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Effect of High Concentrations of Initial Surface P
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EFFECT OF HIGH CONCENTRATIONS OF INITIAL SURFACE P ON THE LANGMUIR ADSORPTION ISOTHERM

By

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ABSTRACT

Effect of High Concentrations of Initial Surface P
on the Langmuir Adsorption Isotherm

By
Daniel C. O'Neill

The effect of high levels of applied P on the adsorption maxima (b) and k values as predicted by the Langmuir adsorption isotherm was examined for seven Michigan soil types. The use of P extracted by Bray P_1, NH_4F, and $Na_2B_4O_7$ as well as isotopically exchangeable P to estimate the initial level of surface adsorbed P was examined.

The b value along with the k value were affected by the soil type and initial level of freshly applied P. In one case the change in k value could not be corrected by any method used in this study.

Bray P_1 corrected b and k values for high and low P concentrations had correlations with ^{32}P corrected b and k values significant at the one percent level.

Bray P_1 extracted P correlated at the one percent level of significance with surface P estimated by ^{32}P isotopic exchange.

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INTRODUCTION

The Langmuir adsorption isotherm was originally proposed to describe adsorption of gases on solid surfaces. More recently it has been expanded to describe adsorption of ions from solutions onto solid surfaces. In the study of adsorption of ions by soils numerous investigators have made use of this isotherm to explain many different soil properties. A few which pertain to the study of P are: prediction of P movement in soils which have been heavily fertilized (Susuki, 1963), evaluation of P requirement of soils (Fox, 1970), mathematical model for P movement in soils (Fox, 1970), mathematical model for P movement in soils (Shah et al., 1975) and mechanism of P sorption (Muljadi, 1966).

In the study of P adsorption by soils, Olsen and Watanake (1957) used the Langmuir equation in the following form:

$$\frac{C}{x/m} = \frac{C}{b} + \frac{1}{kb} \qquad (1)$$

Where: x/m = amount of P adsorbed per weight of soil (mg P/100 g soil)

b = the adsorption maximum (mg P/100 g soil)

c = the equilibrium P concentration (moles/liter)

k = a constant related to the bonding energy of the adsorbent for the adsorbate (liter/mole)

A plot of $\frac{C}{x/m}$ versus C should yield a straight line with a slope of 1/b and an intercept of 1/kb. Deviations from the theoretical straight line (equation 1) with its single value for maximum adsorption (b) and its single value for the constant (k) have frequently been observed for soils and soil minerals. At higher equilibrium solution concentrations (C) the observed values of $\frac{C}{x/m}$ versus C fall below the line defined by the low C values. This type of deviation can be

resolved into two intersecting straight lines suggesting that two different reactions control the adsorption of P on soils (Taylor, 1977). The two lines result in two pairs of b and k values.

In discussing the use of the Langmuir adsorption isotherm to study P adsorption by soils, Olsen and Watanabe (1957) pointed out that the intercepts of a plot of $\frac{C}{x/m}$ versus C increased as the initial level of surface P increased. Therefore, soil containing appreciable surface P initially gave erroneous k values. A correction was made by adding the amount of initial surface P (determined by a separate analysis) to the x/m value of the P adsorbed from the equilibrium solution. This assumed that the initial surface P was bonded by the same mechanism as P adsorbed from an added solution of KH_2PO_4 (Olsen and Watanabe, 1957).

The method generally recognized as a measure of initial surface P is isotopic dilution with a solution containing a known concentration of ^{32}P. This principle was apparently first applied to soils by McAuliffe et al. (1948). If surface ^{31}P is the original exchanging ion on the soil surface to which ^{32}P has been added in a water solution, the exchange with chemically identical ions can be described at equilibrium of the equation:

$$\frac{\text{surface } ^{32}P}{\text{solution } ^{32}P} = \frac{\text{surface } ^{31}P}{\text{solution } ^{31}P} \qquad (2)$$

Since solution ^{31}P can be experimentally determined as the ratio of activities between solid and solution, the surface ^{31}P can be calculated.

Isotopic dilution was used by Olsen and Watanabe (1957) to correct for initial surface P. Although this appears to be an accurate method of estimating surface P, it is expensive and time consuming. A procedure based upon a simple extraction would eliminate the need for radioactive precautions and special instrumentation and would facilitate the use of the Langmuir adsorption isotherm. The extractant which would be a practical alternative to ^{32}P should be easy to use and should yield an extract from which P can be easily measured. The P value obtained should be the same as the surface P estimated by ^{32}P or give a highly correlated value which could be related with linear regression to ^{32}P. A preliminary study (appendix) suggested that three extract solutions would have the greatest potential. These are 0.03 N NH_4F-0.025N HCl (Bray P_1)(Doll, 1972), neutral NH_4F(Bray, 1941) and $Na_2B_4O_7$.

Materials and Methods

Soil Samples

Seven soil types common to Michigan were selected for this study (Table 1). Soil samples were collected from the south-end of Michigan State University campus as part of a soil characterization for the Institute of Water Research. Each sample was air dried, ground to pass a 10 mesh screen and stored in a cardboard container. Because these soils were low in surface P two hundred grams were separated from each soil and ammended with 10 mg P as $Ca(H_4PO_4)_2$ with enough water to bring each soil to field capacity. This quantity of P was 50 mg P/kg soil and ranged from 25 to 78 percent of the b value for individual soils with an average of 47 percent. This set of soils was used to determine the

Table 1. Description and properties of soils used in this study.

Series	Class	Drainage*	Depth	Texture**	Horizon
			cm		
Spinks	Hapludalf	W	5 - 30	l f s	A
			30 - 119	l f s	B^p_{21}
Riddles	Typic	W	5 - 30	f s l	A
	Hapludalf		48 - 127	s c l	B^p
Hillsdale	Typic	MW	5 - 35	f s l	A
	Hapludalf		35 - 91	c s l	B^p
Miami	Typic	WP	0 - 25	l	A
	Hapludalf		25 - 88	c l	B^p
Brookston	Argiaquoll	PD	5 - 27	l	A
			35 - 71	c l	B^p_{22t}
Celina	Typic	MW-SPD	0 - 33	l	A
	Hapludalf		58 - 101	c l	B^p
Conover	Ochraqyalf	SPD	0 - 25	l	A
			35 - 104	c l	B^p

* W = Well
MW = Moderately Well
PD = Poorly Drained
SPD = Somewhat Poorly

** l f s = Loamy fine sand
c l = Clay loam

effect of large quantities of initial P on the Langmuir adsorption isotherm. The soils were covered with polyethelene to prevent evaporation and yet allow passage of O_2, incubated for one week at room temperature, then air dried and ground to pass a 10 mesh screen.

Soil Analysis

Initial P was extracted with 0.05 N NH_4F (2 g soil in 50 ml), 0.05N $Na_2B_4O_7$ (2 g soil in 50 ml) and 0.03 N NH_4F - 0.025 N HCl (5 g soil in 40 ml) by shaking on a rotary shaker at 200 r.p.m. for five minutes. Clear extract was obtained by use of Darco charcoal and filtration through Whatman No. 42 filter paper.

Isotopic Dilution

One gram of soil was equilibrated with 99 ml of H_2 at 24° C by shaking on a rotary shaker at 200 r.p.m. for one hour. To this was added 1 ml of a solution containing a known amount of ^{32}P. Samples were then shaken for 24 hrs., centrifuged and an aliquot was taken for analysis of ^{32}P and ^{31}P in solution. Radioactive ^{32}P was counted by Cerenkov radiation by the method by White and Ellis (1968).

Langmuir Adsorption Isotherm

Phosphorus adsorption isotherms were measured on duplicate soil samples by equilibrating 5 g. of soil (ground to pass a 18 mesh screen) for 24 hrs. at 24° C with 50 ml of 0, 2, 4, 6, 8, 10, 12, 15, 20, 30 ppm P in 0.01 M $CaCl_2$. At the end of 24 hrs. the samples were centrifuged and an aliquot taken for analysis. The quantity of P in solution was subtracted from the amount added and the difference was regarded as the quantity adsorbed.

P Analysis

Phosphorus in all extracts and equilibrium solutions was analyzed by ammonium molybdate ascorbic acid method (Murphy and Riley, 1962).

Results and Discussion

The b and k values for low P soils were affected relatively little by any method used for the correction of initial surface P (Table 2). There was a trend for larger b and k values when corrected by either ^{32}P or Bray P_1 estimate. The need for a correction became evident when the k values for high P concentration were compared with the k values for low P concentration increased. In only two of these deviations did Bray P_1 or ^{32}P fail to correct the k value back to the initial k values, (low P) where no correction was made. The k vlaues of the Spinks soil A horizon decreased by a factor of eight and no method used was able to correct back to the k value (Low P). The k value for the A horizon of the Celina soil also decreased by a factor of eight. Both Bray P_1 and ^{32}P estimate of surface P partially corrected this.

Isotopic dilution with ^{32}P was considered the standard method of estimating surface P and all resultant values were referenced to this. Linear correlations were calculated for b values and for k values between those corrected by ^{32}P and those corrected by the extractants (Table 3). Bray P_1 corrected b values had the highest correlation with ^{32}P corrected b values both for all soils and high level P soils. Sodium borate corrected b values correlated nearly as well. For correcting k values Bray P_1 correlated better with the k values corrected by ^{32}P than the other extractant.

Fig. 1 shows the relationship between Bray P_1 extracted P and surface adsorbed P measured by ^{32}P. The r^2 was significant at the one percent level but did not account for 25 percent of the variation. The slope indicated almost a one to one agreement between Bray P_1 and ^{32}P

Table 2. Influence of P level and extractant on correction of b and k values.

Soil Series	Depth	Extractant	b		k	
			Low P	High P	Low P	High P
	cm		mg/100 g		1/m x 10^{-5}	
Spinks	5 - 30	None	14.2 ± .85	11.4 ± .68	5.1 ±1.3	.63 ± .16
		$Na_2B_4O_7$	14.0 ± .84	12.5 ± .75	5.8 ±1.5	.97 ± .24
		Bray P_1	14.2 ± .85	14.6 ± .88	8.6 ±2.2	1.5 ± .38
		NH_4F	14.0 ± .84	13.0 ± .78	5.7 ±1.3	1.1 ± .28
		^{32}P	14.2 ± .85	13.2 ± .79	9.1 ±2.3	1.1 ± .28
Spinks	30 - 120	None	12.1 ± .73	9.5 ± .57	6.3 ±1.6	1.1 ± .28
		$Na_2B_4O_7$	12.1 ± .73	12.2 ± .73	6.5 ±1.6	2.6 ± .65
		Bray P_1	13.2 ± .79	19.1 ±1.15	8.7 ±2.2	8.7 ±2.2
		NH_4F	12.3 ± .74	13.8 ± .83	7.0 ±1.8	3.7 ± .93
		^{32}P	12.7 ± .76	14.5 ± .87	8.6 ±2.2	4.0 ±1.0
Riddles	5 - 30	None	8.9 ± .53	6.6 ± .40	.19 ± .05	.25 ± .06
		$Na_2B_4O_7$	8.9 ± .53	7.9 ± .47	.20 ± .05	.49 ± .12
		Bray P_1	9.0 ± .54	12.5 ± .75	.24 ± .06	1.1 ± .28
		NH_4F	8.9 ± .53	8.3 ± .50	.20 ± .05	.55 ± .14
		^{32}P	9.8 ± .59	10.3 ± .62	.60 ± .10	.82 ± .21
Riddles	10 -130	None	16.2 ± .97	21.6 ±1.30	.60 ± .15	.37 ± .09
		$Na_2B_4O_7$	16.3 ± .98	21.5 ±1.29	.61 ± .15	.50 ± .13
		Bray P_1	16.5 ± .99	23.2 ±1.39	.67 ± .17	.79 ± .20
		NH_4F	16.3 ± .98	21.5 ±1.29	.61 ± .15	.44 ± .11
		^{32}P	16.8 ±1.01	23.6 ±1.42	.75 ± .19	.79 ± .20

Table 2. Influence of P level and extractant on correction of b and k values (con't).

Soil Series	Depth	Extractant	b		k	
			Low P	High P	Low P	High P
	cm		mg/100 g		$1/m \times 10^{-5}$	
Miami	0 - 25	None	6.4 ± .38	5.9 ± .35	.32 ± .02	.37 ± .09
		$Na_2B_4O_7$	6.5 ± .39	5.9 ± .35	.32 ± .08	.58 ± .15
		Bray P_1	6.9 ± .41	6.4 ± .38	.44 ± .11	1.3 ± .30
		NH_4F	6.5 ± .39	5.8 ± .35	.32 ± .08	.77 ± .19
		^{32}P	7.1 ± .43	7.8 ± .47	.43 ± .11	2.2 ± .55
Miami	25 - 90	None	7.2 ± .43	8.6 ± .52	3.6 ± .90	2.0 ± .50
		$Na_2B_4O_7$	7.4 ± .44	10.7 ± .62	3.5 ± .88	2.9 ± .80
		Bray P_1	7.2 ± .43	14.1 ± .85	3.5 ± .98	3.2 ± .80
		NH_4F	7.2 ± .43	14.1 ± .85	3.5 ± .88	5.1 ± .98
		^{32}P	7.7 ± .46	12.2 ± .73	4.3 ±1.1	3.9 ± .98
Hillsdale	5 - 30	None	8.8 ± .53	7.3 ± .44	.27 ± .07	.50 ± .13
		$Na_2B_4O_7$	8.8 ± .53	8.9 ± .53	.28 ± .07	.51 ± .13
		Bray P_1	9.5 ± .57	10.2 ± .61	.35 ± .09	.78 ± .20
		NH_4F	8.8 ± .53	9.0 ± .54	.31 ± .08	.55 ± .14
		^{32}P	9.7 ± .58	9.4 ± .56	.36 ± .09	.62 ± .16
Hillsdale	35 - 90	None	14.8 ± .89	8.7 ± .52	1.3 ± .33	.89 ± .22
		$Na_2B_4O_7$	14.9 ± .89	9.3 ± .56	1.3 ± .33	1.33 ± .33
		Bray P_1	15.2 ± .91	10.7 ± .64	1.4 ± .35	2.03 ± .51
		NH_4F	15.6 ± .94	9.4 ± .56	1.5 ± .38	1.42 ± .36
		^{32}P	16.2 ± .97	9.8 ± .59	1.6 ± .40	1.65 ± .41

Table 2. Influence of P level and extractant on correction of b and k values (con't).

Soil Series	Depth	Extractant	b		k	
			Low P	High P	Low P	High P
	cm		mg/100 g		1/m x 10^{-5}	
Brookston	5 - 30	None	8.3 ± .50	7.3 ± .44	1.0 ± .25	.12 ± .03
		$Na_2B_4O_7$	11.5 ± .69	7.6 ± .46	2.2 ± .55	.24 ± .06
		Bray P_1	10.7 ± .65	11.3 ± .68	1.9 ± .48	.65 ± .16
		NH_4F	8.4 ± .50	7.5 ± .45	1.1 ± .28	.19 ± .05
		^{32}P	11.4 ± .68	11.1 ± .67	2.1 ± .53	.62 ± .16
Brookston	35 - 70	None	14.5 ± .87	16.3 ± .98	.46 ± .12	.15 ± .04
		$Na_2B_4O_7$	14.5 ± .87	16.3 ± .98	.51 ± .13	.22 ± .06
		Bray P_1	16.0 ± .96	19.3 ±1.2	.82 ± .21	.42 ± .11
		NH_4F	14.5 ± .87	16.1 ± .97	.49 ± .12	.18 ± .05
		^{32}P	14.8 ± .89	18.2 ±1.1	.62 ± .16	.36 ± .09
Celina	0 - 30	None	7.5 ± .45	9.6 ± .58	1.3 ± .33	.15 ± .04
		$Na_2B_4O_7$	7.8 ± .47	9.6 ± .58	1.5 ± .38	.17 ± .04
		Bray P_1	9.3 ± .56	13.7 ± .82	2.4 ± .60	.62 ± .16
		NH_4F	7.7 ± .46	10.2 ± .61	1.5 ± .38	.31 ± .08
		^{32}P	10.5 ± .63	13.3 ± .80	3.0 ± .75	.59 ± .15
Celina	60 - 100	None	14.1 ± .85	12.3 ± .74	1.6 ± .40	1.2 ± .30
		$Na_2B_4O_7$	14.9 ± .89	13.3 ± .80	1.8 ± .45	1.5 ± .38
		Bray P_1	15.8 ± .95	14.9 ± .89	2.1 ± .53	2.0 ± .50
		NH_4F	14.3 ± .86	12.9 ± .77	1.7 ± .43	1.3 ± .33
		^{32}P	15.8 ± .95	15.1 ± .91	2.1 ± .53	2.0 ± .50

Table 2. Influence of P level and extractant on correction of b and k values (con't).

Soil Series	Depth	Extractant	b		k	
			Low P	High P	Low P	High P
	cm		mg/100 g		1/m x 10^{-5}	
Conover	5 - 25	None	9.0 ± .54	6.2 ± .37	.61 ± .15	.15 ± .04
		$Na_2B_4O_7$	9.5 ± .57	8.0 ± .48	.71 ± .08	.34 ± .09
		Bray P_1	12.5 ± .75	12.2 ± .73	1.1 ± .28	.93 ± .23
		NH_4F	9.4 ± .56	8.5 ± .51	.69 ± .17	.43 ± .11
		^{32}P	12.3 ± .74	11.2 ± .67	1.1 ± .28	.81 ± .20
Conover	35 - 100	None	19.9 ±1.2	11.1 ± .67	1.2 ± .30	1.4 ± .35
		$Na_2B_4O_7$	20.1 ±1.2	11.8 ± .71	1.3 ± .33	1.8 ± .45
		Bray P_1	21.2 ±1.3	13.9 ± .83	1.5 ± .38	2.8 ± .70
		NH_4F	20.0 ±1.2	11.7 ± .70	1.2 ± .30	1.8 ± .70
		^{32}P	21.8 ±1.2	13.9 ± .83	1.6 ± .40	2.8 ± .70

Table 3. Correlation between ^{32}P corrected b and k values and extractant corrected b and k values.

Extractant	b		k	
	All Soils	High P soils	All Soils	High P Soils
	r^2			
Bray P	0.95	0.94	0.98	0.91
NH_4F	0.91	0.86	0.90	0.84
$Ha_2H_4O_7$	0.93	0.94	0.95	0.72
None	0.89	0.92	0.75	0.73

Any r^2 greater than 0.5 is significant at the 1% level.

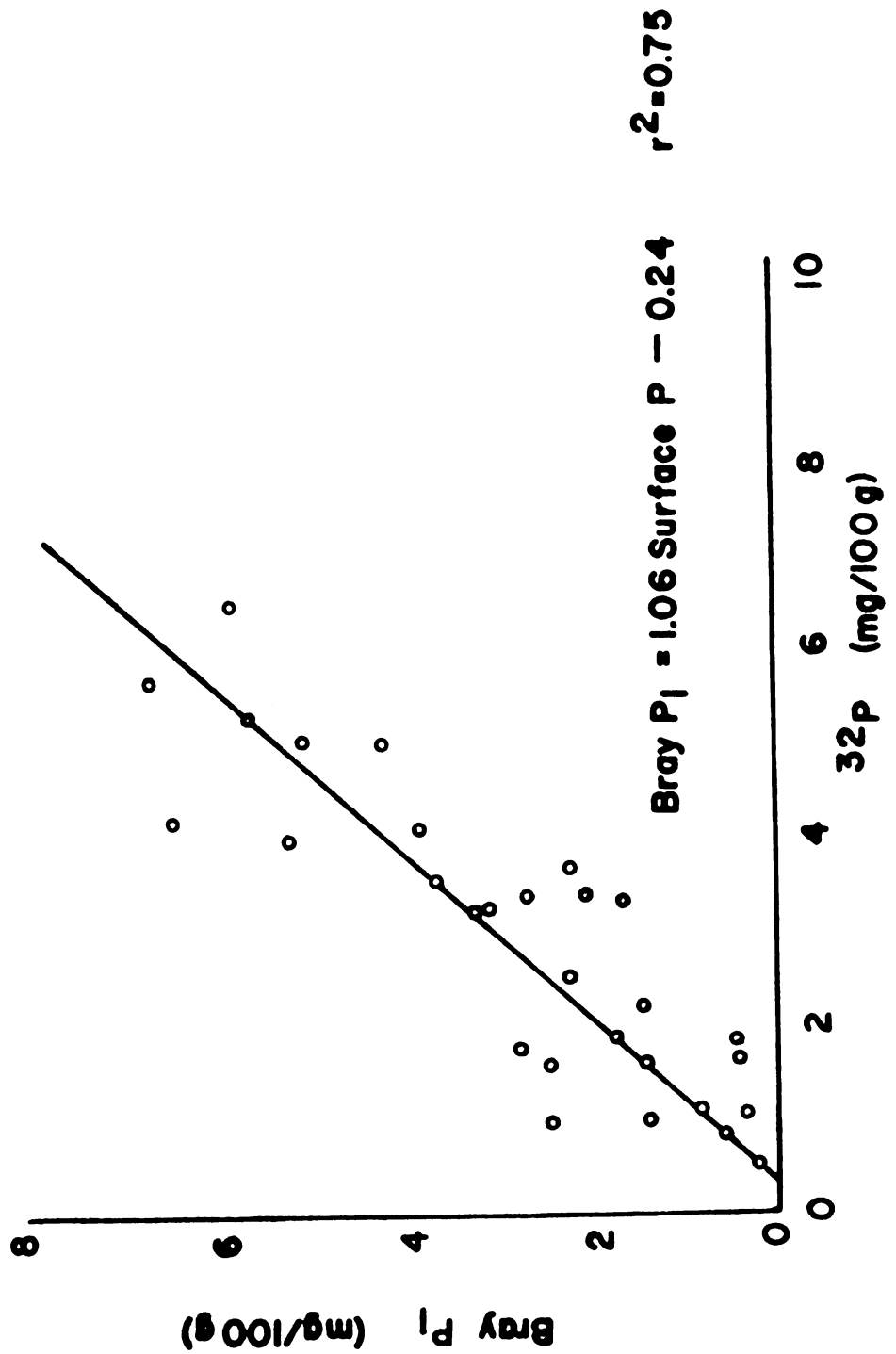

Figure 1. Correlation Between Bray P_1 and ^{32}P Surface P.

although ^{32}P estimated surface P is slightly greater than Bray P_1 by an amount of 0.24. This relationship between surface P and Bray P_1 is similar to results obtained by Doll (1972)[1]. No meaningful relationship between NH_4F extracted P or $Na_2B_4O_7$ extracted P and surface adsorbed P estimated by ^{32}P was obtained.

A four-way analysis of variance of levels of initial P, soils type, soil depth and extracts was conducted for the parameter b. It revealed that there was a significant interaction (.05%) for the b values with P level, soil series, and depth. The ability of a soil to adsorb P has been shown to be dependent on soil texture and horizon (Ellis, 1973). Sandy soils adsorb less P than heavy textured soils and the A horizon adsorbs less P than the B horizon in soils. In this study the type of soil was shown to have an interaction with depth significant at the .05% level. But the soil also had an interaction with the level of P which was significant at the .05% level. Changes in the b value would be expected because theoretically the slope (and therefore b) should not be affected by the initial P status of the soil.

The average of the mean b values for low and high levels of P gives the impression that the b values decrease as the initial level of surface P increases (Table 4). But since the analysis of variance showed a three way significant interaction this may not be a valid conclusion.

Influence of initial P level and extractant on correction of b values showed that eight of the 14 soils decreased in b value for an

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[1]Doll, E. C. 1972. Unpublished Report.

Table 4. Change in b value by correction for estimated surface adsorbed P.

P Level	Extractant Used to Estimate Surface P					
	None	$Na_2B_4O_7$	Bray P_1	NH_4F	^{32}P	Average
			b (mg/100 g)*			
Low	11.5	11.9	12.7	11.7	12.9	12.1
High	10.2	11.1	13.8	11.6	13.1	11.9

* Each value reported is a mean of 14 soil samples.

increase in initial surface P when no correction was made and three remained the same. For the Bray P_1 corrected b values six were unchanged and six increased. For NH_4F corrected b values none were the same and three increased. Sodium borate correction resulted in six unchanged and five decreased.

The decrease in predicted maxima with increasing P in the uncorrected isotherms and the increase in b values with increasing P in the Bray P_1 corrected isotherms can be accounted for if something has occurred in the P amended soils which altered adsorption sites or rendered them unavailable. The maxima predicted for uncorrected soils would then show a decrease. Precipitation of $AlPO_4$ (without creation of new sites) or crystallization (eg. $FePO_4$) could account for this. Bray P_1 extraction could, however, measure either of these as adsorption sites when the correction is made.

The large number of NH_4F and $Na_2B_4O_7$ corrected b values which were unchanged is evidence that $AlPO_4$ compounds may be involved, because these two extracts remove P from Al fractions.

Summary and Conclusions

The purpose of this study was to examine several extraction techniques which could be used in place of ^{32}P when correcting the Langmuir adsorption isotherm for initial surface P. Based upon regression analysis and analysis of variance, Bray P_1 can readily be used in place of ^{32}P. The use of the isotherm would be greatly facilitated, since this extraction is routinely carried out on soils in the humid region.

Ammonium fluoride appeared to be quite capable of correcting the adsorption isotherm, but did not correlate with ^{32}P correction as well as Bray P_1, nor did it show any type of agreement with ^{32}P exchangeable P.

Analysis of variance shows that correction of the isotherm is dependent upon the initial concentration of surface P. The data obtained indicates that the correction was necessary as the concentration of initial P increased but when soils with low initial P were corrected by ^{32}P or Bray P_1 no change in the isotherm values occurs.

Two important points which should be examined in the future are the deviation in k values which could not be accounted for by any method used in this study for correcting initial P and the fact that the maxima did decrease as the initial surface P increased.

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APPENDIX

APPENDIX

A number of anions which have been reported in the literature to be capable of replacing P from soils were examined to select the few that might be most likely to correlate with surface P as determined by ^{32}P isotopic dilution with ^{32}P. A preliminary experiment was conducted on four soils considered to be low in P and two known to be high in adsorbed P. The results are given in Table 1A. Both KSCN and NH_4OAc failed to extract P from the low P soils and removed a much smaller portion of P from the two high P soils (Wayland and Middleville). The other three extracts removed large quantities of P from the two high P soils and varying small quantities form the low P soils. Bray P_1 removed the largest quantities of P in all cases. From these data it was decided to use Bray P_1, NH_4F and $Na_2B_4O_7$ for the thesis study. Both KSCN and NH_4OAc were eliminated because of their inability to extract P from soils which contained greater than 10 ppm P as Bray P_1 extractable.

Table 1A. Soil P extracted using various extracting solutions.

Soil Type or Location	Depth	Bray P_1	NH_4F	$Na_2B_4O_7$	KSCN	NH_4OAc
	cm	ppm P				
Spinks	5 - 30	14.87	2.81	2.98	0.0	0.0
	30 - 120	14.10	3.00	1.00	0.0	0.0
Hillsdale	5 - 30	17.78	1.61	1.13	0.0	0.0
	35 - 90	4.35	0.93	1.81	0.0	0.0
Riddles	5 - 30	5.23	1.00	1.10	0.0	0.0
	50 - 130	3.61	0.13	1.13	0.0	0.0
Miami	0 - 25	6.25	0.39	0.35	0.0	0.0
	25 - 90	4.81	0.20	0.20	0.0	0.0
Wayland	0 - 15	68.77	30.00	25.00	13.44	10.00
Middleville	0 - 15	117.95	71.90	48.62	16.00	18.13