



## Technical Note

## Field and laboratory assessments on dissolution and fractionation of Pb from spent and unspent shots in the rhizosphere soil



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## HIGHLIGHTS

- We determined the effect of plant root growth on Pb dissolution from shot pellets.
- Dissolution of Pb from shot was significantly induced more in rhizosphere than bulk soils.
- Acid extractable-Pb concentration was 13-fold greater in rhizosphere than bulk soils.
- Abundance of soil CaCO<sub>3</sub> derived from shot clay-targets decreases plant Pb uptake.

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## ABSTRACT

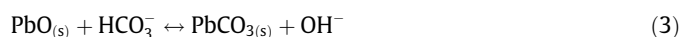
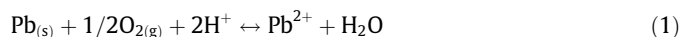
The objective of this study was to determine the effect of plant root growth on Pb dissolution from shot under laboratory and field-scale conditions. For a laboratory study, a 100-d incubation experiment was conducted to assess Pb dissolution from unspent shot (new) and spent shot (>10 yr in fields) in rhizosphere and non-rhizosphere (bulk) soils using the Toxicity Characteristic Leaching Procedure (TCLP) and sequential extraction methods. This study found that increasing the soil pH value to 7.5 by liming significantly reduced Pb dissolution from unspent and spent shot (<5 mg L<sup>-1</sup>). Dissolution of Pb from shot was induced more in rhizosphere than bulk soils. Regardless of shot types, the averaged TCLP-Pb concentration in acidic and limed soils was 12.9- and 8.1-fold greater in rhizosphere than in bulk soils, respectively. For a field-scale investigation, a total of 31 individual plant samples of 6 different species and their rhizosphere soils were collected from a clay-target shooting range (<35 000 mg Pb kg<sup>-1</sup>). The Pb concentration in plant aboveground tissues depended on species with a mean value of 72 mg kg<sup>-1</sup> (15–254 mg kg<sup>-1</sup>), which was far smaller than that reported in previous studies. Regardless of high soil Pb levels, aboveground tissue Pb concentrations of *Solidago altissima* (i.e., Canada goldenrod, 15 mg kg<sup>-1</sup>) and *Andropogon virginicus* (i.e., broomsedge, 18 mg kg<sup>-1</sup>) were below the toxicity threshold, suggesting that these indigenous species could have phytostabilization potentials. The limited Pb accumulation by vegetation was attributed to the abundance of soil calcite derived from spent clay-target fragments.

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## 1. Introduction

Shooting ranges can constitute important sources of heavy metal contamination in terrestrial ecosystems. Toxic metals in shooting ranges are derived via dissolution of spent pellets released in the site. On average, a new shot commercially available in Japan consists of Pb (~97%) and Sb (~3%) and other elements including Zn to a lesser extent (Japan Environment Ministry, 2007). Because it is the most abundant contaminant in the shooting range, Pb has widely been studied to investigate risk and environmental impacts on soils and ecosystems. The environmental impact of Pb around shooting ranges is closely related to the chemical speciation of Pb in the soil. When a shot pellet has been released in the soil,

the surface of the metallic Pb<sub>(s)</sub> is gradually oxidized to PbO (reactions (1) and (2)). The secondary Pb species most abundant in shooting range soils were found to be cerussite (PbCO<sub>3</sub>) and hydrocerussite [Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>] (Cao et al., 2002; Hashimoto et al., 2009a).



These Pb-carbonates appear to control aqueous Pb<sup>2+</sup> activity in shooting range soils (Cao et al., 2003; Hashimoto et al., 2009a). Lead shot is relatively soluble with a dissolution rate of about 1% per year in the soil, depending on pH and soil mineralogical

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properties (Jorgensen and Willems, 1987; Takamatsu et al., 2010). Such high solubility of shot can be attenuated by increasing soil pH using lime amendments since the kinetic reaction governing oxidation and dissolution of Pb shot in soils is primarily dependent on pH conditions. Rooney et al. (2007) demonstrated the liming effects of shot-containing soil on Pb dissolution and found that the dissolved Pb concentration in the limed soil was one to two orders of magnitude less than in the acidic soil.

*In situ* immobilization technologies have widely been accepted as a remediation program of metal contaminated sites. This technology uses soil amendments to transform the original metal species into geochemically more stable phases via chemical processes (i.e., sorption and precipitation). Immobilization technologies can be applied with a vegetation cover as a form of phytostabilization. Hashimoto et al. (2008) and Kucharski et al. (2005) demonstrated that the use of soil amendment in combination with indigenous vegetation coverage decreased metal solubility and the volume of metal-containing leachate. Solís-Dominguez et al. (2011) stated the roles of vegetation for phytostabilization of mine tailing site, which include (i) mitigation of water and wind erosion, (ii) stabilization of metal contaminants in the rhizosphere, (iii) avoidance of uptake of metal contaminants to aboveground tissues, and (iv) development of a long-term sustainable covers. The use of phytostabilization technology is also critical for a remediation program of shooting ranges where the similar metal and vegetation problems occurring in mine tailing site are often found.

To formulate phytostabilization technologies in a shooting range site, understanding how weathering processes of shot pellets are affected by rhizosphere processes is critical. Plants can enhance weathering of soil minerals via rhizosphere processes that physically and biochemically modify the properties of the soil at root interfaces by secreting protons, and organic acids and exchanging ions with the soil solution (Gobran et al., 2005). For example, diffusion of root  $O_2$  into the rhizosphere matrix along with transport of dissolved Fe(II) toward the roots through a transpiration flux can result in the oxidation of Fe(II) and precipitation of Fe hydroxides on the root surface (Otte et al., 1995). Such processes may oxidize metallic  $Pb_{(s)}$  (i.e., Pb shot) and accelerate the transformation  $Pb_{(s)}$  into  $PbO$  (reaction (1)). Rhizosphere processes have been reported to alter metal speciation in soils. Recent studies employing X-ray spectroscopy reported the evidence that preexisting Pb and Zn species in soils were transformed into different ones after plant growth (Panfili et al., 2005; Hashimoto et al., 2011). In elevated  $H^+$  conditions at root interfaces, it is expected that the chemical reaction driving dissolution of Pb shot are likely to be accelerated (reaction (1)). There is however no information on the effect of plant root growth on weathering of Pb shot in the soil. In addition, results of previous studies on Pb dissolution from shot were obtained by the experimentation using unspent (new) pellets. There are few studies regarding the dissolution behavior of spent (or already weathered) pellets, which have already undergone prolonged exposure to field conditions over decades.

The objective of this study was to determine the effect of plant root growth on Pb dissolution from shots under laboratory and field-scale conditions. A laboratory incubation study was conducted to assess Pb dissolution from spent and unspent shots under the rhizosphere and non-rhizosphere soils with different pH conditions. The present study selected a grass plant that may have potential for phytostabilization on a shooting range site. Grass (*Poaceae*) species have been chosen for phytostabilization studies (Panfili et al., 2005; Solís-Dominguez et al., 2011) since those have low root-to-shoot transfer coefficients, and thus limit the propagation of metals into the food chain. A field investigation was conducted to determine the solubility of trace elements in the rhizosphere soils and their accumulation (mainly Pb) by vegetation

growing in a shooting range site, with a view to identifying plant species that may have potential for metal immobilization.

## 2. Materials and methods

### 2.1. Laboratory study

#### 2.1.1. Experiment setup

An uncontaminated brown forest soil was collected at the 0–10 cm surface from a forested area near the Agricultural Experimental Station of Mie University and prepared for the shot weathering study. Brown forest soil represents a typical soil in which many shooting ranges are located in Japan. The soil had a pH value of 4.59 ( $H_2O$ ) and 3.79 (KCl) measured by a soil/solution ratio of 1:2.5. The soil had an organic matter content of  $9.4 \pm 0.2\%$ , and was classified as sandy loam based on the USDA classification (12% clay, 18% silt, and 70% sand fractions). The total Pb concentration was  $20 \text{ mg kg}^{-1}$ , which was below the median value of uncontaminated soils (Essington, 2004). Acidic and limed soils were used for the experiment. An aliquot of 150 g of 2 mm-sieved soil was filled in an acrylic pot without the pH adjustment (acidic soil treatment). The limed soil was prepared by adding a powdered liming material [ $Ca(OH)_2$ , >99% purity] and the soil was mixed well and homogenized. The amount of liming material to adjust the soil pH value of 7.5 was determined by conducting a preliminary study. Unspent and spent shot pellets ( $7.500 \pm 0.050 \text{ g}$ ) were added in the pot soil. Unspent Pb shot was purchased (2.4 mm diameter with  $0.092 \pm 0.006 \text{ g}$  per pellet), and spent shot pellets were collected from a shooting range site ( $0.073 \pm 0.012 \text{ g}$  per pellet). Spent shot pellets have been exposed to the natural environment for over 10 yr since the shooting range was closed. For a model plant, ryegrass (*Lolium perenne* L.) was grown in a pot to reproduce a rhizosphere soil condition with a dense root system (0.4 g seeds per pot). Periodical watering was conducted to the pot to adjust the water volume content to 30%. All pots were placed in a growth chamber under a fluorescent light with a 12/12 h d/night cycle at 25 °C. The pots were prepared with four replicates for plant growth and with three for without plant growth.

#### 2.1.2. Soil and plant analyses

Aboveground plant tissues were harvested around 100 d after seeding. Harvested aboveground tissues of plants were rinsed twice with deionized water and dried at 60 °C for 48 h in a forced-draft oven. The dry weights were measured. Dried plant material (0.25 g) was digested using a block digester with 5 mL of concentrated  $HNO_3$  and 2 mL of  $H_2O_2$  at 200 °C for 6 h. After digestion, the solution was filtered, diluted with deionized water, and analyzed for Pb by atomic absorption spectrometry (AA-6800F, Shimadzu Corporation, Japan). When the plants were harvested, the pots were dismantled to collect the soils and pellets. A hand-shaking operation was performed to allow the separation of soils falling from the roots, and the soil that remained adhered to the roots was considered the rhizosphere soil (Seguin et al., 2005). Soils and pellets were air-dried and used for the chemical analysis. The weight of collected pellets was measured. However, the data varied among the pots and the effect of treatments could not be clearly determined based on the weight loss of shot pellets (data not shown). Therefore, we used the single and sequential extraction methods to determine the effect of lime and rhizosphere treatments on pellet dissolution in the soil. Toxicity Characteristic Leaching Procedure (TCLP) solution (USEPA Method 1311) was used to determine extractable Pb in the soil. Twenty mL of TCLP solution (i.e.,  $CH_3COOH$ ) was added to 1.0 g soil, and the mixture was equilibrated for 24 h on a shaker. The TCLP-Pb concentration

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