

Annual Report to the Delaware Water Resources Center

**Mechanisms of Phosphorus Stabilization in the Soil Environment:
A Molecular Scale Evaluation**

Investigators: Donald L. Sparks and Stefan Hunger
Department of Plant and Soil Sciences
University of Delaware

Background and Justification

Eutrophication has been recognized as a major threat to water resources worldwide. Nutrient enrichment causes increased growth of undesirable algae and aquatic weeds and the decomposition of the dead biomass decreases the oxygen content, severely threatening the aquatic ecosystem. Although it is in general a naturally occurring aging process of surface water, eutrophication can be accelerated by the input of nutrients from wastewater or - more important in rural areas - from agriculture (Sharpley et al., 1999). Of the more abundant nutrients (nitrogen, carbon and phosphorus), phosphorus is considered to be the limiting nutrient for eutrophication to occur in fresh water.

Modern agriculture requires the application of fertilizers to ensure production. Quite often the unavailability of information about the nutrient status of the soil and the bioavailability of the nutrients present leads to application of fertilizers in excess of the crop requirements. Manure and litter material from animal production are often used to supply nutrients and improve soil quality. Since manure contains variable amounts of nutrients, an application practice that provides the required amount of one nutrient might provide an excess of another. This is especially a problem with poultry litter, which has a high P:N ratio due to the P-rich diet of the poultry.

In Delaware, confined animal operations result in large amounts of animal wastes every year that are applied to sandy soils with high ground water tables. The poultry industry alone raised 248 million chickens in 2000, valued at \$497 million. As a byproduct, more poultry litter (PL), that is rich in P, was produced than could be safely applied to the soils, which are already high in P. One of the approaches for reducing phosphorus contamination of waters resulting from application of manure and PL is the use of chemical amendments such as aluminum, calcium or iron salts. These have been shown to reduce the levels of water extractable phosphorus in PL (Moore and Miller, 1994; Shreve et al., 1995). Calcium hydroxide/oxide, iron sulfates and alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$) were all found effective in reducing water-soluble phosphorus in PL (Moore and Miller, 1994). However, the use of iron salts was not recommended due to adverse effects on broiler health and the use of calcium bases was discouraged due to their high pH, which causes ammonia volatilization. Ammonia is harmful to broilers and workers and its volatilization increases the P:N ratio in the litter. However, the long-term effect of chemical amendments on phosphorus stability, release and speciation and on aluminum toxicity and availability when alum is used are poorly understood.

The mobility and bioavailability of P in the soil environment and related systems such as manure and poultry litter are determined by its speciation. P speciation is controlled by surface reactions with calcium and magnesium minerals in neutral to basic soils; with aluminum and iron minerals in more acid soils; and with soil organic matter (SOM). In most soils, surface reactions predominantly occur on aluminum and iron hydroxide coatings on mineral grains. Even in more basic soils, the importance of aluminum and iron hydroxide coatings on other soil minerals in controlling phosphate speciation has been recognized (Hamad et al., 1992).

Two basic P-sorption reactions are distinguished with Al and Fe oxides and hydroxides, which differ in the time scale over which they take place and the stability of products formed. The initial adsorption appears to be a fast ligand exchange of surface hydroxyl groups with phosphate and the formation of inner-sphere surface complexes. Spectroscopic evidence for these complexes has been presented by various researchers (Laiti et al., 1996, 1998; Nanzyo, 1984, 1986; Nanzyo and Watanabe, 1982; Parfitt et al., 1975; Persson et al., 1996; Tejedor-Tejedor and Anderson, 1990; Tejedor-Tejedor and Anderson, 1986).

Less information is available on the slower P-sorption reaction, which can continue over months. Two mechanisms have been suggested for this reaction. One proposed mechanism involves slow diffusion of phosphate into micropores or through a metal phosphate coating (van Riemsdijk et al., 1984; van Riemsdijk and Haan, 1981; van Riemsdijk and Lyklema, 1980) and subsequent adsorption to internal surfaces. The slow weathering of the surface in the presence of phosphate and the formation of a surface precipitate of metal phosphate has been proposed as another possible mechanism. Both mechanisms explain the increasing irreversibility of phosphate sorption with time. Spectroscopic evidence (Bleam et al., 1991; Laiti et al., 1996, 1998; Lookman et al., 1996; Lookman et al., 1997; Lookman et al., 1994) as well as evidence from potentiometric titrations (Li and Stanforth, 2000) exist in favor of the surface precipitate hypothesis. A very recent study by Arai and Sparks (Arai and Sparks, 2001) has, however, placed this hypothesis in doubt by showing very clearly using P X-ray Absorption Near Edge Spectroscopy (XANES) that no metal phosphate phase is formed during the sorption of phosphate to soils and hydrous ferric oxide. Thus, the mechanism of the slow reaction involved in the fixation of phosphate to aluminum and iron minerals in soils and the structure of the products formed, which mainly affect the bioavailability of P, is still elusive.

The reactions of P in soils and related systems such as amended PL are furthermore affected by dissolved anions, cations, and organic matter in the soil solution. Low molecular weight organic acids are known to compete with phosphate in surface reactions with iron and aluminum minerals, thus increasing the amount of water soluble phosphate (Afif et al., 1995; Geelhoed et al., 1998; Iyamuremye et al., 1996a, b, c; Kafkafi et al., 1988; Ohno and Crannell, 1996; Ohno and Erich, 1997; Traina et al., 1986). Information is still lacking on interactions between organic acids and phosphate at the mineral surface and on changes in the speciation of phosphate in the presence of organic acids.

The sorption reactions of phosphate to aluminum and iron hydroxides are very likely affected by calcium cations in limed acid soils and calcareous soils. Rietra and coworkers describe a synergistic effect of calcium and phosphate on the goethite surface (Rietra et al., 2001). They observe that more phosphate is sorbed in the presence of calcium than in its absence and more calcium is sorbed in the presence of phosphate. This effect is explained with the reduction of positive surface charge by the adsorption of phosphate and less repulsion for the positive Ca ions. However, the surface catalyzed precipitation of calcium phosphate even below saturation or the formation of ternary surface complexes can not be ruled

out. Information on a molecular level to fully understand this synergistic sorption mechanism is still lacking.

To study the speciation of P on a molecular level, one has to employ molecular spectroscopy. In recent years, synchrotron-based X-ray absorption spectroscopy (XAS) has been extensively used in the environmental sciences. In particular x-ray absorption near edge structure spectroscopy (XANES) has proven useful in the study of P speciation. Furthermore, advances in solid state nuclear magnetic resonance (NMR) spectroscopy allow one to study more heterogeneous systems, and as is the case with synchrotron-based XAS, modern facilities are available for environmental research.

XANES has proven to be an excellent tool to detect surface precipitates of metal phosphates. Cross-polarization/ magic-angle-spinning (CP-MAS) ^{31}P -NMR and proton-decoupled, single-pulse ^{31}P -NMR on the other hand, gives more detailed information on surface complexes. The two techniques can thus complement each other in the study of phosphate speciation at mineral surfaces.

Objectives

Accordingly, the objectives of the research conducted in 2001 were:

- To complete the ^{31}P -NMR spectroscopic study on the P speciation in alum-amended poultry litter started in 2000;
- To further investigate the effect of reaction conditions and competing organic acids on the sorption reaction of phosphate to gibbsite, using ^{31}P -NMR spectroscopy;
- To extend the study of the effects of reaction conditions to the sorption of phosphate to gibbsite in the presence of calcium using a combination of P-XANES and ^{31}P -NMR spectroscopy.

Methodology

Samples of phosphate adsorbed to gibbsite were prepared by reacting gibbsite suspensions (1.0 g/L in a 0.1 M NaCl background electrolyte) with phosphate while keeping pH and temperature constant. Initial phosphate concentrations were 0.45 mM and 4.5 mM, respectively, reaction times were chosen between 10 minutes and 30 days. The pH was kept constant a pH 4 and pH 7, first by using an automated titrator and later by manually adding appropriate amounts of acid or base. The solids were recovered using a centrifuge (2500 rpm for 10 minutes); any entrained solution was removed by washing with ethanol. The solids were then freeze dried, leaving approximately 5% of surface-bound water, as determined by thermo-gravimetric analysis (TGA).

Samples of calcium and phosphate sorbed to gibbsite for XANES analysis were prepared in a similar fashion using a suspension containing 2.5 g/L gibbsite in a 0.1 M NaCl background electrolyte. Initial concentrations of phosphate were 0.7 mM and 0.15 mM, calcium concentrations were 0.5 mM. Even at initial concentrations, the suspensions were under-saturated with respect to hydroxyl-apatite, the most

stable calcium phosphate phase to be expected in this system. The reaction was started by adding calcium stock solution to the gibbsite suspension while stirring and adding phosphate stock solution after 30 seconds. In this fashion, the risk of local over-saturation while adding the reagents was minimized.

Poultry litter samples were provided by Dr. J.T. Sims. Their properties are summarized in Table 1. Samples 125 through 197 are taken from houses that were treated with alum and samples 502 through 597 are from untreated houses and were analyzed for comparison.

Table 1: Properties of the PL samples studied

Sample	final pH	% total P	% total Al	water soluble P [ppm]	water soluble Al [ppm]
125	7.23	1.97	1.77	322	18.9
134	7.37	2.32	1.09	783	23.1
182	7.03	1.94	1.63	1167	19.5
191	6.89	1.91	2.16	542	18.8
197	7.32	2.09	1.54	355	18.7
502	7.82	1.94	0.08	1635	2.5
511	7.6	1.99	0.12	1754	1.6
541	8.23	1.96	0.10	1308	6.1
559	8.21	2.08	0.10	1570	7.9
597	7.73	2.14	0.09	2534	2.7

Proton-decoupled and CP-MAS ^{31}P -NMR spectra were recorded using a triple resonance probe and 5.0 mm Zirconia Pencil MAS rotors spinning at 10 kHz. The frequencies of ^1H and ^{31}P were 299.99 MHz and 121.43 MHz, respectively. For the single pulse experiments a 90° pulse of 3.7 μs and a recycling delay of 0 s were used. A minimum of 256 scans were averaged for each sample, depending on the phosphate concentration, to give an acceptable signal-to-noise ratio. For the cross polarization experiments a ^1H 90° pulse of 4 μs , a contact time of 1.5 ms and a recycling delay of 2 s were used. Between 1000 and 10,000 scans were averaged for each sample to give an acceptable signal to noise ratio. All spectra were recorded at room temperature. The isotropic chemical shifts in the Fourier-Transform spectra are referenced to 85% phosphoric acid as an external standard. Overlapping peaks were deconvoluted and fit to peaks of Gaussian or Lorentzian line shape using either the Chemagnetics or NUTS NMR data processing software package. NMR studies were conducted at the Environmental Molecular Sciences Laboratory, located at the Pacific Northwest National Laboratory, Richland, WA.

All XANES spectroscopic studies were conducted at beamline X19-A of the National Synchrotron Light Source at Brookhaven National Laboratory in Upton NY. Samples were covered with a thin mylar film and placed inside a helium-purged sample compartment. A solid state PIPS detector collected spectra in fluorescence mode. XANES spectra were collected from 10 eV below the P k edge (2.15 keV) until 50 eV beyond the edge, which encompasses the near edge region. Multiple scans of each sample were collected and averaged together to improve the signal to noise ratio. Data reduction was done with WinXAS 2.1. The background was removed with a linear fit, and the spectra were all normalized.

Results and Discussion

Investigation of P speciation in alum-amended PL. The single-pulse, proton-decoupled spectra and the CP-MAS spectra of the unamended and the alum-amended PL samples are shown in Fig. 1 through 4 respectively. In the single-pulse spectra, the relative signal intensity measured as the area under the signal is proportional to the concentration of the species in question. In CP-MAS spectra, certain species are selectively enhanced and the spectra are therefore not quantitative.

The single pulse spectra of both the amended and unamended samples (see Figure 1 and Figure 2) show broad, complex resonances centered around 0 ppm. One or two relatively sharp peaks can be distinguished. Deconvolution of the signals reveals a set of up to four peaks, all of which are present in some of the amended samples (samples 182, 134 and 125 in Figure 2), whereas in some unamended samples only two peaks are found (samples 541 and 597 in Figure 1). One sharp peak with a chemical shift of 2.8 ppm and varying intensity and a broad peak centered between 0 and 1 ppm are present in all of the samples investigated. Another sharp peak at 6.4 ppm (see for example samples 502, 511, and 559 in Figure 1) can be found in most of the samples. The spectra of the amended samples are dominated by one very broad resonance centered between -4 and -6 ppm, which appears as a tailing on the negative side of the composite signal (see Figure 2).

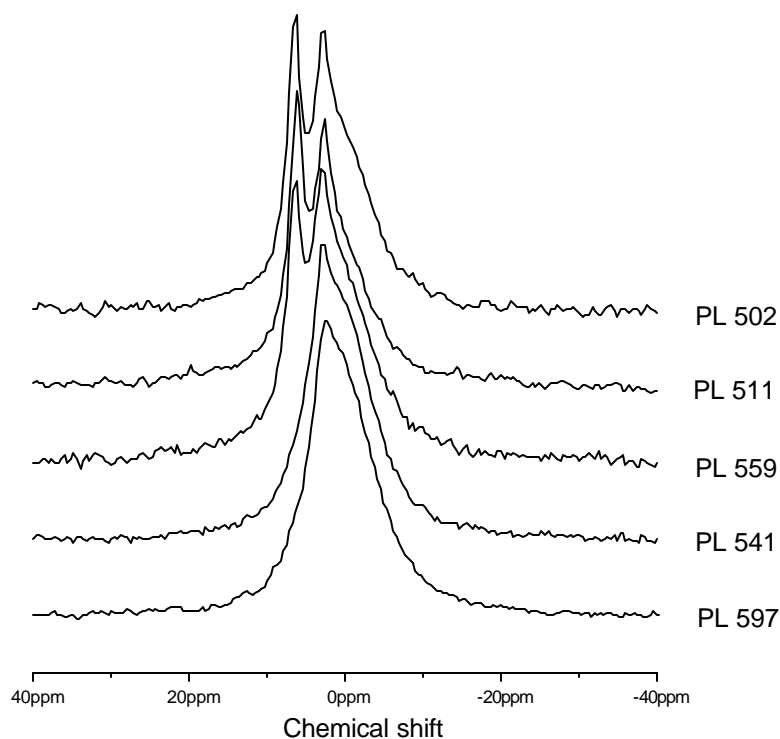


Figure 1: Single-pulse spectra of unamended PL samples

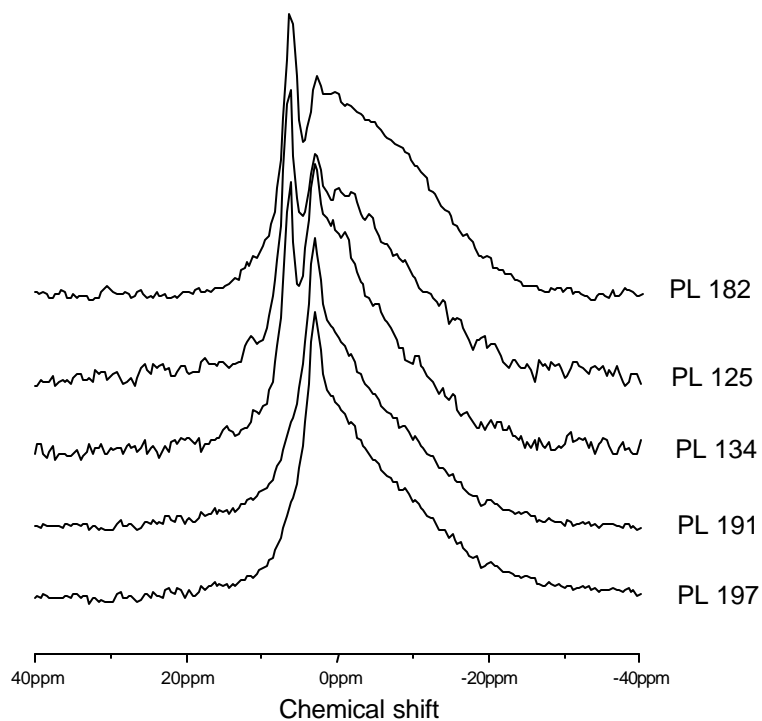


Figure 2: Single-pulse spectra of alum-amended PL samples

Comparison of the single pulse and cross-polarized spectra shows that the peak at 64 ppm is selectively enhanced by cross-polarization and that it is present in all samples but sample 541 (Figure 3). The peak at 2.8 ppm can not be detected in the cross-polarized spectra. Additionally, a weak resonance at -20 ppm appears in the cross-polarized spectra of two of the amended samples (samples 125 and 182 in Figure 4) and in one of the unamended samples (sample 541 in Figure 3).

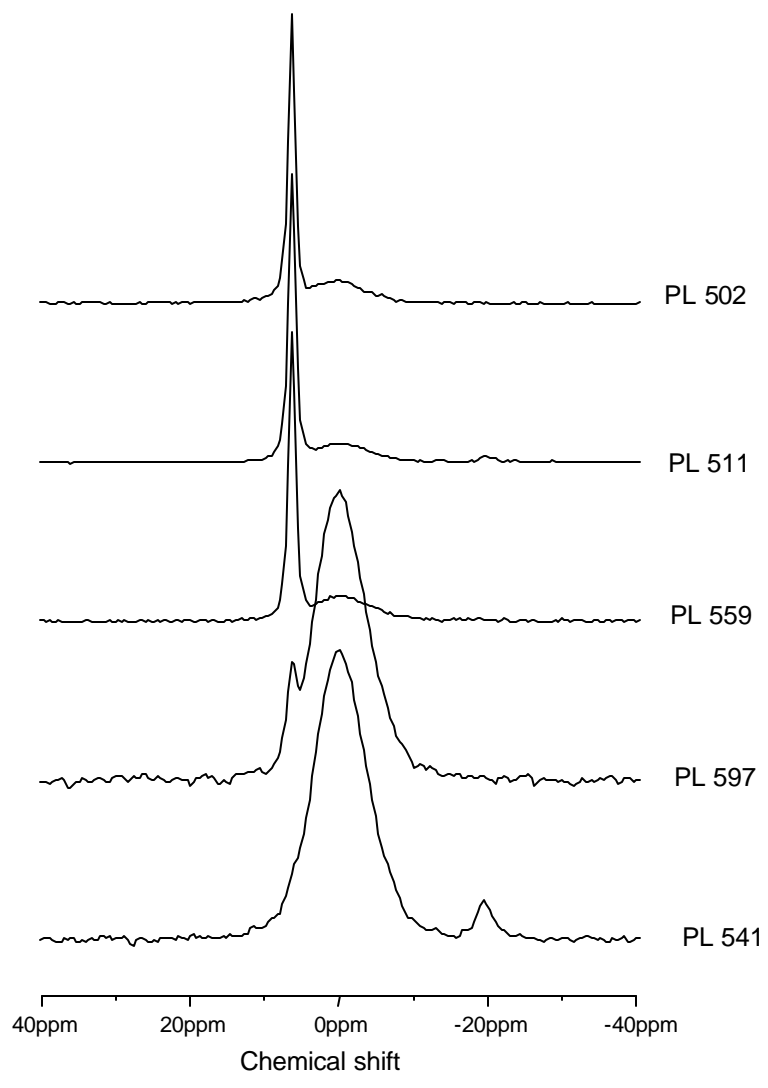


Figure 3: CP-MAS spectra of unamended PL samples

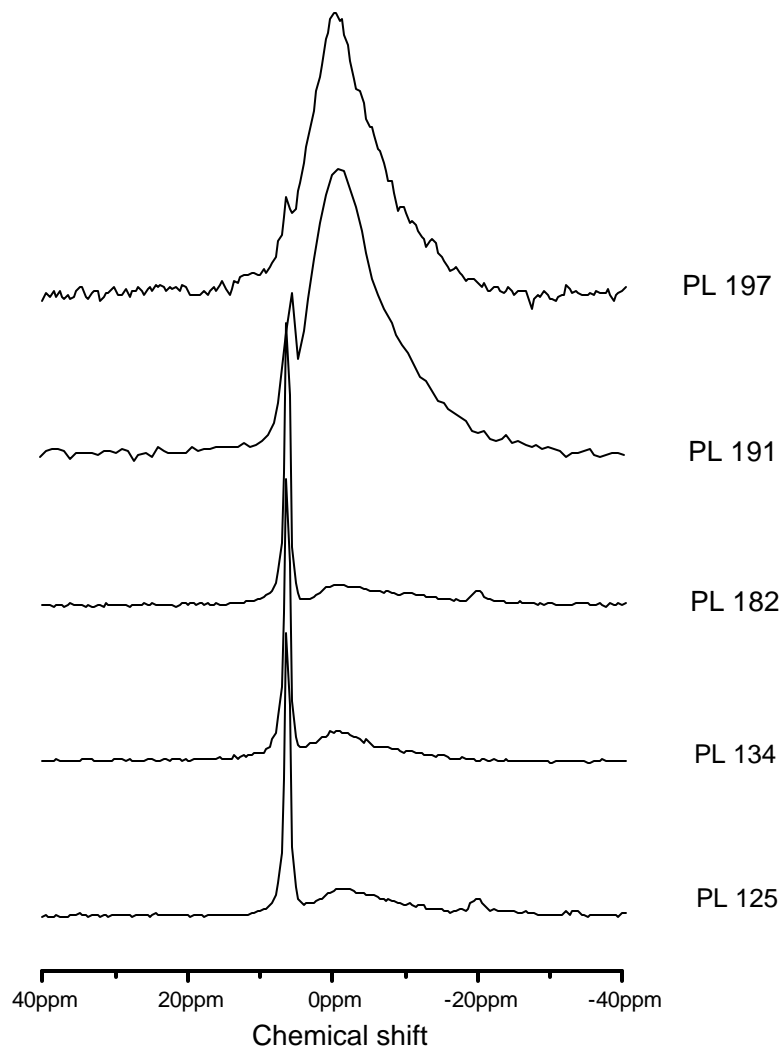


Figure 4: CP-MAS spectra of alum-amended PL samples

The chemical shift of inorganic phosphate in solution is reported at 6.4 ppm. Although the samples have been dried, surface-bound water molecules were not removed. Physically adsorbed phosphate anions can therefore form hydrogen bonds and are thus in a similar chemical environment as in solution, giving rise to the resonance peak at 6.4 ppm.

A P-XANES study of the same samples indicated the presence of a calcium phosphate phase tentatively characterized as a dicalcium phosphate (D. Peak, personal communication). Since the birds' feed contains calcium phosphate in excess of the dietary requirements, it is safe to expect calcium phosphate in significant amounts in the litter material. Chemical shifts for several calcium phosphate phases have been reported, ranging from -1.5 ppm and 0 ppm in anhydrous dicalcium phosphate (monetite); 1.7 ppm in dicalcium phosphate dihydrate (brushite); -0.2 ppm and 3.4 ppm in octacalcium phosphate; to 2.8 to 3.0 ppm in hydroxyl apatite (Elliott, 1994; Rothwell et al., 1980) as well as in generic

calcium phosphate (Turner et al., 1986). In general, the peaks shifted upfield are attributed to hydrogen phosphate anions, whereas the downfield peaks are attributed to deprotonated phosphate. The phosphate species giving rise to the downfield shifts of 2.8 ppm to 3.4 ppm are referred to as being located in “apatitic” layers (Elliott, 1994).

The peak at 2.8 ppm that appears in all spectra could be attributed to hydroxyl apatite in the samples, but the formation of a crystalline apatite is very unlikely in the heterogeneous litter material. It has been reported that the crystal growth of hydroxyl apatite is inhibited by organic acids due to adsorption and blocking of crystal growth sites. Usually, the less stable compounds DCP and OCP hydrolyze to eventually form hydroxyl apatite. This process, however, is inhibited in the presence of polymeric organic acids, such as humic and fulvic acids (Grossl and Inskeep, 1991; Inskeep and Silvertooth, 1988).

Since crystalline calcium phosphates are very unlikely to form, an amorphous precipitate with a short range ordering similar to that in apatite might form, resulting in a resonance with the observed chemical shift. Growth of the precipitates and formation of crystalline phases in this system is inhibited by the complex organic materials present.

Organic phosphate compounds from metabolic processes are present in PL and show up as a broad resonance centered at 0 ppm. This chemical shift range has been reported to be characteristic for phosphate diesters such as occur in phospholipids and nucleic acids (Cade-Menun and Preston, 1996). Since the litter material is very heterogeneous with many slightly different phosphate esters present, the signals for the single compounds overlap and can not be resolved.

The peak centered at -4 ppm to -6 ppm, which accounts for 50 - 75% of the signal intensity in the spectra of the alum-amended samples (Figure 2), can be attributed to phosphate sorbed to aluminum hydroxide. Since this peak appears only in the alum-amended samples, it has to be due to the alum-treatment. Phosphate sorbed to gibbsite at high pH values comparable to the PL samples, shows broad resonances in the same chemical shift range (see next chapter).

Chemical shifts for AlPO_4 are reported in the literature and range from -18 to -24 ppm, depending on crystallinity and water content. A weak signal of AlPO_4 at -20 ppm can only be detected in the CP-MAS spectra of three samples, PL 125 and PL 182 in Figure 4 and PL 541 in Figure 3. It is very curious to find aluminum phosphate in the latter sample, because it was not treated with alum.

Contrary to the widely accepted opinion (Moore and Miller, 1994), the precipitation of aluminum phosphate seems to be negligible compared to the fixation of phosphate by an aluminum hydroxide gel. This gel forms by hydrolyzation of aluminum cations released from alum in the basic poultry litter. This process appears to be kinetically preferred to a precipitation reaction yielding aluminum phosphate. Fixation of phosphate by an aluminum hydroxide gel is nevertheless very effective, as has been demonstrated by Sims and coworkers (Sims et al., 2000). The amount of water-soluble phosphate was reduced significantly by the alum-treatment.

An attempt was made to relate the ratio of water soluble P to total P to the ratio of the signal intensity of the physically adsorbed inorganic phosphate to the total signal intensity. No linear relationship was found (data not shown). This can be explained by the fact that not only inorganic phosphate contributes to the water-soluble portion. Organic phosphate species can hydrolyze to a different extent under the conditions at which phosphate is determined colorimetrically using the Murphy-Riley method. The organic phosphate pool is too heterogeneous to be quantified, an estimate of the portion that will be soluble in water is therefore not possible.

Investigation of the influence of reaction conditions on phosphate sorption. Spectra of samples reacted at pH 4 through pH 7 for 24 hrs are shown in Figure 5. One can clearly see a general trend to lower chemical shifts with decreasing pH values. The broad signals are an indication of the presence of several phosphate species, the signals of which overlap. The samples at pH 5 and pH 6 have a lower phosphate concentration than the samples at pH 4 and pH 7 and result in poorer data quality.

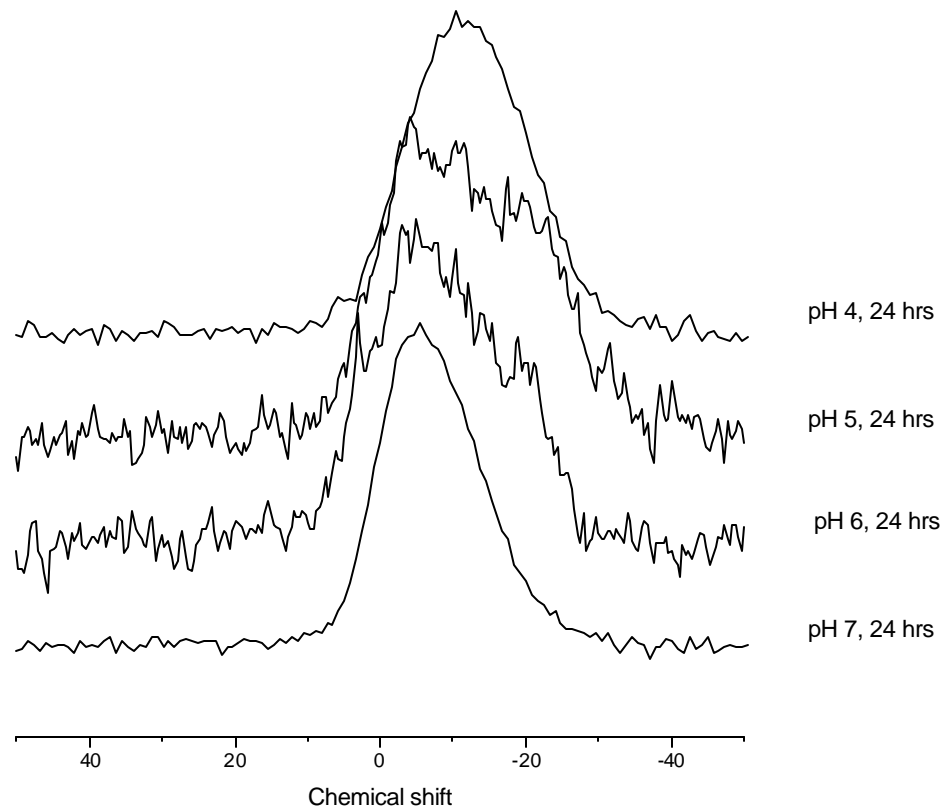


Figure 5: Effect of pH on the NMR spectra of phosphate sorbed to gibbsite

Several general trends in the chemical shifts of phosphate anions have been reported. The chemical shift decreases with decreasing pH in solution from pH 6.4 to pH 0 due to the increasing number of protons bound. Model calculations of chemical shifts of phosphate in glasses containing aluminum cations indicated that the chemical shift decreases with an increasing number of aluminum cations directly bound to phosphate (Cody et al., 2001).

The decrease in chemical shift observed in the shown spectra can therefore be attributed to two effects. With increasing pH, the surface bound phosphate anions can lose protons, resulting in a higher chemical shift. With decreasing pH the phosphate speciation can change from predominantly monodentate, mononuclear, to predominantly bidentate, binuclear complexes, resulting in a lower chemical shift of the resulting sum of overlapping signals.

The effect of time on the NMR spectra of phosphate sorbed to gibbsite is shown in Figure 6 for samples reacted at pH 4.

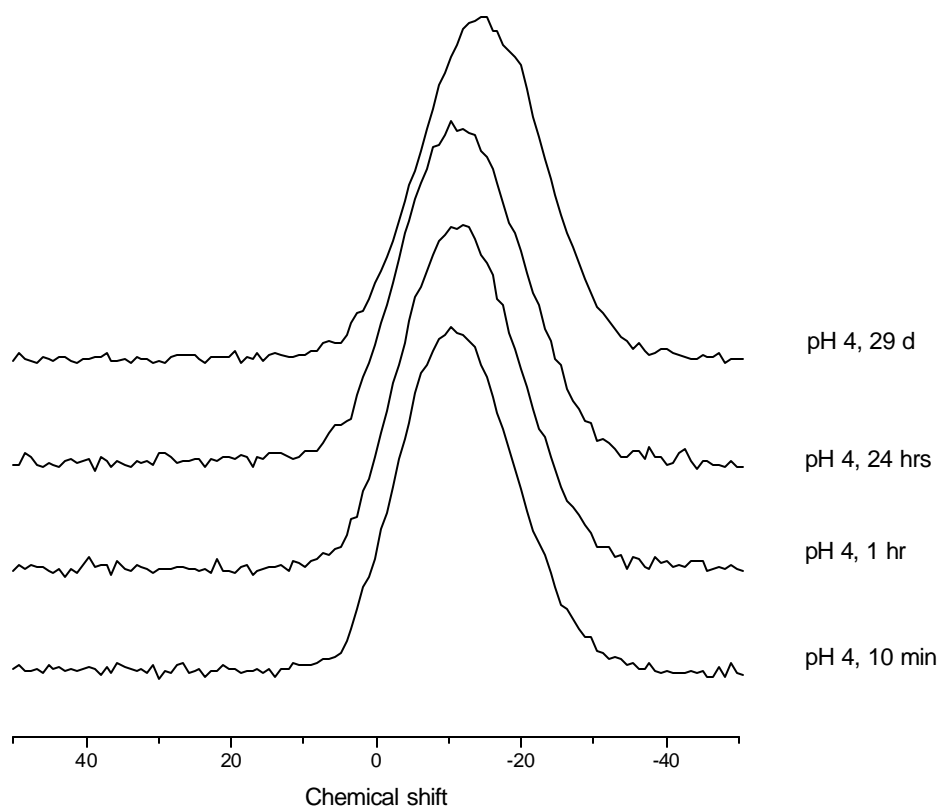


Figure 6: Effect of time on the NMR spectra of phosphate sorbed to gibbsite

With increasing reaction time the chemical shift decreases. Following the arguments employed earlier, this can be due to increasing protonation over time or a change to a higher proportion of bidentate, binuclear, over mononuclear, monodentate complexes.

The spectra of phosphate sorbed to gibbsite in the presence of citric acid show similar general trends of pH and reaction time (data not shown).

An aluminum phosphate surface precipitate was not detected in any of the spectra; the P speciation seems to be therefore dominated by surface complexes.

It is desirable to resolve the single peaks to make a conclusive assignment of the species. An attempt was made to deconvolute the asymmetric signals and assign single peaks to different species, but the results are not consistent and more experiments to identify species are clearly needed.

It was reasoned that a fast proton exchange between sorbed phosphate anions and surrounding adsorbed water molecules is responsible for the broadening of the signals. This effect is usually observed when exchange or conversion reactions happen in a shorter time frame than the data acquisition during the NMR experiment. To reduce the thermal motion of the water molecules at the surface and slow down proton exchange reactions, the samples were cooled down to -60°C during the experiment. No changes in the spectra were observed (data not shown).

To reduce water content, some of the samples were dried at 60°C . Spectra of freeze-dried and oven-dried samples are compared in Figure 7 and Figure 8.

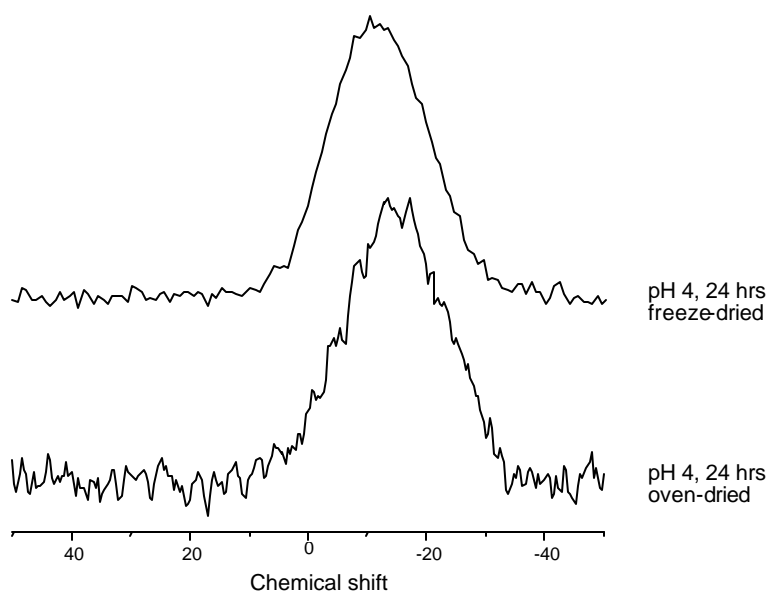


Figure 7: Effect of oven-drying samples

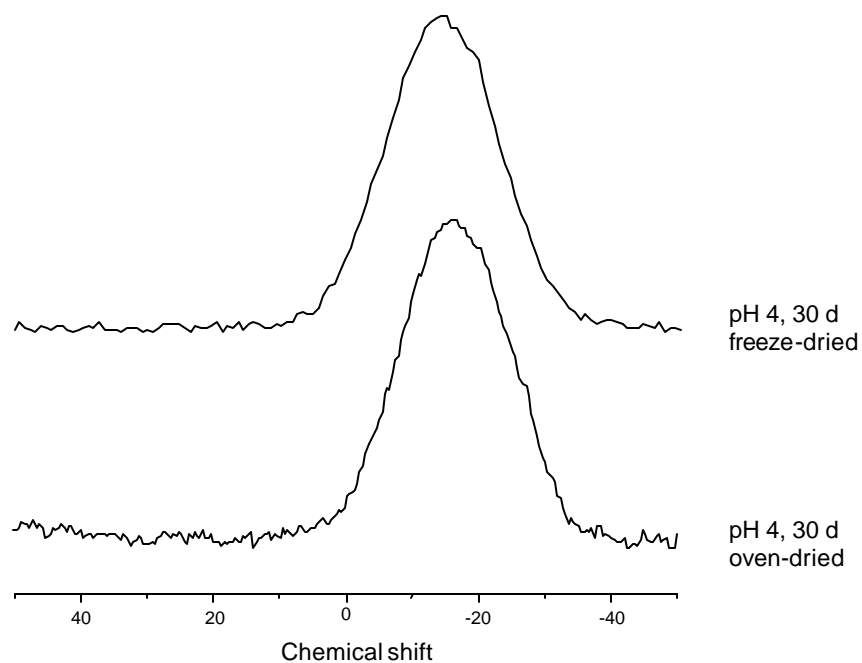


Figure 8: Effect of oven-drying samples

Upon drying the samples at 60°C a shift of the signals to a lower chemical shift is clearly visible, but no better resolution is achieved. This indicates that increasing the temperature can change the phosphate speciation at the gibbsite surface, either by protonating the sorbed phosphate, which is rather unlikely considering the reduced number of water molecules at the surface, or by changing from mononuclear to binuclear complexes or even to a three-dimensional aluminum phosphate network.

Spectroscopic investigation of the co-sorption of Ca and P on gibbsite. Figure 9 shows P-XANES spectra of samples of phosphate sorbed to gibbsite in the presence of calcium at initial molar ratios of 3:2 and 1:3. The spectrum of hydroxyl-apatite is shown for comparison. The two spectral features at the high-energy side of the K-edge in the spectrum of hydroxyl-apatite can be found as a shoulder and a weak peak, respectively, in the spectra of samples reacted at pH 4 (low initial P:Ca ratio only) and pH 7 (arrows). This is indicative of the presence of a calcium phosphate phase, albeit in a very low concentration, which does not necessarily have to be hydroxyl-apatite, because similar features appear in the spectra of other calcium phosphate phases (data not shown).

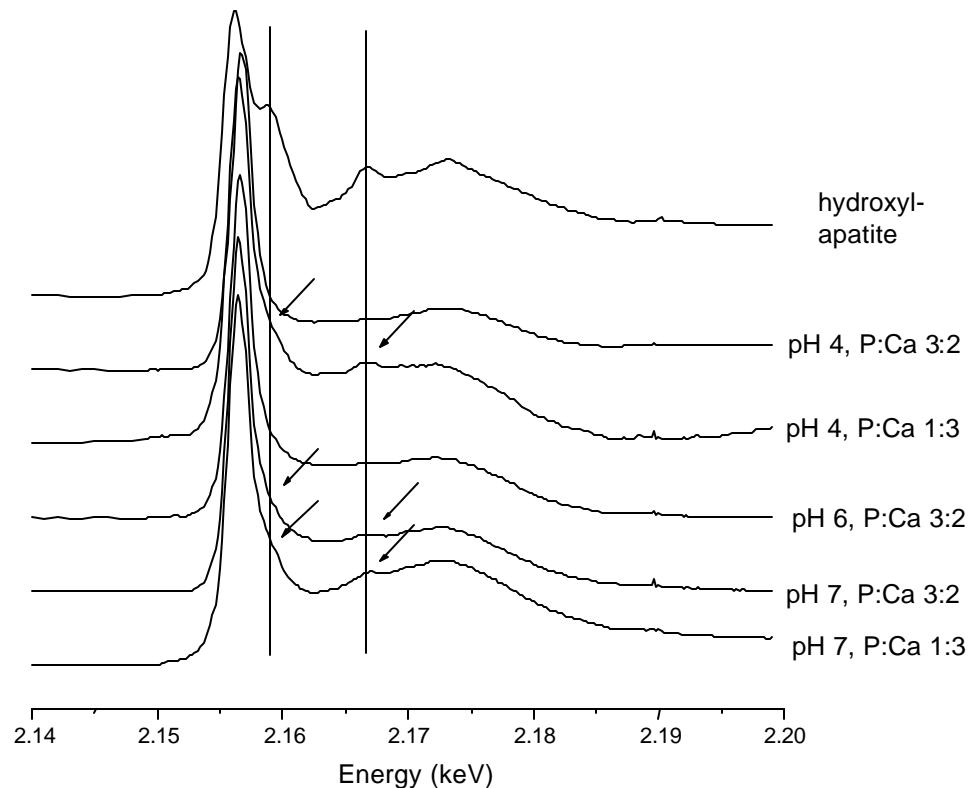


Figure 9: P-XANES spectra of phosphate on gibbsite in the presence of calcium

Figures 10 through 12 show the ^{31}P -NMR spectra of phosphate sorbed to gibbsite in the presence of calcium at pH 4, 6 and 8, respectively. The poor data quality is due to the low initial concentrations that had to be used to avoid super-saturation with respect to solid calcium phosphate phases.

As was mentioned earlier, calcium phosphate phases show relatively sharp signals with characteristic chemical shifts in the ^{31}P -NMR spectra. However, no new signals besides the broad resonances of phosphate sorbed to gibbsite can be detected. Calcium phosphate phases are either not present, or are present in such low concentrations, that the NMR signal can not be distinguished from the background noise. A surface precipitate can therefore not be ruled out, especially if one compares these results with the insights gained from XANES spectroscopy. NMR spectroscopy seems to be less sensitive compared to XANES spectroscopy.

Another possible mechanism of interaction on the gibbsite surface is the formation of a ternary complex, in which the calcium cation is complexed by an adsorbed phosphate anion. Calcium and

phosphate form stable complexes in solution, similar complexes attached to the mineral surface are therefore possible. The complexation of calcium, however, is expected to give rise to a discernible signal in the ^{31}P -NMR spectra. A further spectroscopic investigation is clearly needed to conclusively rule out any direct interactions between calcium and phosphate at the gibbsite surface.

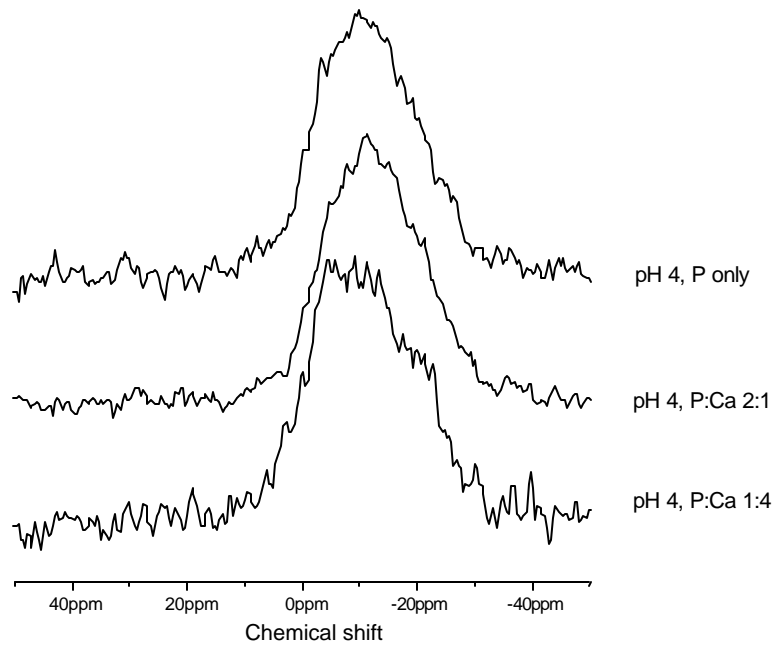


Figure 10: P-NMR spectra of phosphate on gibbsite in the presence of calcium

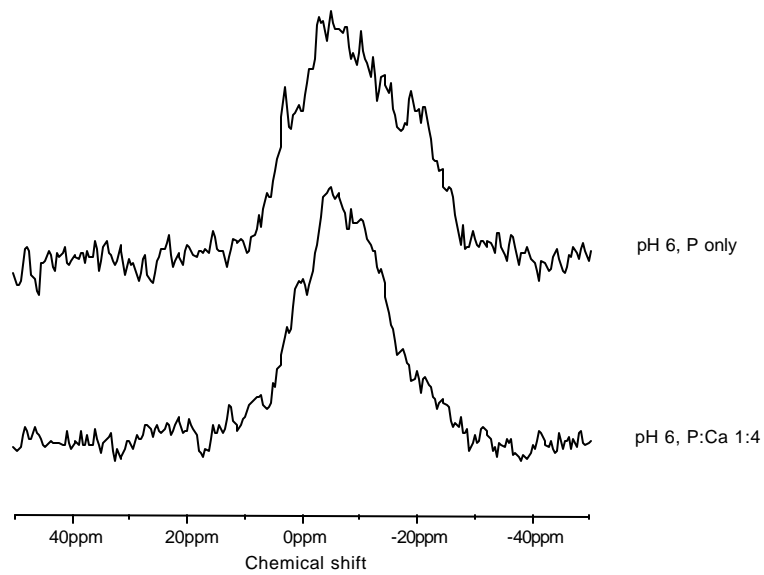


Figure 11: P-NMR spectra of phosphate on gibbsite in the presence of calcium

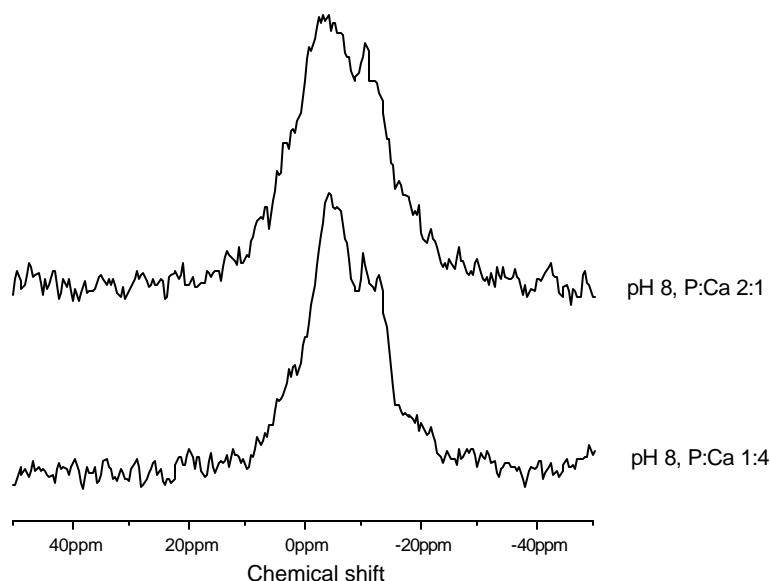


Figure 12: P-NMR spectra of phosphate on gibbsite in the presence of calcium

Besides the direct interaction of phosphate and calcium at the gibbsite surface, adsorption of phosphate can facilitate the adsorption of calcium by reducing the surface charge. Calcium is adsorbed by variably charged soil minerals such as the aluminum and iron hydroxides via an ion exchange mechanism at pH values above the point of zero charge (PZC), which is between pH 8 and 9 for aluminum and iron hydroxides. Adsorption of phosphate decreases the surface charge and facilitates calcium adsorption at pH values below the PZC.

Conclusions and Implications

This research corroborates findings that P is fixed in alum-amended PL as phosphate sorbed to aluminum hydroxide gel rather than precipitating as an aluminum phosphate. This reaction has, however, proven to be very effective in reducing the amount of P soluble in water. Little is still known about reactions occurring during the aging of the alum-amended PL and more research is clearly needed.

Sorption studies of phosphate to gibbsite seem to indicate that even in the presence of organic acids or calcium the P speciation does not change significantly and that it is still dominated by inner-sphere surface complexes. More important is the fact that the concentration of P in the soil solution is determined by various processes, which can counteract each other. Organic anions compete with phosphate for sorption sites on the surface of soil minerals, while calcium cations facilitate phosphate sorption. More research is still needed to investigate changes in the desorption reactions of P adsorbed in the presence of organic acids or calcium.

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