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Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering

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Abstract

Contamination of shooting range soils from the use of Pb bullets is under increasing scrutiny. Past research on Pb contamination of shooting ranges has focused on weathering reactions of Pb bullets in soil. The objective of this study was to determine the significance of abrasion of Pb bullets in contributing to soil Pb contamination. This was accomplished by firing a known mass of bullets into sand and analyzing for total Pb after removing bullets, through field sampling of a newly opened shooting range, and a laboratory weathering study. 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 at 0.5 m height, and from the rifle range berm soil was 1142 mg/kg 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 μg/l (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 ($Pb_3(CO_3)_2(OH)_2$), as well as to a lesser extent cerussite ($PbCO_3$) and massicot (PbO) within one week. Our study demonstrated that abrasion of lead bullets and their subsequent weathering can be a significant source of lead contamination in soils of a newly opened shooting range.

Keywords: Metal contamination; Weathering; Shooting range; Lead; Hydrocerussite; Abrasion

1. Introduction

Approximately 80 000 tons/year of Pb was used in the production of bullets and shot in the United States in the late 1990s (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.

Lead contamination in the environment is of concern as it is a known toxin, which has deleterious effects on the human neurological system. Lead present in soil and dust has been directly related to the Pb levels in blood (Davies, 1995). 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,

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and if the Pb were 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 excluding pellets have been reported in shooting range soils (Manninen and Tanskanen, 1993).

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 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; and (3) to determine the weathering rate of this abraded Pb through a laboratory experiment.

2. Materials and methods

2.1. 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 m^3 wood box was constructed with an opening at one end. The box was transported to a shooting range located in Ocala, Florida (OSR) (Fig. 1), where the experiment was performed. At the shooting range, the box was half filled with play sand. The sand was slightly compacted within the box to simulate a shooting range berm. The box was then set up, with the opening toward the shooter.

Two hundred rounds of 0.22-caliber non-jacketed bullets were fired into the sand within the box from a revolver at a distance of approximately 7 m. 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 five buckets that had been previously rinsed with nitric acid and deionized water to prepare for transport. The bullets were kept in plastic sample bags.

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: Acid Digestion of Sediments, Sludges, and Soils).

2.2. Field sampling

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

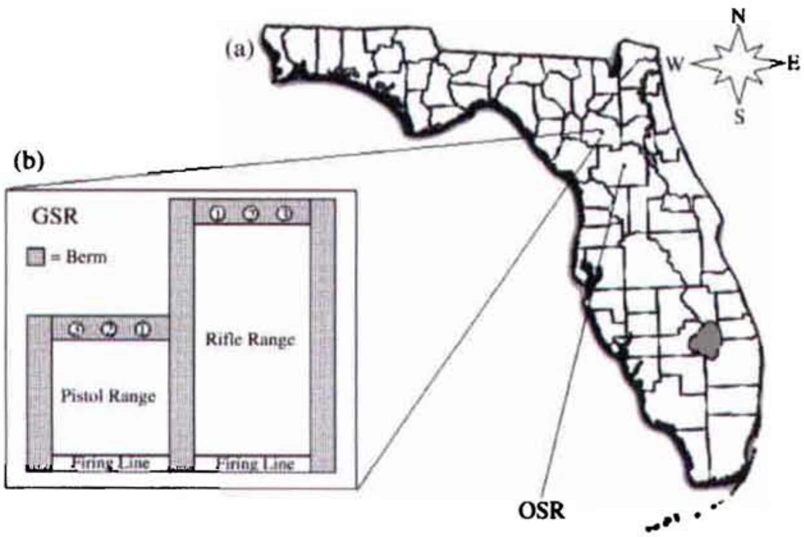

Fig. 1. The position of the study sites in Gainesville (GSR) and Ocala (OSR), Florida (a) and schematic of GSR pistol and rifle range. (b) Sampling locations on berms are numbered.

and rifle ranges are approximately 30 and 100 m from the firing line to the berm. There are also berms that line both sides of the ranges, separating the pistol from the rifle range. The soil on both ranges is very 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. 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 m from the bottom of the berm. Soil samples were not taken from the same exact location, 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.

Samples were collected at positions 1–3 on the pistol range, and position 1 on the rifle range (Fig. 1). 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: Acid Digestion of Sediments, Sludges, and Soils). Bullets and bullet fragments that were larger than 2 mm were manually removed and excluded from the digestion.

2.3. Laboratory studies

2.3.1. 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 (Cao et al., 2003; 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 elements present in soils according to the USEPA.

2.3.2. 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 200-mesh Pb powder to simulate abraded Pb. Final treatments consisted of 150 g of soil within 100 ml glass beakers. Triplicates of the soil were incubated at 25±2 °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 7 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 270-mesh sieve to filter Pb particles from soil.

The mineral components that passed through the 270-mesh 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., 2003; Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995).

2.4. 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).

Table 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

3. Results and discussions

3.1. Field abrasion experiment at ocala shooting range (OSR)

Total and SPLP Pb concentrations from the five buckets of sand that were collected from the field abrasion experiment are presented in Table 1. The average Pb concentration on a mass basis for the five buckets was 91 mg/kg, which translated to 8 g of abraded Pb for all 200 0.22-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 four and five were significantly less than those of the other buckets (Table 1). These buckets represent the sand that was removed last from the wood box. Typically, the 0.22-caliber 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.

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 occured 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 1). All but one sample exceeded the

15 $\mu g\ l^{-1}$ 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 [$PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$] (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., 2003), in contrast to metallic Pb.

The high SPLP concentrations seen in these samples (Table 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.

3.2. Field sampling at Gainesville shooting range (GSR)

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

The highest total Pb concentration from the pistol range berm soil was 193 mg/kg at 0.5 m (Fig. 2a). The highest total Pb concentration from the rifle range berm soil was 1142 mg/kg at 1.0 m (Fig. 2b). At each position, the lowest total (Fig. 2) and SPLP Pb (Fig. 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 $Pb_3(CO_3)_2(OH)_2$] 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.

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). Three of the four samples (Fig. 3b) taken from the rifle range exceeded the 15 $\mu g\ l^{-1}$ critical level of a hazardous waste (USEPA, 1995). However, only two samples (Fig. 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 latter would be less

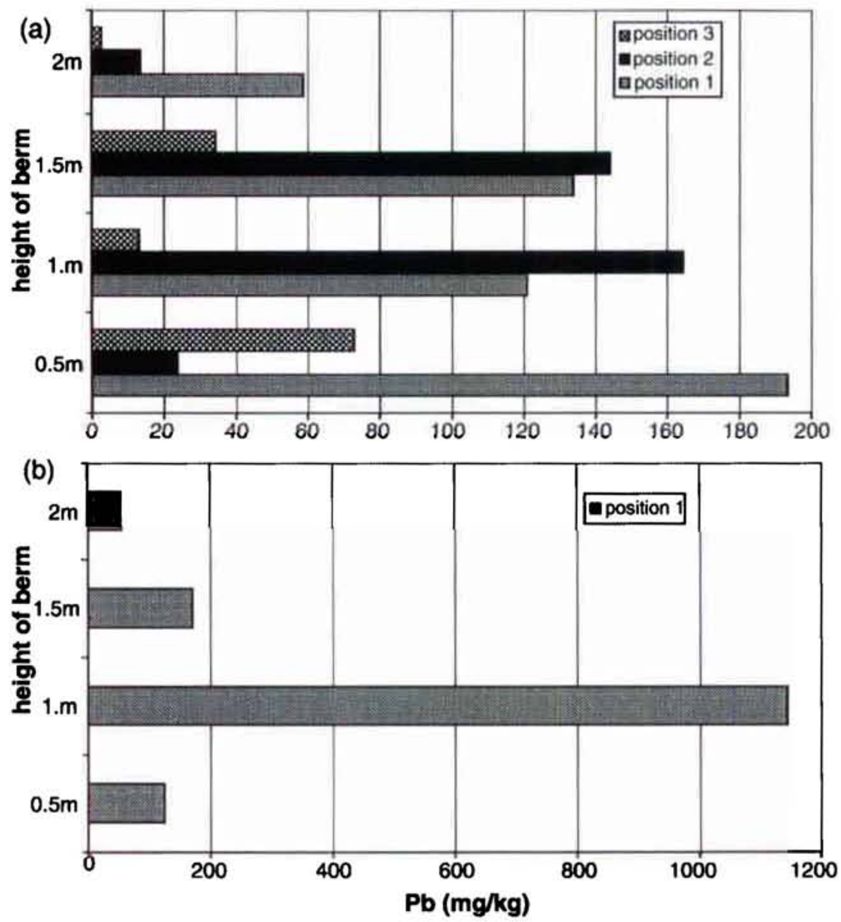

Fig. 2. Total Pb concentration in GSR Pistol (a) and Rifle (b) Range berm soils after 3 months of operation.

representative of the shooting range soil environment.

3.3. 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 200-mesh metallic Pb powder to simulate abraded Pb. Fig. 4a shows the XRD pattern for the metallic Pb used in this experiment, as well as standard hydrocerussite. The predominate metallic Pb peak from the powder was at a *d*-spacing of 2.84, as well as a secondary peak at $d=2.47$. The predominate peak for hydrocerrusite is at $d=2.62$, with secondary peaks at $d=3.27$ and $d=3.60$.

Fig. 4b 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). This suggests that abraded Pb in shooting range is weathered at an accelerated rate and rapidly converted to Pb-minerals. Virtually all metallic Pb was transformed to hydrocerussite as well as other Pb minerals within 7 days. Previous

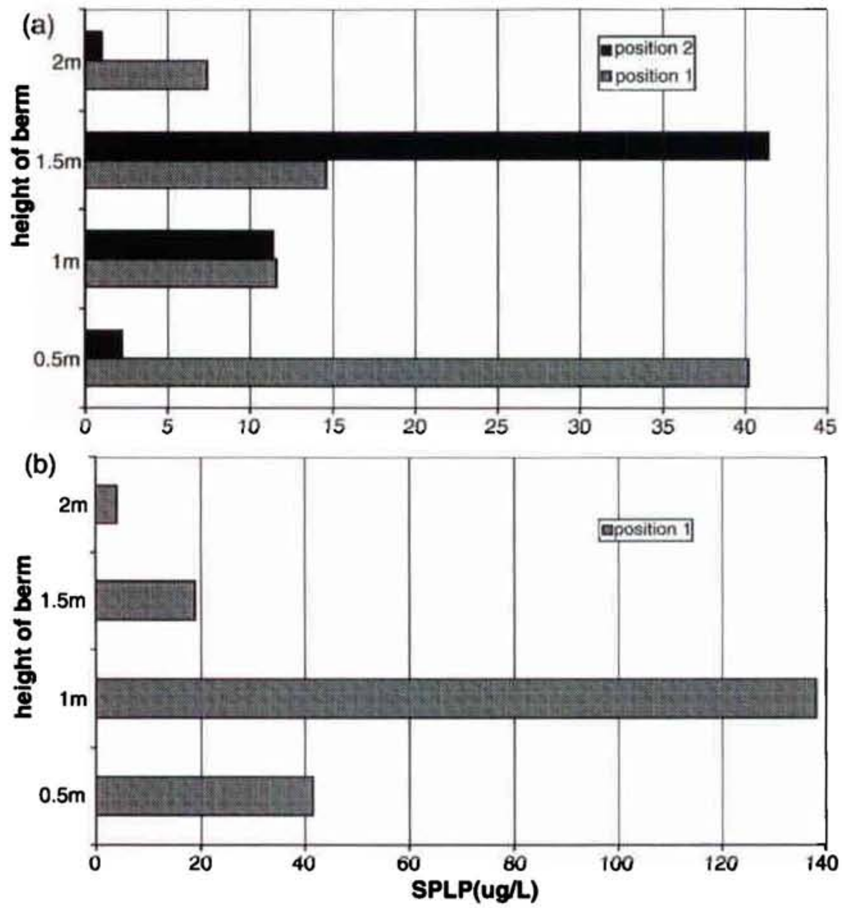

Fig. 3. SPLP Pb concentration in GSR Pistol (a) and Rifle (b) Range berm soils after 3 months of operation.

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). 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 is a cost effective way to remediate Pb-contaminated soils. Lead phosphates are extremely insoluble compared to other Pb compounds (Lind-

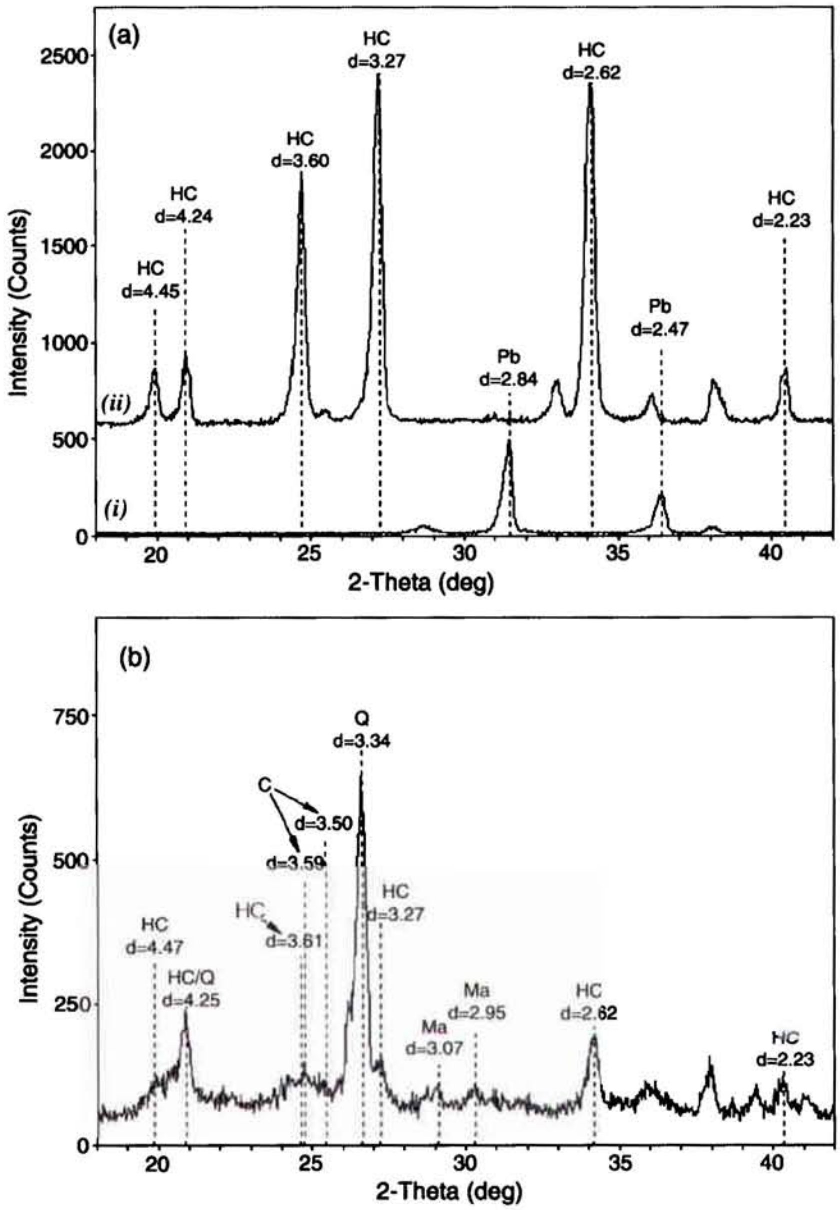

Fig. 4. X-Ray diffraction patterns for Pb powder (i) used in the incubation experiment, and standard hydrocerussite (ii) (a) and for Pb powder after 7 days of incubation in soil (b) at field moisture capacity: Q – quartz, HC – hydrocerussite, C – cerussite, Ma – massicot (PbO) Pb – metallic Pb.

say, 1979; Rickard and Nriagu, 1978), thus reducing the leachability of Pb in soils.

4. Conclusions

This study demonstrated that physical abrasion of Pb bullets passing through soil contributes substantially to soil Pb contamination in shooting ranges. The 0.22-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.

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