



ELSEVIER

The Science of the Total Environment 307 (2003) 179–189

**the Science of the  
Total Environment**

An International Journal for Scientific Research  
into the Environment and its Relationship with Man

www.elsevier.com/locate/scitotenv

## Lead transformation and distribution in the soils of shooting ranges in Florida, USA

Xinde Cao<sup>a</sup>, Lena Q. Ma<sup>a,\*</sup>, Ming Chen<sup>b</sup>, Donald W. Hardison<sup>a</sup>, Willie G. Harris<sup>a</sup>

<sup>a</sup>Soil and Water Science Department, University of Florida, Gainesville, FL 32611, USA

<sup>b</sup>Everglades Research and Education Center, University of Florida, Belle Glade, FL 33430, USA

Received 26 July 2002; accepted 18 October 2002

### Abstract

The use of lead bullets and shot at shooting ranges is under increasing scrutiny as a potentially significant source of Pb pollution. This study assessed Pb contamination in the soils of two shooting ranges (TRR and MPR) in Florida. Soil samples were collected from the two ranges and analyzed for total Pb to determine Pb contamination. Selected spent bullets and berm soil samples were mineralogically characterized to identify Pb transformation. Total Pb in the range soils was significantly elevated with the highest (up to 4.84% by weight) in the berm soils. Most soils failed the synthetic precipitation leaching procedure (SPLP) test. Also, at the MPR shooting range, a substantial amount of Pb migrated down in the subsurface soil, possibly due to the enhanced solubilization of organic Pb complexes at alkaline pH, whereas high cation exchange capacity of the profile soil may be responsible for Pb retention in the subsoil. The weathering products on the surface of the spent bullets were predominantly hydrocerussite  $[\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]$  and cerussite ( $\text{PbCO}_3$ ). Hydrocerussite was mainly found in the MPR range soils, whereas Pb was transformed into hydroxypyromorphite  $[\text{Pb}_5(\text{PO}_4)_3\text{OH}]$  in the TRR range soils because of the presence of more P. Sequential extraction and lead activity ratio modeling showed that the soil Pb solubility was controlled by Pb carbonate minerals in the MPR shooting range, and by less soluble Pb phosphate minerals in the TRR shooting range. This research suggests that it is important to develop and implement efficient management practices to minimize adverse impacts of Pb at shooting ranges. Phosphate-induced Pb immobilization may be an effective alternative for reducing Pb mobility in the shooting range soils.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Lead bullets; Transformation; Distribution; Shooting range; Soil; Model

### 1. Introduction

Due to its widespread use in industrial and commercial activities, Pb has seen a greater distortion of its biogeochemical cycle than many other toxic metals (Alloway et al., 1995). Over time,

the Pb loading rate in soil exceeded its natural removal rate by approximately 20-fold or more (Nriagu, 1990). As a result, large amounts of anthropogenic Pb is stored in the biosphere, which is defined as significant contamination. Large amounts of metallic Pb from the use of lead pellets (bullets and shot) as ammunition have been deposited on the soil of shooting ranges worldwide. For example, approximately 500–600 t of Pb are used

\*Corresponding author. Tel.: +1-352-392-1951; fax: +1-352-392-3902.

E-mail address: lqma@ufl.edu (L.Q. Ma).

annually in shotgun ammunition in Sweden (Lin, 1996). (Scheuhammer et al., 1995) estimated that 2000 metric tons of lead pellets are deposited each year into the environment in Canada. In the US, the total amount of Pb expended as munitions in hunting and recreational shooting has exceeded 3 million metric tons in the last century (Craig et al., 1999). Such a high intensity of Pb-loading at shooting range soils has drawn much environmental concern (Chen et al., 2002; Lin et al., 1995).

Lead weathering generally occurs whenever lead pellets come into contact with soil and exposed to air and water. All of the metallic Pb in a pellet will be ultimately transformed into particulate and ionic lead species and will be dispersed into the environment to some degree. Analyses of spent lead pellets collected from target shooting ranges have been shown to be visibly corroded and covered with a crust of white, gray or brown material (Jorgensen et al., 1987; Lin, 1996). These crusts are composed of various Pb compounds, predominantly cerussite ( $\text{PbCO}_3$ ), hydrocerussite [ $\text{Pb}(\text{CO}_3)_2(\text{OH})_2$ ] and small amounts of anglesite ( $\text{PbSO}_4$ ). Within 6–13 years, 5–17% of the metallic Pb pellet was transformed, and complete transformation is estimated to take 100–300 years (Jorgensen et al., 1987). The weathering rate of metallic lead pellets depends on various physical and chemical factors. Aerobic and acidic conditions in soil enhance the rate of pellet breakdown, whereas anaerobic and/or alkaline conditions may slow it down (Scheuhammer et al., 1995). Physical factors such as high water flow rates, soils dominated by the presence of coarse sand and frequent disturbance of contaminated soils all serve to enhance weathering of lead pellets (Scheuhammer et al., 1995).

Although spent lead pellets are removed periodically at some ranges, particulate metallic Pb and Pb minerals resulting from lead pellet weathering may remain in soils. This results in the elevation of total Pb concentration in the soils. It has been reported that soil Pb concentrations at shooting ranges in the Northern Hemisphere, range from 800 to 55 000 mg/kg (Rooney et al., 1999). Recent investigations of outdoor shooting ranges in the US documented Pb soil levels of >1000 mg/kg at six out of eight sites investigated. Lead

concentrations of 3400–5000 mg/kg in skeet shooting ranges in northern England and central Sweden were reported as well (Lin et al., 1995; Mellor et al., 1994). Murray et al. (1997) observed elevated Pb levels in the subsurface soil where there was a high Pb concentration in surface soil, indicating Pb mobilization through the soil profile.

The principal cause of Pb mobilization appears to be the oxidation of metallic Pb to form carbonates or sulfates, which were found in the crust materials that coated the lead pellets, followed by the dissolution of these compounds. Lead mobility in soils is affected by soil redox potential, available anions, (e.g. carbonate, phosphate and sulfate), pH, and cation exchange capacity (CEC) (Basta et al., 1993; Dragun et al., 1998). Solid phase organic carbon can enhance lead adsorption (Basta et al., 1993) but dissolved organic carbon can enhance Pb mobility (Sauve et al., 1998). Soil organic matter can dissolve with increasing pH, significantly enlarging the pool of organic ligands in the soil solution that can mobilize Pb (Sauve et al., 1998).

Lead contamination at shooting ranges is of special concern in Florida, where the combination of high moisture and year-round elevated temperatures present an especially robust Pb-transforming environment (Chen et al., 2002). The objectives of this research are: (1) to determine Pb concentrations in the surface and soil profile at two rifle shooting ranges in Florida; (2) to identify Pb species in the soils and the weathering products of the bullets; and (3) to apply a geochemical model to predict which Pb minerals likely control Pb activity in the soils.

## 2. Materials and methods

### 2.1. Characteristics of shooting range soils

The present study focused on two 100-yard outdoor rifle shooting ranges (TRR and MPR) in Florida, USA. Each range is approximately  $100 \times 100 \text{ m}^2$ , with a backstop berm built on top of the original ground surface at 100 m distance from the shooting stands by using the soil excavated behind the berm. The TRR shooting range, built on a phosphatic clay soil, is located in central

Table 1  
Selected chemical properties of soils from TRR and MPR shooting ranges

Shooting ranges	pH	CEC <sup>b</sup> cmol/kg	OC <sup>c</sup> %	Total P g/kg	Total Al g/kg	Total Fe g/kg
TRR	5.76±0.43 <sup>a</sup>	8.51±1.97	0.74±0.54	4.24±1.31	1.32±0.86	1.69±0.73
MPR	7.36±0.57	43.2±6.42	10.7±3.60	0.51±0.31	2.35±0.75	1.53±0.65

<sup>a</sup> Mean ± standard deviation ( $n=11$ ).

<sup>b</sup> Cation exchange capacity.

<sup>c</sup> Organic carbon.

Florida and has been operated for 3 years. The MPR shooting range, established on a calcareous soil in south Florida, has been open for 16 years. Selected chemical properties for the soils at the two shooting ranges are provided in Table 1. The soil at the TRR shooting range is acidic and contains a high concentration of P, while the MPR shooting range soil shows high soil pH, high CEC and high organic carbon.

## 2.2. Soil sampling and characterization

Soil samples were collected in November 2000 and April 2001 for the TRR and MPR shooting ranges, respectively. For each shooting range, surface soils (0–10 cm) were collected at 1.5, 31.5, 61.5 and 91.5 m from the firing line along a central transect. Background soils were sampled from the areas that were not impacted by lead bullets near the range. Profile soil samples (0–10, 10–30, 30–50, 50–100 cm) were collected at 91.5 m, just before the backstop berm. Samples were collected in triplicate at each site. After air-drying and sieving through a 2-mm sieve, soils were digested for Pb analysis following the HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> extraction procedure (USEPA Method 3050a).

Composite berm soil samples were collected by mixing samples from the bottom, middle and the top of the berm. After air-drying, the berm soils were sieved (2 mm) to separate the spent bullets from the soils. Most of the collected bullets were visibly corroded. The crusts were removed by ultrasonification (Jorgensen et al., 1987). Crusts and clay fractions of the berm soil were examined by X-ray diffraction using CuK<sub>α</sub> radiation at 35 kV and 20 mA. XRD patterns were obtained from

2 to 60° 2θ. The berm soil was digested for lead analysis using the USEPA Method 3050a.

## 2.3. Leaching test

The synthetic precipitation leaching procedure (SPLP) has been used recently during site investigations to determine if shooting range soils contaminated with Pb might impact groundwater quality (Peddicord, 1998). The test utilizes unbuffered acid rain at a solid to liquid ratio of 1:20. In this study, SPLP Pb in range soils was extracted with extraction fluid No. 1 (pH 4.20±0.05), and determined following the USEPA Method 1312 (USEPA, 1995).

## 2.4. Soil Pb fractionation

A sequential extraction procedure developed by Tessier et al. (1988) was used to separate berm soil Pb into different fractions. The method operationally fractionates Pb into the following forms: water-soluble and exchangeable (WE); carbonate (CB); Fe-Mn oxides (FM); organic (OC); and residual (RS). However, the method is limited by metal redistribution and non-specificity during the extraction. To ensure quality, a summation of all fractions were compared to the total Pb obtained via digestion (USEPA 3050a) using Standard Reference Material SRM2710 (US NIST, Gaithersburg, MD). Total Pb by fraction summing averaged 92±8.2% of the total digested Pb, indicating satisfactory recovery of the fractionation.

## 2.5. Modeling minerals in relation to soil lead activity

To determine ion concentrations in the soils, 20 ml of 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> was added to 2 g of berm

Table 2  
Total Pb, and SPLP-Pb in soils of TRR and MPR shooting ranges

Ranges	Distances from firing lines (m)	Total Pb (mg/kg)	SPLP ( $\mu\text{g/l}$ )
TRR	1.5	7.3	36
	31.5	22.6	10
	61.5	21.7	10
	91.5	736	410
	Berm soil	12 710	6850
	Background soil	1.83	– <sup>a</sup>
MPR	1.5	1066	280
	31.5	562	110
	61.5	1018	1820
	91.5	2715	2706
	Berm soil	48 400	19 910
	Background soil	4.28	–

<sup>a</sup> Not determined.

soil collected from the two ranges. The mixture was shaken at 25 °C for 24 h, which was shown to be long enough to attain equilibrium (McGowen et al., 2001). After the equilibration period, the solution was filtered through a 0.45  $\mu\text{m}$  membrane filter followed by analysis of pH and anions (Cl, Br, F,  $\text{NO}_3$ ,  $\text{SO}_4$  and  $\text{PO}_4$ ) using ion chromatography (Waters 2690 Separations Module, Waters Corporation, USA). Remaining portions were acidified to a  $\text{pH} < 2$  for metal analysis (K, Ba, Al, Ca, Fe, Pb, Cu, Zn and Cd) using ICP-AES. The results were then put into the chemical speciation model Visual MINTEQ (version 1.03, compiled by Jon Petter Gustafsson, KTH, Division of Land and Water Resources, Stockholm, Sweden) to determine Pb activity in the soil solution. A Pb activity ratio diagram was developed based on the dissolution equilibria of Pb minerals. Chemical speciation data obtained from Visual MINTEQ were plotted to identify potential minerals controlling Pb solubility in soils.

## 2.6. Chemical analysis

Soil pH was measured with a 1:1 ratio of soil/water. Soil organic carbon was determined using the Walkley–Black procedure (Nelson et al., 1982). Soil dissolved organic carbon (DOC) was extracted using the method of Zhou et al. (2001), and determined using a carbon analyzer (TOC-5050A, Shimadzu, Kyoto, Japan). Cation exchange

capacity (CEC) was determined using the method of Rhoades (1982). Total phosphorous was measured colorimetrically with a Shimadzu 160U spectrometer using the molybdate ascorbic acid method (Olsen et al., 1982). Metal concentrations were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES; Thermo Jarrell Ash ICP 61-E, Franklin, MA) or using a graphite furnace atomic absorption spectrometer (Perkin-Elmer SIMAA 6000, Perkin-Elmer Corp, Norwalk, CT). Quality control samples included 2709 San Joaquin soil and 2710 Montana soil standard reference materials (US NIST, Gaithersburg, MD).

## 3. Results and discussions

### 3.1. Lead contamination in the soils

#### 3.1.1. Total Pb and SPLP-Pb concentrations in shooting range soils

Distributions of Pb concentrations in the two shooting range soils are shown in Table 2. Total Pb concentrations in the surface soils were significantly elevated, exceeding the average background soil Pb concentration by 10–10 000 times. The highest Pb concentration (up to 4.84%) was observed in the berm soils, which had the highest accumulation of bullets. A positive relationship has been found between the numbers of lead bullets and Pb concentrations in the soil (Mellor

et al., 1994). It should be pointed out that Pb concentrations in berm soils were determined after first picking out the large bullets and then passing through a 2-mm sieve. This indicated that substantial accumulation of Pb in fine soil particles was primarily due to weathering of lead bullets. It was also possible that fine Pb powder may be produced as lead bullets travel through the berm. As expected, total Pb concentrations increased as the range operation time increased. Soil Pb in the MPR shooting range (16 y) was consistently greater than that in the TRR shooting range (3 y), and most soils in the MPR range contained more than 1000 mg/kg, exceeding the EPA critical level of 400 mg/kg (USEPA, 1996).

Total Pb distributions in the surface soil differed in the two shooting ranges (Table 2). In the TRR shooting range, Pb concentrations in the soils near the firing lines were the lowest, whereas berm soil had the highest Pb concentrations, followed by the soil samples that were closest to the berm. Thus, Pb distribution in surface soils was related to accumulation of lead bullets, i.e. the greater the number of bullets, the greater the soil Pb concentrations. However, this was not the case for the MPR shooting range. Substantial amounts of Pb were detected in the surface soils near the firing lines (up to 1066 mg/kg). This implies that discharge of Pb powder produced as bullets rifle through the barrel of the gun may have contributed to the greater Pb concentration. This effect may be more obvious in older shooting ranges.

The SPLP test has been used to assess lead mobility in soils from active shooting ranges (Pedicord, 1998). In the current study, the SPLP-extractable Pb in most soils, especially in the MPR soils, exceeded the 15  $\mu\text{g}/\text{l}$  critical level suggested by EPA for Pb mobility (USEPA, 1995). This result suggested that acid rain (pH of 4) could mobilize significant amounts of Pb and leach it to the groundwater. Since these soils were heavily contaminated with Pb (Table 2), they may pose a risk for groundwater contamination. Similar to the distribution of the total Pb, SPLP-extractable Pb was elevated with the highest in the berm soil (up to 20 mg/l; Table 2). Lead in shooting range soils results mostly from the weathering of bullets and consists mainly of lead carbonates (Jorgensen et

al., 1987; Lin et al., 1995). These carbonate minerals, therefore, can be easily extracted from the soil using SPLP. A significant positive correlation ( $R^2=0.98$ ,  $n=8$ ) existed between total Pb and SPLP Pb concentrations in these shooting range soils. Both total Pb and SPLP-Pb are important in assessing the toxicity and mobility of Pb in shooting range soils.

### 3.1.2. Lead concentrations in soil profiles

For the TRR shooting range, soil Pb was mostly concentrated in the surface (736 mg  $\text{kg}^{-1}$ ), with little found in the subsurface (<17 mg/kg; Table 3). Possibly, the presence of adequate P at the TRR range transformed Pb into the least soluble Pb phosphate compounds, preventing leaching down. However, substantial amounts of Pb (up to 522 mg/kg) were detected in the subsurface soils at the MPR shooting range, indicating substantial downward movement of Pb. This could be attributed to three factors. Firstly, it may be a result of relatively high Pb-loading in the surface soil since it is an older range (Table 3); secondly, a high content of organic matter in the surface soil may have increased the dissolved Pb-organic complexes at the alkaline pH; and thirdly,  $\text{CaCO}_3$  and high pH (7.47–7.69) in the subsurface soil may have contributed to a greater Pb holding capacity (Table 3).

The presence of organic matter increases not only soil cation holding capacity (as a solid), but also the mobility of Pb in the soil (dissolved), which may be due to enhanced solubilization of organo-Pb complex at alkaline pH. From Table 3, we see DOC content was high (89.3–267 mg/kg) in the MPR range soil profile. DOC may facilitate metal transport, especially in calcareous soil by acting as a carrier through the formation of soluble organo-metal complexes (Zhou et al., 2001). Organic colloids/particles are of great importance in transporting Pb from the surface soil to subsurface soil. McBride et al. (1997) estimated that these mobile, organically complexed forms of Pb could account for large cumulative losses of Pb from the surface soil. Due to the high cation exchange capacity in the soil profile, the released Pb from the surface layer is reimmobilized in the subsurface soil (Wang et al., 1996). Since the

Table 3

Soil pH values, total Pb, organic carbon (OC) and dissolved organic carbon content (DOC) in the soil profiles of TRR and MPR shooting ranges

Ranges	Profile depth <sup>a</sup> (cm)	pH	OC <sup>b</sup> (g/kg)	DOC <sup>c</sup> (mg/kg)	CaCO <sub>3</sub> (%)	Total Pb (mg/kg)
TRR	0–10	5.53	7.40	235	1.23	736
	10–30	6.00	1.21	96.7	1.42	17
	30–50	5.91	0.31	49.2	0.91	2.60
	50–100	6.11	0.12	29.8	1.07	1.80
MPR	0–10	6.73	107	267	5.87	2715
	10–30	7.47	16.1	96.6	12.6	276
	30–50	7.56	23.2	123	7.12	522
	50–100	7.69	19.3	89.3	10.2	262

<sup>a</sup> Samples were collected at 91.5 m from the firing line along a central transect.

<sup>b</sup> Organic carbon.

<sup>c</sup> Dissolved organic carbon, extracted at a 1:10 ratio of soil/water for 1 h.

groundwater occurs at a depth of slightly less than 1 m below the soil surface in many parts of Florida, there is a high probability that the groundwater quality at the MPR range may have been impacted by this downward migration of Pb. Murray et al. (1997) reported that subsurface soil Pb concentrations were in excess of 200 mg/kg at a depth of 90–100 cm at a shooting range. It was suggested that Pb movement through the soil profile was caused by formation of Pb carbonate or sulfate compounds from which Pb could subsequently be mobilized in the acidic soil at the shooting ranges.

### 3.2. Lead chemical transformation

#### 3.2.1. X-Ray diffraction patterns for the soil Pb

In shooting range soils, the overall chemical transformation of lead pellets includes weathering on the surface of pellets and further transformation in the soil. A two-step mechanism is proposed to account for the weathering process of lead pellets, i.e. oxidation of metallic lead followed by hydration and carbonation in the presence of H<sub>2</sub>O and CO<sub>2</sub>. It is possible that when lead pellets are exposed to air, Pb oxide (PbO) forms readily on their surfaces, and then CO<sub>2</sub> and H<sub>2</sub>O allow the formation of Pb carbonates from PbO. Lead oxide or Pb carbonate may remain on the surface of the pellets or may move into the soil through natural disturbance such as rain and wind. When they

come into contact with soil, a series of transformation processes may occur. Lead oxide or Pb carbonate may be stable in soils with high pH and/or high organic matter content. However, they may become soluble and mobile in an acidic sandy soil. In the presence of an adequate amount of sulfate and phosphate, Pb carbonate may be further transformed into less soluble Pb compounds of sulfate and phosphate.

In this experiment, XRD patterns showed that the weathering products of lead bullets differed between the TRR and MPR shooting ranges (Fig. 1). Hydrocerussite [Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>], cerussite (PbCO<sub>3</sub>) and trace amount of massicot (PbO) were formed on the surface of weathered bullets collected from the TRR shooting range, whereas only hydrocerussite was observed in those collected from the MPR shooting range (Fig. 1). Lead carbonate was found in both ranges, which agrees with the assumption that when lead bullets are in contact with soil, they will be readily transformed into oxidized species (Jorgensen et al., 1987; Lin et al., 1995). However, the weathering products are site-specific. Soil pH is one of the most important factors. Only hydrocerussite was detected at the MPR shooting range with a high soil pH of 7.36, whereas both hydrocerussite and cerussite were found in the TRR shooting range with a low soil pH of 5.76. It has been reported that the metallic Pb of three Danish shooting ranges was transformed into Pb compounds including hydro-

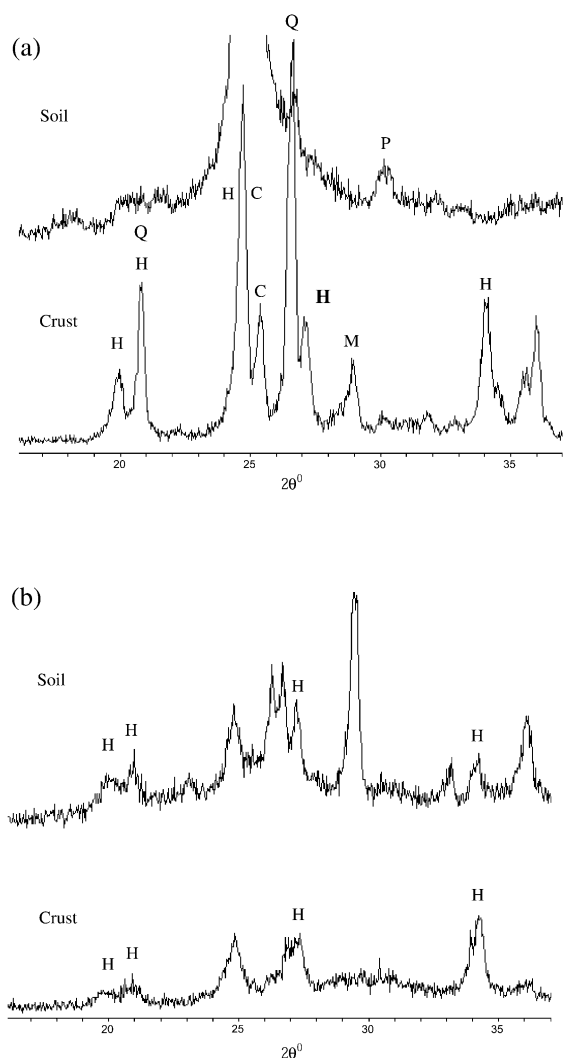


Fig. 1. X-Ray diffraction patterns of Pb compounds in crusts of weathered lead bullet and berm soils from TRR (a) and MPR (b) shooting ranges in Florida. H, Hydrocerussite; C, Cerussite; M, Massicot; P, Hydroxypyromorphite; Q, Quartz.

cerussite, cerussite, anglesite ( $\text{PbSO}_4$ ) and massicot (Jorgensen et al., 1987; Sever, 1993). Mineral contents of bullet crusts from eight shooting ranges in Sweden were composed of approximately 70–80% as hydrocerussite, 10% as anglesite, 5.0–10% as massicot and 5.0% as cerussite (Lin, 1996). The fact that no anglesite was found in the current investigation may be the combination of the solu-

bility of anglesite and differences in the soil environment. Anglesite is unstable and is readily converted to Pb carbonate (Krishnamurthy, 1992). Other researchers found that anglesite existed as a crystalline form found only in a small amounts (0.5 to 2.5%) of the soil Pb (Chaney et al., 1988).

Weathering products of lead bullets differed not only between ranges but also between the bullet crusts and the soil at a given range (Fig. 1). When the crusts exist in soil, they may undergo a number of geochemical processes, which include oxidation/reduction, precipitation/dissolution, adsorption/desorption and complexation/chelation. Soil properties greatly impact these transformation processes, thus Pb minerals present in the soil may differ from those on bullet crusts. Berm soils from the MPR shooting range had the same Pb species, (i.e. hydrocerussite) as the weathering products of corresponding lead bullets (Fig. 1b). The alkaline soil environment may have made hydrocerussite more stable at the MPR shooting range. However, neither hydrocerussite nor cerussite was detected in the berm soils from the TSR shooting range (Fig. 1a), instead hydroxypyromorphite [ $\text{Pb}_5(\text{PO}_4)_3(\text{OH})$ ] was found (Fig. 1a). The phosphate concentration in the soil of range TRR was 4240 mg/kg, which was apparently high enough to form hydroxypyromorphite. The formation of Pb phosphate has been reported in contaminated soils in the presence of adequate P. Ruby et al. (1994) demonstrated that the weathering of galena ( $\text{PbS}$ ) to insoluble chloropyromorphite [ $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ ] in the soil at a port facility historically used for shipment of ore concentrates in the presence of adequate soil P. Cotter-Howells (1996) reported the presence of substantial amounts of pyromorphite in contaminated garden, and urban and motorway roadside soils. Among Pb compounds, pyromorphite has the lowest water solubility (Lindsay, 1979). Formation of pyromorphite in the P-rich TRR shooting range soil is important for lead retention, thus reducing Pb mobility (Table 3). It implied that P addition may be an alternative for controlling Pb impacts in the outdoor shooting ranges.

### 3.2.2. Lead fractionation in the berm soils

Sequential extraction has been extensively used to assess the distribution of heavy metals in soils.

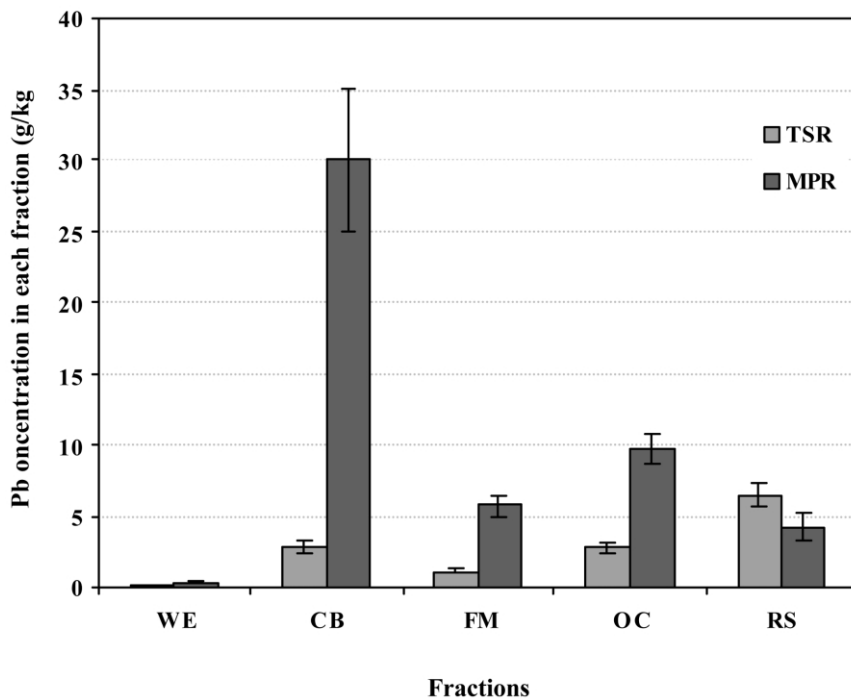


Fig. 2. Lead distribution in different fractions of berm soils from TRR and MPR shooting ranges. WE, water soluble and exchangeable; CB, carbonate; FM, Fe–Mn oxides; OC, organic; RS, residual.

There is a significant difference in Pb distribution in the soils of the TRR and MPR shooting ranges (Fig. 2). Lead in the MPR soils was primarily associated with the carbonate fraction (59.8%), followed by organic > Fe–Mn oxides > residual > water soluble/exchangeable, which is consistent with the XRD data since hydrocerussite was mainly identified in the MPR soil. This result is also in agreement with that of McNear et al. (2000) who found that the carbonate phase constituted 31–52% of total Pb in the berm soils of a shooting range in Pennsylvania, but differed from that of Bruell et al. (1999) who reported that over 40% of the total Pb was held in the exchangeable phase or in the organic fraction of a shooting range soil in Connecticut. However, in this experiment, the sum of Pb associated with the water soluble/exchangeable and carbonate fractions accounted for over 60% of the total Pb, indicating that Pb in the MPR soil is readily mobile. Contrary to the MPR range, residual Pb was predominant (20.7%)

in the TRR soil primarily due to formation of hydroxypyromorphite. Less than 22.3% of total Pb was associated with the water-soluble/exchangeable and carbonate fractions, indicating that Pb in the TRR range showed a relatively low solubility.

### 3.3. Minerals as related to soil Pb activity

The solubility of Pb-bearing minerals is of great significance in controlling Pb concentrations in soils of shooting ranges. At equilibrium, the least soluble lead compounds determine the concentration of dissolved Pb in the soil solution. Graphic methods such as an activity-ratio diagram can be used to describe and qualitatively interpret mineral solubility data (McGowen et al., 2001). Probable equilibrium reactions for Pb minerals and complexes used in the model Visual MINTEQ and the Pb activity-ratio diagram are listed in Table 4. According to the Pb activity ratio diagram, the

Table 4  
Equilibrium reactions for lead minerals and complexes at 25 °C

Minerals	Equilibrium reactions	<sup>a</sup> logK <sup>0</sup>
Massicot	$\text{PbO} + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{H}_2\text{O}$	12.72
Hydrocerussite	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 + 6\text{H}^+ \leftrightarrow 3\text{Pb}^{2+} + 2\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}$	17.51
Cerussite	$\text{PbCO}_3 + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$	4.65
Anglesite	$\text{PbSO}_4 \leftrightarrow \text{Pb}^{2+} + \text{SO}_4^{2-}$	-7.79
PbHPO <sub>4</sub>	$\text{PbHPO}_4 + \text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{H}_2\text{PO}_4^-$	-4.25
Hydroxypyromorphite	$\text{Pb}_5(\text{PO}_4)_3\text{OH} + 7\text{H}^+ \leftrightarrow 5\text{Pb}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	-4.14
Chloropyromorphite	$\text{Pb}_5(\text{PO}_4)_3\text{Cl} + 6\text{H}^+ \leftrightarrow 5\text{Pb}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{Cl}^-$	-25.05

<sup>a</sup> Data from Lindsay (1979).

solubilities of lead minerals decrease in the order of  $\text{PbO} > \text{PbCO}_3 > \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 > \text{PbSO}_4 > \text{PbHPO}_4 > \text{Pb}_5(\text{PO}_4)_3\text{OH} > \text{Pb}_5(\text{PO}_4)_3\text{Cl}$  for most soils (Lindsay, 1979). PbO is the most soluble mineral of those depicted here. There was no PbO detected in the TRR or MPR shooting ranges (Fig. 1). For the MPR shooting range, calculated  $\text{Pb}^{2+}$  activities were supersaturated with regard to cerussite and hydrocerussite for both the surface soil and berm soil (Fig. 3). It indicated that Pb carbonates may control Pb solubility in the soils of the MPR range, which agreed with the XRD (Fig. 1b)

and fractionation data (Fig. 2). However, in the TRR shooting range soil,  $\text{Pb}^{2+}$  activities were related to PbHPO<sub>4</sub> and Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH, showing that Pb solubility may be controlled by the less soluble lead phosphate, which also agreed with the XRD (Fig. 1a) and fractionation data (Fig. 2). The high content of phosphate could reduce lead mobility in the TRR shooting range soil through formation of lead phosphate. This is supported by the previous research (Santillan-Medrano et al., 1975) which suggested that lead pyromorphite is the primary mineral controlling Pb solubility in

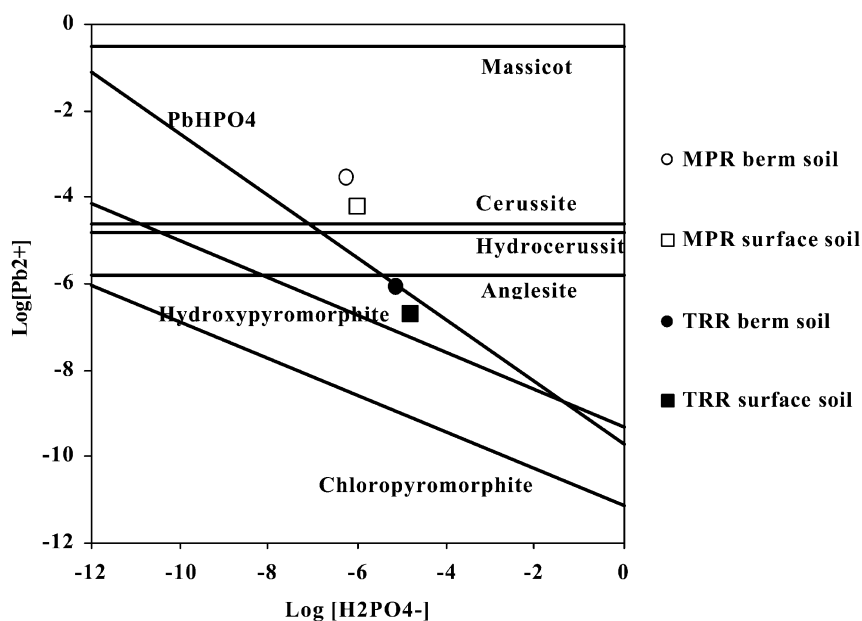


Fig. 3. Lead activity-ratio diagram at 25 °C with soil solution speciation data. Plotted lines assume  $[\text{Cl}^-] = 10^{-4}$  M,  $[\text{SO}_4^{2-}] = 10^{-3}$  M,  $[\text{H}^+] = 10^{-6.5}$  M and  $[\text{CO}_2(\text{g})] = 10^{-3.5}$  M.

many soils amended with various forms of phosphate.

#### 4. Conclusions

Total Pb concentrations in the soils from two shooting ranges (TRR and MPR) were significantly elevated due to the weathering of lead bullets. SPLP-Pb in most soils exceeded the 15  $\mu\text{g/l}$  critical level and, therefore, these soils may impact surface and groundwater quality. In the MPR shooting range, a substantial amount of Pb migrated into the subsurface soil. This was possibly due to the enhanced solubilization of organo-Pb complexes at an alkaline pH, whereas high cation exchange capacity of the profile soil may be responsible for Pb retention in the subsoil. XRD patterns showed that the weathering products of lead bullets were mainly composed of Pb carbonate. For the MPR shooting range hydrocerussite is the predominant fraction of soil Pb. In the TRR shooting range soil, Pb was transformed into hydroxypyromorphite due to the presence of adequate P in the soil. Sequential extraction and lead activity ratio modeling suggested that Pb carbonates controlled soil Pb solubility in the MPR shooting range, while in the TSR soil Pb activity was determined by less soluble Pb phosphates. Our investigation demonstrates the importance of properly managing shooting ranges to minimize Pb environmental impacts. Phosphate-induced Pb immobilization may be a remedial solution where such work is necessary.

#### Acknowledgments

This research is sponsored in part by the Florida Center for Solid and Hazardous Waste Management (Contract No. 0132004). The authors would like to thank Mr Thomas Luonguo for his assistance in chemical analysis.

#### References

- Alloway BJ. Heavy metals in soils, vol. 1. London: Blackie Academic and Professional, 1995. p. 120–190.
- Basta NT, Pantone DJ, Tabatabai MA. Path analysis of heavy metal adsorption. *Soil Agron J* 1993;85:1054–1057.
- Bruell R, Nikolaidis NP, Long RP. Evaluation of remedial alternatives of lead from shooting range soil. *Environ Eng Sci* 1999;16:403–414.
- Chaney RL, Mielke HW, Sterrett SB. Speciation, mobility and bioavailability of soils lead. In: Davies BE, Wixon BG, editors. Lead in soils: issues and guideline. Supplement to vol. 9 (1989) of *Environmental Geochemistry and Health*. 1988, pp. 105–129.
- Chen M, Daroub SH, Ma LQ, Harris WG, Cao X. Characterization of lead in soils of a rifle/pistol shooting range in central Florida, USA. *Soil Sediment Contam* 2002;11:1–17.
- Cotter-Howells J. Lead phosphate formation in soils. *Environ Pollut* 1996;93:9–16.
- Craig JR, Rimstidt JD, Bonnaffon CA, Collins TK, Scanlon PF. Surface water transport of lead at a shooting range. *Bull Environ Contam Toxicol* 1999;63:312–319.
- Dravgen J. The soil chemistry of hazardous materials. second ed. Amherst MA: Amherst Scientific Publishers, 1998.
- Jorgensen SS, Willems M. The fate of lead in soils: the transformation of lead pellets in shooting range soils. *Ambio* 1987;16:11–15.
- Krishnamurthy S. Extraction and recovery of lead species from soil. *Environ Prog* 1992;256–260.
- Lin Z. Secondary mineral phases of metallic lead in soils of shooting ranges from Orebro County, Sweden. *Environ Geol* 1996;27:370–375.
- Lin Z, Comet B, Qvarfort U, Herbert R. The chemical and mineralogical behavior of Pb in shooting range soils from central Sweden. *Environ Pollut* 1995;89:303–309.
- Lindsay WL. Chemical equilibria in soils. New York, USA: John Wiley, 1979.
- McBride MB, Richards B, Steenhuis T, Russo JJ, Sauve S. Mobility and solubility of toxic metals and nutrients in soils fifteen years after sludge application. *Soil Sci* 1997;162:487–496.
- McGowen SL, Basta NT, Brown GO. Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil. *J Environ Qual* 2001;30:493–500.
- McNear DH, Chorover J. Speciation of lead in soils from bullets in firing ranges. In: ASA/CSSA/SSSA Annual Meeting, Minneapolis, MN, 2000, pp. 51.
- Mellor A, McCartney C. The effects of lead shot deposition on soils and crops at a clay pigeon shooting site in northern England. *Soil Use Manage* 1994;10:124–129.
- Murray K, Bazzi A, Carter C, Ehlert A, Harris A, Kopec M, Richardson J, Sokol H. Distribution and mobility of lead in soils at an outdoor shooting range. *J Soil Contam* 1997;6:79–93.
- Nelson DW, Sommers LE. Total carbon, organic carbon, and organic matter. In: Page AL, Miller AH, Keeney DR, editors. *Methods of soil analysis, part 2 chemical and microbiological properties*, vol. 9. Madison, Wisconsin: ASA, 1982. p. 539–577.
- Nriagu JO. Global metal pollution: poisoning the biosphere? *Environment* 1990;32:7–33.

- Olsen SR, Sommers LE. Phosphorus. In: Page AL, Miller AH, Keeney DR, editors. *Methods of soil analysis, part 2 chemical and microbiological properties*, vol. 9. Madison, Wisconsin: ASA, 1982. p. 403–427.
- Peddicord D. *Synopsis of application and limitation of TCLP and SPLP at outdoor shooting ranges*. Newtown, CT: National Shooting Sports Foundation, 1998.
- Rhoades JD. Cation exchange capacity. In: Page AL, Miller AH, Keeney DR, editors. *Methods of soil analysis, part 2 chemical and microbiological properties*, vol. 9. Madison, Wisconsin: ASA, 1982. p. 149–157.
- Rooney CP, McLaren RG, Cresswell RJ. Distribution and phytoavailability of lead in a soil contaminated with lead shot. *Water Air Soil Pollut* 1999;116:534–548.
- Ruby MV, Davis A, Nicholson A. In situ formation of lead phosphate in soils as a method to immobilize lead. *Environ Sci Technol* 1994;28:646–654.
- Santillan-Medrano J, Jurinak JJ. The chemistry of lead and cadmium in soil: solid phase formation. *Soil Sci Soc Am Proc* 1975;39:851–856.
- Sauve SM, McBride M, Hendershot W. Soil solution speciation of lead: effect of organic matter and pH. *Soil Sci Soc Am J* 1998;62:618–821.
- Scheuhammer AM, Norris SL. A review of the environmental impacts of lead shotshell ammunition and lead fishing weights in Canada, Rep. No. 88. Minister of Environment Canadian Wildlife Service, Ottawa, Ontario. 1995, pp 3–23.
- Sever C. Lead and outdoor ranges. In: *National Shooting Range Symposium Proceedings*, Salt Lake City, UT, 1993, pp. 87–94.
- Tessier A, Campbell PGC. Partitioning of trace metals in sediments. In: Krmar JR, Allen HE, editors. *Metal speciation: theory, analysis and application*. Chelsea: Lewis Publisher, 1988. p. 183–199.
- USEPA. *Test methods for evaluating soil waste*. Vol. IA: Laboratory manual physical/chemical methods. Washington, DC 20460. EPA-SW-846, 1995.
- USEPA. *Soil screening guidance: User's Guidance*. In Office of Solid and Emergency Response, Vol. EPA 540/R-96/018, Washington, DC 20460, 1996.
- Wang EX, Benoit G. Mechanisms controlling the mobility of lead in the spodosols of a northern hardwood forest ecosystem. *Environ Sci Technol* 1996;30:2211–2217.
- Zhou LX, Wong JWC. Effect of dissolved organic matter from sludge and sludge compost on soil copper sorption. *J Environ Qual* 2001;30:878–883.