

THE FATE OF PHOSPHATE FERTILISERS IN SOIL

Phosphorus participates in many of the reactions that keep plants and animals alive, and is thus essential for all living organisms. Phosphorus is found in two different forms in soil: inorganic and organic.

Inorganic phosphorus

The main inorganic forms of phosphorus in soil are H_2PO_4^- and HPO_4^{2-} . This is the form in which phosphorus is used by plants. However, these ions can also adsorb onto the surface (or adsorb into) solid matter in the soil. This phosphorus is then unavailable to plants.

Organic phosphorus

Between 50 and 80% of phosphorus in soil is organic phosphorus. This comes from the breakdown of dead plants etc., as phosphorus is found in cell membranes and DNA in living organisms.

Phosphorus is thus naturally available in the soil. However, there isn't usually enough available for plants to grow well. Phosphorus levels are reduced by animals eating the plants then dying elsewhere so that the phosphorus is removed, and also by phosphorus being adsorbed into soil particles or washed away by excess rain. For this reason phosphate fertilisers are widely used. The ways in which this influences phosphate cycling in the soil are discussed in more detail in the following article.

INTRODUCTION

All living plants and animals require phosphorus. Phosphorus containing compounds are essential for photosynthesis in plants, for energy transformations and for the activity of some hormones in both plants and animals. They occur in cell membranes and calcium phosphate (hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}$) is the principle component of bones and teeth.

Grazing animals obtain their phosphorus from plants. Plants obtain their phosphorus from the soil in which they grow and, if no fertiliser has been used, the phosphorus in the soil is derived from the parent material from which the soil was formed. The concentration of phosphorus in unfertilised New Zealand soils varies between 200 and 2000 mg P kg^{-1} soil with an average of 650 mg P kg^{-1} soil; this is similar to concentrations in overseas soils and is equivalent to about 1000 kg per hectare of phosphorus in the top, root containing, layer of soil.

A hectare of pasture producing 14 tonnes of plant material (dry matter) containing 0.35% phosphorus will absorb 49 kg of phosphorus in one year. Thus there is up to 20 times more phosphorus in the surface, root containing layer of an average New Zealand soil than is taken up by the pasture on that soil in a single year. Despite this the majority of our soils were originally deficient in phosphorus for maximum pasture growth; yields on unfertilised soils are typically 25% of the production which is obtained when adequate amounts of phosphate fertilisers are used. Even if enough phosphate fertiliser is applied to produce maximum plant growth, production declines in each successive season if phosphate fertiliser is not reapplied regularly. This article reviews the chemistry of phosphate in the soil and attempts to explain why we need to use phosphate fertilisers on a regular basis.

INORGANIC PHOSPHORUS IN SOIL

Water in soil typically contains about 0.05 mg L^{-1} of inorganic phosphate in solution; this is equivalent to about 15 g of phosphorus in solution in one hectare of land.

These very small amounts and concentrations of phosphates in the solution in soils compared with plant requirements, and the apparently small recovery of fertiliser phosphate in plants, have stimulated a tremendous amount of research. Studies have concentrated on the reactions of added phosphate with soil constituents and on mechanisms controlling the amount of phosphate in solution.

Although the phosphate ion can occur in three states of protonation, at pH values normally found in soils (4.5 - 6.2) H_2PO_4^- and HPO_4^{2-} are the dominant species.

Two types of inorganic reactions control the concentration of phosphate ions in solution; these are precipitation-dissolution and sorption-desorption processes. Precipitation-dissolution reactions involve the formation and dissolving of precipitates. Sorption-desorption reactions involve sorption and desorption of ions and molecules from the surfaces of mineral particles. The role of biological immobilisation-decomposition will be dealt with in the section of organic phosphates. The movement of phosphate into plants also influences soil solution concentrations and promotes dissolution and desorption reactions.

Soils contain a range of crystalline and near-amorphous minerals in clay-sized particles ($< 2 \mu\text{m}$ diameter). These are combined with an equally wide range of poorly characterised organic compounds which modify both the chemical and physical properties of the clays. As a result, much research was done on the reactions between pure samples of individual soil components and phosphate solutions. Hydrous iron and aluminium oxides and aluminosilicates occur widely in soils. They will react with phosphate solutions to produce an isomorphous series of iron and aluminium phosphates [strengite-barrandite-variscite $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ - $(\text{Al,Fe})\text{PO}_4 \cdot 2\text{H}_2\text{O}$ - $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$]. While these materials have been identified by X-ray diffraction in laboratory experiments they have not been seen in natural soils. This was assumed to be due to the very small size of their crystals.

Workers in the 1950's believed that the solubility equilibria of such compounds controlled the concentration of phosphate in the soil solution. This now seems unlikely. While they may be formed in the very acid, high phosphate conditions surrounding a freshly applied fertiliser granule (pH 1.5, 4 M P), it is unlikely that they persist for long. Evidence for this comes from studies of ion activities in soil solutions. It has now been shown that phosphate concentrations are largely independent of pH over the range of 4 to 8 and that the solution is invariably undersaturated with respect to all phosphate compounds. It is therefore unlikely that solubility product principles apply, with the possible exception of the period immediately after fertiliser has been applied.

Other studies have shown that the iron and aluminium phosphates which were assumed to occur in soils are more soluble than the corresponding hydrous metal oxides, which definitely do occur in soils. Phosphate ions are strongly adsorbed by hydrous metal oxide surfaces. This suggests that it is unlikely that metal phosphates could persist for long in soils containing hydrous metal oxides. However, there is also evidence that hydrous ferric oxide coatings can form on the surface of metal phosphates and effectively slow the rate at which they dissolve. It is now generally accepted that iron and aluminium phosphates and precipitation-dissolution reactions do not play an important role in controlling the

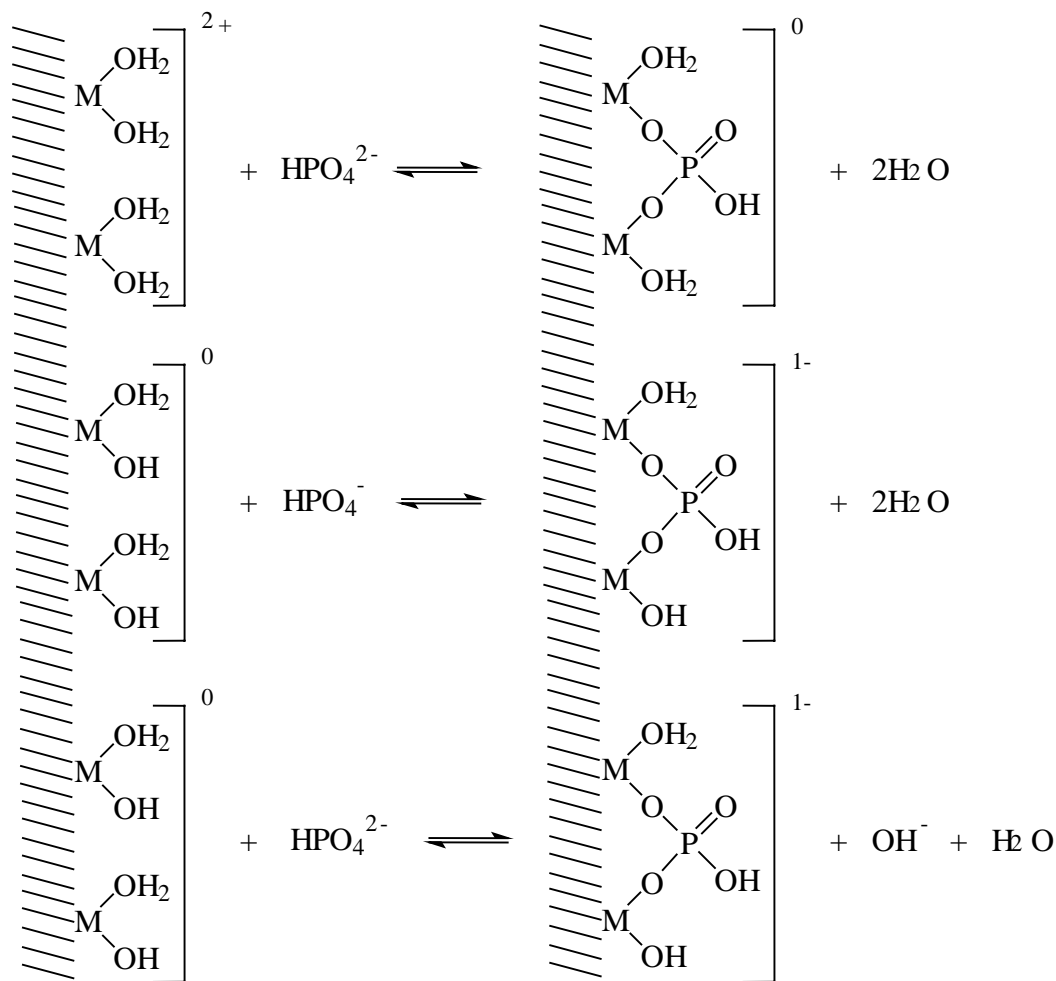
concentration of phosphate in the solution of the majority of soils and hence in the phosphate nutrition of plants.

The only important exception to this is the precipitation of calcium phosphates, including dicalcium phosphate and possibly apatite (tri-calcium phosphate) in soils above pH 6 and particularly those containing free calcium carbonate. Mono-calcium phosphate is soluble whilst tri-calcium phosphate is virtually insoluble.

This means that the second type of reaction, sorption-desorption must be more important. "Sorption" in fact describes two processes. "Adsorption" occurs when phosphate ions are removed from solution and become attached to the surface of soil particles. If the adsorbed phosphate ions then diffuse into the solid, they are "absorbed". Some authors use the term "penetrated phosphate" to avoid confusion between adsorbed and absorbed; "sorption" covers the combined processes. Adsorbed phosphate may become trapped on the surface of soil minerals if any Fe or Al oxide coating is precipitated on the mineral. The trapped phosphate is then described as being occluded. Adsorption, absorption and occlusion are illustrated in **Figures 1 and 2**.

Adsorption was originally thought to be a simple exchange reaction which took place on the surface of iron and aluminium hydroxides. It now seems more likely that chemisorption reactions are involved. Binuclear, or bridging complexes are formed between HPO_4^{2-} ions and metal oxide surfaces and OH_2 and OH^- are displaced. The precise nature of these reactions depends on pH which influences the proportions of OH_2 and OH^- groups on the solid surface and hence its surface charge. A number of both organic and inorganic soil components exhibit this pH dependent, or variable charge, property and it is common to most New Zealand soils.

When soluble phosphate is added to a soil, its solubility first declines very rapidly. This is followed by a more gradual decrease in solution concentrations which can continue for weeks. Experiments which compare the rate at which a soil or soil component decreases solution phosphate concentrations with the rate at which adsorbed phosphate can be extracted from phosphate-treated soils are used to investigate these reactions. Adsorbed phosphates can be extracted from soil with 10^{-1} M NaOH solution. This reagent can be used to show that surface adsorption is responsible for the initial, rapid removal of phosphate from solution but that once this phase is completed, there is no further increase in the amount of adsorbed phosphate present. If the phosphate treated soil is further extracted with a buffered citrate-dithionite reagent which removes phosphate present within the matrices of hydrous ferric oxides, evidence is provided which indicates that the second, slower stage of phosphate sorption is due to the diffusion of phosphate below the adsorbing surfaces; in other words,



M = Al or Fe

Figure 1 – Examples of phosphate adsorption mechanisms

due to absorption or penetration.

A second, large scale mechanism having the same effects as the surface adsorption/absorption processes occurring on single particles, occurs with soil aggregates, or crumbs. Soil aggregates are clusters of soil components held together by a number of mechanisms which include both organic and inorganic cements and the effects of charged surfaces. Aggregates contain a fine network of pore spaces while the aggregates themselves are separated by a coarser system of pores responsible for water and air movement within soil. When a phosphate containing solution passes through the soil, phosphate is removed from the solution by adsorption on soil particles located at the surface of soil aggregates. Some of this adsorbed phosphate subsequently diffuses into the aggregates. As with the adsorption/absorption reactions on single particles, this has the effect of regenerating adsorption sites at the surface of aggregates and of decreasing the accessibility of penetrated phosphate for desorption and hence plant use.

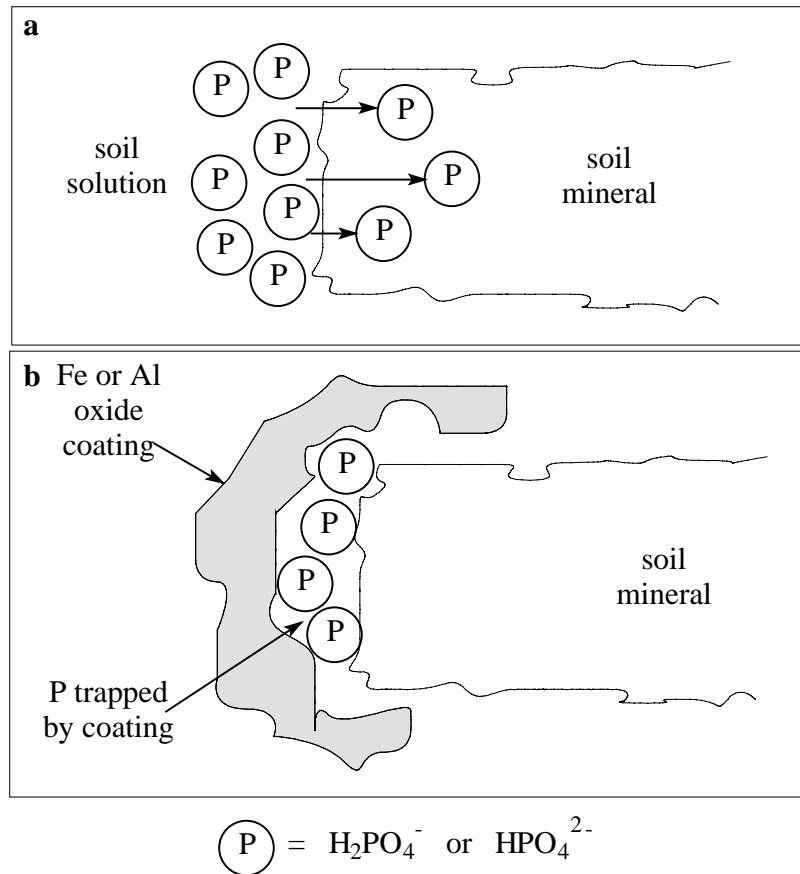


Figure 2 - The absorption of adsorbed P into soil minerals (a) and the subsequent occlusion of adsorbed P (b)

ORGANIC PHOSPHORUS IN SOIL

The composition and transformations of organic phosphorus compounds in soils have received less attention than inorganic forms. This is partly because inorganic phosphates predominate in temperate arable soils and partly because organic phosphates are even more difficult to study than the inorganic phosphates. The latter point results from difficulties in extracting all the organic phosphate components without altering them chemically.

Since the first edition of this article was published in 1981 there have been considerable developments in our understanding of the nature of organic phosphorus compounds in soil science. These have resulted from the development of an analytical technique called 'nuclear magnetic resonance (NMR) spectroscopy'. The advantage of NMR spectroscopy is that it is analytically less complex than the partition chromatography techniques previously used to identify specific organic P compounds in soils. Most NMR studies of soil organic P compounds involved extracting the compounds with 0.5 M NaOH. However this often extracts less than half the total organic P; techniques involving sequential acid and alkaline extractions extract a much greater proportion of organic P but increase the risks of modifying compounds during extraction. Solid state NMR overcomes this problem but is not sufficiently sensitive for detailed quantitative analysis.

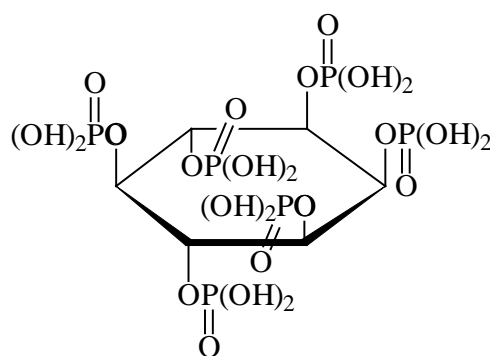
The organic phosphate fraction is much more important in pasture soils, where it may account for 50 to over 80 percent of the total phosphorus present. This is particularly true in New Zealand soils since they contain more than average concentrations of organic matter.

The organic phosphorus fraction is important to the phosphorus economy of these soils since it represents a very large pool of phosphates, part of which actively contributes to the phosphate nutrition of plants and hence grazing animals, while the remainder appears to be relatively stable and hence not available for plant use.

While the parent material from which a soil forms has some influence on the amount of organic phosphate in virgin soils, other soil forming factors and soil properties probably have more influence. Organic phosphate increases as soils become more acid; cultivation decreases organic phosphate content and climatic conditions which favour the accumulation of organic matter in soils increase their organic phosphate content.

Soil organic matter consists largely of carbon, oxygen, hydrogen, nitrogen, sulphur and phosphorus. When soils develop or when virgin or arable soils are put under permanent pasture, their organic matter content generally increases. While organic nitrogen and sulphur components increase to equilibrium values within a relatively short period of time (5 - 20 years), organic phosphate compounds appear to accumulate for much longer. As a result, the phosphorus content of soil organic matter is much more variable than its carbon, nitrogen or sulphur contents. This has led to the suggestion that organic phosphates can be divided into two fractions; one in association with carbon, nitrogen and sulphur in soil humus and the other as independent organic phosphate compounds. However it is likely that the individual organic phosphate compounds identified in extracts are combined into complexes of high molecular weights in soils and that a continuum exists over the range of organic phosphate compounds in soils.

The nature of phosphorus in ill defined soil humic materials is largely unknown. Of the organic phosphate compounds identified in soil extracts, inositol phosphates such as inositol hexaphosphate are the most abundant and can represent up to 50 percent of the total organic phosphates present. A number of stereo isomers have been identified. Only one of these, the myoinositol hexaphosphate, has been reported in plants so presumably the other isomeric forms are synthesised in the soil by microorganisms. The myoform appears to be the most abundant isomer in soils.



Inositol hexaphosphate

An average of 1 percent of the organic phosphates in soils is present as phospholipids (range 0.5 - 7.0%). Phosphoglycerides are probably the dominant fraction but little is known about the other phospholipids in soils. They are probably derived from plant debris, animal wastes and microbial activity and may be more important to plant nutrition and phosphate cycling in soils than their relative proportion suggests. They are much more abundant in plants, suggesting that, unlike inositol phosphates, they are rapidly mineralised in the soil.

Nucleic acids and their derivatives come in the same category as phospholipids. While added in plant and animal remains in greater amounts than other phosphate esters, they represent less than 3 percent of the organic phosphates in soils, again implying that they are rapidly mineralised by microbes.

NMR analysis of organic phosphate compounds extracted by alkaline solution shows that in native soils, the total organic P fraction consists of 83-95% of the phosphate monoester P, 4-9% of the phosphate diester P and up to 12% teichoic acid P (an orthophosphate diester form of organic P which consists of sugar units linked by phosphate groups). The latter two forms are more easily mineralised than the monoester and were not found in soils which had a long history of cultivation.

ORGANIC PHOSPHORUS IN THE SOIL SOLUTION

Somewhat surprisingly, there is normally more organic phosphorus in the soil solution than there is inorganic phosphorus. In light textured soils (sands) as much as 90 percent of the total phosphorus in solution may be organic. This has considerable implications to the role of organic phosphates in the movement of phosphates in soils and to plant nutrition.

Much of the organic phosphate in the soil solution appears to be myo-inositol phosphates although a range of other soluble compounds may be released from damaged microbial cells. There is some confusion over the availability of soluble organic phosphate compounds to plants. While some appear to be as available as inorganic phosphate in aseptic culture solutions, they are of much less value in the soil. As already mentioned, the relatively simple organic phosphates in soil extracts are probably in high molecular weight complexes in the soil. In addition, inositol phosphates are strongly adsorbed on charged surfaces while the sparingly soluble Fe and Al complexes they can form may also decrease plant availability. However, there is evidence that plant roots and rhizosphere organisms which are found around plant roots excrete phosphatase enzymes capable of hydrolysing some organic phosphate compounds, releasing inorganic phosphate for absorption by the plants. Mycorrhizal fungi found on plant roots are known to increase the uptake of phosphates by plants in some circumstances. This may be partly due to their phosphatase activity although their role in physically extending the absorbing root surface into larger volumes of soil is probably more important.

DYNAMICS OF ORGANIC PHOSPHATES

The conversion of plant available inorganic phosphates into unavailable organic forms is termed immobilisation. The reverse is termed mineralisation. Both processes can occur concurrently in the soil but in developing soils immobilisation predominates, resulting in organic phosphate compounds accumulating. The proportion of fertiliser phosphate added to soil which is effectively removed from the pool of cycling phosphate by immobilisation is not accurately known but it is likely to be appreciable. The very large initial dressings of fertiliser phosphate required to establish good quality pasture species in place of native grasses are often assumed to be required to satisfy the capacity of soils to absorb inorganic phosphate. There is evidence however, that a considerable proportion of the phosphate applied at this time is immobilised in organic forms, some of which are sufficiently stable to be valueless sources of plant available phosphate. Subsequently organic phosphate accumulates more slowly, coinciding with a decrease in the rate of fertiliser phosphate which

must be applied. One New Zealand experiment showed that after many years of pasture development, 10 kg of fertiliser phosphate (out of an annual application of 18 kg P/ha) were immobilised in organic forms. Although this process stopped when the soil's acidity was decreased by adding lime, it did not decrease the demand for fertiliser immediately as the lime increased the accumulation of sparingly soluble di-calcium and tri-calcium phosphate, which was no more available to plants than the organic compounds it replaced. There are other experiments however, which show that lime can decrease the amount of phosphate fertilisers required in some circumstances. One possible mechanism for this involves a change in the relative rates of immobilisation and mineralisation, resulting in a more rapid cycling of phosphates through organic forms and a decrease in the rate at which organic phosphate accumulates.

The formation of sparingly soluble iron, aluminium and calcium inositol phosphates by soil components and the sorption and inactivation of phytase enzymes could all protect inositol phosphates from microbial mineralisation and result in their accumulation in soils.

THE FATE OF FERTILISER PHOSPHATE ADDED TO SOILS

The descriptions of inorganic phosphate sorption and the wide range of organic phosphate materials in soils suggest that the fate of fertiliser phosphate and its subsequent availability to plants may follow similar patterns in both organic and inorganic systems.

The probable sequence of reactions after a monocalcium phosphate fertiliser such as superphosphate is added to soils is that, as has already been discussed, there may be the temporary formation of iron and aluminium phosphates in the low pH, high phosphate concentrations surrounding the fertiliser particle. The remaining monocalcium phosphate will be mainly converted to dicalcium phosphate. As a result of these two reactions, the immediate effect of the fertiliser on the concentration of phosphate in the soil solution will be controlled by the solubility of the newly formed phosphates. This is only a temporary phase.

Inorganic phosphate will then be rapidly adsorbed from the soil solution, its resulting concentration depending on the extent and nature of the adsorbing surfaces. Rapid adsorption is followed by a slower penetration of phosphate beneath the adsorbing surface. Release of phosphate to recharge the soil solution follows a similar pattern. Rapid release from particle surface is followed by a much slower release of phosphate from within particles as it diffuses back to the surface. The release of "penetrated phosphate" only occurs when surface adsorbed phosphate has been depleted and it occurs too slowly to maintain solution concentrations great enough for rapid plant growth.

Fertiliser phosphate in the soil may be taken up by plants or incorporated into soil microorganisms. The life cycle of soil organisms is relatively short. When they die the phosphate they contain is released in both organic and inorganic forms. There is evidence that this is either rapidly recycled by new generations of organisms or is made available for higher plants. Some organic phosphate compounds, on the other hand, are relatively resistant to microbial decomposition and tend to accumulate, especially in acid conditions. The phosphorus they contain is unavailable to plants. While some of this immobilised phosphate may ultimately be mineralised, this is unlikely to occur unless the overall phosphate status of the soil is depleted to such a low value that economic agriculture production is no longer possible.

The processes which influence the concentration of phosphates in the soil solution are summarised in **Figure 1**. Forms of phosphate and the transformations between fractions within the central box in **Figure 1** are those most closely involved with the phosphate nutrition of plants and hence grazing animals. They constitute the pool of cycling phosphate in the soil/plant/animal system. Gains and losses from this pool are shown by fractions and transfers across the boundary. Fertiliser inputs and phosphate losses in production, dung transfer, leaching and erosion are obvious. The transfer of once plant-available phosphate to absorbed inorganic or bound organic forms may not constitute a loss from the soil, but the rate of release from these forms is probably too slow to support active plant growth. As a result phosphate in these forms is effectively lost from the cycling pool. The distinction between “free” and “bound” organic phosphates is not as distinct as **Figure 1** implies, there is probably a range of compounds of varying stability.

There has been much debate about the efficiency with which phosphate is used in agricultural production. In grazed pastures in New Zealand, it can be shown that plants absorb an average of 80% of the total phosphate added to the soil each year (this included fertiliser and recycled P). This annual input is made up of decomposing plant residues, animal dung and fertilisers. The remaining 20% is lost in the soil, the majority by incorporation into stable organic or inorganic forms. Soil losses assume greater significance when compared with fertiliser inputs. Measured in this way, the average for New Zealand soils would be closer to 50%. However, we have seen that once fertiliser phosphate enters the soil, it can take part in one of a series of reactions or transformations, so that it rapidly loses its identity. As a result we cannot say that 50% of a particular application of fertiliser is going to be immobilised in soil before it can benefit plant and animal production. Only by using phosphates labelled with the radioisotope ^{32}P can scientists trace the path of a particular application.

MINIMISING PHOSPHATE IMMOBILISATION

There are a few practical methods available to farmers for decreasing phosphate losses in soil. The most important is to ensure that fertilisers are not applied at excessive rates for a particular set of soil and plant conditions. Just how much fertiliser is needed will be discussed later. Adjusting the pH of soil to about six will minimise effective losses in organic forms through promoting a more active microbial population. The selection of plant species capable of achieving maximum growth at relatively low soil solution phosphate concentrations will decrease the amount of fertiliser phosphate required to achieve maximum production and hence soil phosphate losses. However, the amount of fertiliser phosphate subsequently required to maintain plant production will not be decreased proportionately, since it is also required to replace losses in production and dung transfer. Efficient mycorrhizal fungi will have a similar effect to using species with a low solution phosphate requirement. It has been suggested that fertilisers which dissolve more slowly than the conventional superphosphates and ammonium phosphates will also decrease effective losses in highly absorbing soils. This is because they will result in a much more gradual increase in solution phosphate concentrations than do the highly soluble phosphate fertilisers. If the rate of release of phosphate from the fertiliser is similar to the demand of the plant for phosphate, the plant will be able to compete more effectively with adsorption and microbial immobilisation and effective losses from the cycling pool will be decreased. The tendency for plants to take up more phosphate than they need, termed ‘luxury consumption’, will also be limited, further diminishing losses in dung transfer. However, there is little experimental evidence for this in practice.

ESTIMATING THE NEED FOR FERTILISER PHOSPHATE

The processes in **Figure 1** indicate that measuring the concentration of phosphate in the soil solution is of limited value unless other soil properties are also considered. It is the amount and rate of release of phosphate fractions in the surface adsorbed and “free organic phosphate” pools which will control the ability of the soil to supply plants with phosphate. There is no single chemical test which can estimate this ability directly. In New Zealand fertiliser advice is based on two approaches. Chemical tests are used to estimate the potential phosphate supply and the potential of a soil to remove the phosphate from solution. A 0.5 M solution of sodium bicarbonate at pH 8.5 is used to extract phosphate in the soil solution and that adsorbed on charged surfaces. This solution also extracts a proportion of the organic phosphates from the soil but these are not measured in current procedures. This is an empirical test; the precise nature of the phosphates extracted is not known and its value depends on its calibration with the results of field trials with phosphate fertilisers. These must be done in the soil and climatic conditions in which the test is to be used. The second chemical test involves measuring the ability of a soil sample to decrease the concentration of phosphate in solution when the soil is shaken with a solution initially containing 1000 mg/kg P soil.

Both tests are used to predict the amount of fertiliser phosphate required to establish pastures on newly cleared or badly neglected land. The smaller the amount of bicarbonate-extractable phosphate the greater the amount of fertiliser phosphate required to increase the phosphate supplying power to the soil to satisfy the demands of high producing pasture species. The greater the phosphate retention capacity value the greater the amount of fertiliser required.

Once the bicarbonate-extractable phosphate test indicates that the soil can supply enough phosphate in plant available forms for the required rate of pasture production, fertiliser is required for a different purpose. Rather than increasing the soil phosphate status, the aim

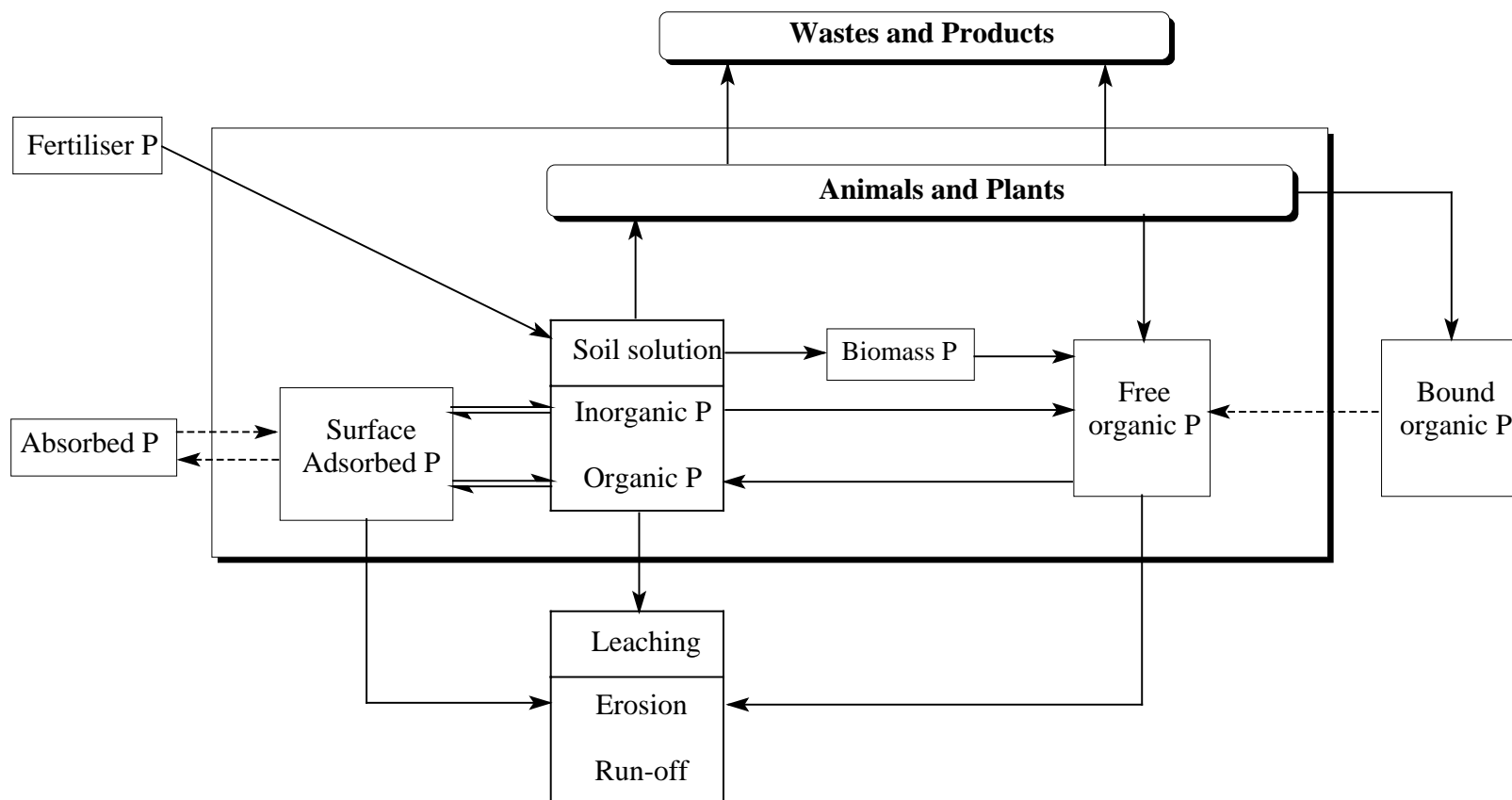


Figure 3 – Phosphorous fractions in grazed pastures

Fractions within the shadow box are components of the cycling pool. Transformations indicated by broken arrows occur much more slowly than other transformations shown.

now is to maintain it at near constant, adequate value. This is done by estimating the amount of phosphate lost from the cycling pool each year. These losses occur in produce (meat, milk, wool), by the transfer of dung off the productive area of paddock, and by losses within the soil (inorganic and organic immobilisation, leaching and erosion). Leaching is normally slight in all but very light soils with a low adsorbing capacity. The amount of fertiliser phosphate required each year is equal to the total of the various types of losses. The bicarbonate-extractable phosphate test is used to monitor the size of the pool of cycling phosphate in the soil and to modify the amount of fertiliser estimated as being required by the balance method. **Figure 3** illustrates the phosphorous cycling pool.

CONCLUSION

This brief discussion indicates that chemical, physical and biological processes influence the fate of phosphate fertiliser added to soils. An understanding of these processes, the measurement of the size of the various fractions or pools of phosphates in soils and the rate at which phosphate transfers from one pool to another are all important if we are to help farmers make the most economically efficient use of phosphate fertilisers.

Article written by I.S. Cornforth (Department of Soil Science, Lincoln University) with reference to:

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- McLaren, R.G.; Cameron, K.C. 1990. *Soil Science, an introduction to the properties and management of New Zealand soils*.
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