

Distribution of Pb and As in Soils at a Shooting Facility in Central Florida

M. Chen*, L. Q. Ma, and W. G. Harris

ABSTRACT

Lead (Pb) and arsenic (As) are trace elements of environmental concern due to their adverse impacts on humans and animals. The objective of this study was to determine the extent of Pb and As contamination in soils at a target shooting facility located in central Florida. This facility has been in operation for 14 yr and includes a fixed-target rifle range and a moving-target shotgun range. Soil samples were collected from both surface (0-10 cm) and profile (depths of 0-10, 11-30, 31-50, 51-100, 181-200 cm) from this site. Concentrations of Pb, As, P, Fe, and Al were determined using USEPA Method 3051a (microwave, $\text{HNO}_3/\text{HCl} = 3:1, \text{v/v}$). Total Pb in surface soils varied from 330 to 17 850 mg Pb kg^{-1} , with the greatest concentration in the middle of the backstop berm at the rifle range. Total As in surface soils varied from 0.50 to 107 mg As kg^{-1} with the greatest concentration found on the central transect at 30 m from the shooting stand at the shotgun range. Elevated soil pH levels were associated with elevated soil Pb concentration. A Toxicity Characterization Leaching Procedure (TCLP) test indicated that Pb in all surface soils from the rifle range exceeded the 5 mg Pb L^{-1} critical level of federal regulation for solid wastes and hazardous wastes provided by the Resource Conservation and Recovery Act (RCRA) and would be characterized as hazardous waste.

Lead and As are both trace metals of environmental concern due to their adverse impacts on humans and animals. Many anthropogenic processes, such as use of Pb shots at shooting ranges, have significantly increased concentrations of these metals in the environment. Lead contamination of soils at shooting ranges from the use of Pb shot and Pb bullets is under increasing scrutiny as a potentially significant source of Pb pollution (Rooney et al., 1999; Craig et al., 1999). Annual deposition of metallic Pb of up to 6 000 Mg was reported for the Netherlands, Denmark, Canada, England, and U.S.A. (Scheuhammer and Norris, 1995). Lead shot is 950 to 970 g Pb kg^{-1} comprised of Pb (by weight), 4.0 to 20 g Sh kg^{-1} , and 2.0 to 8.0 g As kg^{-1} (Fisher and Hall, 1986). A study of outdoor shooting ranges in the U.S. documented soil Pb levels exceeding 1 000 mg kg^{-1} at six of eight sites investigated (Murray et al., 1997). In addition, Pb absorbs very strongly to soil particles and colloids, which provides an exposure risk to human by direct ingestion and inhalation (Bruell et al., 1999). The USEPA has set up a soil screening level of 400 mg kg^{-1} (USEPA, 1996). When Pb concentration was elevated, the TCLP and the synthetic precipitation leaching procedure regulated by RCRA and its state counterparts can be used to examine the Pb toxicity and mobility, respectively (USEPA, 1995; Bruell et al., 1999).

M. Chen, Institute of Geography and Natural Resources, Chinese Academy of Sciences, Building 917, Datun Road, Beijing 100101, China; L. Q. Ma and W. G. Harris, Soil and Water Science Dep., Univ. of Florida, Gainesville, FL 32611-0290. This research was supported by the Florida Agric. Exp. Sin. and is approved for publication as Journal Series, Nu N-02082.

*Corresponding author (mchen@mail.ifas.ufl.edu).

Contribution published in

Soil Crop Sci. Soc. Florida Proc. 60:15-20 (2001).

Shooting is a popular recreational sport. Based on our preliminary survey, there are ~238 gun clubs operating in Florida alone. Natural background concentrations of Pb and As in Florida soils are extremely low relative to soils from other regions of the world (Chen et al., 1999). High amounts of accumulated Pb at shooting ranges are of particular concern in Florida due to a combination of natural factors (low soil pH, low soil clay and organic matter content, high rainfall, shallow groundwater level) that tend to accelerate Pb-shot weathering. In addition, many shooting ranges are located adjacent to environmentally sensitive wetlands, streams, and lakes, and Pb products from the rapid weathering of Pb shot from these shooting ranges may be disbursed directly into wetland and aquatic environments (Scheuhammer and Noms, 1995). Currently, the impact of these accumulated Pb shot in recreational shooting ranges on the environment in Florida is not well understood.

The purpose of this study was to investigate i) total Pb and As concentration distributions in a recreational shooting range soils, and ii) leaching characteristics of elevated Pb in these soils. Quantifying these parameters will help establish approach management procedures at recreational shooting ranges in Florida especially designed to minimize environmental impact.

MATERIALS AND METHODS

Following a preliminary survey of shooting ranges in Florida, a public shooting range was selected in central Florida. This shooting range is operated through a special-use permit with the USDA Forest Service. The 14-yr-old shooting range includes two different shooting areas: rifle and shotgun ranges. The rifle range is approximately 91 m in length, with targets set at 14, 23, 46, and 91 m (Fig. 1). A backstop berm is built on top of the original ground with soil excavated from the backside, forming a water impoundment. The shotgun range provides an area where shooters can shoot at clay targets. Both ranges were constructed in 1987, and apparently there never has been a systematic cleanup and removal of spent bullets in the rifle range backstop berm or Pb shot dispersed over a wide area in the shotgun range. It is estimated that in excess of 25 000 people utilize this facility annually.

In March of 2000, seven composite surface soil samples (0-10 cm) at the rifle range were collected along a single transect at 9, 18, 27, 36, 54, 72, and 91 m from the firing stands. Two additional soil samples were collected from the top and middle of the backstop berm. Five samples (0-10, 11-30, 31-50, 51-100, and 181-200-cm depths) were collected within the soil profile at the rifle range roughly 27 m from the shooting stands. Four surface soil samples (0-10 cm) were collected along a single central transect at the shotgun range at 30, 60, 120, and

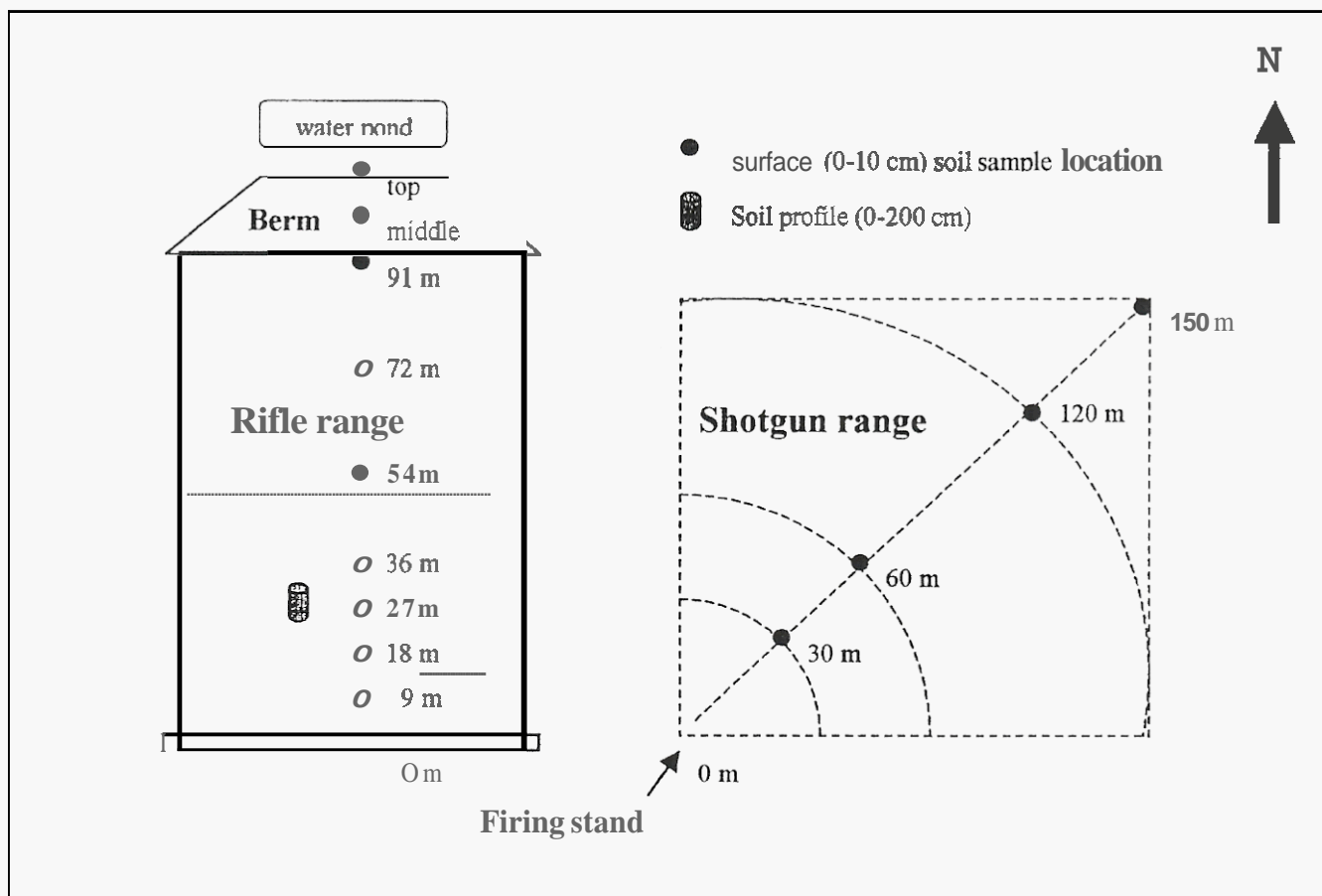


Fig. 1. Schematic of the rifle and the shotgun shooting ranges in central Florida.

150 m from the firing stand (Fig. 1). A clay-pigeon sample was also collected to check these targets for their potential as a source of Pb.

Soil samples were airdried, sieved (2 mm), and digested using USEPA method 3051a by a microwave-assisted $\text{HNO}_3\text{-HCl}$ (v/v = 3:1) digestion (USEPA, 1997), which is equivalent to the hot-plate digestion procedure for Florida soils (Chen and Ma, 1998). Intact Pb shot was separated from the coarse soil fraction (removed by 2-mm sieve) and counted. Toxicity Characterization Leaching Procedure Pb concentrations in the soils were extracted and determined using extraction fluid No. 1 ($\text{pH} = 4.93 \pm 0.05$) following a modified procedure of USEPA Method 1311 (USEPA, 1995), which is a test used to determine the toxicity of waste in a highly buffered environment. A 5.7-mL aliquot of glacial acetic acid in 500 mL of D.I. water and 64.3 mL of 1N NaOH, was diluted to a volume of 1 L. A 100-mL aliquot of this extracting solution was added to a plastic bottle containing 5.0 g of soil. The bottle was sealed with a screw-cap lid and placed on an end-to-end shaker at 30 rpm for 18 ± 2 h. Lead and As concentrations were analyzed using a Perkin-Elmer SIMMA 6000 (Norwalk, CT) graphic-furnace, atomic absorption spectrophotometer. Concentrations of Al, Fe, and P were analyzed on a multi-channel inductively coupled plasma spectrometry (ThermoJarrell Ash ICAP 61-E, Franklin, MA). Soil pH

was determined by using a combination electrode after mixing 5.0 g soil with 5 mL distilled deionized water for 24 h. Elemental recoveries of As, Al, Fe, and P from a National Institute of Standard and Technology standard reference material (NIST SRM 2710) by USEPA method 3051a (USEPA, 1997) were 1080, 280, 800 and 1140 g kg^{-1} , with relative percent differences of 9.4, 26, 1.2, and 35 g kg^{-1} , respectively. Lead recovery was 870 g kg^{-1} , with a relative percent difference of 17 g kg^{-1} . The relative percent difference was a measure of the precision of the chemical analysis. Relations between the soil analytical data were investigated by Pearson correlation analysis.

RESULTS AND DISCUSSION

Distribution of Total and TCLP Pb in Rifle Range Soils

In the rifle range, many brass cartridges were observed within 20 m of the firing stands, whereas Pb bullets were predominantly found in the backstop berm. The highest density of Pb bullets (180 g bullets kg^{-1} soil) was found in the middle of the berm. This is comparable to the results of Astrup et al. (1999), who reported that in a 30-yr-old shooting range in Denmark, up to 40% of the backstop material consisted of Pb bullets. High Pb content of bullets (47 g kg^{-1} soil) was also found in soils from the top of the berm, suggesting that some

Pb bullets could be off-target or could have ricocheted to the top and backside of the backstop berm when hitting other bullets. No bullets or bullet fragments were found in soil samples through the 0 to 72 m central transect. Bullet and bullet fragments within soil samples at the 91-m sampling location collectively represented 91 g Pb kg⁻¹ soil.

The natural background concentration of total Pb in Florida surface soils ranges from 0.1 to 290 mg Pb kg⁻¹, with a geometric mean of 5.4 mg Pb kg⁻¹ (Chen et al., 1999). Distribution of total Pb (determined after removal of Pb bullets by sieving through a 2-mm screen) in soils along the sampling transect showed that soil in the rifle range was contaminated with Pb (Fig. 2). Total Pb concentrations in surface soils (excluding the berm) ranged from 875 to 4 448 mg Pb kg⁻¹, with the highest concentration at 27 m and the lowest at 72 m from the shooting stands. Most soils had Pb concentrations much greater than the Florida DEP soil-cleanup goals (500 mg Pb kg⁻¹ for residential and 1 000 mg Pb kg⁻¹ for industrial soils). They are also higher than the USEPA soil screening level of 400 mg Pb kg⁻¹, which is a risk-based value that provides a reference point for establishing site-specific clean up (USEPA, 1996). The highest Pb concentration (17.8 g Pb kg⁻¹) was in the middle of the backstop berm, which includes Pb associated with the soil particles as well as bullet fragments of Pb bullets <2 mm. This is less but comparable to the total Pb concentration (40.4 g Pb kg⁻¹) in surface soils close to the target of a 30-yr-old

shooting range in Denmark (Astrup et al., 1999). The high Pb contents associated with the soil in the backstop berm, however, suggested that even after removing the Pb bullets by sieving, the soil was strongly contaminated with Pb and would require special handling.

When concentrations of total Pb in soils are above the soil screening level of 400 mg kg⁻¹, TCLP-Pb concentration could be important in assessing the toxicity of wastes (Bruell et al., 1999). In the current study, the modified TCLP test results showed that all soil samples from the rifle shooting ranges exceeded the 5 mg Pb L⁻¹ critical level and would be characterized as hazardous waste by the TCLP (USEPA, 1995). The distribution pattern of TCLP-Pb in soils of the rifle range was similar to that of total Pb concentrations (Fig. 2). The correlation was highly significant (r = 0.98) between total and TCLP-Pb concentrations in the rifle range soils, suggesting that total Pb concentration is important in assessing the toxicity and mobility of Pb in Pb-bullet contaminated soil.

Distribution of Total and TCLP Pb in Shotgun Range Soils

In the shotgun range, total Pb concentrations in soils were greatest at 30 m from the shootingstand (15 368 mg Pb kg⁻¹ soil) and decreased to 330 mg Pb kg⁻¹ at 150 m (Fig. 3). These results differ from studies conducted in England (Mellor and McCartney, 1994) and New Zealand (Rooney et al., 1999), who reported greatest Pb

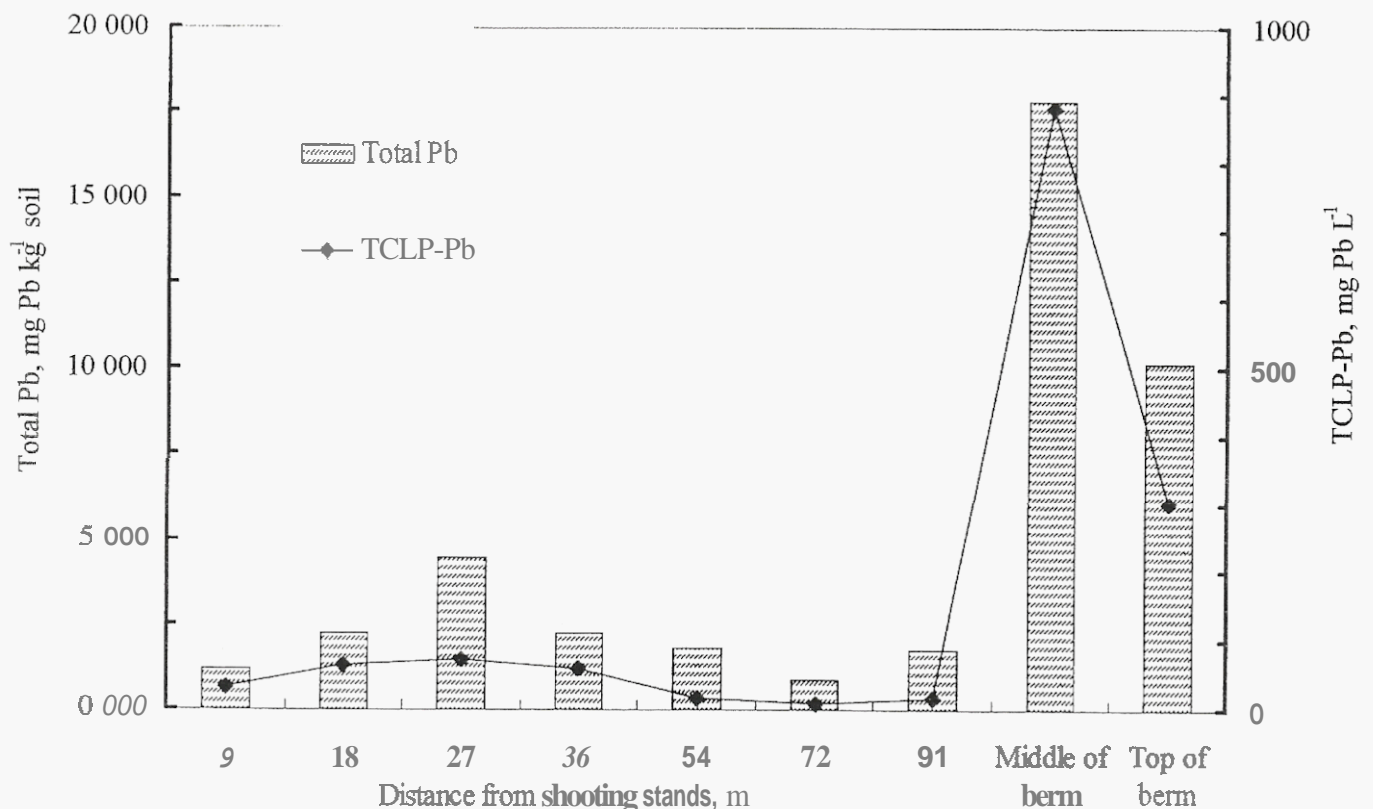


Fig. 2. Spatial distribution of concentrations of total Pb and Toxicity Characterization Leaching Procedure (TCLP) Pb in 0- to 10-cm depths soils of a rifle range in central Florida.

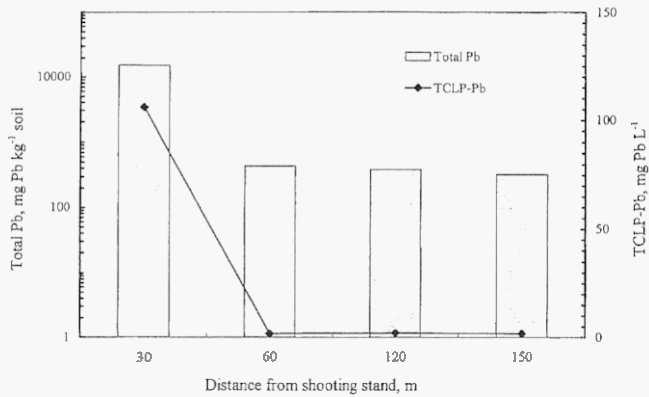


Fig. 3. Distribution of concentrations of total Pb and Toxicity Characterization Leaching Procedure (TCLP) Pb in 0- to 10-cm depth soils of a shotgun shooting range in central Florida.

concentrations were found at 80 to 140 m from the shooting stands. This difference may reflect different shotgun shooting habits or target trajectories used at the various sites. At the Florida sites, the greatest density of clay target fragments (300 g clay target kg⁻¹ soil) was also observed at 30 m from the shooting stand. However, total Pb concentration in the clay target debris was low (26.6 mg Pb kg⁻¹), suggesting little impact of the clay targets on total concentration of Pb in soil at the shotgun range.

It has been reported that Pb-shot densities in the upper 7.5 cm of soil in the shot-fall zone of trap and skeet ranges in New Jersey ranged from 4.15×10^6 to 3.70×10^9 shot ha⁻¹ (Stansley et al., 1992). A 2-mm sieve removed approximately 85% of the total Pb from the soil at a clay target shooting facility in New Zealand (Rooney et al., 1999). In the current study, the pattern of Pb-shot accumulation along the sampling transect was different from that of total Pb concentration. Lead shot was approximately 50 shots 100 g⁻¹ soil (or 44 g Pb-shot kg⁻¹ soil) at 30 m from the shooting stand, but increased to 83 shots 100 g⁻¹ soil (67 g Pb-shot kg⁻¹ soil) at 60 m and 61 shots 100 g⁻¹ soil (28 g Pb-shot kg⁻¹ soil) at 120 m. Thereafter, shots decreased to 9 shots 100 g⁻¹ soil (6.7 g Pb-shot kg⁻¹ soil) at 150 m from the shooting stand. This is consistent with data from a clay pigeon shooting site in northern England (Mellor and McCartney, 1994).

The results of TCLP-Pb in soils at the shotgun range showed that only surface soil at 30 m from the shooting stand (106 mg Pb L⁻¹) exceeded the 5 mg Pb L⁻¹ critical level and would be characterized as hazardous waste by the TCLP (USEPA, 1995) (Fig. 3). The distribution pattern of soil TCLP-Pb for the shotgun range was similar to trends recorded for total Pb concentration. The very high concentrations of both total and TCLP-Pb suggested that at the shotgun range, surface soils at approximately 30 m from the shooting stand were strongly contaminated with Pb and would require Pb-clean up or special management practices.

Distribution of Total and TCLP Pb in Soil Profile

Total Pb concentration decreased dramatically with depth from 0 to 200 cm (Fig. 4). The greatest soil total

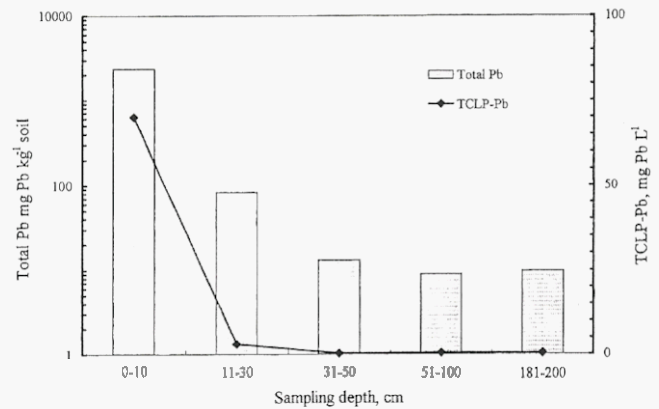


Fig. 4. Distribution of concentrations of total Pb and Toxicity Characterization Leaching Procedure (TCLP) Pb in soil profile of the rifle range in central Florida.

Pb (2357 mg Pb kg⁻¹) remained in the surface horizon (0-10 cm) and the lowest Pb concentration (9.0-9.8 mg Pb kg⁻¹) was found within the 51 to 200-cm depth, comparable to the background concentrations found in Florida surface soils (Chen et al., 1999). However, a relatively high concentration (83 mg Pb kg⁻¹) in the subsurface horizon (11-30 cm) and the trend of rapidly decreasing Pb concentrations with depth indicates that downward movement is minimal (Astrup et al., 1999). Other investigators have suggested that the movement of Pb through the soil profile is mediated by the formation of Pb carbonate or sulfate compounds from which Pb is subsequently mobilized under conditions of slightly acid soils at the study site (Murray et al., 1997; Rooney et al., 1999).

The distribution of the TCLP-Pb in the soil profile was similar to that of the total Pb concentrations (Fig. 4). As expected, soil TCLP-Pb levels exceeded the 5 mg Pb L⁻¹ critical level only for surface horizon soils (70 mg Pb L⁻¹), and would be characterized as hazardous waste (USEPA, 1995). Concentrations of TCLP-Pb in the subsurface and lower soil horizons were less than 5 mg Pb L⁻¹, indicating that Pb in surface soils does not readily migrate downward.

Distribution of Concentrations of Total As

Background concentration of As in Florida surface soils ranges from 0.01 to 52.6 mg As kg⁻¹, with a median of 0.42 mg As kg⁻¹ (Chen et al., 1999). Concentration of total As in soils along the transect at the rifle range varied from 1.05 to 6.12 mg As kg⁻¹, with the greatest concentration at the middle of the backstop berm and the lowest at 36 m from the shooting stands (Table 1). All these values exceeded the Florida DEP soil cleanup goal for As in residential soil (0.80 mg As kg⁻¹) based on direct exposure (Tonner-Navarro et al., 1998). The high As contents associated with the soil in the middle of the backstop berm (6.12 mg As kg⁻¹) exceeded the Florida DEP As target for industrial soil (3.70 mg As kg⁻¹) based on direct exposure (Tonner-Navarro et al., 1998), suggesting the soil was strongly contaminated with As and would require special handling. Total concentrations of As in the soil profile at

Table 1. Distribution of pH and total concentrations of As, P, Al, and Fe and their correlation coefficients with total and TCLP-Pb in 0- to 10-cm depth soils of a rifle shooting range in central Florida.

Distance from the firing line	Soil pH	As	P	Al	Fe
		----- mg kg ⁻¹ -----		----- g kg ⁻¹ -----	
m					
9	6.7	1.37	77.1	2.37	1.88
18	6.7	1.88	61.6	2.65	1.55
27	6.1	3.69	160	3.93	2.28
36	6.3	1.05	53.6	1.34	0.87
54	5.6	1.84	74.0	1.26	1.13
72	5.4	2.90	120	2.51	1.75
91	5.5	1.71	131	2.50	1.43
Top of berm	6.8	3.57	88.6	4.43	2.32
Middle of berm	7.7	6.12	44.0	1.70	1.44
Total Pb (r)	0.78*	0.89**	-0.35	0.13	0.19
TCLP-Pb (r)	0.80*	0.87**	-0.44	4.05	0.04

*,**Spearman's rank correlation coefficient is significant at the P < 0.05 and 0.01, respectively.

the rifle range varied from 0.54 mg As kg⁻¹ at 180- to 200-cm horizon to a maximum value of 1.88 mg As kg⁻¹ at 11 to 30 cm (Table 2). Distribution of total As in soils of the rifle range is similar to that of total Pb. A strong positive correlation (r = 0.89) exists between concentrations of total As and total Pb in rifle range soils (Table 1), suggesting that elevated concentrations of both elements are from the same sources. However, the fact that the greatest As concentration was found in the subsurface horizon instead of the surface horizon may suggest that As is more mobile in soils than Pb.

The greatest As concentration (107 mg As kg⁻¹) in shotgun range soils at the shotgun range was found at 30 m from the shooting stand. At 120 to 150 m, As concentrations fell rapidly to <0.80 mg As kg⁻¹, comparable to the background concentration of As in Florida surface soils (Chen et al., 1999).

Interrelationships with Soil pH and Total P, Al, and Fe

Soil properties such as pH, clay contents, organic C, total Fe and Al, as well as P, are important factors that influence metal distributions in Florida surface soils (Chen et al., 1999). Elevated soil pH was associated with soils contaminated with Pb shot at a shooting range in Denmark and was attributed to the corrosion of the Pb bullets (Astrup et al., 1999). In the current investigation, reference soil samples collected at -300 m from the shooting facility had pH values <5. At the rifle range, elevated soil pH was found <36 m from the shooting

stands and at soils on the backstop berm of the rifle range (Table 1), as well as in the surface horizon of the soil profile (Table 2). Strong positive correlations existed between soil pH and concentrations of total Pb (r = 0.78), as well as TCLP-Pb (r = 0.80) at the rifle range (Table 1), suggesting that the elevated soil pH could be a result of the soil contaminated with Pb bullets.

At the shotgun range, soil pH reached a maximum of 7.8 at 30 m from the shooting stand, which is consistent with results of Mellor and McCartney (1994), who found the greatest soil pH at 50 to 60 m from the shooting area of a clay pigeon shooting site in northern England. Concentrations of total Al, Fe, and P in soils of the shotgun range were also high at 30 m from the shooting stand. However, no significant correlation coefficients existed between total Al, Fe, and P with either total Pb or TCLP-Pb (Table 1).

CONCLUSION

This study indicated that concentrations of total Pb and As were elevated in surface soils at the shooting range in central Florida, especially soils from the backstop berm of the rifle range and at 30 m from the shooting stand of the shotgun shooting area. Toxicity Characterization Leaching Procedure tests confirmed that Pb in most surface soils exceeded the 5 mg Ph L⁻¹ critical level and should be treated with special handling. However, since soil pH tended to be elevated, migration of the elevated Pb in the soil was limited.

ACKNOWLEDGMENT

This research was sponsored in part by the Florida Center for Solid and Hazardous Waste Management (Project contract No. 990111). The authors would like to thank Captain Ed Tyer and Lt. Greg Workman of the Florida Fish and Wildlife Conservation Commission. Their permission and assistance in soil sampling made this study possible. The helpful suggestion made by Drs. R. Gilbert, R. W. Rice, J. B. Sartain and two anonymous reviewers is greatly appreciated.

Table 2. Distribution of pH and total As in the soil profile of a rifle shooting range in central Florida.

Depth of sampling	Soil pH	As
		mg kg ⁻¹
cm		
0-10	6.7	1.37
11-30	5.9	1.88
31-50	5.0	0.86
51-100	4.8	0.89
181-200	5.1	0.54

REFERENCES

- Astrup, T., J. K. Boddum, and T. H. Christensen. 1999. Lead distribution and mobility in a soil embankment used as a bullet stop at a shooting range. *J. Soil Contam.* 8:653-665.
- Bruell, R., N. P. Nikolaidis, and R. P. Long. 1999. Evaluation of remedial alternatives of lead from shooting range soil. *Environ. Eng. Sci.* 16:403-414.
- Chen, M., L. Q. Ma, and W. G. Harris. 1999. Background concentrations of 15 trace metals in Florida soils. *J. Environ. Qual.* 28:1173-1181.
- Chen, M., and L. Q. Ma. 1998. Comparison of four EPA digestion methods for trace metals using certified and Florida soils. *J. Environ. Qual.* 27:1294-1300.
- Craig, J. R., J. D. Rimsstidt, C. A. Bonnaffon, T. K. Collins, and P. F. Scanlon. 1999. Surface water transport of lead at a shooting range. *Bull. Environ. Contam. Toxicol.* 63:312-319.
- Fisher, F. M., and S. L. Hall. 1986. Heavy metal concentrations of duck tissues in relation to ingestion of spent shot. p. 3742. *In*: J. S. Feierabend and A. B. Russell (ed.). Lead poisoning in wild waterfowl—a workshop. Cooperative Lead Poisoning Control Information Prog., Washington, DC.
- Mellor, A., and C. McCartney. 1994. The effects of lead shot deposition on soils and crops at a clay pigeon shooting site in northern England. *Soil Use and Manage.* 10:124-129.
- Murray, K., A. Bazzi, and H. Sokol. 1997. Distribution and mobility of lead in soils at an outdoor shooting range. *J. Soil Contam.* 6:79-93.
- Rooney, C. P., R. G. McLaren, and R. J. Cresswell. 1999. Distribution and phytoavailability of lead in a soil contaminated with lead shot. *Water Air Soil Pollut.* 116:535-548.
- Scheuhammer, A. M., and S. L. Norris. 1995. A review of the environmental impacts of lead shotshell ammunition and lead fishing weights in Canada. Occas. Pap. N. 88. Can. Wildlife Serv., Nat. Wildlife Res. Cent., Hull, QC.
- Sever, C. W. 1993. Lead and outdoor ranges. p. 87-94. *In*: North American hunting club. National shooting range symposium proceedings, 17-19 Oct. 1993. Minnetonka, MN.
- Stansley, W., L. Widjeskog, and D. E. Roscoe. 1992. Lead contamination and mobility in surface water at trap and skeet ranges. *Bull. Environ. Contam. Toxicol.* 49:640-647.
- Tonner-Navarro, L., N. C. Halmes, and S. M. Roberts. 1998. Development of soil cleanup target levels (SCTLs) for Chapter 62-785. Univ. of Florida, Gainesville.
- U.S. Environmental Protection Agency. 1995. Test methods for evaluating solid waste. Vol. 1A: Laboratory manual physical/chemical methods, SW846, 3rd ed. U.S. Gov. Print Office, Washington, DC.
- U.S. Environmental Protection Agency. 1996. Soil screening guidance: User's guidance. USEPA 540/R-96/018. U.S. Gov. Print. Office, Washington, DC.
- U.S. Environmental Protection Agency. 1997. Method 3051a: Microwave assisted acid dissolution of sediments, sludges, soils, and oils. U.S. Gov. Print. Office, Washington, DC.