



5 Phosphorus

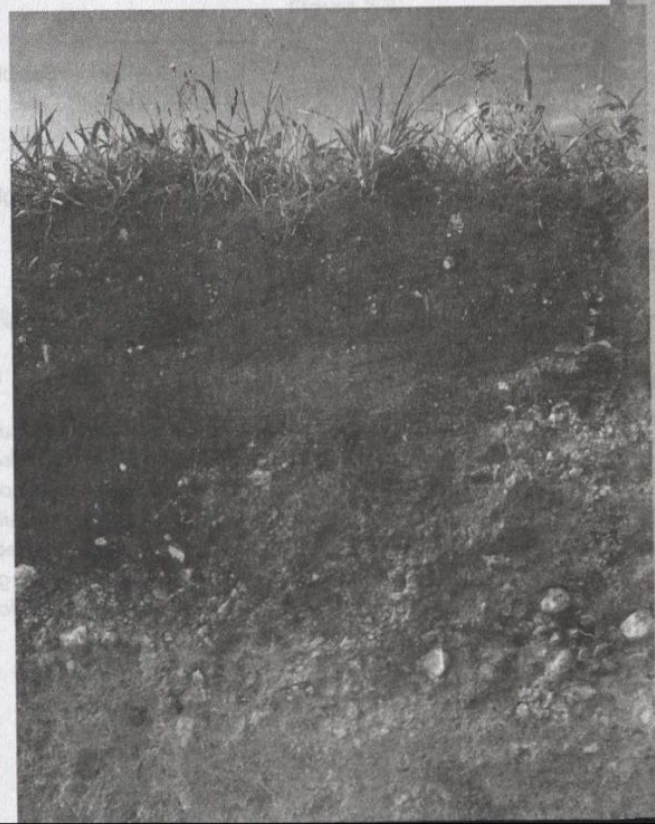
Total phosphorus (P) in surface soils varies from 0.005 to 0.15%, and decreases with increasing weathering intensity. Thus, total soil P is much lower in humid and tropical region soils compared to semi-arid and arid region soils. Unfortunately, the quantity of total soil P has little or no relationship to P availability to plants. Although semi-arid region soils are often high in total P, many are low in plant available P. In contrast, loading soils with P in excess of plant requirements, which is common in soils where manure is continuously applied, may increase potential for P transport to surface and ground waters. Therefore, understanding the relationships and interactions of P in soils and the factors that influence P availability to plants is essential for efficient P management and protection of water quality.

THE P CYCLE

As with N, the relationships between the various P forms in soils can be illustrated in a P cycle (Fig. 5-1). The decrease in soil solution P with absorption by plant roots is buffered by both inorganic and organic P fractions in soils. Primary and secondary P minerals dissolve to resupply H_2PO_4^- and HPO_4^{2-} in solution. Inorganic P (H_2PO_4^- , HPO_4^{2-}) adsorbed on mineral and clay surfaces can also desorb to buffer solution P (Fig. 5-2). Soil microorganisms digest plant residues and other organic amendments (manures, biosolids, etc.) producing organic P compounds that are mineralized through microbial activity to supply solution P.

Water-soluble fertilizer or waste P applied to soil increases P in soil solution. In addition to P uptake by roots, inorganic and organic P fractions buffer the increase in solution P through P adsorption on mineral surfaces, precipitation as secondary P minerals, and immobilization as microbial or organic P. Maintaining solution P concentration (*intensity*) for adequate P nutrition depends on the ability of adsorbed, mineral, and organic P (*quantity*) to replace soil solution P taken up by the plant. The ratio of *quantity* to *intensity* factors defines buffer capacity (BC) or the relative ability of the soil to buffer changes in soil solution P (Fig. 2-15 and 2-16). The larger the BC, the greater the ability to buffer changes in solution P concentration and provide plant available P.

Understanding the dynamics of P transformations in soils will provide the basis for sound management of soil and fertilizer P to ensure adequate P availability to plants (Chapter 10) and to reduce P losses to surface and ground waters (Chapter 12).



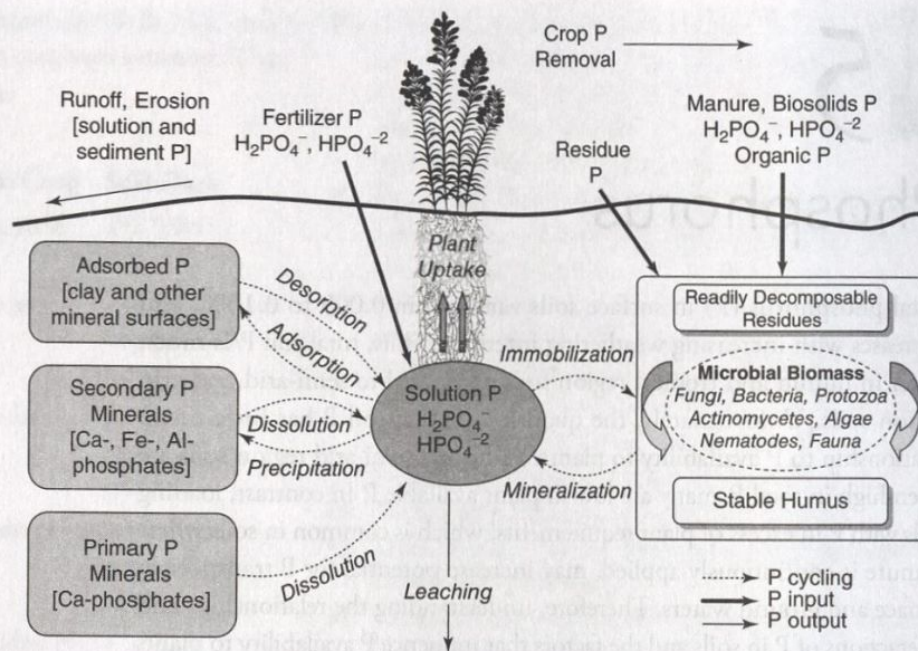


Figure 5-1

P cycling in soil. Internal *P* cycling (dashed lines) between soil solution *P* and adsorbed *P*, solid mineral *P*, and organic *P* controls *P* availability to plants. Removal of *P* from the system occurs primarily through crop removal; however, *P* losses occur from soil erosion, runoff, and leaching.

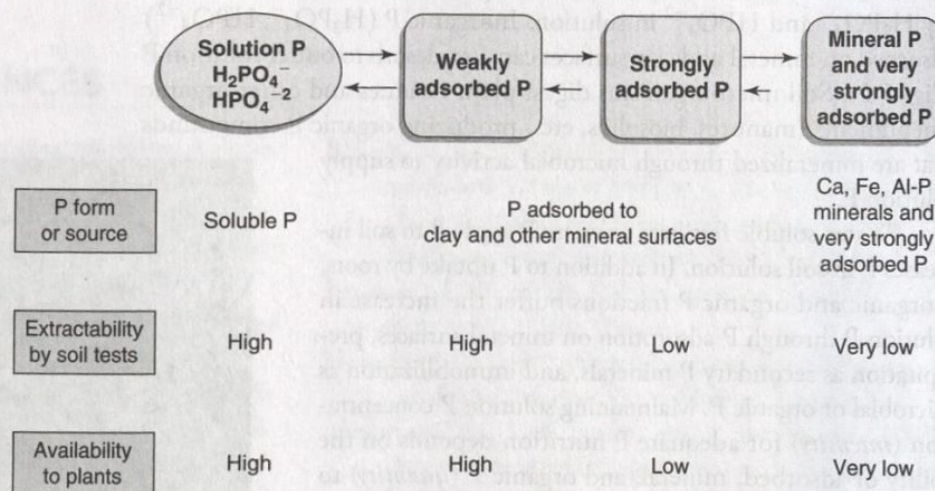


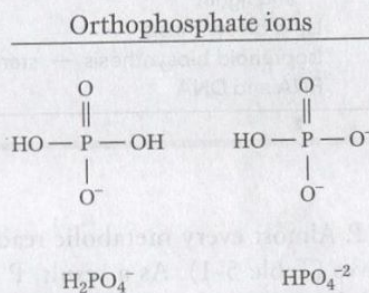
Figure 5-2

Relative plant availability and extractability of inorganic *P* forms in soil. H_2PO_4^- or HPO_4^{2-} in soil solution or weakly adsorbed to AEC sites on mineral surfaces are the dominant *P* sources immediately available to plants. The strongly adsorbed and *P*-containing minerals provide little immediate plant available *P*. The arrows between *P* forms indicate that solution *P* can be converted to any adsorbed or mineral *P* form. While weakly adsorbed *P* (labile *P*) can be readily desorbed to solution (long arrow), strongly adsorbed (non-labile *P*) and mineral *P* conversion to soluble *P* is substantially lower (short arrow).

FORMS AND FUNCTIONS OF P IN PLANTS

Forms

P concentration in plants ranges between 0.1 and 0.5%, considerably lower than N and K. Plants absorb either H_2PO_4^- or HPO_4^{2-} (orthophosphate) depending on soil pH (see p. 191).



Although it has been suggested that plants also absorb soluble, low-molecular weight organic P compounds (i.e., nucleic acid and phytin), these P compounds are likely converted to H_2PO_4^- in the rhizosphere.

Functions

The most essential function of P in plants is in energy storage and transfer. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP) act as "energy currency" within plants (Fig. 5-3). When the terminal H_2PO_4^- molecule from either ADP or ATP is split off, a large amount of chemical energy (12,000 cal/mole) is liberated. Energy obtained from photosynthesis and metabolism of carbohydrates is stored in phosphate compounds for subsequent use in growth and reproductive processes. Phosphorylation is the transfer of energy-rich H_2PO_4^- molecules from ATP to energy-requiring substances in the plant. In this reaction ATP is converted to ADP. ADP and ATP are formed and regenerated in

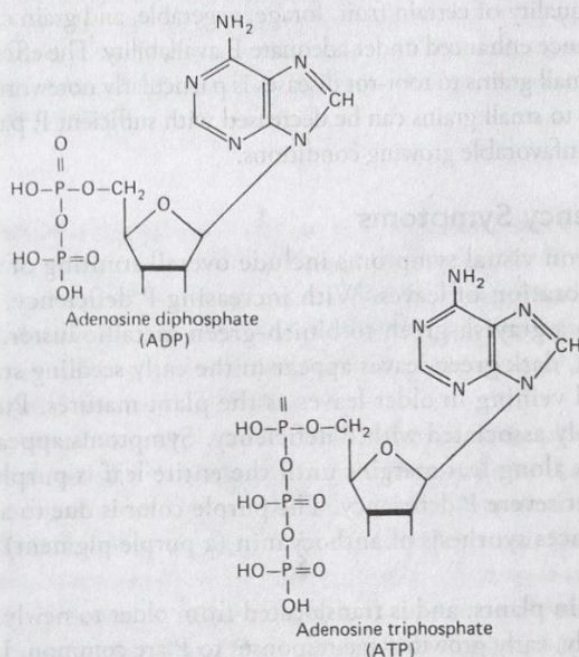


Figure 5-3
Structure of ADP and ATP.

TABLE 5-1
PROCESSES AND FUNCTIONS OF ADP AND ATP IN PLANTS

Membrane transport	Generation of membrane electrical potentials
Cytoplasmic streaming	Respiration
Photosynthesis	Biosynthesis of cellulose, pectins, hemicellulose, and lignin
Protein biosynthesis	Lipid biosynthesis
Phospholipid biosynthesis	Isoprenoid biosynthesis → steroids and gibberellins
Nucleic acid synthesis	RNA and DNA

the presence of sufficient P. Almost every metabolic reaction of any significance involves H_2PO_4^- derivatives (Table 5-1). As a result, P deficiency is associated with restricted growth and development.

P is an essential element in deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) that contain the genetic code of the plant to produce proteins and other compounds essential for plant structure, seed yield, and genetic transfer. Phospholipids, phosphoproteins, coenzymes, and nucleotides are important structural components of membrane chemistry and related functions. Thus, P is essential for vigorous growth and development of reproductive parts (fruits, seeds, etc.).

Adequate P is associated with increased root growth. When soluble H_2PO_4^- is applied in a band, plant roots proliferate extensively in P-treated soil. Similar observations are made with both NO_3^- and NH_4^+ applied in a band near roots (Fig. 5-4). The increased root proliferation should encourage extensive exploitation of the treated soil areas for nutrients and water. Adequate P is essential for fruit and seed development. P also enhances crop maturity and reduces the time required for seed and fruit ripening (Fig. 5-5).

Adequate P increases straw strength in cereals and increases N_2 -fixation capacity of legumes. The quality of certain fruit, forage, vegetable, and grain crops is improved and disease resistance enhanced under adequate P availability. The effect of P on raising the tolerance of small grains to root-rot diseases is particularly noteworthy. Also, the risk of winter damage to small grains can be decreased with sufficient P, particularly on low P soils and with unfavorable growing conditions.

Visual Deficiency Symptoms

The most common visual symptoms include overall stunting of the plant and a darker green coloration of leaves. With increasing P deficiency, the dark green color changes to a grayish-green to bluish-green metallic luster. In some crops (i.e., sugar beets), dark green leaves appear in the early seedling stage, developing to brown, netted veining in older leaves as the plant matures. Purple leaf coloration is commonly associated with P deficiency. Symptoms appear on lower leaf tips and progress along leaf margins until the entire leaf is purple. Lower leaves are necrotic under severe P deficiency. The purple color is due to accumulation of sugars that enhances synthesis of anthocyanin (a purple pigment) in the leaf (see color plates).

P is mobile in plants, and is translocated from older to newly developing tissues. Consequently, early growth stage responses to P are common. In the reproductive stage, P is translocated to fruit and seeds. Thus, P deficiencies late in the growing season affect both seed development and crop maturity.

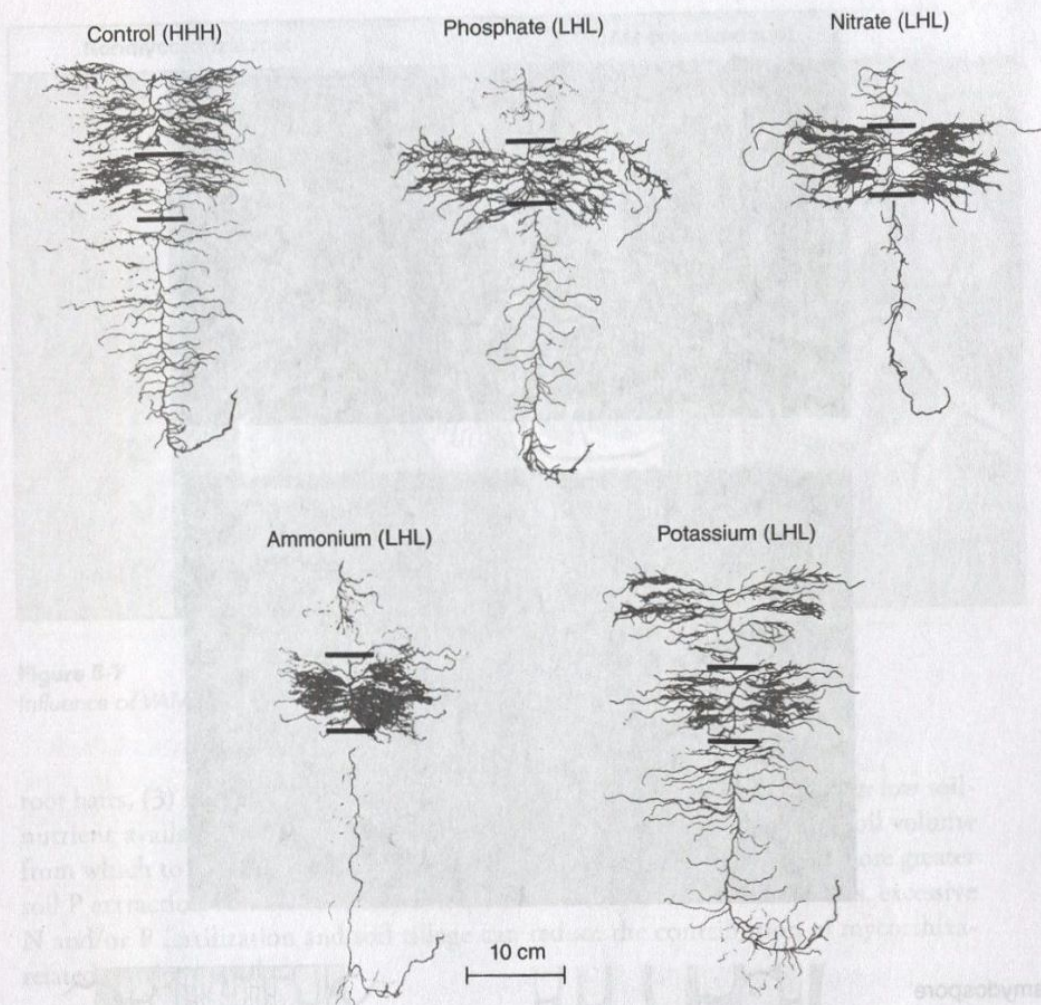


Figure 5-4

Effect of a localized supply of phosphate, nitrate, ammonium, and potassium on root growth. Control plants (HHH) received the complete nutrient solution to all parts of the root system. The other roots (LHL) received the complete nutrient solution only in the middle zone, the top and bottom being supplied with a solution deficient in the specified nutrient.

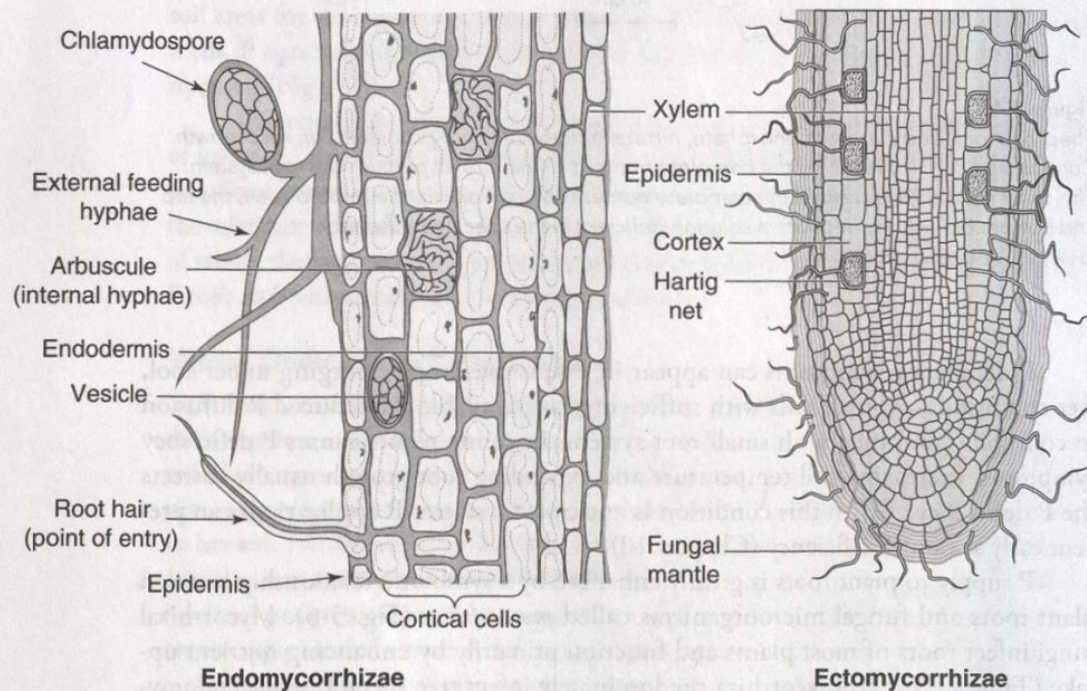
(Drew, 1975, *New Phytol.*, 75:486.)

P deficiency symptoms can appear in P sensitive crops emerging under cool, wet conditions, even in soils with sufficient plant available P. Reduced P diffusion in cool soils combined with small root systems in young plants causes P deficiency symptoms. Increasing soil temperature and expanding root growth usually corrects the P deficiency. When this condition is anticipated, starter P applications can prevent early season P deficiency (Chapter 10).

P supply to plant roots is greatly enhanced by a symbiotic relationship between plant roots and fungal microorganisms called *mycorrhizae* (Fig. 5-6). Mycorrhizal fungi infect roots of most plants and function primarily by enhancing nutrient uptake (Table 2-7). Ectomycorrhiza predominately infect tree species, while endomycorrhiza (vesicular-arbuscular mycorrhiza [VAM]) infect most other plants, although plants vary in the degree of fungal infection. As new roots develop, mycorrhizal fungi infect or enter the root and develop extensive structures extending into and beyond the rhizosphere influenced by root hairs. Plants with a high dependency on VAM generally exhibit (1) low root surface area due to low root branching, (2) few or short

Figure 5-5

Effect of P fertilization on grain sorghum (top) and winter wheat (bottom) maturity. Notice the advanced maturity of both crops receiving P (left) in contrast to those that received no P (right).

**Figure 5-6**

Schematic of primary types of symbiotic mycorrhizal infection of plant roots. Endomycorrhizae, commonly associated with many annual and perennial plants, infect the plant through the root hair, occupying intercellular space and cell membranes in the cortex (arbuscules, vesicles), enhancing nutrient supply to the plant. Ectomycorrhizae, common to woody plants, form a sheath or mantle over the root tips and a cover (Hartig net) over cells in the cortex, which enhances nutrient supply to plant cells.

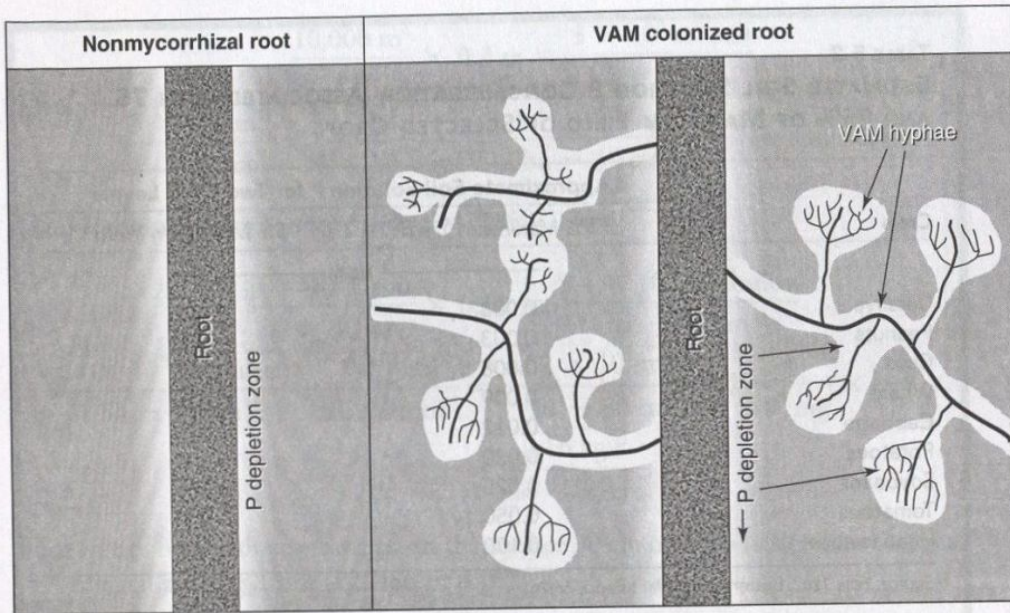


Figure 5-7
Influence of VAM-colonized roots on soil volume accessed for P uptake.

root hairs, (3) slow root growth rate, and (4) reduced root exudation. Under low soil-nutrient availability, VAM-infected roots explore a substantially larger soil volume from which to absorb nutrients. For example, VAM-dependent plants explore greater soil P extraction volume to satisfy P requirement (Fig. 5-7). In many cases, excessive N and/or P fertilization and soil tillage can reduce the contribution of mycorrhiza-related nutrient uptake.

FORMS OF SOIL P

Solution P

The amount of H_2PO_4^- and HPO_4^{2-} present in solution depends on soil pH (Fig. 5-8). At pH 7.2, $\text{H}_2\text{PO}_4^- \approx \text{HPO}_4^{2-}$. Below this pH, $\text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-}$, whereas $\text{HPO}_4^{2-} > \text{H}_2\text{PO}_4^-$ above pH 7.2. Plant uptake of HPO_4^{2-} is much slower than with H_2PO_4^- . Soil solution P concentration varies widely among soils from 10^{-7} (very low) to 10^{-4} M (very high), or 0.003–3 ppm P (average ~0.05 ppm).

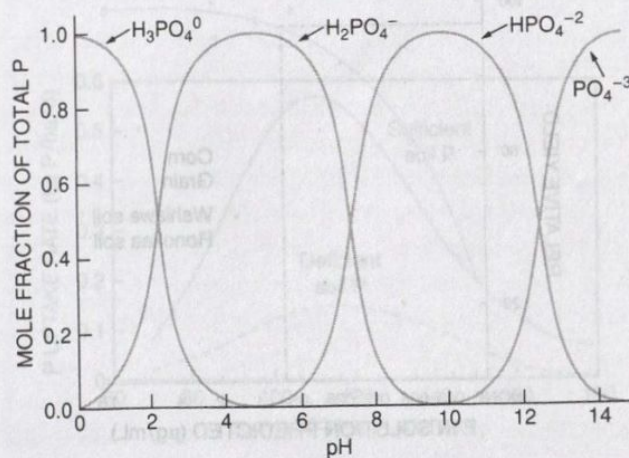


Figure 5-8
Influence of pH on the distribution of orthophosphate species in solution.

TABLE 5-2
ESTIMATED SOIL SOLUTION P CONCENTRATION ASSOCIATED WITH 75
AND 95% OF MAXIMUM YIELD OF SELECTED CROPS

Crop	Approximate Soil Solution P for Two Yield Levels	
	75% Maximum Yield	95% Maximum Yield
	ppm	
Cassava	0.003	0.005
Peanuts	0.003	0.010
Corn	0.008	0.025
Wheat	0.009	0.028
Cabbage	0.012	0.040
Potatoes	0.020	0.180
Soybeans	0.025	0.200
Tomatoes	0.050	0.200
Head lettuce	0.100	0.300

Source: Fox, 1982, Better Crops Plant Food, 66:24.

Soil solution P required by plants depends on crop species and level of production (Table 5-2). For example, maximum corn yields may be obtained with 0.01 ppm P if yield potential is low, but ≥ 0.05 ppm P is needed with high yield potential (Fig. 5-9).

With relatively low solution P concentration (~ 0.05 ppm P), supplying the quantity of P needed or accumulated by plants ($\sim 0.3\%$ P) requires soil solution P to be frequently replenished. The following example illustrates the rate of solution P replenishment needed to meet plant P requirement.

Assume soil solution P concentration = 0.3 ppm P

Calculate kg P/ha in the soil solution:

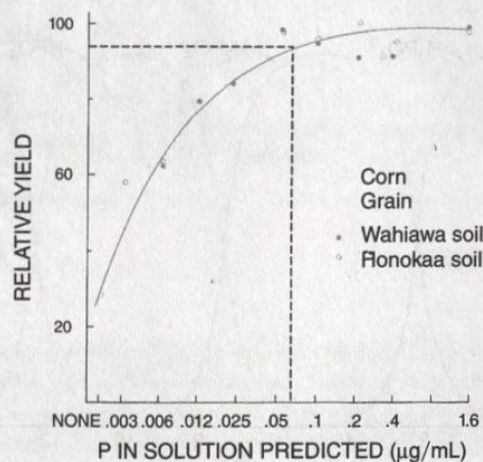
$$0.3 \text{ ppm P} = \frac{0.3 \text{ mg P}}{\text{L solution}} \quad [\text{see note on pg. 193}]$$

Estimate soil water volume (L):

Assume 1 ha area - 30 cm soil depth

Figure 5-9
 Influence of inorganic P in soil solution on corn grain yield.

(Fox, 1981, Chemistry in the Soil Environment, p. 232, ASA, Madison, Wis.)



$$\frac{10,000 \text{ m}^2}{\text{ha}} \times 0.3 \text{ m} = \frac{3 \times 10^3 \text{ m}^3 \text{ soil}}{\text{ha} - 30 \text{ cm}}$$

$$\frac{3 \times 10^3 \text{ m}^3}{\text{ha} - 30 \text{ cm}} \times \frac{1 \text{ L}}{1 \times 10^{-3} \text{ m}^3} = \frac{3 \times 10^6 \text{ L soil}}{\text{ha} - 30 \text{ cm}} \quad [\text{see note below}]$$

Assume volumetric soil water content = 18%

$$\frac{3 \times 10^6 \text{ L soil}}{\text{ha} - 30 \text{ cm}} \times 0.18 = \frac{5.4 \times 10^5 \text{ L solution}}{\text{ha} - 30 \text{ cm}}$$

$$\frac{5.4 \times 10^5 \text{ L solution}}{\text{ha} - 30 \text{ cm}} \times \frac{0.3 \text{ mg P}}{\text{L solution}} = \frac{1.62 \times 10^5 \text{ mg P}}{\text{ha} - 30 \text{ cm}} \times \frac{\text{g}}{10^3 \text{ mg}} \times \frac{\text{kg}}{10^3 \text{ g}}$$

$$= \frac{0.16 \text{ kg P}}{\text{ha} - 30 \text{ cm}}$$

Since we are basing these estimates on the surface 30 cm or 1 ft soil depth, we assume 25% of total rooting depth (120 cm or 4 ft.).

$$\frac{0.16 \text{ kg P}}{\text{ha} - 30 \text{ cm}} \times 0.25 = \frac{0.04 \text{ kg P}}{\text{ha} - 30 \text{ cm}}$$

Thus, 0.3 ppm P in solution represents 0.04 kg P/ha; however, plants generally require 0.3–0.5 kg P/ha/day (Fig. 5-10). Therefore, soil solution P must be resupplied about 10 times each day. Under P deficiency where solution P is tenfold less at 0.03 ppm P (Fig. 5-9), then only 0.004 kg P/ha is available and solution P must be resupplied about 100 times each day.

Note:

Converting ppm to mg/L:

$$0.3 \text{ ppm P} = \frac{0.3 \text{ g P}}{10^6 \text{ g H}_2\text{O}} \times \frac{10^3 \text{ mg}}{\text{g}} \times \frac{1 \text{ g H}_2\text{O}}{\text{mL}} \times \frac{10^3 \text{ mL}}{\text{L}} = \frac{0.3 \text{ mg P}}{\text{L solution}}$$

Converting m³ to L:

$$\frac{1 \text{ mL}}{\text{cm}^3} \times \frac{\text{L}}{10^3 \text{ mL}} \times \left(\frac{10^2 \text{ cm}}{\text{m}}\right)^3 = \frac{\text{L}}{1 \times 10^{-3} \text{ m}^3}$$

where,

$$\left(\frac{10^2 \text{ cm}}{\text{m}}\right)^3 = \frac{10^6 \text{ cm}^3}{\text{m}^3}$$

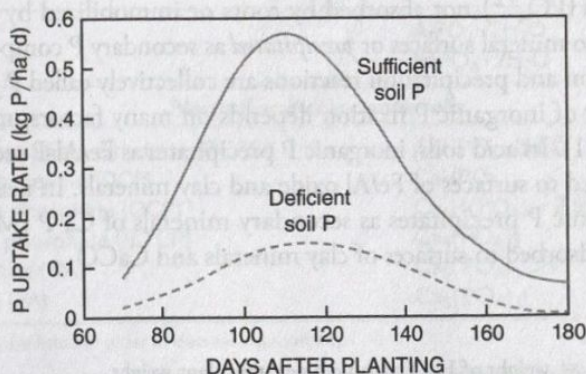


Figure 5-10

Influence of soil P availability on rate of P uptake in spring barley.

(Adapted from Leigh and Johnston, 1986, J. Agric. Sci., 107:329-333.)

TABLE 5-3
DIFFUSION COEFFICIENTS AND DIFFUSION RATE OF SELECTED IONS IN SOIL SOLUTION

Ion	Diffusion Coefficient		Diffusion Rate mm/day
	Range	Average	
	m^2/sec		
NO_3^-	10^{-10} to 10^{-11}	5×10^{-11}	3.0
K^+	10^{-11} to 10^{-12}	5×10^{-12}	0.9
$H_2PO_4^-$	10^{-12} to 10^{-15}	1×10^{-13}	0.13

The actively absorbing surface of plant roots is the young tissue near the root tips. Rapid replenishment of solution P is important where roots are actively absorbing P. As roots absorb P from soil solution, diffusion and mass flow transport additional P to the root surface (Chapter 2). Mass flow in low P soils provides very little of the P requirement. For example, assume a transpiration ratio¹ of 400 and 0.3% P in the crop. If the average solution concentration is 0.05 ppm P, then the quantity of P moving to the plant by mass flow is:

$$\frac{400 \text{ g H}_2\text{O}}{\text{g plant}} \times \frac{100 \text{ g plant}}{0.3 \text{ g P}} \times \frac{0.05 \text{ g P}}{10^6 \text{ g H}_2\text{O}} \times 100 = 0.67\%$$

In fertilized soil with a solution concentration of 1 ppm P, mass flow contributes approximately 13% of the total requirement. The very high P concentrations (2–14 ppm) that exist temporarily in and near fertilizer bands are expected to encourage further P uptake by mass flow and diffusion. Since mass flow provides little P to the root surface, P diffusion is the primary mechanism of P transport, especially in low P soils (Chapter 2).

In soil solution, $H_2PO_4^-$ diffusion rate is also low compared to other ions (Table 5-3). Using an average diffusion coefficient of $1 \times 10^{-13} m^2/sec$, $H_2PO_4^-$ diffusion would be only 0.13 mm/day, which explains why sufficient supply of readily available P throughout the soil volume explored by roots is essential to meet crop P demand. Low solution P and low P diffusion rate help explain why plants frequently respond to P fertilizer placed in concentrated bands near active roots (Chapter 10).

Inorganic Soil P

As organic P is mineralized to inorganic P or as P is added to soil, inorganic P in solution ($H_2PO_4^-/HPO_4^{2-}$) not absorbed by roots or immobilized by microorganisms can be *adsorbed* to mineral surfaces or *precipitated* as secondary P compounds (Fig. 5-1). Surface adsorption and precipitation reactions are collectively called P *fixation* or retention. The extent of inorganic P fixation depends on many factors, most importantly soil pH (Fig. 5-11). In acid soils, inorganic P precipitates as Fe/Al-P secondary minerals and/or is adsorbed to surfaces of Fe/Al oxide and clay minerals. In neutral and calcareous soils, inorganic P precipitates as secondary minerals of Ca-P (Mg-P in high Mg soils) and/or is adsorbed to surfaces of clay minerals and $CaCO_3$.

¹Transpiration ratio = weight of H_2O transpired per unit plant weight.

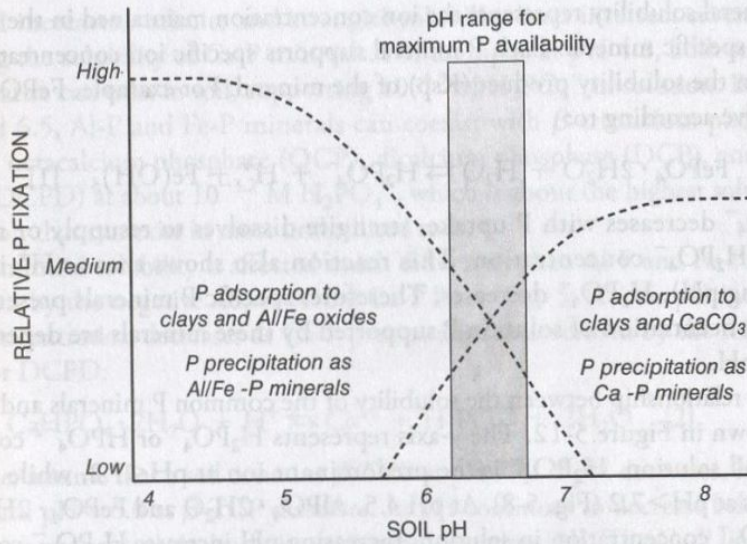


Figure 5-11
Relative effect of soil pH on P adsorption and precipitation.

P fixation is a continuous sequence of precipitation and adsorption. With low solution P concentrations, adsorption dominates, while precipitation reactions proceed when solution P exceeds the solubility product (K_{sp}) of the specific P-containing mineral (Chapter 2). Where water-soluble fertilizers or organic wastes are applied, soil solution P concentration increases greatly depending on P rate and method of application (band vs. broadcast). Both adsorption and precipitation reactions occur, to some extent, immediately following P addition. P precipitation reactions occur as solution P exceeds a specific mineral solubility, while adsorption occurs when adsorption capacity is not saturated with P. Regardless of the contributions of adsorption and precipitation, understanding P fixation processes is important for optimum P nutrition and efficient fertilizer P management.

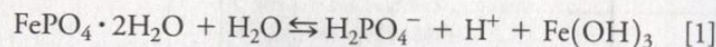
P Mineral Solubility The P cycle illustrates that solution P levels are buffered by adsorbed P on mineral surfaces, organic P mineralization, and P mineral dissolution (Fig. 5-1). Ultimately, solution P concentration is controlled by P mineral solubility. The most common P minerals found in acid soils are Al-P and Fe-P minerals, while Ca-P minerals predominate in neutral and calcareous soils (Table 5-4).

TABLE 5-4
COMMON P MINERALS FOUND IN ACID, NEUTRAL, AND CALCREOUS SOILS

<i>Acid soils</i>	
Variscite	$AlPO_4 \cdot 2H_2O$
Strengite	$FePO_4 \cdot 2H_2O$
<i>Neutral and calcareous soils</i>	
Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4 \cdot 2H_2O$
Dicalcium phosphate (DCP)	$CaHPO_4$
Octacalcium phosphate (OCP)	$Ca_8H(PO_4)_3 \cdot 2.5H_2O$
β -tricalcium phosphate (β -TCP)	$Ca_3(PO_4)_2$
Hydroxyapatite (HA)	$Ca_5(PO_4)_3OH$
Fluorapatite (FA)	$Ca_5(PO_4)_3F$

Note: Minerals are listed in order of decreasing solubility.

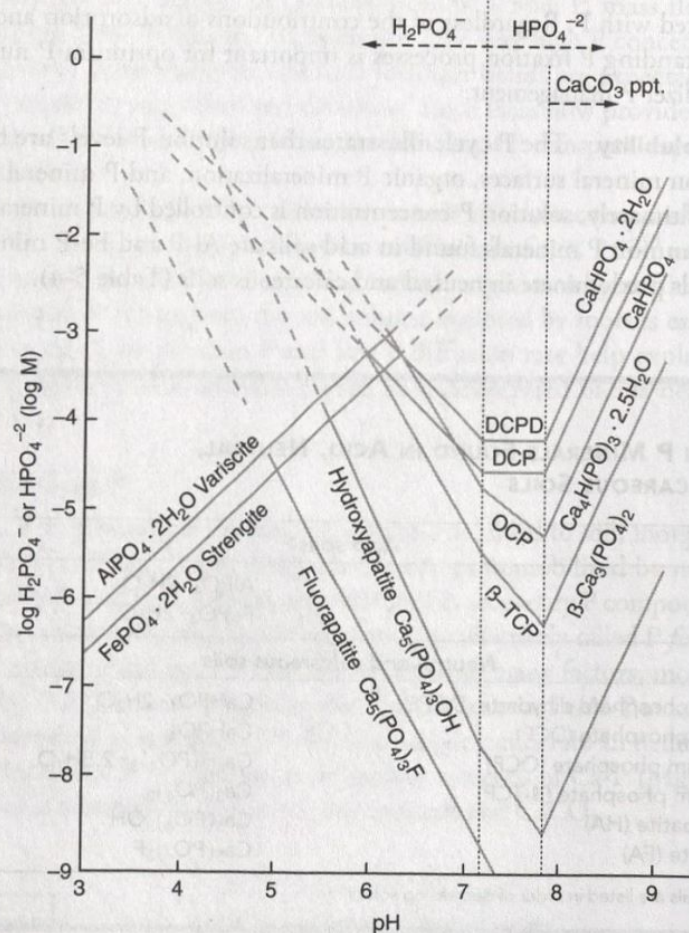
Mineral solubility represents the ion concentration maintained in the soil solution by a specific mineral. Each P mineral supports specific ion concentrations that depend on the solubility product (K_{sp}) of the mineral. For example, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ will dissolve according to:



As H_2PO_4^- decreases with P uptake, strengite dissolves to resupply or maintain solution H_2PO_4^- concentration. This reaction also shows that as H^+ increases (decreasing pH), H_2PO_4^- decreases. Therefore, specific P minerals present in soil and the concentration of solution P supported by these minerals are dependent on solution pH.

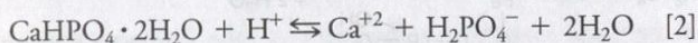
The relationship between the solubility of the common P minerals and solution pH is shown in Figure 5-12. The y-axis represents H_2PO_4^- or HPO_4^{2-} concentration in soil solution. H_2PO_4^- is the predominant ion at $\text{pH} < 7.2$, while HPO_4^{2-} dominates at $\text{pH} > 7.2$ (Fig. 5-8). At pH 4.5, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ control H_2PO_4^- concentration in solution. Increasing pH increases H_2PO_4^- concentration because the Al-P and/or Fe-P minerals dissolve according to reaction [1], which is also depicted in the diagram as a positive slope. Increasing P availability is often observed when acid soils are limed. Also, hydroxyapatite or fluorapatite can be used as a fertilizer in low pH soils ($\text{pH} < 4.5$), as shown by their high solubility at low pH (Fig. 5-12). In contrast, they cannot be used to supply plant available P in neutral or calcareous soils because of their low solubility.

Figure 5-12
Solubility of Ca, Al, and Fe phosphate minerals in soils.
See text for discussion.
(Adapted from Lindsay, 1979,
Chemical Equilibria in Soils, Wiley
Interscience, p. 181.)



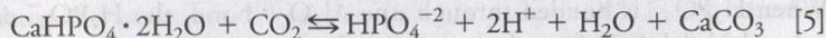
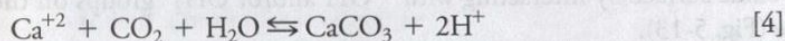
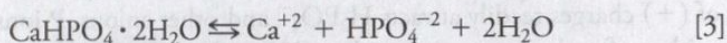
As pH increases, variscite and strengite solubility lines intersect several lines representing the solubility of Ca-P minerals. For example, at pH 4.8, both strengite and fluorapatite can exist in soil, supporting $10^{-4.5}$ M H_2PO_4^- in solution. Between pH 6.0 and 6.5, Al-P and Fe-P minerals can coexist with β -tricalcium phosphate (β -TCP), octacalcium phosphate (OCP), dicalcium phosphate (DCP), and DCP dihydrate (DCPD) at about $10^{-3.2}$ M H_2PO_4^- , which is about the highest solution P concentration that can exist in most unfertilized soils.

Ca-P mineral solubility is affected much differently than Al-P and Fe-P minerals, as shown by the negative slopes of the Ca-P lines (Fig. 5-12). As pH increases, H_2PO_4^- concentration decreases as Ca-P precipitates, as described by the following equation for DCPD:



For example, assume that a soil contains β -TCP at pH 7.0. If pH decreases, H_2PO_4^- increases until pH \approx 6.0 as β -TCP dissolves. As pH continues to decrease below 6.0, H_2PO_4^- decreases as strengite/variscite precipitate (reaction [1]). The Ca-P lines (Fig. 5-12) change slopes at pH > 7.2 because HPO_4^{-2} predominates in solution compared with H_2PO_4^- . The solubility lines represent only HPO_4^{-2} at pH > 7.2.

Above pH 7.8, Ca-P solubility lines exhibit a positive slope, which means that as pH increases above 7.8, HPO_4^{-2} concentration increases. The change in solubility is due to the competing reaction of CaCO_3 solubility given by:



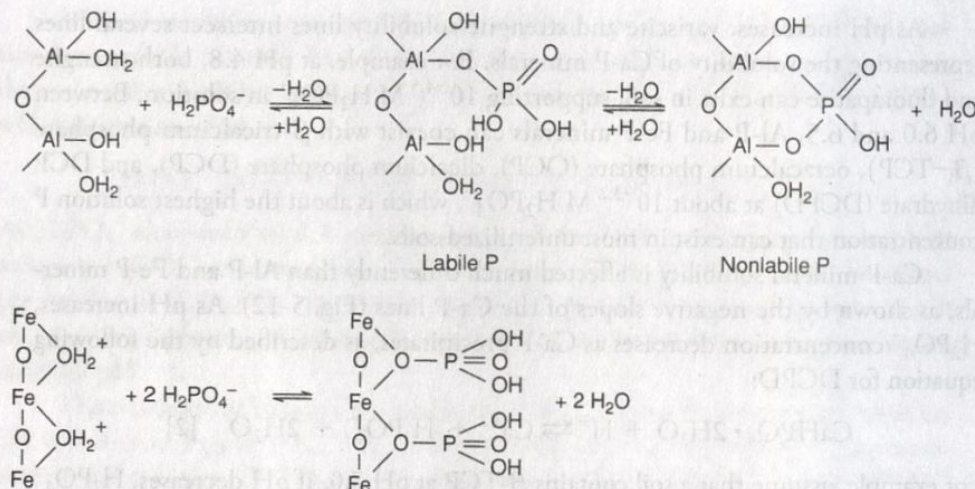
CaCO_3 precipitation occurs at pH 7.8 and above. As solution Ca^{+2} decreases with CaCO_3 precipitation (reaction [4]), DCPD will dissolve (reaction [3]) to resupply solution Ca^{+2} . When DCPD dissolves, HPO_4^{-2} increases (reaction [5]), which is the sum of reactions [3] and [4]. All Ca-P minerals (Table 5-4) behave similarly in calcareous soils. Even though these P solubility relationships show solution P concentration increasing above pH 7.8, P availability to plants can decrease by HPO_4^{-2} adsorption to the precipitating CaCO_3 .

P minerals that support the lowest P concentration (lowest P solubility) are the most stable in soils. For example, apatite minerals (β -TCP and OCP) are more stable than DCPD in slightly acid and neutral soils. Therefore, P mineral-solubility relationships (Fig. 5-12) can be used to understand the fate of inorganic P applied to soils (see "Behavior of P Fertilizers in Soils").

An important fertilizer P source is monocalcium phosphate (MCP) [$\text{Ca}(\text{H}_2\text{PO}_4)_2$], which is very soluble in soil. When MCP dissolves, H_2PO_4^- concentration is much higher than P concentrations supported by native P minerals (Fig. 5-12). Because soil P minerals have lower solubility, H_2PO_4^- from fertilizer will likely precipitate as these minerals. For example, in an acid soil, fertilizer H_2PO_4^- reacts with solution Al^{+3} and Fe^{+3} to form AlPO_4 and FePO_4 compounds, respectively. As a result, solution H_2PO_4^- decreases once the precipitation reactions begin. In neutral and calcareous soils, fertilizer H_2PO_4^- initially precipitates as DCPD and DCP within the first few weeks after application. After 3–5 months, OCP begins to precipitate, with β -TCP forming after 8–10 months. After long periods of time, apatite minerals may eventually form. Thus, after MCP is applied to soil, reactions occur that decrease the elevated solution H_2PO_4^- concentration as insoluble P minerals precipitate. These reactions cannot be controlled and explain why plant recovery of applied P is lower than recovery of soluble nutrients such as NO_3^- and SO_4^{-2} .

Figure 5-13

Mechanism of P adsorption to Al/Fe oxide surface. Phosphate bonding through one Al-O bond results in readily desorbed (labile) P; however, bonding through two Fe-O or Al-O bonds produces a stable structure that results in very little P desorption.



P Adsorption Reactions H₂PO₄⁻ and/or HPO₄⁻² will adsorb to mineral surfaces (Fig. 5-1). In acid soils, Al and Fe oxide and hydroxide minerals are primarily involved in P adsorption. Because of the acidic solution, the mineral edge surface has a net (+) charge, although both (+) and (-) sites exist (Chapter 2). The predominance of (+) charges readily attracts H₂PO₄⁻ and other anions. P ions adsorb to the Fe/Al oxide surface by interacting with -OH and/or OH₂⁺ groups on the mineral surface (Fig. 5-13).

When H₂PO₄⁻ is bonded through one Al-O-P bond, the H₂PO₄⁻ can be readily desorbed (labile P) from the mineral surface to soil solution. When H₂PO₄⁻ bonds with two Al-O, a stable six-member ring is formed (Fig. 5-13). Consequently, desorption is more difficult (non-labile P), reducing plant available P. In acid soils, P adsorption also readily occurs on the broken edges of kaolinite clay minerals (Fig. 2-9). Again, exposed -OH groups can exchange for H₂PO₄⁻ similarly to surface exchange with Fe/Al oxides. Cations held to the surface of silicate clay minerals also influence P adsorption by developing a small (+) charge near the mineral surface saturated with cations. This small (+) charge attracts small quantities of anions such as H₂PO₄⁻. As discussed earlier, precipitation of Al-P minerals in acid soils and Ca-P minerals in neutral and calcareous soils occurs at high P concentrations.

In calcareous soils, small quantities of P can be adsorbed through replacement of CO₃⁻² on CaCO₃ surfaces. At low P concentrations, surface adsorption predominates; however, at high P concentrations, Ca-P minerals precipitate on the CaCO₃ surfaces. Other minerals, mostly Al(OH)₃ and Fe(OH)₃, also contribute to adsorption of solution P in calcareous soils.

Adsorption Equations

Many equations can be used to describe the adsorption of ions or compounds on mineral surfaces (Fig. 5-14). Freundlich and Langmuir equations are commonly used and are helpful in understanding the relationship between quantity of P adsorbed per unit soil weight and the concentration of P in solution. The Freundlich equation is represented by:

$$Q = aC^{-x}$$

where Q = quantity of P adsorbed on mineral surface (per unit soil weight)

C = solution P concentration

a, x = coefficients that vary among soils

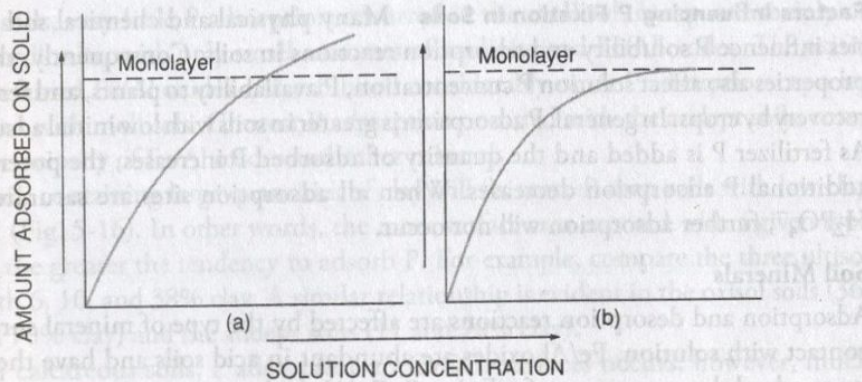


Figure 5-14
Graphical representation of adsorption isotherms of the Freundlich (a) and Langmuir (b) equations used to describe P adsorption in soils.

The Freundlich equation does not include a maximum adsorption capacity and therefore is reliable at low solution P concentrations (Fig. 5-14). Since P adsorption data exhibit a maximum P adsorption capacity at some solution P concentration, another equation is needed to describe situations in which the adsorption sites are saturated with P.

The Langmuir equation includes a term for the maximum P adsorption described by:

$$Q = \frac{abC}{1 + aC}$$

where Q, C, a = defined as before
b = P adsorption maximum

P adsorption maximum "b" implies that a monolayer of P ions is adsorbed on the surface of the mineral, which occurs at relatively higher solution P concentrations than described by the Freundlich equation. The Langmuir equation also shows that further increases in solution P concentration do not increase P adsorption.

Adsorption equations provide no information about adsorption mechanisms or whether Fe/Al oxides, silicate clays, or CaCO₃ dominate adsorption reactions. P adsorption is initially rapid, slowing with time, as the adsorption sites become saturated with P. Once maximum P adsorption is attained, if P is continually added to soil, the solution P concentration will rapidly increase with no additional increase in adsorbed P. Under this scenario, potential soluble P transport by surface runoff or leaching enhances risk to water quality (Chapter 12).

In general, adsorbed P is not readily desorbed. *Hysteresis* occurs when the quantity of adsorbed P (or other ion or compound) is greater than can be desorbed (Fig. 5-15). The extent of desorption depends on the nature of the adsorption mechanism at the mineral surface. With P adsorption on Al/Fe oxides, formation of ring structures limits P desorption (Fig. 5-13), and contributes to hysteresis of P in soils.

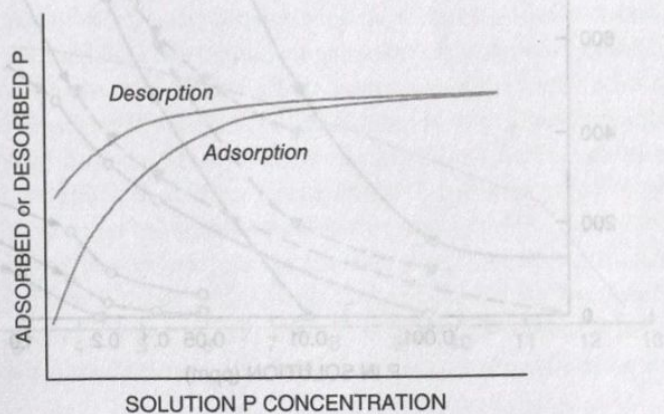


Figure 5-15
General depiction of hysteresis in soil, where the quantity of P desorbed is less than the quantity of P adsorbed.

andepht soils, very little P adsorption occurred in the mollisol, composed mainly of montmorillonite, with only small amounts of kaolinite and Fe/Al oxides. The oxisol soils contained Fe/Al oxides and exhibited considerably more P adsorption capacity compared with mollisols. Greatest P adsorption occurred with the andepht soils, composed principally of Fe/Al oxides and other minerals.

Soils containing large quantities of clay will fix more P than soils with low clay content (Fig. 5-16). In other words, the more surface area exposed with a given type of clay, the greater the tendency to adsorb P. For example, compare the three ultisol soils with 6, 10, and 38% clay. A similar relationship is evident in the oxisol soils (36, 45, and 70% clay) and the andepht soils (11 and 70% clay).

In calcareous soils, P adsorption to CaCO_3 surfaces occurs; however, much of the adsorption is attributed to Fe oxide impurities. The amount and reactivity of CaCO_3 will influence P fixation. Impure CaCO_3 with large surface area exhibits greater P adsorption and more rapid precipitation of Ca-P minerals. Calcareous soils with highly reactive CaCO_3 and high Ca-saturated clay content will exhibit low solution P levels, since P can readily precipitate or adsorb.

In relative terms, acid soils fix twice as much P per unit surface area than neutral or calcareous soils. In addition, adsorbed P is held with five times more bonding energy in acid soils than in calcareous soils. To maintain a given level of solution P in soils with a high fixation capacity, it is necessary to add larger quantities of P fertilizers (Fig. 2-16). Larger additions of P are required to reach a given solution P concentration in fine-textured compared with coarse-textured soils. Consequently, high clay soils often require more fertilizer P than loam soils to optimize yields.

Soil pH

P adsorption by Fe/Al oxides declines with increasing pH. Gibbsite [$\text{Al}(\text{OH})_3$] adsorbs the greatest amount of P at pH 4–5, while P adsorption by goethite (FeOOH) decreases steadily between pH 3 and 12 (Fig. 5-17).

P availability in most soils is at a maximum near pH 6.5 (Fig. 5-11). At low pH, P fixation is largely from reaction with Fe/Al oxides and precipitation as AlPO_4 and FePO_4 (Fig. 5-12). As pH increases, solution Fe and Al decreases, which reduces P adsorption/precipitation and increases solution P concentration. Above pH 7.0, Ca^{+2} precipitates with P as Ca-P minerals (Fig. 5-12) and P availability decreases. Minimum P adsorption at pH 6.0–6.5 (Fig. 5-11) corresponds with the pH range of maximum P solubility (Fig. 5-12). Liming acidic soils generally increases P in solution. Overliming can depress P solubility due to the formation of insoluble Ca-P minerals.

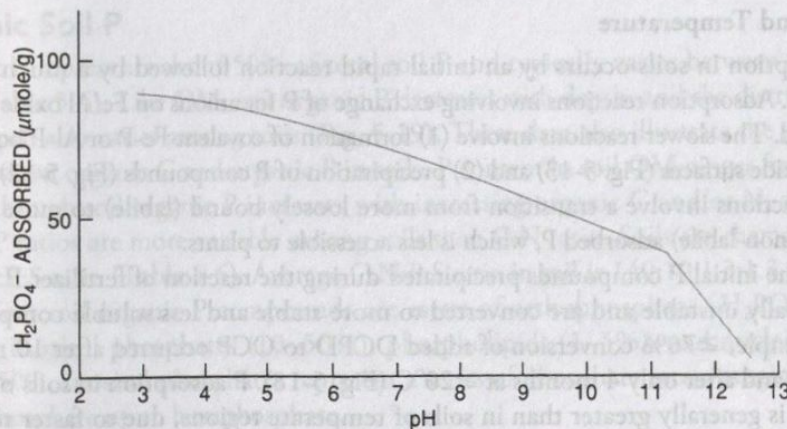


Figure 5-17
Percentage of H_2PO_4^- converted to DCP as a function of time and temperature. Adapted from Shogren and Price, 1981, *Soil Science Society of America*, 45: 173.

Figure 5-17
The adsorption of P by Fe oxide (goethite) as influenced by soil pH.

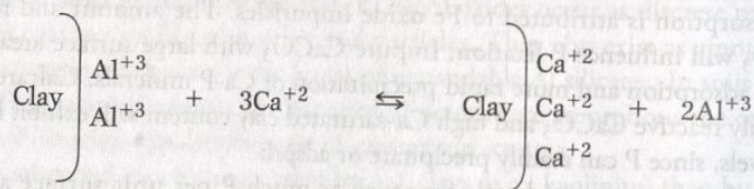
(Adapted from Hingston et al., 1968, *Trans. 9th Int. Cong. Soil Sci.*, 1:1459–1461.)

Cation and Anion Effects

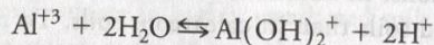
Divalent cations on the CEC enhance P adsorption relative to monovalent cations. For example, clays saturated with Ca^{+2} retain greater amounts of P than those saturated with Na^+ or other monovalent ions. Divalent cations increase the accessibility of (+)-charged edges of clay minerals to P. This occurs at $\text{pH} < 6.5$, because at greater soil pH Ca-P minerals would precipitate.

Concentration of exchangeable Al^{+3} is also an important factor in P adsorption in soils since 1 meq of exchangeable Al^{+3} /100 g soil may precipitate up to 100 ppm P in solution. The following illustrates how hydrolyzed Al^{+3} adsorbs soluble P.

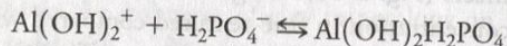
Step 1. Cation exchange



Step 2. Hydrolysis



Step 3. Precipitation and/or adsorption



Both inorganic and organic anions can compete with P for adsorption sites, resulting in decreased P adsorption. Weakly held inorganic anions such as NO_3^- and Cl^- are of little consequence, whereas adsorbed OH^- , H_3SiO_4^- , SO_4^{-2} , and MoO_4^{-2} can be competitive. The anion adsorption strength determines the competitive ability. For example, SO_4^{-2} is unable to desorb much H_2PO_4^- , since H_2PO_4^- is capable of forming a stronger bond than is SO_4^{-2} .

Soil OM

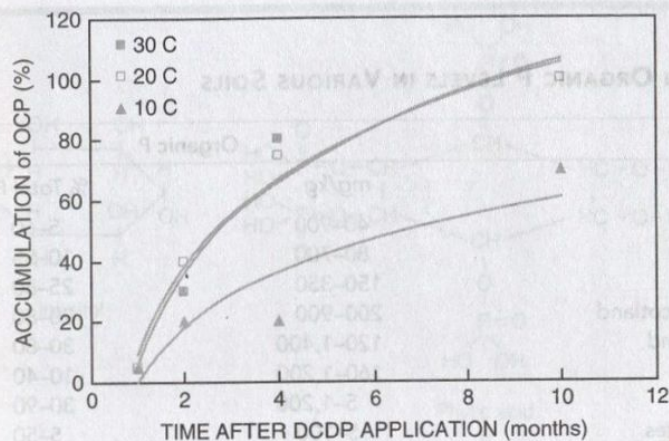
Organic compounds in soils increase P availability by (1) formation of organophosphate complexes that are more soluble, (2) organic anion replacement of H_2PO_4^- on adsorption sites, (3) coating of Fe/Al oxides by humus to form a protective cover and reduce P adsorption, and (4) increasing the quantity of organic P mineralized to inorganic P.

Organic anions produced from OM decomposition form stable complexes with Fe and Al, preventing reaction with H_2PO_4^- . These complex ions exchange for P adsorbed on Fe/Al oxides. Anions that are most effective in replacing H_2PO_4^- are citrate, oxalate, tartrate, and malate.

Time and Temperature

P adsorption in soils occurs by an initial rapid reaction followed by a much slower reaction. Adsorption reactions involving exchange of P for anions on Fe/Al oxide surface are rapid. The slower reactions involve (1) formation of covalent Fe-P or Al-P bonds on Fe/Al oxide surfaces (Fig. 5-13) and (2) precipitation of P compounds (Fig. 5-12). These slow reactions involve a transition from more loosely bound (labile) to more tightly bound (non-labile) adsorbed P, which is less accessible to plants.

The initial P compounds precipitated during the reaction of fertilizer P in soils are initially unstable and are converted to more stable and less soluble compounds. For example, $\geq 70\%$ conversion of added DCPD to OCP occurred after 10 months at 10°C and after only 4 months at $\geq 20^\circ\text{C}$ (Fig. 5-18). P adsorption in soils of warm regions is generally greater than in soils of temperate regions, due to faster reaction

**Figure 5-18**

Percentage of DCPD converted to OCP as a function of time and temperature.

(Adapted from Sheppard and Racz, 1980, Western Canada Phosphate Symp., p. 170.)

rates and higher Fe/Al oxide content associated with a greater mineral weathering environment. Mineralization of P from soil OM or crop residues depends on soil biological activity, which increases with increasing temperature. Usually, mineralization rates double with each 10°C increase in temperature (Fig. 4-22).

Flooding

In most soils plant available P increases after flooding, largely due to a conversion of Fe⁺³-P minerals to more soluble Fe⁺²-P minerals. Other mechanisms include increased mineralization of organic P in acid soils and increased solubility of Ca-P in calcareous soils. These changes in P availability explain why response to applied P by irrigated rice is usually less than an upland crop grown on the same soil.

Fertilizer P Management Considerations

An important practical consequence of P adsorption and precipitation reactions is the time after application during which the plant is best able to utilize the added P. On soils with high P-fixation capacity, this period may be short, whereas with other soils it may last for months or even years. The reaction time will determine whether fertilizer P should be applied at one time in the rotation or in smaller, more frequent applications.

Adsorption of fertilizer P is greater in fine-textured soils because the reactive mineral surface area is greater than in coarse-textured soils. Also, if fertilizer P is broadcast applied, P is exposed to a greater amount of soil; hence, more P fixation occurs than if the same amount of P is band applied. Band placement reduces contact between soil and fertilizer, with a subsequent reduction in P adsorption (see Chapter 10). Although this is only one factor to consider in P fertilizer placement, it is very important for crops grown on low P soils with a high P adsorption capacity, where band placement generally increases plant utilization of fertilizer P.

Organic Soil P

Organic P represents about 50% of total soil P and typically varies between 15 and 80% (Table 5-5). Like OM, soil organic P decreases with depth, and the distribution with depth also varies among soils (Fig. 5-19). These data also illustrate the correlation between organic C and organic P in soils. P content in soil OM ranges from 1 to 3%. Although soil organic P increases with increasing organic C and/or N, the C:P and N:P ratios are more variable among soils than C:N ratio. Soils are characterized by C:N:P:S ratio (Table 5-6). Average C:N:P:S ratio in soil is 140:10:1.3:1.3.

Most soil organic P compounds are esters of orthophosphate (H₂PO₄⁻) including inositol phosphates (10–50%), phospholipids (1–5%), and nucleic acids (0.2–2.5%). Inositol phosphates represent a series of phosphate esters ranging from monophosphate up to hexaphosphate.

TABLE 5-5
RANGE IN ORGANIC P LEVELS IN VARIOUS SOILS

Location	Organic P	
	mg/kg	% Total P
Australia	40-900	5-60
Canada	80-700	10-55
Denmark	150-350	25-80
England, Scotland	200-900	20-80
New Zealand	120-1,400	30-80
Nigeria	160-1,200	10-40*
Tanzania	5-1,200	30-90
United States	5-100	5-50

Figure 5-19

Distribution of organic P and C with depth in lowa mollisol and alfisol soils.
 (Adapted from Stevenson, 1986, Cycles of Soil, p. 261, John Wiley & Sons.)

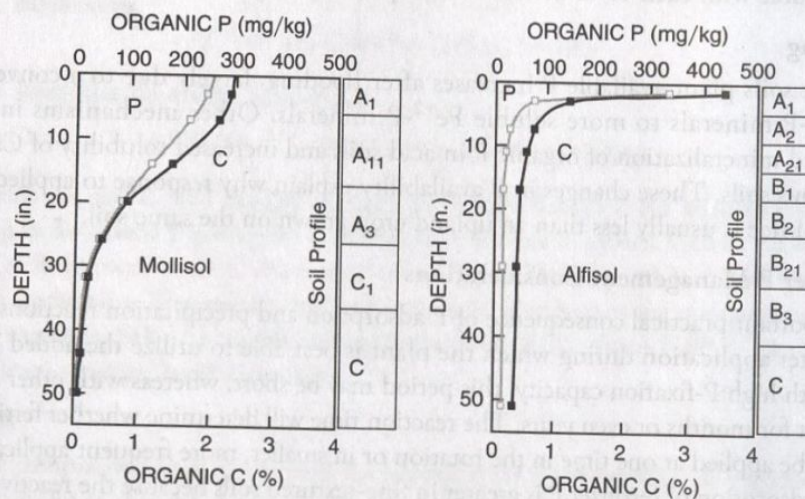


TABLE 5-6
ORGANIC C:N:P:S RATIO IN SELECTED SOILS

Location	Number of Soils	C:N:P:S
Iowa	6	110:10:1.4:1.3
Brazil	6	194:10:1.2:1.6
New Zealand ¹	22	140:10:2.1:2.1
India	9	144:10:1.9:1.8
Scotland ²		
Calcareous	10	113:10:1.3:1.3
Noncalcareous	40	147:10:2.5:1.4

¹Values for subsurface layers (35-53 cm) were 105:10:3.5:1.1.

²Values for S given as total S.

Source: Stevenson, 1986, Cycles of Soil, p. 262, John Wiley & Sons.

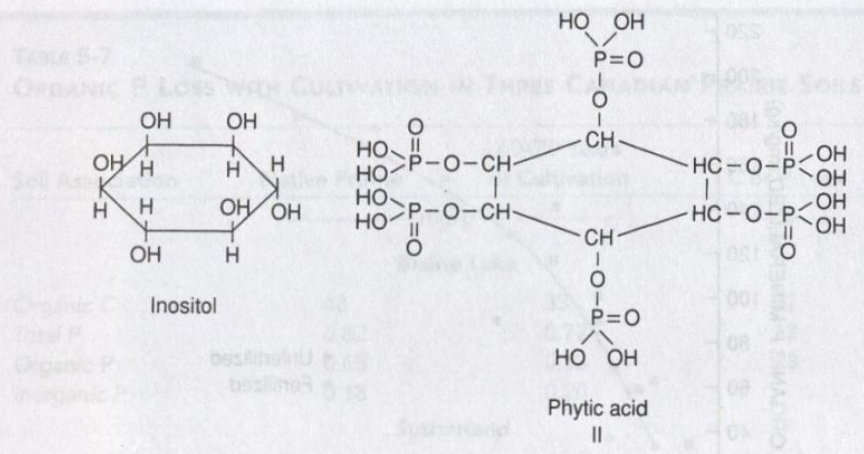
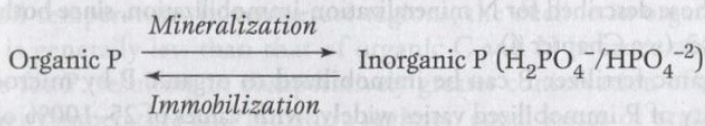


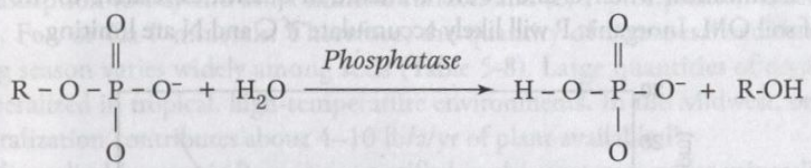
Figure 5-20
Chemical structure of inositol and inositol phosphate (phytic acid).

Phytic acid (myoinositol hexaphosphate) has six H_2PO_4^- groups attached to each C atom in the benzene ring (Fig. 5-20). Successive replacement of H_2PO_4^- with OH^- represents the other five phosphate esters. For example, the pentaphosphate ester has five H_2PO_4^- groups and one OH^- . Inositol hexaphosphate is the most common phosphate ester and comprises $\approx 50\%$ of total soil organic P. Most inositol phosphates and nucleic acids in soils are products of microbial degradation of plant residues. Two distinct nucleic acids, RNA and DNA, are released into soil in greater quantities than inositol phosphates. Since nucleic acids are rapidly degraded by soil microbes, they represent a small portion of total soil organic P. The common phospholipids are derivatives of glycerol and are insoluble in water, but also readily degraded by soil microbes. Thus, phospholipids also represent a small proportion of total organic P. The remaining soil organic P compounds originate from microbial activity, where, bacterial cell walls contain large amounts of stable P esters.

P Mineralization and Immobilization in Soils In general, P mineralization and immobilization are similar to N in that both processes occur simultaneously in soils and can be depicted as follows:

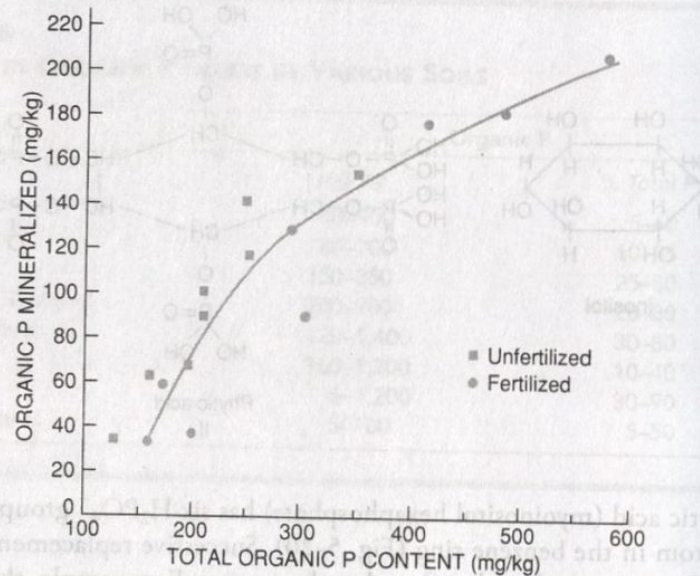


Soil organic P originates from plant and animal residues, which are degraded by microorganisms to produce other organic compounds and release inorganic P (Fig. 5-1). Phosphatase enzymes catalyze the mineralization reaction of organic P by:



The quantity of P mineralized in soils increases with increasing organic P content (Fig. 5-21). In contrast, the quantity of inorganic P immobilized is inversely related to soil organic P, such that as the ratio of soil organic C:P increases (i.e., decreasing organic P), P immobilization increases (Fig. 5-22). Residue C:P ratio determines the predominance of P mineralization over immobilization, just as residue C:N

Figure 5-21
Mineralization of organic P
in soil as influenced by total
organic P.
(Sharpley, 1985, SSSAJ, 49:907.)



influenced N mineralization and immobilization. The following guidelines have been suggested:

C:P Ratio	Mineralization/Immobilization
<200	Net mineralization of organic P
200-300	No gain or loss of inorganic P
>300	Net immobilization of inorganic P

Expressed as % residue P, net P immobilization occurs when residue P < 0.2% and net mineralization occurs with >0.3% residue P. When residues are added to soil, net P immobilization occurs during the early stages of decomposition, followed by net P mineralization as the C:P ratio of the residue decreases.

P mineralization-immobilization processes are similar to N (Fig. 4-2). Factors affecting the quantity of P mineralization/immobilization are temperature, moisture, aeration, pH, cultivation intensity, and P fertilization. The environmental effects are similar to those described for N mineralization-immobilization, since both are microbial processes (see Chapter 4).

Inorganic fertilizer P can be immobilized to organic P by microorganisms. The quantity of P immobilized varies widely, with values of 25-100% of applied P reported. Continued fertilizer P applications can increase organic P content and subsequently increase P mineralization. Increases of 3-10 lb/a/yr in organic P mineralization with continued P fertilization are possible. In general, organic P will accumulate with P fertilization when C and N are available in quantities relative to the C:N:P ratio of soil OM. Inorganic P will likely accumulate if C and N are limiting.

Figure 5-22
Relative effect of C:P ratio
in soil on organic P
immobilization.

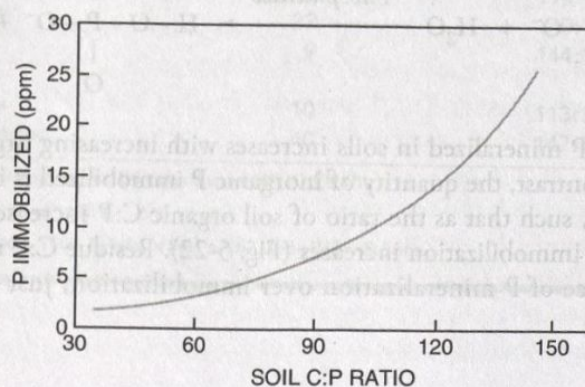


TABLE 5-7
ORGANIC P LOSS WITH CULTIVATION IN THREE CANADIAN PRAIRIE SOILS

Soil Association	60-70 Years of Cultivation		C or P Loss — % —
	mg/g		
Blaine Lake			
Organic C	48	33	32
Total P	0.82	0.72	12
Organic P	0.65	0.53	18
Inorganic P	0.18	0.20	
Sutherland			
Organic C	38	24	37
Total P	0.766	0.66	12
Organic P	0.50	0.41	17
Inorganic P	0.26	0.25	
Bradwell			
Organic C	32	17	46
Total P	0.75	0.53	29
Organic P	0.45	0.32	29
Inorganic P	0.30	0.21	29

Source: Tiessen et al., 1982, Agron. J., 74:831.

As with N, continued cultivation increases organic P mineralization decreasing soil organic P. When virgin soils are brought under cultivation, the soil OM decreases (see Chapter 12). As soil OM is oxidized, organic P is mineralized to inorganic P. For example, in the Northern Plains, organic C and P decreased an average of 38 and 21% after 60–70 years of cultivation, respectively (Table 5-7). Studies in the Midwest showed that after 25 years of cultivation, mineralization reduced organic P by 24% in the surface soil, which was less than the loss in organic C and N. In the Southern Plains, organic P losses are greater because of increased soil temperature. In temperate regions, the decline in organic P with cultivation is generally less than that of organic C and N because of fewer loss mechanisms for P, resulting in comparatively greater conservation of organic P. Under higher temperature and moisture regimes, equal losses of organic C, N, and P have been observed.

Measuring organic P cycling in soils is more difficult than for N because inorganic P produced through mineralization can be removed from solution by (1) P adsorption to clay and other mineral surfaces and (2) P precipitation as secondary Al-, Fe-, or Ca-P minerals. Therefore, the quantity of P mineralized during a growing season varies widely among soils (Table 5-8). Large quantities of organic P are mineralized in tropical, high-temperature environments. In the Midwest, organic P mineralization contributes about 4–10 lb/a/yr of plant available P.

Mineralizable organic P can be quantified in the same manner as mineralizable organic N (Chapter 4). For example, assume a soil contains 2% OM in the surface 6 in., 1% OM degradation rate, 5% N in OM, and a 10:1.3 N:P ratio. Organic P mineralized is estimated by:

$$(2 \times 10^6 \text{ lb soil/afs}) \times 4\% \text{ OM} \times 1\% \text{ OM loss} \times 5\% \text{ N in OM} \\ \times 1.3/10 \text{ P:N ratio} = 5.2 \text{ lb P/afs mineralized}$$

Since P removal with most crops ranges 10–40 lb P/a, mineralizable P generally cannot meet crop P requirement.

TABLE 5-8
ORGANIC P MINERALIZED IN A GROWING SEASON FOR SEVERAL SOILS

Location	Land Use	Soil	Period	Organic P	Mineralized
			yr	kg/ha/yr	%/yr
<i>Slightly weathered, temperate soils</i>					
Australia	Grass	—	4	6	4
	Wheat	—	55	0.3	0.3
Canada	Wheat	Silt loam	90	7	0.4
		Sandy loam	65	5	0.3
England	Grassland	Silt and sandy loam	1	7-40	1.3-4.4
	Arable	Silt and sandy loam	1	2-11	0.5-1.7
	Woodland	Silt loam	1	22	2.8
	Cereal crop	—	—	0.5-8.5	—
	Deciduous forest	Brown earth	1	9	1.2
	Grass	Brown earth	1	14	1.0
Iowa	Row crops	Clay loam	80	9	0.7
Maine	Potatoes	Silt loam	50	6	0.9
Minnesota	Alfalfa	Silty clay loam	60	12	1.2
Mississippi	Cotton	Silt loam	60	5	1.0
	Soybean	Silty clay loam	40	8	1.0
New Mexico	Row crops	Loam	30	2	0.4
Texas	Sorghum	Clay	60	7	1.0
<i>Weathered, tropical soils</i>					
Honduras	Corn	Clay	2	6-27	6-12
Nigeria	Bush	Sandy loam	1	123	24
	Cocoa	Sandy loam	1	91	28
Ghana	Cleared shaded	Fine sandy loam	3	141	6
	Tropical half shaded		3	336	17
	Rainforest exposed		3	396	17

Source: Stewart and Sharpley, 1987, SSSA Spec. Publ. No. 19, p. 111.

Immobilization and mineralization processes for P, C, N, and S cycling are similar and related. For example, if adequate amounts of N, P, and S are added to soils to which crop residues are returned, some of the added nutrients may be immobilized. However, continued cropping of soils without the addition of N, P, and S results in their depletion in soils through mineralization and crop removal.

P SOURCES

Inorganic P

P Fertilizer Terminology Terms used to describe P content in fertilizers are *water soluble*, *citrate soluble*, *citrate insoluble*, *available*, and *total P* (as P_2O_5). A fertilizer sample is first extracted with water, and the P contained in the filtrate represents the water-soluble fraction. The remaining water-insoluble material is extracted with 1 N ammonium citrate to determine citrate-soluble P. The sum of water-soluble and citrate-soluble P represents plant available P. The P remaining after the water and citrate extraction is citrate-insoluble P. The sum of available and citrate-insoluble P represents total P.

P Content of Fertilizers Fertilizer P content is expressed as P_2O_5 instead of elemental P. Although attempts have been made to change from $\%P_2O_5$ to $\%P$, the industry still expresses P concentration in fertilizers as $\%P_2O_5$. Similarly, the concentration of

K in fertilizers is expressed as %K₂O instead of %K. As a matter of interest, N was formerly guaranteed as %NH₃ rather than as %N, as is now done.

The conversion between %P and % P₂O₅ is:

$$\begin{aligned} \%P &= \%P_2O_5 \times 0.43 \\ \%P_2O_5 &= \%P \times 2.29 \end{aligned}$$

The conversion factors are derived from the ratio of molecular weights of P and P₂O₅:

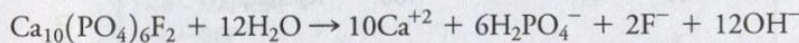
$$\frac{2 \times P \text{ (g/mole)}}{P_2O_5 \text{ (g/mole)}} = \frac{2 \times 31}{142} = 0.43$$

P Fertilizer Sources

Rock Phosphate

Rock phosphate (RP) is the primary raw material used in the manufacture of P fertilizers (Fig. 5-23). The major RP materials are sedimentary deposits found in Morocco, China, the United States, and Russia, representing nearly 72% of total world production. The United States produces about 18% of the world's RP. RP minerals are apatites [Ca₁₀(PO₄)₆(X)₂], where X is F⁻, OH⁻, or Cl⁻. Fluorapatite [Ca₁₀(PO₄)₆F₂] is the most common RP. RP contains numerous impurities of CO₃, Na, and Mg, with some heavy metals, particularly Cd.

None of the P in RP is water soluble, although the citrate solubility varies 3–20% of total P. Finely ground RP can be applied directly to soil and reacts as:



Increasing soil acidity (lower pH) will increase dissolution of RP, since soil acids will neutralize OH⁻ produced and force the above reaction to the right. The solubility of RP (fluorapatite) increases as soil pH decreases (Fig. 5-12); therefore, use of RP as a P fertilizer is restricted to very acidic soils in warm, moist climates characteristic of tropical regions. Since the % available P in RP is relatively small (Table 5-9), RP rates are two to four times superphosphate rates. However, at these rates several years of residual availability can occur, which is important for permanent crops such

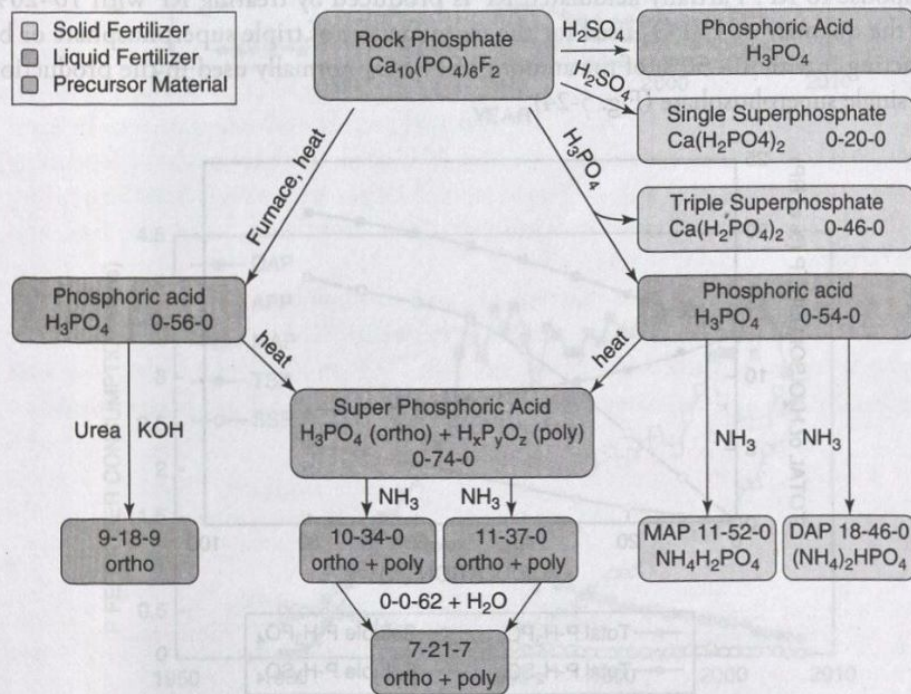


Figure 5-23
Manufacturing process for common solid and liquid P fertilizers from rock phosphate.

TABLE 5-9
COMMON ORTHO- AND POLYPHOSPHATE FERTILIZERS

Fertilizer	Commonly Used Abbreviations	Analysis (%)				% Total Available P	P Compound
		N	P ₂ O ₅	K ₂ O	S		
Calcium phosphates							
Rock phosphate	RP		25-36			3-20	Ca ₁₀ (PO ₄) ₆ · F ₂ · (CaCO ₃) _x · (Ca(OH) ₂) _x
Single superphosphate	SSP		16-22		11-12	80-85	Ca(H ₂ PO ₄) ₂
Triple superphosphate	TSP		44-52		1-2	90-95	Ca(H ₂ PO ₄) ₂
Ammonium phosphates							
Monoammonium phosphate	MAP	11-13	48-62		0-2	100	NH ₄ H ₂ PO ₄
Diammonium phosphate	DAP	18-21	46-53		0-2	100	(NH ₄) ₂ HPO ₄
Ammonium polyphosphate ¹	APP	10-15	35-62			100	(NH ₄) ₃ HP ₂ O ₇ · NH ₄ H ₂ PO ₄
Urea ammonium phosphate ¹	UAP	21-34	16-42			100	(NH ₄) ₃ HP ₂ O ₇ · NH ₄ H ₂ PO ₄
Potassium phosphates							
Monopotassium phosphate			51	35		100	KH ₂ PO ₄
Dipotassium phosphate			41	41		100	K ₂ HPO ₄

¹Contains a mixture of ortho- and polyphosphates.

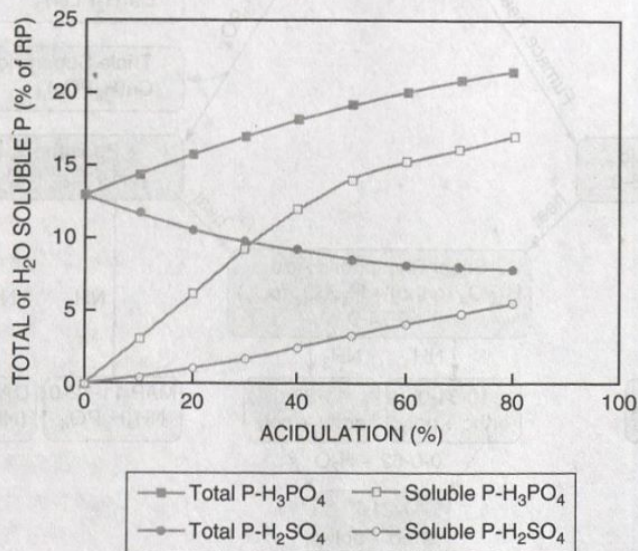
as rubber, oil palm, and cocoa. Ground RP can also be used for restoration of low P soils on abandoned farms and on newly broken lands, usually at rates of 1-3 t/a.

In situations where RP reactivity is inadequate for immediate crop response and P fixation capacity of the soil reduces fertilizer P available to plants, partially acidulated RP can increase the water-soluble P content and improve short-term crop response to RP. Partially acidulated RP is produced by treating RP with 10-20% of the quantity of H₃PO₄ used for the manufacture of triple superphosphate or by reacting it with 40-50% of the amount of H₂SO₄ normally used in the production of single superphosphate (Fig. 5-24).

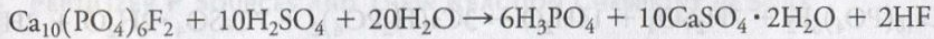
Figure 5-24

Acidulation of North Carolina rock phosphate increases soluble P and ultimately plant available P. Total P increases since P is being added with H₃PO₄.

(Adapted from Schultz, 1986, Inter. Fert. Dev. Center, IFDC-T-31, Muscle Shoals, Ala.)



Reacting RP with H_2SO_4 produces phosphoric acid (H_3PO_4), commonly referred to as green or wet-process acid, containing 17–24% P (39–55% P_2O_5).



A by-product of green acid production is gypsum ($CaSO_4 \cdot 2H_2O$) that can be used as an S and Ca fertilizer, as an amendment for sodic soils, and for other industrial purposes.

Heating RP in an electric furnace produces elemental P that is reacted with O_2 and H_2O to form H_3PO_4 , called white or furnace acid (Fig. 5-23). White acid has a much higher degree of purity than green acid; however, high energy costs involved in manufacturing limits its use in agriculture.

While green acid can be injected in soil or irrigation water, particularly in alkaline and calcareous areas, almost all green acid is used to acidulate RP to make Ca and NH_4 phosphates (Fig. 5-23). Common P fertilizers are produced from either acid- or heat-treated RP to increase water-soluble P (Fig. 5-23; Table 5-9).

Calcium Phosphates

Once the most important P fertilizer, single superphosphate (SSP) and triple superphosphate (TSP) use have decreased relative to NH_4 phosphate sources (Fig. 5-25). Use of SSP in the United States has nearly disappeared (Fig. 5-26).

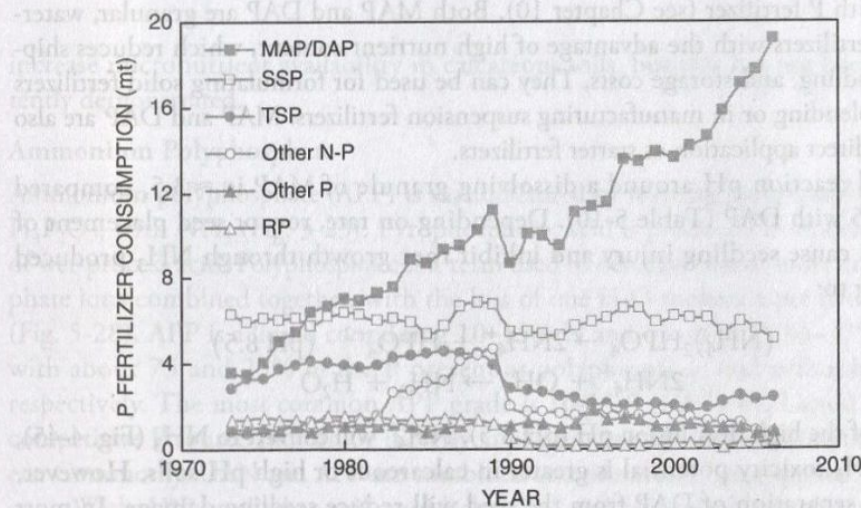


Figure 5-25

World use of common P fertilizers in metric tons of P. MAP/DAP, diammonium phosphate/monoammonium phosphate; SSP, single superphosphate; TSP, triple superphosphate; RP, rock phosphate used for direct application.

(Adapted from International Fertilizer Industry Association, 2009.)

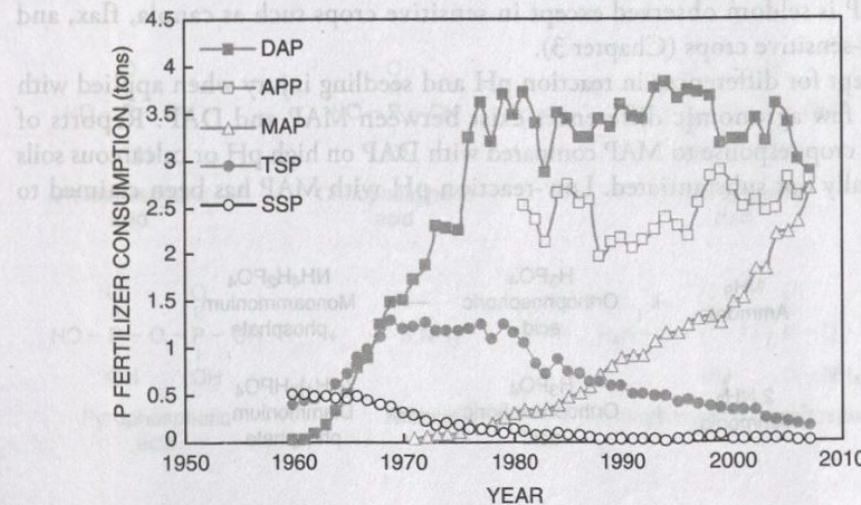
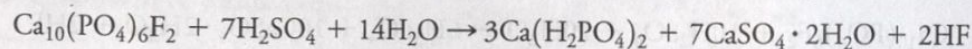


Figure 5-26

Use of common P fertilizers in the United States. DAP, diammonium phosphate; APP, ammonium polyphosphate (also includes other N-P fertilizer); MAP, monoammonium phosphate; TSP, triple superphosphate; SSP, single superphosphate.

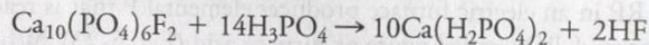
(USDA ERS, 2009.)

SSP contains 7–9.5% P (16–22% P_2O_5) and is an excellent source of S (Table 5-9). Similar to production of green acid, SSP is produced by:



The gypsum by-product is utilized as described before.

TSP contains 17–23% P (44–52% P_2O_5) and is produced by treating RP with H_3PO_4 :

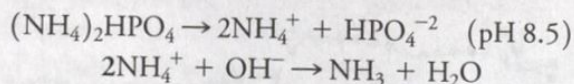


TSP was the most common P source used in the United States until the 1970s, when NH_4 phosphates became popular (Fig. 5-26). Its high P content is an advantage because transportation, storage, and handling comprise a large fraction of total fertilizer cost.

Ammonium Phosphates

NH_4 phosphates are produced by reacting wet-process H_3PO_4 with NH_3 (Figs 5-23; 5-27). Monoammonium phosphate (MAP) contains 11–13% N and 21–24% P (48–55% P_2O_5); however, the common grade is 11-22-0 (11-52-0). Diammonium phosphate (DAP) contains 18–21% N and 20–23% P (46–53% P_2O_5); the most common grade is 18-20-0 (18-46-0). Although MAP use has increased significantly, DAP is more widely used than any other P fertilizer in the United States (Fig. 5-26). Increased global use of MAP/DAP results from increased P uptake when NH_4^+ is placed with P fertilizer (see Chapter 10). Both MAP and DAP are granular, water-soluble fertilizers with the advantage of high nutrient content, which reduces shipping, handling, and storage costs. They can be used for formulating solid fertilizers by bulk blending or in manufacturing suspension fertilizers. MAP and DAP are also used for direct application as starter fertilizers.

Soil reaction pH around a dissolving granule of MAP is ≈ 3.5 , compared to pH 8.5 with DAP (Table 5-10). Depending on rate, row or seed placement of DAP can cause seedling injury and inhibit root growth through NH_3 produced according to:



Because of the high dissolution pH (pH 8.5), NH_4^+ will convert to NH_3 (Fig. 4-45), where NH_3 toxicity potential is greater in calcareous or high pH soils. However, adequate separation of DAP from the seed will reduce seedling damage. In most cases, DAP rate should not exceed 15–20 lb N/a applied with the seed (depending on crop, row width, soil pH and texture, and application rate). Seedling injury with MAP is seldom observed except in sensitive crops such as canola, flax, and other salt-sensitive crops (Chapter 3).

Except for differences in reaction pH and seedling injury when applied with the seed, few agronomic differences exist between MAP and DAP. Reports of improved crop response to MAP compared with DAP on high pH or calcareous soils are generally not substantiated. Low-reaction pH with MAP has been claimed to

Figure 5-27
Reactions of ammonia with orthophosphate to produce monoammonium phosphate (MAP) and diammonium phosphate (DAP).

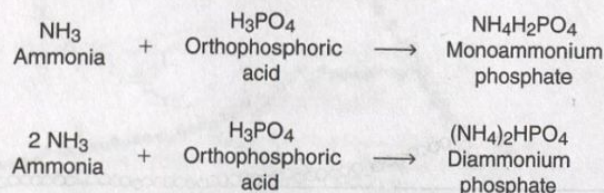


TABLE 5-10
FERTILIZER P SOURCES AND THEIR REACTION CHEMISTRY IN SOILS

Compound	P Source		Saturated Solution Properties			
	Formula	Symbol	pH	P (m/L)	Primary Cation	m/L
<i>Highly water soluble</i>						
Monocalcium phosphate	Ca(H ₂ PO ₄) ₂	TSP	1.5	4.5	Ca	1.3
Monoammonium phosphate	NH ₄ H ₂ PO ₄	MAP	3.5	2.9	NH ₄	2.9
Ammonium polyphosphate	(NH ₄) ₃ HP ₂ O ₇	APP	6.0	6.8	NH ₄	10.2
Diammonium phosphate	(NH ₄) ₂ HPO ₄	DAP	8.5	3.8	NH ₄	7.6
<i>Sparingly soluble¹</i>						
Dicalcium phosphate	CaHPO ₄	DCP	6.5	≈0.002	Ca	0.001
Dicalcium phosphate dihydrate	CaHPO ₄ · 2H ₂ O	DCPD	6.5	≈0.002	Ca	0.001
Hydroxyapatite	Ca ₁₀ (PO ₄) ₆ (OH) ₂	HA	6.5	≈10 ⁻⁵	Ca	0.001

¹Compounds not used as fertilizers, included for comparison purposes.

Source: Sample et al., 1980. In F. E. Khasawneh et al. (Eds.), Phosphorus in Agriculture, p. 275, ASA, Madison, Wis.

increase micronutrient availability in calcareous soils, but this has not been consistently demonstrated.

Ammonium Polyphosphate

Ammonium polyphosphate (APP) is manufactured by reacting pyrophosphoric acid, H₄P₂O₇, with NH₃ (Fig. 5-23). Pyrophosphoric acid is produced from dehydration of wet-process acid. Polyphosphate is a term used to describe two or more orthophosphate ions combined together, with the loss of one H₂O molecule per two H₂PO₄⁻ (Fig. 5-28). APP is a liquid containing 10–15% N and 15–16% P (34–37% P₂O₅), with about 75 and 25% of the P present as polyphosphate and orthophosphate, respectively. The most common APP grade is 10-15-0 (10-34-0). Liquid APP is a competitive P source and can be directly applied or mixed with other liquid fertilizers. Commonly, UAN and APP are combined and subsurface band applied.

With APP applied to soil, rapid chemical and biological hydrolysis of polyphosphate produces H₂PO₄⁻. Several factors control hydrolysis rates. Phosphatase associated with plant roots and rhizosphere organisms are responsible for biological

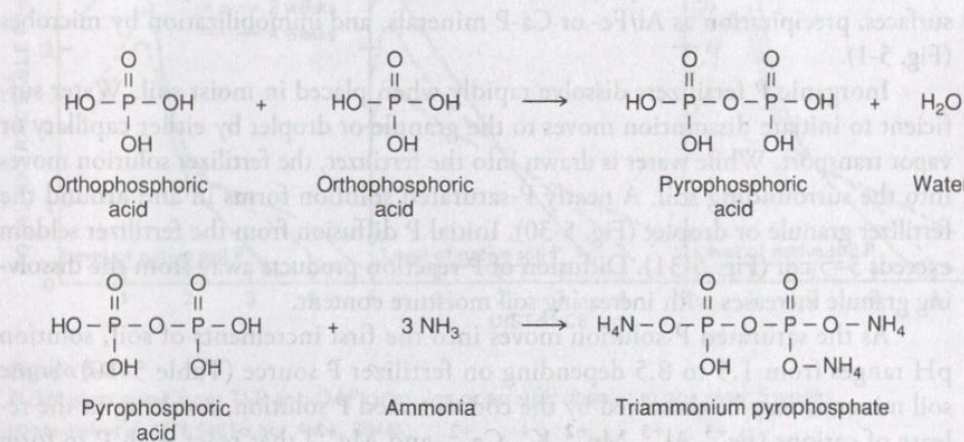
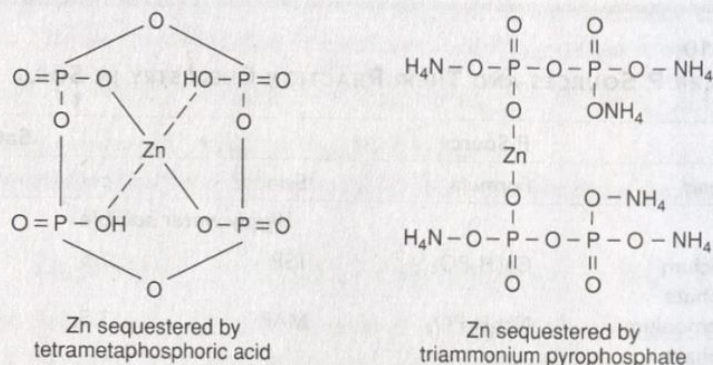


Figure 5-28
Reaction of two H₃PO₄ molecules to produce pyrophosphate. The reaction continues to form longer chains called polyphosphates. Adding NH₃ to pyro- and polyphosphates produces ammonium polyphosphate (APP).

Figure 5-29

Sequestering of Zn by polyphosphate molecules can maintain a greater Zn concentration in solution than Zn added to orthophosphate fertilizers.



hydrolysis of polyphosphates. Temperature, moisture, soil C, pH, and various conditions that encourage microbial and root growth favor phosphatase activity and polyphosphate hydrolysis. Temperature is the most important environmental factor, where hydrolysis of polyphosphate increases substantially as soil temperature increases.

Polyphosphates are as effective as H_2PO_4^- sources for crops. One unique property of APP is chelation or sequestering reaction with micronutrient cations, which maintains higher micronutrient concentration in APP than possible with H_2PO_4^- solutions (Fig. 5-29). APP can maintain 1–3% Zn in solution compared with only 0.05% Zn with H_2PO_4^- .

A granular fertilizer, urea ammonium phosphate (UAP), is produced by reacting urea with APP. The fertilizer grade is 28-12-0 (28-28-0), containing 20–40% polyphosphate. UAP can be easily blended with other granular fertilizers. Like DAP, seedling damage may occur when UAP is applied with the seed.

Potassium Phosphate

Potassium phosphate products include KH_2PO_4 and K_2HPO_4 (Table 5-9). They are water soluble and commonly used in the horticulture industry. Their high P and K content makes them ideally suited for solanaceous crops such as potatoes, tomatoes, and many leafy vegetables sensitive to high levels of Cl^- associated with KCl (see Chapter 6). Their low-salt index reduces injury to germinating seeds and to young seedlings when placed close to the seed.

Behavior of P Fertilizers in Soils

Fertilizer P Reactions

Many of the factors affecting native P availability, discussed earlier, also influence fertilizer P reactions and availability in soil. P fertilizer added to soil initially increases solution P, but subsequently solution P decreases through P adsorption to mineral surfaces, precipitation as Al/Fe- or Ca-P minerals, and immobilization by microbes (Fig. 5-1).

Inorganic P fertilizers dissolve rapidly when placed in moist soil. Water sufficient to initiate dissolution moves to the granule or droplet by either capillary or vapor transport. While water is drawn into the fertilizer, the fertilizer solution moves into the surrounding soil. A nearly P-saturated solution forms in and around the fertilizer granule or droplet (Fig. 5-30). Initial P diffusion from the fertilizer seldom exceeds 3–5 cm (Fig. 5-31). Diffusion of P reaction products away from the dissolving granule increases with increasing soil moisture content.

As the saturated P solution moves into the first increments of soil, solution pH ranges from 1.5 to 8.5 depending on fertilizer P source (Table 5-10). Some soil minerals may be dissolved by the concentrated P solution, resulting in the release of cations (Fe^{+3} , Al^{+3} , Mn^{+2} , K^+ , Ca^{+2} , and Mg^{+2}) that react with P to form

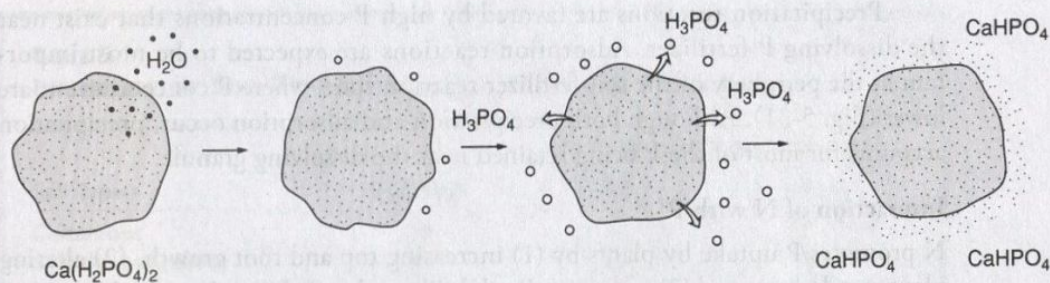


Figure 5-30
 Reaction of a monocalcium phosphate (MCP) granule in soil. Water vapor moves toward the granule, which begins to dissolve. Phosphoric acid forms around the granule resulting in a solution pH of 1.5. The acidic solution causes other soil minerals to dissolve, increasing cation (and anion) concentration near the granule. With time the granule dissolves completely and the solution pH increases, with subsequent precipitation of a dicalcium phosphate (DCP) reaction product.

specific compounds, referred to as soil-fertilizer reaction products. For example, as MCP [$\text{Ca}(\text{H}_2\text{PO}_4)_2$] dissolves, H_3PO_4 forms near the granule and lowers pH to 1.5 (Table 5-10). Other soil minerals in contact with H_3PO_4 may dissolve, increasing solution cation concentration near the granule. Subsequently, the solution pH will increase as H_3PO_4 is neutralized. Within a few days or weeks, DCP and/or DCPD will precipitate as the initial fertilizer reaction product (Fig. 5-12). Depending on the native P minerals initially present in the soil, OCP, TCP, HA, or Fe/AlPO_4 may eventually precipitate.

In acid soils, reaction products formed from MCP include DCP and eventually AlPO_4 and/or FePO_4 precipitates (Fig. 5-12). In calcareous soil, DCP and OCP are the dominant initial reaction products. Because MAP has a reaction pH of 3.5 compared with pH of 8.5 for DAP, P should be more soluble near the dissolving granule (Table 5-10). The acid pH with MAP may temporarily reduce the rate of P reaction product precipitation in calcareous soils.

Although differences in reaction pH among P fertilizers cause differences in reaction products, the overall effect is temporary because the volume of soil influenced by the P granule or droplet is small. Differences in availability of P sources to crops are small compared with differences in other P management factors such as P placement.

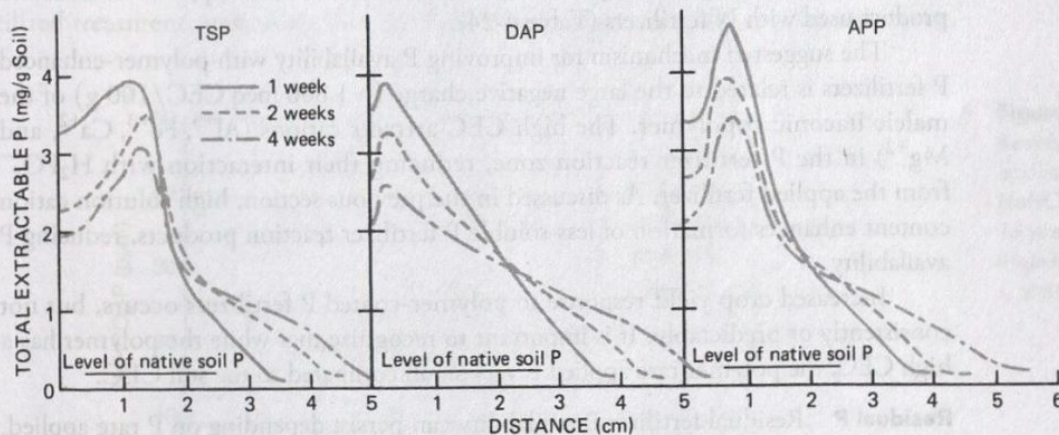


Figure 5-31
 P diffusion away from TSP and DAP granules or an APP droplet in soil over 5 weeks.
 (Khasawneh et al., 1974, Soil Sci. Soc. Am. J., 38:446.)

Precipitation reactions are favored by high P concentrations that exist near the dissolving P fertilizer. Adsorption reactions are expected to be most important at the periphery of the soil-fertilizer reaction zone, where P concentrations are lower (Fig. 5-31). Although both precipitation and adsorption occur, precipitation accounts for most of the P being retained near the dissolving granule.

Interaction of N with P

N promotes P uptake by plants by (1) increasing top and root growth, (2) altering plant metabolism, and (3) increasing P solubility and availability. Increased root mass is largely responsible for increased crop uptake of P. NH_4^+ fertilizers have a greater stimulating effect on P absorption than NO_3^- . Improved fertilizer P effectiveness can occur with P placed close to NH_4^+ sources (see Chapter 10).

Effect of Granule or Droplet Size

Since water-soluble P is rapidly converted to less-soluble P reaction products, decreasing contact between soil and fertilizer generally improves plant response to P fertilizer. Increasing granule or droplet size and/or band application of the fertilizer decreases soil fertilizer contact and maintains a higher solution P concentration for a longer time compared with broadcast P and/or fine particle size.

Soil Moisture

Soil moisture content influences the effectiveness and availability of applied P. At field capacity, 50–80% of the water-soluble P can diffuse from the fertilizer granule within 24 hours. Even at 2–4% moisture, 20–50% of the water-soluble P moves out of the granule within the same time.

Rate of Application

Even though fertilizer P eventually forms less-soluble P compounds, the P concentration in solution increases with P application rate. With time the P concentration decreases as less-soluble P compounds precipitate. The duration of elevated solution P levels depends on the rate of P fertilizer applied, the method of P placement, the quantity of P removed by the crop, and soil properties that influence P availability.

Modification of Chemistry in Soil Fertilizer Reaction Zone Modification of the chemical environment around fertilizer P particles or bands of fluid P by coatings or additions of a specific family of polymers has been investigated since 1999 on a wide range of crops and soils. The most common polymer is *maleic itaconic copolymer* solution used with solid or liquid P fertilizers (AVAIL®). Nutrisphere® is a similar product used with N fertilizers (Table 4-24).

The suggested mechanism for improving P availability with polymer-enhanced P fertilizers is related to the large negative charge ($\sim 1,800$ meq CEC/100 g) of the maleic itaconic copolymer. The high CEC attracts cations (Al^{+3} , Fe^{+3} , Ca^{+2} , and Mg^{+2}) in the P fertilizer reaction zone, reducing their interaction with H_2PO_4^- from the applied fertilizer. As discussed in the previous section, high solution cation content enhances formation of less-soluble P fertilizer reaction products, reducing P availability.

Increased crop yield response to polymer-coated P fertilizers occurs, but not consistently or predictably. It is important to recognize that while the polymer has a high CEC, the polymer rate applied is very small compared to the soil CEC.

Residual P Residual fertilizer P availability can persist depending on P rate applied, crop P removal, and soil properties that influence P reaction product chemistry. P-fixation reactions influence residual P availability in acid soils more than in basic soils (Table 5-11). These data show that approximately 45% of fertilizer P was plant

TABLE 5-11
INFLUENCE OF SOIL TYPE ON RESIDUAL FERTILIZER P AVAILABILITY

Soil Type	# of Soils	% P Available After 6 Months	
		Mean	Range
Calcareous	56	45	11-72
Slightly weathered	80	47	7-74
Moderately weathered	27	32	6-51
Highly weathered	40	27	14-54

Note: Resin extractable P measured 6 months after P application.

Source: Sharpley, 1991, Soil Sci. Soc. Am. J., 55:1038.

available after 6 months over a wide range of soil properties; however, residual P availability was lower in highly weathered, acid soils compared to slightly weathered and calcareous soils.

With increasing P rate, the initial and residual fertilizer P availability increases (Fig. 5-32). After more than 10-12 years, soil test P decreased to its initial level except with the highest P rate. These data demonstrate that relatively high P rates are needed to substantially increase and maintain residual available P over a long time period.

Figure 5-33 illustrates the change in plant available P influenced by P rate and frequency of application. First, plant removal of P in the unfertilized soil caused initial soil test P to decrease substantially over 6 years. Annual application of 100 lb/a P_2O_5 maintained soil test P slightly above the initial soil test level, whereas the intermediate P rate (50 lb/a P_2O_5) resulted in soil test levels between 0 and 100 lb/a P_2O_5 annual rates. Triennial application of 150 lb/a P_2O_5 increased available P in the first year; however, soil test P subsequently decreased below the initial soil test level until the next triennial application. Similarly, 150 lb/a P_2O_5 applied only in the first year maintained soil test P at or above the initial level during the first 3 years, followed by decreasing soil test P in subsequent years. These data illustrate the importance of soil testing for accurately determining when additional fertilizer P is needed for optimum production (Chapter 9).

P placement also influences residual fertilizer P (Fig. 5-34). On this low P soil, broadcast P applied at 45 lb P_2O_5 /a did not increase soil test P over the unfertilized treatment, indicating that fertilizer P not taken up by the crop converted to

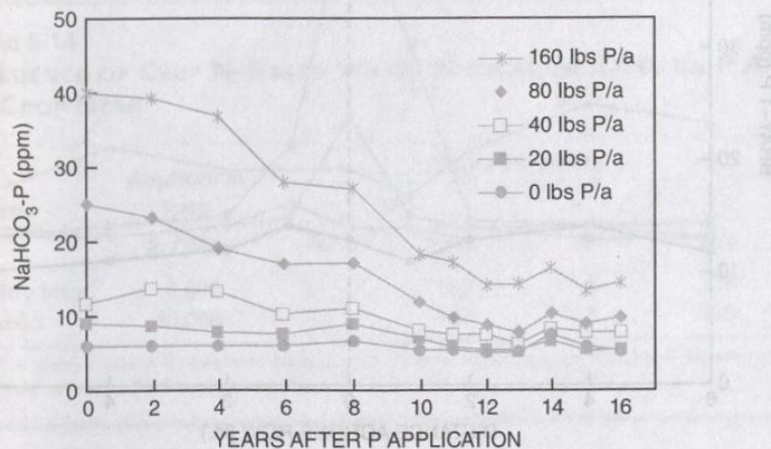
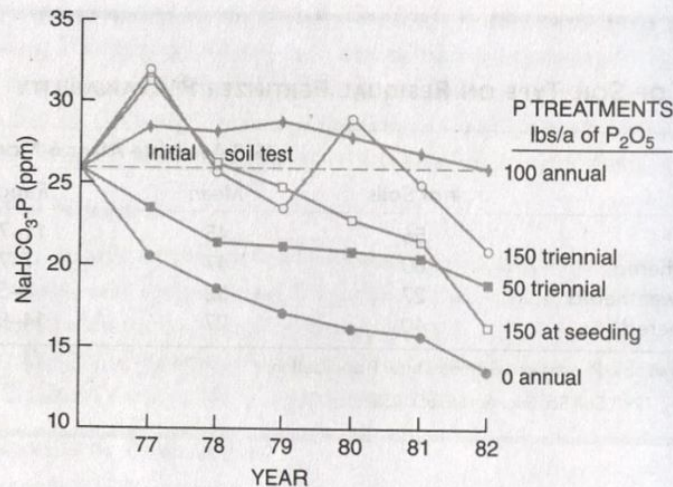


Figure 5-32
 Residual effect of single applications of P on $NaHCO_3$ extractable P over 16 years of production. (Havlorson, 1989, Soil Sci Soc. Am. J., 53:839.)

Figure 5-33
Influence of broadcast fertilizer P on buildup or decline in soil test P over 6 years.
(Havlin et al., 1984, SSSAJ, 48:332.)



P compounds with a solubility similar to that of the native P minerals. In contrast, 75 lb P_2O_5/a (broadcast) increased soil test P. Increasing band-applied P from 45 to 75 lb/a P_2O_5 dramatically increased soil test P in the band, indicating that the solubility of the P reaction products is greater than that of the native P minerals and that they persist for several years after application.

There is some question about the need for additional P even when residual P levels are high. Low rates of P in starter fertilizers placed with or near the seed row are potentially beneficial on high P soils when the crop is stressed by cold, wet conditions and diseases such as root rots. Although residual P contributes significantly to crop yields, additional banding of P may be required to maximize crop production (Chapter 10).

Organic P

Organic wastes are excellent sources of plant available P, with manure accounting for 98% of organic P applied to cropland. The form and content of P in fresh organic materials vary widely depending on source and storage/handling prior to application. With animal wastes, inorganic P ranges from 0.3 to 2% of the dry weight, while

Figure 5-34
Influence of band-applied fertilizer P on soil test P in the band 23 months after application. Band P 1 in. below the seed.
(Havlin et al., 1990, Proc. FFF Symposium, p. 213.)

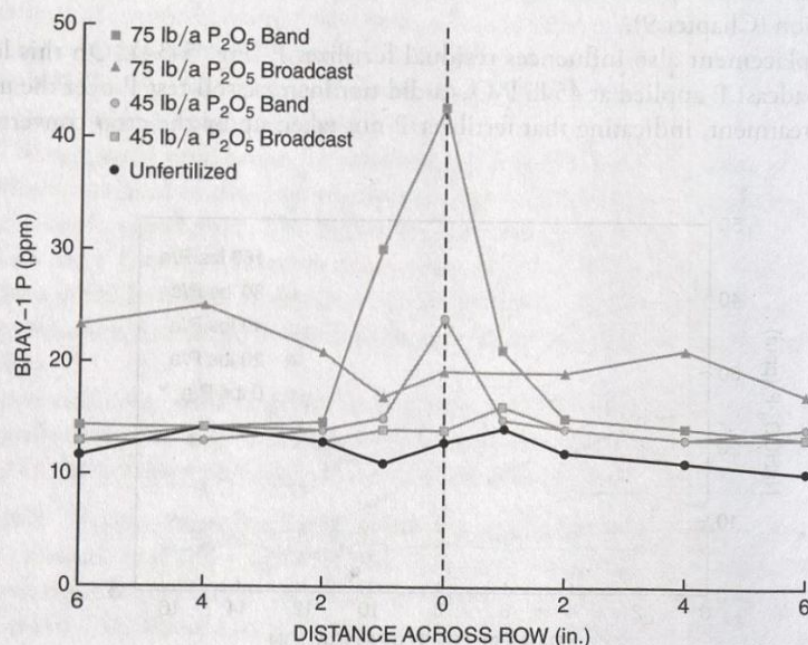


TABLE 5-12
P CONTENT OF SELECTED ANIMAL WASTES AND COMPOSTS

Source	% of Dry Matter	
	Total P	Inorganic P
<i>Animal waste</i>		
Swine	1.5-2.5	0.8-2.0
Beef cattle	0.7-1.2	0.5-0.8
Dairy cattle	0.5-1.2	0.3-1.0
Poultry	0.9-2.2	0.3-1.2
Horses	0.4-1.4	0.2-0.8
<i>Compost</i>		
Poultry manure	1.1-2.4	0.5-1.2
Lawn clippings, leaves	0.1-0.4	0.05-0.2
Biosolids	1.5-7.0	0.7-4.0

organic P ranges from 0.1 to 1% (Table 5-12; Table 4-30). In fresh manure, organic P represents 30-70% of total P. Composting organic wastes generally increases total P content.

As discussed with N, manure storage and handling can change the nutrient content of manure. Mineralization of organic P during storage usually increases inorganic P content and decreases organic P. For example after 3-4 months of liquid swine waste storage, inorganic P increased from 60-70 to 85% of fresh manure dry weight (Table 5-13).

TABLE 5-13
DISTRIBUTION OF P FRACTIONS IN LIQUID SWINE MANURE AFTER STORAGE

Animal	Total P (% dry matter)	% of Total P
Total inorganic P	1.5-2.0	85
Total organic P	0.2-0.3	15
Inorganic P in solution	0.01-0.20	5
Organic P in solution	0.01-0.03	<4
Microbial P	0.02-0.04	<2

Source: Van Faassen, 1987. In V. D. Meer (Ed.), *Animal Manure on Grassland Crops*, pp. 27-45.

TABLE 5-14
INFLUENCE OF CROP N-BASED WASTE APPLICATION RATES ON P APPLIED IN EXCESS OF CROP NEED

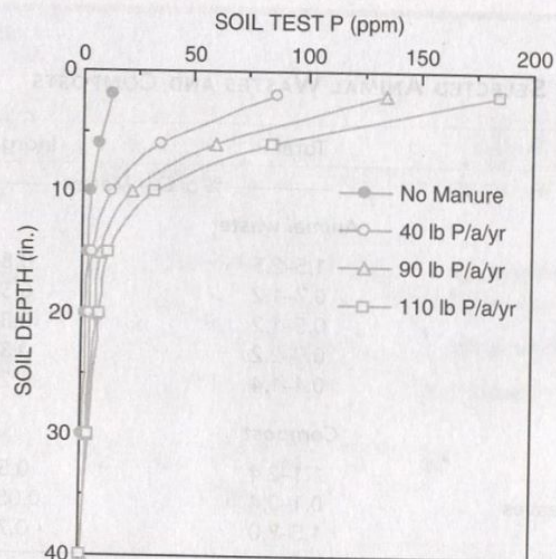
Source	Application Rate lb DM/a	Waste Nutrients				Crop Requirement ¹		Excess P Applied lb/a
		N		P		N	P	
		%	PAN ¹	%	lb/a	lb/a		
Poultry litter	8,000	2	160	1.7	136	160	25	111
Biosolid	10,000	1.6	160	2.5	250	160	25	225

¹PAN = plant available N represents the amount of N required by the crop. Waste rate determined by crop N needed. Crop P required based on 200 bu/a corn at ~0.2% P content.

Figure 5-35

Increase in Mehlich P with increasing manure P rates applied annually for 10 years.

(Adapted from Sharpley et al., 1984, *J. Environ. Qual.*, 13:211-215.)



P content in biosolids ranges from 2 to 7%, with most present as inorganic P (Table 5-12). Thus, 40–140 lb P/a would be applied per ton of material. If 80% is inorganic P and plant available during the first year, then 32–175 lb P/a would be applied per ton. Because of relatively high transportation and processing expenses, application rates generally exceed 1 t/a, and therefore the total amount of P applied can greatly exceed typical crop requirements. See Chapter 10 for detailed discussion of manures and manure management.

Animal waste application rates based on the N requirement of the crop also results in P application in excess of crop requirement (Table 5-14). This example illustrates that waste P was applied at rates 4–9 times that needed by the crop. Continued application of wastes based on crop N requirements will substantially increase soil P (Fig. 5-35), and increase risk of P transport to surface and ground waters (Chapter 12).

STUDY QUESTIONS

- Describe P deficiency symptoms in grasses and broadleaf plants and explain why P-deficient plants exhibit severe stunting.
- Give brief descriptions of the main pathways of transporting soil P to plant roots. How can P fertilization alter the importance of these pathways?
- Compare typical soil solution concentrations of P with P content in plants. If a soil contains 0.05 ppm P in solution, calculate the number of times the solution P must be replenished to meet a 0.5 kg P/ha/day demand by the plant.
- Define P intensity and quantity factors. What is labile soil P?
- What are the various mechanisms of P retention in acid and calcareous mineral soils?
- What soil properties influence fixation of fertilizer P and what can be done to reduce the amount of P fixation?
- Estimate the quantity of P mineralized, if a soil contains 2.5% OM content and the rate of mineralization is 1.5%.
- How is P availability influenced by soil pH?
- Refer to Figure 5-12 (P solubility diagram) and answer the following:
 - A soil contains β -TCP and strengite minerals. The soil pH would be _____ and the soil solution P concentration would be _____ M.
 - After 20 years of fertilizer N use, the soil pH dropped 2 units. The P mineral present at this pH would be _____ and the solution P concentration would be _____ M.
 - Assuming the critical P level is 10^{-5} M, the minimum pH for adequate P supply to plants would be _____.

- d. Assume the initial soil pH is 8. Circle one answer in each group. If the pH is slowly decreased, the concentration of P in solution will (increase, decrease, not change) until about pH (7.2, 6.2, 7.8), at which point the solution P level generally (increases, decreases, or stays the same) until pH (7.0, 6.0, 5.0) at which point solution P (increases, decreases, stays the same).
- e. A soil contains octacalcium phosphate and variscite. What is the soil pH range where solution P would be enough for adequate P availability (assume the critical P level is 10^{-5} M)? Soil pH = _____.
- f. Why does P solubility increase above pH 7.8 for the Ca-phosphate minerals?
- g. Fertilizer P is added to a soil at pH 7.2. The P compound in this soil is hydroxyapatite. What is the initial P compound that precipitates in the soil and what is the final P compound to precipitate?
10. What is the original source of most fertilizer P?
 11. Under what types of soil and cropping conditions might the use of RP give satisfactory results? Explain.
 12. What acids are commonly used to acidify RP? Why does acid treatment of RP render the P more plant-available?
 13. Describe the soil and management conditions that you might expect an appreciable downward movement of P through the soil profile.
 14. Under what soil conditions would band placement of P result in its greatest utilization by the plant?
 15. What advantages or disadvantages exist with high-analysis sources such as DAP, MAP, and TSP?
 16. Describe how the presence of N improves plant utilization of P fertilizers. Which of the two forms, NH_4^+ or NO_3^- , is more beneficial?
 17. What is residual P? Why is it important agriculturally?
 18. What are polyphosphates? Describe the hydrolysis reaction of polyphosphates. Do you expect any difference in crop response to equal rates of APP and MAP?
 19. Briefly describe the sequence of events that takes place during the dissolution of P fertilizers.
 20. What are typical distances for the initial movement of P from fertilizer application sites? Will P in the reaction zones eventually become more uniformly distributed in the soil? Why or why not?
 21. For a crop yield of 3 t/a (0.5% P), estimate the annual excess P applied with 3 t/a swine waste (2% N; 1.52% P).
 22. For a transpiration ratio of 500 and 0.4% P in the crop, if the average solution concentration is 0.08 ppm P, calculate the quantity of P in percentage moving to the plant by Mass flow.
 23. What is the role of microorganisms in producing P compounds in soil?
 24. Discuss the functions of P in plants
 25. Why P is considered as an essential element for the growth and development of the reproductive parts of a plant?
 26. What are the characteristics of VAM-infected roots?
 27. Distinguish between endomycorrhizae and ectomycorrhizae.
 28. Using Figure 5.9, briefly explain the influence of inorganic in soil solution on corn grain yield.
 29. Explain the mechanism of P adsorption using
 - a. Freundlich and
 - b. Langmuir equations.
 30. Write a note on P mineralization and immobilization in soils.
 31. Explain the manufacture of P-fertilizers from Rock phosphate.
 32. What is the Mechanism of improving P availability using polymer-enhanced fertilizers?

SELECTED REFERENCES

- Barker, A. V., and D. J. Pilbeam. 2007. *Handbook of plant nutrition*. Boca Raton, Fla.: CRC Press.
- Khasawneh, F. E. (Ed.). 1980. *The role of phosphorus in agriculture*. Madison, Wis.: American Society of Agronomy, Crop Science Society of America, Soil Science Society of America.
- Marschner, H. 2003. *Mineral nutrition of plants*. Boston, Mass.: Academic Press.
- Mortvedt, J. J., L. S. Murphy, and R. H. Follett. 1999. *Fertilizer technology and application*. Willoughby, Ohio: Meister Publishing Co.
- Pierzynski, G. M., J. T. Sims, and G. F. Vance. 2005. *Soils and environmental quality*. Boca Raton, Fla.: CRC Press.
- Sims, J. T., and A. N. Sharpley (Eds.). 2005. *Phosphorus: Agriculture and the environment*. Madison, Wis.: ASA, CSSA, SSSA.
- Stevenson, F. J. 1986. *Cycles of soil: Carbon, nitrogen, phosphorus, sulfur, micronutrients*. New York: John Wiley & Sons.