

ENVIRONMENTAL FATE OF LEAD IN FLORIDA SHOOTING RANGE SOILS

By

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Donald William Hardison Jr.

This thesis is dedicated to my grandfather, Paul Aubrey Mixon (deceased), the best friend I will ever know. I will always miss you greatly.

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Abstract of Thesis Presented to the Graduate School
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Contamination of shooting range soils from the use of Pb bullets is under increasing scrutiny. This study determined 1) the significance of abrasion of Pb bullets in contributing to soil Pb contamination, 2) the influence of soil properties and soil amendments on the corrosion/weathering of Pb as well as secondary minerals formed, and 3) the mobility of Pb in two shooting range soils through column leaching experiments. Forty-one mg of Pb were abraded per bullet as it passed through the sand, which accounted for 1.5% of the bullet mass being physically removed. At a shooting range that had been open for 3 months, the highest Pb concentration from the pistol range berm soil was 193 mg kg^{-1} at 0.5 m height, and from the rifle range berm soil was $1,142 \text{ mg kg}^{-1}$ at 1.0 m height. Most soils from the field abrasion experiment as well as soil collected from the rifle range had SPLP-Pb $>15 \text{ } \mu\text{g L}^{-1}$ (Synthetic Precipitation Leaching Procedure). Typically, Pb concentration in the rifle range was greater than that of the pistol range. Based on a laboratory weathering study, virtually all metallic Pb was

converted to hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$], as well as to a lesser extent cerussite (PbCO_3) and massicot (PbO) within one week. It was found that an increase in soil moisture level increased the rate at which metallic Pb was transformed to Pb-carbonates. Soil organic matter was necessary for Pb transformation, but transformation was inhibited as soil pH increased. At a higher soil pH, only Pb-oxides were formed. Soil microorganisms did not play a direct role in the transformation of metallic Pb. Aggregates, composed of quartz cemented by hydrocerussite and possibly pyromorphite in untreated and phosphate rock amended soils, formed in the soil after 11 weeks of incubation. Water-soluble Pb was decreased in soil treated with amendments. Lead concentration in the effluent from a sandy Florida shooting range was typically below the $15 \mu\text{g L}^{-1}$ EPA critical limit. This suggested that Pb was immobile in soils with low CEC and low pH even with high total Pb concentrations. Our study demonstrated that abrasion of lead bullets and their subsequent weathering can be a significant source of lead contamination in newly opened shooting range soils, and that soil properties such as pH and OM significantly influenced the weathering rate and products of Pb bullets.

CHAPTER 1 INTRODUCTION

Background

Lead (Pb) contamination in both shotgun and rifle shooting range soils is of increasing environmental concern, due to the elevated concentrations of Pb in these soils. There are an estimated 9,000 non-military outdoor shooting ranges in the United States that collectively shoot millions of pounds of Pb on an annual basis (US Environmental Protection Agency [USEPA], 2001). Over 400 outdoor ranges operate in the state of Florida alone (Florida Department of Environmental Protection [FDEP], 2002). Approximately four percent ($80,000 \text{ tons year}^{-1}$) of all Pb produced in the United States is made into bullets and shot, with an estimated $58,300 \text{ tons year}^{-1}$ of shot and munitions being deposited into the American landscape through shooting activities (Hui, 2002; USEPA, 2001).

Environmental contamination due to the use of Pb ammunition is a worldwide issue. The deposition of metallic Pb in the form of shotgun ammunition has been reported from 200 to 6,000 tons in the countries of the Netherlands, Denmark, Finland, Sweden, Canada, and England (Jorgensen and Willems, 1987; Lin, 1996; Mellor and McCartney, 1994; Scheuhammer and Norris, 1995; VanBon and Boersema, 1988). While contamination at rifle shooting ranges is typically localized due to berm backstops, shotgun and skeet ranges show more extensive areas of elevated concentrations of Pb in soils. In only seven years of operation, a shotgun range in Virginia accumulated 11.1 metric tons of Pb in an area of $66,000 \text{ m}^2$ (Craig et al., 2002).

Due to the extensive amounts of Pb that are being deposited in the environment as a result of activities that are taking place at shooting ranges, it is not surprising that both state and federal regulatory agencies have begun to seriously investigate the use of Pb as munitions in shooting ranges. In fact, the use of Pb shot for waterfowl hunting and shotgun hunting near wetlands and national wildlife refuges has been banned since 1991 (USEPA, 2001). Citizen groups have been the most active in bringing legal suits against outdoor shooting ranges.

The Resource Conservation and Recovery Act (RCRA) and the Clean Water Act (CWA) allow citizens the right to sue in situations where the human or environmental health is threatened (USEPA, 2001). Federal Courts have made several rulings involving Pb contamination in shooting ranges. The United States Court of Appeals for the Second Circuit ruled that Pb shot met the statutory definition of solid waste, and if Pb in shooting ranges is not removed it could be labeled hazardous waste and subject to RCRA on March 29, 1993 (USEPA, 2001). Also, the United States District Court for the Southern District of New York found that the mechanized target throwers, concrete shooting platforms and the shooting range of the New York Athletic Club were considered point sources as defined by CWA; and that shot, target debris, and even non-toxic shot left in the water are pollutants defined by the CWA.

High quality, non toxic metal alloys that are being manufactured as alternatives to Pb shot and bullets do exist for avid shooters including bismuth/tin (Bi/Sn), steel (Fe), zinc (Zn), tungsten/iron (W/Fe), and tungsten/polymer (FDEP, 2002; Scheuhammer and Norris, 1995; USEPA, 2001). However, due to increased cost and/or inferior ballistic properties, these alloys are typically less popular among shooting enthusiasts

(Scheuhammer and Norris, 1995; USEPA, 2001). Another alternative that is relatively less toxic in soils is copper (Cu) or brass jacketed Pb bullets. However, due to the tendency of bullets to fracture upon entering berm soils (Astrup et al., 1999), Cu jacketing offers limited protection against Pb exposure to soils. In addition, Cu should not be used in aquatic environments due to its known toxicity to fish (Bugenyi and Lutalobosa, 1990).

Present Study

The state of Florida provides a unique environment for studying the chemistry of Pb compared with the rest of the United States. Soils found within the state of Florida are typically sandy (low clay and organic matter content) as well as have a low soil pH. While these factors alone may not contribute to the migration of Pb in soils (Chen and Ma, 1998), an average yearly rainfall of 54 inches increases the risk of migration.

The objectives of this study were 1) to investigate the physical contamination (abrasion) of Pb bullets as they pass through berm soils, 2) to determine the rate and effect of soil properties on weathering of metallic Pb, and 3) to investigate factors that contributed to migration of Pb in a Florida shooting range soil. The study was carried out in three parts. First, a field experiment was conducted by firing 22 caliber rounds of Pb bullets into sand. Field sampling was also conducted from a newly open shooting range to determine rate of contamination with time. Total and SPLP Pb concentrations were monitored to determine the contribution of abraded Pb.

Second, the rate and mechanisms by which Pb weathers in a Florida surface soil were investigated. To accomplish this, a laboratory incubation study was carried out in which metallic Pb powder was incubated in soils in which soil properties were

manipulated. Results were determined through identification of mineral products through X-ray diffraction (XRD), as well as monitoring soil pH and water soluble Pb.

Last, intact soil cores were collected from a shooting range that exhibited migration of Pb to the subsurface and a shooting range soil that exhibited no migration of Pb. Leaching studies were conducted to determine desorption of Pb from these soils. Other conditions such as effluent pH and inorganic and organic carbon concentrations were monitored to draw relationships describing mobility of Pb in soils. The last chapter is a synthesis of ideas from the results of these studies, compiled to give a better understanding of the fate and mobility of Pb contamination in shooting range soils, with the ultimate goal of aiding the development of best management practices (BMP's) for shooting range operators.

CHAPTER 2 LITERATURE REVIEW

Overview

Lead is the 36th most abundant element and the most abundant heavy metal in the earth's crust with an average concentration of 13 mg kg⁻¹ (Brown et al., 1999; Nriagu, 1978). Lead is also readily found in soils. Mean concentrations of Pb, in soils worldwide, range from 10 to 84 mg kg⁻¹ (McBride, 1994). Lead has a long residence time compared to most other pollutants when released into the environment due to its extreme insolubility (Davies, 1995). Its concentrations are elevated in the environment due to its past and present use in batteries, paints, alloys, solder, ammunition, gasoline additives, and other commercial products, in addition to mining and smelting activities (Brown et al., 1999). However, serious concern, due to the deleterious health effects from exposure to Pb, has curtailed its use in recent times. Lead use in solder, plumbing pipes, paints, potter glazes, crystal ware, and gasoline have been banned or severely reduced in many countries (Scheuhammer and Norris, 1995).

Once Pb enters the environment, its chemistry is dominated by the plumbous ion (Pb²⁺) (Davies, 1995; McBride, 1994). Lead has oxidation states of Pb (II) and Pb (IV) beyond elemental Pb; however, virtually no stable region exists for Pb⁴⁺ except at very high oxidation potentials and basic conditions (Graedel, 1994; Stumm and Morgan, 1996). This is especially true for soils. It is virtually impossible for the higher state Pb-oxides (PbO₂ and Pb₃O₄) to form in soils since soils are almost always more reduced than $p_e + pH$ of 20.61 (Lindsay, 1979). For this reason, Pb⁴⁺ is rarely seen in soils, and

oxidation-reduction processes will be negligible in atmospheric environments (Graedel, 1994).

Lead has been used extensively throughout the history of man due to its extreme durability. The durability of Pb is due to the formation of a protective layer that consists primarily of the mineral products cerussite (PbCO_3) and hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] (Edwards et al., 1997). Metallic Pb is only stable under extremely reducing conditions and at high pH values (Luo and Hong, 1997; Pourbaix et al., 1966). However, when exposed to the atmosphere it readily transforms to Pb-oxides (Graedel, 1994; Pourbaix et al., 1966). Litharge (PbO), or red Pb, forms when Pb is first exposed to air and is the most common Pb-oxide found on the surface of metallic Pb (Graedel, 1994).

Lead oxides are typically too soluble to provide any protection for Pb against corrosion (Luo and Hong, 1997; Pourbaix et al., 1966). Therefore, they are rapidly replaced in leaching environments by more stable Pb compounds. Another Pb-oxide typically found in the environment is massicot (PbO), or yellow Pb (Blair, 1998; Lindsay, 1979). While both litharge and massicot have the same chemical formula, they are different due to their crystalline structures in the environment. Litharge has an orthorhombic crystalline structure, whereas massicot has a tetragonal crystalline structure (Blair, 1998). Another mineral form of Pb-oxide, minium (Pb_3O_4) (also referred to as red Pb) can be obtained by the oxidation of PbO or formed in alkaline solutions of divalent Pb (Pourbaix et al., 1966). Further oxidation of minium may lead to the formation of PbO_2 . However, as previously discussed, these minerals rarely exist in soils due to their instability under most soil conditions.

Lead oxides have a very narrow region of stability in the environment, and combine readily with CO₂ to form cerussite, hydrocerussite and hydrated products (Blair, 1998; Graedel, 1994). This reaction generally occurs very rapidly due to the presence of an aqueous film on the surface of metallic Pb that allows CO₂ and other gases to diffuse and dissolve, and result in anion reaction with surface metallic Pb to form corrosive products (Graedel, 1994; Rocca and Steinmetz, 2001). In the environment, a layer of these mineral products typically coats metallic Pb and prevents further corrosions of Pb.

The most common weathering products of Pb typically found in the environment are anglesite (PbSO₄), cerussite, and hydrocerussite (Graedel, 1994; Rocca and Steinmetz, 2001; Sposito, 1983). These compounds usually appear on the surface of Pb as a white crust material (Jorgensen and Willems, 1987; Rocca and Steinmetz, 2001). Weathering products of Pb have been identified at different types of Pb contaminated sites. “White rust” has been identified as the corrosion products of Pb roofs from historical buildings due to condensation corrosion (Rocca and Steinmetz, 2001). Mineral forms of Pb that have been found in historical slags from Roman, Medieval, and Industrial times include lead oxides, pyromorphite [Pb₅(PO₄)₃Cl], cerussite, hydrocerussite, galena (PbS), anglesite, and leadhillite [Pb₄SO₄(CO₃)₂(OH)₂] (Gee et al., 1997). Lead compounds found at Pb battery recycling sites include galena, Pb-oxides, Pb⁰ (elemental), cerussite, and hydrocerussite (Nedwed and Clifford, 1997). Lead minerals found at Pb smelting sites include Pb-oxides, Pb-carbonates, and pyromorphite (Maskall and Thornton, 1998). Lead minerals, cerussite and galena, were identified in soils and sediments of a former gold (Au) mine in Korea (Song et al., 1999). Hydrocerussite and cerussite form on the surface of crab shell particles used to treat Pb contaminated wastewater (Lee et al., 1997).

They are typically the most stable forms of Pb found in drinking water (Luo and Hong, 1997).

Health Effects and Bio/Phyto Availability of Pb

Lead is a known toxin and cumulative metabolic poison, and it has been shown to impair the renal, hemopoietic, and nervous systems (Posner et al., 1978). Lead poisoning has been documented throughout the history of human civilizations. In fact, the toxic properties of Pb were documented in Ebers and Hearst medical papyruses prior to 1550 B.C. (Nriagu, 1983). It could be said that the earliest disease of mankind due to occupational hazard is Pb poisoning (Nriagu, 1983).

Children are particularly at risk to Pb poisoning. Lead toxicity has been shown to cause mental impairment in young children (Davies, 1995). Their elevated risk is due to their tendency to ingest substances such as soil and paint chips. Consumption of more than one gram of soil containing $5,000 \text{ mg kg}^{-1}$ Pb for several months would result in the development of clinical Pb poisoning in young children (Mahaffey, 1978). Lead concentrations in both skeet and rifle shooting ranges (Table 2-1) soils have been shown to far exceed $5,000 \text{ mg kg}^{-1}$ (Cao et al., 2003; Cao et al., In Press; Chen et al., 2001; Manninen and Tanskanen, 1993; Mellor and McCartney, 1994; Murray et al., 1997). Studies suggest that children prone to consuming soil will far exceed the amount causing toxicity on a weekly basis (Mahaffey, 1978). While acute exposure in the human population has been diminishing due to better knowledge of health issues, there is increasing concern that continued exposure to lower levels of Pb, due to widespread environmental contamination, may also result in adverse health effects (Posner et al., 1978).

Lead toxicity is of particular concern in shooting ranges, due to the increased bioavailability of Pb compounds generally found in soils. The exposure to Pb from both indoor and outdoor firing ranges doubled the blood Pb concentration in a recreational shooter (Gulson et al., 2002). The Pb minerals cerussite, hydrocerussite and massicot are the typical Pb compounds found in shooting range soils (Cao et al., 2003; Cao et al., In Press; Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995). Hemphill et al (1991) modeled the dissolution of Pb from ingested soils, and predicted complete dissolution of the minerals massicot and cerussite due to the acidic nature of the stomach. The study concluded that aqueous solubility of a mineral is an important factor controlling its Pb bioavailability (Hemphill et al., 1991). Based on this, it can be concluded that mineral hydrocerussite would have a similar bioavailability as cerussite, since these compounds have identical solubility (Table 2-2) at 0.0003 atm of CO₂ (Lindsay, 1979).

Elevated Pb concentrations in soils of shooting ranges may also be toxic to plants and animals that inhabit these areas. Lead concentrations in shooting ranges have been shown to be phytoavailable to several species of plants that inhabit shooting range soils. Elevated concentrations of Pb have been documented primarily in the roots of plant species on these soils (Mellor and McCartney, 1994; Rooney et al., 1999; Turpeinen et al., 2000). However, translocation of Pb has been shown to occur in plants located on shooting range soils, with the Pb concentration in the leaves being well above what is typically allowed for foodstuffs (Hui, 2002; Manninen and Tanskanen, 1993; Rooney et al., 1999). The guidelines for Pb concentrations in edible vegetables set by WHO/FAO (World Health Organization/Food and Agriculture Organization) is 0.3 mg Pb kg⁻¹, whereas Pb concentrations in the leaves of white clover (*Trifolium repens*) grown in a

shooting range soil were reported to exceed $130 \text{ mg Pb kg}^{-1}$ (Rooney et al., 1999). Therefore, organisms that depend on these plants for food are at risk for Pb toxicity. Another significant concern is in ranges that shoot into or over water. Waterfowl are highly susceptible to ingestion of Pb shot as a result of mistaking it for food or grit (Scheuhammer and Norris, 1995; USEPA, 2001).

In addition to plants and higher organisms, invertebrates and microbes that depend on the soil for habitat are at an even greater risk to Pb toxicity within these soils. Hui (2002) found that Pb concentration in the Horn snail (*Cerithidea californica*) within a skeet shooting range averaged $1,987 \text{ mg Pb kg}^{-1}$. Lead concentration in shooting range soils may also affect microbial activity, by limiting enzymatic activity (Manninen and Tanskanen, 1993). While studies have shown that resistance of soil bacteria to Pb is typically greater than that of other heavy metals due to the low solubility of Pb (Davies, 1995), the extremely high concentrations of Pb typically found in shooting range soils will likely enhance the bioavailability of Pb to microbial communities in the soil.

Lead in Shooting Range Soils

Lead Contamination and Weathering in Shooting Range Soils

Extremely high concentrations of total Pb have been documented in the soils of both shotgun and rifle ranges (Table 2-1). Astrup et al (1999) found concentrations as high as 5-10% associated with soil particles, and as high as 40% when factoring in metallic Pb bullets removed from the soil. While rifle ranges tend to have more localized contamination of metallic Pb, high Pb levels have also been shown in shotgun ranges as well. Total Pb levels as high as 300 g kg^{-1} have been reported in the topsoil of a clay-shooting range in The Netherlands (VanBon and Boersema, 1988). Rooney et al (1999)

concluded that over 30% of the sampling area of a clay target area exceeded 300 mg Pb kg⁻¹ after 85% of metallic Pb in the form of shot was removed by sieving.

Table 2-1 Lead concentrations and Pb minerals found in various shooting range soils.

Location	Type	Ref.	Pb minerals	Pb (mg kg ⁻¹)
Denmark	Rifle	1	-	100,000
Florida	Rifle	2	Hydrocerussite, cerussite, massicot, hydroxypyromorphite	48,400
Florida	Shotgun	3	-	15,368
Florida	Rifle	4	Hydrocerussite, cerussite, massicot	17,850
California	Shotgun	5	-	16,200
Denmark	Shotgun	6	Hydrocerussite, cerussite, anglesite	1,000
Sweden	Shotgun	7	Hydrocerussite, massicot, anglesite	24,500
Sweden	Shotgun	8	Hydrocerussite, cerussite, anglesite	3,400
Finland	Shotgun	9	-	54,000
England	Shotgun	10	-	10,620
Michigan	Shotgun	11	Pb-carbonate, anglesite	2,256
New Zealand	Shotgun	12	-	8,300
Finland	Shotgun	13	-	9,804

¹Astrup et al., 1999; ²Cao et al., 2003; ³Chen et al., 2001; ⁴Chen et al., 2002; ⁵Hui, 2002; ⁶Jorgensen and Willems, 1987; ⁷Lin, 1996; ⁸Lin et al., 1995; ⁹Manninen and Tanskanen, 1993; ¹⁰Mellor and McCartney, 1994; ¹¹Murray et al., 1997; ¹²Rooney et al., 1999; ¹³Turpeinen et al., 2000

As mentioned previously, metallic Pb readily corrodes when exposed to the atmosphere and a protective layer of Pb minerals generally forms on the surface of

metallic Pb in the environment, protecting against further corrosion. This holds true in shooting range soils as well. Lin (1996) found that 10% of the Pb pellets removed from a shotgun range is composed of an encrusted outer rim of decomposed and transformed secondary minerals. These rims consisted of an outer rim that was approximately 10 to 150 μ m composed of hydrocerussite, and an inner rim that was approximately 10 to 30 μ m composed of massicot and anglesite (Lin, 1996). The relationship between these rings suggests that Pb-oxides are being replaced by Pb-carbonates as the pellets remain in soil (Lin, 1996).

These Pb minerals, which form encrustation on the surface of the Pb bullets present in soil, have been seen in several shooting ranges, and the Pb minerals found in these soils are presented in Table 2-1. In addition to hydrocerussite, anglesite and massicot; the Pb mineral cerussite (Table 2-1) is also commonly found on the surface of these bullets (Cao et al., In Press; Chen et al., 2002; Jorgensen and Willems, 1987; Lin et al., 1995; Murray et al., 1997). In addition, hydroxypyromorphite [$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$] was found (Table 2-1) in the berm soil of a shooting range built on phosphorus (P) rich soil (Cao et al., In Press). Equilibrium reactions for Pb minerals and complexes at 25°C found in shooting range soils are presented in Table 2-2.

While these layers do form on the surface of metallic Pb bullets in shooting range soils, they do not provide adequate protection against further corrosion of metallic Pb due to the highly reactive nature of soils. Jorgensen and Willems (1987) concluded that within 6-13 years, 5-17% of metallic Pb in the form of shot would be transformed to Pb minerals with complete transformation in 100-300 years. Mechanical soil treatment may reduce this complete transformation to within 30-90 years, since Pb pellets from

cultivated land had six times as much crust material as pellets from grassland (Jorgensen and Willems, 1987). Lin et al (1995) found that in a period of 20-25 years, an average of 4.8% metallic Pb was transformed to secondary Pb minerals. This figure increased to 15.6% in soils that were rich in humus most likely due to soil organic matter (Lin, 1996). Organic acids have been implicated in the accelerated corrosion of metallic Pb (Edwards et al., 1997; Jorgensen and Willems, 1987). In addition, the oxidation of organic matter by microbial communities produces elevated levels of CO₂ in soil increasing the concentration of the carbonate ligand, which increases the amount of Pb-carbonate formed in these soils (Lin, 1996).

These secondary minerals act as sinks for Pb in the shooting range soils (Lin, 1996). At equilibrium, the least soluble Pb compounds determine the Pb concentration in soil solution (Lin, 1996). Soil pH has been shown to increase in shooting ranges due to the weathering and transformation of metallic Pb bullets to secondary minerals. Astrup et al (1999) found that in soil with metallic Pb bullets present, the soil pH was between 6 and 7, whereas the pH of the soil underneath was 5. Chen et al (2002) found a positive correlation between total Pb and soil pH in a shooting range soil. Of the Pb compounds typically found in shooting range soils, cerussite and hydrocerussite are more stable at high soil pH values (>6) (Lindsay, 1979). This suggests that the addition of Pb shot limits the solubility of Pb in the shooting range soils due to its natural liming ability. Gee et al (2001) found that as soil pH drops from 5 to 4, cerussite in soil is no longer stable, and is involved in the buffering reaction with CaCO₃. The role of secondary Pb minerals as natural metal ion buffers is often overlooked (Gee et al., 2001).

However, these secondary Pb minerals may become a source of contamination should soil conditions change (Lin et al., 1995). The most obvious situation where this would occur would be a drop in soil pH. Soil pH plays an important role in the solubility of Pb in shooting range soils (Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995). The dissolution of both hydrocerussite and cerussite require 2 moles of H⁺ (requires a pH < 4.5) per mole of Pb (Table 2-2) if CO₂ is produced in the dissolution process (Jorgensen and Willems, 1987). While Pb solubility is repressed at alkaline pH values, these minerals would dissolve rapidly in the soil environment if the pH were lowered (Jorgensen and Willems, 1987; Zimdahl and Skogerboe, 1977).

Table 2-2 Equilibrium reactions for select Pb minerals and complexes at 25°C

Pb mineral	Equilibrium reaction	log K°
Massicot	$\text{PbO} + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{H}_2\text{O}$	12.89
Cerussite	$\text{PbCO}_3 + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$	4.65
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
Anglesite	$\text{PbSO}_4 \leftrightarrow \text{Pb}^{2+} + \text{SO}_4^{2-}$	-7.79
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

Data from Lindsay (1979)

Lead Mobility in Shooting Range Soils

Secondary Pb minerals may be removed from the bullet crust material by leaching as hydrated Pb ions or as soluble Pb-organic complexes (Jorgensen and Willems, 1987). Once in solution, Pb is likely to precipitate as less soluble Pb compounds, adsorb on to mineral or organic soil components, or be taken up by plants or other organisms that inhabit the soil (Jorgensen and Willems, 1987). Once in soil, Pb has a long residence time due to its low solubility and its strong affinity for soil (Matos et al., 2001; Mellor

and McCartney, 1994; Rooney et al., 1999; Strawn and Sparks, 2000; Turpeinen et al., 2000). The estimated half-life of Pb in soils range from 740-5900 years (Rooney et al., 1999).

The concentration of dissolved Pb in shooting ranges typically diminishes and downward transport is impeded due to adsorbing surfaces within the soil (Jorgensen and Willems, 1987). Retention of Pb in shooting range soils is most likely due to a combination of soil pH, organic matter content, soil cation exchange capacity (CEC), and soil leaching rate in addition to precipitation reactions (Astrup et al., 1999; Lin et al., 1995).

While mobility of Pb in soils is typically very low, downward migration of Pb has been found in several shooting range soils. Murray et al (1997) found that the distribution of Pb in the subsurface soil corresponded to the distribution of Pb in the surface soils suggesting downward migration of Pb even in clay rich soils. Levels in excess of 200 mg kg⁻¹ have been noted at depths of up to 90-100cm at a shooting range soil (Murray et al., 1997). Turpeinen et al (2000) concluded that half of total water soluble Pb in a shooting range soil exhibited low sorption potential to soil particles and plant roots, and may pass deeper in soil layers with drainage water. Astrup et al (1999) found that the migration of Pb in a shooting range soil was greater than sorption/desorption reactions should have allowed, and attributed this translocation of Pb to factors such as grass roots, repair of soil embankment, and dissolved organic carbon in the soil solution. They concluded that Pb migration rate at the shooting range site was approximately 2mm per year (Astrup et al., 1999).

The results of Turpeinen et al (2000) and Cao et al (2002) support the theory that dissolved organic matter may increase Pb mobilization in shooting range soils.

Turpeinen et al (2000) found that water soluble Pb significantly increased in shooting range soil that was limed. Liming also increased the dissolved organic carbon (DOC), and a significant positive correlation was found between the solubility of Pb and the concentration of DOC in soil water (Turpeinen et al., 2000). Cao et al (2002) found total Pb concentrations of 262 mg kg^{-1} at a depth of up to 100cm in a calcareous shooting range soil that exhibited soil properties such as high organic carbon and high soil pH. One of their possible conclusions was that organo-Pb complexes were being mobilized due to the high pH of the soil (Cao et al., In Press).

Soil organic matter becomes more soluble at higher soil pH values as dissociation increases the surface negative charge of the individual organic molecules (McBride, 1994). The increase in surface negative charge also increases the attraction of cations in soil to sorb onto organic molecules. The highest sorption capacity for Pb has been exhibited in calcareous soils (Elkhatib et al., 1991). Therefore, at high soil pH values the solubility of Pb is enhanced due to the solubilization of organic matter. Complexation with DOC has been found to be more significant for Cu and Pb than any other metals (Weng et al., 2002).

Lead in Surface Water of Shooting Ranges

Several sources have reported elevated concentrations of Pb in surface water on shooting ranges. Stansley et al (1992) reported elevated values of total Pb ($1,270 \mu\text{g L}^{-1}$) and filterable ($83 \mu\text{g L}^{-1}$) in surface water within the shot fall zone of trap and skeet (shotgun) ranges compared to nearby control areas ($< 1 \mu\text{g L}^{-1}$ total Pb). VanBon and

Boersema (1988) found similar values of total Pb ($1,300 \mu\text{g L}^{-1}$) in surface water on a clay shooting range (shotgun). Elevated Pb has also been found in surface water on rifle shooting ranges (Cao et al., 2003). They found elevated total Pb ($289 \mu\text{g L}^{-1}$) and filterable Pb ($234 \mu\text{g L}^{-1}$) near the firing line of a rifle range in Florida. Craig et al (1999) also found elevated levels of filterable Pb ($473 \mu\text{g L}^{-1}$) in a rifle range near the berm backstop. While all of these ranges exhibited levels of Pb above the Environmental Protection Agency (EPA) action level for Pb ($15 \mu\text{g L}^{-1}$) in drinking water, concentration of Pb in surface water dropped significantly with distance in most of the range soils (Craig et al., 1999; Stansley et al., 1992). This was most likely due to the tendency for Pb-carbonates to precipitate out of surface water.

Stabilization Remediation Technologies

Lime Amendments

The liming of soils has been very effective in controlling heavy metal mobility in soils (Matos et al., 2001). Lime amendments buffer the pH of soil in order to reduce the mobility of Pb. This is especially important in Eastern United States soils that typically have pH values lower than 6 (USEPA, 2001). The application of lime may also be a cost effective form of remediation since 50 pounds usually only costs between 2 and 4 dollars, and may be applied by the range owners themselves (USEPA, 2001). The addition of lime has been shown to decrease the availability of Pb to plants due to the decreased solubility of Pb carbonates (Zimdahl and Skogerboe, 1977). Liming metal contaminated sewage sludge reduced the DTPA-extractable Pb by as much as 8 to 14% (Fang and Wong, 1999). However, it is important to monitor the conditions before lime application,

as well as the amount of lime applied due to the possible mobilization of organo-Pb complexes as previously discussed.

Plants

Plants may be used to control contamination via surface run-off. Planting grass is an important and easy erosion control method (USEPA, 2001). Vegetation may also help to stabilize Pb. Turpeinen et al. (2000) reported that Pine roots played an important role in the immobilization of Pb in a former shooting range soil. In addition, some species of plants have even been reported to accumulate Pb in the above ground biomass.

Manninen and Tanskanen (1993) reported total Pb concentrations as high as 70 mg kg^{-1} in the leaves of *Betula pendula*. However, Pb uptake by plants is typically at a minimum, and the highest concentrations of Pb typically remain in the roots.

Phosphate Addition

Lead phosphates (in particular fluoropyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2]$ and chloropyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$) are extremely insoluble forms of Pb compounds in soils under a wide range of environmental conditions compared to other Pb compounds (Lindsay, 1979; Nriagu, 1974; Rickard and Nriagu, 1978; Traina and Laperche, 1999), thus reducing the leachability of Pb in soils. The formation of pyromorphite minerals has been reported in urban and roadside Pb contaminated soils (Cotter-Howells, 1996).

Phosphate may be applied in several forms. The most common and easiest to find would be in the form of lawn fertilizer. Lawn fertilizers typically cost \$7.00 per 40 pound bags (USEPA, 2001). This form of phosphate is extremely soluble, and care should be taken not to apply this form near bodies of water in order to prevent runoff that results in algal blooms and eutrophication of the body of water.

Another source of phosphorus that may be used to remediate Pb contaminated soils is hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$]. Ma (1996) found that application of hydroxyapatite significantly reduced the aqueous Pb concentrations in soils contaminated with PbHAsO_4 insecticide. Ryan et al (2001) found that at least 10% of Pb in smelter contaminated soil had been transformed to pyromorphite minerals after 240 days incubation with hydroxyapatite.

Phosphate rock is the raw material used for phosphate fertilizer production. Hettiarachchi et al. (2001) stated that phosphate rock was relatively insoluble compared to other sources of phosphate and should reduce P losses in runoff. Ma et al (1995) demonstrated that the use of phosphate rock was a cost effective way to remediate Pb-contaminated soils. Basta et al. (2001) reported that phosphate rock immobilization products were more stable under acidification than other treatments, and that phosphate rock treatment would reduce bioavailability of Pb associated with the ingestion of contaminated soils by humans. Hettiarachchi et al. (2001) reported that phosphate rock was equally or more effective than Triple Super Phosphate. It has been reported that 15-20 pounds of pure phosphate per 1,000 square feet will effectively control Pb migration (USEPA, 2001).

Other Stabilization Methods

Lead may also be stabilized in soil by addition of cement. Bruell et al. (1999) reported that Pb contaminated shooting range soil that had been bound with cement passed the Toxicity Characterization Leaching Procedure (TCLP), but failed the Synthetic Precipitation Leaching Procedure (SPLP) test. The TCLP test is used to determine the leaching capacity of the soil under landfill conditions, and the SPLP is used to test the leaching capacity of soils in unbuffered simulated rainwater (Reid and Cohen,

2000; USEPA, 1994). Bruell et al. (1999) also heat-treated the soil by heating it to 400°C for 24 hours. This reduced the total organic carbon in the soil from 2.66 to 0.024% without changing the total Pb in soil. This method passed both the TCLP and SPLP tests. Originally, up to 30% of the Pb was organically bound, and thus by heating the soil, Pb was present as more stable fractions.

Summary

While many studies have investigated mobility and remediation of Pb in contaminated soils, studies involving Pb contaminated shooting range soils have primarily focused on characterization of Pb contamination. Issues such as contamination and mobility of Pb have been documented, but the processes have not been well defined. While a few remediation technologies have been discussed in this review, they primarily have been studied in the context of different forms of Pb contaminated soils. It is possible these studies may be applicable to shooting range soils as well, however, validation would be necessary to eliminate the site-specific aspects of these remediation techniques.

The establishment of best management practices (BMPs) for shooting ranges has been advocated and developed by regulatory agencies at the state and federal level. The establishment of these BMPs requires an understanding of the mechanisms by which soils are contaminated with Pb shot and bullets as well as the factors that result in the mobilization of Pb in shooting range soils. The present study was done to better understand the processes of Pb contamination and weathering and mobility of Pb in shooting range soils, in an effort to help these ranges and regulatory agencies establish BMPs that will result in better environmental stewardship of our resources.

CHAPTER 3
LEAD CONTAMINATION IN SHOOTING RANGE SOILS FROM ABRASION OF
LEAD BULLETS AND SUBSEQUENT WEATHERING

Introduction

Approximately 80,000 tons year⁻¹ of Pb was used in the production of bullets and shot in the United States in the late 1990's (USEPA, 2001). It can be hypothesized that the vast majority of this Pb finds its way into the soils of the many civilian and military shooting ranges across the country. The deposition of metallic Pb in the form of shotgun ammunition has been reported in the Netherlands, Denmark, Finland, Sweden, Canada, and England (Jorgensen and Willems, 1987; Lin, 1996; Mellor and McCartney, 1994; Scheuhammer and Norris, 1995; VanBon and Boersema, 1988).

Lead contamination in the environment is of concern as it is a known toxin, which has deleterious effects on the human neurological system. Lead poisoning has been documented throughout human history, and has even been invoked as a factor in the decline of Rome (Nriagu, 1983). Lead present in soil and dust has been directly related to the Pb levels in blood (Davies, 1995). Second-hand Pb poisoning has been documented among the children of Pb workers (Mahaffey, 1978). Even low-level exposure to Pb has been linked to lower intelligence, diminished cognitive function, and delinquent behavior in children (Odum, 2000). In the past, the federal government has not regulated shooting ranges. However, on March 29, 1993 the United States Court of Appeals for the Second Circuit ruled that Pb shot in shooting ranges met the statutory

definition of solid waste, and if the Pb was not reclaimed it could be labeled hazardous waste subject to the Resource Conservation and Recovery Act (USEPA, 2001).

Many recent studies have quantified the amount of Pb contamination in the soils of shooting ranges. Total Pb concentration levels up to 54,000 mg kg⁻¹ excluding pellets have been reported in shooting range soils (Manninen and Tanskanen, 1993). Up to 40% metallic Pb and 5 to 10% Pb associated with soil particles was found in a shooting range in Denmark (Astrup et al., 1999). Elevated Pb concentrations were also reported at up to 100 cm depth suggesting that Pb was being mobilized through the soil profile (Murray et al., 1997). Elevated Pb concentrations have been reported in surface water samples (Craig et al., 1999; Stansley et al., 1992); however, these levels decreased significantly with distance from the shooting range (Craig et al., 1999).

Lead contamination in the state of Florida is of particular concern due to the soil and weather conditions that typify the state. The conditions that contribute to the risk of Pb migration in Florida soils include: low soil pH, low clay and organic matter content, and high amounts of rainfall (Chen and Ma, 1998). Another concern is that Florida groundwater is usually very shallow. This means that once Pb is in solution it has a short distance to travel before encountering the groundwater.

Past research on soil Pb contamination has focused on the contamination and geochemical weathering reactions of Pb bullets in the soil of shooting ranges that have been operated for many years (Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995). Contamination of soils due to the abrasion of Pb bullets passing through soil would result in a contamination of the soil with smaller metallic Pb particles. It was hypothesized that this material would contribute more to immediate contamination of these soils as well as

environmental risk due to its quick buildup as fine particles and rapid transformation to more reactive compounds. Rooney et al (1999) reported that residual Pb particles (<2 mm) in soil were completely dissolved by EDTA. Astrup et al (1999) reported that small Pb bullet fragments in the soil (<2 mm) may have contributed to the total content of Pb in the soils they examined. This type of contamination has implications regarding the age of a shooting range for which best management practices must be implemented.

The objectives of this study were: 1) to quantify the amount of Pb that is physically abraded as a bullet passes through a berm soil, 2) to corroborate these results through field sampling in a newly opened shooting range, 3) to determine the increase in soil Pb concentration in a newly opened shooting range as a function of time, and 4) to determine the weathering rate of this abraded Pb through a laboratory experiment.

Materials and Methods

Field Abrasion Experiment

This experiment was performed to quantify the amount of Pb contamination in a shooting range berm that results from physical abrasion of the bullet as it passes through the berm soil. A 0.6 m³ wood box was constructed with an opening at one end. The box was transported to a shooting range located in Ocala, Florida (OSR) (Fig. 3-1), where the experiment was performed. At the shooting range, the box was half filled with play sand. The sand was slightly compacted in the box to simulate a shooting range berm. The box was then set up, with the opening toward the shooter.

Two hundred rounds of 22-caliber non-jacketed bullets were fired into the sand in the box from a revolver pistol at a distance of approximately 7 meters. The bullets were immediately removed from the sand on site at the completion of the experiment with a 2 mm sieve. This was done immediately at the shooting range to impede any weathering of

the bullets that would result in further contamination of the sand beyond physical abrasion of the bullets as they passed through the sand. The sand was then transferred to 5 buckets that had been previously rinsed with nitric acid and deionized water to prepare for transport. The bullets were kept in plastic sample bags.

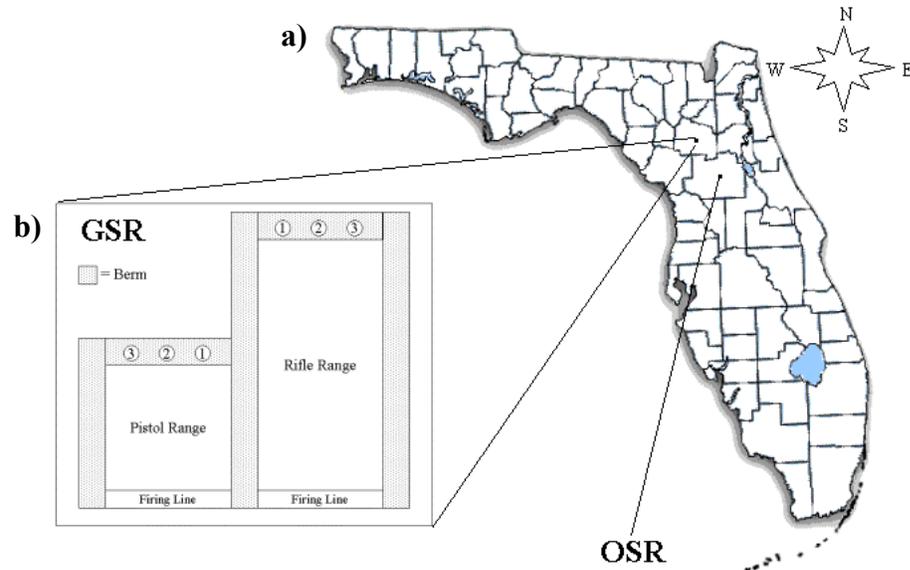


Figure 3-1 The position of the study sites in Gainesville (GSR) and Ocala (OSR), Florida (a), and schematic of GSR pistol and rifle range (b). Sampling locations on berms are numbered.

The bullets were weighed upon returning to the laboratory, and their mass was recorded. The sand was oven dried at 105°C for 1 day, weighed, and homogenized per bucket. Four sub-samples were taken from each bucket. Sand samples were digested using the hot-block digestion procedure (USEPA Method 3050a).

Field Sampling

To corroborate the above experimental results, soil samples were collected at a newly opened shooting range (GSR) in Gainesville, Florida (see Fig. 3-1). Figure 3-1

also shows a rough schematic of the shooting range, which had been in operation for 3 months prior to the first sampling. The pistol and rifle ranges are approximately 30 and 100 meters from the firing line to the berm. There are also berms that line on both sides of the ranges, separating the pistol from the rifle range. The soil on both ranges is primarily sandy, and vegetation is sparse on the range in the form of patches of grass. There is also very little vegetation on the berms at the end of the shooting range from which the samples were taken. Shrubs have been planted on the berms separating the two shooting ranges.

Soil samples were collected from three locations on the berm in both the pistol and rifle ranges (Fig. 3-1). Position numbers were located in the front of benches that were positioned along the firing line. At each location, samples were taken at 0.5, 1, 1.5, and 2.0 meters from the bottom of the berm. Soil samples were not taken from the same exact location on each trip, but from the same general area.

Four soil samples from each location height were collected using a soil probe, and then composited. Only the surface 15-cm of the berm soil was sampled to minimize the effect of whole bullets. It was hypothesized that the majority of bullets would go deeper into the berm soil than the surface 15 cm. Occasional bullets were found in the samples that were collected, but they were few, and visible weathering appeared to be at a minimum in most situations.

On the first visit, samples were collected at positions 1-3 on the pistol range, and position 1 on the rifle range (Fig. 3-1). On subsequent visits, samples were collected from each location. Sampling was continued at 4.5, 6.5, and 11 months to establish a

trend for the addition of abraded Pb in the newly opened shooting range as a function of time.

Field soil samples were transported back to the laboratory where they were air dried, sieved to 2-mm and digested using the hot-block digestion procedure (USEPA Method 3050a). Bullets and bullet fragments that were larger than 2 mm were manually removed and excluded from the digestion.

Laboratory Studies

Leaching test

Synthetic Precipitation Leaching Procedure (SPLP) was used to determine leachable Pb concentrations in the soils collected from the field abrasion experiment as well as field sampling. The SPLP method is believed to be an appropriate test for determining the mobility of Pb in the soils of shooting ranges (Peddicord, 1998; Reid and Cohen, 2000). It was done using extraction fluid No. 1 (pH 4.20 ± 0.05), which simulates unbuffered acid rain for sites east of the Mississippi. The SPLP Pb concentration was determined following the procedure of USEPA Method 1311 at a solid to liquid ratio of 1:20 (USEPA, 1994). This procedure is used to determine the mobility of inorganic analytes present in soils according to the USEPA

Abraded Pb weathering study

A study was performed to determine the weathering rate of abraded Pb, and the resulting weathering products. A Florida surface soil was collected, air dried, and sieved to 2-mm. The soil was elevated to 5% Pb by using a 53 μm Pb powder to simulate abraded Pb. Final treatments consisted of 150 grams of soil in 100 ml glass beakers. Triplicates of the soil were incubated at $25 \pm 2^\circ\text{C}$ for 7 days at field moisture capacity. Deionized water was added daily to maintain the soil at field moisture capacity. At the

end of seven days, samples were taken via straws that removed cores from the beakers. Samples were then allowed to air dry in weighing boats. Soil samples were sieved using a 53 μm sieve to filter Pb particles from soil.

The mineral components that passed through the 53 μm sieve were characterized by x-ray diffraction (XRD) using a computer-controlled X-ray diffractometer equipped with stepping motor and graphite crystal monochromator. Samples were scanned from 2 to 50° 2 θ using Cu K α radiation at 35 kV and 20 mA. XRD has been successfully used to determine Pb-minerals in the crust of pellets and bullets in shooting ranges (Cao et al., In Press; Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995).

Chemical analysis

Lead concentrations were determined by flame atomic absorption spectrometry (Varian 220 FS with SIPS, Varian, Walnut Creek, CA). Lead concentrations <1.0 mg L⁻¹ were reanalyzed by graphite furnace atomic absorption spectrometry (Perkin-Elmer SIMMA 6000, Perkin-Elmer Corp, Norwalk, CT). Quality control samples including a standard reference material for soil (2709 San Joaquin Soil) were used with sample digestion (US Department of Commerce National Institute of Standards and Technology, Gaithersburg, MD 20899).

Results and Discussion

Field Abrasion Experiment at Ocala Shooting Range (OSR)

Total and SPLP Pb concentrations from the 5 buckets of sand that were collected from the field abrasion experiment are presented in Table 3-1. The average Pb concentration on a mass basis for the 5 buckets was 91 mg kg⁻¹, which translated to 8 grams of abraded Pb for all 200 22-caliber bullets (data not shown). This represented

1.5% of the bullet mass being physically removed by abrasion. Total and SPLP Pb concentrations of samples removed from buckets 4 and 5 were significantly less than those of the other buckets (Table 3-1). These buckets represent the sand that was removed last from the wood box. Typically, the bullets did not penetrate past the surface 15 cm of sand. Therefore, the sand that was removed from the box last should have the least exposure to abraded metallic Pb.

Table 3-1 Total and SPLP Pb from field abrasion experiment

Sample	Total Pb (mg kg ⁻¹)	SPLP Pb (µg L ⁻¹)
Bucket 1	118.1 ± 32.7	71.7 ± 6.3
Bucket 2	126.4 ± 28.2	97.2 ± 4.6
Bucket 3	166.5 ± 30.3	109.1 ± 36.6
Bucket 4	14.9 ± 5.3	11.7 ± 0.6
Bucket 5	31.6 ± 5.3	15.9 ± 1.6

It should be noted that a gray powder was clearly visible in the white sand as it was being removed from the box at the range. This possibly consisted of a fine Pb powder that results from friction that occurs on the surface of the bullet as it passed through the sand. Also, the SPLP Pb concentration was considerably higher in these samples, with concentrations as high as 109 µg L⁻¹ (Table 3-1). All but one sample exceeded the 15 µg L⁻¹ critical level of a hazardous waste (USEPA, 1995). This suggests that the material that is removed from the bullet is immediately bioavailable, as well as being susceptible to leaching. It has previously been reported that the mineralized forms of Pb commonly found in shooting ranges are predominantly Pb carbonates [PbCO₃ and Pb₃(CO₃)₂(OH)₂] (Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995). These minerals are prone to leaching and are easily extracted by the SPLP method (Cao et al., In Press), in contrast to metallic Pb.

The high SPLP concentrations seen in these samples (Table 3-1) suggest that Pb minerals were present in the samples. This implies that the metallic Pb that had been physically removed from the bullet may have weathered and mineralized from the time of the experiment to the time at which the tests were performed. This may result from high weathering rate of this material due to the small size and increase in surface area compared to an intact bullet. Therefore, weathering studies were initiated to determine the weathering rate and products from abraded Pb. Based on the data it can be concluded that physical abrasion of Pb is a significant contributor to soil Pb contamination in shooting ranges, and may pose a more immediate concern for shooting range owners.

Field Sampling at Gainesville Shooting Range (GSR)

Total and SPLP Pb concentrations at 0.5, 1.0, 1.5, and 2.0 meters from the bottom of the berm at 2 positions of the pistol range are presented in Figures 3-2a and 3-3a. Total and SPLP Pb concentration at the first position on the rifle range are presented in Figures 3-2b and 3-3b.

The highest total Pb concentration from the pistol range berm soil was 193 mg kg^{-1} at 0.5 m (Fig. 3-2a). The highest total Pb concentration from the rifle range berm soil was $1,142 \text{ mg kg}^{-1}$ at 1.0 m (Fig. 3-2b). At each position, the lowest total (Fig. 3-2) and SPLP Pb (Fig. 3-3) concentrations were found at the 2-m height on the berm. It should be noted that Pb bullets and fragments above 2 mm were removed by sieving prior to digestion. Therefore, only abraded Pb and Pb solubilized or mineralized from bullets are included in total Pb data. The latter is hypothesized to be a smaller fraction of the total Pb due to previously reported rates of chemical weathering of Pb pellets. Jorgensen and Willems (1987) reported that within 6-13 years, only 5-17% of metallic Pb was transformed in Pb shotgun pellets. Lin et al. (1995) reported that in a period of 20-25

years, an average of only 4.8-16% of metallic Pb in these pellets had been transformed to lead carbonates [PbCO_3 and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] and PbSO_4 . These data would suggest that after only 3 months of operation, little transformation of Pb would have occurred in the bullets within the range. However, it should be pointed out that accelerated weathering of Pb pellets could occur in Florida shooting ranges due to its tropical/subtropical climate. Sampling of the newly opened shooting facility corroborated the results from the field abrasion experiment, confirming that physically abraded Pb was a significant contributor to Pb contamination in the soils of shooting ranges.

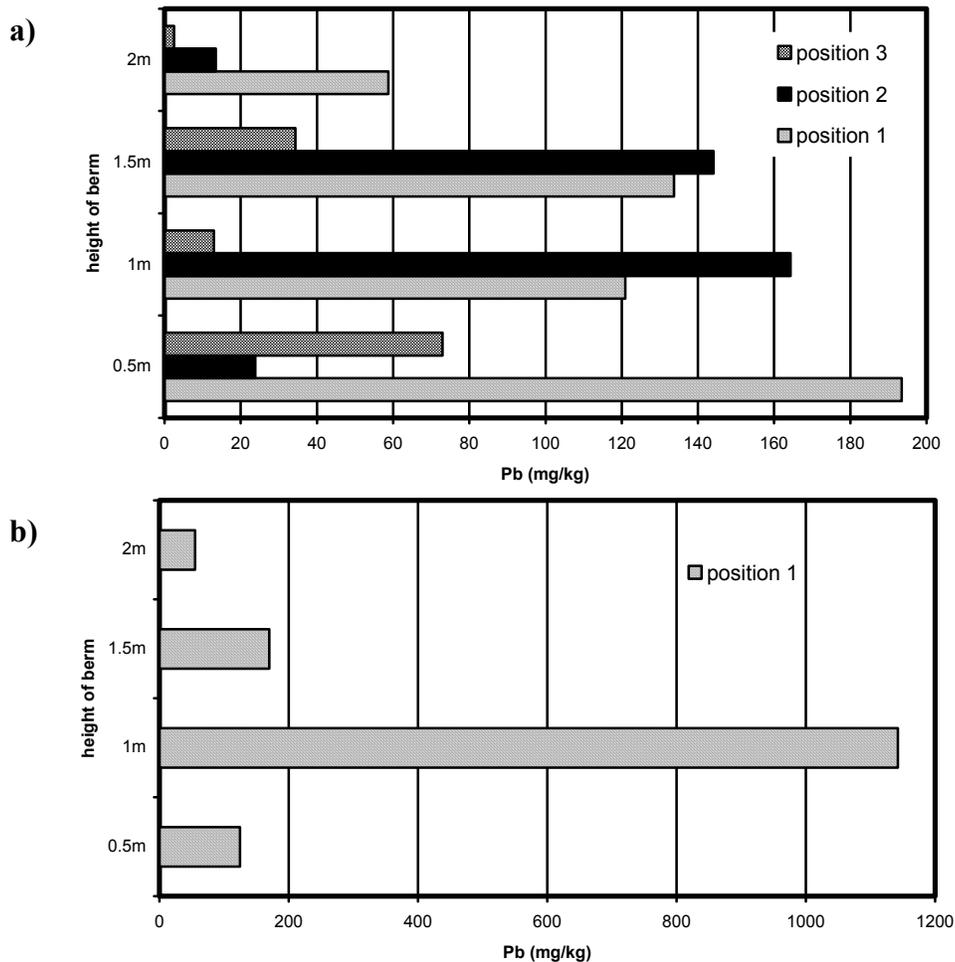


Figure 3-2 Total Pb concentration in GSR Pistol (a) and Rifle (b) Range berm soils after 3 months of operation.

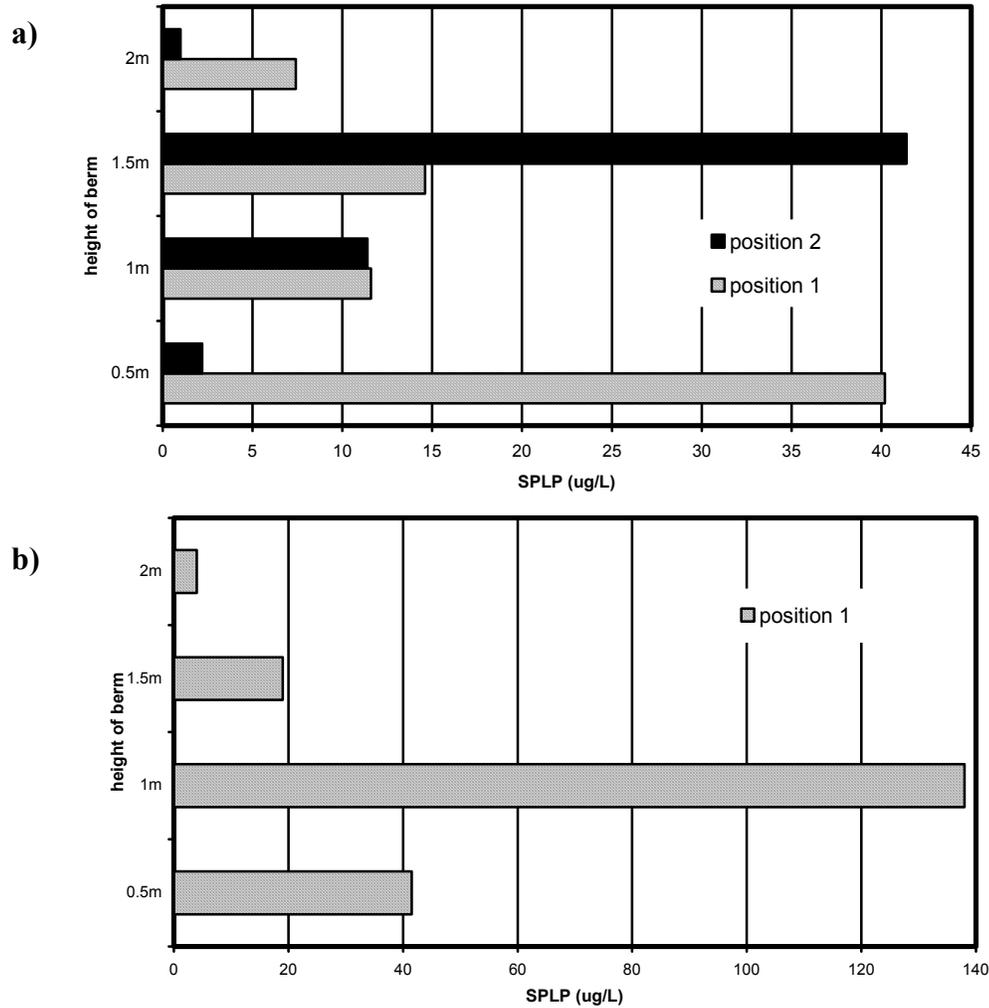


Figure 3-3 SPLP concentration in GSR Pistol (a) and Rifle (b) Range berm soils after 3 months of operation.

The SPLP Pb concentrations in the shooting range samples were lower in proportion to total Pb concentrations than what was seen in the abrasion experiment (Table 1 and Fig. 3-3). Three of the four samples (Fig. 3-3b) taken from the rifle range exceeded the $15 \mu\text{g L}^{-1}$ critical level of a hazardous waste (USEPA, 1995). However, only 2 samples (Fig. 3-3a) from the pistol range exceeded this level. The ratio of SPLP

Pb to total Pb in the abrasion experiment was on average 0.066%, while those in shooting range samples was on average 0.014% (data not shown). This can be significant and suggest that some of the Pb is being leached out from the soil in the shooting range. It has been suggested that the SPLP test is a more appropriate test than the Toxicity Characteristic Leaching Procedure (TCLP) when assessing Pb mobility in shooting range soils (Reid and Cohen, 2000). The difference between these two procedures involves the extraction fluid used. The SPLP solution simulates unbuffered acid rain water, whereas the TCLP solution simulates buffered landfill leachate. The later would be less representative of the shooting range soil environment.

Total Pb concentrations for the three positions on both pistol and rifle ranges for the 11 months of sampling are presented in Figures 3-4 and 3-5. Typically, total Pb concentrations in the rifle range were greater than that of the pistol range. This was probably due to more bullets being fired in the rifle range, and/or greater amounts of jacketed bullets being fired in the pistol range.

Jacketed bullets are Pb bullets that are coated in metallic Cu. A typical Pb bullet is composed of 97% metallic Pb, while a jacketed bullet is composed of 90% metallic Pb, with a 9% outer coating of metallic Cu (Lin et al., 1995; Tsuji and Karagatzides, 1998). It is hypothesized that jacketed bullets will decrease the amount of physically abraded Pb, because there will be no Pb on the surface of the jacketed bullet to be physically removed. In fact, visible observation of jacketed bullets found in samples revealed that in most cases the metallic Cu outer shell was still intact after being fired and entering the berm soil. The instances when this did not occur appeared to be when the jacketed bullet struck another bullet as it entered the berm.

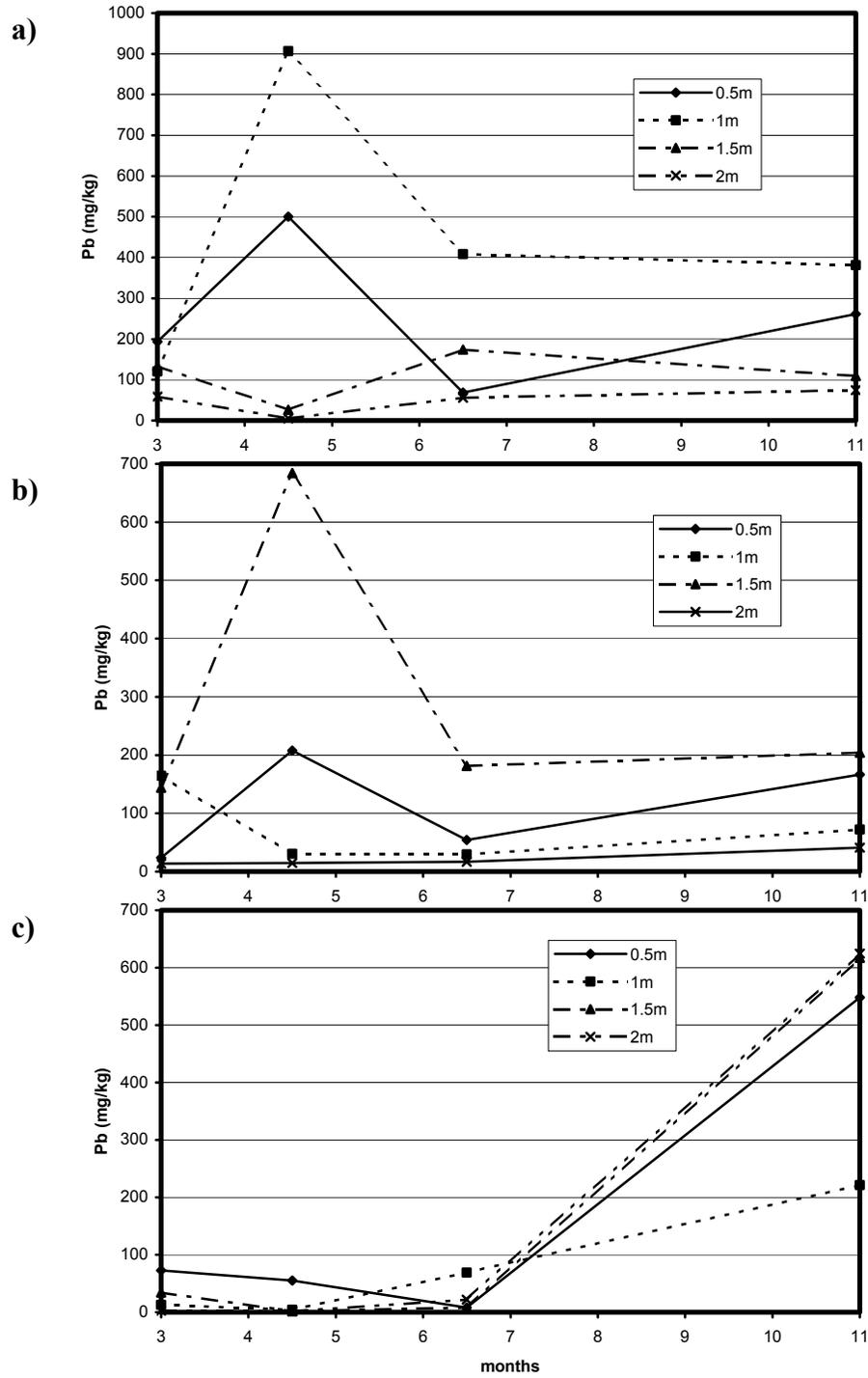


Figure 3-4 Total Pb concentration in GSR Pistol Range berm soil for position 1 (a) position 2 (b) and position 3 (c) as a function of time.

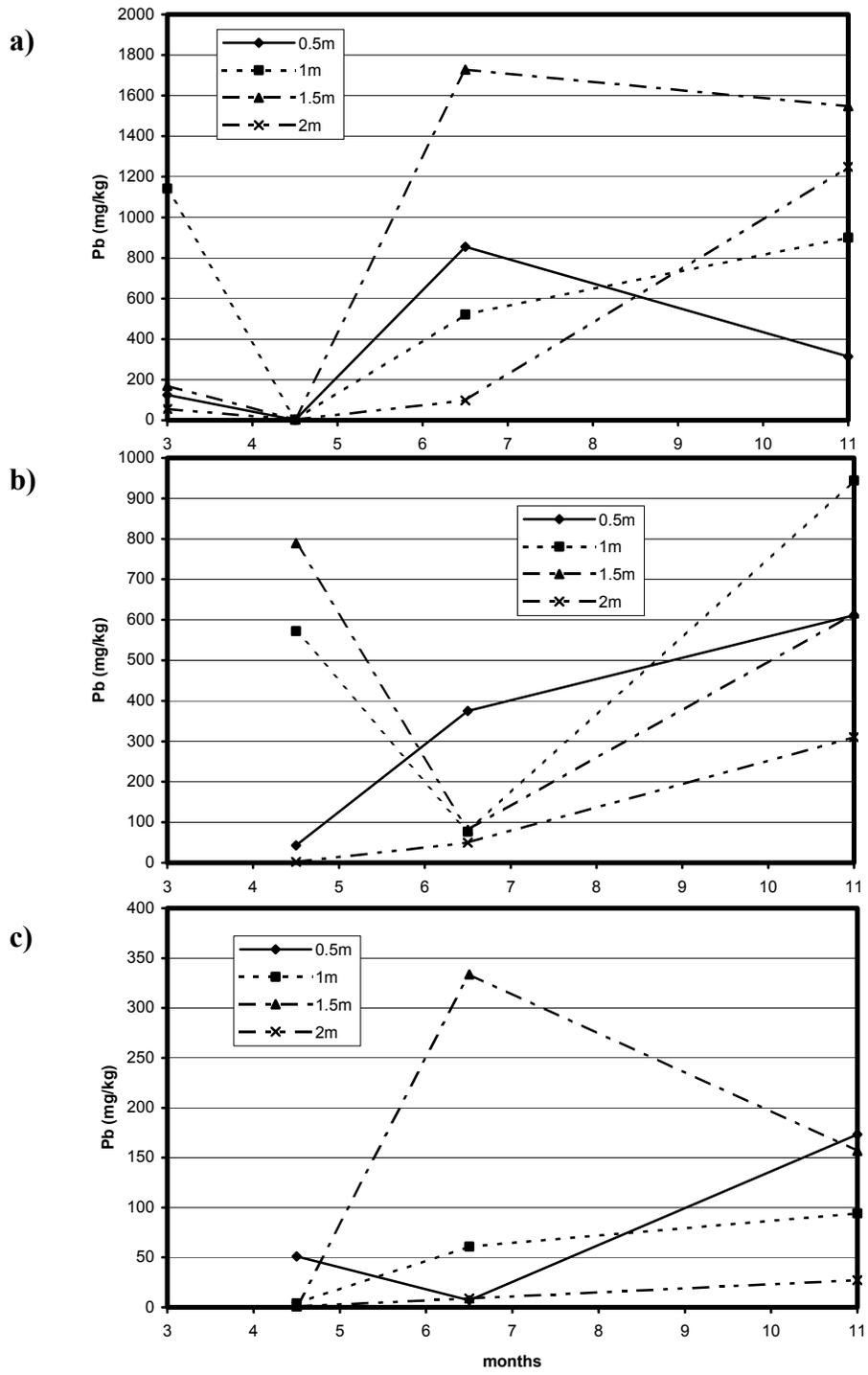


Figure 3-5 Total Pb concentration in GSR Rifle Range berm soil for position 1 (a) position 2 (b) and position 3 (c) as a function of time.

On each sampling trip, positions 1 at 0.5 m, 1.0 m and 1.5 meters sampling heights on the berm were among the highest in total Pb concentrations (Fig. 3-4 and 3-5). These positions are in front of firing line positions that are closest to the entrance of the shooting range, therefore it is hypothesized that there are more bullets fired at these positions. At 4.5 months, 0.5 m and 1 m heights at position 1, as well as 0.5 m and 1.5 m heights at position 2 in the pistol range were abnormally high compared to other months (Fig. 3-4a and 3-4b). This suggests that there are hot spots on the berm in which more rounds are entering resulting in higher concentrations of metallic Pb deposition. This was also the case at 4.5 months in the rifle range at 1 m and 1.5 m at position 2 (Fig. 3-5b).

One noteworthy aspect is that position 3 on the pistol as well as the rifle range consistently had the lowest total Pb concentrations with the exception of the pistol range position 3 samples on the 11-month sampling trip. All four berm heights showed a significant increase compared to the previous sampling trip (Fig. 3-4c). The considerable rise in Pb concentrations at position 3 on the final trip may be attributed to a fundraising day using full automatic weapon that was held at the range the week before the sampling trip. In this case, increase in total Pb was attributed to mostly Pb abrasion from bullets with minimum contribution from chemical weathering of the bullets.

Abraded Pb Weathering Study

Based on the field abrasion experiment, it was concluded that abraded Pb consists of a fine Pb powder that is removed from the bullet as it passes through berm soil. It was hypothesized that this material would weather at an accelerated rate based on its small particles size and high SPLP Pb. A weathering study was thus performed using metallic Pb powder ($< 53\mu\text{m}$) to simulate abraded Pb. Figure 3-6a shows the XRD pattern for the

metallic Pb used in this experiment, as well as standard hydrocerussite. The predominant metallic Pb peak from the powder was at a d-spacing of 2.84, as well as a secondary peak at $d=2.47$. Litharge (PbO) is also present in the Pb powder with small peaks (Fig. 3-6a) at $d=3.11$ and $d=2.81$. The predominant peak for hydrocerussite (Fig. 3-6a) is at $d=2.63$, with secondary peaks at $d=3.27$ and $d=3.60$.

Figure 3-6b shows an XRD pattern for the Pb in soil at field moisture capacity after one week. It is evident that while there are no apparent peaks for metallic Pb, hydrocerussite peaks are visible, as well as to a lesser extent cerussite (PbCO_3) and massicot (PbO) (Fig. 3-6b). This suggests that abraded Pb in shooting range is weathered at an accelerated rate and rapidly converted to Pb-minerals. The result of this experiment was a transformation of virtually all metallic Pb to hydrocerussite as well as other Pb minerals within 7 days.

Previous weathering rates of Pb shotgun pellets reported were 5-17% within 6-13 years (Jorgensen and Willems, 1987), and 4.8-15.6% within 20-25 years (Lin et al., 1995). The dramatic increase in weathering rate is most likely a result in the decrease in size of the material. When a Pb pellet weathers, the pellet is covered by a crust of the resulting weathered minerals (Jorgensen and Willems, 1987), resulting in a protective coat that inhibits further weathering of the inner metallic Pb. In contrast, the Pb powder is too small for a coat to form, and it is completely converted to Pb minerals.

This has implications when considering time periods and techniques for remedial action in shooting ranges. Typical techniques for the remediation of shooting range soils include mechanical sieving (USEPA, 2001), washing soils with EDTA (Samani et al., 1998), and soil amendments (USEPA, 2001).

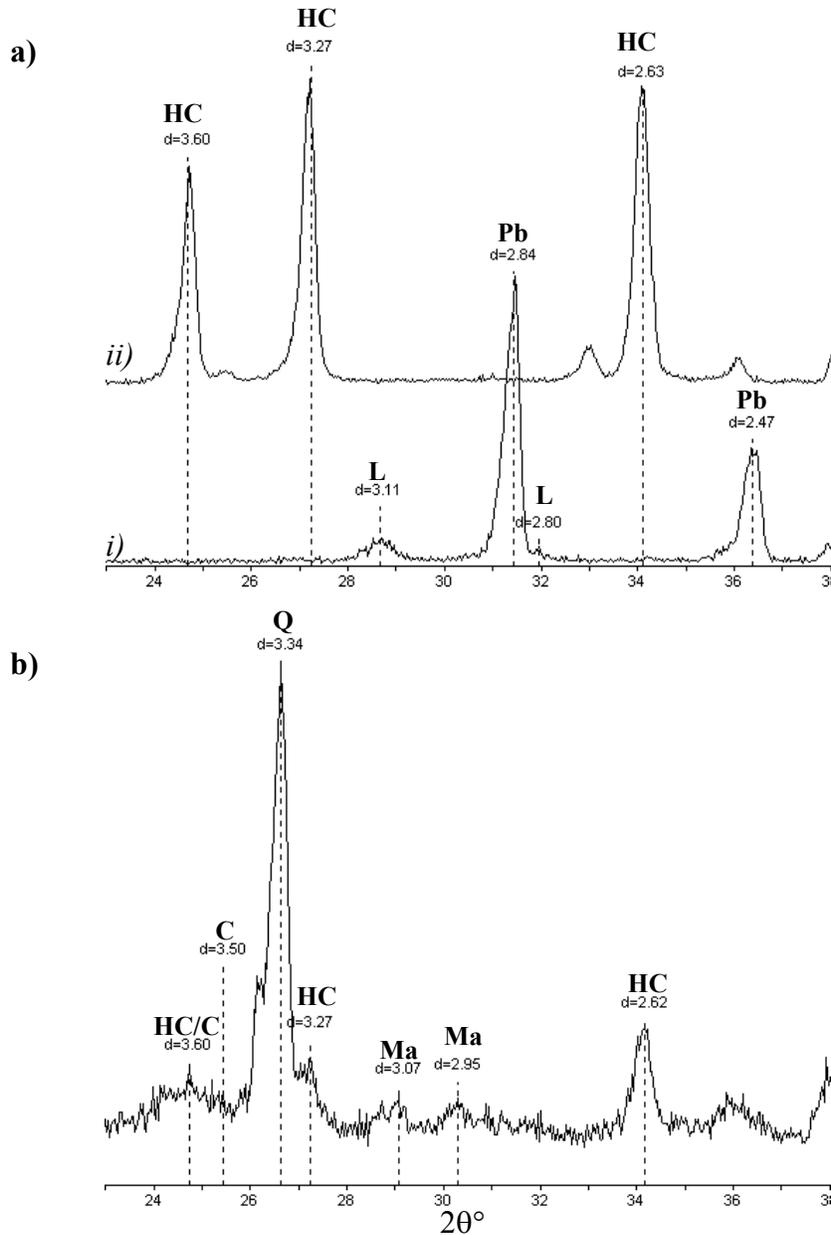


Figure 3-6 X-ray diffraction patterns for Pb powder (i) used in the incubation experiment, and standard hydrocerussite (ii) (a), and for Pb powder after 7 days of incubation in soil (b) at field moisture capacity: Q- quartz, HC- hydrocerussite, C- cerussite, L-litharge (PbO), Ma- massicot (PbO), Pb- metallic Pb.

Mechanical sieving is not applicable in remediating abraded Pb, because this material would easily pass through a sieve due to its size. Washing soils with EDTA would remove abraded Pb from soil; however, time would be an important issue when

using this remediation technique. Due to the rapid weathering rate of this material, washing the soil with EDTA on a regular basis would not be economically feasible. Ma et al (1995) demonstrated that the use of phosphate rock was a cost effective way to remediate Pb-contaminated soils, which may be applied to shooting range soils. Lead phosphates are extremely insoluble compared to other Pb compounds (Lindsay, 1979; Rickard and Nriagu, 1978), thus reducing the leachability of Pb in soils.

Conclusions

This study demonstrated that physical abrasion of Pb bullets passing through soil contributes substantially to soil Pb contamination in shooting ranges. The 22-caliber bullet used in the field abrasion experiment is the smallest caliber that is typically used in shooting ranges. An increase in Pb contamination in the form of physical abrasion would probably result from an increase in the size of caliber. This would be due to an increase in surface area of the bullet that is susceptible to physical abrasion as it passes through soil, as well as the fact that higher caliber rounds travel at higher velocities resulting in an increase in friction.

This fine form of metallic Pb is rapidly converted to Pb-minerals, and may pose a risk to groundwater contamination in shooting range soils. Our research has demonstrated that Pb contamination (elevation of Pb concentrations in soils) as well as Pb transformation (from inert metallic Pb to more reactive Pb compounds) in shooting range soils occurs rapidly in newly opened ranges. Therefore, it is important to develop best management practice to minimize the adverse impacts of Pb in all shooting ranges regardless of their ages.

CHAPTER 4
INFLUENCE OF SOIL PROPERTIES ON THE CORROSION/WEATHERING OF
METALLIC PB

Introduction

The rate and mechanisms by which metallic lead (Pb) transforms to more reactive Pb compounds in shooting range soils, as well as the influence these soils have on the transformation process has not been well documented. Weathering of Pb bullets leads to the accumulation of Pb in the soils of shooting ranges (Cao et al., 2003), and transformation of Pb bullets into soluble secondary minerals may provide a mechanism for mobilization of Pb into the vadose zone (Murray et al., 1997). Most importantly, weathering of Pb bullets may increase Pb bioavailability to organisms that come into contact with contaminated soils. The health of individuals that work and participate in recreational shooting at these ranges may be at risk due to the secondary minerals that are present in the Pb contaminated soil. Hemphill et al (1991) modeled the conditions within the human stomach, and concluded that the aqueous solubility of the Pb mineral in the soil consumed was an important factor in controlling the bioavailability of Pb.

Metallic Pb is only stable under extremely reducing conditions at high pH (Cao et al., 2003; Luo and Hong, 1997), and as a result, it undergoes atmospheric corrosion fairly readily (Graedel, 1994). In stability diagrams for metals, there exists a passive zone in which the stable solid is not the metal but an oxide, hydroxide or salt (Pourbaix, 1966). Under these conditions the metal becomes coated with these secondary minerals, which may form a non-porous film in which the metal is protected from solution, and/or a

porous film in which the metal is partially protected from solution (Pourbaix, 1966). In the case of Pb, there are only small regions for stability for surface oxides, and as a result Pb-oxides are typically too soluble to provide any protection against further corrosion (Graedel, 1994). However, Pb-carbonates, such as cerussite (PbCO_3) and hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] generally form a protective layer that prevents further weathering on the surface of metallic Pb (Edwards et al., 1997; Pourbaix et al., 1966).

These protective layers have been found on the surface of metallic Pb pellets and bullets in shooting range soils. White crust material found on the surface of Pb pellets and bullets were identified as secondary Pb minerals such as hydrocerussite, cerussite, anglesite (PbSO_4), and occasionally massicot (PbO) in shooting range soils in Sweden, Denmark, Canada, and the US (Craig et al., 1999; Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995; Murray et al., 1997; Scheuhammer and Norris, 1995). Lin (1996) found that the crust material consisted of two layers with the inner layer being predominantly massicot, and the outer layer being predominantly hydrocerussite. This suggested that Pb-oxides were being replaced by Pb-carbonates in the shooting range soils.

While anglesite was typically found in most shooting range soils, it was not found in shooting range soils in the state of Florida (Cao et al., 2003; Cao et al., In Press). The sulfate ion will compete with carbonate as a complexing agent in soils when the carbonate ligand is depleted (Jorgensen and Willems, 1987; Lin et al., 1995), suggesting that carbonate was in excess in the Florida shooting range soils.

Immobilization of heavy metals via soil amendments has been used extensively in remediating contaminated soils. It has been suggested that soil amendments such as

phosphorus and lime may be a potential approach towards limiting Pb solubility and mobility in shooting range soils (USEPA, 2001). The relationship between solubility of Pb and soil pH has been well documented. The addition of lime to soil has been shown to reduce Pb availability due to an elevation in soil pH (Geebelen et al., 2002), however it may increase Pb solubility at high pH due to the formation of organo-Pb complexes (Turpeinen et al., 2000). Lead phosphates are extremely insoluble, and may be important in controlling Pb in soil environments (Nriagu, 1974). Phosphorus in the form of rock phosphate (Cao et al., 2002; Ma and Rao, 1999; Ma et al., 1995; Ma et al., 1997a) has been used to effectively reduce the solubility of Pb in contaminated soils.

Bullet fragments (<2mm) have been found in shooting range soils, and are believed to contribute to total Pb concentration in these soils (Astrup et al., 1999; Rooney et al., 1999). Results from Chapter 3 concluded that this Pb material likely comes from abrasion of Pb bullets as they pass through soil, and that this form of Pb weathers at an accelerated rate (Hardison Jr. et al., In Review). The objectives of the present study were: 1) to determine the mechanisms by which metallic Pb weathers in Florida surface soils, 2) to determine the influence of soil properties on the rate of corrosion of metallic Pb as well as the final weathering products, and 3) to determine the impact of soil amendments on the rate of corrosion of metallic Pb, the solubility of Pb, and the final weathering products.

Materials and Methods

Metallic Pb Weathering Incubation Study

Metallic Pb powder (Alfa Aesar, MA, 99.9% metals basis, <53 μ m) was used in determining the effects of soil properties and soil amendments on the weathering of Pb in Florida surface soil (FSS) and a commercial sand (CS). The FSS used in all studies was

collected; air-dried and sieved to less than 2 mm. In all studies except the amendment study, the FSS was sieved to be a soil fraction greater than 106 μm . While the soil was sieved to greater than 106 μm , some silt fraction remained in soils, and is evident through quartz and kaolinite peaks that exist in XRD patterns after separation. CS was air dried and sieved to be a soil fraction less than 2 mm and greater than 106 μm . The term sand refers to the product and not the size fraction of CS, and is also evident in quartz and kaolinite peaks that exist in XRD patterns after separation. An excess of soil was used and sub-samples were taken in determining the influence of moisture level, sand and soil amendments. Smaller amounts of soil were used and plots were sacrificed for sampling in determining the influence of soil organic matter (SOM), soil pH, and soil microbes. The total Pb concentration in the FSS and CS was initially at trace levels (Table 4-1), and therefore Pb minerals already present in soil were likely not a factor in mineralogical results.

Table 4-1 Selected physicochemical properties of soil used in this study

	Pb _T ^a (mg kg ⁻¹)	P _T (mg kg ⁻¹)	pH ^b	OM ^c (%)
FSS ^e	3.69 ± 0.09	498 ± 21	4.16 ± 0.05	ND
FSS (> 106 μm)	ND ^d	ND	4.52 ± 0.04	1.812 ± 0.001
H ₂ O ₂ digested FSS	ND	ND	4.74 ± 0.01	0.149 ± 0.002
CS ^f	3.63 ± 0.60	ND	7.41 ± 0.17	ND

^a Total concentration (Nitric acid and Hydrogen Peroxide digestion)

^b pH was determined with a 1:1 ratio of soil/water

^c Organic matter

^d Not determined

^e Florida Surface Soil

^f Commercial Sand

Metallic Pb weathering in soils at different moisture levels

The FSS (>106 μ m) was elevated to 5% Pb using Pb powder. The final treatments consisted of 100 grams of soil in glass beakers. Triplicates of the amended soils were incubated at $25 \pm 2^\circ\text{C}$ for 5 days at both field moisture capacity and 80% field moisture capacity. Soil moisture was adjusted on a daily basis using deionized water. At the end of 5 days, samples were taken via a straw that removed cores from the beaker. The soil samples were allowed to air-dry overnight in weighing boats. Soil samples were sieved using a 53 μ m sieve to filter Pb particles from soil for XRD analysis. This size sieve was used for separation since metallic Pb powder placed in soil was of a size fraction less than 53 μ m.

Metallic Pb weathering in a commercial sand

The CS (>106 μ m) was elevated to 5% Pb using Pb powder. The final treatments consisted of 250 grams of soil in glass beakers. Triplicates of the amended soils were incubated at $25 \pm 2^\circ\text{C}$ for 5 days at both field moisture capacity and 80% field moisture capacity. Sand was incubated for 62 days as previously discussed, and sampling and separation of Pb from soil was conducted prior to XRD analysis.

Metallic Pb weathering in soils without organic matter

Soil organic matter was removed from the FSS by digestion in H_2O_2 (Kunze and Dixon, 1986). Soil organic matter was determined for Florida soil as well as the digested Florida soil using the Walkley-Black procedure (Nelson and Sommers, 1982). The percent organic matter was significantly lowered (Table 4-1) compared with the initial concentration of organic matter in the FSS. The digested soil was air-dried and sieved to less than 2 mm, and greater than 106 μ m. The soil was elevated to 5% Pb using Pb

powder. The final treatments consisted of 30 grams of soil in glass beakers. Soil was incubated for 12 days as previously discussed. The sampled soil was allowed to air-dry overnight in weighing boats. Separation of Pb from soil was conducted prior to XRD analysis.

Metallic Pb weathering in soils of different pH

The pH of the FSS was adjusted with the addition of 0.1 M NaOH until the desired pH was reached. The pH-adjusted soil was air dried and sieved to less than 2 mm, and greater than 106 μm . The soil was elevated to 5% Pb using Pb powder. The final treatments consisted of 30 grams of soil in glass beakers. Soil was incubated for 9 days as previously discussed. The sampled soil was allowed to air-dry overnight in weighing boats. Separation of Pb from soil was conducted prior to XRD analysis.

Metallic Pb weathering in the absence of soil microbes

The above FSS ($>106\mu\text{m}$) was placed in beakers. Moisture was added to the soil, and the container was capped with glass wool and aluminum foil to prevent microorganisms from reentering the soil. The soil was then autoclaved in the container twice over a period of two days. A control FSS was also included without autoclaving. The soils were elevated to 5% Pb using Pb powder. The final treatments consisted of 30 grams of soil in glass beakers. Soils were incubated for 4 days as previously discussed, with soils being sacrificed for samples. The beakers were capped with glass wool and aluminum foil throughout the incubation process to prevent the outside input of microorganisms. The adjustment of soil moisture was not necessary during the short incubation periods because of capping. Separation of Pb from soil was conducted by wet sieving prior to XRD analysis.

Metallic Pb weathering in soils with amendments

Three treatments were performed at 2 different soil moisture levels. Final treatments consisted of 150 grams of soil in glass beakers. The FSS was elevated to 5% Pb by using Pb powder. The treatments used were an untreated FSS, FSS treated with 2% CaCO₃, and FSS treated with 2% phosphate rock. The phosphorus concentration (Table 4-1) in the FSS prior to the addition of phosphate rock was slightly lower than what is typically seen in Florida surface soils. The amended soils were incubated at 25 ± 2°C for 77 days at both field moisture capacity and 80% field moisture capacity. Soil moisture was adjusted on a daily basis using deionized water. Treatments were in triplicate. This resulted in a total of 16 treatments.

Samples were taken via straws that removed cores from the beakers. Samples were then allowed to air dry over night in weigh boats. Water-soluble Pb was extracted by the method detailed in Ma and Rao (1997b). Soil pH was determined from the samples by equilibrating a 1:1 mixture of soil to deionized water, and measuring the pH of the supernatant. The soil samples were allowed to air-dry overnight in weighing boats. Separation of Pb from soil was conducted prior to XRD analysis.

Identification of Weathered Products

The mineral components that passed through the 53 µm sieve were characterized by x-ray diffraction (XRD) using a computer-controlled X-ray diffractometer equipped with stepping motor and graphite crystal monochromator. Samples were scanned from 2 to 50° 2θ using Cu Kα radiation at 35 kV and 20 mA. XRD has been previously used to determine Pb-minerals in the crust of pellets and bullets in shooting ranges (Cao et al., In Press; Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995). Aggregates removed at

the end of the soil amendment study were broken apart, and the finer material was suspended in solution via ultrasonification for characterization.

Chemical Extraction and Analysis

Soil organic matter was determined using the Walkley-Black procedure (Nelson and Sommers, 1982). Total phosphorus was measured colorimetrically with a Shimadzu 160U spectrometer using the molybdate/ascorbic acid method (Olsen and Sommers, 1982). Soil samples were air dried, sieved to 2 mm and digested with HNO₃ and H₂O₂ using the hot-block digestion procedure (USEPA Method 3050a). Lead concentrations were determined by flame atomic absorption spectrometry (Varian 220 FS with SIPS, Varian, Walnut Creek, CA). Lead concentrations <1.0 mg L⁻¹ were reanalyzed by graphite furnace atomic absorption spectrometry (Perkin-Elmer SIMMA 6000, Perkin-Elmer Corp, Norwalk, CT). Quality control samples including a standard reference material for soil (2709 San Joaquin soil and 2710 Montana soil) were used with sample digestion (US Department of Commerce National Institute of Standards and Technology, Gaithersburg, MD 20899). Satisfactory precision and accuracy were required to be within ± 20%.

Data Analysis

Water-soluble Pb and soil pH results are expressed as an average of triplicates; except soil pH at weeks 0, 1 and 2, which are duplicates; with standard deviation. The effects of treatments were determined by analysis of variance with the generalized linear model procedure using the Statistical Analysis System (SAS Institute Inc.) computer program. Significance was tested at the 0.01 probability level.

Results and Discussion

Impact of Soil Moisture

The XRD patterns (Fig. 4-1) for Pb powder that has been incubated in soil at 80% field moisture capacity and field moisture capacity for 5 days suggest that soil moisture played a significant role in the transformation of metallic Pb to more reactive Pb compounds in the Florida surface soil. Peaks in both patterns (Fig. 4-1) are seen for litharge (PbO) and hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$], however the soil incubated at 80% field moisture capacity still shows a considerable peak for elemental Pb. This suggests that all metallic Pb powder has been converted in the treatment at field moisture capacity, but not all metallic Pb is converted in the treatment at 80% field moisture capacity.

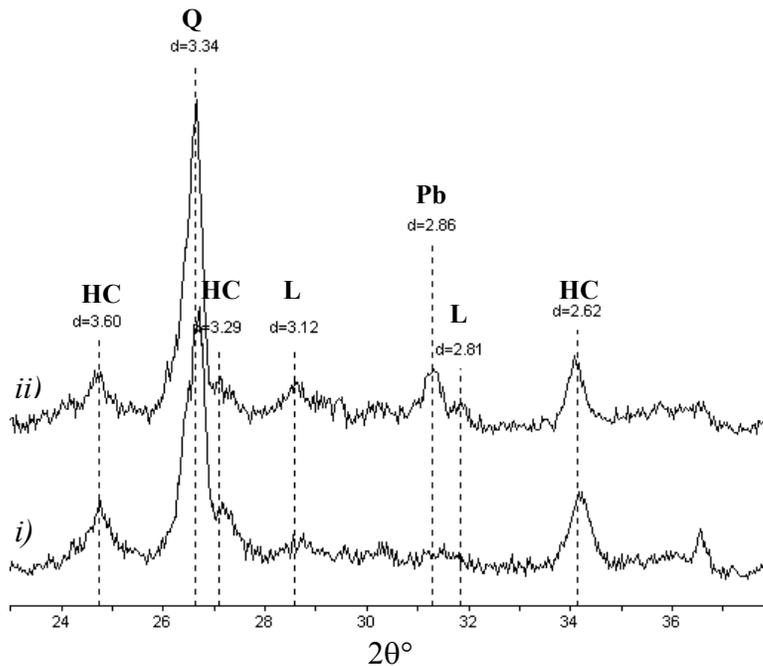


Figure 4-1 X-ray diffraction patterns for Pb powder after 5 days of incubation in Florida surface soil at field moisture capacity (i) and at 80% field moisture capacity (ii): Q- quartz, HC- hydrocerussite, L- litharge (PbO) Pb- elemental Pb.

This was most likely due to less water coating the surface of metallic Pb in the 80% field moisture capacity treatment. It has been shown that the corrosion of Pb is

dependent on a water layer that forms on the metal surface, which acts as a medium for the diffusion of atmospheric gases, which attack the metal surface and leads to the formation of secondary Pb minerals and subsequent dissolution of Pb into solution (Blair, 1998; Graedel, 1994; Rocca and Steinmetz, 2001). It must be noted that pure water is not corrosive to metallic Pb, but the oxidizing agents that diffuse through this water layer are what lead to the formation of secondary Pb minerals (Pourbaix, 1966). The impact of moisture on the corrosion of metallic Pb has been seen in the natural environment in the form of damp roof conditions that have been shown to increase the failure of Pb roofs on historical buildings due to 'condensation corrosion' (Edwards et al., 1997).

Metallic Pb Weathering in Commercial Sand

The XRD patterns (Fig. 4-2a) for Pb powder that has been incubated in autoclaved CS at both 80% field moisture capacity and field moisture capacity show that while peaks for minium (Pb_3O_4) and litharge (PbO) have formed after only 7 days; there is still a considerable peak for elemental Pb suggesting very little Pb transformation had taken place. It should be noted that while a considerable peak existed for minium in the sand incubated at 80% field moisture capacity, no such peak existed in the sand incubated at field moisture capacity. Based on the previous results, that suggested that an increase in moisture increased the weathering rate of metallic Pb, it suggests that minium is possibly an early weathering product of metallic Pb, and not stable enough to persist in the soil after a longer period of time. XRD patterns for Pb powder that has been incubated in autoclaved CS at both 80% field moisture capacity and field moisture capacity (Fig. 4-2b) shows that even after 2 months the majority of the Pb is still in the form of elemental Pb with only a small peak for litharge (PbO).

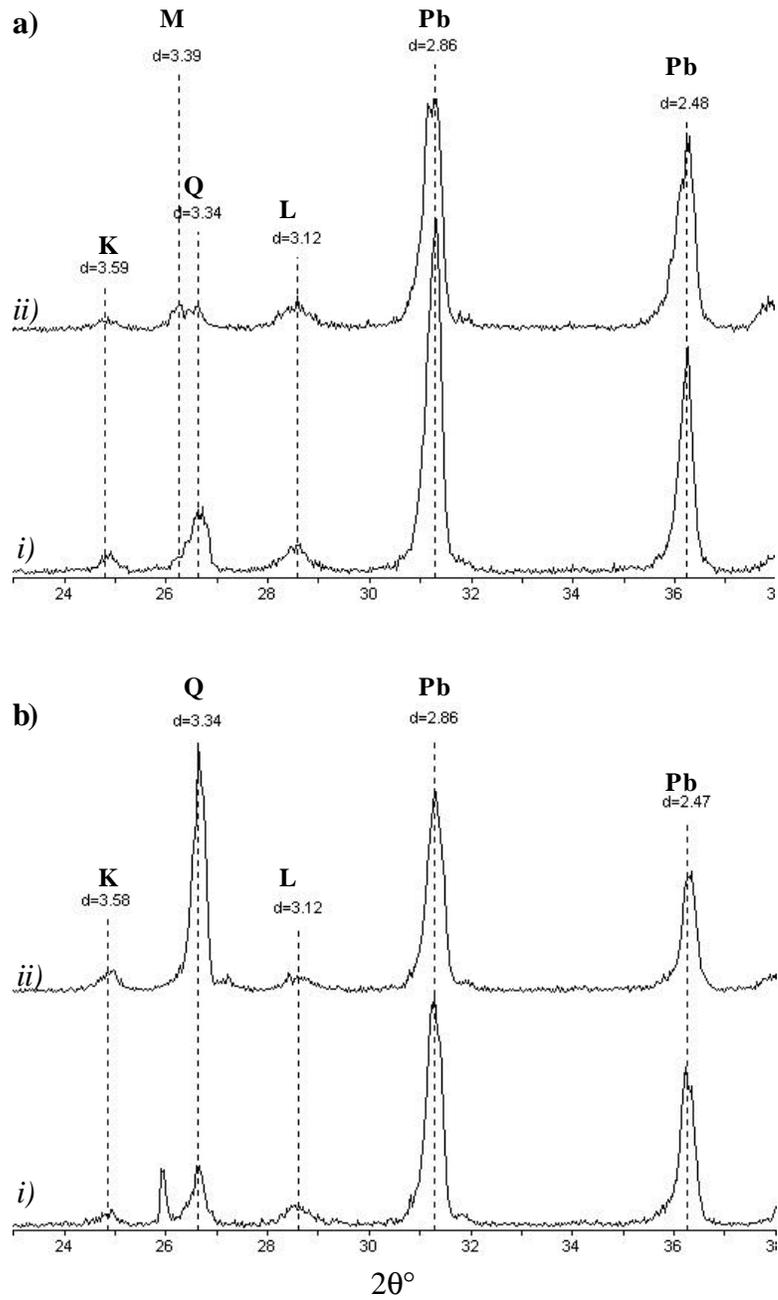


Figure 4-2 X-ray diffraction patterns for Pb powder after 7 days (a) and 62 days (b) of incubation in play sand at field moisture capacity (i) and at 80% field moisture capacity (ii): M-minium (Pb_3O_4), K-kaolinite.

This suggested that transformation of metallic Pb to more reactive Pb compounds was somehow inhibited in the autoclaved CS. It was shown in Chapter 3 that when Pb is incubated in soil, the complete transformation of Pb powder from metallic Pb to more reactive Pb compounds is rapid (Hardison Jr. et al., In Review). At this point the question became, why Pb was not transforming in the commercial sand. It was concluded that the differences between the CS and the FSS, which could be responsible for inhibition of Pb corrosion, include: soil organic matter, soil pH, and soil microorganisms (which elevates CO₂ in soil).

Impact of Soil Organic Matter

It was determined, that soil organic matter in the FSS used in these incubation experiments was 1.8% (Table 4-1). The soil organic matter in the FSS that had been digested in H₂O₂ was reduced to 0.15% (Table 4-1) prior to incubation. The XRD patterns for Pb powder after it had been incubated for 5, 9, and 12 days in the FSS in which organic matter had been removed are presented in Figure 4-3. Significant peaks for elemental Pb are seen in each of the XRD patterns at 5, 9, and 12 days (Fig. 4-3). It is evident that after 12 days no peaks (Fig. 4-3) for secondary Pb minerals exist, except possibly minium.

These results suggest that the absence of soil organic matter impedes the transformation of metallic Pb to PbO and Pb-carbonates. This was most likely due to a decrease in CO₂ concentration in this soil as a result of the removal of organic matter. Lin et al (1995) noted that within soil rich in humus, the rate (15.6%) of Pb transformation to secondary minerals within a 20-25 year span, increased compared to mineral soils (4.8%) over that same time period.

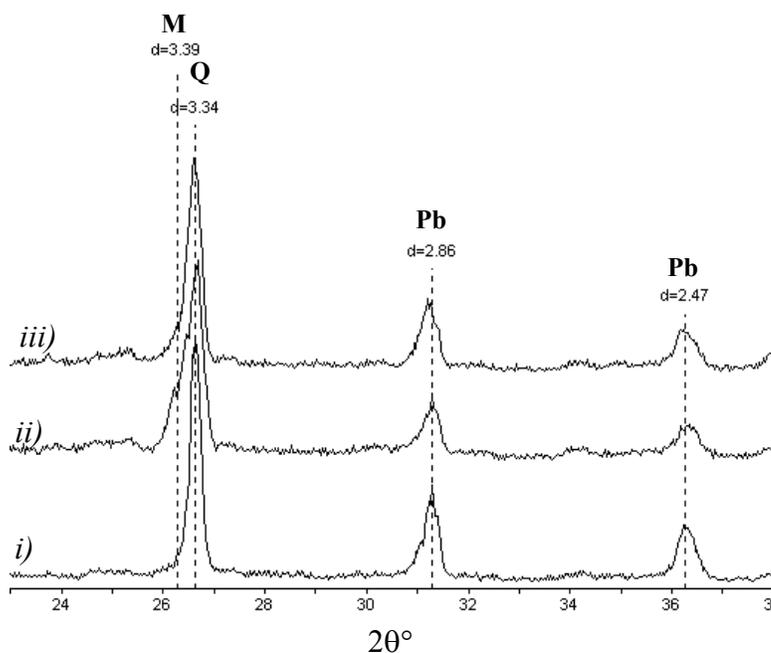


Figure 4-3 X-ray diffraction patterns for Pb powder after 5 days (i) 9 days (ii) 12 days (iii) of incubation in Florida surface soil in which organic matter had been removed at field moisture capacity.

Microbial communities in soil are responsible for the oxidation of organic matter, which produces CO_2 . As a result, CO_2 in soil air is often several hundred times more concentrated than what is typically found in the earth's atmosphere (Brady and Weil, 2000). Therefore, soil will be a more ideal environment for the corrosion of Pb than any other environment. This also suggests that as organic matter content increases in soil, the rate of metallic Pb transforming to Pb carbonates will also increase (Lin, 1996). The high CO_2 concentration in soil also influences which Pb secondary minerals are stable.

Lindsay (1979) concluded that due to the high concentration of CO_2 in soils, cerussite is the more stable mineral.

In addition, organic acids (such as formic and acetic acid) have been implicated in the accelerated corrosion of Pb bullets in shooting range soils (Jorgensen and Willems, 1987), as well as the accelerated corrosion and failure of Pb roofs on historic buildings

(Edwards et al., 1997; Graedel, 1994). This is most likely due to the destruction of the protective layer formed on the surface of metallic Pb by secondary Pb minerals in the weathering process (Edwards et al., 1997). Chelating agents such as EDTA and humic and fulvic acid may also bind with Pb, and subsequently remove it from the surface of metallic Pb exposing new surface (Jorgensen and Willems, 1987).

Impact of Soil pH

The transformation of Pb to reactive Pb-carbonates was influenced considerably by the elevation in soil pH. The XRD patterns (Fig. 4-4) for Pb powder that has been incubated in soils at pH 4.5, 6.1, and 8.5 for 9 days show that as soil pH increased the amount of Pb that was transformed was dramatically decreased. The patterns for Pb powder that was incubated in soil at pH 4.5 (Fig. 4-4) follow a similar trend as previous results, with metallic Pb rapidly transforming to hydrocerussite. However, as pH increases to 8.5 less Pb was converted (larger Pb peaks), and less hydrocerussite was produced. Soil pH also influenced the final Pb-mineral that was produced as metallic Pb weathered. The predominate peaks of Pb powder incubated in the soil at pH 4.5 are Pb-carbonates (Fig. 4-4), whereas in the soil at pH 8.5, the predominate peaks for secondary Pb minerals are Pb-oxides. It appears that at elevated soil pH, Pb weathered to Pb-oxide, and the transformation then stopped there. This agrees with the following chemical equations of the proposed Pb transformation to secondary Pb minerals in the Florida surface soil.



The chemical transformation of PbO to hydrocerussite must consume protons. At higher pH the hydronium ion concentration is low, and protons are in demand. Therefore, as these XRD plots (Fig. 4-4) depict, the transformation of metallic Pb to hydrocerussite was impeded by the lack of protons at a higher soil pH, and only Pb-oxides were formed. Gee et al (1997) concluded that soil pH is a more important factor than age for determining the weathering characteristics of slag material at a particular site.

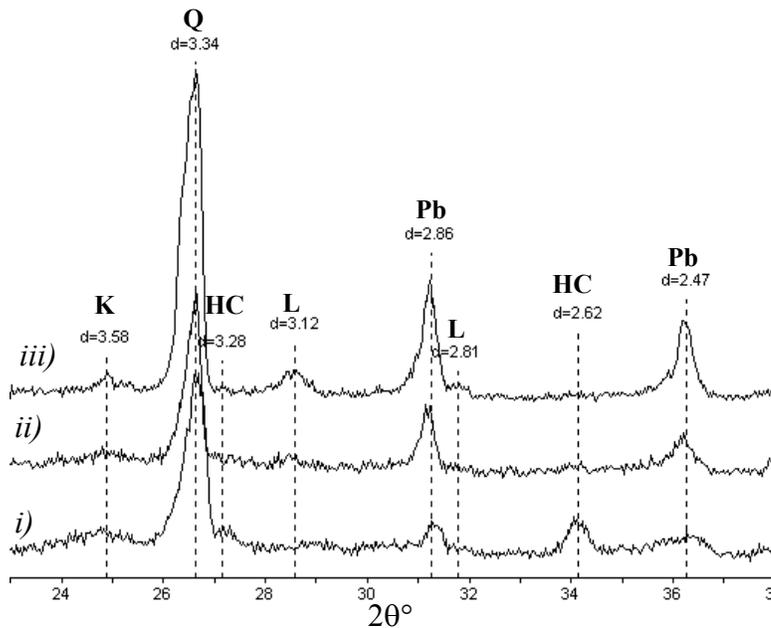


Figure 4-4 X-ray diffraction patterns for Pb powder after 9 days of incubation in Florida surface soil in which the soil pH had been adjusted to pH 4.8 (i) pH 6.1 (ii) and pH 8.5 (iii) at field moisture capacity.

In addition, a lower pH will also influence the rate of metallic Pb transformation to secondary minerals by solubilizing these secondary minerals and exposing new metallic Pb surfaces for corrosion. Soil pH plays an important role in the solubility of Pb in shooting range soils (Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995). The

dissolution of both cerussite and hydrocerussite require 2 moles of H^+ per mole of Pb when CO_2 is the product (Jorgensen and Willems, 1987). Thus, at higher pH values the solubility of Pb is repressed (Zimdahl and Skogerboe, 1977), and Pb minerals are more stable and may form a protective layer, which will prevent further corrosion.

This influence of soil pH on the corrosion of metallic Pb in soil was not seen in soil absent of organic matter. The soil that had been digested in H_2O_2 had a considerably low pH of 4.74 (Table 4-1). However, the fact that no corrosion of metallic Pb (Fig. 4-3) was taking place, suggests that soil organic matter is a more important factor than soil pH in the weathering of Pb. This is important when considering that soils in the state of Florida typically are sandy with low soil organic matter and a low soil pH. This should also be considered when trying to develop best management practices for shooting range operators.

Impact of Soil Microorganisms

Removing soil microorganisms had little effect on the rate of transformation of metallic Pb powder in the FSS, or the resulted weathering products. In both the control (Fig. 4-5a) and the autoclaved soil (Fig. 4-5b), XRD patterns for metallic Pb followed a similar trend over time. However, while results suggest soil microorganisms do not directly effect the transformation of metallic Pb to secondary Pb minerals, previous results discussed suggest soil microorganisms influence Pb transformation indirectly through metabolic activities that produce CO_2 .

While these patterns have shown no influence of soil microorganisms on the corrosion of metallic Pb, they do give a good indication of the progression and rate of corrosion of metallic Pb to more reactive Pb compounds.

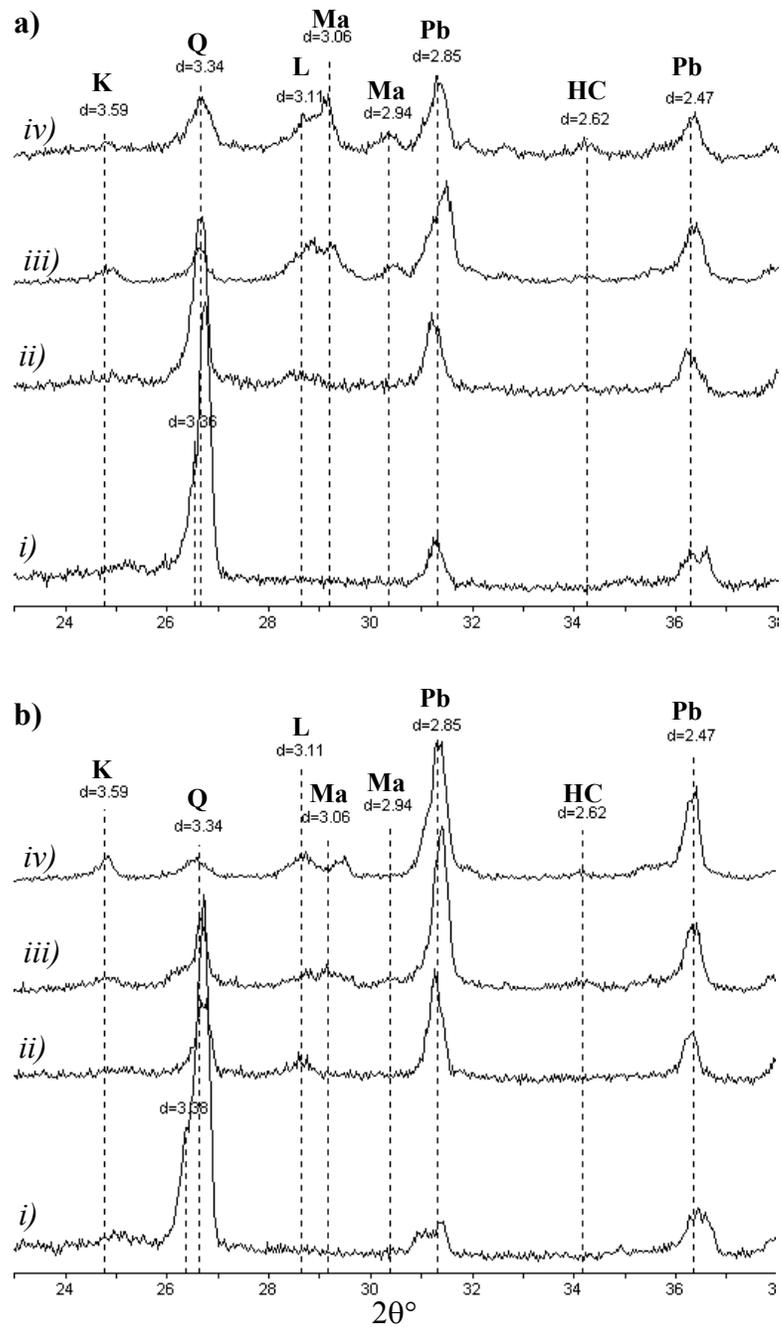


Figure 4-5 X-ray diffraction patterns for Pb powder after incubation in reference Florida surface soil (a) and autoclaved Florida surface soil (b) for 1 day (i) 2 days (ii) 3 days (iii) and 4 days (iv) at field moisture capacity: Ma- massicot (PbO).

It is seen that after 1 day there has been little or no Pb conversion, except for a possible elbow (Fig. 4-5b) on the quartz peak, which would suggest the formation of minium. After 2 days, peaks for litharge may be seen in both treatments (Fig. 4-5a,b), however the majority of Pb still remains in the metallic form. After 3 days (Fig. 4-5a,b) of incubation, 2 forms of Pb-oxide have formed (litharge and massicot), and a slight hydrocerussite peak. At the end of 4 days (Fig. 4-5a,b) of incubation, hydrocerussite has increased, and metallic Pb powder incubated in both the control soil as well as the autoclaved soil appeared to be weathering at the same rate with similar weathering products. In addition, quartz peaks decrease in intensity with time (Fig. 4-5a,b). This is possibly associated with the cementing capacity of secondary Pb minerals that will be discussed in greater detail within the soil amendment study.

Results suggest that metallic Pb weathered in the following progression in the Florida surface soil: $\text{Pb}^0 \rightarrow \text{Litharge (PbO)} \rightarrow \text{Massicot (PbO)} \rightarrow \text{Hydrocerussite } [\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]$. While peaks exist for minium in Figure 4-2a as well as elbows to quartz peaks after 1 day in Figures 4-5 a and b, it has been previously suggested that it is impossible for the higher oxidation state Pb-oxides to form in soils due to the high oxidation potentials required (Lindsay, 1979). For this reason it was hypothesized that minium had formed on the surface of metallic Pb powder prior to being amended to the soil. However, XRD patterns as seen in Fig 3-6a for the metallic Pb powder show peaks for only metallic Pb and litharge. Minium is obtained through the oxidation of PbO or alkaline solutions of divalent Pb (Pourbaix et al., 1966); therefore it is possible that litharge already present in the metallic Pb powder was oxidized to minium when placed

into moist soil. The fact that litharge is typically the first secondary Pb mineral formed from metallic Pb powder are consistent with previous results (Graedel, 1994).

While it is not evident from this study that soil microorganisms influence the corrosion of metallic Pb in shooting range soils, it should be noted that Pb might influence microbial activity due to toxicity. Manninen and Tanskanen (1993) suggested that Pb contamination in shooting range soils may affect microbial activity by limiting enzymatic activity, which will result in a buildup in incompletely decomposed organic matter. This suggests that Pb may inhibit its own transformation due to toxicity of soil microorganisms, which will limit CO₂ in soils. However, previous studies have shown that the resistance of soil bacteria to Pb is typically greater than resistance to other heavy metals (Davies, 1995). This is most likely due to the lower solubility and bioavailability of Pb compared with these other heavy metals (Davies, 1995).

Based on the influence of soil properties, a three-step mechanism (Fig. 4-6) for the corrosion of metallic Pb in the Florida surface soil is proposed. First of all, a layer of water on the surface of metallic Pb is necessary for the diffusion of gases that will react with metallic Pb. Oxygen diffuses through this layer of water and oxidizes metallic Pb to the divalent Pb form, which is typically found in the environment (Brown et al., 1999). Gaseous CO₂ will dissolve within the aqueous surface layer and form carbonate ligands that will react with Pb oxides to form Pb carbonates (Graedel, 1994). Dissolution will occur to secondary Pb minerals due to acidity within the soil water (Luo and Hong, 1997), or through ligands and chelating agents that will react with secondary species (Jorgensen and Willems, 1987).

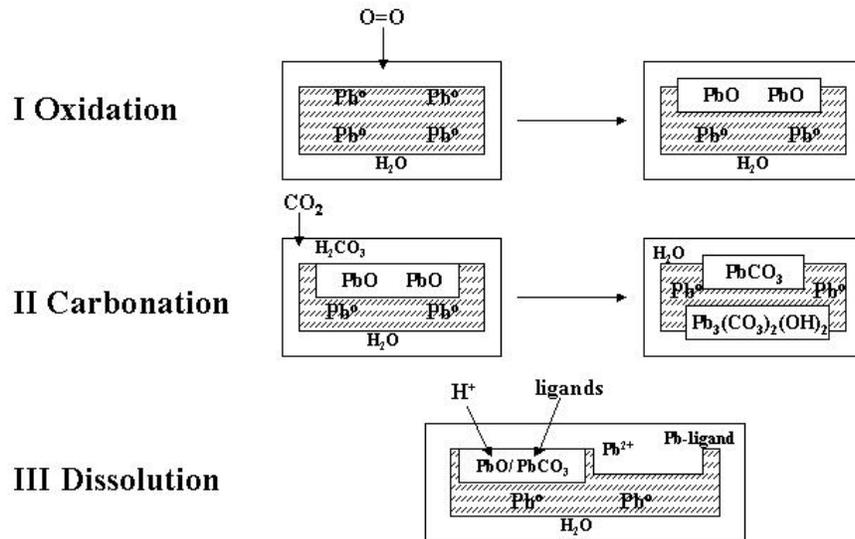


Figure 4-6 Proposed three-step mechanism for the weathering of metallic Pb in the Florida surface soil.

Impact of Soil Amendments

Soil pH was monitored over a period of 11 weeks in different soil treatments at both moisture levels (Figure 4-7a and b). Triplicate samples were taken from each treatment at each moisture level. The pH (Fig. 4-7a,b) of the soil rose considerably in all treatments with the addition of the Pb powder within the first week. Soil pH (Fig. 4-7a,b) then decreased to below a pH of 7 before increasing back above 7 after week 6. However, no significant difference in soil pH (Fig. 4-7a,b) was seen between treatments or moisture levels over the period of 11 weeks. This suggests that Pb ultimately buffers the soil at these high concentrations in soil. Elevated soil pH has been associated with contamination of soils with Pb shot (Astrup et al., 1999; Chen et al., 2001), as well as historical smelting sites (Gee et al., 1997). As previously discussed, the conversion of

oxide to carbonate and the dissolution of these solids could ultimately cause pH to increase (Luo and Hong, 1997). Gee et al (2001) concluded that the role of Pb secondary minerals as natural metal ion buffers is often overlooked. Therefore, it appears that metallic Pb has a natural liming effect when soil is contaminated with Pb bullets, and it will ultimately prevent further corrosion due to this process.

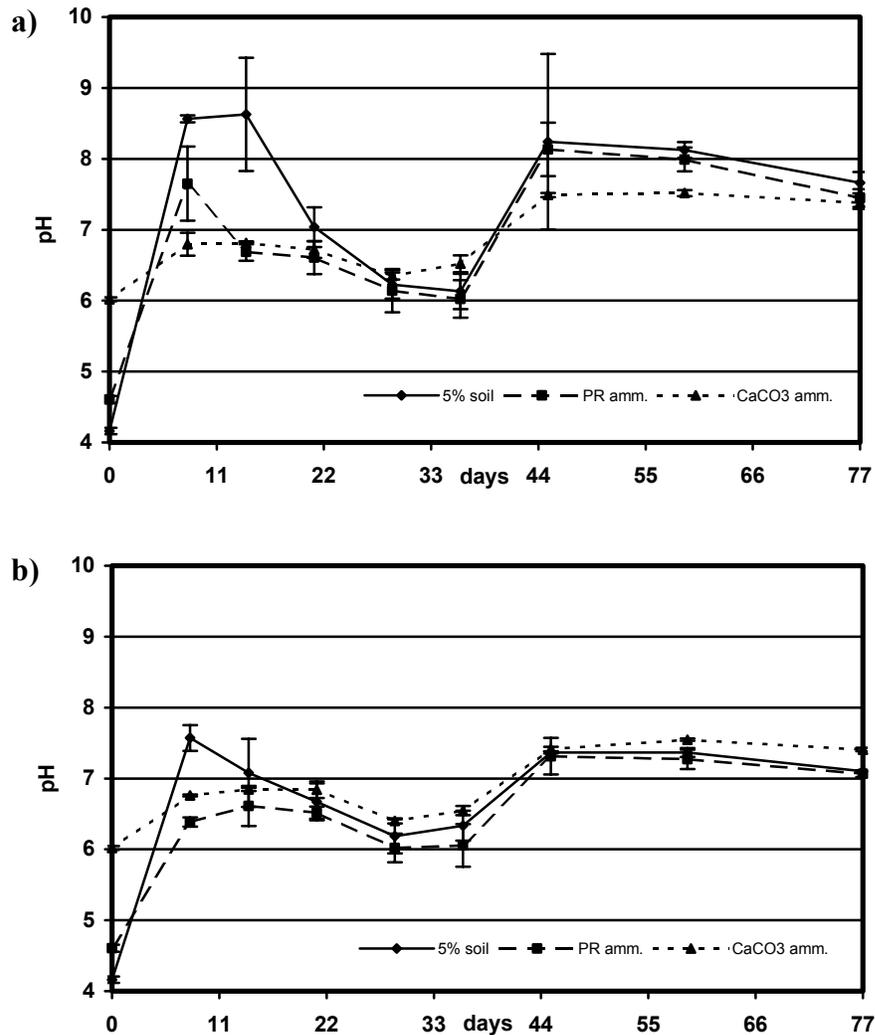


Figure 4-7 Effects of amendments on pH at field capacity (a) and 80% field capacity (b) moisture level over a 77-day incubation period.

Water-soluble Pb was also monitored over the 11-week incubation study at two moisture levels (Figure 4-8 a and b). Triplicate samples were taken from each treatment at each moisture level. There was no significant difference between treatments at field moisture capacity (Fig. 4-8a) over time. However, there was a significant difference between treatments at 80% field moisture level (Fig. 4-8b) over time with the 5% metallic Pb unamended soil typically having the highest concentration of water-soluble Pb. The 5% metallic Pb/phosphate rock amended soil typically had lower values (Fig. 4-8b) of water-soluble Pb, and the 5% metallic Pb/CaCO₃ amended soil generally had the lowest water-soluble Pb over time. From these results, it appears that moisture level played a role in that at field moisture capacity there was no impact of treatments on Pb solubility. However, at 80% field moisture capacity level, phosphate rock lowered solubility of Pb, while the soil amended with CaCO₃ had the lowest solubility of Pb. It should be mentioned that one water-soluble Pb result from the un-amended, at field capacity at 36 days, was thrown out as an outlier after graphing Q/Q plots with the data.

Past studies have shown that the presence of carbonate species in soils leads to elevated pH levels, which enhance the precipitation of metal-carbonates (Maskall and Thornton, 1998). Zimdahl and Skogerboe (1977) concluded that liming soil reduced the solubility of Pb due to the formation of Pb-carbonate, and subsequently reduced the availability of Pb to plants. The addition of lime has also been shown to reduce DTPA-extractable Pb content during a composting period in metal contaminated sewage sludge (Fang and Wong, 1999). However, in the present study, the formation of Pb-carbonates was suppressed at higher pH since transformation from Pb-oxides to Pb-carbonates requires available protons. This suggests that the suppression of Pb solubility at high pH

in these soils is a result of lack of transformation from metallic Pb to Pb-carbonates.

Liming soils may also increase solubility of Pb. Turpeinen et al (2000) found that in soils of a former shooting range, liming significantly increased the water-soluble and bioavailable Pb in amended soils. They concluded that it was most likely due to an increase in dissolved organic carbon in the soil as pH increased.

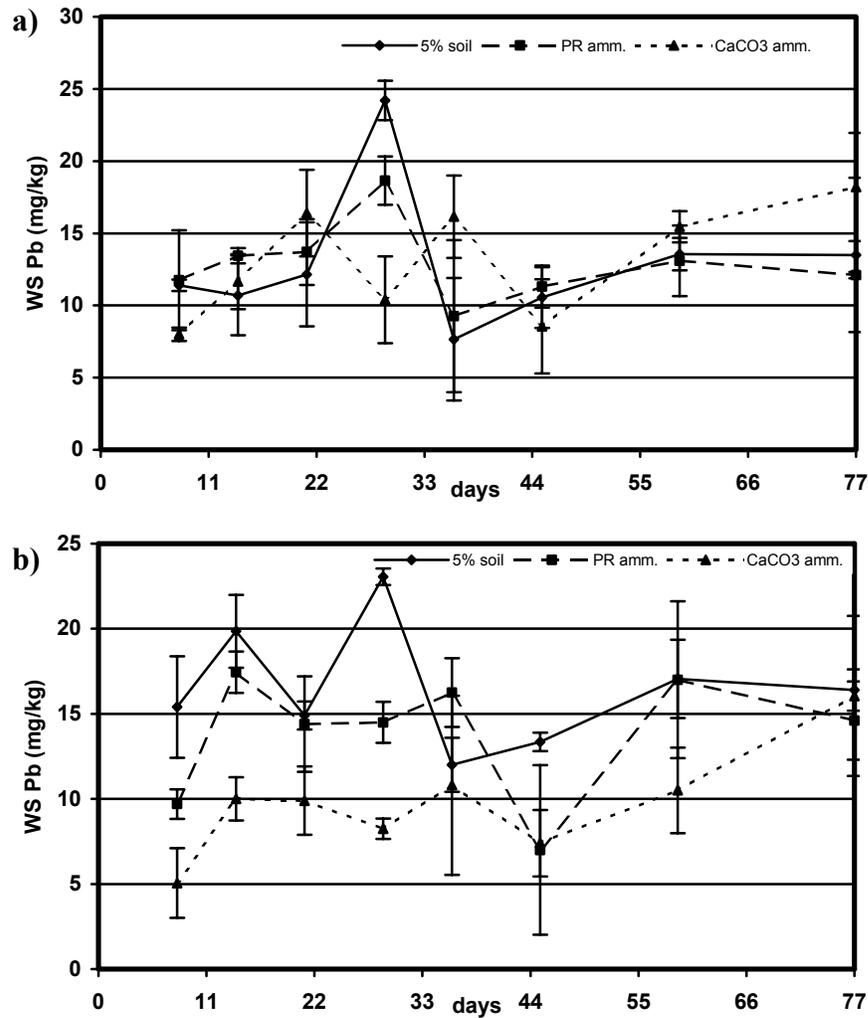


Figure 4-8 Effects of amendments on water soluble Pb at field capacity (a) and 80% field capacity (b) moisture level over a 77-day incubation period.

Figure 4-9 shows an XRD pattern for metallic Pb powder taken from the unamended and phosphate rock amended treatments at field moisture capacity after one week. It is evident that while there are no peaks for metallic Pb in the treatments, peaks are visible for hydrocerussite, massicot, litharge and possibly minium in both the unamended and phosphate rock amended soils.

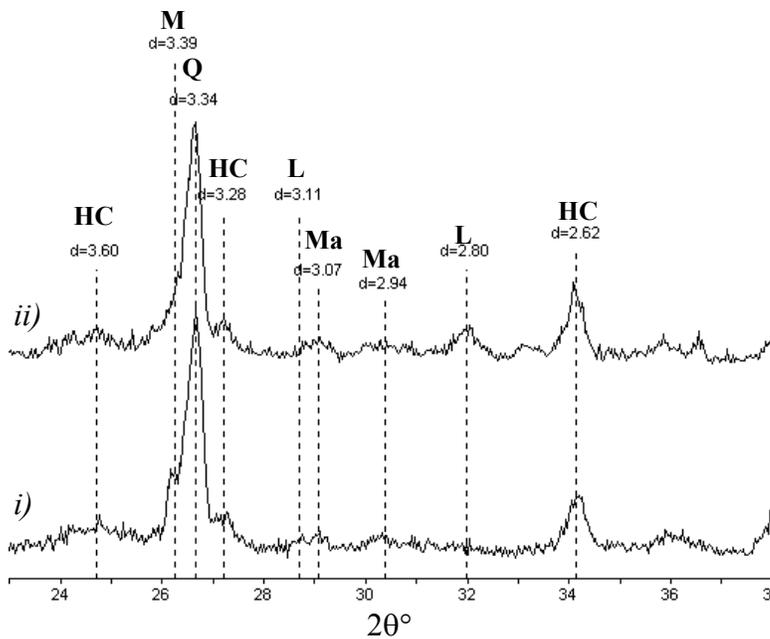


Figure 4-9 X-ray diffraction patterns for Pb powder after 7 days of incubation in Florida unamended surface soil (i) and Florida surface soil amended with ground rock phosphate powder (ii) at field moisture capacity.

This suggests that the dramatic increase in pH in all treatments, which is seen in Figures 4-7a and b, is a result of the transformation of virtually all metallic Pb to hydrocerussite. This is a reaction that has previously been described as one that consumes protons, which accounts for the rise in pH. It should be noted that neither metallic Pb nor hydrocerussite was seen in the XRD pattern (not shown) for the CaCO_3 -amended soil. This is most likely due to the fact that calcite overwhelmed the sample

used for the XRD pattern. This did not occur in the phosphate rock amended soil, since the phosphate rock was a larger soil fraction and did not pass through the sieve.

After 11 weeks of incubation, aggregates formed in the soil, were removed for characterization. Figure 4-10b shows a 2X magnification of one of the aggregates that were removed from the soil. From this picture, it can be seen that the aggregates appeared to be composed of quartz that has been cemented together by a precipitated material. Figure 4-10a shows the XRD patterns for the finer material that cemented these aggregates. It should be noted that observation of the aggregates concluded that those removed from the unamended as well as the phosphate rock amended soils were much more unyielding, whereas the aggregates from the lime amended soil broke apart very easily. The XRD pattern (Fig. 4-10a) shows that the aggregates in the unamended and phosphate rock amended soils were composed of quartz being cemented together by hydrocerussite, massicot as well as possibly pyromorphite (Pb-phosphate) in the phosphate rock amended soil, whereas the sample collected from the CaCO_3 amended soil (not shown) was dominated by calcite.

The absence of a clear distinguishable secondary peak for pyromorphite does not allow a definitive conclusion that pyromorphite has formed. However, the size of the primary peak suggests that pyromorphite appears to have been formed in the phosphate rock amended soil, and that based on previous studies, phosphorus amendments may be considered as a possible approach for immobilizing Pb in shooting range soils.

Chloropyromorphite is the least soluble mineral under most anaerobic and aerobic conditions (Nriagu, 1974), as well as more importantly over a wide pH range (Traina and Laperche, 1999).

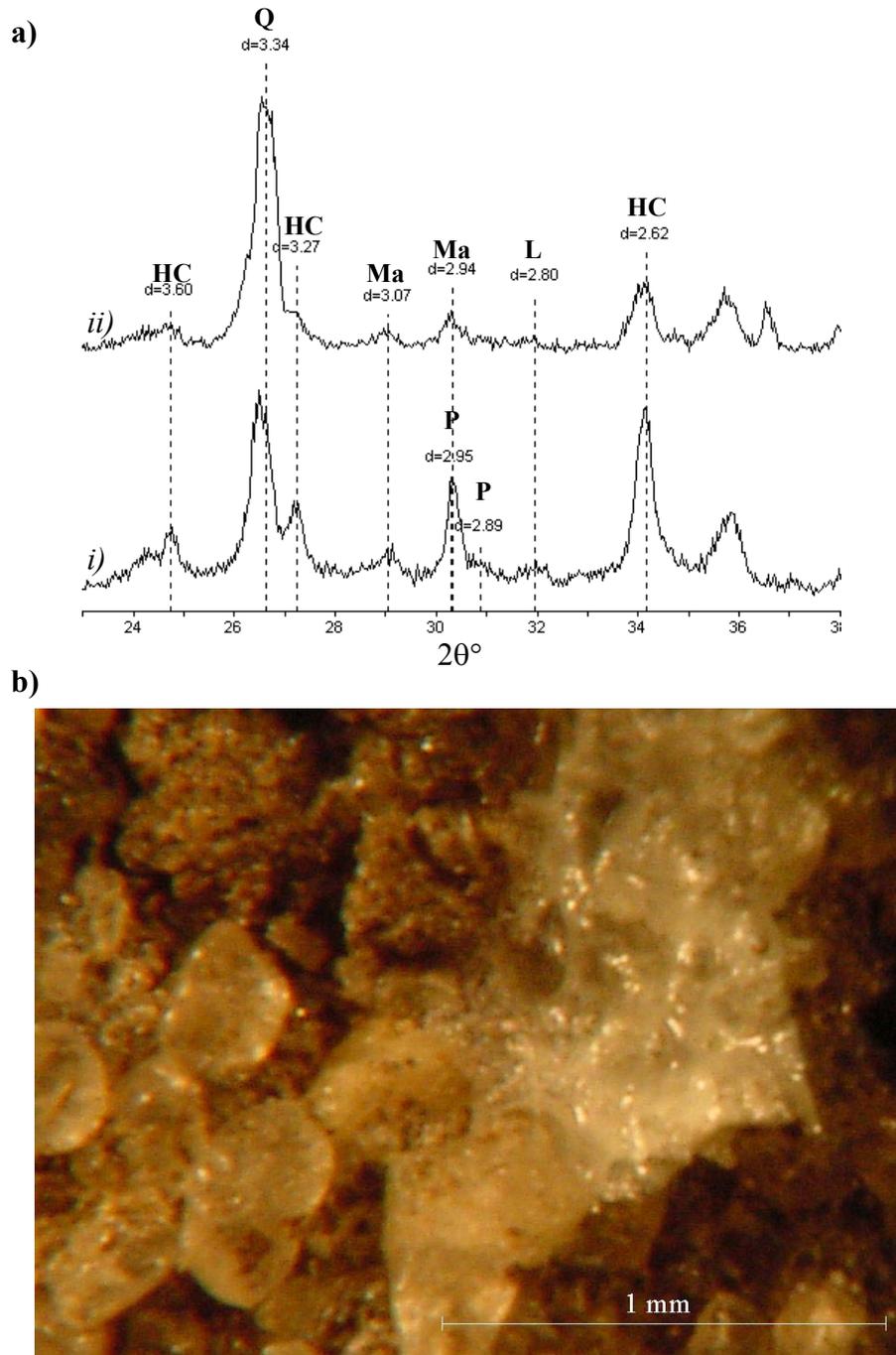


Figure 4-10 X-ray diffraction patterns of precipitated cementing material (a) from the aggregates removed from Florida surface soil amended with ground rock phosphate (*i*) as well as the Florida unamended surface soil (*ii*) and a 2x magnification of one aggregate (b) that were removed after 11 weeks of incubation: P-Pyromorphite (Pb-phosphate)

Amending soils with phosphate rock has previously been identified to significantly reduce the solubility of Pb in different types of Pb contaminated soils (Cao et al., 2002; Ma and Rao, 1997b; Ma and Rao, 1999; Ma et al., 1997a). In addition, hydroxypyromorphite has been found in the phosphorus rich berm soil of a shooting range in Florida (Cao et al., 2003; Cao et al., In Press).

While pyromorphite appeared to form in the phosphate rock amended soils in the present study, Pb solubility was not reduced significantly when compared with other treatments. This suggests that the dominant Pb species in these soils are still Pb-carbonates. This is most likely due to the highly insoluble nature of phosphate rock. Ma et al (1995) concluded that the primary mechanism for the immobilization of Pb by phosphate rock was through dissolution of phosphate rock, and then precipitation of pyromorphite. In soils of the present study, it would also be necessary to dissolve Pb-carbonate species already present. The dissolution of phosphate rock and Pb-carbonates could be accomplished by simultaneous additions of phosphoric acid as well as phosphate rock. While studies have shown phosphoric acid may not be as effective as phosphate rock in immobilizing Pb in soils (Cao et al., 2002; Hettiarachchi et al., 2001), it is possible, that when used in conjunction immobilization of Pb will be more effective.

Conclusions

Soil properties and amendments influenced the corrosion and weathering products of Pb. It was found that an increase in soil moisture level increased the rate at which metallic Pb was transformed to Pb-carbonates. When soil organic matter was absent from soil, there was no corrosion or transformation of Pb to secondary minerals. Soil pH significantly influenced the weathering products as metallic Pb corroded. At a higher soil pH, only Pb-oxides were formed. Soil microorganisms did not play a direct role in the

transformation of metallic Pb. However, it is hypothesized that they played an indirect role due to metabolic activities that oxidized organic matter and elevated CO₂ in soil.

Soil amendments influenced the secondary minerals produced as a result of Pb weathering. Water-soluble Pb was decreased in soil treated with CaCO₃ and phosphate rock. After 11 weeks of incubation, aggregates, composed of quartz cemented by secondary Pb minerals formed in both untreated and phosphate rock amended soils. This study clearly demonstrated that soil properties and amendments influence the corrosion of metallic Pb in soils. Best Management Practices for shooting range soils may be established with these factors in mind.

CHAPTER 5 DESORPTION OF PB IN TWO FLORIDA SHOOTING RANGE SOILS

Introduction

In the past, the translocation of Lead (Pb) from contaminated soils has typically not been of concern due to the highly insoluble nature of Pb compounds. In fact, Pb generally shows the highest retardation of any heavy metal in soils, and therefore, has a long residence time in soils compared to other pollutants (Davies, 1995; McBride, 1994; Rickard and Nriagu, 1978; Strawn and Sparks, 2000). This should be especially true in shooting range soils, where the weathering of metallic Pb bullets has been shown to increase the pH in these soils (Astrup et al., 1999; Chen et al., 2001). Soil pH has been shown to greatly influence the adsorption and movement of heavy metals in soils (Matos et al., 2001). In addition to pH, soil conditions such as redox potential, elevated anion concentrations, and cation exchange capacity (CEC) may greatly affect the mobility of Pb in soils (McBride, 1994; Pourbaix et al., 1966).

Complexation with organic matter is a very important aspect of the chemistry of heavy metals in soils (Stevenson, 1982). Lead and Cu are the most rapidly adsorbed and strongly bound metals by soil organic matter, and are also the most slowly desorbed (McBride, 1994). Zimdahl and Skogerboe (1977) concluded that the majority of Pb immobilized in soil is associated with organic matter. However at a high soil pH, organic acids such as humic (HA) and fulvic (FA) acid dissociate in soil by reaction with base (McBride, 1994). Soil organic matter then becomes more soluble as dissociation increases the negative charge of the individual organic particles (McBride, 1994).

Karlik (1995) found that dissolved organic carbon (DOC) in outflows increased by 44.8% in limed soils due to the increase in soil pH. This increase in negative charge also increases the binding of Pb to organic particles (Christl et al., 2001), which leads to increased mobility of Pb in soils with higher pH (Impellitteri et al., 2002; Sauve et al., 1997; Sauve et al., 1998). Weng et al (2002) found that metal complexation with DOC can increase concentration of dissolved metals by more than 2 orders of magnitude.

Soil organic matter consists of mostly humic and fulvic acids (Weng et al., 2002). High acidities and low molecular weight result in metal complexes with FA being more soluble than those of HA (Stevenson, 1982). However, due to the dissociation from soil, increased negative charge makes HA more attractive for complexation with Pb as well as increased mobility at higher soil pH (McBride, 1994; Stevenson, 1982).

Intact soil cores have been used extensively in column leaching studies to determine the mobility of contaminants in soils (Gaston and Locke, 1996; Gaston and Locke, 2000; Kauffman et al., 1998; Singh and Kanwar, 1991). Camobreco et al (1996) found that when homogenized soil columns were used in leaching studies, they retained all of metals whereas intact soil cores showed metal concentration in the effluent solution. This was most likely a result of preferential flow that occurred within the intact soil columns resulting in less interaction between Pb in solution and soil components. Gaston and Locke (1996) concluded that some preferential flow occurred in all intact soil columns used in column leaching study and the same phenomenon also occurs in the field. Homogenized soil columns, however, represent a specific soil condition that most likely does not represent field conditions and therefore results in an overly optimistic view of metal retention in soils (Camobreco et al., 1996).

A previous study on Pb distribution in shooting range soils suggested that Pb became mobile in a shooting range soil in Florida due to soluble organic matter (Cao et al., 2003). The objectives of this study were: 1) to determine the leachability of Pb in two shooting range soils in Florida using intact soil core, and 2) to investigate the role of CEC, humic acid (HA) and fulvic acid (FA), and soil pH on the mobility of Pb in these soils.

Materials and Methods

Collection of Intact Soil Cores and Soil Sampling

The present study involved two outdoor shooting ranges in the state of Florida. Site one (OCR) is located in Ocala National Forest, and site two (MPR) is located in Broward County. Locations are presented in Fig. 5-1. Both sites have been in operation for a similar amount of time (OCR for 15 yrs., and MPR for 16 yrs.). OCR consists of a 100-meter rifle range and a skeet shooting range. MPR consists of a 100-meter rifle range, a 50-meter pistol range, and a skeet shooting range. This study will focus on the rifle ranges. The soil of the OCR site was a typical sandy Florida soil. The MPR soil was disturbed and will be discussed in greater detail later.

The berm on both sites was built with soil excavated on site. Total Pb concentrations in the berm of rifle range had been previously determined and averaged 22,030 mg kg⁻¹ for OCR and 48,400 mg kg⁻¹ for MPR (Cao et al., 2003; Chen et al., 2001). Profile soil samples (0-10, 10-30, 30-50, 50-100 cm) had also been previously collected with a bucket auger approximately 10m in front of the berm. Soil properties for profile samples taken are presented in Table 5-1. The OC site was a more typical Florida sandy soil with low soil organic matter content (Table 5-1), whereas the MP site was high in soil organic matter (Table 5-1) as well as being calcareous.



Figure 5-1 Locations of the studied shooting ranges in Florida.

Intact soil cores were taken approximately 2m in front of the berm soil at both locations. Clear polyvinyl chloride pipe (4.25 cm i.d. by 116 cm long) was inserted into a steel sleeve fitted with a bottom cutting edge and forced into the soil using Geoprobe® Model 5410 (Fig. 5-2a) hydraulic soil probing machine. The intact soil cores were then removed using the hydraulic probe, and sealed before transporting back to the laboratory. Some soil compaction may have occurred during sampling.

Extraction of Humic and Fulvic Acid

The organic matter fractions were extracted using the method described by Schnitzer (1982). Ten grams of soil were shaken in 100 ml 0.1N NaOH for 24 h and the supernatant solution was separated from residual soil by centrifugation at 10,000 rpm for 10 min. The residual soil was suspended and washed with deionized water and then

separated by centrifugation. The washings were then added to the original supernatant and acidified to a pH < 2 using 2N HCl. The soluble FA fraction was then separated from the coagulate HA fraction by centrifugation and purified. Humic acid was brought back into solution by adding 0.1N NaOH, and both fractions were analyzed for total organic carbon.

Table 5-1 Selected physicochemical properties of soil profile for sites one and two.

	Depth (cm)	pH ^{a,b}	OC ^{c,b} (g kg ⁻¹)	CEC ^d (cmol(+) kg ⁻¹)	Pb _T ^{b,e} (mg kg ⁻¹)
OCR	0-10	6.74	2.4	7.3	2360
	10-30	5.88	ND ^f	5.3	83
	30-50	5.02	ND	4.8	13
	50-100	4.80	ND	4.7	9
MPR	0-10	6.73	107	26.6	2720
	10-30	7.47	16.1	12.6	276
	30-50	7.56	23.2	46.6	522
	50-100	7.69	19.3	52.0	262

^a pH was determined with a 1:1 ratio of soil/water

^b Source: Cao et al (2003) and Chen et al (2000)

^c Organic Carbon

^d Cation Exchange Capacity

^e Total concentration (Nitric acid and Hydrogen Peroxide digestion)

^f Not Determined

Column Set Up

The top and bottom of each column (Fig. 5-2b) was fitted with a 150-micron porous polypropylene frit within a rubber cap, which was sealed by a band clamp to the column ends. Two polyvinyl chloride barbed connector nozzles were inserted in each cap, and used to connect column to tubing. Nalgene 180 polyvinyl chloride tubing with internal diameter of 0.4cm was used in column leaching.

a)



b)

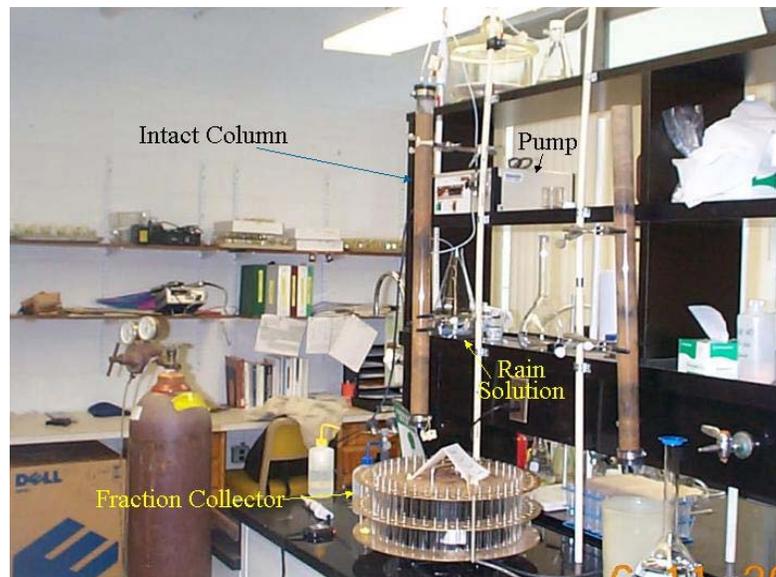


Figure 5-2 Geoprobe® Model 5410 hydraulic soil probing equipment used to take intact soil cores (a) and column set up (b) used in leaching study.

The columns were first saturated from the bottom with a background 0.004M KNO₃ electrolyte solution using a Gilson Model 302 pump (Fig. 5-2b). Saturated flow was then established from the top using a simulated rainwater solution (Table 5-2) using a Gilson Model 302 pump at an effluent rate of 0.5ml per minute. Saturated flow has been previously used to determine the mobility of Pb in the presence of chelating agents in column leaching studies (Kedziorek et al., 1998). Simulated rainwater concentrations (Table 5-2) were determined based on data, from the National Atmospheric Deposition Program, which consisted of the average of seasonal precipitation weighted mean concentrations from 1990-2000 from two sites in Florida located near sampling sites. The simulated rainwater was adjusted to 150 mg L⁻¹ KBr electrolyte solution to increase ionic strength of influent solution and reduce colloidal material in effluent column extract. Monovalent cations were used in background electrolyte solutions to limit exchange with Pb on soil surfaces as well as decrease competition with Pb for complexation with HA and FA. Brown and Elliott (1992) found that Ca and Mg suppressed Pb solubilization by competitive chelation of EDTA.

Table 5-2 Composition of simulated rainwater used in saturated column-leaching experiment.

Analyte	Conc. (mg L ⁻¹)
pH	4.9
Ca(NO ₃) ₂ *4H ₂ O	0.648
MgSO ₄	0.258
NaCl	1.02
NH ₄ Cl	0.326
HNO ₃	0.315
H ₂ SO ₄	0.719
KBr	150.0

Column effluent solution was collected in 20ml test tubes via a fraction collector. Samples were analyzed for pH, inorganic carbon (IC), and organic carbon (OC) within two days of sampling, and then acidified with HNO₃ and stored for Pb analysis. The impact of electrolyte solutions on the solubility of Pb was investigated using the chemical equilibrium model Visual Minteq (version 1.03, compiled by Jon Petter Gustafsson, KTH, Division of Land and Water Resources, Stockholm, Sweden), and found not to considerably increase Pb solubility.

Prior to leaching, one intact soil core from each site was sacrificed and split open, and the soil was sectioned into 10cm increments. The soil was analyzed for total Pb concentrations, and the data are presented in Table 5-3. After leaching, the column soils were weighed under saturated conditions, and dried in an oven at 105°C and reweighed to determine pore volume and material properties of the soil. Upon saturation, there was significant compaction within the columns, and changes in bulk density (ρ_b) and porosity (ϕ) prior to and after saturation are presented in Table 5-4. As a result of compaction, ponding was unavoidable and occurred at the top of the columns throughout the leaching experiment. It must be noted that after sampling it was discovered that a plastic liner existed immediately under the berm soil at the MPR site, thus the bottom 25cm of the MPR intact soil columns were removed prior to leaching due to liner material being in the intact soil columns.

Chemical Extraction and Analysis

Soil pH was determined with a 1:1 ratio of soil/water. Soil organic matter was determined using the Walkley-Black procedure (Nelson and Sommers, 1982). Cation exchange capacity (CEC) was determined by using the method of Rhoades (1982). Soil

samples were air dried, sieved to 2-mm and digested with HNO₃ and H₂O₂ using the hot-block digestion procedure (USEPA Method 3050a). Lead concentrations for soil were determined by flame atomic absorption spectrometry (Varian 220 FS with SIPS, Varian, Walnut Creek, CA). Soil Pb concentrations <1.0 mg L⁻¹ were reanalyzed and column extracts were analyzed by graphite furnace atomic absorption spectrometry (Perkin-Elmer SIMMA 6000, Perkin-Elmer Corp, Norwalk, CT). Quality control samples including a standard reference material for soil (2709 San Joaquin soil and 2710 Montana soil) were used with sample digestion (US Department of Commerce National Institute of Standards and Technology, Gaithersburg, MD 20899). Satisfactory precision and accuracy were required to be within ± 20%. Organic carbon (OC), and inorganic carbon (IC) were determined on a Shimadzu TOC 5050 carbon analyzer (Columbia, MD).

Table 5-3 Total Pb concentration in soil of columns sacrificed for analysis.

Depth (cm)	Pb _T ^a (mg kg ⁻¹)	
	OCR 109	MPR 109
0-10	8,080	26,800
10-20	16,900	7,900
20-30	5,510	6,790
30-40	6,110	4,060
40-50	1,260	25,600
50-60	31	3,650
60-70	28	6,650
70-80	BDL	13,900
80-90	BDL	5,120
90-98	-----	109

^a Total concentration (Nitric acid and Hydrogen Peroxide digestion)

^b Below detection limit

Table 5-4 Changes in bulk density (ρ_b) and porosity (ϕ) after saturation of soil intact columns.

columns	Pre saturation		Post saturation	
	ρ_b^a	$\phi^{b,c}$	ρ_b	ϕ
OCR 104	1.53	0.422	1.77	0.333
OCR 108	1.54	0.420	1.77	0.331
MPR 106	1.35	0.490	1.53	0.424
MPR 114	1.38	0.479	1.59	0.398

^a Porosity

^b Bulk density

^c Calculated assuming a particle density (ρ_m) of 2.65 g cm⁻³

Results and Discussion

Soil Profile Sampling

Results of previous study on the site revealed similar total Pb concentration (Table 5-1) in the surface soil, but the MPR site exhibited much more elevated Pb (Table 5-1) in the subsurface soil suggesting possible migration of Pb down the soil profile (Cao et al., 2003; Chen et al., 2001). However, when considering that the MPR site exhibited elevated CEC values while the OCR site exhibited low CEC values (Table 5-1), it is possible that Pb is actually being retained in the MPR soil due to high CEC. In contrast, the OCR soil is primarily a sandy soil with a lower soil pH, which would seem to favor Pb migration (Chen and Ma, 1998). Based on these data, the first hypothesis is that Pb is being mobilized at the OCR site, and because of its sandy soil nature, it is not being retained in the lower layers of the soil profile.

The OCR site exhibited elevated pH (Table 5-1) in the surface soil, which was most likely due to weathering of Pb and formation of Pb-carbonates as discussed previously in chapter 4. In contrast, the MPR site showed elevated soil pH values (Table 5-1) throughout the soil profile. Elevated HA concentration of 666 mg kg⁻¹ (data not shown)

and FA concentration of 605 mg kg^{-1} (data not shown) in the subsurface (50-100cm) at the MPR site, suggests the possibility of solubilization of organo-Pb complexes due to high soil pH. An increase in Pb solubility due to dissolved organic matter in soils at high pH has been documented in many studies (Dong et al., 2000; Impellitteri et al., 2002; Sauve et al., 1998; Turpeinen et al., 2000). Based on this, the second hypothesis is that Pb is being mobilized at the MPR site resulting from solubilization of Pb-organo complexes due to elevated soil pH.

Intact Soil Core Characterization

One intact soil core from each site was sacrificed for sampling. Total Pb concentrations (Table 5-3) in both columns revealed elevated Pb down the soil profile at both sites. However, Pb concentration (Table 5-3) dropped considerably below 50cm in the OCR column. The total Pb concentration (Table 5-3) from 0-10cm was lower than the concentration at 10-20cm in the OCR column, which suggested some disturbance in the surface layer (20cm) or potential Pb migration down the soil profile.

The MPR column contained extremely high and random Pb concentrations (Table 5-3) throughout the entire column, and showed no trends as far as tapering off until 90cm. The randomness of Pb concentrations (Table 5-3) in the MPR column suggested that the soil profile at this site was once disturbed, which could also account for the elevated organic carbon concentrations (Table 5-1) throughout the soil profile. After contacting the range, it was discovered that the soil was disturbed in an effort to put a liner under the berm, and therefore no conclusions about mobility of Pb could be determined based on total Pb concentrations within the intact soil core.

Column Leaching

Lead concentrations in column leachates from intact soil cores taken from the OCR site were typically low, with the majority of effluent after 2 pore volumes (Fig. 5-3a,b) falling below the $15 \mu\text{g L}^{-1}$ action level for Pb in drinking water established by the EPA. In fact, leachates from column OCR 104 (Fig 5-3a) never rose above $20 \mu\text{g L}^{-1}$ Pb in solution and showed a downward trend after one pore volume. On the other hand, leachates from column OCR 108, rose above $60 \mu\text{g L}^{-1}$ (Fig. 5-3b), and spikes in Pb concentration were seen even at nine pore volumes. However, Pb concentrations were typically low and migration of Pb is not a concern at this site. Matos et al (2000) also found that Pb has the highest retardation factors of any other metals even in sandy soils with low CEC.

While the effluent Pb concentrations from the OCR columns were typically low, Pb concentrations in the effluent from columns taken from the MPR site (Fig. 5-4a,b) were quite high even in the first samples. Lead concentrations in the leachate from the first samples were as high as $1,500 \mu\text{g L}^{-1}$ in column MPR 106 (Fig. 5-4a), and $4,500 \mu\text{g L}^{-1}$ in column MPR 114 (Fig. 5-4b).

The elevated Pb concentrations seen in the first samples in both of these columns were possibly due to a build up in soluble Pb above the liner that was present at the shooting range. A total Pb concentration of $13,905 \text{ mg kg}^{-1}$ was seen at 70-80cm in the MPR column (Table 5-3) that was sacrificed, which was where the column would have been cut off due to the liner. Therefore it is not surprising to see concentrations of water soluble Pb as high as 4.5 mg L^{-1} (Fig. 5-4b) within the first pore volume of leachate. However, the removal of this immediately available Pb should have resulted in a decrease

in the concentration of Pb in effluent with pore volume due to more residual forms of Pb in the soil.

In addition to high initial concentrations, the overall trend of Pb being leached from the columns increased with pore volume. Effluent Pb concentrations from column MPR 106 (Fig. 5-4a) started below $1,000 \mu\text{g L}^{-1}$ after the initial spike, and rose steadily to above $1,000 \mu\text{g L}^{-1}$ after 15 pore volumes. Prior to 21 pore volumes there was a spike in Pb concentration in the effluent of MPR 106 (Fig. 5-4a) to $2,550 \mu\text{g L}^{-1}$. Effluent Pb concentration continued to rise to a final concentration around $1,500 \mu\text{g L}^{-1}$. Effluent Pb concentrations for column MPR 114 (Fig. 5-4b) also increased with pore volume, with the majority of column leachate having Pb concentrations $>1,000 \mu\text{g L}^{-1}$. After three pore volumes there was a decrease in Pb concentration (Fig. 5-4b), but after seven pore volumes the general trend in Pb effluent concentration increased.

The pH of effluent solution from column OCR 104 (Fig. 5-5a) started close to pH 7, but then dropped and buffered around a pH of 6 for the remainder of the column leaching. The pH of effluent solution from column OCR 108 (Fig. 5-5b) was much more inconsistent, but typically remained between a pH of 5 and 6. In contrast, the pH of effluent from columns MPR 106 and 114 (Fig. 5-6a,b) were very similar. The pH of effluent from both MPR 106 and MPR 114 was very well buffered around a pH of 8 due to the presence of calcium carbonate.

Both organic and inorganic carbon concentrations in the effluent from columns OCR 104 and OCR 108 (Fig. 5-7a,b) were typically low. A spike occurred in organic carbon prior to four pore volumes in column OCR 108 (Fig. 5-7b), but this data point could be attributed as being an outlier. Organic and inorganic carbon concentrations in

the effluent from columns MPR 106 and MPR 114 (Fig. 5-8a,b) were elevated compared with what was found in the effluent from the OCR columns. Inorganic and organic carbon concentrations (Fig. 5-8a,b) showed similar trends by peaking within the first three pore volumes and decreasing during the rest of the leaching experiment. In addition, at approximately 18 to 19 pore volumes, DOC concentration decreased and inorganic carbon concentration (Fig. 5-8a,b) increased in both columns.

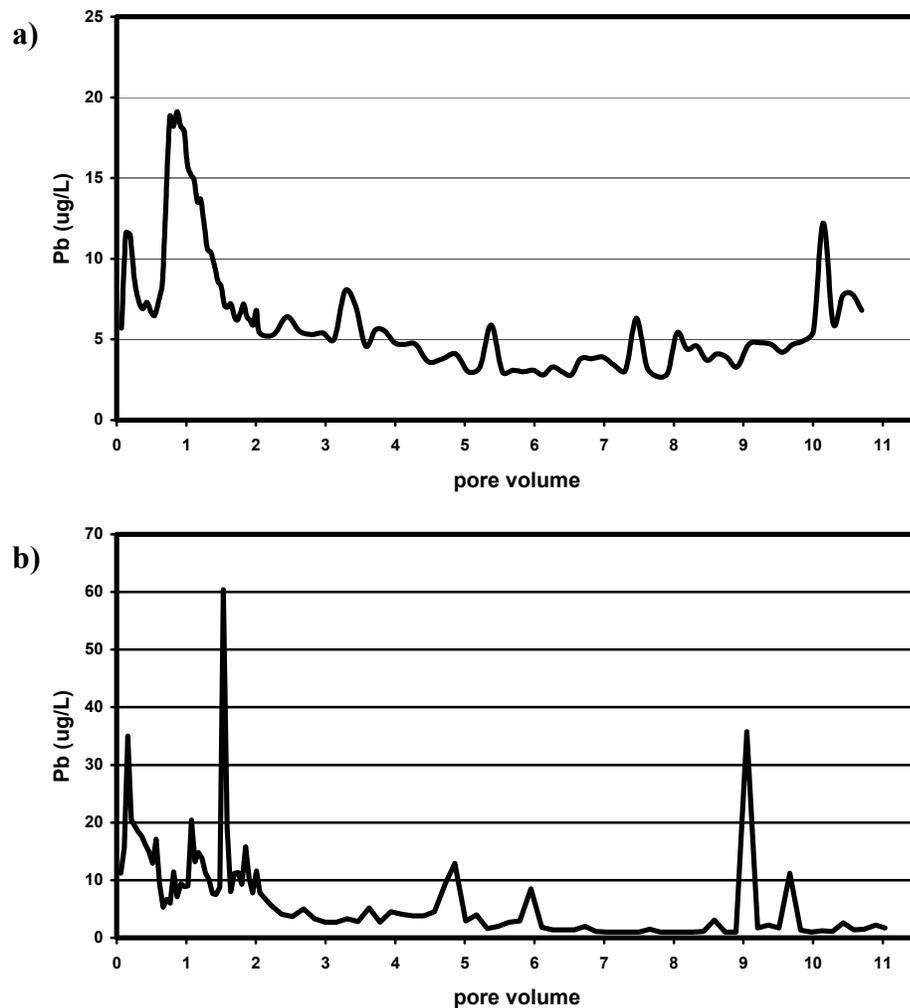


Figure 5-3 Lead concentration of column extracts for column OCR 104 (a) (1 PV=342mL) and OCR 108 (b) (1 PV=312mL) as a function of pore volume.

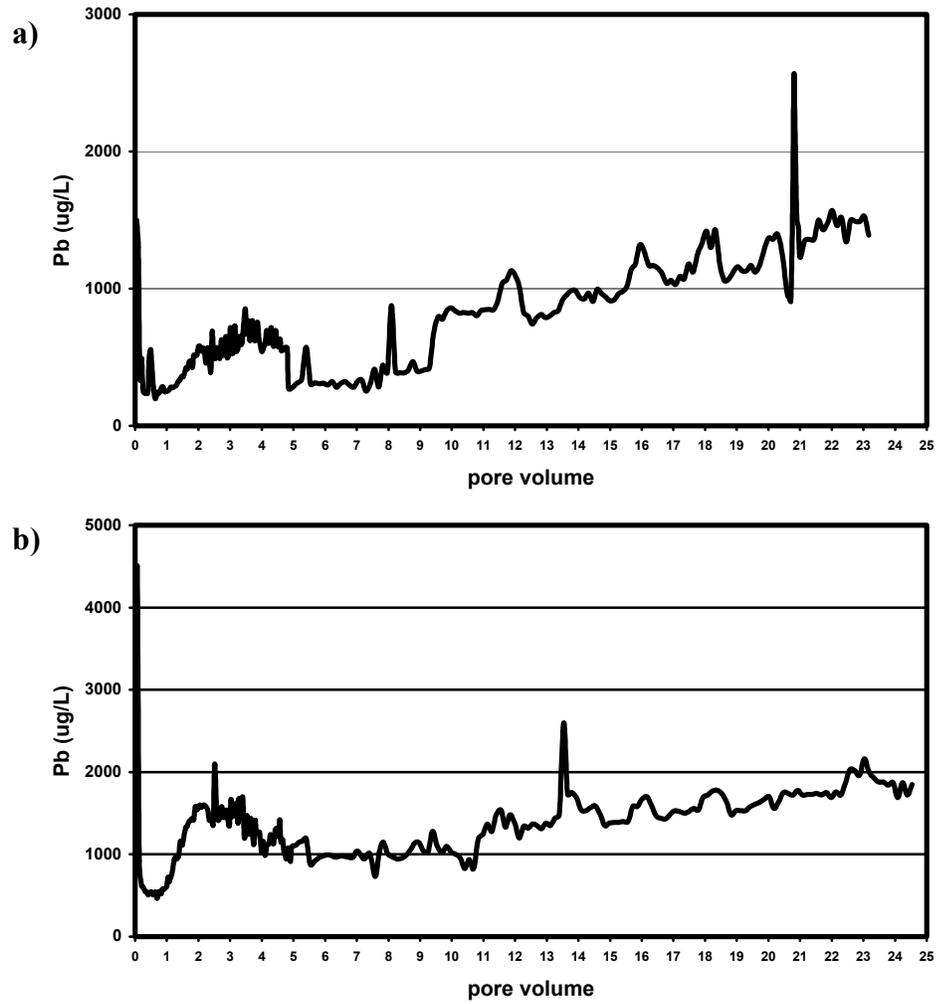


Figure 5-4 Lead concentration of column extracts for column MPR 106 (a) (1 PV=338mL) and MPR 114 (b) (1 PV=322mL) as a function of pore volume.

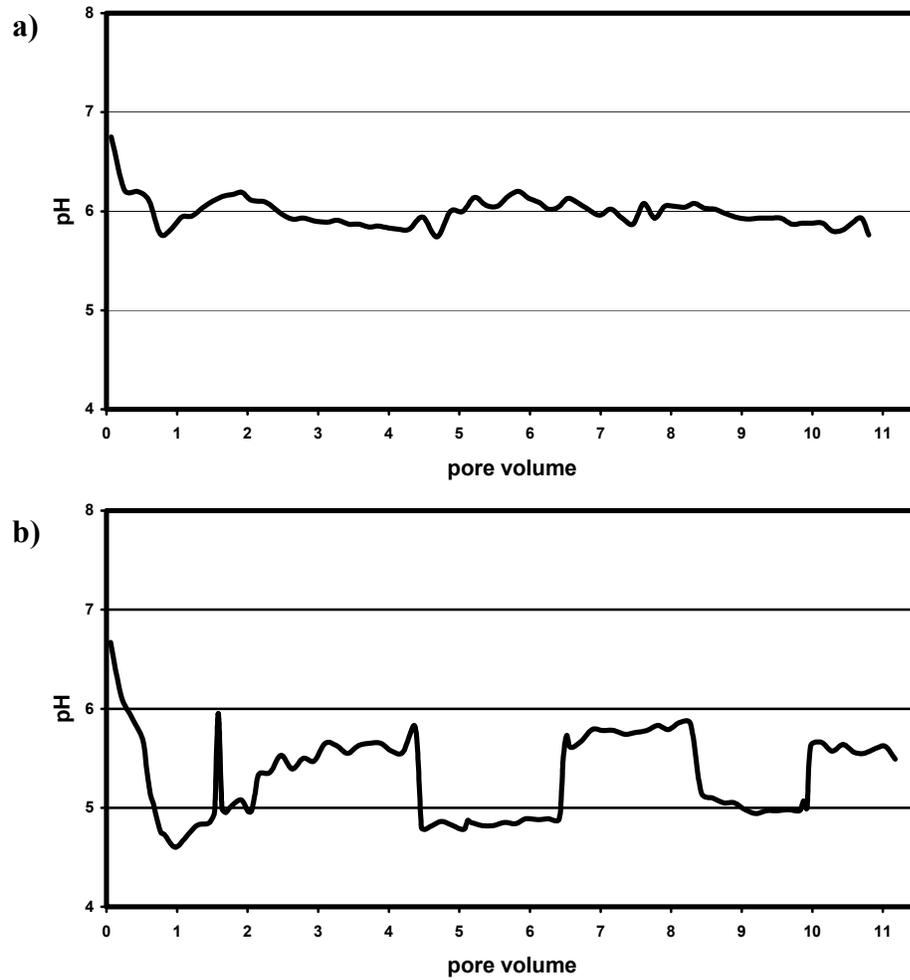


Figure 5-5 pH of column extracts for column OCR 104 (a) and OCR 108 (b) as a function of pore volume.

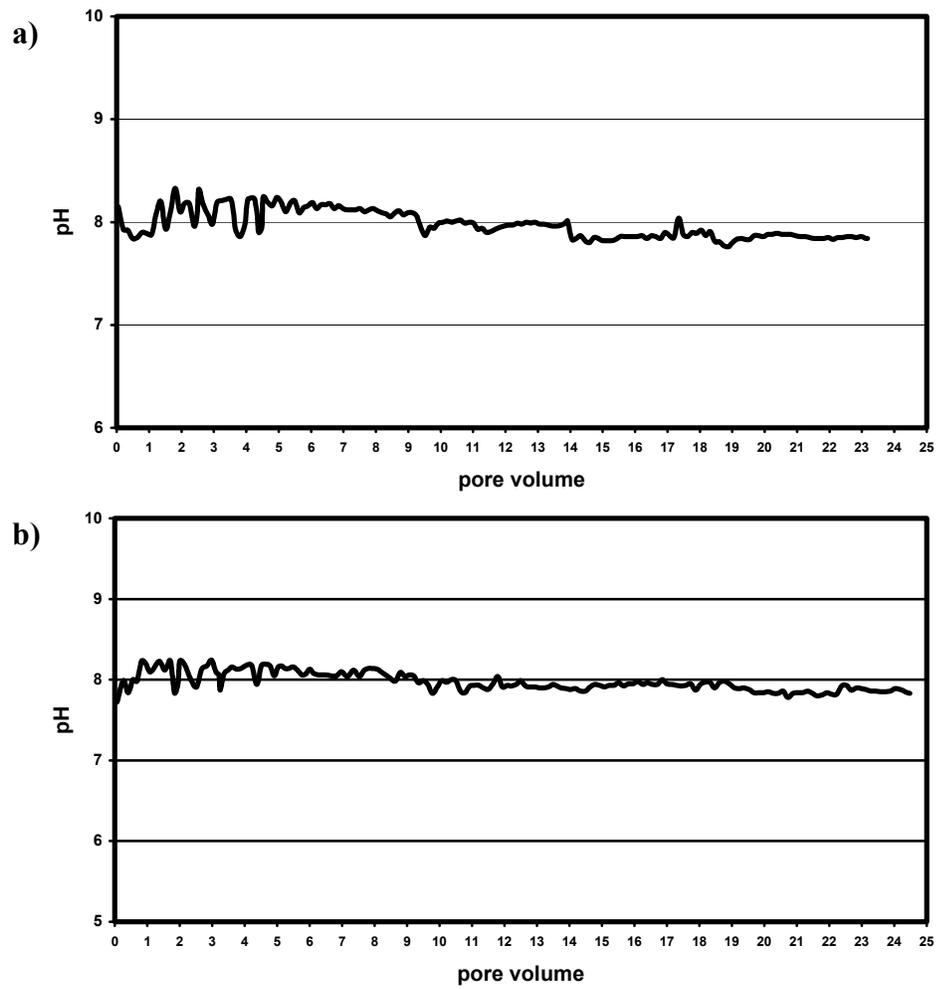


Figure 5-6 pH of column extracts for column MPR 106 (a) and MPR 114 (b) as a function of pore volume.

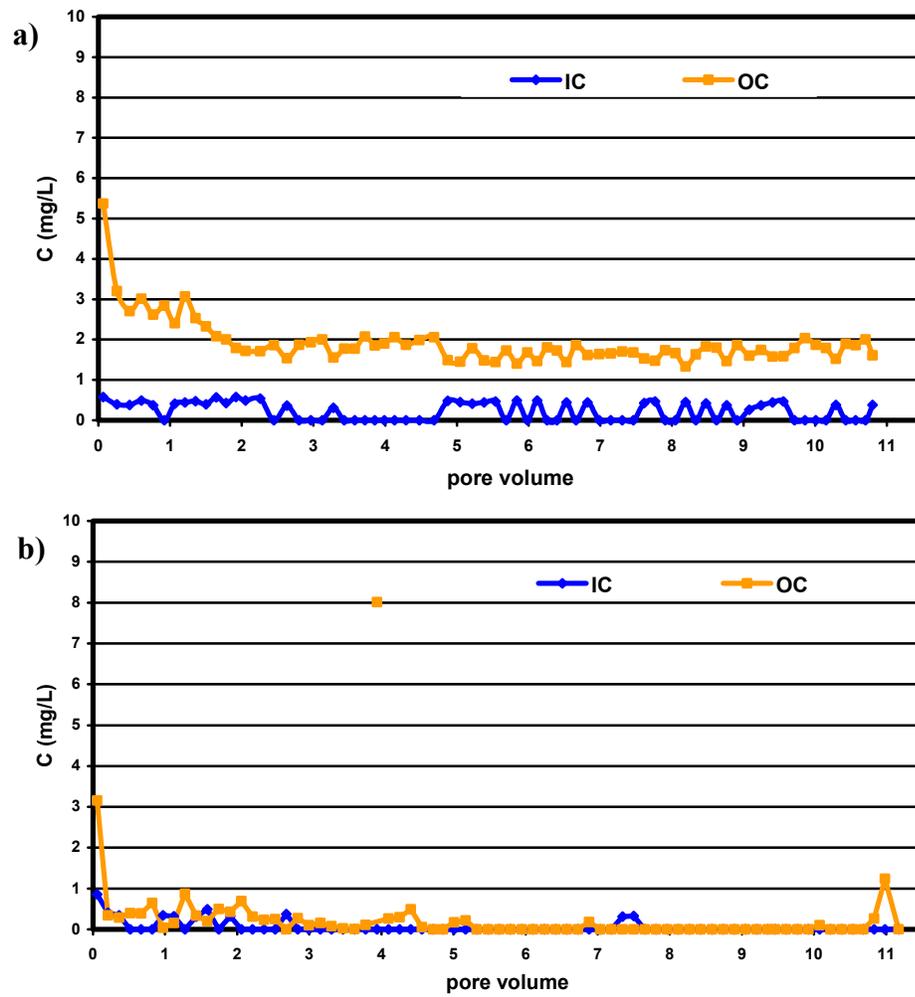


Figure 5-7 Inorganic carbon (IC) and organic carbon (OC) of column extracts for column OCR 104 (a) and OCR 108 (b) as a function of pore volume.

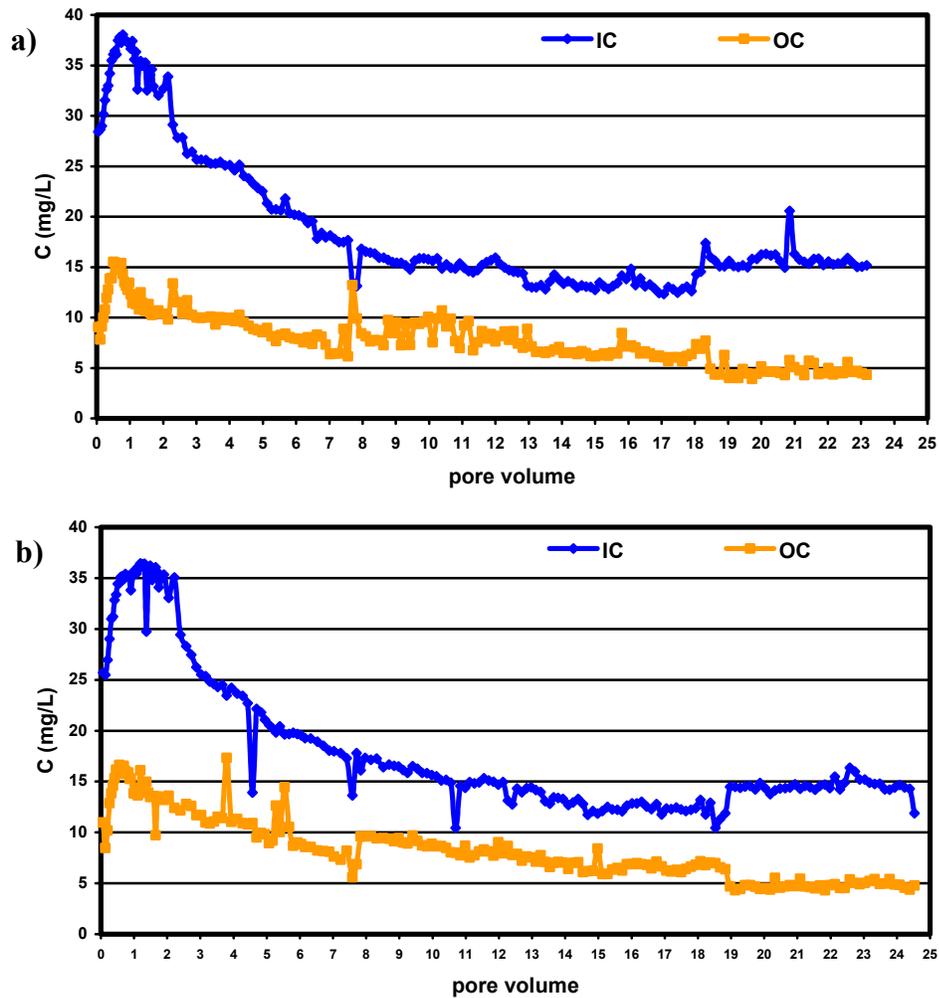


Figure 5-8 Inorganic carbon (IC) and organic carbon (OC) of column extracts for column MPR 106 (a) and MPR 114 (b) as a function of pore volume.

Organic matter facilitated metal transport depends on the mobility of organo-metal complexes within the system (Chirenje et al., 2002). The solubility of Pb has been shown to increase as soil pH rises from 6 to 8 due to solubilization of Pb-organo complexes (Dong et al., 2000; Impellitteri et al., 2002; Sauve et al., 1997; Sauve et al., 1998). The fact that effluent Pb concentration was high in the MPR columns leached in this present study when effluent pH is high, suggested the possibility that Pb-organo complexes are

being mobilized. However, trends in DOC concentration in the effluent did not corroborate this evidence.

While both IC and OC concentrations were elevated in the effluent from both of the MPR columns, the trends did not match any trends seen in Pb concentration in effluent. In fact, they were the complete opposite, with Pb increasing in concentration in effluent with pore volume, and IC and OC concentration decreasing in effluent with pore volume. Therefore, it is not possible to link either DOC or IC effluent concentrations to the enhanced mobility in this soil system.

One other possible explanation for the mobility of Pb at the MPR site is replacement of Pb^{2+} by Ca^{2+} on soil exchange sites. Calcium carbonate was present throughout the disturbed soil within the columns. Ponizovskii et al (2002) found that while Pb^{2+} exchanges with Ca^{2+} and H^+ on soil exchange sites, the exchange is a reversible process. Therefore, Ca^{2+} in soil solution may exchange with Pb^{2+} resulting in elevated Pb in soil solution. Further study is necessary to prove that this will apply to this soil system.

While the mechanisms by which Pb is being mobilized at the MPR site remains unclear, results from the OCR column allow some positive conclusions to be drawn. The conditions that contribute to the risk of Pb migration in Florida soils include: low soil pH, low clay and organic matter content, and high amounts of rainfall (Chen and Ma, 1998). However, it is evident that a low soil CEC and low soil pH values does not appear to be a factor in the mobilization of Pb in intact soil cores taken from the OCR shooting range soil.

Conclusions

This study showed that Pb may become mobile and migrate down the soil profile in a disturbed shooting range soil. In fact, Pb concentration in effluent increased with pore volume. A plastic liner that existed immediately under the berm soil at this site will prevent vertical migration immediately underneath the berm soil, but horizontal movement may lead to vertical movement once the liner is cleared. However, in sandy acidic soils typical of Florida, Pb mobility was suppressed. Results suggest that despite properties such as low soil pH and low soil CEC, Pb is highly immobile in sandy Florida soils despite elevated total Pb concentrations, and there is little risk of groundwater contamination.

CHAPTER 6 SUMMARY AND CONCLUSIONS

Summary

Results from the Pb bullet abrasion study, showed that 1.5% of the mass of a 22-caliber bullet was physically removed as it passed through a berm soil. Sampling of a shooting range that had been open for only 3 months corroborated experimental results. Elevated Pb levels of 1,142 mg kg⁻¹ were seen in the berm soil of the rifle range. Most soils from the field abrasion experiment as well as soil collected from the rifle range had SPLP-Pb concentrations >15 µg L⁻¹ (Synthetic Precipitation Leaching Procedure). Laboratory weathering studies found that virtually all metallic Pb powder was converted to hydrocerussite [Pb₃(CO₃)₂(OH)₂], as well as to a lesser extent cerussite (PbCO₃) and massicot (PbO) within one week.

Laboratory incubation studies found that an increase in soil moisture level increased the rate at which metallic Pb was transformed to Pb-carbonates. The transformation of Pb was completely inhibited in the absence of soil organic matter and no secondary Pb minerals were identified. An increase in soil pH reduced the transformation of metallic Pb to Pb-carbonates. At a higher pH, only Pb-oxides were formed. Soil microorganisms did not play a direct role in the transformation of metallic Pb; however, they probably play an indirect role due to their metabolic processes that oxidize organic matter and elevate CO₂ in soils. Treated soil was found to have reduced water soluble Pb based on an incubation study, with lime amended soils typically having the lowest water soluble Pb concentration compared to phosphate rock amended and un-

amended soil. Aggregates composed of quartz cemented by hydrocerussite in untreated soil and hydrocerussite as well as possibly pyromorphite in phosphate rock amended soils formed after 11 weeks of incubation.

Elevated levels of Pb and dissolved organic matter in the form of humic and fulvic acid were determined in the soil of a shooting range. This soil also had a high soil pH, suggesting that migration of Pb was due to the formation of organo-Pb complexes. Leaching of intact soil cores revealed elevated levels of Pb, pH, inorganic carbon, and organic carbon in the effluent, but trends did not suggest organic matter facilitated transport. However, Pb mobility was minimal when leaching a sandy acidic soil typical of Florida.

Conclusions

As a result of this study, the following conclusions were reached.

- Lead contamination of rifle/pistol shooting range berm soils is rapid as a result of Pb contamination from fine size fractioned Pb produced as the Pb bullet passes through berm soil.
- This fine fraction metallic Pb that is abraded from the bullet will be transformed rapidly to more reactive secondary Pb minerals.
- Soil properties such as high soil moisture content, low soil pH, and high soil organic matter will significantly increase the weathering rate of metallic Pb to more reactive Pb secondary minerals.
- Soil microorganisms do not appear to directly influence the weathering rate of metallic Pb in soils.
- Soil amendments influence the final weathering products, with pyromorphite possibly forming in the phosphate rock treated soil.
- Lead is highly mobile in a disturbed Florida shooting range soil used in column leaching studies, however mechanisms of Pb mobility remain unclear.
- Lead is highly immobile in the sandy shooting range soil typical of Florida used in column leaching studies, despite having elevated total Pb concentrations in the surface soil.

- There appears to be little risk of groundwater contamination when soil is undisturbed.

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BIOGRAPHICAL SKETCH

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