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Routes to improving the efficiency of phosphorus use in arable crop production

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1. Abstract

Phosphorus (P) fertilisers are essential to sustain and improve crop productivity but they contribute to P surpluses in soil and to P exports from crops to livestock and from land to water. Consequences of P use are economic cost, eutrophication, and depletion of finite rock phosphate reserves. This review examines evidence underlying current P nutrition strategies for cropping and assesses scope for innovations to achieve more sustainable approaches.

Current P recommendations largely rely on soil P storage rather than fresh P to optimise crop P supplies. This reliance results from poor capture of freshly-applied P by plant root systems and rapid immobilisation of plant-available P into less available forms in the soil matrix. Soil structure, moisture, temperature, pH and redox conditions can also constrain P supply from soil to root. Some inappropriate P use may also arise through growers justifiably lacking confidence in current soil P tests.

The balance method of assessing efficiency of fertiliser P use appears misleading because it discounts P contributions from non-labile soil sources. Long term studies indicate that soils release at least 5-9 kg/ha/year P without any fertiliser use, and net recoveries of conventional fertiliser P are only 10-15%. The philosophy of feeding the soil rather than the crop must therefore be questioned.

Three key strategies are proposed to improve sustainable P use: (i) minimising crop P requirements, (ii) maximising root recovery of soil P, and (iii) developing targeted fertiliser technologies with as complete P recovery as possible. Large genetic variations in leaf P and crop P (% DM) and in rooting and soil P acquisition offer much potential to improve crops and varieties by breeding; low phytate cereal mutants offer particular promise. Sites should be prepared and maintained to enable testing for and breeding of P-efficient varieties.

Integrated P management strategies including P fertiliser placement, seed P coatings, foliar P applications, industrially re-cycled products, and products that modify soil P availability provide many potential opportunities to improve fertiliser P recovery. These should be developed, and particularly targeted to meet crop P demand at the most susceptible stages (i.e. establishment to stem extension), so as to reduce reliance on soil P fertility. However, current high levels of soil P fertility inhibit P fertiliser improvement; networked experimental sites should be developed and sustained to facilitate development and validation of P fertilisers. New high-precision fertiliser testing methods are also required. Proven reliability of any P targeting technologies will be crucial to their general adoption. Successful innovations in crop P nutrition could offer significant progress in reducing growing costs, preserving finite global P reserves and reducing export of P to livestock and in runoff from land, whilst also facilitating renewed enhancement of crop productivity.

2. Abbreviations

CV%	Coefficient of variation
DM	Dry Matter
Labile P	The P that is immediately able to contribute to plant uptake.
MAP	Mono-ammonium phosphate
N	Nitrogen
P	Phosphorus: To minimise confusion P is usually expressed on an elemental basis throughout this review. P can be converted to P_2O_5 by multiplying by 2.29.
P offtake	‘Crop P removal’ is calculated using harvested weight and P composition.
P uptake	‘Total P uptake’ exceeds ‘offtake’ due to P in haulm or straw and chaff.
SD	Standard Deviation
Soil P	Extractable soil P concentrations are typically quoted as mg/kg (research) or mg/l (advisory) and while not exactly equivalent (depending on bulk density) they are commonly considered as being interchangeable. Soil extractable P concentrations are sometimes converted to an area or volume equivalent basis, such as kg / ha / sample depth. This is particularly helpful when calculating long-term trends in P balances and when comparing with fertiliser applications or crop removal.
STP	Soil Test phosphorus refers to the various soil extraction and analysis procedures used for advisory purposes.
t/ha	tonnes per hectare
TGW	Thousand Grain Weight
TSP	Triple super phosphate

3. Introduction

Phosphorus (P) is an essential nutrient required for food production and human health. The demand for P, which is increasing all the time as the world population grows, has been largely met by fertilisers, feed and food supplements manufactured from phosphate rock (PR). About 80% of mined PR is used for the manufacture of P fertilisers. Since PR reserves take millions of years to form, PR must be treated as a non-renewable resource within the timespan of human existence (Howarth *et al*., 1995). The realisation that P is essentially a finite resource has given rise to various recent estimates of the size and 'geopolitical availability' of exploitable PR (100 – 400 years, Cordell *et al*., 2009; Gilbert, 2009). Supply routes may also become more fragile and vulnerable causing large fluctuations in the price of P fertilisers. Unlike nitrogen (N), which can be produced industrially and potassium (K) where some native sources exist, the UK has no PR reserves and must import all forms of inorganic P. Attempts to increase UK food security through increased 'home' production may therefore be compromised in the future by shortages and/or cost of P imports. Farmers’ response to high fertiliser prices is to omit P fertiliser use, which may (or may not) reduce crop yields and/or the efficiency of use of other nutrients over time (Johnston *et al*., 2001). There are currently no alternative sources of inorganic P on the market that could replace agricultural demand for RP and the need to safeguard these resources and reduce dependence on manufactured fertilisers has therefore become a global priority (Elser & Bennett, 2011).

There is now general consensus that the present day global P cycle is grossly inefficient which suggests there should be large scope to reduce fertiliser P usage. This inefficiency is evident along all parts of the P supply chain, from the mining of the PR to field application of the manufactured product to current patterns of human consumption. Recent estimates suggest that only about 20% of P mined each year ends up in the human diet (Cordell *et al*., 2009; Smit *et al*., 2009). The remaining 80% of unutilized P is either recycled, stored or lost: as it moves along the fertiliser-soil-crop-livestock-human supply chain, some P is recycled via manures and biosolids, some accumulates in the soil, and some is lost to water. Inefficiencies occur because (a) applied fertiliser P is quickly immobilised in soil, (b) the majority of crop P passes through animals before it enters the human food chain, (c) there is unbalanced and limited recycling of excreted P back to crops, and (d) there are ubiquitous losses of P to rivers and ultimately the oceans. These inefficiencies all enhance the need for inorganic fertilisers, and the intensification and specialization of agricultural systems and the increased urbanisation of the population has exaggerated these inefficiencies. This is not only because of increased usage of inorganic P inputs but because P now migrates from areas of arable farming to areas of livestock farming, and from rural areas to urban areas, with little opportunity for returning consumed P back to the land and closing the cycle. A P-balance compiled in 1993 by Withers *et al*. (2001) suggested that the overall efficiency of annual P use in

UK agriculture (total P outputs as a percentage of total inputs) was only 25%, and was considerably poorer in livestock farming (18%) than in crop (arable and grass) production (56%).

This inefficiency is not only economically wasteful but is causing widespread environmental problems during P fertiliser manufacture and following P application. The mining of RP to produce phosphoric acid and fertilisers consumes energy, concentrates potentially harmful metals (e.g. cadmium) in the marketable products, and produces environmentally hazardous by-products (e.g. phosphogypsum) and/or emissions (e.g. fluorides), (Withers *et al*., 2005). The storage and movement of accumulating P within the soil-crop-livestock-human continuum has led to increased transfers of P from land to water causing chronic and acute eutrophication (nuisance growth of algae affecting ecosystem and human health) of inland and coastal waters (Smith, 2003; Edwards & Withers, 1998; Ulén *et al*., 2007). These transfers include sewage and septic tank effluent discharges associated with domestic P consumption (food and detergents), and the P that is mobilised in runoff from agricultural land, farmyards and roads (Edwards & Withers, 2008). Pretty *et al*. (2003) cited the damage costs of aquatic eutrophication to be £75-114 million yr^{-1} in England and Wales alone due to the reduced value of waterfront property, the need to remove N and algal toxins from drinking water, reduced amenity value of water bodies, ecological effects on biota and impacts on the tourist industry. There are real and increasing concerns over declines in the biodiversity of waterbodies, and the degradation of the ecosystem services they provide, that has drawn attention to the overuse and cycling of nutrient inputs, including P (Heathwaite, 2010; Vorosmarty *et al*., 2010).

The cost-effective nature of crop yield response has meant that regular application of fertiliser P has been a standard feature of agricultural production in the UK (and other developed countries) for many years. The continuing need for a supplementary supply of P to support agricultural productivity is not in question. This general point is probably best emphasised through evidence and concerns of a declining soil P status from the organic farming sector (Løes & Øgaard 2001; Oehl *et al*. 2002). However, as P fertiliser manufacture becomes more expensive and increasingly energy demanding, and with growing concerns over the exploitation of a finite resource and the environmental damage from eutrophication, new, innovative and sustainable solutions to the use and management of P are required. Within the water industry, new controls on P levels in detergents are being introduced (EU, 2012) and the amounts of P recycled to agricultural land in biosolids is increasing in the UK; for example, over 75% of biosolids are now returned to the land (Water UK, 2010). It is therefore timely and appropriate to appraise how the use of P in agriculture and the food chain can be reduced and efficiency increased. Recent advances in our understanding of soil-root-crop P interactions and the identification of specific genes for enhanced P uptake, together with advances in fertiliser formulations and nutrient recovery technology (e.g. struvite) suggests P use efficiency could be improved (White & Hammond, 2008; Raboy, 2009;

Lynch, 2011; Simpson *et al*., 2011; Dungait *et al*., 2012). Alongside the ‘looming P crisis’ is the development of a new paradigm in agricultural production that places much more emphasis on the use of biological regulation to manage agroecosystems at field, farm and landscape scales rather than continuing to rely on large chemical inputs; the concepts of ecological intensification, sustainable intensification and integrated production (Russelle *et al*., 2007; Godfray *et al*., 2010; Dore *et al*., 2011). There is also an emerging need to consider global perspectives and to develop solutions that link with the food production crisis in the developing countries (Foley *et al*., 2011; Horlings & Marsden, 2011).

The unsustainability of the global P cycle and the threat this poses for future food security means that the current heavy reliance on inputs of manufactured P must be reduced. Three major strategic goals to achieve this are to (a) improve the efficiency of P use within agricultural systems, (b) maximise the recovery and recycling of P and (c) reduce wastage and losses to water. This review focuses on P use efficiency and is targeted at arable (grain) crops because of their importance for human nutrition. Two important and fundamental aspects of P cycling need to be addressed through crop agronomy and plant breeding. Firstly, the majority of inorganic fertiliser P applied to soils is gradually immobilised by various physical chemical and biological processes (e.g. adsorption, absorption, precipitation) into non-labile inorganic and organic forms of soil P that vary with soil type and are only very slowly available to plants. Secondly, crop P requirement is driven by total biomass production (roots, shoots and grain) and the relationship between P uptake, biomass production and grain yield is controlled by both genetic and environmental factors. Options to meet crop demand by maximising soil P availability (supply) with minimal fertiliser inputs include (a) altering fertiliser formulations to render them less vulnerable to fixation, (b) adapting methods of fertiliser application to improve P capture by the plant, (c) restricting the amount of labile P and improving the acquisition of non-labile soil P by plants and (d) reducing crop P demand (Richardson *et al*., 2011; Rose & Wissuwa, 2012).

Achieving these goals without sacrificing crop yield and downgrading the ecosystem services that soils provide is a major challenge and will require a paradigm shift from past ‘insurance-based’ philosophies which aim to ensure that the crop has access to plentiful quantities of soil P using unlimited supplies of highly-soluble fertilisers. Current fertiliser recommendation systems are largely based on historic field experiments exploring soil P tests for gauging crop response to added P (e.g. MAFF, 1965; Arnold & Sheppard, 1990), but whether these philosophies are still suited to ‘sustainable intensification’ is open to question. For example, current farming systems and methods (varieties, cultivation methods, agrochemical use) are very different to those being used then.

Potential alternative and more sustainable strategies for efficient P use in arable farming systems need to be explored on the premise that their adoption will (i) reduce growing costs and current dependence on elevated soil P-fertility, (ii) help preserve finite global reserves of P and (iii) reduce the eutrophication hazard associated with export of P in runoff from land. Improving the efficiency with which fresh and existing (soil) sources of P are utilised within arable farming systems is the central theme of this review. Following some initial contextual background on the development of arable farming systems and P usage, we critically review current concepts and knowledge of soil P supply and crop P requirements to provide a basis for exploring how P use efficiency might be improved in UK arable crops and the effectiveness of new market products that might facilitate these improvements. Some of the research referred to is not recent and therefore care is needed in its interpretation (e.g. different varieties and a general increase in soil fertility levels).

4. Development of arable farming systems and P usage

4.1. Quantities of P cycling in UK agriculture

Detailed estimates of the amounts of P circulating within UK agriculture have been calculated for 1973 (CAS, 1978), 1993 (Withers *et al*., 2001) and in 2004 (Lord *et al*., 2010). Of relevance to this review is the soil surface balance, which is now calculated annually by Defra for reporting to the EU (Defra, 2011). The methods and commodity values used to derive these estimates have varied slightly but they give a consistent picture of trends in the national P balance. The overall surpluses of P accumulating in soils in 1973, 1993, 2004 and 2010 were 17, 15, 11 and 7 kg P/ha/year when averaged over the productive arable and grassland area (ca. 12 Mha). Trends in the soil surface P balance since 2000 using Defra methodology indicate that surpluses have fallen sharply in recent years largely due to dramatic increases in price and reduction in fertiliser use; inorganic fertiliser consumption has dropped by 40% since 2000 (Figure 1). Indeed, a striking feature of all these balance calculations is that the national P surplus is equivalent to the imports of manufactured fertilisers, so this is clearly a major driver for P cycling within UK agriculture. As fertiliser inputs drop, P balances on arable land and grassland (offtake as a percent of inputs) increase sharply; 51% in 1973, 56% in 1993, 67% in 2000 and 80% in 2011. Fertiliser requirements partly arise from the lack of uniform distribution of the P contained in livestock and manures and wastewater biosolids, which tend to be recycled within close proximity to where they are produced. For example, Bateman *et al*. (2011) calculated that an annual export of 2.8 million tonnes of manure must take place from west to east to balance the supply and demand of P across the country. Overall P balance (P exports as a percent of imports) has therefore been consistently poor: 12% in 1973, 25% in 1993 and 17% in 2004. Withers *et al.* (2001) calculated that since the 1930's the surplus of P which has accumulated in UK soils is ca. 12 million tonnes (equivalent to ca. 1000 kg P or ~2,300 kg P_2O_5) per hectare) and this cumulative input has essentially doubled the average 'background' concentration of total P present in UK soils.

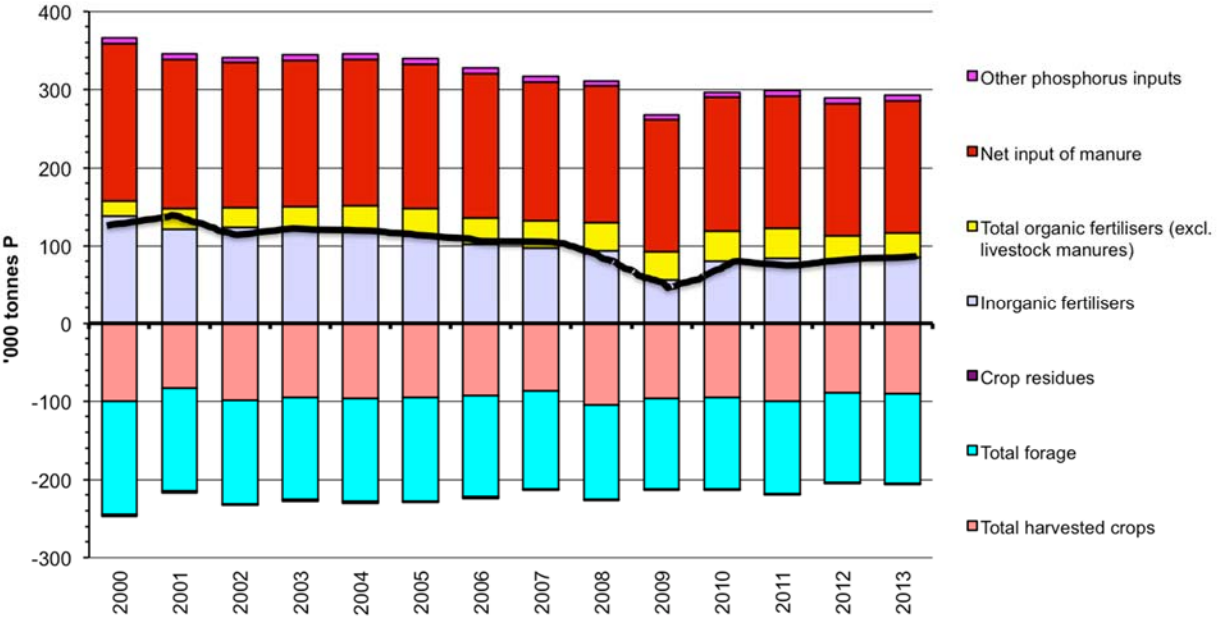

Figure 1. Components of the UK P soil surface balance 2000-2009 (Defra, 2011).

National calculations mask regional variations in P surpluses and differences in P cycling rates between arable and livestock farming systems. Arable cropping systems receive only limited amounts of livestock manure (e.g. 28% of arable area received organic manures in 2011, BSFP, 2011) and biosolids in any single year, although this is steadily increasing. A larger area will receive manures over a rotation. The main P input to arable crops is inorganic fertilisers (ca. 60 kT P in 2011, BSFP (2011)). With the recent drop in fertiliser use, many arable farmers have been omitting P fertiliser and combinable crop rotations may now be in negative balance- with crops relying on the stores of P already present in the soil. Wheat accounts for 60% of all crop P offtake in the UK (Lord *et al*., 2010). The amount of P applied to arable crops in any one year varies with crop type, the area sown and the proportion receiving fertiliser; some average rates for the major arable crops are given in Table 1. The percentage of the wheat area receiving inorganic P fertiliser was only 46% in 2011 but there is often large regional variation in this figure and single crop requirements may be met from larger applications elsewhere in the rotation. The general drop in fertiliser use in 2009 is thought to be due to the large increase in the price of P fertilisers in that year and illustrates how farmers might react if P fertiliser prices increase further.

Table 1. Average field rates (kg P/ha) on major tillage crops, Great Britain 2007 – 2011 (data are the sum of P applied divided by the total area of those fields which received any dressing of the nutrient; from BSFP, 2011).

	Winter wheat	**Spring barley**	**Winter barley**	**Maincrop potatoes**[a]	**Oilseed rape**[b]	**Sugar beet**
2007	27.1	22.3	25.3	65.0	26.6	33.6
2008	26.6	20.9	24.4	64.2	26.6	25.3
2009	23.6	20.9	23.1	69.4	23.6	20.5
2010	26.2	21.8	24.0	60.2	26.2	25.3
2011	27.1	22.3	23.1	58.0	25.7	26.2

[a] Figures for maincrop potatoes include second earlies.

[b] Combined winter and spring oilseed rape areas.

4.2. Current philosophy of fertiliser P management

P fertilizers are required when the supply of P from the soil and other sources such as organic manures is insufficient to meet crop P demand. Sufficiency of soil P supply is estimated by soil analysis (soil test P, STP) procedures that have been calibrated against large numbers of historic field experiments on different soil types (Hanna & Flannery, 1960; Hanway, 1963; Heckman *et al*., 2006). In the UK, these field experiments initially focused on ‘P responsive crops’ such as potatoes and swedes (Cooke, 1956; Cooke & Widdowson, 1959) and then extended to less-responsive crops such as cereals (mainly spring cereals) during the 60’s, 70’s and 80’s (Arnold & Shepherd, 1990; Withers 1999; Johnston & Poulton, 1992). Only a very limited number of long-term experiments are now available for calibrating crop response to added P in the UK (Johnston, 1997). The build up of soil P reserves was a primary objective of P use in the 50s and 60s and soil testing for available P developed in conjunction with soil survey. These experiments and STP analysis provided the basis of practical guidelines for agronomists and extension services that were developed and standardised at the regional scale and subsequently at the national scale to establish clarity and confidence in advice and quality control. These national guidelines are now periodically updated, most recently as the Fertiliser Manual (Defra, 2010) and its associated technical notes in Scotland (SAC, 2012).

A number of basic principles governing fertiliser management evolved during this extensive period of field experimentation. Firstly, following field experiments showing that residual P was better than fresh fertilizer P, it was held that soil P fertility must be increased to a satisfactory ‘critical’ level (Index 2 or 3) to ensure that the developing crop plant has plentiful access to available P. Secondly, some crops such as potatoes responded to very large applications of P fertiliser leaving labile residues of P in the soil that could be utilized by succeeding crops without the need for additional fertiliser (Alison *et al*., 2001). Thirdly, once a satisfactory soil fertility bank had been established, fertilisers could be applied (a) at any point in the rotation, (b) broadcast after the crop was drilled rather than incorporated, and (c) up to 3 years crop P requirements could be applied in one application (Johnston & Poulton, 1992; Withers, 1999; Defra, 2010). The concept of rotational manuring was born and provided farmers with greater speed and flexibility at drilling whilst providing P for several crops in the rotation when conventient. Fourthly, P fertilisers must be in a water-soluble (i.e. immediately available) form to overcome shortages in P supply on soils with low STP. More slowly available P fertilisers (e.g. rock phosphate) could be used to maintain soil fertility on some soil types. Thus maintaining a soil P fertility at soil P Index 2 throughout the crop rotation has become the central philosophy behind P (and K) fertiliser recommendations for arable crops: build up soil fertility by applying more than crop offtake, maintain soil fertility by replacing crop P offtake, and apply bulk fertiliser dressings to the most responsive crop in the rotation (Defra, 2010). Guidelines on the amounts of P fertiliser required to build up STP concentrations were generalised across soil types and use of highly water-soluble single (e.g. TSP) or compound (e.g. di-ammonium phosphate) fertilisers has become the norm.

Current recommendations systems therefore put a heavy reliance on soil P reserves and STP analysis to decide on fertiliser inputs. This soil-based strategy is self-correcting in that more or less P fertiliser can be added until the desired level of soil P fertility has been achieved. Standardised recommendations on soil sampling procedures and a national accreditation scheme for laboratories exist to help reduce errors. In 1955, Hemingway suggested that the ca. 275,000 samples collected annually for advisory purposes represented ca. 10% of the arable and grass acreage of the country (England and Wales); a similar value has been recently calculated for Scotland (Edwards pers. com.). In 1971, 87,215 samples from England and Wales were analysed by the ADAS laboratories of which 26,000 were on all tillage crops (CAS, 1978). In 1993, the number had increased to 45,000 samples. In 2011, the Professional Soil Analysis Group (PAAG) comprising a number of the larger commercial laboratories received 170,000 soil samples from England and Wales of which ca. 65,000 were from arable fields (PAAG, 2012). If one assumes a field is ca. 6 ha, then this represents about ca. 9% of the arable area. A breakdown of the percentages of soil samples in each soil fertility class is shown in Table 2. Whilst these statistics are biased towards the more progressive farmers who send in soil samples, the data show that arable soils in England and Wales are very well supplied with P and that a maximum of ca. 10% of the arable area is probably sampled each year. Over time, fields with either very low or very high STP have declined slightly; the 1971 survey included a high proportion of fields under horticulture and fields receiving pig and poultry manure (CAS, 1978). More objective soil surveys (with statistically stratified samples but) with fewer samples) give a very similar picture (Table 2). There has been surprisingly little change in the distribution of Olsen P since 1970 when the P surplus was at its peak (Withers *et al.*, 2001). This may be due to an increase in topsoil depth with the advent of deeper ploughing. Whilst the concentrations of Olsen-P are similar, there is a greater volume of soil with that concentration.

Table 2. Temporal trends in the percentages of STP (Olsen) in different soil fertility classes based on (a) samples received by commercial laboratories, and (b) stratified surveys since 1970 for England and Wales. PAAG, Professional Soil Analysis Group; RSSS, Representative Soil Sampling Scheme; Skinner & Todd, 1998).

Year	**Sample no.**	**Source**	**Soil P fertility class (P Index; DefraAnon, 2010)**					
			0	**1**	**2**	**3**	**4**	**5+**
(a)								
1971								
all fields	87215	ADAS	12	15	20	22	12	31
arable only fields	26,217	ADAS	5	7	13	19	15	41
1993								
all fields	44607	ADAS	9	16	25	27	12	10
2011/12								
all fields	170,000	PAAG	7	21	30	28	10	4
arable only fields	65,000	PAAG	5	18	29	32	12	4
(b)								
1969-1973								
all fields	2216	RSSS	11	20	26	26	12	6
arable only fields	545	RSSS	9	18	30	30	11	3
1995-1999								
all fields	3503	RSSS	6	20	32	29	10	4
arable only fields	405	RSSS	3	16	32	32	11	5

Concerns over the total reliance on soil analysis for choosing fertiliser P requirements have recently increased. Kuchenbuch & Buczko (2011) reviewed historical fertiliser response data for Germany and concluded that; ‘although site-specific soil and plant properties (e.g., clay and carbon content, pH, crop species) influence the relation between soil nutrient content and fertilizer effectiveness, most of these factors are not accounted for quantitatively when assessing fertilizer demand.’ They also observed that ‘Recent re-evaluations of field observations suggest that even for soil nutrient contents well within the range considered to indicate P or K deficiency, fertiliser applications often resulted in no yield increase.’ This re-analysis of data involved considerable effort and utilised results from about 9000 experimental harvests. The authors suggest that ‘The indication is that soil nutrient contents may not be the predominant factor governing nutrient availability, but other factors related to soil, plant, and climate should be considered.’ This general view is supported by (i) Valkama *et al*. (2011) in their meta-analysis review of 43 Finnish field experiments, (ii) Johnston & Poulton (2012) in their recent review of the Rothamsted long-term experiments and (iii) recent field experiments in Canada (e.g. McKenzie *et al*., 2003). For example, Johnston & Poulton (2012) concluded that ‘maximum yields were obtained from the upper end of Index 0 to P Index 4’.

Recent changes in farming methods may add further uncertainty concerning the usefulness and suitability of a strategy based solely on soil analysis. Relevant changes are (i) uneven distribution of P surpluses (Edwards & Withers, 1998), (ii) both expansion of reduced-cultivation farming (Davies & Finney, 2002) and increased ploughing depth (Edwards *et al*., 1997), (iii) incorporation and decomposition of crop residues since the ban on straw burning and (iv) fertiliser application by top-dressing instead of combine drilling. These will all increase within-field variability in STP, creating increased difficulties and uncertainties in predicting fertiliser P requirements.

5. Concepts and knowledge of soil P supply

Over time, soils develop a vertical profile of different forms and concentrations of P. Under natural conditions, the upper horizons are influenced more by biological processes and so often have higher concentrations of P associated with organic forms and receive continual recycling of P in the form of plant litter/roots. This biologically-active zone passes into a geochemically-dominated zone where various primary and secondary mineral forms of P exist and are slowly supplemented by natural weathering processes. Agriculture has modified the distribution, quantity, form and potential bio-availability of P through direct applications of fertiliser/manure, alteration of pH through liming and mixing of soil constituents through cultivation. To a large extent these changes are confined to the depth of cultivation and have led to a greater proportion of P in inorganic P forms as soil organic matter (SOM) levels have declined with regular cultivation and use of imported inorganic P fertilisers has increased. Total P contents have increased dramatically in agricultural soils due to the surpluses of P that have accumulated as agricultural systems have intensified, with values ranging up to 4500 mg/kg in farmed topsoils (median of ca. 800 mg/kg to a depth of 15 cm), (McGrath & Loveland, 1992; Withers *et al*., 2001). Where large P surpluses have been applied and/or where large applications of P have been applied to well-structured soils, P can migrate to the subsoil (Rubæk et al., 2013).

5.1. Cycling of P in soils

There is continuing debate surrounding the definition of P forms in soil and especially those forms that contribute directly to maintaining labile P plus adequate concentrations of dissolved P in the soil solution for uptake by crops. Four distinct forms of soil P are generally distinguished that display very different trends in response to a change in soil solution P:

Mineral (or native) P – the P that is bound within primary soil minerals and which is released only very slowly by natural weathering and which is relatively insensitive to changes in solution P. The parent material largely governs the range of minerals found in soils and the P that they contain and the rate of weathering is governed by the prevailing climate. This form of P is non-labile.

Organic P – the P that is present in SOM and in the soil microbial population (fungi and bacteria) that breaks down SOM at variable rates depending on the availability of carbon (C) and N and soil conditions (pH, temperature, moisture, redox). Addition of inorganic fertilisers inhibits the microbial cycling of organic P in soils but nevertheless organic P can still represent an important source of P for plants (Turner *et al*., 2005). Organic P forms can be both non-labile (recalcitrant high molecular weight compounds) and labile (low molecular weight compounds).

Sorbed P – the inorganic P that is adsorbed onto the surfaces of primary (e.g. clays) and associated secondary soil particles (e.g. iron (Fe) and aluminium (Al) oxide/hydroxides, calcium and magnesium carbonates) and organic matter with varying degrees of bonding strength (e.g. physical and chemical). The number of sorption sites is dependent on organic matter content, soil particle distribution and pH. Adsorbed P diffuses at variable rates into and out of the soil solution when the P concentration in the soil solution either decreases (plant uptake) or increases (P addition as fertiliser or manure). Adsorbed P is considered the main source of inorganic P for crop plants and the speed of diffusion from particle surfaces into solution is governed by the soils buffering capacity (Holford, 1997). When high soil solution P concentrations are maintained by fertiliser applications, adsorbed P (generally more labile) can become absorbed more strongly within the matrix of soil particles over time, becoming non-labile and less available.

Precipitated P – the P that is precipitated when the concentrations of P and partner metal cations (e.g. Ca, Mg, Fe, Al) in the soil solution exceed solubility thresholds of various precipitate compounds. In agricultural soils, this most often occurs in P-fertilised calcareous soils where high concentrations of Ca are present in the soil solution. Under these conditions, the concentration of P in the soil solution is governed by the specific precipitates present rather than by adsorbed P; when the P concentration of the soil solution drops, the most soluble precipitate will dissolute to replenish soil solution P. This form of P is generally non-labile, but depending on the precipitates formed.

Various interacting factors further influence the concentration of P in the soil at any one time. These are described by Hinsinger (2001) as (i) the pH which influences the number of P sorption sites and the dissolution of primary minerals and secondary precipitates, (ii) the concentrations of organic and inorganic anions that compete with P ions for sorption sites and (iii) the concentrations of metals (Ca, Fe and Al) that can co-precipitate with P ions. These, in turn, are all influenced by the presence of an actively growing root system and an active microbial community, both of which will vary with soil properties (texture and structure), with plant species and their associated mycorrhizae and with the availability of other plant nutrients. The prevailing environmental conditions (redox conditions, soil moisture status and soil temperature) add an additional level of complexity by influencing the rates at which P is mobilised and immobilised by biotic and abiotic processes operating within the rhizosphere.

Soil P dynamics are therefore complex and much research is still required to understand how management can best optimise soil solution P concentrations at a rate that is optimal for crops during the growing season (Dungait *et al*., 2012). The concentration of P in the soil solution varies from 10^{-4} M (low) to 10^{-6} M (high) (Mengel & Kirkby, 1997). Fertiliser P is added to arable crops usually only once (or less) per year and the fertiliser granules are dispersed across the soil surface, or incorporated into the seedbed at drilling (the previously common practice of combine drilling fertiliser with the seed is now seldom practised, except in Scotland). As the granules dissolve, sharp changes in pH and very high P concentrations develop in the micro-environment around the granule, which encourages precipitation with Fe, Al or Ca and adsorption onto soil surfaces (McLaughlin *et al*., 2011). Crops must ‘forage’ for these P concentration hotspots to take up P for the developing shoot, and to further expand their rooting systems. Where monocalcium phosphate (e.g. triple superphosphate) is applied, the microenvironment pH is very low (ca. pH 1-2), whilst for fertilisers such as diammonium phosphate the microenvironment pH is very alkaline (pH 8.0). The current philosophy is therefore one of feeding the soil rather than the plant and the provision of an adequate supply of P during the crop growth cycle is highly dependent on the crop’s foraging ability and the soil environmental conditions (moisture and temperature). Crop roots occupy only about 1% of the soil volume.

5.2. Concepts of soil P availability

Attempts to quantify soil P availability to crops have historically been based on the ease with which soil P is removed by various chemical extractants and the observed correlation between extracted P and crop P uptake in long-term experiments. Four conceptual categories of soil P availability have been recently distinguished (Figure 2). These categories are considered to adequately explain P uptake patterns in long-term experiments (e.g. Syers *et al*., 2008) and are also linked to laboratory extraction procedures that sequentially use increasingly destructive acidic and basic extractants; for example the Hedley extraction (e.g. Hedley *et al*., 1982). The spectrum of availability thus categorised ranges from immediately available to very slowly available and P can move (by diffusion) between these categories in either direction, but the movement of P into slowly-available forms is dominant. Readily-available P (labile P) must be maintained by regular application of fertilisers and if allowed to become depleted, P will slowly diffuse out from the slowly-available (non-labile) categories. However, the rate at which P diffuses from slowly-available to readily-available forms and into solution is considered to be too slow to fully meet crop requirements (Syers *et al*., 2008). The readily-available, or labile, category represents surface-adsorbed and weakly-bonded P which is considered to be the main source of P taken up by crops based on extensive field experimentation. The general lack of accessibility of non-labile P and the continuous gradual migration of P from labile into non-labile forms in well-fertilised soils is one of the main reasons that current P fertilization strategies are inefficient.

This conceptual model may be unnecessarily complex and over-reliant on P sorption processes; it takes no account of soil organic P contributions or the role of rhizosphere processes in P mobilization. For example, reduction processes can occur in microsites resulting in the transient release of labile P (Scalenghe *et al*, 2012). Bhogal *et al*. (1996) and more recently Sattari *et al*. (2012) found that a simple two soil P compartment model (labile and non-labile) was adequate to explain long-term P dynamics in soils. The amount of non-labile P stored in soils is very large. For example, in Australia non-labile P has been estimated to be worth over AU$10billion (Cornish & Millar, 2009). In the UK the store of non-labile P of ca. 7 million tonnes is worth at least £4 billion with over 50% of this store on arable land. A major future challenge for sustainable use of P is to exploit this large reserve of non-labile P and conceptual understanding to-date suggests that the only way to achieve this is by either reducing the store of labile P or enhancing rhizosphere processes (McLaughlin *et al*., 2011).

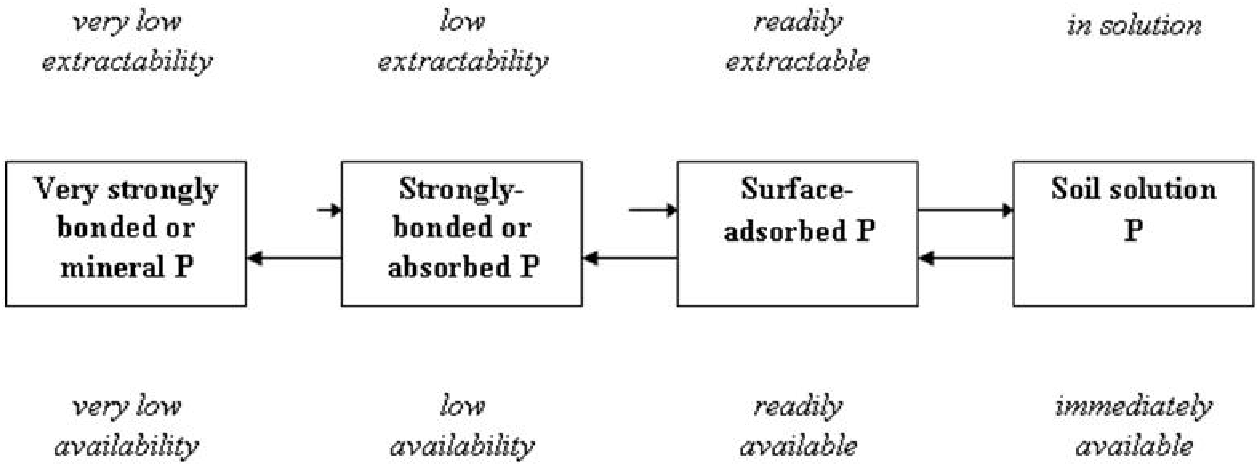

Figure 2. Conceptual diagram of the forms of inorganic P in soils (from Syers et al., 2008). It should not be inferred that these pools are similar in size.

The potential contribution of P from non-labile and labile fractions of soil P can be estimated from long-term experiments where P has not been applied, or where P has been applied but then subsequently stopped. Poulton *et al.* (2012) describes an experiment (Exhaustion Land) where 4 kg P/ha was still being taken by spring barley and winter wheat from soils that had received no P since 1852. Soils that had received P up to 1901, but then subsequently received no P, released 8-11 kg P/ha even though these soils had very low levels of Olsen-P (2-4 mg/L). In contrast, Richards *et al.* (1998) describe an experiment where P offtake on plots receiving no P for 28 years varied 3-fold (7-21 kg P/ha) but did not decline as Olsen-P concentrations fell from 16 to 9 mg/l.

Soil analysis suggested the subsoil contained elevated Olsen-P and may have contributed to the total P uptake. Last *et al.* (1984) also found that Olsen-P at Brooms Barn (22 mg/l) did not decline when the soil did not receive any P for 18 years. The Olsen-P content of the subsoil was also high at the start of the experiment (15 mg/l). Offtake of P on the nil P plots averaged 9 kg P/ha/yr for cereals and 16 kg/ha/yr for sugar beet. These data suggest that substantial amounts of P can be released from soils even though they have not received inorganic P fertiliser for many years.

5.3. Soil Test P (STP)

Many different extractants are used in different countries to quantify the amounts of labile P in soils hence to predict the likely soil P availability to crops and potential yield response to applied fertiliser (Tunney *et al*., 1997; Jordan-Meille *et al*., 2012). These methods can be collectively termed soil test P (STP); they all employ a single extraction that is not too time consuming and that can be routinely carried out at commercial laboratories with a reasonable degree of reliability. The amount of P extracted is related to the likelihood of a yield response based on a large number of historic field experiments. These have shown that there is often a critical level of STP below which crops may suffer yield loss (Arnold & Shepherd, 1990; Johnston & Poulton, 1992; Defra, 2010; Johnston & Poulton, 2012). The critical levels of extractable P vary from site to site, from crop to crop and from season to season to the extent that it has been more pragmatic to relate likelihood of yield response to a soil P fertility index covering a range of STP levels (Defra, 2010). In the UK, there are three STP methods (Olsen, Morgans and Resin) for which the values within each P fertility index are shown in Table 3. It is noteworthy that the values falling within each fertility index differ both between STP methods and between indices using the same STP method. This appears to indicate that (a) different methods extract different amounts of 'labile' P, (b) the allocation of STP values to each index is not regular, and (c) recommendation systems are arbitrary to some extent, being based on calibration with field trials that have significant unexplained variation (and were carried out many years ago). Nevertheless, fertiliser recommendations still rely heavily on STP and a soil fertility indexing system that predicts that crops will not yield to their optimum potential unless the soil P index is at least 2 (or Index 3 for some horticultural crops).

Soil analysis has a number of inherent uncertainties that can potentially undermine its usefulness (Edwards *et al*., 1997); these are summarised in Figure 3. To expect such a general system based on a single STP method to be suitable for all field situations is optimistic; at best STP can only provide an approximate guideline to fertiliser requirements for individual fields, although STP may become to some extent self-correcting after regular soil analysis. Routine soil analysis does also not take account of P that has accumulated in the subsoil and which can contribute to P uptake.

Table 3. Indices and concentration ranges (mg P litre^{-1}) for Olsen, Modified Morgan's and ion (anion) exchange resin methods of soil P analysis.

Olsen		**Modified Morgan**[1]		**Resin**	
Index[2]	***mg P l***$^{-1}$	**Status**	***mg P l***$^{-1}$	**Index**	***mg P l***$^{-1}$
0	0 – 9	Very low	<1.8	0	0 – 19
1	10 -15	Low	1.8 – 4.4	1	20 – 30
2	16 – 25	Moderate	4.5 – 13	2	31 – 49
3	26 – 45	High	14 – 30	3	50 – 85
4	46 – 70	Very high	>30	4	86 – 132
5	71 – 100			5	>132
6	101 – 140				
7	141 – 200				
8	201 – 280				
9	>280				

[1] Ammonium acetate / acetic acid solution.

[2] Index 0 – yield response likely, Index 1 – yield response possible, Index 2 – yield response unlikely, Index 3 – recommended upper limit to avoid eutrophication risks.

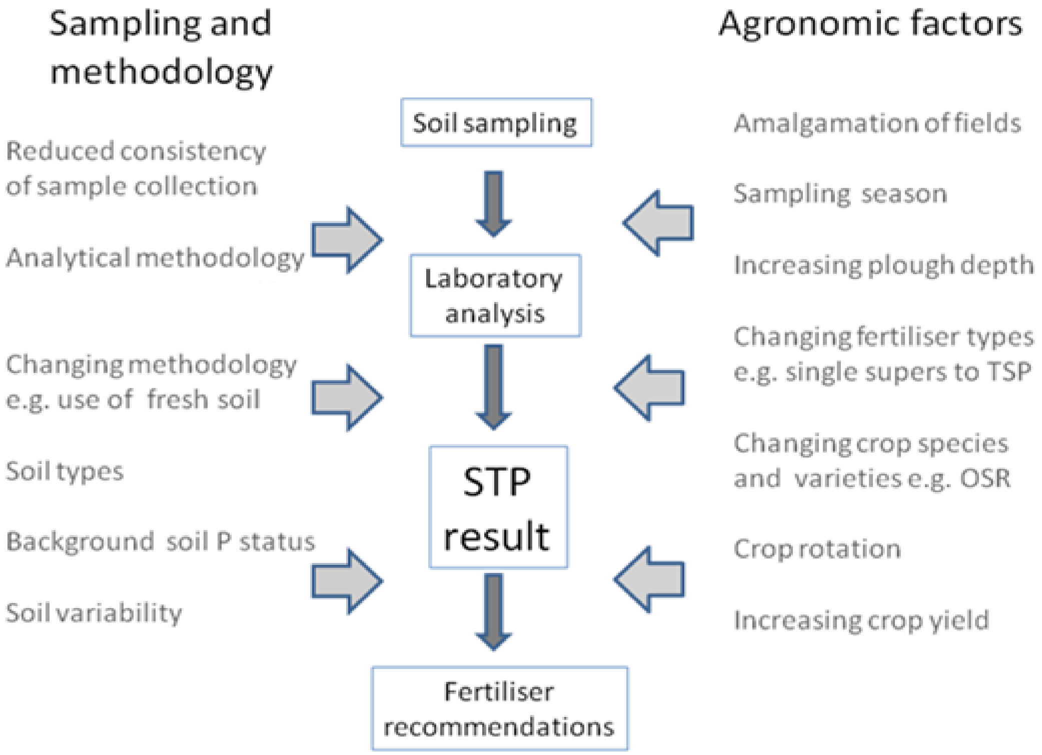

Figure 3. Schematic representation of the direct and indirect factors that have changed over the last 50 years and which may influence STP results and interpretation.

In summary, there are three areas of concern with STP: firstly soil sampling and analysis require consistency in sampling depth, STP methods and lab conditions (especially temperature) under which the analysis is undertaken (Edwards *et al*., 1997). Secondly, changes in agronomic practices (e.g. cultivation depth, method of fertiliser application) may increase the spatial and temporal variability and distribution within the soil profile of P forms; for example minimal cultivation and broadcasting of fertiliser concentrates P more at the surface (Owens *et al*., 2008). Field sampling to 20 cm depth may not represent this variability adequately in terms of the implications for P uptake. Note that a 0.5 kg soil sample is being used to represent ~10,000 tonnes of soil in a 5 ha field, and more in larger fields. Thirdly, there are difficulties inherent in the assumption that any chosen STP method will extract some proportionate amount of the labile P pool that relates to growth and yield. The extent to which STP can represent the contribution of soil organic P to crop P uptake is largely unknown. With P reactions in soils being so complex and variable it seems very unlikely that a single STP method could suit all soils and it is evident that different STP methods can give different P fertiliser recommendations for the same field. For example, the Olsen-P test overestimates labile P in acid soils (e.g., Smith & Sinclair, 1998) but extracts very little P from basaltic soils even though crops thrive on them (Bailey *et al*., 2000). In addition, yield responses to applied P may be limited by factors other than P supply (e.g. soil moisture, rooting restrictions).

In the light of these uncertainties, it seems sensible to constrain the confidence placed on STP and the recommendations that are based on it. A less risky approach might be to ensure that the plant receives more targeted supplies of P that are less dependent on soil and climatic factors that limit soil P supply.

5.4. Soil Organic P

Organic P represents between 30 and 65% of soil total P and will likely become even more important as crop residues and organic manures are recycled in greater quantities in the future. The main forms of organic P in soils are inositol phosphates (mono-esters analogous to phytate), phosphonates, phospholipids and nucleic acids (di-esters), (Harrison, 1987; Condron *et al*., 2005). A significant amount of P (as organic polyphosphate) is also present within microbial cells. Whilst inositol phosphate is the most stable and abundant form of organic P, a range of lower molecular weight breakdown compounds (e.g. phosphoglycerides and amino acids) are mineralised rapidly within the rhizosphere to provide inorganic P for crop uptake. Rates of P mineralisation form organic residues depend on enzyme activity, the availability (accessibility) of suitable carbon substrates for the range of microorganisms present and environmental factors such as wetting and drying. Phosphatase and phytase enzymes are produced by plant roots, mycorrhizae and microorganisms to facilitate organic P mineralization according to their demand for P relative to the availability of inorganic P in the soil (Tarafdar & Claassen, 1988). Phytases attack phytate and phosphatases attack other organic P esters. Enzyme activity is greatly influenced by soil properties and phosphatases can be strongly adsorbed onto clay-sized particles (Jones & Oburger, 2011).

Current STP methods have not been designed to reflect soil organic P or its contribution to crop P uptake. Whilst STP methods such as Olsen (extractant: sodium bicarbonate) do hydrolyse some portion of soil organic P during the extraction process (Hedley *et al*., 1982; Cross & Schlesinger, 1995), it seems unlikely that this would reflect the potential for enzyme-mediated mineralisation of organic soil P within the rhizosphere. Brookes *et al.* (1984) measured net mineralisation rates ranging between 2-11 kg P ha/yr for arable soils and 20-40 kg P ha/yr for grassland soils in lowland England. These rates suggest significant amounts of inorganic P can be mineralised from organic sources, with potential to substitute for the regular inputs of inorganic P fertilisers.

5.5. Subsoil P

Subsoils are rarely considered as a major source of P in plant nutrition, however, their importance should not be overlooked. This is particularly true considering that cereal roots routinely penetrate to depths exceeding 1 m in agricultural soils and allocate a large proportion of their investment in below-ground biomass to the exploitation of subsoils (Gan *et al*., 2011). Subsoils contrast in many ways with topsoils and parallels in P behaviour can rarely be drawn between the two. Firstly, mineral subsoils are highly structured containing large aggregates that may have remained physically stable for centuries. Secondly they contain lower amounts of organic matter and consequently have less microbial activity. Most of their P is inorganic and is held on secondary minerals and particularly on Fe and Al oxyhydroxide films present on aggregate surfaces. The sorption capacity and strength of sorption also tends to be much higher in subsoils. When plant roots penetrate subsoils they tend to preferentially grow within macropores and rarely enter into the aggregates (Dexter *et al*., 2004). This can be due to the high bulk density of the aggregates, and their low O_2 and nutrient contents. Unlike topsoils, therefore it is likely that roots repeatedly occupy the same macropores for many generations (Pierret *et al*., 1999).

Available P contents of subsoils tend to be significantly lower (ca. 5-fold) than fertilised topsoils across a broad range of soil types (Jobbagy & Jackson, 2001). Rates of mineral weathering in subsoils have been estimated to deliver 5 kg P ha y^{-1}, however, P can also be delivered to subsoils by other mechanisms. Firstly, when organic and inorganic fertilizers are added in high amounts, sorption sites in the topsoil can become saturated leading to downward migration of P in response to leaching (Campbell *et al*., 1993; Holford *et al*., 1997). Secondly, P can be transferred directly from the surface to the subsoil via macropore flow (Jensen *et al*., 1998). Thirdly, anecic earthworms can bring plant litter from the surface to lower soil horizons upon which microbial or earthworm decomposition leads to P release (Pankhurst *et al*., 2002). Lastly, and most importantly, P is transferred to subsoils during root turnover and rhizodeposition (Jones *et al*., 2004). In annual plants this P flux may be large even after accounting for retranslocation of P to the seed; however, good estimates of this flux remain lacking.

The importance of subsoils to plant P nutrition is highly context specific, depending on soil type, crop type, management regime and climate. As a general rule, subsoils are likely to be more important in low-input systems especially when P availability in topsoils becomes limiting either directly or indirectly (Richards *et al*., 1995). An experimental study on wheat by Kuhlmann & Baumgärtel (1991) indicated that P uptake from the subsoil accounted for between 37% and 85% of total P uptake, with the amount of P captured inversely correlated with topsoil P supply. In contrast, Barber & Mackay (1986) calculated from modelling that only 4% of the P taken up by maize was from the subsoil in a well-fertilised agricultural soil. In their recent review Kautz *et al*. (2013) found strong evidence to indicate that subsoils can contribute more than two-thirds of plant N, P and K, especially when the topsoil is dry or nutrient-depleted. They conceptualized nutrition from arable subsoils involving three major processes: (i) mobilisation from the subsoil, (ii) translocation to the shoot and long-term accumulation in the topsoil, and (iii) re-allocation to the subsoil. Further work is clearly needed to determine the contribution of subsoil P to a range of crops in a range of soil types to resolve the current discrepancy between the limited experimental and modelling approaches.

Assuming that subsoil can make a significant contribution to plant P nutrition, we need to consider potential management options for optimizing its recovery including:

1. In dry conditions P uptake is often limited by poor root growth, low rates of mycorrhizal infection, slow rates of P diffusion and low rates of P mineralization. To overcome this some or all of the P fertiliser can be placed in the subsoil where moisture is retained for longer periods and where root activity is greater (McLaughlin *et al*., 2011).
2. Crop varieties can be selected with deeper roots which will allow greater exploitation of both subsoil P and water (Streda *et al*., 2012). This deeper rooting may even stimulate the recapture of nutrient resources previously lost from the system to deeper soil layers. This strategy could be particularly effective in shallow rooting grasslands which could be planted with a deeper rooting high biomass annual for one year to recover subsoil nutrients and allow P transfer back to the topsoil organic-P pool.
3. Subsoiling may also prove effective in breaking up compacted layers allowing root penetration but also reduce the size of subsoil aggregates allowing greater root exploration (Himmelbauer *et al*., 2010). For example, Lilley & Kirkegaard, (2011) predicted overall mean yield benefits of 0.3-0.4 t ha^{-1} from a combination of faster growing and more efficient roots. Combining subsoiling with deep placement of organic fertilizer has also proved successful to remediate compacted soils and increase water capture (Espinosa *et al*., 2011; Leskiw *et al*., 2012).

6. Concepts and knowledge of crop P requirements

The definition of crop P requirements varies: it is taken here to be the P contained within an optimally supplied crop, but it can also be taken as the total supply of P (or the supply of fertiliser P) required to achieve optimal growth, thus also taking into account the capacity of roots for P capture. Crop P requirements can be explained qualitatively according to the physiological functions of P in the plant, and they can be quantified empirically by crop response experiments; in addition, modelling approaches may be used to partition P requirements quantitatively between components.

6.1. Crop P constituents and patterns of P uptake

Plant P occurs in many forms: phosphorylated sugars, proteins and lipids, but its primary and vital functions are in enabling energy transfer through formation of adenosine triphosphate (ATP) and as a component of nucleic acids (DNA and RNA). High energy pyrophosphate bonds of ATP, formed mainly in photosynthesis, release energy on hydrolysis. However, quantities of P required for ATP and DNA formation are relatively small; it appears that leaves must contain approximately 0.25% DM as P (Bingham, 1966), or at least 0.12 g m^{-2} of leaf in order to maintain maximum rates of carbon capture (Ghannoum *et al*., 2008). It is possible that leaf P includes some inessential P storage but, assuming this is not so, and given that optimum canopies or crops have Green Area Indices of around six (6 m^{-2} green tissue per m^{-2} land; Sylvester-Bradley *et al*., 2008), this translates to an optimal metabolic P requirement of ~0.75 g m^{-2} land (or ~17 kg P_2O_5 per ha), much less than the normal uptake of P by crops. Given that P is not thought to be involved in structural substances (cellulose and lignin) the discrepancy between ‘metabolic P’ and total crop P is largely accounted for by P storage as phytate (Raboy, 2002; González *et al*., 2010). Phytates are present in all plant tissues where they can be involved in metabolic signalling (Raboy, 2009) but they accumulate to significant quantities in seeds and tubers, providing a reserve from which metabolic P compounds can be reformed during plant regeneration (Catusse *et al*., 2008.).

Maximum P uptake rates generally coincide with the phase of maximum dry matter growth (Figure 4), and the timing of this phase does not appear to be much affected by P deficiency (Figure 5), however the phase of growth most vulnerable to low P supply occurs earlier (Grant *et al.* 2001), indicating that P supply is dependent on development of a satisfactory root system. Uptake appears to continue during grain filling.

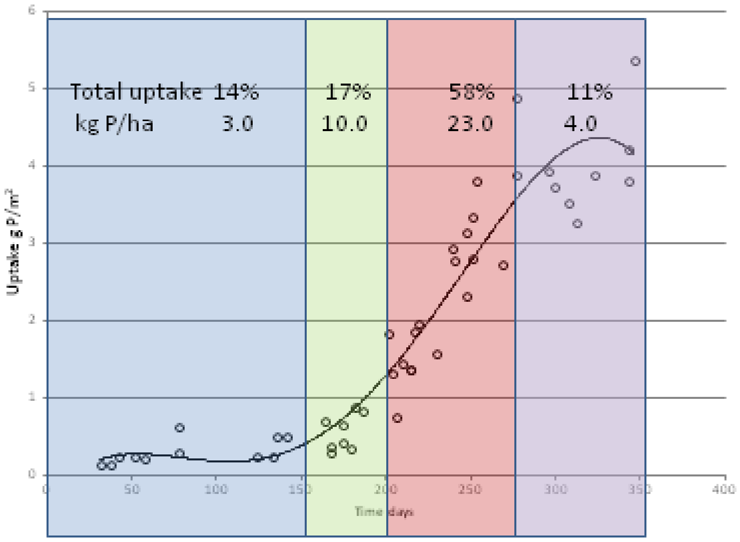

Figure 4. P accumulation by the shoots of winter wheat (4 irrigated crops sown between mid September to mid October at Broadbalk and Woburn, with 9.5 t ha^{-1} average grain yield and ~40 kg ha^{-1} or 4 g m^{-2} average P uptake, re-drawn from Barraclough, 1986). Coloured zones indicate phases of P uptake.

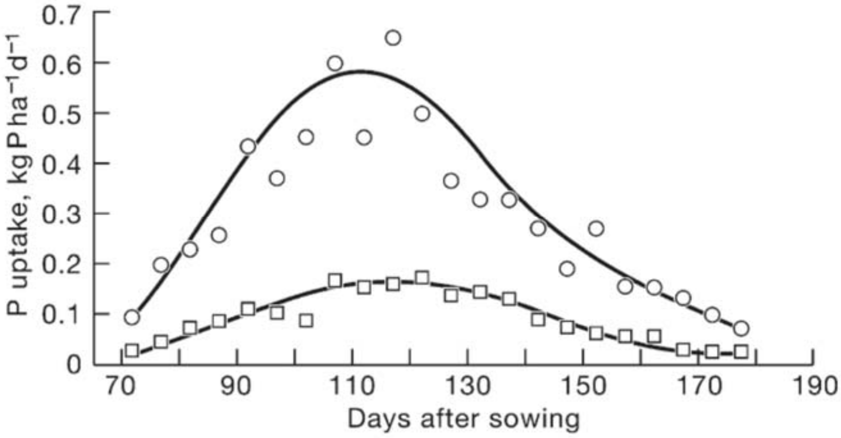

Figure 5. Daily P uptake rate of spring barley grown with adequate (100 mg/kg Olsen P, ○) and deficient (5 mg/kg, □) soil P (from Kirkby & Johnston, 2008, adapted from Leigh & Johnston 1986.)

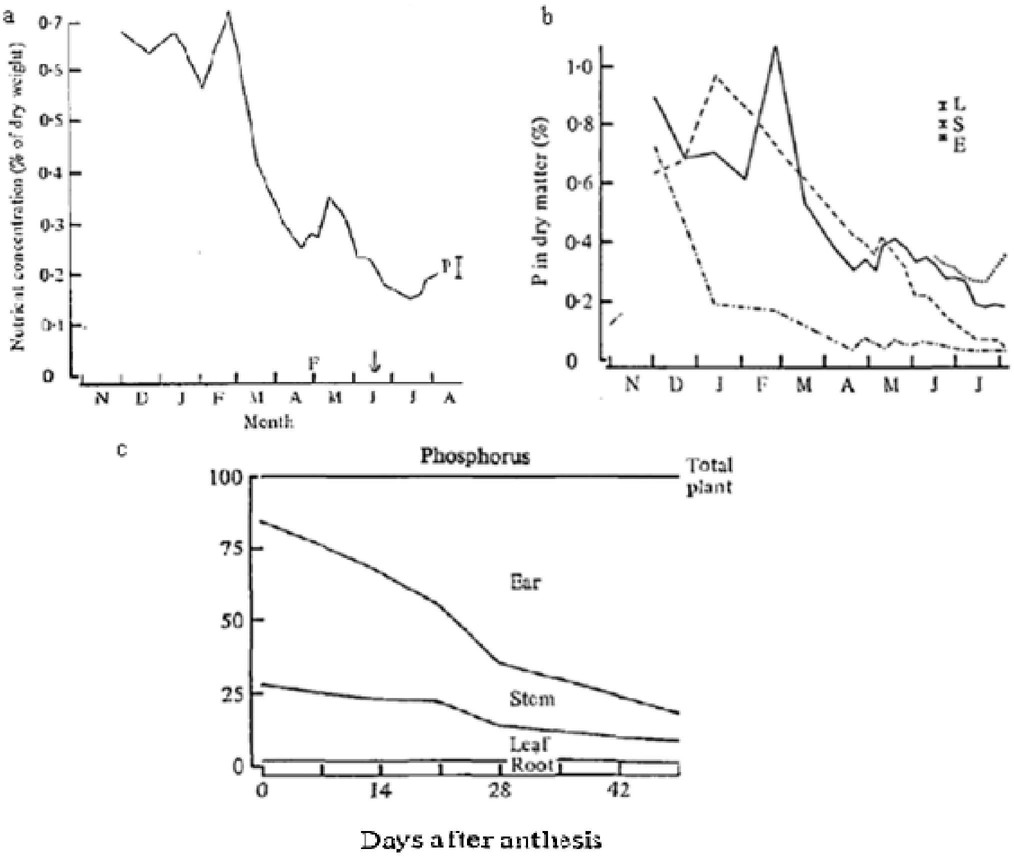

Figure 6. (a) Concentration of P in winter wheat (P, shoot plus root) and (b) leaf (——), stem (— — —), ear (• • •) and root (—•—•). The SE shown (a) is a mean for the whole season and is an under-estimate early in the season and a slight overestimate later. Times of fertiliser application (F) and anthesis (↓) are indicated. (c) P partitioning (of total crop P) between components of the winter wheat crop after anthesis.

P concentrations generally decline in annual plants as they mature, because an increasing proportion of their dry weight is composed of low-P structural and storage tissues (Figure 6; Greenwood *et al*. 2008). Bolland & Paynter (1994) reported that the critical P concentration in wheat shoot DM decreased from 0.91% to 0.23% over the growing season. Elliott *et al*. (1997) reported a critical P concentration of 0.19 to 0.23% in wheat grain (relating to 90% maximum grain yield). There is a final period of remobilisation to the ear during the post anthesis period (Figure 6c).

6.2. Crop P capture

Compared with other macronutrients, soil P is poorly recovered by crops especially where soil P fertility is already high (McKenzie *et al*., 2003). The sorption of P by soils and the rate-limiting, slow diffusion (~0.13 mm per day) of orthophosphate ions (H_2PO_4 and to a lesser extent HPO_4^{2-}) in solution from the soil exchange complexes reduce the immediate effectiveness of untargeted fertiliser applications. Due to this immobility of soil P, very little arrives at the root surface in the transpiration stream: a crop which transpires a typical 370 mm of water during its life will only receive ~1 kg ha^{-1} P from the soil solution. Consequently P uptake depends on creation of a concentration gradient through continuing active P uptake at the root surface. The capacity of roots to generate a concentration gradient (Tinker & Nye, 2000) indicates that mean root length densities required to access all available soil P are about an order of magnitude larger than those needed to capture water and N (van Noordwijk, 1983). However, rather than being related to root length (Otani & Ae, 1996) P uptake may depend more on new root growth (Yanai, 1994) or other mechanisms that increase available P close to the root surface; certainly, to grow successfully, plants have evolved various additional ways of increasing soil P capture (Ramaekers *et al*., 2010; White & Hammond, 2004):

- Soil exploration: by increased branching and root hair formation, the surface area of the root system is maximised, not only to explore the soil volume more effectively but also to exploit any localized patches of high P availability (Lynch & Brown 2001; White *et al*., 2005).
- Endo-symbiotic associations with arbuscular mycorrhizae increase the plant's ability to explore the soil volume and mobilize P from inorganic and organic sources (Smith *et al*., 2011)
- active uptake mechanisms (e.g. P transporter systems)
- exudation of organic acids to mobilize Pi from inorganic P sources (Walker *et al*., 2003)
- exudation of phosphatase enzymes to mobilize Pi from organic P sources (Li *et al*., 1997).

Annual plants appear particularly vulnerable to P deficiency in the early stages of growth before they establish an effective root system. Seed stores of P as phytate (Raboy, 2009) can satisfy requirements over the initial stages of seedling establishment. Thus in solution culture Brechley (1929) found that the critical time period for external P supply to barley was from the 2nd to 4th weeks after sowing, before P requirement was fully satisfied (week 6). In these control conditions, restricted P supply after the 6th week had no influence on number of heads produced. In field conditions many additional factors influence the plant's capacity for P uptake, nevertheless it is generally during the early stages that a readily available source of P is found to be most critical (Grant *et al*. (2001)).

One of the few detailed studies of rooting by winter wheat (Figure 7) shows how root length follows an exponential pattern; roots are largely restricted to surface layers and extend slowly during autumn and the overwinter period, but faster exploration of deeper soil layers coincides with increased shoot growth in spring and summer.

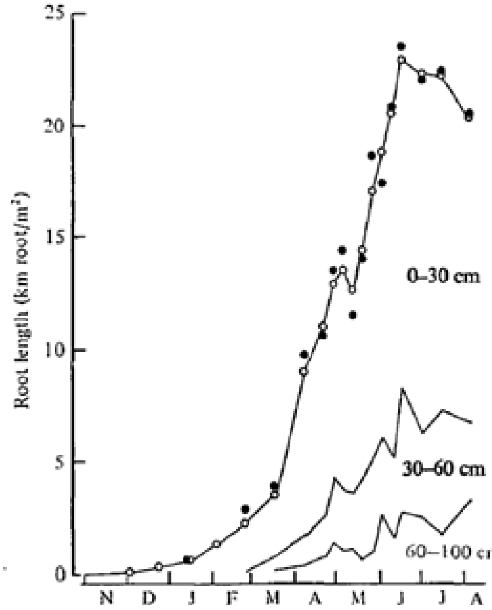

Figure 7. Cumulative measured (●) and smoothed (○) total root lengths of winter wheat for three soil layers (from Gregory et al., 1979a).

P influxes through root surfaces have proved difficult to quantify, partly due to the difficulties in measuring effective root surfaces. For instance values for field-grown wheat were estimated by Barraclough (1986) as being an order of magnitude less than those estimated for young plants in controlled conditions by Brewster & Tinker (1972). Hence the quantity of root necessary for satisfactory P uptake has proved difficult to specify with any confidence.

Nevertheless, different P acquisition strategies must have different attendant costs and benefits, the best balance of which will depend on the particular soil and aerial environment in which a plant grows, hence different strategies have evolved across the plant genera. These different mechanisms are all apparent in cropped species, but the managed environments in which crops are now grown, particularly with the relatively recent availability of inorganic fertilisers, may well have given rise to non-optimal P acquisition strategies for modern cropping systems. Thus P acquisition strategies are potentially open to manipulation and modification for improvement of efficiency of crop P nutrition.

6.3. Field factors influencing P availability

Greenwood *et al.* (2001) describe a complex model which takes into account factors such as the large spatial variation in soil P concentrations that can develop over time in agricultural soils. Various factors can contribute to this variability: broadcasting of fertilisers increases top soil P, placement increases lateral variability, ploughing inverts topsoils, and minimal cultivation decreases mixing. Available P in subsoils generally contrasts with P in topsoils, migration and root transfer to depth being slow. Thus the general pattern of root development for annual species is initially to explore soil with a high P status but a frequently low moisture content, but subsequently to explore soil with a lower-P status but a more commonly high moisture content. However, various additional complicating effects are noted in the literature; for example:

- Ma *et al.* (2007) used a layered soil culture system in glasshouse conditions to investigate effects of water, P & K in upper and lower soil layers. They noted greater reductions in shoot and root growth with a -P/wet than a +P/dry upper soil treatment. Also, root growth was stimulated and plants took up more P and K if the two nutrients were supplied together rather than separately.
- Another glasshouse study on wheat noted an increase in soil water around a P fertiliser band in the topsoil. Apparently the mechanism involved taking up water from the wet subsoil and releasing it into the dry topsoil during the night; as a result, P uptake in the dry topsoil and plant growth were increased (Valizadeh *et al.,* 2003). In the layered pot, roots apparently bridged hydraulically between the upper soil (low water potential) and the lower soil (high water potential) layers (Matzner & Richards 1996; Caldwell *et al.* 1998; Valizadeh *et al.* 2003; Huang 1999), possibly assisted by release of root exudates.

Generally, P is less soluble at lower temperatures and this is important because crops are often sown into cold soils, but it is difficult to distinguish between temperature effects on solubility and on rooting (Sheppard & Racz 1984). Grant *et al.* (2001) suggest that in an agronomic context fresh fertiliser P is less available at lower spring temperatures, increasing the significance of native soil P. However, Sheppard & Racz (1985) showed that at 10°C plants produced more root and shoot dry matter with band-applied P than with the same amount of P broadcast; at higher temperatures (>20°C) plants in the banded soil showed P toxicity.

6.4. Crop responses to applied P

Responses of crops to applied P are commonly tested by experiments conducted over several years because single year experiments do not assess the residual value of the P applications. Figs. 8 & 9 show example responses of winter wheat and winter barley to applied TSP from the long-term experiments at Saxmundham, Suffolk (treatments maintained with modifications for 83 years; Johnston & Poulton, 2011) and Padstow, Cornwall (treatments maintained for >22 years; Richards *et al*. 1998) respectively. Interpretation of multi-year trials is more complex than interpretation of single year effects because results are commonly derived from a rotation of crops, and because the life of the experiment may be insufficient to establish equilibrium STP levels.

Nevertheless, once mean crop output data have been collated over years, crop P requirements have generally been defined according to ‘critical’ levels of STP or annual applied P that maintain 95% or 98% of mean maximum crop yield. In the cases of Saxmundham (Figure 8) and Padstow (Figure 9) economic optima were determined by valuing TSP-P at £0.75 per kg P_2O_5 and grain at £150 per tonne; Olsens’s P was valued at £10/mg/kg/year, based on these prices of grain and

TSP, quantities of TSP-P required to run down or build up soil P, and a half-life of Olsen's P of 9 years (Johnston & Poulton, 2001). Economic optimum P is defined as the annual P application that maximises the average economic margin of crop output over fertiliser input (it is determined by fitting a curve that best describes the response in mean crop yields to mean P applied, and finding the P amount that gives a response equivalent to the P:grain price 'break-even' ratio). Economic optima and critical levels of P cannot be determined with much certainty because the slopes of the responses typically change relatively little over the tested range, and responses and prices vary from year to year. It may be worth exploring further a method of valuing Olsen's P economically, so that the criteria for defining crop P requirements can be less arbitrary than choosing the amount giving 95% or 98% of maximum yield, as at present.

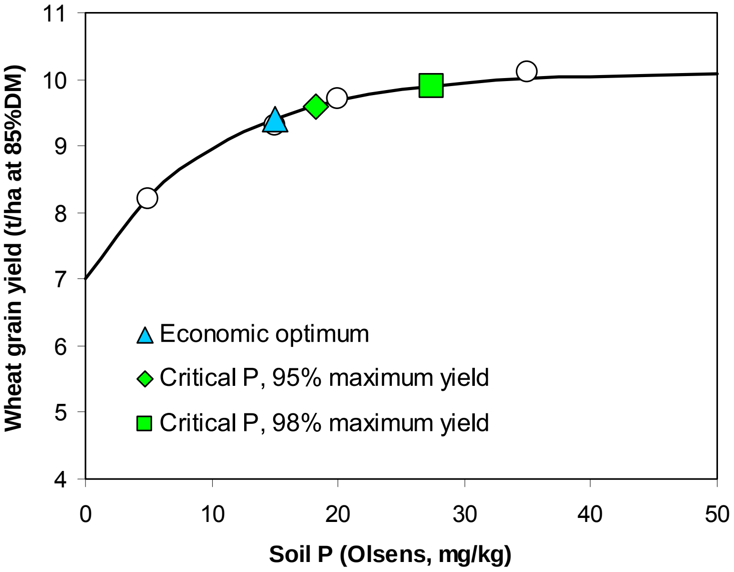

Figure 8. Effect of Olsen's STP on grain yield of winter wheat after winter beans at Saxmundham, Suffolk in 1982. Data (open circles) are taken from Johnston & Poulton (2011; their Figure 8) and an exponential curve fitted allowing critical (green) and economic optimum (blue) soil P levels to be estimated.

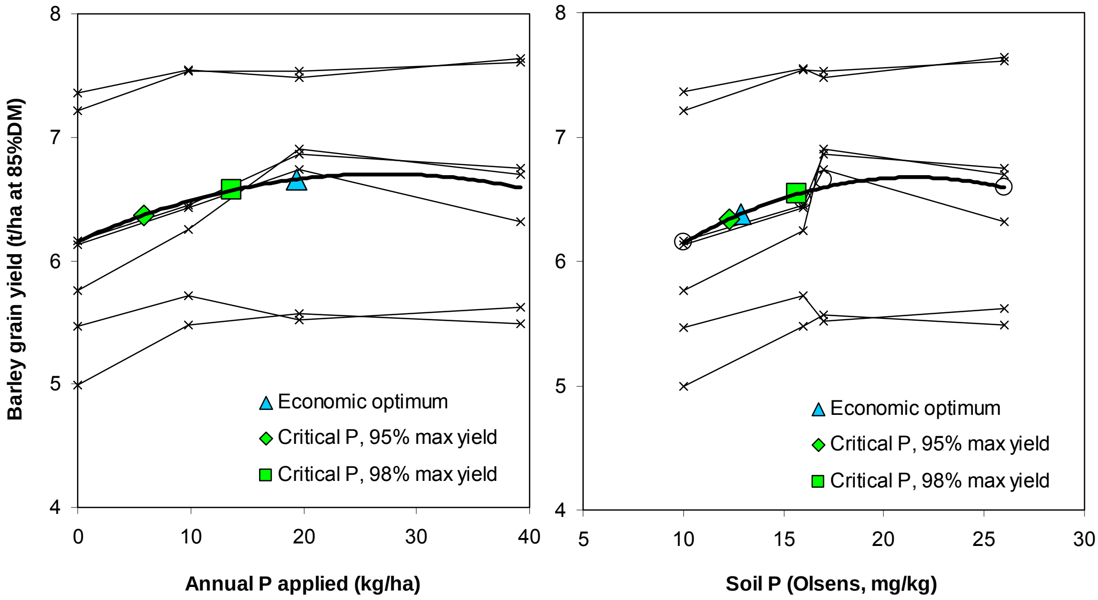

Figure 9. Effect of annual P applications on grain yield of continuous winter barley at Padstow, Cornwall from 1989 to 1996. Data (crosses) are taken from Richards et al. (1998) and a quadratic curve fitted to the means (bold line) allowing critical (green) and economic optimum (blue triangle) values to be estimated for both annual P applied and the levels of Olsen's topsoil P (0-20cm), as observed in 1996.

7. P use efficiency in UK arable crops

P use efficiency is generally understood as a ratio of crop output to nutrient input; however, many different measures of crop output are used and nutrient inputs can also be considered differently, for instance as applied nutrient or as total nutrient (soil plus applied fertiliser and manure) (White & Hammond, 2008, Rose & Wussuwa, 2012). Syers *et al.* (2008) identified five methods that have been used to calculate P use efficiency, as follows:

- ***Direct fertiliser recovery*** – measures the proportion of applied P taken up by the crop using radioisotopes (e.g. ^{33}P- or ^{32}P-labelled) in the year of application (or less commonly across a rotation).
- ***Fertiliser recovery by Difference*** – assumes that the difference in P uptake between crops receiving P and not receiving P is the amount of the applied P that is utilised by the crop. When expressed as a proportion of the total amount of P applied, this method gives a measure of 'apparent recovery' and is the most commonly used measure of P-use efficiency.
- ***Fertiliser recovery by Balance*** – the total P in the crop divided by the total P applied. This method attempts to take into account the role of annual P fertiliser dressings in maintaining the amounts of residual P in the soil.
- ***Partial factor productivity index*** – is the kilograms of product (yield) produced per kilogram of P available. It is the product of P capture efficiency (P uptake per unit of total nutrient available) and P conversion efficiency (crop yield per unit of P uptake).

- ***Physiological efficiency index*** – relates to the effectiveness of fertiliser, and is calculated as the difference in crop yield with and without P fertiliser divided by the difference in P uptake with and without P fertiliser.

Here we choose only to consider efficiency in terms of nutrient recovery; we maintain that ratios involving crop biomass or saleable output have little utility where (as is almost always the case) concerns about crop productivity far exceed concerns about nutritional efficiency; as has been explained for N nutrition by Sylvester-Bradley & Kindred (2009), crop productivity and nutritional efficiency must both be considered but separately; a ratio between them serves no practical purpose because it maximises at low yield levels.

7.1. Defining recovery of P fertiliser

There has been recent debate (involving well respected researchers) about calculation and expression of the apparently simple term ‘P recovery’ (see Syers *et al*., 2008; Johnston & Curtin, 2012; Chein *et al*., 2012a; 2012b). The discussion concerns the validity and usefulness of two apparently simple approaches to its estimation:

Difference method: % recovery of fertilizer P = $[(U_p – U_o) /F_p] \times 100$ (1)
Balance method: % recovery of fertilizer P = $(U_p/F_p) \times 100$ (2)

Terms here are defined (Chein *et al.* 2012a) as: U_p, P uptake from soil treated with fertilizer P (i.e. fertilizer P + soil-P); U_o, P uptake from soil with no fertilizer P applied (soil-P), and F_p, the amount of fertilizer P applied. The two approaches are evidently distinguished by whether U_o is considered significant or not: the difference method considers that U_o is significant whereas the balance method does not.

Table 4. Mean total crop P harvested in 2 cycles of a 4-crop rotation of sugar beet, barley, potatoes, barley in the Saxmundham experiment in Suffolk, 1969-73 (after Syers *et al*. 2008)

	P harvested (kg/ha)		**P recovery (%)**	
P applied over 4 years (kg/ha)	**Olsen P 4 mg/kg**	**Olsen P 33 mg/kg**	**Olsen P 4 mg/kg**	**Olsen P 33 mg/kg**
0	23.3	75.2		
55	46.9	77.0	43%	3%
110	57.2	79.4	31%	4%
165	63.8	82.2	25%	4%

Given that P applications and crop P removals have clear residual effects over-and-above their immediate effects on the growing crop or the next crop to be grown, both approaches need to be considered over specified time periods, and the implications of previous and subsequent applications and cropping need to be recognised, as well as the immediate effects of each fertiliser application. In their thorough discussion of how to assess total efficiency of P use in agriculture Syers *et al*. (2008) advocate using the balance method in preference to the difference method, but they predicate this conclusion by saying *"if the existing level of plant-available P in the soil is to be maintained"*. In this review we are questioning whether existing levels of soil P must be maintained, and we are concerned to maximise recovery of inherent soil P, as well as fertiliser and manure P, thus it is essential that we consider the recoveries of soil P and fertiliser P separately. Also, as is shown by the Saxmundham experiment (Table 4), recoveries of applied P range from being large (up to 43%) where P supplies are deficient for crop growth to being small (3-4%) where P supplies are large. Thus in studying how P recoveries vary, it is important to recognise whether the P supply being tested gave near-optimal crop growth; comparisons that are relevant to commercial crop production need to be made where P supplies were approximately optimal.

In conclusion, the most valid test of P recoveries for our purposes here will be provided by treatments that have been maintained for many years, where soil P status and crop performance can be considered to have reached their equilibria for each treatment, and where the range of treatments straddles the economically optimum supply of P. Further analysis of long-term experiments meeting these criteria is recommended.

7.2. Examples of P fertiliser efficiencies

Syers *et al*. (2008) provide a review of crop P recoveries in some long-term P experiments where soils should have reached equilibrium levels. Although here is scope for a more extensive review of UK evidence, it has not been possible to complete this here because the necessary data for most of the experiments are not readily available, and because significant care is required to ensure that treatments in these experiments (which often change over time) provide a valid test. Potentially useful UK field experiments include the Broadbalk (Syers *et al*. 2008), Exhaustion Land (Johnston & Poulton 1977) and Agdell (experiments at Rothamsted, the Saxmundham (Rotation II) experiment in Suffolk, two experiments started in 1978 at Ropsley, Lincolnshire (Bhogal *et al*. 1996; Hatley, 1999) and the 28 year experiment at Padstow, Cornwall (Richards *et al.* 1998). Here we have examined just the Padstow experiment where total crop P and grain yield of winter barley were measured (Figure 10a), and the Exhaustion Land (Rothamsted) experiment where previously established soil P differences (from before 1901) were augmented for 7 years from 1986 by TSP applications to provide P applications from nil to 131 kg/ha per year (Figure 10b). In both these cases it is possible to calculate economically optimal P applications and so, by using fitted curves to interpolate between treatments, to compare recoveries of the optimum amounts of applied P.

Table 5. Mean total crop P at harvest of wheat receiving fertiliser N in the Broadbalk experiment at Rothamsted (after Syers *et al*. 2008)

	Nil P (or K)	**+ P**	**+ P + K**	**Mean P recovery (%)**
1852-1971	6.5	9.2	11.3	11%
1966-1967	4.8	11.0	12.0	19%
1970-1975	9.0	13.1	17.3	18%
1985-2000	5.7	12.7	17.4	27%

With respect to recovery of inherent soil P, crops at Rothamsted and Saxmundham (Figure 10b; Tables 4 and 5) have continued to take up 5-9 kg/ha P annually without addition of any fertiliser P or manure P since before the experiments began in the mid-19th century. This inherent P supply is presumably derived from weathering of soil parent materials, and can be regarded as ‘free P’. The large supply of 19 kg/ha from inherent soil P at Padstow (Figure 10a) is explained by the much larger levels of subsoil P at this site than on most soils (Figure 11; 17-27 mg/kg Olsen P). Even if this site as atypical in this respect, inherent soil P supplies appear to be generally significant in relation to optimal P requirements of most modern crops (20-30 kg/ha), and it is possible that a significant proportion of sites can mineralise enough soil P to supply the majority of crop requirements. Thus it would seem misleading to attribute these supplies to fertiliser P, as is implied when recoveries of fertiliser P are assessed by the balance method.

Recoveries of fertiliser P (estimated here for optimum applications using the difference method) at Rothamsted and Padstow were relatively similar and ranged from 10% to 16%, levels that agree well with Johnston & Poulton’s (2011) summary that the difference method often gives values in the range 10-15% (however it is unclear whether they were describing steady state conditions here, and whether they are just considering crops receiving economically optimal P supplies). Although these two experiments appeared best suited to assess P recoveries, it is possible that some of the unrecovered P may have been still contributing to trends in available soil P. However, the shortfall between optimum applications of P and their net effects on P recovered is so large that it calls into question the sustainability of current P nutrition strategy – it will be important to question more closely the fate of the 85-90% of applied P that appears normally to be unrecovered when employing the currently recommended P management strategy.

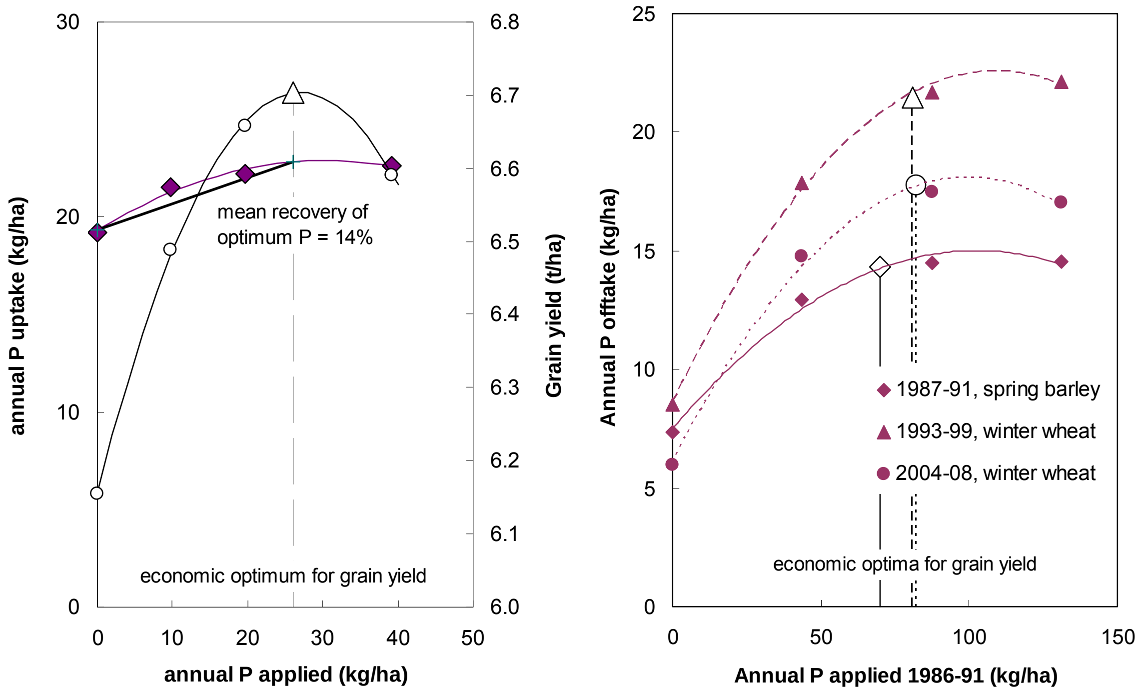

Figure 10. (a) Effect of P applied as TSP annually on mean grain yield (open circles) and total annual crop P uptake (purple diamonds) (1989-1996) of winter barley at Padstow, Cornwall (after Richards et al. 1998). (b) Effect of P applied as TSP annually (for 7 years following further differential P treatments since 1901) on P offtake by spring barley (1987-91; 10% P recovery), winter wheat (1993-99; 16% P recovery), and winter wheat (2004-8; 14.3% P recovery) on Exhaustion Land, Rothamsted (after Johnston & Poulton, 2011, their Table 2).

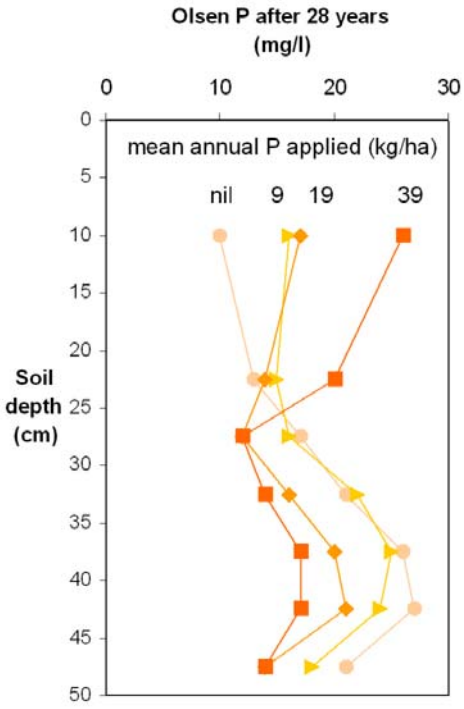

Figure 11. Effect of P applied annually as TSP for 28 years on soil P (Olsen's, mg/l) of topsoil and subsoil at Padstow, Cornwall. Note that SE per plot (d.f. 12) were large and increased with successive depths, being 1.5, 3.5, 7.7, 9.8, 11.9, 14.1 & 10.8 mg/l.
(after Richards et al., 1998)

8. Possible innovations in P use efficiency in UK arable crops

The three key objectives of applied research on crop P nutrition must be to (i) minimise crop P requirements, (ii) maximise root recovery of inherent soil P and (iii) use fertiliser technologies that meet the shortfall between these two quantities with as complete recovery as possible. The outcome of persisting with such P nutrition strategies that involve highly efficient ‘targeted’ fertilisers would be a gradual depletion of soil P supplies and increased reliance on fertiliser P. Thus the reliability of any P targeting technologies will be crucial to their successful adoption. The current strategy, which relies on soil P storage, contrasts with P-targeting in that it puts less dependence on P fertiliser efficiency; however, it must tend to be more expensive economically and environmentally, since P storage must cause some P fixation into irretrievable forms, and higher soil P concentrations will inevitably cause increased P losses to the environment. The optimum strategy is thus likely to be some form of compromise which uses targeted P applications, but does not become totally dependent on them. We will now consider prospects for innovation in each area.

8.1. Minimising crop P requirements

P deficient plants show responses that reduce reliance on ATP-mediated processes for metabolism and on phospholipids for cell membrane structure (Vance *et al*., 2003). With ample P supplies, the majority of P taken up by plants is stored in cell vacuoles as orthophosphate and polyphosphates (Schactman *et al*., 1998). This storage is probably an innate survival mechanism so that plants can remobilise stored P during periods of P shortage. In general, P uptake by crops relates to their biomass yield, but crop species and varieties show significant variation in biomass formed per unit of P (Greenwood *et al*., 2008; Hammond *et al*., 2009). Some of this variation probably relates to levels of P supply, and hence to the extent of P storage in plant tissues (Akhtar *et al*., 2008; White & Hammond, 2008; Richardson *et al*., 2011). Where P supply is supra-optimal, substantial P storage can occur. Hammond *et al*. (2009) found up to 5-fold variation in shoot P concentrations in Brassica crops grown at the same levels of P supply suggesting there is potential scope to breed for maximum yield at low critical tissue P concentrations. By analogy with work on crop N requirements (Sylvester-Bradley & Kindred, 2009), each crop genotype will show an optimum level of P supply which avoids P inhibition of metabolic processes but which minimises P storage. However, discovery of critical tissue P concentrations for crop genotypes will be more problematic than discovery of critical N concentrations because genotypes also show substantial variation in their capacity for P acquisition. Rose & Wissuwa (2012) suggest that reduced P storage should be targeted separately in root, shoot and grain, as each tissue exhibits different storage characteristics. In P-rich environments, tissue P and grain P concentrations are quite variable, which suggests there is potential to reduce crop P demands and hence to grow crops on low P soils without sacrificing yield.

Commercial plant breeders prioritise improvement of crop yield and quality, along with disease and lodging resistances; they have yet to address nutritional efficiency – all commercial breeding takes place with ample nutrient supplies. Inclusion of nutritional efficiency amongst their targets is likely to slow progress in breeding for existing objectives so will depend on easy identification of appropriate traits using genetic markers or other simple assays, and probably on some public support. Breeders have engaged in recent research to identify such traits for N nutrition (e.g. Sylvester-Bradley *et al*. 2010), and work is under way to develop appropriate variety testing methods for N efficiency (Kindred & Sylvester-Bradley 2010); however, the attempts to improve P efficiency have been more limited. Interest has focussed on the availability of mutants in cereal species with dramatically reduced phytate contents. When these are grown with ample P supplies total P content in the seed is not reduced as inorganic P increased at the expense of phytate (Figure 12).

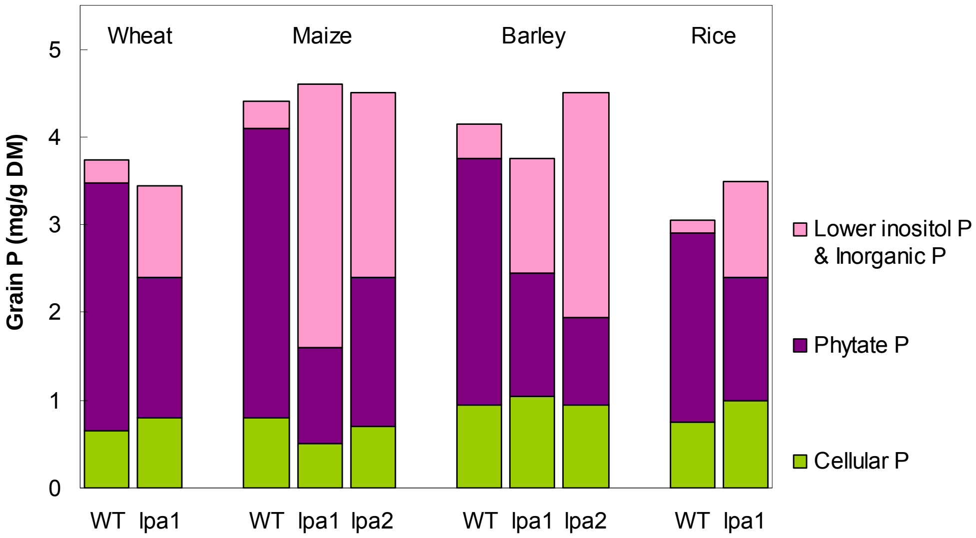

Figure 12. Seed P fractions in wild-type (WT) and low phytic-acid (lpa) iso-lines of wheat (Guttieri et al. 2004) and other cereal species (Raboy 2002).

A backcrossing programme attempted to introduce the low phytate trait, developed in the US (Raboy 2009), into UK elite wheat germplasm (HGCA 2010), but this work was not followed up, partly due to the difficulty in detecting the low phytate trait (the current approach is to detect increased inorganic P; S. Bentley pers. comm.). The main aim of this work was to improve nutritional value of the grain for pig and poultry production; reduced crop P requirements were not expected and poor adaptation of the available lines to UK conditions prevented an adequate test of whether the low phytate trait gave improved performance with low P supplies (M. Broadley, pers comm.), as might be expected. Given the likely potential of low phytate to reduce crop P requirements, it would seem worth seeking specific assays for phytate, or identifying genetic markers for the low phytate mutation, so that adapted lines with low phytate can be investigated for any tolerance of low soil P. In any case, in future it would seem important to maintain more field sites where germplasm can be compared with contrasting soil P supplies, so that P efficient germplasm can be detected more easily.

8.2. Maximising root recovery of inherent soil P

Richardson *et al*. (2011) identify three plant-based mechanisms for improving soil P acquisition and increasing the efficiency of P use: (a) adaptations to root architecture that enhance access to soil P; (b) enhancement of rhizosphere processes responsible for mobilising soil P; and as considered above (c) reducing the plant's demand for P. All three of these mechanisms vary greatly depending on crop genetics and soil and environmental conditions, so there is much scope to investigate how both breeding and management innovations might be used to achieve more efficient use of soil and applied P by arable crops (White and Hammond, 2008; Ryan *et al*., 2008; Rameakers *et al*., 2010; Sylvester-Bradley & Withers, 2012).

8.2.1. Adaptations to root architecture

Root architecture and its reaction to soil P availability have been shown to vary enormously between crop species and varieties. Root growth and development is hormone-regulated and greatly influenced by soil moisture, availability of oxygen and soil density (Vance *et al*., 2003). The main root traits linked positively to P uptake are root length density (e.g. primary roots), root branching (e.g. lateral roots, cluster roots), formation of aerenchyma and root hair formation, and these traits are expressed to varying degrees by crops growing naturally in low P environments (Figure 13). These traits are designed to either increase the root surface area in contact with the soil or to reduce the carbon cost of root extension (Lynch & Ho, 2005; Postma & Lynch, 2010). Roots tend to proliferate in soil regions with high soil P supply, and thereby increase P uptake (Lynch & Brown, 2001); proliferation commonly occurs in topsoils. Plasticity of root architecture provides an ability to 'forage' for P-rich zones in lower P environments; however high soil P supply probably inhibits root proliferation. Intensive plant breeding and testing have only occurred for a little over half a century. But since they have largely taken place with P-enriched topsoils and almost entirely without direct selection for rooting traits, it is unclear the extent to which modern high-yielding varieties have adapted their rooting characteristics to P-rich topsoils; it is possible that their rooting is excessive, encouraged by the high soil P levels, or that they have lost some foraging ability if they were to be grown in low P environments. Research is underway to identify the genes responsible for different rooting traits in different crops; some traits (e.g. lateral branching) have complex genetic controls whilst other traits (e.g. root hair formation) can be traced effectively by single genetic markers (Richardson *et al*., 2011). Root architecture in UK arable crops has been relatively little studied. Reynolds *et al*. (2001) suggested that root length density in the surface soil to be an important trait for soil P acquisition by wheat, however King *et al*. (2003) pointed out that more investment in subsoil rooting is needed for more effective capture of water and N. Hill *et al*. (2005) found that faster growing pasture grasses had a greater ability to forage for P and required less fertiliser to achieve their maximum growth rate. Hammond *et al*. (2009) found that large differences in P use efficiency in *Brassica oleracea* was positively related to differences in lateral root development and architecture. Aerenchyma (internal air channels formed when root cells coalesce) are generally associated with plant growth in anoxic (especially waterlogged) conditions, but they also appear to decrease the carbon cost of root extension in P-deficient conditions as well as drought (Postma & Lynch, 2011). There is considerable genetic variation in the capacity to form aerenchyma (Seago *et al*., 2005).

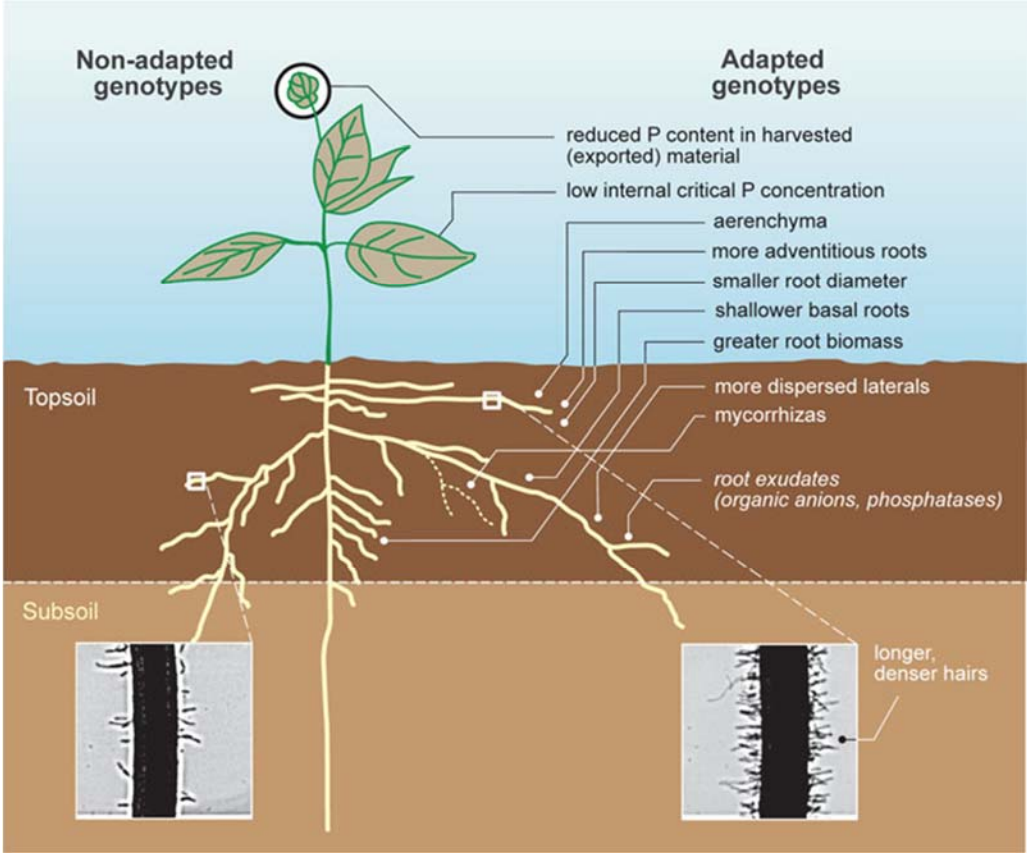

Figure 13. Schematic representation of root and shoot traits that provide adaptation of plants to low soil P (from Richardson et al. 2011, adapted from Lynch 2007).

Many crops (with the notable exception of the Brassicae) have arbuscular mycorrhizal (AM) associations that confer a significant increase in absorption of P through a hyphal mycelium that extends out from roots and root hairs (Bonfante & Genre, 2010). Their role appears principally to be one of extending the root system's surface area hence root-soil contact. AM possess high-affinity transporters in their hyphae and allow accumulation of inorganic P as polyphosphate-P; this P can be translocated rapidly to the host plant. Their beneficial effect on P uptake diminishes with increased soil P fertility, but nevertheless AM have an important role particularly in more sustainable farming systems that have less reliance on high soil P fertility (Richardson *et al*., 2011).

8.2.2. Enhancing P mobilization

Plants and the soil microbial community help to mobilise soil P by influencing the rhizosphere – an area of high biogeochemical activity surrounding the root that is induced by the release of C from plant roots into the surrounding soil (Hinsinger, 2001; Jones *et al*., 2009). These C sources include exuded mucilage at the root tip and root exudates (glucose, amino acids and organic acids) lost passively from the root surface and rapidly utilized by the microbial community. Of importance for P uptake is the release of organic acids (citrate, malate and oxalate), ectoenzymes (phytase and phosphatase) and protons (H+ ions) by plants and microbes. Release of organic acids is increased in response to a shortage of P and this is the main mechanism of P mobilization in plants that develop cluster roots (Lambers *et al*., 2006). Since these organic acids (carboxylates) are rapidly degraded, it is unclear exactly what mechanism is responsible for increased P mobilization, but it is thought that they occupy adsorption sites that might otherwise bind P or substitute for P in precipitates with Fe, Al and Ca (Richardson *et al*., 2011). Release of extracellular enzymes (i.e. phosphatases that can mineralise various soil organic P forms to orthophosphate for uptake by the plant) into the rhizosphere occurs in response to a depletion of P in the soil solution. George *et al*. (2008) found that wheat cultivars exhibited a two-fold variation in phosphatase activity, although this variation did not apparently influence plant P uptake from soil. Bacteria and non-mycorrhizal fungi also release phytases that mineralise more recalcitrant phytates in soils. Plants and microbes increase rhizosphere acidity through the release of protons which is considered to mobilise more occluded forms of soil P such as apatite (Hinsinger, 2001). Positive effects of bio-innoculants (specific bacteria and fungi) that can mobilise inorganic and organic P compounds have been obtained in controlled laboratory studies, but have been less effective under field conditions (Richardson *et al*., 2011). This may reflect competitive effects between innate and introduced microbial communities; futher research is needed to identify which P mobilising species is most suitable for which conditions (Ryan *et al*., 2008).

Plant P uptake is controlled by specific combinations of transporter proteins that enable P transport from the soil (low P concentration) into the root (very high P concentration) and subsequent distribution through the plant (Bucher, 2007). There is variation in P transporter proteins, and genetic markers for specific proteins have been identified, but their combination does not appear to confer a marked improvement in P uptake (Richardson *et al*., 2009). Perhaps the rate limiting step in P capture is more often the exploration and mobilisation of P in the soil, rather than the process of uptake into the root.

P-solubilising microbes (PSM) appear to be common in natural conditions and can be shown to act *in vitro*; however, their performance in soil has been contradictory. They work through production of organic acids (succinic, citric and formic) that attack and dissolve soil phosphates, converting the P to bio-available forms. Organic acids have been used in industrial refinement of RP for selective removal of accessory minerals such as carbonates (Ashraf *et al.* 2005). However, variable performance of PSM has restricted any large-scale application in sustainable agriculture (Khan *et al.* 2007). Potential technical solutions include those where conditions are optimised through biotechnological advances, such as selective screening for P-solubilizing activity (e.g. Harris 2006), and molecular techniques including genetic modification (Rodriguez *et al*., 2006). Commercially available products include Jumpstart™ that contains *Penicillium bilaiane*, whose excretion of H^+ and organic acid anions induce complexing of Ca^{2+} and P mineral dissolution.

8.3. Maximising recovery of applied P

A number of innovative fertiliser products are now on the market or being developed that attempt either to supply P more evenly through the growing season, reduce the fixation of P by soil constituents, or recycle P in wastes. Novel or unusual methods of P application (which may also involve N) include seed dressings, soil placement and foliar applications. Further options include combinations of product types and methods of application. Ultimately it should be possible for crop P demand to be met through a combination of supply from 'native' soil resources together with a variable but timely contribution from various freshly applied fertiliser products. Similarly, it should be feasible to reduce the amount of freshly-applied P by targeting fertiliser type and method so that a greater proportion of applied P is recovered.

8.3.1. Amendment of soluble P fertilisers

The high-analysis fertilisers (e.g. ammonium phosphates, triple-superphosphate) that are used predominantly at present dissolve readily into highly acidic saturated solutions, even under low soil moisture conditions (Sample *et al*., 1980; Sims & Sharpley, 2005). These solutions gradually diffuse into, and react with, soil constituents to form various precipitation products of Fe, Al, and Ca (depending on soil pH and soil type), from which P becomes available for adsorption through gradual dissolution. Solid and liquid ammonium phosphate fertilisers generally precipitate less P at the application site than mono-calcium based fertilisers and in a solid form they dissolve more rapidly (Nash *et al*., 2003). Depending on soil properties, rapidly released P may also become quickly immobilised by inorganic (adsorption) or organic (microbial activity) processes, reducing the opportunity for P uptake by crops. Where this occurs, fertilisers that inhibit this immobilization (e.g. AVAIL), or release orthophosphate more slowly (e.g. Struvite) may be beneficial (Hedley *et al*., 1995; Rajan *et al*., 1994).

8.3.2. Reducing fixation – amendment with AVAIL or Bauxsol

AVAIL is a dicarboxylic co-polymer used to coat granular phosphate fertilisers or to mix into liquid phosphate fertilisers. The polymer is a high-charge density polymer (cation exchange capacity of approximately 1,800 meq / 100 g) that is reported to sequester multivalent cations that would normally form insoluble precipitates with P fertiliser thus creating a zone of access and higher P availability, allowing more P to be taken up and used by plants. There is also the possibility of complexing potentially toxic Al^{3+} ions under acidic soil conditions. The mechanisms associated with AVAIL appear to include a combination of limiting the soil reactions through formation of secondary precipitates while also reducing the adsorption of soluble P by soil, although the degree to which this happens has been questioned by Degryse *et al*. (2013). Varying the coating thickness has also been demonstrated to modify the dissolution of TSP (Murphy & Sanders, 2007). Table 4 shows the effects of AVAIL treatment on MAP; benefits appear to be greater when AVAIL treated P was band applied, as opposed to broadcast (Sanders *et al*., 2004). Extractable P and soil solution P may increase in AVAIL treated soils, but there are doubts about its capacity to complex sufficient cations (Osmond *et al*., 2008; Karamanos & Puurveen 2011).

AVAIL has been tested with a wide range of crop types, soil and management situations with results varying from clear benefits (yield and or P concentration of potatoes, rice, soybean; Ellison *et al*., 2009; corn and soybean Gordon, 2005) to no significant difference (fescue on a low P soil, Murdock *et al*., 2007; bermudagrass Stewart *et al*., 2009; corn and wheat, Ward *et al*., 2010).

Table 4. Effects of the polymer AVAIL and P application method on wheat yields in Arkansas (Sanders *et al*., 2004); all P treatments were 15 kg/ha P; soil P low; soil pH 7.6.

Treatment	Grain yield (bushels / acre)
Control	46.7
MAP banded	54.7
MAP + polymer, banded	76.9
MAP broadcast	58.2
MAP + polymer, broadcast	65.6
MAP + seed, broadcast	55.1
MAP + polymer + seed, broadcast	68.3
LSD (0.05)	7.5

Bauxsol is a high pH by-product of the Bauxite mining industry that contains Fe and Al. Addition of small amounts of Bauxsol to highly water-soluble fertilisers has the potential to both slow down the rates of fertiliser-P release (by binding to Fe & Al) and buffer the extreme acidity that normally develops around a dissolving fertiliser granule, thereby reducing rates of P fixation and enhancing P availability to the crop.

8.3.3. Enhanced solubility – Ground rock phosphate and micronized sulphur

Mixing micronized sulphur with rock phosphate plus aims to enhance solubility of mineral phosphate through manipulating the local conditions within the soil (i.e. increasing acidity). There has been a long established link between the chemistries of phosphate and sulphate in soil science (Lipman and McLean, 1916). A good example of this is the common use of phosphate as an extractant for sulphate. One of the mechanisms involved in the combined rock phosphate and sulphur material might relate to competition between sulphate and phosphate for sorption sites. It is likely that the oxidation of sulphur to sulphate (requiring the presence of oxidizing bacteria, which may be native or inoculated) and the accompanying localized acidification that is more important. This product has the advantage of using materials that are acceptable to organic agriculture. Australian studies indicate that the required amount of S was reduced in more acidic soils; S was also was more effective in situations with higher rainfall (Evans & Price, 2006; Evans *et al*., 2009).

8.3.4. Recycled P – Struvite

Struvite [$(NH_4)MgPO_4 \cdot 6(H_2O)$] can be precipitated from effluent derived from a wide range of origins and contains 12.6%, 9.9% and 5.7% P, Mg and N respectively (Table 5). Struvite has been suggested as a potential source of these nutrients for a considerable period of time. However, the general term ‘struvite’ encompasses a material having a wide range of physical and chemical properties which are likely to influence its dissolution and consequently its reliability to deliver plant available nutrients. For example, evidence on the nature of dissolution is conflicting; Taylor *et al*. (1963) suggest that it forms a precipitate of tri-magnesium phosphate which remains poorly soluble in water but soluble in weak mineral acids whereas Bridger *et al*. (1962) suggest that both forms of magnesium ammonium phosphate (MgAP; Table 5) are only slightly soluble in water but that the MgAP hexahydrate is 100% soluble in ammonium citrate (Table 6).

Technology to recover P from wastewater streams at sewage treatment works (STW) in the form of struvite (ammonium magnesium phosphate) has advanced significantly in recent years and a commercially viable fertiliser product derived from the Ostara process is now sold and used in North America. The Ostara product has a N-P-Mg composition of 5:28:10 and is free of pathogens and metals. Severn Trent Water (STW) have recently made a pilot plant for struvite recovery operational, using the same process, and other water companies have plans to expand nutrient recovery. A recent DEFRA-funded project (HRI, 2008) calculated that struvite could supply 44% of the fertiliser P requirements of Great Britain if all the P arriving at STW could be recovered. Although struvite recovery will only be an option for some water companies, and recovery would not be 100%, struvite represents a potential way of reducing dependence on finite rock phosphate supplies, while also reducing direct losses of soil P to the wider environment. If the agronomic value of struvite can be demonstrated then P recovery might be adopted more widely by the water industry.

Table 5. Theoretical composition of magnesium ammonium phosphates (taken from Bridger *et al*. 1962).

Compound	Molecular weight	N (%)	P (%)	Mg (%)
$MgNH_4PO_4.6H_2O$	245.4	5.71	12.6	9.91
$MgNH_4PO_4.H_2O$	155.4	9 02	19.9	15.65

Table 6. Solubility of $MgKPO_4.6H_2O$ in various solvents (from Salutsky & Steiger, 1964).

	$MgKPO_4.6H_2O$ (Mmoles per litre)		
Solvent	**K**	**Mg**	**P**
Water	8 .5	0.08	3.1
0.001 N-HCl	9.2	0.12	4.1
0.01N HC1	27.5	0.93	10.1
0.001N NaOH	7 .7	<0.08	3.9
0.0l N NaOH	9 .8	<0.08	5.8

Owing to its low solubility in pH neutral solutions, struvite is considered a slow-release fertiliser with the possible advantage that it does not ‘‘burn’’ roots when over applied (Shu *et al*., 2006). Whilst there is a considerable body of literature describing conditions required for precipitation of struvite, there appears to be confusion surrounding the actual agronomic testing of struvite, perhaps best summarised by a recent paragraph taken from Gell *et al*. (2011):

> *‘Struvite has been widely cited in wastewater treatment literature as a good P-fertiliser, and often as a slow-release fertiliser, however, there is limited basis for this claim. P fertilisers are commonly divided into soluble forms such as triple super phosphate, and slightly soluble forms such as rock phosphate. Struvite does not readily fit into either category since it has low solubility (Ronteltap et al., 2007b) but can decompose quickly to soluble fertilisers (Cabeza Perez et al., 2009; Johnston & Richards, 2003).’*

Early studies involving struvite (Owen *et al*., 1964) reported greater dissolution (measured mainly as a change in soluble N content) of MgAP monohydrate in acid soil, at increased levels of soil moisture and, interestingly, where nitrification occurs. These authors suggested surface applications resulted in a slower release of N than from normal fertilisers. Also particle size (through surface area) introduced an additional complication. Adding an ammonium sink, such as ion-exchange resin, or stimulating nitrification, reduced ammonium concentrations in solution and stimulated solubilisation of struvite. Bridger *et al*. (1962) indicated that MgAP monohydrate is hydrated to the (less soluble) hexahydrate in soil. Experimental use of nitrification inhibitors, sterile soil, and varying temperatures support the theory that nitrification of ammonia may be useful in enhancing P release from Struvite.

Many pot and field experiments (Table 7) using various forms of struvite have shown that, although having a very low water solubility, the availability of their P to crops can, under certain conditions, be equivalent to or better than that of water-soluble triple-superphosphate (Johnston & Richards, 2003; HRI, 2008; Cabeza Perez *et al*., 2009). It is unclear why struvite is apparently so effective or, conversely, under what site conditions it would be ineffective. Some studies choose to optimise conditions in order to favour struvite dissolution e.g. maximizing particle surface area by powdering the material (Johnston & Richards, 2003) and ensuring a saturated soil moisture regime. Other factors such as background soil concentrations of ammonium and magnesium will also influence dissolution rates again making direct extrapolation difficult; e.g. Johnston & Richards (2003) applied large amounts of N (~1000 kg/ha equivalent) as ammonium nitrate and dressings of Mg (as $MgSO_4$).

A pot study (Kern *et al*., 2008) using a sand/perlite mixture with 50 mg P/pot added as struvite (the same as struvite No 6 in Johnston & Richards, 2003) indicateded that 3.5% of the total P in struvite was immediately water soluble. Analysis of wheat and maize plants after 53 days suggested 66 and 86% of the P applied had been taken-up, and therefore solubilised, demonstrating a clear potential for struvite to be utilised. However, it is likely that most ‘field’ conditions will provide less than optimum conditions for struvite-P release over at least part of the growing season and direct extrapolation from controlled pot experiments is difficult. However, a synthesised struvite in powder form added to soil with a medium to very high P status (Olsen Index 3-9; Defra 2008) caused an early growth response in potatoes (struvite-treated crops had higher tissue weights and N contents than those supplied with an equivalent amount of TSP) but there were no differences in final commercial yields between equivalent treatments.

Table 7. Summary of experiments using struvite, taken from Gell *et al*. (2011).

Citation	**Year**	**Type**	**Crop**	**Struvite source**	**Crop improvement (%) ***		
Bridger *et al*.	1962	Pot	Herbaceous flowers, tomatoes	USA, Chemical reagents	0-100	NR	SOL
Bridger *et al*.	1962	Field	Shrubs, grasses	USA, Chemical reagents	40-75	NR	
Teman & Taylor	1965	Pot	Maize	USA, Chemical reagents	40	SS	
Ghosh *et al*	1996	Pot	Chickpea, gram	India, Chemical reagents	50	SS	SOL
Goto	1998	Pot	Komatsuma, green vegetables	Japan, recovered struvite	50	SS	SOL
Johnston & Richards	2003	Pot	Ryegrass	UK, Chemical reagents	100	SS	SOL

Citation	Year	Type	Crop	Struvite source	Crop improvement (%) *		
Johnston & Richards	2003	Pot	Ryegrass	Japanese sewage, and Dutch sewage & manure	100	SS	SOL
Johnston & Richards	2003	Pot	Ryegrass	Spanish red dye liquor, US corn liquor	100	SS	SOL
Li & Zaho	2003	Pot	Cabbage, chard, spinach	Hong Kong, landfill leachate	>100	SS	
Rőmer	2006	Pot	Ryegrass	German and USA manure	>100	SS	SOL
Rőmer	2006	Pot	Ryegrass	German, Italian, and Japanese sewage	>100	SS	SOL
Gonzalez Ponce & Lopez-de-Sa	2007	Pot	Perennial ryegrass	Spain, municipal wastewater		SS	>SOL
Montag *et al*	2007	Pot	Unspecified	Germany, sewage sludge		NR	SOL
Plaza *et al*	2007	Pot	Ryegrass	Spain, municipal wastewater	>100	SS	SOL
Ganrot *et al*	2007	Pot	Wheat	Sweden, human urine, also included zeolites	30-100	SS	
Ponce & Lopez-de-Sa	2008	Pot	White lupine	Spain, municipal wastewater		NR	SOL
Cabeza Perez *et al*.	2009	Pot	Maize	Germany, sewage sludge	25-100	SS	SOL
Cabeza Perez *et al*.	2009	field	Rapeseed and winter barley	Germany, sewage sludge	0-40	NS	SOL
DVL	2009	field	Flowers, potatoes, Brussels sprouts	Netherlands, potato wastewater		NR	
Massey *et al*.	2009	Pot	Spring wheat	USA, dairy waste and process	<25	SS	<SOL
Gonzalez ponz *et al*	2009	Pot	Lettuce	Spain, municipal wastewater		SS	SOL
Weinfurtner *et al*.	2009	Pot	Maize	Germany, sewage sludge	20-100	SS	SOL
Yetilmezsoy & Sapci-Zwngin	2009	Pot	Purslane, cress, grass	Turkey, digested poultry manure	>100	NR	
Present study	2010	field	Maize	Netherlands, urine and black water	<30	NS	SOL

*number refers to % improvement over control in P-uptake and/or yield; SS = improvement is statistically significant; NS = improvement is not statistically significant; NR = statistics not reported; SOL = comparable to soluble fertiliser

8.3.5. Placement of fertiliser P

Placement of fertiliser P (and N) either with the seed, or as a concentrated band at some variable distance adjacent to or below the seed, has been shown to benefit early season root development, enhance crop yield and P uptake on low P status soils (MAFF, 1965; Withers, 1999; Grant *et al*., 2001; McLaughlin *et al*., 2011). Early studies by Crowther (1945) and Cooke & Widdowson (1956) on P-responsive soils showed large cereal yield increases (0.6-0.75 t/ha) from combine drilling P fertiliser. Devine *et al.* (1964) describe a large number of field experiments for spring wheat and barley across the main cereal growing areas of Britain and at that time concluded that combine drilled P gave higher mean yields than broadcast on soils with a low P status (using 1% citric acid) but there was little difference between application method on soils having a higher P status. Wager *et al*. (1986) showed that annual seed-placed applications of 10 and 20 kg P ha^{-1} gave average increases in wheat yield and P uptake similar to broadcast applications of 40 kg P ha^{-1}. This confirms early data from Scotland suggesting combined-drilled P is twice as effective as broadcast P (DAFS, 1956). The greater P use efficiency associated with placed P fertiliser is considered to be due to a reduction in the soil volume in contact with the fertiliser, thereby reducing soil immobilisation effects. At low soil temperatures, a high P concentration close to the developing root system will also increase P uptake and is probably a major reason why combine drilling is still widely practised in Scotland where cold short days can slow early root growth. However, placement close to the seed might inhibit germination or root development if too much P is applied (>20 kg P/ha). It should also be recognised that, depending on crop row width, P placement will probably increase variability in residual soil P concentrations, so will affect nutrition of subsequent crops (Grant *et al*., 2001).

Individual crops vary in their ability to exploit placed fertiliser. In one experiment, roots from 4 plant species were forced through an area of P concentration (to represent a banded application) ~100 times that of non-fertilized soil (Strong & Soper, 1974a & b). The order of increasing root zone proliferation was flax, wheat, buckwheat and rape (Table 8). The amount of ^{32}P recovered from the reaction zone was reduced when the availability of P in surrounding soil was increased (Strong & Soper, 1974b). A combined mechanism of increased root proliferation and increased rate at which the roots absorb P was suggested. Rape and buckwheat both appear to be able to make positive adjustments in root performance when they encounter zones of high P concentration. Differential ability of plant species to proliferate roots in zones of high P concentration may result in a variable ability of species to utilize banded P fertilizer effectively. More recently, Rose *et al.* (2009) also found that crops differ in root proliferation around P fertiliser placed either in the topsoil (5 cm) or in the subsoil (50 cm). However, the root proliferation was confined to P hotspots; root length and density above or below the zone were not increased. They concluded that the P placement at depth in the soil did not give any added advantage in avoiding surface drying.

Table 8. Apparent rates of P absorption by flax, wheat, rape and buckwheat roots from soil and from a simulated P reaction zone at three levels of P supply (dicalcium phosphate dihydrate, DPDH; Trt i, 40 mg ^{32}P-labelled DCPD applied to reaction zone; Trt ii, mixed DCPD at 50 mg P kg^{-1} to soil plus 40 mg ^{32}P-labelled DCPD applied to reaction zone; Trt iii, 200 mg P/kg to soil plus 40 mg ^{32}P-labelled DCPD applied to reaction zone). Data from Strong & Soper (1974b).

			P absorption rate from reaction zone (mg P/g root per day)		
Crop	**P source**	**Control**	**Treatment i**	**Treatment ii**	**Treatment iii**
Flax	Soil	0.66a	0.47a	0.81a	1.75b
	Reaction zone		2.69b	2.81b	1.56a
Wheat	Soil	0.59a	0.44a	1.03b	1.25b
	Reaction zone		5.53b	3.00a	1.66a
Rape	Soil	0.22a	0.22a	1.38b	1.66b
	Reaction zone		6.44b	5.94b	3.63a
Buckwheat	Soil	0.41a	0.38a	1.13b	1.84c
	Reaction zone		13.47b	8.84a	6.69a

Means of treatments followed by the same letter are not significantly different at P=0.05

8.3.6. Seed coating with P

The general P uptake profile and potential sources that contribute P for annual plant growth is presented schematically in Figure 14.

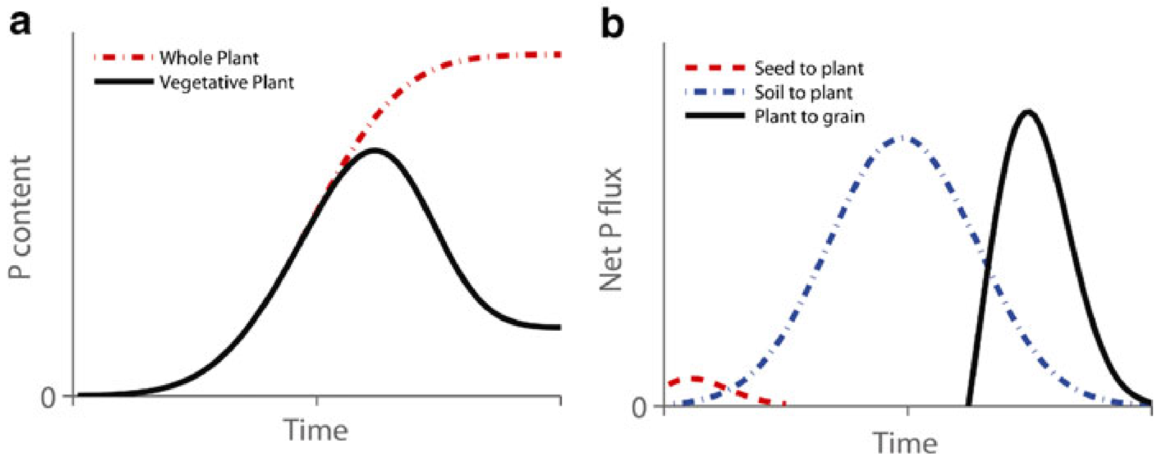

Figure 14. Schematic time course of (a) the P content (kg/ha) of an annual crop from germination to maturity and (b) net P fluxes (kg/ha/day) from seed and soil to plant tissues and from vegetative tissues to the seed (from White & Veneklaas, 2012).

There are three distinct phases of P nutrition of an annual crop (Figure 14b): (i) redistribution from phytate reserves in the seed for a couple of weeks after germination[1]. (ii) uptake from soil, depending on root growth and conditions for good root activity, and (iii) re-distribution to the generative organs (usually the seed). This P uptake profile will vary depending on the extent to which the particular genotype attempts to recycle P from generation to generation via the seed. The optimum green canopy of a cereal crop measures about 6 hectares per hectare (Sylvester-Bradley *et al*., 2008) and contains about 1.25 kg P per ha green leaf (2.5 mg / kg DM; 50g DM / m^2), so photosynthesis can be estimated as requiring only 7-8 kg P per ha land. This compares with 30 kg/ha uptake of P by a high-yielding wheat crop at flowering and 50 kg/ha P uptake by harvest. Thus most of the P requirement of conventional cereal crops appears to be driven by P to maintain structural tissues and P storage, first in the canopy and then in the grain. Each cereal seed contains about 0.2 mg P, or approximately 10% of that plant's photosynthetic P requirement. Addition of inorganic P (either as superphosphate or ammonium triphosphate) sufficient to fully satisfy photosynthetic P requirements would only increase the weight of the seed by 20%, might obviate the need for much plant P storage hence could reduce requirements for P fertilisers. However, such a stratagem would require joint innovation in both genetic composition of seeds as well as in artificial enhancement of seedling P supply after sowing.

A variety of approaches could be adopted to either improve the bioavailability and/or physical accessibility of P to seedlings; soaking seeds in nutrient solutions, coating seeds with nutrients, placing fertiliser products close to the seed or some combination of these.

The aim of seed coatings is to deliver nutrient supplies accurately and precisely to the plant, giving intimate contact with the seedling's developing root system whilst reducing fertiliser-soil interactions. Scott (1989) suggested that the effectiveness of nutrient containing seed coatings depends upon species sown, time of sowing (Watkin & Je Winch, 1974, cited in Scott, 1989), type of coating, soil fertility and soil texture. Scott & Blair (1988) tested mono- (MCP), di- (DCP) and tri-calcium phosphate (TCP) on alfalfa and *Phalaris* and demonstrated that the effectiveness of P seed coating increased with solubility of the material used. They achieved increases (relating to solubility) in P content, leaf number, biomass and yield. At 27 days after sowing heights of *Phalaris* plants grown with a 5 kg P/ha as a coating were equivalent to those that received 20 kg P/ha by drill or broadcast. There are likely to be interactions between product solubility and soil type, for example Terman *et al*. (1958) reported DCP to be more effective than MCP to ryegrass growing in

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[1] There is genetic variation here: Peltonen-Sainio *et al*. (2006) suggested that oat is more sensitive to soil P availability that wheat or barley because it hydrolyses its seed phytate less efficiently.

acid soils[2]. Ascher *et al*. (1989) reported that negative effects of MCP seed coating on time to first emergence and number of emerged plants of both sorghum and wheat showed a non-linear effect of soil clay content in the range 1-6%; negative effects were greatest in coarse textured soils. Table 8 gives a summary of various experiments reported in the literature.

Overall, it is clear that P seed coatings can enhance early growth, especially of herbage and fodder crops where the total above ground vegetation is periodically removed. However, responses have been more mixed with crops where final yields are largely determined later during crop development. Coatings can damage seedlings temporarily or permanently where excess salt concentrations are caused to develop in the vicinity of the seed, and there will be a balance between these negative effects and positive effects on early growth which will constrain amounts of P that can be applied in seed coatings. Thus, especially where seeds are small and few seeds are sown, it seems unlikely that the majority of crop P requirements could be met by seed coatings. In addition, P coatings may have a limited effective period because (i) due to root growth, the zone of active P uptake will move away from the seed zone and (ii) any coated P not taken up quickly will interact with soil and have its availability reduced.

Table 8. Summary of experiments that have employed P containing seed coatings.

Conditions	Crop	Treatment	Finding	Reference
Soil glasshouse	Corn	Coating $NaH_2PO_4.H_2O$ at 6 mg P / seed	Positive effect on yield compared to control.	Guttay *et al*. (1957)
Field, Finland, low P content	Oat cvs. Belinda and Fiia	Coating ~5 kg P / ha	Promoted early growth without increasing economic yield. Positive effects on some structural traits by some treatments; better biomass and grain set.	Peltonen-Sainio *et al*. (2006)
Acidic soils, dry land	Tropical grasses	10 mg NaH_2PO_4 per fascicle (up to ~2 mg P)	Increased germination, establishment and early growth on reseeding of existing pastures.	Silcock & Smith (1982)
Nutrient deficient soil	Tall fescue	MCP, DAP,APP, UP, AMP and NP	Most sources promising but lower P materials required thicker coatings giving possible impedance of germination.	Garrote *et al*. (1989)

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[2] Details of a commercial P dressing product, iSeed, developed by Yara, can be found at http://www.dlf.com/forage/Technical_info/iSeed/iSeed_overseeding.aspx

Conditions	Crop	Treatment	Finding	Reference
Glasshouse	Rice	RP, SSP, MAP or PP	RP quadrupled shoot and root growth. Emergence depressed by all other treatments until 40 DAS, then root and shoot dry weights increased.	Ros *et al*. (2000)
Field, Korea	Tall fescue, orchard grass, alfalfa, birdsfoot trefoil	MCP, TCP	Mixed results on early plant growth but TCP appeared to perform well over most species.	Kim *et al*. (2000)
?	Tobacco (3 cvs)	P seed coatings	Increased germination rate and time but no obvious effects on biomass or total root length.	Wang *et al*. (2009)
Pot experiment in Brazil on 2 soils, with high and low P	Soybean	Phytic acid, bicalcic phosphate @ 0, 0.7, 1.4 and 2.1 g / 100g seeds	Increased productivity with rate of P coating up to a maximum of 14% yield improvement.	Peske *et al*. (2009)
Central Lithuania	Winter wheat	P seed coatings +/- broadcast NPK	Reduced emergence, increased early growth, and affected quality traits but not grain yield.	Mašauskiene *et al*. (2007)
P limiting conditions (pot trial)	Pearl millet	125-500 g P / ha applied adjacent to seed at 5 DAS	Increased plant biomass	Valluru *et al*. (2010)

8.3.7. Foliar P

Foliar P applications are usually used to provide a small amount of often highly soluble P to actively growing crops to overcome a temporary P limitation or promote translocation of P to the developing seed or tuber. The potential for foliar P applications to substitute for much larger applications of soil-applied P has also been suggested (Alison *et al*., 2001). By targeting key physiological growth stages, the aim of foliar applications is usually to maximise utilisation while also minimising possible competition for P from soil processes. There is a considerable amount of related science on sprayer design, droplet size and adherence to leaf surface which greatly influences likely efficiencies of foliar applications (not reviewed here, but see Neumann, 2003, for a general overview). There are well documented examples where foliar applications are regularly recommended and others where timely applications have either improved final yield or improved final product quality (Table 9). The change from vegetative to reproductive growth stages is accompanied by a decrease in root growth and nutrient uptake and a need to translocate P in vegetative parts to the seed. Addition of foliar P during this change may delay premature senescence of leaves, prolong the time before photosynthesis stops, and provide resources for seed growth, especially under dry conditions (Sherchand & Paulsen, 1985; Benbella & Paulsen 1998).

In the 1980s ADAS tested whether phosphate sprays (providing some 2-3 kg/ha P) soon after tuber initiation could substitute for larger quantities of soil applied P on soils with high P reserves. Discounting the reduced residual effects of soil-applied P (as might apply to land leased for potato production) the saving in soil applied P (compared to the standard recommendation) was estimated to be 80-90%, depending on soil P index. However, results were insufficiently consistent for the technique to be adopted generally. Allison *et al*. (2001) considered that foliar P applications for potatoes must increase green leaf area and radiation absorption to affect on yields; applications must be effective before tuber initiation in order to increase tuber numbers. However, these authors could find few positive effects of foliar P on either tuber yield or tuber number in 6 experiments conducted between 1986 and 2000 and concluded there was very little evidence in the literature to support the use of foliar P.

Table 9. A summary of studies where foliar P has been tested.

Situation	Country	Form of P	Comments	Reference
Barley, field grown	India	Phosphate applied to leaves 70-80 days after sowing	Grain responses to foliar P especially for treatments that had initially received basal dressing	Afridi & Samiullah, (1973)
Potatoes, on farm	UK	No details	Applications of foliar P had no effect on number of tubers or tuber yield	Alison et al. (2001)
Field/ glasshouse, corn and soybean	USA	Condensed phosphates and P-N compounds	Mixed responses between crops and P forms. Control plants not deficient.	Barel & Black (1979)
Wheat	USA	5 to 10 kg KH_2PO_4 ha^{-1} (1.1 to 2.2 kg P ha^{-1}) applied after anthesis	Increased wheat grain yields by up to 1 t ha^{-1}.	Benbella & Paulsen (1998)

Situation	Country	Form of P	Comments	Reference
Subterranean clover, pot (sand) solution culture		Several P compounds with repeated applications including ^{32}P	Suggestion that >50% of ^{32}P applied was still on leaf surface 2 days after application. Concluded that foliar P had little scope to hasten recovery from P deficiency	Bouma (1969)
Sweet persimmon		^{32}P tagged fermented mono-calcium di-hydrogen phosphate	P uptake was higher on the underside of leaves; foliar P treatments improved fruit yield and quality.	Hossain & Ryu (2009)
Maize	USA	Various timing and rate (0, 2, 4, 6 and 8 kg P ha^{-1}) combinations of inorganic P	Foliar P could be used as an efficient P-management tool in corn when applied at the appropriate growth stage and rate	Girma et al. (2007)
Wheat grown in field on two soils with marginal P status	Australia	Ortho- and condensed P forms (labelled) at growth stage 39; 1.65 kg P ha^{-1}	Clear response on one soil but not on the other.	McBeath et al. (2011)
Winter wheat	USA	Foliar P applied (as KH_2PO_4) at 0, 1, 2 and 4 kg ha^{-1} that had received 0 or 30 kg ha^{-1} basal (as TSP)	Low rates of foliar P might correct mid-season P deficiency in winter wheat, and might give higher P use efficiencies than soil applications.	Mosali et al. (2006)

The key factors that control the optimal timing of foliar P applications to crops generally were summarised by Noack *et al*. (2010) as:

1. The degree of P deficiency as determined by tissue testing: a very P deficient crop will have limited potential to respond, while P sufficient crops will not be responsive;
2. Leaf area of crop: sets foliar P-uptake potential and depending on physiological age of crop sets photosynthetic potential for grain filling.
3. The physiological age of crop: the potential for yield improvement will decrease with increasing crop age (most likely diminishing beyond anthesis);

But effectiveness of foliar P is also dependent on soil water status, crop type, fertiliser formulation and prevailing climatic conditions (Noack *et al*., 2010). Examples of published information on foliar P are summarised in Table 9. A useful recent discussion of strategies for joint soil and foliar P application to winter wheat (in Australia) has been made by McBeath *et al*. (2011). The main advantages and limitations associated with P nutrition stratgeies involving foliar P are shown in Table 10.

Table 10. Advantages and limitations associated with foliar P application.

Advantages	Limitations
Flexibility in timing, rate and composition (multiple nutrients and specific chemical forms) of application to target specific growth stages or crops.	Requires knowledge of plant condition
Opportunity to correct deficiencies during growth	May require more than one application increasing the cost
Should be capable of achieving a high uptake efficiency	Possible interactions with other nutrients when added in a mixture
Reduces possibility of soil-fertiliser interactions that may restrict uptake	Some weather dependence for application
Should present an opportunity to maximise efficiency of freshly applied P and reduce environmental aspects.	May depend on interpretation of plant P concentrations (sap or leaf)

Much of the literature on foliar P does not address these issues adequately; we conclude that future R&D could usefully seek to:

1. understand the physiology of foliar P leaf retention, penetration and assimilation, possibly using tracer techniques;
2. Develop formulations, application methods, and timings that maximise crop recovery of and response to P, according to soil P status and crop P requirements;
3. Identify feasible combinations of P with other nutrients (in particular N) and the value of appropriate adjuvants.

9. Conclusions and Recommendations

Key issues raised in this review are summarised below, together with recommended actions (as bullet points):

1. Whilst it is unclear whether global P stocks will last more or less than two centuries, P reserves must be regarded as finite. In addition there are substantial economic and environmental costs associated with reliance on mined P, so reduced fertiliser P use through (i) reduced crop P demands, (ii) more efficient fertilisers and (iii) better use of soil P reserves is desirable, especially with a view to further sustainable intensification.

   - The research community should seek to develop reliable means for growers to treat soil P reserves as valuable and exploitable, for breeders to develop crops with lower P demands, and for fertiliser suppliers to provide more efficient fertilisers.
2. Improving the efficiency of P use from soil and fertiliser will compliment other aspects of sustainable P use including increased recovery and recycling of P in wastes and more integration of livestock and arable farming systems at the regional level. The current positive national 'land-surface' P balance obscures an average negative balance in the arable east, due to a larger positive average balance in the west, where most crop P is transferred for livestock production.
   - Farming systems and technologies should be investigated for their potential to achieve more uniform spatial distribution of excreted P.
3. UK arable farmers have more than halved their use of fertiliser P since the 1980s, and especially since 2005 in response to large price increases; no detectable shift in soil P status has yet been detected and consequent yield losses are not yet likely to have affected many crops, but whilst P inputs remain untargeted (broadcast; unsynchronised with crop uptake) and less than half of P offtakes, yield losses are increasingly likely.
4. Current fertiliser P recommendations largely rely on soil P storage rather than fresh P to optimise crop P supplies. This reliance results from poor capture of freshly-applied P by plant root systems and rapid immobilisation of plant-available P into less available forms in the soil matrix. Soil structure, moisture, temperature, pH and redox conditions can also constrain P supply from soil to root. Reduced reliance on soil P storage and more efficient targeting of fertiliser P represents a potentially more sustainable strategy to lessen our dependence on fertiliser P
5. Current P recommendations assume little or no P loss by fixation or leakage, they ignore the large inherent investment necessary to maintain recommended critical soil P levels (we estimate that interest costs of maintaining P Index 2 approximate to £15,000/year on a typical 400 ha farm3), and they are managed using soil P tests which provide poor repeatability and poor predictions of crop P responses, have not been adequately validated for modern cropping practices, and omit availability of organic P, subsoil P, and P acquired by crops from non-labile sources. Some inappropriate P use may arise through growers justifiably lacking confidence in current soil P tests; so there is much room for improvement here. (Note that this strategy has international adherence, yet is inappropriate for countries with poor access to fertilisers.)
   - On farms, soil test P (STP; e.g. Olsen) analysis should be treated as no more than an approximate guide to fertiliser requirements.

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[3] Assumptions here are that the capital P investment of raising Olsen's P in topsoil from 10 to 20 mg/kg costs 1000 kg/ha P_2O_5, equivalent to £0.3 million at £0.75/kg on 400 ha.

   - The role of soil P testing in P fertiliser recommendation systems needs to be re-evaluated as part of an international movement towards modernisation. Revalidation of current methods should also consider the most promising alternatives.
   - The contribution of subsoil P should be determined for the major crops in a range of soil types, and if significant, subsoil P levels should be surveyed.
6. Most P fertilisers are broadcast as simple inorganic salts (TSP, MAP, etc.) with the intention of maintaining soil P above critical levels. Critical levels have been set arbitrarily to achieve 95% or 98% of maximum yield, but the difference between these can be large, and they are poorly defined because of uncertainties in STP, insufficient long-term response experiments (which enable consideration of residual P effects), and small responses to fertiliser P in relation to experimental precision.
   - Means of defining economically optimum P use should be investigated and compared with definitions of critical P. Recommendations should then be made on how best to define optimal P use, recognising inevitable uncertainties in experimental data.
7. The balance method of assessing efficiency of fertiliser P use appears misleading because it discounts P contributions from non-labile soil sources. The most appropriate long-term studies for detecting P recovery indicate that soils release at least 5-9 kg/ha/year P without any fertiliser use. Using the difference method of determining net P recovery, crops grown with conventional technology only appear to acquire 10-15% of fertiliser P. Thus up to 85% or 90% of applied P appears to be unrecovered when employing the currently recommended P management strategy.
   - Justification of current practice on the basis of balance calculations should be questioned on the grounds that these discount the costs of maintaining a large soil P store, and the capacity of many crops to acquire a significant proportion of their optimal P requirements from inherent soil sources.
   - More thorough consideration should be given to the fate of the P not recovered using current P nutrition strategies.
8. Three key alternative strategies offer potential to improve sustainable P use: (i) minimising crop P requirements, (ii) maximising root recovery of soil P, and (iii) developing targeted fertiliser technologies with as complete P recovery as possible. Large genetic variations in leaf P and crop P (% DM) and in rooting and soil P acquisition offer much potential to improve crops and varieties by breeding. Large potential reserves of non-labile P exist in soils and opportunities to exploit this reserve through plant breeding, manipulation of soil microbial communities and precision management need to be investigated. The large genetic variation in plant traits for soil P acquisition suggests that there is scope to achieve this.
   - Sites should be prepared and maintained to enable testing for and breeding of P-efficient varieties.

   - Systematic investigations are required into the determination of and genetic variation in capacities for P acquisition and P demands of UK crop species.
   - Improved assays for phytate should be developed, and work on low phytate cereal mutants should be resumed, focussing on effects on crop P demand as well as on nutritional value for non-ruminants.

9. The stage of crop development most vulnerable to P deficiency is when seed reserves are exhausted, yet photosynthesis, root growth and soil exploration are slow. Seed P reserves are helpful to seedling establishment but they give rise to most of a crop's P requirement and introduce much P into supply chains (esp. in feeds to livestock).
   - The consequences of reducing P in feed grains from 4 to 3 or even 2 kg/t should be investigated for livestock production and manure composition.
   - Depending on whether seed coatings can be developed to reduce the need for seed P reserves, a long-term goal of reducing seed P (hence total crop P demands) should be envisaged.
10. Potential components that might be integrated into future management strategies to provide more efficiently for (perhaps reduced) crop requirements and might be tailored to specific farm, crop, soil and environmental conditions, include P fertiliser placement, seed P coatings, foliar P applications, industrially re-cycled products, and products that modify soil P availability. Fertilisers containing recycled P will be important in reducing requirements for mined P.
    - Novel fertilisers should be developed and tested, and particularly targeted to meet crop P demand at the most susceptible stages (i.e. establishment to stem extension), so as to reduce reliance on soil P fertility.
    - Fertiliser development studies should provide some appreciation of the chemistry and dynamics of their effects, something which fertiliser manufacturers can seldom afford.
11. Research thus far has commonly shown inconsistent or uncertain performance of novel fertiliser products. Proven reliability of any P targeting technologies will be crucial to their general adoption on farms, yet current generally high levels of soil P fertility inhibit improvement of such efficient P fertiliser technologies. Also, the precision with which alternative P fertilisers can be compared, and tailored to soil type, is inadequate when using conventional (replicated, randomised) experiments.
    - Networked experimental sites should be developed and sustained to facilitate development and validation of P fertilisers, and new integrated fertiliser management strategies.
    - New high-precision fertiliser-testing methods should be developed. Precision farming technologies have the potential to enable this, their capacity to make multiple in-field measurements should provide the high degree of replication that is essential for high precision comparisons.

12. The magnitude of the challenges involved in developing alternative P nutrition strategies is large, and their resolution will take significant time and investment. In particular, reduced reliance on soil P storage will require improved confidence in the recoveries of P fertilisers. It is not clear whether improved fertiliser products would make soil P analysis more or less important; possibly it would be less important in directing P fertiliser use but more important in quantifying the risk of failure.
    - Research funders should prioritise the component parts of the overall challenge of establishing efficient P management strategies, so that progress can be made as rapidly as possible.
13. Successful innovations in crop P nutrition can offer significant progress in reducing growing costs, preserving finite global P reserves and reducing export of P to livestock and in runoff from land, whilst also facilitating renewed enhancement of crop productivity.

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