Phosphorus Speciation in Manure and Manure-Amended Soils Using XANES Spectroscopy

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Previous studies suggested an increase in the proportion of calcium phosphates (CaP) of the total phosphorus (P) pool in soils with a long-term poultry manure application history versus those with no or limited application histories. To understand and predict long-term P accumulation and release dynamics in these highly amended soils, it is important to understand what specific P species are being formed. We assessed forms of CaP formed in poultry manure and originally acidic soil in response to different lengths of mostly poultry manure applications using P K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Phosphorus K-edge XANES spectra of poultry manure showed no evidences of crystalline P minerals but dominance of soluble CaP species and free and weakly bound phosphates (aqueous phosphate and phosphate adsorbed on soil minerals). Phosphate in an unamended neighboring forest soil (pH 4.3) was mainly associated with iron (Fe) compounds such as strengite and Fe-oxides. Soils with a short-term manure history contained both Fe-associated phosphates and soluble CaP species such as dibasic calcium phosphate (DCP) and amorphous calcium phosphate (ACP). Long-term manure application resulted in a dominance of CaP forms confirming our earlier results obtained with sequential extractions, and a transformation from soluble to more stable CaP species such as β-tricalcium calcium phosphate (TCP). Even after long-term manure application (>25 yr and total P in soil up to 13 307 mg kg⁻¹), however, none of the manure-amended soils showed the presence of crystalline CaP. With a reduction or elimination of poultry manure application to naturally acidic soils, the pH of the soil is likely to decrease, thereby increasing the solubility of Ca-bonded inorganic P minerals. Maintaining a high pH is therefore an important strategy to minimize P leaching in these soils.

Introduction

Land application of animal manure on agricultural fields generally serves two main purposes: first, it provides essential nutrients to crops; and second, it serves as a means of waste disposal for animal feeding operations. Animal manure supplies phosphorus (P) to the soil (1, 2), and contributes to increased yields of forage and field crops where P was previously limiting production (3–5). However, when land application is aimed primarily at supplying nitrogen (N) to crops and/or reducing the waste volume, P applied with manure can far exceed the amount of P required by most crops (6). For example, a typical N:P uptake ratio for corn is 7.5:1 (7), while the N:P ratio for poultry manure reported in the literature tends to be approximately 2.5:1 (8).

Initially soils will retain most of the P applied in excess of crop uptake through various transformation processes including immobilization, adsorption, and precipitation. Apart from plant uptake, P can be lost by surface erosion (9, 10) and/or subsequently by leaching (11). Such losses have resulted in eutrophication of rivers and lakes in the past decades (12, 13).

Adsorption to surfaces of iron (Fe) and aluminum (Al) oxides and clay minerals and precipitation as secondary Fe- and AlP minerals are predominant reactions for solution P in acidic soils. Despite the generally high adsorption capacity of most soils, P leaching can occur especially when intensive and/or long-term applications of the manure saturate the P adsorption capacity of the soils (14, 15). In neutral and calcareous soils, the fate of P is controlled by adsorption to surfaces of calcium carbonate (CaCO₃) and clay minerals and/or precipitation as secondary calcium phosphate (CaP) minerals. Soil pH plays a critical role in P retention in soils by altering the adsorption capacity of soils, forming CaCO₃ (if pH > 7.8) and changing the solubility of secondary Fe-, Al-, and CaP minerals in soils. Manure is well-known as a liming material (16). However, it is unknown how manure application impacts the solubility and transformation of the secondary phosphate compounds. An understanding of the distribution of P forms in manure and transformation of P forms in soils upon manure application is critical in assessing environmental impacts of land application of manure.

Sequential fractionation, one of the most commonly used methods to determine P forms in soils, has been used for investigating P forms in animal manures (17–19). However, results have been inconsistent. He et al. (20) found that the acid-extractable P fraction in swine manure (11%) was lower than that in the soil (14%) although Ca and P concentrations in the same fraction were higher in the manure. They concluded that it may not be appropriate to exclusively apply soil-based fractionation interpretations (bicarbonate and hydroxide-extractable P either loosely sorbed on the surface or bound to Fe and Al compounds and acid-extractable P associated with CaP) to fractionation results of animal manure, and that the physicochemical properties of their matrices should be taken into account when applying soil-based fractionation methods and interpretations in the animal manure P study.

It seems evident that Ca is abundantly available in poultry litter and manure with a high pH (mostly pH > 7; 21, 22). Application of such litter/manure can raise the pH of naturally acidic soils, and this may play an important role in forming various secondary CaP minerals with different solubility and crystallinity. Wet-chemical P fractionation techniques applied to acidic forest soil (pH 4.1) and close-by manure-amended soils (with varied application history up to 25 yr) revealed higher proportions of CaP (dilute acid-extractable P) than other fractions with longer application history (19). These results suggested that secondary CaP compounds were formed upon poultry manure application. However, it is not clear whether such CaP compounds would readily appear in solution upon P depletion due to P uptake by plants or leaching, or whether these compounds are stable and provide a long-term option for P binding. Such behavior would have
important implications for long-term prediction of P losses from manure amended watersheds. Recent advances in nuclear magnetic resonance (NMR), particularly high-resolution solid state \(^{31}\)P NMR and X-ray absorption near-edge structure (XANES) spectroscopic techniques, have made it possible to investigate molecular species in heterogeneous samples (e.g., soils and poultry litter). These techniques have contributed to a better understanding of the form, distribution, and transformation of CaP in poultry manure and manure-amended soils (21, 22). Studies conducted in Delaware suggested that the most likely CaP phases corresponding to a peak found in the solid state \(^{31}\)P NMR spectra of poultry litter were \(\beta\)-tricalcium phosphate (TCP) or calcium phosphate surface precipitate on CaCO\(_3\) (22). Calcium P comprised on average 7–14% of the total P in these litter samples. Using P K-edge XANES spectroscopy for the same litter samples, dibasic calcium phosphate (DCP) and dibasic calcium phosphate dehydrate (DCPD) were detected. However, thermodynamically more stable CaP minerals such as hydroxyapatite (HAP) were not observed (21).

Phosphorus K-edge XANES spectra of animal manure applied (>25 yr) soils in Québec revealed CaP minerals that differed from the ones found in the manure applied to the soils (24). Least-squares fits of the spectra yielded 18% HAP and 45% octacalcium phosphate (OCP) of the total P present in the Ap horizon, and 11% HAP and 45% octacalcium phosphate (OCP) of the total P present in the underlying Bg horizon. The authors attributed precipitation of CaP in the B horizon to leaching of Ca and P from the A horizon despite the soil being acidic (pH 5.5). It has not been documented, however, whether CaP minerals from poultry materials transform into other forms of CaP minerals in soils, or whether newly formed amorphous CaP minerals in soils transform into more crystalline CaP minerals over time.

The objective of this study was to assess the CaP species formed in an originally acidic soil in response to high and long-term manure applications using P K-edge XANES spectroscopy. Field sites were selected based on estimated history of manure application (short-term (S) <6 yr, medium-term (M) 10–15 yr, and long-term (L) >25 yr of manure application). Three fields were chosen from each application site, and a forest field (FO) without history of cultivation or manure application was included as a reference site (Table 1). The sites are located within an area of about 4 km\(^2\). Fields varied with regard to manure source; the history of some fields was dominated by dairy manure application, while others, including the fields with long-term manure application histories, had received mostly poultry manure (23).

**Sample Collection and Characterization.** Soil samples (composites of 15 subsamples) were taken from the top 0–12.5 cm, air-dried, passed through a 2-mm sieve, and stored in a plastic container. A poultry manure sample was obtained from an in-site poultry house by compiling 10 subsamples with varying depths of the manure layer by using a shovel. The manure sample was dried at 65 °C for 10 h, manually crushed to pass a 2-mm sieve, and stored in a plastic container prior to analysis.

Soil samples were analyzed for Morgan extractable P, Ca, Al, and Fe (26). Samples were shaken in a 1:5 (v/v) ratio for 15 min and filtered through a Whatman No. 2 filter paper. Phosphorus in the extracts was analyzed colorimetrically using the molybdate ascorbic acid method (27) using a Technicon Autoanalyzer I (Pulse Instrumentation Limited, Saskatoon, SK) at a wavelength of 660 nm. Calcium, aluminum, and iron were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP–AES) using a JY70 Type II ICP–AES (Horiba Jobin Yvon Inc., Edison, NJ). Total P in the soil samples was determined using nitric acid digestion according to EPA method 3051 (28) followed by determination of P in solution with ICP–AES using a Spectro Ciros ICP–AES (Spectro Analytical Instruments, Kleve, Germany) and EPA method 6010b (29). Soil pH was measured in distilled water with a soil-to-solution ratio of 1:1 using a SP20 glass electrode (Thermo Orion, Cambridge, MA). Soil organic matter was estimated by loss-on-ignition (30). Particle-size distribution was determined by pipet method (31).

The manure sample was analyzed according to recommended methods for manure analysis (32). Manure pH was measured in distilled water as a 1:2 manure/water slurry using a SP 20 glass electrode. Total N was analyzed by combustion method adapted from AOAC 990.3 (33) using a Vario Max CN combustion analyzer (Elementar Americas Inc., Mt. Laurel, NJ). Ammonium N was determined colorimetrically as adapted from U.S. EPA 351.2 (34) using a QuickChem Autoanalyzer (Lachat Instruments, Milwaukee, WI). Manure P, K, Ca, Mg, and trace elements

### Table 1. Manure Application History and Selected Characteristics of Manured Soils

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were analyzed by nitric acid–perchloric acid digestion method (35) using TJA 61E ICP–AES (Thermo Electron Corporation, Waltham, MA).

**Phosphorus Standards for XANES Spectroscopy.** The following phosphate standards for XANES spectroscopy were either purchased from a chemical supplier, synthesized according to the reference cited, or provided from the sources indicated: DCP (Ca(HPO4), DCPD (CaHPO4·2H2O), β-TCP (Ca₃(PO₄)₂·1/2H₂O; x is depending on the phase), and OCP (Ca₅(PO₄)₃·2H₂O·2H₂O) (36); HAP in mineral form (HAPm) (from Tennessee Valley Authority, Knoxville, TN); strengite (STR; Fe₅O₇·2H₂O) (37); and variscite (VAR; AlPO₄·2H₂O) (38). All P standards were verified for their mineralogical purity by X-ray powder diffraction analysis; and small amounts (< ca. 5%) of impurities were found in HAPm, STR, and VAR. A spectrum for orthophosphate species in aqueous solution (Aq-PO₄) was included (from D. Hesterberg, unpublished data). A species of choice was H₃PO₄ being a dominant species in a pH range of the soil samples studied. The solution contained 50 mM P in a 0.1 M NaCl background solution, the pH of which was adjusted to 4.7 with HCl or NaOH.

**X-ray Absorption Near-Edge Structure Spectroscopy Analysis.** Solid-state characterization of P from the soil samples, manure, and P standards was carried out using P K-edge XANES spectroscopy at beamline X-19A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The P XANES spectra were collected from air-dried silty clay fractions (by dry sieving to <50 μm; 39) of soil samples, air-dried manure, and P standards that had been passed through a 125-μm sieve prior to analysis. The finely ground materials were uniformly spread on Scotch tape, which was pretested for its P level and exhibited a much lower P level than the amount detected from Mylar X-ray film (Complex Industries, NY); commonly used for covering samples), and mounted at the back of a center-through hollow (1.3-cm diameter) 0.5-mm thick acrylic sample holder. The measurements were conducted under standard operating conditions, i.e., after calibrating the X-ray energy to the K-edge of P using variscite as a standard, the spectrum was assigned a reference energy (E₀) value of 2149 eV using the maximum peak of the spectrum and scanned ranging from 40 eV below to 100 eV above the absorption edge of P. Technical limitations of the beamline prohibited going further below the P K-edge, which may make background subtraction in the case of more dilute samples a challenge (21). For this reason, samples were not diluted in boron nitride (BN). The XANES data between 2119 and 2179 eV were collected with a step size of 0.2 eV. Each XANES spectrum was composed of an average of three scans. A monochromator consisting of double crystal Si (III) with an entrance slit of 0.5 mm, electron beam energy of 2.5 GeV, and maximum beam current of 300 mA was used. The spectra were recorded in fluorescence mode using a passivated implanted planar silicon (PIPS) detector (Canberra Industries, Meriden, CT). The beam path from the incident ion chamber to the sample chamber was purged with He gas. The P K-edge data analysis was done using WinXas version 3.1 (WinXas Software, Hamburg, Germany). The energy scale was calibrated to a reference energy (E₀) of 2149 eV as the maximum energy of the first peak in the first derivative spectrum for a variscite standard. The background was corrected by fitting a first-order polynomial to the preedge region from 2119 to 2159 eV; and the spectra were normalized over the region from 2187 to 2210 eV.

Linear combination fitting of soil and manure XANES spectra was conducted over the spectral region from 2130 to 2190 eV using the computer program Kaleidagraph (version 3.6, Synergy Software Co., Reading, PA) (40, 41). All possible binary and ternary combinations of the 11 available standards were fitted without energy shift parameters, and the best fitting results were judged according to their chi-square values. The fitting results were rejected when one or more of the best fit coefficients for the standard spectra were negative. In addition, as discussed by Toor et al. (42), it is not possible to quantitatively distinguish aqueous phosphate from phosphate adsorbed on minerals with XANES technique alone due to a lack of distinctive features to separate them. Therefore, aqueous phosphate in the fitting results is considered as a group of “free and weakly bound (adsorbed) phosphates”.

**Results and Discussion**

**Nutrient Concentrations in Manure and Soil.** The poultry manure used in our study tested 2–4 times higher in P, Ca, Fe, Mn, and Zn than the highest values reported by Edwards and Daniel (Table 2; 8). The N:P ratio of the manure was 1.6:1, lower than the 2.5:1 reported as a mean in the literature (8). The manure pH was high compared to values reported in the literature (21, 22), causing naturally acidic soil (pH = 4.32) to raise pH up to 7.42 by its application (Table 1). The fields with the long-term poultry manure history had greater levels of extractable P and Ca than the other fields (Table 1). The higher availability of these two elements in those soils with long-term poultry manure history is particularly important in our study since a change in their concentrations substantially affects the formation and transformation of the CaP compounds in question. In contrast, extractable Al and Fe concentrations were lower in the fields with long-term manure application histories than in the other fields (Table 1).

**Phosphorus Forms in Standard Materials.** Standards of inorganic phosphate forms were measured for comparison with spectra obtained from the investigated soils (Figure 1). In all spectra, the white line energy occurred at around 2149 eV (Figure 1, position (b), 1b; hereafter only numbers and letters are indicated for figures and spectral features, respectively); and a peak was found at around 2166 eV (1 g), which can be interpreted as oxygen oscillation. Spectral characteristics of the Fe- and AlP, STR and VAR, respectively, were distinctly different from those of the CaP species. Both STR and VAR spectra featured a peak at around 2156 eV (1e), but were able to be distinguished by the presence and absence of a pre-white line peak at around 2146 eV (1a) for STR and VAR, respectively. These spectral features were consistent with Hesterberg et al. (43), Peak et al. (21), and Beauchemin et al. (24); moreover molecular-structural interpretations for the spectra of STR and VAR were provided by Khare et al. (44).

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* Dry matter basis, determined by recommended methods (32).

**TABLE 2. Selected Properties of Poultry Manure**

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* Dry matter basis, determined by recommended methods (32).
Some spectral characteristics of the CaP species were distinct, while others were more subtle. In addition to the white line (1a) and oxygen oscillation (1g), the most characteristic feature for all CaP species spectra was a peak at around 2159 eV (1f), although a slight shift of this peak was observed in DCPD and TCP. Another distinctive shoulder that was commonly seen in the spectra for CaP species occurred at a region between 2151 eV (1c) and 2152 eV (1d). These spectral features were consistent with results from other studies (21, 24).

A closer observation of the shoulder on the high energy side of the white line at the region 2151–2152 eV (1c–1d) revealed this shoulder to be more well-defined for CaP species with decreasing solubility and increasing thermodynamic stability, as partially discussed by Hesterberg et al. (43) and Peak et al. (21). Solubilities of the CaP species studied generally decrease in the following order: DCPD > DCP > ACP ≈ TCP > OCP > HAP (solubility of ACP depended on synthetic reaction time, ACP1 > ACP2 in this study; 45, 46), and their spectra are depicted in the same order from the bottom to top in Figure 1 (HAPc and HAPm are considered to be equally soluble). Our results show that both spectral features (1c–1d and 1f) are required to confirm the presence of any CaP species in samples. However, only DCPD spectrum showed a slightly elevated shoulder toward the high energy end (2152 eV) of the above-mentioned region (1c–1d).

**Phosphorus Forms in Manure and Soils.** The heterogeneity of the manure and soil samples provides a challenge for the interpretation of the P-XANES spectra. However, several distinctive features could be identified on the spectra (Figure 2A–C). Besides the white line (2Ab) and oxygen oscillation (2Ag), the manure spectrum lacked most of the features that could indicate the presence of any phosphate crystals, except for two barely visible shoulders found at around 2151–2152 eV (2Ac–2Ad) and 2159 eV (2Af). These are characteristic for CaP species, however, rather, it most closely resembled those for aqueous phosphate (Figure 1) or phytic acid (inositol phosphate; a visual inspection from result of another study, 21), although the primary source of organic phosphate in the litter appears to be the animal waste itself. Hence, formation of organic phosphate in the litter is relatively minor (21). Nevertheless, the linear combination fitting result shows the studied manure contained 18% DCP, 35% ACP1, and 47% aqueous phosphate (Table 3). Nearly half of the total P in the manure being in a form of aqueous phosphate requires attention; however, as indicated earlier, Aq-PO4 spectrum may also represent weakly adsorbed phosphates on minerals. Hunger et al. (22) speculated CaP surface-precipitated on CaCO3 in poultry litter; and phosphates adsorbed on amorphous aluminum oxides and gibbsite were identified in the litter upon alum addition, where spectra of P adsorbed on those minerals closely resemble the Aq-PO4 and manure spectra in our study (21). A large proportion of P in the studied manure, represented by Aq-PO4, in the linear combination fitting, therefore, could well be characterized by free and weakly bound phosphate. This argument can apply to Aq-PO4 fitting results from other samples studied (Table 3). Nonetheless, overall fit of the manure spectrum captured well the features of CaP species (Figure 2D).

The P-XANES spectrum for the forest soil clearly showed the pre-white line shoulder (2Aa) indicative of FeP. This peak is significantly widened compared to STR (1a), suggesting the presence of a combination of phosphates in strengite and phosphates adsorbed to surfaces of various Fe-oxides such as ferrhydrite and goethite, for which several authors showed a less prominent but wider shoulder than strengite at the same energy point (24, 44). The spectrum for the forest soil showed the shoulder at the region 2151–2152 eV (2Aa), while the peak at 2159 eV (2Af) was not visible. It cannot be concluded from the lack of this peak (2Af) that the forest soil did not contain CaP species, considering that different P species in the soil are able to obscure particular spectral features (e.g., the peak at 2159 eV). The linear combination fitting resulted in 38% ACP1, 32% STR, and 30% Aq-PO4 in the forest soil (Figure 2D) and the high chi-square value (Table 3) may suggest that certain forms of P were present in the forest soil that were not adequately represented by the standards used for fitting. A greater variety of P standards, especially amorphous Fe- and AlP species may need to be considered in future work.

One of the most distinctive features of all spectra for soils with the short-term manure application (Figure 2A, S2 and S3; S1 spectrum was discarded from the result because of its strong spectral noise and unreliable, overall spectral shape) was the widened shoulder (2Aa) prior to the white line, showing the presence of FeP minerals and/or phosphate adsorbed on Fe-oxide surfaces as discussed above. The fact that the shoulders (2Aa) were less prominent in the S-group
spectra compared to the forest soil spectrum can be explained by dissolution of strengite due to the increased pH after manure applications. At these higher pH levels phosphate can be released into solution; and formation of secondary CaP compounds can exceed the proportion of phosphates associated to Fe minerals or oxides. This hypothesis was further supported by the formation of CaP compounds as indicated by the presence of both the shoulder at 2151−2152 eV (2Ac) and the peak at 2159 eV (2Af) in the S-group spectra. In fact, only 8% DCP and 19% ACP1 were computed for the S2 spectrum, while the majority (73%) was categorized as Aq-PO4 in this soil (Table 3). The lower proportions of CaP species in the S2 soil than those in the manure may well be a result of a dissolution of CaP compounds in the high pH manure (pH 8.41) that could occur when the manure was applied to the acidic soil (pH 6.83). Consequently, phosphate forming stronger complexes with CaP compounds in the high pH manure environment.
Mechanisms of appearance of CaP compounds in the soil upon manure application include (i) formation of secondary CaP minerals; (ii) phosphate adsorption to the surface of CaCO₃ (21); and/or (iii) surface precipitates of phosphate with adsorbed calcium on Fe-oxide surface. The secondary CaP minerals that may have been formed in the S-group soils must be relatively soluble minerals, as the intensity of the shoulder at 2151–2152 eV (2Ac) was low. However, the fact that the pH of these soils was not high enough to form CaCO₃ safely rules out interpretation (ii). A recent study of the Ca-phosphate-goethite system under conditions below the saturation index for apatite showed a strong interaction between adsorbed Ca and phosphate (47). The authors found that the adsorption of both Ca and phosphate on goethite surfaces in the mixed system (both Ca and phosphate present) was much higher than in a single system (Ca or phosphate separately present), with the effect being more pronounced at higher pH. Due to elevated concentrations of Ca and phosphate from manure and possibly Ca- and FeP dissolution along with the elevated pH in the manure-amended soils, a coadsorption of Ca and phosphate on Fe-oxide surface may still be a possibility in our studied soils. The S2 and S3 spectra showed a peak at around 2176 eV (2Ah) which was not found in the spectra for any standards or other samples investigated. Future investigations should expand the number and variation of standards to identify peaks in this area.

The spectra for soils with the medium-term manure histories (Figure 2B, M1, M2, and M3) also contained the prewhite line shoulders (2Ba), but the shoulders were less intense than those found in the S-group spectra. The shoulders were still wide indicating the presence of phosphates associated with Fe-oxide surfaces. However, the peak for strengite (2Ba), present in the S-group spectra, was not seen in the M-group spectra. Although the characteristic CaP feature (2Bf) in the M-group spectra was not as pronounced as in the S-group spectra, the other spectral feature for CaP (2Bc) appeared as well-defined as or more pronounced than those found in the S-group soils. The linear combination fitting result from the M1 soil clearly showed increasing crystallinity of CaP species in soils from the short-term to medium-term application; a decreased proportion of DCP (1%) and an increased proportion of ACP1 (55%) compared to those from the S2 soil (Table 3). Yet, nearly half of the phosphates in the M1 soil was represented by Aq-PO₄ in the fitting.

The spectra for soils with the long-term manure histories (Figure 2C, L1, L2, and L3) revealed no detectable shoulders prior to the white line, suggesting no evidences to indicate the presence of FeP compounds. Features found in these spectra were only distinctive for CaP species both at around 2151–2152 eV (2Cc) and 2159 eV (2Cd). The shoulder and peak were clearly greater than those in the S- and M-group spectra and appeared to be more pronounced for soils with higher Morgan extractable Ca and P concentrations within the L-group soils (Table 1; L1 < L2 < L3). It was shown by the fitting results that the L1 soil contained 13% ACP1, the lowest proportion of total P among the fitted samples, and 43% TCP, which did not appear in other fitted samples (Table 3). The long-term manure application appears to have resulted in the transformation of relatively soluble CaP species (DCP and ACP1) into more crystalline CaP species (TCP) over time.

Implications of P Forms for P Losses. Phosphorus-XANES studies showed that the studied manure was dominated by free and weakly bound phosphate and relatively small proportions of soluble CaP species such as DCP and ACP. Upon application of manure to soils over time, phosphates seemed to be initially involved in the release (dissolution) of various P compounds (CaP in manure and Fe- and AlP in soil), adsorption onto surfaces of different soil minerals, and formation of soluble CaP minerals. With continued applications of poultry manure, CaP compounds dominated and proportions of Fe- and AlP were negligible. It was also shown that longer application of poultry manure to soils resulted in the transformation of relatively soluble CaP (DCP and ACP) into more crystalline CaP species (TCP). Yet the most stable CaP species such as HAP was not found in the studied soils. However, the relatively soluble compounds such as DCP and ACP are able to hydrolyze to eventually form thermodynamically more stable species such as HAP. Crystallization from ACP to HAP occurs quicker in solutions with higher Ca/P molar ratios, and moreover a more Ca-rich environment around ACP is expected to be favorable for ACP–HAP conversion (48). The absence of the most stable CaP species in these heavily manured soils could be due to the presence of organic acids that can delay the crystallization and transformations of CaP minerals by either chemically bonding to or adsorbing onto (thus sterically blocking) the crystal growth sites (49, 50). Since DCP and other CaP minerals are least soluble at high pH, maintaining a high pH may be an important strategy to minimizing phosphate leaching in the studied soils.

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Literature Cited


<table>
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<th>TABLE 3. Relative Proportion of Phosphate Standards that Best Fit to Manure and Selected Soil XANES Spectra in Linear Combination Fitting*</th>
<th>DCP (%)</th>
<th>ACP1 (%)</th>
<th>TCP (%)</th>
<th>STR (%)</th>
<th>Aq-PO₄ (%)</th>
<th>(\chi^2)</th>
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<tr>
<td>manure</td>
<td>18 ± 2</td>
<td>35 ± 2</td>
<td></td>
<td></td>
<td>47 ± 1</td>
<td>1.82</td>
</tr>
<tr>
<td>FO</td>
<td>38 ± 8</td>
<td></td>
<td>32 ± 10</td>
<td>30 ± 3</td>
<td>33.84</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>8 ± 3</td>
<td>39 ± 4</td>
<td>73 ± 8</td>
<td>4.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>1 ± 2</td>
<td>55 ± 2</td>
<td>44 ± 0.4</td>
<td>1.02</td>
<td></td>
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</tr>
<tr>
<td>L1</td>
<td>13 ± 12</td>
<td>43 ± 10</td>
<td>44 ± 1.0</td>
<td></td>
<td>2.16</td>
<td></td>
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</table>

* Percentage after normalization to sum = 100% ± standard errors for the linear coefficients.


(22) Morgan, M. F. Chemical soil diagnosis by the Universal soil testing system; Connecticut Agricultural Experiment Station Bulletin No. 459; 1941.

(23) Morgan, M. F. Chemical soil diagnosis by the Universal soil testing system; Connecticut Agricultural Experiment Station Bulletin No. 459; 1941.


(26) Morgan, M. F. Chemical soil diagnosis by the Universal soil testing system; Connecticut Agricultural Experiment Station Bulletin No. 459; 1941.


