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A MODEL FOR THE BEHAVIOUR OF LABILE PHOSPHATE IN SOIL

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SUMMARY

The Langmuir two-surface adsorption equation is used to derive a phosphate adsorption characteristic, the maximum buffer capacity, which integrates the intensive and extensive components of adsorption and is independent of P saturation. Changes in the intensities and quantities of labile P and equilibrium buffer capacities resulting from fertilization of a group of 24 soils are shown to be related to the Lamgmuir high-energy adsorption parameters and in particular the maximum buffer capacity.

INTRODUCTION

The immediate source of phosphate (P) to plant roots is the soil solution which is replenished in most soils by adsorbed P [5]; it follows, therefore, that two parameters describe the plant-availability of soil P: the concentration (c) of P in the soil solution (an intensive parameter) and the quantity (P_s) of adsorbed P (an extensive parameter). The relationship between these variables, termed the buffer capacity (*BC*), defines the change in quantity of adsorbed P (ΔP_s) per unit change in concentration of solution P (Δc). The fundamental problem in evaluating the plant-availability of soil *P* by means of a soil test, whether it be an intensive or extensive parameter [9], is that neither alone gives any information on buffer capacity, which controls the resistance of both c and P_s to change when P is added to or removed from the system.

The buffer capacity of the soil P system may be described by the P adsorption isotherm. It has been previously shown that the Lang-

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muir equation is an excellent model for describing P adsorption from solutions $< 10^{-3}M$P, if it is assumed that adsorption occurs on two types of surface of contrasting bonding energies [3]. For most soils, which are relatively undersaturated with P, this equation may be written as:

$$x = \frac{k'x'_m c}{1 + k'c} + \frac{k''x''_m c}{1 + k''c}$$

where x = adsorption, k = adsorption/desorption equilibrium constant, x_m = monolayer adsorption capacity, and c = equilibrium solution concentration. The superscripts $'$ and $''$ refer to the high and low-energy adsorption surfaces respectively.

According to this model, labile soil P exists in equilibrium between the solution and the high and low-energy surfaces. When soluble phosphate is added to soil, phosphate ions will move from the enriched solution phase on to unoccupied adsorption sites until a new equilibrium is established. The relative amount adsorbed on each surface will be a function of the P affinity and the availability (or frequency) of each type of site. When phosphate ions are removed from the soil as a result of plant uptake or leaching adsorbed P will move into the depleted solution until a new equilibrium is established. The amounts removed from each surface will be a direct function of the frequency but an inverse function of the affinity of P-occupied sites. When phosphate ions are either added to or removed from the soil, the change in total P_s (or x) relative to the change in c is defined by the buffer capacity.

At any point on the adsorption isotherm corresponding to a particular P concentration, the slope of a tangent to the curve will represent the instantaneous buffer capacity of the system *i.e.* $(\mathrm{d}x/\mathrm{d}c)_c$. By differentiating the Langmuir equation, the buffer capacity at any concentration is:

$$\mathrm{d}x/\mathrm{d}c = \frac{k'x'_m}{(1 + k'c)^2} + \frac{k''x''_m}{(1 + k''c)^2}$$

As P is added to or removed from the soil system, the buffer capacity will decrease or increase (respectively), the magnitude of the change depending on the original position on the adsorption isotherm (Fig. 1). The buffer capacity will remain relatively constant as long as the solution concentration is on the steeply-rising part of

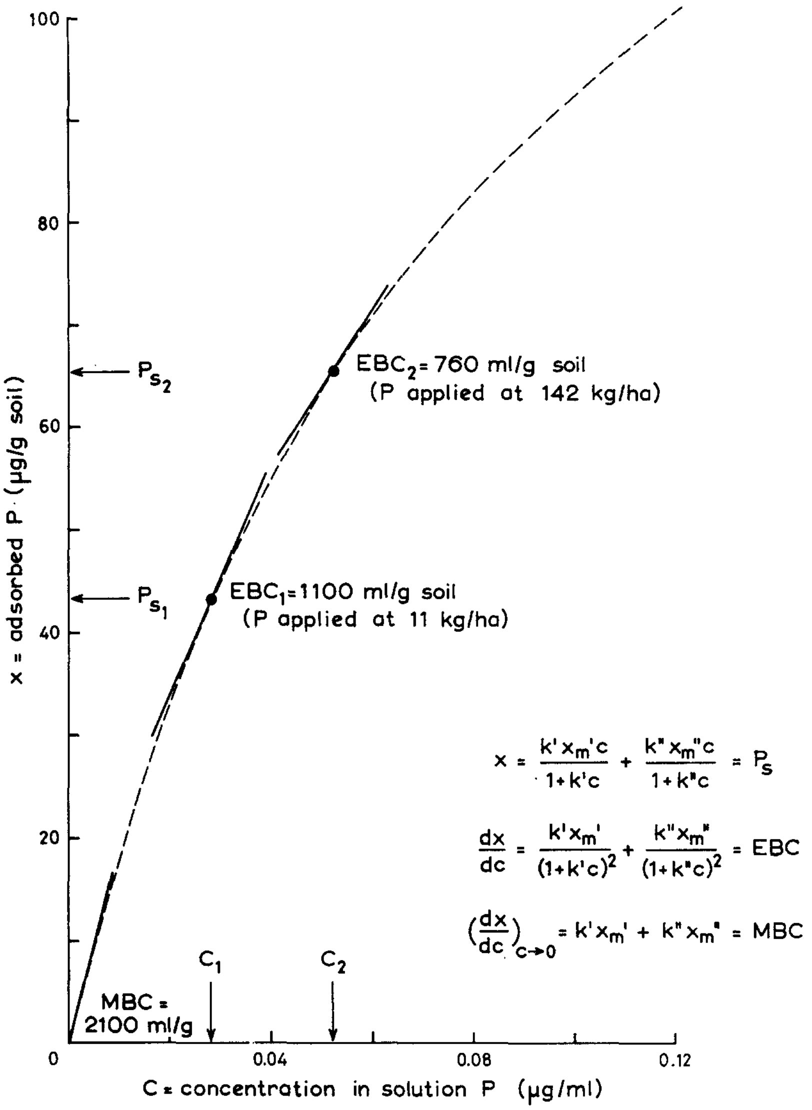

Fig. 1. Phosphorus adsorption isotherm and parameters (P_s; MBC; EBC) related to soil P supply from Andoversford soil.

the isotherm. As the high energy surface becomes nearly saturated, the buffer capacity diminishes rapidly because of the decreasing isotherm slope.

It is reasonable to propose the existence of a maximum or limiting buffer capacity to overcome the problem of a constantly varying capacity. This is the maximum slope of the adsorption isotherm as c tend to zero. From the previous equation it can be seen that:

$$(\mathrm{d}x/\mathrm{d}c)_{c \to 0} = k'x'_m + k''x''_m$$

This parameter remains constant as long as the adsorption properties of the soil are unchanged. This model for the soil P system is illustrated in Figure 1.

The Langmuir equation provides four parameters which determine the buffer capacity of the soil P system which is a function of the adsorption/desorption equilibrium constant (k) of the soil surface and the number of sites (or extent of surface) available for adsorption ($x_m - \mathrm{P}_s$). In a soil in which the high-energy surface is significantly under-saturated with P, most of the buffer capacity is provided by adsorption properties of this surface because of its much higher P affinity. However, as this surface becomes more and more saturated, its relative contribution to buffering decreases by comparison with that of the low-energy surface on which P adsorption does not become appreciable until the high-energy surface is approaching full saturation [3].

The equilibrium buffer capacity (EBC) of soil is therefore determined by the Langmuir adsorption parameters and by the degree of P saturation of the adsorption complex. This effect of P saturation is illustrated by the changes in EBC that result from fertilization of the Andoversford soil (Fig. 1). When unfertilized, this soil had an EBC of 1100 ml/g whereas fertilization with 142 kg P/ha decreased the EBC to 760 ml/g. Fertilization increased the saturation of the high-energy surface from 38% to 49% and the P concentration in the soil solution from 0.028 to 0.052 μg/ml.

These considerations demonstrate the importance of k in understanding the total adsorption properties of soil. The majority of past studies have been concerned only with the extensive parameter (x_m) of adsorption [1 6 8 10]. Both k and x_m determine the buffer capacity, and in any group of soils the more variable parameter will have the largest effect on buffer capacity.

The objective of the following study was to examine the effects of past fertilizer applications in the field on intensities and quantities of labile P and equilibrium buffer capacities in relation to the adsorption properties of 24 related soils from the Sherborne series in south-western England[4].

MATERIALS AND METHODS

Soils

The 24 soils were taken from eight different sites on the Sherborne series, and were described previously by Russell[7]. Three rates of fertilizer P had been applied as superphosphate at each site at least two years before sampling, and each soil represented one of these rates and is described thereby (Table 1).

Adsorption measurements

Adsorption was determined from the change in P concentration of 0.02 *M* KCl (when shaken with soil), whose initial P concentrations, as KH_2PO_4, were 0.78, 1.55, 2.33, 3.10, 4.65, 6.2, 12.4, 18.6, 24.8 and 31.0 μg/ml. Details of the procedures and calculation of the adsorption parameters are given by Holford *et al.*[3].

Soil P supply parameters

From the above measurements, the following estimates of *P* intensity, quantity and buffer capacity were made for each soil:

i. P intensity (*I*): P concentration (μg/ml) of supernatant solution after shaking 2.50 g soil in 50 ml 0.02*M* KCl for 24 h.

ii. P quantity (*Q*): adsorbed P plus isotopically-exchangeable P in the soils determined as described by Holford *et al.*[3].

iii. Maximum buffer capacity (MBC): maximum slope of Langmuir adsorption isotherm $(\mathrm{d}x/\mathrm{d}c)c \rightarrow 0$ calculated from $k'x'_m + k''x''_m$.

iv. Equilibrium buffer capacity (EBC): slope of the tangent to the Langmuir adsorption isotherm $(\mathrm{d}x/\mathrm{d}c)$ at a P concentration (c_1) corresponding to the equilibrium *I* and calculated from

$$\mathrm{d}x/\mathrm{d}c = \frac{k'x'_m}{(1 + k'c_1)^2} + \frac{k''x''_m}{(1 + k''c_1)^2}$$

RESULTS AND DISCUSSION

According to this model, the short-term changes (measured in weeks or several months), in the intensities (ΔI) and quantities (ΔQ) of labile P and the equilibrium buffer capacities (EBC) of the soils at each of the eight sites will be a function of the previous P fertilization and the inherent adsorption properties of each soil.

These changes can be calculated from the Langmuir parameters which have been reported previously [2]. However, the results which we are now discussing represent longterm changes (over a period of at least two years) and these are affected by additional processes which convert adsorbed P into non-labile forms.

The second problem in studying the changes induced by P fertilization at each site is that adsorption properties tend to vary signi-

TABLE 1

Soil P – supply parameters* for Sherborne soils

Soil	P applied	I 0.02 *M* KCl	Q 0.02 *M* KCl	Buffer capacity				P saturation
				Major components		MBC	EBC	
	(kg/ha)	(µg/ml) × 10²	(µg/g)	(k′)	(x_m')	(ml/g) × 10⁻¹		$\left(\frac{P_s}{x_m'} \times 100\right)$
Charlton Abbots	44	4.3	70	9.8	153	156	80	45
	175	4.4	84	17.9	151	279	93	54
	307	14.9	112	6.0	188	117	35	57
Sherborne	44	2.7	63	15.6	169	275	141	37
	175	3.8	65	13.3	155	217	102	41
	307	5.6	103	15.1	182	286	92	56
Andoversford	11	2.8	56	14.1	140	206	110	39
	142	5.2	71	14.4	143	214	76	49
	274	10.8	100	10.1	159	170	48	61
Longborough	44	3.9	95	19.4	194	389	134	49
	175	4.9	112	22.5	188	438	110	59
	307	6.5	128	18.0	202	377	90	63
Dunkirk	44	1.8	85	51.0	169	887	259	50
	153	1.9	97	35.6	191	704	264	51
	263	3.9	105	30.0	182	560	131	57
Castle Cary	44	5.1	212	36.6	297	1102	147	71
	153	6.1	233	25.5	340	883	135	68
	263	7.2	275	43.1	345	1512	112	79
Purse Caundle	0	3.5	79	20.2	168	352	129	46
	110	4.6	100	25.8	175	463	107	57
	219	4.7	109	26.9	181	501	109	60
Badminton	0	3.9	116	20.9	216	468	153	53
	110	6.7	150	17.9	243	449	103	61
	219	8.8	162	14.5	251	377	82	64

* see text for explanation of symbols

ficantly within each site as well as between sites. The total adsorption properties are best expressed by the buffer capacity, which varied (Table 1) from 1700 ro 2140 ml/g soil in the most uniform site (Andoversford) and from 1170 to 2790 ml/g soil in the most variable site (Charlton Abbots). This variability has been described elsewhere [2] and is due primarily to the amount or iron oxides present in the soils. Because of these variations within sites it is impossible to establish simple relationships between changes in the P supply

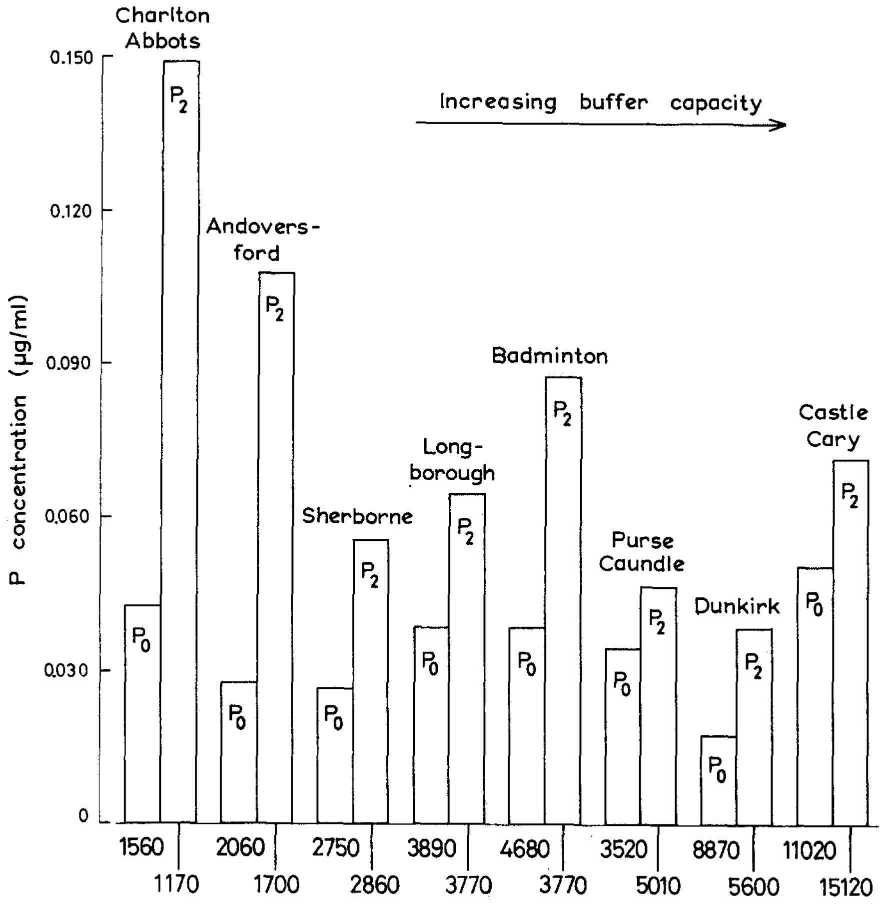

Fig. 2. Effects of maximum buffer capacity (MBC) on increases in soil P concentrations (µg P/ml) at 8 sites following P fertilization. (Maximum buffer capacities (ml/g soil) shown at base of each column).

parameters, P fertilization, and adsorption at each site and the results can only be discussed semi-quantitatively.

Changes in P intensity

The increase in I resulting from P fertilization at each site should be inversely related to the MBC and EBC. In at least half the sites (Sherborne, Longborough, Castle Cary and Badminton) there was a consistent increase in I from each increment of P fertilizer (Table 1). The largest overall increase in I occurred on Charlton Abbots, which is the least buffered soil, and the smallest was on Purse Caundle, which is the third most buffered soil (Fig. 2).

In soils from Charlton Abbots there was no increase in I at the intermediate rate of P because the MBC of this soil was higher than that of the soil receiving the lowest rate of P. By contrast, the very large increase in I at the highest rate of P was due to the very low MBC of this soil.

In soils from Andoversford, Longborough and Dunkirk there was a much larger relative increase in I at the highest than at the intermediate rate of P. In each case, the soil receiving the highest rate of P had a significantly lower MBC than the soil receiving the least P (*i.e.* Charlton Abbots, Andoversford, Badminton and Dunkirk). In each of the latter soils I more than doubled at the highest rate of P. On the other hand, where MBC was much greater on the highest-P soil (as in Purse Caundle and Castle Cary) there was a relatively small increase in I.

Changes in P quantity

Because most of the added fertilizer P initially goes into the labile pool, the absolute increases in Q, in the short-term, should be proportional to the amount of P added irrespective of the MBC. The effect of the MBC will be to control the ratio of ΔQ to ΔI; *i.e.* the greater the buffer capacity, the greater the increase in Q relative to the increase in I. Consequently ΔQ on every site should be similar because approximately the same amount of P was applied to all sites. Table 1 shows, however, that there was more than a threefold variation in ΔQ over the eight sites, indicating that other processes, such as precipitation of stable mineral phosphates, have caused variable amounts of P to be removed from the labile pool.

Although the Castle Cary soil contained the highest concentration of P in solution and would therefore be most susceptible to loss of labile P by precipitation, it showed the largest increase in Q following fertilization. This soil had the largest x_m, whereas the soil (Dunkirk) which showed the smallest ΔQ had the largest k; this suggests that the larger the adsorption capacity of the soil surface, the more added P remained in the labile pool, whereas the more tightly held the adsorbed P, the more it reverts to a non-labile form. The transformation of labile P to a non-labile form is primarily a surface reaction. The higher the bonding energy of the surface, the more adsorbed P is converted into non-exchangeable P either by the formation of stable crystalline phosphates or by penetration of the surface by the P ions.

Changes in equilibrium buffer capacity

As predicted from the model, at most sites the EBC generally decreased with each increment of P fertilizer (Fig. 3). However, at Charlton Abbots and Dunkirk the EBC increased at the first increment while at Purse Caundle there was no change at the second increment. These anomalies are probably due to within-site variability of the adsorption parameters. At Charlton Abbots the soil receiving the middle rate of P had a much higher k' and consequently a higher MBC and EBC. At Dunkirk the corresponding soil had a much higher x'_m and was no more P-saturated than the lowest-P soil; consequently there was little change in EBC. At Purse Caundle, the higher MBC and small change in P saturation explain the lack of change in EBC between the middle and high rates of P.

CONCLUSIONS

Maximum buffer capacity is suggested as a characteristic for defining the P adsorption properties of soil because it integrates the intensive and extensive components of adsorption and is independent of P saturation. It accounts well for the changes that have occurred in the intensity and quantity of labile P and equilibrium buffer capacities of a group of related soils following P fertilization.

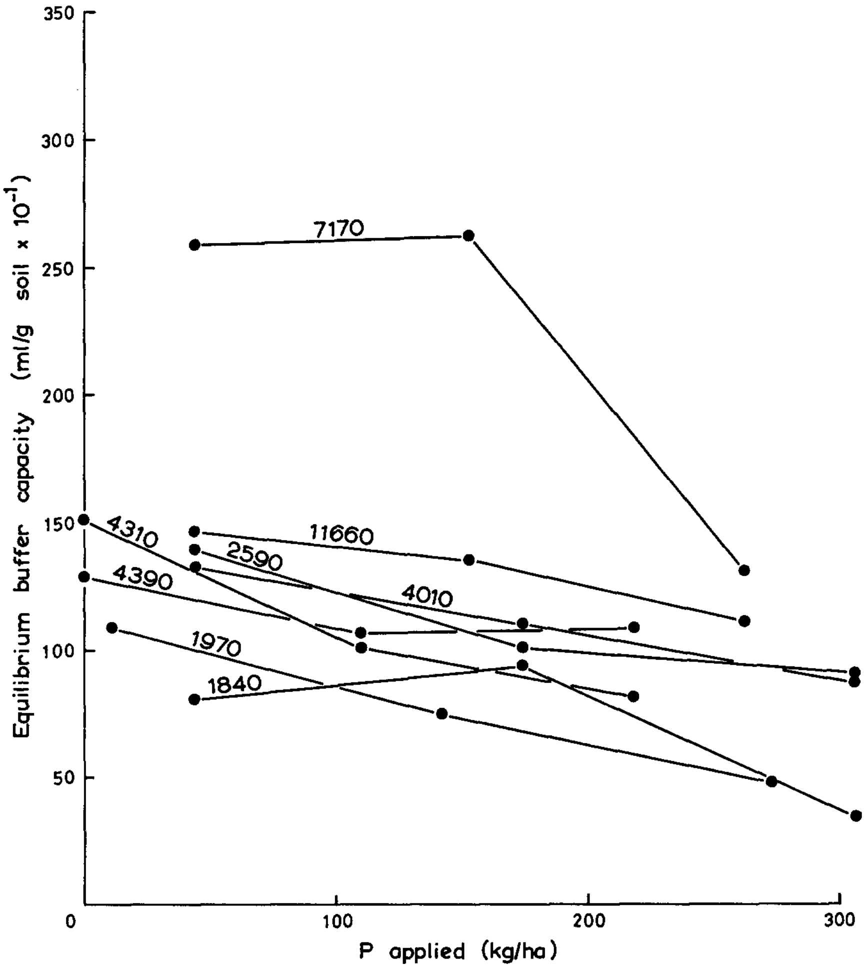

Fig. 3. Effects of the application of fertilizer P on the equilibrium buffer capacity (EBC) of soils. (Mean maximum buffer capacity (ml/g soil) shown on each curve.

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