7 Reactions Controlling The Cycling Of P In Soils

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Soils contain 100 to 3000 mg of phosphorus kg^{-1} almost entirely as orthophosphate (PO_4). The proportion of soil phosphate in organic compounds ranges from 29 to 65% of the total P (Harrison, 1987). Processes involved in P cycling can be inorganic or biological. Inorganic processes include physico-chemical reactions, such as precipitation/dissolution and sorption/desorption. The biological processes are initiated primarily by the uptake by higher plants and microorganisms of P released during the weathering of primary and secondary minerals, and include active solubilisation of soil P minerals. The inorganic P (Pi) generated is then recycled via complex food chains through a series of mineralisation and immobilisation reactions.

DISSOLUTION AND PRECIPITATION

DISSOLUTION

Apatite [$Ca_{10}X_2(PO_4)_6$, where X = OH^- or F^-, Ca may also be substituted with Na, Mg and PO_4 with CO_3] is the most common primary P mineral. It is the main phosphate mineral in the earth's crust, is very stable in calcareous environments, can be sand or silt-sized (and therefore easily identified) and can be occluded in other minerals such as quartz (Syers *et al.*, 1967; Lindsay *et al.*, 1989). The first step of P cycling is the dissolution of apatite.

The dissolution of apatite has been extensively studied with phosphate rock (Olson, 1975) but more seldom in natural systems where it is the first step of the P cycle (Walker and Syers, 1976). Apatite dissolution requires a source of H^+ which can originate from the soil itself or from roots or microbes , and sinks for Ca and P (Simllie *et al.*, 1987; Mackay *et al.*, 1986). Therefore phosphate rocks have lower agronomic value in soils above pH 6.2 (Fardeau *et al.*, 1988a). Gupta *et al.* (1990) attributed the release of P from a sodium dominated soil to the dissolution of calcium phosphates at high alkalinity and pH. The rate of

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dissolution further depends on the accessibility of the apatite particle, its morphology (Kirk and Nye, 1986a) and the rate of substitution of PO_4 by CO_3 within the crystal lattice (McClellan and Gremilion, 1980).

Methodologies for studying precipitation/dissolution (Table 1) have been reviewed by Pierzynski (1991). Solubility equilibrium experiments may have limited validity because of our inability to describe properly the chemical state of the solid phase of the soil (Pierzynski, 1991; Yong *et al.*, 1992). The use of direct methods such as X-ray energy dispersive analysis in conjunction with Scanning Electron Microscopy for high resolution solid state NMR (Hinedi *et al.*, 1989) look more promising since they allow direct observations of P minerals. New NMR spectrometers and ^{31}P solid state probes allow the acquisition of spectra on materials with total P contents as low as 1 g kg^{-1} (Frossard et al. 1994a). Further methodological research on the acquisition and interpretation of ^{31}P NMR spectra on soil samples is required.

PRECIPITATION IN CALCIUM SYSTEMS

As early as the mid-nineteenth century researchers related the retention of P to the presence of Ca carbonates and Al and Fe hydrous oxides in soils (Wild, 1950).

Calcium phosphates can form by precipitation following an initial P adsorption on to calcite (Cole *et al.*, 1953; Freeman and Rowell, 1981; Syers and Curtin, 1989). After an initial adsorption of P on the surface of a pure calcite, monocalcium phosphate [MCP, $Ca(H_2PO_4)_2$] precipitates, it then transforms to dicalcium phosphate dihydrate (DCPD, $CaHPO_4{\cdot}2H_2O$), to octocalcium [OCP, $Ca_8H_2(PO_4)_6{\cdot}5H_2O$] and finally to hydroxyapatite [HAP,$Ca_{10}(PO_4)_6(OH)_2$] (Lindsay *et al.*, 1989). This mineral having the lowest solubility should ultimately control the concentration of P in the soil solution while the intermediate precipitates are unlikely to persist in soils.

Various Ca phosphates have been identified in calcareous soils following P fertilisation (Lindsay *et al.*, 1989). Apatite is seldom observed although it is the thermodynamically most stable P mineral (Bell and Black, 1970; Harrison and Adams, 1987; Pierzynski *et al.*, 1990a). This is because of the presence of impurities such as organic acids or Mg which inhibit the crystal growth of apatite through adsorption on the seed crystal surface (Brown, 1981; Amjad *et al.*, 1984; Amoros *et al.*, 1986; Inskeep and Silvertooth, 1988). Thus organic acids adsorbed on DCPD crystal surfaces can act as new nuclei for DCPD crystals hampering any further transformation to OCP or HAP (Grossl and Inskeep, 1991). This could explain the increased available P contents of calcareous soils amended with an organic P sources (farmyard manure, sewage sludge) compared to those receiving only mineral fertilizer (O'Connor *et al.*, 1986).

PRECIPITATION IN ALUMINIUM AND IRON SYSTEMS

Few well crystallised Al and Fe phosphates have been observed in soils. Many researchers have assumed that amorphous Fe-P or Al-P compounds would transform respectively to strengite [$FePO_4{\cdot}2H_2O$] and variscite [$AlPO_4{\cdot}2H_2O$] after prolonged aging (Lindsay *et al.*, 1989). However the crystallisation of strengite and variscite occurs only under very restricted conditions (high P and

cation concentrations), which seldom occur in soils (Hsu, 1982a and b). Instead, the reaction of P with Al oxides can result either in the formation of amorphous aluminum phosphate (Nanzyo, 1988) or in the formation of organised phases such as sterretite [$(Al(OH)_2)_3HPO_4H_2PO_4$, Van Riemsdjik *et al.*, 1975)]. Similarly the reaction of P with an Fe oxides such as goethite can result in the precipitation of tinticite [$Fe_6(PO_4)_4(OH)_6.7H_2O$, Jonasson *et al.*, 1988)] or griphite [$Fe_3Mn_2(PO_4)2.5(OH)_2$, Martin *et al.*, 1988)] depending on the solution and surface conditions.

Table 1. Summary of the methods used for studying the precipitation/dissolution reactions of P in soils and with soil minerals

DIRECT METHODS, *IN SITU* OBSERVATIONS

IDENTIFICATION OF THE P SOLID PHASE:
petrographic observations
X-ray Diffraction
Differential Scanning Calorimetry
High resolution solid state ^{31}P Nuclear Magnetic Resonance
Limits: high P concentration required
Paramagnetic impurities (Fe, Mn) preclude the observation P by NMR.

MORPHOLOGY AND COMPOSITION OF P-RICH PARTICLES:
Electron microscope (SEM, STEM) coupled with energy dispersive X-ray analysis (EDS) (Electron microprobe)
Limits: Local information at the micrometric scale only (representativeness)

INFORMATION ON THE SURFACE STRUCTURE OF MINERALS:
Scanning auger microscopy/spectroscopy
Infra red spectroscopy, diffuse reflectance IR spectroscopy
Limits: These techniques require "clean minerals"

INDIRECT METHODS

SEQUENTIAL EXTRACTION:
quantification of Ca-P and Fe/Al-P
Limits: solubilisation and re-precipitation of P forms during the extraction

SOLUBILITY EQUILIBRIUM EXPERIMENTS:
identification of the P solid phases controlling the concentration of P in the solution
Limits: solid P phases in soils not in the standard state;
product of solubility of solid P phases in soils underestimated

Various P minerals can be observed under natural conditions in P rich environments (phosphatic parent material, heavy fertilisation). Minerals of the crandallite group [crandallite $CaAl_3(PO_4)_2(OH)_5{\cdot}H_2O$; plumbogummite $PbAl_3(PO_4)_2(OH)_5{\cdot}H_2O$; florencite $CeAl_3(PO_4)_2(OH)_5{\cdot}H_2O$; gorceixite $BaAl_3(PO_4)_2(OH)_5.H_2O$]; wavellite $[Al_3(PO_4)_2(OH)_3{\cdot}5H_2O]$; and barrandite $[(Al,Fe)PO_4{\cdot}2H_2O]$ have been identified in soils (Norrish, 1968; Adams *et al.*, 1973; Kumar *et al.*, 1991; Karathanasis, 1991; Wang *et. al.*, 1989). Vivianite $[Fe_3(PO_4)_2{\cdot}8H_2O]$ has been reported in anaerobic conditions in soils rich in organic matter either under natural conditions [peats, buried alluvial soils, (Lindsay *et al.*, 1989)] or following heavy additions of dairy effluent (Guichet, 1986). Indirect evidence based on solubility equilibrium experiments, indicate that $MnPO_4{\cdot}1.5H_2O$ could control the concentration of solution P in soils (Boyle and Lindsay, 1986; Schwab, 1989). However, such crystallised minerals represent only a small proportion of the total soil P, most of it being precipitated as amorphous compounds (Wang *et al.*, 1991a). Furthermore (Wang *et al.*, 1991b) show that crystalline Fe can not be found in a phosphorus rich environment all the iron being precipitated as amorphous Fe-P compounds. In heavily fertilised soils amorphous mixed Al-Si-P compounds prevail (Pierzynsky *et al.*, 1990b).

SORPTION/DESORPTION

Although precipitation-dissolution reactions are of interest, sorption-desorption reactions usually give a better description of the uptake and release of P by soils (Syers and Curtin, 1989). We use the term "sorption" instead of "adsorption" because it covers the fast surface reaction of adsorption and the long term reaction (Barrow, 1985). There is a theoretical difference between the precipitation/dissolution and the sorption/desorption processes: the concentration of P in solution controls the amounts of sorbed P, whereas the solubility product of the least soluble P compound in the solid phase controls the dissolution and therefore the concentration of P in solution (Syers and Curtin, 1989). In reality, the abiotic retention of P on soils particles must be seen as a continuum between surface reactions and precipitation.

SORPTION

Phosphorus sorption on soil minerals has been extensively studied on clean minerals (Wild, 1950; Parfitt, 1978; Sample *et al.*, 1980; White, 1982; Barrow, 1985; Lindsay *et al.*, 1989; Syers and Curtin, 1989; Barrow, 1990; Sollins, 1991; Pierynski, 1991; Fardeau and Frossard, 1992).

Sorption of P on soil minerals and organic compounds initially proceeds by a rapid reaction. When water soluble orthophosphate ions are added to metal oxi-hydroxide a very rapid exothermic ligand exchange reaction takes place with the reactive surface groups. An OH^- or an H_2O molecule is released from the surface and a phosphated surface complex is formed (Parfitt *et al.*, 1976, 1977; Goldberg and Sposito, 1985; Torrent *et al.*, 1990, 1992). This surface complex has been directly confirmed by X-ray photoelectron spectroscopy (Martin and Smart, 1987).

The greater sorption of P on goethite than on hematite (Figure 1) can be explained by a greater accessibility to phosphates of singly coordinated OH surface groups on {110} faces (Torrent *et al.*, 1990). The sorption of P can be accounted for by a total occupation of these sites by bidendate complexes. The average maximum quantity of sorbed phosphates reaches 2.5 µMol P m^{-2} on goethite but only 0.97 µMol m^{-2} on hematites because reactive surface sites are present only on a small proportion of the total surface (Barrón *et al.*, 1988). Similarly, the polymerisation and crystallisation of aluminum oxide decrease the number of surface sites available for P sorption (Sims and Ellis, 1983).

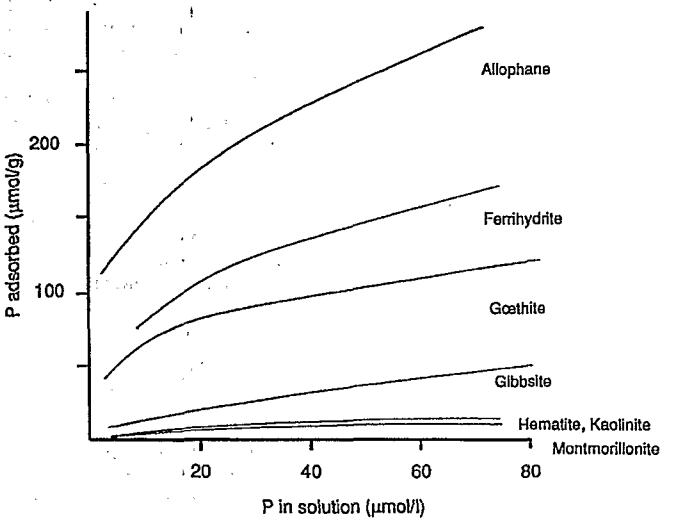

Figure 1. Sorption of P on various minerals (Sollins, 1991).

Monoesters such as glucose-1-P, glucose-6-P and myoinositol hexaphosphate, or phosphonates are adsorbed on the same sites and in similar ways as orthophosphate ions on ordered Al and Fe hydroxides (Shang *et al.*, 1990; Shang *et al.*, 1992; Ognalaga *et al.* 1994). The sorption of P monoesters is a function of the charge density of the PO_4 group (Frossard *et al.*, 1989) and of the spatial conformation of the molecule. Thus, the sorption of DNA on soil is governed both by the amount of sorbing clay and by the molecular weight of the DNA (Ogram *et al.*, 1988). The phosphonate moiety of the herbicide glyphosate [isopropylamine salt of N-(phosphonomethyl)glycine] can form binuclear complexes with surface $-Fe(H_2O)^+$ groups on goethite by ligand displacement of H_2O (McBride and Kung, 1989). The sorption of di- and tri-esters has not been studied in detail probably because of their complexity, but deserve more attention.

The initial rapid sorption of P on soils is followed by slow reactions which have been ascribed to either solid (Barrow, 1985) or liquid state diffusion (Sollins, 1991). Barrow (1985) shows that this slow reaction is endothermic and can occur

by ion exchange within the crystal lattice or by a vacancy mechanism in which an atom moves in one direction and the vacancy in the other direction. The latter would be more likely to occur in imperfect crystals such as those found in soils. The slow reaction may also result from the lower accessibility of surface sorption sites located within the aggregates of poorly crystallised oxides such as ferrihydrite. This porosity then controls the reaction rate (Madrid and De Arambarri, 1985; Willett *et al.*, 1988; Torrent *et al.*, 1990 and 1992).

The sorption of P on oxides is a function of the electrostatic potential in the plane of adsorption (Bowden *et al.*, 1977). Therefore, P sorption by pure oxides decreases with increasing pH, due to a decrease in the electrostatic potential. The effect of ionic composition of the solution on anion sorption varies with pH. Above a certain pH, sorption increases with increasing ionic strength and below this pH the reverse occurs. The pH at which there is no effect of the electrolyte concentration is called Point of Zero Salt Effect (PZSE). For uniform surfaces such as those of synthetic oxides, the PZSE coincides with the Point of Zero Net Charge (PZNC). The effects of pH and electrolyte on the P sorption on goethite have been described by Bowden *et al.* (1980) and Barrow *et al.* (1980) using the mechanistic model developed by (Bowden *et al.*, 1977). This model also describes the effect of time on P sorption by Fe and Al oxides (Bolan *et al.*, 1985).

Organic ligands can affect P sorption. Organic anions compete with orthophosphate for similar sites on the surfaces of oxides (Nagarajah *et al.*, 1970; Sibanda and Young, 1986; Violante *et al.*, 1991; Fontes *et al.*, 1992) and soils (Yuan, 1980; Frossard *et al.*, 1986; Amann and Amberger, 1988; Hue, 1991). The destruction of organic matter by H_2O_2 can increase the accessibility of sorbing sites to PO_4 (Frossard *et al.*, 1992b). Several aliphatic acids (such as oxalic, citric, isocitric, malic, and malonic) are very effective in decreasing P sorption, followed by aromatic acids and phenolics, while sugars, or amino acids are not effective in reducing P sorption (Nagarajah *et al.*, 1970; Amann and Amberger, 1988). The effect is greater when the organic compound is added prior to the P addition (Hue, 1991). Organic compounds can chelate metals and prevent the reaction between metals and phosphates (Earl *et al.*, 1979). An increase in P sorption can occur when the addition of organic compounds to amorphous oxides in soils hampers their crystallisation and increases their specific surface thus increasing P sorption (Huang and Violante, 1986; Borggaard *et al.*, 1990). Citrate, tartrate or formate also can extract metallic ions from mineral surfaces creating new P sorption sites (Traina *et al.*, 1986a).

Complexes of organic matter and Al are an important P sink in allophanic soils (Borie and Zunino, 1983), but additions of various organic compounds did not alter the P sorption in a soil derived from volcanic ash (Appelt *et al.*, 1975). Humic acid-goethite complexes extracted from oxisols could sorb up to 100 μMol P g^{-1} despite their low specific surface (1 m^2g^{-1}) (Fontes *et al.*, 1992).

An indirect effect of organic matter on P sorption can result from the anaerobic decomposition of organic matter, which causes Fe compounds to be dissolved and re-precipitated as amorphous minerals with strong P sorption abilities (Sah and Mikkelsen 1986, 1989; Sah *et al.*, 1989a). Sing and Jones (1976) and Bumaya and Naylor (1988) showed that P sorption could either increase or decrease following the addition of organic residues in highly P-sorbing soils. The P sorbing capacity increased with the duration of incubation and decreased with an increasing P content in the residue.

Complexes of humic compounds with Fe, Al and, to a lesser extent Ca, are able to sorb orthophosphate (Levesque and Schnitzer, 1969; Cegarra *et al.*, 1978; Bloom, 1981; Gerke and Hermann, 1992) possibly by the formation of ternary compounds (HA-Metal-PO_4) (Cegarra *et al.*, 1978). Humic acid from a peat sorbed little P until it was conditioned with a concentrated solution of $AlCl_3$ (White, 1982). The quantity of sorbed P was a function of the degree of hydrolysis of Al on the organic compound. The sorbed P:Al ratio reaches a maximum for the maximum charge of adsorbed Al, i.e. at OH:Al ratios between 1.5 and 2.5 (Appelt *et al.*, 1975). For iron freshly complexed to humic substances, Gerke and Hermann (1992) found a maximum sorption at a molar ratio of sorbed P:Fe of 1. This ratio was 10 fold lower for an amorphous iron oxide. P sorption was influenced by pH and the presence of Ca through changes in the accessibility of sorption sites and electrostatic interactions.

Clay minerals sorb less PO_4 than oxides (Figure 1). Two sorption surfaces can be distinguished on a clay: the edge of the Al layer and the negatively charged surfaces. The broken edges of aluminum layers are variable-charge surfaces containing -Al(OH) groups with P sorption properties similar to those of Al hydroxide surfaces Parfitt, (1978). On 1:1 clays such as kaolinite, P sorption is a function of the specific surface (Schwertmann and Herbillon, 1992).

The quantity of P sorbed on 2:1 clay can greatly exceed the available edge sites and is strongly affected both by the valency and hydration energy of cations or Fe- and Al hydroxides on clay surfaces, and by the ionic strength of the solution (Blanchet, 1960; Coleman *et al.*, 1960; White 1982; Traina *et al.*, 1986b).

Allophane-like materials sorb large amounts of orthophosphate rapidly (Clark and McBride, 1984; Parfitt, 1989) (Figure 1) due to their very high specific surface area (Parfitt, 1980). In addition, the slow reaction is more important in allophane than in goethite, hematite or ferrihydrite (Parfitt, 1989). The slow reaction can result from the formation of alumino-phosphate precipitates disrupting the allophane structure and creating new defect sites (Parfitt, 1989).

The sorption of organic P (Po) compounds on montmorillonite is related to its active Al content (Anderson and Alridge, 1962) and increases below pH 5 (Greaves and Wilson, 1969). Above pH 5, sorption reaches a minimum and is confined to the external surfaces of the clay. Interaction of a phosphonate oxygen from dimethyl methyl phosphonate with interlamellar Ca in montmorillonite was shown by Bowen *et al.* (1988). Such sorbed species may have different properties than free ones (Mingelgrin and Tsvetkov, 1985).

The quantity of P sorbed on calcite depends largely on its specific surface (White, 1982; Borrero *et al.*, 1988). Pure calcites have a low specific surface (1-2 m^2 g^{-1}) while soil calcites can have specific surfaces in the range of 16-500 m^2 g^{-1} (Holford and Mattingly, 1975a) due to intermittent dissolution, reprecipitation and incorporation of impurities. Although pure calcite is slightly negatively charged (White, 1982), orthophosphate can be sorbed at the surface. This sorption occurs only on 5% of the surface of pure calcite (Cole *et al.*, 1953), but these sites then act as nuclei for the 'clustering' of Ca and PO_4 ions with the ultimate formation of a calcium phosphate phase. The induction period prior to nucleation and crystal growth is very long at low P concentration.

For whole soils, there is much evidence that Al and Fe oxides are the most important components determining the soil P sorbing capacity even in calcareous soils (Holford and Mattingly, 1975a; Parfitt, 1978; Ryan *et al.*, 1984; Hamad *et al.*, 1992). However the long term sorption of P in calcareous soils is governed by

calcium carbonate (Solis and Torrent, 1989). The quantity of Fe oxides in a soil determines the P sorption capacity but the type of oxide and their organisation are important as well. Soils with large amounts of hematite sorb less P than soils rich in goethite due to the lower accessibility of sorption sites on hematite (Colombo *et al.*, 1991). The dispersion of an oxisol with a Na^+ resin greatly increases the accessibility of sorbed $^{32}PO_4$ (Frossard *et al.*, 1992b).

Liming can either increase, decrease or have no effect on the P sorption capacity (Haynes, 1982). Liming acid soils can either (i) increase the negative charge of the soils, thus decreasing P sorption, or (ii) cause the precipitation of exchangeable Al as hydroxy Al polymers resulting in the formation of newly active sorbing surfaces (Haynes and Swift, 1985). The net liming effect depends on the magnitude of these two processes.

At high P concentrations, P sorption can be modified by the slow dissolution of Al (Stumm *et al.*, 1983) or Fe (Lin and Benjamin, 1990) oxides, and particularly of amorphous compounds. Large quantities of myoinositol hexaphosphate added to acidic soils extracted Al and Fe (Anderson *et al.*, 1974). Sufficiently high P concentrations (1 M) are reached in soils near dissolving fertilizer particles, where dissolution of minerals has been observed (Lindsay and Stephenson, 1959). The ligand-promoted dissolution may proceed through polarisation, weakening and finally breaking of the metal-oxygen bonds, causing the release of metal to solution (Stumm *et al.*, 1983) (Figure 2). Not all oxides are similarly prone to dissolution; the polarizing effect of a ligand or a surficial complex is not sufficient to release the metal from goethite (Zinder *et al.*, 1986).

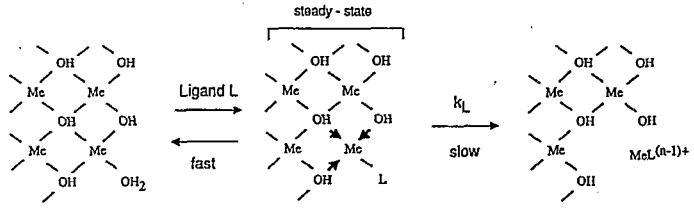

Figure 2. Dissolution of hydrous oxides caused either by protonation of Me-OH surface groups or by sorption of ligand on Me-OH groups (Stumm *et al.*, 1983)

Myoinositol hexaphosphate is more strongly sorbed than orthophosphate on Fe and Al oxides of acidic soils (Anderson *et al.*, 1974). However, after reaching a maximum, sorption declines due to the dissolution of oxide surfaces. No such surface dissolution is observed in neutral or basic soils (McKercher and Anderson, 1989). The sorption appears to be governed by clay and organic matter content and by the number of PO_4 groups in the monoester (Figure 3).

All these studies show that P sorption capacity is closely related to soil properties and that, aside from the short-lived effects around fertilizer granules, it is little affected by fertilizer inputs at levels compatible with financially sound farming practices (Frossard *et al.*, 1992a). Variations in P sorbing capacity of soils in relation to soil properties (type) have been mapped in France on sedimentary

parent materials (Frossard *et al.*, 1992a) and in Albania (Sinaj *et al.*, 1992) on sedimentary and plutonic parent materials.

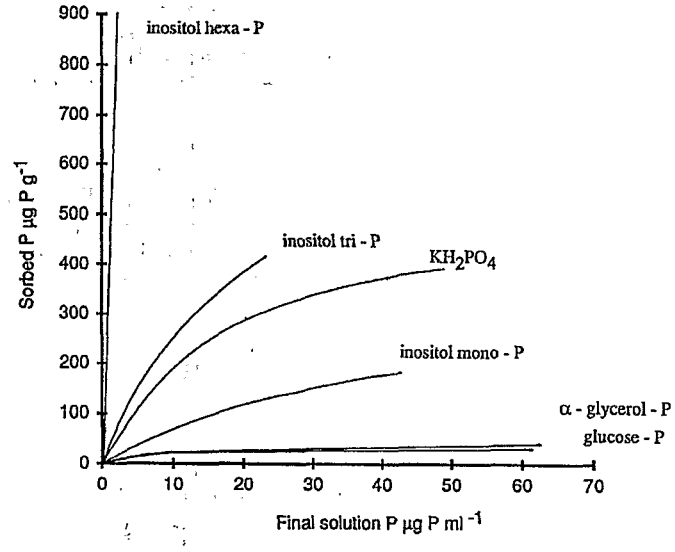

Figure 3. Sorption of organic phosphates on a clayey soil (McKercher and Anderson, 1989)

Barrow (1983b) developed a mechanistic model describing the sorption of P by soils. This model has three assumptions (i) the reaction occurs between divalent phosphate ions and variable charge surfaces; (ii) there is a range of values of surface properties which are distributed normally and (iii) the initial adsorption induces a gradient towards the interior of the particle which drives a solid-state diffusion processes. This model describes the effects of phosphate concentration, pH, temperature and time contact. Furthermore the model suggests, the phosphate that has reacted with a soil for a long enough period is not "fixed" but that it can be recovered slowly if a low enough surface activity is induced.

Sorption curves

The sorption of P can be characterised with parameters calculated from the Langmuir equation:

$$S = \frac{(k\, S_{max}\, c)}{(1 + kc)} \qquad (1)$$

where S is the quantity of sorbed P, c the P concentration in the soil solution, S_{max} the maximum quantity of P that can be adsorbed on the soil and k an "affinity" constant. However the theoretical assumptions of the equation are not realistic since sorbed phosphates carry charges which decrease surface charge and potential of the sorbing surface (Bowden *et al.*, 1977). This leads to large errors in the estimates of maximum P sorption capacity (Kuo, 1988). The Freundlich equation often fits data better (Barrow, 1978; Ratowsky, 1986), but cannot predict sorption maxima. Barrow (1991) modified the Freundlich equation to account for increases in P sorption with sorption time:

$$S_t = c^a(kt)^b \quad (2)$$

where S_t is the quantity of sorbed P at a specific time, c the concentration of P in the solution, k a function of the temperature, and a and b are constants specific to the soil. Fardeau and Frossard (1992) related sorption to the amounts of P added:

$$S_t = Q - V\,c_t \quad (3)$$

where Q is the quantity of P added in a volume V and c_t the concentration of P in the solution at a time t, and the relation $c_t = f(t)$ is described by:

$$c_t = c_1\,[t + (c_1/c_0)^{1/m}]^{-m} \quad (4)$$

At t = 0 the concentration of P in the solution c_0 is Q/V, and after an infinite time c_t reaches 0; c_1, is the concentration of P in the soil solution at t = 1 unit.

DESORPTION

Most of the P taken up by plants is derived from the solid phase of the soil. Therefore, P desorption is useful for describing available P. Four approaches are currently used to estimate the quantity of P that can be desorbed from the soils.

(1) A large number of chemical extractants have been used to desorb phosphate from soils through changes in pH or ionic composition of the soil solution (Roche, 1983; Houmane *et al.*, 1986). However, chemical reagents do not extract homogeneous pools of phosphate but ions presenting a wide range of mobility (Fardeau *et al.*, 1988b) and they ignore the kinetics of P release.

(2) Desorption in P free water or dilute electrolyte is frequently used in sorption/desorption experiments where P was previously sorbed. Often, only small proportions of sorbed P can be desorbed, and this water extraction can rarely be used in unfertilised soil because of the very low concentration of P in solution. The amount of desorbable P increases with increasing soil:solution ratio and increasing desorption time. This has been modeled by Sharpley *et al.* (1981). Desorption decreases with increasing sorption time prior to the desorption (Barrow, 1979). Using a mechanistic model to describe P sorption, Barrow (1983a) quantified the effects of incubation time, temperature and soil/solution ratio on P desorption.

(3) Desorption can be effected through lowering the solution P concentration by introducing a P sink such as an anionic resin or iron oxide coated filter paper into the soil suspension (Amer *et al.*, 1955; Van der Zee *et al.*, 1987). This causes the P from the solid phase to diffuse towards the solution and to be trapped by the resin or oxide (Abrams and Jarrell, 1992). Results obtained are strongly correlated to the amount of P taken up by plants (Roche *et al.*, 1980; Lin *et al.*, 1991; Tran *et al.*, 1992; Menon *et al.*, 1991; Hedley *et al.*, Ch. 5) and algae (Sharpley *et al.*, 1992). The kinetics of P release indicated that P desorption is controlled by diffusion (Pavlatou and Polyzopoulos, 1988; Abrams and Jarrell, 1992).

(4) The amount of P present on the solid phase and able to diffuse to the soil solution can be indirectly assessed by the amount and rate of isotopic exchange of $^{32}PO_4$ (Larsen, 1967; Le Mare and Leon, 1989; He *et al.*, 1991). This technique is based on the homoionic exchange between the radioactive $^{32}PO_4$ introduced in the solution and the $^{31}PO_4$ located on the solid phase of the soil. When $^{32}PO_4$ ions are introduced carrier free into a soil/solution suspension at a steady state, the specific activity of phosphate in solution [$^{32}PO_4/^{31}PO_4$] is equal, at any given exchange time, to the specific activity of the exchangeable phosphate located on the solid phase.

$$\frac{R_t}{c_p \cdot 10} = \frac{R_0 - R_t}{E_P \cdot 10 \cdot c_p} \quad (5)$$

where R_0 is the total radioactivity introduced (MB_q), R_t the radioactivity remaining in the solution after t minutes of exchange (MBq); c_p the concentration of P in solution (mg l^{-1}), E_P the isotopically exchangeable P (mg kg^{-1}). The factor 10 represents the soil:solution ratio of 1 g in 10 ml of water so that c_p*10 is equivalent to the water soluble P content of the soil in mg kg^{-1}. The main problem with this technique is the measurement of low concentrations of water soluble P (Fardeau and Jappé, 1988, Salcedo *et al.*, 1991).

Fardeau *et al.*, (1985) give a theoretical formula describing the decrease of radioactivity with time (t) of exchange:

$$\frac{R_t}{R_0} = \frac{R_1}{R_0}\,[t + (R_1/R_0)^{(1/n)}]^{-n} + \frac{R_\infty}{R_0} \quad (6)$$

where R_0 and R_t are the same as in Eq. (7), and R_1 and R_∞ are the quantity of radioactivity remaining in solution after 1 minute and after an infinite isotopic exchange period; n is an experimental factor between 0 and 0.5. Therefore:

$$E_P = \frac{c_p \cdot 10}{\frac{R_1}{R_0}\,[t + (\frac{R_1}{R_0})^{(1/n)}]^{-n} + \frac{R_\infty}{R_0}} \quad (7)$$

Thus, E_P is a function of R_1/R_0, c_P, R_∞/R_0 and of exchange time. All isotopically exchangeable P present on the solid phase can come into solution and be available to plants. This demonstrates that soil P can not be divided into pools containing available P and unavailable forms of P. Instead, available P is a

function of time and most Pi must be seen as been more or less rapidly exchangeable with the P in solution (Barrow, 1983b).

The E_P values obtained with Eq. 7 can be extrapolated to at least 3 months. Frossard *et al.* (1994b) have shown that the L value of 10 soils (fertilised or not with 100 mg P kg^{-1} soil) experimentally measured after 13 weeks of growth of *Agrostis communis* was not statistically different from their E_P value calculated for an isotopic exchange time of 23 weeks (Figure 4). Validation of the Equation for longer time is difficult due to the 14 day half life of ^{32}P.

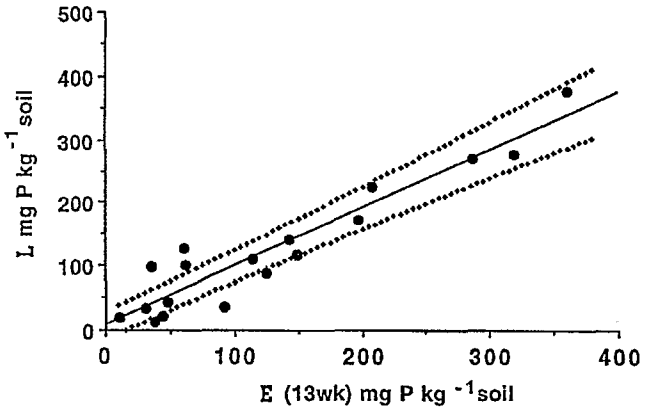

Figure 4. Comparison between the E value calculated for 3 months according to Fardeau et al. (1985) and L values determined experimentally by the method of Truong and Pichot (1976) for 9 soils from widely different origins (from Frossard *et al.* 1994b).

Tran *et al.*, (1988) and Salcedo *et. al.*, (1991) using a double isotopic dilution have shown the existence of an homogeneous pool of free phosphate ions. This pool contains ions in the solution plus ions located on the solid phase with the same mobility as the ions in the solution. This pool is generally not different from the quantity of P isotopically exchangeable within one minute. For t = 1 minute, the Equation 7 can be approximated as follows:

$$E_{P1} = c_P \cdot 10 \cdot (R_0/R_1) \qquad (8)$$

The R_0/R_1 ratio is a measure of the P buffering capacity of soils (Tran *et al.*, 1988; Salcedo *et al.*, 1991; Frossard *et al.*, 1992a; Frossard *et al.*, 1993). Buffering capacity is considered to be very high when R_0/R_1 is higher than 10; high when R_0/R_1 is in the range of 5 to 10; medium when R_0/R_1 is in the range of 2.5 to 5 and low when R_0/R_1 is lower than 2.5.

The results obtained from isotopic dilution kinetics can be interpreted by two complementary analyses: (1) stochastic and (2) compartmental.

(1) In the stochastic analysis, Eq. 6 can be considered as the Laplace transformation of a γ function. This is a probability function describing the distribution of the individual rate of exchange, k_i, between the ions present in the solution and exchangeable ions located on the solid phase, $k = 0$ and $k = \infty$ being excluded (Fardeau *et al.*, 1991). There is a continuum between 0 and the infinite for all k_i values. This means that all phosphate ions in the soil are able to move more or less rapidly to the solution. It is possible to calculate a mean exchange rate, k_m (min^{-1}), of phosphate ions between the soil solution and the solid phase.

$$k_m = \frac{n}{(R_1/R_0)^{(1/n)}} \qquad (9)$$

The mean residence time of phosphate ions in the solution, T_m (min), is:

$$T_m = 1/K_m \qquad (10)$$

And the mean flux of exchange, F_m (mg kg^{-1} min^{-1}) between the solid phase and the solution is:

$$F_m = 10 \cdot c_P \cdot K_m \qquad (11)$$

(2) In the compartmental analysis, a compartment is defined as an homogeneous unit in which all the phosphate ions have the same kinetic properties and exchange at the same rate with phosphate ions present in other compartments.

When $^{32}PO_4$ ions are added to a soil suspension at a steady state, they are introduced in the pool of free phosphate ions and can be exchanged with the $^{31}PO_4$ ions located on the solid phase (Fardeau, 1993). This system is therefore both multi-compartmental and mamellary as defined by Sheppard (1962) and Shipley and Clark (1972), and can be described by the simplified model proposed by Fardeau (1993) (Figure 5).

All compartments are connected to the pool of free phosphate ions which is homogeneous and has a size close to that of E_{P1min}. These ions are almost instantaneously available to plants. Phosphate in this compartment can be exchanged with ions located in:

- The pool of P exchangeable between 1 minute and 24 hours. This represents a period during which a single root can actively take up P.
- The pool of P exchangeable between 24 hours and three months. This corresponds to the growth period of the root system of an annual crop.
- The pool of P exchangeable between 3 months and 1 year.
- And the pool of P exchangeable slowly over periods longer than a year.

The quantity of P ions present in each of these compartments is calculated from Eq. 7. R_∞/R_0 is the maximum possible dilution of the added $^{32}PO_4$ and is approximated by the water soluble P divided by the total mineral P of the soil. It excludes Po whose release is due to hydrolysis and not exchange.

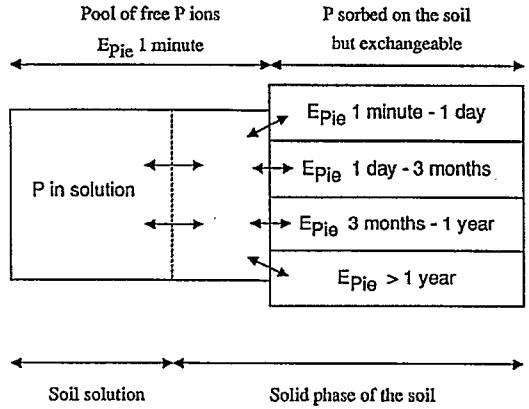

Figure 5. Schematic representation of the multi-compartmental mamellary model of soil exchangeable P (Fardeau, 1993).

Table 2. Total P, organic P, P buffering capacity and water soluble P in 7 soils from various origins

Soil	R_0/R_1	c_p	n	Total P	Org. P
		mg l^{-1}		mg kg^{-1}	
Sandy Feralsol, Burkina Faso	2.44	0.036	0.24	89	55
Clayey Vertisol, Sénégal	33.3	0.008	0.27	265	71
Clayey Cambisol, France	7.58	0.10	0.31	927	251
Silty Luvisol, France	7.40	0.16	0.36	1058	368
Calcareous Rendzina, Morocco	6.67	0.15	0.25	629	266
Calcareous Rendzina, France	3.33	0.12	0.19	1919	348
Andosol, Dominica	142	nd	0.42	2200	909

Data from Frossard *et al.* (1994b); nd: not detected.

The isotopic exchange kinetics for 7 soils are given in Table 2. The sandy soil from Burkina Faso has a very low P buffering capacity while the Vertisol has a very high P buffering capacity. The clayey and silty soils from France and the calcareous soil from Morocco have a high P buffering capacity. The French soil developed on decalcified clay (a "terra fusca" developed on Bajocian limestone) has a medium P buffering capacity. The Andosol has the highest P buffering capacity. Water soluble P ranges from a very low value in the African Vertisol to a high

value in the French Rendzina. Due to a high Si concentration in the solution of the Andosol, the concentration of water soluble P could not be accurately measured. Silica is the major obstacle to a precise measurement of water soluble P (Fardeau and Jappé, 1988; Medeiros and Salcedo, Ch. 20).

The results of the compartmental analysis are presented in the Table 3. The sandy soil from Burkina Faso has a very low available P content. Less than 1 mg kg^{-1} is exchangeable within one minute and only 13 mg kg^{-1} can be exchanged within a year. A soil can be regarded as P limited when E_{P1min} is lower than 5 (Tran *et al.*, 1988). The Vertisol is also very low in available P. In this soil, low in oxides, the slowly exchangeable phosphate must be sorbed either on the clay edges, or on the surface of clay sheets covered by polycationic species. The heavily fertilised clayey and silty French soils have a high available P content. As in the Vertisol, the slowly exchangeable P of the clayey soil probably is sorbed on montmorillonite. In the silty soil, the slowly exchangeable P may be sorbed to iron oxides. The two rendzinas are not P limited. The high proportion (70%) of the Pi which can not be exchanged within a year in the rendzina developed on the terra fusca may be related to its high iron oxide content (Cabrera *et al.*, 1981; Frossard *et al.*, 1992a). The high proportion (57%) of slowly exchangeable P ($E_{P>1year}$) found in the calcareous Moroccan rendzina, might be precipitated with Ca. Due to the small surface area, and to the long reaction times necessary for calcium phosphate precipitation, a significant proportion of the P in this soils can still be exchanged within a year.

Table 3. Calculated P contents in the various exchangeable pools according to the multi-compartmental analysis of Fardeau (1993).

Soil	E_P 1 min	E_P 1min-24h	E_P 24h-3 m	E_P 3m-1 y	E_P >1year
	mg kg^{-1}				
Ferralsol	0.9	3.5	5.9	2.6	21
Vertisol	2.7	15	31	15	130
Cambisol	7.8	59	140	67	400
Luvisol	8.6	92	220	86	290
Rendzina (M)	10	43	72	30	210
Rendzina (F)	37	99	150	68	1200

The results obtained with the stochastic analysis show that all the Pi could arrive in the solution with a mean exchange rate varying from 9.9 min^{-1} in the sandy soil to 118,000 min^{-1} in the Vertisol i.e. the P in the solution will be completely renewed 10 times per minute in the sandy soil and 118,000 times in a minute in the Vertisol (Table 4). The mean flux of exchange varies from 3.55 mg kg^{-1} min^{-1} in the sandy soil to 9,000 in the Vertisol. Fardeau *et al.* (1991) suggest that when E_{P1min} is greater than 5 mg kg^{-1} and when F_m is higher than 80 mg kg^{-1} min^{-1}, P is not a limiting factor for the growth of plants.

Table 4. Mean constants calculated from the stochastic model of Fardeau *et al.* (1991).

Soil	K_m	T_m	F_m
	min^{-1}	min	mg min^{-1} kg^{-1}
Ferralsol	9.85	0.10	3.55
Vertisol	118,000	$8.5 \cdot 10^{-6}$	9,430
Cambisol	213	$4.7 \cdot 10^{-3}$	219
Luvisol	94.5	$10.6 \cdot 10^{-3}$	109
Rendzina (M)	494	$2.0 \cdot 10^{-3}$	741
Rendzina (F)	107	$9.3 \cdot 10^{-3}$	1202
Andosol	56,700	$17.6 \cdot 10^{-6}$	nd

In natural soils, a number of factors affect P desorption. Increasing amounts of oxides decrease P desorption (Sayin *et al.*, 1990; Colombo *et al.*, 1991; Tiessen *et al.*, 1991). The amount of desorbable P is inversely correlated to the P sorbing capacity (Kuo *et al.*, 1988), and to the unoccupied portion of the sorbing capacity (Kuo, 1988). Increasing sodicity can increase the water soluble P (Curtin *et al.*, 1992). Organic compounds such as oxalate can desorb P from acid soils by complexing Al and Fe (López Hernández *et al.*, 1979; Fox *et al.*, 1990; Fox and Comerford, 1992a). The soil water regime can also affect desorption. Bhadoria *et al.* (1991b) showed that the effective diffusion coefficient of P (De) increases strongly when the soil water content increases. Reducing conditions lead to P release followed by a decrease in solution P concentration (Ponnamperuma, 1972). The release has been attributed to the reduction of Fe (III) leading to a dissolution of Fe oxide and to the partial elimination of P sorbing sites. The subsequent decrease of P in solution may be due to the sorption of P on re-precipitated amorphous oxides (Sah *et al.*, 1989b). On the other hand, P sorption may protect Fe oxides against reduction (Willett, 1986), and a rise of solution P in reduced sediments has been observed long before the Eh conditions were low enough to reduce Fe oxide (Nriagu and Dell, 1974). The release of P from waterlogged soils must then be accounted for not only by oxidation-reduction processes but also probably by some biological mechanisms such as the bacterial reduction of iron. Aerobic conditions prevailing in the rice root rhizosphere induce very low pH values due to Fe oxidation, and therefore can lead to the release of soil P to roots (Kirk, 1993). This release may be short-lived, since the succession of flooding and draining periods leads to an overall decrease of P desorption (Sah *et al.*, 1989b).

PLANT UPTAKE AND PHOSPHORUS SUPPLY

ROOT ABSORPTION

Only orthophosphate ($H_2PO_4^-$ and $HPO_4^=$) appears to be taken up directly by the membrane transport systems of plant roots (Anderson, 1980) in an active, energy dependent process (Haynes, 1990) which occurs preferentially in young unsuberised roots, but also along most suberised root surfaces. The process is capable of concentrating phosphates to 10^{-3} *M* within plant root cells and xylem tissue from concentrations ranging between 10^{-5} and 10^{-8} *M* in the soil solution. Uptake takes place against a steep electrochemical gradient and is mediated by a H^+ co-transport. The absorption of phosphate from solutions of low concentration can be described by Michaelis-Menten kinetics. The lowest concentration at which roots can absorb P from soil solution (threshold concentration; Barber, 1984) varies with plant species (reviews by Nye and Tinker, 1977; Mengel and Kirkby, 1982; Barber, 1984) and with genotype (Krannitz *et al.*, 1991). The solution pH and concentrations of mobile cations (e.g. K^+ and NH_4^+) also affect the rate of uptake (Barber and Chen, 1990).

PHYSICO-CHEMICAL SUPPLY

The root absorbing power creates a demand for phosphate at the rhizoplane which is greater than the rate of phosphate transport to the root surface by mass flow of soil water meeting an evapotranspiration demand (Nye and Tinker, 1977; Barber, 1984). The concentration of phosphate in the rhizoplane solution is rapidly depleted through active uptake but, because in most soils the equilibrium condition between solution phosphate (P_L, µmol cm^{-3}) and exchangeable soil surface phosphate (P_S, µmol cm^{-3} soil) is often 1000 fold in favour of the soil surface, the diffusion of phosphate to the depleted zone around the root is slow. As mass flow of P is negligible, in all but heavily fertilised soils, the effective diffusion coefficient of phosphate through soil (D_e, $cm^2 s^{-1}$) becomes a major factor limiting the rate of plant P uptake. D_e can be calculated from the self diffusion coefficient of phosphate in water, (D_L, $cm^{-2} s^{-1}$), by constraining diffusion to the fractional volume of water in a soil, θ, and recognising that the diffusion path has to circumnavigate soil particles and air-filled pores, which effectively reduces the diffusion coefficient by an impedance factor, f. In addition, the power of the soil surface to sorb ($\partial P_S / \partial P_L$) reduces the time allowed for effective diffusion. D_e is thus given by:

$$D_e = D_L \, \theta \, f \frac{\partial P_L}{\partial P_S} \qquad (12)$$

Consideration of root extension rates and the calculated flux of phosphate to the root surface (J_r, µMol cm^{-2} s^{-1}), mostly by diffusion plus a small amount carried in mass water flow (Vo) has proved an effective method of simulating P uptake by plants growing in cultivated soils for short growing seasons (Nye and Tinker, 1977; Barber, 1984), using the equation:

$$J_r = D_e \frac{\partial P_S}{\partial r} + V_0 \, P_L \qquad (13)$$

where $\partial P_S / \partial r$ is the concentration gradient of soil phosphate at radial distances (r) away from the root surface.

The most important soil factors influencing P uptake are those that influence D_e described in Equation [12] (i.e. soil moisture content influences both θ and f and soil texture and bulk density influence f), and the soil P sorption characteristics. Within one soil type ($\partial P_S/\partial P_L$) is curvilinear with respect to P_S and is represented by the differential of the Freundlich isotherm (Kirk and Nye, 1986a). P_S and the nature of the sorption isotherm used to calculate P_L and D_e are sensitive parameters in calculating P uptake (Silberbush and Barber, 1983). However the sorption isotherms may not be sufficient to predict the uptake of P. Shaviv *et al.* (1992) showed that the predicted uptake of P was strongly reduced when P sorption kinetics were also taken into account. Bhadoria *et al.* (1991a) stressed the importance of using desorption rather than adsorption isotherms to describe P uptake in soils of low P status.

Although only limited validation of these physico-chemical models of P supply to plants has been carried out, they are believed to provide a mechanistically correct description of short-term P uptake processes. Deviations of predicted from observed P uptake are likely to be due to factors that influence the most sensitive parameters of a model, for example: factors influencing root extension, such as soil acidity and Al toxicity, lack of other growth limiting nutrients, and adverse soil physical properties; and factors influencing D_e, such as, heterogeneous soil structure, soil pH (Barber and Chen, 1990) and a P_S pool which may sorb P during the period of plant growth. A low P supply induces an increase of the root surface mostly through increased production of root hairs (Anghinoni and Barber, 1980; Dinkelaker *et al.*, 1989; Anuradha and Narayanan, 1991; Föhse *et al.*, 1991) and/or enhanced myccorizhal association (Plenchette, 1991).

SOLUBILISATION OF INORGANIC P BY ACIDIFICATION, CHELATION AND REDUCTION

The modeling approach described above should be restricted to those plants which use only isotopically exchangeable P such as rye grass (Fardeau and Jappé, 1976) or *Agrostis* (Figure 4). Other plants (e.g. *Lupinus* spp., *Brassica* spp, *Beta* spp) and associated microorganisms modify the chemistry and biochemistry of rhizosphere soil in a number of ways which can influence the pool of P_S through the solubilisation of soil Pi and the mineralisation of Po. Claassen (1992) recently reported significant deviations between the uptake of P as predicted from the model and the actual uptake by sugar beet (*Beta vulgaris*). This difference can be attributed to biological processes causing the dissolution of insoluble forms of Pi and/or Po in the sugar beet rhizosphere (Heck and Saive, 1983). The dissolution of the mineral P in the rhizosphere are effected by the excretion of H^+ and organic acids by roots, fungi and bacteria.

The excretion of H^+ is related to the cation-anion balance of root uptake and exudation. A plant supplied with NH_4^+ as the sole source of N excretes H^+, while OH^- is excreted with NO_3^- uptake (Gahoonia and Nielsen, 1992). A net H^+ efflux also occurs when NO_3^- fed plants are grown in a P-deficient solution (Le Bot *et al.*, 1990), due to a greater uptake of cations than anions (Moorby *et al.*, 1988). This process was invoked by Hedley *et al.* (1982) to explain the solubilisation of calcium phosphate by *Brassica napus*. Bekele *et al.* (1983) reported higher yields and P uptake of plants grown on rock phosphate with NH_4^+ than with NO_3^-. Legumes acidify their rhizospheres (Haynes, 1983) through surplus cation uptake

as a result of N_2 fixing activity, and can be efficient users of acid-soluble P (Bekele *et al.*, 1983, De Swart and Van Diest, 1987). Kirk and Nye (1986b) have incorporated H^+ excretion by roots and subsequent P solubilisation into a computer simulation of plant uptake of P from soil fertilised with calcium phosphates.

Hoffland *et al.* (1989a) showed that while P deficient plants continue to show a net surplus of anion uptake under NO_3 nutrition, areas behind the root tip still excreted H^+. In young rapeseed plants this was associated with accumulation and excretion of malic and citric acids (Hoffland *et al.*, 1989b) in quantities sufficient to solubilise more P from a phosphate rock than was actually taken up by the plant (Hoffland 1992). Similar organic acid excretion has been noted for P deficient, proteid roots of lupins (Gardner *et al.*, 1983) and of *Banksia integrifolia* (Protaceae) (Grierson, 1992). White lupine (*lupinus albus*) can excrete up to 23% of its total weight as citric acid when grown on a calcareous P deficient soil (Dinkelaker *et al.*, 1989). The excretion of citric acid not only allowed for the dissolution of calcium phosphate but also for the precipitation of Ca-citrate which acts as a sink for Ca ions. Ae *et al.* (1990) showed that pigeon pea can solubilise Fe phosphate with chelating organic acids. Strains of carrot root cells which produce large amounts of citric acid are able to use $AlPO_4$ as the sole source of P (Koyama *et al.*, 1990), and have maximum P uptake rates three fold higher than non adapted cells (Koyama *et al.*, 1992).

Further research is required to determine how the physical stage of plant growth and the nutrient status of plant and soil influence acid excretion. Plants that excrete acid as undissociated organic acids have advantages because the organic anion concentrated in the rhizosphere may have chelation and reduction abilities (Gardner *et al.*, 1983). Plants that are net anion absorbers are expected to raise the pH of their rhizospheres. Increased rhizosphere pH has been shown to convey Al-tolerance in cereals (Haynes, 1990) which presumably can improve root extension and sustain P uptake in acid soils.

The rhizoplane and rhizosphere host a large number and variety of free-living microflora and microfauna, mostly living within 20 μm of the root surface (Foster, 1986). The microflora metabolises rhizo-deposited carbon, which in young plants can account for 5-30% of the photosynthetically fixed carbon (Lynch and Whipp, 1990). In this process such microflora may generate low molecular weight organic compounds which have the power to release soil P (reviews Tinker, 1983; Richards, 1987) by acidification (e.g. 2-ketogluconate), chelation (e.g. citrate, oxalate) and reduction (e.g. sugars, citrate, hydroxamates). Whether these compounds are produced in sufficient quantity to influence plant nutrition remains a matter for debate (Tinker, 1984). The activity of iron-reducing bacteria can release P sorbed on iron oxides. In soils, the solubilisation of P minerals may result from the synergistic action of a group of microflora rather than just one microorganism. Leyval and Berthelin (1987) showed that the solubilisation of $Ca_3(PO_4)_2$ was 2-5 times higher when a bacterium (*Agrobacterium radioabacter*) was introduced with the ectomycorhizal fungi *Laccaria laccata* or *Paxillus involutus* than when the bacterium was alone (Figure 6). On the other hand *A. radiobacter* inhibited the growth of *L. laccata* in the presence of $FePO_4$. The effects of rhizosphere microflora are further complicated by other trophic interactions of microflora that result in root microflora being both sinks and sources of plant available P (Baas, 1990).

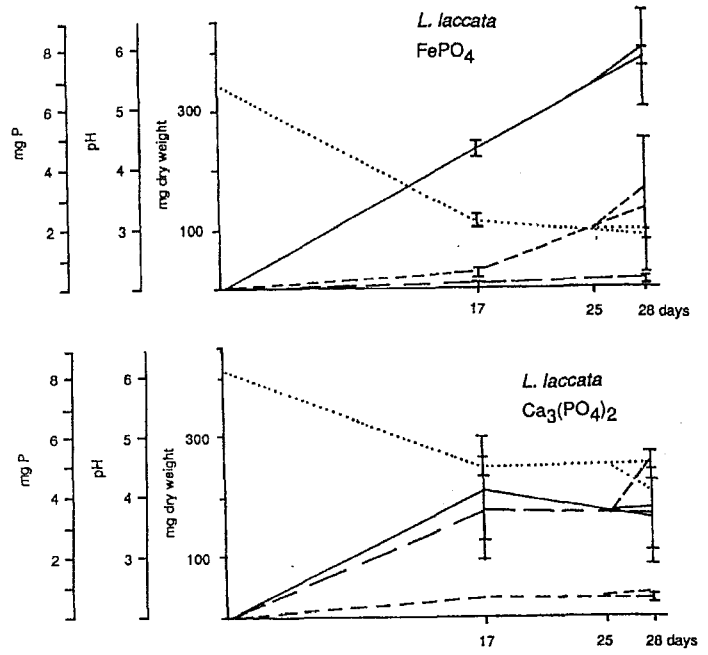

Figure 6. Growth (____), pH decrease (.....), phosphorus solubilisation (_ _ _) and immobilisation (----) kinetics of an ectomycorrhizal fungus (*P. involutus*) inoculated after 25 days with *A. radiobacter* (Leyval and Berthelin, 1987)

ENZYMATIC HYDROLYSIS

Research on cropped soils (Sharpley, 1985) supports the concept that Po mobilisation occurs when Pi supply limits plant growth and phosphatase enzymes of plant and microbial origin are induced. The turnover (Helal and Sauerbeck, 1984) and depletion (Tarafdar and Jungk, 1987) of soil Po are greatest in rhizosphere soil. Phosphatase activity is greater in the rhizosphere of young and perennial plants than in bulk soil (Burns, 1985; Burns *et al.*, 1989; Häussling and Marschner, 1989; Fox and Comerford, 1992b). This has permitted the observation *in vivo* of acid phosphatase activity in the rhizosphere of soil-grown plants (Dinkelaker and Marschner, 1992).

Roots under sterile conditions produce phosphatases able to hydrolyze a wide range of Po and polyphosphates (Dick and Tabatabai, 1986; Tarafdar and Claassen, 1988; Juma and Tabatabai, 1988). Phosphatase activity varies with plant species and variety (Helal, 1990) and along roots (Adams and Pate, 1992). Kroehler and Linkins (1988) showed that Pi produced by the hydrolysis of Po at the root surface

could provide up to 65% of the annual need of P of *Eriophorum vaginatum*, while the amount of Po mineralised through enzymatic activity by oats, barley, clover or wheat surpassed by a factor of 20 the plant uptake of P under both sterile and non sterile conditions (Tarafdar and Claassen, 1988; Tarafdar *et al.*, 1992).

Microbial phosphatases may also be of importance for plant nutrition (Tarafdar and Claassen, 1988). The uptake of P by *Pinus caribea* from phytic acid was strongly enhanced when the plant was inoculated with both phosphate solubilising bacteria and the ectomycorrhizal fungus *Pisolithus tinctorius*. (Chakly and Berthelin, 1983). Macrofauna, such as earthworms can affect the production of microbial phosphatase (Satchell *et al.*, 1984), possibly through increasing microbial activity (Lavelle *et al.*, 1992).

The production of phosphatase either by roots or associated micro-organisms is an efficient strategy for the acquisition of P by plants. The factor limiting plant utilisation of Po is the availability of these Po sources rather than the production of enzymes (Tarafdar and Claassen, 1988). It is not clear to what extent roots and micro-organisms compete for P sources.

Enzymatic activity is a function of soil properties (pH, water content, surface charge, redox condition etc.) and soil fabric (microsites) (Nannipieri, 1984). The sorption of enzymes on clay, oxides or humic substances can change enzyme conformation and reduce activity (Dick and Tabatabai, 1987; Quiquampoix, 1987, Nannipieri *et al.*, 1988).

MYCORRHIZAL ASSOCIATION

Mycorrhizal fungi increase the uptake of less mobile nutrient ions such as, P and Zn from soils (Bolan, 1991; Plenchette, 1991, Lajtha and Harrison, Ch. 8). More than 80% of the higher plants can enter into mycorrhizal associations (Gianinazzi, 1991). These associations have occurred at least since the Devonian, allowing substantial co-evolution (Gianinazzi, 1991) and genetic adaptation (Lu and Koide, 1991). Root exudates stimulate P uptake and increase growth of hyphae (Johnson *et al.*, 1991; Thomson *et al.*, 1991; Lei *et al.*, 1991). The uptake and translocation of P from the soil to the host plant is ultimately regulated by the transfer of carbohydrate from the host to the fungus (Koide and Schreiner, 1992; Schwab *et al.*, 1991). High levels of infection together with high P availabilities have been associated with a depression of host plant growth due to the high carbohydrate demand of the fungus (see references in Koide, 1991).

Mycorrhizae increase the physical exploration of the soil, effectively increasing the rhizosphere volume (Leyval and Berthelin, 1991; Jakobsen *et al.*, 1992a; Li *et al.*, 1991a). The dependence of plants on mycorrhizal infection for nutrient acquisition may be related to P requirement (Plenchette, 1991; Koide, 1991) and is inversely correlated to the fineness of the root system (Baylis, 1975; Hetrick *et al.*, 1988). Mycorrhizal infection also enhances the transfer of P between living roots and from dying roots to living roots. Inter root transfer of P overcomes the loss of P likely to occur through soil adsorption, leaching and immobilisation by microorganisms (Newman, 1988; Newman and Eason, 1989).

Numerous studies have shown that mycorrhizae dissolve insoluble P minerals (Leyval and Berthelin, 1986) through the excretion of H^+ and organic acids (Li *et al.*, 1991b; Lapeyrie *et al.*, 1990; 1991), and hydrolyse Po through phosphatases (Fabig *et al.*, 1989; Antibus and Linkins, 1992). The presence of a varied microflora may enhance or inhibit the use of these insoluble P compounds by

plants (Chakly and Berthelin, 1983; Leyval and Berthelin, 1987). The extent to which insoluble P can be used by plants in field soils remains to be demonstrated (Gianinnazi-Pearson *et al.*, 1981).

The rate of inflow of P into mycorrhizal roots cultivated under controlled conditions is much greater than that of nonmycorrhizal roots (Sanders and Tinker, 1973; Jakobsen *et al.*, 1992a). However the relationship between arbuscular mycorrhizae (AM) root infection and P inflow is not clear under field conditions (Sanders and Fitter, 1992). The capacity of transport of P from the hyphae to the root varies greatly with the fungus species (Jakobsen *et al.*, 1992b). The variability in the responsiveness of plants to mycorrhizal infection is related to both the plant demand and the soil P supply (Koide, 1991) as well as environmental factors such as the soil water status, or to faunal interactions (Fitter, 1985; Coleman *et al.*, 1988).

SYNTHESIS AND DECOMPOSITION OF ORGANIC P

Organic P constitutes 29 to 65% of topsoil P (Harrison, 1987), most in low molecular weight compounds (Fares *et al.*, 1974; Condron and Goh, 1989). Inositol phosphates can make up to 50% of the identifiable Po, other sugar phosphates, phospholipids, nucleic acids, phosphonates are also present but in minor quantities (Stewart and Tiessen, 1987). A large proportion of Po remains unidentified because of the stable nature of Po-soil complexes, which prevent extraction of these compounds. The Po composition of the soil is quantitatively different from that of living organisms which indicates that specific processes lead to the selective stabilisation of various Po compounds in soils (Stewart and Tiessen, 1987).

Organic P is synthesised in plants and may constitutes approximately 20-80% of P in plant vegetative tissue, depending upon plant part, age and P supply, and 70-83% of P in seeds. The more important Po compounds synthesised are phospholipids (membrane structure), nucleic acids (genetic code) and inositol phosphates (P storage). Their respective tissue concentrations in leaves are in the range 0.01%, 0.01% and <0.0001% and in seeds 0.002%, 0.02% and 0.05%. In general, P concentration is higher in meristematic tissue. It is common for P in older plant parts to be remobilised and transported to meristematic tissue or to seeds (Koide, 1991).

MICROORGANISMS

Brookes *et al.* (1984) estimated that microbial phosphate made up 3 to 24% of the Po in temperate arable or pasture soils. Lee *et al.* (1990) observed that glucose additions to a highly weathered soil increased the quantity of microbial P, but Martin and Correll (1989) detected no Po synthesis by biomass in wheat rhizosphere soil. A possible explanation may be that approximately 5-30% of photosynthetically fixed carbon is rhizodeposited (Lynch and Whipps, 1990) and probably consumed by the population of rhizosphere microorganisms within 20 µm of the rhizoplane (Foster, 1986), so that rhizosphere synthesised-P and root P may not be separable. Rhizosphere organisms commonly are high in P and often contain inositol polyphosphate granules. Away from roots, most bacterial activity is isolated in discrete microsites around organic residues, and the bacteria are

usually smaller and lack polyphosphate granules (Foster, 1986). Most forms of Po are common to both plants and microbes. Scyllo-isomers of inositol phosphates are of microbial origin (Cosgrove, 1966), and phosphonates are produced by the soil microflora or fauna (Newman and Tate, 1980; Nakashita and Seto, 1991).

Only a limited proportion of P is incorporated into high molecular weight organic compounds during humification (Fares *et al.*, 1974; Condron and Goh, 1989). Brannon and Sommers (1985) have shown that P incorporated into synthetic humic compounds could resist both chemical and enzymatic hydrolysis. This stability can be reinforced further by a physical stabilisation or organic colloids with clay particles (Skjemstad *et al.*, 1986).

DECOMPOSITION OF ROOTS, LITTER AND EXCRETA

As ecosystems mature, the proportion of P in organic forms increases and P nutrition becomes more dependent upon the recycling of P by Po decomposition (Walker and Syers, 1976; Harrison, 1985; McLachlan *et al.*, 1988).

Decomposition processes are the result of activities of microbes and small animals (Richards, 1987; Toutain, 1987a; Ponge, 1991) and involve physical breakdown, transport, catabolism and leaching (Swift *et al.*, 1979; Toutain, 1987b). Microorganisms have specific degradative functions. Few bacteria degrade pectin, cellulose or starch while most of the fungi will. Fungi are commonly the initial agents of catabolism (Reisinger *et al.*, 1978), in conjunction with invertebrate animals, protozoa and bacteria (Richards, 1987). Trophic interactions, for example predation of microflora by amœbae and nematodes (Cole *et al.*, 1978; Clarholm, 1981; Anderson *et al.*, 1982; Coleman *et al.*, 1988; Elliot *et al.*, 1988) or interactions between microflora and fauna (Lavelle *et al.*, 1992) increase the turn-over of the microbial populations. This leads to increases in the diversity and activity of enzymes contributing to the degradation of stable organic compounds (Bottner and Billès, 1987). Communition and mixing by earthworm or termite activity allows for a greater surface area of substrate to come into contact with appropriate organisms and enzymes (Kretzschmar, 1987; Garnier-Sillam *et al.*, 1987). As an example of the role of the macrofauna on P cycling, Fardeau and Frossard (1992) showed that the quantity of isotopically exchangeable P at 1 min increased from 2.2 mg kg^{-1} in the bulk soil to 87.0 mg kg^{-1} in the center of a termite (*Trinervitermes geminatus)* nest.

The microstructure of soil fabric offers physical protection to the microflora (Van Veen *et al.*, 1984; Merckx and Martin, 1987). Chotte *et al.* (1994) showed that aggregates >2 cm (isolated by wet sieving without agitation) represented the most important habitat in a Vertisol; 50% of the soil weight containing 30% of the total biomass was associated with fresh or partly decomposed organic skeletons and clay plasma. Access to the substrate by appropriate organisms and their enzymes can be limited, either by aggregation of soil particles and microbial metabolites entombing the residue and the initial decomposer organism (Ladd *et al.*, 1990), or by allelopathy of the incumbent organisms. Aggregation may also cause decomposition to decrease because small, water-filled pores limit oxygen diffusion to intra-aggregate decomposers or limit access to predators (Bamforth, 1988). The size of pore openings depends on soil particle size and orientation, while the strength of the aggregate bonding reflects mineralogy and the nature of the bonding agent (roots, hyphae or microbial metabolite) (Harris *et al.*, 1966; Tisdale and Oades, 1982; Payne, 1988). For example, amorphous alumino-silicates

form particularly strong aggregates with small micropores which are considered to be responsible for the fine structure and high carbon content (10-12%) of some New Zealand Andisols under pastures (Jackman, 1964a).

Factors affecting the rate of decomposition and fate of organic P

The rate of decomposition of Po in litter and excreta, depends initially on the P solubility in the residue and subsequently on the rate of decomposer growth. The rate of decomposer growth depends on substrate accessibility to the organism and its enzymes, the chemical nature and nutrient content of the substrate (extent of lignification, C:N:P ratio, Table 5) and the surrounding soil water (pH, 0_2 partial pressure, N, S and P concentrations) (Vaughan and Ord 1985; Sparling, 1985).

Table 5. Phosphorus, carbon, nitrogen content and C/P, C/N ratios of some plants, animals, and manures.

	P	C	N	C/P	C/N	References
	mg g^{-1} dry weight					
Bacteria	14-32	500	150	16	3	1
Actinomycetes	15	500	110	33	5	2
Yeasts	6-7	470	62	67	8	3
Fungi	4-6	440	34	73	13	3
Soil microbial biomass				10- 26	10-11	4
Earthworms	9	460	100	51	5	2
Maize	2	440	14	220	31	5
Lucerne	3	450	33	161	14	6
Farmyard manure	5	370	28	69	13	2
Tropical manure	3-15		0-26			7
Sewage sludge	25	39	68	159	6	8

[1] Roberts *et al.*, (1955) cit. in Jenkinson (1981); Brookes *et al.*, (1982);
[2] Jenkinson (1981); [3] Jenkinson (1981), Brookes *et al.*, (1982);
[4] Singh *et al.*, (1991), Brookes *et al.*, (1984); [5] Miller (1938); [6] Bertrand (1939), cit. in Jenkinson (1981); [7] Pieri (1989); [8] Brossard *et al.*, 1991

Fifteen to 50% of plant P may be soluble (Pi and monoesters, Table 6). If plant residues are incorporated into soils this P can be rapidly adsorbed by soil surfaces (Friesen and Blair, 1988; McLachlan *et al.*, 1988). Sorption of simple Po compounds by reactive clay surfaces will decrease their rate of decomposition and may lead to their stabilisation (Tate, 1985). Chopping or grinding plant residues and incorporation into soil improves residue-soil contact and speeds this process (Friesen and Blair, 1988; Jenkinson, 1988). In highly competitive root zones of

permanent pasture, roots or mycorrhizal hyphae can grow into litter and utilise soluble P (Thibaud *et al.*, 1988; Newman and Eason, 1989) preventing sorption by soil surfaces or immobilisation by free-living soil flora.

The non-water soluble P (mostly diesters: nucleic acids, phospholipids, and phosphoproteins) remaining in the residues are used by fast growing saprophytic fungi, followed by slower growing fungi with suites of polysaccharases. If there is adequate moisture and the solution does not become acidic, bacteria will be able to colonise residues quickly (Richards, 1987). The rate of decomposition at this stage is controlled by nutrient availability, particularly N (Jenkinson, 1988). Much of the residue P will be immobilised into decomposers and their predators. For example, clearfelling increases biomass P in the Oh horizon as a result of debris input to the forest floor (Hughes and Reynolds, 1991). The new microbial Po may last for one season because the mean turnover time of microbial biomass in cultivated temperate soils appears to be greater than 1 year (Sparling, 1985).

Table 6. Water soluble phosphorus in *Digitaria d.* and maize roots (Brossard et Laurent, unpublished)

		Digitaria decumbens	Maize
		---------- µg g^{-1} root ----------	
Total P		175	644
Water soluble	total P	37.1	107.9
	Pi	16.9	56.7
	Po	20.2	51.2
	C	5041	16463
	C/N	26	17
	C/Po	250	322

Results of McLachlan *et al.* (1988) support these ideas. Seven to ten days after applying ^{33}P labeled, medic residues to a wheat seed bed, 40-50% of the litter P (approximately equivalent to the soluble P content of the litter) could be found in soil Pi, whereas the remaining residue Po remained either as soil Po or biomass P for the remainder of the wheat growing season, showing that little P mineralisation occurred due to biomass cycling. The medic residues initially contained 0.3% P, thus after initial soluble P loss (50%), the non water-soluble P residue probably had a C:P ratio exceeding 300. The generalised equation (14) derived by White (1981) shows that little P mineralisation is expected:

$$\frac{\text{Amount of P mineralised}}{\text{Amount of C-CO}_2\text{ mineralised}} = \frac{[C_{om}/P_{om} - C_y(C_m/P_m)]}{(1-C_y)} \qquad (14)$$

where C_{om}/P_{om} and C_m/P_m are the C:P ratios of the organic matter being decomposed and the biomass respectively, and C_y is the growth yield.

If the C_m/P_m is taken to be 15 and the long term growth yield $C_y = 0.5$, then it can be calculated that net mineralisation of P is unlikely to occur until the 4th

generation of decomposers on the medic residues. As C:P ratios of most plant residues are 140 or greater (Brossard and Laurent, 1992; Tiessen and Stewart, 1983), initial P mineralisation is probably due to the release of soluble P by cell lysis (Friesen and Blair, 1988). Mineralised biomass P is more likely to be derived from substrates with C:P ratios near 30-50. This suggests that most P mineralised by the biomass is derived from the decomposition of microflora and fauna which have C:P ratios ranging from 12-45 (Tate, 1985; Brookes *et al.*, 1984). Evidence for rapid biomass growth on residues applied to cultivated soils followed by periods of no net P mineralisation from the fresh residue but extensive P mineralisation from old residues is provided by McLachlan *et al.* (1988). During the first 7 days after adding ^{33}P labeled medic residues to the soil they found rapid incorporation of 25-30% of the label into microbial biomass and the percentage of ^{33}P remaining as Po remained constant for the next 88 days.

This sequence of events is consistent with observations that at any one time <15% of biomass in arable soils is active (Sparling, 1985) but carries high adenylate energy charge and can respond rapidly to inputs of easily decomposable residue for short periods of time before returning to an inactive state. During the active period of P cycling in McLachan *et al.*'s experiment 83% of the increase in biomass P was derived from unlabelled soil P reserves which also supplied 60-70% of the P taken up by the wheat crop. Presumably this resulted partly from the limited spatial distribution of the ^{33}P labeled, medic residue in the bulk soil and partly from the more widespread mineralisation of previously "protected" Po residues made available by cultivating the soil.

Decomposition in an arable soils may proceed as follows. Cultivation and residue incorporation or root exudation activate microflora (Billès *et al.*, 1986) . Decomposers grow on insoluble P residues and immobilise soil Pi and any P released by hydrolytic enzymes. Decomposer activity then is reduced because the carbon substrates become more complex and the initial decomposers may lack the appropriate hydrolases to complete decomposition. Access to the substrate by organisms and their enzymes may be limited by environmental factors (changes in soil fabric, aggregation and climate).

Mechanical disturbance of soils affect these processes, reducing aggregation (Harris *et al.*, 1966) and promoting Po mineralisation (Hedley *et al.*, Ch. 5). Cultivation, freeze/thaw or wet/dry cycles (Harris *et al.*, 1966) and root growth through weak aggregates (Payne, 1988) also provide such disturbance. Cultivation decreases the Po content of unfertilised soils (Tiessen and Stewart, 1983; Condron *et al.*, 1990) and limits Po synthesis in favour of Pi accumulation in fertilised soils (Johnston, 1989; Ivarsson, 1989). Cultivation causes preferential mineralisation of diester-P while monoesters remain (Condron *et al.*, 1990) due to their greater stabilisation through sorption.

In undisturbed soils, like permanent pastures, the degree of protection of Po is high, and addition of inorganic P fertilizer results in rapid accumulation of organic P (Jackman, 1955; Walker *et al.*, 1959; Jackman, 1964a, 1964b; Brossard and Laurent, 1992). The rate of accumulation of Po in regularly fertilised pastures decreases per unit increase of total soil P (Perrott *et al.*, 1989). The rate of Po accumulation is a function of plant productivity and the rate of Po mineralisation. In legume-based pastures the rate of organic matter mineralisation is also a function of soil nitrogen status.

MODELLING THE P CYCLE

Most models of P dynamics have concentrated on a specific set of soil and plant processes operating over time scales of hours to months. While annual P budgets have been constructed for a variety of ecosystems, there have been few attempts to develop dynamic models of P cycling at ecosystem level over a number of years.

The P cycle in grazed temperate perennial pasture in New South Wales, Australia was modeled by Blair *et al.* (1977). The model is based on an available P pool comprising soil solution P plus bicarbonate extractable P. Mineralisation, fixation, fertilizer dissolution, plant uptake and litter return, and animal transfers were included in the model (Figure 7). A similar P model by Katznelson (1977) gives typical pool sizes and a qualitative description of the controls on the flows of P for pastoral ecosystems.

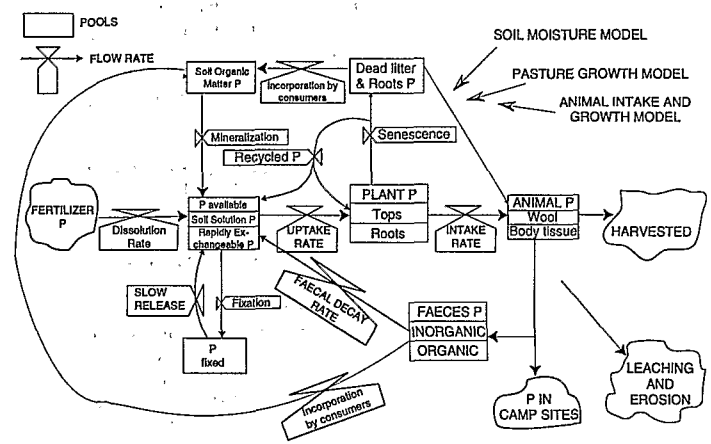

Figure 7. P cycling model (Blair *et al.*, 1977)

The simulation model of P cycling in semiarid North American grasslands by Cole *et al.* (1977) considers solution P, labile and stable Pi and Po, decomposers, litter, standing dead, live plants partitioned into shoots, crowns and roots, and consumers. Labile Pi was defined as P which can enter soil solution by isoionic exchange within an appropriate time. Processes represented include plant uptake and translocation of P, uptake by decomposers, and mineralisation of labile and stable Po. Soil solution P is used to control the rates of P uptake by plants and decomposers but, because the model was designed to run at time steps of one day or more, P flows are taken directly from the labile Pi pool. The P uptake by decomposers was the largest annual flow in the simulation. Long term stability of the model was sensitive to the rate of Po mineralisation.

The decomposition of soil organic matter was the focus of a model of C, N, P, and K dynamics described by Smith (1979). The initial disintegration phase of the

decomposition of plant or microbial organic matter yields free Po, which can in turn yield Pi or be sorbed onto soil colloids in competition with Pi sorption. The sorbed Po is protected from microbial degradation and is only slowly released to soil solution Po. The sorption of both Pi and Po is described by a Langmuir isotherm. The dissolution of slowly soluble mineral P or fertilizer P are described separately. Microbial and plant uptake of P is modeled with Michaelis-Menten kinetics with maximum uptake rate dependent on the labile P concentration in the cell. Growth and death of the microbial population are allowed for.

P and N cycles in *Calluna* heathland ecosystems have been modeled by de Jong and Klinkhamer (1983) using an annual time step. The model has state variables for total soil Pi, ash from the burning of plants or litter, root zone and sub-root zone humus, live and dead roots, green and brown shoots, flowers, wood and litter. Plant uptake, senescence, burning, litter decomposition, dead roots, and humus are represented. The only P input considered is rainfall, while leaching of Pi and downward movement of P in humus are the outputs from the ecosystem.

The P cycle in *Calluna* heathland has been modeled again by Chapman *et al.* (1989) using either annual or monthly time steps. The model includes a water soluble P pool with P sorption and the dissolution of P from ash and mineral compartments considered. Plant production is controlled by available P equal to the sum of the water soluble and adsorbed pools. The P content of aboveground plant material is a function of plant age. The model allows for two optional approaches to mineralisation of P from organic matter. Rates of P release can be related to organic matter decomposition, or the composition of other relevant compartments can be made to remain constant, with transfers to the soil solution calculated accordingly. Both approaches give similar results. A leaching loss of Pi is calculated from drainage and the concentration of P in soil solution. Aeolian losses of P by burning are also considered.

A model of C, N, P, and S cycling in perennial pastures in New South Wales, Australia (McCaskill and Blair, 1988) accounts the soil biomass, organic and inorganic soil pools, grass and clover, sheep and excreta. Inorganic P was split into plant available P and two fixed pools representing native soil P and P of fertilizer origin. Uptake of S, P and N was based on diffusion and plant uptake kinetics (McCaskill and Blair, 1990). Relationships were simplified to reduce the computer time required. Nutrient uptake was allowed to occur within an effective radius calculated from the root radius plus root hair length, the half distance between roots, and the effective diffusivity coefficient. Mycorrhizal infection was simulated by increasing the effective root length. Plant uptake could be limited by either diffusion to the root, root uptake capacity or plant demand. To account for the effects of rhizosphere acidification, variation of the buffer capacity with distance from the root and other factors, it was necessary to calibrate the effective rooting radius against field data for plant tissue concentrations.

As a submodel for the Erosion-Productivity Impact Calculator (EPIC) model Williams (1990) and Jones *et al.* (1984) developed a soil and plant P model based on a labile P pool equivalent to P extractable with anion exchange resin. The labile pool is buffered by an active Pi pool, the size of which is estimated from the size of the labile pool and an availability index calculated from P sorption over 6 months. Relationships to derive labile P and the availability index have been established using other soil P tests and soil properties such as the clay content (Sharpley *et al.*, 1984; Sharpley *et al.*, 1989). The active pool is in slow equilibrium with a stable mineral P pool. Plant P uptake is controlled either by

plant demand or by a function of the size of the labile P pool, the root mass in each soil layer, and soil moisture. The model has pools for fresh and stable organic matter. Mineralisation from the fresh Po pool is controlled by the C:N and C:P ratios, soil water, temperature and the stage of residue decomposition. The stable organic matter pool is subdivided into mineralisable and non-mineralisable fractions depending on the length of time under cultivation. P can be lost from the ecosystem in plant produce, eroded sediments and surface runoff. The effects of agricultural management are a key feature of the model.

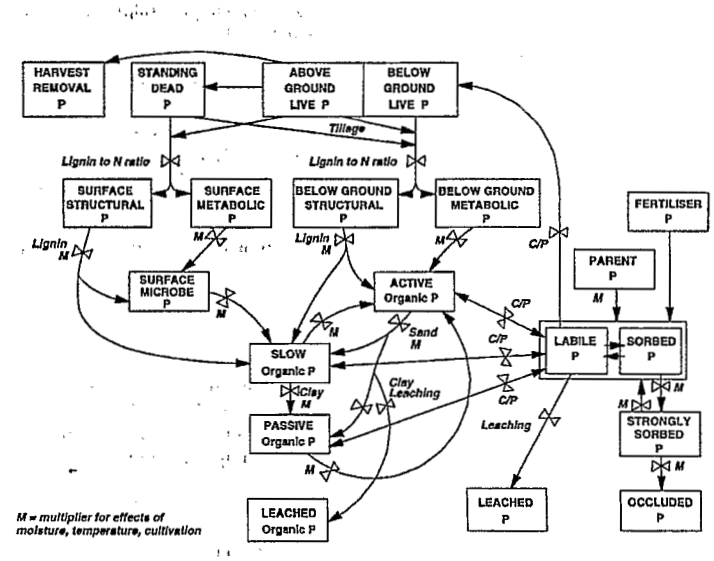

Figure 8. The pools and flows of phosphorus in the CENTURY model

The CENTURY model (Parton *et al.*, 1988; Figure 8) simulates long-term C, N, P, and S dynamics in a variety of ecosystems with an emphasis on soil organic matter. Plant residues and animal excreta are partitioned into structural and metabolic components, while soil organic matter is divided into active, slow and passive pools. Each pool has a characteristic turnover time and range of C:N, C:P and C:S ratios. Turnover times and the efficiency of organic matter stabilisation are functions of soil texture. The C:P ratio of organic matter entering each of the active, slow and passive pools varies as a function of the labile P level where labile P is defined as phosphate which is isotopically exchangeable or extractable with anion exchange resin. Plant P status varies with the balance between supply from the labile pool and plant demand. Increasing N status is assumed to increase the availability of P to plants. Given the monthly timestep of the model, the labile pool is assumed to be in equilibrium with a sorbed pool equivalent to 0.1M NaOH extractable P, in a curvilinear relationship described by sorption affinity and

sorption maximum parameters. This pool is in slow equilibrium with a strongly sorbed pool. P can enter the cycling pool by weathering of a parent material and can be slowly fixed in an occluded pool.

There is still considerable scope for the development of mechanistical P cycling models which can be applied over long time scales in order to study the transformations of P between various inorganic and organic soil pools and to account for losses from the ecosystem. Transport of P between ecosystem components in the landscape with runoff, eroded sediments and animal excreta also needs to be considered in ecosystem level models. Model development needs to characterise processes at an appropriate level for application to a wide variety of soils and managed and natural ecosystems. Plant and microbial uptake of P and the rate of organic matter decomposition can be limited by the availability of other nutrients, particularly N, K, and S. Hence it is desirable that models of ecosystem P dynamics also consider these other elements.

An alternative approach has been to model the residual value of P fertilizer in agricultural systems where empirical relationships are derived between crop or pasture yields and a labile P pool (Helyar and Godden, 1977b; McCall and Thorrold, 1991). The approach lends itself to economic analysis (Godden and Helyar, 1980; Scobie and St. Pierre, 1987). P is lost from the labile pool either by first order linear kinetics or by an inverse function of time since fertilizer application (Probert and Williams, 1985).

CONCLUSIONS

The most noticeable advances of the last 15 years have been the integration of abiotic processes with biological processes into more complex models, stressing the role of the soil fabric and of the biological interactions (between organisms, or between organic components and minerals). Concerning the abiotic processes significant recent advances have been:

- some understanding of the influence of reaction time on the fate of sorbed P, especially for long reaction periods;
- expansion of the results obtained with pure minerals to more complex minerals such as Al-substituted iron oxides or minerals of soil origin;
- appreciation of the importance of the soil fabric;
- design of new methods allowing for the determination of soil exchangeable P, e.g., the isotopic exchange kinetics or the use of iron oxide impregnated paper.

Concerning the biological aspects of P cycling important recent advances are:

- the understanding of plant strategies for the acquisition of P, such as the role of root exudates;
- the recognition of the importance of microbially mediated processes
- the consideration of microflora - fauna interactions which allows for an holistic view of decomposition processes;
- the use of NMR allowing for the observation of the full range of Po types.

The major processes, described in this review, are summarised in the Figure 9. The abiotic and biological regulations of the phosphate supply to the soil solution are strictly related to the organisation of the soil at different scales and to biologically active surfaces (represented for example by the microbial biomass:root surface ratio in different zones of the rhizosphere).

In light of this review some directions for future researches on the processes of P cycling can be proposed. Eventually all processes should be integrated at various times and space scale levels from the soil horizon, to the profile and even to the landscape in order to provide a comprehensive understanding of P cycling. The current development of non-invasive new techniques (X-ray energy dispersive analysis in conjunction with electron microscopy or high resolution solid state ^{31}P NMR) will allow for an improved resolution in observation of the elementary processes (from weathering to biological transformations). The quantification of P mineralised from organic matter or present in the microbial biomass could now be improved with the knowledge acquired through the use of radioactive tracer P in soils. It should also be determined at which soil available P level plants begin to actively solubilise P minerals or Po. Models look promising as integrative tools allowing for a formalised conceptualisation of the P cycle, for the identification of missing links and eventually predicting the influences of given environmental conditions or anthropogenic effects on P cycling.

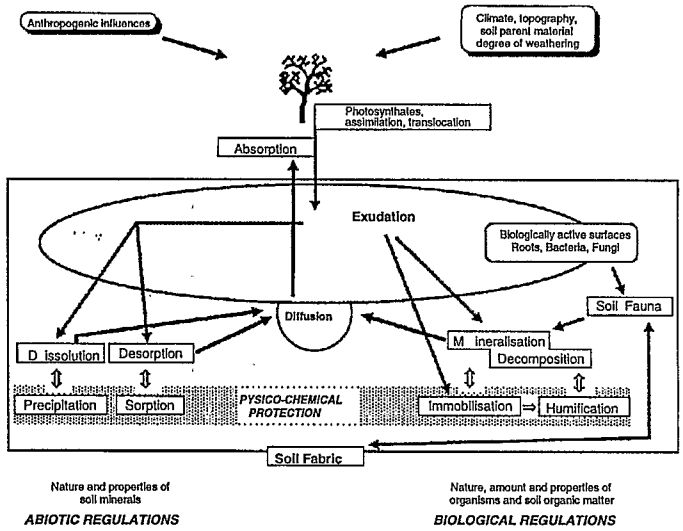

Figure 9. Processes of phosphorus transformations and their regulations in plant-soil systems

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