

Phosphate Desorption from Some Argentine Soil Samples. I. Constant Temperature¹

*E.J. Bottani**, *E.A. Fertitta***,
*L.E. Cascarini de Torre****

ABSTRACT

Phosphate ion desorption from four Argentine soil samples is studied, and the kinetics are analyzed. Two different kinds of adsorbed phosphate ion are identified, one corresponding to low concentrations of added phosphate. From the desorption isotherms, it is possible to determine the Bray-Kurtz phosphorus. Phosphate released by soil without previous additions is also analyzed.

INTRODUCTION

In a previous paper (Bottani *et al.* 1993), several soil samples were characterized by analysis of gas adsorption data. The characteristics deduced were employed to explain adsorption of the phosphate ion from solutions.

To increase knowledge of the mechanisms and state of phosphate ion adsorption in soils, we studied the desorption process at constant and variable temperatures. In this paper, we present the results obtained at constant temperature; in the second paper, we present the results obtained at different temperatures; in the third paper, we relate the characteristics deduced from adsorption of simple gases in the same soil samples.

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* Fellowship of the CIC, Provincia de Buenos Aires, Arg

* Researcher of the CIC, Provincia de Buenos Aires, Arg

RESUMEN

Se estudia la desorción de iones-fosfato en cuatro muestras de suelos argentinos y se analiza la cinética del proceso. Se postula la existencia de dos tipos diferentes de iones fosfatos adsorbidos, uno correspondiente a bajas concentraciones de fosfato agregado y otro a altas. A partir de las isothermas de desorción es posible obtener un valor de fósforo comparable con el obtenido por el método Bray-Kurtz. También se examina el fósforo liberado por el suelo cuando no hay agregado previo.

The desorption data may give information about of strength of the phosphate ion-soil- site bond, and the analysis of this process could explain how the phosphate ion is retained and released by soils (Gardner and Preston 1973; Imai *et al.* 1981).

Although Langmuir's model (De Blas Varela *et al.* 1989; Camara *et al.* 1987), when applied to adsorption isotherms of phosphate, can give a good fit, it is shown that the deduced parameters may be meaningless, especially the energy-dependent one.

MATERIALS AND METHODS

Soil samples studied in this paper are from different regions of Buenos Aires province. Soil LUJ is from Lujan, LP from La Plata, LE from La Emilia district, and LT from the region close to La Tigra lake. LP is an argiudoll-like soil, while LE is a typical haplustol, LT is an argiudoll petrocalcic, and LUJ is a typic argiudoll (Table 1).

Phosphate ion concentration was determined following the standard technique of the phosphomolybdate blue complex using ascorbic acid as a reducing agent. This experimental technique has been previously described (Bottani *et al.*; Jackson 1964; Chen *et al.* 1956).

The desorption of the phosphate ion was done as follow: Soil samples of approximately 2.5 g were

Table 1. Main characteristics of the soils employed.

Soil	LUJ	LE	LP	LT
pH (1:2.5)	5.4	6.2	5.8	6.3
%OM ¹	3.55	1.79	1.98	3.16
%N ²	0.218	0.112	0.21	0.148
P ³ (ppm)	5.31	3.59	16.40	4.04
Ca ⁴ (mEq/100g)	14.69	8.44	8.20	13.57

- 1: Organic matter content determined according to Walkley-Black method
- 2: Kjeldahl Nitrogen content
- 3: Bray and Kurtz #1
- 4: Exchangeable calcium.

put in contact with 25 ml of phosphate solutions in Pyrex glass flasks during five days at 303.2 ± 0.1 K, as in the determination of the adsorption isotherms (Barrow 1978; López-Hernández *et al.* 1981). Formal concentrations of phosphate solutions were 1, 3, 5, 7, 10, 12, 15, 25 and 30 ppm (mg/ml). Once the equilibrium was reached, the liquid was extracted and both the pH and the remaining phosphate in the solution were determined. In this way, the adsorbed quantity was known, and taken as soil-starting phosphate content. Then, 25 ml of pure water were added to each sample and kept at 303.2 K during several days. The new solution was extracted, without reaching equilibrium, to determine the released phosphate quantity and fresh water was added (always 25 ml). Finally, the process was repeated until the released phosphate was negligible, usually after a maximum of 96 days. We always included a flask containing soil where only pure water was added, which was replaced by pure water, in order to measure the phosphate released by the soil. In all cases, manual discontinued agitation (twice a day) was practiced.

The analysis of the pH values obtained from these experiences has not shown any dependence on the adsorption-desorption process in terms of pH.

The adsorption isotherms of the phosphate ion were determined at 303.2 K in order to obtain the desorption isotherms; in addition the adsorption isotherms at 313.2 K were determined (Mehadi and Taylor 1988). In Figures 1-4 the adsorption isotherms of phosphate at both temperatures are shown.

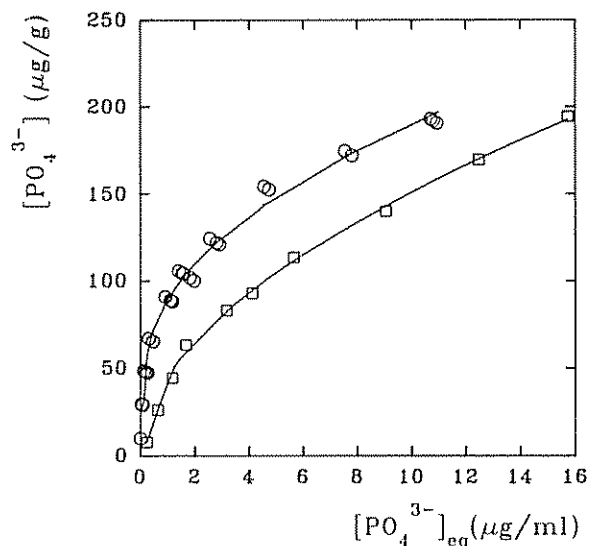


Fig. 1. Phosphate adsorption isotherms on soil LE. °: 303.2 K; □ : 313.2 K.

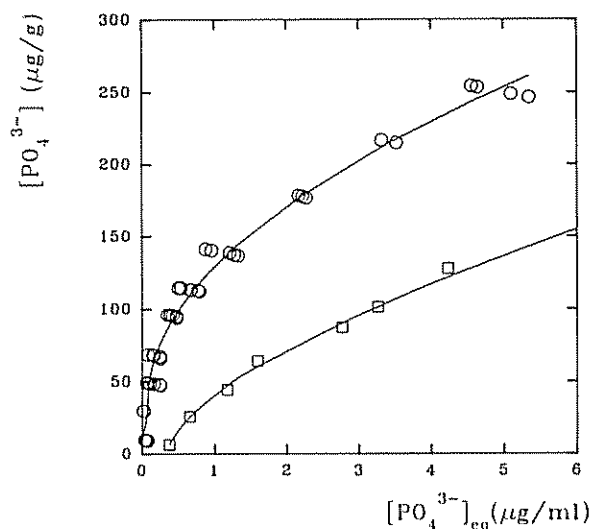


Fig. 2. Phosphate adsorption isotherms on soil LP. °: 303.2 K; □ : 313.2 K.

RESULTS AND DISCUSSION

All the adsorption isotherms were fitted to Langmuir's model equation:

$$\frac{C}{X} = \frac{C}{X_m} + \frac{1}{K_T X} \quad (1)$$

where C represents the phosphate ion remaining in solution, X is the adsorbed phosphate, X_m is the phosphate ion necessary to form a monolayer and K_T

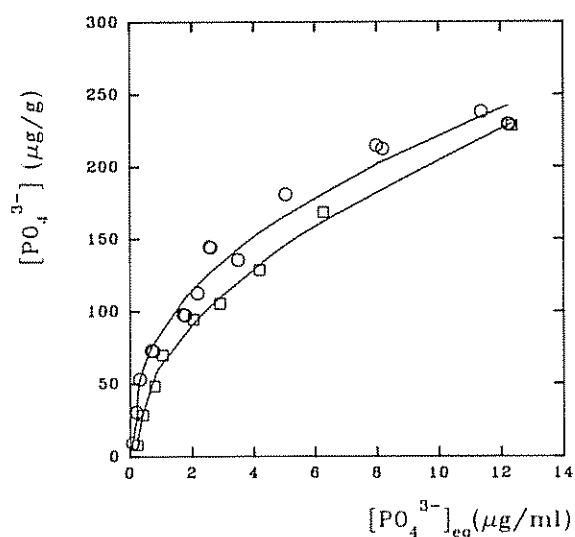


Fig. 3. Phosphate adsorption isotherms on soil LT. \circ : 303.2 K; \square : 313.2 K.

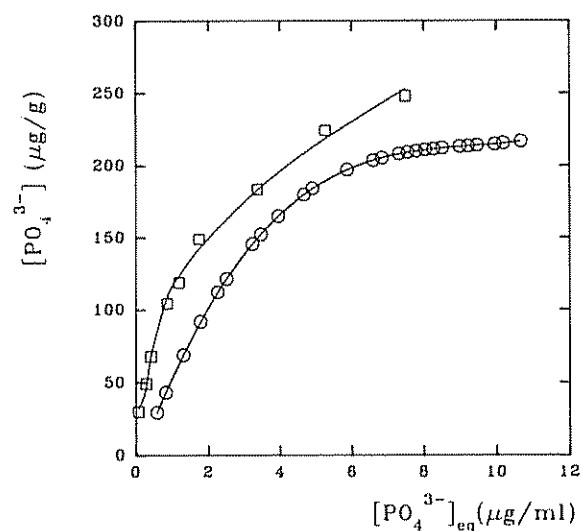


Fig. 4. Phosphate adsorption isotherms on soil LUJ. \circ : 303.2 K; \square : 313.2 K.

is a constant related to the bonding energy between the phosphate ion and the soil surface:

$$K_T = A_0 \exp \left(\frac{E_{ad}}{RT} \right) \quad (2)$$

where A_0 is a preexponential factor, E_{ad} is the adsorption energy, R is the universal gas constant and T the absolute temperature. If it is assumed that A_0 does not strongly depend on temperature, it is

possible to determine the E_{ad} from the K_T values obtained at two temperatures. In our case, the temperature difference between the adsorption isotherms was 10 K; therefore perhaps the adsorption energy did not change. The values obtained for X_m , K_T and E_{ad} are quoted in Table 2. It can be seen that the values obtained for the adsorption energy are very large, making impossible the desorption process, at least in the experimental conditions used in this work. The X_m values do not reflect the expected values from graphic representations of the adsorption isotherms (see Figures 1-4). Therefore, these results indicate that any good agreement between experimental data and the Langmuir model is only due to mathematical reasons and not to the physical reality of this simple model.

Table 2. Langmuir's parameters for adsorption isotherms.

Soil	KT1	KT2	Ead	Xm,T1	Xm,T2
LE	0.8796	0.14044	142.8	197.1	268.0
LP	1.2160	0.08816	206.9	264.4	457.6
LT	0.3346	0.22548	30.9	283.2	282.0
LUJ	0.2936	0.63150	-60.6	295.3	289.3

T1=303.2 K; T2=313.2 K; Ead in kJ/mol; Xm in mg/g

Before presenting the desorption data we need to define some variables, as follows:

P_{ad}^0 is the quantity of the phosphate ion initially adsorbed as determined by the adsorption isotherm; P_{ad}^n is the remnant adsorbed phosphate after the n -th extraction with pure water, and P_{des}^n is the phosphate-ion-recovered quantity at the n -th extraction. P_{ad}^n is calculated from:

$$P_{ad}^n = P_{ad}^{n-1} - P_{des}^n \quad (3)$$

Thus:

$$P_{ad}^1 = P_{ad}^0 - P_{des}^1 \quad (4)$$

$$P_{ad}^2 = P_{ad}^1 - P_{des}^2 \quad (5)$$

equations (4) and (5) can be combined to give:

$$P_{ad}^2 = P_{ad}^0 - P_{des}^1 - P_{des}^2 \quad (6)$$

and the generalization of this equation is straightforward:

$$P_{ad}^n = P_{ad}^0 - \sum_{i=1}^n P_{des}^i \quad (7)$$

We can easily see that the limit of expression (7), when n tends to infinity, is zero, meaning that after infinite extractions, all the initially adsorbed phosphate must be recovered.

If it is assumed that the desorption process is of first order of P_{ad}^n , and using equation (7), the final expression is:

$$\ln P_{ad}^n = C - kt \quad (8)$$

where $C = \ln P_{ad}^0$, k is the rate constant and t is the time. The units are always: mg for P_{ad}^n and day for t , unless anything else is explicitly indicated. In fact, there are a set of equations (8) for each initial phosphate concentration. In Figures 5-8, the corresponding profiles for all soils are shown. All straight lines have correlation coefficients that are greater than 0.998. These graphs demonstrate that the desorption process is a first-order one.

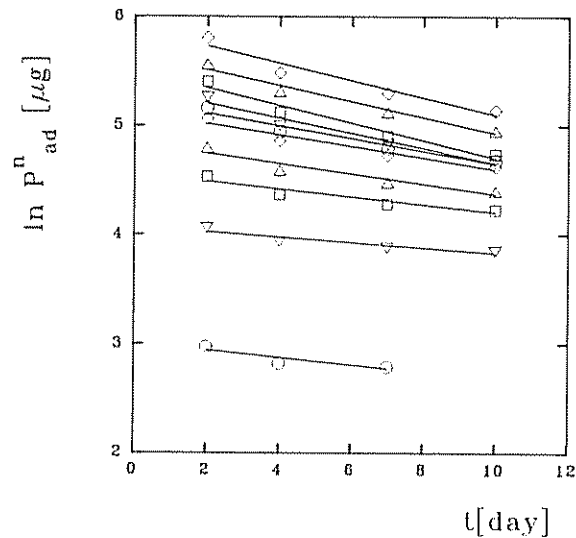


Fig. 5. Soil LE profiles calculated with Equation (8) for all initial added phosphate quantities (see text). $T = 303.2$ K.

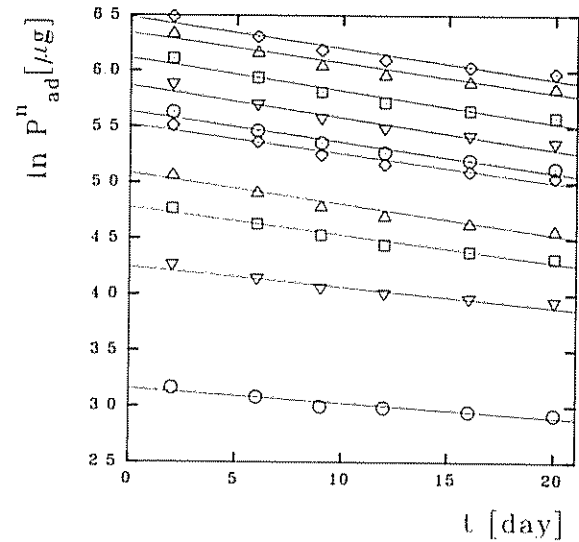


Fig. 6. Soil LP profiles calculated with Equation (8) for all initial added phosphate quantities (see text). $T = 303.2$ K.

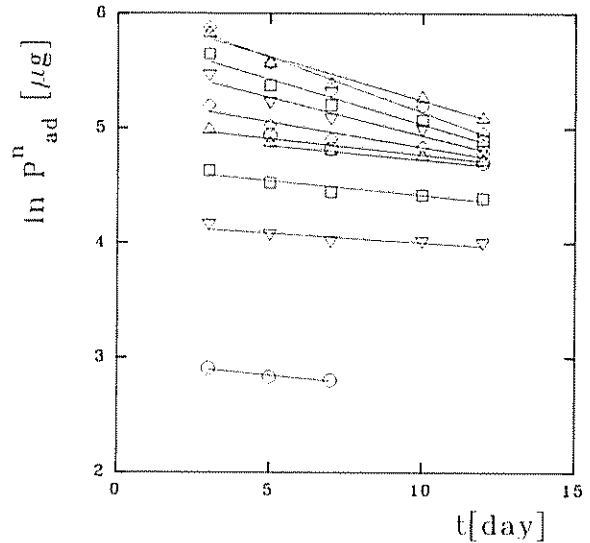


Fig. 7. Soil LT profiles calculated with Equation (8) for all initial added phosphate quantities (see text). $T = 303.2$ K.

We can now discuss the obtained values for P_{ad}^0 by extrapolation of equation (8). If the extrapolated values of P_{ad}^0 are compared to the experimental values, two straight lines are obtained for each soil sample. In Figure 9, the profile obtained for soil LUJ is presented as an example; the other soils show similar profiles. One has low phosphate quantities (< 230 mg) and the other higher concentrations (> 230 mg). Table 3 quotes the values obtained for each soil. In

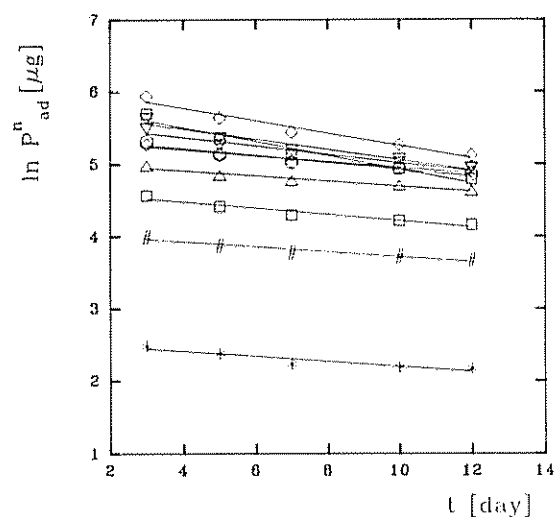


Fig. 8. Soil LUJ profiles calculated with Equation (8) for all initial added phosphate quantities (see text). $T = 303.2$ K.

Table 3, the mean values of the slopes are included to show that there are only two values, except for soil LT high phosphate quantities. In the last two columns, the values of P^0_{rec} (the total quantity of phosphate ion recovered after 96 days of successive extractions in the flask without phosphate addition) and P^0_{iso} (the total quantity of phosphate ions recovered in the reference flask employed in the adsorption experiment). In other words, P^0_{rec} is the phosphate ion released in non-equilibrium conditions (extractions at variable periods of time) and P^0_{iso} is the phosphate ion liberated by the soil in equilibrium conditions.

The intercepts of the straight lines obtained (Table 3) are in good agreement with these two quantities for

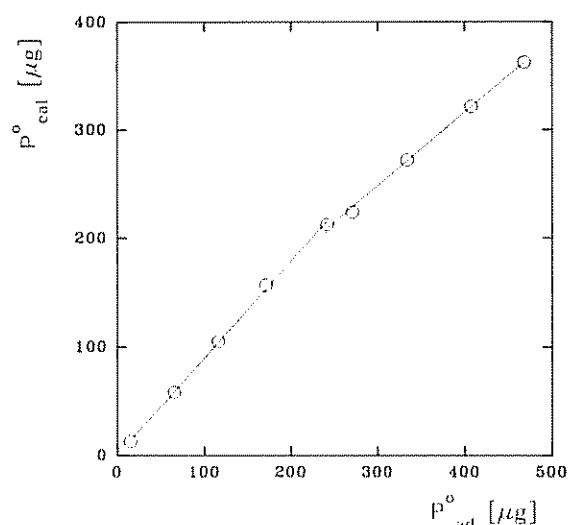


Fig. 9. P^0_{ad} extrapolated with Equation (8) as a function of the experimental values for soil LUJ. $T = 303.2$ K.

each soil sample. This behavior confirms the reasonable assumption that at low quantities of added phosphate the equilibrium is reached in shorter times than at higher concentrations of phosphate ions. In addition, it indicates that soil in equilibrium with a solution releases a certain quantity of phosphate ions, much less than the actual phosphate content of the soil but large enough to stop the liberation process due to reasons that we can not support by experimental evidence. One possible way to explain this is to assume that there are different kinds of phosphate ions bonded to the surface in such a way that, in the equilibrium experiment, only the loosely bonded phosphate is released, while in successive extractions (non-equilibrium situation) almost all phosphate is liberated.

Table 3. Parameters calculated from Equation 8.

Soil	$P^0_{ad} < 230 \mu\text{g}$		$P^0_{ad} > 230 \mu\text{g}$		P^0_{rec}	P^0_{iso}
	C	k	C	k		
LUJ	1.086	0.8885	45.942	0.67511	57.279	4.167
LT	2.495	0.8662	14.200	0.81098	15.701	2.437
LP	3.209	0.8679	50.025	0.68093	50.485	3.313
LE	2.666	0.8215	19.057	0.69945	14.840	2.341
		0.8610		0.6852		
c2		$6 \cdot 10^{-4}$		$1 \cdot 10^{-4}$ *		

where is the mean value of b and c2 is the deviation

* Excluding the value for soil LT (see the text).

Regarding to the slopes of the straight lines, it can be said that both processes discussed above are soil-independent. In the case of soil LT, the same slope is obtained for both straight lines—indicating that phosphate ions are loosely bonded to its surface.

If P_{ad} raised to the third power is represented against time for each added phosphate quantity, straight lines are obtained; this kind of representation maximizes experimental errors. The intercepts to the origin of these lines are the extrapolated phosphate quantities initially added. In an ideal situation, the extrapolated value should coincide with the experimental phosphate quantity initially adsorbed, as indicated by equation 7. If the extrapolated quantity is less than the experimental one, it means that some phosphate is retained by the soil and cannot be recovered by extraction. On the other hand, if the extrapolated quantity is greater than the experimental one, as in our case, it means that some of the recovered phosphate was released by the soil itself. This fact could be easily verified by plotting the extrapolated values as a function of the experimental quantities:

$$P_{ad,x}^{cal} = a + bP_{ad,x}^{exp} \tag{9}$$

where $P_{ad,x}^{cal}$ is the phosphate quantity adsorbed when no phosphate was previously added, the superscripts cal and exp indicate the extrapolated and experimental values respectively; in other words, $P_{ad,x}^{cal}$ is the phosphate quantity of the soil itself.

The parameters calculated with equation 9, for all soils, are quoted in Table 4. It is important to notice that the cubic root of the intercept coincides with the phosphorus content determined by the Bray-Kurtz #1

Table 4. Parameters calculated with Equation 9.

Soil	a	b	PBray-Kurtz	D%
LUJ	14.98	0.72398	13.28	13
LP	39.19	0.67375	41.0	-4
LT	12.57	0.61789	10.1	24
LE	9.04	0.55759	8.975	0.7

$c_1 = 0.64330, c_2 = 0.004$

where a and b are the cubic root of the intercept and the slope of the line respectively, D% is the relative error between a and total Bray-Kurtz phosphorus

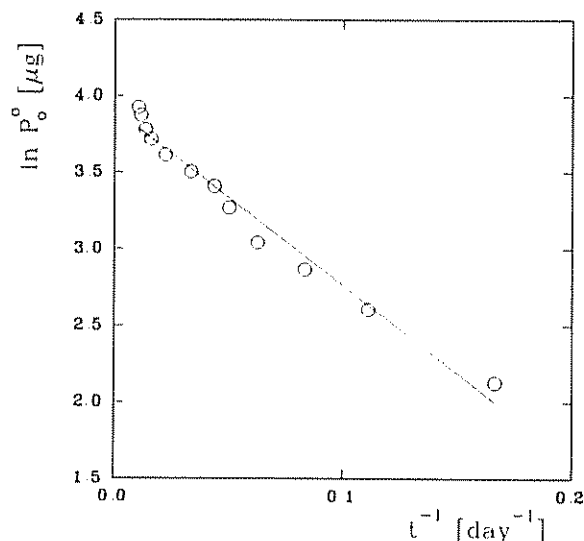


Fig. 10. Representation of Equation (10) for soil LP. T = 303.2 K.

method supporting the ideas mentioned above. The slope of the lines are very similar, indicating that the process is soil-independent.

Table 5. Parameters calculated with Equation 10.

Soil	a	b	Poext	PBray-Kurtz
LP	3.90557	-11.436	49.68	41.0
LE	2.17666	-2.954	8.82	8.975
LUJ	3.91510	-5.7765	0.151	3.28
LT	2.66630	-6.6571	4.39	10.1

During each desorption experiment, a flask containing soil with no phosphate added was used as a reference. The accumulated desorbed phosphate in the reference flask is denoted as P_0 ; if a linear dependence of the natural logarithm and the inverse of time (t) is assumed:

$$\ln P_0 = \alpha - \frac{\beta}{t} \tag{10}$$

straight lines are obtained for each soil sample. Figure 10 shows as an example the results obtained for soil LP. It must be noted that the inverse of time is taken in order to simplify the parameter interpretation; similar lines are obtained by plotting against

time. In equation 10, a_1 is the logarithm of the released phosphate quantity at infinite extraction time (P_{∞}). In Table 5, the values of a , b and Bray-Kurtz phosphorus are quoted. It can be seen that, except for soil LUJ, P_{∞} and Bray-Kurtz phosphorus are in good agreement.

CONCLUSIONS

The inadequacy of Langmuir's adsorption model to produce parameters with physical meaning has been shown with the examples presented in this and in a previous (Bottani *et al.* 1993) paper. It should be possible to test the validity of this model for soils of different characteristics to the ones studied here.

The analysis of the desorption process proved to give valuable information. This process is in principle a first-order one. The analysis of our data indicates that there are phosphate ions bonded to the soil surface with different strengths: Only the loosely bonded phosphate is liberated under equilibrium conditions. To release almost all the phosphate contained in the soil, it is necessary to apply non-equilibrium conditions (extractions with water).

From plots of remnant adsorbed phosphate raised to the third power as a function of time, it is possible to determine the phosphorus content of these soils, one in good agreement with that determined by Bray-Kurtz #1 method.

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