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CELEBRATING THE 350TH ANNIVERSARY OF DISCOVERING PHOSPHORUS—FOR BETTER OR WORSE

Phosphorus in Agriculture: A Review of Results from 175 Years of Research at Rothamsted, UK

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Abstract

Insight into the role of phosphorus (P) in soil fertility and crop nutrition at Rothamsted, UK, and its involvement in associated environmental issues, has come from long-term field experiments initially started by J. B. Lawes in 1843 and continued by others, together with experiments on different soils. Results from the 1940s confirmed that residues of P applied in fertilizers and manures build up reserves of P in soil. There is a strong relationship between crop yield and plant-available P (Olsen P), and a critical level of Olsen P can be determined. For soils near the critical level, P-use efficiency is high when the P applied and offtake by the crop is nearly equal. Soil inorganic P is associated with various soil components and is held there with a range of bonding energies so that when no P is applied, the decline in Olsen P follows a smooth curve. We conceptualize inorganic soil P as being in four pools of vastly varying size, availability for uptake, and extractability by reagents used in routine soil analysis, and with reversible transfer of P between pools. For very disparate soils at Rothamsted and in the United States, there is a strong relationship between the change in Olsen P and P removal/input ratios, suggesting an underlying similarity in inorganic P behavior. Maintaining soil near the critical level should optimize yield and the use of the global P resource while minimizing the risk of transfer of large amounts of P to the aquatic environment.

Core Ideas

- Lawes started long-term experiments on P in the 1840s.
- Insights into role of P in soil fertility and crop growth comes from field experiments.
- P residues build up a reserve of plant-available P.
- Olsen's method is used to establish critical level of available P in soil for optimum yield.
- Inorganic P transfers between 4 pools of different size/extractability/availability.

Long-term field experiments initially begun at Rothamsted, UK, have provided insight into the role of phosphorus (P) in soil fertility and crop nutrition, as well as its involvement in associated environmental issues. In this review, we focus mainly on the agronomic role of P in crop production and soil fertility, illustrated with examples from the Rothamsted long-term experiments and those at Woburn and Saxmundham, UK (Table 1). Descriptions of the recent long-term experiment at North Wyke, UK, which became part of Rothamsted Research in 2009, are included, together with some preliminary results.

The first Rothamsted experiments showed the essential need to apply water-soluble P to soil, to increase yield, and to ensure a response to other nutrient additions, especially nitrogen (N). Despite enormous problems, P imports into the United Kingdom doubled during World War II as more land was brought into food production and farmers sought to maximize yields. The rationing of phosphate fertilizers was introduced in 1942 (Crowther, 1948). From the 1940s, the efficient use of newly applied P fertilizers and manures, and of the soil P reserve from the accumulated residues (P applied to a crop minus that removed in the crop) from past fertilizer and manure applications, became the focus of much research.

Frequently, a new program of research develops to answer questions identified in earlier research. Aware that organic P was important in crop production systems in many parts of the world, G.E.G. Mattingly initiated a program in the 1960s to determine the total organic P and its rate of mineralization in the top 23 cm soil in the long-term experiments. The results (Chater and Mattingly, 1980) in summary showed that as much as 30% of the total P was organic P but the annual rate of mineralization was only 0.5 to 1.5 kg P ha^{-1} on the old arable soils, far too little to produce economic yields of cereals in UK conditions. The annual rate of mineralization was higher (7.7 to 8.5 kg P ha^{-1}) where soils had been plowed out from permanent grass or as much as 100 t ha^{-1} of farmyard manure (FYM) had been applied. As a consequence of these very small rates of organic P mineralization, and organic P not being determined in most methods used in routine soil analysis for plant-available P, research at Rothamsted had mainly focused on inorganic P. However, the role of organic P in agriculture and the wider environment is still much debated (George et al., 2018).

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Abbreviations: FYM, farmyard manure; SOM, soil organic matter.

Other topics on P in soil fertility have been the subject of research at Rothamsted. They include the role of P in soil microbial biomass (Brookes et al. 1984), and energy relationships (Brookes et al., 1983) and in mycorrhizal fungi (Stribley et al., 1980). Losses of P in eroded soil and in drainage have also been measured in Rothamsted experiments (Catt et al., 1998).

Background

Phosphorus, the 12th most abundant element in the earth's crust, was discovered in 1669 by Hennig Brandt in Hamburg, Germany. In the 1830s, some 170 years later, John Bennet Lawes, owner of the farm at Rothamsted near Harpenden, UK, 40 km north of London, began experiments both in the laboratory and the field on the use of P in agriculture. Lawes had left Oxford University when still an undergraduate in 1834, to manage the farm on behalf of his widowed mother and sister. At that time, and only in England, crushed bones were widely used to increase the yields of crops, particularly of turnip (*Brassica rapa* L.) and grassland, but Lawes found that they did not increase yields on his farm. Intrigued by this, Lawes made and tested several inorganic ammonium salts on small plots and pots in the late 1830s and early 1840s and showed that ammonium phosphate, in which the phosphate was water soluble, gave the largest yields of cabbage (*Brassica oleracea* L.) and turnip (Lawes, 1842, 1843a). Lawes then did a series of trials to solubilize the phosphate in bones and in 1842 was granted a patent for his process of treating bone ash and other phosphatic materials with sulfuric acid to produce a dry reaction product, single superphosphate together with calcium sulfate, which, when crushed to a powder and spread on land, improved crop yields. By June 1843, Lawes was advertising for sale the phosphate of lime he was manufacturing at a factory in London (Lawes, 1843b).

With his factory in production, Lawes was keen to start larger-scale field experiments on the nutrient requirements of the arable crops then widely grown in the United Kingdom. The rigor of his approach and the methodology used was probably influenced by that of Jean-Baptiste Boussingault, who in the early 1830s had started field experiments on crops grown in rotation on his farm at Bechelbronn in Alsace (Boussingault, 1845). In addition to weighing and analyzing the manures used and the crops grown, Boussingault produced nutrient balance sheets, including one for N. Lawes' approach was more detailed than that of Boussingault. Lawes grew the same crop year after year in most of his experiments because he considered that he would better understand its nutrient requirements (Lawes and Gilbert, 1895). He also tested N, P, potassium (K), magnesium (Mg), and sodium (Na) singly and in combination as inorganic salts (fertilizers) and compared their effects with those of FYM.

The Start of the Rothamsted Field Experiments

In June 1843, Lawes started the first large-scale experiment on turnip on Barnfield, and in autumn the second on winter wheat (*Triticum aestivum* L.) on Broadbalk. That year he also appointed Joseph Henry Gilbert, a chemist, to assist him in the management of the experiments and to analyze crop and soil samples, mostly for N. At the first harvest of both wheat and turnip, the yields showed the need for fertilizer N. But with additional plant-available P, from the applied superphosphate, yields were even larger. These were the first important results on increasing crop yield from Rothamsted Experimental Station (now Rothamsted Research).

Having established the Barnfield, Broadbalk, and other experiments (Table 1), Lawes and Gilbert concentrated on managing them, recording the yields with notes on the growth of the crop, and analyzing crop and soil samples for N. The results, with much detail and discussion, were published, and by 1900, there were some 169 papers. A complete list is in the electronic Rothamsted Archive (e-RA; Rothamsted Research, 2019). It is our present good fortune that Lawes started several long-term experiments (at his own expense), and that others have been

Table 1. Long-term experiments† at Rothamsted, Hertfordshire, Woburn, Bedfordshire and Saxmundham, Suffolk, UK.

Experiment	Duration	Crop	Comment	Reference
Rothamsted‡				
Barnfield	1843–current	Root crops	Grass since 1975	Warren and Johnston, 1962
Broadbalk	1843–current	Winter wheat	Parts of the experiment have included rotations since 1968	Johnston and Garner, 1969; Poulton et al., 2018
Agdell	1848–1990	Arable crops	Half in grass, 1958–1969	Johnston and Penny, 1972; Johnston et al., 2013, 2016
Hoosfield	1852–current	Spring barley	Parts of the experiment included rotations 1968–1978	Warren and Johnston, 1967; Johnston et al., 2016; Poulton et al., 2018
Exhaustion Land	1856–current	Arable crops		Johnston and Poulton, 1977; Poulton et al., 2013; Johnston et al., 2016
Park Grass	1856–current	Permanent pasture	Pasture since ca. 1700	Warren and Johnston, 1964; Silvertown et al., 2006; Johnston et al., 2016
Residual P	1960–1981	Arable crops		Updated from Chater and Mattingly, 1980
Woburn§				
Long-term P	1968–1981	Arable crops		Updated from Johnston et al., 1976
Saxmundham¶				
Rotation II	1899–1986	Arable crops		Johnston et al., 1986, 2016

† For a more complete list of long-term experiments managed by Rothamsted Research, see Macdonald et al. (2018).

‡ Rothamsted soil is a flinty silty clay loam over Clay-with-Flints and is classified as a Chromic Luvisol (IUSS Working Group WRB, 2015).

§ Woburn soil is a sandy loam and is classified as a Cambic Arenosol (IUSS Working Group WRB, 2015).

¶ Saxmundham soil is a sandy clay loam derived from boulder clay and is classified as a Eutric Gleysol (IUSS Working Group WRB, 2015).

started subsequently, because one or another experiment is invariably generating results of interest and importance.

The second half of the 19th century can be considered perhaps a period of consolidation, when the experiments were continued and managed with great care, yields were recorded, and samples of crops and soils were archived for future analysis (Lawes and Gilbert, 1873). Lawes and Gilbert were aware that new analytical techniques were likely to be introduced and that an archive of samples might prove valuable; in this they were remarkably far-sighted. One major development was the start of analyzing soils from the field experiments for P.

Introduction of Soil Analysis for Phosphorus Reserves

It is perhaps simplistic to comment that advances in most sciences require appropriate, reliable, reproducible analytical methods, and this is especially so for the determination of readily plant-available P in soil. Hermann von Liebig (1872), analyzing soils from Broadbalk, showed that those with P since 1852 contained more P soluble in dilute nitric acid than did unmanured soils. Later, Dyer, with Lawes and Gilbert, made a P balance (P applied minus P removed) for the first 38 years of the Hoosfield Continuous Barley experiment and later for 50 years on Broadbalk. Dyer determined both "total" P by digesting the soil for 48 h with constant boiling HCl and P soluble in 1% citric acid and showed that, within the errors of soil sampling and analysis, the total P accounted for 80 to 90% of the positive P balance for soils with P applied. When data for soils with and without P were compared, total P varied by 2:1 but citric-soluble P varied by 8:1 or 9:1, suggesting that citric-soluble P was a better index of P availability (Dyer, 1894, 1901, 1902).

Dyer's results supported two earlier observations. In laboratory experiments, Way (1850), percolated an aqueous, water-soluble phosphate solution through a column of soil and showed that the P was retained in the soil. This was confirmed for the field situation when Voelcker (1874) analyzed drainage collected during 1866 to 1868 from plots on Broadbalk and showed that although 33 kg ha^{-1} P as water-soluble phosphate had been applied each year since 1843, little of this P was in the drainage. These and similar results elsewhere, showing that P was retained in the soil, led to the widely held view that P was so fixed in soil that it would not be available to plants; consequently, fresh water-soluble fertilizer should be added each year. The concept of P fixation was supported by many laboratory studies on precipitation reactions of water-soluble P and the production of insoluble solid phase reaction products, but the laboratory conditions were far removed from those in soils in the field. Wild (1950), however, noted that phosphate ions were likely to be removed initially from the soil solution by adsorption. These early laboratory studies paid little attention to the availability of P for uptake by roots. Coleman (1942), however, suggested that perhaps crops did not respond to P not because it was fixed but because there was already sufficient plant-available P in the soil. This observation has been well supported by later work that also showed that there was no response to P if lack of other nutrients, especially N and K, limited yield and weeds, pests, and diseases were not adequately controlled.

Soil Analysis for Plant-Available Phosphorus

During the last two centuries, many alkaline, neutral, and acidic extractants for plant-available have been tested on a wide range of soil types. Often, one was chosen in the belief that it extracted P held in some combination with specific soil constituents such that the P was, or would become, plant available. Extractants that have remained in common use are those that extract amounts of P that correlate well with crop response, either to soil P or freshly applied P. However, Holford and Mattingly (1976a, 1976b, 1979) showed a negative relationship between an effective soil test and P buffering capacity when buffering properties are controlled by phosphate adsorption characteristics. Recently, several studies in Europe have been made to compare soil tests in common use and their suitability for assessing fertilizer P requirements (Jordan-Meille et al., 2012; Nawara et al., 2017).

In the early 1950s, we did not have any extractant suitable for use with our mainly, slightly calcareous clay loam soils at Rothamsted. The best was 0.01 M $CaCl_2$ ($CaCl_2$-P) (Schofield, 1955) because this salt concentration is very similar to that in the soil solution of our soils. Thus, the P concentration in the extract could be considered very similar to that in the soil solution. But at that time, it was difficult to determine low concentrations of P in the solution. In 1954, we received a typescript of Olsen's method (Olsen et al., 1954), and we have used this method almost exclusively to determine readily plant-available P because it best classifies our soils according to the response of crops to applied P (Warren and Johnston, 1965). With the increased sensitivity in many analytical techniques, it is now much easier to determine P in $CaCl_2$ extracts, and $CaCl_2$ has been used occasionally to determine very readily available P in the soils from some long-term experiments (see "Environmental Issues" section below). Interestingly, we have determined total, Olsen P, and $CaCl_2$-P in soils receiving similar total amounts of P either as fertilizers or FYM in three long-term experiments. The increase in total and Olsen P was quite similar with both P sources, but there was twice as much $CaCl_2$-P in soils with extra soil organic matter (SOM) from FYM additions (Johnston et al., 2009).

Long-term Release of Phosphorus Reserves from Soil

One of the most important results from our long-term experiments at Rothamsted has been that P added to soil in fertilizers and manures has *not* been fixed irreversibly in these soils and probably not in many others. Following the observation that soil P reserves increased the yields of spring barley (*Hordeum vulgare* L.) on the Exhaustion Land in 1949 and subsequently (see below), we have monitored the removal of P in the crops grown each year on Plots 7 and 9 (N–P–K or P, 1856–1901) and Plot 3 (FYM, 1876–1901) compared with the P removed from Plots 1 and 5 (no P, 1856–1901). The P offtake in the crops grown in various periods between 1856 and 1975 was calculated by Johnston and Poulton (1977) and measured annually since 1976. Table 2 shows the offtake of P in the crops grown after 1901 when applications of P and FYM ceased. From 1902 to 2012, 394 kg P ha^{-1} was removed from plots without P since

Table 2. Exhaustion Land; P removed from 1902 to 2012 by arable crops growing on soils without P since 1876 or on soils with residues of P applied as fertilizer from 1856 to 1901 or in farmyard manure from 1876 to 1901 and none since.†

Period	Crop	Plots 1, 5 No P since 1856		Plots 7, 9 1410 kg P ha^{-1} applied 1856–1901 as superphosphate		Plot 3 1260 kg P ha^{-1} applied 1876–1901 in farmyard manure	
		Amount of P removed in the crop					
		Total	per year	Total	per year	Total	per year
		kg ha^{-1}					
1902–1940‡	Spring barley	102	2.6	207	5.3	200	5.1
1941–1985§	Spring barley	189	4.2	394	8.8	478	10.6
1986–1991¶	Spring barley	28	4.7	51	8.5	60	10.1
1992–2012#	Winter wheat	75	3.6	175	8.3	200	9.5
1902–2012	Total	394	–	827	–	938	–

† Table adapted from Johnston and Poulton (2014).

‡ Mainly spring barley grown during this period; no fertilizers or manure applied.

§ Fertilizer N applied at various rates since 1941; fallow in 1967 and 1975.

¶ Basal K and N applied since 1986.

Spring wheat in 2001.

1856 (at an average annual rate of 2.6–4.7 kg P ha^{-1}) while more, 827 or 938 kg P ha^{-1}, was taken up from soils with reserves of P from past fertilizer or FYM additions (Johnston and Poulton, 2014). More than 100 years after fertilizer P or FYM was last applied, the P reserves are still being recovered at 4 to 6 kg P ha^{-1} yr^{-1}. Thus, the residue of applied P has *not* been fixed irreversibly in soil but is an important P reserve. Also, if residues of applied P fertilizer were fixed irreversibly in soil, it would not be possible to increase plant-available P in soil as seen in many soils worldwide.

Forms in which Phosphorus Is Held in Soil

The long-term removal of P from soils with and without P reserves raises the question, How is that P held in soil? One approach we used was to sequentially extract P from soil with chemical reagents thought to remove P in different chemical forms (Chang and Jackson, 1958; Hedley et al., 1982; Maher and Thorrold, 1989; Tiessen and Moir, 1993). This was done for archived and current soils from the same plot in six of our long-term experiments with a range of treatments to determine the effect of treatment and time on the amount of P extracted by each reagent (Blake et al., 2003). Table 3 shows data for Exhaustion Land soils and the order in which the first five extractants were used; three further extractions were used to determine the residual P, but the amounts were small (Blake et al., 2003). The first determination was equilibration with an anion-exchange resin (Hislop and Cooke, 1968; Tiessen and Moir, 1993), followed by extraction with $NaHCO_3$. While both these reagents are used individually to determine plant-available P in routine soil analysis, in sequential extractions, $NaHCO_3$ is used after resin. In this paper, we call P extracted by 0.5 M $NaHCO_3$ during routine soil analysis Olsen P and that extracted in sequential extraction $NaHCO_3$-P (or bicarbonate P). The other extractants, and the forms of P they were thought to remove, are described in Blake et al. (2003).

The P balance and changes in extracted P for the Exhaustion Land soils are for the top 23 cm, two sources of P and two periods: the first for plots initially with superphosphate from 1856 to 1901 and then none from 1902 to 1993, and the second for plots with FYM from 1876 to 1901 and then none from 1902 to 1993. Both organic P and inorganic P (not shown separately here but given by Blake et al., 2003) were determined analytically in the P removed by 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1 M NaOH. For soils with P fertilizer and with FYM, when the P balance was positive, the amount of P extracted by each of the first five extractants increased and then decreased when the P balance was negative (Table 3). These negative and positive changes in all five fractions in this soil account for almost 90% of the total P determined separately for each soil in each period.

Table 3. The P balance at the end of each treatment period and the change in P fractions in soils taken in 1903 and 1993, Exhaustion Land, Rothamsted.†

Plot no., treatment, and period	P balance‡	Change in first five P fractions					
		Resin	0.5 M $NaHCO_3$	0.1 M NaOH	1 M NaOH	0.25 M H_2SO_4	Total change
	kg ha^{-1}	kg P ha^{-1}					
1. No P since 1856							
No P applied, 1902–1993	−300	−49	−20	−195	−82	−19	−365
9. P fertilizer							
Applied, 1856 –1901	1222	158	126	79	7	270	640
Not applied, 1902–1993	−644	−234	−138	−114	45	−253	−694
3. Farmyard manure							
Applied, 1876–1901	1035	193	129	133	107	355	917
Not applied, 1902–1993	−752	−259	−123	−159	−112	−164	−817

† Table adapted from Blake et al. (2003).

‡ P balance is the amount of P applied minus the amount removed by the crop.

The sequential extraction of P was made for a heavier textured, sandy clay loam soil to which 230 and 490 kg P ha^{-1} were added in both FYM and superphosphate between 1965 and 1967. In spring 1969, the sum of the inorganic P extracted by resin and 0.5 M $NaHCO_3$ was only 56 and 58%, respectively, of the total increase in inorganic P in the first five extractants. This suggests that P had moved quickly into other P fractions. The data in Blake et al. (2003) showed, for all the soils investigated, that each of the eight soil P fractions increased during periods of P addition or decreased when P was no longer applied. Importantly, these changes were not confined to any one P fraction. Thus, water-soluble P added to soil is transferred to fractions that require stronger chemical reagents to extract the P. When soils are cropped without P addition, this more strongly bound P is released, confirming that the transfer of P between pools is reversible.

Evidence for Crop Yields Being Increased by Soil Phosphorus Reserves

Rothamsted became increasingly interested in assessing the value of P reserves accumulated in soil from past applications of P fertilizer and FYM when, in 1949, yields of spring barley on the Exhaustion Land were increased by P residues accumulated from these two sources of P (Johnston and Poulton, 1977). Large reserves of total P had accumulated from annual applications of superphosphate from 1856 to 1901 and FYM from 1876 to 1901 (Johnston and Poulton, 1977). No P or other nutrients were applied after 1901 until basal N was applied from 1941. In the very dry spring of 1949, early growth of the spring barley varied greatly across the site and the boundaries of the 10 original plots were re-established from archived field plans. Grain yields also varied, the largest being on plots that had P as fertilizer or FYM before 1901 but none since, good evidence suggesting that P added before 1901 was still available for uptake by plant roots and had not been fixed irreversibly in soil. This important result was confirmed by the yields in subsequent years (Table 4), and analysis of grain and straw showed that the effect was mainly due to P (Johnston and Poulton, 1977).

The extent to which P reserves from past applications of fertilizer and FYM could be recovered by grass and arable crops was tested by modifying treatments in the Agdell experiment, 1848 to 1951 (Warren, 1958). Growing either grass or arable crops on one half of each of the original six very large plots between 1958 and 1969 increased SOM in the grass plots to 2.4% compared with 1.5% where arable crops were grown. Also, in this 12-yr period, a range of Olsen P levels was built up on subplots on each of the original six plots (Johnston and Penny, 1972). Potato (*Solanum tuberosum* L.), sugar beet (*Beta vulgaris* L.), and spring barley were each grown twice between 1970 and 1972 and the yield–Olsen P relationship was determined (Table 5). To get 95% of the maximum yield required more Olsen P on the soil with less SOM and the percentage variance accounted for was less. When the soils from the 48 plots were sampled and sown to ryegrass (*Lolium perenne* L.) in pots in the greenhouse, the Olsen P required to achieve 95% of the maximum yield together with the percentage variance accounted for were the same irrespective of the level of SOM (Table 5). Thus, both the field and pot experiment suggested that yield and its associated Olsen P were affected by SOM and thus presumably by soil structure and the ability of roots to search the soil for nutrients. The importance of soil structure was confirmed later (Johnston and Poulton, 2011).

Table 4. Mean yields of spring barley grain, 1949–1974, grown on soils with and without P residues; Exhaustion Land, Rothamsted.†

Period	Plot numbers and treatment		
	1, 2, 5, 6 No P since 1856	7, 8, 9, 10 P applied 1856–1901 as superphosphate	3, 4 P applied 1876–1901 in farmyard manure
	Mean yield grain at 85% dry matter		
	t ha^{-1} yr^{-1}		
1949–1953	1.59	2.88	3.03
1954–1959	1.80	3.02	3.32
1960–1963	1.99	2.72	3.14
1964–1969‡	1.71	3.60	4.28
1970–1974	1.83	4.18	4.75

† Table adapted from Johnston and Poulton (1977).

‡ The experiment was fallowed in 1967.

The Critical Level for Olsen P in Soil

The results from Agdell encouraged us to determine the yield–Olsen P relationship and the factors effecting this relationship on other soils, especially on the sandy clay loam at Saxmundham, Suffolk (Johnston et al., 1986), and on the silty clay loam at Rothamsted (Johnston and Poulton, 1977). Both experiments had large plots that had soils with a range of Olsen P from earlier treatments, and this range was extended by dividing the large plots into smaller ones and adding further amounts of P, which were cultivated into the topsoil to allow the added P to equilibrate with existing soil P. Each year, sufficient N and K were applied so as not to limit yields. In both experiments, the relationship between yield and Olsen P was best described by a Mitscherlich-type asymptotic regression equation; for examples, see Poulton et al. (2013) and Fig. 1. From the equation, the Olsen P associated with 98% of the asymptotic yield together with its associated standard error was determined. We considered this level of Olsen P to be the critical level for that crop and soil because the yield was not increased either with larger concentrations of Olsen P or by addition of fresh P fertilizer.

Table 5. Effect of soil organic matter on the critical level of Olsen P for three arable crops and grass grown on a silty clay loam soil, Rothamsted.

Crop	Soil organic matter	Yield at 95% of the asymptote	Olsen P associated with the 95% yield	Variance accounted for
	%	t ha^{-1}	mg kg^{-1}	%
		Field experiments		
Spring barley grain, t ha^{-1}	2.4	5.00	16	83
	1.5	4.45	45	46
Potato tubers, t ha^{-1}	2.4	44.7	17	89
	1.5	44.1	61	72
Sugar, t ha^{-1},	2.4	6.58	18	87
from sugar beet	1.5	6.56	32	61
		Pot experiments in the greenhouse		
Grass, dry matter, g pot^{-1}	2.4	6.46	23	96
	1.5	6.51	25	82

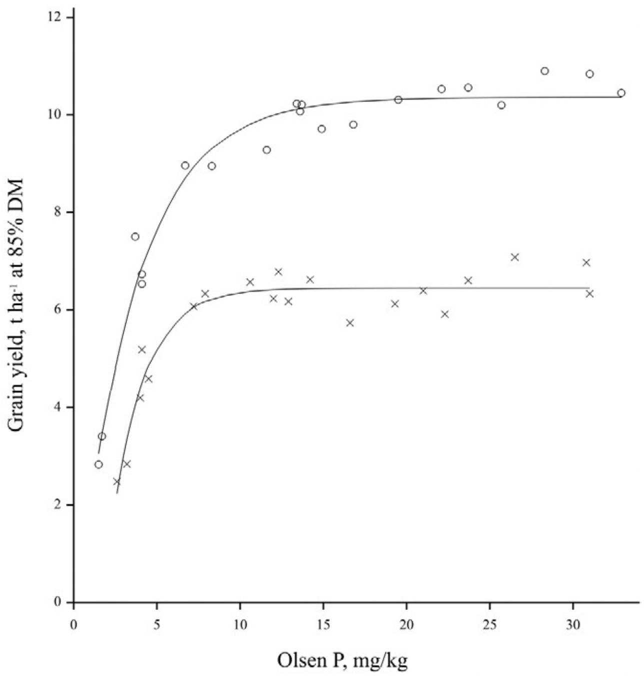

Fig. 1. Asymptotic regression of winter wheat grain on Olsen P in soil in two years with different maximum yields and similar critical Olsen P; 2003 (x); 2008 (●); Exhaustion Land, Rothamsted. DM, dry matter.

At Saxmundham, adding P to existing plots in 1965 to 1968 established soils with Olsen P ranging from 3 to 67 mg P kg^{-1} by autumn 1968 (Johnston et al., 1986). The plots were divided into four groups of five subplots to grow different crops on each group. From 1969, fresh P was added to four of the subplots, while one subplot had no further P. The yield–Olsen P relationship was determined initially for potato, sugar beet, and spring barley grown in rotation (Johnston et al., 1986) and later for winter wheat (Johnston et al., 2013).

On the Exhaustion Land, the five adjacent, odd-numbered main plots were each divided into four smaller ones (each 6.0 by 25.6 m) in 1986, and P was tested in three periods: (i) from 1986 to 1992, P was applied annually as triple superphosphate to each of the four subplots at 0 vs. 44 vs. 87 vs. 131 kg P ha^{-1}, respectively; (ii) from 1993 to 1999, no fresh P was applied; and (iii) since 2000, a maintenance dressing of P has been applied to maintain Olsen P on those subplots that had received P from 1986 to 1992. Spring barley was grown from 1986 to 1991, and winter wheat has been grown since 1992, except in 2001, when spring wheat was grown. Each year, the asymptotic grain yield and critical Olsen P, with their associated standard errors, were determined from the yield–Olsen P relationship (Poulton et al., 2013). To illustrate this relationship, we show two years when the asymptotic yield was very different but the critical Olsen P was similar (Fig. 1).

The percentage variance accounted for in the yield–Olsen P relationship ranged from 83 to 97% (with only two exceptions in 23 yr), which confirms that the Olsen method is a good indicator of plant-available P and that P was the principal soil factor controlling growth (Poulton et al., 2013). The high percentage variance accounted for in these experiments compares with that, ~50%, reported by Boyd (1965) for a series of national experiments in England, which were done on a range of farms where the soil type, weather, and management were not always identical. The results that we report here were on plots with a range of Olsen P levels within the one field, on one farm under the one management. We consider that although such experiments require foresight and commitment to establish and maintain, they give the best opportunity to more accurately define the relationship between crop yield and Olsen P.

The critical Olsen P value will vary with soil type, but our experience suggests that soil structure, and thus the ability of a crop to produce a root system capable of exploring the soil for nutrients, is a major cause of this variation. Knowledge of the critical value enables farmers to manage the P status of their soils; the soil should be sampled once every 3 to 5 yr to ensure that the level is being maintained. Once a protocol for soil sampling has been established, it should be followed rigorously to monitor changes of plant-available P with time, and the method of analysis should be simple and reproducible (Johnston, 2011). There is no reason to limit P applications to water-soluble P fertilizers; any source of P can be used provided it maintains the critical level of plant-available P. Knowing the critical level also helps when there are environmental issues such as the transfer of P from soil to surface water on eroded soil particles or as water soluble P. If the soil has been maintained near the critical value to ensure optimum crop production, then it is appropriate to seek methods to control losses rather than restrict the amount of P a farmer can apply.

The Buildup and Decline in Plant-Available Phosphorus Reserves in Soil

Buildup of Plant-Available Phosphorus

In our long-term experiments on a silty clay loam, a sandy loam, and a sandy clay loam where P has been applied for many years, there is a linear relationship between the increase in Olsen P and the increase in total P when both are expressed in kilograms P per hectare, but the increase in Olsen P is only about 13% of the increase in total soil P (Johnston, 2001). Of more practical importance is the amount of P required and the time needed to build up Olsen P above the critical level. On the Exhaustion Land, the range of Olsen P was increased (Table 6) by the large amounts of P applied to the subplots newly created in 1986 (see above) and spring barley grown from 1986 to 1991 and winter wheat in 1992. From the total P offtake in grain plus straw of these two cereals, it was possible to calculate the increase in Olsen P both as a percentage of the P applied and as a percentage of the P balance (Table 6). Interestingly these percentage increases were remarkably consistent and independent of either the amount of P applied or the P balance on the original nil and superphosphate plots and a little more variable on the original FYM-treated plot. A possible explanation for this result is discussed below.

Decline in Plant-Available Phosphorus

In 1903, soils on the Exhaustion Land that had received fertilizer P from 1856 to 1901 or FYM from 1876 to 1901 had 60 to 70 mg kg^{-1} Olsen P in the top 23 cm; these levels had declined to 5 to 19 mg kg^{-1} by 1965 (Johnston and Poulton, 1977). From the limited number of Olsen P values available, there appeared to be a smooth curvilinear decline relating Olsen P and time.

Table 6. Increase in Olsen P as a percentage of the P applied and of the P balance, Exhaustion Land.

Original treatment 1856–1901	P treatment† 1986–1992	Olsen P		Change in Olsen P‡	P applied 1986–1992	P offtake grain + straw 1986–1992	P balance§	Increase in Olsen P	
		1985	1992					as % of P applied	as % of P balance
		mg kg^{-1}		kg ha^{-1}				%	
Nil¶	P0	2	2	0	0	33	−33	–	–
	P1	2	14	36	306	93	212	12	17
	P2	2	30	85	611	109	502	14	17
	P3	2	44	127	916	111	806	14	16
P#	P0	5	4	−3	0	62	−62	–	–
	P1	6	18	36	306	105	201	12	18
	P2	8	38	91	611	119	492	15	18
	P3	6	54	145	916	120	796	16	18
FYM††	P0	8	5	−9	0	78	−78	–	–
	P1	10	23	39	306	113	193	13	20
	P2	9	53	133	611	122	489	22	27
	P3	7	57	152	916	120	797	17	19

† P0, P1, P2, P3 received 0, 44, 87, 131 kg P ha^{-1} yr^{-1} as triple superphosphate.

‡ Using a weight of 3030 t ha^{-1} for topsoil, 0-23 cm.

§ P balance is the amount of P applied minus the amount removed by the crop.

¶ No P applied 1856–1901 and none between 1902–1985; mean of data from two main plots.

\# Fertilizer P applied 1856–1901, no P applied 1902–1985; mean of data from two main plots.

†† Farmyard manure applied 1876–1901, no P applied 1902–1985; data from one main plot.

Intrigued by this and its possible implication for the forms of P held in soil and their release, we took the opportunity to measure the decline in Olsen P in more detail. At Saxmundham by 1968, Olsen P ranging from 3 to 67 mg kg^{-1} had been established on the subplots started in 1965 (see above and Johnston et al., 1986). One of the plots in each group of five received no more P, and Olsen P measured in alternate years declined over the next 14 yr (Fig. 2a). The decline on the subplots without fresh P on each of the eight main plots could be fitted with a quadratic curve. Subsequently, these eight curves could be shifted horizontally onto an extended *x* axis (years) and, using an exponential model, a unified curve produced. (Fig. 2b). From the unified curve, the half-life of the Olsen P, that is, the time in years for it to halve relative to the lowest level measured in the soil, can be calculated. To determine the half-life does not require knowledge of the P offtake, only the change in Olsen P.

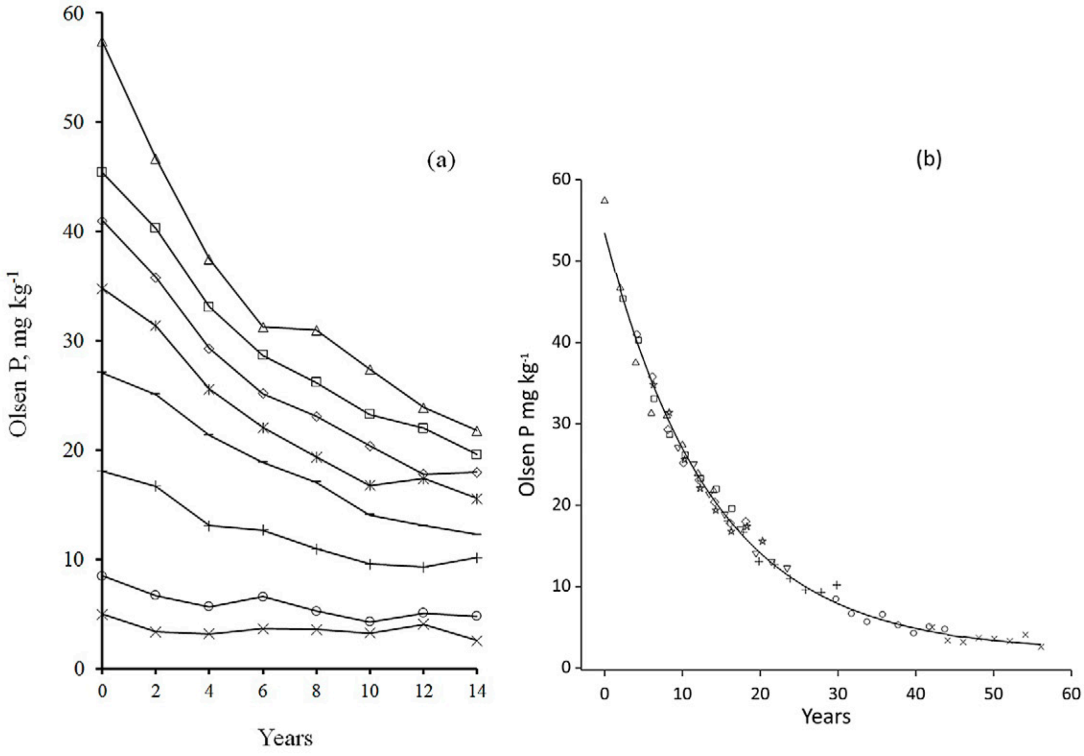

Fig. 2. (a) The change in Olsen P in eight treatments given no more P after 1968; (b) an exponential curve fitted to the data from the eight treatments once the curves have been bought into coincidence by a series of horizontal shifts; Saxmundham RII, Suffolk.

Knowledge of the half-life is useful when planning long-term policies for managing the P status of soils, especially when there is a need to lower the level of plant-available P for agricultural, environmental, and ecological reasons (Johnston et al., 2016). As fertilizer prices continued to increase in the 1980s, farmers wishing to optimize their use of P fertilizers and maintain the critical level of Olsen P for their soil wanted to know for how long they could withhold P applications if their soil was above the critical level. This question could be answered from a decline curve like that in Fig. 2b. In experiments on different soil types (Table 1), we measured the decline in Olsen P over short periods on subplots with a wide range of Olsen P. This range was created when fresh P fertilizer was added for a few years to soils with pre-existing levels of Olsen P. For each experiment, a unified decline curve was produced, as described above. The horizontal shifts of the individual curves to bring them into coincidence and the half-lives of the Olsen P were determined. These half-lives ranged from 4.5 to 16.1 yr (Table 7), the different values being related to soil type, crop grown, the initial level of Olsen P, the time over which the measurements were made, and the P balance (Johnston et al., 2016).

Efficient Use of Phosphorus in Crop Production

Much comment in recent years about the inefficient use of P, particularly of inorganic P fertilizer in agriculture, is based on the low percentage recovery of applied P determined by either of two methods. First is the direct, but expensive, method using ^{32}P-labeled fertilizer, which has limited applicability because of the short half-life of the labeled fertilizer. In field experiments at Rothamsted with ^{32}P, average P recovery ranged only from 5 to 25% (Mattingly, 1957; Mattingly and Widdowson, 1958a, 1958b). Second is the difference method, where percentage P recovery of added P, is calculated as follows:

$$[(U\text{p} - U\text{o})/F\text{p}] \times 100$$

where Up and Uo are the uptake of P by crops with and without added P, respectively, and Fp is the amount of P applied. Percentage recovery of P is often in the range 5 to 10%. The method is suitable for comparing the recovery of P from a range of P sources in 1- or 2-yr experiments. But it tells us nothing about longer-term P recovery and its appropriateness has been questioned. If not more than 25% of freshly applied P is taken up by a crop, then the remainder of the P in the crop must have come from the plant-available P reserve in the soil. Consequently, the amount of recently added P that replaces that in the plant-available soil P reserve can be considered as part of the efficient use of the newly added P (Syers et al. (2008). Thus, P use efficiency is determined as the total P removed in the harvested crop (the offtake, Up, part of which comes from the added fertilizer and part from soil reserve, which is being replaced) divided by the total P applied (the input, Fp). Percentage P-use efficiency is calculated as Up/Fp × 100, and the method is called the balance method because only the balance between Up and Fp is considered. In the United States, when only Up and Fp are known, they are expressed as a ratio, the offtake/input ratio, or Up/Fp ratio. This ratio can be related to the change in plant-available P.

When soil is at the critical Olsen P for optimum yield and this level is maintained by replacing the P removed in the harvested crop, then P-use efficiency, determined by the balance method, can exceed 90%. For example, on the silty clay loam of the Exhaustion Land, five plots had a range of Olsen P from 9 to 31 mg P kg^{-1}, and winter wheat was grown each year for 4 yr. The average annual grain yield increased with Olsen P to reach a plateau above the critical value, and the total amount of P removed in grain plus straw in 4 yr increased also (Table 8). Each autumn, “maintenance” P at 20 kg P ha^{-1} was applied to maintain the initial Olsen P values. Where the total P application in 4 yr more nearly matched the P removed, P-use efficiency was about 95% when calculated as the Up/Fp ratio (Table 8).

Developing Concepts Describing the Behavior of Soil and Fertilizer Phosphorus

The need for a simple, visual method to explain the ideas presented here for the relationship between soil P and crop production led Johnston (2001) and Johnston et al. (2001) to suggest a

Table 7. Half-life, rate of decline, variance accounted for and standard errors associated with fitted Olsen P decay curves.†

Site and experiment	Asymptote‡ constrained to	SE of observations	Variance accounted for	Rate of decline (SE)	Half-life (SE)
	mg kg^{-1}		%	k	yr
Saxmundham					
Rotation II	2.0	1.28	99.0	0.072 (0.0019)	9.6 (0.25)
Woburn					
Long-term P	6.0	2.36	97.6	0.081 (0.0064)	8.5 (0.67)
Rothamsted					
Exhaustion Land	1.8	1.40	98.9	0.105 (0.0040)	6.6 (0.25)
Residual P	1.8	2.32	97.9	0.116 (0.0100)	4.5 (0.30)
Agdell					
1.5% SOM	2.0	4.22	92.0	0.057 (0.0042)	12.1 (0.88)
2.4% SOM	2.0	4.79	92.5	0.096 (0.0065)	7.2 (0.49)
Park Grass					
No P, 1856–1964	0.6	1.03	99.3	0.067 (0.0015)	10.3 (0.24)
P–K, 1898–1964	0.6	7.85	96.2	0.043 (0.0015)	16.1 (0.57)

† Table adapted from Johnston et al. (2016).

‡ The lowest measured value for Olsen P after many years without P addition.

Table 8. Maintaining Olsen P by replacing the P removed in the grain and straw of four winter wheat crops, Exhaustion Land, 2005–2008.

	Olsen P, mg kg^{-1}, in 2004†				
	9	14	20	23	31
Mean grain yield, t ha^{-1} yr^{-1}	7.6	8.3	8.1	8.5	8.5
Total P applied, kg ha^{-1}	80	80	80	80	80
P balance, kg P ha^{-1}	24	12	14	3	5
Olsen P, mg kg^{-1}, in 2008†	8	13	18	24	31
% P use efficiency by the balance method	70	85	82	96	94

† Olsen P in soils sampled in autumn.

simple model. Inorganic P in soil is considered to be in four pools of vastly varying size and greatly varying plant-availability with reversible transfer of P between the pools. This simple model was further developed by Syers et al. (2008) (as shown in Fig. 3). The descriptions used are essentially operational definitions. The plant availability of P is linked to its accessibility to roots (soil structure) and extractability by reagents used in routine soil analysis. The P is considered to be retained on soil components with a continuum of bonding energies, related to the nature of its physical association with these components, and may be largely reversible with time. Such bonding may also explain why increasingly "strong" reagents, like 1 M NaOH and 0.25 M H_2SO_4, are required to extract this P in sequential extraction.

Least P is in Pool 1, the soil solution. Pool 2 represents the readily available/easily extractable P that can be measured with reagents used in routine soil analysis, and this P is released to replace that in the soil solution when it is taken up by roots. Pool 3 is a reserve of P accumulated from past applications of P; it is more strongly bonded but can become available over periods of months or years. The P in Pool 4 is very strongly bonded or is native soil P that may only become very slowly plant-available by weathering. The long-term release of soil P from the Exhaustion Land soils is most likely that in Pools 3 and 4. Routine soil tests measure P in Pools 1 and 2, but this is not a finite quantity because it varies with the reagent used to extract it. However, in terms of the concepts in Fig. 3, it can be defined provided there is a strong relationship between the amount of P extracted and the response of a crop to either soil P or freshly applied P fertilizer.

Crucial to this model is the reversible transfer of P between the pools, which explains the rapid loss of Olsen P when water-soluble P is added to soil and why the critical level on any soil is largely independent of the yield when this varies with the weather or competition with weeds, pests, and diseases. The data in Table 6 strongly support the concept that only a fraction of either the added P or the P balance remains as plant-available P in Pools 1 and 2, with the remainder being transferred to Pools 3 and 4. Table 6 shows that the same proportion of the P balance, ranging approximately from 200 to 800 kg P ha^{-1}, was present as Olsen P in 1992, and this is of considerable interest. It suggests that there may be a ratio between the P in Pools 2 and 3; if this is so, then it could give information about the amount of P available to replace P in Pool 2 as it is taken up by crops.

Relating Changes in Plant-Available Soil Phosphorus to Input/Output Ratios for Data from Rothamsted and North America

We have expressed our P balance data as output/input ratios and related them to the change in Olsen P. These values have been plotted together with similar data from the International Plant Nutrition Institute for the central plains in North America in Fig. 4 (Johnston et al., 2014). A log function (not shown) fitted to all the data has an r^2 of 0.84. This relationship is of considerable interest given that it is for a vastly disparate set of soils on two continents and from both controlled experiments in England and derived statewide aggregate data in the United States. This relationship makes a powerful and convincing statement suggesting that for the agricultural soils from which these data were obtained, there is an underlying similarity in the behavior of plant-available inorganic P in soil.

Environmental Issues: Phosphorus and Eutrophication

Although P has a vital, irreplaceable role in food production through crop and animal nutrition, environmental issues have come to the fore in recent decades, one of which is the transfer of P from both point and diffuse sources to surface water bodies. Increasing P concentrations in inland fresh waters have been implicated as a major cause of disturbance in the biological balance, with many adverse effects on this important aquatic resource (Mekonnen and Hoekstra, 2018). Addition of P from point sources, such as sewage treatment works, has declined in recent years by removing P from the discharged treated water. Consequently, the proportion of P coming from diffuse sources, such as intensively managed agricultural land, has increased. Heckrath et al. (1995) measured the concentration of total P in drainage water from plots with and without P on Broadbalk between October 1992 and March 1995. Although the P concentration varied between years, it was not linearly related to the concentration of Olsen P in the top 23 cm, but each year the concentration increased rapidly above a change point (or threshold value) of about 60 mg kg^{-1} Olsen P. This

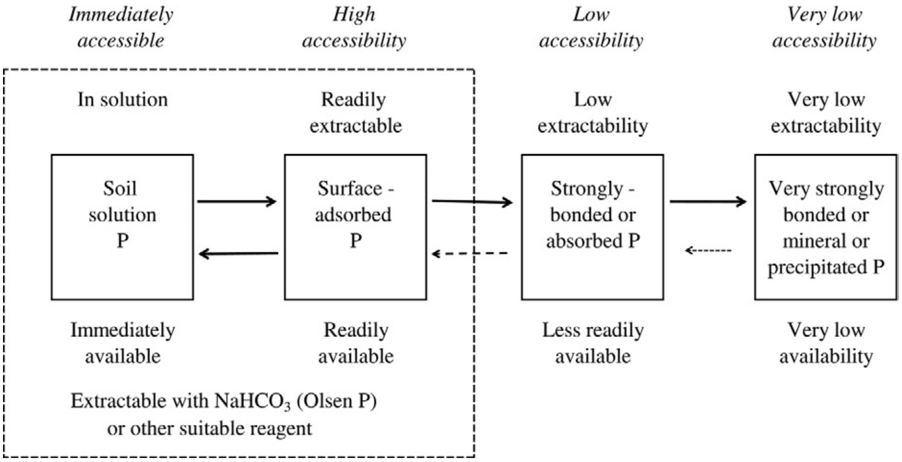

Fig. 3. Conceptual diagram for the forms of inorganic P in soil, categorized in terms of their accessibility, extractability, and plant availability.

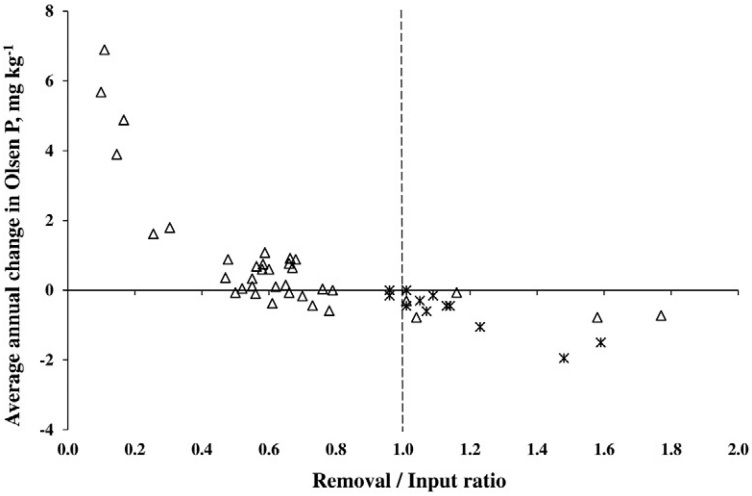

Fig. 4. Relationship between the removal/input ratio (P removed by the crop divided by the P input in fertilizer or manure) and the change in Olsen P for long-term experiments in the United Kingdom (∆) and 12 states in the United States (x).

level of Olsen P was well above the critical level, 15 to 25 mg kg^{-1} Olsen P, for optimum crop production on this soil.

These data from Heckrath et al. (1995) were possibly unique at that time because the drainage water could be collected and analyzed; a similar facility was rarely available in other experiments. Consequently, attention was focused on trying to find a surrogate analysis that could give an indication of the concentration of P in the soil solution. Phosphorus soluble in 0.01 M $CaCl_2$ was suggested because this P would be most at risk to loss in drainage. Soils from five long-term experiments were extracted both with 0.01 M $CaCl_2$ and 0.5 M $NaHCO_3$ (Johnston and Poulton, 1992; Brookes et al., 1997), and a similar sharp increase was observed in $CaCl_2$-P above a threshold value (or change point) of Olsen P. Similar relationships between Olsen P and $CaCl_2$-P have been produced for several Rothamsted and other experiments (McDowell et al., 2001) and show a wide range in change points from 20 to 60 mg kg^{-1} Olsen P for arable soils and higher values for grassland soils. Experiments would be required to check if the change point is specific to individual soil types.

Johnston (1997, Fig. 12) used a schematic relationship between crop yield and Olsen P to suggest that the important factor was the difference between the critical Olsen P for crop production and the threshold value for the concentration of P in the soil solution. This was illustrated by Withers et al. (2017) using Rothamsted data where the change point was at about 60 mg kg^{-1} Olsen P and the critical Olsen P about 20 mg kg^{-1}—an adequate margin of "safety." But soils at Saxmundham (McDowell et al., 2001) had a change point at 20 mg kg^{-1} Olsen P while the critical Olsen P for cereal yields ranges from <10 to about 34 mg kg^{-1} Olsen P (Johnston et al., 2013). This raises the question, Should the opportunity to achieve optimum yield be sacrificed because of the possible risk of loss of P from soil to water?

Many questions about P in relation to food production and its loss from agricultural soils need to be answered by monitoring at the farm and landscape scales (Powlson, 1998). We need to identify critical source areas for the loss of P (Pionke et al., 1997) and determine whether these are source areas because of loss of P to water by leaching and/or surface runoff or by soil erosion. Such areas must be related to the food production potential of the agricultural area and the level of plant-available P (e.g. Olsen P) required to achieve that potential. More recently, several papers have highlighted the value of farm-scale experiments to our understanding of soil processes and the implications for ecosystem services in grassland systems (Cardenas et al., 2016).

In 2010, a long-term, farm-scale grassland experiment, the North Wyke Farm Platform, was established at the Rothamsted Research site at North Wyke, Devon. The experiment, with three differently managed "farmlets" for beef and sheep production, each comprising five hydrologically separated catchments, is intensively instrumented. All inputs and losses are measured, including losses of P in surface and subsurface drainage. Full details of this complicated experiment are given in Orr et al. (2016). Reporting some of the early findings from this experiment, Peukert et al. (2014) found that in these conventional grassland systems, suspended sediment and total P concentrations in run-off often exceeded water quality limits recommended by the European Freshwater Fisheries Directive (25 mg total P L^{-1}) and the European Water Framework Directive (0.04 mg soluble reactive P L^{-1}) (UK TAG, 2008).

Looking to the Future

In 1889, Lawes and Gilbert attended the first meeting of the Lawes Agricultural Trust, which Lawes had endowed with £100,000 (about £10,000,000 today) to provide an income to defray the cost of maintaining the long-term experiments at Rothamsted. Gilbert was asked to prioritize each experiment, to which he replied that they had equal importance. Further qualifying this, Lawes noted that the yields of the crops showed the danger of allowing soil fertility to decline. Lawes then went on to say that the crop and soil samples he had collected (and retained) took first place in importance, having indicated that future generations of scientists could perhaps make good use of them (Lawes Agricultural Trust, 1896). How prescient was that? The archive of data and samples has been mined for information and analyzed to seek answers to questions that often only long-term data can provide. Published papers by authors around the world are testament to that. The archive, which now comprises >300,000 samples, together with the continuing long-term experiments is a valuable resource that can still be used to answer questions that may arise in the future—even though we do not necessarily know what those questions might be. Much information and data are available through e-RA (Rothamsted Research, 2019).

In more general terms, P use efficiency will improve if all our accumulated knowledge is applied to current crop and animal production systems. This requires adoption by farmers and growers through education and incentives. Knowledge is still imperfect on aspects of the behavior of P in soil; for example, the relation between the P held in Pools 2 and 3 in Fig. 3. At a more practical level, there is a need for a better understanding of the importance of good soil structure in facilitating root exploration of soil for nutrients, and greater use could be made of soil analysis to guide P applications both as fertilizers and organic manures.

To help ensure that the world's P resource is used as efficiently as possible, it will be essential to adopt and manage a whole-life-cycle approach to close the global P cycle (Hilton et al., 2010). Three aspects of this are (i) improving the sustainability of P mining, (ii) managing soil erosion to minimize P losses, and (iii) adopting a policy of "from waste to P recovery and recycling." The latter will require research into the removal of inorganic and organic pollutants from organic wastes to be applied to land so that these do not enter the food chain.

Conclusions

Our desire to explain many of the results from field and laboratory experiments at Rothamsted has led to our thinking of inorganic P existing in soil in four pools. These vary in size, the availability of the P for uptake by roots, and the extractability of the P used to determine its availability to crops. Very importantly, the concept recognizes the transfer of P between the pools. Inorganic P is associated with a variety of soil components, and the plant-availability of the P is related to the P being held to them with a range of bonding energies, weakly held P being the most readily available to crops. For the soils at Rothamsted, the most suitable extractant for plant-available P is sodium bicarbonate (Olsen's method). There is a very strong relationship between crop yield and Olsen P from which the critical level of Olsen P at which a soil should be maintained to optimize crop yield and P-use efficiency can be determined. Efficiency, calculated by the balance method, can exceed 90% when the amount of P applied is nearly equal to that removed in harvested crops. Maintaining sufficient plant-available P in soil to ensure food security by adding P in fertilizers and manures must not lead to the transfer of P to the aquatic environment where it can disturb the biological balance.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgments

This review has been possible because of the foresight of those who started the long-term experiments whose data we have used. First, Lawes and Gilbert at Rothamsted in 1840s–1850s; then the Royal Agricultural Society of England at Woburn in 1876; and then East Suffolk County Council at Saxmundham in 1899; and to those who continued the tradition by starting similar experiments. Our thanks also go to the innumerable members of the staff at all three stations who helped in so many ways with the field and laboratory experiments. We also thank the Lawes Agricultural Trust. Rothamsted Research receives strategic funding from the Biotechnology and Biological Sciences Research Council (BBSRC) of the UK. P research is supported by BBSRC Grant BBS/E/C/00005197 and the Rothamsted Long-term Experiments National Capability by BBSRC Grant BBS/E/C/000J0300.

References

Blake, L., A.E. Johnston, P.R. Poulton, and K.W.T. Goulding. 2003. Changes in soil phosphorus fractions following positive and negative phosphorus balances for long periods. Plant Soil 254:245–261. doi:10.1023/A:1025544817872

Boussingault, J.B. 1845. Rural economy, in its relation with chemistry, physics, and meteorology, or, chemistry applied to agriculture. Translated by G. Law. Appleton & Co., New York.

Boyd, D.A. 1965. The relationship between crop response and the determination of soil phosphorus by chemical methods. In: Soil phosphorus. Technical Bull. 13. Ministry of Agriculture, Fisheries and Food. HMSO, London. p. 94–102.

Brookes, P.C., G. Heckrath, J. De Smet, G. Hofman, and J. Vanderdeelen. 1997. Losses of phosphorus in drainage water. In: H. Tunney, O.T. Carton, P.C. Brookes, and A.E. Johnston, editors, Phosphorus loss from soil to water. CABI, UK. p. 253–271.

Brookes, P.C., D.S. Powlson, and D.S. Jenkinson. 1984. Phosphorus in the soil microbial biomass. Soil Biol. Biochem. 16:169–175. doi:10.1016/0038-0717(84)90108-1

Brookes, P.C., K.R. Tate, and D.S. Jenkinson. 1983. The adenylate energy charge of the soil microbial biomass. Soil Biol. Biochem. 15:9–16. doi:10.1016/0038-0717(83)90112-8

Cardenas, L.M., A.L. Collins, J.A.J. Dungait, J. Hawkins, A. Chabbi, and C. Hawes. 2016. The contribution of farm-scale experiments to the understanding of soil processes and implications for ecosystem services. Eur. J. Soil Sci. 67:359. doi:10.1111/ejss.12360

Catt, J.A., K.R. Howse, R. Farina, D. Brockie, A. Todd, et al. 1998. Phosphorus losses from arable land in England. Soil Use Manage. 14(s4):168–174. doi:10.1111/j.1475-2743.1998.tb00636.x

Chang, S.C., and M.L. Jackson. 1958. Soil phosphorus fractions in some representative soils. J. Soil Sci. 9:109–119. doi:10.1111/j.1365-2389.1958.tb01903.x

Chater, M., and G.E.G. Mattingly. 1980. Changes in organic phosphorus contents of soils from long-continued experiments at Rothamsted and Saxmundham. In: Rothamsted Experimental Station Report for 1979, Part 2. Lawes Agricultural Trust, Hertfordshire, UK. p. 41–61. doi:10.23637/ERADOC-1-34288

Coleman, R. 1942. Utilization of adsorbed phosphate by cotton and oats. Soil Sci. 54:237–246. doi:10.1097/00010694-194210000-00003

Crowther, E.M. 1948. Fertilizers during the war and after. Pamphlet 13. Bath and West and Southern Counties Society. Bath, UK.

Dyer, B. 1894. On the analytical determination of probably available "mineral" plant food in soil. J. Chem. Soc. Trans. 65:115–167. doi:10.1039/CT8946500115

Dyer, B. 1901. A chemical study of the phosphoric acid and potash contents of the wheat soils of Broadbalk field, Rothamsted. Philos. Trans. R. Soc. B 194:235–290.

Dyer, B. 1902. Results of investigations on the Rothamsted soils. USDA Bull. 106. Office of Experiment Stations, USDA, Washington, DC.

George, T.S., C.D. Giles, D. Menezes-Blackburn, L.M. Condron, A.C. Gama-Rodrigues, et al. 2018. Organic phosphorus in the terrestrial environment: a perspective on the state of the art and future priorities. Plant Soil 427:191–208. doi:10.1007/s11104-017-3391-x

Heckrath, G., P.C. Brookes, P.R. Poulton, and K.W.T. Goulding. 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. J. Environ. Qual. 24:904–910. doi:10.2134/jeq1995.00472425002400050018x

Hedley, M.J., J.W.B. Stewart, and B.S. Chauhan. 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. Soil Sci. Soc. Am. J. 46:970–976. doi:10.2136/sssaj1982.03615995004600050017x

Hilton, J., A.E. Johnston, and C.J. Dawson. 2010. The phosphate life-cycle: Rethinking the options for a finite resource. Proc. Int. Fert. Soc. 668:1–42.

Hislop, J., and I.J. Cooke. 1968. Anion exchange resin as a means of assessing soil phosphate status; a laboratory technique. Soil Sci. 105:8–11. doi:10.1097/00010694-196801000-00003

Holford, I.C.R., and G.E.G. Mattingly. 1976a. Model for behavior of labile phosphate in soil. Plant Soil 44:219–229. doi:10.1007/BF00016969

Holford, I.C.R., and G.E.G. Mattingly. 1976b. Phosphate adsorption and availability plant of phosphate. Plant Soil 44:377–389. doi:10.1007/BF00015889

Holford, I.C.R., and G.E.G. Mattingly. 1979. Effects of phosphate buffering on the extraction of labile phosphate by plants and by soil tests. Aust. J. Soil Res. 17:511–514. doi:10.1071/SR9790511

IUSS Working Group WRB. 2015. World reference base for soil resources 2014, update 2015: International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Rep. 106. FAO, Rome.

Johnston, A.E. 1997. Fertilisers and agriculture: Fifty years of developments and challenges. Proceedings 396. The Fertiliser Society, York, UK. p. 19–48.

Johnston, A.E. 2001. Principles of crop nutrition for sustainable food production. Proc. Int. Fert. Soc. 459:1–39.

Johnston, A.E. 2011. Assessing soil fertility: The importance of soil analysis and its interpretation. Potash Development Association, York, UK.

Johnston, A.E., and H.V. Garner. 1969. Broadbalk: Historical introduction. In: Rothamsted Experimental Station Report for 1968, Part 2. Lawes Agricultural Trust, Hertfordshire, UK. p. 12–25. doi:10.23637/ERADOC-1-34916

Johnston, A.E., P.W. Lane, G.E.G. Mattingly, P.R. Poulton, and M.V. Hewitt. 1986. Effects of soil and fertilizer P on yields of potatoes, sugar beet, barley and winter wheat on a sandy clay loam soil at Saxmundham, Suffolk. J. Agric. Sci. 106:155–167. doi:10.1017/S0021859600061864

Johnston, A.E., G.E.G. Mattingly, and P.R. Poulton. 1976. Effect of phosphate residues on soil phosphorus values and crop yields: I. Experiments on barley, potatoes and sugar beet on sandy loam soils at Woburn England. In: Rothamsted Experimental Station Report for 1975, Part 2. Lawes Agricultural Trust, Hertfordshire, UK. p. 5–35. doi:10.23637/ERADOC-1-34502

Johnston, A.E., and A. Penny. 1972. The Agdell experiment. In: Rothamsted Experimental Station Report for 1971, Part 2. Lawes Agricultural Trust, Hertfordshire, UK. p. 38–68. doi:10.23637/ERADOC-1-37287

Johnston, A.E., and P.R. Poulton. 1977. Yields on the Exhaustion Land and changes in NPK content of the soils due to cropping and manuring, 1852–1975. In: Rothamsted Experimental Station Report for 1976, Part 2. Lawes Agricultural Trust, Hertfordshire, UK. p. 53–85. doi:10.23637/ERADOC-1-34447

Johnston, A.E., and P.R. Poulton. 1992. The role of phosphorus in crop production and soil fertility: 150 years of field experiments at Rothamsted, United Kingdom. In: J.J. Schultz, editor, Phosphate fertilizers and the environment: Proceedings of an international workshop. Spec. Publ. 18. International Fertilizer Development Center, Muscle Shoals, AL. p. 45–63.

Johnston, A.E., and P.R. Poulton. 2011. Response of cereals to soil and fertilizer phosphorus. HGCA Research Review 74. Agriculture and Horticulture Development Board, Warwickshire, UK.

Johnston, A.E., and P.R. Poulton. 2014. Changing concepts for the efficient use of phosphorus in agriculture. Proc. Int. Fert. Soc. 757:1–38.

Johnston, A.E., P.R. Poulton, and K. Coleman. 2009. Soil organic matter: Its importance in sustainable agriculture and carbon dioxide fluxes. Adv. Agron. 101:1–57. doi:10.1016/S0065-2113(08)00801-8

Johnston, A.E., P.R. Poulton, P.E. Fixen, and D. Curtin. 2014. Phosphorus: Its efficient use in agriculture. Adv. Agron. 123:177–228. doi:10.1016/B978-0-12-420225-2.00005-4

Johnston, A.E., P.R. Poulton, and J.K. Syers. 2001. Phosphorus, potassium, and sulphur cycles in agricultural soils. Proc. Int. Fert. Soc. 465:1–44.

Johnston, A.E., P.R. Poulton, and R.P. White. 2013. Plant-available soil phosphorus: Part II. The response of arable crops to Olsen P on a sandy clay loam and a silty clay loam. Soil Use Manage. 29:12–21. doi:10.1111/j.1475-2743.2012.00449.x

Johnston, A.E., P.R. Poulton, R.P. White, and A.J. Macdonald. 2016. Determining the longer term decline in plant-available soil phosphorus from short-term measured values. Soil Use Manage. 32:151–161. doi:10.1111/sum.12253

Jordan-Meille, L., G.H. Rubaek, P.A.L. Ehlert, V. Genot, G. Hofman, et al. 2012. An overview of fertilizer-P recommendations in Europe: Soil testing, calibration and fertilizer recommendations. Soil Use Manage. 28:419–435. doi:10.1111/j.1475-2743.2012.00453.x

Lawes Agricultural Trust, 1896. Report of the Lawes Agricultural Trust Committee. J. R. Agric. Soc. England. Series 3, Vol. 7. p. 324–332.

Lawes, J.B. 1842. Ammoniacal manure. Gard. Chron., 2 April, p. 221.

Lawes, J.B. 1843a. Ammonia. Gard. Chron., 7 October, p. 692.

Lawes, J.B. 1843b. J.B. Lawes's Patent Manures. Gard. Chron., 1 July, p. 442.

Lawes, J.B., and J.H. Gilbert. 1873. Reports of experiments on the growth of barley for twenty years in succession on the same land. J. R. Agric. Soc. England, Vol. IX, Part I, 5–79; Part II, 79–178

Lawes, J.B., and J.H. Gilbert. 1895. The Rothamsted experiments; being an account of some of the results of the agricultural investigations conducted at Rothamsted in the field, the feeding shed, and the laboratory, over a period of fifty years. Trans. Highl. Agric. Soc. Scotl. Fifth Series, Vol. 7.

Liebig, H. von. 1872. Soil statics and soil analysis. J. Chem. Soc. 25:318, 837.

Macdonald, A., P. Poulton, I. Clark, T. Scott, M. Glendining, S. Perryman, J. Storkey, J. Bell, I. Shield, V. McMillan, and J. Hawkins. 2018. Guide to the classical and other long-term experiments, datasets, and sample archive. Rothamsted Research, Hertfordshire, UK. doi:10.23637/ROTHAMSTED-LONG-TERM-EXPERIMENTS-GUIDE-2018

Mattingly, G.E.G. 1957. Effects of radioactive phosphate fertilisers on yield and phosphorus uptake by ryegrass in pot experiments on calcareous soils from Rothamsted. J. Agric. Sci. 49:160–168. doi:10.1017/S0021859600036133

Mattingly, G.E.G., and F.V. Widdowson. 1958a. Uptake of phosphorus from P^{32} labelled superphosphate by field crops. Part I. Effects of simultaneous application of non-radioactive phosphorus fertilizers. Plant Soil 9:286–304. doi:10.1007/BF01394156

Mattingly, G.E.G., and F.V. Widdowson. 1958b. Uptake of phosphorus from P^{32} labelled superphosphate by field crops: Part II. Comparison of placed and broadcast applications to barley. Plant Soil 10:161–175. doi:10.1007/BF01394262

McDowell, R., A. Sharpley, P. Brookes, and P. Poulton. 2001. Relationships between soil test phosphorus and phosphorus release to solution. Soil Sci. 166:137–149. doi:10.1097/00010694-200102000-00007

Mekonnen, M., and A.Y. Hoekstra. 2018. Global anthropogenic phosphorus loads to freshwater and associated grey water footprints and water pollution levels: A high-resolution global study. Water Resour. Res. 54:345–358. doi:10.1002/2017WR020448

Nawara, S., T. van Dael, R. Merckx, F. Amery, A. Elsen, et al. 2017. A comparison of soil tests for available phosphorus in long-term field experiments in Europe. Eur. J. Soil Sci. 68:873–885. doi:10.1111/ejss.12486

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L.A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939. USDA, Washington, DC.

Maher, F.W., and B.S. Thorrold. 1989. Accumulation of phosphorus fractions in yellow-brown pumice soils with development. N. Z. J. Agric. Res. 32:53–62. doi:10.1080/00288233.1989.10423477

Orr, R.J., P.J. Murray, C.J. Eyles, M.S.A. Blackwell, L.M. Cardenas, et al. 2016. The North Wyke farm platform: effect of temperate grassland farming systems on soil moisture contents, runoff and associated water quality dynamics. Eur. J. Soil Sci. 67:374–385. doi:10.1111/ejss.12350

Peukert, S., B.A. Griffith, P.J. Murray, C.J.A. Macleod, and R.E. Brazier. 2014. Intensive management in grasslands causes diffuse water pollution at the farm scale. J. Environ. Qual. 43:2009–2023. doi:10.2134/jeq2014.04.0193

Pionke, H.B., W.J. Gburek, A.N. Sharpley, and J.A. Zollweg. 1997. Hydrological and chemical controls on phosphorus loss from catchments. In: H. Tunney, O.T. Carton, P.C. Brookes, and A.E. Johnston, editors, Phosphorus loss from soil to water. CABI, UK. p. 225–242.

Poulton, P.R., A.E. Johnston, A.E. Macdonald, R.P. White, and D.S. Powlson. 2018. Major limitations to achieving "4 per 1000" increases in soil organic carbon stock in temperate regions: evidence from long-term experiments at Rothamsted Research, UK. Glob. Change Biol. 24:2563–2584. doi:10.1111/gcb.14066

Poulton, P.R., A.E. Johnston, and R.P. White. 2013. Plant-available soil phosphorus. Part I: The response of winter wheat and spring barley to Olsen P on a silty clay loam. Soil Use Manage. 29:4–11. doi:10.1111/j.1475-2743.2012.00450.x

Powlson, D.S. 1998. Phosphorus, agriculture and water quality. Soil Use Manage. 14:123. doi:10.1111/j.1475-2743.1998.tb00629.x

Rothamsted Research. 2019. e-RA: The electronic Rothamsted Archive. http://www.era.rothamsted.ac.uk.

Schofield, R.K. 1955. Can a precise meaning be given to "available" soil phosphorus? Soils Fert. 18:373–375.

Silvertown, J., P. Poulton, E. Johnston, G. Edwards, M. Heard, and P. Biss. 2006. The Park Grass experiment 1856–2006: Its contribution to ecology. J. Ecol. 94:801–814. doi:10.1111/j.1365-2745.2006.01145.x

Stribley, D.P., P.B. Tinker, and R.C. Snellgrove. 1980. Effect of vesicular-arbuscular mycorrhizal fungi on the relations of plant-growth, internal phosphorus concentration, and soil phosphate analyses. J. Soil Sci. 31:655–672. doi:10.1111/j.1365-2389.1980.tb02112.x

Syers, J.K., A.E. Johnston, and D. Curtin. 2008. Efficiency of soil and fertilizer phosphorus. FAO Fertilizer and Plant Nutrition Bull. 18. FAO, Rome.

Tiessen, H., and J.O. Moir. 1993. Characterisation of available P by sequential extraction. In: M.R. Carter, editor, Soil sampling and methods of analysis. Lewis, London. p. 75–86.

UK TAG. 2008. UK environmental standards and conditions (phase 2). UK Technical Advisory Group on the Water Framework Directive.

Voelcker, A. 1874. On the composition of waters of land drainage. J. R. Agric. Soc. Engl. 30:132–165.

Warren, R.G. 1958. The residual effects of the manurial and cropping treatments in the Agdell Rotation experiment. In: Rothamsted Experimental Station Report for 1957. Lawes Agricultural Trust, Hertfordshire, UK. p. 252–260. doi:10.23637/ERADOC-1-35007

Warren, R.G., and A.E. Johnston. 1962. Barnfield. In: Rothamsted Experimental Station Report for 1961. Lawes Agricultural Trust, Hertfordshire, UK. p. 227–247. doi:10.23637/ERADOC-1-37013

Warren, R.G., and A.E. Johnston. 1964. The Park Grass experiment. In: Rothamsted Experimental Station Report for 1963. Lawes Agricultural Trust, Hertfordshire, UK. p. 240–262. doi:10.23637/ERADOC-1-56

Warren, R.G., and A.E. Johnston. 1965. Notes on the use of soil analysis for estimating available P in Rothamsted soils. In: Soil phosphorus. Ministry of Agriculture Fisheries and Food Technical Bull. 13. H.M. Stationery Off., London. p. 30–37.

Warren, R.G., and A.E. Johnston. 1967. Hoosfield continuous barley. In: Rothamsted Experimental Station Report for 1966. Lawes Agricultural Trust, Hertfordshire, UK. p. 320–338. doi:10.23637/eradoc-1-47796

Way, J.T. 1850. On the power of soils to absorb manure. J. R. Agric. Soc. Engl. 11:313–379.

Wild, A. 1950. The retention of phosphate by soils: A review. J. Soil Sci. 1:221–238. doi:10.1111/j.1365-2389.1950.tb00734.x

Withers, P.J.A., R.A. Hodgkinson, A. Rollett, C. Dyer, R. Dils, et al. 2017. Reducing soil phosphorus fertility brings potential long-term environmental gains: A UK analysis. Environ. Res. Lett. 12:063001. doi:10.1088/1748-9326/aa69fc