

PHOSPHORUS DYNAMICS IN ORGANIC MATTER-AMENDED SOILS

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ABSTRACT

Generally, phosphorus (P) is considered immobile in calcareous soils. Yet, numerous studies have found that the addition of organic wastes (e.g. manures) can enhance P mobility in these soils. We believe that the soluble organic matter present in these wastes increases P solubility by inhibiting the sorption of inorganic P on soil colloidal surfaces and subsequently preventing the formation of insoluble calcium phosphates. This results in increased P bioavailability. Likewise, tests used to assess phosphorus (P) status in manure amended calcareous soils may inaccurately estimate the amount of potentially mobile P due to the influence of soluble organic matter. This can lead to incorrect applications of manure – possibly an increase in mobile P – which potentially threatens the quality of receiving waters. We examined P dynamics in calcareous systems in order to understand and determine which test most accurately predicts the fate of P in these environments. This study included batch and kinetic experiments using mineral phases found in calcareous soils such as calcite, brushite, and the iron oxide ferrihydrite. Humic acid obtained from the International Humic Substances Society was used as an analogue for manure. Our hypothesis was that the soluble organic matter from the manure inhibits the sorption of P and possibly affects the extractability of P by commonly used soil tests such as the Olsen bicarbonate extract or a calcium chloride extract. Sorption kinetics may be responsible for differences observed between the extractants (water, CaCl₂, and NaHCO₃) and solid phases responsible for regulating soluble P levels in soils. By fully understanding P dynamics in organic matter-amended soils the proper tests can be chosen that accurately assess P status and ultimately lead to sustainable waste management.

INTRODUCTION

Agricultural runoff has been implicated in accelerated eutrophication of surface waters in developed farmland areas (Sharpley and Menzel, 1987). This is particularly the case where P has accumulated in surface soils due to high inputs of fertilizer, municipal biosolids, or manure and is compounded by situations facilitating erosion, whereby bioavailable P enters a surface water body. Ultimately, phosphate sorption/desorption on soil surfaces is the factor controlling soluble phosphate levels in natural waters. Sorption reactions include precipitation of metal phosphates and adsorption-desorption processes occurring at aqueous/solid interfaces. Mineralization of organic P forms also provides a source of P; however, phosphate bioavailability is still controlled

by sorption/desorption processes on soil surfaces. In calcareous systems, with pH values ranging from near neutral and above, dicalcium phosphate dihydrate (DCPD), octacalcium phosphate (OCP), and hydroxyapatite (HAP) are major P solid phases (Lindsay, 1979). DCPD and OCP are important reaction products of P fertilizers in soil and are precursors to the formation of thermodynamically more stable HAP (Lindsay, 1979; Stumm and Morgan, 1981; Fixen et al., 1983; O'Connor et al., 1986; Amacher et al., 1995).

The presence of soluble organic matter is ubiquitous in natural systems. It is widely documented that soluble organic constituents enhance phosphate solubility and mobility (Traina et al., 1986; Inskeep and Silvertooth, 1988; Grossl and Inskeep, 1991, 1992). Recent studies indicate that organic matter, associated with animal waste applications, enhances the solubility of phosphate in soils (O'Connor et al., 1986; Harris et al., 1994; James et al., 1996; Erich et al., 2002; Maughn, 2002; Siddique and Robinson, 2003). Common organic acids have been shown to inhibit the precipitation of calcium phosphate minerals (Inskeep and Silvertooth, 1988, Grossl and Inskeep, 1991, 1992). The proposed mechanism of inhibition is the adsorption of organic acids onto crystal surfaces, which block sites acting as nuclei for new crystal growth. Others report that organic ligands compete with phosphate for sorption sites on oxide and clay surfaces (Nagarajah et al., 1970; Lopez- Hernandez et al., 1986; Violante et al., 1991; Violante and Gianfreda, 1993). Commercial humic acid products are currently available and marketed to increase available soil P. Yet, Jones et al. (2007) report that the recommended rates of application of these humic acid products may be too low to enhance spring wheat growth or available P levels.

We surmise that when manure is applied to calcareous soils, soluble organic matter prevents precipitation of insoluble Ca phosphates, and phosphate activity in these soils is controlled by rapid adsorption/desorption on colloid surfaces and formation of more soluble Ca phosphates, metastable to HAP. This results in enhanced phosphate bioavailability. Calcium phosphate precipitation can be conceptually explained using principles of chemical kinetics and reaction pathways (Grossl and Inskeep, 1992). Starting with a solution supersaturated with respect to DCPD, OCP, and HAP, precipitation can proceed either through a parallel or series reaction pathway. In either case, DCPD would precipitate first and since the formation of OCP and HAP are inhibited to a greater extent by DOC, present at levels realistic for many soil environments, DCPD would remain as a metastable solid phase controlling the activity of phosphate in soil solutions and prolonging the bioavailability and mobility of P in pastures.

Tests used to assess phosphorus (P) status in manure-amended calcareous soils are often inaccurate and underestimate the amount of potentially mobile P. This could lead to over applications of manure and an increase in mobile P which potentially threatens the quality of receiving waters. The "*Change-Point*" determined with a 0.01M CaCl₂ extract could be a useful indicator of the soil Olsen P-test concentration where P becomes mobile – this occurs at an Olsen P test value of approximately 60 ppm (Hesketh and Brookes, 2000). This *change point* was also observed for a calcareous Millville silt loam fertilized with increasing rates of inorganic P, however, not when this soil was fertilized with poultry manure.

The **objective** of this study was to measure the sorption behavior of P on different soil constituents with and without exposure to soluble organic matter. We hypothesize that soluble organic matter from manure inhibits the sorption of P and consequently influences soil test P levels.

MATERIAL AND METHODS

Supersaturated solutions of phosphate and Ca^{2+} were equilibrated with the soil solid combinations listed in Table 1. Soil solids included the iron oxide ferrihydrite (F); CaCO_3 or calcite (C), and dicalcium phosphate dihydrate (DCPD, also coded as P in Table 1) known as brushite. Combinations of these were added to a quartzite sand base resulting in 9 g total of solid material. The ferrihydrite was prepared as described by Amacher (2001), and reagent grade CaCO_3 and brushite were used. Experiments were conducted by adding 290 mL of 10.3mM CaCl_2 solution (pH 7.5) into containers to which no humic acid would be added, and 270 mL of 11.1mM CaCl_2 solution was added to containers to which 20 mL of 75mM C humic acid solution (pH 7.5) was added. This gave a final humic acid (Leonardite, Humic Acid Society Standard) concentration of 5mM C. To each container, 10 mL of $3,000 \mu\text{g P mL}^{-1}$ (as Naphosphate) solution was added, followed immediately by the pre-weighed solid materials for that treatment and the time recorded. This process was repeated for each container. The pH was adjusted to pH 7.5 if necessary with 0.5M NaOH or HCl, and then each container was sampled at 5 minutes after the addition of solids. The pH was again adjusted after 5 minutes, 2.5 hours, 6 hours and then daily thereafter. Containers were sampled at 5, 20 and 60 minutes, and 0.5, 1, 3, 7, 14, 21 and 28 d after P and solid addition.

Table 1. Weight (grams) of the soil constituents in each treatment.

Trt. name	Sand	Ferrihydrite	CaCO_3	DCPD	Humic acid
F	8.1	0.9	–	–	–
F+C	6.3	0.9	1.8	–	–
F+C+P	5.4	0.9	1.8	0.9	–
F+P	7.2	0.9	–	0.9	–
C	7.2	–	1.8	–	–
C+P	6.3	–	1.8	0.9	–
P	8.1	–	–	0.9	–
Sand	9	–	–	–	–
F	8.1	0.9	–	–	5mM C
F+C	6.3	0.9	1.8	–	5mM C
F+C+P	5.4	0.9	1.8	0.9	5mM C
F+P	7.2	0.9	–	0.9	5mM C
C	7.2	–	1.8	–	5mM C
C+P	6.3	–	1.8	0.9	5mM C
P	8.1	–	–	0.9	5mM C
Sand	9	–	–	–	5mM C

At sampling, 15 mL of solution was removed from each container and filtered through a $45\mu\text{m}$ nitrocellulose filter. Solutions were stored in a refrigerator before being colorimetrically analyzed for P (Murphy and Riley, 1962). At the end of the experiment, treatment samples were centrifuged at 3,500 rpm for 10 min then filtered through a $45\mu\text{m}$ nylon membrane. The filtrate was analyzed for P and the remaining solids (on the filter paper, in the bottom of the centrifuge

tube, and left in the beaker) were dried at 30°C overnight. The solids were scraped off the centrifuge tubes, filter paper and beaker from each replicate of each treatment and were recombined and thoroughly mixed. A subsample of air-dried solid material (750 g) was then extracted with 15mL of NaHCO₃ at pH 8.5 for 20 min (Olsen et al. 1954) then centrifuged at 3,500 rpm and filtered (Whatman No. 42). A further 2 g sample was extracted with 10 mL of 0.01 M CaCl₂ for 15 minutes, then centrifuged and filtered. The Olsen, CaCl₂ and solution extracts were then analyzed for P using the colorimetric method of Murphy and Riley (1962).

RESULTS AND DISCUSSION

The presence of humic acid (HA) completely inhibited the kinetics of P sorption for systems containing only calcite (C), only brushite (P), and calcite together with brushite (C + P) (Figure 1). Even without HA, sorption kinetics were slower for the C, P, and C+P systems than for the system containing ferrihydrite only (F) (Figure 1). Thus, in the C, P, and C+P systems, P solubility was controlled by precipitation/dissolution of Ca phosphate solid phases, and the slower kinetics of Ca phosphate precipitation was subject to greater inhibition by HA. The kinetics of adsorption of P onto F was much faster – faster than the adsorption of HA onto the F surface (Figure 1). Interestingly, when F was present in the C, P, and C+P systems with and without HA, the sorption kinetics followed the behavior of the system containing only F. Iron oxides such as ferrihydrite are ubiquitous in soils, even calcareous soils, thus, iron oxides may play a much more important role than previously thought in regulating P solubility in calcareous soils. This warrants further investigation.

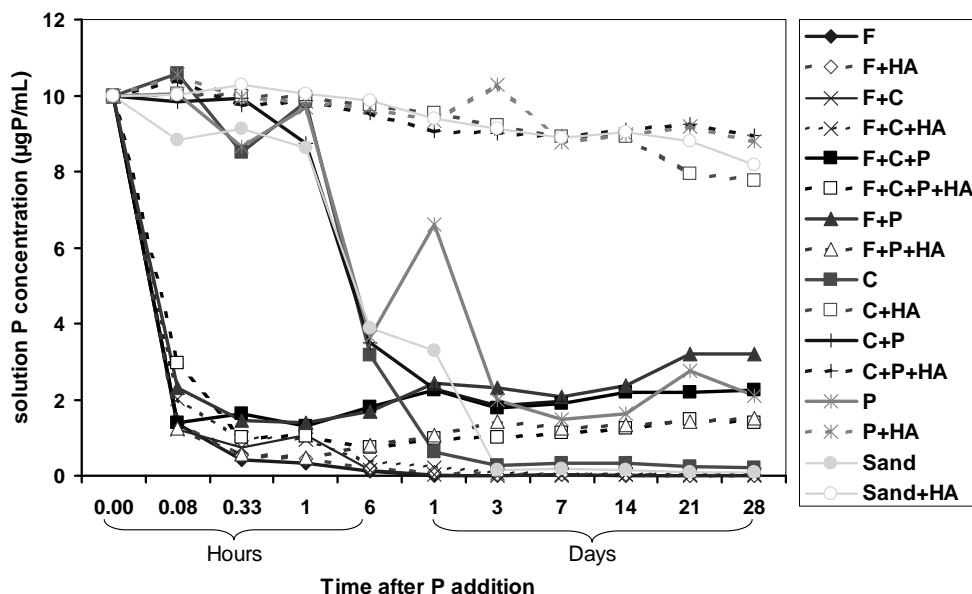


Figure 1. Changes in solution P concentration over time.

When we evaluated the amount of P extracted from the treatment solids using either NaHCO₃ (Olsen method), CaCl₂, or water we found that very little sorbed P was extracted from F surfaces. The (C) and (P) systems with HA had lower levels of NaHCO₃ extractable P than without HA (Table 2). For clarity, it should be noted that Table 2 only lists the amount of P that was extracted from the solids collected at the end of each experiment, and does not list solution data collected during the course of the experiments. The P only systems with HA had lower

levels of water and CaCl₂ extractable P than without HA, while the opposite was observed for C and C+P treatments (Table 2).

Table 2. P extracted from treatment solids.

Treatment	P extracted (µgP/g 'soil')		
	Water	CaCl ₂	NaHCO ₃
C	4.22	1.06	69
C+HA	16.17	7.87	27
C+P	58.92	7.29	1884
C+P+HA	36.24	11.14	90
P	294.02	47.12	1086
P+HA	81.80	20.81	433

SUMMARY

Humic acid (HA), which acted as an analogue to the soluble organic matter present in organic wastes, inhibited the formation of insoluble calcium phosphates, thus, rendering P more bioavailable. Sorbed HA also decreased the amount of soil test P extracted from Ca phosphate solid phases. Surprisingly, ferrihydrate, with and without HA, was a dominant sorbent of P. Sorption kinetics may be responsible for differences observed between the extractants (water, CaCl₂, and NaHCO₃) and solid phases responsible for regulating soluble P levels in soils. Care must be taken when determining manure application rates on calcareous soils that are solely based upon NaHCO₃ extractable P levels.

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