

2 Phosphorus

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Introduction

Phosphorus (P) is one of the most important mineral nutrients for biological systems, yet it is also one of the most scarce nutrients in terms of its demand in both terrestrial and aquatic environments (Moss, 1988). In nat-

ural systems, P is tightly cycled through the plant–soil continuum, but in agricultural systems soil P is removed in the crop or animal products and must be replaced if P deficiency is to be avoided. Therefore, mineral PO_4^{3-} fertilizers and animal manures are applied to agricultural land to raise soil

P levels and maintain crop yields (Sibbesen and Sharpley, 1997).

Phosphorus fertilizer has traditionally been applied to agricultural land with no concern over losses to water, because inorganic P is strongly fixed in the soil and prevented from leaching (Sample *et al.*, 1980). However, while this is true from an agronomic standpoint, the small amounts of P lost from the soil can have severe impacts on water quality in receiving catchments, especially in terms of eutrophication and the growth of undesirable algae (Moss, 1996). In aquatic ecosystems, P can contribute to eutrophication, toxic algal blooms and a general deterioration of water quality. Known far-reaching consequences of these aquatic processes include the disappearance of sensitive ichthyofauna, the increased cost of drinking water purification and loss of income from recreational tourism. In particular, accumulations of P can occur under heavy manure or fertilizer application (Breeuwsma *et al.*, 1995), which can eventually reduce the capacity of the soil to retain P and accelerate the loss of P in runoff to watercourses. Examples of areas with severe eutrophication problems that are directly attributable to agricultural P include the Chesapeake bay area of north-eastern USA and the Gippsland Lakes area in south-eastern Australia (Burkholder *et al.*, 1992; EPA, 1995).

In this chapter we discuss the role of agricultural management of P in contributing to water quality problems. The main areas of consideration are the imbalances in P use at the farm scale, the dynamics of soil P and the transfer of P from soils to watercourses. Emphasis is placed on understanding the mechanisms and pathways of losses from soil to water and forms of P in surface waters. Finally, options for improved management of agricultural P for the prevention of surface water pollution are considered.

Phosphorus Use on Farms

Agricultural soils receive P from livestock (direct excreta and manures), mineral fertilizers and municipal sludges and waste-

waters. Imbalances originate because P is applied at levels that are in excess of the amounts required for optimum crop yields. This is often exacerbated where areas requiring P fertilizer (e.g. crop producing areas) are spatially separated from areas with large P surpluses (e.g. areas of intensive livestock production). The following sections examine the basic sources and pathways of P in agricultural systems that can lead to the over-application and consequent acceleration of transfer to watercourses.

Livestock feeding and manure production

Dietary P supplements are often used to maintain the optimum P requirements of livestock, because P deficiency can exert a number of negative effects on animal growth, productivity and fertility. The optimal requirement of digestible P in animal feeds ranges from 0.12–0.26% dry matter for pigs to 0.4–0.8% dry matter for poultry; ruminants have an intermediate requirement of 0.2–0.6% dry matter (Jongbloed and Everts, 1992). The digestibility of plant P ranges between 15 and 35% depending on the type of plant, while the availability of P in mixed feed for ruminants is c. 45–50% (Lynch and Caffrey, 1997). Balancing plant P and animal requirements for digestible P can be achieved by the supplementation of diets, as Ca-, NH₄- or Na-phosphate or phosphoric acid. Alternatively, deficiency can be avoided by the use of enzyme supplements to animal diets to increase the digestibility. Between 60 and 90% of the P in animal feeds occurs as phytic acid (inositol hexabisphosphate), an organic P compound found widely in the environment (Turner *et al.*, 2002). Phytic acid is poorly available to monogastrics (pigs, poultry), which have low levels of intestinal phytase enzymes. Phytase catalyses the release of PO₄³⁻ from phytic acid. Therefore, the uptake of P from phytic acid can be improved by the use of phytase as a dietary supplement. Phytase supplements are also used for ruminants, although these animals can use phytic acid to a larger extent because of a

because P is in excess of the crop yields. Areas requiring large P inputs (livestock manure) examine the over-fertilization of

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When used to improve the efficiency of P use in animals, the addition of P can exert a positive effect on animal growth. The optimal level of P in animal feed varies depending on the dry matter content of the feed; for example, the requirements for poultry are higher than for cattle (Jongbloed *et al.*, 1997). The availability of P in the feed depends on the availability of plant nutrients such as calcium, magnesium, and phosphorus (Nisbet *et al.*, 1997). Requirements for P are determined by the availability of calcium, NH_4 , and phosphoric acid. The addition of P to animal feed is necessary to avoid deficiencies. Between 1980 and 1990, the use of phosphate fertilizers increased significantly (Nisbet *et al.*, 2002). The use of P fertilizers to improve the efficiency of P use in animals has low environmental impacts. The use of PO_4^{3-} from animal manure is a good alternative to synthetic P fertilizers. The use of P fertilizers can be reduced by the use of P supplements. The use of P supplements is necessary for animals that are deficient in P because of a

greater level of intestinal phytase. Phosphorus uptake efficiency can be greatly improved through the use of phytase supplements, reducing P contents in excrement by up to 25–35% (Oloffs, 1998). This has environmental as well as financial benefits, because increased efficiency in livestock production reduces the P returns to land. It should be noted, however, that P in manures from animals fed with phytase supplements may be present in more soluble forms and, hence, may actually increase the likelihood of manure-derived P transfer to watercourses.

Mineral fertilizers

The addition of mineral P fertilizer to crops is commonly based on soil tests and the resulting fertilizer recommendations. More than ten different soil tests are used in European countries (Tunney *et al.*, 1997). These include various lactate methods such as double lactate (DL), calcium-ammonium lactate (CAL) and ammonium acetate (AL) (Austria, Belgium, Germany, Hungary, The Netherlands, Norway, Poland, Romania, Sweden), the Olsen method (sodium bicarbonate (NaHCO_3): Denmark, Greece, Italy, Spain, UK) and the water-extractable P method (Austria, Netherlands, Switzerland). A more recent development is the extraction of soil with 0.01 M calcium chloride (CaCl_2), which is used for multi-element determination and evaluation for various nutrients and contaminants. The

critical soil value to obtain the desired high crop yield varies widely, even if the same soil P test is used (Table 2.1). This results from differences in soil and climatic conditions, P requirements and uptake by crops, and also from differences in the experimental basis used to derive these critical levels. Therefore, a re-evaluation of experimental data to match P requirements of crops and minimize the risk of P losses from soils is urgently needed.

Clearly, the differences in soil P test methods and their evaluations result in widely different P fertilizer recommendations in various regions (Sibbesen and Sharpley, 1997; Tunney *et al.*, 1997). Mineral P applications are typically in the range of 10–20 kg P ha⁻¹ year⁻¹. Common types of P fertilizer are superphosphate (8–10% P), triple superphosphate (20% P), ammonium phosphates (21–24% P) and rock phosphates (apatites, 13% P) (Mengel and Kirkby, 1987). Examples of current mean fertilizer P applications in European countries are given in Table 2.2. In calculating fertilizer application rates, it is necessary to consider the manure-P inputs so that the farmer can reduce mineral fertilizer application, thereby saving money, avoiding undesirable soil P enrichments and reducing the potential impacts of P transfer to aquatic ecosystems. However, this is not always the case, especially when manure applications are calculated on the basis of N, rather than P, content, which can result in disproportionate quantities of P being applied to the land.

Table 2.1. Examples of soil-test phosphorus (P) levels for 95% relative yield or no yield response (data from Sibbesen and Sharpley, 1997).

Soil P test method	Critical level (mg P kg ⁻¹)	Crops	Number and duration of trials	Region, soils
H ₂ O	5	Rotation	105 trials, 1 year	Germany, loess
H ₂ O	14	Potatoes	37 trials, 1 year	The Netherlands
DL	26	Rotation	150 trials, 1–3 years	Germany, various
DL	50–60	Rotation	1 trial, 42 years	Germany, Pheozem
Olsen	5	Maize	25 trials, 1 year	Iowa, various
Olsen	21–35	Rotation	7 trials, 20 years	Denmark, various
Bray-1	11	Maize	25 trials, 1 year	Iowa, various
Bray-1	22	Wheat	4 trials, 12 year	Nebraska, Mollisols

Table 2.2. Phosphorus field balances in some European Countries (Isermann, 1999).

	The Netherlands (1997)	Denmark (1996)	Poland (1997/98)	Greece (1988)
Input (kg ha ⁻¹ year ⁻¹)	58	28	14	> 22
Animal manure	41	18	6	n.d.
Fertilizer	14	8	8	22
Deposition	1	n.d.	n.d.	n.d.
Other	2	2	n.d.	n.d.
Output (kg ha ⁻¹ year ⁻¹)				
Plant products	31	20	14	9
Surplus	27	8	> 0	> 13
Efficiency of use (%)	53	71	98	< 41

n.d. = Not determined.

Soil phosphorus

Soils are the source of P for plant uptake and also for transfer to watercourses, so an understanding of soil P dynamics underpins the two fundamental aspects of agricultural P research.

Phosphorus contents and forms

Total P contents of topsoils in temperate regions typically range between 300 and 2000 mg kg⁻¹ depending on parent material, soil type, land use and fertilizer/manure application method (Frossard *et al.*, 1995; Leinweber, 1996). In contrast, some soils in densely stocked areas of Western Europe and the USA are greatly enriched in P (Barberis *et al.*, 1996). The proportions of organic P can range between 25 and 50% of total P in mineral soils and up to 60–90% in organic soils (Harrison, 1987). Soil management (e.g. arable vs. permanent grassland and biological vs. conventional farming) and rates of P fertilizer/manure application all affect soil P contents and the ratio of inorganic to organic compounds.

Inorganic P-containing minerals include the various calcium phosphates, such as Ca(H₂PO₄)₂, CaHPO₄, Ca₄(HPO₄)₃ and Ca₅(PO₄)₃OH. The solubility of calcium phosphates depends on pH and the Ca²⁺ concentrations in soil solution. In alkaline soils, the availability of freshly applied fertilizer P gradually decreases through precipitation of less soluble calcium phos-

phates. In neutral and acidic soils, the dynamics of inorganic P are dominated by PO₄³⁻ sorption on to the edges of clay minerals and to pedogenic Al and Fe oxides. Sorbed PO₄³⁻ can diffuse inside pedogenic oxides and become less soluble. These sorbed and occluded insoluble phosphates of Al and Fe predominate in acid soils. This presents a serious problem in highly weathered soils rich in Al and Fe oxides, like Ferralsols and Sesquisols, especially in tropical regions. Low molecular organic anions and higher molecular organic acids such as fulvic and humic acids compete with PO₄³⁻ and, possibly, organic P compounds, for sorption sites. Furthermore, chelating organic compounds may also contribute to the desorption of PO₄³⁻. Hence, agronomic treatments that enhance soil organic matter content often also improve PO₄³⁻ availability. There is substantial evidence that redox dynamics are closely linked to the dynamics of sorbed and dissolved PO₄³⁻ in soil which can directly affect the amounts and forms that leach from soils.

Quantitatively, the most important organic P compound in most soils is phytic acid, which can form up to 80% of the organic P (Turner *et al.*, 2002). Other measurable organic P compounds include phospholipids and nucleotide phosphates (Harrison, 1987). Despite their prevalence, soil organic P compounds remain poorly understood, especially in terms of their availability to plants and transfer to watercourses (Frossard *et al.*, 2000). Indeed, a large proportion of the soil

Greece
(1988)

> 22

n.d.

22

n.d.

n.d.

9

> 13

< 41

organic P has eluded even basic chemical characterization (Harrison, 1987). This is partly attributable to the fact that recoveries of organic P compounds are often < 50% in common extractants such as sodium hydroxide (NaOH) (Cade-Menun and Preston, 1996). This may result from the 'trapping' of organic P compounds by more complex organic macromolecules, such as fulvic and humic acids, which makes their direct determination difficult.

The soil microbial biomass can contain a large and active P fraction, which can be determined by the fumigation-extraction method (Brookes *et al.*, 1982). Typical proportions of microbial P range from 2 to 5% of organic P in arable soils (Brookes *et al.*, 1982) and up to 24% in grassland soils (Turner *et al.*, 2001). Estimated annual fluxes of P through the microbial biomass of 5 (arable) to 23 (grassland) kg ha⁻¹ year⁻¹ (Brookes *et al.*, 1984) indicate that microbial biomass P is an important pool for plant nutrition and possible losses to water.

Advances in the characterization of organic P in soils have been achieved by the application of solution-state ³¹P nuclear magnetic resonance (³¹P NMR) spectroscopy to soil extracts (Newman and Tate, 1980). This technique enables the characterization of functional classes of P in alkaline extracts with NaOH (Table 2.3).

In general, these studies have shown that, as well as PO₄³⁻, monoester P is the dominant class of compounds in most soils. Individual studies have shown the effects of land use and manuring or fertilizer practice on the relative abundance of P compounds. However, the data in Table 2.3 do not show a significant influence of P applications on the relative proportions of P compounds. Direct comparison between studies is often difficult because of the differences in P forms extracted by the various extraction methods employed in these studies (Cade-Menun and Preston, 1996). Solid-state ³¹P NMR spectroscopy has been used to investigate Ca-P and Al-P compounds in soils, but bonds between P and Fe cannot be observed because of the paramagnetic character of Fe (Frossard *et al.*, 1994; Lookman *et al.*, 1994).

Sequential extractions have been widely used to distinguish P forms of different solubilities and, thus, with different ecological significance (Hedley *et al.*, 1982). The basic sequential extraction starts with the removal of PO₄³⁻ ions by an anion exchange resin (resin P). The following NaHCO₃ and NaOH extracts usually contain inorganic and organic P, which are considered as labile and moderately labile fractions, respectively (Cross and Schlesinger, 1995). The sulphuric acid (H₂SO₄) or hydrochloric

lic soils, the dominated by of clay mineral Fe oxides. de pedogenic labile. These e phosphates cid soils. This highly weath- oxides, like cially in trop- rganic anions acids such as te with PO₄³⁻ mpounds, for e, chelating contribute to e, agronomic rganic matter)₄³⁻ availabil- ce that redox the dynamics in soil which ts and forms

rtant organic phytic acid, the organic P measurable phospholipids rison, 1987). ganic P com- od, especially o plants and ssard *et al.*, n of the soil

Table 2.3. Ranges (and median) percentage of phosphorus (P) compounds from total signal area as compiled from investigations by ³¹P NMR spectroscopy. The samples included humic acids (HA), fulvic acids (FA) and NaOH extracts of whole soils, and particle-size fractions which were either native (Soil - P) or received organic or mineral P applications (Soil + P) (Leinweber *et al.*, 1997b).

Sample	No. of studies	Phos-phonate	Ortho-P	Mono-ester-P	Teichoic acid P	Diester-P	Pyro-P	Poly-P	Unknown P
HA	3	3-7 (4)	3-4 (3)	51-59 (53)	1-3 (1)	30-38 (37)	+ -2 (1)		
FA	3	n.d. ²	15-18 (16)	54-64 (54)	20-24 (21)	+	+ -8 (6)		
Soil + P	24	n.d.-0.6 (n.d.)	47-89 (81)	10-39 (15)	n.d.-20 (n.d.)	n.d.-10 (3.0)	n.d.-3.0 (1.6)	n.d.-1.4 (n.d.)	n.d.-10 (5.4)
Soil - P	42	n.d.-3.0 (0.69)	9.0-76 (36)	22-72 (49)	n.d.-9.7 (6.0)	n.d.-34 (12)	n.d.-18 (7.0)	n.d.-3.9 (0.84)	2.9-13 (5.0)

+ = Below quantification limit.

n.d. = Below detection limit.

acid (HCl) soluble P is assumed to be linked with Ca. After this strong acid extraction, a residual P fraction remains comprising stable inorganic and organic P. Examples of the differences in P forms among soil types are shown in Table 2.4. Heavily manured soils in an area of intensive livestock production in north-west Germany contained P contents an order of magnitude larger and also a disproportional enrichment in PO_4^{3-} ions and labile P fractions compared with the other soils.

The distribution of P compounds between soil particle size fractions is an important property with regard to P transfer in runoff, because of the different susceptibilities of physical fractions to detachment, erosion and transport. The P content of soil particles often increases with decreasing particle size. For example, the contents of PO_4^{3-} (resin-P), NaHCO_3 -P, NaOH -P, H_2SO_4 -P and residual-P decreased from the clay fraction to the sand fraction of two loam soils under originally native prairie (Tiessen *et al.*, 1983). Despite the decreasing P contents with increasing particle size, large proportions of soil P are associated with the sand fraction. For example, in sandy soils receiving large amounts of manure, the proportions of NaHCO_3 -P and residual-P were larger in sand than in clay (86–87% sand) (Fig. 2.1). This P probably comes from manure-derived specific light particles, which enter the sand fraction. Under the geographical conditions of north-west Germany, this P may be especially susceptible to losses by wind erosion.

Soil phosphorus dynamics and transformations

According to turnover rates, slow and rapid cycling organic and inorganic P pools can be distinguished (Fig. 2.2). Inorganic and organic P compounds can be assigned to these pools on the basis of sequential soil P fractionation methods. For instance, resin-P, NaHCO_3 -P and microbial biomass P represent most of the rapid cycling P. These fractions, along with organic NaOH -P (which is interpreted as moderately labile organic P), can be involved in biotic processes controlling P release to the soil solution (Frossard *et al.*, 2000).

Determination of the concentrations and forms of P in soil solution is important for the investigation of P uptake by plants and of leaching losses. This requires soil solution collection by zero-tension lysimeters or suction cups. However, the exchange of P ions between the solid phase and soil solution is time-dependent, so isotopic exchange methods can be used to quantify P transfer and determine the effects of soil type, P concentration in solution and time on the kinetics of P transfer. Morel *et al.* (2000) showed that more reliable predictions of the crop response to soil P were obtained with isotopic exchange methods compared with traditional soil extraction methods and concluded that the isotopic exchange approach could be helpful in estimating P loss to water. Applications of P to soils in fertilizer or manures initially reach the rapidly cycling fractions. The P that is not taken up into the biomass or removed

Table 2.4. Typical contents of total phosphorus (P) (g kg^{-1}) and proportions of sequentially extracted forms of phosphorus in topsoils of different origin (% of total P).

Material	Total P	Resin P	NaHCO_3 -P	NaOH -P	H_2SO_4 -P
Mollisol ^a	0.3–0.7	1–9	1–17	1–12	10–42
Vertisol ^a	0.3–0.7	1–6	1–2	3–7	22–46
Spodosol ^b	0.4	3	15	43	3
Histosol	0.5–0.9	1–9	3–8	11–28	0–2
Gleysol	0.5–0.8	2–9	4–8	4–25	16–24
Manured soils ^c	0.5–8.1	2–17	4–33	2–62	1–41

^a Sharpley *et al.* (1985).

^b Beck and Elsenbeer (1999).

^c Leinweber (1996).

ics and

slow and rapid P pools can be inorganic and organic. With respect to these pools, P fractionation methods such as H₂SO₄-P, NaHCO₃-P, NaOH-P, and DOWEX-P represent most of the methods, along with others, which can be interpreted as different P release mechanisms (Morel *et al.*, 2000).

Concentrations and dynamics are important for plant growth and soil solution. In lysimeters, the exchange of P between the soil and plants is so isotopic that it is difficult to quantify the effects of soil P dynamics and time. Morel *et al.* (1997) used reliable prediction models for soil P extraction. The isotopic method is helpful in estimations of P to initially reach the P that is sorbed or removed.

forms of

H ₂ SO ₄ -P
10-42
22-46
3
0-2
16-24
1-41

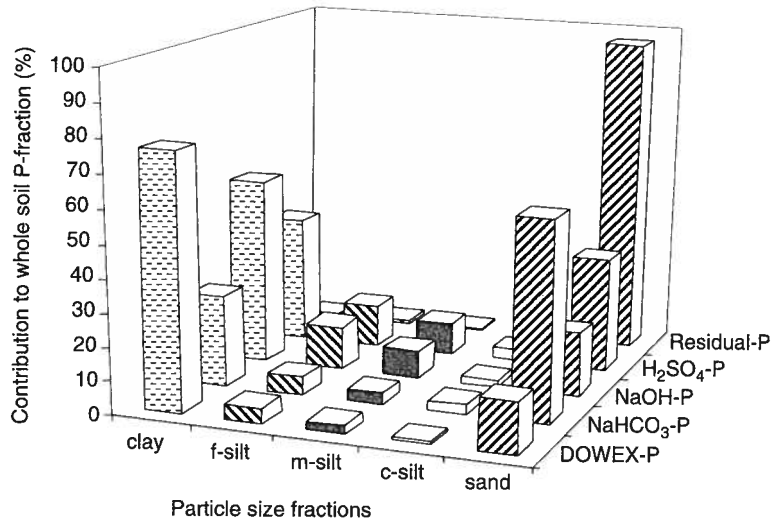


Fig. 2.1. Distribution of sequentially extracted P fractions in organic-mineral particle size fractions averaged for two soils.

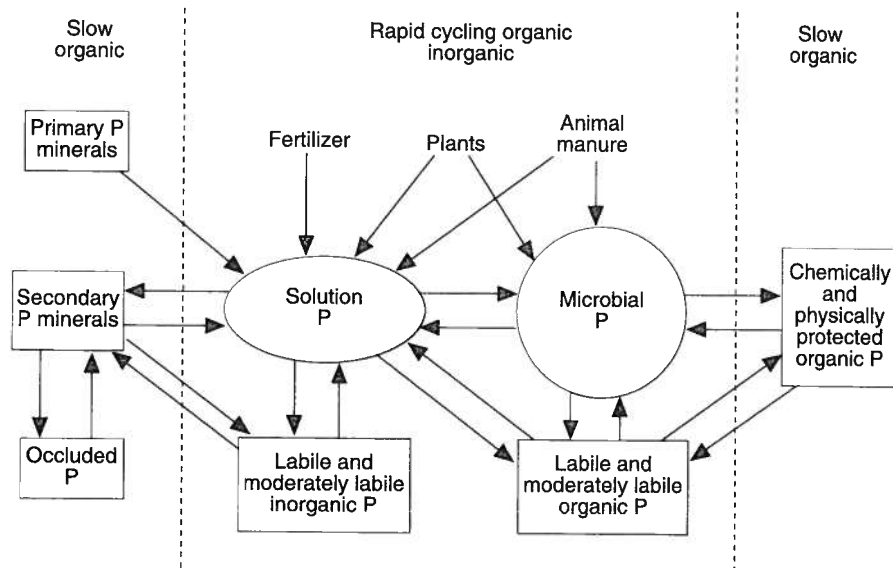


Fig. 2.2. The soil phosphorus cycle: its components and measurable fractions (adapted from Stewart and Sharpley, 1987).

from the soil can be sorbed, occluded or incorporated into soil organic matter. These reactions reduce the rate of P turnover and explain why soils can be a sink for P. This is especially valid for soils with large amounts of pedogenic oxides or Ca, which tend to adsorb PO₄³⁻ strongly or form sec-

ondary P minerals. Processes such as mineralization of soil organic matter, mineral solubilization and PO₄³⁻ desorption, result in P inputs into the labile and mobile pool. This may be one reason why long-term cessation of P fertilizer application does not necessarily lead to decreasing yields.

Phosphorus uptake by crops

Soil P is taken up by crops as dihydrogen phosphate ions (H_2PO_4^-) under acid conditions and as hydrogen phosphate ions (HPO_4^{2-}) under neutral and alkaline conditions. To maintain equilibration, crop roots release anions such as OH^- or HCO_3^- . In plant physiology, P is essential to the production of a variety of organic P compounds that are building blocks or part of coenzymes in many synthesis processes. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP) take part in energy metabolism, which is involved in all syntheses in plant cells. The hydrogen-transferring coenzymes, such as nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP), are involved in oxidation and reduction reactions. Phosphates are also building blocks of nucleic acids and phospholipids; the latter are important cell wall components. In addition to these and other organic P containing compounds, inorganic P occurs in larger quantities in the vegetative organs of crops. Total P contents of plant materials range from 2 to 8 g kg^{-1} . They tend to be smaller in root crops than in grain crops and smaller in the vegetative than in the generative organs. Phosphorus uptake from the soil ($\text{kg ha}^{-1} \text{ year}^{-1}$) at mean crop yields follows the order of cereals and potatoes (25) < forage maize (30) < sugarbeets (35) < oilseed rape (38).

Agricultural crops have different strategies to acquire soil PO_4^{3-} . Some grasses and cereals increase their root systems under P-deficient conditions. Other plants, such as maize, oilseed rape and some legumes and inter-cultures (e.g. buckwheat), exude protons, organic acids and phosphatase enzymes into the rhizosphere to enhance P availability. In this way, inter-cultures can mobilize P from insoluble fractions and provide this in plant-available form for use by the main crops (Eichler and Köppen, 1998). Deficiency of P results in a general reduction of most metabolic processes and, therefore, in reduced crop yields. The large concentrations of Al and Fe oxides in the soil present problems for the supply of P to plants,

because they strongly adsorb PO_4^{3-} and prevent availability for biological uptake. Traditionally, P fertilizer recommendations have aimed to maintain large amounts of P in the soil, but the current concerns over P loss to water from over-fertilized soils has challenged this approach. However, the experimental bases for target levels of soil P ensuring the economical yield optimum and protecting aquatic ecosystems from inevitable P inputs are not well established.

Imbalances of agricultural phosphorus

Imbalances in agricultural P use can result from the use of P in livestock feeding, P excretion and manure disposal, mineral P fertilizers and P turnover in soils, which together provide total and available P above the P requirements of crops. The magnitude of these imbalances can be calculated by various approaches and at different scales. These scales can be the field, farm or catchment scale, or for political units they can be districts or nations.

Tables 2.2 and 2.5 show examples of P balances in European countries. From the farmer's point of view, field or farm balances are most important. Mean values show a P surplus ranging from > 0 (Poland) to 27 $\text{kg ha}^{-1} \text{ year}^{-1}$ (The Netherlands). However, even at low field balances, such as in Poland (Table 2.2), individual farms with a large stocking density (e.g. c. 5 animal units ha^{-1}) can have large surplus values of up to 50 $\text{kg P ha}^{-1} \text{ year}^{-1}$ (Marcinkowski and Sapek, 1998). For 596,000 farms in North Rhine-Westphalia, the median P surplus value did not indicate a P surplus, but for 24,800 farms with intensive livestock feeding, a median of 35 $\text{kg P surplus ha}^{-1} \text{ year}^{-1}$ was calculated (Werner and Brenk, 1997). Maximal P surplus values of > 80 $\text{kg P ha}^{-1} \text{ year}^{-1}$ were reported in this study. Often, regional P balances disclose such great surplus values, especially if stocking density on the basis of imported feeds contributes to excessive manure P. For the county of Vechta (Lower Saxony, north-west Germany), one of the areas with the largest

PO_4^{3-} and pre-geological uptake. Recommendations on amounts of P concerns over P-limited soils has. However, the levels of soil P optimum and systems from established.

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use can result in over-fertilization, P deficiency, mineral P in soils, which reduces available P for crops. The balance can be calculated and at different levels, for political reasons.

Examples of national P balances for different countries. From field or farm level, mean values of P balance > 0 (Poland, Netherlands). National balances, such as individual farms (e.g. c. 5 kg ha⁻¹ year⁻¹ large surplus ha⁻¹ year⁻¹ (1998). For North-Westphalia, did not indicate 10 farms with a median of 10 kg ha⁻¹ year⁻¹ as calculated. Maximal P ha⁻¹ year⁻¹ ten, regional level, great surplus density on contributes to the county of North-Westphalia the largest

Table 2.5. Mean values of phosphorus farm balances in European countries (Isermann, 1999 and references cited therein).

	Austria (1992)	Germany (1995)	Switzerland (1995)	UK (1993)
Input (kg ha ⁻¹ year ⁻¹)	11	21	20	13
Mineral fertilizer	8	13	10	9
Imported feeds	2	7	5	3
Deposition	< 1	n.d.	< 1	< 1
Sludge, compost	< 1	1	4	< 1
Output (kg ha ⁻¹ year ⁻¹)	5	9	6	3
Plant products	3	6	2	< 1
Animal products	2	3	4	> 2
Surplus	6	12	14	10
Efficiency of utilization (%)	45	43	30	23

n.d. = Not determined.

stocking density in Europe, the mean P surplus originating from manure is 37 kg ha⁻¹ year⁻¹ (von Hammel, 1994).

National P balances have revealed surplus values ranging from 0.8 (Lithuania) to 6.4 (Poland) and c. 7 kg ha⁻¹ year⁻¹ (Sweden and Denmark) (data for 1995 compiled by Marcinkowski and Sapek, 1998). A national P balance for Germany showed that the contribution of animal excrement is on average c. 17 kg P ha⁻¹ agricultural area year⁻¹. This confirms that livestock feeding is an important source of P inputs to soils (Fleischer, 1997).

Impact of excess fertilizer application on the amounts and forms of soil phosphorus

The application of excess mineral fertilizer, manures and sewage sludges to soil increases the total P concentration. In a European Community research project, over-fertilized soils had total P concentrations of 890–1168 mg kg⁻¹ (Germany), 333–1400 mg kg⁻¹ (Spain), 1331–1920 mg kg⁻¹ (UK) and 709–1067 mg kg⁻¹ (Italy) (Barberis *et al.*, 1996). In a region with intensive livestock feeding in north-west Germany, total P contents ranging from 565 to 8173 mg kg⁻¹ with mean values of 1335–2693 mg P kg⁻¹ clearly indicated large P enrichments (Leinweber, 1996).

Three farms with alternative agricultural management systems in that area had smaller total P concentrations (1580–1690 mg kg⁻¹) than farms with known high livestock densities (mean 3113 mg P kg⁻¹).

Soil P test values are often unequivocal indicators of over-fertilization and P accumulation from manure application and waste disposal. In Delaware, north-eastern USA, which has a large and growing poultry industry, even the maximum values of P soluble in 0.05 M HCl + 0.0125 M H₂SO₄ of up to 632 mg P kg⁻¹ were in the range of normal total P concentrations of other soils (Mozaffari and Sims, 1994; and see Sims and Coale, Chapter 16, this volume). Figure 2.3 shows the frequency distribution of double lactate extractable P (DL-P) contents in soils from Vechta, north-west Germany. Forest soils, which serve as a reference, contained low to medium DL-P contents. Soils under agricultural use had much higher DL-P concentrations: about 95% of samples from grassland, horticulture (raspberries, asparagus) and arable land had DL-P concentrations above the levels for crop response to P fertilizer addition. Soils in counties with a large stocking density in North Rhine-Westphalia had mean calcium-ammonium lactate extractable P (CAL-P) contents of 100–115 mg P kg⁻¹. About 60–80% of soils in these counties had CAL-P contents classified as 'high' or 'very high' (Werner and Piehl, 1998).

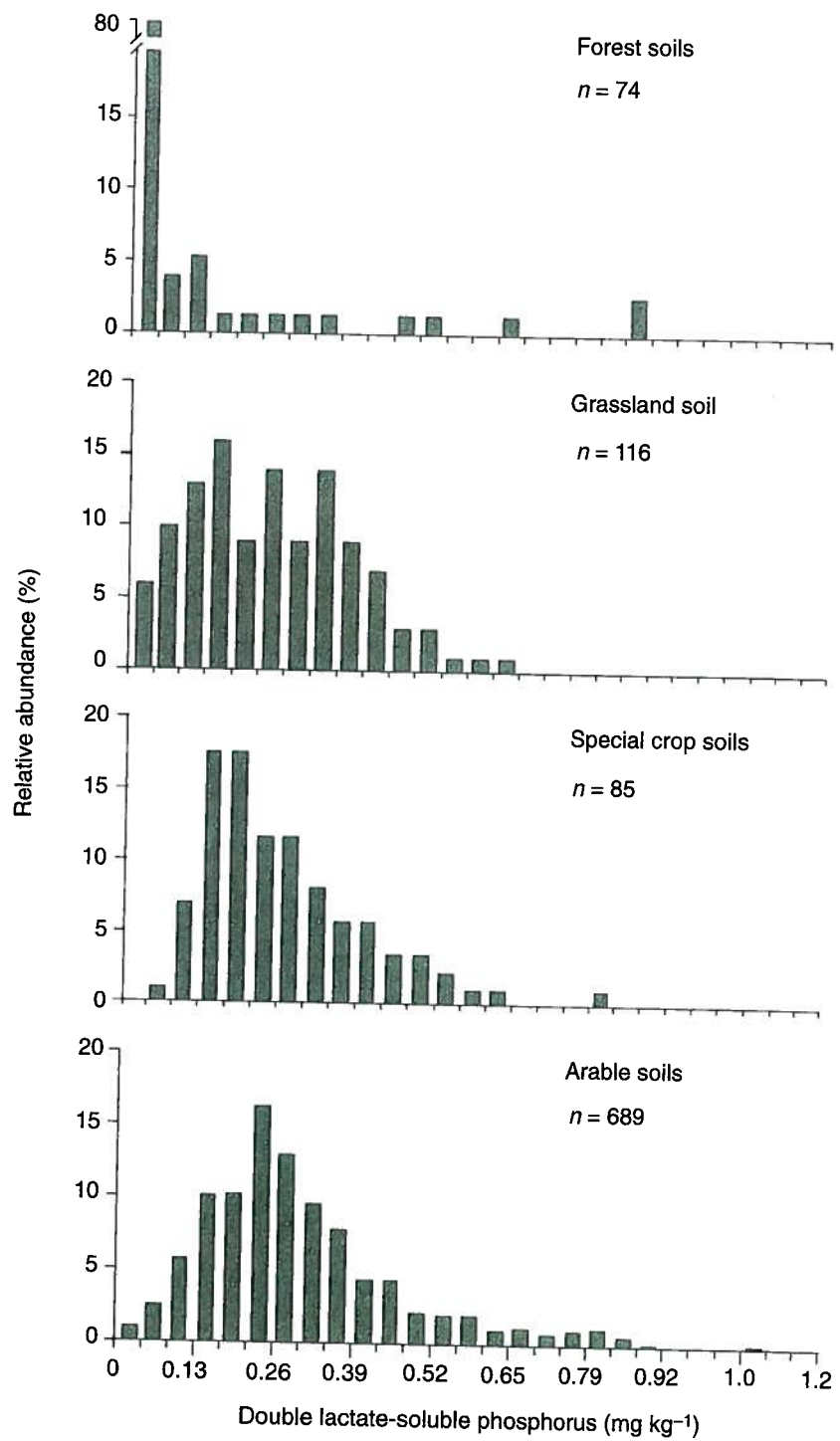


Fig. 2.3. Frequency distribution of soil phosphorus test values in a densely stocked area in north-west Germany (Leinweber *et al.*, 1993).

In The Netherlands, soil P accumulations were recognized in the early 1980s. Studies of the regional P distribution were based on PO_4^{3-} saturation characteristics (Breeuwsma *et al.*, 1995). According to these authors, the degree of PO_4^{3-} saturation is defined as:

$$\text{DPS (\%)} = P_{\text{ox}} / \text{PSC} \times 100$$

where DPS = degree of phosphate saturation, P_{ox} = sorbed P (extracted by oxalate) (mol kg^{-1}) and PSC = PO_4^{3-} sorption capacity, often determined by $0.5 \times (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})$ (mol kg^{-1}).

These detailed studies revealed that 70% of farmland soils were P saturated, with values of 88% for maize and 69% for grassland. More than 21% of farmland was strongly (DPS > 50%) and 6% very strongly (DPS > 75%) P saturated. In north-west Germany, Leinweber *et al.* (1997a) determined DPS values from 14 to 145% in soils from a catchment with relatively low stocking density. In contrast, in an area with high stocking densities the DPS ranged from 13 to 179%, with most frequent values in the range of 70 to 90%. The differences between the two areas clearly originated from the contents of P_{ox} and not differences in the PSC, hence they could be assigned to the P input with manure rather than to differences in the P sorption.

Besides these effects on total P contents, soil P test values and DPS, excessive fertilizer application and waste disposal also alter the amounts and proportions of soil P fractions, as shown by sequential extraction and spectroscopic investigations. Mineral fertilizer application usually increases the proportions of inorganic P in labile and moderately labile fractions. Repeated manure applications can increase the amounts and percentages of Ca-P phases and residual P.

Combinations of inorganic and manure P increase the P proportions over a wider range of differently soluble fractions (Zhang and MacKenzie, 1997). Extensive soil management can lead to reduced proportions of resin-P, NaHCO_3 -P and NaOH -P, whereas intensively used arable soils with organic and mineral fertilization contain high levels

of resin-P, H_2SO_4 -P and residual-P (Leinweber *et al.*, 1999). Generally, there are various interactions between amounts and forms of P application, fertilization with other nutrients, soil type and properties, crop rotation and the contents and the proportions of inorganic and organic P forms. Sequential fractionation of P forms in 69 soils from the densely stocked area in north-west Germany yielded results in the order: resin-P (2–17%) < NaHCO_3 -P (4–33%) < NaOH -P (2–62%). Soil management influenced the percentages of the different P fractions. Grouping of the samples according to different soil use gave the order, arable > horticultural crops and grassland for the mean concentrations of resin-P and NaHCO_3 -P. This was in accordance with the large proportions of labile P in manure and the particular use of arable soils for its disposal. The large proportions of resin-P and NaHCO_3 -P show that, as well as greater total P concentration, the soils of this densely stocked area have more soluble P (Leinweber, 1996). In particular, liquid pig manure and poultry litter contain large amounts of P, of which large proportions occur as PO_4^{3-} (Leinweber, 1996). Therefore, it can be expected that soils receiving large amounts of these materials will be enriched in these labile P compounds. This is a serious problem in regions with high livestock densities, such as north-west Germany (Vechta, Lower Saxony), where it has been calculated that the P contents in some soils could only be explained by annual manure-P inputs of up to $180 \text{ kg P ha}^{-1} \text{ year}^{-1}$ over the last 40 years (Leinweber *et al.*, 1993). Such high P inputs may increase the potential for losses of P to water.

Environmental Consequences of Excessive Phosphorus Enrichment in Soils

Introduction and general problem

As described above, large stocking densities and excessive manure applications are reasons for surplus P inputs to agricultural

soils. The perception that fertilizer P is strongly held in soil and prevented from leaching has meant that P fertilizer recommendations have often been above the requirements of plants and have not adequately considered the P inputs from manures. As a consequence, P contents have gradually increased in many European soils, which can accelerate the transfer of P to watercourses in runoff. In the following section we describe the effects of oversupply on the contents and forms of soil P. The movement of P from soil to surface waters is described, including the mechanisms of P release and pathways of P transfer from soil to water: this is not only affected by the soil P contents and forms, but also by land use. Finally, an assessment of the environmental consequences of excessive P enrichment of soils requires basic information on the forms of P in soil solution and runoff and on critical concentrations and loads in drainage waters.

Forms of phosphorus in soil solution and runoff waters

Phosphorus forms in water are conventionally determined on the basis of operational procedures, which are used throughout the world. These procedures involve: (i) chemical fractionation, based on the reaction of inorganic P with molybdate followed by subsequent reduction and spectrophotometric detection; and (ii) physical fractionation, based on filtration through a sub-micron filter. The spectrophotometric procedures are based on an original method described by Murphy and Riley (1962) for the determination of dissolved PO_4^{3-} . The P determined by this procedure is termed reactive P (RP) rather than inorganic P (Haygarth and Sharpley, 2000) because the procedure can overestimate true PO_4^{3-} . The sample preparation and reaction conditions can result in other forms of P, such as labile organic P species, being hydrolysed in the strongly acid conditions required for colour development (Tarapchak, 1993), while interference from silica (Ciavatta *et al.*, 1990) and sample tur-

bidity has also been noted. Recent studies using alternative methods of detecting PO_4^{3-} , such as ion chromatography, have indicated the extent of this problem in soil runoff and lake waters (Baldwin, 1998; Halliwell *et al.*, 2000).

Total P can be determined in the sample using an appropriate digestion procedure (recently reviewed by Rowland and Haygarth, 1997), which allows the UP fraction to be determined by difference. This fraction generally represents organic P compounds, including monoester P (e.g. inositol phosphates, sugar phosphates or mononucleotides), diester P forms (e.g. nucleic acids and phospholipids), phosphonates (e.g. aminoethylphosphonic acid) and condensed organic P forms (e.g. ATP), although only a few of these have been directly identified in soil waters (Espinosa *et al.*, 1999). However, UP (< 0.45) cannot strictly be termed organic P, because inorganic condensed forms that are not Mo-reactive, such as pyrophosphate, are included in the UP fraction (Ron Vaz *et al.*, 1993). Alternative methods for the determination of the true 'organic' P fraction using ultraviolet light induced persulphate oxidation are available, but are not widely employed (Ron Vaz *et al.*, 1992; Benson *et al.*, 1996). However, some studies have indicated that condensed inorganic P can represent a large part of the soil solution P (Ron Vaz *et al.*, 1993).

Samples can be further fractionated by filtration through a sub-micron filter, most commonly of pore size 0.45 μm , although 0.2 μm filters are used in some countries where a sterile sample is required. Filtration is often used to define 'dissolved' (< 0.45 μm) and 'particulate' (> 0.45 μm) P fractions, but this is incorrect, because soil waters have been shown to contain a continuum of particles in the < 0.45 μm size range (Haygarth *et al.*, 1997; Sinaj *et al.*, 1998). Particles of size < 0.45 μm are often referred to as colloidal, although this term strictly defines particles ranging in size from 1 nm to 1 μm , composed of specific mineral forms (Kretzschmar *et al.*, 1999).

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Therefore, four fractions are directly determined on the basis of Mo reaction with or without digestion and on filtered and unfiltered samples (TP, TP (< 0.45), TRP and RP (< 0.45)). From these, five additional fractions can be determined by difference (Fig. 2.4).

Identification of the various P forms is complicated by changes within the solution after release from the soil (Sharpley *et al.*, 1981). For example, rapid sorption or desorption of orthophosphate between the solid soil, solution particles and solution can occur, in addition to the hydrolysis of organic forms by enzymes and immobilization by biomass uptake. These changes can occur rapidly, as noted by Haygarth *et al.* (1995), who discovered that RP (< 0.45) concentrations in soil leachate were substantially reduced within 8 hours of sampling. Clearly, it is strictly wrong to describe RP as 'inorganic', UP as 'organic', filtered P as 'dissolved' and unfilterable P as 'particulate'. These ambiguities mean that is only correct to use strict operational definitions for the fractions determined.

Movement of phosphorus from soils to watercourses

The transfer of P from agricultural soils to watercourses is now regarded as a serious problem in many areas of the world, highlighted by recent major conferences on the subject (Tunney *et al.*, 1997; Foy and Dils, 1998). Phosphorus transfer is a complex phenomenon, but can be defined as a function of the forms of P, the mechanisms of their release from soil to water and the hydrological pathways by which the mobilized P moves from the land (Haygarth and Jarvis, 1999). The following sections present brief reviews of these three aspects of P transfer from the soil shown conceptually in Fig. 2.5. Each aspect is important for a comprehensive understanding of P transfer.

Mechanisms of phosphorus release from soil to water

The critical first step in the transfer process is release from the soil solid phase to soil

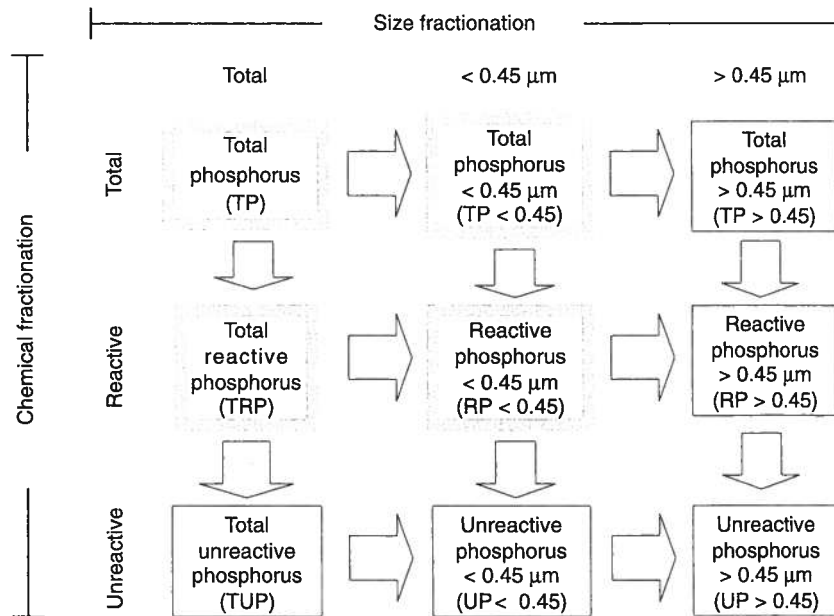


Fig. 2.4. Operationally defined phosphorus fractions determined in water, showing the directly determined fractions (in boxes with shaded borders) and fractions determined by difference.

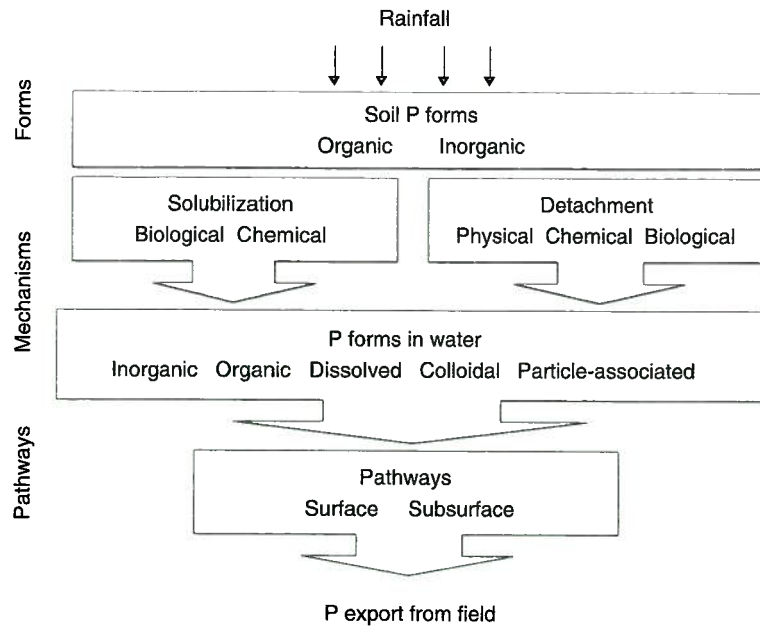


Fig. 2.5. A conceptual illustration of the transfer process (adapted from Haygarth and Jarvis, 1999).

water. This occurs through various mechanisms of P release. These can be classified into solubilization and detachment mechanisms of solid colloids and particles.

The processes controlling the solubilization of soil inorganic P have received considerable attention, mainly in terms of the cycling and plant availability of inorganic P (Barrow, 1978; Frossard *et al.*, 1995; Barberis *et al.*, 1996), and a limited amount of information also exists on organic P sorption by chemical mechanisms (Anderson *et al.*, 1974; Frossard *et al.*, 1989). However, relatively little attention has been paid to the implications of these processes for P transfer (Haygarth and Jarvis, 1999). Solubilization of inorganic P results primarily from desorption of PO_4^{3-} from solid surfaces. Similar processes apply to sorbed organic P. Release of PO_4^{3-} to solution is largely controlled by the amount of readily desorbable P in the soil. Desorption of inorganic P from soil to solution appears to involve a readily exchangeable pool of inorganic P, which can move rapidly between the solid-liquid phases, at timescales of seconds to minutes (Cole *et al.*, 1977; Lopez-Hernandez *et al.*, 1998). The steady-state

concentration of PO_4^{3-} in solution is termed the equilibrium P concentration (EP_0). Removal of inorganic P from the soil solution, for example by plant uptake, results in the movement of P ions into solution. Conversely, an increase of inorganic P in solution, for example through fertilizer application, results in P movement on to the solid phase. Whether equilibrium will be reached in drainage water will depend on the rate of water movement through the soil and the equilibrium P concentration, but should be fairly rapid where the amounts of P in the soil are low (Cole *et al.*, 1977; Fardeau, 1996). Other factors that affect desorption from the soil include ionic strength, pH and temperature. Effects of pH, which can result from the release of plant root exudates or lime additions, can be variable, because increasing pH has been shown to both increase (Barrow, 1984) and decrease (Wild, 1988) the inorganic P concentration of the soil solution. Waterlogging of soil can release P through the reduction of Fe^{3+} compounds and the mobilization of clay-humic complexes (and associated P) through reduction of the metal (Fe) bridge (Ryan and Gschwend, 1990; Frossard *et al.*, 1995).

Biological mechanisms can exert strong controls on the solubilization of P, but represent the most under-investigated aspect of P transfer. Most studies have centred on the role of the soil microbiology in soil P cycling and the availability of P to plants, although even this information has been fairly scarce until relatively recently. This is highlighted by the fact that reliable techniques for measuring P in the microbial biomass were only developed as late as the 1980s (Brookes *et al.*, 1982; Hedley and Stewart, 1982). However, biological mechanisms appear to be critically important in determining soil solution P concentrations (Cole *et al.*, 1977; Lee *et al.*, 1990; Seeling and Zasocki, 1993; Turner and Haygarth, 2002) and, therefore, have the potential to exert a considerable influence on P solubilization. Indeed, recent studies of leaching indicate that seasonal patterns of microbial release in the soil translate into P concentrations in leachate water at depth (Turner and Haygarth, 2000).

Growing plants and microorganisms immobilize inorganic P from the soil solution in their biomass. The immobilized P is released on cell death and decay, mostly as organic P, particularly through lysis of microbial biomass cells. Therefore, these biological mechanisms transform inorganic forms into organic P. These processes maintain a low soil solution inorganic P concentration, with a relatively large organic P concentration (Lee *et al.*, 1990; Seeling and Zasocki, 1993). The cycle is completed by phosphatase enzymes, released into the soil from plants and microorganisms, which catalyse the release of inorganic forms from organic compounds (Spier and Ross, 1978; Turner and Haygarth, 2002). Phosphatase enzymes appear to have a fundamental, but poorly understood, role in the P transfer process, by regulating the availability of P to the microbial biomass and the forms of P available for transfer in runoff. In addition to microbial controls, macrofauna such as earthworms play a major role through the mineralization and translocation of P in the soil profile (Sharpley *et al.*, 1979), while plants release substantial amounts of water-soluble P after defoliation (Bromfield and Jones, 1972).

Soil detachment and transport processes are well described in standard texts (e.g. Hudson, 1995; Morgan, 1995). Detachment of P primarily involves the erosion of soil particles by the hydraulic action of flowing water or by raindrop impact. However, chemical mechanisms, such as changing ionic strength or pH, can also result in the detachment of particle-associated P forms sorbed to the soil. In addition, the release of some biological P may be classed as detachment, such as the cell fragments released by cell lysis.

Erosion mechanisms have been relatively well investigated, partly because of the traditional perception of P transfer being dominated by P export in overland flow (see Sharpley and Smith, 1990, for review). Erosion is frequently associated with P transfer by overland flow, especially from arable land, where losses of particulate P can be extremely high and constitute most of that transferred (e.g. Burwell *et al.*, 1977; Sharpley and Syers, 1979; Haith and Shoemaker, 1987). This is often associated with the preferential transport of fine clay-sized materials, which are relatively enriched in P because of their high P sorption capacities (Sharpley, 1985; Kretzschmar *et al.*, 1999). Erosion can also result from rapid subsurface drainage, with particles eroded from the edges of wormholes, cracks and underground fissures. This can contribute to high concentrations of particulate P in subsurface drainage through macropores (Dils and Heathwaite, 1996) and in tile drainage (Turtola and Jaakkola, 1995; Grant *et al.*, 1996; Ulen, 1999). Fine colloidal sized (1 nm–1 µm) particles may be particularly efficient at transporting P through subsurface pathways, because they have high capacities to sorb P but are not easily stabilized in the soil profile (Kretzschmar *et al.*, 1999). Therefore, although physical release of P has traditionally been associated with surface pathways, there is the potential for particle-associated P forms to make a significant contribution to P transfer through subsurface pathways.

Chemical detachment can result from changes in ionic strength, which controls the

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release of particle-associated P in terms of clay and organic matter. For example, CaCl_2 solution suppresses the release of these particles to solution (Wild and Oke, 1966), while high Na^+ and low ionic strength can result in the release of particulate P through dispersion of aggregates (Kaplan *et al.*, 1996). These processes have been suggested as particularly important in P movement through soils (Chardon *et al.*, 1997).

Surface applied P in animal manure or mineral fertilizer can be directly lost from the field without ever becoming part of the soil P. This process cannot be classed by a mechanism of release, because the P never actually becomes part of the soil matrix. This type of P loss has recently been termed 'incidental' (Haygarth and Jarvis, 1999) and can be especially important in grassland systems where surface applied manure is used, especially when 'best management practices' are not employed. Incidental losses may account for substantial losses of P from the land (Harris *et al.*, 1995), but little information currently exists on this potentially important aspect of P transfer.

Pathways of phosphorus transfer from soil to water

The driving force behind P transfer from the land is the hydrology, because water provides the energy and the carrier for P movement (Haygarth and Jarvis, 1999). The route taken by water as it carries P off the land describes the pathway of P transfer. Pathways can be broadly separated into surface (overland flow) and subsurface pathways and the pathways taken are of critical importance in determining the extent of P loss from agricultural land. Comprehensive details and definitions of the pathways within these broad separations can be found in Ryden *et al.* (1973) and Haygarth and Sharpley (2000).

The traditional perception of P being strongly fixed in the subsoil has meant that research into transfer traditionally has focused on surface pathways (Baker *et al.*, 1975; Burwell *et al.*, 1977; Sharpley and Syers, 1979). Detachment mechanisms and

loss as particulates are considered to dominate transfer in overland flow, but all forms and release mechanisms can contribute to loss via overland flow. Overland flow is often associated with catastrophic events, which are considered to be the most severe in terms of loss, although there is evidence that lower frequency events that occur for a much greater time throughout the drainage period are equally important in P transfer (Fraser *et al.*, 1999). This is because overland flow preferentially erodes and transports clay-sized material (Sharpley, 1985). As shown in Fig. 2.1, total P and desorbable PO_4^{3-} are enriched in clay fractions. Using ^{32}P studies, overland flow has been found to interact with only the top few mm of soil, termed the effective depth of interaction (Ahuja *et al.*, 1981). This coincides with the depth of soil that often contains the greatest amount of P and can result in especially high concentrations in overland flow.

Subsurface pathways include lateral flow through the soil, vertical drainage, preferential flow through macropores and artificial drainage channels. Until recently, subsurface P losses were considered to be negligible, because of the propensity for P to be retained at depth in the soil profile (Baker *et al.*, 1975; Burwell *et al.*, 1977; Sharpley and Syers, 1979). This was exacerbated by the fact that measured losses of P in subsurface flows were small compared with the total amount of P in the soil (Sample *et al.*, 1980). However, the change from an agronomic to an environmental perspective on soil P has refocused attention on subsurface P transfer, because small concentrations of P can cause significant problems for water quality (Tunney *et al.*, 1997; Turner and Haygarth, 2000). This phenomenon is not restricted to waterlogged soils (Khalid *et al.*, 1977) or sandy-textured soils under heavy fertilizer addition as traditionally thought (Ozanne *et al.*, 1961; Breeuwisma and Silva, 1992), but includes many soil types, especially clay soils that are susceptible to cracking and preferential flow (Stamm *et al.*, 1998; Simard *et al.*, 2000; Turner and Haygarth, 2000).

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Studies using lysimeters have revealed that P concentrations in leachate water from a range of soil types occur at levels that could present problems for water quality. For example, Leinweber *et al.* (1999) and Turner and Haygarth (2000) measured TP concentrations routinely in excess of $100 \mu\text{g l}^{-1}$ in leachate from a range of contrasting grassland soil types and management conditions. Organic P constitutes a large proportion of the total P transported in leachate (Magid and Nielsen, 1992; Espinosa *et al.*, 1999; Turner and Haygarth, 2000), where its mobility in the soil compared with inorganic P forms makes it an important mechanism by which P may escape from the soil. Inorganic P is readily fixed in the soil and prevented from leaching by precipitation with Ca, Fe and Al, or sorption to clays and other soil particles (Frossard *et al.*, 1995). However, some organic P is not strongly sorbed and can move easily through the soil to surface waters (Rolston *et al.*, 1975; Frossard *et al.*, 1989; Chardon *et al.*, 1997), where it can contribute to algal growth after the release of inorganic P by phosphatase enzymes (Whitton *et al.*, 1991).

Preferential flow pathways may be important in subsurface P transfer. The high concentrations of $> 0.45 \mu\text{m P}$ forms in leachate water indicates the importance of preferential flow even in sandy-textured soils (Turner and Haygarth, 2000). The potential for P transport through macropores was demonstrated by Simard *et al.* (2000), while Dils and Heathwaite (1996) detected P concentrations in macropore flow through agricultural grassland soils of $> 1 \text{ mg l}^{-1}$. The large amounts of TP (> 0.45) present in subsurface drainage water indicate that erosion mechanisms within macropores may contribute to P transfer. The importance of TP (> 0.45) transport confirms that process terms such as leaching (which is synonymous with all subsurface transport, but actually means the release and movement of exclusively dissolved P) can be very misleading (Haygarth and Sharpley, 2000).

Colloidal P can facilitate export through soil, through protection by sorption in the

soil profile, and is a large component of P in overland flow (Matthews *et al.*, 1998) and in river waters (Haygarth *et al.*, 1997). Colloidal P may be an especially important component of P transfer through preferential flow pathways, because the low ionic strength water that results from the minimal contact between rainfall and soil results in the mobilization of colloids and associated P (Chardon *et al.*, 1997).

Subsurface export from artificially drained land can be responsible for considerable amounts of P transfer (Turtola and Jaakkola, 1995; Grant *et al.*, 1996; Haygarth *et al.*, 1998; Ulen, 1999), despite the fact that artificially drained soils are mainly loams and clays that are low in P. Much of the P can occur in dissolved forms, although large amounts also occur as particulates, probably by detachment from the walls of drainage channels. High P concentrations in artificial drainage water are probably a result of the rapid movement of water to depth, thereby bypassing the soil matrix and minimizing removal from solution by sorption. However, artificial drainage has the overall effect of reducing P transfer from the land, by as much as 30% compared with undrained plots (Haygarth *et al.*, 1998).

Effects of land use on phosphorus losses

Arable land can be susceptible to substantial P losses, especially by erosion and overland flow, because the land is left bare at certain times of the year. An increase in winter cereal cropping has exacerbated this problem, because it combines the period of maximum rainfall with long periods of bare soil. Under these circumstances, vast amounts of P can be lost in 'catastrophic' events, associated with the removal of large amounts of soil by rill and gully erosion. For example, Haith and Shoemaker (1987) reported exports of up to $24 \text{ kg ha}^{-1} \text{ year}^{-1}$ from maize fields in Delaware, USA, mainly as $> 0.45 \mu\text{m P}$. The amounts of P lost depend greatly on factors such as slope, rainfall intensity and soil type. In addition, arable land often receives large inputs of mineral fertilizer, which results

in large amounts of P available for loss through leaching (Heckrath *et al.*, 1995). However, higher rates of mineral fertilizer applications do not necessarily result in larger P losses. Experience from long-term lysimeter studies showed that P concentrations in leachates and leaching losses depend on soil texture, cropping, mineral fertilizer applications and intensity of soil management. Phosphorus losses were larger in sands than in loamy sands and were greater in arable soils than in grassland soils (Meissner *et al.*, 1995). In lysimeters of a loamy sand under a winter barley-oats rotation, the mean leaching losses were largest ($657 \text{ g P ha}^{-1} \text{ year}^{-1}$) with the smallest fertilizer rate ($12.5 \text{ kg P ha}^{-1} \text{ year}^{-1}$) and decreased by more than $100 \text{ g P ha}^{-1} \text{ year}^{-1}$ if the fertilizer rates used were up to three times larger. Interestingly, intensively used arable soils with organic and mineral P fertilizer inputs had the smallest leaching losses (Leinweber *et al.*, 1999).

Even if arable land is found on light-textured soils on relatively flat land, it can still be susceptible to overland flow and erosion through soil 'capping' (Fraser *et al.*, 1999). Sandy soils under heavy manure applications can also result in high concentrations of P in leachate water (Breeuwisma and Silva, 1992; Chardon *et al.*, 1997; Meissner *et al.*, 1997).

Grasslands appear to transfer a smaller proportion of soluble inorganic P than arable land, especially on soils with low extractable P contents. However, this does not account for organic and particulate P exports, which can be substantial from grasslands. For example, exports of P of between 2 and $3 \text{ kg ha}^{-1} \text{ year}^{-1}$ have been recorded from 1 ha grassland lysimeters in south-west England (Haygarth and Jarvis, 1997; Haygarth *et al.*, 1998). Because grasslands are often located on heavy, poorly draining soils on steeply sloping ground, they can lose large amounts of $> 0.45 \mu\text{m P}$ by detachment, erosion and overland flow; in one extreme storm event, in excess of 0.5 kg P ha^{-1} was lost by this pathway (Haygarth and Jarvis, 1997). Large P concentrations have also been observed in

leachates from grassland established in sandy soils, although mean annual concentrations did not reflect the rate of mineral P fertilizer applications (Leinweber *et al.*, 1999). Grasslands are also susceptible to incidental losses of P from ill-timed manure applications; for example, Harris *et al.* (1995) measured RP (< 0.45) concentrations of $267 \mu\text{g l}^{-1}$ from plots that had received slurry applications just prior to heavy rainfall, compared with $30 \mu\text{g l}^{-1}$ from control plots.

Compaction of soil by farm machinery and poaching by livestock can further promote the occurrence of overland flow. The high P concentrations in overland flow from grasslands can be exacerbated by an intense surface accumulation (Haygarth *et al.*, 1998), because of the permanent (untilled) nature of the soil and high inputs from fertilizer, slurry applications and excretal returns from grazing animals. In one extreme case, concentrations of RP (< 0.45) of $> 7 \text{ mg l}^{-1}$ have been reported in overland flow from high input pasture plots in south-eastern Australia (Nash and Murdoch, 1997).

Pleistocene landscapes covering the northern parts of central Europe have melt-water valleys that are nowadays filled in by peat and were used in the past for intensive grassland. This practice led to the oxidation of peat, accelerated especially if the soils were ploughed to establish a closed new grass population. In more recent years, the restoration of fenlands, set-aside and wetland programmes have been started to prevent the Histosols from further severe degradation. However, a novel problem emerged: the undesired mobilization of dissolved organic matter and PO_4^{3-} if the groundwater level was elevated. For example, Kalbitz *et al.* (1999) measured PO_4^{3-} concentrations in the soil solution and near-surface groundwater ranging from 0.001 to $0.622 \text{ mg P l}^{-1}$ which were negatively correlated to the redox potential. Thus, dramatic changes in land use or setting aside land should not be planned and carried out without consideration of possible undesired side-effects and consultation of the pertinent literature.

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Critical phosphorus concentrations and loads

The pollution of watercourses with P is a serious problem in many parts of the developed world. In unpolluted freshwaters, TP concentrations are typically below 25 $\mu\text{g P l}^{-1}$. In water management, it is generally assumed that concentrations above 50 $\mu\text{g P l}^{-1}$ are the result of anthropogenic influences. In Germany, the quality classification in Table 2.6 is applied to running surface waters.

A survey of rivers in Europe (European Environment Agency, 1998) revealed that a large proportion of *c.* 1000 monitoring stations observed TP concentrations exceeding 50 $\mu\text{g l}^{-1}$. Only *c.* 10% of the monitoring stations reported mean TP concentrations below 50 $\mu\text{g P l}^{-1}$. The lowest concentrations of P were found in the streams and rivers of the Nordic countries where 91% of the monitoring stations reported mean concentrations below 30 $\mu\text{g P l}^{-1}$ and 50% below 4 $\mu\text{g P l}^{-1}$. This pattern results from a low human population and the presence of slowly weathering bedrock poor in nutrients. Higher P concentrations were found in a band stretching across central Europe, from southern England to Romania.

A similar pattern of P levels can also be found in lakes with low concentrations in the Nordic and Alpine regions. Lakes can be severely affected by eutrophication after P enrichments. This can be a particularly difficult problem because P may accumulate in lake sediments and be released (for example, by climatic events, changes of redox-conditions or the action of fish) into the water column, maintaining a eutrophic status.

Phosphorus levels in surface waters generally declined across Europe between 1987 and 1996. This trend occurred for annual average concentrations of both total and dissolved P, but it appears that high peak concentrations still occur even where improvements have been achieved. Such improvements originate to a great extent from a more intensive treatment of urban and industrial wastewater and some decline in fertilizer use. In recent years, great efforts have been undertaken in Europe to reduce and control aquatic P pollution and eutrophication in general. These activities (policies, legislation, conventions, etc.) were started at the national and international scale, especially within the framework of the European Union.

It is important to note that some pressure for action comes from international conventions to protect marine environments. These include HELCOM (The Helsinki Convention to protect the Baltic Sea), OSPAR (The Paris and Oslo Conventions to protect the North Sea and Atlantic) and The Barcelona Convention to protect the Mediterranean Sea. The HELCOM and OSPAR conventions focused particularly on reductions of nutrient pollution (N and P). However, Table 2.7 shows that this was not achieved by all countries. Great efforts are necessary to solve this problem. The proposed Water Framework Directive of the European Union is currently under intensive debate within the legislative process. It will provide the basis for an overall management framework for surface (including estuarine and coastal) waters and groundwaters. This is a major

Table 2.6. Threshold values for total phosphorus (TP) in running surface waters as used in Germany (Umweltbundesamt, 1997).

Quality class	Degree of pollution	TP-concentration ($\mu\text{g l}^{-1}$)
I	Not anthropogenic polluted	≤ 50
I-II		≤ 80
II (target class)	Moderately polluted	≤ 150
II-III		≤ 300
III	Raised polluted	≤ 600
III-IV		≤ 1200
IV	Highly polluted	≥ 1200

Table 2.7. Annual discharges of total phosphorus (106 kg year⁻¹) to the North Sea, the north-east Atlantic Ocean and to the Baltic Sea (European Environment Agency, 1998).

Country	1991	1995
<i>North Sea, Atlantic Ocean</i>		
Belgium ^a	2.0	4.0/5.0
Denmark	2.3	2.0
France	n.d.	n.d.
Germany	11.6	11.5
Ireland	6.3	7.3
The Netherlands	17.0	34.1
Norway	3.3	3.9
Portugal	3.1	3.1
Sweden	0.2	1.3
UK ^a	39/40	36
<i>Baltic Sea</i>		
Denmark	5.3	2.3
Estonia	2.8	1.3
Finland	3.4	3.6
Germany	1.2	0.6
Latvia	3.2	2.2
Lithuania	1.7	1.4
Poland	15.0	14.2
Russia	9.5	7.1
Sweden	4.0	4.7

^a Low/high estimate.
n.d. = Not determined.

new development for water legislation and a fundamental basis for sustainable protection of water resources against pollution.

Options for Mitigation and Conclusions

To establish successful management options for reducing P losses to water-courses, it is necessary that farmers, other stakeholders and politicians are aware of the problem and accept that improper P use in agriculture is a main reason for surface water pollution with P. Much evidence has been compiled to show that uneven distribution of livestock results in particular enrichments in total and labile P in certain regions. Hence, political and economic measures are necessary to achieve a more even distribution of animal production. However, the socio-economic impacts of such measures on rural and urban communities need to be considered, as emphasized by Sharpley and Tunney (2000).

Besides this international or national level, a lot can be done locally to improve agricultural P management. Phosphorus use in animal production can be reduced by improving utilization (e.g. precise recommendations, improved P utilization, better choice of inorganic P supplements, plant breeding, etc.; Damgaard-Poulsen, 2000), so that better farm balances can be achieved without loss in productivity (Valk *et al.*, 2000). Improved P use in animal production offers the opportunity to reduce inputs to soils, provided it is not compensated for by increases in stocking densities. In any case, all P entering the soil, including that in manure, must be considered in the calculation of fertilizer recommendations. A European-wide re-evaluation of the experimental data that fertilizer recommendations are traditionally based on, is being carried out in the framework of the European Union. More precise recommendations with lower safety margins will help farmers to avoid inefficient fertilizer applications and undesired P enrichments in soil.

Novel techniques such as isotopic exchange (Morel *et al.*, 2000), ^{31}P NMR spectroscopy, or microbiological measurements, will improve the general understanding of P transformations in soil and thus potential for P solubilization. This will enable a closer matching of fertilizer applications with plant requirements. In plant production, various measures can reduce the risk of losses. These include: (i) reducing P availability in excessively fertilized soils by lowering inputs and either increasing removal in produce or increasing the sorption capacity of soil; and (ii) modification of the cropping systems to achieve optimum utilization of soil and fertilizer P (Frossard *et al.*, 2000). One example for increasing the sorption capacity of soil is the application of aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$) to poultry litter (Moore *et al.*, 2000). This amendment reduces P in runoff and NH_3 loss from poultry litter broadcast on to grassland. However, from an environmental perspective, all options for avoiding surplus P balances and improving utilization are preferable to 'technical solutions' for temporal immobilization.

The identification of critical source areas and assessment of the risks of eutrophication requires a comprehensive understanding of movement from soil to water, and of the P forms and critical concentrations and loads in water bodies. A first step is to evaluate how agronomic and environmental soil tests predict P losses to water. Studies using lysimeters have revealed that DPS predicts P in leachate better than a range of agronomic tests (Leinweber *et al.*, 1999). For acid sandy soils in The Netherlands, Schoumans and Groenendijk (2000) concluded from model calculations that the water-extractable P used for fertilizer recommendations was a good predictor of pollution risk. They also demonstrated that it will take several decades to reduce P contents in over-fertilized soils to levels that are acceptable from an environmental perspective. This calls for an immediate reduction of inputs along with increasing removal by crops and stabilizing mobile fractions in P enriched acid sandy soils.

If critical source areas within catchments are identified, the risk of P mobilization and transport to surface waters can be minimized. Surface application of manure can

be followed by substantial losses in over-land flow, so manure should immediately be incorporated into soil. The method of tillage is also important: mouldboard ploughing can exacerbate erosion by creating pathways for water flow, while least damage occurs from direct drilling or no-tillage systems, which are now common in the grain belt of the USA. Contour ploughing and other practices that minimize erosion are equally valid for minimizing P loss from arable land. For example, McDowell and McGregor (1984) found that no-till cropping reduced TP loss ninefold compared with conventional maize cropping practices, although this was at the expense of an eightfold increase in dissolved P loss.

Possible effects of land use on losses must be considered in conjunction with overall P management. These call for a critical evaluation of possible effects on P losses in advance of large-scale land use changes. The same need applies for setting aside land and Histosol re-wetting measures. However, research in Nordic countries has shown that small-scale measures such as buffer zones, constructed wetlands and ponds may be very efficient in retaining P from agricultural runoff. For example, Uusi-Kämpä *et al.* (2000) reported that total P concentrations decreased by 27–97% ($0.24\text{--}0.67 \text{ kg P ha}^{-1} \text{ year}^{-1}$), depending on the width of buffer zones. Constructed wetlands and ponds retained 17 and 21% of their P loads, respectively. However, the retention of RP (< 0.45) was inconsistent. Therefore, more data are needed on the availability of P, influences of soil types, and effects of cutting and harvesting.

Finally, the setting of scientifically based threshold values for algal-available P in waters of various quality classes, and the continuation and fulfilment of international conventions such as HELCOM and OSPAR will initiate and assist efforts to reduce agricultural P losses. The proposed Water Framework Directive of the European Union is a novel approach in the right direction. Last but not least, more interdisciplinary and international research is needed to fill in the gaps in our knowledge concerning agricultural P cycles, and the forms, pathways and consequences of P losses from land to water.

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