PHOSPHORUS ADSORPTION AND MOVEMENT IN SOILS

Dissertation for the Degree of Ph. D.

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ROBERT WALTER TAYLOR

1977

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ABSTRACT

PHOSPHORUS ADSORPTION AND MOVEMENT IN SOILS

By

Robert Walter Taylor

The movement of phosphorus (P) through heavily fertilized agri-
cultural soil profiles into groundwater is potentially an important
source of its enrichment in rivers and lakes. Therefore, it is
desirable to understand the mechanism by which it is adsorbed and
moved through soils.

The Langmuir adsorption isotherm has been widely used to relate
soil solution P to surface adsorbed P. However, deviations from the
straight line predicted by the linear form of the equation have been
reported for both soil and homogeneous soil minerals. Elucidation
of the mechanism of P adsorption may explain the deviations and indicate
whether the Langmuir equation accurately characterizes P adsorption
by soils.

Langmuir plots of P adsorption isotherms of four soils were
shown to fit two intersecting lines. The adsorption data were also
found to fit the BET equation. The monolayer capacities computed from
the BET equation corresponded closely with the adsorption maxima com-
puted from initial slopes of the Langmuir plots.

Studies of P adsorption on energetically homogeneous sites of the
anion exchange resins Dowex 1-X8 and Dowex 2-X4 (Cl-forms) at 25 C

gave results similar to those obtained with soils. Measurements of Cl^- released during adsorption indicated that initially 2 mMole of Cl^- were released per mMole of P adsorbed, and this value decreased at higher equilibrium P concentrations eventually approaching 1 mMole of Cl^-. Measurements of the pH of equilibrium P solutions suggested that there was deprotonation of $H_2PO_4^-$ during the initial stages of adsorption. Similar results were obtained when Dowex 1-X8 was saturated with IO_3^- and P adsorption on the resin studied.

The differential isoteric heat of adsorption, $\overline{\Delta H}$, of P adsorption on Dowex 1-X8 was computed between 11 C and 25 C. $\overline{\Delta H}$ decreased sharply over the first region of the isotherm and became almost constant over the second.

It was concluded that P was bonded by two points of attachment after deprotonation of $H_2PO_4^-$ followed by one point of attachment during adsorption on the resin surface. This resulted in the deviation from linearity predicted by the Langmuir equation. This hypothesis for the mechanism of P adsorption is presented to explain the deviation observed on soil and homogeneous soil mineral surfaces.

The vertical movement of P was studied by sampling agricultural soils at 15 cm intervals to a depth of 152 cm. Bray Pl extractable P measurements were made on all samples and Langmuir adsorption maxima determined from isotherms of the 0-15 cm samples. Significant downward movement of P was not discernible on loam soils. Sandy loam soils generally showed appreciable downward movement of P. Movement was not solely related to Bray Pl levels of surface soils. To determine if P movement was related to the fraction of adsorbed P at 1 ppm P in solution, ratios of Bray Pl extractable P to adsorbed P were calculated. Little relationship was found between this ratio and movement of P in soil profiles.

PHOSPHORUS ADSORPTION AND MOVEMENT IN SOILS

By

Robert Walter Taylor

A DISSERTATION

Submitted to
Michigan State University
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DOCTOR OF PHILOSOPHY

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Department of Crop and Soil Sciences

1977

DEDICATION

to my parents, wife, and son

ACKNOWLEDGEMENTS

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INTRODUCTION

The liberal application of phosphate fertilizers is the most extensively used procedure for improving P fertility of soils. Since the efficiency of P fertilizers is low, it usually requires relatively large applications to produce maximum yields. Such applications are generally profitable and are therefore adopted by some Michigan farmers. But these large applications over many years may result in gradual movement of P down through the soil profiles and into the groundwater. Once in the groundwater, P may enter streams, rivers and lakes resulting in pollution of these natural waters.

Many of the rivers and lakes in Michigan are polluted by high levels of P from detergents in domestic and industrial wastewaters. However, since the source of these additions is known, their input into natural waters can be controlled. What is not generally recognized is the input from the groundwater resulting from heavy application of P fertilizers to agricultural soils. Because of this, there is a need to identify at what levels of available P and on which agricultural soils P movement into groundwater can be expected in Michigan.

In addition, soils are increasingly being considered for treatment and renovation of agricultural, domestic and industrial wastewaters and materials. It is essential that we identify soils which would best serve this purpose for a satisfactory length of time.

If a procedure is to be developed to determine when appreciable downward movement of P may occur, the establishment of a level, or

1

levels, of extractable soil P (measured in Michigan by the Bray P1 extraction) above which downward movement would be significant seems feasible. Phosphorus must be in solution to move, so some method must be devised to relate Bray P1 extractable P to concentrations of P in the soil solution.

A number of Michigan soils showed a high linear correlation between Bray P1 extractable P and surface adsorbed P (Susuki et al., 1963). This correlation appeared only above 20 ppm Bray P1 extractable P. However, values below 20 ppm are not in the range where P movement would be expected. This suggests that Bray P1 extractable P could be used as a good measure of surface adsorbed P.

The linear form of the Langmuir adsorption isotherm has been widely used to study P adsorption by soils. There are certain assumptions that must be made when applying this equation to P adsorption by soils, and the equilibrium concentration of P determined experimentally is probably not precisely the same as the concentration in the soil solution at field capacity. A rigorous discussion of the applicability of the Langmuir isotherm to studies of soil phosphorus is given by Fried and Broeshart (1967). Deviations from the straight line predicted by the linear form of the Langmuir equation have been reported for both soil and homogeneous soil minerals. These deviations were fitted by two intersecting lines suggesting that two different reactions were controlling the soil P adsorption system--one that dominated at relatively high concentrations of P in solution and the other that dominated at much lower P concentrations. Elucidation of the mechanism of P adsorption on soil and soil mineral surfaces may explain the deviations observed and may indicate whether the Langmuir equation accurately characterizes P adsorption by soils.

The latter should be determined before constants obtained from the

Langmuir equation are used in the interpretation of P movement data.

CHAPTER I

A MECHANISM OF PHOSPHORUS ADSORPTION ON SOIL
AND ANION EXCHANGE RESIN SURFACES

Introduction

The mechanism of P adsorption on soil and homogeneous soil

mineral surfaces is not clearly defined in the literature. However,

it is generally agreed that on clay and sesquioxide mineral surfaces,

phosphate ions replace exposed OH groups and/or other adsorbed anions.

Whether the bonds between the phosphate ions and the Fe (III) and Al

(III) atoms in the colloidal surface are ionic, covalent, or coordinate

covalent is not agreed upon.

Stout (24) and other investigators (5,12), working with kaolinite,

soils, and hydrated sesquioxides, respectively, suggested that phos-

phate adsorption represents a physicochemical anion exchange equilibrium

whereby phosphate ions replace exposed OH ions from the colloidal

materials. Dickman and Bray (6) presented clear evidence that the

exposed OH groups of kaolinite are replacable. Lutz et al. (17),

Muljadi et al. (18), and Kafkafi et al. (11) also suggested that P is

adsorbed by exchange of edge OH groups in kaolinite and hydrated

sesquioxide minerals. Kuo and Lotse (13) disagreed with this and

suggested that a coordinate covalent bond is formed between Al of the

surface and O of the phosphate ion by replacement of coordinated H_2O

or another anion. The research of Rajan and Watkinson (22) indicated

that, during P adsorption on an allophane clay, adsorbed SO_4, SiO_4,

4

H_2O and OH groups were exchanged for phosphate. Parfitt et al. (21) and Atkinson et al. (1), using infrared spectroscopic techniques, presented evidence of the formation of a binuclear surface complex of the type $Fe-O-P(O_2)-O-Fe$ in which two of the O atoms of the phosphate ion are coordinated, each to a different Fe^{+3} ion, when phosphate reacts with Fe oxides.

Although adsorption isotherms by themselves do not indicate the mechanism involved, they do illustrate the equilibrium relationship between the amounts of adsorbed and dissolved species at a given temperature. The Langmuir equation has been used to characterize the adsorption of P by soils (20) and soil minerals (4,10). Deviations from a single linear Langmuir relationship at high equilibrium P concentrations in soils (20) and soil minerals (4) as well as at low equilibrium concentrations (7,25) have been reported. Griffin and Jurinak (7) found that the deviation at low equilibrium P concentration, when P interacted with calcite, could also be represented by the BET equation which gave a single straight line.

The purpose of this research was to investigate the mechanism of P adsorption at low equilibrium concentrations.

Materials and Methods

The physical and chemical properties of the air-dried surface soils as well as the equilibrium phosphate data were obtained from Srisen (23). The necessary calculations were performed on the equilibrium data and the resulting isotherms plotted (Figures 1 and 2).

The sorption of phosphate by Dowex 1-X8 and Dowex 2-X4 was studied by shaking (on a wrist action shaker) 1 g of resin in 50 ml centrifuge tubes containing 20 ml of KH_2PO_4 solution. The Cl-resin

was washed with deionized H_2O until free of excess Cl^- and dried overnight at 60 C in an oven. The concentrations of the initial solutions ranged from 4.0 to 25.0 ppm P for the low equilibrium range and from 120 to 190 ppm P for the high. The centrifuge tubes were covered with Parafilm and shaken in a constant temperature chamber at 25 C for 3 hours, filtered, and the filtrate analyzed for P content. Phosphate was determined by the method of Murphy and Riley (19), modified for use with a Technicon Auto Analyzer II. The P sorbed was calculated from the difference between initial and final concentrations of P in solution.

Dowex 1-X8 and Dowex 2-X4 had anion exchange capacities of 3.2 and 3.1 meq per g (dry weight), respectively. Chloride released during adsorption was measured using a specific ion Cl-electrode with a double-junction reference electrode. Iodate was measured by the method of Salcedo and Shields (unpublished) as follows: 5 ml of sample is added to 15 ml of acetonitrile, 1 ml of acetic acid, 0.2 ml of a supersaturated KI solution, and the volume made up to 25 ml with deionized H_2O. The resulting yellow color is measured at 360 mμ and compared to a standard curve. Iodate saturated Dowex 1-X8 was obtained by treating the resin successively with 1 liter of 1N KIO_3, 0.1N KIO_3, 0.01N KIO_3 and finally with deionized H_2O until the wash was free of excess IO_3^- and Cl^-. The drying procedure was the same as described above.

The Langmuir (14) and BET (3) equations were used to interpret the equilibrium adsorption data. The linear form of the Langmuir equation is:

$$\frac{c}{x/m} = \frac{1}{Kb} + \frac{c}{b}$$

[1]

where c is the equilibrium P concentrations, x/m is the amount of P

adsorbed per unit mass of adsorbent, b is the P adsorption maximum,

and K is a constant related to the energy of adsorption.

The BET equation in its linear form is:

$$\frac{c}{x/m \ (c_o - c)} = \frac{1}{kX_m} + \frac{(k-1)}{kX_m} \frac{c}{c_o} \qquad [2]$$

where c is the equilibrium P concentration, c_o is the maximum concen-

tration of P that can exist in solution before precipitation can

occur, x/m is the amount of P adsorbed per unit mass of adsorbent,

k is related to the free energy of transfer of P from the bulk solu-

tion to the surface of the adsorbent and is assumed to be constant (7).

The monolayer capacity (X_m) may be calculated graphically using the

above equation.

The differential isosteric heat of adsorption, $\overline{\Delta H}$, was obtained

by collecting adsorption data at 11 C and 25 C and applying the

Clausius-Clapeyron equation to the system where the surface coverage,

Θ, is maintained constant (7).

$$Log \ [\frac{c_2}{c_1}]_\Theta = \frac{\overline{\Delta H}}{2.303 \ R} \ [\frac{1}{T_1} - \frac{1}{T_2}] \qquad [3]$$

where c_1 and c_2 are the equilibrium concentrations at temperatures T_1

and T_2, respectively, and R is the molar gas constant.

Results and Discussion

Some of the physical and chemical properties of the soils used

in this study are presented in Table 1. The adsorption isotherms of

two of the four soils used are shown in Figure 1. The data represent

averages of triplicates and were shown to fit a two slope Langmuir

plot. Some workers (4,20) obtained a single linear Langmuir

Table 1. Physical and chemical properties of soils used[*]

Soil type	Taxonomic placement	pH	Organic matter (%)	Bray Pl (ppm)
Hillsdale sandy loam	Typic hapludalf coarse-loamy	5.82	1.66	57.9
Locke sandy loam	Aquallic hapludalf coarse-loamy	6.00	2.72	41.7
Sims clay loam	Mollic haplaquept fine-mixed	6.23	6.77	39.5
Hoytville clay loam	Mollic ochraqualf fine-illitic	6.50	3.16	7.5

[*]Data taken from Srisen (23).
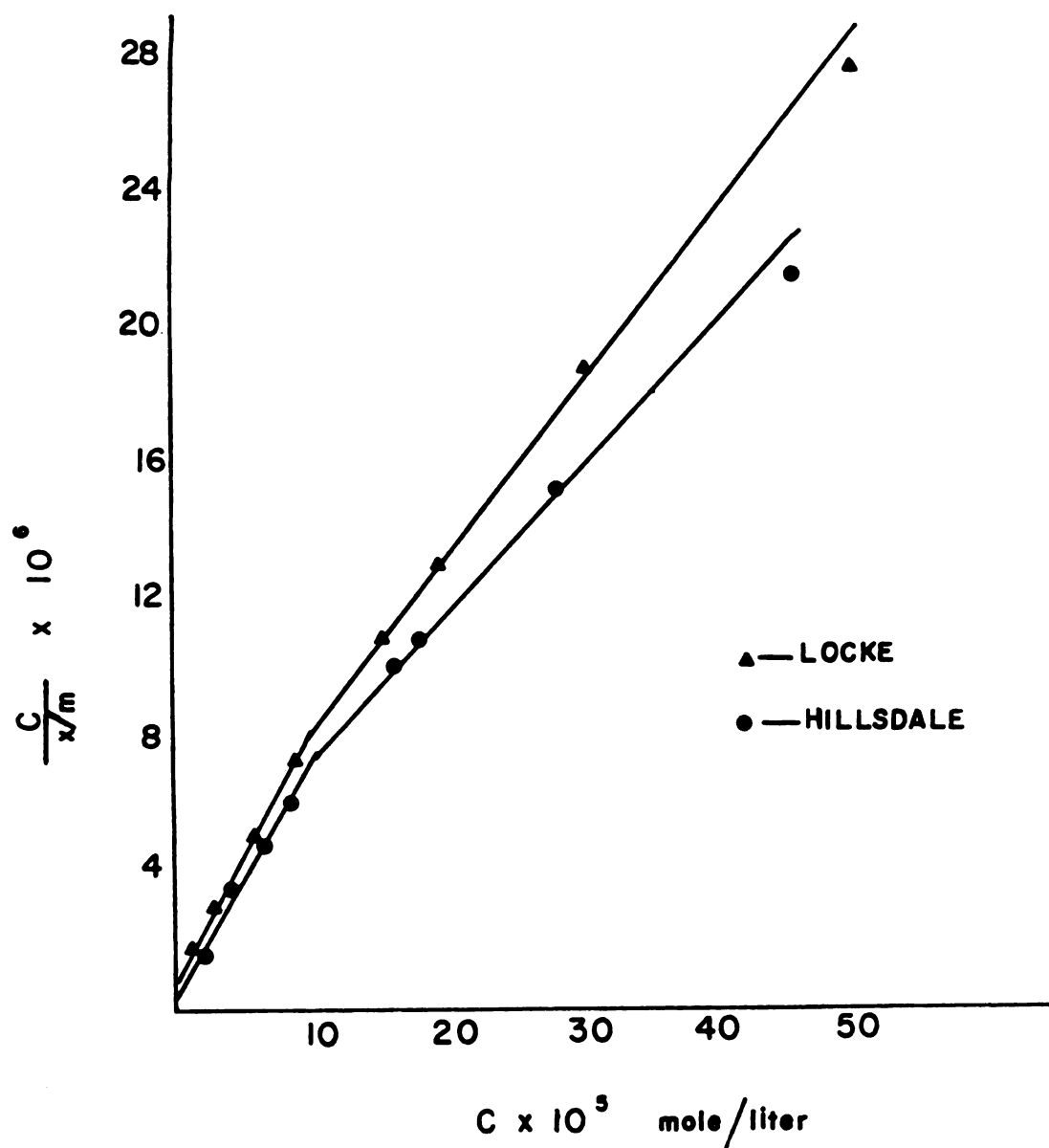
Figure 1. Langmuir isotherm for P adsorption on Locke sandy loam and Hillsdale sandy loam. (data from Srisen, 23)

relationship over the same equilibrium P concentration range (up to 14 µg/ml). Syers et al. (25), however, obtained a two slope Langmuir plot for three soils over this equilibrium P concentration range. They interpreted this as an indication of two populations of sites on the soil surface which have a widely differing affinity for P. Gunary (8) reported that P adsorption data for 24 soils fitted curvilinear lines. This was interpreted to signify that the soil will adsorb P with decreasing energies of binding. It should be noted that some two-slope Langmuir plots can be fitted to curvilinear lines and vice versa.

The adsorption data of the four soils used in this study were also found to be described by the BET equation (curves for two soils are illustrated in Figure 2). The c_o term was computed from the pH of the soils and the pK of 6.66 for $CaHPO_4$ assuming a pCa of 2.5 (15) and by the use of the Debye-Huckel equation for estimating the activity of the individual ion species in an ionic strength of 0.01M $CaCl_2$.

The data in Table 2 show that the monolayer capacities, X_m, computed by the BET equation, agree closely with the adsorption maxima, b_1, obtained from the initial slopes of the Langmuir isotherms. Griffin and Jurinak (7) reported similar results. Although the BET equation is linear for the entire region, this is not a sufficient criterion to conclude that P adsorption on soil and soil mineral sur-faces is a multilayer phenomenon. But the linear fit does suggest that P is being adsorbed with at least two different energies of binding making no commitment as to the actual location of these sites with respect to the surface.
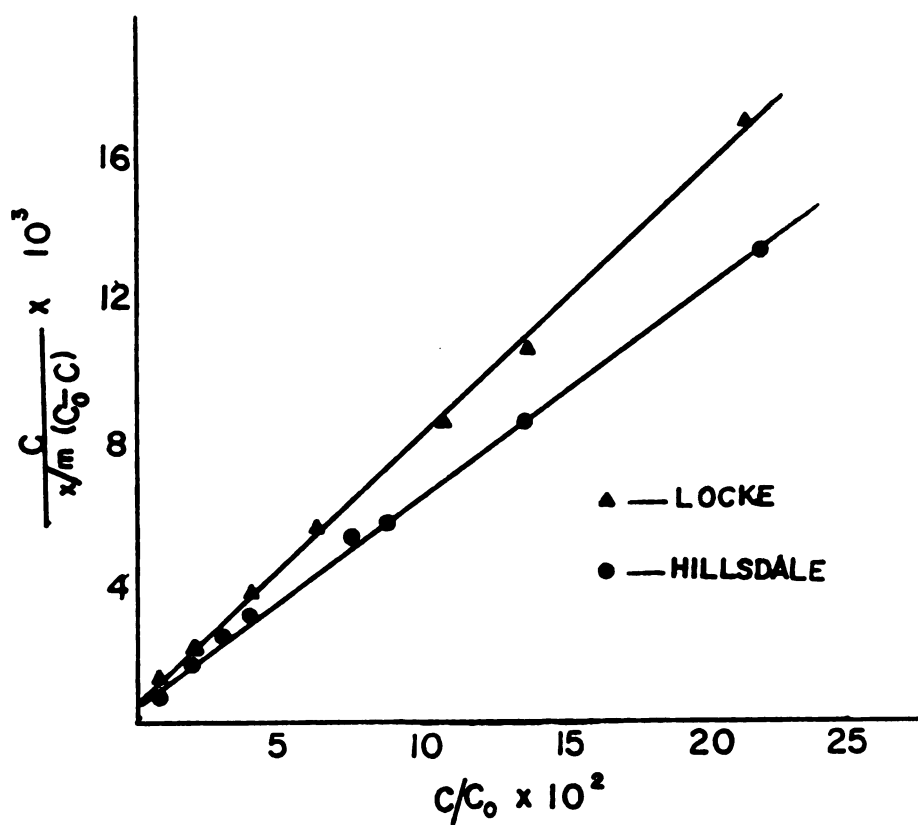
Figure 2. BET isotherm for P adsorption on Locke sandy loam
(c_0 = 1.43 x 10^{-3} M P) and Hillsdale sandy loam (c_0 = 2.08 x 10^{-3}
M P) (data from Srisen, 23).

Table 2. Computed Langmuir adsorption maxima and BET monolayer
capacities of soils

Soil	Langmuir adsorption maximum[*]	BET monolayer capacity
	————————mg P/100 g of soil————————	
Hillsdale A	15.3	16.8
Locke A	13.3	13.4
Sims A	15.5	14.9
Hoytville A	15.0	17.6

[*]Correction made for adsorbed P assuming adsorbed P is equivalent to Bray P1 extractable P.

The different slopes noted in Figure 1 may be due to a) adsorption taking place at energetically different sites on the surface, b) adsorption occurring in layers on the surface, and c) precipitation of the phosphate ion. Griffin and Jurinak (7) and Muljadi et al. (18) reported that P is adsorbed with different energies of binding at low equilibrium concentrations on homogeneous soil mineral surfaces. The relatively low equilibrium P concentrations at which the deviations in those studies occurred should exclude precipitation as a factor. Also, the expected homogeneity of the surfaces suggests that another mechanism of adsorption other than the existence of energetically different binding sites for P may be responsible for this effect. In order to investigate this mechanism, P adsorption on anion exchange resin surfaces, Dowex 1-X8 and Dowex 2-X4, was studied. The anion exchange resin system should have energetically homogeneous

surface sites, should not precipitate P, and should have known

replaceable anions which can be easily measured in equilibrium

solutions.

Langmuir adsorption isotherms for P adsorption on Dowex 1-X8

(Cl^- and IO_3^- forms) are shown in Figure 3. The data represent

averages of duplicates and, like the soils data, fit two lines.

The same result was obtained for Dowex 2-X4. A linear fit was

obtained with the BET equation. However, in the case of the resin,

a c_o term could not be calculated since no precipitation of P is

expected in this system. A value for c_o was obtained by iteration

until the best fit for the straight line was obtained. The Langmuir

adsorption maxima and BET monolayer capacities for Dowex 1-X8 and

Dowex 2-X4 are given in Table 3. As in the case of the soils, close

Table 3. Computed Langmuir adsorption maxima and BET monolayer
capacities of anion exchange resins (Cl-forms)

Resin	Langmuir adsorption maximum	BET monolayer capacity
	————mg P/100 g of resin————	
Dowex 2-X4	31.0	33.9
Dowex 1-X8	29.2	26.4

agreement was obtained. The fact that the data from the two slope

Langmuir isotherm (Figure 3) can fit a single line BET isotherm

(Figure 4) may indicate P adsorption on the resin surface with at

least two different energies of binding in spite of the expected

homogeneity of the resin surface sites.
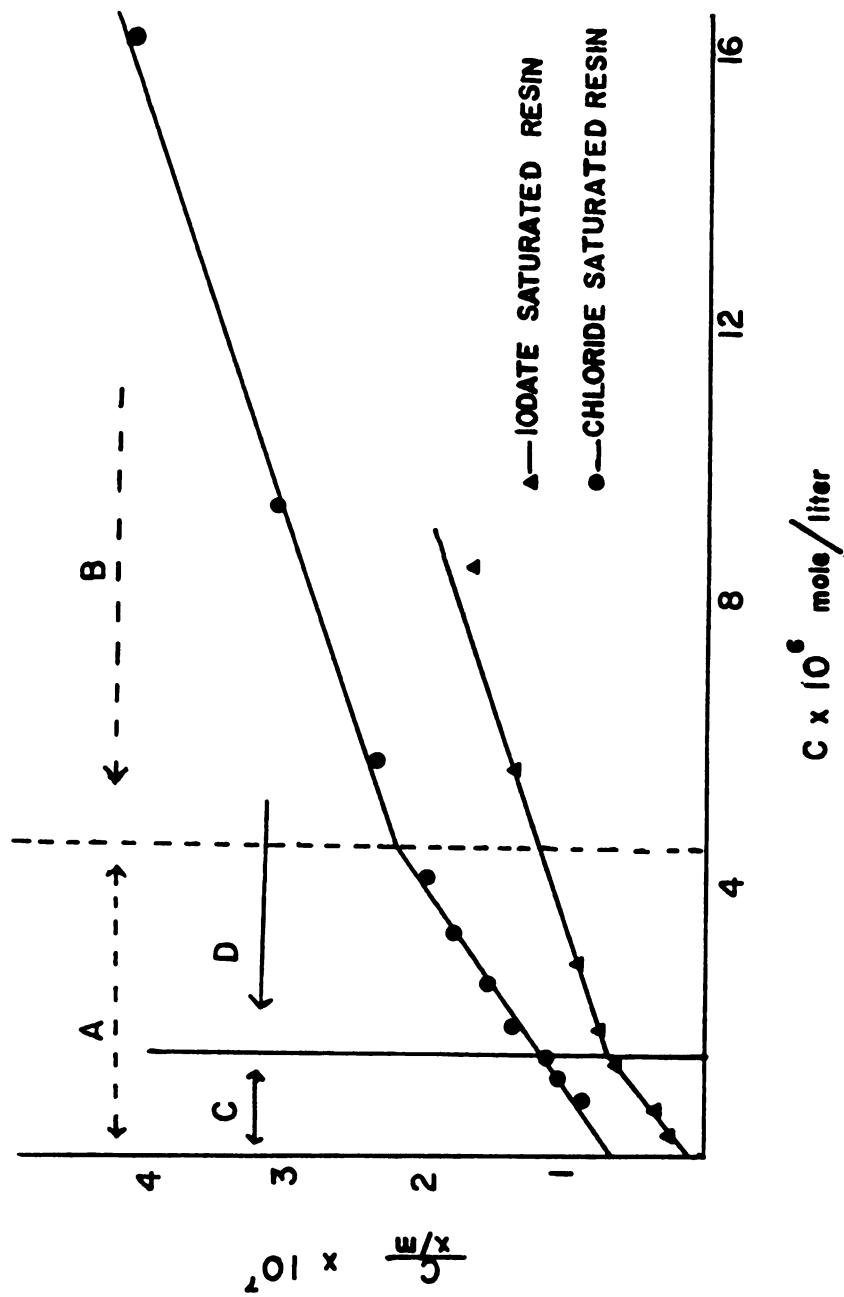
Figure 3. Langmuir isotherm for P adsorption on iodate and chloride saturated resins (Dowex 1-X8). A and B are regions 1 and 2, respectively, of the chloride saturated resin. C and D are the same for the iodate saturated resin.
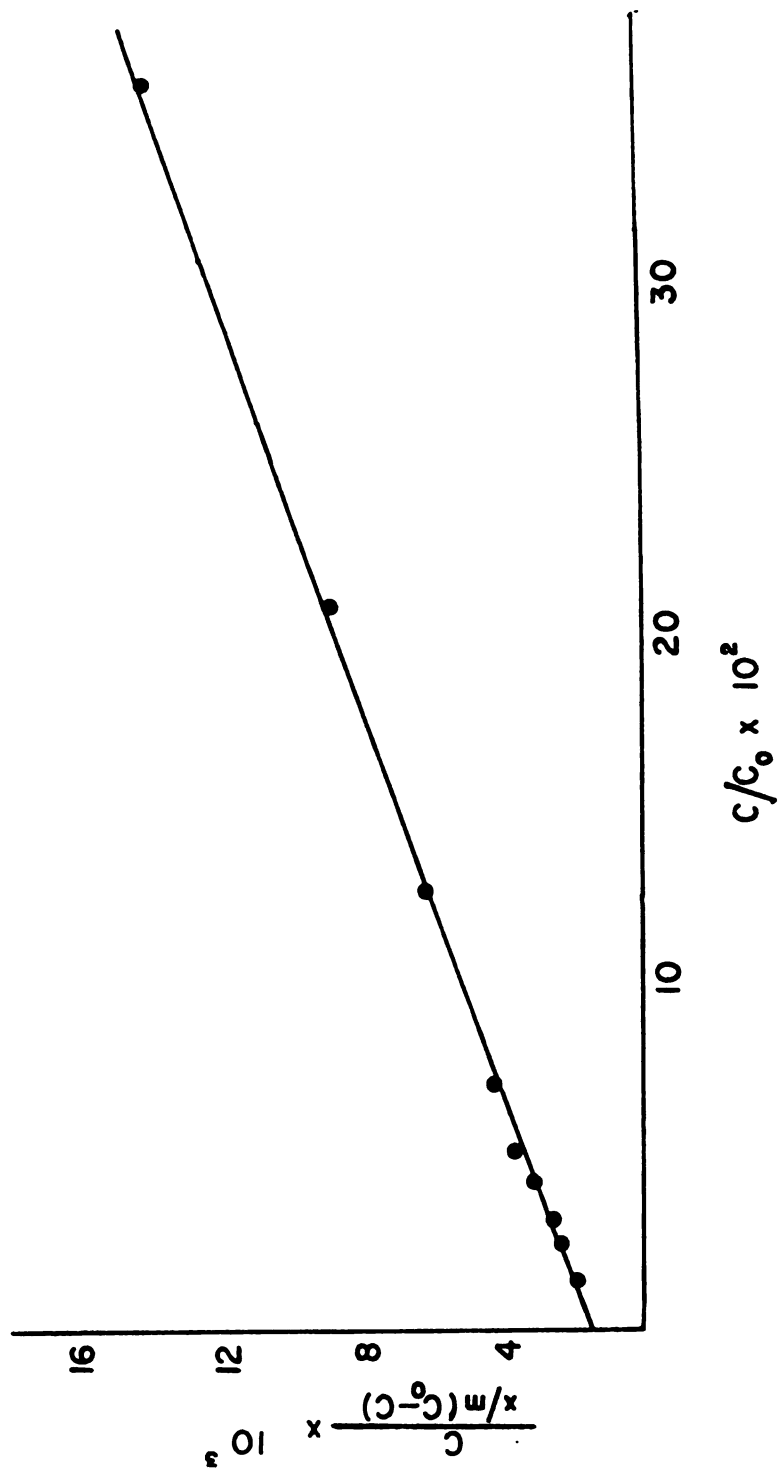
Figure 4. BET isotherm for P adsorption on the Cl⁻ saturated resin (Dowex 1-X8).

Computations derived from measurements made on the equilibrium

P solutions of the isotherms in Figure 3 are presented in Tables 4

and 5. Measurements of the Cl^- released during P adsorption (Table

4) indicate that over region 1 two Cl^- ions were initially released

per phosphate ion adsorbed. This value decreased and continued to

decrease over region 2, approaching a 1:1 ratio. pH measurements

of the equilibrium solutions showed a decrease from the 0 ppm to the

7 ppm initial P treatments. There was no significant change in pH

from the 7 ppm to the 20 ppm initial P treatments. This suggests

very little or no deprotonation at higher equilibrium concentrations.

The above results suggest P adsorption initially as $HPO_4^=$ (two point

attachment) followed by adsorption as $H_2PO_4^-$ (one point attachment).
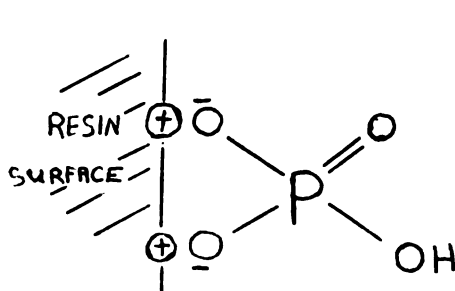
"Two-point attachment"   "One-point attachment"
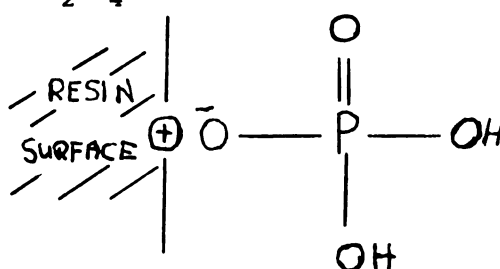
"Two point attachment" of P on kaolinite and soil surfaces was

suggested by Kafkafi et al. (11) and Barrow and Shaw (2), respec-

tively. This type of bonding would be particularly stable because

the distance between the two O atoms of the phosphate tetrahedron

(2.85 - 3.20Å) is very close to the distance between the two Al

atoms (2.96Å) on the edge face of a kaolinite crystal. Using infrared

spectroscopic techniques to study phosphate adsorption on Fe oxides,

Parfitt et al. (21) and Atkinson et al. (1) obtained evidence for

"two point attachment." This mechanism of bonding to soil mineral

and other surfaces would produce a stable bonding between P and the

Table 4. Chloride released during adsorption of P on Dowex 1-X8 and
pH values of the equilibrium solutions[*]

Initial P conc. (ppm)	P Adsorbed (mMole/l)	Cl⁻ Released (mMole/l)	$\frac{Cl^-}{P}$	Equilibrium pH [†]
0	0	0	0	4.38
4.09	0.131	0.288	2.20	3.91
5.15	0.165	0.340	2.06	3.87
6.13	0.197	0.396	2.01	3.85
7.11	0.228	0.426	1.87	3.80
8.04	0.257	0.482	1.88	3.79
9.00	0.287	0.506	1.76	3.79
9.96	0.318	0.562	1.76	3.79
12.00	0.382	0.643	1.68[††]	3.83
15.00	0.475	0.774	1.63	3.81
20.00	0.630	0.914	1.45	3.81

[*]All equilibrium measurements represent averages of duplicates.

[†]pH of Cl form of resin in H_2O = 4.43 (average of triplicates).

[††]Indicates where deviation from initial linear line begins.

surface. The limit to "two point attachment" may be availability of the sites that can accommodate this type of bonding on the colloidal surfaces.

Approximately the same results as those given in Table 4 were obtained when the Cl^- on the resin was replaced by IO_3^- (Table 5) and P adsorption on this system studied. Preliminary experiments showed the release of both Cl^- and IO_3^- after adsorption, indicating incomplete replacement of Cl^- by IO_3^-. Apparently replacement resulted in some Cl^- being adjacent to IO_3^-. This might be due to the large size of IO_3^-. For some sites, there appeared to be insufficient space for IO_3^- ions to be adjacent to each other. This would support the deduction that some resin surface sites are close enough (i.e., those sites occupied by Cl^- which were not replaced by IO_3^-) to accommodate "two point attachment." As a result of this finding, following P adsorption on the IO_3^- saturated resin, both Cl^- and IO_3^- released were measured (Table 5).

On the other hand, at very high initial concentrations, P adsorption on Dowex 1-X8 resulted in a single linear Langmuir isotherm (Figure 5 and Table 6). The data indicate that at high P concentrations, one Cl^- ion was released per $H_2PO_4^-$ ion adsorbed. Therefore, it appears that over this region of the isotherm, there is a 1:1 replacement of Cl^- by P and, as a result, conformity to one line predicted by equation [1].

The heat released or absorbed during adsorption is the differential molar heat of adsorption, $\overline{\Delta H}$. The values of $\overline{\Delta H}$ were computed for Dowex 1-X8 (Cl-form) between 11 C and 25 C using equation [3]. The results are plotted as a function of P adsorbed and shown in Figure 6. The adsorption process was found to be endothermic, which
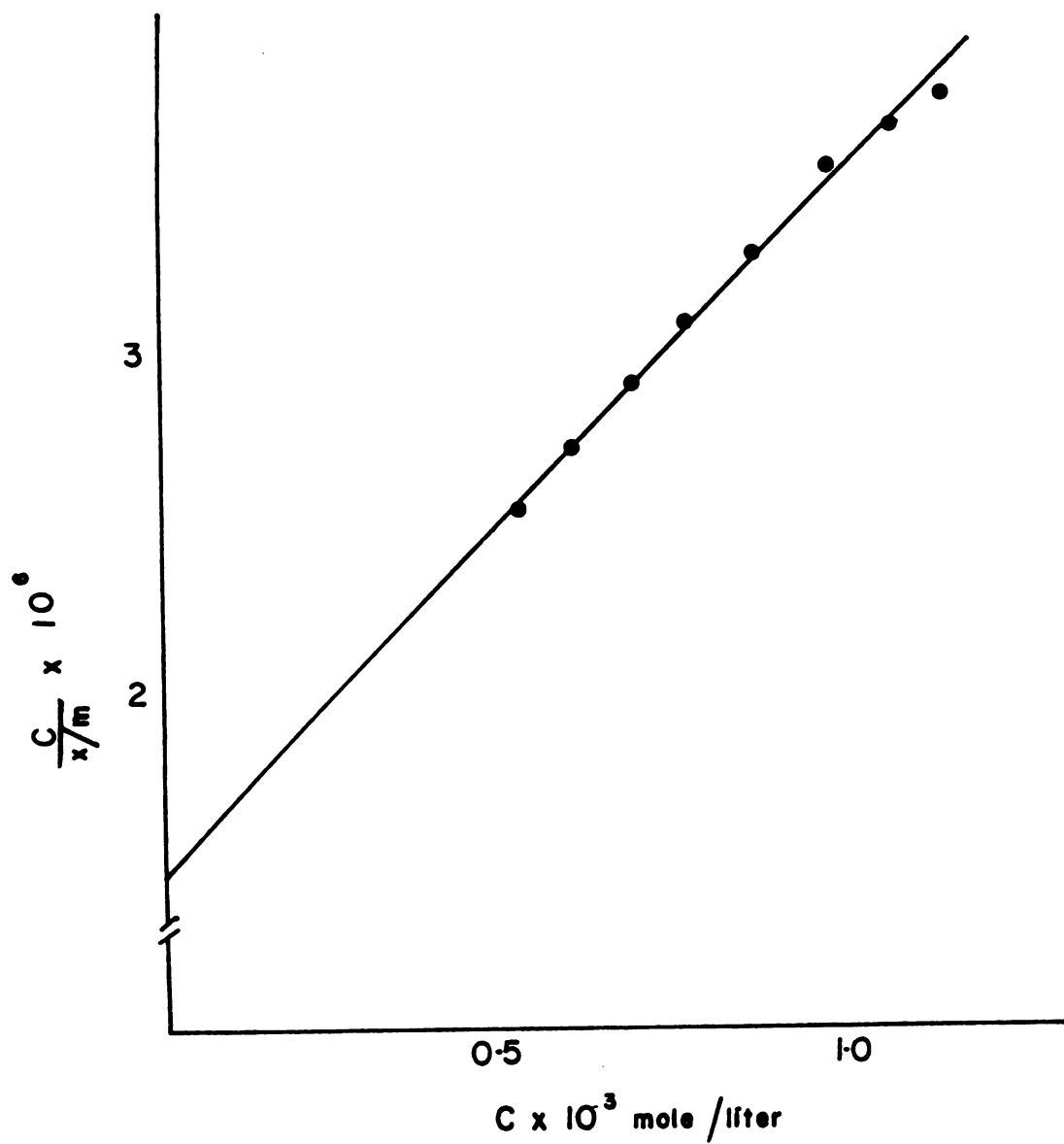
Figure 5. Langmuir isotherm for P adsorption on the Cl$^-$ saturated resin (Dowex 1-X8) at high equilibrium concentration.

Table 5. Chloride plus iodate released during adsorption of P on Dowex 1-X8 (after partial replacement of Cl^- by IO_3^-) and pH values of the equilibrium solutions*

Initial P conc. (ppm)	P Adsorbed (mMole/l)	(IO_3^- plus Cl^-) Released (mMole/l)	$\dfrac{IO_3^- + Cl^-}{P}$	Equilibrium pH
0	0	0	0	4.26
5.0	0.161	(0.209 + 0.101)	1.93	3.95
8.0	0.258	(0.286 + 0.151)	1.69	3.94
10.0	0.322	(0.360 + 0.164)	1.63	3.90
12.0	0.386	(0.431 + 0.186)	1.60[†]	3.89
15.0	0.482	(0.516 + 0.203)	1.49	3.87
20.0	0.640	(0.658 + 0.281)	1.46	3.85
25.0	0.799	(0.806 + 0.333)	1.42	3.81

*Chloride on Dowex 1-X8 replaced by IO_3^- (average of duplicates).

†Indicates where deviation from initial linear line begins.

Table 6. Chloride released during P adsorption at high initial P
concentration on Dowex 1-X8 (Cl-form) and pH values of
the equilibrium solutions[*]

Initial P conc. (ppm)	P Adsorbed (mMole/l)	Cl^- Released (mMole/l)	$\dfrac{Cl^-}{P}$	Equilibrium pH [†]
0	0	0	0	4.36
120	3.347	3.735	1.11	3.71
130	3.591	3.932	1.09	3.79
140	3.830	4.284	1.12	3.79
150	4.066	4.411	1.08	3.79
160	4.293	4.707	1.09	3.81
170	4.500	5.030	1.11	3.77
180	4.735	5.256	1.11	3.77
190	4.976	5.523	1.11	3.79

[*]All equilibrium measurements represent averages of duplicates.

[†]pH of Cl-form of resin in H_2O = 4.43 (average of triplicates).

is in agreement with Griffin and Jurinak (7) and Low and Black (16)

for P adsorption on $CaCO_3$ and kaolinite, respectively. The heat

evolved or consumed in the course of an ion exchange reaction is

approximately 2 K cal/Mole (9). Therefore, consumption of approxi-

mately 6 K cal/Mole during the initial stages of adsorption is

probably in agreement with the formation of two electrostatic bonds

between $HPO_4^=$ and two resin surface sites after deprotonation of the

$H_2PO_4^-$ ion which may also consume energy. The energy consumed over

region 2 (a change from 3.00 -- 1.42 K cal/Mole) is in agreement

with the formation of one electrostatic bond between $H_2PO_4^-$ and the

resin surface site.

The adsorption process on the resin surface can be visualized

as the initial adsorption taking place with P being adsorbed as

$HPO_4^=$, although the phosphate ion is present in solution as $H_2PO_4^-$.

Apparently, the greatest heat of adsorption is attained (or the most

active sites on the homogeneous surface of the resin produced) and

the lowest free energy of the system acquired by deprotonation of

the $H_2PO_4^-$ ion resulting in adsorption of P as $HPO_4^=$. It is assumed

that deprotonation and "two point attachment" would occur only if,

in the total population of sites on the resin surface, there is a

limited number of specific sites which are so positioned that they

can sterically accommodate the phosphate ion as $HPO_4^=$. Some systems

studied may not have these sites with the correct distance apart, or

they may already be occupied; therefore, the isotherm remains linear

over the whole concentration range used.

As the adsorption process continues, P is adsorbed both as $HPO_4^=$

and $H_2PO_4^-$ with the former species decreasing and the latter increasing.

This causes a sharp decrease in the overall heat of adsorption, $\overline{\Delta H}$,

from that value obtained initially when only $HPO_4^=$ ions were being

adsorbed (Figure 6). With the continuation of adsorption, $\overline{\Delta H}$ con-

tinues to decrease until it falls below one-half of its initial

value. At this point, the isotherm begins to deviate from the

initial straight line. Region 2 of the isotherm, defined by the

change in slope of the line, is entered. In this region $H_2PO_4^-$

adsorption continues to increase, while that of $HPO_4^=$ approaches zero.

$\overline{\Delta H}$ becomes essentially constant and, should the adsorption process

continue, would reflect only adsorption of P as $H_2PO_4^-$. It is in

this region of the isotherm that a straight line Langmuir relation-

ship is obtained over the whole concentration range used (Figure 5).

The above mechanism of P adsorption as hypothesized for the resin

system is proposed as one possible explanation for the deviation from

linearity predicted by equation [1] which is observed on soil and

homogeneous soil mineral surfaces at low equilibrium P concentrations.

The type of bond formed between P and the colloidal surfaces may be

covalent, but this should not change the overall mechanism of

adsorption.
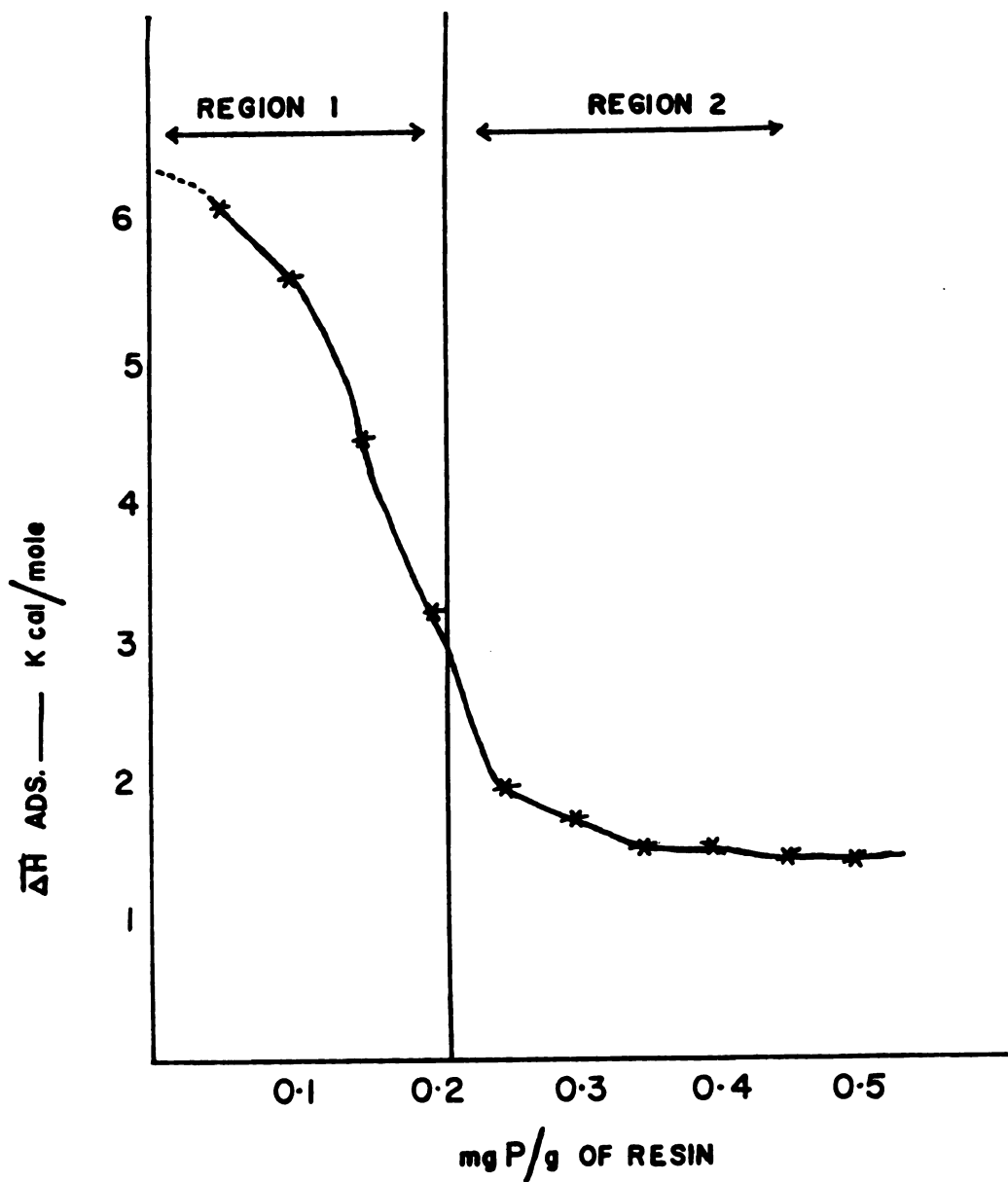
Figure 6. The isosteric differential heat of adsorption, $\overline{\Delta H}$, as a function of phosphate adsorbed on Dowex 1-X8.

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CHAPTER II

VERTICAL MOVEMENT OF PHOSPHORUS AS RELATED TO
AVAILABLE PHOSPHORUS IN SOIL PROFILES

Introduction

Application of phosphorus (P) fertilizer in Michigan has

increased from an average rate of 14 kg P per hectare in 1962 to 27

kg P per hectare in 1971 (Doll et al., 1972). This has resulted in

an increase in the average soil test value for P from 39 to 84 kg P

per hectare. In Michigan, P fertilization is recommended for all

soils which test below 44 kg P per hectare (20 ppm). The number of

samples testing in this range decreased from 74% to 40% during the

10-year period 1962 through 1971. There is some indication that

appreciable downward movement of P may occur when soils test above

224 kg P per hectare (100 ppm) and the number of samples in this

range increased from less than 1% to 7% from 1962 to 1971 (Doll et

al., 1972).[1]

Levels of soil P are related to soil texture. In 1971, 69% of

the clay soils and 20% of the sand soils tested below 20 ppm, while

only 10% of the clay soils and 43% of the sand soils tested above

50 ppm (Doll et al., 1972).[1] This would suggest that downward move-

ment of P would be likely to occur on coarse-textured soils especially

if they were heavily fertilized.

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[1]Doll, E. C., J. F. Demeterio and R. P. White. 1972. Accumu-
lation and movement of phosphorus in Michigan soils. Unpublished
data, Michigan State University.

Reports of the downward movement of P are not unusual. Neller (1946), using lysimeters, found that P applied on or incorporated in the surface horizon of a Leon fine sand would be diffused throughout the soil mass above the impervious hardpan layer 2.54 to 61 cm below the surface. Doll et al. (1959) noted that P topdressed at annual rates of 59 and 138 kg P per hectare on the surface of pasture sod moved downward 7.6 cm in 2 years in Kentucky. Spencer (1957) reported that P applied to a fine sand soil in Florida had in some cases leached to 213 cm over a 15-year period. Kao and Blanchar (1973) noted that between the B_2 and C_2 horizons of a Mexico silt loam there was a trend for total P level to be higher both in available and total inorganic P. They attributed this to the downward movement of P resulting from the illuviation of P in soil water.

To determine if significant amounts of P (and other elements) were being leached from the soil into tile drains and streams, Erickson and Ellis (1971) monitored drainage water from tile drains on 4 farms and from 4 small streams. Their data suggested little loss of P from the heavily fertilized fine textured soils.

Ellis (1975) reported very little movement of P below the surface layer of soil if the adsorbed P was below the predicted Langmuir adsorption maximum of the soil. However, when soils received applications of fertilizer to levels approaching the adsorption maximum movement of P occurred. In certain sandy soil, this movement progressed to a depth exceeding 0.50 meter.

The objective of this research was to determine whether coarse textured soils are more likely to allow the vertical movement of P than fine textured soils, and to establish a level, or levels, of Bray

Pl extractable P above which appreciable downward movement of P may be anticipated.

Materials and Method

Soil Sample

Soil samples were collected from three counties in Michigan: Tuscola, Gratiot and St. Joseph. These counties were chosen because they represent ranges of landforms in Michigan, namely lake plains, moraines and outwash plains which would give soils of fine and coarse textures and different natural drainage. The farms chosen as sites for sampling were picked after consultation with county agents in the respective counties on the basis of P fertilization history in an attempt to obtain soils which have been heavily, moderately, and lightly fertilized. Eleven sites were sampled in Tuscola County, 17 sites in Gratiot County, and 20 sites in St. Joseph County.

At each site (farm) samples were collected from the field at 15 cm intervals with a bucket auger to a depth of 122 cm in Tuscola County and 152 cm in the other counties. Sampling was terminated at any site after the groundwater was encountered. The samples were temporarily placed in plastic bags and transported to the laboratory at Michigan State University, where they were air-dried, screened through a 2 mm sieve and stored in small glass jars before being analyzed.

Soil Analyses

Each sample was analyzed in duplicate for extractable P by the Bray Pl method and pH in $0.01M$ $CaCl_2$ (1:2 soil to solution). Langmuir

adsorption isotherms were determined on all 0-15 cm surface samples to obtain the adsorption maxima.

Langmuir Adsorption Isotherm

Twenty milliliters of P solutions ranging in concentration from 0-25 ppm P in 0.01M $CaCl_2$ were added to 2 g of soil in 50 ml centrifuge tubes and shaken on a wrist action shaker for 24 hours in a constant temperature chamber at 25 C. The soil suspensions were then centrifuged at 9,750 rpm for 15 minutes and the centrifugate filtered through Whatman No. 42 filter paper. Equilibrium P concentration was determined using a Technicon Autoanalyzer II.

Results and Discussion

Given any accepted level of P activity in the soil above which movement will occur, the Langmuir equation may be used to determine the fraction of the adsorption maximum, Θ, that would maintain this level in solution. The most useful form of the Langmuir equation for this purpose is:

$$K = \frac{\Theta}{(P)\ (1-\Theta)}$$

where: K = Langmuir constant
P = P activity in solution (moles/liter)
Θ = fraction of the possible sites occupied by P.

Tuscola County

Bray P1 extractable P and pH measurements of the loam soils from Tuscola County are presented in Table 1. To determine if P movement could be correlated with the percentage of the Langmuir adsorption maximum which would give movement if the soil solution concentration was 1 ppm P (Ellis, 1975), a ratio of Bray P1 extractable P to that

Table 1. Bray P1 extractable P and pH measurements of the loam soils from Tuscola County

Site	Depth (cm)	0-15	15-30	30-45	45-60	60-75	75-90	90-105	105-120
1	Bray P1 (ppm)	1.3	1.1	0.76	0.88	0.70	0.62	0.86	-
	pH	7.45	7.48	7.62	7.56	7.60	7.60	7.63	-
2	Bray P1 (ppm)	13	27	3.4	3.6	3.0	3.0	3.9	4.2
	pH	6.65	6.42	6.85	7.05	7.50	7.60	7.30	7.48
3	Bray P1 (ppm)	17	1.6	1.1	2.6	1.6	2.0	2.3	2.1
	pH	7.33	7.45	7.62	7.56	7.69	7.70	7.60	7.60
4	Bray P1 (ppm)	23	5.9	3.6	3.7	2.8	3.0	3.0	1.7
	pH	6.60	6.73	7.00	7.25	7.43	7.62	7.57	7.61
5	Bray P1 (ppm)	28	11	4.2	3.6	1.2	1.3	1.8	1.7
	pH	7.23	7.15	7.42	7.51	7.65	7.72	7.60	7.60
6	Bray P1 (ppm)	30	21	3.6	3.6	2.9	3.1	4.0	-
	pH	6.55	6.73	7.05	7.24	7.31	7.44	7.15	-
7	Bray P1 (ppm)	31	22	4.1	4.2	3.0	3.3	4.4	4.2
	pH	7.20	7.05	7.00	7.32	7.25	7.55	7.40	7.43
8	Bray P1 (ppm)	32	3.4	6.7	6.5	4.7	3.1	4.3	-
	pH	7.35	7.41	7.35	7.46	7.42	7.48	7.40	-
9	Bray P1 (ppm)	34	16	8.6	3.9	3.3	3.0	4.0	4.0
	pH	7.00	6.75	6.93	7.05	7.50	7.33	7.30	7.41
10	Bray P1 (ppm)	35	9.7	4.0	4.0	3.0	3.1	4.1	4.0
	pH	6.92	7.12	7.22	7.46	7.63	7.65	7.58	7.60
11	Bray P1 (ppm)	46	31	7.2	4.0	3.1	3.1	2.9	2.1
	pH	7.28	7.15	7.15	7.24	7.50	7.60	7.60	7.59

fraction of the adsorption maximum of the 0-15 cm samples was calcu-
lated (Tables 2 and 3). A ratio above which movement would be
expected and below which no movement would be anticipated cannot be
established since these soils show no phosphorus movement.

The fine textured soils of Tuscola County do not show appreciable
downward movement of P. The Bray P1 extractable P levels in the 0-15
cm samples are all below 50 ppm P. Generally, downward movement of
P would not be expected at these relatively low levels in fine
textured soils.

It should be noted that most of the soils from the 3 counties
used in this study gave Langmuir isotherms which fitted two lines.
However, only the adsorption maximum, b_1, and the constant related
to the energy of binding K_1, from the first region of the isotherms
were used because the experimental equilibrium P concentrations from
this region are more in the range of the expected soil solution P
concentration even in heavily fertilized soils.

Gratiot County

The Bray P1 extractable P and pH measurements of the loam soils
from Gratiot County are shown in Table 4. Three (17%) of the 0-15
cm surface samples (sites 15, 16 and 17) have Bray P1 extractable P
levels which are above 50 ppm P. Their values are still not in the
range where appreciable downward movement of P would be expected.
However, two of them indicate a little P movement into the 30-45 cm
layer. Three other sites (farms), numbers 10, 11 and 14, having Bray
P1 extractable P levels in the 0-15 cm samples below 50 ppm P show
a minor accumulation of P in the 30-45 cm layer. In all cases where
movement can be discerned (in these soils only a very small amount of

Table 2. Langmuir adsorption parameters for surface samples from
Tuscola County

Site	Region 1		Θ_1 at 1 ppm P in soil solution
	K_1	b_1	
	$X\ 10^{-4}$	mg/100 g soil	
1	3.3	9.5	0.51
2	4.4	11.2	0.58
3	2.4	15.5	0.44
4	0.9	25.3	0.22
5	1.1	26.7	0.26
6	5.0	10.0	0.61
7	2.2	15.3	0.41
8	0.5	24.5	0.15
9	2.6	15.0	0.46
10	2.1	16.2	0.40
11	1.2	24.0	0.25

Table 3. The ratio of Bray P1 extractable P to adsorbed P at 1 ppm P
in soil solution for surface samples from Tuscola County

Site	$\dfrac{\text{Bray P1}}{b_1 \times \Theta_1}$	Movement indicated
1	0.27	$-^{*}$
2	0.20	-
3	0.25	-
4	0.41	-
5	0.40	-
6	0.50	-
7	0.50	-
8	0.86	-
9	0.50	-
10	0.53	-
11	0.69	-

*(-) indicates no discernible downward movement of P and (+)
indicates discernible downward movement of P to a specified depth.

Table 4. Bray P1 extractable P and pH measurements of the loam soils from Gratiot County

Site	Depth (cm)	0-15	15-30	30-45	45-60	60-75	75-90	90-105	105-120	120-135	135-150
1	Bray P1 (ppm)	6.1	5.1	2.4	2.5	2.7	2.7	2.3	1.0	0.96	--
	pH	6.66	6.45	6.75	6.95	7.29	7.34	7.66	7.66	7.70	--
2	Bray P1 (ppm)	6.8	3.5	2.3	2.2	2.5	2.3	3.0	2.9	2.8	2.0
	pH	7.08	7.28	7.05	7.03	7.15	7.24	7.25	7.24	7.26	7.76
3	Bray P1 (ppm)	8.8	7.8	2.8	2.5	2.5	2.7	2.7	1.9	1.1	1.9
	pH	5.95	6.02	6.50	6.87	7.00	7.37	7.56	7.63	7.64	7.64
4	Bray P1 (ppm)	9.4	9.6	3.4	1.7	1.5	1.4	1.5	0.95	--	--
	pH	7.20	7.37	7.00	7.13	7.66	7.69	7.67	7.69	--	--
5	Bray P1 (ppm)	15	8.3	3.6	2.2	2.2	2.2	2.6	3.0	3.0	3.2
	pH	6.91	6.83	6.86	6.93	7.04	6.94	7.06	7.24	7.11	7.59
6	Bray P1 (ppm)	16	24	5.3	2.8	2.4	2.3	2.6	2.2	2.1	--
	pH	7.00	6.90	6.67	6.97	7.01	7.40	7.64	7.63	7.59	--
7	Bray P1 (ppm)	20	19	3.3	3.3	1.1	1.2	1.2	1.2	1.4	1.5
	pH	6.92	6.99	7.02	7.14	7.70	7.65	7.84	7.82	7.73	7.71
8	Bray P1 (ppm)	21	19	3.5	2.5	2.2	1.5	1.3	0.98	1.1	1.2
	pH	7.27	7.36	7.48	7.46	7.51	7.77	7.70	7.74	7.84	7.78
9	Bray P1 (ppm)	22	16	2.3	2.3	2.7	2.7	2.8	2.4	1.0	1.0
	pH	6.25	6.53	6.60	6.76	7.41	7.46	7.40	7.54	7.60	7.67
10	Bray P1 (ppm)	29	92	8.4	2.2	2.1	2.2	3.0	2.8	2.9	3.3
	pH	6.17	5.55	6.20	6.65	6.77	6.94	7.05	7.29	7.54	7.61

Table 4 (continued)

Site	Depth (cm)	0-15	15-30	30-45	45-60	60-75	75-90	90-105	105-120	120-135	135-150
11	Bray P1 (ppm)	29	36	9.3	1.8	1.2	1.2	1.4	1.3	1.4	1.6
	pH	5.62	5.73	6.31	6.84	7.59	6.67	7.65	7.66	7.69	7.72
12	Bray P1 (ppm)	33	25	6.3	2.1	2.4	2.5	3.1	3.1	2.8	1.3
	pH	6.09	6.30	7.15	7.23	7.32	7.32	7.46	7.61	7.63	7.63
13	Bray P1 (ppm)	40	35	3.5	2.4	2.1	1.4	1.3	1.1	1.1	0.88
	pH	6.92	6.87	7.07	7.38	7.42	7.67	7.69	7.71	7.81	7.75
14	Bray P1 (ppm)	42	52	14	7.2	5.3	6.0	3.4	3.0	2.6	2.8
	pH	6.78	7.03	7.41	7.61	7.48	7.54	7.52	7.61	7.54	7.62
15	Bray P1 (ppm)	53	34	2.8	2.2	2.3	2.4	2.4	-	-	-
	pH	6.13	6.21	6.57	6.75	6.72	6.76	6.91	-	-	-
16	Bray P1 (ppm)	62	73	10	6.0	4.8	4.4	1.0	1.2	1.2	1.2
	pH	6.96	7.00	7.13	7.10	7.35	7.48	7.71	7.67	7.72	7.70
17	Bray P1 (ppm)	76	119	12	5.0	3.5	4.2	3.0	2.2	2.0	1.1
	pH	6.92	7.01	7.19	7.23	7.20	7.11	7.34	7.54	7.50	7.60

Table 5. Langmuir adsorption parameters for surface samples from
Gratiot County

| Site | Region 1 | | Θ_1 at 1 ppm P in soil solution |
| | K_1 | b_1 | |
	$\times 10^{-4}$	mg/100 g soil	
1	8.3	12.0	0.73
2	3.9	11.0	0.56
3	1.0	14.0	0.25
4	2.5	19.3	0.45
5	4.1	13.3	0.57
6	50.0	10.0	0.94
7	1.0	17.0	0.25
8	2.0	15.8	0.39
9	2.7	14.2	0.46
10	2.1	14.5	0.41
11	2.6	10.1	0.45
12	1.4	17.0	0.31
13	2.7	11.6	0.47
14	5.1	14.0	0.62
15	9.0	23.2	0.74
16	2.0	14.7	0.39
17	2.3	17.5	0.42

P movement was indicated) the Bray Pl phosphorus levels of the 15-30 cm layer are higher (sometimes much higher) than those of the corresponding 0-15 cm samples. This might be due to mechanical mixing of the surface soils during plowing followed by crop removal of some of the P from the 0-15 cm layers prior to soil sampling. That might also explain why the extractable P levels of sites 10, 11 and 14, being in a range where movement is not expected in a fine textured soil, do show a little movement. The ratio of Bray Pl extractable P to that fraction of the adsorption maximum which would give movement if the soil solution concentration was 1 ppm P are shown in Table 6. When the ratio is above 1.0 (sites 16 and 17) some movement is indicated. Movement is manifested in some cases when the ratio is approximately 0.5 (sites 10 and 14) and 0.6 (site 11), but other sites having the same (sites 7 and 12) and higher (site 13) ratios show no movement. This suggests that other factors (i.e., actual texture of entire soil profile, actual amount of water that moved through the soil profile, etc.) not taken into consideration here also affect P movement in these soils. A critical ratio value above which P moves and below which it does not move cannot be established from the data presented in Table 6.

Generally, the soil profiles (sites) from Gratiot County have lower pH values (below 7.0) between 0-60 cm than the sites from Tuscola County; however, the pH increased between 60-152 cm depth to values (above 7.0) similar to those obtained from the Tuscola County soils (Tables 1 and 4). Any effect of pH on P movement cannot be discerned.

Table 6. The ratio of Bray Pl extractable P to adsorbed P at 1 ppm P
in soil solution for surface samples from Gratiot County

Site	$\dfrac{\text{Bray Pl}}{b_1 \text{ X } \Theta_1}$	Movement indicated	Depth of movement (cm)
1	0.07	-*	
2	0.11	-	
3	0.25	-	
4	0.11	-	
5	0.19	-	
6	0.17	-	
7	0.48	-	
8	0.34	-	
9	0.34	-	
10	0.49	+	30-45[†]
11	0.64	+	30-45[†]
12	0.63	-	
13	0.74	-	
14	0.48	+	30-45[†]
15	0.31	-	
16	1.08	+	30-45[†]
17	1.03	+	30-45

*(-) indicates no discernible downward movement of P and (+)
indicates discernible downward movement of P to a specified depth.

[†]Apparent movement at this depth but little accumulation of P.

St. Joseph County

Table 7 shows the Bray Pl extractable P and pH measurements of the sandy loam soils from St. Joseph County. Thirteen of the 20 sites show appreciable downward movement of P. Of these, movement advanced to the greatest depth in site 14, showing P enrichment of the 90-105 cm layer. One-fourth, or 5 sites (16, 17, 18, 19 and 20) have Bray Pl extractable P values above 100 ppm P, the level above which appreciable downward movement of P may occur in soils (Doll et al., 1972).[1] One of the five (site 16) exhibits no movement while the others indicate definite movement. Again, some of the sites which manifest movement have higher Bray Pl levels in the 15-30 cm layers than the corresponding 0-15 cm layers. This is not observed in sites which show no movement. The same explanation as put forth for similar findings in the surface soils of Gratiot County is presented here. The Bray Pl extractable P data for these sandy loam soils reveal that at higher levels (above 80 ppm P), P movement is evident for most sites but at the lower levels (below 50 ppm P) some sites also exhibit movement. Generally, the soil profiles from St. Joseph County are more acid than those from the other two counties. However, the degree of movement seems to be determined more by soil texture rather than soil pH.

The absence of a relationship between the ratio of Bray Pl extractable P to that fraction of the adsorption maximum which would allow movement if the soil solution concentration was 1 ppm P is shown in Table 9. A critical ratio value (explained earlier) for P movement

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[1]Doll, E. C., J. F. Demeterio and R. P. White. 1972. Accumulation and movement of phosphorus in Michigan soils. Unpublished data, Michigan State University.

Table 7. Bray P1 extractable P and pH measurements of the sandy loam soils from St. Joseph County

Site	Depth (cm)	0-15	15-30	30-45	45-60	60-75	75-90	90-105	105-120	120-135	135-150
1	Bray P1 (ppm)	24	9.0	7.4	5.3	6.8	6.2	5.9	6.8	5.4	--
	pH	5.12	4.99	4.75	4.65	4.55	4.71	4.80	7.28	7.21	--
2	Bray P1 (ppm)	35	33	35	15	9.2	5.6	4.3	4.7	4.4	4.1
	pH	4.64	5.44	5.57	5.55	5.59	5.60	5.70	5.60	5.66	5.65
3	Bray P1 (ppm)	36	18	18	19	18	8.5	6.8	9.4	10.6	--
	pH	4.58	6.45	4.51	5.96	4.73	4.91	4.85	4.87	4.75	--
4	Bray P1 (ppm)	37	32	18	9.4	6.7	6.6	7.5	6.7	6.2	5.7
	pH	6.30	6.50	6.25	4.90	4.61	4.70	4.84	5.50	6.91	6.30
5	Bray P1 (ppm)	38	32	51	43	29	28	10	9.1	8.3	15
	pH	5.68	5.92	5.85	5.81	5.81	5.76	5.71	5.67	5.77	5.66
6	Bray P1 (ppm)	54	72	65	34	27	--	--	--	--	--
	pH	7.03	7.00	7.03	7.05	7.03	--	--	--	--	--
7	Bray P1 (ppm)	60	63	57	50	24	14	12	13	11	8.9
	pH	5.54	6.34	6.08	6.02	5.91	5.90	5.84	5.90	5.87	5.77
8	Bray P1 (ppm)	61	48	12	6.3	4.7	7.9	6.2	6.0	0.86	1.1
	pH	6.26	6.38	6.59	6.57	6.50	6.85	6.56	6.98	7.60	7.81
9	Bray P1 (ppm)	62	50	33	20	19	15	12	11	11	11
	pH	6.27	6.90	6.79	6.63	6.56	6.58	6.57	6.52	6.70	6.5
10	Bray P1 (ppm)	64	57	21	16	14	11	12	9.7	9.6	7.5
	pH	4.08	4.04	5.55	5.01	4.82	4.50	4.66	4.66	5.32	7.18

Table 7 (continued)

Site	Depth (cm)	0-15	15-30	30-45	45-60	60-75	75-90	90-105	105-120	120-135	135-150
11	Bray P1 (ppm)	66	55	31	22	-	16	14	14	12	4.7
	pH	4.05	4.16	4.80	4.75	-	4.77	4.83	4.88	5.34	5.46
12	Bray P1 (ppm)	72	65	34	18	9.2	7.1	7.1	7.0	5.3	7.5
	pH	4.24	5.19	4.58	4.48	4.42	4.45	4.43	4.46	4.53	4.57
13	Bray P1 (ppm)	79	52	24	28	13	11	13	11	11	9.1
	pH	5.88	5.89	5.10	5.23	5.31	5.39	5.39	5.29	5.22	5.04
14	Bray P1 (ppm)	82	154	47	440	168	86	33	11	10	10
	pH	4.13	4.43	4.14	5.17	4.29	4.07	4.05	4.08	4.25	4.45
15	Bray P1 (ppm)	82	79	11	4.1	4.0	4.4	3.5	4.4	5.3	6.8
	pH	5.47	5.47	4.24	3.87	3.92	3.96	4.13	4.11	4.22	4.38
16	Bray P1 (ppm)	127	49	13	9.0	10	9.0	11	13	10	10
	pH	5.64	6.00	6.32	6.15	6.10	5.82	5.82	5.61	5.73	5.87
17	Bray P1 (ppm)	132	141	41	23	13	11	11	9.1	7.3	12
	pH	5.44	5.66	6.20	6.66	6.53	6.27	6.20	6.20	6.20	6.18
18	Bray P1 (ppm)	132	114	55	17	18	6.4	7.9	5.6	7.2	9.1
	pH	5.67	5.37	4.97	5.15	4.74	4.83	4.74	4.78	4.97	5.15
19	Bray P1 (ppm)	184	158	71	59	7.0	8.0	6.8	7.7	7.7	5.6
	pH	5.09	5.30	5.63	5.75	5.81	5.77	5.84	5.84	5.84	5.92
20	Bray P1 (ppm)	329	334	185	96	45	27	14	11	12	15
	pH	5.84	5.82	5.17	5.33	5.33	5.46	4.87	4.52	4.57	4.91

Table 8. Langmuir adsorption parameters for surface samples from St. Joseph County

Site	Region 1		θ_1 at 1 ppm P in soil solution
	K_1	b_1	
	$\times 10^{-4}$	mg/100 g soil	
1	8.9	14.0	0.74
2	2.3	12.5	0.43
3	4.2	20.0	0.57
4	6.3	11.3	0.67
5	4.4	12.5	0.58
6	7.1	14.0	0.69
7	7.3	13.7	0.70
8	3.7	13.7	0.54
9	5.4	13.2	0.63
10	10.7	15.5	0.77
11	17.5	19.0	0.84
12	12.5	20.0	0.80
13	5.5	15.0	0.63
14	17.5	19.0	0.84
15	6.0	16.7	0.65
16	3.6	20.0	0.53
17	5.8	21.4	0.65
18	1.7	25.0	0.35
19	6.6	25.0	0.68
20	4.9	40.5	0.61

Table 9. The ratio of Bray P1 extractable P to adsorbed P at 1 ppm P
in soil solution for surface samples from St. Joseph County

Site	$\dfrac{\text{Bray P1}}{b_1 \times \theta_1}$	Movement indicated	Depth of movement (cm)
1	0.23	-[*]	
2	0.66	+	30-45
3	0.32	-	
4	0.50	-	
5	0.52	+	75-90
6	0.56	+	60-75
7	0.63	+	60-75
8	0.83	-	
9	0.75	+	30-45
10	0.54	-	
11	0.41	+	30-45
12	0.45	+	30-45
13	0.84	+	45-60
14	0.51	+	90-105
15	0.76	-	
16	1.20	-	
17	0.95	+	30-45
18	1.51	+	30-45
19	1.08	+	45-60
20	1.33	+	75-90

[*](-) indicates no discernible downward movement of P and (+)
indicates discernible downward movement of P to a specified depth.

cannot be established. Of the sites which show a ratio above 1.0, one of them does not display movement (unlike the soils from Gratiot County). Other factors (i.e., actual texture of the entire soil profile, amount of water which actually moved through the profiles, etc.) other than the ratio seem to control P movement.

Generally, these sandy loam soils have higher Bray P1 extractable P levels in the 0-15 cm layer and show greater downward movement of P than the loam soils from Tuscola and Gratiot Counties. The higher levels of extractable P might be due to heavier application of P fertilizers to these soils. The above results confirm the supposition that appreciable downward movement of P is likely to occur on heavily fertilizes coarse textured soils.

CONCLUSIONS

Chapter I

1). The Langmuir adsorption isotherm can be used to illustrate P adsorption on soil surfaces although two separate reactions seem to be involved even at low equilibrium P concentrations. These reactions yield two sloped isotherms when the linear form of the Langmuir equation is used.

2). It is hypothesized that the deviation from linearity observed on soil and homogeneous soil mineral surfaces when using the Langmuir equation is due to P adsorption initially by "two point attachment" followed by "one point attachment."

Chapter II

1). Coarse textured Michigan soils, when heavily fertilized, will permit appreciable downward movement of P. Over many years, movement may actually progress as far as the groundwater.

2). Significant downward movement of P is not observed in heavily fertilized fine textured Michigan soils.

3). A level or levels of Bray Pl extractable P of surface soils above which P movement is expected cannot be established from the data obtained in this study. Levels of Bray Pl extractable P of surface soil does not seem to correlate well with P movement.

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6	0.56	+	60-75
7	0.63	+	60-75
8	0.83	-	
9	0.75	+	30-45
10	0.54	-	
11	0.41	+	30-45
12	0.45	+	30-45
13	0.84	+	45-60
14	0.51	+	90-105
15	0.76	-	
16	1.20	-	
17	0.95	+	30-45
18	1.51	+	30-45
19	1.08	+	45-60
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