Evidence for Struvite in Poultry Litter: Effect of Storage and Drying

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The use of spectroscopic techniques (especially phosphorus-31 nuclear magnetic resonance [^{31}P-NMR] and X-ray absorption near edge structure spectroscopy) has recently advanced the analysis of the speciation of P in poultry litter (PL) and greatly enhanced our understanding of changes in P pools in PL that receive alum (aluminum sulfate) to reduce water-soluble P and control ammonia emissions from poultry houses. Questions remain concerning changes of P species during long-term storage, drying, or after application of PL to cropland or for other uses, such as turfgrass. In this study, we investigated a set of six PL samples (of which three were alum-amended and three were unamended) that had been characterized previously. The P speciation was analyzed using solid-state ^{31}P-NMR spectroscopy, and the mineralogy was analyzed by powder X-ray diffraction (XRD) after storing the samples moist and dried for up to 5 yr under controlled conditions. The magnesium ammonium phosphate mineral struvite was identified in all but one PL samples. Struvite concentrations were generally lower in dried samples ($\leq$14%) than in samples stored moist (23 and 26%). The moist samples also had higher concentrations of phosphate bound to aluminum hydroxides. Solid-state NMR spectroscopy was in general more sensitive than XRD in detecting and quantifying P species. Although phosphate associated with calcium and aluminum made up a large proportion of P species, they were not detected by XRD.

Agricultural fields that have received animal manures to provide nutrients and improve soil quality can be nonpoint sources for nutrients in adjacent streams, lakes, and estuaries if not managed properly. Increased nutrient loads cause eutrophication and the deterioration of water quality, posing a severe threat to fresh water resources worldwide. Reducing water-soluble P in animal manures by chemical amendments such as aluminum sulfate (alum) (Arai et al., 2005; Smith et al., 2004; Staats et al., 2004), lime (Maguire et al., 2006), or iron sulfate has been suggested as a best management practice to reduce nutrient losses from fields by runoff (Moore and Miller, 1994; Moore et al., 2000; Shreve et al., 1995; Sims and Luka-McCafferty, 2002). Recent advances in characterizing animal manures have increased our understanding of the speciation or chemical form of P, which allows us greater insight into biochemical and chemical processes in animal manures and the mobility and bioavailability of P in manure-amended soils (Toor et al., 2006). Phosphorus K-edge X-ray absorption near edge structure (XANES) (Maguire et al., 2006; Peak et al., 2002; Shober et al., 2006; Toor et al., 2005a, 2005b) and solid-state phosphorus-31 nuclear magnetic resonance (^{31}P-NMR) spectroscopy (Hunger et al., 2004, 2005) have been used to characterize and quantify solid forms of P in manures, identifying them as mostly calcium phosphate phases, phosphate associated with aluminum- and iron hydroxides, and phytic acid (inositol hexakisphosphate). Solution ^{31}P-NMR spectroscopy is the technique of choice to determine organic phosphate esters and inorganic phosphate (orthophosphate, pyrophosphate, and polyphosphates) in extracts of animal wastes (for a review of the literature in this area, see Toor et al. [2006]). A standard NMR method has been developed for routine analyses (Turner, 2004) that is increasingly being used to study changes in soluble phosphate species in manures with changes in diet and during storage (Leytem et al., 2004, 2007; Maguire et al., 2004; McGrath et al., 2005; Turner and Leytem, 2004).

Poultry litter (PL) offers ideal conditions for microbial life and therefore undergoes significant changes while aging during storage for later field application or by composting for litter mass and volume reduction and biological stabilization (Dao et al., 2001; McGrath et al., 2005; Moore et al., 1995b; Sharpley and Moyer, 2000). McGrath et al. (2005) showed that storing PL for more than 1 yr at approxi-

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Abbreviations: CP-MAS, cross-polarization, magic angle spinning; DCP, dicalcium phosphate; DI, deionized; HAP, hydroxyapatite; MAS, magic angle spinning; NMR, nuclear magnetic resonance; OCP, octacalcium phosphate; PL, poultry litter; TCP, tricalcium phosphate; XANES, x-ray absorption near edge structure; XRD, X-ray diffraction.

Table 1. Selected properties of the poultry litter samples used for X-ray diffraction and 31-phosphorus nuclear magnetic resonance spectroscopy.

Sample†	Initial moisture content‡	pH§ (fresh)	Total	Water soluble	Total Al	pH§ (after storage)
	%			—— g kg^{-1} ——		
PL 125	31.5	7.23	19.7	0.32	17.7	5.81¶
PL 134	34.5	7.37	23.2	0.78	10.9	6.04¶
						7.33#
PL 191	20.3	6.89	19.1	0.54	21.6	5.48¶
PL 502	21.3	7.82	19.4	1.64	0.7	6.56¶
PL 541	32.8	8.23	19.6	1.31	1.0	7.18¶
PL 559	28.7	8.21	20.8	1.57	1.0	6.88¶
						7.92#

Column header note: Concentrations§ / P (Total, Water soluble), Total Al

† Samples PL 125, 134, and 191 were alum amended; PL 502, 541, and 559 were unamended. Samples were homogenized and ground to pass a 0.8-mm screen and analyzed by inductively coupled plasma–optical emission spectroscopy for water-soluble P after extraction with deionized water (1:10 litter to water ratio) and for total P and Al concentrations after digestion with HNO_3/H_2O_2. Subsamples were dried at 65°C and stored up to 66 mo at room temperature in the dark. Moist samples were stored up to 63 mo at 4°C in the dark.

‡ Expressed on a dry-weight basis.

§ Determined as a suspension in deionized water (1:4 litter to water ratio).

¶ Sample was stored dried.

\# Sample was stored moist.

mately 40% moisture increased the proportion of water-soluble inorganic P at the expense of organic phosphate esters, such as phytic acid. Storage closer to the initial moisture content (approximately 20%) resulted in less hydrolysis of organic phosphate, a higher proportion of phytic acid, and some assimilation of inorganic P. Information on the mineral phases in PL was not reported by McGrath et al. (2005). Shand et al. (2005) studied the P speciation and solubility in sheep feces after application to the field using solution and solid-state ^{31}P-NMR spectroscopy and powder X-ray diffraction. They observed that the mineral phases struvite ($MgNH_4PO_4 \cdot 6H_2O$) and brushite ($CaHPO_4 \cdot 2H_2O$), which were the only identifiable solid phosphate phases, were removed over the study period of 84 d by dissolution or assimilation; changes in the organic phosphate species as determined by solution ^{31}P-NMR spectroscopy were not consistent.

Spectroscopic techniques are routinely used to study P speciation in animal manures in general and PL in particular (Hunger et al., 2004; Peak et al., 2002; Shober et al., 2006; Toor et al., 2005b; Toor et al., 2006); however, the changes in P speciation over time under different storage conditions (McGrath et al., 2005) or in the field (Shand et al., 2005) remain largely unexplored. In this research we investigated changes in solid P species occurring in dried samples of alum-amended and unamended PL during storage over 5 yr at room temperature and at 4°C. We also discuss the more general differences in P-speciation between samples that had been stored dry at room temperature and moist at 4°C. A combination of powder X-ray diffraction (XRD) and solid-state ^{31}P-NMR spectroscopy was used to identify crystalline phases and quantify P-species, respectively. Using XRD for the investigation of crystalline phases in PL is a rather novel approach that enabled us to unambiguously identify a previously unconsidered phosphate phase, struvite.

Materials and Methods

Poultry Litter Samples

Samples of PL were obtained from an on-farm evaluation of the effectiveness of alum as an amendment for PL. The details of this study have been reported elsewhere (Sims and Luka-McCafferty, 2002). In brief, 194 poultry houses were chosen, of which 97 received alum (100 series of samples) and 97 served as a control group (500 series of samples). The alum was applied and incorporated at an average rate of 90 g alum per bird shortly after the previous flock and the upper crust of litter had been removed (approximately every 5–6 wk). Samples were collected from the entire depth of the litter layer after removal of the last flock in the study (May 2000) and then homogenized. Upon arrival at the University of Delaware, the litter samples were split into two batches. One set of samples was stored at initial moisture content at constant 4°C in the dark in closed containers for 63 and 64 mo after sampling and allowed to dry at room temperature the day before NMR and XRD analysis. A second set of samples was dried immediately on arrival at 65°C, ground to pass a 0.8-mm screen and stored in airtight sample bags at room temperature. Using thermal analysis, Hunger et al. (2004) demonstrated that the dried PL samples had a residual water content of approximately 10%.

A first set of NMR spectra was recorded in January 2002 after 20 mo of storage of the dried subset of these samples, and the reminder was stored in the dark at room temperature in sealed containers. The second set of NMR experiments was conducted in 2005 after a total of 63 to 66 mo of storage. For comparison, one set of NMR spectra was recorded of the PL samples that had been kept at initial water content after 63 to 64 mo of storage. Before NMR or XRD analysis, samples were ground again using mortar and pestle to break up clumps that had formed during storage. The pH of the fresh and aged samples was determined in deionized (DI) water (1: 4 w/v) using a combination glass electrode. Water-soluble and total P, total Al concentrations, and moisture content of the fresh samples and pH values of the fresh and aged samples are given in Table 1.

Struvite Synthesis

All reagents were analytical grade; DI water with a resistivity of ≥18 MΩ was used to prepare reagent solutions. Struvite was synthesized by titrating an equimolar solution of $MgCl_2 \cdot 6H_2O$ and KH_2PO_4 (pH 3.6) to pH 9 with 1.0 mol dm^{-3} NH_4OH (Nelson et al., 2003). The precipitate was stirred over night, filtered, washed with DI water and acetone, and allowed to dry at room temperature in air. The colorless solid was confirmed to be struvite by powder XRD. Preliminary experiments had shown that struvite loses water by crystallization on drying in the oven to yield a mixture of struvite and dittmarite, a fact that has also been reported by Sarkar (1991).

Powder X-ray Diffraction

X-ray powder diffraction was performed on a Philips (Eindhoven, The Netherlands) PW 1050 Goniometer with a Philips PW 1730 generator using Cu K$_\alpha$ radiation. Samples were mounted in aluminum holders by pressing into the aperture of

the holders to achieve a flat surface and scanned over a 2θ range from 5 to 70° in 0.01° increments. The software TRACES (Diffraction Technology, Canberra, Australia) was used to analyze the data. Individual scans were calibrated to the quartz (111) peak, and phases were consecutively identified by comparison with powder diffraction files from the ICDD PDF2 (International Centre for Diffraction Data Powder Diffraction Files) database.

Solid-State ^{31}P-NMR Spectroscopy

Solid-state ^{31}P-NMR spectra were recorded on a Chemagnetics CMX Infinity spectrometer (Varian Inc., Palo Alto, CA) with an Oxford 300-MHz wide-bore magnet operating at a magnetic field of 7.04 Tesla, corresponding to resonance frequencies of 121.4 MHz for ^{31}P and 299.9 MHz for [1]H. To afford uniform distribution and homogeneous spinning of the rotor in the magic angle spinning (MAS) probe, dried and ground samples were used. Spinning speeds were maintained constant at values from 5 to 10 kHz ± 5 Hz. The spinning speed mostly depended on the rotor diameter and was limited to 6 kHz for the 6 mm pencil rotors used at University of Leeds.

Cross-polarization, magic angle spinning (CP-MAS) experiments used a proton π/2-pulse of 3.5 μs in 2002 (EMSL, Richland, WA) and of 4.0 μs in 2005 (University of Leeds, UK), a contact time of 1.3 ms, and a pulse delay of 2 s. Depending on the P concentration, 2000 to 8000 scans were accumulated to give a signal-to-noise ratio of at least 30:1 for the most intense peak. Single-pulse, proton-decoupled spectra were recorded using a [31]P π/2-pulse of 3.7 μs in 2002 and 4.0 μs in 2005 and a relaxation delay of 60 s. For these experiments, a minimum of 256 scans was accumulated. Experimental parameters were optimized for both locations to achieve the best signal-to-noise ratio and to ascertain that any differences observed in the spectra were not instrumental artifacts.

The spectra were processed and analyzed using the NUTS NMR utility transform software by Acorn NMR (2000). A line broadening of 50 to 100 Hz was applied before Fourier transformation and phase correction. Isotropic chemical shifts are reported in ppm relative to the signal of 85% H_3PO_4 as an external reference; positive values correspond to low-field or high-frequency shifts.

Peaks of P species in close proximity to protons as a protonated phosphate group, a phosphate group receiving a hydrogen bond, or in a crystalline species with protons on fixed crystallographic positions, are selectively enhanced in CP-MAS spectra (Hartmann and Hahn, 1962; Pines et al., 1973). Only single-pulse spectra are therefore quantitative and are used to determine the relative proportions of P species. Cross-polarization, magic angle spinning spectra were used to help in the identification of P species.

The single-pulse spectra were deconvoluted using a minimal set of peaks as described by Hunger et al. (2004). The Lorentzian/ Gaussian ratio was fixed at a value of 1 (Lorentzian peak) for the relatively sharp peaks at δ = 3.0 and 6.5 ppm and allowed to float for all other peaks. No further constraints were used. Chemical shifts of the fitted peaks are accurate within ±0.1 ppm. An error margin of ±5% of the combined signal intensity of all signals was assumed for the peak areas of the deconvoluted peaks. Spinning
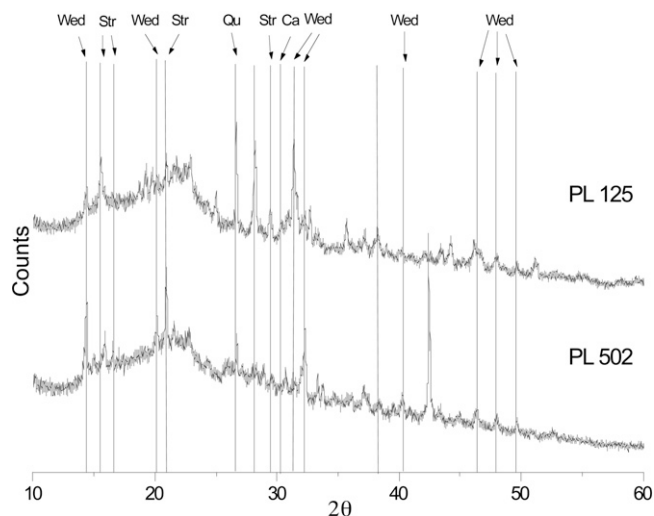

Fig. 1. X-ray diffraction patterns of the dried and powdered poultry litter (PL) samples PL 125 and PL 502 after 4 yr of storage. PL 125 was alum amended, and PL 502 was unamended. Identified phases: Wed, wedellite ($CaC_2O_4 \cdot 2H_2O$); Str, struvite ($NH_4MgPO_4 \cdot 6H_2O$); Qu, quartz; Ca, calcite.

side bands were not observed at spinning speeds ≥7 kHz. In the spectra of the samples spinning more slowly, spinning side bands were fitted separately, and their intensity was added in proportion to that of the one or two broad peaks that were observed. Preliminary experiments with mineral standards and careful analysis of the positions of the spinning side bands have shown that they are caused by the broad resonances.

Results and Discussion
Crystalline Phases Detected by Powder XRD

We did not attempt to assign every peak observed in the XRD traces of the dried PL samples 125, 134, 502, and 559 (Fig. 1 and 2) because we were primarily interested in the phosphate
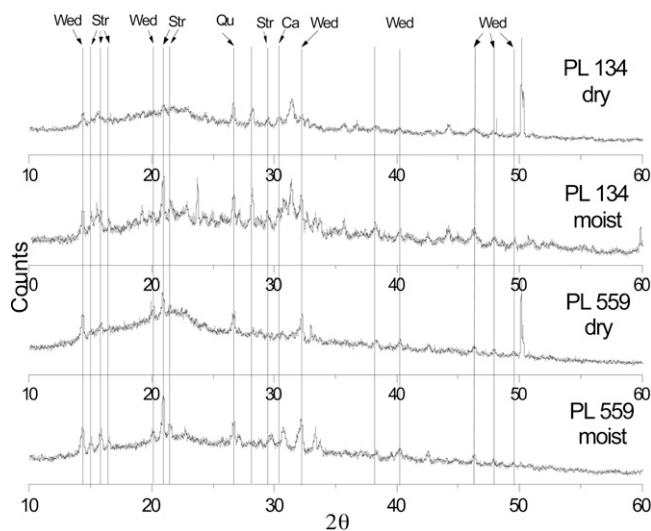

Fig. 2. Comparison of the X-ray diffraction patterns of poultry litter (PL) stored moist and dried for 64 mo. PL 134 was alum amended, and PL 559 was unamended. Identified phases: Wed, wedellite ($CaC_2O_4 \cdot 2H_2O$); Str, struvite ($NH_4MgPO_4 \cdot 6H_2O$); Qu, quartz; Ca, calcite.

Table 2. Fitting results of the single-pulse 31-phosphorus magic angle spinning nuclear magnetic resonance spectra.

		Jan. 2002			Sept. 2005		
	Peak†	Chem. shift‡	Peak width§	Proportion¶	Chem. shift‡	Peak width§	Proportion¶
		ppm	Hz	%	ppm	Hz	%
PL125	1	6.44	356	10.7	6.45	219	9.2
	2	2.98	302	5.3	3.06	242	6.7
	3	−0.68	1517	58.7	2.07	1273	31.5
	4	−10.53	1726	25.3	−6.43	2121	52.6
PL134	1	6.47	213	5.8	6.38	243	9.6
	2	3.09	235	4.0	3.08	243	5.4
	3	1.35	1378	62.9	1.63	1169	46.0
	4	−7.73	1891	27.4	−7.60	1783	39.1
PL191	1	–	–	–	6.40	208	12.4
	2	2.79	346	12.8	3.00	223	2.3
	3	0.79	1080	40.8	1.38	1467	40.5
	4	−7.19	1780	46.5	−8.36	1749	44.8
PL502	1	6.51	191	13.5	6.41	185	11.8
	2	2.80	207	8.1	2.98	163	3.1
	3	1.20	1348	78.4	2.2	1312	85.1
PL541	2	2.98	407	18.0	2.95	301	9.4
	3	−0.11	1209	82.0	1.37	1174	90.6
PL559	1	6.44	230	11.1	6.46	241	13.8
	2	2.97	252	7.3	3.05	289	4.5
	3	1.49	1311	81.3	1.68	1347	81.7
PL134 moist	1	n.a.#	n.a.	n.a.	6.40	830	26.2
	2	n.a.	n.a.	n.a.	3.15	334	10.2
	5	n.a.	n.a.	n.a.	0.46	357	8.7
	4	n.a.	n.a.	n.a.	−4.60	1981	54.8
PL559 moist	1	n.a.	n.a.	n.a.	6.40	329	22.8
	2	n.a.	n.a.	n.a.	3.38	344	10.1
	5	n.a.	n.a.	n.a.	0.76	468	13.2
	3	n.a.	n.a.	n.a.	4.45	1438	53.9

† Identified peaks: struvite (6.5 ± 0.1 ppm, peak 1), calcium phosphate (2.9 ± 0.1 ppm, peak 2), unresolved organic and inorganic phosphate (peak 3), phosphate sorbed to aluminum hydroxide (−5 to −10 ppm, peak 4), and amorphous magnesium phosphate (0.5 ± 0.1 ppm, peak 5).

‡ ±0.1 ppm.

§ Full width at half height.

¶ ±5%.

n.a., not available.

mineralogy of PL and those mineral phases that are known to influence P speciation in manures. In addition to excreta and bedding (sawdust), the various samples possibly contain clay minerals (scraped from the floor of the chicken houses) and simple salts containing potassium, ammonium, chloride, sulfate, etc.

Several major phases emerge: Quartz is identified and used to calibrate the traces of all samples. Slight shifts in observed values for 2θ are due to particle size heterogeneity, which caused an uneven loading of the sample holder and displacement of the sample surface from the focal plane. The quartz calibration corrected for most of these shifts, but they nevertheless introduce some uncertainty to the identification of mineral phases. A weak reflection attributable to calcite can be detected in the traces of samples 125 and 134. Calcium carbonate is an important part of the chickens' diet and finds its way into the litter directly from the feeding trough or indirectly through the chickens' digestive system. This fact is reflected in the high Ca content generally reported for PL (Hunger et al., 2005; Jackson et al., 2003; Moore et al., 1995b; Sato et al., 2005).

The two phases most clearly identified in all PL samples analyzed by XRD are the minerals struvite ($NH_4MgPO_4 \cdot 6H_2O$) and wedellite ($CaC_2O_4 \cdot 2H_2O$), of which a series of reflections can be observed (Fig. 1 and 2). Struvite has only recently been identified by powder XRD and solid-state ^{31}P-NMR spectroscopy in sheep manure (Shand et al., 2005) or by XRD and P XANES spectroscopy in dairy manure (Güngör et al., 2007) but not, to our knowledge, in PL (see below). Its formation should not come as a surprise, however, considering the elevated concentrations of phosphate, magnesium, and ammonium in PL.

Two reflections at 28° and 38° 2θ, which are only present in the alum-amended PL samples 125 and 134, might be assigned to the boehmite reflections (120) and (031), respectively. However, the strong (020) diffraction peak at 14.5° 2θ, which is characteristic for boehmite, could not be observed together with these peaks. A peak is observed at approximately 14° 2θ, but it is strongest in the unamended PL samples 502 and 559, and its intensity seems to be correlated with the intensity of the series of peaks assigned to wedellite. The presence of crystalline boehmite can therefore be ruled out. The formation of aluminum hydroxide phases has been predicted for alum-amended PL and indirectly confirmed via the identification of sorbed phosphate species (Hunger et al., 2004; Peak et al., 2002). The XRD data indicate that the aluminum hydroxide formed in alum-amended PL is amorphous. Crystalline aluminum hydroxide phases were also not observed in biosolids amended with alum and incubated for 4 mo (Huang and Shenker, 2004).

Besides these major phases, crystalline calcium, iron, or aluminum phosphates are conspicuously absent. Two strong reflections at 28° and 31° 2θ, which are present in all samples, could be assigned to the whitlockite (β-TCP) diffraction peaks (214) and (2010). Besides these two peaks, no further whitlockite peaks, especially the strong (220) reflection, could be observed, and the presence of this phase is therefore uncertain. Shand et al. (2005), on the other hand, identified struvite and brushite (dicalcium phosphate) in sheep feces in the field by powder XRD. Extensive spectroscopic evidence (solid-state ^{31}P-NMR and P K-edge XANES spectroscopy) exists for dicalcium phosphate (DCP; $CaHPO_4$) (Peak et al., 2002; Sato et al., 2005) and tricalcium phosphate (TCP; $Ca_3(PO_4)_2$) in PL (Hunger et al., 2004; Sato et al., 2005; Shober et al., 2006) and for DCP and hydroxylapatite (HAP; $Ca_5(PO_4)_3(OH)$) in turkey litter (Toor et al., 2005b) and PL (Maguire et al., 2006; Shober et al., 2006), but if these phases were present in the litters used in our study, they were of insufficient crystallinity and/or particle size to be detected.

Phosphorus Species Detected by Solid-State ^{31}P-NMR Spectroscopy

Up to three sharp peaks can be distinguished in the single-pulse MAS NMR spectra as individual peaks or as shoulders, but usually only one or two are present. The sharp peak at 6.5 ± 0.1 ppm (Peak 1 in Table 2) is present in the spectra of most alum-amended and unamended samples (Fig. 3–6) and is absent only in sample PL 541 (Table 2). This peak is selectively enhanced by cross-polarization and was originally interpreted as hydrogen phosphate
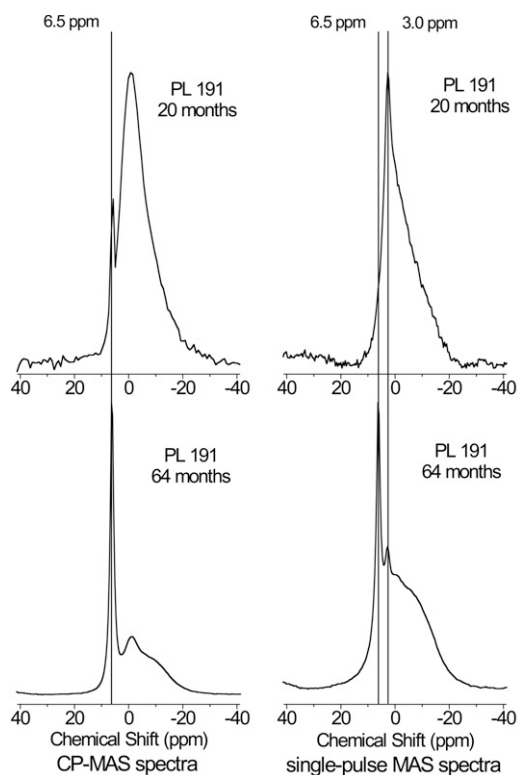
Fig. 3. Comparison of the single-pulse and cross-polarization, magic angle spinning (CP-MAS) solid-state 31-phosphorus nuclear magnetic resonance spectra of sample PL 191 (alum amended). The sample was dried at 65°C and stored in the dark at room temperature for 20 and 64 mo. Identified species: struvite (6.5 ppm), calcium phosphate (3.0 ppm) (see Table 2).

Fig. 4. Comparison of the single-pulse and cross-polarization, magic angle spinning (CP-MAS) solid-state 31-phosphorus nuclear magnetic resonance spectra of sample PL 502 (unamended). The sample was dried at 65°C and stored in the dark at room temperature for 20 and 64 mo. Identified species: struvite (6.5 ppm), calcium phosphate (3.0 ppm) (see Table 2).

anions surrounded by water molecules in the organic matrix of the litter material (Hunger et al., 2004). Only circumstantial evidence existed for this interpretation, most importantly the chemical shift similar to that of hydrogen phosphate in solution and the selective signal enhancement by CP-MAS. None of the phosphate phases considered in the earlier interpretation had similar spectral characteristics. However, positive identification is only possible by direct comparison with spectra of standard compounds or published chemical shift values. The selection of standards is therefore crucial to the interpretation of NMR spectra. We identified the phosphate phase struvite ($NH_4MgPO_4\cdot6H_2O$) in these PL samples using XRD. The published chemical shift (Bak et al., 2000) and the chemical shift of the synthetic compound confirm the assignment of the peak at 6.5 ± 0.1 ppm to struvite. At concentrations of 6 to 13% in dried litter and up to 26% in moist litter (Table 2), struvite clearly is an important component of PL.

In addition to struvite, a comparatively sharp peak at 2.9 ± 0.1 ppm (Peak 2 in Table 2) has been assigned to a calcium phosphate phase (Hunger et al., 2004) (Fig. 3–6). An unambiguous identification is not possible because this chemical shift is shared by HAP and TCP (Elliott, 1994; Rothwell et al., 1980) and phosphate sorbed to the calcium carbonate surface (Hinedi et al., 1992). Both TCP and HAP have been identified in PL by XANES spectroscopy (Maguire et al., 2006; Shober et al., 2006). Because neither crystalline HAP nor TCP was identified in the XRD traces of the samples but calcite was recognized as a com-
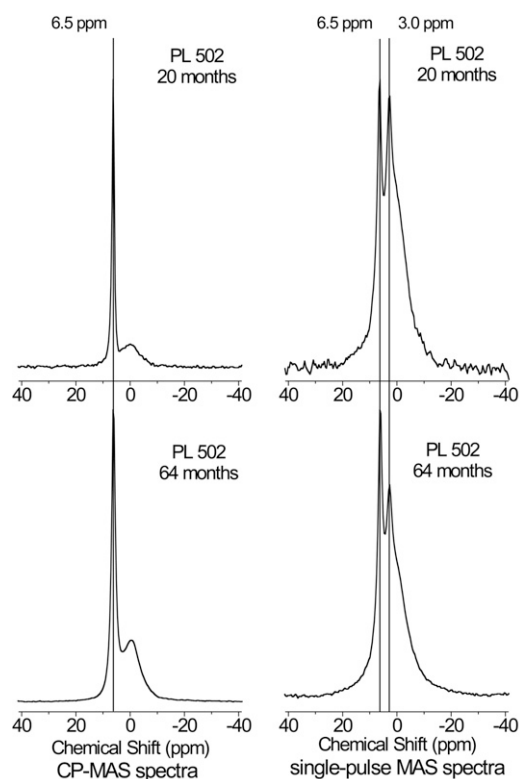
ponent, the assignment to phosphate sorbed to the calcite surface (as surface complexes or nanoparticles of TCP or HAP) seems to be the most likely. In the spectra of the moist samples, this peak is shifted to slightly higher values. This is indicative of the formation of octacalcium phosphate (OCP) (or a surface precipitate of OCP at the calcite surface), which exhibits a chemical shift of 3.4 ppm (Elliott, 1994; Rothwell et al., 1980). Because the peak of the calcium phosphate phase is broader in the moist samples than in the dried samples, the most probable species is a combination of TCP and OCP or HAP and OCP.

The moist samples PL 134 and 559 have an additional narrow peak at 0.46 ± 0.1 and 0.76 ± 0.1 ppm, respectively (Fig. 5 and 6; peak 5 in Table 2). A chemical shift of 0.5 ppm has been reported for amorphous $Mg_3(PO_4)_2$ (Aramendía et al., 1998a,b), which is a likely candidate in this magnesium-rich system. The fact that this peak is as narrow as the peaks of calcium phosphate and struvite suggests that this resonance is due to a specific chemical species rather than the unresolved phosphate species usually observed in this chemical shift range (see below). Besides the amorphous $Mg_3(PO_4)_2$, these samples contain 26 and 23% of poorly crystalline struvite, respectively, indicated by the broad resonance peaks at 6.5 ± 0.1 ppm. Phosphorus-speciation in the moist samples is therefore dominated by magnesium phosphate phases, which are discussed in more detail below.

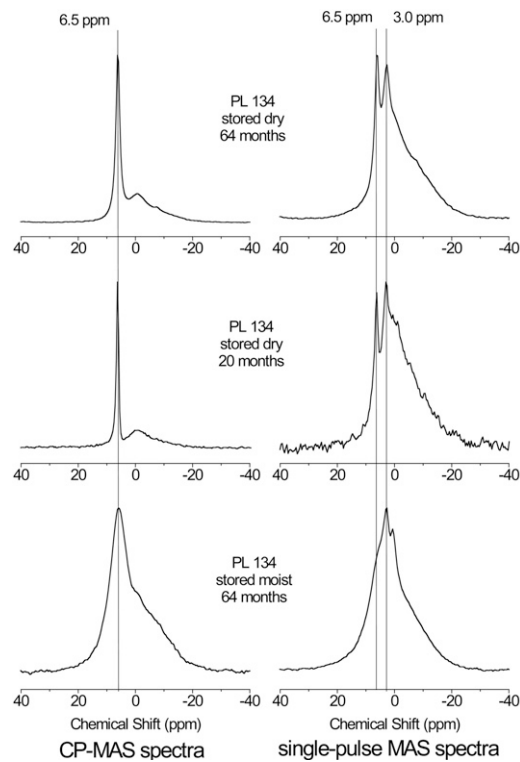Using [31]P{[27]Al} TRAPDOR (TRAnsfer of Polarization during DOuble Resonance), Hunger et al. (2004) showed that

Fig. 5. Comparison of the single-pulse and cross-polarization, magic angle spinning (CP-MAS) 31-phosphorus nuclear magnetic resonance spectra of sample PL 134 (alum-amended). The sample was stored dried (65°C) for 20 and 63 mo at room temperature in the dark and moist at 4°C in the dark for 63 mo before analysis. Identified species: struvite (6.5 ppm), calcium phosphate (3.0 ppm) (see Table 2).

Fig. 6. Comparison of the single-pulse and cross-polarization, magic angle spinning (CP-MAS) 31-phosphorus nuclear magnetic resonance spectra of sample PL 559 (unamended). The sample was stored dried (65°C) for 20 and 66 mo at room temperature in the dark and moist at 4°C in the dark for 64 mo before analysis. Identified species: struvite (6.5 ppm), calcium phosphate (3.0 ppm) (see Table 2).

40 ± 14% of phosphate in alum-amended PL samples was associated with aluminum hydroxide phases. These phases appear as broad peaks centered between −4 and −10 ppm (Peak 4 in Table 2), often tailing to more negative chemical shift values. Possible structures are mononuclear and binuclear inner-sphere surface complexes of phosphate on poorly crystalline aluminum hydroxide or on boehmite (Bleam et al., 1991). A poorly ordered, uncondensed aluminum phosphate polymer with a structure similar to that of wavellite ($Al_3(OH)_3(PO_4)_2 \cdot 5H_2O$, −11 ppm) (Bleam et al., 1989; Hunger et al., 2004) is also likely to form. No crystalline aluminum phosphate phases have been detected in PL by XRD.

A significant proportion of the ^{31}P-NMR signal cannot be assigned to individual chemical species, between 30 and 60% in alum-amended PL samples and up to 90% in the unamended samples (Peak 3 in Table 2). However, this signal can be fitted with one broad peak of predominantly Gaussian line-shape centered between −1 and 2 ppm in most samples and 4.4 ppm in the moist, unamended sample (Table 2). The Gaussian line-shape is an indication of a range of similar chemical environments and therefore chemical shifts. All P species that have no unique chemical environment are included in this peak, such as inorganic phosphate complexed by various metal cations and organic phosphates such as nucleic acids, phospholipids, and phytic acid, which is an important component of PL (Taylor, 1965). These organic phosphate
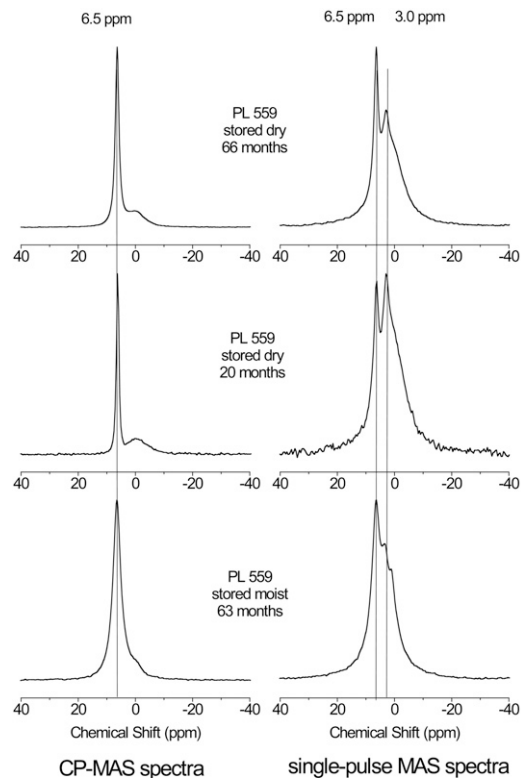
compounds are easily detected in alkaline extracts of soils (Turner and McKelvie, 2002; Turner et al., 2003a, 2003b) and dairy manures (Toor et al., 2005a) using solution ^{31}P-NMR spectroscopy but give only uncharacteristic, broad resonances in the solid state because of the random orientation of the molecules in a matrix, limiting their mobility (Hunger et al., 2004). This results in a range of peaks with slightly different chemical shift values, which overlap to give the observed broad resonance.

Organic and unspecific bound inorganic phosphate species are difficult to detect in the solid state using P K-edge XANES spectroscopy (Peak et al., 2002) due to the similarity of their XANES features. This group of P species is therefore usually fitted as aqueous P and phytic acid (Peak et al., 2002; Shober et al., 2006; Toor et al., 2005b).

Changes Observed during Drying and Storage

The pH of the dried samples decreased by at least one unit during storage, whereas the pH of the two samples stored moist remained approximately constant. Aging of the dried PL samples caused significant changes in P speciation in some samples, whereas others were relatively unchanged. Storing the alum-amended samples PL 125 and 134 increased the relative proportion of aluminum hydroxide–bound phosphate, indicating a further stabilization of phosphate in the amended litter with time. However, the same fraction was constant within the error range of ±5% in

PL 191. It is therefore not possible to generally conclude that storing dried alum-amended litter further reduces the proportion of soluble phosphate. In samples PL 125 and 134, the increase of the aluminum hydroxide–bound fraction was concomitant with a decrease in the unresolved fraction of organic and inorganic phosphate species. Struvite shows the biggest variation in the alum-amended samples: The struvite content remains constant in sample PL125, whereas it increases in samples PL134 and PL191.

In the unamended samples, the struvite content remains approximately constant, whereas the proportion of calcium phosphate decreases and the unresolved fraction increases. Organic phosphate compounds and inorganic orthophosphate are readily bioavailable and subject to biotic reactions. This can be seen most clearly in the change of the chemical shift of this fraction to more positive values for all litter samples: Organic phosphate species have in general positive chemical shifts in solution, with phosphate monoesters (4–5 ppm) exhibiting higher shifts than phosphate diesters (0–1 ppm) (Turner et al., 2003a). The change in chemical shift might be indicative of biotic or abiotic hydrolysis of phosphate diesters to monoesters. It is not possible to draw more detailed conclusions for the potential chemical and biochemical reactions in PL over time from solid-state ^{31}P-NMR spectra alone. Using solution ^{31}P-NMR spectroscopy, McGrath et al. (2005) showed increased hydrolysis of phosphate esters during storage of moist PL (approximately 40% moisture) but some assimilation (formation of organic phosphate esters) during the storage of PL closer to the initial moisture of approximately 20%.

Because solid-state ^{31}P-NMR spectra of the initial moist samples were not recorded, effects of drying on the P chemistry of PL cannot be deduced from this data set. Furthermore, all samples were dried before analysis: The "dry" samples were dried at elevated temperatures and stored for up to 5 yr, whereas the samples stored "moist" were dried at room temperature immediately before analysis. The most drastic changes in P chemistry likely occurred during the initial drying process at 65°C.

Keeping this in mind, this data set allows for some degree of generalization. Major differences between samples stored moist and dry can be seen in the ^{31}P-NMR spectra and to some extent in the XRD patterns. The struvite content is higher in the moist samples than in the dried samples (Table 2 and Fig. 2). The line-width of the struvite NMR resonance is higher in the moist sample (Table 2), which is indicative of poorer crystallinity. The XRD pattern of struvite shows no broadening attributable to poor crystallinity (Fig. 2). Both moist samples exhibit a narrow NMR peak that was identified as amorphous magnesium phosphate (Fig. 5 and 6, Table 2), which is not observed in the dried samples. By comparing the proportions of struvite and amorphous magnesium phosphate of the moist samples with that of the dried samples, it can be seen that those phases are better preserved in the moist samples. The lower concentration of struvite in the dried samples in combination with the lower pH after 5 yr of storage suggests that the samples probably lost ammonia during drying. Ammonia volatilization releases protons, lowering the pH of the PL (Eq. [1]). Most likely, the bulk of the ammonia volatilization occurred during the initial drying at 65°C by forcing Eq. [1] to the right.

$$NH_4^+ \overset{\Delta T}{\leftrightarrow} NH_3(g) + H^+ \qquad [1]$$

It has been shown that amending PL with alum reduces ammonia volatilization during storage (Moore et al., 1995a, 1995b, 2000). The hydrolysis of alum releases protons (Eq. [2]), which subsequently force Eq. [1] to the left.

$$Al_2(SO_4)_3 \cdot 14H_2O + 6H_2O \rightarrow 2Al(OH)_3 \\ + 3SO_4^{2-} + 6H^+ + 14H_2O \qquad [2]$$
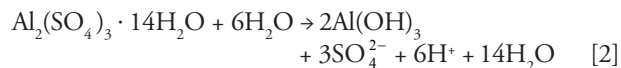
The pH value of the alum-amended PL sample stored moist remained constant, and that of the unamended sample stored moist decreased by 0.3 units. The fact that the pH value of all dried samples had decreased by at least one unit after drying and storage demonstrates that drying PL causes ammonia loss regardless of alum amendments. The observed drop in pH could have also been caused by nitrification because biological activity was not suppressed during storage of the litter. However, the PL samples were not analyzed for NH_3–N or NO_3–N, and any conclusions as to the nitrogen chemistry in dried and/or stored PL are speculative. The observed changes in the solid-state NMR spectra and of the pH values are indicative of some loss of ammonia from the struvite pool that might be coupled with ammonia volatilization or other chemical or biological pathways that fix ammonia in a less soluble form.

The ^{31}P-NMR spectra also indicate better preservation of the calcium phosphate phase in the moist samples (Peak 2 in Table 2, approximately 10% vs. approximately 5% in the dried samples). The peak of the calcium phosphate phase detected in moist PL is wider than that in the dried samples (>300 Hz compared with 200–300 Hz for moist and dried samples, respectively), which suggests a mixture of OCT (3.4 ppm) and TCP (3.0 ppm). Tricalcium phosphate seems to be favored as the thermodynamically stable phase in the dried samples.

Conclusions

Struvite has, to our knowledge, not previously been identified in PL. It was detected by solid-state ^{31}P-NMR but not identified correctly in 10 out of 11 PL samples by Hunger et al. (2004), and it was identified in sheep manure. It has been suggested that concentrations of ammonium and phosphate in anaerobic swine lagoon effluent can be decreased by precipitation and removal of struvite or magnesium phosphate. Struvite seems to play an important role in the speciation of P in animal wastes but has previously not been considered in the spectroscopic analysis of PL. This clearly shows that the selection of standards is crucial for the analysis and quantification of ^{31}P-NMR and P K-edge XANES spectra and that overlooking a likely phase in the analysis can bias the interpretation of the data.

Our finding that struvite and other sparingly soluble forms of P, such as calcium phosphate (TCP or HAP) or phosphate bound to aluminum hydroxide, form during storage of PL under moist or dry conditions is relevant to the environmentally sound management of PL as a nutrient source. We suggest that opportunities to process and store PL in a manner that enhances struvite formation

will increase its fertilizer value and reduce the risk of nonpoint P pollution of ground and surface waters. For example, although the oven-drying method used in our study is more extreme than the drying that occurs under on-farm conditions, new technologies are being adopted that will process PL into drier, value-added fertilizers that may be stored for longer periods before use. One example is a pelletization and granulation plant operating in Delaware that processes about 60,000 Mg yr^{-1} of PL for use in agronomic and horticultural settings. Temperatures from 80 to 110°C are reached during the production of these pellets and granules.

Temperatures similar to those used for oven-drying the PL samples analyzed by solid-state NMR are easily reached during composting. Poultry litter is usually composted to assimilate soluble forms of N, reduce moisture content and litter volume and mass, and kill pathogens. Although the moisture content of finished compost is greatly reduced compared with the initial moisture content, the compost is by no means oven-dry and can be reasonably similar to the "moist" PL samples used in our study. However, the above-mentioned chemical reactions induced by elevated temperatures, such as ammonia volatilization or crystallization of struvite and calcium phosphate phases, can be expected.

In summary, our research shows the practical value of using advanced analytical methods to provide a detailed knowledge of the actual P species present in animal manures and other biosolids. Although more research on the factors affecting struvite formation in PL is needed, it is clear that the presence of struvite in PL pellets or composts will improve their quality as fertilizer because struvite is considered a slow-release fertilizer. The conversion of soluble forms of P in PL to struvite also reduces the potential for dissolved P loss by runoff when PL is surface applied, as occurs in no-tillage agriculture, and when PL is used as a turf grass fertilizer. From an economic perspective, pelletized or composted PL is drier and lower in mass and volume, facilitating handling and transport to areas with a higher fertilizer demand, including nonfarming applications such as athletic fields, turf, and urban or suburban gardens. Together, these factors suggest that technologies to enhance struvite formation in PL should be pursued in the future.

Acknowledgments

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