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PHOSPHORUS SPECIATION IN MANURE AND MANURE-AMENDED SOILS USING XANES SPECTROSCOPY

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It is important to know what inorganic phosphorus (P) species are being formed in soils subjected to high, long-term poultry-manure application in order to understand P accumulation and release patterns. Phosphorus K-edge XANES spectra of fresh manure showed no evidence of crystalline P minerals, but did exhibit a dominance of soluble calcium phosphates (CaP) and free and weakly bound phosphates. Soils with a short-term manure history contained both Fe-associated phosphates and soluble CaP. Long-term application resulted in a dominance of CaP and a transformation from soluble to more stable CaP species. However, none of the amended soils showed the presence of crystalline CaP. Maintaining a high pH is therefore an important strategy that can be used to minimize P leaching in these soils.

Poultry manure is frequently applied to agricultural fields to supply essential nutrients to crops, subsequently increasing yields. However, apart from plant uptake, manure P can be lost as the result of surface erosion and/or leaching. Such losses have resulted in the eutrophication of watersheds in the past. Soil pH plays a critical role in P retention in soils by, for instance, changing the solubility of secondary Fe, Al, and CaP minerals in soils. Manure is a well-known liming material; however, it is unknown how manure application impacts the solubility and transformation of these secondary P compounds. Our previous studies suggest an increase in the proportion of CaP in the total P pool in soils with long-term manure application. Using P K-edge XANES, this study aims to assess the CaP species formed in an originally acidic soil in response to high and long-term (up to 25 years) manure applications.

We measured standards of inorganic phosphate forms for comparison with spectra of the investigated soils (**Figure 1**). Both the spectra of the Fe-oxide strengite (STR) and the Al-oxide variscite (VAR) featured a peak at 2156 eV (**Figure 1e**), but

were distinguished by the presence and absence of a peak at 2146 eV (**Figure 1a**) for STR and VAR, respectively. The most characteristic feature for all of the CaP species was a peak at 2159 eV (**Figure 1f**) and a shoulder between 2151 eV (**Figure 1c**) and 2152 eV (**Figure 1d**). A closer observation of the shoulder (**Figure 1c-1d**) revealed this shoulder to be better expressed for CaP species with decreasing solubility. The solubilities of these CaP species generally decrease as follows: dibasic calcium phosphate dehydrate (DCPD) > dibasic calcium phosphate (DCP) > amorphous calcium phosphate (ACP) \approx β -tricalcium phosphate (TCP) > octacalcium phosphate (OCP) > hydroxyapatite (HAP).

The manure spectrum showed only two small shoulders that are characteristic of CaP species (**Figure 2Ac-d and 2Af**), but the overall spectra rather resembled that for Aq-PO₄. The linear combination fitting result showed that this manure contained 18% DCP, 35% ACP1, and 47% Aq-PO₄. Aq-PO₄ in the fitting results is considered a group of "free and weakly bound (adsorbed) phosphates," since it is not possible to use XANES alone to quantitatively distinguish Aq-PO₄ from phosphate adsorbed on minerals. The forest soil spectrum showed a shoulder (**Figure 2Aa**) that is indicative of FeP but was significantly widened compared to STR, suggesting the presence of a combination of phosphates in strengite and phosphates adsorbed to the surfaces of various Fe-oxides. The linear combination fitting resulted in 38% ACP1, 32% STR, and 30% Aq-PO₄ in the forest soil. Spectra of the manure-applied soils showed a decrease and disappearance of the FeP shoulder (**Figure 2A-2Ca**) and an increase in the



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intensity of the CaP shoulder (**Figure 2A-2Cc**) and the CaP peak (**Figure 2A-2Cf**) as the application history increased. In fact, the linear combination fitting suggested that long-term manure application resulted in the transformation of relatively soluble CaP species (**Figure 2A**, S2 soil: 8% DCP and 19% ACP1) into more crystalline CaP species

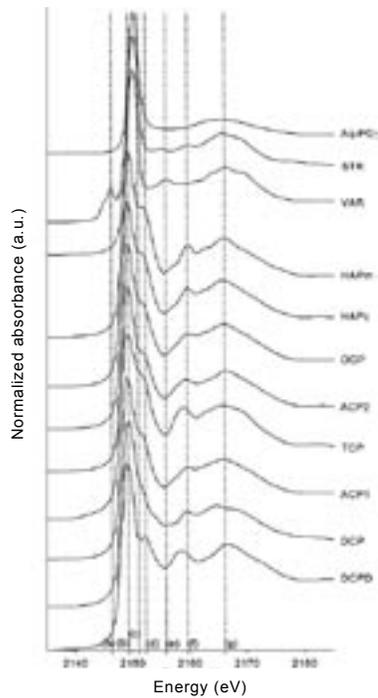


Figure 1. Phosphorus K-edge XANES spectra for different inorganic phosphate standard species. The dashed lines show energy levels of importance to indicate unique spectra features for different species: (a) STR; (b) absorption edge (white line); (c)–(d) CaP species related to their solubility; (e) STR and VAR; (f) CaP species; (g) oxygen oscillation. Aq-PO₄ is H₂PO₄⁻ species in 0.1 M NaCl solution. STR: strengite, VAR: variscite, HAP: hydroxyapatite, OCP: octacalcium phosphate, ACP: amorphous calcium phosphate (phase 1 and 2), TCP: β -tricalcium phosphate, DCP: dibasic calcium phosphate, and DCPD: dibasic calcium phosphate dehydrate.

(**Figure 2C**, L1 soil: 13% ACP1 and 43% TCP) in soils over time. Yet, the most crystalline and therefore least soluble CaP form, such as HAP, was not found in the studied soils. Since CaP minerals are least soluble at high pH, maintaining a high pH may be an important strategy for minimizing P leaching in these soils.

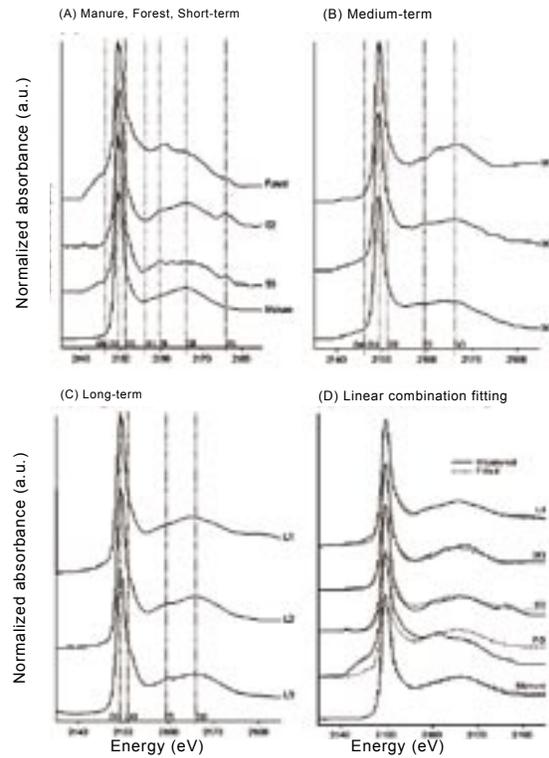


Figure 2. Phosphorus K-edge XANES spectra for poultry manure, forest, and manure-applied soils with different histories of application: (A) manure, forest, and short-term; (B) medium-term; (C) long-term; and (D) linear combination fits of selected spectra. The dashed lines in (A), (B), and (C) correspond to those in Figure 1. The dotted lines in (D) represent the best fitted result to respective spectra by linear combination fitting.