Chapter 1

Introduction

RATIONALE FOR THE REPORT

The essential need to increase the plant availability of phosphorus (P) in soils to produce adequate yields of crops was demonstrated some 200 years ago, and P fertilizer use has increased in response to the need to feed an increasing population. In the developed countries, the increase in the annual use of P fertilizers was gradual from the mid-1850s; it then increased rapidly between the early 1950s and the mid-1970s before stabilizing or declining slightly thereafter. However, there is still a need for P inputs to maintain crop production in the developed countries. Perhaps the greater need today is to increase the use of P fertilizers in the least- developed countries (LDCs), where many soils are deficient in P and increased food production is essential to feed their increasing population.

Improving the efficiency of P use in agriculture is a contribution to many agricultural and environmental issues. These include maintaining or improving the P fertility of soils by the judicious use of P fertilizers and other sources of P, such as organic manures including animal manures, composts and biosolids. There is also the need to conserve the finite global P resource. However, in the developed countries (and increasingly in LDCs), there is the additional need to minimize the transport of P to water, by various pathways, because of the adverse effect of P on water quality in some situations. A major contribution to these issues can come from improving the understanding of the fate of P added to soils and its effective use in crop production. In turn, this could result in an economic benefit for farmers if it were possible to demonstrate that using less P fertilizer does not have an adverse impact on the financial viability of the farm enterprise and does not lead to a decline in soil fertility.

Although there has been much research and extension work on P fertilizer use since commercial production of single superphosphate (SSP) first began in the United Kingdom in 1843, a review is timely. This is because in the last four decades there have been major changes in the understanding of the properties and behaviour of soil and fertilizer P and their interrelationships with crop yield. This report seeks to provide a sound technical basis for improving P-use efficiency in agriculture, so that the best possible advice is available to agricultural scientists, extension workers, farmers and environmental managers.

Following a brief background review in this chapter, Chapter 2 outlines the role of P in crop nutrition. The main focus of the report is in Chapter 3, which discusses changing concepts of the behaviour of soil and fertilizer P. Partly as a result of these changing concepts, there is a need to define and measure the recovery of fertilizer P. Chapter 4 addresses these aspects and discusses indicators of the efficiency of soil and fertilizer P use. It also illustrates the recovery of soil and fertilizer P, supported by data from nine detailed case studies from different agro-ecological zones (Annex 1). These studies have measured P recovery over a number of years. Chapter 5 discusses ways for improving the efficiency of soil and fertilizer P use in agriculture, and Chapter 6 presents the conclusions drawn from this report.

BACKGROUND

Phosphorus is an essential element for all living organisms. As a component of every living cell, P is indispensable because no other element can replace it in its vital role in many physiological and biochemical processes. As a consequence, the production of crops for food, feed, fuel and fibre requires an adequate supply of P in the soil. Of the plant nutrients required by crops in large amounts, P is of most concern because of the rate of exploitation of this non-renewable resource to meet current demand.

Phosphorus is a common element, ranking 11th in order of abundance in the earth's crust. However, the concentration in many rocks is usually very small. Globally, phosphate deposits consist of reserves and resources (or potential reserves). Reserves are deposits that are currently exploitable in an economically viable way. Resources are deposits that could be used subject to advances in processing technology or their use becoming economically viable. Both the reserves and resources have a finite life span. In 2006, the US Geological Survey estimated the world phosphate rock (PR) reserves at about 18 000 million tonnes, while resources were about 50 000 million tonnes (Jasinski, 2006). The International Fertilizer Industry Association (IFA) estimated world PR production at 171 million tonnes in 2005 (Prud'homme, 2006). At this rate of use, the reserves and resources could last between 105 and 470 years. However, it is difficult to ascertain the true extent of world P reserves and resources (IFDC/ UNIDO, 1998). Based on some estimates of potential resources, the global P supply could last between 600 and 1 000 years at the current rate of use (Isherwood, 2003). These estimates do not include the possibility of finding as yet unknown P deposits. However, the fact remains that the total global P supply is finite and that it is necessary to use it efficiently in order to maximize its life span.

Besides recognizing the essential need to apply P to many soils in order to increase crop production, soil scientists have been intrigued by the fate of P added to soils in fertilizers since the first publication of a study by Way in 1850. Currently, the role of the scientist in increasing the life span of world P reserves lies in increasing the efficiency of use of P in agriculture. This may be P applied in mineral fertilizers, in organic manures, e.g. animal manures, composts and biosolids, but also soil P reserves accumulated as residues from past applications of fertilizers and manures. Currently, of the total global production of PR, mineral fertilizers account for about 80 percent, animal feeds about 5 percent, while 15 percent goes to industrial uses, such as detergents (12 percent) and metal treatment (3 percent) (Heffer *et al*., 2006).

As noted above, environmental issues are now a driver of the need to improve the efficient use of P in agriculture. Enrichment of surface waterbodies with P causes their eutrophication, on which their own biological productivity depends. This relies on the transfer of P from land, which may be both undisturbed and human-managed, and from urban and industrial effluents discharged to water, e.g. from sewage treatment works. However, excessive nutrient enrichment of surface freshwater bodies can cause undesirable changes in their ecology, including the balance of species of plants, fish and other aquatic organisms. In many cases, these changes in the biological balance are seen first as algal blooms, which usually occur owing to an increase in the concentration of bio-available P in the water and, in some cases, nitrogen (N). Widespread problems associated with the eutrophication of freshwaters came to the fore in the 1960s, most notably in the Great Lakes Basin of Canada and the United States of America (Rohlich and O'Connor, 1980). In the following two decades, studies found that many other lakes had varying degrees of eutrophication, i.e. in the United States of America (Federico *et al*., 1981), in Finland (Rekolainen, 1989), in Ireland (Foy and Withers, 1995), and in Germany and the Netherlands. Sharpley and Rekolainen (1997) later reviewed the role of P in agriculture and the environment.

Initially, studies linked eutrophication in lakes primarily to sewage-derived P inputs. Jenkins and Lockett (1943) estimated that as much as 40–60 percent of the total P in crude sewage entering treatment works was discharged as effluent to rivers in the United Kingdom. Much of the P in the effluent was water-soluble and, therefore, immediately bio-available for use by aquatic plants and animals. By the 1970s, although steps had been taken to limit P discharges to rivers from larger sewage treatment works, water quality had not improved in many lakes. This led to the suggestion that P from agriculture was a contributing factor to the P load in rivers and lakes. In consequence, there has since been much research on P and water quality in both North America and Europe. However, even in many developed countries, there are few sewage treatment plants with tertiary treatment facilities to remove P from the effluent. In LDCs, large volumes of untreated wastewater are usually discharged directly to surface waters.

It now appears that much of the P transferred from agriculturally-managed land to streams, rivers and lakes derives from specific areas ("hot spots") within a river catchment and that these are related to farming system, soil type, and hydrology (Gburek *et al*., 2002). It is possible to consider these areas as: (i) critical source areas – permanent features within a catchment from which P may be lost readily; and (ii) variable source areas – temporary features, often near streams, that lead to overland water flow carrying P, often associated with mineral or organic particles. Most of the P transported from soil to water is in eroded soil particles enriched with P (Ryden, Syers and Harris, 1973) or from excessive amounts of P fertilizer or animal manure applied to soil when conditions are not suitable (Johnston and Dawson, 2005).

This report recognizes the need to consider both the agricultural and the environmental dimensions of the use of P applied in fertilizers and organic manures to benefit crop growth, and it explores the basis of the concept of P-use efficiency and the rationale and prospects for its improvement.

Chapter 2

Plant availability of soil and fertilizer phosphorus

SOIL–PLANT INTERACTIONS

Phosphorus is taken up from the soil solution by plant roots as orthophosphate ions, principally $H_2PO_4^-$ and to a lesser extent HPO_4^{2-}. Several factors can influence both the rate and amount of P taken up by the plant and, therefore, can affect the recovery of a single application of P fertilizer. The same factors can also affect the recovery of P reserves accumulated in the soil from past additions of P as fertilizer or manure.

The most important factors controlling the availability of P to plant roots are its concentration in the soil solution and the P-buffer capacity of the soil. The latter controls the rate at which P in the soil solution is replenished, i.e. the rate of desorption of P from the solid phase of the soil, which is faster in soils with a high buffer capacity. Also important are the size of the root system and the extent to which roots grow into the soil, and the efficiency with which roots take up P. When considering a single application of P fertilizer, the efficiency with which it is used also depends on how well it was mixed with the volume of soil exploited by roots. Other factors that affect crop yield, and hence the requirement for P, can influence P uptake by the crop and thus the recovery of P and the efficiency with which the applied P was used. These factors include soil moisture and the extent to which weeds, pests and diseases have been controlled. Because the effects of these factors vary from year to year, it is essential to average estimates of P recovery over a number of years in order to obtain reliable data.

CONCENTRATION OF PHOSPHORUS IN THE SOIL SOLUTION

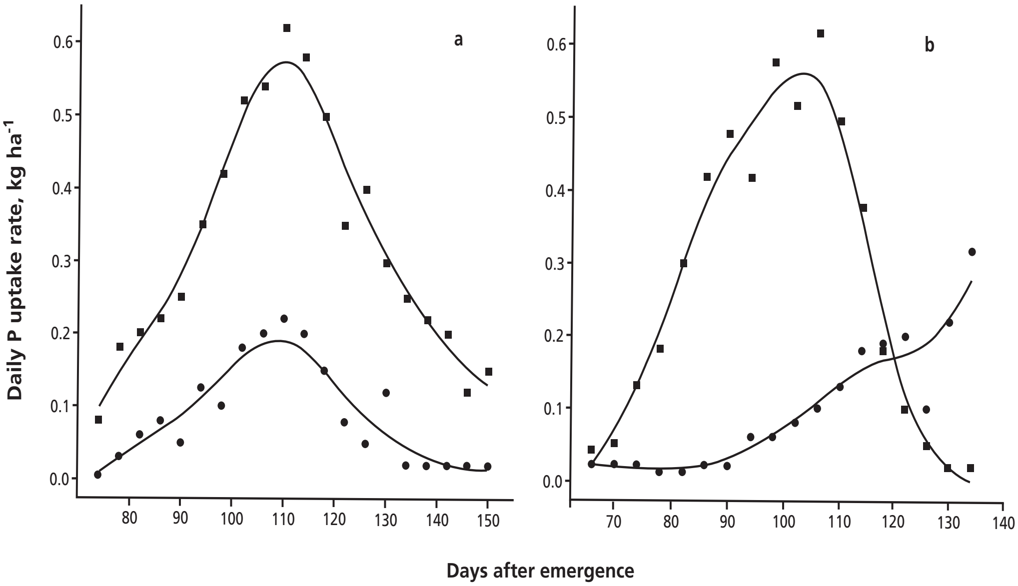
The concentration of P in the soil solution can range from 10^{-4} M, very high, to 10^{-6} M, deficient, to as low as 10^{-8} M in some very low-fertility tropical soils. These concentrations can be related to the amount of P in the soil solution and crop uptake of P. For example, a concentration of 10^{-5} M corresponds to 0.31 mg P per litre in the soil solution. Assuming that the top 30 cm of soil holds 6 cm of water (equivalent to 600 m^3 per hectare) there will be less than 0.2 kg P ha^{-1} in the soil solution to that depth. If a crop uses 37 cm of water during its growth, there will only be about 1 kg P ha^{-1} dissolved in the soil solution, yet it may take up 20–40 kg P ha^{-1} during the growing season. This much larger uptake is possible because roots can absorb P from solutions with very small P concentrations and P is maintained in solution by desorption from the solid phase of the soil. Provided that there is sufficient P on adsorption sites, from which it can be desorbed readily, and that the rate of release is adequate, plants will obtain enough P to meet their changing demand during the growing season. The rate of P release is an important factor (Frossard *et al.*, 2000), but it is difficult to measure routinely because radioisotopes and expensive counting equipment are required.

The minimum concentration of P to which the roots of soil-grown plants can deplete the external concentration of P in the rhizosphere soil solution is about 1 µM (Hendriks, Claassen and Jungk, 1981). The amount of P in the bulk soil solution required to replenish this concentration of P in the root hair cylinder can be estimated as follows. If the concentration of P is 5 µM, equivalent to 0.15 mg P per litre, and the amount of solution in the top 30 cm of soil is 500 000 litres per hectare, then the quantity of P is 0.075 kg ha^{-1}. However, the crop requirement for P during its phase of rapid growth can range between 0.3 and 0.5 kg P ha^{-1} per day. To meet this requirement for P during the period of maximum demand, the P in the root hair cylinder has to be replenished at least 10–20 times each day. This is because roots explore only about 25 percent of the topsoil in any one growing season (Jungk, 1984), but this depends on the crop grown.

Figure 1 illustrates the importance of maintaining an adequate supply of readily-plant-available P in soil to satisfy the maximum daily demand of a crop for P. Spring barley, given sufficient N and K, was grown in 1980 and 1981 on two soils, one well supplied with readily-plant-available P, the other with little. Figure 1a shows that in 1980 the maximum daily P-uptake rate occurred some 106–114 days after sowing and differed by a factor of three for the crops grown on the two soils. After the 114th day, the daily uptake rate declined on both soils. This large difference in P uptake was reflected in the final grain yield: the yield on the soil with adequate P was 6.88 tonnes ha^{-1} but it was only 2.88 tonnes ha^{-1} on the P-deficient soil. The following year (1981), the same cultivar was grown on the plots but the results were slightly different (Figure 1b). On the soil adequately supplied with P, maximum uptake occurred between the 94th and 106th day, and reached a maximum value of just under 0.6 kg P ha^{-1} per day, a difference in timing but similar in the amount of P to the previous year. On the soil with too little P, daily P-uptake rate by the crop continued to increase until the onset of senescence, but at the maximum the rate was less than 0.3 kg P ha^{-1}. As in 1980, the difference in soil P availability, and the effect on the daily P-uptake rate, resulted in a large difference in grain yield at harvest, namely 5.07 and 2.48 tonnes ha^{-1} on soil with and without an adequate supply of readily-plant-available P, respectively. The different pattern of P uptake between years on the P-deficient soil probably reflected the available moisture. In 1980, rainfall was less than average in May and, apparently, there was too little root activity to take up what P was available. In 1981, rainfall was more than average and the roots continued to take up the small amounts of P that were available. The difference in rainfall patterns did not affect P-uptake rates with adequate amounts of available soil P.

FIGURE 1

Daily P uptake by spring barley after emergence



Note: The two crops were grown in the same experiment on soils with adequate (▪) and less than adequate (•) amounts of plant available P in 1980 (a) and 1981 (b).

Source: Adapted from Leigh and Johnston (1986).

MOVEMENT OF PHOSPHORUS TO ROOTS

Plant root systems have two main functions; first, to provide an anchor for the plant in the soil, and second, to take up water and nutrients from the soil solution. Roots do not grow throughout the whole volume even of the surface soil and, as noted above, roots explore perhaps as little as 25 percent of the topsoil in one growing season. Roots can intercept nutrients (Barber, Walker and Vasey, 1963) but less than 1 percent of the available soil nutrients are supplied in this way (Barber, 1984). Nutrients are taken up from the soil in the region of the root, and this process is largely dependent on nutrients moving to the root by two distinct processes, mass flow and diffusion (Barber, 1984).

The amount of nutrient transported by mass flow is related to the amount and rate of water movement to the root, the water use by the crop, and the concentration of the nutrient in the soil solution. For example, assuming the concentration of P in the soil solution is 0.15 mg per litre and a crop transpires 3 million litres of water per hectare during its growth, then the total amount of P delivered to the roots is about 0.45 kg P per hectare. This quantity is only 2–3 percent of the total amount of P required by many crops to produce acceptable yields.

Diffusion is the main process by which P moves to the root surface. Diffusion involves the movement of ions along a concentration gradient, i.e. from a higher to a lower concentration. Thus, when plant roots remove nutrient ions from the soil solution and the concentration is lowered relative to that in the bulk solution, a concentration gradient develops and nutrient ions move down this gradient. The extent of depletion at the root surface depends on the balance between the supply from the soil and the demand by the plant. If the "absorbing power" of the root is large, this creates a sink to which nutrients diffuse (Tinker and Nye, 2000). The root-absorbing power is not constant but depends on root metabolism and the nutrient status of the plant (Barber, 1984). The amount of P required at the root surface depends on the depletion profile that develops with time. The shape of this profile will depend on the balance between P uptake by roots, the rate at which P is replenished in the soil solution, and the mobility of the phosphate ions by diffusion.

The mobility of an ion is defined in terms of a diffusion coefficient, which is usually orders of magnitude smaller in soils than in homogeneous media, such as water, because of the tortuosity (complexity of shape and length) and small diameter of most water-filled pores in the matrix of the heterogeneous soil system. Marschner (1995) gives estimated diffusion coefficients of $H_2PO_4^-$ (the most common form of inorganic orthophosphate in solution in weakly-acid aqueous systems) in water as 0.9×10^{-9} m^2 s^{-1}, but in soil estimated values range from 10^{-12} to 10^{-15} m^2 s^{-1}. At an average value of 1×10^{-13} m^2 s^{-1}, the movement of $H_2PO_4^-$ would be about 0.13 mm per day. This very limited movement of phosphate ions explains why it is necessary to have a sufficient supply of readily-available P throughout the volume of soil explored by roots if the demand for P by a crop is to be met during its most active period of growth. It also explains why good responses are often obtained to placing P fertilizer near where the roots of a crop are expected to grow.

PLANT ROOT SYSTEMS AND PHOSPHORUS UPTAKE BY ROOTS

Plant roots take up P from the soil solution as orthophosphate ions, principally $H_2PO_4^-$ and to a lesser extent HPO_4^{2-}, except in calcareous and saline soils. Plant roots can absorb P from soil solutions having very low P concentrations (Loneragan and Asher, 1967), in which case P uptake is against a very steep P concentration gradient. This is because the P content of root cells and xylem sap is 100–1 000 times larger than that of the soil solution (Mengel and Kirkby, 1987). The transport of P across the cell membrane varies between plant species. Cultivars within the same species can differ in their capacity for active P uptake, and these differences are probably largely genetically controlled.

Many plants have extensive root systems, which frequently have root hairs that extend out into the rhizosphere (the cylinder of soil surrounding the root), thereby increasing the effective surface area of the root system for the uptake of water and nutrients. Root hair formation is modified by environmental factors such as nutrient supply, especially that of N and P, and it differs between species.

In non-mycorrhizal plants, the extent of the zone of P depletion in the soil as a result of active P uptake by roots is often closely related to root hair length. For example, the extent of the P-depletion zone around maize and oilseed rape roots is nearly the same as the maximum root hair length, 1.8 mm for maize and 2.6 mm for rape, respectively (Hendriks, Claassen and Jungk, 1981). Itoh and Barber (1983) found a strong positive correlation between P-uptake rate per unit root length and the volume of the root hair cylinder. Caradus (1982) also showed differences in the efficiency of P uptake between genotypes of white clover that were related to root hair length.

Root hairs are more effective in absorbing P than is the root cylinder when the influx per unit area of each is compared because the smaller diameter and geometric arrangement of the root hairs maintain higher diffusion rates for P (Jungk and Claassen, 1989; Claassen, 1990). In soils with little readily-available P, uptake by root hairs can account for up to 90 percent of total P uptake by the plant (Föhse, Claassen and Jungk, 1991).

However, a close relationship between root hair length and the extent of the P-depletion zone in the rhizosphere is not always found. For example, the P-depletion zone around cotton, with short root hairs (about 0.2 mm) greatly exceeds the root hair cylinder (Misra, Alston and Dexter, 1988). For non-mycorrhizal plants, this suggests root-induced changes in the rhizosphere, e.g. the release of root exudates (particularly low-molecular-weight organic acids), pH changes, or a higher efficiency of uptake per unit length of root.

Many plants have developed a symbiotic association with arbuscular mycorrhizal (AM) fungi. The spores, which are found in many soils, develop hyphae that penetrate the root, remove carbohydrates from it, and grow out into the soil immediately surrounding the root, extending the capacity of the root to take up water and nutrients, especially P and micronutrients (Tinker, 1984). In soils with adequate plant-available P, this fungal association is usually not well developed, suggesting that mycorrhizae are not important in such soils. In mycorrhizal plants, the extent of the P-depletion zone greatly exceeds the diameter of the root hair cylinder (Jungk and Claassen, 1989), and it can be as large as 11 cm in white clover (Li, George and Marschner, 1991). Some plants do not have a mycorrhizal association. These include species of the order Chenopodiaceae, which includes agriculturally-important crops such as sugar beet. Compared with crops with mycorrhizae, such crops can be disadvantaged considerably when grown on soils with very small amounts of readily-available P (Johnston *et al*., 1986).

Differences between genotypes in P-use efficiency may be caused by differences in P uptake by roots, P transport within roots, P transport from root to shoot and between organs within shoots, and the utilization of P within the plant (Marschner, 1995). Perhaps the most important factor causing differences between genotypes is the acquisition of P by roots. Differences in P uptake per unit root length may be caused by higher influx rates, longer root hairs or differences in root/shoot ratios relative to the availability of P in the soil solution. As these differences are genetically controlled, there should be good prospects for developing more

P-efficient genotypes. If such genotypes become available, it should be possible to maintain soils at lower critical P concentrations than those required for current cultivars. Such P-efficient genotypes, whether produced by conventional breeding techniques or genetic manipulation, would have to be high-yielding and not more susceptible than current cultivars to other nutrient deficiencies and abiotic and biotic stress. Brown, Clark and Jones (1977) showed that some P-efficient genotypes are more susceptible to iron (Fe) and copper (Cu) deficiencies.

There may be reasonably good prospects for improving the efficiency of P use by plants by selecting appropriate genotypes with characteristics for root hair length, organic acid production in the rhizosphere, and mycorrhizal associations for soils with low P status. This approach to improving P-use efficiency may be more appropriate than seeking to modify root architecture, i.e. the shape and branching of the root system, which is often suggested as a way of improving nutrient uptake. Field evidence shows that root distribution in soil is much more dependent on soil physical characteristics than on the inherent shape of the root system. Almost 30 years ago, Drew and Saker (1978) showed that plant roots proliferated in soil zones that are enriched in P rather than following some specific pattern of spatial distribution.

PHOSPHORUS UPTAKE, ROOT SYSTEMS AND SOIL CONDITIONS

For nutrients such as P that are taken up by roots from the soil solution, the size of the root system and the efficiency with which it takes up nutrients are important in nutrient acquisition. The size of the root system is genetically controlled and varies between species. However, external factors also affect root growth and function. These factors include soil properties (such as acidity), depth, structure, stoniness, moisture retention, and composition of the soil atmosphere. Root diseases and nematodes also decrease the size of the root system, limiting the opportunity for nutrient uptake.

Many plants have extensive root systems, a feature possibly related to the time when they had to acquire nutrients from soils with very low concentrations of plant-available nutrients. Although both ryegrass and winter wheat have large root systems, they differ greatly in that ryegrass has fine roots, most of which are in the surface soil, while the roots of winter wheat are coarser and many are found below a depth of 1 m. A crop of winter wheat yielding 10 tonnes of grain per hectare can have a root system weighing about 1.5 tonnes ha^{-1} (dry matter) and extending to 300 000 km ha^{-1}, or about 100 m of root for each plant. Although the root system can be so large, root tips can only enter soil pores of larger than a certain diameter. For example, cereal roots cannot enter pores that are narrower than about 0.05 mm (Johnston *et al.*, 1998).

The rhizosphere, extending about 1–2 mm from the root surface into the bulk soil, is particularly important for plant nutrient availability. Estimates suggest that as much as half of the organic carbon translocated from the topsoil to the roots passes into the soil during the period of active growth. Much of this carbon is in excreted mucilage and dead cells (sloughage) shed by the root. This organic material ensures close contact between the root surface and the soil, and facilitates nutrient uptake. These materials, together with other organic compounds excreted by roots, are an energy source for micro-organisms living in the rhizosphere. Microbial activity in the rhizosphere can increase P availability by both lowering the pH and solubilizing iron-bound and aluminium-bound P, probably by complexing (or chelating) the Fe and aluminium (Al). Plant roots can also excrete organic acids that could solubilize considerable amounts of P in hydroxylapatite. Many species of brassicas, such as oilseed rape, and some legumes are particularly effective at doing this. Applying N as ammonium sulphate, or N sources such as urea that are converted to ammonium, can lower the pH in the rhizosphere by as much as 1 pH unit, and this also helps to solubilize P.

Soil pH has a controlling influence on the release of Al from various clay minerals as well as the dissolution of Al hydroxy compounds in soil. Soil acidity has adverse effects on plant growth and these are more the consequence of the free Al in the soil solution than the large concentration of H^+ ions. At elevated Al concentrations in the soil solution, root tips and lateral roots become thickened and turn brown, and P uptake is reduced. A large concentration of Al within the upper parts of the plant decreases the translocation of P and also interferes with P metabolism. Where liming materials are not readily available in the large quantities needed to increase soil pH, then adding sufficient material to remove free Al ions from the soil solution is generally adequate to ensure unhindered P uptake.

The composition of many soils is such that there are approximately equal volumes of mineral material and voids or pores in a complex array. The pores are important because they contain both air and water, and both are essential for root function. The relation between the water and air content in the pores is important because roots respire and an adequate level of oxygen in the soil air is required to ensure adequate root respiration for active P uptake. The diameter of the pores varies greatly. They tend to be larger in coarse-textured sandy soils than in clayey soils. In the latter, the mineral particles can be aggregated, and this creates larger pores. Excess water drains through larger pores, while smaller-diameter pores retain water to supply the needs of the plant. Compaction, for example by heavy traffic on soil with a small load-bearing capacity, tends to eliminate larger pores, and roots cannot grow in severely compacted soil because the pore diameter is too small. Compaction also decreases the diffusion of phosphate ions in soil by increasing the path length or tortuosity (complexity) of the system, with a further reduction in P uptake by the roots.

The slow movement of P by diffusion is frequently ascribed to the tortuosity of the pore system (above). However, the reactive sites for P adsorption on soil minerals lining the sides of the pores can also retain phosphate ions, temporarily or permanently, slowing or preventing their movement along the pore.

Soils devoid of air in the pores, for example as a result of waterlogging, become anaerobic. Reducing conditions in the soil as a result of anaerobic conditions, defined by the redox potential, affect many inorganic and biological processes. For example, the end products of the anaerobic microbial decomposition of organic matter can be toxic to higher plants. However, there can be benefits in relation to P nutrition for some specialized plants, including paddy rice, that grow in waterlogged soil. Oxygen required by the root for respiration passes to the root through air-filled channels (aerenchyma) in the stems and roots. Under anaerobic conditions, the reduction and dissolution of ferric oxides typically releases P into solution from sites where it is strongly adsorbed, e.g. on hydrous ferric oxides. This P is available for uptake by the roots. As the soils dry after harvest and ferrous iron reverts to ferric iron, hydrous ferric oxides in the soil will again retain readily plant-available P. In addition, PR can be used on paddy soils because anaerobic decomposition of organic matter produces soluble organic compounds that can increase the solubility of P in apatite materials through their ability to complex calcium (Ca) during the dissolution of apatite. Even in normally aerobic soils, it is probable that at certain times of the year there will be anaerobic microsites, especially in small-diameter pores, where the reduction of ferric to ferrous iron will release adsorbed P.

It is difficult to demonstrate the effects of soil structure on the response of a crop to an application of P fertilizer. However, in an experiment on a silty clay loam soil in the United Kingdom, there was a relationship between the content of soil organic carbon and the response of three crops to different levels of Olsen P (Table 1). For each of the three crops (spring barley, potatoes, and sugar beet), the percentage variance accounted for in the relationship between crop yield and Olsen P was appreciably larger for the soil with more soil organic matter (SOM). Moreover, much less Olsen P was required to achieve optimal yield when the crops were grown on the soil with more SOM. When a soil sample was taken from

TABLE 1
Effect of soil organic matter on the relationship between the yield of three arable crops and Olsen P in a silty clay loam soil, Rothamsted

Crop	Soil organic matter (%)	Yield at 95% of the asymptote (tonnes ha^{-1})	Olsen P asociated with the 95% yied (mg kg $^{-1}$)	Variance accounted for (%)
		Field experiments		
Spring barley	2.4	5.00	16	83
Grain (tonnes ha^{-1})	1.5	4.45	45	46
Potatoes	2.4	44.7	17	89
Tubers (tonnes ha^{-1})	1.5	44.1	61	72
Sugar beet	2.4	6.58	18	87
Sugar (tonnes-ha^{-1})	1.5	6.56	32	61
		Pot experiments in the greenhouse		
Grass dry matter	2.4	6.46*	23	96
(g pot^{-1})	1.5	6.51*	25	82

* The response curves at the two levels of soil organic matter were not visually different.
Source: Adapted from Johnston and Poulton (2005).

each plot in the field experiment and cropped with ryegrass in the greenhouse under controlled conditions, the relationship between yield and Olsen P showed the same critical value for Olsen P, irrespective of the level of SOM. This suggests strongly that the different critical Olsen P values, observed for each crop grown in the field, on the different soils was a consequence of the effect of the difference in SOM on soil structure. Similar effects of SOM have also been reported in an experiment with a sandy loam soil (Johnston, 2001).

Thus, the process of P diffusion in soil and the factors that influence diffusion substantially influence soil–plant P interactions. Root distribution and particularly the presence of root hairs, also play an important role in P acquisition by plant roots. All of these factors contribute to the recovery of P from soils and, thus, influence the efficiency with which plants use soil and fertilizer P.

A major factor that affects crop yield, and hence the requirement of the crop for P, is the adequacy of all other nutrients required in order to produce optimal yields. The sufficiency or insufficiency of other nutrients *per se* does not necessarily affect the uptake of P from the soil solution, but there can be important interactions between nutrients that affect yield. Two or more nutrients are said to interact when their individual effect is modified by the presence of one or more of the other nutrients. If the combined effect exceeds the sum of the individual effects then the interaction is positive or synergistic; if less than the sum of the individual effects, the interaction is negative or antagonistic.

Sumner and Farina (1986) discuss the agronomic implications for crop yield of interactions between P and other nutrients. They point out that many studies on nutrient interactions have been done in the laboratory or the greenhouse, but few in the field. They give a diagrammatic representation of the response of a crop to a number of limiting factors to show how replacing them, one by one, can affect yield. This effect is illustrated by the interaction between plant-available soil P (Olsen P) and N applied to maize (Table 2). The response to both P and N was

TABLE 2

Interactive effects of soil phosphorus and applied nitrogen on maize grain yields

Olsen P (mg kg^{-1})	N applied (kg ha^{-1})			
	0	60	120	180
	Maize grain yield (tonnes ha^{-1})			
3	2.31	2.22	3.11	3.41
16	4.74	6.68	7.91	7.84
27	4.06	7.14	9.12	9.74
46	4.54	8.17	9.42	9.96

Source: Adapted from Sumner and Farina (1986).

small at deficient levels of the other nutrient but increased markedly as soil P and applied N increased. Sumner and Farina (1986) also discuss, in detail, P by lime interactions, where there are considerable contradictions in the published literature. Many references are given to each of three possibilities, i.e. liming increased, decreased, or did not change soil P availability, as measured by various soil extraction techniques. There are similar contradictory reports for the effect of modifying soil pH on the recovery of P by plants.

Chapter 3

Changing concepts of the behaviour of soil and fertilizer phosphorus and reconciling these with agronomic information

WORK IN THE NINETEENTH CENTURY

The landmark field experiments established at Rothamsted, the United Kingdom, in the mid-nineteenth century revolutionized thinking on soil fertility and plant nutrition. These experiments tested the effects of fertilizers supplying N, P, potassium (K), magnesium (Mg), and sodium (Na), applied singly and in various combinations, and compared their effects with those of farmyard manure (FYM) on the growth of a range of arable crops (Johnston, 1994). They soon demonstrated that it was necessary to apply more P than was removed in the harvested crop to achieve an acceptable yield on what were then P-deficient soils (Johnston, 1970).

The need to apply more P than was removed in the harvested crop raised the question as to what happened to the residual phosphate. In the early 1870s, Liebig received samples of soil from some of the plots from the Broadbalk Winter Wheat experiment (started at Rothamsted in 1843), which had treatments with and without P since the beginning. On extracting the soils with dilute mineral acids, Liebig showed that the P-treated soils contained more readily soluble P than the untreated soils (Liebig, 1872). Later, Dyer (1894) produced a P balance (P applied minus P removed) for the first 38 years of the Hoosfield Continuous Barley experiment at Rothamsted. Where superphosphate (SP) had been applied annually at 33 kg P ha^{-1}, the P balance was positive. Most of this positive P balance could be accounted for by the extra total P accumulated in the 0–23 cm soil layer.

Subsequently, Dyer (1902) estimated a P balance for the first 50 years of the Broadbalk Winter Wheat experiment where P had been applied annually as SSP at a rate of 33 kg P ha^{-1}. Dyer related the positive P balance where P had been applied to the change in both total and 1 percent citric acid soluble P in the 0–23, 23–46, and 46–69 cm layers of soil sampled in 1893. Dyer calculated that, on the five plots receiving N and P fertilizer, 80–90 percent of the positive P balance had been retained in the top 23 cm of soil. Dyer assumed that the P that could not be accounted for (3.7 kg P ha^{-1} each year, or about 10 percent of that added in SSP) had moved downwards in the soil profile. However, the variability in both total and 1 percent citric-acid-soluble P in the 23–46 and 46–69 cm soil layers did not allow Dyer to demonstrate, with certainty, any subsoil enrichment with P. While recognizing that some of the P could have moved below 69 cm, Dyer concluded that errors in sampling and analysis of the soil precluded the possibility of obtaining a more accurate estimate of the amount of residual P in the soil. A very important consequence of this pioneering work was the thinking that, because only a small proportion of the P balance could not be accounted for as an increase in total P in the soil, most of the residual P was retained or "fixed" in the surface soil.

Further interest in residual fertilizer P in soil was stimulated in the United Kingdom at the beginning of the twentieth century. There was considerable discussion as to whether, when a tenant farmer left a farm, the owner of the land should pay the tenant compensation for the residual value of any fertilizers the tenant had applied but had not had the time to obtain any benefit from by way of increased crop yields. For each nutrient, the residual value was determined by measuring the increase in crop yield in the years following the initial application, compared with the yield on soil that had not received that nutrient. For fertilizer P, the residual benefit was estimated to be small and short-lived. In part, this was because the experiments attempted to measure the residual value of only one or a few applications of small amounts of P fertilizer added to very P-deficient soils, and sufficient N and K were not always applied to ensure that these nutrients were not limiting yield. The lack of response to residual P was taken as further evidence that if P was applied to a soil to grow a crop and it was not taken up by that crop, then the P was fixed in soil in unavailable forms. This stimulated interest in developing an understanding of the forms, amounts and availability to plants of P in soils, particularly of inorganic P.

WORK IN THE EARLY PART OF THE TWENTIETH CENTURY

Early studies, dating back to the mid-nineteenth century, e.g. Way (1850), demonstrated that soils could remove phosphate ions from solution. This process was called "P fixation" or "P retention" (Sample, Soper and Racz, 1980), the two terms often being used synonymously. The reaction was usually attributed to specific soil components, e.g. calcium carbonate in calcareous soils, and hydrous iron and aluminium oxides in acid soils (Wild, 1950). This early work, which started in earnest in the 1920s, stimulated subsequent interest in the interactions of phosphate solutions with pure minerals, and the mechanisms involved. The review by Wild (1950) indicates that although precipitation of calcium, iron and aluminium phosphates was widely suggested, up to that time the dominant mechanism was thought to involve the removal of phosphate ions from solution by adsorption. This is supported by much of the work reviewed by Kurtz (1953), where adsorption received a degree of prominence, although Kurtz made the observation that "in many respects, a distinction between the reactions in which phosphate ions are precipitated from solutions of iron and aluminium, and reactions in which phosphate ions are removed from solution by hydrated oxides is arbitrary, because the final products, if both reactions went to completion, would be identical." With hindsight, if the final product of these two very different processes were identical then the subsequent rate and extent of release of P would be the same, and there is no evidence for this. In addition to the review by Wild (1950), Pierre and Norman (1953), Khasawneh, Sample and Kamprath (1980), and Larsen (1967) provide summaries of the earlier work.

Most of the early studies produced conflicting results and conclusions, in part related to the conditions used in the experiments, and also because insufficient attention was directed to the actual plant availability of soil P, as measured by plant uptake of P and crop response. Although some researchers did pay due attention to the plant dimension, most of their work did not receive adequate recognition. Of the studies prior to the 1950s, that by Coleman (1942) is particularly interesting. It had commonly been assumed that the failure of a crop to respond to fertilizer P was because of the rapid fixation of P by the soil. Coleman showed that this could also be due to a sufficiency of plant-available P already in the soil and that large amounts of P "formerly considered fixed" are available to plants. Kurtz (1953) concluded that P reacts quickly in acid and neutral soils by becoming adsorbed but is still readily available to plants. With time, this initial form of P is converted gradually to less extractable and less plant-available forms. Kurtz argued that the explanation that P is held in soil by simple precipitation "sometimes leads to rather questionable conclusions." Kurtz asserted that if the P in a given soil were present as a series of insoluble phosphate compounds, then there would be a stepwise decrease in "solubility" when the same reagent was used for sequential extractions of the soil. The observed solubility showed no such stepwise changes; rather, solubility decreased very gradually with repeated extractions or dilutions. Kurtz concluded that the gradual decrease in extractability of added P provides evidence, but not necessarily proof, that definite phosphate compounds are not present in a fertilized soil.

A further complicating factor, in retrospect, has been the rather loose terminology used initially, and some still persists today. As mentioned previously, some workers in this field frequently used the terms fixation and retention interchangeably. However, others used the term fixation to indicate an irreversible removal of phosphate ions from solution, and retention to describe only the removal of phosphate from solution, regardless of the mechanism involved. Both terms ignore the implications for the availability of added P for uptake by plants. In retrospect, it was also incorrect to regard fixation and precipitation of P as being one and the same thing because precipitated phosphates are usually metastable, or transient, as discussed below.

FROM 1950 TO 1980: A PERIOD OF CHANGE

The 1950s saw a major shift in thinking, especially in the United States of America, regarding the reactions that occur when water-soluble phosphates are added to soil. These studies may be divided into laboratory studies and modelling.

Many laboratory studies focused on the formation of “discrete-phase”, “water-insoluble” compounds, particularly variscite (aluminium phosphate) and strengite (iron phosphate) under acid conditions, and a range of calcium phosphates under near-neutral and alkaline conditions. This led to the thinking that these compounds were the products of interactions between water-soluble P added in fertilizer and soil components. It was claimed that the very large concentrations of P (1.5 to in excess of 6 M) and cations (as large as 12 M) in the soil solution following the addition of a highly water-soluble P fertilizer react rapidly to form phosphate minerals with low water-solubility, and that this explained why the plant-availability of fertilizer P was so low in many soils. Much of this work was done in the United States of America by Jackson and co-workers at Wisconsin (Jackson, 1963) and by an active group at the Tennessee Valley Authority (Huffman, 1962, 1968). Early work in this area was reviewed by Kurtz (1953) and Hemwall (1957); subsequent work was reviewed by Larsen (1967) and Sample, Soper and Kamprath (1980), among others. There is strong evidence to suggest that, under the conditions used in many of the laboratory experiments, i.e. very large phosphate concentrations, often in reactions with pure minerals and sometimes at elevated temperatures, phosphate minerals having very low water solubility can form. Whether such insoluble reaction products commonly form in the heterogeneous environment of the soil is debatable (Barrow, 1983a). Furthermore, even if strengite and variscite do form as reaction products, they are unlikely to persist in soils having pH values higher than 1.4 and 3.1, respectively (Bache, 1964), and thus are unlikely to explain the chemistry of P in fertilized soils.

Much work was done on the reactions of P with calcium carbonate, used as a model system for calcareous soil, beginning more than 50 years ago but continuing subsequently (Kuo and Lotse, 1972). The early work of Cole, Olsen and Scott (1953) showed that adsorption reactions were dominant when dilute P solutions were added to calcium carbonate in the laboratory, but that dicalcium phosphate (DCP), or a compound with similar properties to DCP, precipitated when more concentrated P solutions were added. Lindsay, Frazier and Stephenson (1962) concluded that DCP and dicalcium phosphate dihydrate (DCPD) were formed as initial reaction products when a saturated solution of monocalcium phosphate (MCP) was reacted with calcium carbonate or calcium magnesium carbonate. These compounds were also thought to form in calcareous soils when highly water-soluble triple superphosphate (TSP), containing MCP, was added to soil. However, Sample, Soper and Racz (1980) have pointed out that there have been very few studies conducted with moist soil in which reaction products have been isolated and identified successfully. Most of the compounds considered to form as reaction products have been inferred from simulation of the chemical environment near a fertilizer granule or from solubility isotherm data, the limitations of which are discussed below. For example, using data from experiments in Colorado, the United States of America, Fixen, Ludwick and Olsen (1983) inferred – but did not demonstrate – that in two calcareous soils with extractable P concentrations of more than 35 mg kg^{-1}, octocalcium phosphate (OCP) was controlling solution

P concentrations, whereas with less-extractable P (concentrations in the range of 10 to 25 mg kg^{-1}), tricalcium phosphate (TCP) or a similar mineral dominated the concentration of P in the soil solution. However, Fixen, Ludwick and Olsen (1983) concluded, as did many other workers, that most P minerals are too soluble to persist in many soils. For example, it was earlier believed that DCPD reverted to OCP and even to colloidal hydroxylapatite relatively quickly (Lehr and Brown, 1958; Larsen, 1967), although this was not always the case. For example, Larsen, Gunary and Devine (1964) could not demonstrate the formation of a new crystalline phase when DCPD was incubated in both acid and alkaline soils for periods of up to 26 months. As suggested by Mattingly and Talibudeen (1967), the rate of removal of P from solution by soil components in acid and neutral soil is faster than OCP can be formed, indicating that OCP, if formed, is unlikely to persist. A similar conclusion was reached by Bache (1964) for the stability of strengite and variscite in most soils. Even if these compounds form, which seems unlikely in most soil environments, their persistence is doubtful. Thus, secondary, discrete-phase P compounds are unlikely to control solution P concentrations in soils and the availability of P to plants, except for short periods in some soils receiving water-soluble P fertilizer.

The preoccupation with precipitation reactions and the likely importance of solid-phase reaction products had an important side-effect. Much time and effort was spent in attempting to find methods for fractionating soil inorganic P using sequential extraction with a series of reagents of increasing extraction severity (Dean, 1938; Chang and Jackson, 1957). It was thought that the different chemical reagents, when used sequentially, would extract different forms of discrete-phase inorganic P. If this proved to be the case, it would support the view that added water-soluble P was precipitated in soil in a range of chemical compounds related to iron, aluminium and calcium phosphates, depending on soil pH. However, as discussed later, an alternative explanation is that these chemical reagents remove P associated with soil components with varying bonding energies. Today, soil P fractionation is being used in an attempt to identify soil P fractions associated with the plant-availability of soil P. This has led to a less prescriptive terminology that reflects the improved understanding of the behaviour of phosphate ions at the surfaces of soil and soil components (Chapter 4 and Annex 1). The preoccupation with P precipitation also ignored the fact that much P would be sorbed on particulate matter in soil and involve both adsorption and absorption reactions.

In a comprehensive review of the reactions of fertilizer phosphate added to soil, Sample, Soper and Racz (1980) concluded that both sorption reactions and precipitation are likely to occur simultaneously. However, it was recognized that it is difficult to assess sorption reactions in the presence of precipitation. Some of the initial reaction products undergo dissolution, and the P released may be taken up by plant roots or be adsorbed by soil components. The initially adsorbed P may be replaced and moved to new adsorption sites. According to Sample, Soper and Racz, the overall trend with time is for both initially precipitated and adsorbed forms of P to slowly become more stable and support progressively lower concentrations of P in the soil solution. The mechanisms involved are complicated and, to a significant extent, this explains the rather slow progress in developing an adequate understanding of the P fertilizer–soil system.

In the late 1950s and in the 1960s, modelling studies made extensive use of thermodynamic models, particularly solubility isotherms, to explain the behaviour of P in soil. Much of this work was done by Lindsay and co-workers (e.g. Lindsay and Moreno, 1960; Huffman, 1962; Lindsay, Frazier and Stephenson, 1962) and has been reviewed by Larsen (1967) and subsequently by Lindsay (1979). Using solubility isotherms for pure, crystalline phosphate compounds, Larsen (1967) concluded that the solubility of "hydroxylapatite" controls phosphate equilibria in soils, a view that now finds little acceptance. Although such models can produce elegant descriptions of products that might form, they largely ignore the kinetics of reactions and the fact that it is necessary to achieve a given level of supersaturation (defined by the supersaturation index) before a particular reaction product actually forms. Barber (1984) has indicated that a major limitation of using solubility isotherms is that they are constructed assuming that pure crystalline compounds are in equilibrium with phosphate ions in solution. Barber suggests that P compounds in soils are not pure crystalline forms but are rather impure with an unknown solubility. Most importantly, the fit of data-points to a solubility isotherm does not constitute proof that a particular compound controls phosphate solubility. This puts a question mark against the significance of much of the earlier evidence, inferred from solubility isotherms, that claimed to support the precipitation of P added to soil in fertilizer.

A MAJOR CHANGE IN DIRECTION

Pioneering work in Australia in the late 1960s and 1970s by Posner and co-workers (Posner and Barrow, 1982) and later by Barrow (1983b) on P adsorption in soils and its reversibility (desorption) led to a change in thinking. The slow reaction between phosphate and soil was attributed to the diffusive penetration of adsorbed phosphate ions into soil components. This would explain the decrease in extractability, isotopic exchangeability, and plant availability of P with time (Barrow, 1980). Earlier, Evans and Syers (1971) used the stable P isotope, ^{31}P, and the low-energy (0.25 Mev) radioactive ^{33}P isotope with a longer half-life (25 days) relative to ^{32}P to study the distribution of P added to soil. Using autoradiography on a medium-grained film, Evans and Syers (1971) showed that when P was added to aggregates of an iron-rich, Brazilian Oxisol (Syers *et al.*, 1971), the surface sorption of P was initially rapid and this was followed by diffusive penetration (or absorption) over time. Significantly, phosphate was not concentrated in discrete areas. This suggested that P was retained by a sorption reaction, presumably initially by adsorption at external surfaces, followed by absorption, which may be thought of as adsorption at internal surfaces. If the P removed from solution had been precipitated as strengite (in this goethite/hematite-rich soil), then the volume of soil occupied by phosphate would have been appreciably less than that indicated on the autoradiograms. Significantly, the exchangeability (even in 1 hour) of the sorbed, added P was small and decreased between 7 and 21 days of contact with the soil aggregates. The small exchangeability of the sorbed, added P and its spatial distribution, in conjunction with changes in P penetration into soil components over time, substantiate the hypothesis that the penetration of added P and the isotopic exchange of that sorbed, added P are diffusion-controlled processes.

Barrow (1980) suggested that the P that had become absorbed could be released over time; in other words the adsorption or absorption of P was largely reversible over time, but that testing for complete reversibility might involve a period of years. Barrow used results from Leamer (1963) to support this view. In an irrigated rotation experiment in the southwest of the United States of America, two-thirds of an addition of 235 kg P ha^{-1} had been recovered after growing alfalfa for four years and sorghum for one year. Subsequent crops responded to freshly added fertilizer P, but there continued to be a slow, cumulative increase in the proportion of the original fertilizer recovered, up to almost 80 percent after nine years. At lower levels of P application, the recovery was even larger and was essentially complete after nine years.

Barrow (1980) acknowledged useful discussions with Mattingly (Rothamsted), and some of the topics reviewed by Barrow would have been supported by data supplied by Mattingly. Among these were data on the residual value of P when different P sources had been applied to soil; the work reported in Mattingly (1971) was especially relevant. Mattingly probably drew Barrow's attention to the recovery of P residues more than 70 years after the last application of P fertilizer in the Exhaustion Land experiment at Rothamsted. Annex 1 provides a full discussion of these results in the case study on arable cropping in the United Kingdom. Furthermore, at about this time, a number of research workers were considering how P was retained in soil if it was not precipitated as discrete-phase inorganic phosphates.

Further evidence that fertilizer P is sorbed reversibly comes from experiments at Rothamsted. In these experiments, Olsen P was used to monitor P availability over time. In the Exhaustion Land experiment, SSP was applied annually at 33 kg P ha^{-1} from 1856 to 1901. The P balance was positive but the increase in Olsen P (167 kg P ha^{-1}) accounted for only 14 percent of the positive P balance (1 217 kg P ha^{-1}). After 1901, no more P was applied, and between 1901 and 1974 there was a negative P balance of 509 kg P ha^{-1}. However, the decrease in Olsen P in the top 23 cm accounted for only 182 kg P ha^{-1} or 36 percent of the total P removed in the crops grown in this period (Johnston and Poulton, 1977). This shows that P was retained at sites in the soil from which it was not extracted by the Olsen reagent when the P balance was positive. However, it was released from these sites when the P balance was negative, indicating a degree of reversibility of sorbed P (details in Annex 1).

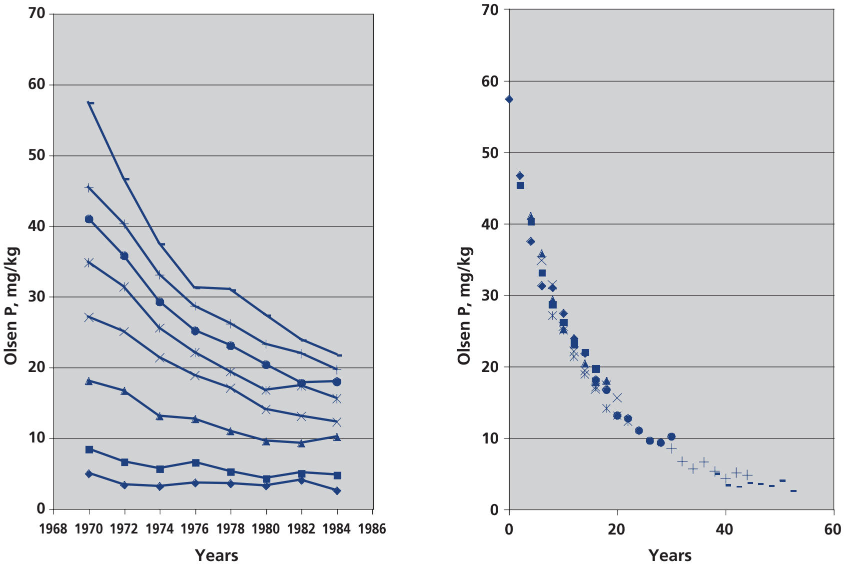
In another experiment started in 1899 on a silty clay loam soil at Saxmundham in Suffolk, the United Kingdom, treatments with and without P were applied annually to eight plots. By 1967, these eight plots had soils with Olsen P values ranging from 3 to 67 mg kg^{-1}. Potatoes, sugar beet, spring barley, winter wheat and field beans (*Vicia faba*) were grown in rotation without further addition of P but with adequate N and K between 1968 and 1984. The harvested crops were analysed for P while the soils were sampled in alternate years and analysed for Olsen P. On the soils with most Olsen P, the decline in Olsen P accounted for 26–46 percent of the P uptake. On the soils with 21 and 28 mg kg^{-1} Olsen P, the decline in Olsen P accounted for 12 and 21 percent, respectively, of the P uptake. On the soils with the least Olsen P, the change in Olsen P was less than 10 percent of the P uptake (Johnston, Poulton and Syers, 2001).

Although the data from this experiment at Saxmundham are only for a period of 16 years, it was observed that the decline curve for Olsen P on each of the eight plots appeared to be a segment of a single decay curve. It proved possible to bring the eight individual decay curves into coincidence and this unified curve (Figure 2) described the decline in Olsen P over a 50-year period (Johnston, Poulton and Syers, 2001).

From this curve, it was possible to calculate that it took nine years for the amount of Olsen P to halve as a result of P removal in the harvested crops. Similar unified decay curves have been found for experiments on silty clay loams growing arable and grass crops at Rothamsted.

FIGURE 2

Olsen P values over 16 years in eight soils having different initial Olsen P values and with no further additions of phosphorus (left) and development of a coincident decline curve by making horizontal shifts (right)



Source: Adapted from Johnston and Poulton (1992).

These results are critically important to the present discussion because this type of decay curve would be expected if there were different soil P pools in equilibrium with one another, with the readily-plant-available pool of P being buffered by one or more pools of less readily-available soil P. It also suggests that there are no specific, well-defined and discrete fractions of soil P, as previously widely believed, because these would become available in a stepwise progression.

AN OVERALL ASSESSMENT

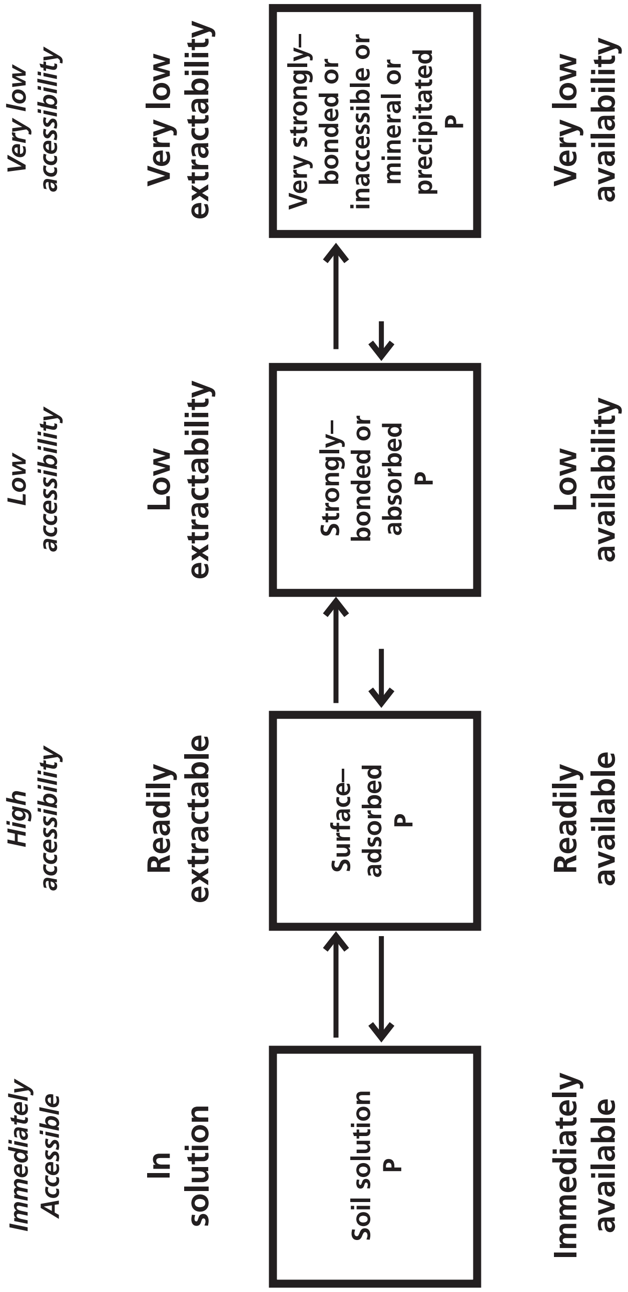
As discussed above, much of the work done up to about 1980 led to a preoccupation with the concept of P fixation and, hence, to an underestimate of the likely recovery over time of fertilizer P residues in soil. In retrospect, the persistence of the notion that fertilizer P residues are fixed irreversibly in soil may seem somewhat surprising, given that as early as 1953 Kurtz (1953) noted that: "Contrary to the apparent belief of two decades ago, more recent evidence indicates that the reactions of phosphate with soils are not entirely irreversible and that for most soils the term fixation is an exaggeration." The present understanding among most researchers is that changes in the extractability of soil and fertilizer P, and the decrease in plant availability of added P with time, can be explained reasonably well by current concepts relating to P equilibria in soils. These primarily involve adsorption and absorption reactions, which may be largely reversible with time. What now requires attention is the extent to which this concept of reversible adsorption can be reconciled with agronomic information when assessing P residual effects and the efficiency of P fertilizer use. This is a major thrust of the present report.

RECONCILING CURRENT CONCEPTS WITH AGRONOMIC INFORMATION

Using the ideas presented above, the concept that inorganic P is more likely to be retained by soil components with a continuum of bonding energies was developed and substantiated. This concept suggests that the more strongly bound the P is, the less available it is for uptake by plant roots. Moreover, sorbed P has a varying extractability or availability, related to the nature of its physical association with retaining components in the soil. However, this concept of the behaviour of P in soil needs to be reconciled with information on crop response to P. This can be done by categorizing soil P in terms of its availability to plants, i.e. by describing soil P as being readily and less-readily available to plants. These descriptions are essentially operational definitions and relate to the ability to characterize them by chemical extractants because it is important to have a methodology that is suitable for routine advisory purposes. This approach can be conceptualized and expressed diagrammatically, as in Figure 3, in which soil P is represented as being in four pools. Analytical procedures such as equilibration with resin and 0.5 M $NaHCO_3$, which remove weakly-bonded P that equates to P that is readily plant-available, can be used to assess the response of a crop to an application of P fertilizer.

Phosphorus is considered to be in the four different pools shown in Figure 3 on the basis of its accessibility and extractability, and thus its availability to the plant.

FIGURE 3
Conceptual diagram for the forms of inorganic P in soils categorized in terms of accessibility, extractability and plant availability



In the soil solution, P is immediately available for uptake by plant roots. The second pool represents readily-extractable P held on sites on the surface of soil components. This P is considered to be in equilibrium with P in the soil solution, and it can be transferred readily to the soil solution as the concentration of P in the latter is lowered by P uptake by plant roots. The P in the third pool is less readily extractable and is the P that is more strongly bonded to soil components or is present within the matrices of soil components as absorbed P (i.e. P adsorbed on internal surfaces) but can become plant-available over time. The P in the fourth pool has a low or very low extractability. This is because the P is very strongly bonded to soil components, or it has been precipitated as slightly soluble P compounds, or it is part of the soil mineral complex, or it is unavailable because of its position within the soil matrix. Whatever the reason, this P is only very slowly available (often over periods of many years) for plant uptake.

Electron microprobe analysis has shown that P may also be dispersed within certain minerals (presumably through isomorphous substitution reactions at the time of initial crystallization) or is present as apatite inclusions within other minerals (Cescas, Tyner and Syers, 1970). However, these modes of occurrence are of little direct interest to the behaviour of fertilizer P, even though they may affect the availability of soil P over extended periods of time (Syers *et al.*, 1967) and be important in certain natural ecosystems.

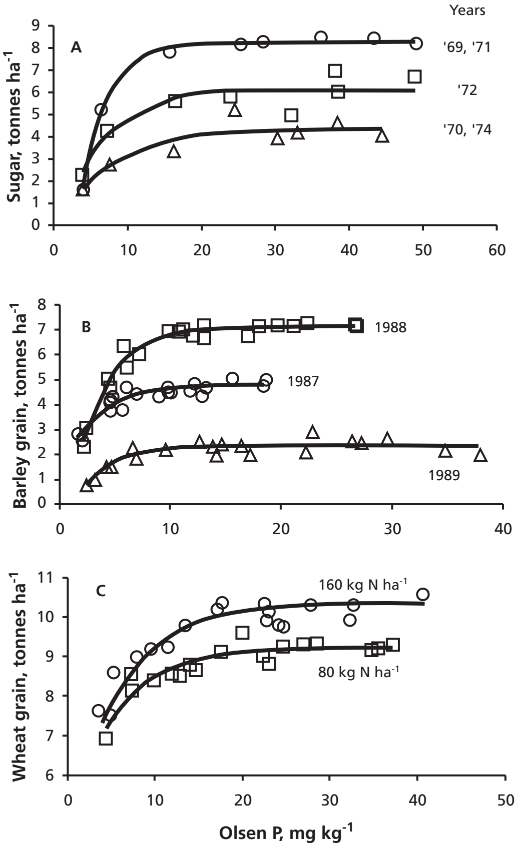
Routine soil tests measure P that is in the soil solution and in the readily plant-available soil pool. Thus, it is not a definite quantity but will vary with the reagent used. However, provided that there is a strong relationship between the amount of P extracted and the response of a crop to an application of P fertilizer, then this fraction of soil P can be thought of as being reasonably well defined.

The most important concept illustrated in Figure 3 is the reversible transfer of P between the first three pools. It is in this respect that current thinking about the behaviour of P in soil is fundamentally different from the belief that P is irreversibly fixed in soil. Irreversible fixation of P cannot be invoked to explain satisfactorily this behaviour of P added to soils in fertilizers.

When a fertilizer containing water-soluble P is added to soil, a very small proportion remains in the soil solution, and a small part may undergo initial precipitation reactions in some calcareous soils. However, the majority of the P rapidly becomes distributed between the readily-available and less readily-available pools by processes of adsorption and then absorption. For example, in the long-term (40+ years) experiments at Rothamsted, Woburn and Saxmundham, in the United Kingdom, where P has been applied as fertilizer and organic manure, only about 13 percent of the increase in total soil P is extracted by the Olsen reagent, which is used routinely to estimate readily-available P in soils. This experimental observation offers an explanation as to why attempts to estimate the value of residual P were not successful in the early twentieth century. If less than 15 percent of any residual P remains immediately available to plants, then it is unlikely that the small increase in Olsen P from any positive P balance resulting from a few small applications of P fertilizer would have a measurable effect on yield.

FIGURE 4

Response to Olsen P of sugar beet, barley and winter wheat grown on different soils at three sites in the southeast of the United Kingdom



Source: Adapted from Johnston (2005)

An important outcome from the above analysis is that, if the P in the readily-extractable pool (pool 2) supplies the bulk of available P for plants, then it is only necessary to accumulate a certain amount of P in this pool in order to achieve optimal yield; this is consistent with the concept of a “critical P” value for a particular crop in a given situation. This point is well illustrated by the data in Figure 4. Figure 4 shows that when sugar beet, barley and winter wheat were grown on contrasting soils at three sites, there was a critical P value for each crop. This was about 15 mg kg^{-1} Olsen P for sugar beet, 10 mg kg^{-1} Olsen P for spring barley, but nearer 20 mg kg^{-1} Olsen P for wheat. Compared with values for wheat from other soils, this value for wheat was rather large, probably because the soil on which this experiment was conducted had a poor structure and root growth was restricted. Above this critical value, there was no further increase in crop yield with further increases in Olsen P.

It is concluded that applying the concept of a critical P value for a specific soil growing a given crop can lead to a more efficient use of P from an agronomic standpoint. If this minimizes the excessive use of P, there will also be environmental benefits. The erosion of excessively P-enriched soil into surface freshwater bodies is a major cause of the increasing load of P in these waterbodies. Such P enrichment (eutrophication) leads to adverse effects on the biological balance in the aquatic environment (Johnston and Dawson, 2005).

Chapter 4

Measuring the recovery of soil and fertilizer phosphorus and defining phosphorus-use efficiency

INTRODUCTION

The outcome of any discussion about the recovery and efficient use of soil and fertilizer P is partly dependent on the definitions adopted and whether crop yield, P uptake and soil analysis data are used in making the calculation. A large percentage recovery of added P is taken to imply an efficient use of P by the plant.

There are a number of agronomic indices and methods for measuring the efficiency of plant-nutrient use in agriculture. In summary, the methods and indices, based on those of Cassman *et al.* (1998), are: direct method; difference method; partial factor productivity index; physiological efficiency index; and balance method.

The direct method can only be used for those nutrients where the fertilizer can be labelled, e.g. using ^{32}P-labelled or ^{15}N-labelled fertilizer, to measure nutrient uptake from the fertilizer directly. The index is the proportion of added nutrient recovered in the crop.

Results obtained by this method are often expressed as percentages.

The difference method can be used in two ways:

- Using yield, $(Y_N - Y_O)/F_N$, where Y_N and Y_O, are the crop yields with and without the nutrient being tested, and F_N is the amount of nutrient applied, all in kg ha^{-1}. This is frequently considered to be the “agronomic efficiency” of the applied nutrient.
- Using nutrient uptake, $(U_N - U_O)/F_N$, where U_N and U_O are the nutrient uptake by crops with and without the applied nutrient, all in kg ha^{-1}. This is frequently considered to be the “apparent recovery” or “apparent efficiency” of the applied nutrient.

Results obtained by this method are often expressed as percentages.

The partial factor productivity of the applied nutrient is calculated in terms of kilograms of product produced per kilogram of nutrient applied, Y_N/F_N (Y_N and F_N as above).

The physiological efficiency of the applied nutrient is calculated in terms of kilograms of product increase per kilogram of increase in nutrient taken up, $(Y_N - Y_O)/(U_N - U_O)$. (Y_N, Y_O, U_N and U_O as above).

In all the above, P can replace N (nutrient) in the formulae. Examples are given below.

In addition, a balance method is used here, i.e. total P in the crop divided by the P applied (U_P/F_P), expressed as a percentage. This method has been used occasionally (e.g. Chambers, 1953). It is an appropriate method for calculating P recovery and efficiency for a number of important reasons. For N fertilizers, the difference method, which has been used widely for many years, is appropriate because very little of an N application remains in the soil as mineral N in autumn to benefit a subsequent crop. However, where P is added to soil in fertilizers or manures, there can be a large P residue, which may increase the yields of subsequent crops for a number of years. When P in a fertilizer or manure is added to the heterogeneous and complex biological, chemical and physical environment of the soil, it can undergo several biological and chemical reactions that remove phosphate ions from the soil solution. However, this does not imply that the P becomes unavailable to plants. As measured by the direct method, rarely is more than 25 percent of the added fertilizer P taken up by the crop to which it was applied. The remainder of the P in the crop must come from soil P reserves, and this P must be returned if the existing level of plant-available P in the soil is to be maintained. Thus, P-use efficiency can be measured by expressing total P uptake as a percentage of the P applied. In one sense, Dobermann *et al.* (2005) have used this approach by suggesting that nutrient management and efficiency of nutrient use can be considered at a system level where changes in all nutrient pools are taken into account.

In this report, the direct and balance methods have mainly been used to assess the efficiency of use of P based on the recovery of added and soil-derived P, but other methods have also been considered to illustrate how they may be used.

Soil analysis can also be used to assess any residual value of applied P. This approach is not sensitive to the other factors that can affect crop yields but an appropriate method of soil analysis is required. Some suggestions are discussed below.

If the recovery of added P is of interest not only in the year of application but in subsequent years as well, this raises two questions:

- Over what time scale should recovery be measured?
- Can the residual P produce yields that are economically viable for the farmer?

Both of these issues are discussed below (with examples in Annex 1).

Where very large amounts of P are added to soil, they can have a residual effect over many years (Kamprath, 1967). However, it is more important to consider the residual effect and hence recovery over time of smaller, annual applications of P more similar to those used in normal farming practice. However, assessing the residual effect of P should only be done relative to that of an application of “fresh” (i.e. newly-applied) P in the year of the experiment (Mattingly, 1971). Thus, a welldefined response curve to freshly-applied P is required, and the response to it can be measured as yield or P uptake. In pot experiments, these two measures give similar indications of residual value (Barrow and Campbell, 1972), but this is not always the case in field experiments (Mattingly and Widdowson, 1963). In field experiments, P uptake may indicate a larger residual value than that indicated by yield alone.

The ultimate measure of the recovery of a P fertilizer, determined as its continued uptake over many years, is time-consuming; this may explain why there is a paucity of such data. Of equal interest is whether residual P is able to produce acceptable yields over a period of years. This is why other methods of estimating P efficiency (but not recovery) have been suggested. These include: the quantity of added P that remains in a labile form in the soil over time (Larsen, Gunary and Sutton, 1965); the effect of P additions on P-sorption isotherms (Fox and Kamprath, 1970); and changes over time in Olsen P values (Power *et al.*, 1964; Fitter, 1974). More recently, changes in the various pools of P extracted sequentially from soil have been used (Beck and Sanchez, 1996; Aulakh *et al.*, 2003; Blake *et al.*, 2003); this approach is discussed in more detail below.

ASSESSING THE RECOVERY OF ADDED PHOSPHORUS FROM CROP YIELDS

This section provides assessments of the recovery of applied P by the direct, difference and balance methods together with a comparison of the difference and balance methods.

Yield can be used in the calculations using the latter two methods, and P uptake in all three methods. Both the yield of a crop and the amount of P it takes up can be affected not only by the availability of soil P, but also by a range of other factors that vary from year to year. These factors include: climate (e.g. rainfall and sunshine) during the growing season; agronomy, including the availability of other essential plant nutrients, especially N and K; biotic stress (e.g. pests and diseases); and soil factors, such as soil structure. For annual experiments, the result will also depend on how well the added P was incorporated into the volume of soil explored by the roots.

For longer-term experiments, the result will depend on the number of years the experiment lasts. This is particularly important for P because, for soils where P can be accumulated in plant-available forms, plants may continue to take up the residual P from one or more applications of P fertilizer for many years. Thus, the recovery of residual P will depend on the time scale over which it is measured. Often, this residual effect has either been ignored or considered simply to be a benefit to yield by building up soil P reserves, without considering the recovery of residual P as part of the efficiency with which the initial application has been used over time.

There are two major problems with measuring P recovery over a number of years. The first is having the guarantee that the experiment will continue for an appropriate period of time; this explains why the most useful data for assessing the efficiency of P fertilizer use are usually obtained from experiments conducted on research stations where there is "security of tenure". The second relates to the distribution of P within the soil profile where plant roots are taking up nutrients actively, and the risk of loss of P from the soil. In long-term experiments, it is not correct to assume that all the residual P will be in the topsoil, which is usually the only soil horizon sampled and analysed. The data in Table 3 show that soil P has increased at different depths in some long-term experiments. However, little is known about the relative contribution of the P from different soil horizons to the total uptake of P by plants, because there is no information on root activity at different depths in these experiments.

Estimates of P recovery in long-term experiments can also be affected where P has been lost in surface runoff, especially in eroded soil (Sharpley and Syers, 1979; Tunney *et al.*, 1997; Johnston and Dawson, 2005) and also in subsurface runoff (Ryden, Syers and Harris, 1973). Both dissolved and particulate forms of P can be lost by any of these routes. Where P is lost from the soil, then the amount of P available for crop uptake will be less than that added originally. Thus, the recovery, when calculated as a percentage of the total P added, will be underestimated, whereas the recovery would be larger if it were calculated on the basis of the actual amount of residual P in the volume of soil explored by the roots.

Losses of P by movement down through and out of the soil profile are likely to occur on coarse-textured soils (Neller *et al.*, 1951; Ozanne, Kirton and Shaw, 1961). Mattingly (1970) observed that residual P from applications of SSP was leached from a coarse-textured, sandy surface soil but was retained by a clayey horizon in the subsoil. The amount of P recovered from this clayey layer would depend on the concentration and proliferation of roots in this soil layer, and the amount of P recovered would influence substantially the estimated P recovery. Similarly, Russell (1960) calculated the P balance for the period 1919–1957 for a permanent pasture grazed by sheep at Kybybolite, Australia. The soil was a light grey loamy sand passing to very light grey sand. Less than half of the increase in the P balance was found as an increase in total P in the top 20 cm of soil, and Russell presumed that much P had leached below this depth on this coarse-textured soil.

TABLE 3

Total phosphorus at different depths in long-term experiments at Rothamsted where superphosphate was applied for many years to a silty clay loam surface soil at pH 6.5

	Arable crops		Permanent grassland	
Soil depth	None	P	None	P
(cm)		(mg kg^{-1})		
0–23	780	1 295	575	1 425
23–30	465	525	555	785
30–46	415	450	500	600
< 46	400	395	n.d.	n.d.

Source: Adapted from Johnston and Poulton (1992).

Reviewing results from other experiments in Australia, Russell noted that, on other coarse- textured soils, P appeared to have been lost from the surface soil although the magnitude of the loss was not consistent. Unlike the results reported by Mattingly (1970), where P leached from the sandy surface soil was retained in the heavier-textured subsoil, the P leached from the surface soil described by Russell could well have been transported out of the soil profile.

Improving P-use efficiency on coarse-textured soils requires considerable management skills and a greater understanding of the progressive “saturation” of soil with P, as well as the role of maintenance applications, especially on permanent pastures, from which little P is removed in animal products. One potential option is to use a slow-release P fertilizer in these situations; a second option is to try to increase soil organic matter but this is not easy on coarse-tesxtured soils.

Direct method

Labelling a P fertilizer with a radioactive isotope of P (usually ^{32}P) is the main direct method of estimating the recovery by a crop of P from a single application of P fertilizer. The half-life of ^{32}P is too short (14.3 days) for it to be used over periods longer than about three months, so most studies are inevitably short-term. The method is also expensive. A second radioisotope of P, ^{33}P (Evans and Syers, 1971), has a longer half-life (25 days) but it is appreciably more expensive than ^{32}P.

A large number of studies on the uptake by plants of P from fertilizers labelled with ^{32}P were reported in the 1950s (Mattingly, 1957). Before then the difference method (below) had been used (Russell and Watson, 1940; Crowther *et al.*, 1951). However, the difference and radiochemical methods do not always give the same result; the reasons for this, which are related mainly to technique, were discussed by Mattingly (1957).

In a greenhouse experiment in 1952, Mattingly (1957) used soil samples from a long-term experiment where the plots had received either no P, or SP (1856–1901), or FYM (1876–1901) with no P added to any of these plots after 1901 (Johnston and Poulton, 1977). To 400 g of soil in each pot, 10 mg of ^{32}P-labelled SP was added and mixed uniformly with the soil. Ryegrass was grown and harvested three times in a period of 87 days. Between 18 and 21 percent of the added P was recovered during this time. In a second, similar pot experiment, the recovery of ^{32}P-labelled SP was measured using soils taken from a field experiment where P had been applied for some years as either SP or PR. The recovery of added P ranged from 21 to 24 percent for SP-treated soils, and was somewhat less (18 to 19 percent) where PR had been applied (Mattingly, 1957).

Subsequently, Mattingly and Widdowson (1958) conducted a series of nine field experiments between 1952 and 1954 to estimate P recovery from placed, ^{32}P- labelled SP applied to root crops and cereals grown on contrasting soils. In 1952, the recovery of the placed SP was 7, 18 and 36 percent, by potatoes, swedes and fodder beet, respectively. In 1953 and 1954, only fodder beet was grown, and the recovery of the placed SP was 38 percent in 1953 (similar to that in 1952) but only 6 percent in 1954, when yields were smaller. Sequential samples of the fodder beet taken during the growing season showed that the proportion of the total P in the crop that was derived from the placed, labelled SP declined during growth.

Experiments with spring barley in 1953 and 1954 on two soils, with pH_{water} values of 7.4 and 5.3, gave an average P recovery of 15 percent. Another series of field experiments with spring barley in 1953 and 1954 compared broadcast and placed ^{32}P-labelled SP (Mattingly and Widdowson, 1959). At harvest, the recovery of the placed SP varied less (ranging from 10 to 15 percent) and was larger than that (range 5–12 percent) from the broadcast application in spring.

There was little variation between estimates of percentage P recovery in greenhouse experiments, where only ryegrass was grown, but results from field experiments varied considerably, both between crops and between years for the same crop. For the field experiments, the variation between seasons was related to soil conditions and yield. Based on the results from all the field experiments, the recovery of ^{32}P-labelled SP ranged from 5 to 25 percent.

In contrast, Larsen (1952) reported much larger recoveries (about 85 percent) of the P from MCP added to soils in pots growing ryegrass in a greenhouse. More recently, Sisworo *et al.* (1998) used ^{32}P labelling to compare different PRs with either TSP or SP-36 in field experiments with rice grown both in the lowlands and uplands in Indonesia. Yields of lowland rice were very similar with both TSP and PR at each level of P tested. At 32 days after planting, 66–75 percent of the P in crop was derived from the added P. Yields of upland rice were larger with SP-36 than with any of the PRs tested. With SP-36, 40 percent of the P in the crop was derived from the added P. The smaller yields of upland rice with PR were associated with 25–32 percent less P in the crop compared with the percentage of P in the crop grown with SP-36.

Difference method

For many years, the difference method has been used widely to estimate the recovery of fertilizer P added to soil. Russell and Watson (1940) and Crowther *et al.* (1951) provide reviews of early work. If the calculation (above) is based on yields, the result is frequently considered as the agronomic efficiency of the applied P. If the calculation is based on P uptake, the result is considered to be the apparent recovery or efficiency. Many factors can affect the result, some of which have been discussed above. The percentage recovery of applied P determined in this way depends on the yield and P uptake by the crop grown on the soil to which no P was applied, and this, in turn, depends on the amount of plant-available P in the control soil.

In greenhouse experiments, growing conditions can be controlled well, and because roots tend to grow throughout the soil mass, optimal conditions exist for P uptake if the added P is mixed uniformly with the soil. In a recent greenhouse experiment, Johnston and Richards (2003) measured the recovery of P by ryegrass grown on ten soils with available soil P (Olsen P) ranging from very low to high (from 4 to 40 mg P per litre) and pH_{water} values ranging from 4.9 to 8.1. The P was added as MCP at four rates: 44, 66, 88, and 110 mg P per pot, each pot containing 1 kg of soil.

The recovery of added P was measured during one growing season. Calculated by the difference method for soils with very low to medium P status (4–20 mg kg^{-1} Olsen P), recovery (range 38–44 percent) was largely independent of the amount of P added (Table 4). Averaged over the four amounts of P tested, recovery was 41 and 43 percent for the low and the medium soil P groups, respectively. This was despite the fact that there was a large difference in the total P uptake from the control soils of the low and medium soil P groups: 14.0 and 35.8 mg P per pot, respectively. Even on soils with 28 and 40 mg kg^{-1} Olsen P, the recovery of added P was, on average, 34 percent.

Several field experiments were analysed by the difference method. The effect of N on yield, P uptake, and P-use efficiency over time is clear in the Broadbalk experiment at Rothamsted. There, the same annual amounts of N (96 kg ha^{-1}), P (33 kg, then 35 kg ha^{-1} from 1974) and K (90 kg ha^{-1}) have been applied to plots growing winter wheat since 1852. In the absence of N, the recovery of the added

TABLE 4

Recovery of P by the difference method in a greenhouse experiment with P added as MCP at four rates to soils with a range of plant-available P values

		P added (mg P pot^{-1}) as MCP				
		44	66	88	110	
Olsen P	Total P uptake on control			Recovery of added P		Mean
(mg kg^{-1})	(mg pot^{-1})			(%)		
4–11	14.0	44	42	40	38	41
16–21	35.8	44	43	44	41	43
28–40	61.7	34	35	34	33	34

Source: Adapted from Johnston and Richards (2003).

TABLE 5

Change in P recovery over time determined by the difference method, Broadbalk, Rothamsted

		Annual treatment*				
		Without N		With N		
Period		None	PK		P	PK
1852–71	P in crop** (kg ha^{-1})	4.9	6.6	6.5	9.2	11.3
	% recovery		5		8	14
1966–67	P in crop (kg ha^{-1})	4.5	5.7	4.8	11.0	12.0
	% recovery		4		19	22
1970–75	P in crop (Kg ha^{-1})	6.2	6.8	9.0	13.1	17.3
	% recovery		2		12	24
1985–2000	P in crop (kg ha^{-1})	3.7	4.7	5.7	12.7	17.4
	% recovery		3		20	33

* Annual treatment (kg ha^{-1}): N, 96; P, 33 (35 since 1974); K, 90.

** Total P in grain plus straw.

P was less than 5 percent and has not changed over 150 years (Table 5). With the increasing yield potential of the cultivars grown and where the crop always received 96 kg N ha^{-1}, P-use efficiency has increased over time.

The effect of plant-available soil P on the recovery of added P by three arable crops was examined in the Agdell experiment at Rothamsted. There, two levels of SOM and a range of Olsen P levels were established over a 12 year period before spring barley, potatoes, and sugar beet were each grown for two years in the three-year period 1970–72. The data in Table 6 are from soils with 2.4 percent SOM and are averaged over two years. On the soil with 6 mg kg^{-1} Olsen P, the recovery of added P varied with the crop grown. However, on the soil with adequate Olsen P there was no response to added P, except for a small response by spring barley.

Balance method

The balance method does not make any comparison between crop yield and P uptake on soils with and without added P. It simply considers yield and P uptake relative to the amount of P applied. The reasons for adopting this method have been discussed above. As an example, P recoveries by the balance method can be calculated from the data in Table 5; the results are shown in Table 7. Percent P recoveries calculated by the balance method are larger than those calculated by the difference method. The data in Table 7 show that where N and K supply is adequate, percent recovery has increased as the yield potential of the wheat crop has increased. The data in Table 7 suggest that in recent years about 50 percent of the added P can be accounted for in that experiment. Further examples of the balance method are given below.

TABLE 6
Effect of level of plant-available soil P on the recovery of P applied to three arable crops, Agdell, Rothamsted

	Olsen P (mg kg^{-1}) at the start of the experiment			
	6		59	
	P applied*			
	no P	P	no P	P
Spring barley				
P in crop** (kg ha^{-1})	8.3	12.6	17.5	19.1
% recovery		16		6
Potatoes				
P in crop (kg ha^{-1})	9.4	16.2	16.8	17.0
% recovery		8		0
Sugar beet				
P in crop (kg ha^{-1})	8.1	22.9	36.0	35.1
% recovery		27		0

*P applied to each crop, kg ha^{-1}: barley, 27; sugar beet, 54; potatoes, 82.

** P uptake: barley grain + straw; potatoes, tubers; sugar beet, tops + roots.

Note: Basal applications (kg ha^{-1}): N: barley, 95; potatoes, 250; sugar beet, 190; K: barley, 50; potatoes, 250; sugar beet, 250.

The difference and balance methods compared

A comparison of the data in Tables 5 and 7 shows that the percent recovery of P added in fertilizers is larger when calculated by the balance method, and there are valid reasons for calculating recovery in this way. Table 8 provides a more comprehensive example. Rotations of three arable crops (sugar beet–spring barley–potatoes–spring barley) were started in 1969 and in 1970 on soils with a range of Olsen P values. Three amounts of SSP (27.5, 55 and 82.5 kg P ha^{-1}) were tested at each level of Olsen P but were only applied to the potatoes and sugar beet. Thus, in four years, a total of 55, 110 and 165 kg ha^{-1} P were applied. The P uptake in the harvested crops was measured each year and the total P uptake in four years was calculated and averaged over the two rotations. Table 8 presents data for only two levels of soil P (4 and 33 mg kg^{-1} Olsen P). On the soil with only 4 mg kg^{-1} Olsen P, the recovery estimated by the difference method ranged from 43 to 24 percent, declining with the amount of P applied. Yields and, hence, P uptake were much larger on the soil with 33 mg kg^{-1} Olsen P and recovery was much less (3 – 4 percent). Estimated by the balance method, recovery of the added P ranged from 85 to 39 percent on the soil with least Olsen P, again declining with the amount of P applied. On the soil well supplied with Olsen P, recovery varied from 140 to 50 percent. The value of 140 percent arises because there were excellent yields on this soil without adding any P and adding 27.5 kg ha^{-1} P to the potatoes and sugar beet increased yield and P uptake by only a small amount. Where recovery determined by the balance method exceeds 100 percent, this implies that the added P has not replaced all the P removed in the harvested crop and that P reserves are being depleted.

TABLE 7
Change in P recovery over time determined by the balance method, Broadbalk, Rothamsted

		Annual treatment*		
		Without N	With N	
Period		PK	P	PK
1852–71	P in crop **	6.6	9.2	11.3
	% recovery	20	28	34
1966–67	P in crop	5.7	11.0	12.0
	% recovery	17	33	36
1970–75	P in crop	6.8	13.1	17.3
	% recovery	21	40	52
1985–2000	P in crop	4.7	12.7	17.4
	% recovery	13	36	50

* Annual treatment (kg ha^{-1}): N, 96; P, 33 (35 since 1974); K, 90.
** Total P in grain plus straw, kg ha^{-1}.

TABLE 8

Percentage recovery of three amounts of applied P at two levels of Olsen P, sandy clay loam soil, Saxmundham

P applied* (kg ha^{-1})	Olsen P (mg kg^{-1})					
	4	33	4	33	4	33
	P uptake in 4 years (kg P ha^{-1})		% recovery by the difference method		% recovery by the balance method	
0	23.3	75.2				
55	46.9	77.0	43	3	85	140
110	57.2	79.4	31	4	52	72
165	63.8	82.2	24	4	39	50

Notes:
Data are the mean of two 4-year rotations, 1969–1972 and 1970–73.
Rotation: sugar beet, barley, potatoes, barley.
Total P applied in 4 years was 55, 110 and 165 kg P ha^{-1}.
* P tested at 27,5, 55 and 82,5 kg P ha^{-1} but applied only to potatoes and sugar beet.

EFFICIENCY DETERMINED IN RELATION TO YIELD PER KILOGRAM OF PHOSPHORUS APPLIED OR TAKEN UP BY THE CROP

The efficiency with which the crop uses P can also be expressed in terms of the increase in yield per unit of P applied, and this is often known as “partial factor productivity”. The data from the greenhouse experiment given in Table 4 can be used to illustrate this method of calculating efficiency (Table 9). One feature arising from this method of presentation is that, at each of the three levels of Olsen P, although yield increased with the amount of added P, the efficiency of P use decreased, whether expressed as milligrams of dry matter (DM) per milligram of P applied or as milligrams of DM per milligram of P uptake. Thus, although yield increased with the amount of applied P, the applied P was used less efficiently. The yield and the milligrams of DM per milligram of P applied both increased with increasing Olsen P, but the milligrams of DM per milligram of P uptake decreased with increasing Olsen P (Table 9).

Another feature of the results is the relationship between yield, Olsen P, and P-use efficiency. For example, the total yield of ryegrass per pot (23.5 and 24.6 mg) was similar for the second rate of P addition (65.5 mg P pot^{-1}) at the medium level of Olsen P (16-20 mg kg^{-1}) and for the largest rate of P addition (109 mg P pot^{-1}) at the lowest level of Olsen P (4 - 11 mg kg^{-1}). However, in terms of efficiency, expressed as milligrams of DM per milligram of P applied, the P was used more efficiently at the medium level of Olsen P, 612 compared with 225 mg DM. A similar comparison can be made for the smallest amount of P applied at the highest level of Olsen P and the largest amount of P added at the medium level of Olsen P (Table 9). Again, P was used more efficiently when the smallest amount of P was applied to the soil with the largest Olsen P value. Both sets of results suggest that there is an advantage to be gained from maintaining soils at an adequate level of readily-available soil P to achieve maximum efficiency of applied fertilizer P.

TABLE 9
Efficiency of P applied as MCP when expressed as unit of DM per unit of P applied or unit of DM per unit of P uptake

Olsen P	P applied (mg P pot^{-1})				
(mg kg^{-1})	0	44	66	88	110
			Ryegrass yield (mg pot^{-1})		
4 to 11	9.32	19.17	21.62	23.27	24.62
16 to 20	19.81	23.51	24.21	25.26	25.63
28 to 40	26.02	26.70	27.26	27.69	28.35
			mg DM per mg P applied		
4 to 11		440	330	266	225
16 to 20		539	370	289	235
28 to 40		612	419	317	260
			mg DM per mg P uptake		
4 to 11		579	524	480	443
16 to 20		428	380	341	321
28 to 40		350	322	305	289

SUMMARY OF METHODS FOR ESTIMATING THE RECOVERY OF PHOSPHORUS FERTILIZERS

The various methods of estimating P-use recovery or efficiency can be best summarized by data from the Broadbalk Winter Wheat experiment at Rothamsted for the period 1985–2000. Table 10 presents the effects of Olsen P and added N on the average yield of wheat grown continuously and in the rotation used in the 16 year period.

When determined by the difference method, the recovery of applied P was less for wheat grown in rotation than for wheat grown continuously. The reason is that yields are larger when wheat is grown in rotation because the effects of soil-borne pathogens on root growth and uptake of applied nutrients are minimized in the rotation. However, when calculated by the balance method, wheat grown in rotation recovered more P than did continuous wheat. When calculated by both the difference and the balance method, recovery of P added in FYM is smaller than that of P added in P fertilizer when sufficient fertilizer N is given with the fertilizer P.

When efficiency of P use was calculated as kilograms of grain per kilogram of P uptake, the largest values were for the crops given N, but no P, i.e. the crop was using soil P very efficiently but not effectively, because without N, yields were very small and not financially viable. Where the same amount of fertilizer P was applied each year, the range in terms of kilograms of grain (306–334) per kilogram of P uptake was small, which suggests a fairly constant concentration of P in both grain and straw.

These data indicate that different methods of calculating P recovery or efficiency can give very different results. In addition, the recovery of added P depends not only on the crop grown, but also on all those factors, such as other inputs, soil conditions, and weather during the growing season, that affect the final yield and, thus, the amount of P taken up by the crop. These factors need to be borne in mind when evaluating the data and the information generated in the case studies included in Annex 1.

SOIL ANALYSIS

Another approach to estimating the recovery or efficiency of P added in fertilizers is to use soil analysis to assess whether P residues have remained in soil P pools from which they can be recovered by crops.

TABLE 10

Effect of Olsen P and N on the yield and efficiency/recovery of P by winter wheat, Broadbalk, Rothamsted, 1985–2000

	Treatment						
Continuous wheat	Nil	N_2K	N_2PK	N_4PK	N_6PK	FYM	FYM + N_2
Olsen P (mg kg^{-1}) in 1992	7	4	115	76	73	85	74
Grain yield (tonnes ha^{-1})	1.17	2.46	5.32	6.58	7.29	6.04	8.07
P in grain+straw (kg P ha^{-1})	3.7	5.0	17.4	20.6	22.8	22.9	28.6
% recovery							
Difference method			35	45	51	39	51
Balance method			50	59	65	50	62
Efficiency of P use							
kg grain per kg P uptake	316	492	306	319	320	264	282
kg grain per kg P applied			152	188	208	131	175
Rotational wheat	Nil	N_2	N_2PK	N_4PK	N_6PK	FYM	FYM + N_2
Olsen P (mg kg^{-1}) in 1992	9	6	86	80	77	111	93
Grain yield (tonnes ha^{-1})	2.25	5.53	7.26	8.76	8.67	7.78	9.36
P in grain+straw (kg P ha^{-1})	6.7	13.2	21.9	26.8	27.5	27.0	33.7
% recovery							
Difference method			25	39	41	30	44
Balance method			63	77	79	58	73
Efficiency of P use							
kg grain per kg P uptake	336	421	334	327	316	289	278
kg grain per kg P applied			207	250	248	169	203

Notes:

Cultivars grown: Brimstone, 1985–1990; Apollo, 1991–1995; Hereward, 1996–2000.

Treatment per hectare annually: N_2, N_4, N_6: 96, 192, 288 kg N; P, 35 kg; K, 90 kg. FYM, 35 tonnes ha^{-1} supplying 46 kg P and 225 total N.

For rotational wheat treatment N_2 had to be used instead of N_2K.

Assessing the increase in readily plant-available soil phosphorus

On soils where P residues can accumulate in readily plant-available forms (Chapter 3) the concentration of P in the available pool can be measured by appropriate methods of soil analysis such as Olsen, Morgan, Bray, Mehlich and CAL (Kamprath and Watson, 1980). The concentration of P, i.e. in milligrams per kilogram of soil, measured using these reagents will increase as the amount of total P in a given soil increases. However, relative to the increase in total P, the increase in the P extracted by the reagents is usually small (Johnston, Poulton and Syers, 2001). In Rothamsted experiments, the increase in Olsen P is only about 13 percent of the increase in total P. In order to determine the amount of P, i.e. in kilograms per hectare, in the readily-available pool, the weight of soil per unit area to the depth of sampling must be known with accuracy.

Figure 3 indicates reversible transfer of P between the readily-available and less readily-available pools of soil P, and thus the P in the latter pool does become available to plants. There is ample evidence for this (Johnston, 2001). The amount of P in the less readily-available pool cannot be determined by routine soil analysis methods. Therefore, little is known about the relative amounts of P in these two pools for a range of soils. Unless the quantity of P in the soil P reserves is known together with its rate of release, it is not possible to predict how long the reserves will last. Chapter 3 described an experiment in which the decline in Olsen P was measured over a 16 year period of arable cropping. Because the decline curves for eight soils could be brought into coincidence, it was possible to estimate from the combined curve that it would take about 50 years for Olsen P to decline from 60 to 5 mg kg^{-1} with a half-life of 9 years.

Optimizing the use of soil phosphorus reserves

On soils where plant-available P can accumulate, the response of crops to increasing levels of these P reserves will follow the law of diminishing returns, i.e. as readily-available P reserves increase, the yield will increase rapidly at first and then more slowly to reach an asymptote (Figure 5).

The level of readily-available soil P (assessed by a well-tried and accepted method of analysis, at least for weakly acid, neutral and calcareous soils) at which the yield asymptote is approached can be considered to be the critical value for that soil type and farming system. The critical value will vary with these two factors, and at the critical value, readily plant-available soil P is used with maximum efficiency and maximum effectiveness. Below the critical value, there is a serious risk of loss of yield. Above the critical value, applying P is inefficient because there is no increase in yield, and there is also an unnecessary cost to the farmer. Where such P-enriched soils are transferred to surface waterbodies by erosion, there is an increased risk of eutrophication. At the critical level, P is used most effectively when the amount applied replaces that removed in the harvested crop (maintenance or replacement applications). To check whether this approach is maintaining the critical level, the soil can be sampled every 4–5 years. This approach is applicable where comprehensive information for soils and farming systems exists (Johnston and Dawson, 2005).

FIGURE 5

The theoretical realtionship between crop yield and the level of readily-plant-available P and K in soil

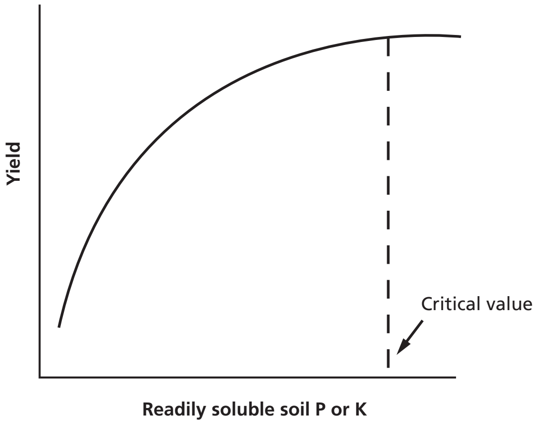
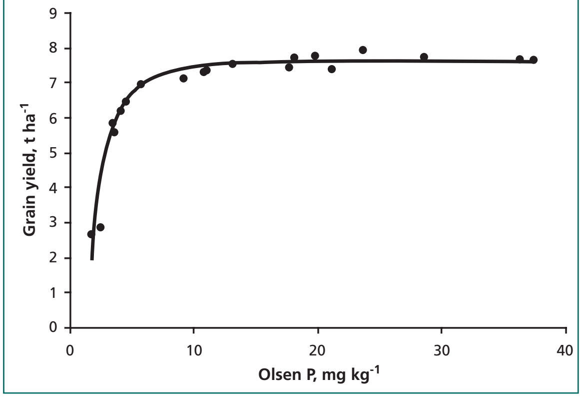


FIGURE 6

The relationship between Olsen P and the yield of wheat grain on a silty clay loam soil

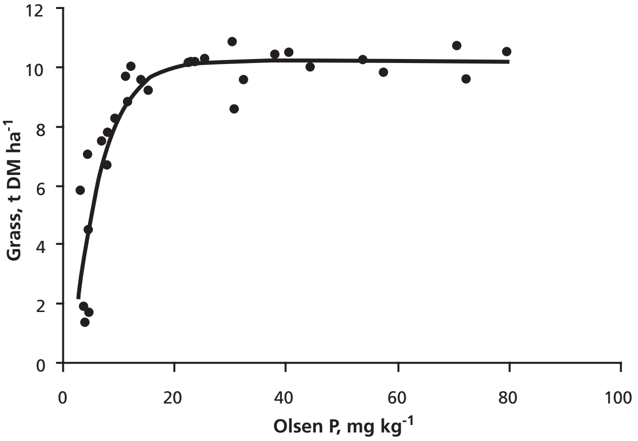


Figures 6 and 7 show examples of the relationship between Olsen P and the yields of winter wheat and grass (DM) grown on a silty clay loam soil. Figure 4 shows other examples of this relationship. For each of the three crops shown in Figure 4, the Olsen P value at which the yield approached the asymptote was similar irrespective of the large annual differences in yield, which in this case were caused by weather and N supply. Although the critical value was essentially independent of the yield, more P will have to be applied to make good the larger uptake of P in the larger yield, i.e. the use of applied P will be efficient because only the P removed will be replaced. The data in Table 1 show that the level of SOM had a large effect on the critical Olsen P value for spring barley, potatoes and sugar beet grown on one site where the lower level of SOM was far below the optimum. This effect of SOM could be explained by its positive effect on soil structure in the field and, in consequence, better root growth. In this situation, it would be better to improve soil structure, perhaps by increasing SOM, rather than applying excessive amounts of P to achieve very high levels of available soil P.

Sequential analysis of soil phosphorus

Chapter 3 has described a method for categorizing soil P according to its ease of extraction and availability for crop uptake, using sequential extraction of the P in soil (Figure 3). Another approach to describing soil P has sought to identify different chemical forms of P in soil. This has involved sequential extraction of the soil with chemical reagents that have an increasing ability to remove P from the soil. For this purpose, various methods have been described by, among others, Chang and Jackson (1958), Hedley, Stewart and Chauhan (1982), Perrot, Maher

FIGURE 7
The relationship between Olsen P and the yield of grass DM on a silty clay loam soil



and Thorold (1989), and Tiessen and Moir (1993). It was initially thought that sequential extraction would give some insight into the chemical association of the P removed by each extractant. However, with improved understanding, it seems preferable to consider a continuum of P adsorbed or absorbed by mineral components in the soil, as well as P in more or less discrete chemical forms. Consequently, no specific P compounds can be related to each extractant. Although sequential extraction of a single soil sample gives data that are little more than a “snapshot in time”, Blake *et al.* (2003) have shown how the usefulness of such data might be extended. In experiments with contrasting P treatments, it is possible to see how the amount of P extracted by each reagent has been affected by a treatment. Where there are archived soil samples, it is sometimes possible to assess how P extracted by each reagent has changed with treatment and time, and to relate these changes to P balances and plant availability of the P in each fraction. This approach to using sequential extraction of soil P is illustrated here using an example from a long-term experiment at Rothamsted. Other examples are given in the Peru and India case studies in Annex 1. Knowledge about the amount of P in those soil fractions that are known not to be immediately plant available, identified as less-labile P pools in some reports, could lead to a better understanding of soil P dynamics. This could lead to improved management of P fertilizer use and, hence, higher P-use efficiency.

There is ample evidence that P extracted by an anion-exchange resin or by 0.5 M $NaHCO_3$ is usually well related to the amount of P that is available for crop uptake. These two reagents are used as the first and second extractants, respectively, in several methods of sequential extraction. It is unlikely that the P extracted by 0.5 M $NaHCO_3$ following equilibration of the soil with resin will be the same in quantity or form as the P extracted by the Olsen method for routine soil analysis. Repeated extraction of a soil with 0.5 M $NaHCO_3$ following a first extraction, as in the Olsen method, continues to extract P, but in decreasing amounts, for about ten extractions. Hence, extraction with bicarbonate following equilibration with resin would be expected to remove more P from the soil. Here the amount of P extracted by 0.5 M $NaHCO_3$ in the sequential extraction method will be identified as $NaHCO_3$ P (or bicarbonate P) to distinguish it from the Olsen P in routine soil analysis. Rarely does the sum of the amount of P extracted by resin and bicarbonate relate directly to the P balance. This is because much of the residual P moves rapidly to the less-readily-available pool (Figure 3); it is the continuing availability of the P in this pool of P that is of particular interest.

Using archived and current soil samples and estimates of P balances in long-term experiments managed by Rothamsted Research on contrasting soil types at Rothamsted, Woburn, and Saxmundham, it has been possible to evaluate sequential extraction of soil P. Blake *et al.* (2003) give details of the soil, experimental treatments, P balances for three long-term experiments, and the sequential extraction method used. Here, data for the Exhaustion Land experiment at Rothamsted (case study on arable cropping in Annex 1) are summarized. Started in 1856, there were three P treatments: none, SP (1856–1901), and FYM (1876–1901). Since 1901, no P has been applied. The top 23 cm of soil has always been sampled, and there are samples for 1856, 1903 and 1993. The two-year difference between the last application of P in 1901 and the soil samples in 1903 has no effect on the interpretation of the data to derive P balances because of the long time scales of P accumulation and depletion.

The extractants used were, in order: (i) an anion-exchange resin; (ii) 0.5 M $NaHCO_3$; (iii) 0.1 M NaOH; (iv) 1 M NaOH; (v) 0.5 M H_2SO_4; (vi) hot concentrated HCl; and (vii) analysis of the residue to determine residual organic P (Po) and recalcitrant residual inorganic P (Pi). The P removed by extractants (ii), (iii) and (iv) was determined analytically as both Po and Pi. However, for simplicity, only the sum of Po and Pi is given here, and the discussion is restricted to the P extracted by the first five reagents. Before 1901, the P balance was positive where both fertilizer and FYM were applied; P accumulated in the soil and there were increases in all the first five soil P fractions. During the period of P depletion (1901–1993 on all plots), there were negative changes in all five P fractions (Table 11). These positive and negative changes account for almost 90 percent of the increase or decrease in total soil P determined separately for each soil in each period. Inorganic P changed much more than Po in these soils growing arable crops. The change in resin P contributed most (25 percent) to the change in total P.

In another experiment, it was seen that added P distributed itself between the different soil P fractions quite quickly (Blake *et al.*, 2003). On a sandy clay loam soil, 230 and 490 kg P ha^{-1} were added in FYM and SSP, respectively, between 1965 and 1967. By spring 1969, the sum of the Pi extracted by resin and 0.5 M $NaHCO_3$ was only 56 and 58 percent, respectively, of the total increase in the Pi in the first five fractions. The sum of the change in P in all five fractions (expressed as kilograms per hectare) did not account for all the P balance. This was probably because the authors were calculating differences between analytical values, and any small error in the determination of P in each fraction contributes to the overall error.

The data from both these experiments indicate that there were both increases and decreases in all five fractions of soil P related to the known accumulation and depletion of soil P, i.e. there was reversible transfer of P between these fractions. Thus, the P accumulated in more strongly-held forms was subsequently released and taken up by the crops grown (Johnston and Poulton, 1977).

USING OMISSION PLOTS TO ASSESS THE NEED FOR PHOSPHORUS

Applying fertilizer P when the soil supply is sufficient to meet the requirement of a crop is an inefficient use of P. To apply this concept to large areas of farmland, for which little is known about past fertilizer additions and soil fertility status, an "omission plot" technique has been developed (Dobermann *et al.*, 2003). The technique entails establishing a series of plots in farmers' fields, and applying to one of them all major nutrients as well as those micronutrients that might be deficient. On each of the remaining plots, one of the nutrients given to the fully fertilized plot is omitted. Comparing the yields on these plots with those on the fully fertilized plot gives an estimate of the indigenous supply from the soil of that nutrient for that crop and year. By combining this site-specific crop-based data with modelling the expected yield response as a function of nutrient interactions and climatic yield potential (Dobermann *et al.*, 2002), a site-specific nutrient management (SSNM) approach has been developed that can be used on similar soils within a region. A consortium consisting of the Swiss Development Cooperation (SDC), IFA, International Potash Institute (IPI) and International Plant Nutrition Institute (IPNI) co-sponsored a multinational project to evaluate SSNM at numerous locations in many rice-growing areas in Asia (Wang *et al.*, 2001; Dobermann *et al.*, 2002; 2003). This project has had considerable success in indicating the indigenous nutrient supply of soil at the different sites and the need

TABLE 11

Relationship between P balance at the end of each treatment period and the change in soil P fractions, Exhaustion Land, Rothamsted

		Change in firt five P fractions,kg P ha^{-1}					
Plot, treatment & period	P balance	Resin	0.5 M $NaHCO_3$	0.1 M NaOH	1 M NaOH	0.5 M H_2SO_4	Total change
	(kg ha^{-1})				(kg P ha^{-1})		
No P							
1903–1993	-300	-49	-20	-195	-82	-19	-365
FYM applied							
1876–1901	1 035	193	129	133	107	335	917
Not applied							
1903–1993	-752	-259	-123	-159	-112	-164	-817
P fertilizer applied							
1856–1901	1 222	158	126	79	7	270	640
Not applied							
1903–1993	-644	-234	-138	-114	45	-253	-694

Source: Adapted from Blake *et al.* (2003).

to apply P fertilizer when the soil supply was too small. When used for N, the timing and amount of N to apply can be fine-tuned to the needs of a crop based on leaf chlorophyll content (Peng *et al.*, 1996). For P, the omission plot only indicates whether or not to apply P. To determine the efficiency with which the applied P has been used, the grain and straw should be sampled and analysed.

SUMMARY

A variety of methods have been used to measure P recovery and to estimate the efficiency of use of soil and fertilizer P. These methods often give widely different results depending on the basis of the calculation. Of the methods used, the direct and balance methods have been emphasized. Of the two, the balance method is preferred because this includes allowance for the plant-available soil P derived from previous fertilizer or organic manure applications; that is, it takes into account residual P. Results obtained using the balance method are invariably higher than those using the direct method. However, as the former takes into account residual P, it is considered to be both more realistic and more useful.