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# EFFECTS OF SOIL MICROSTRUCTURE ON
# PHOSPHORUS SORPTION IN SOILS OF THE HUMID TROPICS

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The cycling of P, more than that of any other major nutrient element, is controlled by inorganic chemical reactions. What are these reactions? What are the important controls? This paper reviews recent studies suggesting that the physical characteristics of soil constituents, as opposed to their chemical characteristics, may be more important than previously thought in determining patterns of P availability in acidic soils of the humid tropics.

Some understanding of the inorganic chemical reactions that affect P availability in acidic soils is prerequisite to discussion of the physical factors controlling them. Precipitation reactions have been touted as important but in fact the evidence suggests otherwise. Microprobe studies fail to reveal variscite or strengite as coherent grains in soils (Norris and Rosser 1983), and equilibrium and kinetic considerations suggest that these minerals would be unstable in soils except below pH 3.1 and 1.4, respectively (Bache 1963, Syers and Curtin 1989).

Instead, ligand exchange appears to be the only inorganic reaction of any significance in the acid soils of the humid tropics. The reaction consists of replacement of surface hydroxyls by the phosphate ligand. Three factors affect the rate of ligand exchange (per unit soil volume) and thus the P adsorption capacity of soils: (1) the amount of hydroxyl groups per unit surface area, (2) the extent to which the hydroxyl groups enter into ligand exchange, and (3) the total amount of reactive surface area in the soil. Reactive surface area is provided mainly by layer-silicate clays, by oxides and hydrous oxides of Al and Fe, and by highly disordered aluminosilicates such as allophane. All of these soil constituents are clays with regard to their physical properties and are referred to as "clays" hereafter.

The first factor, amount of hydroxyls per unit surface area, depends on the types of clays present in the soil, that is to say, their mineralogy. Fig. 1 shows P adsorption curves for the clays present commonly in soils of the humid tropics. Of these, allophane and ferrihydrite adsorb most strongly, largely because of their extremely large surface area. Goethite, an Fe oxide, adsorbs at an intermediate level, followed by gibbsite and hematite. Kaolinite, a 1:1 layer-silicate clay, adsorbs relatively little P because its specific surface area is low and because surface hydroxyls are present only along broken edges. The 2:1 layer-silicate clays, such as montmorillonite, adsorb hardly at all.

Methods can affect P adsorption values. Most researchers have used NaCl or KCl as the background electrolyte. Use of $CaCl_2$, however, may give very different results (Barrow 1989). The correct choice of electrolyte may be soil specific. Gillman and Bell (1978), for example, extracted solutions from six North Queensland soils (0-10 cm depth). Na was dominant in one of the six, K in two, Mg in two, and Ca in one. Length of reaction time is also problematic. As discussed later, adsorption is generally

monitored for at most a few days. In fact, P continues to be taken up from solution for long periods, although at reduced rates. Nonetheless, the patterns in Fig. 1 indicate the large range in P adsorption capacity of the clays present commonly in soils of the humid tropics.
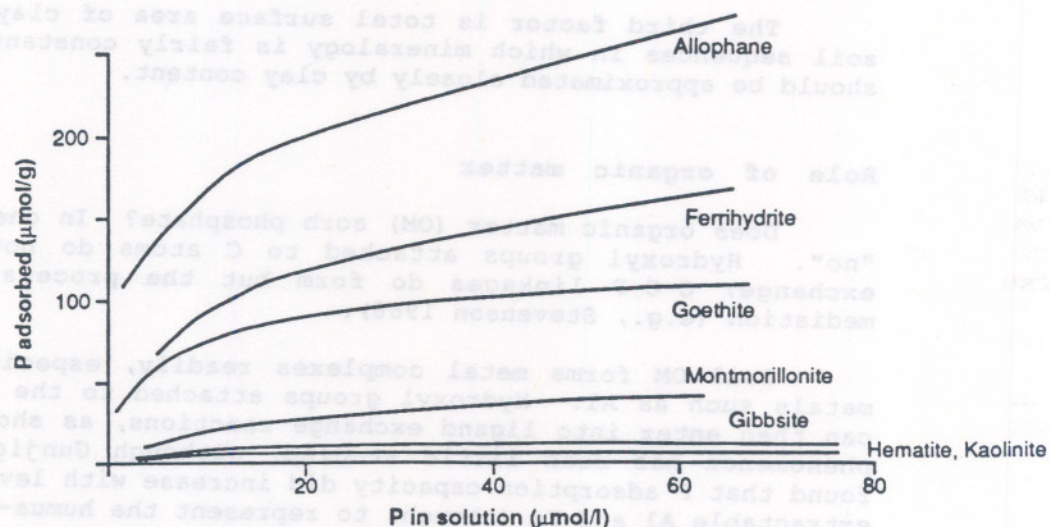


Figure 1. Adsorption curves for phosphate on various minerals (per g of mineral). Except for gibbsite and montmorillonite, all data are for 25 C, 16-h shaking, and 0.002 M CaCl2 (Parfitt 1989). Data for gibbsite are for 0.1 M NaCl (Parfitt et al. 1977). Data for kaolinite and montmorillonite are for 0.02 M KCl and 2-day equilibration (Bar-Yosef et al. 1988).

The second factor, in effect the equilbrium constant for the ligand-exchange reaction, involves the nature of the material in which the hydroxyl groups occur. Most studies with infra-red spectroscopy and other techniques (e.g., Parfitt et al. 1975, Martin and Smart 1987, Parfitt 1989) suggest that, at least for the Fe oxides, P is adsorbed only as a binuclear complex (Fig. 2), the formation of which requires a certain minimum spacing between adjacent OHs. Closely paired OHs occur on only some of the various faces that each clay presents. Thus variations in the proportion of the total hydroxylated surface on which OHs are paired closely enough to permit formation of a binuclear complex might explain some of the variation in P adsorption capacity among minerals and between different preparations of the same mineral.
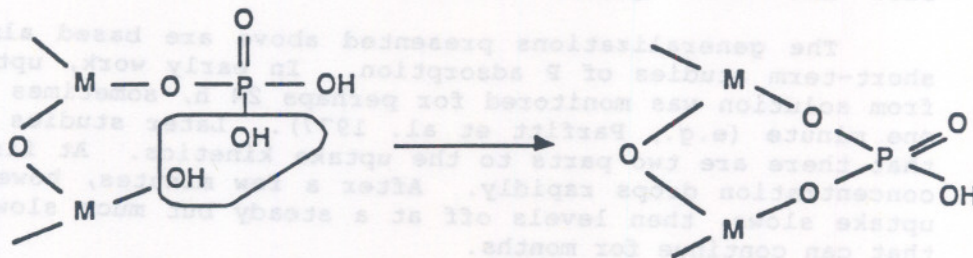


Figure 2. Formation of binuclear phosphate surface complex (after Mott et al. 1981).

Barrón et al. (1988) used differences in spacing of surface hydroxyls to explain variation in P adsorption in aluminous hematites of different crystal shapes. They were able to explain some of the variability on the basis of estimates of relative surface area accounted for by each crystal face. Possibly, their approach can be extended to other oxide types.

The third factor is total surface area of clays in the soil. Over soil sequences in which mineralogy is fairly constant, this surface area should be approximated closely by clay content.

## Role of organic matter

Does organic matter (OM) sorb phosphate? In one sense the answer is "no". Hydroxyl groups attached to C atoms do not enter into ligand exchange; C-O-P linkages do form but the process requires enzymatic mediation (e.g., Stevenson 1986).

Soil OM forms metal complexes readily, especially with transition metals such as Al. Hydroxyl groups attached to the Al in such complexes can then enter into ligand exchange reactions, as shown in Fig. 3. This phenomenon has been little studied, although Gunjigake and Wada (1981) found that P adsorption capacity did increase with levels of pyrophosphate-extractable Al and Fe (thought to represent the humus-bound Al and Fe).

Figure 3. Schematic representation of phosphate surface complex with humus-bound Al.

In fact it is difficult to distinguish between allophane and Al-humus complexes and until recently soils containing such materials were lumped together as Andepts (Soil Taxonomy) or Andosols (FAO). The new Andisol order within Soil Taxonomy separates the soils with Al-humus complexes as Humands, and it will be interesting to compare long-term kinetics of P adsorption in Humands vs. the true allophanic soils.

## Slow and fast uptake kinetics

The generalizations presented above are based almost entirely on short-term studies of P adsorption. In early work, uptake of phosphate from solution was monitored for perhaps 24 h, sometimes for as little as one minute (e.g., Parfitt et al. 1977). Later studies showed, however, that there are two parts to the uptake kinetics. At first the phosphate concentration drops rapidly. After a few minutes, however, the rate of uptake slows, then levels off at a steady but much slower rate (Fig. 4) that can continue for months.

Until about 1982, the so-called "slow reaction" was virtually unstudied. Barrow (1985) called attention to its importance, pointing out that the slow part of the reaction kinetics, not the fast part, was likely

to govern availability of P to plants.  Fortunately, recent data suggest that short- and long-term rates of uptake correlate well across a range of natural and synthetic minerals (Parfitt 1989).  Consequently, the earlier studies are still useful, and the discussion presented above of factors controlling short-term rates of P adsorption can be expected to hold also for the long-term rates of P uptake from solution.  In addition, the fast part of the kinetics may be worth studying further as a factor important in controlling the balance between immobilization and adsorption of P.  The measurement of microbial P may also be affected.  When P is released from microbial cells during $CHCl_3$ fumigation, the amount obtained with an extracting solution may be governed mainly by the fast part of the reaction kinetics.
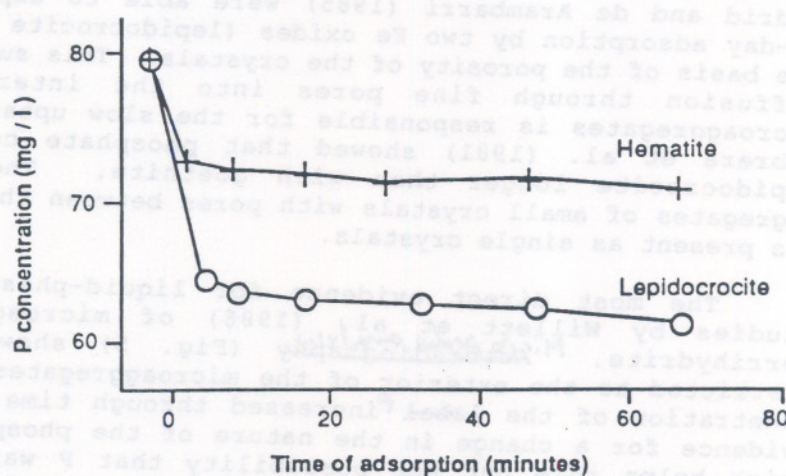


Figure 4.  Uptake of phosphate from solution by lepidocrocite and hematite (after Madrid and de Arambarri 1985).

Some recent studies are helping to unravel the mechanisms responsible for the two-part uptake kinetics.  Empirical studies of the temperature dependence of P uptake show that, under most conditions, the rate of long-term uptake increases with temperature (see Barrow 1985, Fig. 13).  This is unexpected ligand exchange *per se* is an exothermic reaction (Barrow 1985, p. 217), so adding heat, a product of the reaction, should slow it down.  In fact, this slowing is seen, but only under very restricted conditions.  That the opposite is the case more commonly indicates that ligand exchange is not the only process at work.

There is now consensus that the "slow reaction" is caused by a diffusion process but there is little agreement about its nature.  Barrow (1989) noted that the activation energy for the slow part of the P uptake kinetics is large, suggesting that solid- rather than liquid-phase diffusion was involved.  Barrow's view is supported by other lines of experimental evidence that point toward solid-phase migration of the phosphate ion into the interior of clay crystals.  Such diffusion would be most likely where atoms such as Si have previously migrated into the crystal, replacing the original Fe or Al and creating defects in the crystal structure.  For example,  Norrish and Rosser (1983) showed that P adsorption in Fe-rich soils correlates with their Al content, not with their Fe content, which suggests that it is not gibbsite but rather the degree of Al substitution in the goethite that controls P uptake.

Parfitt (1989) compared long-term P adsorption rates (30-d) for a synthetic preparation of goethite and for four minerals obtained nearly pure *in situ* (allophane, ferrihydrite, goethite, and hematite). The synthetic goethite was highly crystalline and equilibrated rapidly with phosphate. The natural goethite was more Al-substituted, appeared to be less highly crystalline, and equilibrated more slowly. These results were interpreted as implying solid-phase diffusion through crystal defects. Porosity, however, was not measured and would be expected to be higher in the Al-substituted, natural goethite than in the synthetic material. Thus, the slower equilibration of the natural goethite might also be explained by liquid-phase diffusion through its pore structure.

Other studies point to liquid-phase diffusion of phosphate to adsorption sites as the cause of the slow part of the uptake kinetics. Madrid and de Arambarri (1985) were able to explain the difference in 13-day adsorption by two Fe oxides (lepidocrocite and hematite) simply on the basis of the porosity of the crystals. This suggests that liquid-phase diffusion through fine pores into the interiors of crystals and microaggregates is responsible for the slow uptake kinetics. Likewise, Cabrera et al. (1981) showed that phosphate continued to react with lepidocrocite longer than with goethite. The lepidocrocite formed aggregates of small crystals with pores between them, whereas the goethite was present as single crystals.

The most direct evidence for liquid-phase diffusion comes from studies by Willett et al. (1988) of microaggregates of synthetic ferrihydrite. Microprobe analysis (Fig. 5) showed that sorption was restricted to the exterior of the microaggregates, but that the depth of penetration of the P increased through time. IR spectra showed no evidence for a change in the nature of the phosphate bond through time, which helps rule out the possibility that P was replacing Si that had previously substituted for Fe or Al in the crystal structure.
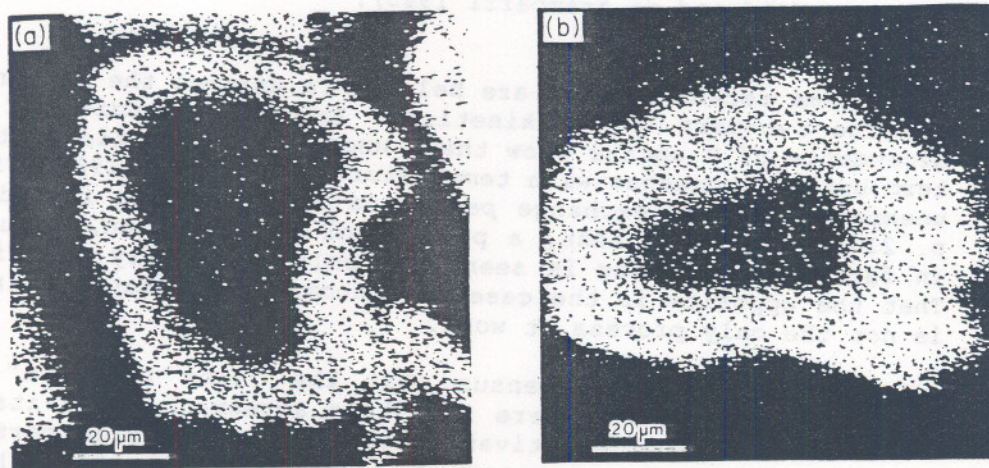


Figure 5. Distribution of phosphate in microaggregates of ferrihydrite (from Willett et al. 1988): (a) after 1 h, (b) after 1 d.

Results for allophane and other poorly ordered clays are hard to interpret. Solid-phase diffusion is unlikely to explain the slow reaction because the spherule walls are only 3-4 atoms thick (Parfitt 1989).

Structural properties of the allophane spherules do seem to affect adsorption. Adsorption seems to occur preferentially in conjunction with defects and/or pores in the allophane spherules (Parfitt 1989), and P adsorption capacity of allophane tends to increase with the degree of substitution of Fe for Ae (Parfitt and Hemni 1980). In any case, allophane spherules flocculate very strongly; so liquid-phase diffusion may well be involved also. Moreover, since allophane is gel-like, allophanic surfaces are constantly being buried and uncovered as the allophane flows and coalesces. Thus the adsorbed phosphate may stay put and the *site* of adsorption may migrate.

The importance of solid- vs. liquid-phase diffusion thus appears to vary with the minerals involved. Dispersion methods, such as ultrasonication, could perhaps be used in conjunction with autoradiography to gain insight into the relative importance of the two modes of diffusion. If P adsorption/desorption are limited by rates of liquid-phase diffusion into the interiors of micro-aggregates, then dispersion of those micro-aggregates should greatly speed desorption. On the other hand, if a solid-state diffusion process limits P adsorption/desorption, then dispersion should have little effect. The experiment could be done first with a defined artificial material, such as the synthetic ferrihydrite aggregates used by Willett et al. (1988). If the ultrasonic dispersion in fact speeds desorption, autoradiography after the ultrasonication could then serve to indicate whether the ultra-sonication had successfully dispersed the labelled exteriors of the aggregates. It is unclear whether the approach would work for highly porous crystals which might be very difficult to break up, but the autoradiography would indicate unequivocally whether dispersion had been achieved. If the overall approach could be shown to work with synthetic materials, it might then be useful for judging which diffusion process is more important in whole soil.

## P budgets: inorganic vs. organic reactions

The above papers dealt with well defined, synthetic materials, not whole soil. In recent work with an Oxisol and two Andepts, Parfitt et al. (1989) compared long-term P adsorption (218 d) with P uptake by microflora and clover. Uptake by the microflora ranged from 5-25 mg P kg$^{-1}$; uptake by the clover ranged from near 0, at low levels of P addition, to 40-60 mg P kg$^{-1}$ of soil at high levels. Phosphorus adsorption was much higher: 50 to 400 mg P kg$^{-1}$ soil depending on the amount of P added. Of the three soils, the Oxisol gave the lowest P adsorption and the highest uptake by microflora. McLaughlin et al. (1988) measured fluxes of P to plants and microflora, along with uptake of P into relatively unavailable organic and inorganic forms. Even though the soil they studied did not adsorb P strongly (a Calci-xerollic Xerochrept), inorganic reactions were estimated to remove about 1/3 of the P added as organic residues, and about 3/4 of the P added as fertilizer. Experiments combining MacLaughlin's and Parfitt's approaches in more strongly P adsorbing soils seem warranted.

Lastly, it should be noted that it may be difficult to rule out microbiological activity as the explanation for the slow part of the uptake kinetics, especially in experiments with whole soil. Some, but not all, investigators mention adding a biocide to retard microbial uptake of P. Even if biocide was added, its effectiveness should not be assumed; plate counts and respiration measurements are easy and would settle the issue. Also, many biocides themselves adsorb strongly on mineral surfaces, a process that might affect P adsorption.

## Conclusion

Researchers have concluded that the physical structure of the soil, not just its chemical composition, must be understood in order to predict rates of chemical and biological processes (see recent reviews by Duxbury et al. 1989; Theng et al. 1989). The studies reviewed here suggest that physical arrangement of reactive surfaces in the soil is also important in controlling P transformations and availability. It thus seems likely that techniques based solely on use of chemical extractants will never adequately explain differences in P availability between soils or through time. New approaches are needed that deal with the physical arrangement, not just chemical composition, of soil constituents.

## Acknowledgement

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