Speciation of phosphorus and zinc in soils receiving swine manure compost for nearly a quarter of a century

The accumulation of phosphorus (P), zinc (Zn), and copper (Cu) is a common issue in farmland soils receiving a large amount of swine manure (SM) compost from pig production. The SM contains relatively high levels of Zn and Cu owing to the extensive use of veterinary medicinal products in pig production [1]. Therefore, the continual application of SM in the farmland results in the elevation of these elements in the soil. The mobility and potential bioavailability of an element in soil depend on their oxidation states and chemical species. It is largely unknown how the chemical species of elements in SM have been altered in the soil over a decade or an even longer time span. The objective of this study was to investigate the concentration and chemical species of Zn and P in soil collected from a field where SM compost has been continuously applied for 23 years. Long-term field experiments are essential for revealing the changes in the accumulation and speciation of manure-derived metals and P in the soil.

The experimental plots were located at Western Region Agricultural Research Center, NARO, Kyoto, Japan and were established in 1993. The plots had been treated twice a year with chemical fertilizer (CF) and SM compost for 23 years. Air-dried soil samples were analyzed by XAFS. P *K*-edge XANES measurements were conducted at Aichi Synchrotron Radiation Center using beamline BL6N1, equipped with an InSb (111) monochromator, at ambient temperature under He atmosphere. References for P compounds and mineral-adsorption phases were also analyzed. Zn *K*-edge XAFS measurements were conducted at SPring-8 **BL01B1** and **BL14B2** beamlines, equipped with a Si(111) monochromator, at ambient temperature. References for Zn compounds and mineral-adsorption phases were also analyzed [2].

The continual application of SM compost notably increased the soil P concentration to about three times greater (SM soil, 4.5 g·kg^{-1}·yr^{-1}) than that in the chemical-fertilizer-applied soil (CF soil, 1.6 g·kg^{-1}·yr^{-1}) after 23 years of field application (Fig. 1(a)). The Zn concentration in the SM soil in the 23rd year of the field trial reached 224 mg·kg^{-1} (Fig. 1(b)). In contrast, the concentration of Zn remained virtually unchanged with CF application for 23 years.

The P *K*-edge XANES spectra of soils were characterized by the pre-edge at around 2145 eV (Fig. 2), indicating the presence of PO_4 associated with Fe minerals. The XANES spectrum of SM-compost-applied soil collected in 2015 (SM2015) was similar to that of the hydroxyapatite reference and exhibited a distinctive feature of a shoulder on the high-energy side of the whiteline peak. Because of the high similarity in XANES spectra even among the reference compounds, linear combination fitting (LCF) of soil XANES spectra using reference standards was reported as a group of PO_4 associated with Fe (Fe–P), Ca (Ca–P), and Al (Al–P) [3]. The original soil (Soil1992) contained 55% Al–P (0.67 g·kg^{-1}) and 39% Fe–P (0.47 g·kg^{-1}) as major species. The continual application of CF for 23 years (CF2015) did not induce any notable change in Al–P concentration, but an increase in the Fe–P concentration from 39% to 49% of the total P was observed. In contrast, the continual application of SM compost for 23 years (SM2015) rapidly increased the concentrations of Fe–P to 3.4 g·kg^{-1} (76%) and Ca–P to 0.86 g·kg^{-1} (19%) with a concomitant decrease in Al–P to 0.23 g·kg^{-1} (5%). The accumulation of these P species in the SM2015 soil corresponded to the P species in SM itself, which is enriched with Fe–P (59%) and Ca–P (41%).

The overall structure of the Zn EXAFS spectrum for the original soil (Soil1992) and CF-applied soil (CF2015) was similar to that of Zn associated with kaolinite (Fig. 3). These soils exhibited marked

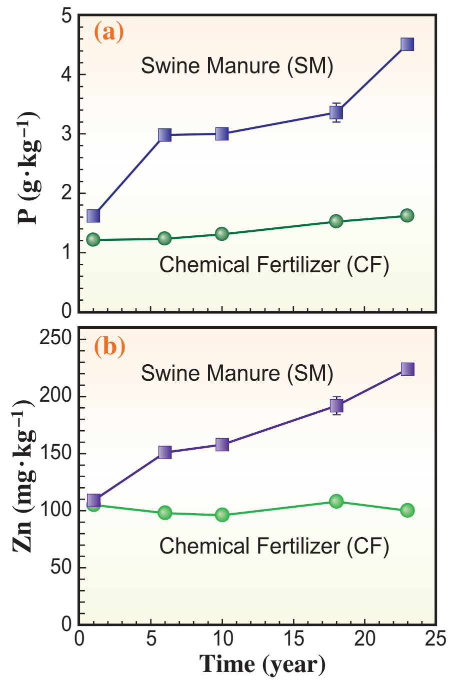

Fig.1. Concentrations of P **(a)** and Zn **(b)** in soils treated with chemical fertilizer (CF, circles) and swine manure (SM) compost (squares) for 23 years.

splitting in the first oscillation of their EXAFS spectra at 3.7 $Å^{-1}$, corresponding to the reference Zn associated with kaolinite. The original soil (Soil1992) contained 95% Zn associated with phyllosilicates (99 mg·kg^{-1}), which included kaolinite and hydroxyl-interlayered montmorillonite. The continual application of CF to the soil (CF2015) essentially did not change the distribution of these Zn species. In contrast, the continual application of SM compost for 23 years (SM2015) induced the accumulation of hopeite (60 mg·kg^{-1}, 27%) and Zn associated with humus (72 mg·kg^{-1}, 32%) in addition to the inherent species of Zn associated with phyllosilicates (78 mg·kg^{-1}, 35%).

Our study revealed that the continual application of SM compost to soils significantly increases the concentrations of Zn and P. Agricultural soils receiving a large amount of SM from swine production can be a primary source of Zn in the environment. In soils receiving repeated land applications of SM and pig slurry, the concentration and speciation changes of Zn and P over time are critical in predicting the long-term fate and potential mobility of these elements. Our study suggests that in the long-term land application of SM, the accumulation and speciation of Zn and P over time should be monitored to minimize the environmental loss of these elements.

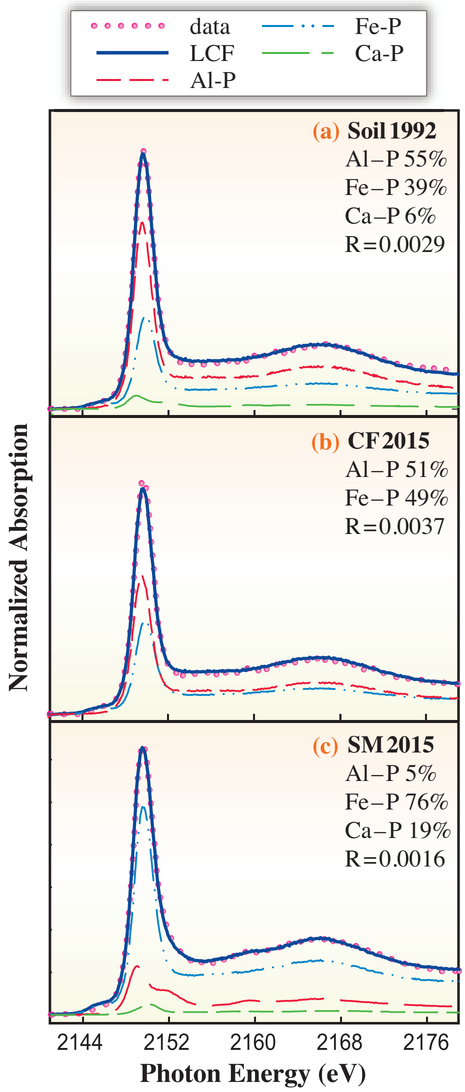

Fig. 2. P *K*-edge XANES spectra for **(a)** original soil (Soil1992), **(b)** soil treated with chemical fertilizer (CF2015), and **(c)** soil treated with swine manure compost (SM2015) and their linear combination fits using P reference spectra. Al–P, Fe–P and Ca–P represent P associated with Al, Fe, and Ca, respectively.

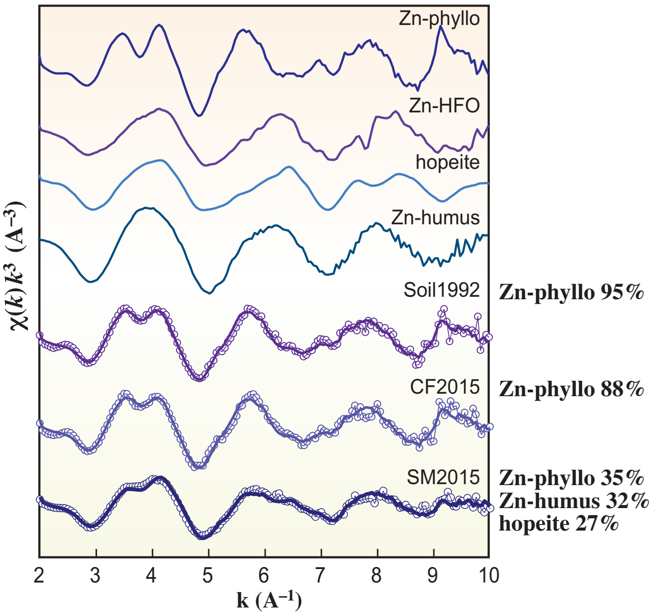

Fig. 3. Spectra of Zn *K*-edge EXAFS of selected references relative to original soil (Soil1992), soils treated with chemical fertilizer (CF2015) and swine manure (SM2015), and their linear combination fits using reference spectra (solid lines). The best results of LCF are shown on the right side of each panel. The sum of components of LCF on each sample is not adjusted to 100%. Zn phyllo: sum of Zn associated with kaolinite and montmorillonite. Zn-humus and Zn-HFO represent Zn associated with humus and ferrihydrite, respectively.

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