

Chemical speciation of Pb in contaminated soils: (Im)mobilization by plant root growth and chemical amendments

The environmental impact of soil contamination around shooting ranges is closely related to the chemical speciation of Pb in spent pellets. When a shot pellet has been released into the soil, the surface of the metallic Pb is gradually oxidized to PbO and subsequently transformed into carbonate phases (e.g., PbCO₃). These species are thermodynamically labile and have been recognized as a primary phase controlling Pb solubility in soils. In addition to these Pb species, recent investigations using synchrotron-based XAFS have revealed that Pb in shooting range soils is also present in association with organic matter and Fe/Mn (oxy)hydroxides [1]. These characterizations of soil Pb were achieved using synchrotron-based XAFS. In the next phase of our study, we have investigated how Pb solubility and speciation of shooting range soils were affected by plant root growth and chemical amendments [1,2]. Lead in contaminated shooting range soils (Japan and South Korea) and over 20 reference compounds were analyzed by Pb L_{III}-edge EXAFS spectroscopy at beamline BL01B1 in transmission and fluorescent modes.

Plant roots can alter metal solubility via rhizosphere processes that physically and biochemically modify the properties of the soil at root interfaces. The rhizosphere processes are derived from root exudates containing protons and various organic acids, and such chemicals induce metal (mineral) dissolution in soils. To examine the effect of root growth on the dissolution of Pb pellets, plants were grown in a soil amended with Pb pellets for 100 days, and then acid-extractable Pb concentrations were measured. Figure 1(a) illustrates how the growth of roots induces the dissolution of Pb from pellets to soils. The average extractable Pb concentration in the pH 4.5 soil was about 13-fold greater in rhizosphere (with root growth) than in bulk (without root growth) treatments (Fig.1 (a)). Compared with the acid soil, the acid-extractable Pb concentration

was decreased in the alkaline soil (pH 7.5), although Pb dissolution from pellets still occurred more in the rhizosphere than in the bulk soils.

To assess the effect of root growth on Pb speciation, buckwheat and grass were grown in a Japanese shooting range soil, and their Pb L_{III}-edge EXAFS spectra were simply compared (Fig. 2(a)). Compared with the bulk soil, the growth of buckwheat and grass modified the fine structure in EXAFS spectra. Also, the EXAFS spectra of buckwheat and grass soils were different in fine structure. These results indicate that (i) transformations of preexisting soil Pb species were induced by plant root growth, and (ii) such transformations depended on plant species. The linear-combination fitting (LCF) procedure with known Pb references revealed that Pb in the bulk soil existed in the form of PbCO₃ (37%), and Pb sorbed on ferrihydrite (Pb-Fe, 36%) and on organic matter (Pborg, 15%) (Fig. 2(a)). The predominance of these Pb species could be supported by soil chemical constraints, including the abundance of Fe hydroxides, organic matter and carbonate minerals. The buckwheat-grown soil had more Pb-Fe (51%) and less PbCO₃ (25%) than the bulk soil. These notable modifications of Pb species occurred owing to the acidification of buckwheat rhizosphere soil whose pH value was significantly lower than that of the bulk soil. Compared with the buckwheat soil, the grass-grown soil had a subtle difference in the proportion of each Pb species, although their EXAFS spectra were notably different in fine structure. This result suggests that a subtle difference in the relative abundance of metal species may not be determined by using the LCF procedure.

There have been several investigations regarding remediation studies of Pb-contaminated shooting range soil, with the main emphasis being on immobilization technologies. The mechanism of immobilization is based on the formation of inert and highly insoluble species of metals using soil amendments. We have studied several types of natural waste materials, including egg and oyster shells, as metal immobilizing amendments, and demonstrated their effectiveness on reducing metal solubility [3]. According to X-ray diffraction results, the mineralogical structure of egg and oyster shells is basically CaCO₃ (Fig. 3). The structure of these shells can be altered to CaO by heating at high temperatures (calcination). The calcination process increases the pH and surface area of the material, which induces a much greater ability to immobilize metals in contaminated soils.

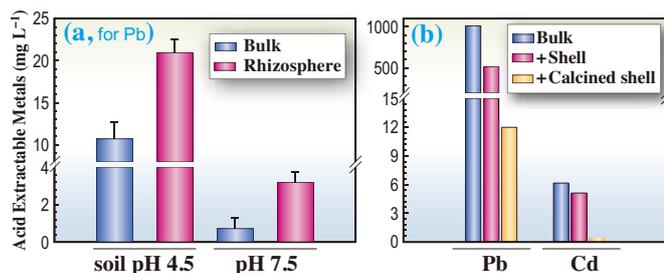


Fig. 1. Acid extractable metals from contaminated bulk and rhizosphere (plant grown) soils (a) and from contaminated soil with non-calcined and calcined shell additions (b).

Figure 1(b) shows the acid extractable Pb and Cd from a contaminated soil amended with calcined and non-calcined shells, demonstrating a significant decrease in metal solubility with the addition of these amendments.

We performed XAFS spectroscopy to identify the Pb species were present in the soils with these amendments. Unlike a Japanese soil, Pb in the soil collected from a Korean shooting range was mainly present in association with kaolinite and humus (Fig. 2(b)). The Pb-EXAFS spectra obtained from the soils amended with calcined and non-calcined shells were visually different in structure, suggesting that Pb in these soils was immobilized in different forms. Although the exact Pb species were not identified, the EXAFS spectrum for the calcined-shell-amended soil was similar to that of $Pb(OH)_2$ and $PbSiO_3$, and it was

clearly different from that for bulk and shell-amended soils. The association of Pb with Si was likely derived from the dissolution of (phyllo)silicate minerals under highly elevated soil pH conditions by the addition of calcined shells. The increases in soil pH and Ca concentration in the soil amended with calcined shells may enhance the formation of calcium silicate hydrate with Pb in its structure [4]. The association of Pb with Si and Ca are supported by the elemental distribution map illustrating the presence of these elements at the same position on the soil surface [2]. Owing to the large possible number of heavy metal species in soils, identifying at least the major species is a challenging task but critical in understanding the metal behavior in a certain environment.

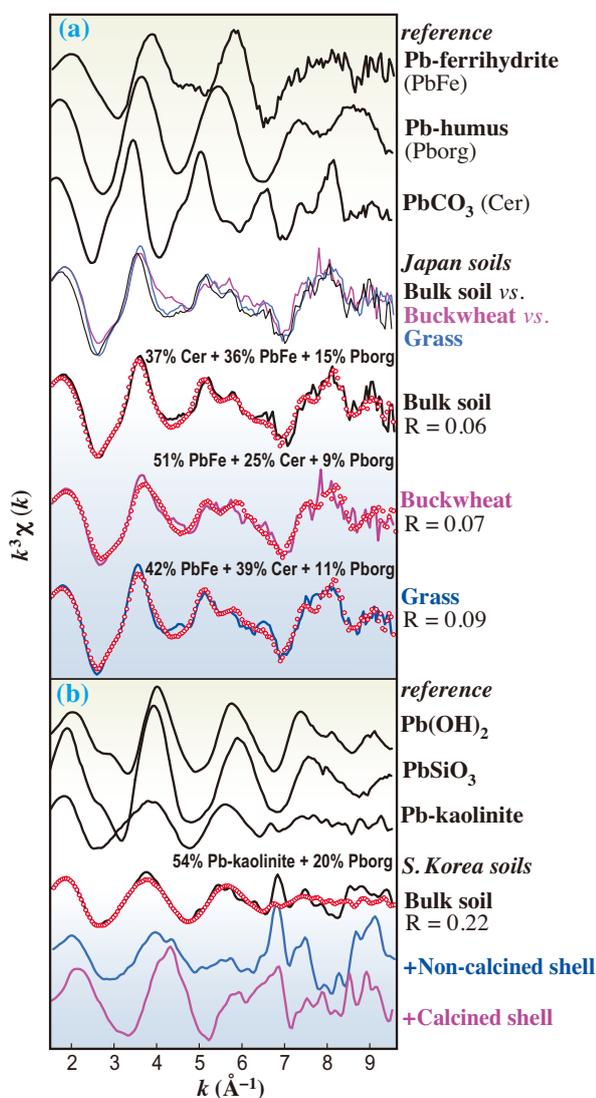


Fig. 2. L_{III} -edge Pb EXAFS spectra of selected references and contaminated shooting range soils grown with different plants (a) and amended with non-calcined and calcined shells (b). Open circles indicate the best LCF spectra obtained using the Pb references.

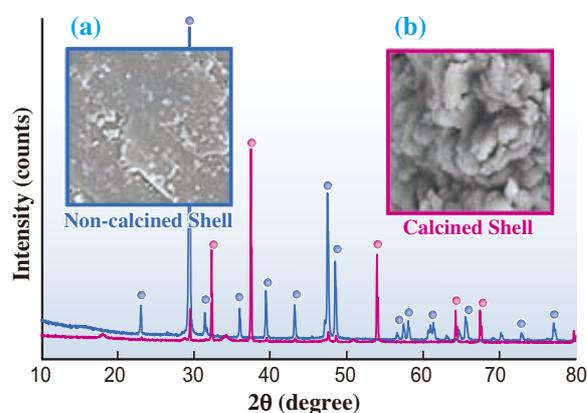


Fig. 3. XRD spectra of non-calcined and calcined oyster shells. Filled blue and magenta circles indicate $CaCO_3$ and CaO phases, respectively.

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