

**Original Article**

# **Evaluation of lead movement from the abiotic to biotic at a small-arms firing range**

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**Received:** 18 February 2004 / **Accepted:** 27 April 2004

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**Abstract** An investigation to characterize the extent and speciation of lead contamination in water, soil, and surrounding biota was conducted at a small-arms firing and skeet range in West Point, New York. Specifically, lead concentrations were examined in sediment, soil, water, plants, fish and invertebrates. There is an elevated concentration of lead in the soil and sediment up to 11,000 µg/g and 340 µg/g and also evidence of bioconcentration of the lead by the surrounding biota. Earthworms had up to 90% higher concentrations of lead while tadpoles showed 20% higher concentrations compared with their controls. Lead uptake by indigenous plants gave varying results. Two species bioconcentrated lead 20 and 55 times greater than the control plants. These differences were significant ( $P < 0.05$  level) when tested by the student's t test. Further studies show that the total leachable lead was highest in the invertebrates and vertebrates but not in the plants.

**Keywords** Lead · Firing ranges · Plant bioconcentration · Bioavailability

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# Introduction

Lead contamination on firing ranges is the most abundant metal found in bullet and shot fragments (DeShields and others 1998). Ecological impacts of the contamination will vary from site to site due to variations in soil conditions, speciation of the lead, and ability of the local plant life to absorb or bioaccumulate the species of lead that is present. Subsequent effects on invertebrates, birds, and mammals help to determine whether action must be taken to “clean” the range or work towards lead remediation.

Previous studies evaluating lead contamination at firing ranges include work by DeShields and others (1998) who looked specifically at the uptake of lead by two species of buckwheat plants growing in inactive beach firing ranges of Fort Ord California (DeShields and others 1998). The purpose was to study the effects of lead on an endangered butterfly by evaluating the lead in its food supply. Correlations were demonstrated between lead in the soil and that found in the plant tissue. Another study was conducted at an inactive skeet range at the Naval Weapons Station, at Seal Beach, California (Hui 2002). In this case, the author’s objective was to “determine how thoroughly lead from the skeet range has been incorporated into the biota...and its potential threat to avifauna.” Soil, sand, and silt were evaluated along with seven species of plants and the invertebrate California horn snail. Results indicate that the snail had 100 times greater lead concentrations than the plant leaves, which had variable uptake of lead themselves, leaving the correlation unconfirmed. Danish and Finnish shooting ranges have also shown elevated lead contamination in soil and humus (Jorgensen and Willems 1987; Manninen and Tanskanen 1993). Three plant species showed variable uptake of lead from 10 to 70  $\mu\text{g/g}$  (Manninen and Tanskanen 1993) yet, again no correlation was determined.

More recently, a study confirmed the lead poisoning of songbirds at a trap and skeet range (Vyas and others 2000). Yet, the authors did not establish the specific source of the lead poisoning, i.e., contamination in the food chain, soil or direct ingestion of lead shot. A more encompassing study was carried out at the Firearms Training Facility at the Federal Law Enforcement Training Center in Glynn County, Georgia (Lewis and others 2001). In this study, 22 different species of mammals and birds were evaluated for exposure to lead and other trace metals at an active firing range. Significantly elevated tissue lead levels resulted in the mandatory restructuring of the ranges and development of bullet recovery methodologies to reduce future lead contamination (Lewis and others 2001).

Gettysburg Range is a small-arms firing and skeet range at Camp Buckner, a training camp for the cadets of the United States Military Academy at West Point, New York. A preliminary undergraduate research project conducted in 1999 by cadet A.C. Elliot and supervisor Richard Lonardo, revealed elevated levels of lead in water, soil, and sediment at sites A, B, and C (Fig. 1). However, until now, no studies have been conducted to evaluate the extent or correlation of lead uptake by local biota. Thus, the goal of the present work is to confirm the water, soil, and sediment concentrations of lead and to evaluate whether the lead is being bioconcentrated by the indigenous plants, invertebrates and/or fish. Fifteen plant species were evaluated along with a variety of invertebrates and two vertebrates.

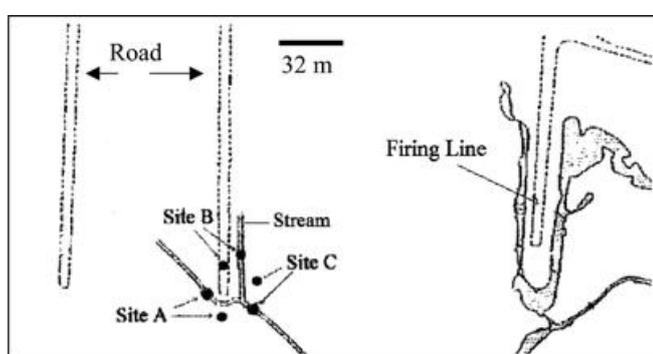


Fig. 1 Map of the sampling area

## Materials and methods

### Sampling

Samples were obtained on two dates from sites A, B and C (Fig. 1). Sediment samples were taken near the edge of the stream via brass grab sampler. Soil samples were taken 3–20 cm below the surface. One-liter water samples were obtained at a depth of 15 cm below the surface of the stream. Plant samples were branches, containing numerous leaves, cut from the parent plant. Aquatic biota were acquired using a mesh seine. Snails, insects, a roach, fish and shrimp were collected and stored in plastic bags in a refrigerator until analysis. All control samples were taken from an uncontaminated site outside of the range fan.

### Sample preparation

The biological samples were digested as described by the Association of Analytical Chemists Official Methods of Analysis (Helrich 1990). The samples were weighed, ashed overnight at

350 °C, and digested in 10 ml of 1 M HCl with heat. The samples were filtered and the final volume adjusted to 25 ml with deionized water.

The water, soil, and sediment samples were treated as described by Enseco (1991). A 1.0-g wet weight soil or sediment sample was added to 10 ml of 1 M HNO<sub>3</sub> and heated without boiling for 10 min. Five ml of concentrated nitric acid was added with an additional 30 min of heating. The sample was allowed to cool; then 10 ml of 30% H<sub>2</sub>O<sub>2</sub> was added, followed by warming for 10 min. Lastly, the sample was filtered and adjusted to a final volume of 100 ml with deionized water. A sequential chemical extraction (SCE) of the lead species present was performed on the soil fraction from each site (Tessier and others 1979). Table 1 presents the reagents used for each extraction phase.

**[Table 1 will appear here. See end of document.]**

Water samples (50-g) were amended with 1 ml of 30% H<sub>2</sub>O<sub>2</sub> and 0.5 ml of 1 M HNO<sub>3</sub>. The samples were heated without boiling until the volume was reduced to 15–20 ml. The samples were then filtered and brought to 100 ml with deionized water.

## Analysis

Flame atomic absorption (AA) (Varian SpectrAA Spectrometer) was used to measure ppm concentrations, while Graphite Furnace AA (Thermo Jarrell Ash Smith-Heiftje 1000 Spectrometer) was used for samples with ppb levels of lead. All samples were run in triplicate using lead lamp at wavelength 217 nm. The deposit time for the samples evaluated by GFAA was 10 s at a temperature of 300 °C with atomization for 1 s at a temperature of 1,750 °C.

## Results

The samples were collected on two different dates but from the same sites: A, B and C (Fig. 1). The collection dates were 22 September and 6 October 1999. Therefore, data will be specified as to the collection site by a letter, and will have a 1 or 2 designating the collection date, respectively. All controls were collected on the first date.

Table 2 indicates the variability of the lead concentrations of the water samples. The first collection indicated site C as being the highest concentration of lead while the second collection indicates site A. However, site B remained constant (within standard deviation) for the two collections. Both collections indicate elevated lead concentrations when compared with the control site.

[Table 2 will appear here. See end of document.]

The sediment and soil data demonstrate high levels of lead (Table 2). The concentration of lead in the sediment is highly variable between the sites and collection days. However, there is clearly noticeable elevation of lead concentration compared to the control. The soil data indicates much more constancy. Table 2 shows very high lead concentrations for both collections at sites A and B when compared to the controls.

The results of the SCE are presented in Fig. 2. The largest fraction of lead in the control sample was found in the carbonate phase, which is the most stable phase of lead in many soils (Chen and others 2002). At sites A and B, where the total lead concentration was ca. 2 orders of magnitude greater, the lead appeared to be more evenly distributed. As presented in Fig. 3, over 40% of the lead at each site was either bound as exchangeable ions or bound to carbonates, the two most labile lead fractions. Site C was found to have the highest fraction of labile lead.

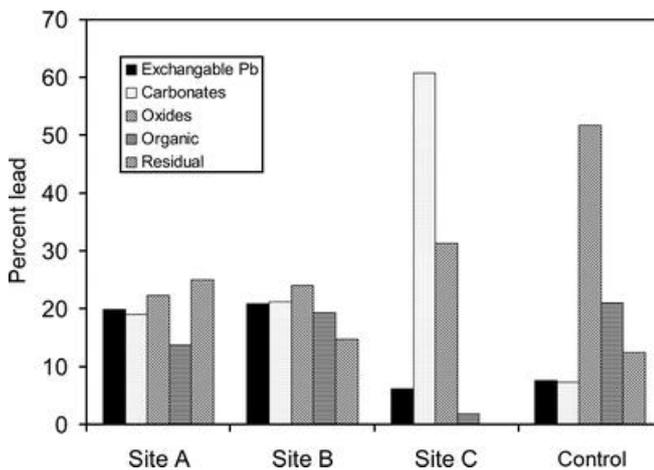
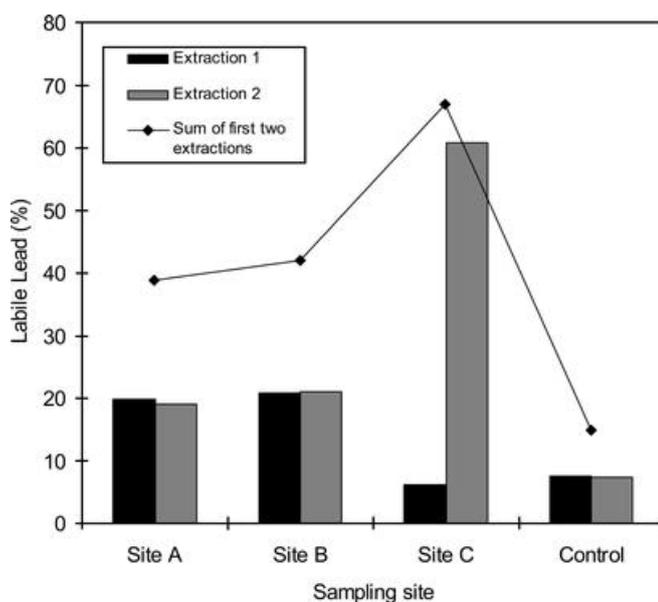


Fig. 2 Sequential chemical extraction—percent of lead in each fraction



**Fig. 3** Labile lead in the first two extraction phases of the sequential chemical extraction

Table 3 indicates the variability in lead uptake by plants at the three sites for both collections. The bioaccumulation of lead by plants is species-specific and heavily depends on soil conditions (DeShields and others 1998). In the present study, there were two species, *Phalaris aruncia* sp. and *Carex* sp., for which control data was available. The first species shows approximately 55 times the amount of lead as the control, while the second species contains about 22 times the amount of lead found in the control. These differences were significantly different ( $P < 0.05$ ) when tested by the student's *t* test. *Solidago* sp. and *Spirea* sp. both show greater than 100  $\mu\text{g/g}$  amounts of lead. In general, there seemed to be more lead uptake measurable in plants from sites A and B, which is consistent with the higher lead concentrations at those sites.

**[Table 3 will appear here. See end of document.]**

Invertebrates and vertebrates were also collected for evaluation (Table 4). The data indicate that worms collected from site A contained 90 times the concentration of lead found in the control and worms from site C contained about 27 times that in the control. Also of note are the tadpole lead concentrations. At sites A and C there is about 20 and 16 times, respectively, the amount of lead determined for the controls at these sites. All of these findings were significant when tested by the student's *t* test ( $P < 0.05$ ). While control data was not available for the fish, the levels of lead exceed the World Health Organization (WHO) guidelines of 0.3  $\mu\text{g/g}$  (wet weight) at both sites (WHO 1972). The shrimp and insects collected from site C may also contain significant amounts of lead.

**[Table 4 will appear here. See end of document.]**

## Discussion

The soil at the small arms and skeet range at West Point, N.Y. was found to have high but variable levels of lead (Table 2). This variability was expected due to the presence of lead shot. In many areas the lead shot is clearly visible on the surface of the soil and entrapped in the roots of plants. The lead shot was highly corroded and the source of lead in the soil. These results are consistent with other findings of lead contamination due to deposition of lead shot and bullets (Desields and others 1998; Lewis and others 2001; Hui 2002). It was also determined that the lead was not confined to the soil but was leaching into the nearby streams and into the sediment.

Movement of the lead into the abiotic phase allows for its uptake by the plants and animals in that region. Plants are capable of extracting lead from soil (Xiong 1998; Qian and others 1999), particularly at contaminated firing ranges (Manninen and Tanskanen 1993; Barona and Romero 1997). There was a great degree of variability in the concentration of lead found in the plants growing at the sampling site (Table 3). Two species, *Phalaris aruncia* sp. and *Carex* sp., had significantly higher levels of lead than did the same species found at the control site. The other two plants which had very high levels of lead, *Solidago* sp. and *Spirea* sp., were subsequently found to bioconcentrate lead under laboratory conditions (Gowdy and Labare 2004). This demonstrates the potential of these sites to serve as a source of plants for phytoremediation.

It was hypothesized that high levels of labile lead might correspond with plant uptake regardless of plant species. However, the site with the highest percentage of labile lead (site C) did not contain plants with the highest level of lead uptake. It is concluded that total lead and possibly extractions four and five (tightly bound lead) are better indicators of plant uptake of lead. On the other hand, lead uptake by invertebrates and vertebrates at site C was comparable to that in sites A and B, even though the total lead concentration at site C was 2 orders of magnitude lower. This observation may be consistent with the higher percentage of labile lead at site C.

In addition to plants, significantly elevated lead levels were found in tadpoles and earthworms. Both organisms are a potential route for the lead to move up to higher trophic levels. For example, earthworms are an important link between the soil lead content and secondary consumers in the food chain due to their ability to accumulate heavy metals from contaminated soil (Pankakoski and others 1994). It is possible that the lead might move up the food chain as deer graze on the local plants (Martin and others 1951).

**Acknowledgements** The authors would like to thank Dr. David Loehle and Mr. Anand Shetty for their technical assistance. This work was supported by the two departments' student research programs.

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**Table 1** Operationally defined sequential chemical extraction fractions and their respective reagents

Soil fraction	Reagent
1. Exchangeable	MgCl <sub>2</sub>
2. Carbonates	NaOAc/HOAc
3. Oxides	NH <sub>2</sub> OH*HCl in HOAc
4. Organic	HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> and NH <sub>4</sub> OAc
5. Residual	HNO <sub>3</sub> (Digestion)

**Table 2** Concentration of lead in environmental samples

Sample	Date	Control site	Site A	Site B	Site C
Water <sup>a</sup>	22 Sept	0.0035±0.0019	0.0048±0.0004	0.0054±0.0029	0.015±0.0042
	6 Oct		0.011±0.0005	0.0061±0.0006	0.0079±0.0020
Soil <sup>b</sup>	22 Sept	11.4±0.9	9830±5190	12400±2830	385±31
	6 Oct		7320±1870	11800±6650	821±165
Sediment <sup>c</sup>	22 Sept	11.7±1.6	42000±55000	706±242	224±64
	6 Oct		186±32	119±8	344±5

<sup>a</sup> µg of Pb/g water sample±standard deviation

<sup>b</sup> µg of Pb/g soil (wet weight)±standard deviation

<sup>c</sup> µg of Pb/g sediment (wet weight)±standard deviation

**Table 3** Lead concentration in variety of plant species

Plant	Site and collection <sup>a</sup>	µg Pb/g wet weight
<i>Vitis</i> sp.	(A1)	3.63±.03
<i>Prunus</i> sp.	(A1)	6.771±.002
<i>Betula</i> sp.	(A1)	1.73±.01
<i>Dryopteris</i> sp.	(A1)	6.41±.02
<i>Vitis</i> sp.	(B1)	38.8±2.6
<i>Acer rubra</i> sp.	(B1)	45.2±1.2
<i>Solidago</i> sp.	(B1)	137.6±9.6
<i>Cornus</i> sp.	(C1)	2.0±0.5
<i>Salix</i> sp.	(C1)	0.70±.08
<i>Phleum</i> sp.	(C1)	4.1±.9
<i>Typha</i> sp.	(C1)	0.7±.2
<i>Phalaris aruncia</i> *	(A2)	43.3
<i>Betulas</i> sp.	(A2)	2.473±.001
<i>Spirea</i> sp.	(A2)	152.2±9.2
<i>Pranus</i> sp.	(A2)	10.9±.7
<i>Ribes</i> sp.	(B2)	53.9±3.4
<i>Viburnum</i> sp.	(B2)	0.9±.1
<i>Spirea</i> sp.	(B2)	1.133±.007
<i>Celastrus</i> sp.	(C2)	10.9±.5
<i>Solidago</i> sp.	(C2)	0.20±.16
<i>Carex</i> sp.*	(C2)	0.8700
Plant Controls		
<i>Phalaris aruncia</i> *		0.79
<i>Carex</i> sp.*		0.04

<sup>a</sup>Sample locations are described in Fig. 1. Sampling times were 22 September 1999 (1) and 6 October 1999 (2)

**Table 4** Lead concentration ( $\mu\text{g/g}$ ) in invertebrates and vertebrates at sample sites and times<sup>a</sup>

Sample	Control	C1	A2	B2	C2
Worms	0.61	27.6	54.9		16.2
Snails			7.00		39.9
Tadpoles	1.3	22.7	26.8	11.0	18.1
Fish			0.129		4.49
Shrimp					7.41
Insects			6.02	5.27	12.1

<sup>a</sup>Sample locations are described in Fig. 1. Sampling times were 22 September 1999 (1) and 6 October 1999 (2)