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The effect of bullet removal and vegetation on mobility of Pb in shooting range soils

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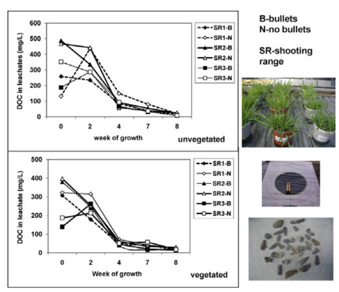
HIGHLIGHTS

- Two best management practices for shooting ranges, bullet removal and vegetation, were evaluated in a green house study.
- Bullet removal reduced total soil Pb and increased DOC in leachates.
- Bullet removal increased bio-available Pb in un-vegetated soils.
- Vegetation reduced leaching of Pb in two shooting range soils.
- St. Augustine grass accumulated up to 5021 mg Pb/kg in roots.

GRAPHICAL ABSTRACT



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ABSTRACT

Lead (Pb) contamination at shooting ranges is a public health concern because Pb is a toxic metal. An experiment was conducted to determine the effect of two best management practices; bullet removal and vegetation, on bioavailability and leachability of Pb in three shooting range (SR) soils. St. Augustine grass was grown in sieved (2 mm) and un-sieved SR soils for 8 weeks after which leachates, soil and plant samples were analyzed. Bullet removal reduced total soil Pb, increased Mehlich-3 Pb in unvegetated soils and increased dissolved organic carbon (DOC) in all soils. Bullet removal increased leaching in two SR soils while grasses reduced leaching but increased water soluble Pb in two SR soils. The roots of the grasses were able to accumulate more Pb in the root (1893–5021 mg kg^{-1}) than the aboveground biomass (252–880 mg kg^{-1}) due to mobilization of Pb in the rhizosphere. Grasses had a higher plant biomass in unsieved soils suggesting tolerance to the presence of bullets in the unsieved soils. Results suggest that bullet removal probably increased microbial activity and Pb bioavailability in the soil. The leaching and bioavailability of Pb in shooting range soils depends on biological activities and chemical processes in the soil.

1. Introduction

Soil contamination with lead (Pb) has been reported in shooting ranges (SR) worldwide (Dermatas et al., 2006; Siebielec and Chaney, 2012; Sanderson et al., 2014). 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, 2005; Hardison et al., 2004).

Bullets are fragmented and pulverized upon impact with ground, backstop, berms or bullet trap at SR (O'Connor et al., 2009). It has been reported that soil and Pb metallic fragment particle sizes play a dominant role in the rate and amount of Pb release in SR soils

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(Dermatas et al., 2006). Weathering of fragmented Pb bullets eventually results in elevated total Pb concentrations in SR soils especially those that have been in operation for a long period of time.

Some of the best management practices (BMP) used to mitigate Pb contamination in SR includes sieving to remove the bullet fragments and vegetation to provide a cover for the soil (USEPA, 2005). Removal of used bullets from contaminated SR soils is expected to reduce Pb contamination at these sites. However, previous studies have reported that the abrasive action of mechanical sieving transferred metallic Pb to the soil fraction (<2 mm) and increased total Pb in the soil (Yin et al., 2010; Liu et al., 2013).

It is imperative to evaluate the effect of bullet removal on Pb bioavailability since total concentrations do not provide adequate information on toxicity of heavy metals to the users and biota at these sites. The total amount of metals in the soil is not available because they are adsorbed or bound by organic and inorganic solid phases in the soil such as organic matter, Fe and Al oxides and clay minerals (Fayiga and Saha, 2016). Since bioavailability is the portion that is available or can be absorbed by living organisms, it is a better estimate of environmental risk and toxicity (McLaughlin, 2001; Hettiarachchi and Pierzynski, 2004).

The speciation of Pb is also important because it's the key to understanding the fate and bioavailability of Pb in the environment (Beak et al., 2006). Water-soluble concentration has also been said to be the most eco-toxicologically relevant fraction in the environment due to its high contamination potential of the surface and ground water through leaching and runoff (Meers et al., 2006; Levei et al., 2010). It may also control plant uptake in vegetated soils.

The presence of vegetation in SR is significant because some plants are tolerant to metals and can immobilize contaminants in the root zone (Cao et al., 2003a). The metal tolerant plants can be used for revegetation of contaminated sites (Shu et al., 2002). Butler et al. (2010) reported that vegetation alone reduced metal concentrations in run-off water by about nine times compared to the control.

The combination of vegetation (Houben et al., 2012) and bullet removal in SR may be a cost efficient and sustainable method of remediation for contaminated SR soils. Therefore, the objectives of this study were to determine the effect of bullet removal and vegetation on Pb leachability and bioavailability in SR soils.

2. Materials and method

2.1. Experimental set up

The soils used in this experiment were collected from the berms of three rifle shooting ranges (SR1, SR2 and SR3) in Florida. SR1 has been in operation for 6 years whereas the SR2 and SR3 have been in operation for 15 and 30 years respectively. We took random samples from top, bottom and middle of the berms and mixed them up to make a representative 100 kg composite sample. The soils were hand mixed and air-dried for a week, with 50 kg passed through a 2-mm sieve (no bullets), while the other 50 kg was not sieved (with bullets).

Shooting range soil weighing 1.6 kg was thoroughly hand mixed with 2 g of slow release fertilizer (18-9-18, N-P_2O_5-K_2O) and placed in a plastic pot with a diameter of 0.14 m and height 0.16 m (2.5 L). One plug of St. Augustine grass (*Stenotaphrum secundatum*) was planted in pots containing sieved or un-sieved soil, with soil alone as controls with four replications. The plants were grown in the University of Florida greenhouse where the average temperature ranged from 14 (night) to 30 °C (day), with an average photosynthetic photon flux density of 825 μmol m^{-2} s^{-1}. The plants were watered with deionized water and a petri dish was placed under each pot to collect potential leachates during the experiment.

Leachate was collected every two weeks and analyzed for pH, DOC and Pb content. The grasses were harvested after 8 weeks and separated into aboveground and belowground biomass (roots). Fresh plant samples were rinsed with deionized water, dried in the oven for 3 days at 65 °C and then ground in a mill. The weights of fresh and dry biomass of grass in each pot were determined. Soil samples were collected after harvesting and analyzed for pH, water-soluble Pb, Mehlich-3-Pb and total Pb. Rhizosphere soil collected from the roots was separated from the bulk soil and analyzed for water-soluble Pb and soil pH. Unsieved soils were sieved after harvest and bullet mass determined.

2.2. Chemical analysis

Characterization of sieved soils were done before the experiment by routinely analyzing for CEC, organic matter, particle size distribution, soil pH and water soluble Pb. Detailed methods of analysis can be found in a previous publication (Fayiga et al., 2011). Non-crystalline aluminum and iron in the soils were extracted by shaking 2 g soil in 10 ml acid ammonium oxalate for 4 h in the dark (McKeague and Day, 1966). Fe and Al in the extract were measured by using a flame atomic absorption spectrophotometer (FAAS, Varian 220 FS with SIPS, Walnut Creek, CA). Results are presented in Table 1.

Soil and plant samples from experiment were digested with nitric acid and hydrogen peroxide using the Hot Block Digestion System (Environmental Express, Mt. Pleasant, SC; EPA Method 3050a). Total Pb contents of soil/plant digest; filtrate/extracts and leachates were analyzed on FAAS.

Dissolved organic carbon in leachates from soils was analyzed using a total organic carbon analyzer (TOC-5050 A, Shimadzu Corporation, Japan) which was calibrated with standards. Water-soluble Pb was determined in a soil:solution of 1:5 after shaking for one hour, centrifuged at 5000 rpm for 5 min and then filtered through 0.2 μm cellulose membrane filter. Mehlich-3 extractant was used in this study because it has been recommended as a screening tool to estimate bioaccessible Pb (Minca et al., 2013).

Three grams of dry soil was extracted with 25 ml of Mehlich-3 solution and filtered through 0.2 μm membrane filter to determine Mehlich-3 Pb. The Mehlich-3 solution was prepared in-house by mixing the following solutions; 0.2 N acetic acid, 0.25 N ammonium nitrate, 0.013 N nitric acid, 0.015 N ammonium fluoride and 0.001 M EDTA. All chemical analyses were performed following the QA/QC guidelines of NELAC-certified Laboratory at University of Florida using certified reference materials, spikes, duplicates, blanks and instrument calibration with standards.

Table 1
Selected soil characteristics of shooting range soils.

Properties	SR 1	SR 2	SR 3
Total Pb (mg kg^{-1})	12,689 ± 347	70,350 ± 241	10,068 ± 234
Soil pH	6.11 ± 0.15	6.72 ± 0.15	6.68 ± 0.25
CEC (Cmolc/Kg)	24.8 ± 0.23	11.1 ± 0.65	8.34 ± 0.48
Ox-Fe (mg kg^{-1})	959 ± 92	838 ± 26	379 ± 34
Ox-Al (mg kg^{-1})	278 ± 21	162 ± 15	219 ± 23
OM (%)	1.01 ± 0.05	0.21 ± 0.02	0.67 ± 0.03
Total Ca (mg kg^{-1})	1829 ± 45	900 ± 34	152 ± 13
% sand	86.6	89.4	88.0
% silt	9.46	7.90	7.07
% clay	3.93	2.67	4.96

CEC-cation exchange capacity; Ox-oxalate; OM-organic matter; SR-shooting range. Values are means ± standard error, n = 4, .Error includes instrumental error, instrumental drift error, analytical error.