a very low redox potential condition. Typical soil water conditions occupy a higher level of Eh (McBride, 1994). As a result, metallic lead will probably be converted into other oxidized forms (e.g., PbO, $PbCO_3$, $PbSO_4$) in most natural soil environments. The mineral phase of hydrocerussite is stable between pH 7.7 and 10.1, while cerussite is stable between pH 5.9 and 7.7. This is consistent with our data in that only hydrocerussite was detected at Ranges 4 and 5 with alkaline soil pH (>7.20), while in Ranges 1, 2, and 3 with acidic soil pH, hydrocerussite, cerussite, and massicot were all present on the surface of weathered bullets. However, the stability range of $Pb_3(CO_3)_2(OH)_2$ and $PbCO_3$ may differ slightly due to the variations in reported thermodynamic constants and total soluble Pb concentration (Luo and Hong, 1997).

The weathered products from the bullets may remain

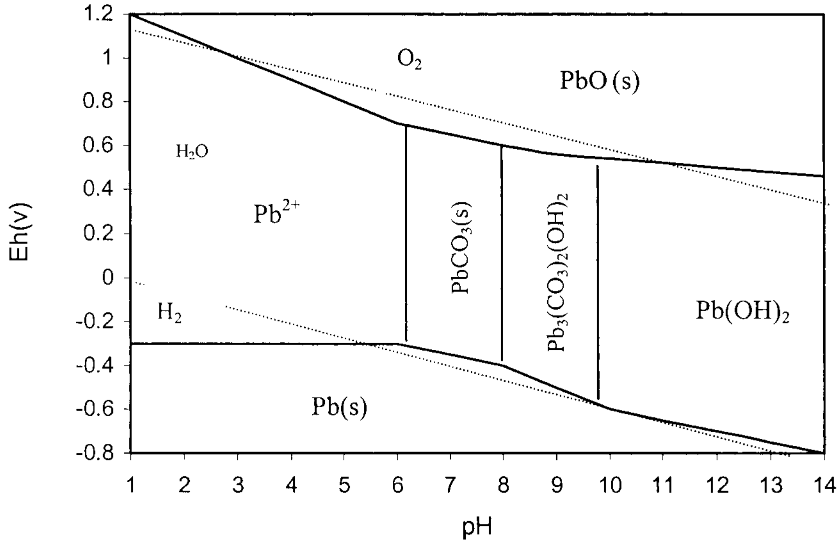

Fig. 3. Equilibrium stability field diagram for solids and dominant solute species in a system of Pb + CO_2 + H_2O at 25°C and 0.101 MPa pressure (ionic strength [*I*] = 5 × 10^{-3}, CO_2 = 1 × 10^{-3} mol L^{-1}, Pb = 1 × 10^{-6} mol L^{-1}) (slightly modified from EA Engineering, Science, and Technology, 1996).

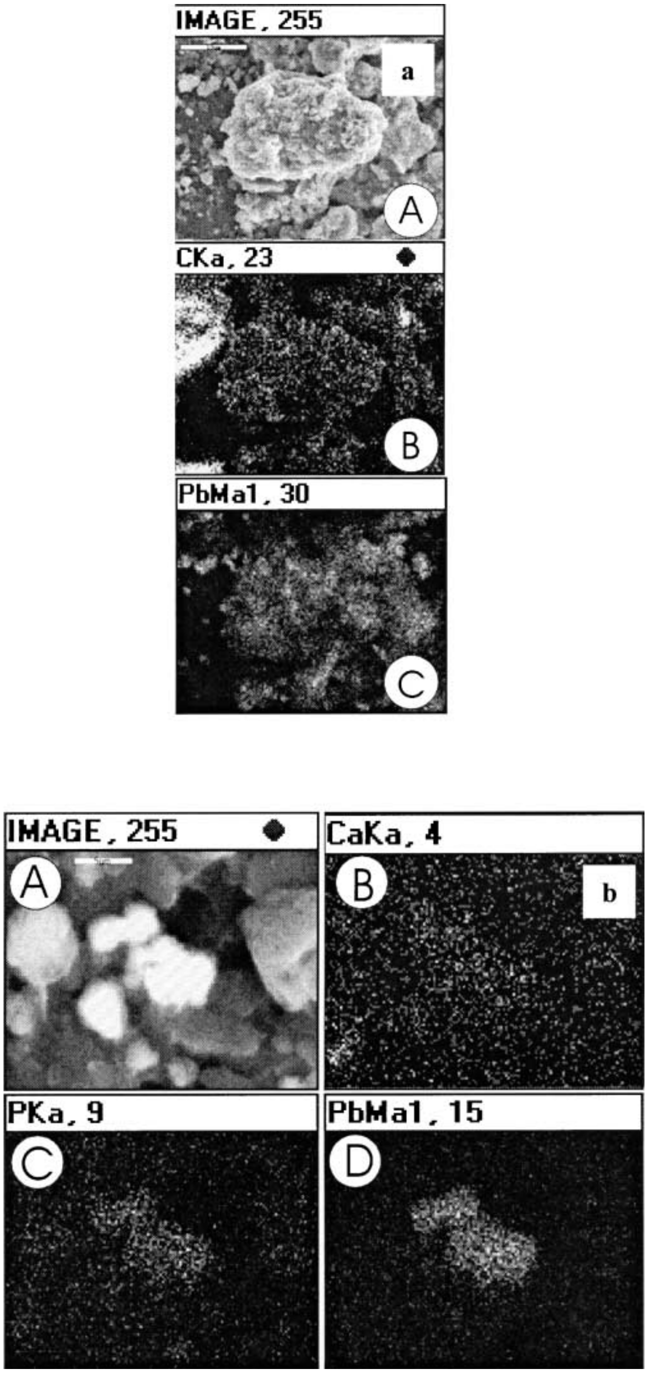

Fig. 4. Scanning electron microscopic images and elemental distribution maps. (*a*) Weathered bullet crust: A, lead carbonate; B, carbon; C, elemental lead. Scale bar = 10 μm. (*b*) Berm soil from Range 1: A, chloropyromorphite; B, calcium; C, phosphorus; D, elemental lead. Scale bar = 5 μm.

as crusts on the bullet surface, whereas some will find their way into the soil. For those in soils, some will stay the same, some will undergo further transformation, and some will be lost from soil through dissolution and subsequent leaching. Among the five shooting ranges analyzed, only berm soils from Ranges 4 and 5 had the same Pb compounds as their corresponding bullet weathering products (i.e., hydrocerussite) (Fig. 2), possibly due to high soil pH, which kept hydrocerussite in berm soils as in weathering crusts. Another possibility is that these two shooting ranges are the oldest, and thus there was more hydrocerussite accumulated in the soil to be detected by X-ray diffraction. Neither hydrocerussite or cerussite was detected in the berm soils from the other three relatively new shooting ranges (Fig. 2). Acidic soil pH in these soils may dissolve Pb carbonates from weathering crusts, which accounted for the detection failure of Pb carbonates. However, hydroxypyromorphite [$Pb_{10}(PO_4)_6(OH)_2$] was found in the berm soil of Range 1 (Fig. 2), which was built on a P-rich soil and has been operated for only two years (Table 1). The phosphate concentration in the berm soil of Range 1 was 3360 mg kg^{-1}, apparently high enough to form hydroxypyromorphite (Lindsay, 1979). Lead in the weathered bullet crust of Range 1 was mainly associated with carbon (i.e., hydrocerussite and cerussite) (Fig. 4a), whereas Pb in the berm soil of Range 1 was primarily associated with P as evidenced by scanning electron microscopy–energy dispersive X-ray elemental spectroscopy (SEM–EDS) (Fig. 4b). In fact, formation of lead phosphate can occur in contaminated soils in the presence of adequate P. Ruby et al. (1994) demonstrated that weathering of galena (PbS) to insoluble pyromorphite [$Pb_{10}(PO_4)_6Cl_2$] in soils at a port facility historically used for shipment of ore concentrates is due to the presence of adequate soil P. Cotter-Howells (1996) reported the presence of substantial amounts of pyromorphite in contaminated urban, garden, and motorway–roadside soils. Among Pb compounds, pyromorphite shows the lowest solubility (Lindsay, 1979). Thus, formation of pyromorphite in the P-rich Range 1 soil implied that P addition may be an alternative for best controlling Pb effects in the outdoor shooting ranges.

Total Lead Concentrations in Range Soils

Weathering of lead bullets results in accumulation of lead in shooting range soils. The distribution of lead concentrations in the central transect soils in five 100-yard (91.4-m) rifle shooting ranges in Florida is shown in Table 2. Total lead concentrations in the surface soils were significantly elevated. As expected, the highest Pb concentration (1.27–4.84%) was observed in the berm soils, which had the highest accumulation of bullets. It is important to point out that lead concentrations in berm soils were determined after large bullets were removed by sieving (2 mm). Sieved samples were digested. This indicates that substantial accumulation of lead in fine soil particles was primarily due to weathering. The possible production of fine lead powder as the bullet travels through the soil profile is currently under investigation.

As expected, total lead concentrations increased with the operation time of shooting ranges. Most soils are considered to be contaminated with lead as they contained greater than 200 mg kg^{-1}, the upper limit for a common soil (Lindsay, 1979). For Ranges 4 and 5, which have been used for more than 15 years, most soils contained more than 1000 mg kg^{-1}, exceeding USEPA critical levels of 400 mg kg^{-1}.

Table 2. The pH values, total Pb, toxicity characteristic leaching procedure (TCLP) Pb, and ratios of TCLP to total Pb in soils of five 100-yard (91.4-m) rifle shooting ranges.

Range	Distance from firing line	pH	Total Pb	TCLP	TCLP to total Pb ratio†
	m		mg kg^{-1}	mg L^{-1}	%
1 (high P)	1.5	5.90	7.3	0.07	19.1
	31.5	5.61	22.6	0.17	15.0
	61.5	5.62	21.7	0.17	15.6
	91.5	5.53	736	17.3	47.0
	berm	5.82	12 710	352	55.4
2	1.5	5.01	323	1.0	6.19
	31.5	4.74	107	0.6	11.2
	61.5	4.82	45	10.4	46.2
	91.5	5.18	63	1.3	41.2
	berm	5.32	16 225	537	66.2
3	1.5	7.27	354	12.1	68.3
	31.5	5.42	148	2.35	31.8
	61.5	5.63	464	10.6	45.8
	91.5	5.44	6 800	110	32.5
	berm	6.91	19 520	729	74.7
4	1.5	6.72	1 201	32	53.3
	31.5	6.11	4 448	74	33.3
	61.5	5.55	1 793	25	27.9
	91.5	5.52	1 723	27	31.3
	berm	7.23	22 030	880	79.9
5 (high pH)	1.5	7.29	1 066	0.78	1.45
	31.5	7.13	562	0.21	0.74
	61.5	7.02	1 018	18.2	35.7
	91.5	6.93	2 715	67.6	49.7
	berm	7.62	48 400	991	40.9

† Expressed as percent (mass) of total Pb in the soil sample.

It is clear that the distribution of lead concentrations in surface soils of different shooting ranges is variable (Table 2). However, we observed that berm soils had the highest lead concentrations, followed by the soil samples taken close to the berm. Thus, lead distribution in surface soils was related to the number of lead bullets (i.e., the more the bullets, the greater the soil lead concentrations). Nevertheless, lead concentrations in soils close the firing lines did not always show the lowest Pb content in our study. Substantial amounts of lead were detected in the surface soils near firing lines in all shooting ranges (up to 1201 mg kg^{-1}). This implies that discharge of lead powder produced as bullets rifle through the gun may cause high lead concentrations in the soils at the firing lines.

Toxicity Characteristic Leaching Procedure Lead Concentrations in Range Soils

The toxicity characteristic leaching procedure simulates leaching of toxic elements in landfill environments. When concentrations of total Pb in soils are above the soil screening level of 400 mg kg^{-1}, a TCLP test could be important in assessing the toxicity of wastes (Bruell et al., 1999). Generally, there is a positive correlation between total Pb and TCLP Pb. In the current study, the modified TCLP test results showed that all surface soil samples exceeded the 5 mg kg^{-1} critical level and would be characterized as hazardous waste (USEPA, 1990). To some extent, it could be assumed that the ratio of TCLP to total Pb reflects the mobility of Pb in shooting range soils. The ratios of TCLP to total Pb in surface soils of five shooting ranges varied significantly, ranging from <1 to 80%. The variation in these data suggested that Pb retention was site dependent. Phosphate levels are important in controlling lead solubility because lead phosphates are highly insoluble (Ma et al., 1993). In Range 1, high levels of P resulted in the formation of immobile hydroxypyromorphite (Fig. 2), which greatly reduced the lead mobility. Several other studies have also shown that phosphate effectively controls the solubility of lead (McGowen et al., 2001; Seaman et al., 2001). In addition, calcareous Range 5 soil had a high CEC, which may induce the adsorption of lead by $CaCO_3$ or exchange of Pb^{2+} with Ca^{2+} (Turpeinen et al., 2000). In these two ranges, less soil Pb was leached by TCLP reagent (0.70 to approximately 55% of total Pb compared with 6.0 to approximately 80% in the other three range soils; Table 2). The fact that up to 80% of the total Pb was TCLP extractable suggests that most of the lead in shooting range soils was present as lead carbonates, which are readily soluble in acidic TCLP extractant solution.

Lead Concentrations in Soil Profiles

Except for Range 5 soils, lead was mostly concentrated in the surface (Table 3). However, low Pb concentration in the subsurface soil may not indicate that Pb was not leached into ground water. Instead, it may reflect the reduced Pb holding capacity of subsurface soil. For example, substantial amounts of lead were detected in the subsurface soils in Range 5. This is because the soil had a high organic matter content throughout the soil profile. The presence of organic matter may increase the Pb-holding capacity of the soil, or may increase the mobility of Pb in the soil when soil pH is alkaline, which may be due to the enhanced solubilization of Pb–organic matter complex at alkaline pH. From Table 3, we see that dissolved organic carbon contents were higher in the Range 5 soil profile relative to other ranges. Dissolved organic carbon can facilitate metal transport, es-

Table 3. The pH values, dissolved organic carbon (DOC) content, and total Pb in the soil profiles of three 100-yard (91.4-m) rifle shooting ranges.†

Range	Profile depth	pH	DOC	Total Pb
	cm		mg C L^{-1}	mg kg^{-1}
1	0–10	5.53	23.5	736
	10–30	6.00	9.67	17
	30–50	5.91	4.92	2.6
	50–100	6.11	2.98	1.8
4	0–10	6.74	12.8	2357
	10–30	5.88	9.23	83
	30–50	5.02	7.23	13.2
	50–100	4.80	6.00	9
5	0–10	6.73	26.7	2715
	10–30	7.47	9.66	276
	30–50	7.56	12.3	522
	50–100	7.69	8.93	262

† Samples were collected along a central transect at 91.5 m from firing line.

pecially in calcareous soil, by acting as a carrier through formation of soluble metal–organic complexes (Zhou and Wong, 2001). Organic colloids and/or particles are of great importance in transporting lead from surface soil to subsurface soil. McBride et al. (1997) estimated that these mobile, organically complexed forms of lead could account for large cumulative losses of lead from surface soil. Due to the high cation exchange capacity in the subsurface soil (data not shown), the released lead from the surface layer is reimmobilized in subsurface soil (Wang and Benoit, 1996). Considering that ground water occurs at a depth of slightly less than 1 m below the soil surface in certain parts of Florida, there is a high probability that ground water quality at this site has been affected by this downward migration of Pb from the surface.

Lead Concentration in Surface Water

The total and dissolved Pb concentrations in the surface water of some shooting ranges are shown in Table 4. Compared with those in the nearby background, Pb concentrations in the surface water of Range 3 were elevated, greatly exceeding the USEPA drinking water standard of 15 μg L^{-1}. This suggests that lead from bullet weathering and fine Pb particles in this range were mobile, possibly carried to the ponds with surface runoff water. The surface water from Ranges 1 and 5, however, showed low levels of Pb concentrations, close to background. This may be attributed to the formation of immobile lead phosphate due to a high P level present in Range 1, and the high pH value due to calcareous soils at Range 5. Formation of hydroxypyromorphite and sorption to carbonate of lead may have reduced the Pb content in runoff water. Lead shot erosion leading to elevated lead levels in water was reported by Stansley et al. (1992) in an investigation of eight target shooting ranges in the USA that had surface waters (ponds, marshes, etc.) in their shotfall zones. From Table 4, we could also see that in Range 3 dissolved Pb in surface water was close to total Pb, indicating that soluble lead is predominant in retention pond water, and perhaps only soluble lead entered the pond with runoff water. In the retention pond at Range 5, total Pb is more than twice that of dissolved Pb. There was a large amount of nonfilterable Pb suspended in water. This could be explained by a suspension of crust materials in the water column due to a high water pH value (Table 4). However, no significant correlation existed between the total Pb concentration in the surface water and water pH as well as total soil Pb concentration, implying that soil properties may play an important role in controlling the mobility of Pb from soil to water. High levels of P and CEC in soil reflect low Pb mobility. Low Pb concentrations were found in the surface water from Range 1 (Table 4). This again indicated that P application may be effective for properly managing shooting ranges to minimize Pb mobility.

Lead Concentration in Plants

In soil with low Pb concentrations (15–30 mg Pb kg^{-1}), only trace amounts of Pb are taken up by plants, but the amount is usually increased with Pb concentration in soil (Turpeinen et al., 2000). The lead concentrations in bermudagrass along the central transect of Ranges 3 and 5 are shown in Table 5. Generally, lead concentrations in grasses grown close to berms contained more lead, which is attributable to the fact that soils close to the berms contained more total Pb and plant-available Pb (Table 5). This was consistent with the results of Mellor and McCartney (1994), showing that concentrations of lead in oilseed rape (*Brassica napus* L.) plants were highest in the area of most intense lead shot deposition. Compared with the Pb concentrations in the roots (up to 1342 mg kg^{-1}), Pb concentrations in grass shoots were lower (<806 mg kg^{-1}). However, there is still a considerable amount of Pb being transported into the aboveground biomass.

Observation of elevated Pb (up to 806 mg kg^{-1}) in the

Table 4. Total and dissolved lead concentration in the surface water of shooting ranges.

		Before filtration		After filtration	
Range	Sample	pH	Total Pb (n = 3)	pH	Dissolved Pb (n = 3)
			μg L^{-1}		μg L^{-1}
1	background	ND†	ND	ND	<1
	retention pond	ND	ND	ND	2.2 ± 0.2
3	background	7.16	3.3 ± 0.2	7.25	3.1 ± 0.4
	retention pond	5.96	33.9 ± 1.1	6.13	33.7 ± 1.3
	pond close to firing line	7.27	289 ± 10.6	7.49	234 ± 9.8
5	background	ND	BDL‡	8.10	BDL
	retention pond	8.26	30.5 ± 1.9	8.35	13.6 ± 0.9
	shallow lake close to Range 5	8.12	10.2 ± 4.3	8.22	4.4 ± 1.2

† Not determined.

‡ Below detection limit (<0.8 μg L^{-1}).

Table 5. Total Pb concentrations in soils and in bermudagrass growing on the sites.†

Range	Distance	Soil total Pb	Plant-available Pb‡	Pb in roots	Pb in shoots
	m	mg kg^{-1} dry wt.			
3	1.5	354	12.1	512	324
	31.5	148	5.61	115	86.7
	61.5	464	73.2	1166	511
	91.5	6800	136	1342	806
5	1.5	1066	6.75	438	134
	31.5	562	46.3	769	500
	61.5	1018	28.2	698	518
	91.5	2715	68.2	952	500

† Mean of three analyses.
‡ Plant-available Pb extracted with 0.5 mol L^{-1} acetate solution (pH = 5.0) (Mellor and McCartney, 1994).

aboveground biomass in the grass growing on shooting range soils has an important implication. Grasses in these ranges are periodically mowed and grass clippings are recycled back to the range. It is possible that Pb released from plant biomass is more available to the plant. If this is the case, Pb available in these soils will be increased gradually with time. In addition, precautionary measures should be taken while mowing the grass, minimizing worker exposure to airborne Pb. Furthermore, elevation of Pb in the aboveground biomass potentially increases wildlife exposure to lead. This is because the vegetation serves as attractive habitat for birds and wildlife (EA Engineering, Science, and Technology, 1996). Crop production should be avoided and planting of vegetation in general at shooting ranges must be undertaken with caution.

Total Lead and Toxicity Characteristic Leaching Procedure Lead Interrelationships with Soil Properties

Soil pH is an important factor that influences metal distribution in soils. Elevated soil pH was observed in soils contaminated with Pb shot at a shooting range in Denmark and was attributed to the corrosion of Pb bullets (Astrup et al., 1999; Chen et al., 2002). In the current investigation, a similar trend was also observed. From Table 3, we can see that soil pH value was positively correlated with the Pb concentration in soil ($r = 0.74$, $p < 0.05$). This fact was also demonstrated by a batch experiment, in which an unfired new Pb bullet was shaken with 0.02 M $CaCl_2$ solution (1:20). After an 18-h equilibration, the solution pH value was elevated from 5.45 to 7.58 (data not shown), suggesting that Pb oxidation–dissolution induces an elevation of the pH value.

The toxicity characteristic leaching procedure attempts to simulate buffered landfill leaching. Adsorption of Pb on the Fe and Al oxides and precipitation of lead phosphate would reduce Pb mobility in the soils. Statistic analysis showed that total P, Al, and Fe inversely correlated with TCLP Pb. Their correlation coefficients were 0.43, 0.52, and 0.50 ($p < 0.05$, $n = 35$), respectively. High levels of P, Al, and Fe were favorable for Pb stability. No significant relationship between TCLP Pb with pH and organic matter was observed. Sauve et al. (1998) indicated that Pb mobility is not a linear function of pH; rather, Pb mobility decreases with increasing pH until more organic matter becomes dissolved. It is possible that adding organic matter to a shooting range soil with low pH may reduce Pb mobility since organic matter will sorb Pb. On the other hand, adding organic matter to a shooting range soil with high pH may enhance Pb mobility. At an elevated pH, organic matter tends to be solubilized and dissolved organic carbon–Pb complexes are formed, thus increasing Pb mobility.

CONCLUSIONS

Lead weathering occurs when Pb bullets come into contact with soil. The weathering products depend on soil properties at shooting ranges, among which soil pH is the most important. Lead carbonates were predominantly present in the weathering products and in the berm soils. In shooting range soils containing adequate amounts of phosphorus, insoluble lead phosphate (pyromorphite) can be formed.

The weathering and transformation of Pb in shooting ranges resulted in a significant elevation of Pb concentration in soil, water, and vegetation. In alkaline soils containing high amounts of organic matter, lead is expected to migrate down the profile. High $CaCO_3$, Fe, Al, and P contents were favorable for immobilization of Pb in shooting ranges. The study results suggest that it is necessary to develop best management practices for minimization of Pb pollution at outdoor shooting ranges. In situ lead stabilization through phosphate amendment may provide a cost-effective method for reducing the effects of lead in shooting range soils.

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