

SOIL PHOSPHORUS CHEMISTRY: AGRONOMIC AND ENVIRONMENTAL APPLICATIONS

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Introduction

Phosphorus (P) has been a heavily researched topic in soil science for many years. For example, a search of the AGRICOLA database from 1970 to present turned up nearly 6000 citations under the key words soil and phosphorus. The fact that P is essential to all forms of life has promoted these research activities, as one would expect. In addition, the complexity of the soil P cycle has yet to be fully understood and appreciated by the scientific community. Further, while early research focused on correcting P deficiencies in crops, more recently we have had to focus on soils that have P levels far in excess of what can be justified from an agronomic viewpoint. The potential environmental impacts of P in surface waters has forced the agricultural community to examine the possibility that P may have offsite impacts and that high levels of soil P or practices that allow P to move offsite may need to be restricted. In summary, given the renewed and continued interest in soil P, one would not predict a decline in P research activities in the near future.

The Basics

The soil P cycle is complicated despite the fact that it does not involve gaseous forms or changes in oxidation state of P, similar to forms and processes found in the soil nitrogen cycle. The cycle is strongly influenced by the nature and quantities of inorganic and organic solid phases present and by the chemistry of the soil solution (pH, ionic strength, redox potential, etc.) Still, there are some basic observations and conclusions that can be made to help our understanding. The purpose of this section is to provide a synopsis of the basic behavior of P in soils and to discuss the primary methods that are used to study P in soils.

One key characteristic of P is its propensity for accumulating in the soil, as measured by total P concentrations, which begs the question as to the fate of P in soil. It clearly does not reside in the soil solution, as the soil solution typically contains less than 1% of the total amount of P in the soil system, and suggests that the P is strongly associated with the soil solid phases. These solid phases can be either organic or inorganic in nature. Soils typically have between 3 and 90% of the total P present as organic P, leaving 10 to 97% as inorganic P (Stevenson, 1986). Cultivated soils generally have a higher proportion of inorganic P than organic P. The role of organic P in supplying plant available P is subject to some debate. In general, organic P as a source of plant available P is most important in low P soils found in forest or grassland systems while in cultivated and fertilized soils the inorganic P fraction generally provides most of the plant available P.

Figure 1 presents the influence of time and P application on soil solution P (P_1) concentrations in an incubated soil sample without crop uptake of P. It is clear that between 3 weeks and 6 months there was a significant drop in P_1 with little additional decrease after 6 months. The data demonstrate the ability of a soil alone to remove P from the soil solution. The key processes responsible for this decrease are adsorption and precipitation of secondary P-containing solids. Use of the word mineral is avoided because mineral implies an ordered atomic arrangement in a solid and that may not be the case.

Adsorption is the formation of chemical bonds between soil constituents and P from the soil solution. Examples are shown in Figure 2. The cations most often involved are Al, Ca, Fe or Mn. The bonding may be monodentate, bidentate, or binuclear (Fixen and Grove, 1990). Adsorption occurs whenever these cations are in contact with the soil solution. The most obvious examples of this are Al, Fe, or Mn (hydr)oxide minerals or CaCO_3 in calcareous soils. In addition, adsorption may also occur on clay minerals when these cations are exposed along the edges of clay particles, most notably with Al. Adsorption may also occur with soil organic C through cation bridges between functional groups and P in the soil solution. Phosphorus adsorption is pH dependent. For the Al, Fe, and Mn (hydr)oxides P adsorption decreases as pH increases with little adsorption above pH of 7. The pH relationships are more complicated with CaCO_3 because of precipitation reactions that occur as pH increases.

Adsorption is studied using P adsorption isotherms, or adsorption curves, that relate the quantity of P adsorbed by the solid phase to the P concentration in solution in equilibrium with the solid phase. In practice, the soil or mineral phase in question is exposed to a range of solutions containing varying initial P concentrations. After a predetermined amount of time, the P concentration in the solution is measured and the adsorbed amount of P is calculated from the change in solution P concentration. The data can be modeled with a number of equations, the most commonly employed being the Freundlich and the Langmuir equations. Examples are shown in Figure 3. The key differences between the two are that the Langmuir predicts an adsorption maximum while the Freundlich does not. The theory behind these equations is beyond the scope of this paper. In practice, the equation that best describes the data or fits the purpose is the one that is used.

When P fertilizers are added to soils the P concentration in the soil solution increases dramatically and the solubility product of a number of P solid phases is exceeded. Precipitation of a solid phase containing P and one of the major soil cations is likely. If a number of solids are possible with the mix of cations present, thermodynamics dictates that the least soluble solid phase should form. Above a pH of approximately 7.0, Ca phosphates would be less soluble than Al or Fe phosphates with apatite being the least soluble of the possible Ca phosphates. Below a pH of 7.0, Al or Fe phosphates would be less soluble than Ca phosphates. Lindsay (1979) has presented a unified P solubility diagram that suggests maximum P solubility at a pH of approximately 6.8. This is the point of intersection between the least soluble Ca, Fe, and Al phosphates.

Study of the P solid phases in soils is very difficult. Direct methods for determining the presence of a given solid phase, such as x-ray diffraction, are generally not sensitive enough to detect the solid phases even in soils with high P concentrations. This has led to the use of indirect methods such as solubility equilibrium experiments. In this approach either soil solution is collected or a solution is brought into contact with the soil. In both cases, an equilibrium state between the aqueous and solid phases is assumed. Under these conditions, it is possible that the composition of the aqueous phase could be used to infer the presence of a solid phase that is controlling P solubility. Many such studies have been published. In general, the studies support our notion that under low pH conditions the Al, Fe, or Mn phosphates seem to be involved with control of P solubility and under high pH conditions the Ca phosphates serve the same role. However, the solubility data rarely coincide exactly with what we would expect for the pure P solid phases based on thermodynamics. There are numerous examples of this problem. One of the more common ones is the fact that solubility equilibrium experiments do not often suggest that apatites control P solubility in high pH soils when thermodynamics predicts that they would. There are numerous possible causes for these discrepancies ranging from procedural shortcomings to violations of the basic thermodynamic assumptions. Again, these topics are beyond the scope of this paper.

Pierzynski et al. (1990a; 1990b) examined P-rich particles separated from high P soils with energy dispersive x-ray analysis, a technique that determined the elemental composition of the particles. Solubility equilibrium studies were conducted on the same samples. The particles from a given soil were highly variable in composition. Nearly all of the particles examined had detectable quantities of both Al and Si. Calcium did not dominate the elemental composition of particles separated from high pH soils, as thermodynamics would suggest. In general, the element composition of the particles did not support conclusions drawn from solubility equilibrium studies with the exception of low pH soils where the predominance of Al was consistent with both approaches. These studies suggest that solid phase control of P solubility is quite complicated.

Practical Applications of Soil Phosphorus Chemistry

The complexity of soil P chemistry and the difficulty in using chemical principals to predict the behavior of P in soils has led to a more empirical approach for describing the fate and transport of P in the environment. These approaches represent a blend of good chemistry and correlations between measurable soil properties and something that we would like to predict.

Nomenclature for P in soil is certainly an example of finding convenient terms to describe the behavior of P without identifying the chemical processes responsible. The term *fixation* is often used to describe the process by which plant available P in soil is converted to forms that are no longer available for plant uptake. In reality *fixation* represents a combination of adsorption and the precipitation of P containing solid phases. Laboratory studies suggest that adsorption is the dominant process when initial soil P levels are low with precipitation becoming more likely as P levels increase. There are

situations where both processes occur simultaneously. Earlier it was suggested that <1% of the soil P resides in the soil solution, suggesting that this P must be replaced many times over the life of a plant if the plant is to receive adequate P nutrition. Soil P that rapidly equilibrates with an aqueous solution is often referred to as *labile P* while forms of soil P that are slow to equilibrate with an aqueous solution are termed *nonlabile*. Again, the chemical processes involved are not identified but the behavior is described.

Soil test procedures for P are another example of how our knowledge of soil P chemistry can be put to good use. One might conclude that water or a weak salt solution would be the best soil extractant to use to predict P availability for plants since these solutions approximate the composition of the soil solution. In practice, however, these solutions would have P concentrations too low to measure on a routine basis and measure only the intensity of P availability and do not assess capacity. The use of F^- in a soil extractant overcomes both problems by assessing P that is associated with Al in soils. The F^- forms stronger complexes with Al than does P so Al-bound P is released into the extracting solution. It is not known, nor does it matter, whether this P is released from adsorption sites, from a pure crystalline Al phosphate solid, or from some other form of P associated with Al. Similarly, the use of HCO_3^- in an extracting solution for calcareous soils promotes the formation of $CaCO_3$, which releases Ca-bound P. The obvious requirement here is that the results correlate with some useful parameter such as probability of yield response to fertilizer.

The use of P sinks is another approach for assessing the availability of P in soils to plants or even to algae if that soil produced sediment in surface runoff that entered an aquatic ecosystem. Phosphorus sinks include anion exchange resins or membranes or iron oxide coated filter paper. Generally, the procedures using P sinks put the soil in a container along with the sink and a weak salt solution or water. Phosphorus sinks can also be used *in situ*. The sinks place the soil under a strong P concentration gradient because the sink maintains a very low P concentration in the solution. This is quite different than batch extractions where the P concentration in the extractant is increasing over the course of the procedure. Phosphorus that can desorb or dissolve within the time frame of the experiment will be measured. Some authors have argued that this approach is theoretically better than batch extractions because the P sinks mimic the behavior of a root absorbing P from the soil solution. While P uptake by roots is more complicated than acting as a simple sink for P, the general thought is valid and the use of P sinks to predict plant available P would probably be more popular if the batch extractions didn't work so well. Recent use of P sinks to predict potential algal-available P levels in soil also has theoretical merit since sediment entering a surface water body with a low P concentration would be subjected to a strong P concentration gradient in a manner similar to the P sink procedures.

Recent research has demonstrated strong correlations between extractable P, from both batch and P sink methods, and algal-available P and the EPC_0 for a given soil sample (Sims, 1998). The EPC_0 value can be obtained from a P adsorption isotherm and is the equilibrium P concentration at which adsorption equals desorption (Figure 3). Both of these parameters relate to the potential impacts of P on an aquatic ecosystem and suggest

that routine soil test procedures may have some utility in predicting potential environmental impacts of offsite movement of P. This concept will be discussed in more detail in subsequent papers in this session.

The unified P solubility diagram presented by Lindsay (1979) suggests maximum P solubility at a soil solution pH of around 6.8. This pH also approximately corresponds to the point at which P adsorption onto Fe, Mn and Al (hydr)oxides is minimal and where adsorption by carbonates is not an issue. The combination of these two phenomena leads to the generalization of maximum plant availability of P in the pH range of 6.5 to 7.0. This is often used as one reason to lime acid soils to this pH range.

The strong tendency for P to react with Al and Fe can also be used to our advantage. Recent work has shown that adding Al- or Fe-containing substances such as alum (aluminum sulfate) to wastes can reduce P losses in runoff when those wastes are land applied (Shreve et al., 1995; Table 1). The Al and Fe may form (hydr)oxides, which then serve as adsorbents for P or the P may precipitate out directly as Al or Fe phosphates.

Summary

The cycling of P within soils is a combination of complex processes that are not fully understood. Attempts to understand the soil P cycle using principals of pure chemistry has met with limited success. Generalizations about reactions between P and Fe or Al under acidic conditions, and with Ca under alkaline conditions, can be made but the exact mechanisms or species involved cannot always be identified. This has led to nomenclature that is descriptive of the behavior of P in the soil rather than descriptions of processes. Still, our knowledge of soil P chemistry can be put to good use for managing soil P for agronomic and environmental benefits. Examples include development of soil test methods, estimating the pH range of maximum P availability to plants, and development of amendments for waste materials that reduce offsite movement of P.

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Table 1. Reductions in soluble reactive and total P concentrations and loadings in runoff after alum or ferrous sulfate additions to poultry litter. First runoff event, from Shreve et al., 1995.

Treatment	---- concentration ----		----- loadings -----	
	SRP [#]	Total P	SRP	Total P
	----- mg/L -----		----- kg/ha -----	
Litter + alum	10.8b [@]	17.6b	0.083b	0.126b
Litter + ferrous sulfate	19.0b	23.5b	0.226b	0.275b
Litter alone	83.0a	89.3a	0.590a	0.630a
Control	0.7b	1.2c	0.006b	0.010b

[#]SRP=soluble reactive P.

[@]means within a column followed by the same letter are not significantly different at P=0.05.

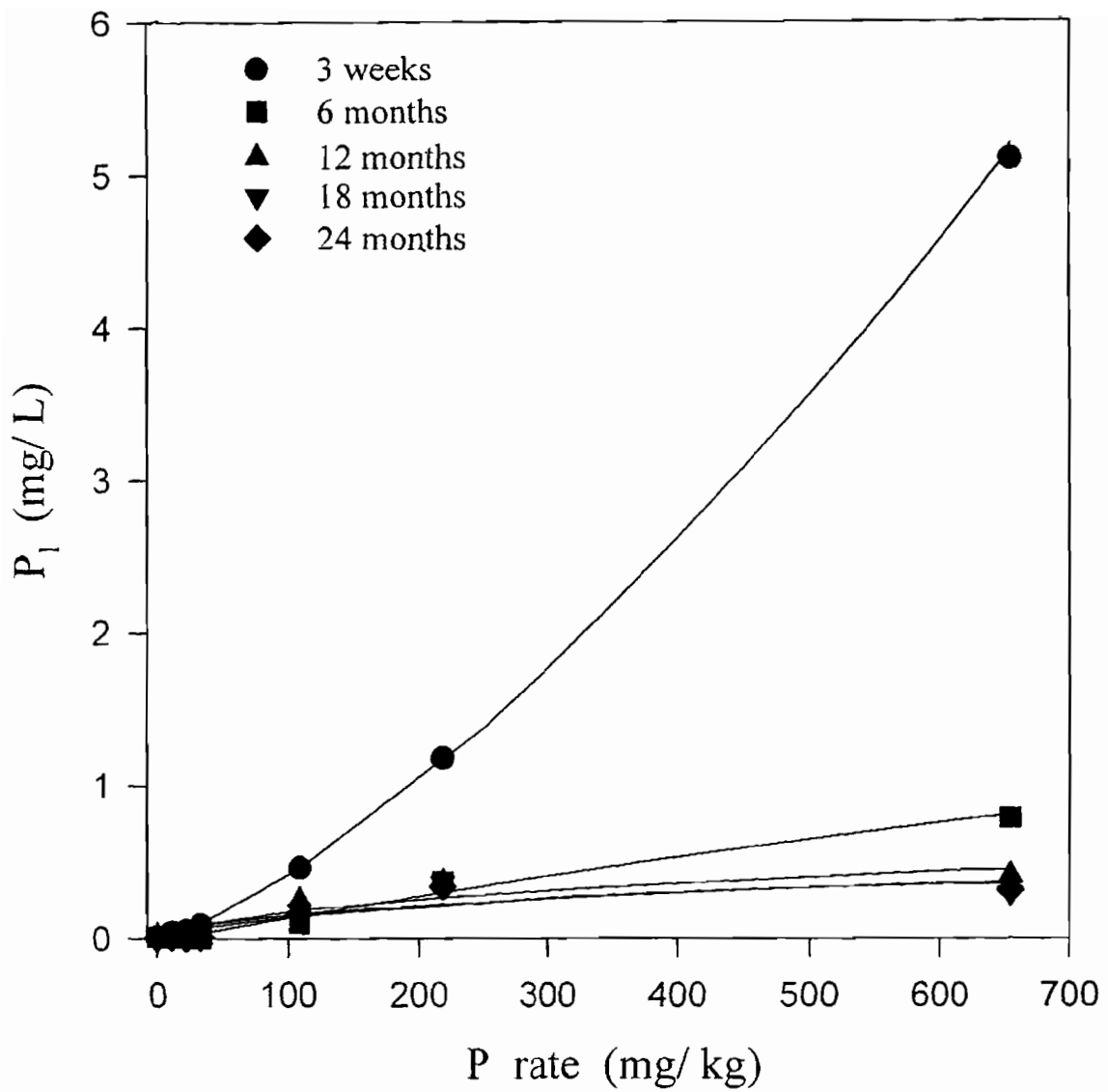


Figure 1. The effect of time and P applications on soil solution P concentration in an acid soil. From Hettiarachchi (1995).

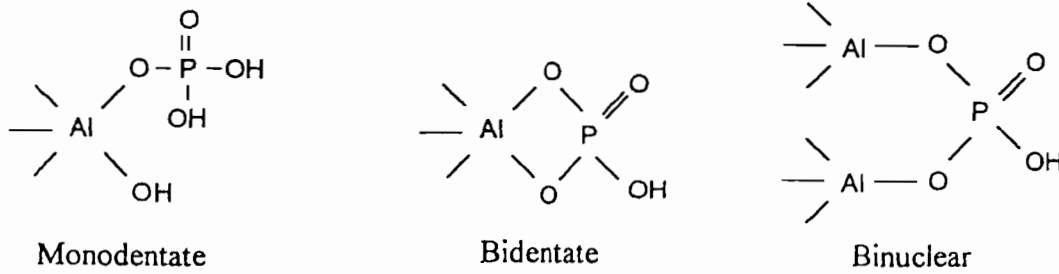


Figure 2. Three forms of P bonding to Al (hydr)oxide minerals. Adapted from Fixen and Grove.(1990).

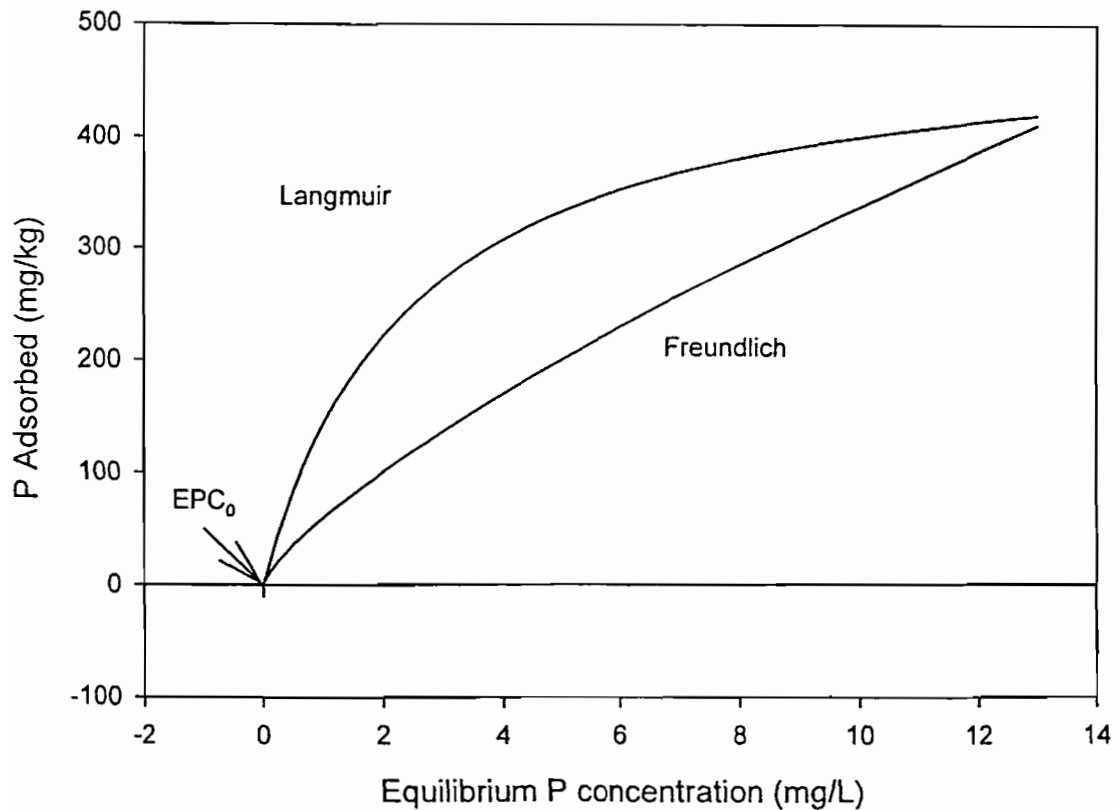


Figure 3. Idealized P adsorption isotherms. The Langmuir predicts an adsorption maximum while the Freundlich does not. The EPC_0 is the point at which there is not net adsorption of P from solution.

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