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### Isotopic Exchange of Phosphates in Soil

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# ISOTOPIC EXCHANGE OF PHOSPHATES IN SOIL

*Review of Experimental Techniques and Results at Rothamsted  
1952-1960*

BY

G. E. G. MATTINGLY & O. TALIBUDEEN

Paneth and Vorwerk first used radiotracers to measure the surface-exchangeable ions of solids in suspension; their now classic experiments, done in 1922, used the lead isotope, Th B, to investigate insoluble lead salts. Only much later was this technique extended to the soil-phosphate system, using growing plants to sample the soil solution (Fried & Dean, 1952; Larsen, 1952). The historical development of this subject has been reviewed earlier (Mattingly, 1957a); this article summarises laboratory experiments and pot and field experiments at Rothamsted since 1952 to evaluate soil phosphate, using the isotope  $^{32}\text{P}$ . The final section shows the extent of agreement between measurements in the laboratory and in pot experiments with soils from Rothamsted and Saxmundham Experimental Stations and Nurseries of the Forestry Commission.

## LABORATORY MEASUREMENTS

(O. Talibudeen)

### *Introduction*

In heterogeneous systems, isotopic exchange methods can be used to measure: (1) the concentration of the exchanging species at the surface of the dispersed phase, and (2) the bulk diffusion rate of the exchanging species into the dispersed phase. When applied to the soil phosphate : water equilibrium, it is difficult to separate these two measurements because adsorption sites on the soil surface and the surface chemistry of exchanging solid phosphates both vary.

These experiments were concerned with the extent and the rate of isotopic exchange in a fully dispersed soil : water system as influenced by intrinsic soil properties (e.g., carbonate content, pH, organic C content, mechanical composition, etc.) and extrinsic variables (e.g., soil : solution ratio, temperature, phosphate manuring, chelating and non-chelating organic anions, nature of the electrolyte in the equilibrating solution). The methods used are described in a series of papers (Talibudeen, 1954, 1957, 1958; Arambarri & Talibudeen, 1959, a, b, c).

Because of the complex nature of the soil-phosphate system, it is difficult to obtain unique constants for the rate of isotopic exchange which can be quantitatively related to extrinsic and intrinsic variables. However, semi-empirical constants have been obtained that are specific to each soil. To measure isotopic exchange rates,



it is convenient to maintain a constant concentration of the exchanging species in solution. In soil-phosphate equilibria this condition can be realised by maintaining equilibrium concentrations which are either very high (by adding excess soluble phosphate) or very low (by adding neutral salts). Each addition inevitably changes the soil-phosphate complex irreversibly, so that the resultant system bears little relation to the system it is desired to investigate. In our work the soil was brought to equilibrium with the phosphate concentration it would maintain in soil solution, small changes during isotopic exchange being corrected for by chemical analyses of the phosphate in solution.

Interpretation of the rate measurements presents two basic difficulties. Stable organic orthophosphates (e.g., nucleotide and phytate phosphorus) exchange isotopically at rates incomparably slower than adsorbed and particulate forms of inorganic phosphate. The isotopically exchangeable phosphate measured in the laboratory is principally related to the inorganic soil phosphate. Reliable estimates of the inorganic phosphate are therefore required to calculate the phosphate in the soil which could exchange isotopically in infinite time. Secondly, an approximate calculation shows that, on average, a *minimum* of 60 days would be required for complete isotopic exchange of the total inorganic phosphate, *if* the first-order rate constant for the slowly exchanging fraction controlled the exchange of *all* the slowly exchanging inorganic phosphate. Laboratory measurements show that small changes in specific activity of the phosphate in solution continue even after 12–14 days of continuous shaking. When these changes, measured at 48-hour intervals, are smaller than the mean error of the measurements ( $\pm 3.8\%$ ), a nearly constant figure for the isotopically exchangeable phosphate in the soil is evaluated.

The relation between the specific activity (SA) of the solution and time can be analysed semi-empirically in different ways by considering that: (1) two types of adsorption sites are responsible for isotopic exchange—those in which  $\log(\text{SA})$  and  $(\text{SA})$  are linearly related to  $(\text{time})$  and  $\log(\text{time})$  respectively; (2)  $\log(\text{SA})$  at small time-values decreases linearly with time; at large time-values  $(\text{SA})$  decreases because of self-diffusion into the solid phosphate phase and therefore as a linear function of  $(\sqrt{\text{time}})$ ; (3) the observed curvilinear decay in  $\log(\text{SA})$  with  $(\text{time})$  in laboratory experiments is composed of two or more simultaneous first-order rate processes whose rate constants are a measure of the relative ease of exchange of groups of phosphate-adsorption sites in the soil complex.

Specific activity data for over a hundred arable soils from England and Wales have been examined by the third method; the results show that at least three groups of exchanging sites are involved with half-times of exchange 10–30 minutes, 5–15 hours and 40–60 hours. The phosphate in the equilibrium solution, which is removed from the soil during equilibration, is a part of the more rapidly exchanging groups of the total isotopically exchangeable phosphate. Experimental confirmation of this is given later. In aqueous suspension (0.02M-KCl) the phosphate in solution is less than a quarter of the total isotopically exchangeable phosphate, the rapidly exchanging fraction between a quarter and a third, the



slowly exchanging group between a half and two-thirds, and with few exceptions, the middle group is less than a twentieth. The phosphate in solution, the rapidly exchanging groups and the middle group make up  $P_r$ , the phosphate adsorbed on rapidly exchanging sites;  $P_r$  expressed as a fraction of  $P_e$ , the total exchangeable phosphate, is one of the semi-empirical constants  $P_r/P_e$  used to characterise the phosphate status of a soil.

In routine work, the amount of phosphate exchanged in 20 hours is taken to be the rapidly-exchanging phosphate  $P_r$ , and that exchanged in 170 hours as the "total" isotopically exchangeable phosphate  $P_e$ . Routine  $P_r$  values are over-estimated on average by about 25% of  $P_{\text{slow}}$  (where  $P_{\text{slow}}$  is the slowly-exchanging phosphate with an average half-time of exchange of 50 hours).  $P_e$  is usually only slightly under-estimated, because about 98% of the equilibrium  $P_{\text{slow}}$  exchange is completed in 170 hours. Hence  $P_r/P_e$  is an approximate value in routine determinations and less accurate than that derived from a full-scale rate-analysis.

The second "constant" used is the ratio  $P_e/P_t$ , where  $P_t$  is the total soil phosphate determined by perchloric acid digestion. This is a less sensitive and less accurate index than  $P_r/P_e$ , principally because  $P_t$  includes the inert and isotopically non-exchangeable organic phosphate, which cannot be estimated accurately.

#### *Materials*

Soils from four sources were used: (a) the classical plots at Rothamsted; (b) the nurseries of the Forestry Commission (Benzian, 1959); (c) N.A.A.S. experimental plots at Shardlow, Nr. Derby (Blood, 1957); (d) calcareous soils from selected arable sites supplied by the Soil Survey of England and Wales.

#### *Extrinsic factors affecting the isotopically exchangeable phosphate*

Various procedures have been suggested in the last 10 years to measure the isotopically exchangeable phosphate in soils. The aim has been to develop a routine laboratory procedure which gives values that not only correlate well with those in pot experiments but are equal to them. Before establishing a routine procedure it was necessary to evaluate quantitatively the influence of external variables on the isotopically exchangeable soil phosphate and to avoid any which significantly altered this numerical equality. The degree of success attained is discussed below (p. 261).

(a) *Soil : solution ratio.* The phosphate concentration in solution increased with soil : solution ratio, but the isotopically exchangeable phosphate measured at any one time *decreased* at a fixed and optimum rate of agitation (Talibudeen, 1954). The effect of increasing soil : solution ratios diminished at larger reaction times; the measurements indicated that soil : water ratios below 2 g. : 100 ml. did not alter the isotopically exchangeable phosphate.

(b) *Concentration of soluble phosphate added with  $^{32}\text{P}$  for measuring isotopically exchangeable phosphate.* Most methods suggested for determining isotopically exchangeable phosphate use  $^{32}\text{P}$  solutions of low specific activity (high phosphate content), and although good correlation is obtained with plant-derived indices, numerical equality is rarely observed. Experiments on a neutral Rothamsted soil



(Highfield) showed that, in the range of  $3.2 \times 10^{-7}M$  to  $1.5 \times 10^{-4}M$  phosphate, higher concentrations significantly decreased the isotopically exchangeable phosphate at any one reaction time (Talibudeen, 1957). To obtain a specific soil index it is necessary to add  $^{32}P$  in a phosphate solution which does not appreciably alter the phosphate level in the equilibrium soil solution.

(c) *Organic anions.* Moderately high concentrations of anions (e.g., citrate and bicarbonate) which chelate cations in combination with soil phosphate are commonly used for evaluating phosphate residues; non-chelating anions (e.g., acetate) have also been used for this purpose. Isotopic exchange measurements are difficult with soils of very low phosphate status, because the phosphate concentrations to be measured in solution are so small. Very low concentrations of citrate ions were used to raise this phosphate concentration (Talibudeen, 1958). Two Rothamsted soils showing moderate response to phosphate were examined to estimate the influence of chelating and non-chelating organic anions at a  $0.001M$  level (Arambarri & Talibudeen, 1959a). Table 1 shows that soil pH directly influences the interaction of organic anions. The chelating citrate ion increases the total  $P_e$  in the slightly acid soil, but diminishes total  $P_e$  in the calcareous soil, although the rate of

TABLE 1

*Influence of soil pH and chelating constants on the interaction of 0.001 Molar concentrations of organic anions with the isotopically exchangeable phosphate in Rothamsted soils.*

Organic anion	Chelating constant for Ca log ( $K_{Ca}$ )	Isotopic exchangeability of soil phosphate					
		Highfield pH 6.7			Exhaustion land (superphosphate plot) pH 7.5		
		$P_e$	$P_r/P_e$	$R_{slow}^*$	$P_e$	$P_r/P_e$	$R_{slow}^*$
No organic anion ...	—	11.3	0.284	0.013	11.5	0.331	0.020
Phenyl-barbiturate	0.66	9.1	0.486	0.040	7.1	0.491	0.020
Citrate ...	3.15	16.3	0.760	0.044	9.5	0.476	0.037

\*  $R_{slow}$   $\equiv$  1st-order rate constant of slowly exchanging phosphate, in mg.  $P/100$  g. soil/hour.

exchange  $R_{slow}$  of phosphate is increased equally in both soils. In contrast, the non-chelating barbiturate ion decreases total  $P_e$  in both soils, increasing  $R_{slow}$  in the acid soil but not altering  $R_{slow}$  in the calcareous soil. These figures illustrate some of the difficulties in using foreign ions, even in such low concentrations, to aid isotopic exchange determinations of the soil phosphate;  $P_e$  values with and without  $0.001M$ -citrate are compared below (p. 261).

(d) *Nature of electrolyte in equilibrating solution.* Although isotopic exchange measurements in soil:water suspensions avoid specific ion interactions, they are impracticable in most soils. To ensure rapid and efficient separation of soil and solution and to provide a constant ionic strength without unduly diminishing the equilibrium phosphate concentration in solution,  $0.02M$ -KCl solution was used. Experiments with NaCl, KCl and  $CaCl_2$  solutions show that in strong electrolytes the valency of the cation has little effect on the total  $P_e$  (Arambarri & Talibudeen, 1959b).



(e) *Temperature.* Equilibrium phosphate concentrations in soil solution have a positive temperature coefficient, for which Aslyng (1950) gave an average value of 1–2% per °C. The temperature coefficient of the total labile phosphate for calcareous soils between 25° and 45° was between 0.8 and 6.6%, which emphasises the need to control temperature within  $\pm 1^\circ$  in measurements of isotopically exchangeable phosphate (Arambarri & Talibudeen, 1959c).

*The influence of intrinsic soil properties on the extent and rate of isotopic exchange of soil phosphate*

The soils examined were divided into two broad groups—(a) calcareous soils containing >0.1% carbonate with pH values >7.2 in 0.01M-CaCl<sub>2</sub> or 0.02M-KCl; (b) non-calcareous soils containing <0.1% CaCO<sub>3</sub> in the pH range 3.7–7.0. Phosphate-retaining mechanisms and soil properties which would influence the extent and distribution of the soil phosphate in the two groups are quite different. The only common factor affecting soil phosphate distribution is the mechanical composition of the soil.

(a) *Calcareous soils.* The phosphate-retaining phase of primary importance is the carbonate fraction; this is conventionally referred to in soil analysis as *calcium* carbonate, although it may also often contain the carbonates of Mg, Fe, Mn and Zn.

Isotopic exchange measurements at Rothamsted on more than 50 soils from the United Kingdom and Spain showed that, although the rapidly exchanging phosphate,  $P_r$ , was unrelated to the carbonate content, the ratios  $P_r/P_e$  and  $P_e/P_t$  both increased linearly with decreasing carbonate content (Arambarri, 1960). Later work on four groups of soils selected from arable sites, where the carbonate and other mineral constituents were of similar origin within each group, showed that the ratio  $P_r/P_e$  decreased with increasing

TABLE 2

*Decrease in the distribution of rapidly exchanging phosphate with increasing carbonate content in different soil groups (four soils in each group)*

Origin of carbonate	Decrease in $P_r/P_e$ per g. CaCO <sub>3</sub>
Upper/Middle Chalk	$1.6 \times 10^{-3}$
Oolitic Limestone A	4.2
Magnesian Limestone	5.5
Lower Lias	9.3

carbonate content. In two of these soil groups with a large range of carbonate contents this relationship consisted of two linear portions. Up to 10% carbonate content the decrease in  $P_r/P_e$  was larger; at higher carbonate contents the change in  $P_r/P_e$  per unit change in carbonate content was less. Within the accuracy of measurement, the inverse linear relation between  $P_r/P_e$  and carbonate content was different for each soil group (Table 2). The surface exchangeable calcium (measured by isotopic exchange using the <sup>45</sup>Ca isotope in a "difference" method), in soils with similar carbonate contents from six sites, showed that  $P_r/P_e$  was



inversely proportional to the surface-calcium in the carbonate fraction. Surface areas, based on the surface density of  $\text{Ca}^{2+}$  ions on calcite surfaces, suggested that the "carbonate" crystallites in calcareous soils have an "effective" diameter of  $0.25 \mu$ , and therefore carbonate particles in size fractions larger than this diameter are very porous. In soils containing carbonate with the lowest specific surface, the first-order rate constant of the slow-exchanging phosphate fraction is at least three times as great as in soils with carbonate of high specific surface (Table 3). This table also illus-

TABLE 3

*Relation between the first order rate constant of the slowly exchanging surface phosphate groups and the specific surface of the carbonate fraction in soils with similar carbonate contents (25–35%  $\text{CaCO}_3$ ) of different geological origin*

Carbonate	Specific surface (sq. m./g. $\text{CaCO}_3$ )	$R_{\text{slow}}$ (mg. P/100 g. soil/hour)
Coral Rag and Coralline Oolite ...	2.1	0.065
Portland Limestone ...	2.8	0.088
Magnesian Limestone ...	3.9	0.036
Chalk Marl Limestone ...	4.7	0.023
Lake Marl Limestone *	7.9	0.008
Synthetic Calcite ( $25 \mu$ diameter) †	0.15	—

\* Containing 52%  $\text{CaCO}_3$ .

† *Rep. Rothamst. exp. Sta. for 1958, p. 50.*

trates the variation in specific surface of the soil carbonate of different geological origins together with that of synthetic calcite. Isotopic exchange measurements show that added phosphate reverts to less-exchangeable forms at rates and in amounts that are directly proportional to: (1) the carbonate content (and thus to the total surface exchangeable Ca) in soils from one group containing carbonate of the same origin; (2) the surface-exchangeable calcium per g.  $\text{CaCO}_3$  (or the specific surface) of the carbonate fraction in soils of similar carbonate content but of different geological origin.

Also, in each soil,  $P_e$  (as the quantity of phosphate exchanging) is linearly related to the phosphate in solution (as the intensity of phosphate), for the untreated soil and the phosphate-treated soil after 1, 2 and 6 months.

(b) *Non-calcareous soils.* Increase in soil acidity increases the aluminium (and iron) concentration (in particular, the activity of the  $\text{Al}^{3+}$  ion) in the soil solution, and the surface concentration of positively charged sites on soil minerals. The increase in  $\text{Al}^{3+}$  activity lowers the phosphate concentration in solution in several pairs of soils, where the soil, treated with equal amounts of superphosphate, has been maintained at different pH levels (Chakravarti, 1959). Table 4 shows that, in addition, decreasing soil pH affects  $P_e$  and  $P_r/P_e$  in the same way. The effect of soil pH on the isotopically exchangeable phosphate clearly illustrates the need for a reliable method for measuring the concentration of these positively charged sites on the soil surface. This may help to define the composition of surface-adsorbed layers formed in acid soils treated



with average agricultural levels of superphosphate. Table 4 also illustrates how the organic carbon content of the soil modifies the effect of soil pH on the water-soluble phosphate and the isotopically exchangeable phosphate. Thus, in a soil with less organic carbon the water-soluble phosphates and  $P_e$  decrease more with decreasing pH than in a soil with more organic carbon. This qualitatively indicates the blocking of positive adsorption sites by organic molecules or anions in soils with high organic carbon content, especially at lower pHs.

TABLE 4  
*Effect of soil pH and organic carbon content on water soluble phosphate and isotopically exchangeable phosphate*

Soil	% Organic carbon *	pH	Total soluble aluminium phosphate ( $\times 10^{-6}$ Molar)	Soluble phosphate	$P_e$ (mg. P/ 100 g. soil)	$P_r/P_e$
<i>Park Grass</i>						
Plot 4(i) Unlimed	3.07	5.2	5.1	17.0	36.5	0.647
4(i) Limed ...	3.05	6.8	1.2	25.0	41.4	0.727
<i>Shardlow Unmanured plots</i>						
Plot A5 ...	1.58	4.0	28.0	0.58	17.6	0.472
C5 ...	1.67	5.0	3.1	1.5	21.3	0.545
E5 ...	1.87	6.0	2.6	4.1	28.8	0.392(?)
<i>Broadbalk Section V, Plot 8</i>						
Sample 2 ...	1.19	5.3	—	4.4	22.9	0.477
3 ...	1.21	6.0	—	5.7	21.6	0.601
5 ...	1.19	7.5	—	9.7	30.7	0.635

\* Walkley-Black Method (with acknowledgements to J. M. d'Arifat).

Cropping modifies the contrasts in  $P_r$  and  $P_e$  between unmanured and phosphate-treated soils, especially in soils with higher pHs from which much more of the added phosphate is removed. However, the effect of soil pH on the nature of phosphate residues can be evaluated by isotopic exchange measurements. Table 5 gives ratios calculated from differences in the  $P_r$ ,  $P_e$  and  $P_t$  values for untreated and phosphate-treated soils from Shardlow at pH 4.0, 5.0 and 6.0. Thus,  $\Delta P_r/\Delta P_e$  and  $\Delta P_e/\Delta P_t$  values indicate that at lower pHs the residual phosphate is held in less exchangeable forms.

TABLE 5  
*The effect of pH on the isotopic exchangeability of phosphate residues in soils from N.A.A.S. Centre, Shardlow*

Soil pH	$\Delta P_r/\Delta P_e$	$\Delta P_e/\Delta P_t$
4.0	0.436	0.700
5.0	0.805	0.828
6.0	0.831	0.722(?)

(c) *Phosphate manuring*. Much new information has been added to that already published (Talibudeen, 1958). It shows that:

(a) When water-soluble forms of phosphate are added to acid or calcareous soils the absolute values of  $P_r$  and  $P_e$ , as well as the proportion of added phosphate on rapidly exchanging sites (defined



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by the ratios  $P_r/P_e$  and  $P_e/P_t$ , are significantly increased. In any one soil, this increase depends on: (1) the level of phosphate added; (2) the phosphate status of the soil initially; (3) the length of time the added phosphate has been in contact with the soil; and (4) in cropped soils the amount of phosphate removed from the soil by the crop before sampling. The effects of manuring and cropping are described below (pp. 257-259). The influence of the first three factors is briefly illustrated.

The  $P_r/P_e$  index is sensitive enough to detect the *residual* effect of 0.5 and 1.0 cwt.  $P_2O_5$ /acre (added as superphosphate) after 2 years, even when superimposed on the residual effect of previous manuring (Table 6). Larger changes in  $P_r/P_e$  have also been

TABLE 6

*Isotopic exchangeability of soil phosphate in Exhaustion Land two years \* after a dressing of 0.5 and 1.0 cwt.  $P_2O_5$  per acre as superphosphate*

Previous manuring †	Plot 5 No phosphate Ammonium salts (1856-1901)			Plot 9 Superphosphate (1856-1901)		
	0	0.5	1.0	0	0.5	1.0
Cwt. $P_2O_5$ /acre as superphosphate in 1957						
Crop				$P_r/P_e$ values		
Kale ... ..	0.540	0.570	0.595	0.589	0.605	0.620
Swede ... ..	0.490	0.557	0.576	No sampling		

\* One year's cropping (kale or swede) followed by ploughing and one year's fallow.

† For full details, see Warren & Johnston, 1960.

observed (together with increases in  $P_r$  and  $P_e$ ) under two very different sets of conditions (Talibudeen, 1958). In laboratory incubations when the soil was dressed with 10 mg. P/100 g., the isotopic exchangeability of the residue after 3 months' incubation was lower on the unmanured soil which also had the smaller  $P_r/P_e$  value (Table 7).

TABLE 7

*Isotopic exchangeability after three months incubation at field capacity of phosphate added (10 mg. P/100 g. soil) to Exhaustion Land soils in relation to their phosphate status*

Manurial history	Phosphate status of untreated soil $P_r/P_e$	Isotopic exchangeability of 10 mg. P addition after three months	
		$\Delta P_r/\Delta P_e$	$\Delta P_e/\Delta P$
No manure ... ..	0.532	0.677	0.65
FYM (1856-1901) ... ..	0.689	0.743	0.70
Superphosphate (1856-1901)	0.666	0.771	0.70

(b) When very insoluble forms of phosphate (e.g., apatites) are added to calcareous soils little change in isotopic exchangeability of the soil phosphate can be detected (Talibudeen, 1958). However, the isotopic exchangeability of phosphate residues in acid soils



treated with rock phosphate or basic slag are not very different from superphosphate residues (Table 8).

(d) *Nature of exchangeable cations in the soil.* The isotopic exchangeability of soil phosphate is principally affected by the factors described above, although the exchangeable cations play a secondary but significant part in influencing it. In non-calcareous soils divalent exchangeable cations decrease the rate of exchange of the slowly exchanging phosphate without altering its extent;

TABLE 8

*Isotopic exchangeability of phosphate residues from different sources in soils (pH 4.9–5.4) from Wareham Nursery, sampled in 1955*

Phosphate source	$\Delta P_r$	$\Delta P_e$	$\Delta P_i$	$\Delta P_r/\Delta P_e$	$\Delta P_e/\Delta P_i$
Gafsa rock phosphate	2.25	2.70	7.3	0.833	0.370
Basic slag ...	1.60	1.78	5.0	0.900	0.356
Superphosphate ...	1.70	1.85	4.9	0.920	0.378

this rate of exchange is also less sensitive to temperature than with soil saturated with monovalent cations. Thus, manurial treatments which shift the cation balance in the soil in favour of monovalent cations increase the rate of exchange of the slowly exchanging phosphate. It is suggested that this is caused by the decrease in  $Al^{3+}$  activity at the soil : water interface when changing from a divalent-cation-dominated soil to a monovalent one (Arambarri & Talibudeen, 1959b).

#### FIELD AND GREENHOUSE EXPERIMENTS (G. E. G. Mattingly)

##### *Radiation effects from $^{32}P$*

Conflicting reports have appeared on the magnitude and reproducibility of the effects of radiation on the growth of plants. Most workers have detected slight alterations in growth with both low and high levels of  $^{32}P$  (see Mattingly, 1957a for references). In preliminary experiments in the greenhouse using ryegrass, dry weight and phosphorus uptake were the same when either 5 and 10  $\mu C$  or 10 and 50  $\mu C$   $^{32}P$ /pot were compared. However, less fertiliser phosphorus was taken up at the higher levels of radioactivity. There was no difference between effects of  $^{32}P$  at different  $^{31}P$  levels, or with different soils (Mattingly, 1957b). With barley,  $^{32}P$ -labelled superphosphate gave the same yield of grain, straw and roots in the greenhouse and the same distribution of phosphorus in the crop as an equivalent amount of commercial superphosphate (Mattingly & Widdowson, 1958b). The effects of  $^{32}P$  on growth and fertiliser uptake in greenhouse experiments were always small but reproducible, probably because the fertiliser was mixed uniformly throughout the soil. In field experiments, using superphosphate labelled with 0.7–1.4 mC  $^{32}P$ /g. P, yields of barley and uptakes of phosphorus in the field were slightly lower than with commercial superphosphate (Mattingly & Widdowson, 1958b).



### *Field experiments*

The main purpose of the field experiments using  $^{32}\text{P}$ -labelled superphosphate was: (a) to establish whether the increased yields that usually result from applying water-soluble phosphates near the seed of cereals could be attributed to greater uptake of soil phosphorus, of fertiliser phosphorus, or both; (b) to measure by isotope dilution the total "pool" of isotopically exchangeable phosphate in the soil at different stages of growth and the increase in this "pool" from applying different non-radioactive phosphate fertilisers.

*The uptake of soil phosphorus by barley.* When barley grew rapidly, more total phosphorus and more phosphorus from the soil was removed in 26 days from plots receiving superphosphate than from plots without phosphate fertilisers. This effect was largest when the superphosphate was drilled with the seed; the *extra* phosphorus in the plants taken up from soil was then comparable with the phosphorus taken up from the fertiliser. Barley given broadcast superphosphate removed smaller amounts of *extra* soil phosphate. This effect did not persist until the crop was harvested, when, in seven out of eight comparisons, *less* soil phosphorus had been taken up when superphosphate was applied. Very similar results have been obtained elsewhere with wheat (Mitchell, 1957) and with oats (Verma *et al.*, 1959).

There are three possible explanations of the changes in uptake of soil phosphorus during growth: (i) radioactive superphosphate damages plants; (ii) superphosphate alters the growth pattern of roots; (iii) superphosphate "blocks" the removal of soil phosphorus. The first is unlikely, because increasing levels of  $^{32}\text{P}$  usually decrease fertiliser uptake without greatly altering the total phosphorus removed by the crop. Consequently, the uptake of soil phosphorus should *increase* on applying a radioactive superphosphate. There is some evidence (Cooke, 1954) that the root system of peas, and presumably of other crops, is considerably more diffuse without phosphorus fertilisers than when superphosphate is either drilled or broadcast. This suggests that the roots of unmanured plants are in contact with a larger soil surface than those of plants receiving superphosphate. The exchangeable phosphate sites on soil surfaces may also be "blocked" by fertiliser phosphates, as in laboratory experiments (Talibudeen, 1957), which would further limit the removal of soil phosphate.

*Isotope dilution with non-radioactive phosphate fertilisers.* Experiments with  $^{32}\text{P}$ -labelled fertilisers not only give information on the uptake of phosphorus from the fertiliser and soil but they also estimate the total "pool" of soil phosphorus sampled by the crop at different stages of growth. In the greenhouse, when soil and fertiliser are well mixed, the ratio of  $^{32}\text{P}/^{31}\text{P}$  in the crop decreases only slightly during growth, as progressively more soil phosphate exchanges. In the field, however, this ratio falls more rapidly as roots take up phosphate from soil which is not mixed with the labelled fertiliser.

The total "pool" of soil phosphorus sampled by barley and fodder beet in the presence of drilled superphosphate (i) increased during growth, (ii) varied between the crops, and (iii) varied very



greatly in different years on the same site (Mattingly & Widdowson, 1958a).

The total "pool" sampled at harvest on one site was 37 and 55 lb. P/acre for fodder beet and barley respectively; both values are larger than the total amount of phosphate removed by the crops. The smaller "pool" with fodder beet indicates that the root system of this crop does not remove phosphate from soil far from the fertiliser zone. When commercial non-radioactive phosphate fertilisers were broadcast in these experiments the increase in total labile phosphate in the soil was equal for fodder beet to the amount of phosphorus applied as superphosphate or dicalcium phosphate. With barley the increase was less than the total applied. Gafsa rock phosphate did not significantly increase either the "pool" of soil phosphate sampled or the yield of the crop in any experiment.

The conclusions from these experiments confirm and provide some quantitative explanations for results in other field experiments on fertiliser placement. Barley produces higher yields when superphosphate is drilled with the seed than when broadcast (Crowther, 1945). The experiments with  $^{32}\text{P}$  show that (i) a higher proportion of phosphate is taken up from drilled than broadcast superphosphate, (ii) drilled superphosphate usually increases uptake of soil phosphate in the early stages of growth, and (iii) only part of the phosphate in superphosphate, when applied broadcast, increases the "pool" of labile soil phosphate sampled by the crop. In contrast, placing superphosphate for sugar beet, which has a similar root system to fodder beet, is very little more effective than broadcasting (Prummel, 1957), probably because the "pool" of phosphate sampled is restricted to the soil which is mixed with the broadcast fertiliser.

There is a fundamental difference between the interpretation of isotope dilution experiments in the field and in the greenhouse. In the greenhouse the root system is restricted to a known weight of soil. The amount of phosphate that exchanges *in unit weight of soil* can be calculated from the  $^{32}\text{P}/^{31}\text{P}$  ratio in the crop.

In field experiments the amounts of soil phosphorus accessible *per acre* to the crop can be calculated from the  $^{32}\text{P}/^{31}\text{P}$  ratio. However, phosphorus derived by the crop from soil mixed with the fertiliser cannot be directly distinguished from that derived from lower layers of soil, unless the limiting value of the  $^{32}\text{P}/^{31}\text{P}$  ratio for unit weight of soil is known from a greenhouse experiment. In a field experiment in 1953, when barley grew very rapidly, all the dilution of fertiliser phosphorus by  $^{31}\text{P}$  from the soil could be accounted for at harvest by the isotopically exchangeable phosphate estimated, from greenhouse experiments, to be present in the plough layer. In 1954, when the crop grew more slowly, the  $^{32}\text{P}/^{31}\text{P}$  ratio was very small at harvest, and indicated that about one-half of the  $^{31}\text{P}$  in the crop had come from below the layer of soil with which the fertiliser phosphate was mixed by harrowing (Mattingly & Widdowson, 1958b).

*Evaluation of residues of phosphate fertilisers by isotope dilution.* Similar methods using  $^{32}\text{P}$  have been used to estimate the residual value of superphosphate in a field experiment with barley. The value in 1955 of the residues of superphosphate applied in 1954 was estimated from (a) yield, (b) phosphorus uptake and (c) changes in



the  $^{32}\text{P}/^{31}\text{P}$  ratio in the crop. Six weeks after sowing, all three methods of evaluation showed that the residues were equivalent to about one-quarter as much superphosphate broadcast in 1955, and yields of grain at harvest also gave this value. Evaluations using phosphorus uptake and changes in the  $^{32}\text{P}/^{31}\text{P}$  ratio in the crop were higher and equal to 40–50% of the amount of superphosphate applied in 1955. These results suggest that at harvest the root system of barley reached residues of superphosphate that had been buried by ploughing. The phosphorus taken up from these residues ("luxury uptake") did not increase yield but decreased the ratio  $^{32}\text{P}/^{31}\text{P}$  in the crop (Mattingly & Widdowson, 1956).

#### Greenhouse experiments

Preliminary work (Mattingly, 1957b) established a standard technique for greenhouse experiments. A solution of monocalcium phosphate containing 2.0 mg. P, labelled with  $10\ \mu\text{C}\ ^{32}\text{P}$ , was mixed mechanically with 400 g. air-dry soil and 200 g. coarse quartz per pot. Perennial ryegrass (*Lolium perenne*, S23 strain), used as the test crop in most experiments, was cut at intervals of 3–4 weeks. This level of radioactivity was enough to measure the  $^{32}\text{P}/^{31}\text{P}$  ratio in the grass up to 16 weeks from sowing. A few experiments were done using 100 g. soil labelled with 0.5 mg. P containing  $5\ \mu\text{C}\ ^{32}\text{P}/\text{pot}$ .

For the first cut of grass, the total amount of phosphate that exchanges per 100 g. soil during the greenhouse experiment is given by the equation

$$A = 0.5 \left\{ \frac{(^{32}\text{P}/^{31}\text{P}) \text{ fertiliser}}{(^{32}\text{P}/^{31}\text{P}) \text{ crop}} - 1 \right\}$$

For several cuts of grass  $(^{32}\text{P}/^{31}\text{P})_{\text{crop}}$  is replaced by  $(\sum_1^n ^{32}\text{P}/\sum_1^n ^{31}\text{P})$ , where  $\sum_1^n$  is the sum of  $^{31}\text{P}$  or  $^{32}\text{P}$  removed in  $n$  cuts.

*Comparison of phosphate fertilisers by isotope dilution.* Experiments, similar in principle to those in the field, were done in the greenhouse to evaluate different phosphate fertilisers. Commercial, non-radioactive phosphate fertilisers were added to soils and compared with superphosphate by measuring (i) yield, (ii) phosphorus uptake, and (iii) changes in the ratio  $^{32}\text{P}/^{31}\text{P}$  in the crop.

All three methods of evaluation showed that powdered dicalcium phosphate and silico-phosphate were equivalent to superphosphate in the greenhouse. However, rock phosphates gave much higher values by the isotope dilution method than from measurements of yield and phosphorus uptake, probably because  $^{32}\text{P}$  was distributed unevenly in soil around particles of rock phosphate which dissolve slowly (Mattingly & Widdowson, 1956).

*Measurement of the residual value of phosphate fertilisers.* The principle of isotope dilution with  $^{32}\text{P}$ -labelled orthophosphate has been used by several workers to estimate the residual phosphate in soil that remains isotopically exchangeable in greenhouse experiments. Table 9 gives estimated changes since 1901 in the "A" value of soils from the Hoosfield Exhaustion Land experiment at Rothamsted. Details of this experiment are given elsewhere (Warren, 1956; Warren & Johnston, 1960).

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The values in line *a* were calculated, assuming 1 acre of soil weighs 2 million lb., from the average removals of phosphate by barley in the field reported by R. G. Warren in *Guide to the Experimental Farms* (Rothamsted, 1959, p. 26). "A" values in 1901 are not known, but were estimated from measurements on other plots at Rothamsted. Values in line *c* were determined in a greenhouse experiment.

TABLE 9  
Removal of P by cropping and changes in "A" values on  
Hoosfield Exhaustion Land, 1901-1957  
(All results in mg. P per 100 g. soil)

	Plot 1 (no P; no K)	Plot 3 (FYM before 1901)	Plot 9 (Superphosphate before 1901)
(a) P removed by cropping 1901-1957 ...	12	26	23
(b) "A" value in 1901 (estimated) ...	10	21	21
(c) "A" value in 1957	3	10	9
(d) Decrease in "A" between 1901 and 1957 ...	7	11	12

Although the results involve some assumptions, they indicate that during 60 years only one-half of the phosphate removed by cropping came from the isotopically exchangeable "pool". The remainder has been derived from soil phosphate in an unknown chemical form that was not isotopically exchangeable in 1901.

In short-term field experiments the amount of phosphate taken up by the crops almost equals the decrease in "A". The "A" values of soils from the Four-Course rotation at Rothamsted decreased each year after applying superphosphate, but remained constant (at lower values than the superphosphate plots) after applying Gafsa rock phosphate. Rock phosphate appears to dissolve slowly in this calcareous soil, at a rate approximately equal to the rate at which phosphate is removed by the crops in the rotation (Mattingly, 1957b).

The increase in total phosphate content of soils ( $\Delta P_t$ ) from applying phosphate fertilisers can be determined by chemical analysis. The quantity of the residual phosphate in calcareous soils that is isotopically exchangeable has been measured in some greenhouse experiments from the increase in "A" values ( $\Delta A$ ) on plots receiving phosphate fertilisers. The values obtained for the ratio  $\Delta A/\Delta P_t$  vary from 20 to 70% of the total residual phosphate (*Rep. Rothamst. exp. Sta.* for 1957, p. 61; for 1959, p. 50). This is greater than the range 26-56% quoted by Olsen *et al.* (1954) for calcareous soils in the U.S.A.

Some of the most important factors influencing the amount of residual phosphate that remains isotopically exchangeable are (i) pH, (ii) the quantity of phosphate removed by cropping, (iii) soil type, and (iv) the form of nitrogen fertilisers applied for long periods with superphosphate. The relative importance of (i), (ii) and (iv) is difficult to determine because they are interrelated, but the most



important single factor, on any soil type, appears to be removal of phosphate by cropping. This is illustrated below using soils from a rotation experiment on calcareous Boulder Clay at Saxmundham, details of which are given by Cooke *et al.* (1958).

TABLE 10

*Effect of cropping in the field on the percentage of the residual phosphate ( $\Delta A/\Delta P_t$ ) that is isotopically exchangeable in calcareous soils from Saxmundham*

Field treatment	Mean yields of barley 1899-1956 (bushels/acre)	$\Delta A/\Delta P_t$ (%)
P ... ..	21	73
PK ... ..	23	71
NP ... ..	34	64
NPK ... ..	36	56

(P = 2 cwt. superphosphate/acre; N = 2 cwt. sodium nitrate/acre; K = 1 cwt. of potassium chloride/acre.)

Yields and amounts of phosphate removed by the crops were low without added nitrogen, and more of the residual phosphate in these soils now remains isotopically exchangeable.

Saxmundham soils have higher  $\Delta A/\Delta P_t$  values than the calcareous soils at Rothamsted, on which this ratio varies from about 20 to 50%. The highest values at Rothamsted are on plots that have, at some time in their history, been acid from applying ammonium sulphate. The average value for  $\Delta A/\Delta P_t$  in acid and very acid soils taken from nine field experiments in Great Britain and Japan was 70% (*Rep. Rothamst. exp. Sta.* for 1959, p. 49).

There are several limitations to experiments of this type using soil samples taken from field experiments. When the amounts of phosphate applied as fertiliser are small compared with total soil phosphate,  $\Delta P_t$  is determined from the difference between two large quantities. In the experiments so far completed increases in phosphorus content shown by analysis have generally agreed closely with increases calculated by assuming the plough layer of 1 acre of soil weighs between 2.0 and 2.5 million lb.

The experiments referred to above show how much of the phosphate applied to soils as superphosphate remains isotopically exchangeable. They do not, however, give any direct evidence of the chemical form in which the phosphate residues exist in soil. Phosphate ions are probably adsorbed, rather than precipitated, because so large a proportion remains isotopically exchangeable.

*Relationships between "A" values and crop growth.* Yield of ryegrass, grown in the greenhouse and given optimum N, K and minor elements, is exponentially related, and uptake of phosphate by the crop linearly related, to the "A" values of soils. The equations below give typical relationships between yield ( $y$ ) of ryegrass and the "A" values ( $x$ ) for two groups of soils with very different physical properties:

Rothamsted soils (calcareous; 20-30% clay)  

$$y = 17.3 - 25.2e^{-0.161x}$$

Forest Nursery soils (acid; 1-10% clay)  

$$y = 17.5 - 18.4e^{-0.161x}$$



The maximum yields (17.3–17.5 g./pot) were the same for both groups when the experiments were continued for 4 months; this suggests that growth in the greenhouse was limited by phosphate and not by physical differences between the soils. The yield, per unit of isotopically exchangeable phosphate ("A"), was much greater on the lighter acid soils from nurseries of the Forestry Commission than on the heavier soils from Rothamsted. The more rapid growth of grass on the nursery soils has been attributed to the higher phosphate concentration, measured in 0.01M-CaCl<sub>2</sub>, they maintain per unit of exchangeable phosphate (*Rep. Rothamst. exp. Sta. for 1957*, p. 59).

Table 11 shows the relationships between the uptake of phosphorus by ryegrass in three to four months and "A" values, found in four greenhouse experiments.

TABLE 11

*Linear regression equations and correlation coefficients between uptake of phosphorus by ryegrass in the greenhouse (y) and "A" values of soil (x)*

(All results in mg. P/100 g. soil)

Experiment	Brief description of soils	No. of soils	Regression equation	Correlation coefficient
P9	Rothamsted; calcareous	9	$y = 0.546x - 0.52$	0.998
	Forest Nurseries; acid	12	$y = 0.668x - 0.37$	0.986
P12	Rothamsted; calcareous	7	$y = 0.217x - 0.42$	0.977
	Saxmundham; calcareous	9	$y = 0.290x - 0.41$	0.991
P11	Acid and calcareous arable soils from C. and E. England	15	$y = 0.418x - 1.31$	0.870
P14	Acid and very acid soils from England, Wales, N. Ireland and Japan	24	$y = 0.335x - 1.15$	0.879

Phosphorus uptake and "A" are very highly correlated, especially so with soils from the same location. The differences between the regression lines for the different groups of soils in experiments P9 and P12 were both significant. The greater release of phosphate from the forest nursery soils agrees with the more rapid growth on them. No satisfactory explanation has yet been found for the differences between calcareous soils of similar clay content and composition derived from the Clay-with-Flints at Rothamsted and the Boulder Clay at Saxmundham in which the ratio  $P_r/P_e$  (Table 13) and phosphate concentrations in 0.01M-CaCl<sub>2</sub> are similar.

The high correlations in these experiments, and the fact that there is no outstanding discrepancy, may be partly explained by the technique used. In all experiments a "starter dose" of phosphate (0.5 mg. P/100 g. soil) was mixed with the soil. Although this is small compared with the "A" values of most soils (5–25 mg. P/100 g.), it may have maintained the concentration of phosphate high enough after germination for the root system to develop. This explanation is supported by evidence with both acid and calcareous soils that the *initial* rate of growth of grass in the greenhouse on soils with the same "A" value is most rapid when the phosphate concentrations in 0.01M-calcium chloride are high (*Rep. Rothamst. exp. Sta. for 1957*, p. 59; for 1959, p. 44).



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The initial rate of growth of grass depends principally on phosphate potential, as predicted by Schofield (1955), but total yield and uptake of phosphorus increase with "A" and can, on some soils, be almost independent of phosphate potential. However, in Rothamsted soils phosphate potential (phosphate concentration) and quantity ("A") are closely correlated, so that either measurement predicts their phosphate status satisfactorily.

## RELATIONSHIPS BETWEEN LABORATORY AND GREENHOUSE MEASUREMENTS OF ISOTOPICALLY EXCHANGEABLE PHOSPHATE

*Correlation of "A" and  $P_e$* 

Table 12 summarises the correlations obtained between greenhouse ("A") and laboratory ( $P_e$ ) values for isotopically exchangeable phosphate in arable soils.

TABLE 12

*Summary of relationships between "A" and  $P_e$  measured in 0.02M-KCl or in 0.02M-KCl + 0.001M-NH<sub>4</sub> citrate for arable soils*

No. of soils	Description	Electrolyte	Regression equation	Correlation coefficient
37	Acid, neutral and calcareous	0.02M-KCl	$A = 1.067P_e + 0.21$	+0.985
12	Acid	0.02M-KCl + 0.001M-NH <sub>4</sub> citrate	$A = 0.771P_e + 0.09$	+0.966
12	Calcareous	0.02M-KCl + 0.001M-NH <sub>4</sub> citrate	$A = 1.238P_e + 1.18$	+0.993

The 37 soils tested had clay contents between 1 and 30%, pH values (in 0.01M-CaCl<sub>2</sub>) between 3.9 and 7.6, and  $P_e$  values between 1 and 32 mg. P/100 g. Values of "A" and  $P_e$ , measured in 0.02M-KCl, were very highly correlated, and "A" was numerically about 7% higher than the  $P_e$  values determined by the routine method. The regression equation shows that the total "pool" of soil phosphate sampled by ryegrass grown for 3-4 months in the greenhouse can be estimated quantitatively by isotopic exchange in the laboratory in about 7 days. The close correlations previously established between "A" and phosphorus uptake from soils (Table 11) will, therefore, also hold for  $P_e$  and phosphorus uptake in the greenhouse.

Values for  $P_e$  measured in 0.02M-KCl + 0.001M-NH<sub>4</sub>Cit are also highly correlated with "A" (Table 12), but are about 30% higher than "A" on acid soils. This suggests that even 0.001M-NH<sub>4</sub>Cit removed phosphate from acid soils with which <sup>32</sup>P ions do not exchange in the greenhouse. Acid reagents (0.3N-HCl; 0.002N-H<sub>2</sub>SO<sub>4</sub>; 0.5N-CH<sub>3</sub>COOH and citric acid) often used in soil analysis also dissolve soil phosphate that does not exchange with <sup>32</sup>P ions in the greenhouse (*Rep. Rothamst. exp. Sta.* for 1958, p. 51). For calcareous soils  $P_e$  values in the presence of citrate are very highly correlated with, but less than, "A"; this is consistent with measurements in the laboratory (Table 1).

The correlations summarised above were obtained with arable soils.  $P_e$  is not always numerically the same value as "A" measured



by growing grass in the greenhouse for 3–4 months if the soils contain either mineral or bone phosphates, which continue to dissolve slowly during a greenhouse experiment, or organic phosphates from plant residues or soil organic matter, which mineralise slowly. The slow release of  $^{31}\text{P}$  (with which  $^{32}\text{P}$  did not exchange during the first few weeks in the greenhouse) from all these materials decreases the specific activity of the later cuts of grass. "A" values calculated in these circumstances may be anomalously high (Mattingly & Widdowson, 1956).

TABLE 13

*Comparison of isotopically exchangeable P values in laboratory and greenhouse experiments and yields of ryegrass in the greenhouse*

Manurial treatment in the field			mg. P/100 g. soil		$P_r/P_e$ ratio	g. dry matter per pot	
		$A_1$	A	$P_e$			
Agdell Rotation, Rothamsted:							
NPK	(f)	...	9.4	10.9	9.1	0.621	3.10
NPK	(c)	...	6.6	7.5	7.8	0.483	1.87
PK	(f)	...	8.7	9.5	9.3	0.619	3.28
PK	(c)	...	5.0	6.4	6.7	0.544	2.02
O	(f)	...	2.7	2.8	3.8	0.547	1.11
O	(c)	...	2.6	2.4	3.5	0.352	0.78
Barnfield, Rothamsted:							
No nitrogen—							
PKNaMg	...	...	19.7	21.5	22.2	0.695	4.20
P	...	...	20.4	23.8	21.8	0.685	4.37
O	...	...	9.4	10.7	11.0	0.628	3.58
Sodium nitrate—							
PKNaMg	...	...	18.2	20.7	20.2	0.679	4.79
P	...	...	17.8	21.0	20.0	0.689	4.42
O	...	...	5.9	7.1	7.5	0.587	2.68
Ammonium sulphate—							
PKNaMg	...	...	32.4	33.9	29.6	0.750	4.65
P	...	...	31.0	36.1	30.1	0.810	4.40
O	...	...	9.3	10.4	12.0	0.585	3.09
Saxmundham, Rotation I:							
P	...	...	11.2	14.4	10.8	0.669	4.19
O	...	...	2.8	3.4	2.8	0.533	1.32
NP	...	...	10.9	13.2	9.3	0.621	4.16
N	...	...	2.6	3.3	2.8	0.473	1.20

## Notes

Agdell Rotation: (f) = fallow rotation; (c) = clover rotation. Manuring 1848–1951; all fertilisers were applied at the following rates per acre once in four years. N = 2 cwt. ammonium sulphate + 18 cwt. rape cake; P = 4 cwt. superphosphate; K = 3 to  $3\frac{1}{2}$  cwt. potassium sulphate. For details of the rotation and soils see Warren (1958).

Barnfield: Rates of manuring/acre/year: N = 4 cwt. ammonium sulphate or 5 cwt. sodium nitrate; P =  $3\frac{1}{2}$  cwt. superphosphate; K =  $4\frac{1}{2}$  cwt. potassium sulphate; Na = 2 cwt. sodium chloride; Mg = 2 cwt. magnesium sulphate.

Saxmundham: Rates of manuring/acre/year: N = 2 cwt. sodium nitrate; P = 2 cwt. superphosphate; K = 1 cwt. potassium chloride. For details of the rotation and soils see Cooke *et al.* (1958).

*Effects of manuring and cropping in the field on "A" and  $P_e$* 

Table 13 gives values for  $P_e$ , the ratio  $P_r/P_e$  and "A" obtained with soils from long-term field experiments at Rothamsted and



Saxmundham Experimental Stations. Yields of ryegrass on these soils in a greenhouse experiment are also given. Values for  $P_r$  and  $P_e$  were obtained by the routine laboratory method (p. 248).  $P_r$  was measured after isotopic exchange for 20 hours and  $P_e$  after 170 hours. Two values are given for "A". The first,  $A_1$ , was calculated from the specific activity of the first cut of grass; the second is the weighted mean value during the experiment (p. 257).

Yields of beans and clover in 1956 and 1957 and phosphate solubility in 0.5M-NaHCO<sub>3</sub> show that soils from the clover rotation on Agdell now supply less phosphate to crops than soils from the fallow rotation (Warren, 1958). The "A" and  $P_e$  values, the  $P_r/P_e$  ratio, and yields in the greenhouse, are also lower on soils from the clover rotation (Table 13).

Yields in the greenhouse,  $P_e$  and  $P_r/P_e$ , are all higher on the *unmanured* soil from Barnfield "No N" plots than on NPK plots from the adjacent Agdell rotation. The application of 4 cwt. superphosphate/acre once in 4 years on Agdell has resulted in a net gain of 8 lb. P/acre/year on the NPK (fallow) and 5 lb. P/acre/year on the NPK (clover) plots (Warren, 1958). This gain has not maintained the total "pool" of isotopically exchangeable phosphate on the more heavily cropped Agdell soils at the present level of the unmanured Barnfield soil. Superphosphate applied at 2 cwt./acre annually at Saxmundham for 60 years, however, has maintained "A" values at higher levels (Table 13) than on Agdell. Yields in the greenhouse on soils from the P and NP treatments at Saxmundham were near the maximum for the experiment.

The supplementary manuring on Barnfield with K, Na and Mg, in the presence of superphosphate, for over 80 years has not affected either  $P_e$  or the ratio  $P_r/P_e$ . Continuous application of ammonium sulphate for 80 years lowered the pH of the soil to about 5.5 by 1955. These plots were limed in 1956 and are now neutral. The "A" and  $P_e$  values on plots receiving P or PKNaMg are 50% higher (Table 13) than the corresponding plots receiving sodium nitrate which have never been acid. This suggests that phosphate was dissolved by ammonium sulphate from particles of chalk and then adsorbed in an isotopically exchangeable form after liming.

#### *Comparison of phosphate removed by ryegrass in the greenhouse with changes in $P_e$*

Preliminary experiments (*Rep. Rothamst. exp. Sta.* for 1957, p. 60) showed that the differences between  $P_e$  values of soils before and after cropping in the greenhouse were *greater* on acid soils and *smaller* on calcareous soils than the total phosphate removed by ryegrass. These conflicting results were probably obtained because  $P_e$  values were measured by exchange in 0.02M-KCl + 0.001M-citrate in which  $P_e$  values are greater than "A" in acid soils and less than "A" in calcareous soils (Table 12).

Table 14 gives more recent results, in which  $P_e$  values were measured in 0.02M-KCl, for soils from two nurseries of the Forestry Commission. At both centres the soils have received superphosphate annually for over 10 years and have been maintained at



different pH values. The Kennington Extension nursery is on an old arable soil (ca. 10% clay) and the Wareham nursery on sand (ca. 1% clay).

TABLE 14

Comparison of phosphate removed by ryegrass with changes in  $P_e$  for soils of different pH from Wareham, Dorset and Kennington, Oxon.

	Kennington (KE27)					Wareham (W27)					Mean of all soils
	4.3	4.8	5.3	6.2	7.0	3.8	4.8	5.6	6.5	6.8	
Approximate pH ...	4.3	4.8	5.3	6.2	7.0	3.8	4.8	5.6	6.5	6.8	—
$P_e$ (before cropping), mg. P/100 g. ...	14.4	13.6	15.4	17.6	18.3	12.6	13.6	16.1	19.9	17.1	15.9
$P_e$ (after cropping), mg. P/100 g. ...	4.0	3.1	3.2	3.4	3.3	2.0	2.0	2.6	4.4	4.2	3.2
Difference, mg. P/100 g.	10.4	10.5	12.2	14.2	15.0	10.6	11.6	13.5	15.5	12.9	12.7
P removed by ryegrass, mg. P/100 g. ...	11.6	12.6	12.4	14.2	14.4	10.0	12.6	15.4	17.4	16.2	13.7

The decrease in  $P_e$  by cropping on both soils is almost equal to the phosphate removed by the ryegrass. This confirms that the laboratory method used here to measure  $P_e$  estimates quantitatively the "pool" of isotopically exchangeable phosphate in soil taken up by ryegrass over the whole pH range from 3.8 to 7.0.

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