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PHOSPHATE ADSORPTION AND AVAILABILITY PLANT OF PHOSPHATE

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SUMMARY

The effects of phosphate buffer capacity on the plant-availability of labile soil phosphate, when measured as intensity (I) or quantity (Q), are described and tested using results from a greenhouse experiment on 24 Sherborne soils. In multiple regression studies, phosphate buffer capacity with I or Q measurements as independent variables accounted for up to 94% of the variance in P uptake by ryegrass, the maximum buffer capacity being generally more useful than the equilibrium buffer capacity.

When the quantity of soil P is measured (Q), its availability (*i.e.* ease of desorption) to plant roots is inversely related to the Langmuir bonding energy parameter and the buffer capacity. When the intensity of soil P is measured (I), its availability (*i.e.* resistance to change) is directly related to the adsorption and buffer capacities. The levels of Q or I, therefore, which are optimal for plant uptake vary with the buffer capacity of the soil. There is little or no correlation between the adsorption capacity and the bonding energy in many soils and consequently phosphate buffer capacity is only poorly correlated with the total adsorption capacity.

INTRODUCTION

It was shown earlier that phosphate buffer capacity is a function of the adsorption processes in soil[5]. As P is removed from soils, buffer capacity measures the amount of P desorbed as the equilibrium intensity (I) of P in solution decreases; as P is added to the system buffer capacity measures the amount of P adsorbed as I increases. However, in both situations, either the existing I or labile adsorbed P (P_s) must be known for buffer capacity to provide any quantitative information on the plant-availability of soil P. The equilibrium

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(EBC) and maximum buffer capacities (MBC) were defined elsewhere[5].

If it is assumed that buffer capacity remains relatively constant (as when the adsorption surface is very under-saturated) it will have the following effects on plant availability:

(i) In two or more soils of equal P intensity, plant uptake will be directly proportional to buffer capacity because the higher the capacity the more P is desorbed as I is decreased by root uptake. This

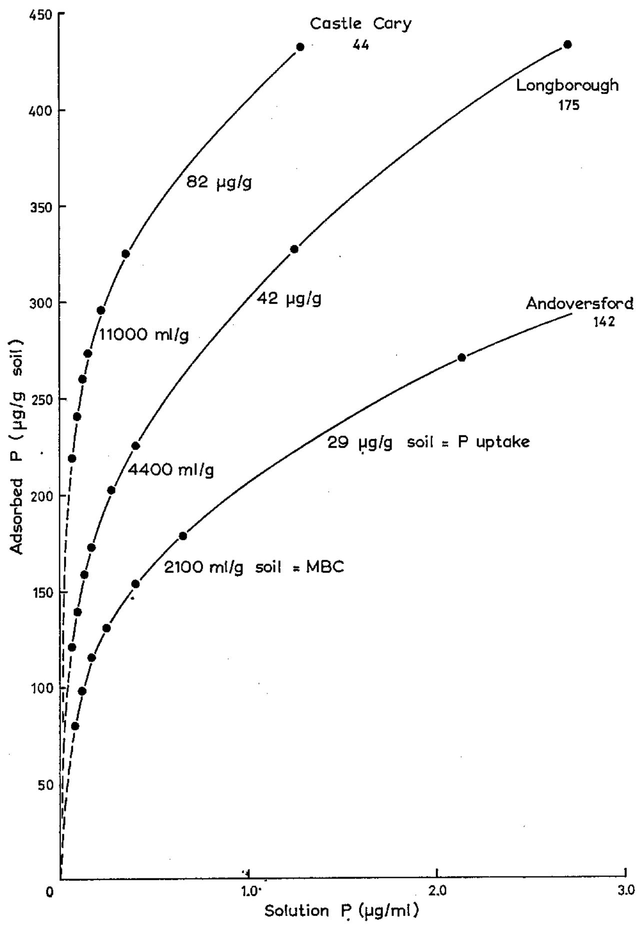

Fig. 1. Phosphorus adsorption isotherms for three soils (Sherborne Series) with different maximum buffer capacities (MBC) but similar initial P concentrations (0.05 μg P/ml). (Plant uptake is shown on each isotherm).

effect is illustrated in Fig. 1, which gives the adsorption isotherms of three soils with the same I (0.05 μg P/ml). It can be seen that the P_s in equilibrium with I is directly proportional to the maximum buffer capacity (MBC), and the total P uptake by ryegrass (in experiments described later in this paper) from these soils was also directly proportional to the MBC.

(ii) In two or more soils containing equal quantities of adsorbed P, plant uptake will be inversely proportional to buffer capacity because the higher the capacity the lower will be the P concentration in solution. Fig. 2 shows adsorption isotherms for three soils containing 100 μg P_s/g. Plant uptake was inversely proportional to the

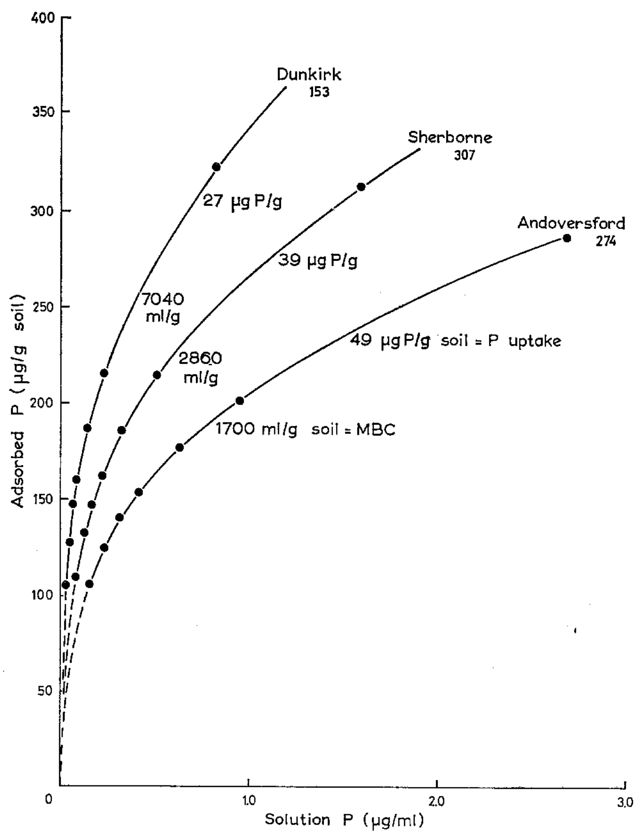

Fig. 2. Phosphorus adsorption isotherms for three soils (Sherborne Series) with different maximum buffer capacities (MBC) but similar initial quantities of labile P (100 μg P/g soil). (Plant uptake is shown on each isotherm).

buffer capacity because increasing buffer capacity depresses I. Similar concepts were discussed by Khasawneh[6].

The limitation of buffer capacity as a definitive parameter in the soil P system is that it may change significantly as P is added to or withdrawn from the system. However, the maximum buffer capacity (MBC) provides a parameter which is independent of the P saturation of the soil and gives a complete measure of its adsorption properties[5].

The objective of the following study was to determine the effect of the P adsorption parameters and derived buffer capacities on the uptake of P by ryegrass when related to the intensity and quantity of labile P in soil.

METHODS AND MATERIALS

The P uptake data were taken from a greenhouse experiment[7] using 24 soils from the Sherborne series[9] in south-west England. At each of the eight sites the soils had been given three rates of superphosphate in the field. No further P was applied in the greenhouse experiment. The ryegrass was cut 40, 77 and 117 days after sowing, and the tops were weighed (oven-dry) and analysed for P.

Table 1 gives the cumulative P uptakes from each harvest; the P-supply parameters have already been published[5]. The cumulative P uptake at each harvest was related to I or Q (independent variable 1) and the various adsorption parameters (independent variable 2) by multiple regression analyiss.

RESULTS

Because of the wide range of buffer capacities and the suggestion by Olsen and Watanabe[8] that P uptake is proportional to the square root of buffer capacity, this transformation of the BC data as well as the linear form was used in the multiple regressions. The square root transformation accounted for up to 9 per cent more variance in P uptake when related to I but there was no improvement when related to Q.

Effect of adsorption parameters and derived buffer capacities on plant P uptake in relation to P intensity

Table 2 gives the coefficients for the regressions of cumulative P uptake by ryegrass at 40, 77 and 117 days after sowing on intensity and buffer capacity measurements for the 24 Sherborne soils.

TABLE 1

Cumulative P uptake by ryegrass tops on Sherborne soils at 40, 77 and 117 days after sowing

Soil	P applied in field kg/ha	P uptake (µg/g soil)		
		40 days	77 days	117 days
Charlton Abbots	44	8.4	14.9	20.4
	175	11.8	22.6	32.8
	307	21.8	39.6	56.0
Sherborne	44	6.1	11.8	16.0
	175	11.7	21.8	31.1
	307	13.6	26.8	39.1
Andoversford	11	5.1	10.0	13.2
	142	12.2	21.0	28.8
	274	21.0	35.5	48.8
Longborough	44	10.4	20.8	32.2
	175	14.4	28.1	42.3
	307	17.8	34.5	54.0
Dunkirk	44	5.3	11.8	18.3
	153	7.2	16.7	26.8
	263	13.7	28.3	45.8
Castle Cary	44	20.6	46.8	82.3
	153	22.5	49.1	87.2
	263	26.9	60.9	104.1
Purse Caundle	0	9.6	20.6	32.1
	110	16.0	30.9	47.4
	219	17.8	33.8	48.4
Badminton	0	14.7	32.9	53.0
	110	18.5	41.5	64.1
	219	26.2	53.1	76.9

Intensity measurements (I) alone accounted for progressively less of the variance in P uptake at each successive harvest of ryegrass. MBC was correlated with uptake only at the second ($r = 0.52$) and third harvest ($r = 0.63$), but when combined with I in multiple regressions it greatly increased the variance accounted for by I alone, so that at each harvest the two parameters together accounted for 78–79 per cent of the variance in P uptake. The equilibrium buffer capacity (EBC), on the other hand, did not improve the regression.

TABLE 2

Coefficients of regression of P uptake by ryegrass on P intensity and measures of P buffer capacity

Days after sowing	Intensity coefficient	Buffer capacity		Variance accounted for %
		Parameter	Coefficient × 10^3	
40	161*** ± 31			53
77	290** ± 79			35
117	417* ± 149			23
40	211*** ± 29	$\sqrt{k'}$	2612** ± 762	68
77	424*** ± 71	$\sqrt{k'}$	7118*** ± 1830	61
117	681*** ± 128	$\sqrt{k'}$	14034*** ± 3320	56
40	132*** ± 19	x_m'	63*** ± 10	84
77	209*** ± 36	x_m'	174*** ± 19	87
117	257*** ± 54	x_m'	343*** ± 27	90
40	189*** ± 22	$\sqrt{MBC}$	152*** ± 29	79
77	366*** ± 48	$\sqrt{MBC}$	418*** ± 63	78
117	565*** ± 80	$\sqrt{MBC}$	825*** ± 107	79
40	200*** ± 48	$\sqrt{EBC}$	204 ± 194	53
77	433** ± 118	$\sqrt{EBC}$	750 ± 474	39
117	721** ± 219	$\sqrt{EBC}$	1598 ± 878	30

* $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

The superiority of MBC over EBC suggests that MBC is more characteristic of the overall buffering properties of the soils. Measurements of EBC, which correspond to the Q/I relation of Beckett and White[2], would be expected to be less effective as they change as P is withdrawn from the system by plant growth[11].

The two major components of buffer capacity significantly increased the variance accounted for by I alone, and their relative effects increased at each harvest. The larger effect of x_m', compared with k′, indicates that the most important component of buffering, when related to I, is the extensive parameter. However, the very high correlation (r = 0.98) between x_m' and Q may partly account for its large effect on the variance.

The inter-relationships between the buffer capacity measurements and their two major components help to explain the adequacy of each measurement. Thus MBC was closely related to both k′

(r = 0.87) and x_m' (r = 0.79) whereas EBC was only correlated with k′ (r = 0.76), the least important of the two buffering components.

The positive effect of buffer capacity (MBC) on plant P uptake, when related to P intensity, shows that the higher the buffer capacity, the lower the I required to achieve any particular level of plant P uptake (Fig. 3 and 4). Fig. 3 shows that to achieve an uptake of 50 μg P/g soil, a soil with MBC of 9000 ml/g requires an I of 0.022 μg/ml whereas a soil with MBC of 3000 ml/g requires an I of 0.077 μg/ml. For any group of soils, therefore, the critical I will be inversely related to the MBC and directly related to the time of uptake.

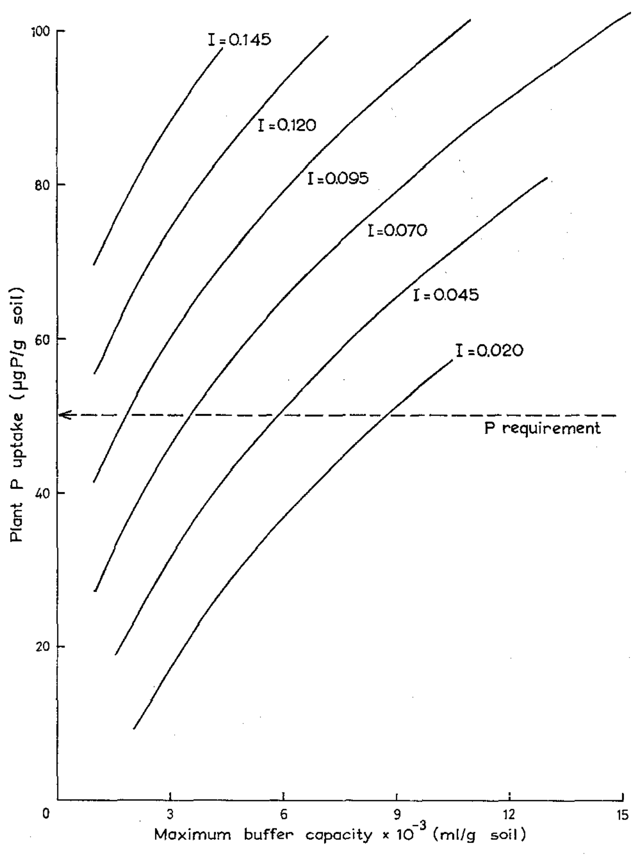

Fig. 3. Effects of maximum buffer capacity (MBC) on uptake of P by ryegrass at various initial P concentrations (I); data for 24 soils. (Uptake = $565\ I + 0.825\ MBC^{\frac{1}{2}}-38$; $r^2 = 0.79$).

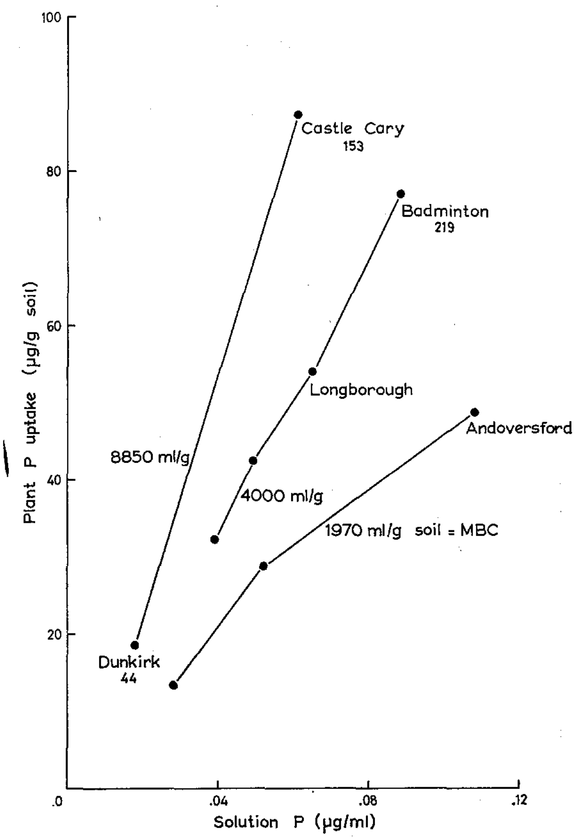

Fig. 4. Effects of initial P concentrations (I) in solution on uptake of P by ryegrass from soils with different maximum buffer capacities (MBC). (Soils with the same buffer capacities are joined by lines).

Experimental data for three groups of soils, whose MBC vary, show the same positive interaction between I and MBC on plant P uptake (Fig. 4). In the least buffered group (Andoversford) there was an increase of 36 µg P/g soil in uptake relative to an increase of 0.08 µg P/ml in I from the lowest to the highest fertilized plot. However, the increase in P uptake from the much more buffered Dunkirk – Castle Cary group of soils was 69 µg P/g soil relative to an increase in I of only 0.04 µg P/ml. The same effect is shown in Fig. 1 for three individual soils of contrasting buffer capacities but about the same I (0.049–0.052 µg P/ml). The uptake of P varied from 29 µg/g soil in the least buffered Andoversford soil to 82 μg/g soil in the most buffered Castle Cary soil.

Effect of adsorption parameters and derived buffer capacities on plant P uptake in relation to P quantity

At each successive harvest of ryegrass, Q alone accounted for an increasing and very significant percentage (from 61 to 90) of the variance in P uptake (Table 3). Both measurements of buffer capacity, however, significantly improved the multiple regression, the relative improvement decreasing from the first to the final harvest. Both measures of buffering had the same effect on the variance although EBC tended to be slightly better at the first harvest.

The bonding energy component of buffering significantly increased the variance accounted for by Q alone and was only slightly inferior to the BC measurements. The effect of x_m' was only signifi-

TABLE 3

Coefficients of regression of P uptake (by ryegrass) on P quantity and measures of P buffer capacity

Days after sowing	Quantity coefficient × 10^3	Buffer capacity		Variance accounted for %
		Parameter	Coefficient × 10^3	
40	91*** ± 15			61
77	221*** ± 24			79
117	407*** ± 29			90
40	113*** ± 13	k'	−249** ± 66	76
77	254*** ± 22	k'	−380** ± 109	86
117	444*** ± 27	k'	−433** ± 135	93
40	243*** ± 62	x_m'	−150* ± 60	69
77	415*** ± 104	x_m'	−192 ± 100	81
117	603*** ± 128	x_m'	−195 ± 124	90
40	159*** ± 17	MBC	− 1.41*** ± 0.28	81
77	326*** ± 28	MBC	− 2.18*** ± 0.47	89
117	526*** ± 36	MBC	− 2.47*** ± 0.59	94
40	91*** ± 10	EBC	− 5.58*** ± 1.03	83
77	221*** ± 17	EBC	− 8.22*** ± 1.81	89
117	406*** ± 22	EBC	− 9.38*** ± 2.29	94

* $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

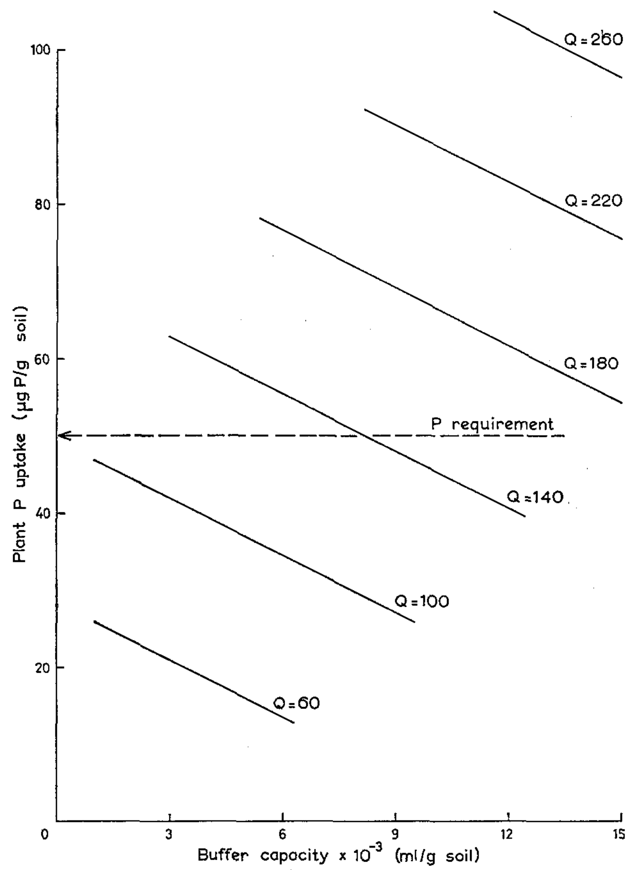

Fig. 5. Effects of maximum buffer capacities (MBC) on uptake of P by ryegrass from soils containing different initial quantities of labile P (Q); data for 24 soils. (Uptake = 0.526 Q − 0.0025 MBC − 3.3; r^2 = 0.94).

cant at the first harvest and, when related to Q, the most important component of buffering is the intensive parameter, k', the equilibrium constant between adsorbed P and solution P.

The negative effect of buffering (MBC) on plant P uptake, when related to Q, is shown in Fig. 5. It follows that the higher the buffer capacity, the larger the Q required to achieve any particular level of plant P uptake. In order to reach an uptake of 50 µg P/g, a soil with MBC of 9000 ml/g requires a Q of 144 µg P/g whereas a soil with MBC of 4000 ml/g requires a Q of 120 µg P/g. In other words, the higher the buffer capacity the greater the initial level of labile P required in the soil. As with I, increasing the time of uptake will also increase the critical Q.

DISCUSSION

The problem of analysing soil for so-called plant-available P has long exercised the minds of soil chemists. Recognition of the I and Q aspects of soil P has helped to clarify the problem[12] but the role of the adsorption process has not been fully understood. Two approaches have been used in previous research that are relevant to adsorption processes: one is the effect of P saturation of the adsorption complex[3 13], and the other is an equilibrium buffer capacity measurement derived from a Q/I curve[2].

This study has analysed the adsorption process and demonstrated the relative importance of the two fundamental adsorption parameters, both of which contribute to the buffering[5]. It has also shown the relationships between Q, I, and buffer capacity parameters of the soil P system.

An important conclusion is that the critical levels of Q or I alter according to the buffer capacity of the soil and the time of cropping. Critical levels of Q increase and I decrease as the buffer capacities of soils increase. It is impossible, therefore, to set a universal value for either quantity or intensity of P in a group of soils, unless the buffer capacity and time of cropping are uniform. The 13-fold variation in the buffering of the 24 soils used here (all from one soil series) demonstrates the great variability of buffer capacities. In a group of unrelated soils, buffer capacity could be much more variable.

Both an intensive and an extensive parameter are required to measure the plant-availability of soil P adequately. If the primary measurement of soil P is I, the extensive component of buffer capacity, or the adsorption capacity, is the important factor to plant-availability. If the primary measurement of soil P is Q, the intensive component, k, is the major factor in buffering. Being related to the bonding energy, k has a negative effect on availability because the higher the k the more the adsorption/desorption equilibrium tends to move towards the solid phase (P_s). Consequently, I will be inversely correlated with k so that for two or more soils of equal Q (or P_s), the buffer capacity will be inversely correlated with I.

In spite of Schofield's[10] emphasis on the energy factor in the soil

P system, its significance in the process of P adsorption/desorption has been largely overlooked. Previously published studies[3 13] have been primarily concerned with the effect of the P adsorption maximum on P availability. More recent studies[1 4] have aimed at determining P adsorption capacities on the assumption that they were the major adsorption parameter in the soil P system. Consequently, the full significance of the adsorption process in controlling the Q/I equilibrium, as it is expressed in the buffer capacity parameter*, has not been appreciated. Our results show that there is little or no correlation ($r = 0.43$) between the adsorption capacity and the bonding energy parameter and consequently buffer capacity can only be poorly correlated with adsorption capacity in many soils.

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REFERENCES

1 Bache, B. W. and Williams, E. G., A phosphate sorption index for soils. J. Soil Sci. **22**, 289–301 (1971).
2 Beckett, P. H. T. and White, R. E., Studies on the phosphate potentials of soils. III. The pool of labile inorganic phosphate. Plant and Soil **21**, 253–282 (1964).
3 Cole, C. V. and Olsen, S. R., Phosphorus solubility in calcareous soils: II. Effects of exchangeable phosphorus and soil texture on phosphorus solubility. Soil Sci. Soc. Am. Proc. **23**, 119–121 (1959).
4 Gunary, D., A new adsorption isotherm for phosphate in soil. J. Soil Sci. **21**, 72–77 (1970).
5 Holford, I. C. R. and Mattingly, G. E. G., A model for the behaviour of labile phosphate in soil. Plant and Soil **44**, 219–229 (1975).
6 Khasawneh, F. E., Solution ion activity and plant growth. Soil Sci. Soc. Am. Proc. **35**, 426–436 (1971).
7 Mattingly, G. E. G., Russell, R. D. and Jephcott, B. M., Experiments on cumulative dressings of fertilisers on calcareous soils in south-west England. II. Phosphorus uptake by ryegrass in the greenhouse. J. Sci. Food Agr. **14**, 629–637 (1963).
8 Olsen, S. R. and Watanabe, F. S., Diffusion of phosphorus as related to soil texture and plant uptake. Soil Sci. Soc. Am. Proc. **27**, 648–653 (1963).
9 Russell, R. D., Experiments on cumulative dressings of fertilisers on calcareous

* This is illustrated by the close correlation ($r = 0.98$) between the Q/I ratio at equilibrium and EBC for the Sherborne soils (excluding Castle Cary soils).

soils in south-west England. I. Description of field experiments and soil analysis for phosphorus residues. J. Sci. Food Agr. **14**, 622–628 (1963).

10 Schofield, R. K., Can a precise meaning be given to 'available' soil phosphorus. Soil and Fertilizers **18**, 373–375 (1955).

11 White, R. E., Buffering capacity of soil on uptake of phosphorus by plants. Trans. 9th Intern. Congr. Soil Sci. **2**, 787–794 (1968).

12 Williams, E. G., The intensity and quantity aspects of soil phosphate status and laboratory extraction values. Anales Edafol. Agrobiol. (Madrid) **26**, 525–546 (1967).

13 Woodruff, J. R. and Kamprath, E. J., Phosphorus adsorption maximum as measured by the Langmuir isotherm and its relationship to phosphorus availability. Soil Sci. Soc. Am. Proc. **29**, 148–150 (1965).