Transformations of soil Pb species by plant growth and phosphorus amendment: Phytoremediation and metal immobilization technologies

Shooting range areas are one of the highly concerns of heavy metal contamination. Over 400 shooting ranges are present in Japan. The environmental impact of soil contamination around shooting ranges is closely related to chemical speciation of lead (Pb) in spent pellets. If Pb species present in the soil are readily soluble, then these species are predicted to be bioavailable. When a spent pellet has been released in the soil, the surface of the metallic Pb(0) is gradually oxidized to Pb(II) (e.g. PbO) and subsequently transformed into carbonate phases (e.g., $PbCO_3$). These species are labile and have been recognized as a primary phase controlling Pb solubility and availability in shooting range soils. Recent investigations using synchrotron-based X-ray spectroscopy have revealed that organically bound Pb is one of the predominant species in a shooting range soil with abundant organic matter [1]. Lead sorbed to pedogenic Fe and Mn (oxy)hydroxides is another important phase for moderating solubility and bioavailability [2]. These Pb phases occurring in soil systems are illustrated in Fig. 1.

The success of *in situ* remediation programs of Pb contaminated shooting range soil relies on the transformation of comparably soluble Pb species into thermodynamically more stable species. A technology attracting attention concerning the remediation of contaminated shooting range soil is the immobilization of Pb using phosphorus-containing amendments. The mechanism of Pb immobilization using phosphorus (P) amendments is based on the rapid kinetic formation of Pb phosphates [e.g., $Pb_5(PO_4)_3Cl$], which are thermodynamically the most stable in a wide range of pH and redox status under earth surface conditions. Used in conjunction with plant growth, phosphorus-amended immobilization technologies can be used to reduce the leaching potential of both dissolved phosphorus and metal contaminants in the soil profile [3]. This remediation technology is called phytostabilization, which reduces the risk of metal toxicity and mobility by transforming metal speciation in the soil. However, it remained unclear how chemical speciation of preexisting Pb is affected in the soil surrounding plant roots (i.e., rhizosphere soils).

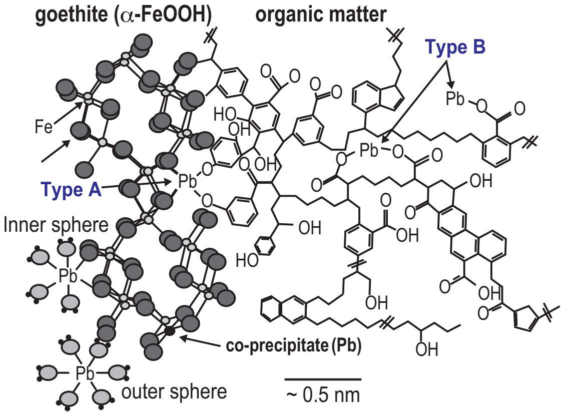

Fig. 1. Molecular mechanisms of Pb(II) bonding to an Fe oxide-organic matter assemblage. Mechanisms involving the mineral component include inner- and outer-sphere surface complexes, and coprecipitation by isomorphic substitution into the mineral structure. A Type A ternary complex is a bridging cation between the organic and mineral components, and a Type B ternary complex involves the mineral-bound organic matter. Figure modified based on Hesterberg *et al.* [5].

Plant roots can alter metal speciation via rhizosphere processes that physically and biochemically modify the properties of the soil at root interfaces. Plants and mycorrhiza (fungi) closely associated with roots locally modify the chemical properties of rhizosphere soils by exuding exchanging ions and organic acids. From the perspective of Pb immobilization, biochemical alternation of rhizosphere soils compared with the bulk soils may have a distinct effect on the solubility of amendment and Pb minerals, which eventually promotes transformations of preexisting Pb species. For the development and evaluation of phosphorus-amended phytostabilization technology for shooting ranges, it is necessary to assess how the plant rhizosphere affects the speciation and solubility of Pb in soil.

We investigated the effect of phosphorus amendment on the solubility and speciation of Pb in a highly contaminated shooting range soil under rhizosphere conditions. A Pb-contaminated soil collected from a shooting range was treated with a phosphorus amendment, and buckwheat plants were grown in the pot. After 100 days, the soil was collected and analyzed for Pb L_{III}-edge EXAFS spectroscopy at beamline **BL01B1** in a fluorescent mode. To provide qualitative and quantitative estimates of Pb speciation, the Pb-EXAFS spectra of soil samples were modeled by least-squares fitting using a linear combination (LCF) of known standard Pb species. Knowledge from soil mineralogical and chemical properties and related studies [2] was employed to narrow down the standard spectra used for the fitting procedure. Detailed information is available in Hashimoto *et al.* [4].

To assess the effect of root growth and P amendment on the soil Pb speciation, Pb L_{III}-edge EXAFS spectra of selected soil samples were simply compared (Fig. 2). The P amendment modified the overall spectral shape, which differed from that of unamended soil (Fig. 2(a)). In addition to the molecular spectroscopic analysis, a soil extraction procedure showed a significant reduction of soluble Pb concentration in the P-amended soil, indicating the modification of soil Pb species to less soluble phases. In the soil growing buckwheat, the overall shape of the Pb L_{III}-edge EXAFS spectrum was altered as compared with that of bulk soil (Fig. 2(b)). These results indicate the modifications of preexisting soil Pb species by the P amendment and plant root growth. The overall structure of EXAFS spectrum was also different among the plant species [4], suggesting that modifications of soil Pb species could be dependent on biochemical processes of plant roots.

The LCF procedure on the EXAFS spectra revealed that Pb in the *bulk* soil was present in the form of $PbCO_3$ (37%), and Pb sorbed on Fe minerals (Pb-Fe, 36%) and on organic matter (Pborg, 15%) (Fig. 3). The predominance of these Pb species could be supported by the soil chemical constraints, including the abundance of Fe (oxy)hydroxides, organic matter and carbonate minerals [3]. The *buckwheat* soil contained more Pb-Fe (51%) and less $PbCO_3$ (25%) than the *bulk* soil. These notable modifications of Pb species occurred due to acidification of buckwheat rhizosphere soil whose pH value was significantly lower than that of the *bulk* soil. The reduced Pb solubility in the *buckwheat + P* soil resulted from the transformation of preexisting $PbCO_3$ and Pborg into thermodynamically more stable $Pb_5(PO_4)_3Cl$ (26%) and Pb-Fe (57%) phases. It was expected that the mechanism of Pb immobilization by P amendments relies entirely on the formation of Pb phosphate compounds. Our study, however, concluded that the inner-sphere complex of Pb with Fe minerals is an alternative mechanism of soil Pb immobilization [4]. This study demonstrated that root growth modifies Pb speciation in P-amended soils, and for the purpose of phytostabilization, some plant species with strong rhizosphere processes may impair the efficiency of Pb immobilization by P amendments.

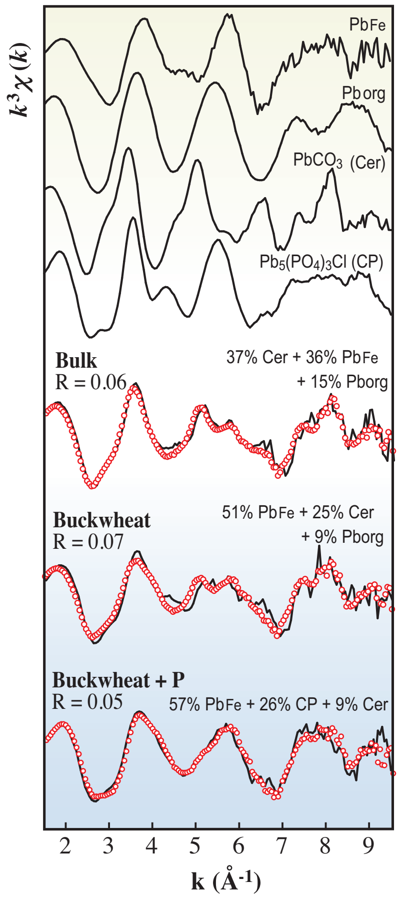

Fig. 3. Pb L_{III}-edge EXAFS spectra (solid line) of soil samples and their best linear combination fits (circle) using the standard spectra of known Pb species. Cer, cerussite ($PbCO_3$); CP, chloropyromorphite [$Pb_5(PO_4)_3Cl$]; PbFe and Pborg, Pb sorbed on ferrihydrite and on organic matter, respectively.

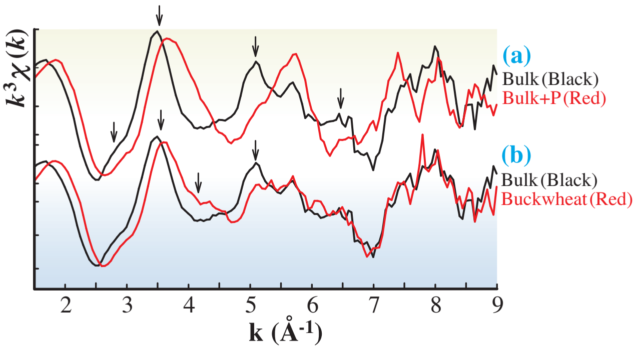

Fig. 2. Pb L_{III}-edge EXAFS spectra of soil samples comparing **(a)** the effect of the P amendment in the bulk (non-rhizosphere) soils, and **(b)** the effect of plant growth in the unamended soils. Arrows point to spectral modifications caused by the amendment or the plant growth.

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