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LEAD LEACHING FROM SOILS AND IN STORM WATERS
AT TWELVE MILITARY SHOOTING RANGES
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ABSTRACT
Soils from impact berms at 12 military shooting ranges were evaluated for lead leaching by particle-size distribution, sequential extractions, storm water analysis, batch studies with amendments of crushed apatite (FB) and triple-super phosphate (TSP), and column leaching studies with amendments of ashed apatite (FBa) and TSP. Soil particle fractions were determined by ASTM D422-63 and by x-ray diffraction; lead leaching was found by EPA's SPLP and TCLP. Total and dissolved lead in soils and storm waters were determined by ICP-MS. The residual fraction averaged 79.8% of total mass of lead in all soils. There was significant correlation between TCLP results and lead in the less than 0.075-mm-size fraction for all soils in the study (r² = 0.82, P << 0.001, n = 13), along with a significant correlation of lead in storm water and soil Fe (r² = 0.56, P = 0.03, n = 8) and Mn (r² = 0.59, P = 0.03, n = 8). Average dissolved lead in storm water = 104 μg/L (SD = 152, n = 17). Batch studies of FB 3% and 5% amendments sorbed 85.3% and 88.2% lead, respectively. TSP 3% and 5% amendments created phosphate precipitates that captured 97.6% and 92.7% lead, respectively. In column studies, FBa-amended soils had mixed effectiveness as lead adsorbents, and TSP-amended soils leached more lead than control in all but Virginia (VA) soils. Control, nonamended soils did not leach lead for three soil combination types: New Mexico range b (NMb), Nevada (NV), and South Dakota range 2 (SD2). NMb soil had no lead leachate, presumably due to the high organic matter, pH = 8.2, and very high sulfides. In the NV range soil, a combination of pH = 8.7, low moisture = 1.2%, and mostly fine gravels had no lead leachate. SD2 range had no leachate with pH = 8.2, moderate clay, and organic matter content. Both TSP and FBa amendments leachate pH were significantly different than control leachate pH (FBa: F = 9.47, P = 0.003, n = 120; TSP: F = 115.5, P << 0.001, n = 135). Leachate pH dropped an average 3.7 standard units (SD = 0.93, n = 13) in the first week for TSP-amended soils. Soil pH was the most significant indicator of soil leaching behavior. While TSP can be an effective lead-immobilization mechanism, reduction of soil pH can have an unintended consequence for lead ions not precipitated as phosphates. Range operators would be prudent to monitor soil pH regularly and to know their soil clay and organic matter content.

Key words: lead leaching, column study, storm water pollutant, soil particle size, shooting range

INTRODUCTION
Shooting range soils have elevated concentrations of elemental lead as high as 10 to 100 times background levels (Murray et al., 1997). Concern for migration of this anthropogenic source has been a focus of research by many (Abdel-Fattah et al., 2003; Bruell et al., 1999; Cao et al., 2003; Craig et al., 1999; Dermatas et al., 2006; Hardison et al., 2004; Jorgensen and Willems, 1987; Lin et al., 1995; Murray et al., 1997; Scheuhammer and Norris, 1995; Stansley et al., 1992; U.S.EPA, 2001). Shooting ranges contain large amounts of lead-contaminated soil that may become mobile through two primary pathways: physical abrasion and weathering. The physical abrasion of bullets has been found to be a significant source of lead contamination in the soils (Hardison et al., 2004). Abraded residue transforms into hydrocerussite (2Pb(CO₃)(OH)₂) and to a lesser degree, cerussite (PbCO₃) and massicot (PbO) in as little as one week (Cao et al., 2003; Hardison et al., 2004; Jorgensen and Willems, 1987). Weathering of elemental lead forms from shooting ranges has also been documented as visible corrosion on lead
fragments as crusts of white, gray, or brown material and as hydrocerussite, cerussite, and some amounts of anglesite (PbSO$_4$) (Cao et al., 2003; Lin et al., 1995). The lead of weathered bullets exists as particulate or ionic forms and may provide a steady source of potentially labile constituents, which can appear in various soil fractions and in storm waters (Cao et al., 2003). These oxidized lead compounds in earthen bullet-impact berms provide a constant source of lead in the soil matrix, where the rate of elemental lead dissolution is regulated by both physical and chemical factors.

**Lead Dissolution**

Lead mobility in soil is driven by redox potential, available anions (e.g. carbonates, phosphates, and sulfates), pH, soil organic matter, and cation exchange capacity (Basta et al., 1993; Dragun, 1998; Pickering, 1986). Both aerobic and acidic conditions in soils increase elemental lead dissolution, whereas anaerobic and alkaline conditions decrease it (Scheuhammer and Norris, 1995). Organic carbon has been found to enhance lead adsorption (Basta et al., 1993; Sauve et al., 1998). Soil colloids have been found to be active participants in transporting lead to groundwater and limiting lead interaction with reactive soil constituents (Citeau et al., 2003). Surface and sub-surface soil’s lead migration has been reported (Abdel-Fattah et al., 2003; Craig et al., 1999; Murray et al., 1997). Dissolution and subsequent migration may require implementation of best management practices (BMPs) to control and immobilize lead complexes.

**Lead immobilization**

*Insitu* immobilization of lead may be accomplished by soil amendments with phosphoric acid (H$_3$PO$_4$) (Yang et al., 2001); TSP (triple-super phosphate), which in concentrated form is composed of monocalcium phosphate hydrate, Ca(H$_2$PO$_4$)$_2$·H$_2$O, and generally contains 43-50% P$_2$O$_5$ (Budavari, 1989); or apatites (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) to convert soluble lead to pyromorphite species [Pb$_5$(PO$_4$)$_3$(OH, Cl, F…)]. Pyromorphite is extremely stable ($K_{sp} = 10^{-80}$) and its precipitate formation is an immobilization objective. Pyromorphite can be formed from soil lead compounds like cerrusite (PbCO$_3$), anglesite (PbSO$_4$), and galena (PbS) when exposed to phosphates. Some studies have suggested pyromorphites can also be a natural weathering product in soil (Cotter-Howells et al., 1994; Klein and Hurlburt, 1993). Changing the available lead to less soluble forms using phosphates has been shown effective (Brown et al., 2005; Fayiga and Ma, 2006; Ownby et al., 2005). TSP-amended 3.2% and 1% phosphoric acid soils have been reported as the most effective lead treatments to reduce bioavailability in fescue grass
(Brown et al., 2005). Hydroxyapatite has also been shown to be an effective calcium phosphate-based, 
\[\text{Ca}_5(\text{PO}_4)_3(\text{OH})\] lead-immobilizing amendment (Ryan et al., 2001). Phosphate sources of various types
have been used, as well as other fish hard parts, as effective metal adsorbents (Wright et al., 1995).

**Objectives**

Researchers, previously mentioned, have studied and reported distribution of lead contamination
at shooting ranges, distribution and geochemistry of metals in range soils, effectiveness of different
amendments and mechanisms of metal sorption, remediation technologies, and other edaphic topics.
These research efforts have advanced our understanding of shooting range environmental knowledge.
The challenge to range managers is to translate this information into effective range BMPs. In this study,
key soil characteristics of shooting range impact berms are identified to assist the range environmental
professional to predict the lead leaching behavior of range soils. To clarify lead leaching characteristics
of range soils, the objectives of this research focused in three areas: 1) quantification of the physical
and mineralogical associations of lead in shooting range-impact berm soils; 2) measurement of lead
concentrations in range storm waters, and 3) characterization of the soil lead leaching behavior via
laboratory batch and column studies with apatite and TSP amendments. Statistical correlations are
presented where appropriate.

**Range site description**

The 12 small-arms firing ranges (SAFRs) were located in nine states and are hereafter referred
to by alphanumeric codes: CA: California - one range; LA1, LA2, and LA3: Louisiana – three ranges
at same site; MO: Missouri - one range; NE: Nebraska - one range; NMa: New Mexico – one range and
NMb: New Mexico - one range (note: The two ranges in New Mexico were at two different military
installations approximately 350 km apart.); NV: Nevada - one range; SC: South Carolina - one range;
SD2: South Dakota - one range (note: SD2 is used to differentiate from range SD1 at this same site, but
SD1 was not included in this paper); and VA1 and VA2: Virginia - one range with two berms, one five-
year aged berm in front of a 40-year aged berm, respectively. Site approximate locations are depicted in
Figure 1.

Each range consists of a firing line, target line, and impact berm located behind the target line,
except the NV range did not have an impact berm. Distance from the firing line to the target line was 25
m to 100 m for pistol ranges, and 100 m to 950 m for rifle ranges. Impact earthen berms varied in height
from 1.5 m to 15 m, with an average height of 6 m. Soil volumes in these impact berms ranged from 75 m$^3$ to 15,000 m$^3$. In 2003, these small-arms training ranges averaged approximately 371,430 rounds of 5.56-mm, 7.62-mm, and 9-mm-size fired per range complex per year, adding about 1,960 kg of lead to each range complex annually. Typical operations and maintenance for SAFR berms included periodic sieving soil to remove and recycle lead shot from the berm areas, repairing berm erosion caused by storm events and bullets, and replacement of berm soils to reduce ricochet (ITRC 2004).

MATERIALS AND METHODS

Soil Characterization

Approximately 25 kg of berm soil from surface depths of 2 to 20 cm was collected at each shooting range using stainless steel shovels and trowels. Soil was collected across the face of berms equal distance apart within impact zones and along a single transect. Aliquots of soil were thoroughly mixed and homogenized. Large, visible organic constituents including roots, twigs, or leaves were removed. Berm soils, although likely indigenous to the area, were not necessarily from the immediate location of the shooting ranges. Range operators were not aware of the original source of berm soils. Geotechnical characteristics of soil are shown in Table 1. Soil-particle fractions were determined by ASTM D422-63. Lead particle sizes were evaluated using standard sieve sizes 4, 10, 60, and 200. Lead chemical associations were determined by sequential extraction following Ryan et al. (2001). EPA’s synthetic precipitation leaching procedure (SPLP) SW846-1312 and toxicity characteristic leaching procedure (TCLP) SW846-1311 were completed on each size fraction, and chemical analysis for metals in soils followed SW846-6010B and 3050B (USEPA, 1999). Soil clays and crystalline components were characterized by Perkin Elmer XRD using Cu K$\alpha$ radiation. Measurements were made using continuous scanning techniques, and XRD patterns were obtained from 2 to 60° 20. Triplicate distilled/de-ionized (DDI) blanks, triplicate reverse-osmosis water blanks, and triplicate quality control (QC) reagent standards were used for each analysis. The percent standard deviation of the reagent QC standards was < 5 percent. Blank values were subtracted from measured values. Soil crystalline phases are reported in Table 2.

To evaluate lead leaching from operational ranges into storm water, runoff samples were taken when possible during field visits. Storm water samples were collected from ranges at CA, LA1, LA3, MO, NMa, SD2, VA1, and VA2. Storm water samples at the other sites were not collected. Two to four
samples were collected with one duplicate sample from surface storm waters down gradient of berms
in natural swales or constructed drainage, and from 1 to 150 m from range boundaries. Samples were
collected in the middle of streams or channels considering both width and storm water depth. Dissolved
samples were filtered using a 0.45-μm hourglass filter. Samples were analyzed for total and dissolved
metals following USEPA method SW846-6020.

Batch study

Batch studies were completed on each soil with and without amendments. Amendments for batch
studies were added at 3% and 5% by mass. Crushed apatite II (FB) was used as supplied by PIMS NW
Inc., and TSP was used as potassium phosphate (KH₂PO₄) and phosphoric acid (H₃PO₄), which generally
contains 43-50% P₂O₅ (Budavari, 1989). Soils and amendments were air dried after mixing in the batch
test vessel. Amended-soils’ TCLP solutions were added to batch samples and continuously shaken for
24 ± 2hr. Leachates from each batch sample were filtered with a 0.45-μm filter and analyzed using the
Perkin Elmer Inductively Coupled Plasma Optima 4300 DV.

Column Setup

A preliminary screening batch analysis of the VA1 and VA2 soils found the 3% amendment
effective and equilibrated at 28 d. Therefore, 150 g of hand-mixed soil was added with 3% ashed apatite
II (FBa) and 3% triple-super phosphate (TSP) to 4-cm, inside-diameter borosilicate columns that were
30 cm long. Ashed apatite II was utilized to avoid the buildup of biofilm experienced in the preliminary
28-d study with VA soils.

Columns of each soil with no amendment were prepared as controls. The soil for the test filled
approximately 20 cm of each column. TSP and FBa were supplied as previously referenced, but FBa
was further prepared to remove organics by heating it in a muffle furnace for 24 h at 450 °C. To each
column, 35 mL of tap water was added daily, Monday through Friday, for five weeks (approximately 35
days). Effluent was collected in Nalgene bottles twice weekly (Mondays and Fridays) and analyzed for
total As, Cr, Cu, Fe, Ni, P, Pb, Mn, Mo, Sb, Sn, V, W, and Zn by EPA SW846 method 6010B ICP-MS.
Only total lead results are reported in this paper. Effluent pH was recorded ±0.05 and masses within
±0.05 g. Each analytical run included triplicate DDI blanks, triplicate RO water blanks, and triplicate
QC reagent standards. Percent standard deviation of the reagent QC standards was typically less than
5%. Leachates from columns were analyzed by ICP-MS.
RESULTS AND DISCUSSION

Physical soil parameters from berm soils had a CEC average = 15.8 meq/100 mL (SD = 8.1, from 31.5 (SD2) to 4.4 (SC), n =12); pH average = 7.7 (SD = 0.6, from 6.8 (LA1) to 8.7 (NV), n = 12); moisture content average = 15.3% (SD = 8.3; from 1.2% (NV) to 25.8% (LA1), n = 12); and soil texture generally as sand, with some silt and clay elements (Table 1). Berm average age = 33.7 y (SD = 19.8, from 5 y (VA1) to 60 y (LA1, LA3, MO), n = 13), indicating seasoned and well-weathered impact earthen berms. Iron and manganese concentrations were within typical U.S. soil nationwide averages. Edaphic lead associations were reviewed and are presented below in three areas: 1) particle size and physical characteristics, 2) crystalline phases as determined by XRD, and 3) metal partitioning by sequential extraction. Results and discussions of field storm water sampling, and batch and column leaching studies are then presented.

Particle Size and Physical Characteristics

Particle-size distributions are depicted in Figures 2 and 3. The order from largest to least percent clay for the first three soils were SD2 > LA3 > MO, which were the same soils as the XRD analysis, but in a slightly different order, LA3 > MO > SD2 (Table 2). Tables 3, 4, and 5 provide results of the sequential extraction, lead associations by fraction and leaching, and storm water lead concentrations, respectively. The SD2 and LA3 soils also had small exchangeable lead associations; however, the MO soil had the highest lead associations in the exchangeable fraction of any soil in this study (Table 3). The silt-clay fraction has been shown to be an effective transporting mechanism of heavy metals in storm waters (King, 1988). Heavy metal associations generally decreased with smaller size fractions (Table 4), contrary to findings by Zhang et al. (2003) who noted heavy metal attachment increased with smaller aggregate size. This phenomenon may have been due to lead fragments in the larger size fractions as it is well established that surface attachment mechanisms have dominant control of the distribution of heavy metals among the various fragment sizes (Zhang et al., 2003).

Lead in storm waters with suspended solids seems to corroborate the potential for lead migration. For example, storm water dissolved lead concentrations for SD2 and MO were 440 and 118 μg/L, respectively (Table 5). The topography of SD2 and MO ranges had been graded to direct-range surface runoff to storm water collection basins and ditches where samples for this study were collected. LA3 had a much lower dissolved concentration at 4.2 μg/L, which likely was a result of the application of
TSP approximately one year prior to this study, implementation of a storm water BMP that re-sloped the range infield to reduce storm water surface velocity, and seeded indigenous Bermuda grass (*Cynodon dactylon*) in the drainage pattern. The high clay-content soil of LA3, and prior to the BMP implemented in previous work to this study, found 2001 storm waters had total lead = 2,350 μg/L and in 2002 = 3,730 μg/L (Abdel-Fattah et al., 2003).

The size and lead association relationship may be further supported in part by the correlation of the smallest soil fractions and TCLP results. For example, TCLP and lead in the < 0.075-mm fraction was significantly correlated for all soils in the study ($r^2 = 0.82$, $P << 0.001$, $n = 13$). Similarly, but not as strong was the TCLP and lead correlation in the fraction from 0.075 to 0.250 grain size ($r^2 = 0.54$, $P = 0.004$, $n = 13$), and TCLP and lead in the fraction from 0.250 to 2.00 grain size ($r^2 = 0.38$, $P = 0.02$, $n = 13$). Less lead leached with the smaller fractions, similar to results by Dermatas et al (2006).

Storm water field sample results are in Table 5. Order of largest to smallest dissolved-lead concentrations were SD2 > LA1 > MO > VA1 > CA > VA2 > LA3 > NMa. SD2 and LA1 soils lead associations had 13,623 and 172,800 mg/kg in the 0.250 to 2.00 mm soil fraction; 5,548 and 2,441 mg/kg lead in the 0.075 to 2.50 mm fraction; and 817 and 11,137 mg/kg in the less than 0.075 mm fraction, respectively (Table 4). Suspended colloids may be contributing to total and dissolved lead in shooting range storm waters; however, no statistical correlation with storm water total or dissolved lead and grain size was found. The second soil in the series was LA1, which had storm water from a combined M-9 (pistol) and M-60 (machine gun) range. The LA3 storm water was from a M-16 range that had the TSP treatment previously mentioned. This analysis seems to indicate that the LA3 soil treatment may have reduced lead mobility compared with the LA1 soil with no treatment.

The third soil in the dissolved-lead storm water series, MO, did not show a tendency to lead leaching in the batch and column studies. Iron content in the MO soil at 18,210 mg/kg was greater than any other soil in this survey (Table 1) and may be inhibiting lead-cation exchange with soil micelles, and therefore, contributing to elevated lead in storm waters.

The fourth, fifth, and sixth soils in the series were VA1, CA, and VA2 soils, respectively. These soils had high lead amounts in the <0.075-mm fraction 8,294 mg/kg, 18,587 mg/kg, and 6,111 mg/kg, respectively, potentially providing a ready source of lead-cation, surface-attached colloids (Table 4). The NMa soil had the least dissolved lead of those measured (Table 5). The NMa soil also had high gypsum
content (75%), which decreases the electrical double layer between the clay surface and the soil solution as the double-charged calcium ions balance the charge rather than monovalent ions such as sodium (Quirk, 1994). Because the double-charge calcium ions are more strongly attracted to clay surfaces, sulfate anions are available to bind with free cations such as Pb$^{2+}$ to form the insoluble-lead sulfate salt.

Lead storm water concentrations were positively correlated with Fe soil concentration ($r^2 = 0.56$, $P = 0.03$, $n = 8$) and Mn soil concentration ($r^2 = 0.59$, $P = 0.03$, $n = 8$), which agree with King (1988). However, this disagrees with findings reported by Amacher et al. (1986) who found a negative correlation. The correlation may be attributable simply to the soil colloidal transport mechanism that can carry metal cations in storm waters.

Heavy metal contaminants in soils have been reported to interfere with adsorption by apatite. This may have had similar impacts on the natural adsorbent mechanisms in MO soils of this study and contributed to the observed correlation. Seaman et al. (2001) found other metals in the soil can reduce the amount and rate at which PO$_4$ becomes available for precipitation with the heavy metal of concern, changing the formation of secondary phosphate precipitates. For example, the MO soil with 18,210 mg/kg Fe could form strengite (FePO$_4$·2H$_2$O), inhibiting the formation of the desired Pb phosphate precipitates. Lead also sorbs readily to manganese hydroxides over iron oxides by a factor of 40, potentially further restricting mobilization of lead (Hettiarachchi et al., 2000). MO soil was 875 mg/kg Mn, the highest of the range soils studied.

**Crystalline Phases**

Most soils were dominated by sand or crystalline-phase quartz (70-85%) (Table 2). Sandy soils are characteristic of soil types used for small-arms firing range impact berms to reduce ricochet (ITRC, 2004; US EPA, 2001). There were two soils that were not dominated by quartz; NMa and NV soils had quartz = 5% and 40%, respectively.

The NV soil contained 50% carbonates and 40% quartz, and this range did not have a constructed impact berm. The NV soil was sampled along the firing-lane beds of an alluvial fan and had the least amount of clay soil of those surveyed. The NV soil also had the highest gravel content of soil types, which does not readily adsorb heavy metals (Bradl, 2004). NV soil also had a very low exchangeable lead association (Table 3).
Pb(II) Metal Partitioning

The sequential extraction found in the residual had an average of 10,114 mg/kg lead (SD = 7,783, from 13 to 44,500 mg/kg, n = 13), representing 79.8% of the total lead mass. This would suggest lead in the earthen berms is mostly in metallic form and not likely bioavailable or tending to dissolution naturally (Tessier et al., 1979). However, research by others has found lead pellets and fragments can transform quickly into other lead compounds on the surface of lead fragments and soils (Jorgensen and Willems, 1987). Berm average age = 33.7 y would provide ample time for oxidization of lead to hydrocerussite (2Pb(CO₃)(OH)₂), cerussite (PbCO₃), and massicot (PbO), the most commonly found Pb(II) forms in range soils (Hardison et al., 2004; Jorgensen and Willems, 1987). The high lead residual association differed from Cao et al. (2003), who found shooting range soils in Florida primarily associated with the carbonate fraction, and Bruell et al. (1999) found 40% of the total lead at a Connecticut shooting range was in the exchangeable fraction. This difference suggests lead-fraction associations will be uniquely defined for each shooting range.

The exchangeable lead fraction averaged 105 mg/kg (SD = 260.8, from non-detect to 797 mg/kg, n = 13) for all soils (Table 3). The two soils with the highest exchangeable amounts were CA = 797 mg/kg and SC = 85.1 mg/kg. Average lead in soils extracted as lead carbonates was 1055 mg/kg (SD = 3,059, from non-detect to 10,270 mg/kg, n = 13); with the highest carbonates CA =10,270 mg/kg, SD2 = 379 mg/kg, and NE = 303.4 mg/kg. The top four OM and sulfide associations in decreasing order were CA = 6,312 mg/kg, SD2 = 1,793 mg/kg, NE = 448 mg/kg, and SC = 372.1 mg/kg. Soil organic matter, sulfides, and carbonates affect the desorption of lead as observed by Suavé et al. (1998), where soils from pH 6.5 to 8 and with higher OM content contribute to a more labile lead species. There was no correlation between OM and sulfide and lead leachate (less than 0.075 mm fraction) observed, probably because these fractions were such low percentages of the total lead in the sample. For example, the SD2 soil for all fractions, excluding the residual, was 0.1% of the lead mass (Table 3).

Total soil lead was negatively correlated with moisture and not statistically significant in this study ($r^2 = 0.24$, $P = 0.10$, n = 12). This negative correlation agrees with Lee et al. (2002), who found a significant negative correlation with moisture content ($r^2 = 0.95$, $P \leq 0.001$). There was no correlation found between storm water lead concentrations and moisture content (Table 5).
**Batch results**

The batch test procedure was used to determine the adsorption effectiveness of amended versus non-amended soils. Non-amended soils served as control. FB and TSP, as supplied, were both generally effective adsorbents of lead cations with some exceptions (Table 6). Immobilization of lead for all soils by FB 3% and 5% amendments averaged 85.3% (SD = 24.5, from 12.4 to 99.7%, n=13) and 88.3% (SD = 24.3, from 19.5 to 100%, n=13), respectively. TSP 3% and 5% amendments’ average lead-adsorption results were 97.6% (SD = 3.13, from 90.8 to 99.7%, n=13) and 92.7% (SD = 22.7, from 17.3 to 99.8%, n=13), respectively.

CA, NMB, and SD2 soils had less than optimum adsorption performance by both amendments. The CA had 631 mg/L OM and sulfides and pH = 7.2, which the combination OM and near-neutral pH has been shown to preferably form lead OM complexes (Sauvé et al., 1998). NMB and SD2 had high OM compared to other soils in this study at 593 and 179 mg/L, respectively. However, soil pH = 8.2 for both. Although a pH = 8.2 is not near neutral, it is still within the less-soluble range for lead compounds and would partially contribute to reduced leachate in the NMB and SD2 soils. Likely, the combination of pH and OM content synergistically operates to sorb metal cations. Increasing OM was likely a significant contributor to the decreased sorption in all three soils (Strawn and Sparks, 2000).

The CA soil also had other significant presence of other metals, which has been shown to inhibit heavy metal immobilization by apatite (Seaman et al., 2001). The CA soil had 12,727 mg/kg iron. Coupled with the higher CA exchangeable (797 mg/L) and OM and sulfide (6,312 mg/L) lead fractions, this could further explain the low FB sorption of the CA soil. In other soils, total iron for MO soil = 18,210 mg/kg, NMB soil = 5,833 mg/kg, and SD2 soil = 16,993 mg/kg (Table 1). Each of these three soils, MO, NMB, and SD2, also showed reduced FB adsorption.

The TSP 5% amendment was not effective on the NMA soil (17.3%). The NMA soil had the highest CEC of the soils in this study group (26 meq/100 mL) and, uniquely, was the only soil with 75% gypsum content (Table 2). Gypsum (CaSO₄) calcium cations likely dominated the soil colloid exchange sites and inhibited PO₄²⁻ from reacting with lead cations. TSP 5% amendment for NMA soil performed poorly, and this was the only soil with inhibited TSP lead adsorption. TSP performance may be less effective in soils with high Pb concentrations, although no statistical correlation was found in this data set and the control Pb concentration range was significant from 1.04 to 1,294 mg/L.
The 3% FB amendment had the lowest overall general adsorption performance (85.3%, from 12.4 to 99.7%, SD = 24.5, n = 13) and the 3% TSP the best (97.6%, from 90.8 to 99.7%, SD = 3.1, n = 13). Brown et al. (2005) also found TSP amended 3.2% acidic soils effective for lead immobilization.

**Pb Soil Leaching Behavior in Column Studies**

Results of soil-column leaching with and without amendments are shown in Figures 4 and 5. The FBa-amended soils leached less lead than control for LA3, NMa, SC, SD2, VA1, and VA2 soils. The TSP amendment leached less lead than control for the VA1 and VA2 soils, likely due to the more porous soil allowing phosphate precipitate compounds to form more readily. All soils leached lead from control soils except NMb, NV, and SD2 soils. For NMb, the combination of pH = 8.2, low clay content, and high OM/sulfides yielded no lead in leachate during the five-week period. In the NV soil, a combination of pH = 8.7, very low moisture = 1.2%, mostly fine gravel, and a moderate lead amount in the < 0.075 mm fraction also resulted in no leaching. The SD2 control soil did not leach during the five-week study, but for different reasons than the NMb and NV soils. SD2 had the common denominator of higher pH = 8.2, a higher CEC = 31.5 meq/100 mL, and moderate clay and OM content, which was sufficient to hold metal cations.

The change in leachate pH from control was an important result as depicted in Figures 6 and 7. For both amendments, leachate pH was significantly different than control leachate pH (FBa: F = 9.47, P = 0.003, n = 120; TSP: F = 115.5, P << 0.001, n = 135). In general, in the first week, leachate pH dropped an average of 3.7 (SD = 0.93, n = 13) standard units for the TSP-amended soils. The TSP leachate pH gradually increased and approached the control pH by week five and did not return to original values except for the NMa soil as gypsum is known to ameliorate soil acidity. Effects of the TSP leachate pH reduction can be illustrated by observing the MO soil. The MO soil pH at week one = 4.0, week two = 4.6, week three = 5.0, week four = 5.3, and week five = 5.6 (Figure 6). The MO leachate control pH at end of week one = 8.5 and by the end of the five-week study = 8.8. The MO soil at low pH would see orthophosphate ions precipitated or adsorbed by species of Fe(III) and other metal divalent cations, capturing available surface and inter-phase micelle Pb(II) adsorption sites. Then, presumably, available lead cations were released. The MO soil had the highest iron content of all soils in the study.
An analysis of variance of only the control leachate amounts between the highest six clay-content soils and the remaining six soils, as reported above in particle-size distribution, found a significant difference in the two groups. This held true using either the particle-size series sequence or XRD series order (F = 11.0, P = 0.002, n = 60 and F = 7.5, P = 0.007, n = 60, respectively). This observation of clay correlation with lead retention in soils agrees with others (Bradl, 2004; King, 1988; Zhang et al., 2003).

CONCLUSIONS

Soils and storm waters from impact berms at 12 military shooting ranges were evaluated for lead leaching. The residual fraction accounted for 79.8% of total lead mass in all soils studied. All soils leached lead in excess of the EPA RCRA hazardous waste TCLP limit of 5 mg/L, except the MO soil, which had high clay content. Clay content and grain size are factors in the transport of lead in storm waters. Significant correlation was found between lead in storm water and total iron and manganese in soils. Total soil lead was negatively correlated with moisture content. FB-FBa., and TSP-amended soils generally performed as effective lead adsorbents, although ashed apatite may have impacted performance from a degraded internal structure presumably caused by the high-temperature ash process. Column studies found most soils tended to leach lead, except for those soils with high clay (MO) or high pH (NMb and NV). Amendments containing 3% TSP caused a significant decrease in pH. TSP pH changes may have caused increased lead leaching in soils as; pH was reduced to less than five in the first week of application. The FBA 3% amendment pH generally reflected the control pH for the study period. Apatite and phosphorus can be effective amendment soil treatments.

The 12 range soils were uniquely characteristic; however, essential range edaphic data can provide the necessary information to effectively manage and control lead leaching. While no single soil parameter can explicitly predict lead leaching behavior, each range environmental steward should understand the impact on berm soil of pH; particle-size distribution; CEC; and soil concentrations of iron, manganese, and organic matter. With this minimal information, shooting range managers can tailor appropriate BMP responses, minimize soil leaching behavior, and estimate the propensity of lead-cation migration to storm water.

ACKNOWLEDGEMENTS

The support provided by the U.S. Air Force for this study and the support of Parsons Inc. staff Mr. Bob Kull, Mr. John Ledbetter, Ms. Dawn DeMartino, and Mr. Ken Rice, who completed
the field and analytical work, is gratefully acknowledged. Special thanks to Dr. Steven Larson, U.S. Army, Vicksburg, Miss., for volunteering to complete the soil-column study, help interpret the data, and provide his corporate expert knowledge of shooting range soil chemistry; and to Ms. Michelle Thompson, U.S. Army, Vicksburg, Miss., who spent many hours laboring to make sure all the sequential extraction, daily pore volumes, and analysis got done. Thank you to Dr. Judith Wright, PIMS NW Inc., whose professional skill, knowledge, and advice were greatly appreciated. A grateful thank you to the reviewers who made very useful and constructive improvements to the manuscript. The views expressed in this article are those of the author and do not necessarily reflect the official views of the U.S. Air Force or Department of Defense.

REFERENCES


Figure 1. Locations of military small-arms firing ranges in nine states.
Table 1. Geotechnical characteristics of shooting-range berm soils. Soil color followed Munsell method, that is 2.5YR6/8 is hue or measure of chromatic composition – 2.5yellow-red, value is degree of lightness or darkness – 6 (black = 0; white = 10), and chroma is strength of spectral color – 8 (neutral = 0; strongest = 8). Berm ages are estimates based on interviews with range operations personnel. Soil texture abbreviations are Cly-clay, Fn – fine, Lm – loam, Slty – silty, Snd – sand, Sndy – sandy. LA2 and SD1 impact-berm soils were not analyzed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CA</th>
<th>LA1</th>
<th>LA3</th>
<th>MO</th>
<th>NE</th>
<th>NMa</th>
<th>NMb</th>
<th>NV</th>
<th>SC</th>
<th>SD2</th>
<th>VA1</th>
<th>VA2</th>
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<tbody>
<tr>
<td>Moisture %</td>
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<td>20.9</td>
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<td>24</td>
<td>14.4</td>
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<td>23.8</td>
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<td>17.7</td>
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<td>1.58</td>
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<td>1.61</td>
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<td>Fe (mg/kg)</td>
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<td>4237</td>
<td>18210</td>
<td>1312</td>
<td>1068</td>
<td>5834</td>
<td>6971</td>
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<td>16993</td>
<td>653</td>
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<tr>
<td>Mn (mg/kg)</td>
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<td>37.9</td>
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<td>875</td>
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<td>5YR3/4</td>
<td>10YR4/3</td>
<td>7.5YR3/1</td>
<td>5YR6/6</td>
<td>5YR4/6</td>
<td>10YR6/3</td>
<td>2.5YR4.5/8</td>
<td>10YR4/2</td>
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<td>Soil Texture</td>
<td>Lm</td>
<td>Cly Lm</td>
<td>Slty Cly</td>
<td>Slty Cly</td>
<td>Lm</td>
<td>Sndy Lm</td>
<td>Sndy Cly Lm</td>
<td>Fn Slty Snd</td>
<td>Sndy Cly Lm</td>
<td>Cly</td>
<td>Sndy Lm</td>
<td>Sndy Lm</td>
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<tr>
<td>Berm Age (yr)</td>
<td>41</td>
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<td>60</td>
<td>60</td>
<td>34</td>
<td>39</td>
<td>10†</td>
<td>22‡‡</td>
<td>18‡‡</td>
<td>15</td>
<td>5</td>
<td>40</td>
</tr>
</tbody>
</table>

† SAFR was constructed in 1961. In 1994, an earthen berm was constructed 25 m from firing line. Old berm at 100 m was abandoned.

‡‡ There is no impact earthen berm at this range. Sample was taken approximately 350 m on centerline from firing line.

‡‡‡ SAFR was constructed in 1967, but after a storm in 1986, the berm was pushed back and a new berm constructed.
Table 2. Percent soil crystalline phases as determined by XRD. Quartz and cristobalite are forms of SiO₂. Impact berm soil crystalline phases were predominantly sands with some clay. ND = not detected

<table>
<thead>
<tr>
<th>Crystalline Phases</th>
<th>CA</th>
<th>LA1</th>
<th>LA2</th>
<th>LA3</th>
<th>MO</th>
<th>NE</th>
<th>NMa</th>
<th>NMb</th>
<th>NV</th>
<th>SC</th>
<th>SD2</th>
<th>VA1</th>
<th>VA2</th>
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<tbody>
<tr>
<td>Clay</td>
<td>~12-14</td>
<td>~16-18</td>
<td>~18-20</td>
<td>~25</td>
<td>~20-22</td>
<td>~14-16</td>
<td>~5-7</td>
<td>~13-15</td>
<td>~4-6</td>
<td>~12-14</td>
<td>~17-19</td>
<td>~16-18</td>
<td>~10-12</td>
</tr>
<tr>
<td>Quartz</td>
<td>~70</td>
<td>~75</td>
<td>~75</td>
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<td>~80</td>
<td>~5</td>
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<td>~70</td>
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<td>Cristobalite</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>ND</td>
<td>ND</td>
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<tr>
<td>Feldspar</td>
<td>~2-3</td>
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<td>~5</td>
<td>~2</td>
<td>~5-7</td>
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<td>~2</td>
<td>~5</td>
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<td>~1-2</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>~10</td>
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<td>Gypsum</td>
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<td>ND</td>
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<td>ND</td>
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<td>&lt;0.5</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
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</table>
Figure 2. Particle size distribution.
Sample LA2 was not analyzed for particle sizes.
Figure 3. Particle size distribution. NV soil was collected approximately 350 m from the firing line along a perpendicular transecting firing lane’s center line. Sample SD1 was not analyzed for particle sizes.
Table 3. Bulk soil sequential extraction Pb associations in mg/kg. Values are the average of triplicate samples. Values <0.05 indicate results less than the detection limit of 0.050 mg/L. OM = organic matter; SD = standard deviation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CA</th>
<th>LA1</th>
<th>LA2</th>
<th>LA3</th>
<th>MO</th>
<th>NE</th>
<th>NMa</th>
<th>NMb</th>
<th>NV</th>
<th>SC</th>
<th>SD2</th>
<th>VA1</th>
<th>VA2</th>
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<tbody>
<tr>
<td>Exchangeable</td>
<td>797.0</td>
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<td>&lt;0.05</td>
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<td>24.4</td>
<td>10.6</td>
<td>0.1</td>
<td>2.5</td>
<td>&lt;0.05</td>
<td>85.1</td>
<td>6.9</td>
<td>12.3</td>
<td>&lt;0.05</td>
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<tr>
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<td>0.0</td>
<td>0.0</td>
<td>0.4</td>
<td>1.6</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>36.9</td>
<td>1.3</td>
<td>21.3</td>
<td>0.0</td>
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<tr>
<td>Percent</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>4.3</td>
<td>0.1</td>
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<td>4.6</td>
<td>0.0</td>
<td>2.8</td>
<td>0.1</td>
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<tr>
<td>Carbonates</td>
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<td>&lt;0.05</td>
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<td>303.4</td>
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<td>379.3</td>
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<td>7.6</td>
<td>2.8</td>
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<tr>
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<td>68.6</td>
<td>139.7</td>
<td>127.6</td>
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<td>33.2</td>
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<td>&lt;0.05</td>
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<td>30.1</td>
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<tr>
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<td>12.4</td>
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<td>23.8</td>
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<td>38.2</td>
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<td>11,417.8</td>
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<td>100.0</td>
<td>100.0</td>
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<td>100.0</td>
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Table 4. Lead fractional and soil-leaching associations. Totals are in units mg/kg, and SPLP and TCLP are in units mg/L. Results are averages of triplicates. There was insufficient mass for leaching analysis of two largest grain sizes (except CA and NV soil; see footnote). Blank cells indicate insufficient mass to analyze. <0.05 indicates instrument detection limit. SD = standard deviation.

<table>
<thead>
<tr>
<th>Grain Size (mm)</th>
<th>Analysis</th>
<th>CA</th>
<th>LA1</th>
<th>LA2</th>
<th>LA3</th>
<th>MO</th>
<th>NE</th>
<th>NMa</th>
<th>NMb</th>
<th>NV</th>
<th>SC</th>
<th>SD2</th>
<th>VA1</th>
<th>VA2</th>
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<tr>
<td>&gt; 4.75</td>
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<td>100903</td>
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<td>-</td>
<td>7685</td>
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<td>36710</td>
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<td></td>
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<td>6476</td>
<td>132868</td>
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<td>172</td>
<td>-</td>
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<td>12111</td>
<td>48883</td>
<td>-</td>
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<td>-</td>
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<td>0.250 to 2.00</td>
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† 2.00 to 4.75 mm SPLP: CA = 0.718 mg/L, SD = -0.635; NV = 0.050 mg/L, SD = 0.0 and 0.250 to 2.00 mm TCLP: CA = 967 mg/L, SD = 221 and NV = 0.469 mg/L, SD = 0.030
Table 5. Measured storm water lead concentrations. Measurements are averages where there are multiple samples and all measurements are in μg/L. Average dissolved Pb = 104.0 μg/L (SD = 152, n = 17). At least one field duplicate was taken for each sampling event. NS = not sampled. n = number of samples. Std Dev = standard deviation. Non-applicable fields were left blank.

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<th>LA2</th>
<th>LA3</th>
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<th>NMa</th>
<th>NMb</th>
<th>NV</th>
<th>SC</th>
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Table 6. Batch study results. Amendments with percent adsorbed < 90.3% have been highlighted by bold-lined boxes. Control and adsorbed amounts are in units mg/L. Results are averages of triplicates. FB = apatite II; TSP = triple super phosphate; SD = standard deviation. <0.05 indicates instrument detection limit.

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% Adsorbed | 12.4| 99.1| 97.9| 87.5| 81.0| 61.5| 99.2| 99.0| 97.0| 90.3| 85.2| 99.6| 99.7| 53.7| 99.8| 99.7| 99.0| 100.0|

Mass removed was greater than control.
Figure 4. Lead leaching behavior in soils from column studies. Control had no amendments added. Amounts are accumulative over five week study period. Original soil lead concentration is shown in parenthesis. Amendment 3% FBA reduced the amount of lead released compared to control for L3 and NMa soils. Amendment 3% TSP did not reduce the amount of lead released compared to control for any of these soils.
Figure 5. Lead leaching behavior in soils from column studies. Control had no amendments added. Amounts are accumulative over five-week study period, except VA1 and VA2 where study period was 27 days. Original soil lead concentration is shown in parenthesis. Amendment 3% FBa reduced the amount of lead released compared to control for the SC, VA1, and VA2 soils. Amendment 3% TSP reduced the amount of lead released compared to control for VA1 and VA2 soils.
Figure 6. Column study leachate FBa leachate pH was significantly different than control (F = 9.47, P = 0.002, n = 119), and TSP leachate pH was also significantly different than control (F = 115.5, P << 0.001, n = 135). Initial pH drop after TSP treatment was substantial and in most cases never returned to control value. LA3 soil with TSP amendment had no leachate at the end of week one, and FBa amended soil had no leachate at the end of weeks 1, 3, 4, and 5. NE soil with FBa amendment had no leachate at the end of weeks three and five.
Figure 7. Column study leachate pH. FBa and TSP leachate pH were significantly different than control (see Figure 6 note). VA1 and VA2 soils leachate pH were not measured. TSP leachate pH drop was significant in the first week of use, and returned within one pH standard unit for NV and SD2 soils by the end of the five-week study period.