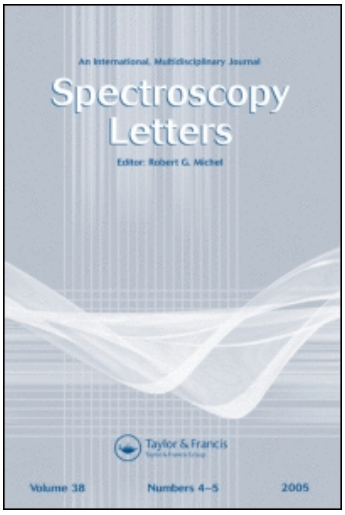

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Lead Analysis in Soils and Sediments at the Saginaw Field and Stream Club

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Abstract: Samples from the Saginaw Field and Stream Club in Saginaw County, Michigan, were collected to determine whether lead levels at the club shooting ranges pose a threat to the environment. Flame atomic absorption spectroscopy (AAS) was used to determine lead levels in soil and sediment samples digested for total lead as well as soluble lead. Lead was present at levels exceeding 10,000 mg/kg in some surface soil samples. In general, lead was pervasive at the site in both metallic and soluble forms. Each of the shooting ranges contains areas where lead occurs at concentrations significantly in excess of the Michigan Department of Environmental Quality criteria and therefore poses a potential risk to the human users of the land as well as to the native wildlife.

INTRODUCTION

Lead in soil is a pervasive environmental problem throughout the world, and many efforts have been taken to control exposure to lead. Lead has been eliminated from paints and gasoline, which has reduced major sources of exposure. However, public concerns about lead has led other agencies to consider their contribution to the problem. In recent years, concerns have been growing over the presence of lead at shooting clubs.[1–5]

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Lead is a common industrial metal that causes severe health effects even at relatively low levels in the body. Lead affects the human nervous system, the production of blood cells, kidneys, reproductive system, and behavior. The risks of lead poisoning are the greatest for small children and women who are pregnant.[6,7] A study done by the Environmental Working Group has shown that shooting ranges account for approximately 4700 pounds of lead pollution each year in the United States, which is 48 times higher than what industrial polluters report each year.[8] For example, a shooting range that has 15 customers each day, each of whom shoots 50 rounds of shot containing 1 oz of lead each, would create 100 lb of lead pollution in just 7.5 days, or 4800 lb of lead contamination per year.

The Saginaw Field and Stream is a conservation group in central Michigan that has been in existence since 1916. The mission of this group is to promote conservation and sportsmanship as well as to guard the waters against pollution. Because a big part of the enjoyment and use of the outdoors in Michigan involves hunting and shooting, in the mid-1960s the club opened several shooting ranges on a 158-acre piece of land it owns in Thomas Township, Saginaw County, Michigan. The club constructed the trap and skeet field seen in Fig. 1A, as well as two pistol ranges and a rifle range. In addition, the club constructed a lake at one end of the trap and skeet field, which they keep stocked with a variety of game fish.[9]

In recent years, the club has become concerned about the amount of lead that may be present on the land and about the movement of lead in the environment. Figure 1B is typical of the ground surface at the trap and skeet field and is evidence of the extent of the problem. A crude estimate of the amount of lead from shot that could be present on the site is more than 70 tons. In an effort to assess the situation, the club solicited a study from nearby Alma College to evaluate the extent of the problem and to provide information and suggestions as to how to address the problem. The study reported on herein includes the analysis of surface and core samples from the field soil and lake sediments to determine the amount of lead present. Using this analysis, a determination can be made as to how much and how far down lead has leached into the soil and thus the extent of the remediation required for the soil at the Saginaw Field and Stream Club.

MATERIALS AND METHODS

After an initial visual survey of the 158-acre site in Thomas Township, Saginaw County, Michigan, as located in the Fig. 2 inset, a sampling plan was created to perform a baseline evaluation. Figure 2 shows the transects along two trap stations, one skeet station, the rifle range, and both pistol ranges where samples were collected. The stars marked on the map at each station indicate sampling locations. At the rifle and pistol ranges, these were at the shooting station, at the end berm and half-way between. On the trap

Figure 1. (A) The trap and skeet field at the Saginaw Field and Stream Club. The black box on the left in the front is the trap launch. Just in front of the tree line in the center of the image is Lake Vitek. The field itself is a cleared area in a mixed evergreen/deciduous forest. (B) A close-up of the ground. The pen is about 15 cm long. Shot is pervasive in this manner across the field from about 300 m out to the lake shore and into the lake.

and skeet field, surface and core samples were collected along a transect from the shooting station at 50-m intervals to the shore of the lake. Soil samples were collected by scraping the surface to remove vegetation or other materials (generally the shattered clay targets) and collecting the soil just beneath. Soil core samples were collected with a 1-ft-long, 1-in-diameter core sampler. The cores were subdivided and each portion separately bottled. All samples were collected in acid-washed, HDPE screw-cap bottles.

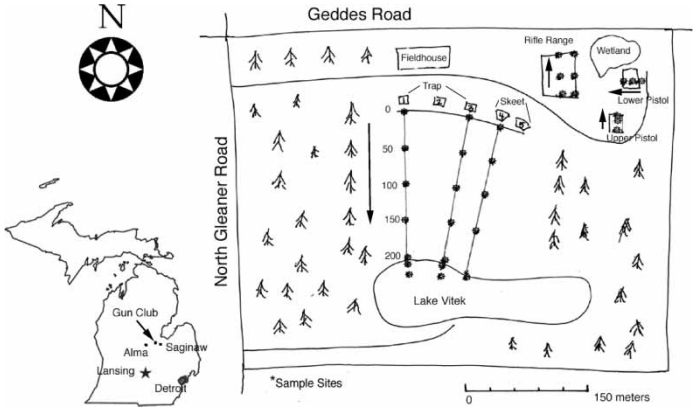

Figure 2. The inset shows the location of the club in central Michigan. The map shows the four shooting ranges sampled and the location of the sample collections. Arrows along the ranges indicate the direction of shooting. Lake Vitek is 1–3 m deep and stocked with game fish. Access to the site is limited to members via a locked gate.

Of great concern is the lake built at the end of the trap and skeet field because the lake is stocked with game fish and is a haven for migratory birds. It is known that shot enters the water because shot is observed on the surface of the ice over the lake in the winter, and is seen in sediment samples collected from the lake. Grab samples of lake sediment were taken at the edge of the lake. In addition, a 4-ft-long polyethylene tube was pushed into sediment in the bottom of the lake about 3 m from the shore. This sample was capped on the top, pulled out and then capped on the bottom. The tube was returned to the lab where the core was subdivided into 5-cm sections. Each section was analyzed separately.

After collection, all samples were returned to Alma College and stored in a refrigerator at 4°C until sample preparation began. Samples were prepared for digestion by drying at 110°C and then removing unwanted materials such as stones and sticks and observable lead pellets. Initially, soil samples were digested to analyze total lead using EPA Method 3050B for acid digestion of soils. Later samples were digested using EPA Method 3051 for microwave-assisted digestion using a CEM MDS-81D (Matthews, NC, USA) microwave oven. In addition, some soil samples were also analyzed for dissolved lead using EPA Method 1311, the Toxicity Characteristic Leaching Procedure, and then digested using either EPA Method 3010A or 3015 as appropriate.[10]

Analysis of all samples was performed on a Varian SpectrAA 20 Atomic Absorption Spectrometer (Palo Alto, CA, USA) using an acetylene (13.5 L/min)/air (20.0 L/min) flame. Analysis was done at a wavelength of 283.3 nm with an 0.5-nm slit and a lamp current of 10.0 mA. All samples, standards, and controls were in a 5% nitric acid matrix.

All reagents used were trace metal grade quality from Fisher Scientific (Pittsburgh, PA, USA). A 1000 mg/kg lead standard from Inorganic Ventures (Lakewood, NJ, USA) was used to prepare calibration standards. An "SQC1 Trace Metals in Soil" standard from NSI Solutions (Raleigh, NC, USA) was used as a calibration check.

RESULTS AND DISCUSSION

Analyses of the samples from the Saginaw Field and Stream Club show significant concentrations of lead are present at the soil surface at all active shooting ranges. All four ranges showed levels of lead well in excess of the EPA recommendation for lead in surface soil (400 mg/kg). In some places, total lead is in excess of 10,000 mg/kg. The analysis has been validated using traditional measures. A *t*-test shows that the measured average of 201 mg/kg Pb for SQC1 Soil Control sample with a certified value of 204 mg/kg is statistically the same at 95% confidence ($t_{calc} = 1.03$; $t_{crit} = 2.28$). The analytical detection limit was 0.10 mg/kg based on (3 × SD of blanks)/slope. At least one sample in each data set was run as a duplicate, and the coefficient of variation for these samples ranged from 0.2 to 5.0. A 10.0 ppm Pb standard run as a confirmation sample with every data set has a 95% confidence interval of 9.94 $\pm$ 0.45 ppm. The calibration sensitivity derived from the calibration line was typically around 0.05 (with a typical line being $A = 0.0571\ (\pm\ 0.0025)\ c + 0.0004\ (\pm\ 0.012)$).

Rifle and Pistol Ranges

In Fig. 3, it can be seen that at the rifle range and both pistol ranges lead was only present at high concentrations in the soil berm at the end of the ranges. These results are similar to those reported in other studies where the field terminated in a berm.[11] Digging a hole into the berm to collect a sample revealed a large number of spent shells and shot. Remediation here will simply involve sieving the soil in the berm, as soil between the shooting stand and the berm is minimally contaminated.

Trap and Skeet Field

Figure 4A shows that at the trap and skeet field, lead increased from the shooting stand out to about 150 meters at each of the three stations sampled. After this point lead levels dropped off but were still significant in the surface sediments at the edges of the lake. Core samples taken at the same location as surface samples along the transects showed that lead concentrations decrease with depth, as seen in Fig. 4B. The concentration of lead

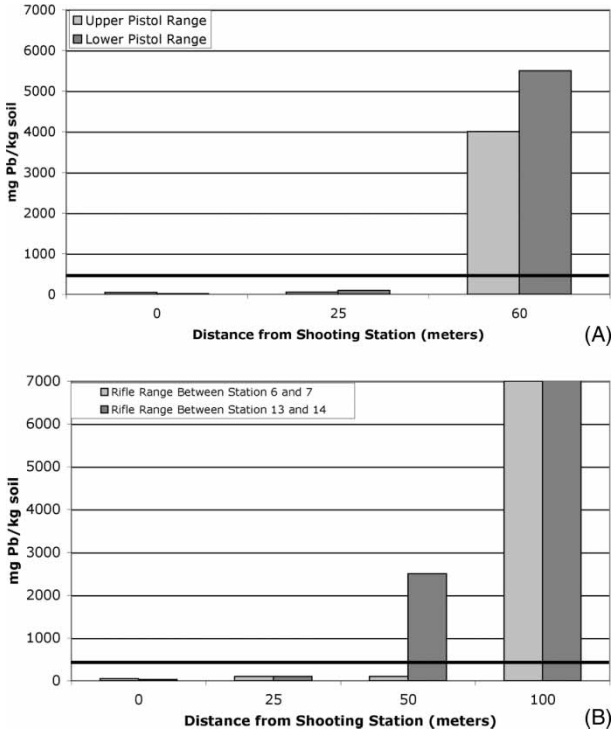

Figure 3. Results along transects at the pistol (A) and rifle (B) ranges. Samples were collected down the center of each range as well as along one edge of the rifle range. The dark horizontal line is at 400 mg/kg, the EPA recommended maximum for lead in residential soils.[6]

dropped to less than 50 mg/kg by 15 cm depth. Again, similar results were observed in other studies looking at both longitudinal and depth analysis at shooting ranges.[12,13]

These results were used by the club to develop criteria for a planned remediation project on the trap and skeet field. This group recommended to the club that the top 6–8 in. of soil be removed from at least 300 yards out to the margins of the lake. The project was carried out in summer 2005. In reality, a remediation was not done; instead an outside company was hired to reclaim the lead that had built up on the field. The lead recovered could then be sold. The reclamation involved scraping off the top 6–8 in. of soil, running it up a conveyor belt and off the top. The heavier material, including the lead, fell closer to the machine into a sieve. The lead pellets were separated from the finer soil by the sieve. The lighter material and the sieved soil was returned to the field. The lead was packed into drums for removal from the site. About half the trap and skeet field was

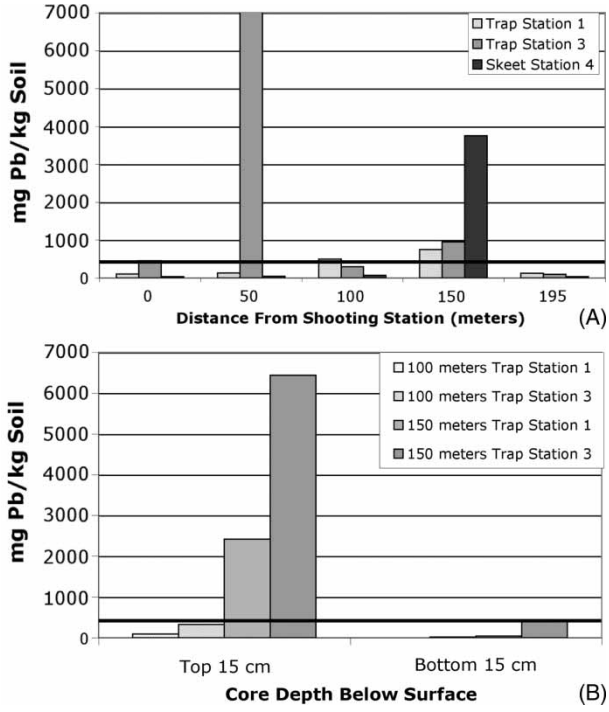

Figure 4. Results from the trap and skeet field before remediation. (A) The distribution of lead on the surface along transects starting at the shooting stand and going out at 50-m intervals to the edge of the lake at about 200 m. (B) Core samples taken at the 100-m and 150-m distances for the trap stations 1 and 3 transects. The dark horizontal line is at 400 mg/kg, the EPA recommended maximum for lead in residential soils.[6]

reclaimed in this fashion. The rest could not be done at the time as a result of extremely wet soil due to excessive rainfall and will be done at a later time. Based on the mass of lead collected, it is estimated that more than 30 tons of lead was removed by the commercial reclamation firm contracted by the club.

Figure 5 shows the results at two stations that were resampled and reanalyzed after the reclaimation. The result may seem surprising, unless one considers the manner of the process: total metal concentrations were higher after the remediation. Early in the work it had been observed that occasional high values were most likely due to lead pellets that had been digested. While more care was taken in later work to remove these pellets from samples, this was apparently not always successful; for example, see 50 meters at Station 3 in Fig. 3 (45,500 mg/kg Pb) and 100 meters at the Practice Station in Fig. 4 (2800 mg/kg Pb). Large pellets can be seen and are usually removed. Smaller pieces remain in the sample, even after sieving, and are thus

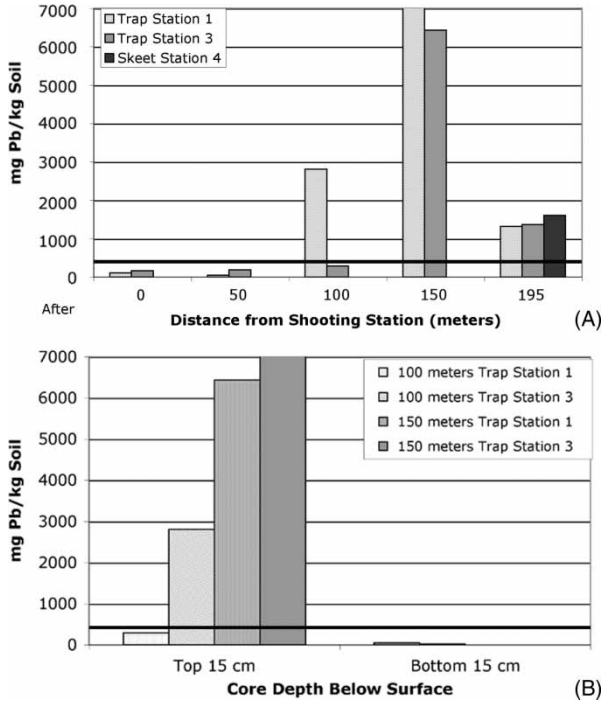

Figure 5. Distribution of lead on the trap and skeet field after the remediation that occurred in summer 2005. (A) Surface samples along the transects. (B) Cores at 100 and 150 m. The dark horizontal line is at 400 mg/kg, the EPA recommended maximum for lead in residential soils.[6]

digested. It has been reported in the literature[12,14] that smaller particles are the result of impact between falling pellets and stationary pellets on the ground, resulting in the shattering of one or both pellets. While earlier, random high values may be due to this, here it is suggested that lead increased at some locations after remediation because, although the reclamation sieved out larger pellets for recovery and reuse, it also broke partially weathered, more fragile pellets into smaller pieces. These smaller pieces are not recognized and removed even by sieving, leading to an apparent increase in concentration.

Soluble Lead

Samples were also analyzed for leachable lead using the Toxicity Characteristic Leaching Procedure (TCLP). Qualitative evaluation of pH (6–8) and phosphate levels (<50 mg/kg) indicate that lead should primarily stay in a solid form and not be susceptible to dissolution. The Eh-pH diagram for

lead indicates that ionic lead will be present as a solid precipitate between a pH of 6 and 12 and a potential greater than +0.4 V, typical levels observed in surface environments and within the pH ranges observed in both the soil and the water. Figure 6 shows that the TCLP protocol verified that levels of soluble lead were dramatically less than total lead. Therefore, the primary concern is the susceptibility of ever smaller particles of lead metal to increased levels of weathering due to increased surface areas.

Lake Vitek

In Fig. 7, it can be seen that lake sediment core samples exhibit lead concentrations that were as high as 40 mg/kg at 20–25 cm below the sediment surface. As the sediment in this man-made lake is made up primarily of sand, dissolved lead can move much more quickly through it than through the soil, which has a greater abundance of organic matter to complex lead ions. Based on these considerations, when lead remediation or reclamation is done on the lake, it needs to take place up to 25 cm in depth to remove the bulk of the lead.

There is concern about the presence of lead in the lake, and the club is investigating ways to reduce the impact of the trap and skeet field on the lake. Water samples from the lake show no evidence of lead within the detection limits of the analysis done. Further work is in progress to more fully investigate the quality of water and sediment across the lake bottom, although no impact is expected on the water because of the pH conditions, which ranges from 6.5 to 8.5 depending on the season.

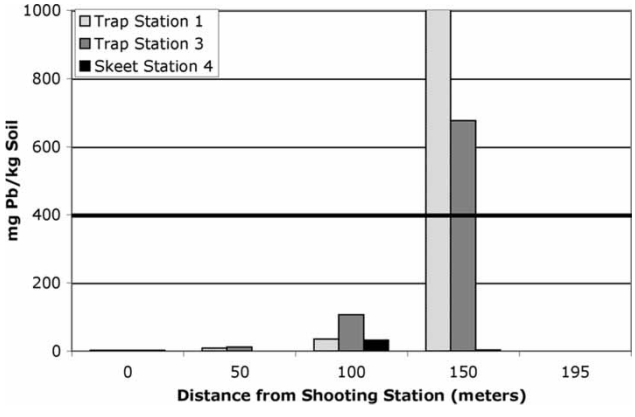

Figure 6. Soluble lead results using the Toxicity Characteristic Leaching Procedure in surface soils along the transects on the trap and skeet field. The dark horizontal line is at 400 mg/kg, the EPA recommended maximum for lead in residential soils.[6] Note that the scale in this graph is different from the earlier graph.

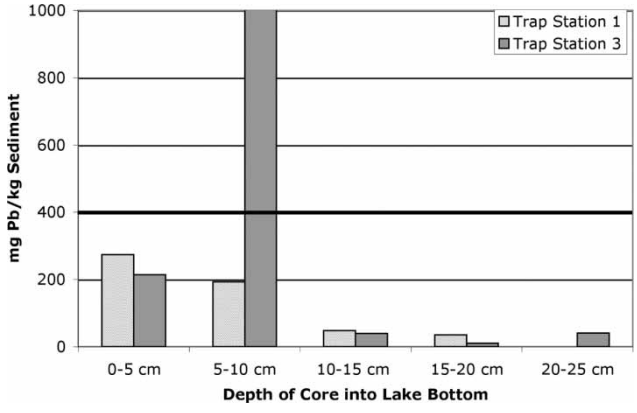

Figure 7. Sediment results from two cores driven into the bottom of the lake about 10 ft from shore. The dark horizontal line is at 400 mg/kg, the EPA recommended maximum for lead in residential soils.[6] Note that the scale in this graph is different from the earlier graphs.

CONCLUSIONS

The work in this study was used by the Saginaw Field and Stream Club to perform a reclamation of the trap and skeet field in summer 2005. More than 30 tons of lead was removed during the work. This work also pointed out additional concerns as to the placement of the trap and skeet field with respect to the lake. The lake is stocked and used for fishing, however, it is also extensively used by migrating birds such as geese. This latter leads to concerns about exposure of the birds to lead pellets present in the lake. The club is currently investigating methods to limit access of the lead to the lake including the construction of a berm at the end of the field as well as the possibility of reorienting the range in another direction to shoot away from the lake. Further investigation will be done by the college to aid the club in their determinations.

Lead is a hazard at shooting ranges, as found in this and other studies[1–5]. Lead dissolution can be controlled by adjusting the pH and phosphate levels in the soil. Lead can be removed by remediation of the land. Lead can also be limited by turning to shot made of less toxic materials, such as steel. This last is expensive and less satisfying to the recreational shooter. Steel shot is significantly more expensive and has a different "feel" to the characteristic of the firing. The monitoring of lead at the Saginaw Field and Stream Club shooting ranges will continue as the college continues to provide exciting opportunities to show the impact of the chemist on the broader world and the club continues in its attempts to promote conservation and guard the waters.

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