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Characterization of Lead in Soils of a Rifle/Pistol Shooting Range in Central Florida, USA

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The distribution of lead in soil samples collected from both surface (0 to 10 cm) and profile (O 0 to 10 cm, E 11 to 30 cm, Eb 31 to 50 cm, Bw 51 to 100 cm, and C 181 to 200 cm) at a 14-year-old rifle/pistol shooting range located in central Florida were determined using EPA Method 3051a (microwave, HNO_3/HCl=3:1, v/v). In addition to total lead analysis, Toxicity Characteristic Leaching Procedure (TCLP) analysis was performed on corresponding samples to determine whether the soils would require special handling as hazardous waste if the soils were to be removed from the range. Total lead in surface soils varied from 330 to 17 850 mg Pb kg^{-1}, with the greatest concentration in the middle of the backstop berm. The TCLP tests indicated that lead in all surface soils exceeded the 5 mg Pb L^{-1} critical level of federal regulation for solid wastes and hazardous wastes provided by the Resource Conservation and Recovery Act (RCRA) and would be characterized as hazardous waste. Sequential fractionation and X-ray diffraction (XRD) analyses revealed that lead carbonate existed predominantly (91.3%) in the berm soil. The weathering of lead bullets in the soil environments formed primarily as hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), with small amounts of massicot (PbO) and cerussite ($PbCO_3$). However, the elevated soil pH, caused by the oxidization and transformation process of elemental lead in lead bullets, could be a significant factor in limiting the migration of lead in the soil.

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INTRODUCTION

Lead is ranked as the number two priority hazardous substance on the Agency for Toxic Substances and Disease Registry and the U.S. Environmental Protection Agency (USEPA) priority list of hazardous substances. Serious human health risks, particularly for children under 6 years of age, are associated with lead poisoning (Xintaras, 1992). In recent years, lead contamination of soils at shooting ranges from the use of lead bullets is under increasing scrutiny as a potentially significant source of lead contamination (Rooney *et al*., 1999; Craig *et al*., 1999). Annual deposition of metallic lead of up to 6000 tons was reported for the Netherlands, Finland, Denmark, Canada, England, and U.S.A. (Manninen and Tanskanen, 1993; Scheuhammer and Norris, 1995). A study of outdoor shooting ranges in the U.S. documented soil lead levels exceeding 1000 mg kg^{-1} at six of eight sites investigated (Murray *et al.,* 1997). In addition, lead adsorbs very strongly to soil particles and colloids, which provide an exposure risk to human by direct ingestion and inhalation (Bruell *et al*., 1999). The USEPA has set up a soil screening level of 400 mg kg^{-1}, which can be used as Preliminary Remediation Goals that provide a reference point for establishing site-specific cleanup levels (USEPA, 1996).

When the lead concentration is elevated, the Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure regulated by the Resource Conservation and Recovery Act (RCRA) and its State counterparts can be used to examine the lead toxicity and mobility, respectively (USEPA, 1995; SAAMI, 1996; Murray *et al*., 1997; Bruell *et al*., 1999). The TCLP procedure was designed to evaluate the environmental activity of a particular waste under conditions typical of municipal landfills containing household refuse. It is a laboratory simulation that attempts to measure the extent to which certain components of the waste will dissolve and leach into water under conditions common in municipal landfills (NSSF, 1998). The TCLP regulatory limit for lead is currently 5 mg Pb L^{-1}. If the concentration exceeds the regulatory limit, the waste fails TCLP and exhibits the regulatory characteristic of toxicity. The waste is then classified as a hazardous waste under RCRA and the site becomes subject to remedial action (Murray *et al*., 1997).

The nature of the oxidation process of metallic lead and the behavior of dissolved lead is highly dependent on the chemistry of the soil environment (Manninen and Tanskanen, 1993). After contacting the soil, the metallic lead in bullets may become oxidized and transformed into dissolved and particulate species and spread over the environment at a decomposition rate of ~10 g Pb kg^{-1} bullet yr^{-1} (Jørgensen and Willems, 1987). It is also estimated that all of the metallic lead bullets deposited in the soil in Denmark will be decomposed within 100 to 300 years. Weathering products of lead bullet include cerussite ($PbCO_3$), hydrocerussite [$Pb(CO_3)_2(OH)_2$], and small amounts of anglesite ($PbSO_4$) (Sever, 1993). Lin *et al.* (1995) found that an average of 5% of metallic bullet lead had been transformed to lead carbonate and lead sulfate in a period of 20 to 25 years in shooting range soils in central Sweden. Manninen and Tanskanen (1993) reported that of the total Pb, 90% was in EDTA-extractable form. McNear and Chorover (2000) found that the majority of lead in surface (0- to 2.5-cm depth) soils of rifle/pistol ranges was organically bound, with carbonate and Fe-Mn oxide phases at greater depths (2.5- to 10-cm, 10- to 18-cm and 18- to 25-cm depths). Murray *et al*. (1997) observed elevated lead levels in subsurface soil (90- to 100-cm depth) where lead concentrations in surface soil (5- to 15-cm depth) were high, indicating lead mobilization through the soil profile. The principal cause of lead mobilization appears to be the dissolution and oxidation of metallic lead to form lead carbonates or sulfate compounds, which were found on crust materials coating lead shots in shotgun shooting areas (Jørgensen and Willems, 1987).

Shooting is a popular recreational sport. Based on our preliminary survey, there are around 238 gun clubs operating in Florida alone. Natural background concentrations of lead in Florida soils ranges from 0.1 to 290 mg Pb kg^{-1}, with a median value of 4.9 mg Pb kg^{-1}, which are extremely low relative to soils from other regions of the world (Chen *et al*., 1999). High amounts of accumulated lead at shooting ranges are of particular concern in Florida due to a combination of natural factors (low soil pH, low soil clay and organic matter content, high rainfall, shallow groundwater level) that tend to accelerate lead bullet weathering. In addition, many shooting ranges are located adjacent to environmentally sensitive wetlands, streams, and lakes, and lead products from the rapid weathering of lead shot/bullets from these shooting ranges may be dispersed directly into wetland and aquatic environments (Scheuhammer and Norris, 1995). Currently, the impact of these accumulated lead bullets in recreational rifle/pistol shooting ranges on the environment in Florida is not well understood.

The purpose of this study was to investigate (1) total lead concentration distributions in an outdoor rifle/pistol shooting range soils, (2) chemical fractionation and leaching characteristics of elevated lead in these soils, and (3) weathering characteristic of lead bullets in soils. Quantifying these parameters will help establish proper regulation and management practices at recreational shooting ranges in Florida especially designed to minimize environmental impact.

Materials and Methods

A 14-year-old public rifle/pistol shooting range was selected in central Florida for this study. This facility is approximately 91 m in length, with targets set at 14, 23, 46, and 91 m (Figure 1). A backstop berm was built on top of the original ground surface with soil excavated from the area behind the berm. The excavated area later formed a pond. The berm is at the bottom 25 m long and at the top 20 m long. The height is about 4 m and the bottom width is about 5 m. It is estimated that in excess of 25,000 people utilize this facility annually. No reclamation of the range has been

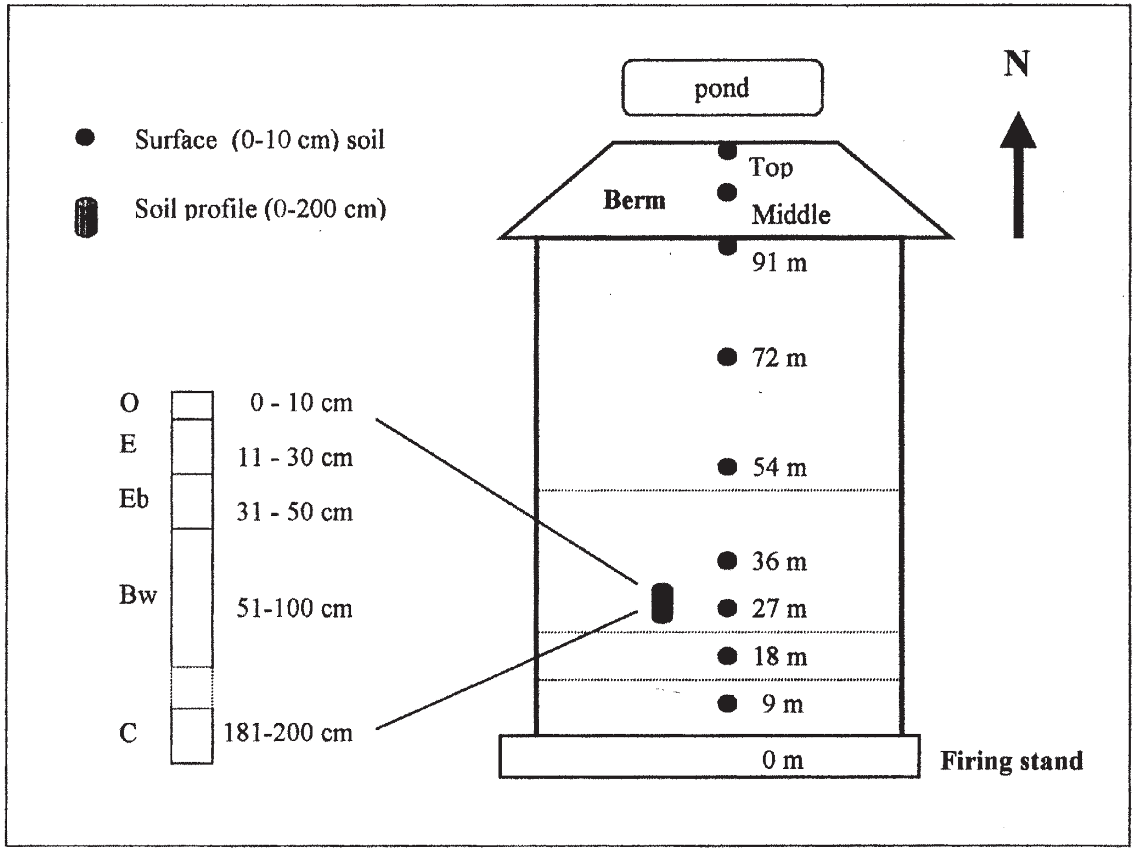

FIGURE 1

Schematic of the soil sampling strategy at a rifle/pistol shooting range in central Florida.

conducted during its existence. Thus, bullets have been accumulating for a period of 14 years.

The soil was characterized as Humod (Soil Survey Staff, 1998) consisting of a thick sequence of well-drained horizons consisting of a thin *O* horizon (0 to 10 cm) underlain by a sequence of *E* (11 to 30 cm), *Eb* (31 to 50 cm), *Bw* (51 to 100 cm), and *C* (101 to 200 cm) horizons (Figure 1). Seven composite surface soil samples (0 to 10 cm) were collected along a single transect at 9, 18, 27, 36, 54, 72, and 91 m from the firing stands at the shooting range. Two additional surface soil samples were collected from the top (4 m height from ground) and middle (2 m height from ground) of the backstop berm. Five bulk soil samples (0 to 10, 11 to 30, 31 to 50, 51 to 100, and 181 to 200 cm depths) were collected within each horizon (*O, E, Eb, Bw,* and *C*) from the soil profile at the shooting range roughly 27 m from the firing line (Figure 1).

Soil samples were air-dried, sieved (2 mm), and digested, by a microwave assisted HNO_3-HCl ($v/v = 3:1$) digestion (USEPA, 1997), which is equivalent to the hot-plate digestion procedure for Florida soils (Chen and Ma, 1998). Intact lead bullets were separated from the coarse soil fraction (removed by a 2-mm sieve) and counted. Toxicity Characteristic Leaching Procedure lead concentrations in the soils were extracted and determined using extraction fluid No.1 ($pH = 4.93 \pm 0.05$) following a modified procedure of USEPA Method 1311(USEPA, 1995), which is a test of leachability as an indicator of potential mobility of waste in a highly buffered environment. A 5.7-mL aliquot of glacial acetic acid in 500 mL of D.I. water and 64.3 mL of 1N NaOH, was diluted to a volume of 1 L. A 100-mL aliquot of this extracting solution was added to a plastic bottle containing 5.0 g of soil sample. The bottle was sealed with a screw-cap lid and placed on an end-to-end shaker at 30 rpm for 18 ± 2 h.

Chemical fractionation was done for the soil sample from the middle of the berm based on the methodology of Tessier *et al*. (1979). The sequential extractions were carried out in 40 mL centrifuge tubes with 1.0 g of soil. The procedure separates lead in the following operationally defined fractions: exchangeable, carbonate bound, Fe-Mn oxides bound, organic bound, and residual. The exchangeable fraction was extracted with 1 *M* $MgCl_2$ (pH 7.0) for 1 h. The carbonate fraction was extracted with 1 *M* NaOAc (adjusted to a pH 5.0 with HOAc). The Fe-Mn oxide fraction was extracted with 0.04 *M* NH_2OH-HCl in 25% (v/v) HOAc at 96°C with occasional agitation for 6 h. The organic fraction was leached with 0.02 *M* HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2.0 and heated to 85°C (Tessier *et al*., 1979). The residual fraction was digested with a mixture of HNO_3 and HCl using USEPA method 3051a (USEPA, 1997).

Lead concentration was analyzed using a Perkin-Elmer 3030 flame atomic absorption spectrophotometer (FAAS) (Norwalk, CT) at wavelengths of 217.5 nm when lead concentration $>1\ \mu g\ Pb\ L^{-1}$ in the solution and otherwise a Perkin-Elmer SIMMA 6000 (Norwalk, CT) graphic-furnace atomic absorption spectrophotometer (GFAAS). Method detection limit of GFAAS was 0.02 mg Pb kg^{-1}. Lead recovery was 87%, with a relative percent difference of 1.7%. The relative percent different was a measure of the precision of the chemical analysis. Soil pH was determined by using a combination electrode after mixing 5.0 g soil with 5 mL distilled deionized water for 24 h. Relations between the soil analytical data were investigated by Pearson correlation analysis.

X-ray diffraction (XRD) analysis was performed in order to identify and characterize the crystalline components of lead in clay fraction (<2 μm) of highly contaminated soils from the berm, with a Philips X-ray diffractometer (Philips Electronic Instruments, Inc., Mahwah, NJ) using Cu Kα radiation at 35 kV and 20 mA. Measurements were made using a continuous scanning technique, and XRD patterns were obtained from 2 to 60° 2θ. Weathering products of the lead bullets collected from the range were also investigated after an ultrasonic treatment of the bullets at 30 k Hz for 3 min.

RESULTS AND DISCUSSION

Distribution of Total Lead in Soils

Lead bullets were predominantly found in the backstop berm. The highest density of lead bullets (180 g bullets kg^{-1} soil) at this rifle/pistol shooting range was found in the middle of the berm. This observation is consistent with results of Astrup *et al*. (1999), who reported that in a 30-year-old shooting range in Denmark, up to 400 g kg^{-1} of the stop butt material consisted of lead bullets. High lead bullet content (47 g bullets kg^{-1} soil) was also found in soils from the top of the berm, suggesting that some lead bullets could be off-target or have ricocheted to the top and backside of the backstop berm when hitting other bullets. No bullets or bullet fragments were found in soil samples through the 0 to 72 m central transect. Bullet and bullet debris within soil samples at the 91 m sampling location collectively represented 91 g Pb kg^{-1} soil.

Based on a study of baseline concentrations of 15 trace elements in Florida surface soils (Chen *et al*., 1999), mean background concentration of total lead in 21 Humods was 5.0 mg Pb kg^{-1}. Concentration distribution of total lead (determined after removal of lead bullets by sieving through a 2 mm screen) in soils along the sampling transect showed that soil in the shooting range was contaminated with lead (Table 1). Total lead concentrations in surface soils in the area in front of the berm ranged from 875 to 4 448 mg Pb kg^{-1}, with the highest concentration at 27 m and the lowest at 72 m from the shooting stands (Table 1). Most soils had lead concentrations much greater than the Florida DEP soil-cleanup goals (500 mg Pb kg^{-1} for residential and 1000 mg Pb kg^{-1} for industrial soils) (Ruddell, 1995). Concentrations are also higher than the USEPA soil screening level of 400 mg Pb kg^{-1}, which is a risk-based value that provides a reference point for establishing site-specific clean up (USEPA, 1996).

TABLE 1
Distribution of Soil pH, Total and TCLP Lead in 0- to 10-cm Depth of a Rifle/Pistol Shooting Range in Central Florida

Distance from the firing line	Soil pH	Total Pb	TCLP-Pb
m		mg kg^{-1}	mg L^{-1}
9	6.7	1201	32
18	6.7	2214	64
27	6.1	4448	74
36	6.3	2213	60
54	5.6	1793	15
72	5.4	875	9
91	5.5	1723	17
Top of berm	6.8	10138	302
Middle of berm	7.7	17850	880
Total lead (r)	0.78 *	1.00	0.98**
TCLP-Pb (r)	0.80 *	0.98 **	1.00

*, ** Spearman's rank correlation coefficient is significant at the 5% and 1%, levels respectively.

The highest lead concentration (17 850 mg Pb kg^{-1}) was in the middle of the backstop berm, which includes lead associated with the soil particles as well as bullet fragments of metallic lead bullets smaller than 2 mm. This is less but comparable to the total lead concentration (40.4 g Pb kg^{-1}) in surface soils close to the target of a 30-year-old shooting range in Denmark (Astrup *et al*., 1999). The high lead content associated with the soil in the backstop berm, however, suggested that even after removing the lead bullets by sieving, the soil was highly contaminated with lead.

Total lead concentration decreased dramatically with depth from 0 to 200 cm (Table 2). The greatest soil total lead (2357 mg Pb kg^{-1}) remained in the *O* horizon (0 to 10 cm) and the lowest lead concentration (9.0 to 9.8 mg Pb kg^{-1}) was found in the *Bw* (51 to 100 cm) and *C* (181 to 200 cm) horizons. This is comparable to the background concentrations found in Florida surface soils (Chen *et al*., 1999). However, a relatively high concentration (83 mg Pb kg^{-1}) was found in the leached (*E*) horizon (11 to 30 cm). The trend of rapidly decreasing lead concentrations with depth indicates that downward movement of lead is minimal (Astrup *et al*., 1999). Other investigators have suggested that the movement of lead through the soil profile is mediated by the formation of lead carbonate or sulfate compounds from which lead is subsequently mobilized under conditions of slightly acid soils at the study site (Murray *et al*, 1997; Rooney *et al*., 1999).

One thing needs to be mentioned is that variation in total lead concentrations from samples taken at approximately the same distance (27 m) from the shooting stands is great (4448 vs. 2357 mg kg^{-1}). Small fragments of lead bullets (<2 mm) present in the soil may have contributed to this spatial variation (metallic lead is dissolved by the digestion procedure used).

Distributions of TCLP Lead in Soils

The TCLP test was designed to simulate potential waste leaching conditions at municipal landfills. When concentrations of total lead in soils is above the soil screening level of 400 mg kg^{-1}, TCLP lead concentration could be important in assessing the toxicity of wastes (Bruell *et al*., 1999). In the current study, the modified TCLP test results showed that all soil samples from the shooting range exceeded the 5 mg Pb L^{-1} critical level and would be characterized as hazardous waste under RCRA (USEPA, 1995) were the site to become subject to remedial action (Murray *et al*., 1997). In addition, the correlation of the TCLP lead to total lead concentrations in soils of the shooting range was significant ($r = 0.98$) (Table 1), suggesting that the total lead in the lead bullet contaminated soil at the range is in relatively soluble forms.

The distribution of the TCLP lead in the soil profile was similar to that of the total lead (Table 2). As expected, soil TCLP lead levels exceeded the 5 mg Pb L^{-1} critical level only for *O* horizon (70 mg Pb L^{-1}) and would be characterized as hazardous

TABLE 2

Distribution of pH, Total and TCLP Lead in Soil Profile at Approximate 27 m of a Rifle/Pistol Shooting Range in Central Florida

Depth	Horizon	Soil pH	Total Pb	TCLP-Pb
cm			mg kg^{-1}	mg L^{-1}
0-10	O	6.7	2357	70
11-30	E	5.9	83	3.1
31-50	Eb	5.0	13.2	0.34
51-100	Bw	4.8	9.0	0.30
181-200	C	5.1	9.8	0.31

waste (USEPA, 1995). Concentrations of TCLP-Pb in the *E, Eb, Bw,* and *C* horizons were less than 5 mg Pb L^{-1}, indicating that the elevated lead in surface soils does not readily migrate downward. However, as TCLP typically removes much more lead from bullets or soil than would be removed under natural conditions occurring at most ranges (Krishnamurthy, 1992; SAAMI, 1996; NSSF, 1998), caution should be employed when using this data for risk assessment or for any regulatory purpose.

Interactions between Lead Elevation and Soil pH

Soil properties are important factors that influence metal distributions in Florida surface soils (Chen *et al*., 1999). Elevated soil pH was associated with soils contaminated with lead bullets at a shooting range in Denmark and was attributed to the corrosion of the elemental lead (Astrup *et al*., 1999). In the current investigation, reference soil samples collected at roughly 300 m west from the shooting facility had pH values around 5.0. Elevated soil pH was found <36 m from the shooting stands and in soils on the backstop berm (Table 1), as well as in the surface horizon of the soil profile (Table 2). Strong positive correlation coefficients were found between soil pH and concentrations of total lead (r = 0.78), and soil pH and TCLP lead (r = 0.80) (Table 1). Two possible explanations for these correlations are (1) the elevated soil pH is a result of the soil contaminated with lead bullets, and (2) soil lead is in relatively soluble forms, such as PbO or $PbCO_{3,}$ extraction of which by acetate was sensitive to pH (Clevenger *et al*., 1991).

Sequential extraction is a procedure to identify various chemical forms of lead in soils. In the current investigation, lead was predominantly (91.3%) found in the carbonate form in berm soil of the shooting range (Table 3). The percentage of lead associated with different fractions was in the order of carbonate > organic > Fe-Mn oxide > exchangeable > residue. This result was agreement with that of McNear and Chorover (2000), who found the carbonate phase constituted 31 to 52% of total lead in berm soils of shooting ranges in Pennsylvania, but differed from that of Bruell *et al*. (1999), who reported that over 40% of the total lead was held at exchangeable sites or in the organic fraction of a shooting range soil in Connecticut. More carbonate and less residual fractions suggested that lead in berm soil at the shooting range in central Florida was relatively soluble and predominantly controlled by the dissolved carbonate concentration, which is pH dependent. At pH values between 5.3 and 7.8, $PbCO_3$ was predicted to be the solubility control component lead in soils (SAAMI, 1996).

Mineralogical Characterization of Soil Lead and Weathering Products of Lead Bullets

The patterns of lead in middle of the backstop berm showed that the dominant part of the lead (~ 90%) was found as lead bullets (>2 mm). The weathering products

TABLE 3
Chemical Fractionations of Soil Lead at Backstop Berm of a Rifle/Pistol Shooting Range in Central Florida

Pb Fraction	Pb Concentrations	Percentage of Total
	mg kg^{-1} soil	%
Exchangeable	208	1.2
Carbonate	16289	91.3
Fe-Mn oxide	484	2.7
Organic	803	4.5
Residue	66	0.37
Total	17850	100

of lead bullets from the shooting range were identified primarily as hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], with small amount of massicot (PbO) and cerussite ($PbCO_3$) (Figure 2). It has been reported that metallic lead on three Danish shooting ranges was transformed into lead compounds such as hydrocerussite, cerussite, anglesite ($PbSO_4$), and massicot (Jørgensen and Willems, 1987; Sever, 1993). Mineral content of bullet crust from eight shooting ranges in Sweden composed around 70 to 80% as hydrocerussite, 10% as anglesite, 5.0 to10% as massicot, and 5.0% as cerussite (Lin, 1996). Strong evidence of elemental lead was identified, but no anglesite lead could be found in the current investigation (Figure 2). The inconsistency is possibly a combination of the soluble nature of anglesite and differences in the soil environments, because anglesite is not stable in soil and is readily converted to lead carbonate in minutes (Kirshnamurthy, 1992). Other researchers found $PbSO_4$ exited as a crystalline form only in a small amount (0.5 to 2.5% of the soil lead) susceptible to XRD (Chaney *et al*., 1988)

According to the XRD analytical data, mineral contents of the clay fraction (< 2 µm) of the berm soil contained quartz, hydrocerussite, and massicot (Figure 3). This further demonstrates the importance of lead carbonate in controlling lead solubility in soil (Table 3). However, little cerussite was identified in the soil (Figure 3), suggesting hydrocerussite could be the only predominant crystalline form of soil lead in central Florida.

Possible Lead Reactions in Soils

Elemental lead can be readily dissolved at low pH (Stumm and Morgan, 1970). Lead oxides (PbO and PbO_2) are potentially the first products resulting from the direct oxidation of metallic lead by oxygen (SAAMI, 1996), which are refractory substances and could be easily converted to other compounds (Krishnamurth, 1992), such as $Pb(OH)_2$, $PbSO_4$, $PbCO_3$, and $Pb_5(PO_4)_3Cl$ in hours (SAAMI, 1996). It has been reported that PbO and PbO_2 were unstable in acid solutions (Stumm and Morgan, 1970) and $PbSO_4$ was too soluble to persist in soils (Krishnamurth, 1992), while $PbCO_3$ was more soluble than $Pb_5(PO_4)_3Cl$ (Chaney *et al.,* 1988) and $Pb_3(CO_3)_2(OH)_2$ (Stumm and Morgan, 1970). Because of the large amount of total lead in the surface soils of shooting ranges, we believe that the solubility limiting compounds in the shooting range soil are those observed in the bullet crusts and in the berm soil, such as $Pb_3(CO_3)_2(OH)_2$ or $PbCO_3$. This could be confirmed by both the chemical fractionation analysis (Table 3) and XRD analysis (Figure 3). It has been reported that the transition from Pb^{2+} to cerussite occurs at pH = 4.8 and the boundary between the predominance of cerussite and hydrocerussite was at pH equals 7.3 (Stumm and Morgan, 1970). Together with the increases of soil pH when the total lead concentration was elevated (pH equals 7.8 at middle of berm) (Tables 1 and 2), possible weathering process of metallic lead from lead bullets could be written as follows: (1) Oxidation of lead to massicot ($Pb + O_2 + H_2O \rightarrow$

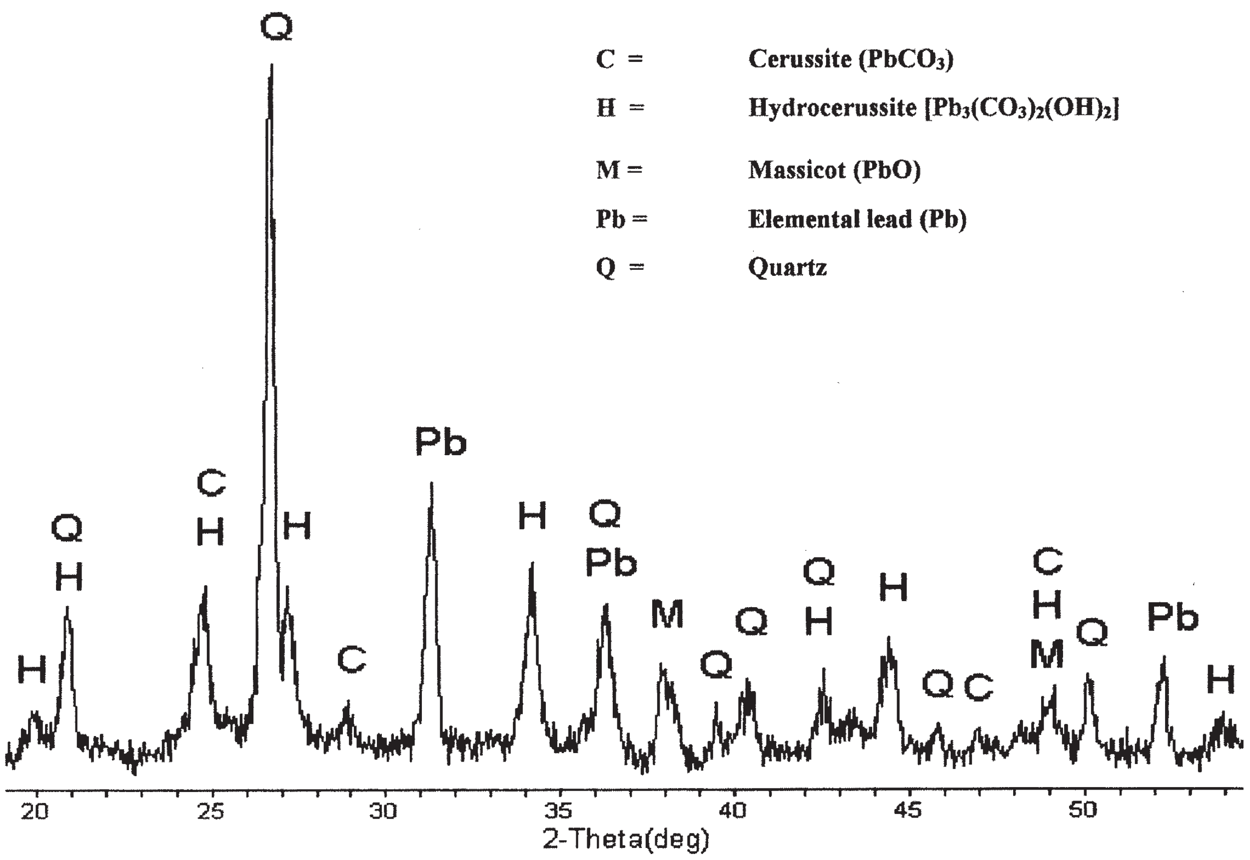

FIGURE 2

X-ray diffraction analysis pattern of the weathering materials of lead bullets form a rifle/pistol shooting range in central Florida.

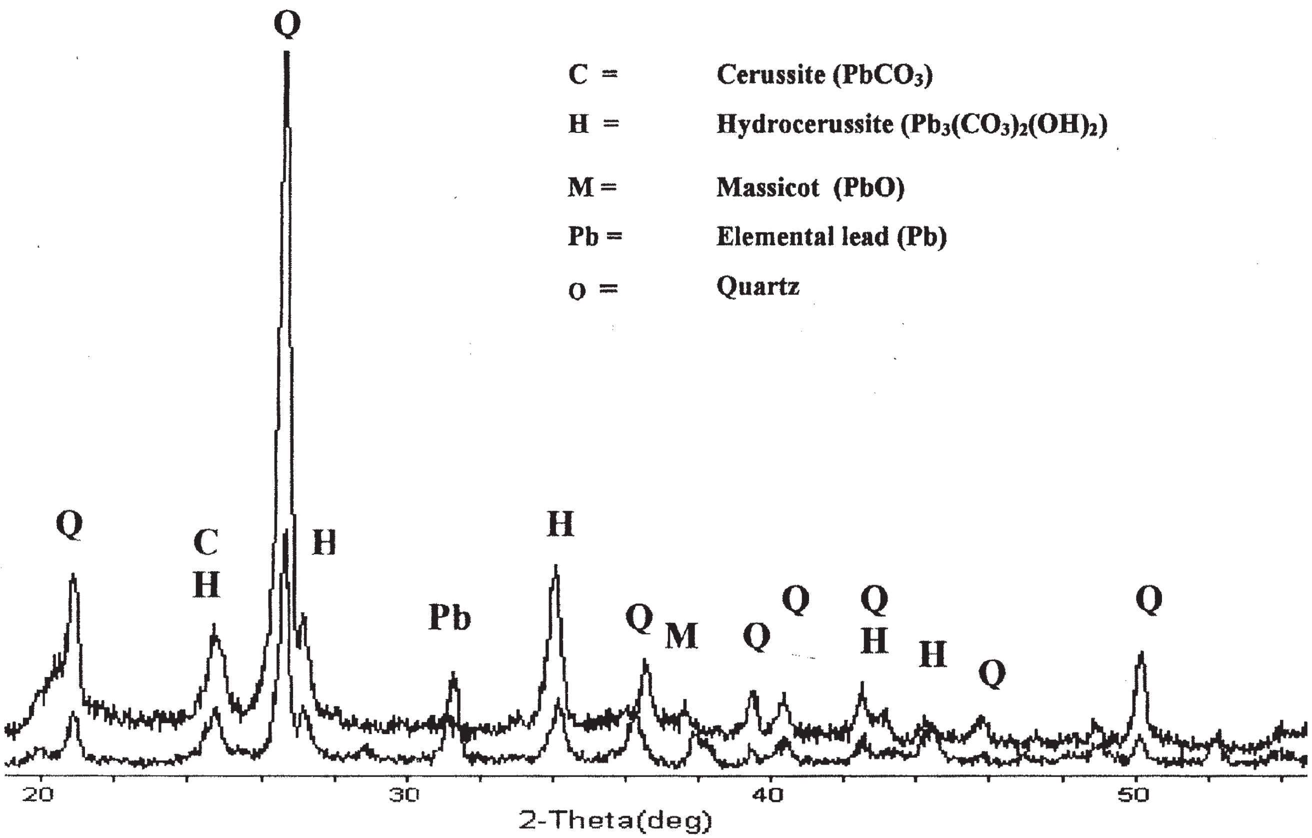

FIGURE 3

X-ray diffraction analysis pattern of lead in berm soil (top curve) in comparison with the weathering materials of lead bullets (bottom curve) from a rifle/pistol shooting range in central Florida.

$PbO + 2\ OH^-$); (2) Formation of cerussite ($CO_2 + H_2O \rightarrow HCO_3^- + H^+$; $PbO + HCO_3^- \rightarrow PbCO_3 + OH^-$); (3) Formation of hydrocerussite [$3\ PbCO_3 + 2\ H_2O \rightarrow Pb_3(CO_3)_2(OH)_2 + H_2CO_3$]; (4) Dissolution of cerussite ($PbCO_3 + 2\ H^+ \rightarrow Pb^{2+} + H_2O + CO_2$) and hydrocerussite [$Pb_3(CO_3)_2(OH)_2 + 6\ H^+ \rightarrow 3\ Pb^{2+} + 4\ H_2O + 2\ CO_2$]. Results of these reactions tended to increase soil pH, which in turn could be a significant factor in limiting the migration of lead in soils (Astrup *et al.,* 1999).

CONCLUSIONS

This study indicated that concentrations of total lead were elevated in surface soils at a 14-year-old rifle/pistol shooting range in central Florida, especially the soil from the backstop berm. Toxicity Characteristic Leaching Procedure tests confirmed that lead in all surface soils exceeded the 5 mg Pb L^{-1} critical level and would require special handling. Sequential fractionation and XRD tests indicated carbonate is the predominant fraction of soil lead at the middle of backstop berm. An investigation of the weathering products of lead bullets discharged in the shooting range suggested hydrocerussite was the primary crystal lead mineral in controlling lead solubility in the soil, with small amount of massicot and cerussite. Because soil pH tended to be elevated, migration of the elevated lead in the soil was limited.

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REFERENCES

Astrup, T., Boddum, J.K., and Christensen, T.H. 1999. Lead distribution and mobility in a soil embankment used as a bullet stop at a shooting range. *J. Soil Contam.* **8**, 653–665.

Bruell, R., Nikolaidis, N.P., and Long, R.P. 1999. Evaluation of remedial alternatives of lead from shooting range soil. *Environ. Eng. Sci.* **16**, 403–414.

Chaney, R.L., Mielke, H.W., and Sterrett S.B. 1988. Speciation, mobility and bioavailability of soils lead. In B.E. Davies and B. G. Wixon (Eds.) *Lead in Soils: Issues and Guidelines*. Supplement to Vol 9 (1989) of Environmental Geochemistry and Health. pp. 105–129.

Chen, M., Ma, L.Q., and Harris, W.G. 1999. Background concentrations of 15 trace metals in Florida soils. *J. Environ. Qual.* **28**, 1173–1181.

Chen, M. and Ma, L.Q. 1998. Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. *J. Environ. Qual.* **27**, 1294–1300.

Clevenger, T.E., Salwan, C., and Koirtyohann, S.R. 1991. Lead speciation of particles on air filters collected in the vicinity of a lead smelter. *Environ. Sci. Technol.* **25**, 1128–1133.

Craig, J.R., Rimsstidt, J.D., Bonnaffon, C.A., Collins, T.K., and Scanlon, P.F. 1999. Surface water transport of lead at a shooting range. *Bull. Environ. Contam. Toxicol.* **63**, 312–319.

Jørgensen, S.S. and Willems, M. 1987. The transformation of lead pellets in shooting range soils. *Ambio* 16, 11-15.

Krishnamurthy, S. 1992. Extraction and recovery of lead species from soil. *Environ. Prog.* **11**, 256–260.

Lin, Z.X., Comet, B., Qvarfort, U., and Herbert, R. 1995. The chemical and mineralogical behavior of lead in shooting range soils from central Sweden. *Environ Pollut.* **89**, 303–309.

Lin, Z. 1996. Secondary mineral phases of metallic lead in soils of shooting ranges from Örebro County, Sweden. *Environ. Geol.* **27**, 370–375.

Manninen, S. and Tanskanen, N. 1993. Transfer of lead from shotgun pellets to humus and three plant species in a Finnish shooting range. *Arch. Environ. Contam. Taxicol.* **24**, 410–414.

Mcnear, D.H., Jr. and Chorover, J. 2000. Speciation of lead in soils from bullets in firing ranges. In *Annual Meetings Abstracts*. pp. 51. ASA/CSSA/SSSA, Minneapolis, MN. Nov. 5–9, 2000.

Murray, K., Bazzi, A. and Sokol, H. 1997. Distribution and mobility of lead in soils at an outdoor shooting range. *J. Soil Contam.* **6**, 79–93.

NSSF (National Shooting Sports Foundation), 1998. *Synopsis of Applications and Limitations of TCLP and SPLP at Outdoor Shooting Ranges*. National Shooting Sports Foundation, Newtown, CT 06470. Facility Development Series, No.4.

Rooney, C.P., McLaren, R.G., and Cresswell, R.J. 1999. Distribution and phytoavailability of lead in a soil contaminated with lead shot. *Water, Air, Soil Pollut.* **116**: 535–548.

Ruddell, J.M. 1995. *Soil cleanup goals for Florida*. Florida DEP Memo. Tallahassee, FL. Sept. 27, 1995.

SAAMI (Sporting Arms and Ammunition Manufacturers' Institute). 1996. *Lead Mobility at Shooting Ranges*. Newtown, CT 06470. Sporting Arms and Ammunition Manufacturers' Institute, Inc. Facility Development Series, No.1.

Scheuhammer, A.M. and Norris, S.L. 1995. *A Review of the Environmental Impacts of Lead Shotshell Ammunition and Lead Fishing Weights cn Canada*. Hull, QC. Can. Wildlife Serv., Nat. Wildlife Res. Cent., Occas. Pap. No. 88.

Sever, C. 1993. Lead and outdoor ranges. In: *National Shooting Range Symposium Proceedings*, pp. 87-94. Salt Lake City, UT.

Soil Survey Staff. 1998. *Keys to Soil Taxonomy*, 8th ed. Washington, DC 20250. USDA-NRCS.

Stumm, W. and Morgan, J.J. 1970. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*. pp 321-327. Wiley-Interscience, John Wiley & Sons, Inc., New York.

Tessier, A., Campbell, P.G.C., and Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844–851.

USEPA (U.S. Environmental Protection Agency). 1995. *Test Methods for Evaluating Solid Waste*. Vol. IA: Laboratory Manual Physical/Chemical Methods. Washington, DC 20460. EPA-SW-846.

USEPA (U.S. Environmental Protection Agency). 1996. *Soil Screening Guidance: User's Guidance*. Office of Solid and Emergency Response. Washington, DC 20460. EPA 540/R-96/018. May, 1996.

USEPA (U.S. Environmental Protection Agency). 1997. *Method 3051a: Microwave Assisted Acid Dissolution of Sediments, Sludges, Soils, and Oils*. Washington, DC 20460. U.S. Gov. Print. Office.

Xintaras, C. 1992. *Impact of Lead-Contaminated Soil on Public Health*. Atlanta, GA 30333. USDHHS Agency for Toxic Substances and Disease Registry. May, 1992.