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1	Phosphorus in agriculture: a review of results from 175 years research at
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19 Abstract

Insight into the role of phosphorus (P) in soil fertility and crop nutrition at Rothamsted, and 20 21 its involvement in associated environmental issues, has come from long-term field 22 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 23 in fertilizers and manures build-up reserves of P in soil. There is a strong relationship 24 between crop yield and plant-available P (Olsen P) and a critical level of Olsen P can be 25 26 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 27 28 components and is held there with a range of bonding energies so that when no P is applied 29 the decline in Olsen P follows a smooth curve. We conceptualise inorganic soil P as being in four pools of vastly varying size, availability for uptake and extractability by reagents used in 30 routine soil analysis, and with reversible transfer of P between pools. For very disparate soils 31 at Rothamsted and in the US there is a strong relationship between the change in Olsen P and 32 P Removal/Input ratios suggesting an underlying similarity in inorganic P behaviour. 33 34 Maintaining soil near the critical level should optimise yield and the use of the global P resource while minimising the risk of transfer of large amounts of P to the aquatic 35 environment. 36

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38 Core ideas

• Lawes started long-term experiments on P in 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 used to establish critical level of available-P in soil for optimum yield

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• Inorganic P transfers between 4 pools of different size/extractability/availability

44 Introduction

This review is mainly about the agronomic role of phosphorus (P) in crop production and soil
fertility illustrated with examples from Rothamsted long-term experiments and those at
Woburn and Saxmundham (Table 1). Descriptions of the recent long-term experiment at
North Wyke, 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, 50 to increase yield and ensure a response to other nutrient additions especially nitrogen (N). 51 52 Despite enormous problems, P imports into the UK doubled during World War II as more land was brought into food production and farmers sought to maximise yields. The rationing 53 of phosphate fertilizers was introduced in 1942 (Crowther, 1948). From the 1940s the 54 efficient use of newly applied P fertilizers and manures and of the soil P reserve from the 55 accumulated residues (P applied to a crop *minus* that removed in the crop) from past fertilizer 56 57 and manure applications, became the focus of much research.

Frequently, a new programme of research has developed to answer questions identified in 58 earlier research. Aware that organic P was important in many crop production systems in 59 many parts of the world, Mattingly instigated a programme in the 1960s to determine the total 60 organic P, and its rate of mineralisation in the top 23cm soil in the long-term experiments. In 61 summary, the results (Chater and Mattingly, 1980) showed that as much as 30% of the total P 62 was organic P but the annual rate of mineralisation was only 0.5 to 1.5 kg P ha⁻¹ on the old 63 arable soils, far too little to produce economic yields of cereals in UK conditions. The annual 64 rate of mineralisation was higher (7.7 to 8.5 kg P ha⁻¹) where soils had been ploughed out 65 from permanent grass or as much as 100 t ha⁻¹ of farmyard manure (FYM) had been applied. 66

As a consequence of these very small rates of organic P mineralisation, and organic P not
being determined in most methods used in routine soil analysis for plant-available P, our
research had mainly focussed on inorganic P. However, the role of organic P in agriculture
and the wider environment is still much debated (George et al., 2018).

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).

75 Background

Phosphorus, the 12th most abundant element in the earth's crust, was discovered in 1669 by 76 Hennig Brand in Hamburg, Germany. In the 1830s, some 170 years later, John Bennet 77 Lawes, owner of the farm at Rothamsted near Harpenden, UK, 40km north of London, began 78 79 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 80 widowed mother and sister. At that time, and only in England, crushed bones were widely 81 used to increase the yields of crops, particularly of turnips (Brassica rapa) and grassland, but 82 Lawes found that they did not increase yields on his farm. Intrigued by this, Lawes made and 83 tested several inorganic ammonium salts on small plots and pots in the late 1830s and early 84 1840s and showed that ammonium phosphate, in which the phosphate was water soluble, 85 gave the largest yields of cabbages (Brassica oleracea) and turnips (Lawes, 1842; 1843). 86 87 Lawes then did a series of trials to solubilise the phosphate in bones and in 1842 was granted a patent for his process of treating bone ash and other phosphatic materials with sulphuric 88 acid to produce a dry reaction product, single superphosphate together with calcium sulphate, 89 which, when crushed to a powder and spread on land, improved crop yields. By June 1843, 90

91 Lawes was advertising for sale the phosphate of lime he was manufacturing at a factory in92 London.

93 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 UK. The rigour of his 94 approach and the methodology used was probably influenced by that of Boussingault who in 95 the early 1830s had started field experiments on crops grown in rotation on his farm at 96 Bechelbronn in Alsace (Boussingault, 1845). Besides weighing and analysing the manures 97 used and the crops grown Boussingault produced nutrient balance sheets, including one for 98 nitrogen (N). Lawes' approach was more detailed than that of Boussingault. Lawes grew the 99 same crop year after year in most of his experiments because he considered that he would 100 better understand its nutrient requirements (Lawes and Gilbert, 1895). He also tested N, P, 101 potassium (K), magnesium (Mg) and sodium (Na) singly and in combination as inorganic 102 salts (fertilizers) and compared their effects with those of FYM. 103

104 The start of the Rothamsted field experiments

In June 1843, Lawes started the first large-scale experiment on turnips on Barnfield, and in 105 autumn the second on winter wheat (Triticum aestivum) on Broadbalk. That year he also 106 appointed Joseph Henry Gilbert, a chemist, to assist him in the management of the 107 experiments and to analyse crop and soil samples, mostly for N. At the first harvest of both 108 wheat and turnips, the yields showed the need for fertilizer N. But, with additional plant-109 available P, from the applied superphosphate, yields were even larger. These were the first 110 111 important results on increasing crop yield from Rothamsted Experimental Station (now Rothamsted Research). 112

Having established the Barnfield, Broadbalk and other experiments (Table 1), Lawes andGilbert concentrated on managing them, recording the yields with notes on the growth of the

crop and analysing 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, http://www.era.rothamsted.ac.uk). It is our present good fortune that Lawes started several long-term experiments (at his own expense), and that others have been started subsequently, because one or other experiment is invariably generating results of interest and importance.

121 The second half of the 19th century can be considered perhaps as "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).

124 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 analysing soils from the field experiments

127 for P.

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

Rothamsted ‡ Barnfield1843 >Root cropsGrass since 1975Warren and Johnston, 1962Broadbalk1843 >W. wheatParts of the experiment have included rotations since 1968Johnston and Garner, 1969 Poulton et al., 2018Agdell1848 - 1970Arable cropsHalf in grass, 1958 - 1969Johnston and Penny, 1972 Johnston et al., 2013; 2016Hoosfield1852 >S. barleyParts of the experiment included rotations 1968-1978Warren and Johnston, 1967 Johnston et al., 2016. Poulton et al., 20Exhaustion1856 >Arable cropsJohnston and Poulton, 1977	
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Exhaustion 1856 > Arable crops Johnston and Poulton, 1977	
Land Poulton et al., 2013, Johnston et al., 2	016
Land Poulton et al., 2013. Johnston et al., 2	2016
Park Grass 1856 > Permanent Pasture since c. 1700 Warren and Johnston, 1964	
pasture Silvertown et al., 2006. Johnston et a	1., 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 [¶]	
Saxmunanam 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).

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131 Introduction of soil analysis for phosphorus reserves

132 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. H. von Liebig (1872), analysing soils from Broadbalk,

- showed that those with P since 1852 contained more P soluble in dilute nitric acid than
- 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
- 138 50 years on Broadbalk. Dyer determined both "total" P by digesting the soil for 48h with

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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 80-90% 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 by 8 or 9 :1 suggesting that citric-soluble P was a better index of P
availability (Dyer, 1894; Dyer, 1901, 1902).

144 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 145 showed that the P was retained in the soil. This was confirmed for the field situation when 146 Voelcker (1874) analysed drainage collected during 1866-1868 from plots on Broadbalk and 147 showed that although 33 kg ha⁻¹ P as water-soluble phosphate had been applied each year 148 since 1843 little of this P was in the drainage. These, and similar results elsewhere, showing 149 that P was retained in the soil led to the widely held view that P was so fixed in soil that it 150 would not be available to plants; consequently, fresh water-soluble fertilizer should be added 151 each year. The concept of P fixation was supported by many laboratory studies on 152 precipitation reactions of water-soluble P and the production of insoluble solid phase reaction 153 products, but the laboratory conditions were far removed from those in soils in the field. Wild 154 (1950) however, noted that phosphate ions were likely to be removed initially from the soil 155 solution by adsorption. These early laboratory studies, paid little attention to the availability 156 of P for uptake by roots. Coleman (1942) however, suggested that perhaps crops did not 157 respond to P, not because it was fixed, but because there was already sufficient plant-158 available P in the soil. This observation has been well supported by later work which also 159 showed that there was no response to P if lack of other nutrients, especially N and K, limited 160 yield and weeds, pests and diseases are not adequately controlled. 161

162 Soil analysis for plant available phosphorus

During the last two centuries many alkaline, neutral and acidic extractants for plant-available 163 have been tested on a wide range of soil types. Often, one was chosen believing that it 164 extracted P held in some combination with specific soil constituents such that the P was, or 165 would become, plant-available. Extractants that have remained in common use are those 166 which extract amounts of P that correlate well with crop response, either to soil P or freshly 167 applied P. However, Holford and Mattingly (1976a, b; and 1979) showed a negative 168 169 relationship between an effective soil test and phosphorus buffering capacity when buffering properties are controlled by phosphate adsorption characteristics. Recently, in Europe, several 170 171 studies 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). 172 In the early 1950s we did not have any extractant suitable for use with our mainly, slightly 173 calcareous clay loam soils at Rothamsted. The best was 0.01 M CaCl₂ (CaCl₂-P) (Schofield, 174 1955) because this is about the salt concentration in the soil solution of our soils, and the P 175 concentration could be considered as that in the soil solution. But, at that time, it was difficult 176 to determine low concentrations of P in the solution. In 1954 we received a typescript of 177 Olsen's method (Olsen et al., 1954) and we have used this method almost exclusively to 178 determine readily plant-available P because it best classifies our soils according to the 179 response of crops to applied P (Warren and Johnston, 1965). With the increased sensitivity in 180 many analytical techniques it is now much easier to determine P in CaCl₂ extracts and it has 181 been used to determine very readily available P in the soils from some long-term experiments 182 (see Section on Environmental Issues). Interestingly, we have determined total, Olsen P and 183 CaCl₂-P in soils receiving similar total amounts of P either as fertilizers or FYM in three 184 long-term experiments. The increase in total and Olsen P was very similar with both P 185 sources but there was twice as much CaCl₂-P in soils with extra SOM from FYM additions 186 (Johnston et.al., 2009). 187

188 Long-term release of phosphorus reserves from soil

One of the most important results from our long-term experiments has been that P added to 189 190 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 191 barley (Hordeum vulgare) on the Exhaustion Land in 1949 and subsequently (see later) we 192 have monitored the removal of P in the crops grown each year on plots 7 and 9 (NPK or P, 193 1856-1901) and plot 3 (FYM, 1876-1901) compared with the P removed from plots 1 and 5 194 (no P, 1856-1901). The P offtake in the crops grown in various periods between 1856 and 195 1975 was calculated by Johnston and Poulton (1977) and measured annually since 1976. 196 Table 2 shows the offtake of P in the crops grown after 1901 when applications of P and 197 FYM ceased. From 1902 to 2012, 394 kg P ha⁻¹ was removed from plots without P since 198 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 199 taken up from soils with reserves of P from past fertilizer or FYM additions (Johnston and 200 Poulton, 2014). More than 100 years after fertilizer P or FYM was last applied the P reserves 201 are still being recovered at 4-6 kg P ha⁻¹ yr⁻¹. Thus, the residue of applied P has not been 202 fixed irreversibly in soil but is an important P reserve. Also, if residues of applied P fertilizer 203 were fixed irreversibly in soil it would not be possible to increase plant-available P in soil as 204 seen in many soils world-wide. 205

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Table 2 Exhaustion Land; phosphorus 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 1856-1901 or in farmyard manure from 1876-1901 and none since.

			1 & 5 nce 1856	1410 kg P 1856	7 & 9 ha ⁻¹ applied 5-1901 phosphate	1260 kg P 1876	lot 3 ha ⁻¹ applied 5-1901 ard manure
			Amou	nts of P remov	ved in the crop, k	ag ha ⁻¹	
Period	Crop	Total	per year	Total	per year	Total	per year
1902-40 ⁺	S. barley	102	2.6	207	5.3	200	5.1
1941-85 [‡]	S. barley	189	4.2	394	8.8	478	10.6
1986-91 [§]	S. barley	28	4.7	51	8.5	60	10.1
1992-2012 [¶]	W. wheat	75	3.6	175	8.3	200	9.5
1902-2012	Total	394	-	827	-	938	-

+ Mainly s. barley grown during this period; no fertilizers or manure applied

‡ Fertilizer N has been applied at various rates since 1941; fallow in 1967 and 1975

§ Basal K and N applied since 1986

¶ S. wheat in 2001

Adapted from Johnston and Poulton (2014)

208 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 209 is that P held in soil?". One approach we used, was to sequentially extract P from soil with 210 chemical reagents thought to remove P in different chemical forms (Chang and Jackson, 211 1958; Hedley et al., 1982; Perrot et al., 1989; Tiessen and Moir, 1993). This was done for 212 archived and current soils from the same plot in six of our long-term experiments with a 213 range of treatments to determine the effect of treatment and time on the amount of P extracted 214 by each reagent (Blake et al., 2003). Table 3 shows data for Exhaustion Land soils and the 215 order in which the first five extractants were used; three further extractions were used to 216 determine the residual P, but the amounts were small (Blake et al., 2003). The first 217 determination was equilibration with an anion-exchange resin (Hislop and Cooke, 1968; 218 Tiessen and Moir, 1993), followed by extraction with NaHCO₃. While both these reagents 219 are used individually to determine plant-available P in routine soil analysis in sequential 220

- extractions, NaHCO₃ is used after resin. In this paper P extracted by 0.5 M NaHCO₃ during
- routine soil analysis we call Olsen P, and that extracted in sequential extraction we call
- 223 NaHCO₃ P (or bicarbonate P). The other extractants, and the forms of P they were thought
- to remove, are described by Blake et al. (2003).

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.,	_	Change in first five P fractions, kg P ha ⁻¹						
treatment	P balance [†]		0.5 M	0.1 M	1 M	0.5 M	Total	
and period	kg ha ⁻¹	Resin	NaHCO ₃	NaOH	NaOH	$\mathrm{H}_2\mathrm{SO}_4$	change	
1. No P since 1856 No P applied, 1902-93	-300	-49	-20	-195	-82	-19	-365	
9. P fertiliser Applied, 1856 - 1901 Not applied, 1902-93	1222 -644	158 -234	126 -138	79 -114	7 45	270 -253	640 -694	
3. Farmyard manure Applied, 1876 - 1901 Not applied, 1902-93	1035 -752	193 -259	129 -123	133 -159	107 -112	355 -164	917 -817	

⁺ The P balance is the amount of P applied *minus* the amount removed by the crop

Adapted from Blake et al., 2003

The P balance and changes in extracted P for the Exhaustion Land soils are for the top 23cm, 227 two sources of P and two periods. The first for plots initially with superphosphate from 1856-228 1901 and then none from 1902-1993, and the second for plots with FYM from 1876-1902 and 229 then none from 1902-1993. Both the organic P (Po) and inorganic P (Pi) (not shown 230 separately here but given by Blake et al., 2003) were determined analytically in the P 231 removed by 0.5 M NaHCO₃, 0.1 M NaOH and 1 M NaOH. For soils with P fertilizer and 232 with FYM, when the P balance was positive the amount of P extracted by each of the first 233 five extractants increased and then decreased when the P balance was negative (Table 3). 234

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235	These negative and positive changes in all five fractions in this soil account for almost 90
236	percent of the total P determined separately for each soil in each period.
237	The sequential extraction of P was made for a heavier textured, sandy clay loam soil to which
238	230 and 490 kg P ha ⁻¹ were added in both FYM and superphosphate between 1965 and 1967.
239	In spring 1969 the sum of the Pi extracted by resin and 0.5 M NaHCO ₃ was only 56 and 58%,
240	respectively, of the total increase in Pi in the first five extractants. This suggests that P had
241	moved quickly into other P fractions. The data in Blake et al. (2003) showed, for all the soils
242	investigated, that each of the eight soil P fractions increased during periods of P addition or
243	decreased when P was no longer applied. Importantly, these changes were not confined to
244	any one P fraction. Thus, water-soluble P added to soil is transferred to fractions that require
245	stronger chemical reagents to extract the P. When soils are cropped without P addition, this
246	more strongly-bound P is released, i.e. the transfer is reversible.

247 Evidence for crop yields being increased by soil phosphorus reserves

Rothamsted became increasingly interested in assessing the value of P reserves accumulated 248 in soil from past applications of P fertilizer and FYM when, in 1949, yields of spring barley 249 on the Exhaustion Land were increased by P residues accumulated from these two sources of 250 P (Johnston and Poulton, 1977). Large reserves of total P had accumulated from annual 251 applications of superphosphate from 1856 to 1901 and FYM from 1876 to 1901 (Johnston 252 and Poulton, 1977). No P or other nutrients were applied after 1901 until basal N was applied 253 from 1941. In the very dry spring in 1949, early growth of the spring barley varied greatly 254 255 across the site and the boundaries of the ten 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 256 before 1901 but none since, good evidence suggesting that P added before 1901 was still 257 available for uptake by plant roots and had not been fixed irreversibly in soil. This important 258

- 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).

	Pl	Plot numbers and treatment							
	1, 2, 5, 6	7, 8, 9, 10	3, 4						
		P applied	P applied						
	No P since 1856	1856-1901	1876-1901						
		as superphosphate	in farmyard manure						
Period	Mean yield grain at 85% DM, t ha ⁻¹ yr ⁻¹								
1949-53	1.59	2.88	3.03						
1954-59	1.80	3.02	3.32						
1960-63	1.99	2.72	3.14						
1964-69 [†]	1.71	3.60	4.28						
1970-74	1.83	4.18	4.75						

Table 4 Mean yields of spring barley grain, 1949-74, grown on soils with and without P residues; Exhaustion Land, Rothamsted

† The experiment was fallowed in 1967

Adapted from Johnston and Poulton, 1977

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The extent to which P reserves from past applications of fertilizer and FYM could be 263 recovered by grass and arable crops was tested by modifying treatments in the Agdell 264 experiment, 1848-1951 (Warren, 1958). Growing either grass or arable crops on one half of 265 each of the original six very large plots between 1958 and 1969 increased SOM in the grass 266 plots to 2.4% compared with 1.5%, where arable crops were grown. Also, in this 12-year 267 period, a range of Olsen P levels was built-up on sub-plots on each of the original six plots 268 (Johnston and Penny, 1972). Potatoes, sugar beet and spring barley were each grown twice 269 between 1970 and 1972 and the yield/Olsen P relationship determined (Table 5). To get 95% 270 of the maximum yield required more Olsen P on the soil with less SOM and the percent 271 variance accounted for was less. When the soils from the 48 plots were sampled and sown to 272 ryegrass (Lolium perenne) in pots in the glasshouse, the Olsen P required to achieve 95% of 273

the maximum yield together with the percent 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 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

	Soil organic	Yield at 95%	Olsen P associated	Variance
	matter	of the asymptote	with the 95% yield	accounted for
Сгор	%	t ha ⁻¹	mg kg ⁻¹	%
		Field ex	periments	
Spring barley grain,	2.4	5.00	16	83
t ha ⁻¹	1.5	4.45	45	46
Potato tubers,	2.4	44.7	17	89
t ha ⁻¹	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,	2.4	6.46	23	96
g pot ⁻¹	1.5	6.51	25	82

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280 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

287	the added P to equilibrate with existing soil P. Each year sufficient N and K were applied so
288	as not to limit yields. In both experiments the relationship between yield and Olsen P was
289	best described by a Mitscherlich type asymptotic regression equation; for examples see
290	Poulton et al. (2013) and Figure 1. From the equation, the Olsen P associated with 98% of the
291	asymptotic yield together with its associated standard error was determined, and this level of
292	Olsen P we considered to be the critical level for that crop and soil because the yield was not
293	increased either with larger concentrations of Olsen P or by addition of fresh P fertilizer.
294	At Saxmundham, adding P to existing plots in 1965-1968 established soils with Olsen P
295	ranging from 3 to 67 mg P kg ⁻¹ by autumn 1968 (Johnston et al., 1968). The plots were
296	divided into four groups of five sub-plots to grow different crops on each group. From 1969
297	fresh P was added to four of these sub-plots while one sub-plot had no further P. The
298	yield/Olsen P relationship was determined initially for potatoes, sugar beet, and spring barley
299	grown in rotation (Johnston et al., 1986) and later for winter wheat (Johnston et al., 2013).
300	On the Exhaustion Land the five adjacent, odd-numbered main plots were each divided into
301	four smaller ones (each 6.0 x 25.6 m) in 1986 and P was tested in three periods. 1) from
302	1986-1992, 0 v 44 v 87 v 131 kg P ha ⁻¹ was applied annually as triple superphosphate, 2)
303	from 1993-1999 no fresh P was applied, and 3) since 2000 a maintenance dressing of P has
304	been applied to maintain Olsen P on those sub-plots which had received P from 1986 to 1992.
305	Spring barley was grown from 1986-1991 and winter wheat since 1992, except 2001 (spring
306	wheat). Each year the asymptotic grain yield and critical Olsen P, with their associated
307	standard errors was determined from the yield/Olsen P relationship (Poulton et al., 2013). To
308	illustrate this relationship, we show two years when the asymptotic yield was very different,
309	but the critical Olsen P was similar (Figure 1).

The percentage variance accounted for in the yield/Olsen P relationship ranged from 83 to 310 97% (with only two exceptions in 23 years) which confirms that the Olsen method is a good 311 indicator of plant-available P, and that P was the principal soil factor controlling growth 312 (Poulton et al., 2013). The high percentage variance accounted for in these experiments 313 compares to that, c 50%, reported by Boyd (1965) for a series of national experiments in 314 England, which were done on a range of farms where the soil type, weather and management 315 316 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 317 318 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 319 Olsen P. 320

The critical Olsen P value will vary with soil type, but our experience suggests that soil 321 structure and thus the ability of a crop to produce a root system capable of exploring the soil 322 323 for nutrients is a major cause of this variation. Knowledge of the critical value enables a farmer to manage the P status of his soils and the soil should be sampled once every three to 324 five years to ensure that the level is being maintained. Once a protocol for soil sampling has 325 been established it should be followed rigorously to monitor changes of plant-available P 326 with time and the method of analysis should be simple and reproducible (Johnston, 2011). 327 There is no reason to limit P applications to water-soluble P fertilizers, any source of P can be 328 used provided it maintains the critical level of plant-available P. Knowing the critical level 329 330 also helps when there are environmental issues like the transfer of P from soil to surface 331 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 332 control losses rather than restrict the amount of P a farmer can apply. 333

334 The build-up and decline in plant-available phosphorus reserves in soil

335 Build-up of plant-available phosphorus

336 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 337 P and the increase in total P when both are expressed in kg P ha⁻¹ but the increase in Olsen P 338 is only about 13% of the increase in total soil P (Johnston, 2001). Of more practical 339 importance is the amount of P required and the time needed to build-up Olsen P above the 340 341 critical level. On the Exhaustion Land the range of Olsen P was increased (Table 6) by the large amounts of P applied to the sub-plots newly created in 1986 (see above) and spring 342 barley grown from 1986-1991 and winter wheat in 1992. From the total P offtake in grain 343 plus straw of these two cereals, it was possible to calculate the increase in Olsen P both as a 344 percentage of the P applied and as a percentage of the P balance (Table 6). Interestingly 345 346 these percent 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 347 on the original FYM-treated plot. A possible explanation for this result is discussed later. 348

						P offtake			
Original	Р			Change	P applied	grain + straw		Increase	in Olsen P
treatment	treatment [†]	Olsen P	, mg kg ⁻¹	in Olsen P [‡]	1986-1992	1986-1992	P balance [§]	as a % of	as a % of
1856-1901	1986-1992	1985	1992	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	P applied	P balance
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
$FYM^{\dagger\dagger}$	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

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

+ 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 top-soil, 0-23 cm

§ The 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 between 1902-1985; mean of data from two main plots

349 ^{††} Farmyard manure applied 1876-1901, no P applied between 1902-1985; data from one main plot

350

351 Decline in plant-available phosphorus

352	In 1903, soils on	the Exhaustion Land	d that had receiv	ed fertilizer P fror	n 1856-1901 or FYM

from 1876-1901 had 60-70 mg kg⁻¹ Olsen P in the top 23 cm, and these levels had declined to

5-19 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.

356 Intrigued by this and its possible implication for the forms of P held in soil and their release

357 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 sub-plots 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 years (Figure 2a).

361 The decline on the sub-plots without fresh P on each of the eight main plots could be fitted

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with a quadratic curve. Subsequently, these eight curves could be shifted horizontally on to 362 an extended x axis (years) and using an exponential model, a unified curve produced. (Figure 363 2b). From the unified curve, the half-life of the Olsen P, that is the time in years for it to 364 halve relative to the lowest level measured in the soil, can be calculated. To determine the 365 half-life does not require knowledge of the P offtake, only the change in Olsen P. 366 Knowledge of the half-life is useful when planning long-term policies for managing the P 367 status of soils, especially when there is a need to lower the level of plant-available P for 368 agricultural, environmental and ecological reasons (Johnston et al., 2016). As fertilizer prices 369 continued to increase in the 1980s, farmers wishing to optimise their use of P fertilizers and 370 maintain the critical level of Olsen P for their soil wanted to know for how long they could 371 withhold P applications if their soil was above the critical level. This question could be 372 answered from a decline curve like that in Figure 2b. In experiments on different soil types 373 (Table 1), we measured the decline in Olsen P over short periods on sub-plots with a wide 374 range of Olsen P. This range was created when fresh P fertilizer was added for a few years to 375 soils with pre-existing levels of Olsen P. For each experiment a unified decline curve was 376 produced, as described above. The horizontal shifts of the individual curves to bring them 377 into coincidence, and the half-life of the Olsen P determined. These half-lives ranged from 378 4.5 to 16.1 years (Table 7), the different values being related to soil type, crop grown, the 379 380 initial level of Olsen P, the time over which the measurements were made, and the P balance (Johnston et al., 2016). 381

Site and	Asymptote [†]	SE of	Variance accounted for	Rate of decline and its SE	Half-life and its SE
	$mg kg^{-1}$		%	k	
experiment	nig kg	observations	⁷ 0	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)
PK, 1898-1964	0.6	7.85	96.2	0.043 (0.0015)	16.1 (0.57)

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

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

Adapted from Johnston et al., 2016

383 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 percent recovery of applied P determined by either of two methods. First is the direct, but expensive method using ³²P-labelled fertilizer, which has limited applicability because of the short half-life of the labelled fertilizer. In field experiments at Rothamsted with ³²P, average P recovery ranged only from 5-25% (Mattingly, 1957; Mattingly and Widdowson, 1958,1959). Second is the difference method, where percent P recovery of added P, is calculated as:

$$Up_{-}Uo/Fp_{-}x_{-}100$$

where Up and Uo is the uptake of P by crops with and without added P and Fp is the amount

of P applied. Percent recovery of P is often in the range 5 - 10%. The method is suitable for

394 comparing the recovery of P from a range of P sources in one- or two-year experiments. But,

it tells us nothing about longer-term P recovery and its appropriateness has been questioned. 395 If not more than 25% of freshly applied P is taken-up by a crop, then the remainder of the P 396 in the crop must have come from the plant-available P reserve in the soil. Consequently, the 397 amount of recently added P which replaces that in the plant-available soil P reserve can be 398 considered as part of the efficient use of the newly added P (Syers et al. (2008). Thus, P use 399 efficiency is determined as the total P removed in the harvested crop (the offtake, Up, part of 400 which comes from the added fertilizer and part from soil reserve, which is being replaced) 401 divided by the total P applied (the input, Fp). Percent P-use efficiency is calculated as Up/Fp 402 403 x 100, and the method called the "balance method" because only the balance between Up and Fp is considered. In the USA, when just Up and Fp are known, they are expressed as a ratio, 404 the "offtake/input ratio" or Up/Fp ratio. This ratio can be related to the change in plant-405 available P. 406

When soil is at the critical Olsen P for optimum yield and this level is maintained by 407 replacing the P removed in the harvested crop, then P-use efficiency, determined by the 408 balance method, can exceed 90%. For example, on the silty clay loam of the Exhaustion 409 Land, five plots had a range of Olsen P from 9 to 31 mg P kg⁻¹, and winter wheat was grown 410 each year for four years. The average annual grain yield increased with Olsen P to reach a 411 plateau above the critical value, and the total amount of P removed in grain plus straw in four 412 vears increased also (Table 8). Each autumn, "maintenance" P at 20 kg P ha⁻¹ was applied to 413 maintain the initial Olsen P values. Where the total P application in four years more nearly 414 matched the P removed, P-use efficiency was about 95% when calculated as the Up/Fp ratio 415 (Table 8). 416

	Olsen P, mg kg ⁻¹ , in 2004 \dagger					
	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	

Table 8 Maintaining Olsen P by replacing the P removed in the grain and straw of four winter wheat crops, Exhaustion Land, 2005-08

417 [†] Olsen P in soils sampled in autumn

418

419 Developing concepts describing the behaviour of soil and fertilizer

420 phosphorus

The need for a simple, visual method to explain the ideas presented here for the relationship 421 between soil P and crop production led Johnston (2001) and Johnston et al. (2001) to suggest 422 a simple model. Inorganic P in soil is considered to be in four pools of vastly varying size and 423 greatly varying plant-availability with reversible transfer of P between the pools. This simple 424 model was further developed by Syers et al. (2008) (as shown in Figure 3). The descriptions 425 used are essentially operational definitions. The plant-availability of P is linked to its 426 accessibility to roots (soil structure) and extractability by reagents used in routine soil 427 analysis. The P is considered to be retained on soil components with a continuum of bonding 428 energies, related to the nature of its physical association with these components, and may be 429 largely reversible with time. Such bonding may also explain why increasingly "strong" 430

reagents, like 1N NaOH and 0.5 N H₂SO₄, are required to extract this P in sequential
extraction.

433 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 434 replace that in the soil solution when it is taken up by roots. Pool 3 is a reserve of P 435 accumulated from past applications of P, is more strongly bonded but can become available 436 over periods of months or years. The P in pool 4 is very strongly bonded or is native soil P 437 that may only become very slowly plant-available by weathering. The long-term release of 438 soil P from the Exhaustion Land soils is most likely that in pools 3 and 4. Routine soil tests 439 measure P in pools 1 and 2 but this is not a finite quantity because it varies with the reagent 440 used to extract.it. However, in terms of the concepts in Figure 3, it can be defined provided 441 there is a strong relationship between the amount of P extracted and the response of a crop to 442 either soil P or freshly applied P fertilizer. 443

444

Crucial to this model is the reversible transfer of P between the pools which explains the 445 446 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 447 weeds, pests and diseases. The data in Table 6 strongly support the concept that only a 448 449 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 450 of the P balance, ranging approximately from 200 to 800 kg P ha⁻¹, was present as Olsen P in 451 452 1992 and this is of considerable interest. It suggests that there may be a ratio between the P in pools 2 and 3, and if this is so then it could give information about the amount of P available 453 to replace P in pool 2 as it is taken up by crops. 454

455 Relating changes in plant-available soil phosphorus to input/output ratios for data from 456 Rothamsted and North America

We have expressed our P balance data as output/input ratios and related them to the change in 457 Olsen P. These values have been plotted together with similar data from the International 458 Plant Nutrition Institute for the central plains in North America in Figure 4 (Johnston et al., 459 2014). A log function (not shown) fitted to all the data has an r^2 of 0.84. This relationship is 460 of considerable interest given that it is for a vastly disparate set of soils on two continents and 461 from both controlled experiments in England and derived 'State-wide' aggregate data in the 462 USA. This relationship makes a powerful and convincing statement suggesting that, for the 463 agricultural soils from which these data were obtained, there is an underlying similarity in the 464 behaviour of plant-available inorganic P in soil. 465

466 Environmental issues - phosphorus and eutrophication

Although P has a vital, irreplaceable role in food production through crop and animal 467 nutrition, environmental issues have come to the fore in recent decades, one of which has 468 been the transfer of P from both point and diffuse sources to surface water bodies. Increasing 469 P concentrations in inland fresh waters have been implicated as a major cause of disturbance 470 in the biological balance with many adverse effects on this important aquatic resource 471 (Mekonnen and Hoekstra, 2018). Addition of P from point sources, like sewage treatment 472 works, has declined in recent years by removing P from the discharged treated water. 473 Consequently, the proportion of P coming from diffuse sources, like intensively managed 474 agricultural land, has increased. Heckrath et al. (1995) measured the concentration of total P 475 in drainage water from plots with and without P on Broadbalk between October 1992 and 476 March 1995. Although the P concentration varied between years, it was not linearly related to 477 the concentration of Olsen P in the top 23 cm, but each year the concentration increased 478

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479 rapidly above a change point (or threshold value) of about 60 mg kg⁻¹ Olsen P. This level of
480 Olsen P was well above the critical level, 15-25 mg kg⁻¹ Olsen P, for optimum crop
481 production on this soil.

This data from Heckrath et al. (1995) was possibly unique at that time, because the drainage 482 water could be collected and analysed; a similar facility was rarely available in other 483 experiments. Consequently, attention was focussed on trying to find a surrogate analysis that 484 could give an indication of the concentration of P in the soil solution. Phosphorus soluble in 485 0.01M CaCl₂ was suggested because this P would be most at risk to loss in drainage. Soils 486 from five long-term experiments were extracted both with 0.01 M CaCl₂ and 0.5 M NaHCO₃ 487 (Johnston and Poulton, 1992; Brookes et al., 1997) and there was a similar sharp increase in 488 CaCl₂-P above a threshold value (or change point) of Olsen P (Figure 5). Similar 489 relationships between Olsen P and CaCl₂-P have been produced for several Rothamsted and 490 other experiments (McDowell et al., 2001) and show a wide range in change points from 20 491 to 60 mg kg⁻¹ Olsen P for arable soils and higher values for grassland soils. Experiments 492 would be required to check if the change point is specific to individual soil types. 493 Johnston (1997, Figure 12) used a schematic relationship between crop yield and Olsen P, to 494 suggest that the important factor was the difference between the critical Olsen P for crop 495 production and the threshold value for the concentration of P in the soil solution. This has 496 497 been illustrated by Withers et al. (2017. Figure 1) 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 498 adequate margin of "safety". But, for soils at Saxmundham, McDowell et al. (2001) give a 499 change point at 20 mg kg⁻¹ Olsen P while the critical Olsen P for cereal yields ranges from 500 <10 to about 34 mg kg⁻¹ Olsen P (Johnston et al., 2013). This raises the question; should the 501 opportunity to achieve optimum yield be sacrificed because of the possible risk of loss of P 502 from soil to water? 503

Many questions about P in relation to food production and its loss from agricultural soils 504 need to be answered by monitoring at the farm and landscape scale (Powlson, 1998). Critical 505 source areas for the loss of P (Pionke et al., 1997) need to be identified and whether these are 506 source areas because of loss of P to water by leaching/surface runoff or by soil erosion. Such 507 areas must be related to the food production potential of the agricultural area and the level of 508 plant-available P (like Olsen P) required to achieve that potential. More recently, several 509 510 papers have highlighted the value of farm-scale experiments to our understanding of soil processes and implications for ecosystem services in grassland systems (Cardenas et al., 511 512 2016).

In 2010, a long-term, farm-scale grassland experiment, the 'North Wyke Farm Platform', was 513 established at the Rothamsted Research site at North Wyke, Devon. The experiment, with 514 three differently managed 'farmlets' for beef and sheep production, each comprising five 515 hydrologically separated catchments, is intensively instrumented. All inputs and losses are 516 measured, including losses of P in surface and sub-surface drainage. Full details of this 517 complicated experiment are given by Orr et al. (2016). Reporting some of the early findings 518 from this experiment, Peukert et al. (2014) found that in these conventional grassland 519 520 systems, suspended sediment and total P concentrations in run-off often exceeded water quality limits recommended by the European Freshwater Fisheries Directive (25 mg TP L^{-1}) 521 522 and the European Water Framework Directive (0.04 mg soluble reactive P L⁻¹) (UK TAG, 2008). 523

524 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

prioritise each experiment to which he replied that they had equal importance. Further 528 qualifying this, Lawes noted that the yields of the crops showed the danger of allowing soil 529 fertility to decline. Lawes then went on to say that the crop and soil samples he had collected 530 (and retained) took first place in importance having indicated that future generations of 531 scientists could perhaps make good use of them. How prescient was that? The archive of data 532 and samples has been mined for information and analysed to seek answers to questions which 533 534 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 535 536 continuing long-term experiments are a valuable resource which can still be used to answer questions that might arise in the future; though we do not necessarily know what those 537 questions might be. Much information and data are available through e-RA 538

539 (http://www.era.rothamsted.ac.uk/).

In more general terms, phosphorus use efficiency will improve if all our accumulated 540 541 knowledge were applied to current crop and animal production systems. This requires adoption by farmers and growers through education and incentives. Knowledge is still 542 imperfect on aspects of the behaviour of P in soil; for example, the relation between the P 543 held in pools 2 and 3 in Figure 3. At a more practical level there is a need for a better 544 understanding of the importance of good soil structure in facilitating root exploration of soil 545 for nutrients, and greater use could be made of soil analysis to guide P applications both as 546 fertilizers and organic manures. 547

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: 1) improving the sustainability of P mining; 2) managing soil
erosion to minimise P losses and 3) 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.

554 Conclusions

To help explain many of the results from field and laboratory experiments at Rothamsted has 555 led to our thinking of inorganic P existing in soil in four pools. These vary in size, the 556 availability of the P for uptake by roots, and the extractability of the P used to determine the 557 its availability to crops. Very importantly, the concept recognises the transfer of P between 558 the pools. Inorganic P is associated with a variety of soil components and the plant-559 availability of the P is related to the P being held to them with a range of bonding energies; 560 weakly-held P being the most readily available to crops. For our soils the most suitable 561 562 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 563 which a soil should be maintained to optimise crop yield and P-use efficiency can be 564 565 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-566 available P in soil to ensure food security by adding P in fertilizers and manures must not 567 lead to the transfer of P to the aquatic environment where it can disturb the biological 568 balance. 569

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781	Figure legends
782	Fig. 1 Asymptotic regression of winter wheat grain on Olsen P in soil in two years with
783	different maximum yields and similar critical Olsen P; 2003 (x); 2008 (•); Exhaustion Land,
784	Rothamsted.
785	Fig. 2 a) The change in Olsen P in eight treatments given no more P after 1968; b) an
786	exponential curve fitted to the data from the eight treatments once the curves have been
787	bought into coincidence by a series of horizontal shifts; Saxmundham RII, Suffolk.
788	Fig. 3 Conceptual diagram for the forms of inorganic P in soil, categorised in terms of their
789	accessibility, extractability and plant availability.
790	Fig. 4 Relationship between the Removal/Input ratio (P removed by the crop divided by the P
791	input in fertilizer or manure) and the change in Olsen P for long-term experiments in the U.K.
792	(Δ) and 12 states in the U.S. (x).
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Table 1 Long-term experiments† at Rothamsted, Hertfordshire, Woburn, Bedfordshire and Saxmundham, Suffolk, UK.

Experiment	Duration	Crop	Comment	Reference
$Rothamsted^{\ddagger}$				
Barnfield	1843 - ongoing	Root crops	Grass since 1975	Warren and Johnston, 1962
Broadbalk	1843 - ongoing	W. wheat	Parts of the experiment have	Johnston and Garner, 1969
			included rotations since 1968	Poulton et al., 2018
Agdell	1848 - 1970	Arable crops	Half in grass, 1958 - 1969	Johnston and Penny, 1972
				Johnston et al., 2013; 2016
Hoosfield	1852 - ongoing	S. barley	Parts of the experiment	Warren and Johnston, 1967
		·	included rotations 1968-1978	Johnston et al., 2016. Poulton et al., 2018
Exhaustion	1856 - ongoing	Arable crops		Johnston and Poulton, 1977
Land		-		Poulton et al., 2013. Johnston et al., 2016
Park Grass	1856 - ongoing	Permanent	Pasture since c. 1700	Warren and Johnston, 1964
		pasture		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	٩			
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).

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Table 2 Exhaustion Land; phosphorus 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 1856-1901 or in farmyard manure from 1876-1901 and none since.

			1 & 5 nce 1856	1410 kg P 1856	7 & 9 ha ⁻¹ applied 5-1901 phosphate	1260 kg P 1876	ot 3 ha ⁻¹ applied 5-1901 ard manure	
		Amounts of P removed in the crop, kg ha ⁻¹						
Period	Crop	Total	per year	Total	per year	Total	per year	
1902-40 ⁺	S. barley	102	2.6	207	5.3	200	5.1	
1941-85 [‡]	S. barley	189	4.2	394	8.8	478	10.6	
1986-91 [§]	S. barley	28	4.7	51	8.5	60	10.1	
1992-2012 [¶]	W. wheat	75	3.6	175	8.3	200	9.5	
1902-2012	Total	394	-	827	-	938	-	

+ Mainly s. barley grown during this period; no fertilizers or manure applied

‡ Fertilizer N has been applied at various rates since 1941; fallow in 1967 and 1975

§ Basal K and N applied since 1986

¶ S. wheat in 2001

797 Adapted from Johnston and Poulton (2014)

Plot No.,	_	Change in first five P fractions, kg P ha ⁻¹						
treatment	P balance [†]		0.5 M	0.1 M	1 M	0.5 M	Total	
and period	kg ha ⁻¹	Resin	NaHCO ₃	NaOH	NaOH	$\mathrm{H}_2\mathrm{SO}_4$	change	
1. No P since 1856 No P applied, 1902-93	-300	-49	-20	-195	-82	-19	-365	
9. P fertiliser Applied, 1856 - 1901 Not applied, 1902-93	1222 -644	158 -234	126 -138	79 -114	7 45	270 -253	640 -694	
3. Farmyard manure Applied, 1876 - 1901 Not applied, 1902-93	1035 -752	193 -259	129 -123	133 -159	107 -112	355 -164	917 -817	

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

⁺ The P balance is the amount of P applied *minus* the amount removed by the crop Adapted from Blake et al., 2003

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Table 4 Mean yields of spring barley grain, 1949-74, grown on soils with and without P residues; Exhaustion Land, Rothamsted

	Plot numbers and treatment						
	1, 2, 5, 6	7, 8, 9, 10	3, 4				
		P applied	P applied				
	No P since 1856	1856-1901	1876-1901				
		as superphosphate	in farmyard manure				
Period	Mean y	ield grain at 85% DM,	t ha ⁻¹ yr ⁻¹				
1949-53	1.59	2.88	3.03				
1954-59	1.80	3.02	3.32				
1960-63	1.99	2.72	3.14				
1964-69 [†]	1.71	3.60	4.28				
1970-74	1.83	4.18	4.75				

† The experiment was fallowed in 1967

Adapted from Johnston and Poulton, 1977

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	Soil organic	Yield at 95%	Olsen P associated	Variance			
	matter	of the asymptote	with the 95% yield	accounted for			
Crop	%	t ha ⁻¹	mg kg ⁻¹	%			
		Field ex	periments				
Spring barley grain,	2.4	5.00	16	83			
t ha ⁻¹	1.5	4.45	45	46			
Potato tubers,	2.4	44.7	17	89			
t ha ⁻¹	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,	2.4	6.46	23	96			
g pot ⁻¹	1.5	6.51	25	82			

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

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

Original	Р			Change	P applied	P offtake grain + straw		Increase	in Olsen P
treatment	treatment	Olsen P	, mg kg ⁻¹	in Olsen P [‡]	1986-1992	1986-1992	P balance [§]	as a % of	as a % of
1856-1901	1986-1992	1985	1992	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	P applied	P balance
Nil [¶]	DO	2	2	0	0	22	22		
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
	Р3	2	44	127	916	111	806	14	16
P [#]	PO	5	4	-3	0	62	-62	-	-
	P1	6	18	36	306	105	201	12	18
	P2	8	38	91	611	119	492	15	18
	Р3	6	54	145	916	120	796	16	18
FYM ^{††}	PO	8	5	-9	0	78	-78	_	-
•	P1	10	23	39	306	113	193	13	20
	P2	9	53	133	611	122	489	22	27
	Р3	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 top-soil, 0-23 cm

§ The 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 between 1902-1985; mean of data from two main plots

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

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Site and	Asymptote [†] constrained to	SE of	Variance accounted for	Rate of decline and its SE	Half-life and its SE
experiment	$mg kg^{-1}$	observations	%	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)
PK, 1898-1964	0.6	7.85	96.2	0.043 (0.0015)	16.1 (0.57)

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

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

Adapted from Johnston et al., 2016

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Table 8 Maintaining Olsen P by replacing the P removed in the grain and straw of four winter wheat crops, Exhaustion Land, 2005-08

	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	

808 [†] Olsen P in soils sampled in autumn

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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.

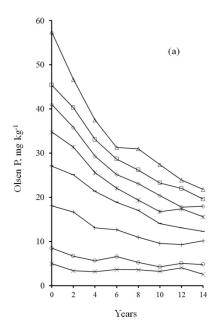


Fig. 2 a) The change in Olsen P in eight treatments given no more P after 1968; b) an exponential curve fitted to the data from the eight treatments once the curves have been bought into coincidence by a series of horizontal shifts; Saxmundham RII, Suffolk.

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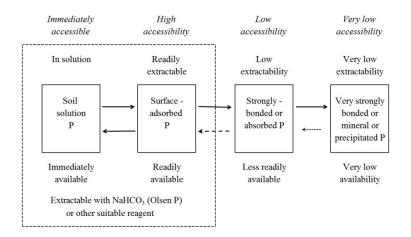


Fig. 3 Conceptual diagram for the forms of inorganic P in soil, categorised in terms of their accessibility, extractability and plant availability.

410x325mm (96 x 96 DPI)

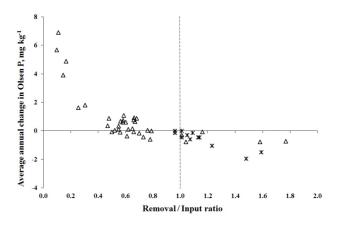


Fig. 4 Relationship between the Removal/Input ratio (P removed by the crop divided by the P input in fertilizer or manure) and the change in Olsen P for long-term experiments in the U.K. (Δ) and 12 states in the U.S. (x).

410x325mm (96 x 96 DPI)