5-1973

A Measure of the Amount of Phosphate Adsorption and the Rate of Release of Indigenous Phosphate from a Desert Soil

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A MEASURE OF THE AMOUNT OF PHOSPHATE ADSORPTION AND THE RATE OF

RELEASE OF INDIGENOUS PHOSPHATE FROM A DESERT SOIL

by

Robert Lindsey Evans

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soil Science

UTAH STATE UNIVERSITY
Logan, Utah

1973

ACKNOWLEDGMENTS

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ABSTRACT

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Release of Indigenous Phosphate from a Desert Soil

by

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Utah State University, 1973

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The capacity of a calcareous desert soil, Thiokol silt loam, to re-
tain natural, as well as added, orthophosphate-P was measured by equili-
brium adsorption employing a batch technique and evaluated using the
two-slope Langmuir adsorption isotherm. From these data, corrected to
account for indigenous soil P, a hypothesis was formulated as to the na-
ture of retention of P by the soil, including the identification of two
interfacial reactions involving P, and a value calculated for the ad-
sorption maximum as defined by the Langmuir isotherm equation for P with
soil at each of two soil depths and three constant temperatures within
the range of biological activity. The initial reaction was considered
to be surface adsorption, where phosphate ions interact with the clay
and lime mineral surfaces at definite sites. The activity of the sec-
ond mechanism was identified as adsorption, and in addition, the hetero-
geneous nucleation of metal phosphates on the lime mineral surfaces.

In addition to these quantitative studies, the flux of P in the
soil was also investigated for the same soil and temperatures by means
of kinetic experiments conducted to identify the nature (mechanisms) and
measure the rates and release maxima of indigenous P release from the

soil. These experiments were carried out using an anion-exchange resin as an infinite sink for P, again applying a batch technique. Ultimately, the release of indigenous P from the soil under saturated conditions was attributed to three simultaneous first-order reactions. The rate constants of the three reactions were found to be of orders of 10^{-4}, 10^{-5}, and 10^{-6} (1/sec), and did not vary significantly with soil depth or temperature. The three reactions above were identified as dissolution of poorly crystalline or amorphous calcium phosphates, the desorption of surface site adsorbed or labile P, and the slow dissolution of calcium hydroxyapatite, respectively.

(72 pages)

INTRODUCTION

Soil phosphate-P is considered to be of importance to the desert ecosystem as a whole because of its relationship to the nutrition of native desert vegetation. The availability of soil P to plant life, a function of its chemical reactivity with many components of the soil system, is a major factor in the determination of plant biomass production and distribution.

Because of the need to understand the conditions of availability of soil P in desert regions, this research was conducted to find both the capacity of deserts to retain P and release rate constants of P for the soil under study, that of Thiokol silt loam.

The capacity of a desert soil to retain P can be measured by equilibrium adsorption and evaluated using the Langmuir adsorption isotherm. Measurements of phosphate adsorption onto clay minerals and selected soils have been expressed and interpreted graphically using adsorption isotherms, which relate the amount of adsorbate to the concentration of the soil solution at equilibrium, and help identify possible occurring mechanisms of adsorption and calculate temperature dependent adsorption maxima for the equilibrium systems.

The flux of P in the soil can be investigated by means of kinetic experiments conducted to measure the nature, the capacity, and the rate of indigenous P release from soil. These experiments were performed using an anion-exchange resin to simulate the uptake factor of the plant root.

This study is a part of the Desert Biome-U.S. International Biological Program and was funded by the National Science Foundation and the Environmental Protection Agency.

LITERATURE REVIEW

Equilibrium Phosphate Adsorption

Measurements of phosphate-P adsorption on soils have been characterized by both the Freundlich (Davis, 1935; Kurtz, DeTurk, and Bray, 1946; Russell and Low, 1954) and Langmuir isotherms (Fried and Shapiro, 1956; Olsen and Watanabe, 1957; Rennie and McKercher, 1959). The Freundlich isotherm was useful in describing the adsorption of soils with widely varying adsorptive capacities and of both large and small initial solution concentrations (Olsen and Watanabe, 1957). The Freundlich isotherm describes adsorption on a solid surface that is considered energetically heterogeneous, i.e., energy of interaction varies from site to site. The Langmuir model assumes that solid surfaces are energetically homogeneous and that the heat of adsorption remains constant, further there is no energy of interaction between adsorbate molecules (Barrow, 1966; Brunauer, Copeland, and Kantro, 1967). The adsorption of phosphate-P onto soil surfaces according to the Freundlich and Langmuir isotherms was tested as to goodness of fit and both were found to be highly correlated (Olsen and Watanabe, 1957).

Both the Langmuir and the Freundlich isotherms incorporate the heat of adsorption (q) into a proportionality constant. The value of this parameter varies with adsorption or surface coverage for the Freundlich equation, but the Langmuir equation functions assuming the value to be a constant for increasing surface coverage, and correspondingly the heat of adsorption is considered constant.

In theory, the Langmuir equations are obeyed by solid surfaces upto

that equilibrium solution concentration where the fractional surface coverage (θ_1) approaches unity. This one characteristic of the Langmuir isotherm makes it possible for the adsorption maximum of the adsorbate to be calculated (Fried and Shapiro, 1956; Olsen and Watanabe, 1957; Rennie and McKercher, 1959). This value cannot be determined using the Freundlich equation. Because a useful relationship is said to exist between the adsorption maximum of a soil and the calculation of a reasonable value for the surface area of a soil, the Langmuir isotherm has become an unique expression of soil adsorption character (Olsen and Watanabe, 1957).

The surface area of a soil can be calculated from the adsorption maximum and compared to the experimental value, assuming that the relationship between surface area and ethylene glycol retention by soils and clays is correct (Dyal and Hendricks, 1949; Bower and Gschwend, 1952). In turn, a reasonable conformation between a calculated value and an experimental value for the surface area of a soil may suggest adsorption with a monomolecular character. The type of silicate clay minerals is believed to be less important than the surface area or degree of weathering in controlling the adsorption maximum of soils (Olsen and Watanabe, 1957).

In comparing the Langmuir and Freundlich isotherms to describe the adsorptive nature of soils (as well as other solid adsorbents), the following advantages favor the Langmuir isotherm: (1) the ability to calculate an adsorption maximum; (2) the ability to calculate (as a result of knowing the adsorption maximum) the amount of adsorbing surface area of a soil; and (3) the ability to find a constant related to the bonding energy of a soil for phosphate-P (Olsen and Watanabe, 1957).

The first use of the Langmuir equation was made to describe the adsorption of gasses on solid surfaces (Langmuir, 1918). Langmuir (1918) admitted that direct evidence did not exist that monomolecular adsorption, as described by his equations and isotherms, occurred on the surfaces of solids. Langmuir believed that solids should not have a greater tendency to adsorb more than a monolayer of molecules than a liquid adsorbent, a fact acceptable prior to Langmuir's work (Harkins, Brown, and Davies, 1917; Harkins, Davies, and Clark, 1917). Langmuir did show that the adsorption of hydrogen gas upon the smooth surface of glass obeyed homogeneous monomolecular adsorption. Although the Langmuir isotherm has since been modified to describe the adsorption of liquids or ions in solution upon solids, such as phosphate-P upon the surfaces of calcium carbonate (Cole et al, 1953), clays (Russell and Low, 1954), and soils (Fried and Shapiro, 1956; Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Woodruff and Kamprath, 1965), the theoretical validity of such adsorption being monomolecular in nature is not conclusive (Langmuir, 1918; Olsen and Watanabe, 1957).

The amount of phosphate-P adsorbed by a soil surface according to the Langmuir isotherm from a phosphating solution was verified with the use of isotopic phosphate exchange to measure the amount of surface phosphate on equilibrated soil (Fried and Shapiro, 1956; Olsen and Watanabe, 1957). This suggests that at least for some soils adsorption of P from the soil solution obeys the mathematical assumptions of the Langmuir equations and isotherm. Whether monomolecular layers are in actuality formed on the surface of the soils without adsorbate interaction is debatable (Olsen and Watanabe, 1957).

In obtaining adsorption data the soil:solution ratio had little

effect upon the Langmuir isotherm within reasonable limits (Olsen and Watanabe, 1957). It appears that the value of $C/(x/m)$, a ratio of the equilibrium solution concentration (C) to the amount of P adsorbed per unit soil (x/m), is affected by the existing soil:solution ratio. Whether the ratio is critical to a single value is not known, but the work of several researchers indicate that soil:solution ratio experiments should be undertaken and a single ratio chosen (Russell and Low, 1953; Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Woodruff and Kamprath, 1965).

Because actual soil samples have surface sites with adsorbed P at them, i.e., indigenous adsorbed P, the method used to determine P adsorption by soil must be corrected. To correct the equilibrium P concentration on the soil for indigenous surface P, the initial P can be extracted, the amount measured, and added to the value of P adsorbed $((x/m)$, mg of P per g of soil) (Olsen and Watanabe, 1957). When the indigenous P in a soil is small, the ultimate correction is minor (Olsen and Watanabe, 1957).

Isotopic phosphate exchange (P-32) and resin adsorption are methods by which P on the surface sites of soil can be measured quantitatively. This is extremely helpful when the measurement of indigenous surface P is desired to correct adsorption data. The fraction of the adsorbed P which is in ready equilibrium with solution P-32 is related to the equilibrium P concentration according to the Langmuir isotherm (Olsen and Watanabe, 1957). It has been suggested that P-32 exchange be used as a method of measuring the "soil quantity factor" for P, and the use of an anion-exchange resin to measure the "soil rate factor" for P, as it is depleted from the soil particles (Larsen, 1964). However, anion-exchange

resins have been used to measure both rate and quantity in relationship to the surface phosphate-P of soil.

<div align="center">

The Release of Phosphorus from Soil
onto an Anion-Exchange Resin

</div>

Methods of phosphorus extraction

The determination of the amount of phosphate-P available to plants from the soil has encouraged a search among soil chemists in recent years to develop an extracting method for soil inorganic P that will produce data which will adequately describe or simulate the adsorption of P by plant roots without (1) destroying or altering the chemical and structural integrity of the soil involved, and (2) altering the ability (quantity) or nature (rate) of the uptake or adsorption.

The major "non-destructive" experimental methods of extracting P from soils are (1) isotopic phosphate (P-32) exchange; (2) equilibrium phosphate concentrations (extractions in water solutions or in salt solutions ($NaHCO_3$)); and (3) the quantity of P removed by an anion-exchange resin (Cooke and Hislop, 1963).

Isotopic phosphate exchange, the use of P-32 to exchange with phosphate groups on soil sites, has been shown to simulate the removal and uptake of phosphate by plant roots (Olsen and Watanabe, 1957). However, phosphate-P transfer from the soil site to the plant root is a one-way process, when there is no phosphate for phosphate replacement from the soil solution. The isotope exchange procedure depends on P-replacement as a means of measuring the amount of available P in the soil (i.e., the amount of P-32 removed from solution, or the amount that can be adsorbed by the plant root) (Amer et al, 1955; Cooke and Hislop, 1963).

The adsorption of soil P by an anion–exchange resin releases anions from the resin sites, but these anions do not necessarily exchange sites with the soil P, rather they remain in solution to stabilize or control the pH of the suspension (Amer et al, 1955; Cooke and Hislop, 1963; Larsen, 1964).

The methods by which P is extracted from soil in water solutions or in dilute salt solutions are not effective over a wide range of P concentrations, and are best employed when P concentrations are small (Cooke and Hislop, 1963). Thompson et al (1960) found that salt solutions, as well as destructive techniques using acids as a part of the extracting procedure, were not as effective as isotopic phosphate exchange in predicting yields of P in crops from samples of the soil in which the crops were grown. However, it was also found that extractions of P by quantities of water were more accurate than isotopic exchange. Likewise, Moser, Sutherland, and Black (1959) found that the $CaCl_2$ and the phosphate potential methods of Schofield (1949) and Aslyng (1954), the $HCl-NH_4F$ method of Bray and Kurtz (1945), and the $NaHCO_3$ method of Olsen et al (1954) (all four methods are outlined by Moser) were not as accurate in predicting yields from soil samples analyzed as was the anion–exchange resin method employed to remove available P from the soil.

Amer et al (1955) showed that the extraction of soil P by an anion-exchange resin is well correlated to the P–extraction method of Kurtz and Bray (1945) and the isotopic dilution technique of Fried and Dean (1952). In addition, Moser, Sutherland, and Black (1959) showed that the quantity of P released from soils to resin is well correlated with the uptake of P by a crop grown in those soils. Cooke and Hislop (1963) found a correlation coefficient of 0.91 existed between plant uptake

and resin uptake of P. Larsen (1964) stated that a correlation coeffi-
cient of 0.73 was found between P uptake by plants and the rate of soil
phosphate dissolution by the resin method. This agreement suggested
that the rate by which P comes into solution at least in part influences
the uptake of P by plants.

The use of an anion-exchange resin

Amer et al (1955) found that the capacity of anion-exchange resin
was quantitative at least upto values of 1000 micrograms (or 1.0 mg) of
P. For natural soils, the quantitative limits of the resin are more
than adequate.

Cooke and Hislop (1963) conducted experiments at different temper-
atures within the range of biological activity and found a distinct tem-
perature dependence existed for the resin with soil. However, the equi-
libration of samples was terminated after 16 hours, and no data were
given to indicate the equilibrium values for each temperature. A 4% in-
crease in the amount of P desorbed from soil onto the resin was found
for every degree of increase from 20 C.

The question of whether the pre-moistening of soil samples had a
statistical effect on the amount of P desorbed was investigated by Amer
et al (1955). They found that the pre-moistening of samples, and then
the air drying of those samples before resin extraction, did not encour-
age an increase in uptake of P by resin.

Amer also investigated the effects of soluble salts and pH on the
quantity of resin adsorption of P. Both Amer and Cooke and Hislop (1963)
recognized that the presence of salts in solution provided anions that
competed with phosphate ions for sites on the resin particles. This

condition increases the concentration of P in solution, and in turn re-
duces the concentration gradient across the water film surrounding the
resin. Linear regression indicated that the effect of salt does
not significantly affect the adsorptive capacity of the resin, even in
arable soils (Amer et al, 1955). Cooke and Hislop suggested that the
competition of soluble salt anions for surface sites on the resin is re-
duced by increasing the volume of the suspension.

Amer found that pH of the suspension significantly influenced the
amount of P adsorbed by the resin between the values of 4.0 and 5.5.
Above 5.5, any variation was attributed to experimental error. The va-
riation of adsorption with pH was attributed to the effect of pH on the
diffusion coefficient of the P, and was not the result of any character-
istic of the resin. Amer and Larsen (1964) showed that the anion-ex-
change resin tends to maintain pH constant in the soil suspension dur-
ing adsorption, with the release of anions to solution as phosphate is
adsorbed onto the resin.

The resin:soil ratio was investigated by Amer et al (1955) to find
the ratio which produced the greatest or maximum rate of P uptake from
the soil. Ratios which favored the resin by weight (2.0) or an equal
ratio of resin to soil appeared to show the greatest uptake of P from
the soil solution.

The interpretation of the nature of adsorption
of an anion-exchange resin

The development and critical testing of the anion-exchange resin
as a method of removing P from soil was achieved by Amer et al (1955),
who, among other things, showed that under certain conditions the rate

of uptake of P by the resin was only dependent upon the rate of release of P from the soil and not on the properties of the resin.

Amer hypothesized that the rate controlling process in adsorption (soil P to resin) was diffusion, and conducted experiments to find whether this rate of diffusion was due to adsorption within the resin (i.e., a function of the resin) or was proportional to the P concentration in solution (i.e., not a function of the resin). The work of Boyd, Adamson, and Myers (1947) provided evidence to support their claim that the diffusion of P within the resin particles was not responsible for controlling the adsorption of P onto the resin and provided an equation which described that adsorption. Amer found experimental data produced a straight line when plotted according to the equation of Boyd, Adamson, and Myers:

$$- \log (1 - (C_o/C)) = kt$$

The value of C_o is equal to the concentration of P adsorbed by the resin at any time t, while C represents the concentration of P adsorbed by the resin at equilibrium. The value of k is associated with the rate of uptake of P by the resin (i.e., the total rate constant of the P uptake by the resin). Linear agreement with the equation above indicated that the rate controlling step, if diffusion, was not a function of (adsorbed) P within the resin, but rather a function of a process occurring in the solution surrounding the resin particles.

The limiting rate factor can then be attributed to one of two phenomena in the soil solution: (1) the rate of diffusion through a thin film of solution surrounding the resin particles, or (2) the rate of ion exchange. The limiting rate factor was delineated by Amer et al (1955),

who found a three-point linear relationship between the P adsorbed by the resin over a single period of time and the P concentration of the solution.

Amer proposed that the rate of diffusion through the interstitial film of water around the resin was responsible for controlling the process of adsorption, rather than ion exchange itself. Their experiments demonstrated that adsorption increased as stirring was increased, a condition that would not affect quantities of adsorption if actual exchange were the limiting factor. Li et al (1972) also attributed the rate determining step to diffusion outside the resin particles, to either film diffusion or intraparticle diffusion.

Amer et al (1955) found that the uptake of P by anion-exchange resin followed a curve that increased very rapidly from time zero and then slowly levelled off as time progressed. They attributed the curve to three simultaneous first-order reactions, the slow and intermediate reactions complete within 72 hours and a very fast reaction complete within two hours. Li et al (1972) also found three first-order reactions of varying rate when exchanging isotopic P (P-32) of solution for surface P of lake sediments. The rate plots for these exchanges demonstrated curves with two distinct breaks in them when plotted to show the removal of isotopic inorganic P from suspension with time to equilibrium. The calculation of the rate constants was achieved in much the same manner as Amer, who found the rate of the slowest reaction by assuming that the other two faster reactions ceased before equilibrium was reached for the third. McAuliffe et al (1948) plotted similar data for isotopic P exchange, but attributed the adsorption to two simultaneous first-order reactions, rather than to three. However, McAuliffe reported only two data points at

time of less than one hour (5 and 30 minutes), which might explain the absence of a fast, short-termed reaction.

Larsen (1967) stated that the agreement between experimental data and the "parabolic diffusion law" (Laidler, 1965) as reported by Cooke (1966) indicated that the rate of P release from soil was controlled by a diffusion step.

THEORY

Equilibrium Adsorption

The Langmuir equations and isotherms

Irving Langmuir (1918) developed an expression for the equilibrium adsorption of gas molecules at constant temperature. Langmuir defined surface adsorption at equilibrium as a "dynamic process" (Brunauer, Copeland, and Kantro, 1967, p. 77) where (at equilibrium) the amount adsorbed has a definite value. Molecules which directly strike the uncovered surface of the adsorbent remain there, or if they acquire enough energy to leave the surface, they are replaced by other molecules striking that uncovered surface. In 1918, Langmuir published his empirical equations and the first experimental data for substantiating their mathematical, if not actual, validity.

According to the kinetic-molecular theory of gases (Barrow, 1966), the rate at which gas molecules (the adsorbate) come in contact with the solid surface (the adsorbent) is defined by the equation:

$$m_g = \sqrt{\frac{M}{2\pi RT}} \ (P) \qquad\qquad [1]$$

where: m_g = the number of grams of gas molecules striking cm^2 of area
on the adsorbent per second ($g/cm^2/sec$)

M = the molecular weight of the gas ($g/mole$)

R = the universal gas constant (8.31×10^7 ergs/degree/mole)

T = the absolute temperature (degrees K)

The number of gram-molecules (grams per molecule) of gas striking each cm^2 of area on the adsorbent is defined by μ:

$$\mu = \frac{m_\text{B}}{M} = \frac{P}{\sqrt{2\pi MRT}} \qquad [2]$$

By incorporating the constant values of the equation above, the relationship becomes:

$$\mu = 4.375 \times 10^{-5} \frac{P}{\sqrt{MT}} \qquad [3]$$

According to Langmuir, the rate of adsorption of molecules per unit area (R_a) is expressed by the identities below (Langmuir, 1918; Brunauer, Copeland, and Kantro, 1967):

$$R_a = \alpha_o (1 - \theta_1) \mu \qquad [4]$$

$$R_a = \alpha_o \theta \mu \qquad [5]$$

where: θ_1 = the fraction of the surface covered by the adsorbed molecules

$\theta = (1 - \theta_1)$ = the fraction of the surface uncovered by molecules

α_o = the ratio of the number of molecules of gas which hit uncovered surface sites without striking adsorbed molecules to the total number of collisions by molecules with the surface; or "condensation coefficient" (Brunauer, Copeland, and Kantro, 1967, p. 78)

It is important to note two things concerning the rate of adsorption. First, the expression α_o was considered by Langmuir to be very close to unity. This assumption was made because the occurrence of "elastic collisions" with uncovered surface sites was considered to be rare (Brunauer, Copeland, and Kantro, 1967, p. 78). And second, at equilibrium the

maximum concentration of the adsorbate molecules on the surface of the
(solid) adsorbent is nearly equivalent to a monolayer of (gas) molecules
and has a definite value (Langmuir, 1918; Brunauer, Copeland, and Kantro,
1967). According to Langmuir, it is not possible for a second layer of
molecules to exist on the surface of the adsorbent. Molecules striking
already adsorbed molecules are "elastically reflected" back into the gas
phase (Brunauer, Copeland, and Kantro, 1967, p. 78). Langmuir (1918)
further stated that the forces which could exist between the surface
monolayer and a subsequent second layer of adsorbed molecules is slight
compared to the forces existing between the solid surface and the mono-
layer molecules.

In order to complete this theory regarding the kinetic-monomolecular
nature of the solid-gas interface, some basic assumptions must be made:

1. Only one type of adsorbing surface exists on the solid, or the
   adsorbing surface has uniform sites. Therefore, all surface
   sites experience a constant heat of adsorption or constant en-
   ergy level.

2. No interaction occurs between adsorbed ions on the surface,
   neighboring ions are independent of one another. An adsorbed
   molecule does not affect a neighboring site.

3. None of the adsorbate initially present in solution or in the
   gas phase is considered adsorbed (Brunauer, Copeland, Kantro,
   1967; Boyd, Schubert, and Adamson, 1947).

The number of molecules desorbing or "evaporating" (Langmuir, 1918,
p. 1369) from a square cm of surface of the adsorbent per unit of time
is represented by v, and is a function of the amount of energy existing
between the surface of the solid and the molecules (not, however, energy

between molecules, which Langmuir considered to be theoretically non-existent on uniform surfaces; or, in other words, Langmuir assumed energy to be directed in one direction only: downward, from adsorbate to the surface site). The term v is therefore expressed by the equation below (Langmuir, 1918; Brunauer, Copeland, and Kantro, 1967):

$$v = k_o e^{-q/RT} \qquad [6]$$

where: k_o = a function of temperature, dependent upon the entropy of adsorption

q = the heat of adsorption

The heat of adsorption can be equated to the heat released when a molecule is adsorbed at a surface site. Therefore, in order for the molecule to desorb from the surface, at least an equal amount of heat energy must be attained by the adsorbate molecule (Brunauer, Copeland, and Kantro, 1967):

$$R_d = v\, \theta_1 \qquad [7]$$

At equilibrium, the rate of adsorption of gas molecules to the surface or the rate of "condensation" is equal to the rate of desorption or rate of "evaporation." Therefore:

$$R_a = R_d \qquad [8]$$

and from [5] and [7]:

$$\alpha_o\, (1 - \theta_1)\, \mu = v\, \theta_1 \qquad [9]$$

When the above equation is solved for θ_1, the ratio of surface sites which are occupied to the total number of surface sites, the expression becomes:

$$\theta_1 = \frac{\alpha_o \, \mu}{v + \alpha_o \, \mu} \qquad [10]$$

Division produces a new expression:

$$\theta_1 = \frac{\alpha_o \, \mu}{v} \Bigg/ (1 + \frac{\alpha_o \, \mu}{v}) \qquad [11]$$

Equations [2] and [6] give equivalent values for μ and v, respectively, and these values help define $(\alpha_o \, \mu/v)$ (from equation [11]) below:

$$\frac{\alpha_o \, \mu}{v} = \frac{\alpha_o (P/\sqrt{2\pi MRT})}{(k_o e^{-q/RT})} \qquad [12]$$

or, by rearrangement:

$$\frac{\alpha_o \, \mu}{v} = \frac{P(\alpha_o/\sqrt{2\pi MRT})}{(k_o e^{-q/RT})} \qquad [13]$$

Rate constants of adsorption and desorption, here defined to be K_1 and K_2, respectively, can be expressed from the values of equation [13]:

$$K_1 = \frac{\alpha_o}{\sqrt{2\pi MRT}} \qquad [14]$$

$$K_2 = k_o e^{-q/RT} \qquad [15]$$

The value of (K_1/K_2) is expressed as the Langmuir constant, and for increasing pressure, it is represented by b:

$$K_1/K_2 = b \qquad [16]$$

From equations [13], [14], [15], and [16], the following expression may

be derived:

$$\frac{\alpha_o \mu}{v} = bP \tag{17}$$

From equations [11] and [17], the ratio of surface sites which are occupied to the total number of surface sites, or θ_1, becomes equivalent to the following:

$$\theta_1 = \frac{bP}{1 + bP} \tag{18}$$

Equation [18] is the expression used with the increasing pressure of a gas. This equation, when expressed for increasing concentration of ions in solution, becomes:

$$\theta_1 = \frac{kC}{1 + kC} \tag{19}$$

where: k = the Langmuir constant

  C = the concentration of the adsorbate

Langmuir considered b or k to be a constant. Therefore, $k_o e^{-q/RT}$ is a constant as well (Brunauer, Copeland, and Kantro, 1967). This assumption implies that q, the heat of adsorption, is also constant, as can be seen from equation [13].

The practical applications of the Langmuir equations in measuring the relationship between adsorbed molecules and pressure on the gas phase system has been defined and restated numerous times in recent literature. Specifically, the use of the Langmuir equation to express the relationship existing when phosphate-P is adsorbed from the liquid phase by clay minerals, calcium carbonate, and soil samples are quite popular among agronomic and soil chemistry researchers.

The term θ_1 expresses the fraction of molecules adsorbed by a surface at any concentration (or pressure). If (x/m) represents the amount of adsorbate (mg) per amount of adsorbent (g), and x_m represents the calculated or experimental adsorption maximum (in this case, the amount of adsorbate needed to create a monolayer of molecules on the surface of the solid), then the following must be true:

$$\theta_1 = \frac{(x/m)}{x_m} \qquad [20]$$

and from equation [19]:

$$\frac{(x/m)}{x_m} = \frac{kC}{1 + kC} \qquad [21]$$

Researchers have tested the mathematical validity of this essentially empirical expression and found it to be true for specific types of adsorption. However, it has been noted that in actuality these specific adsorptions may not follow the Langmuir model, even though they do follow the isotherm equation he developed. It is believed that compensating factors or values within the Langmuir expression allow for its mathematical validity, while the expression is a statement of idealized theoretical adsorptive behavior (Brunauer, Copeland, and Kantro, 1967).

The solid-liquid adsorption isotherm is developed from the linear derivation of the Langmuir expression:

$$\frac{C}{(x/m)} = \frac{1}{x_m k} + \frac{C}{x_m} \qquad [22]$$

or

$$\frac{C}{(x/m)} = \frac{1}{x_m} C + \frac{1}{x_m k} \qquad [23]$$

where: $(1/x_m k)$ = the intercept

   $(1/x_m)$ = the slope

The isotherm is constructed by plotting $C/(x/m)$ against C.

At small concentrations (or at low pressures) the amount of adsorbate adsorbed is linearly proportional to the concentration (or pressure). The phenomenon can be observed by examining the Langmuir expression:

$$\theta_1 = \frac{kC}{1 + kC} \tag{19}$$

At small values of C, $(1 + kC)$ tends toward a unity value:

$$(1 + kC) \simeq 1 \tag{24}$$

or

$$\frac{kC}{1 + kC} \rightarrow kC \tag{25}$$

At large values of C, (kC) tends to differ only slightly from the value of $(1 + kC)$:

$$(1 + kC) \simeq kC \tag{26}$$

or

$$\frac{kC}{1 + kC} \rightarrow 1 \tag{27}$$

The Release of Phosphorus from Soil

onto an Anion-Exchange Resin

Reaction kinetics

Reaction kinetics applied to the release of P from soil found using a strong anion-exchange resin required calculations involving two and three simultaneous first-order reactions.

A graphical resolution to express the depletion of the adsorbate (P) from the suspension onto the adsorbent (resin) and to observe and postulate the kinetics involved in the desorption can be constructed by plotting $\log (C_o - C)$ vs time to equilibrium of the system, where C_o represents the initial surface concentration (of P) at time 0 on the soil which is later removed and C is the concentration of P on the resin at any time t. The first-order kinetics of isotopic P-exchange were shown graphically in this manner by McAuliffe et al (1948). Such a plot for total data should reveal a curve of two slopes, and a rather distinct break between the two, if two simultaneous first-order reactions are occurring at different rates. If one distinctive break cannot be denoted, and an attempt to provide the curve with two slopes also proves fruitless, three reactions may be occurring at the same time, each with its own rate.

The release of P from soil under saturated conditions has been interpreted by Amer et al (1955), who reported the derivation of equations describing three simultaneous first-order reactions. Each reaction is described by the following equations:

$$\log (C_o - C) = \log C_n + \log 10^{-k_n t} \quad [1]$$

[28]

and

$$\log (C_o - C) = - k_n t + \log C_n$$

[29]

where: C_o = the initial amount of adsorbate (surface P) in ppm or mg/l

C = the amount of adsorbate (P) released in ppm or mg/l

t = time in seconds

k_n = the rate constant of a single reaction n in 1/sec

C_n = the initial amount of adsorbate (surface P) due to reaction n in ppm or mg/l

When the log of $(C_o - C)$ is plotted against time, the slope of that line is defined as being the negative of the rate constant of a specific reaction, and the intercept the log of C_n.

It is important to specify that the values of C_o and C, contrary to previous quantitative definition, are variable and change for each of the three reactions they describe. For the slowest of the reactions, C_o is equal to the sum of the release maximums of all three reactions (or the amount of adsorbate initially on the surface (of the soil) that will be removed by the reactions). For the slow reaction C is equal to the total amount of adsorbate removed by all three reactions at any specific time during removal.

Equation [29] can be modified to show the form and quantities used to find the rate and adsorption maximum of the slow reaction:

---

[1]This equation appears incorrectly in Amer et al (1955), but other equations tend to support this integrated root equation.

$$\log (C_{o(1+2+3)} - C_{(1+2+3)}) = -k_3 t + \log C_3 \qquad [30]$$

In the same manner, the specific equations that are used for the inter-
mediate and fast reactions can be expressed:

$$\log (C_{o(1+2)} - C_{(1+2)}) = -k_2 t + \log C_2 \qquad [31]$$

$$\log (C_{o(1)} - C_{(1)}) = -k_1 t + \log C_1 \qquad [32]$$

For the slow and intermediate reactions there are two unknowns, that of
C_n and k_n. However, the fast reaction has only one unknown, k_1, as C_1
is found previously $((C_1 + C_2) - C_2)$ with the resolution of equation
[31].

Larsen (1967), reporting the work of Cooke (1966), claimed that if
a linear relationship existed between C and the square root of time, it
indicated that the rate of P release from soil was controlled by a dif-
fusion step, presumably through the "static water film" which surrounds
solid particles, even when they are shaken in suspension. The relation-
ship described above is indicated by the following linear equation, a
variation of the "parabolic diffusion law" (Laidler, 1965):

$$C = R\sqrt{t} + \text{constant} \qquad [33]$$

The value of R, the universal gas constant, is expressed in kcal/degree-
mole and t is expressed in minutes.

The activation energy of desorption

Arrhenius was able to develop an expression which related the rate
constant k of a single reaction n to the temperature T (degrees K) of

the system by this equation (Laidler, 1965):

$$\frac{d\ln k_n}{dT} = \frac{\Delta E}{RT^2}$$ [34]

where: ΔE = the change in energy with temperature (or according to the

suppositions of Arrhenius, the increase in energy with an

increase in temperature)

Integrating equation [34] gives the linear form of the expression:

$$\ln k_n = \frac{-\Delta E_d}{RT} + \text{constant}$$ [35]

The activation energy of desorption, ΔE_d in kcal/mole, is found by plot-

ting $\ln k_n$ vs $1/T$. The slope of the line is the negative of the activa-

tion energy over R, the universal gas constant (in kcal/degree-mole).

The difference between the activation energies of desorption and adsorp-

tion is equal to the thermodynamic integral heat of adsorption, ΔH.

EXPERIMENTAL PROCEDURE

Measurement of Equilibrium Phosphate Adsorption

Adsorption data for plotting the Langmuir isotherms were obtained
by shaking soil samples of equal mass with phosphate-P aqueous solutions
of varying concentrations until equilibrium was reached.

The soil used for this study was a typic calciorthid Thiokol silt
loam, taken next to the Desert Biome research site at Curlew Valley,
Utah. Two sampling depths, or horizons, were used: the surface crust,
from 0 to 3 cm in depth, which represented the highest measured avail-
able P level of any layer within the accessibility of plant life (consi-
dered a depth of 46 cm); and a subsoil layer, from 28 to 40 cm in depth,
which represented the lowest measured level (Jurinak and Griffin, 1972).

Preliminary kinetic experiments were concerned with determining the
equilibration time period for the adsorption process. Subsoil samples
of equal mass (1.0 g) were shaken with 50 ml of a K_2HPO_4 phosphating so-
lution in a 125 ml Erlenmeyer flask in a constant temperature water bath
for various lengths of time from 0.5 minutes to several days. Equili-
brium was noted to occur between two and three days. A selection of five
days for a reasonable incubation period for the equilibrium adsorption
experiments seemed cautious and unobjectionable.

In addition, once an equilibrium time was established for the pro-
cess, a soil:solution ratio was determined. This ratio was found by
equilibrating numerous amounts of the subsoil, from 0.50 g to 20.0 g,
with equal volumes and concentrations of phosphating solutions. The fi-
nal soil:solution ratio, that of 2.50 g of soil for 50 ml of solution,

was determined by the highest value calculated for the Langmuir isotherm expression $C/(x/m)$ - an indication of the smallest concentration of P adsorption possible with any soil:solution ratio. Among the ratios tested were the experimental ratios reported in the literature (Russell and Low, 1954; Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Woodruff and Kamprath, 1965).

The procedure for equilibrating the soil samples was performed essentially six times, excluding replications. For each of the two soil sampling depths, the equilibrium data were measured at three constant temperatures within the range of biological activity: 11, 25, and 40 C. The temperatures were maintained within ±0.5 degrees C. Each batch experiment measured contained 16 samples, and the concentrations of the phosphating solutions for these samples ranged from 1 to 50 ppm P.

Following equilibration, the phosphating solutions were decanted from each soil sample and centrifuged for 60 minutes at 10,000 rpm to separate remaining suspended soil particles from the supernatants. The supernatants were then decanted from the solid matter onto a Buechner funnel to filter organic matter and other floating material from them. The process of decolorizing the supernatants before analysis for P was not considered as separation from solid particles produced clear, colorless solutions.

The available, equilibrium phosphate-P concentrations of each of the samples were determined by the ascorbic acid method of Murphy and Riley (1962) as reported by Watanabe and Olsen (1965), using a Coleman spectrophotometer at a wavelength of 882 mμ.

The difference between the concentration (the amount) of P measured as being present in the soil solution and the concentration (the amount)

present before equilibrium was the measured amount of P adsorbed by the soil from the phosphating solution (Olsen and Watanabe, 1957). A final value for this amount was found by adjusting for the soil:solution ratio of the equilibrium solution. The accuracy of this value for adsorption at equilibrium is dependent on whether there exists a quantity of indigenous phosphate-P on the soil when it is equilibrated. If indigenous P is present, an adjustment must be made to account for it. Mathematically, the measured amount of adsorbed P is expressed by the equation below:

$$(x/m) = ((A - C)(V_1))/(M_s)$$

where: (x/m) = the amount of P (x, in mg) adsorbed per amount of soil (m, usually expressed in g)

A = the initial concentration of P in ppm or, more conveniently, mg per l

C = the final concentration of P in the soil solution after equilibration in ppm or mg per l

V_1 = the volume of the phosphating solution for each sample in l

M_s = the amount of soil for each sample in g

The surface areas of the two soil samples were measured using the ethylene glycol retention method of Bower and Gschwend (1952) derived from Dyal and Hendricks (1949). The surface soil layer was found to have an exposed surface area of from 108 to 122 m^2/g (3 batches, 3 replicates per batch), and the subsoil a surface area of from 103 to 115 m^2/g. While significant variation occurred between batches, replicates of a batch were measured to have nearly identical values.

Electrical conductivities of saturated extracts of the soil samples were found and the ionic strengths determined from the E.C. readings using the method of Griffin and Jurinak (1973). The E.C. of the surface soil was 0.886 mmhos/cm and the subsoil 2.272 mmhos/cm. The ionic strength of the surface soil was calculated to be 0.013 moles/l and of the subsoil 0.034 moles/l. The pH measurements for saturated pastes were 7.8 for the surface soil and 8.2 for the subsoil.

The calcium carbonate content of separate samples of soil was found by base titration. The lime content of the surface soil was found to be 12.0% and of the subsoil 38.7%.

The Measurement of the Release of Phosphorus
from Soil onto an Anion-Exchange Resin

Use was made of an anion-exchange resin to remove indigenous phosphate-P from the same soil used in the equilibrium study, that of the Desert Biome site at Curlew Valley. The primary purpose for conducting kinetic experiments with the resin on this soil was to help define the specific nature of phosphate at the solid-solution interface and its availability to removal (Amer et al, 1955, Boyd, Adamson, and Myers, 1947; Cooke and Hislop, 1963; Moser, Sutherland, and Black, 1959). Also, the quantitative value of the indigenous P adsorbed by the resin at equilibrium provided a correction factor for each value of the equilibrium phosphate adsorption data (x/m). The correction factor is meant to be an expression of the total amount of indigenous P present on the soil before equilibration with phosphating solution, and provides more accurate data points for plotting the Langmuir isotherms (Olsen and Watanabe, 1957; Rennie and McKercher, 1959).

Amer et al (1955) indicated that an anion-exchange resin provides an infinite sink for P from soil. In addition, Cooke and Hislop (1963) stated that the anion-exchange resin simulates plant root uptake as isotopic phosphate does not. The primary difference between these two methods is that isotopic exchange replaced--ion for ion--an isotope of phosphate for surface, or indigenous, phosphate on the soil, while the resin as the plant root, makes no exchange on the soil surface for the phosphate anion. The anion present on the resin, in this case a carbonate anion, is released to the soil solution to maintain a stabilized solution pH.

The anion-exchange resin used for these adsorption experiments was Dowex (a Dow Chemical trademark) 1-XB (Baker lot 35412). The resin was rinsed with distilled water numerous times before use, and saturated with reagent grade calcium carbonate. The resin was not sieved to eliminate small or broken particles, nor was it dried with acetone following water applications as was performed by Cooke and Hislop (1963).

Soil samples of 1.0 g each were placed with 2.0 g of moist resin in 250 ml Erlenmeyer flasks with a 100 ml volume of distilled water, such that release took place under saturated conditions, and shaken for various lengths of time from 0.50 minutes to equilibrium at five days. For each sample, the resin was separated from the soil particles, and the P removed from the resin for quantitative analysis.

It was believed that a broad spectrum of time intervals was established for the evaluation of release rate or rates, and the reaction or reactions that describe them. The longest time increment was equivalent to the time of equilibration determined for the soils with phosphating

solutions and, at that period of time, the resin was to have adsorbed all of the available phosphate of the soil surfaces.

The resin was separated from the soil by a 60-mesh sieve, which accepted the soil and not the larger resin particles, and was then thoroughly rinsed with distilled water and placed on filter paper (Whatman 42 (slow filter speed) Ashless, 9.0 cm) over a funnel with a flexible plastic stem attached to it. The effective grinding of soil particles, such that they passed through the 60-mesh sieve before being shaken with resin particles in solution, was a necessity to assure that the soil would pass through the sieve upon washing of the resin.

Treatment with 40 ml of a 1.0 N Na_2SO_4 solution (Cooke and Hislop, 1963) removed the P from the resin, and the resulting solution containing the available P was evaluated by the ascorbic acid procedure of Watanabe and Olsen (1965), using a Coleman spectrophotometer at a wavelength of 882 mμ. The Na_2SO_4 solution was held in the funnel for a 24-hour period by clamping the flexible stem to saturate the resin.

Another method endorsed in the literature involved digesting the resin with H_2SO_4, treatments of H_2O_2, and finally with $HClO_4$ (Amer et al, 1955).

RESULTS AND DISCUSSION

Equilibrium Phosphate Adsorption

Figures 1 and 2 show the raw data for equilibrium phosphate adsorption for the surface soil layer and a subsoil layer of Thiokol silt loam, respectively. The adsorption data were collected for each soil at three temperatures: 11, 25, and 40 C. The effect of increasing the temperature is to increase adsorption, which indicates that the reaction process is endothermic. Each graph has been divided into two regions. These regions are defined by the isotherms developed from the application of the linear form of the Langmuir equation (equation [23]) to the adsorption data. These data are shown in Figures 3 and 4, and confer that the application of the Langmuir equation to phosphate adsorption generates two linear curves. The existence of two linear regions suggests that two types of reactions may be occurring at the solid-liquid interface during adsorption.

The first reaction or slope is attributed to surface adsorption as originally defined by Langmuir, where the phosphate ions interact with the clay and lime mineral surfaces at definite sites. The second slope, labelled as Region 2, is considered to be the result of possibly a composite reaction, that of continued interfacial adsorption together with the initiation of calcium or magnesium phosphate nucleation on the surfaces of the soil lime particles. Evidence for the nucleation hypothesis is supplied by Figures 1 and 3, which show that a gross deviation from expected values exists in Region 2 for the surface soil at 40 C. Phosphorus is removed from solution in greater amounts than predicted
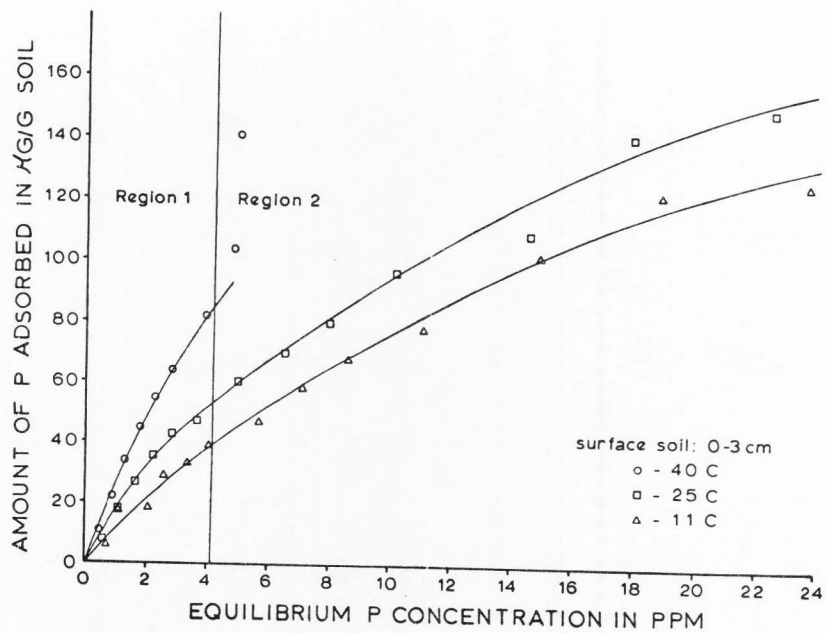
Figure 1. Adsorption isotherms for phosphorus interaction with the surface layer of Thiokol silt loam.
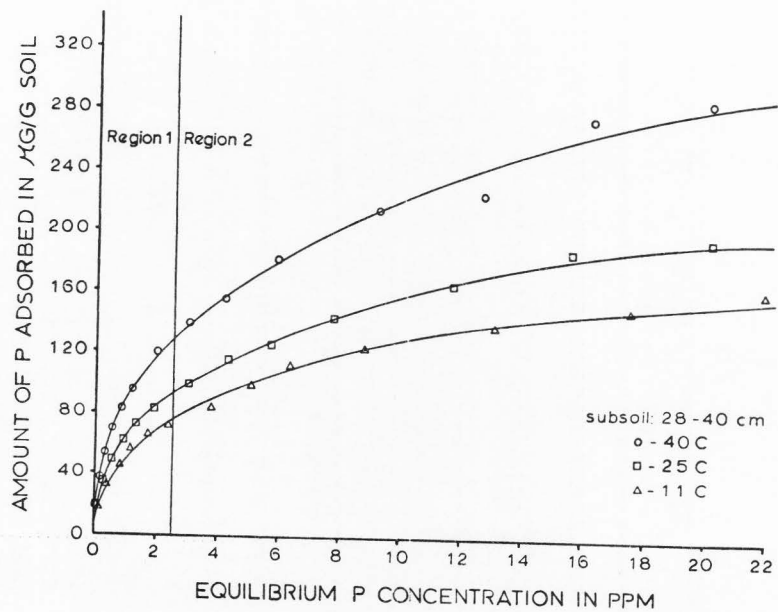
Figure 2. Adsorption isotherms for phosphorus interaction with a subsoil layer of Thiokol silt loam.
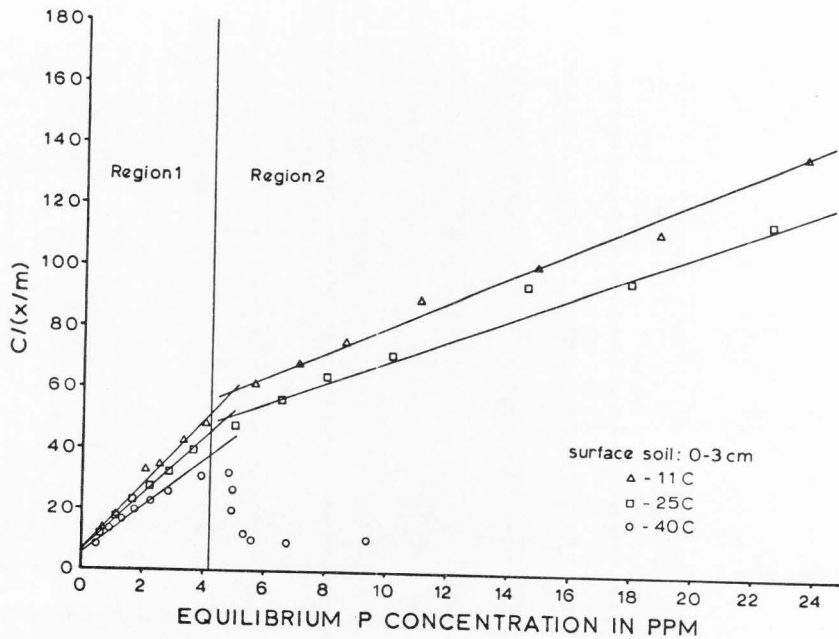
Figure 3. Phosphorus adsorption data for the surface soil plotted according to the Langmuir isotherm equation.
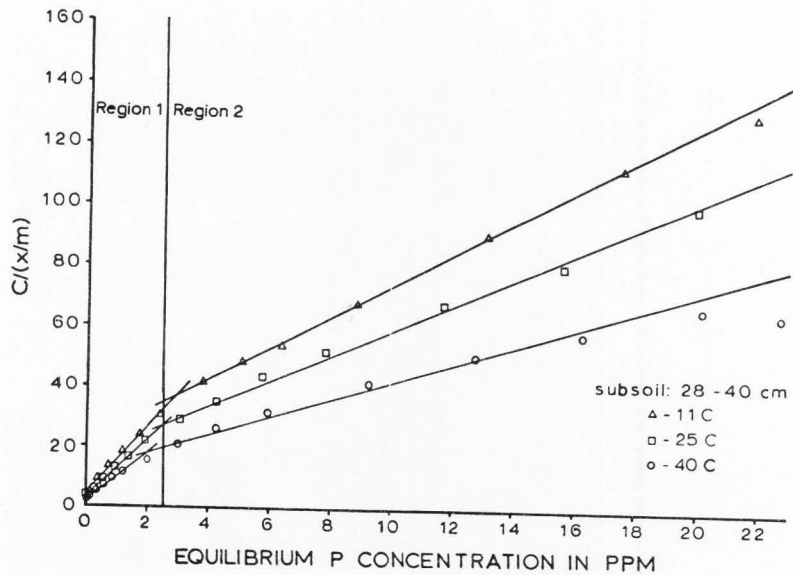
Figure 4. Phosphorus adsorption data for the subsoil plotted according to the Langmuir isotherm equation.

for this soil and temperature as a result. This phenomenon can be explained by the precipitation of metal phosphates, which occurs as a direct result of a higher temperature in the presence of a limited number of nucleating sites on the lime crystal faces. These data appear to corroborate the findings of Griffin (1973), who studied phosphate interaction with calcite.

In general, three statements can be made concerning the equilibrium adsorption data shown in Figures 1-4. First, P adsorption in both the surface soil and subsoil increases as the temperature increases. Second, the subsoil has a greater adsorptive capacity for P than does the surface soil. This is probably caused by the higher lime content in the subsoil. The lime contents of the surface soil and the subsoil are 12.0% and 38.7%, respectively. Finally, at least two mechanisms are operating in P adsorption in both soil samples. The initial reaction is considered to be simple adsorption, where the activity of Region 2 also involves the heterogeneous nucleation of metal phosphate on the lime mineral surfaces.

The data shown in Figures 3 and 4, that of data plotted according to the Langmuir isotherm equation, have been corrected for indigenous soil P. The importance of correcting the raw P adsorption data for indigenous P in soils is shown in Figure 5. Typical corrected and uncorrected adsorption data for the surface soil are shown plotted according to the Langmuir isotherm. As expected, uncorrected data report adsorption quantities less than actual. In addition, correction for indigenous P produces a much better fit of the Langmuir isotherm, particularly at low P concentrations. The correction for the subsoil is much less
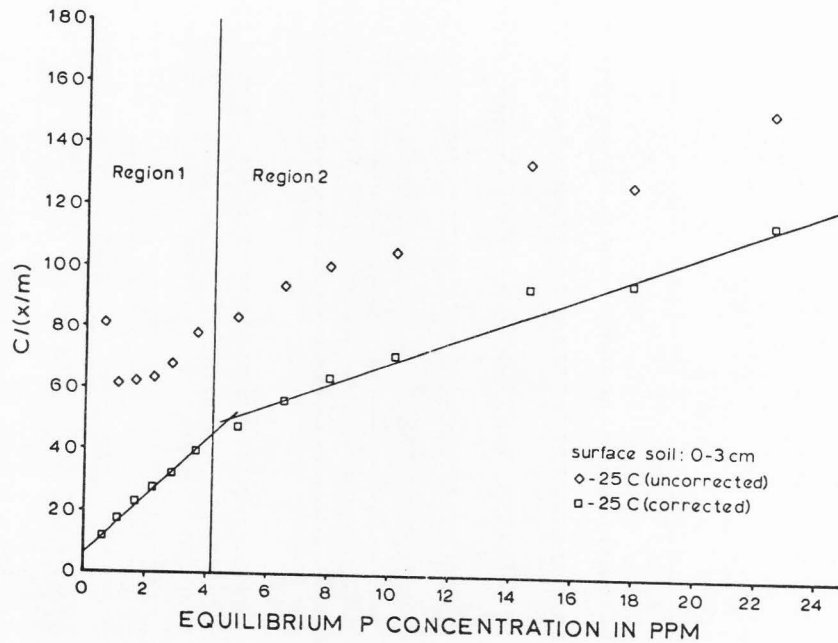
Figure 5. Uncorrected and corrected adsorption data for the surface soil at 25 C plotted according to the Langmuir isotherm equation.

dramatic, but significant. The surface soil contains nearly six times the amount of indigenous P as did the subsoil.

Table 1 reports equilibrium adsorption data for the two samples of Thiokol silt loam at three temperatures. Each set of data includes the following information: (1) the linear equation of the Langmuir isotherm, (2) the correlation coefficient of the points of the isotherm, (3) the Langmuir constant (k), (4) the adsorption maximum (μg P/g soil) for adsorption according to Langmuir, and finally (5) the correction factor for indigenous P (μg P/g soil) for the two soil horizons as found by equilibrating the soils with anion-exchange resin.

The Release of Phosphorus from Soil
onto an Anion-Exchange Resin

Reaction kinetics

The results of the kinetic experiments using an anion-exchange resin to remove indigenous P from the surfaces of Thiokol silt loam are shown in Figures 6 and 7. The data are for the surface soil and the subsoil, respectively, and, in each case, the reported release values are for three temperatures: 11, 25, and 40 C. The data show that upto 2800 minutes (46.5 hours) P release shows little temperature dependence. Figures 8 and 9 show the release during the initial 4 hours of uptake. For this increment of time the effect of temperature is slight though, with the rate of release greater as temperature is increased. Considerably more P was released from the surface soil than from the subsoil at all temperatures.

Figures 10 and 11 show the release data of P from the two soils plotted for kinetic interpretation. Only the 40 C release data are

Table 1. Equilibrium Adsorption Data for Thiokol Silt Loam

surface soil: 0-3 cm

T	linear equation	r	L. const. (k)	ads. max. (x_m) $(\mu g/g)$
11 C	y = 10.40x + 7.54	.989	1.38	96.2
25 C	y = 8.97x + 7.12	.997	1.26	111.5
40 C	y = 7.21x + 6.31	.991	1.14	138.7

Indigenous P $(\mu g/g)$ = 45.6

subsoil: 28-40 cm

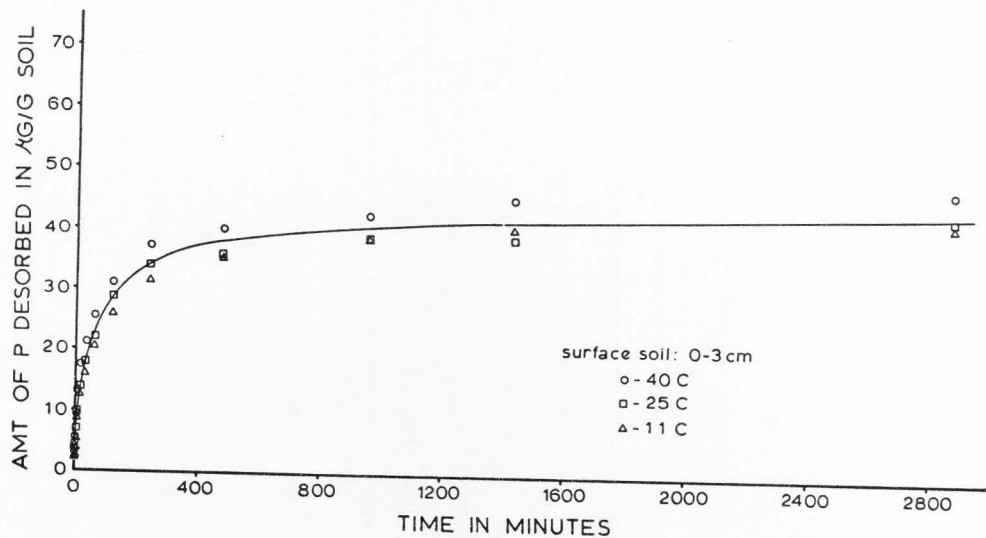| T	linear equation	r	L. const. (k)	ads. max. (x_m) $(\mu g/g)$
11 C	y = 10.89x + 4.64	.995	2.35	91.8
25 C	y = 9.68x + 3.52	.995	2.75	103.3
40 C	y = 8.11x + 2.23	.993	3.64	123.3

Indigenous P $(\mu g/g)$ = 8.3

Figure 6. Kinetics of phosphorus release by an anion-exchange resin for the surface soil.
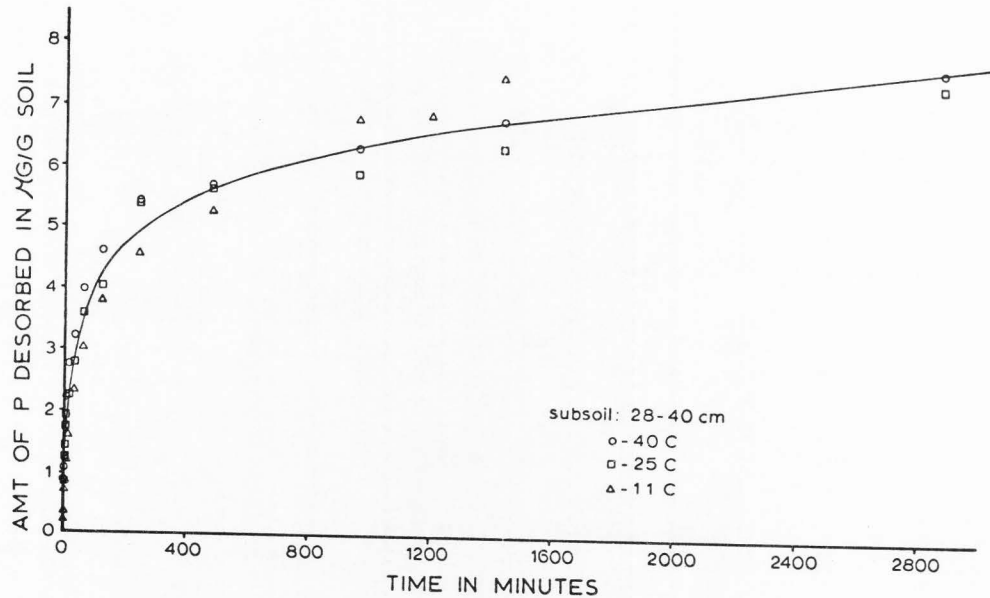
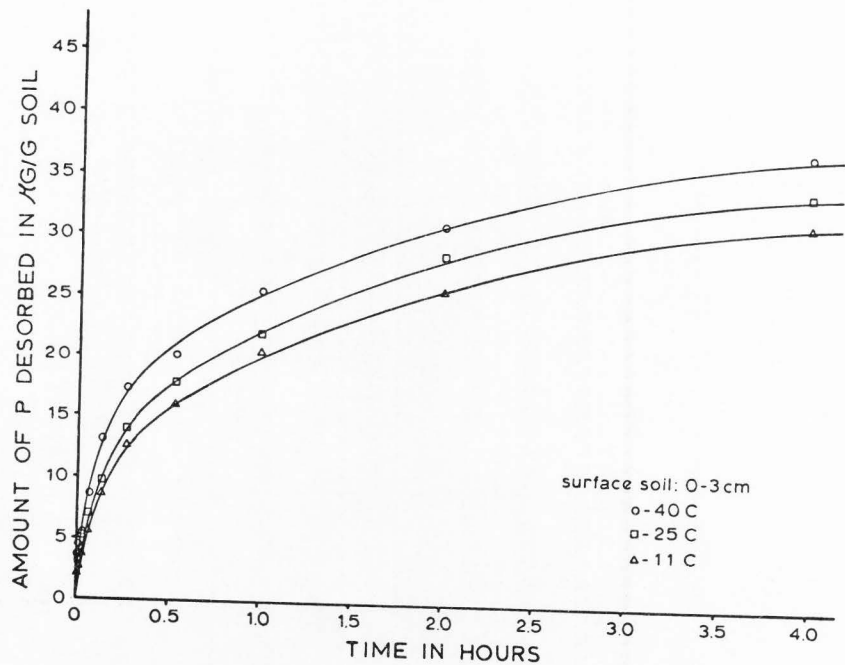Figure 7. Kinetics of phosphorus release by an anion-exchange resin for the subsoil.

Figure 8. Kinetics of phosphorus release by an anion-exchange resin for the surface soil showing the temperature dependence existing during the first 4 hours of uptake.
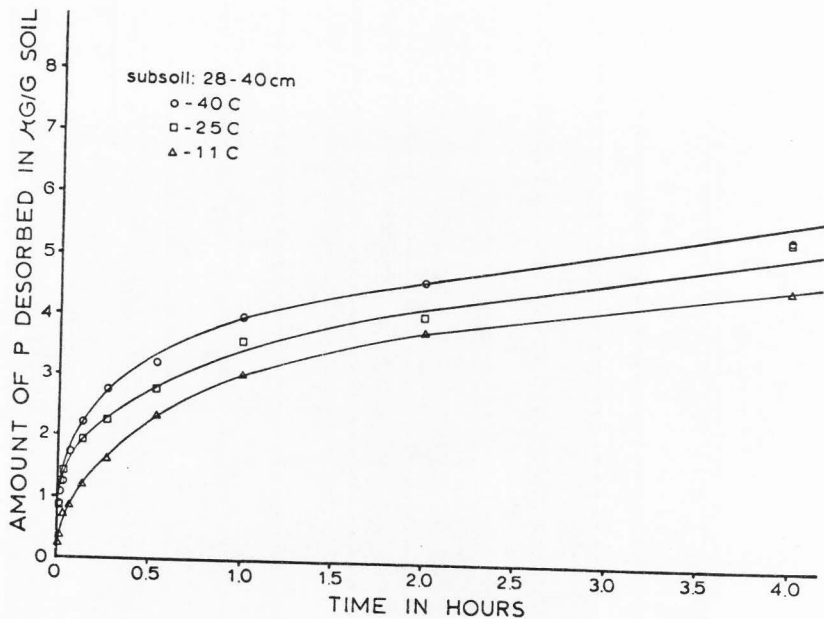
Figure 9. Kinetics of phosphorus release by an anion-exchange resin for the subsoil showing the temperature dependence existing during the first 4 hours of uptake.

Figure 10. A description of the rate of phosphorus uptake by the surface of the resin during the process of release (log C vs t) and of the depletion of phosphorus from the surfaces of the soil (log(C_O-C) vs t), for the surface soil at 40 C over a period of 24 hours.
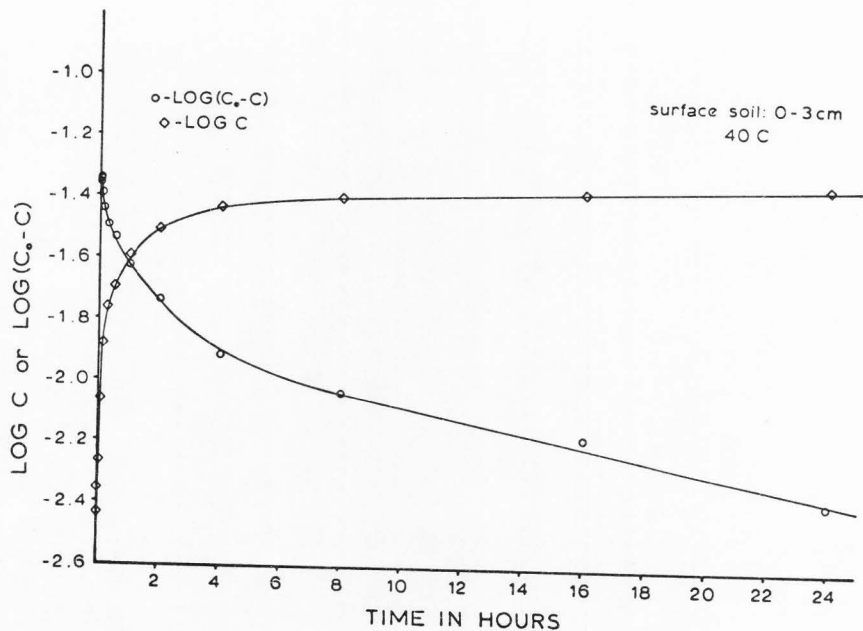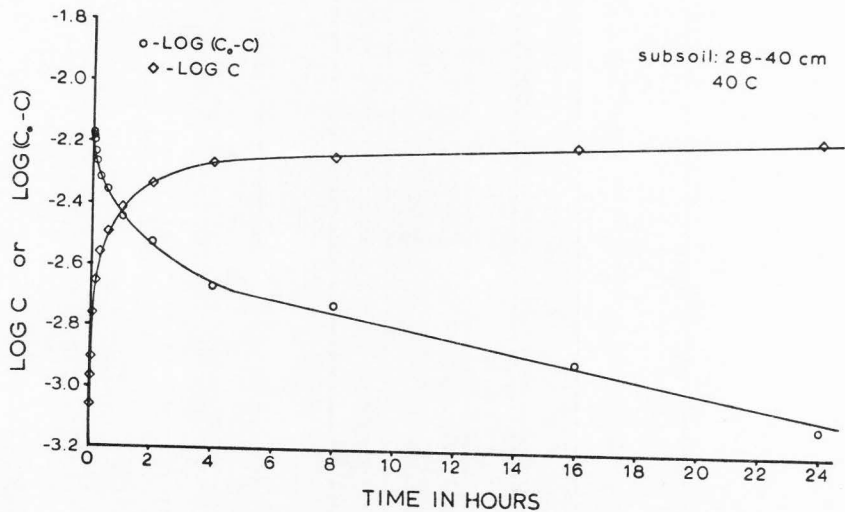
Figure 11. A description of the rate of phosphorus uptake by the surface of the resin during the process of release (log C vs t) and of the depletion of phosphorus from the surfaces of the soil (log(C_o-C) vs t), for the subsoil at 40 C over a period of 24 hours.

shown. The adsorption of P by the anion-exchange resin at any time t is shown by plotting log C vs t for the initial 24 hours, where C is the concentration of P adsorbed by the resin. Since the resin is assumed to be an infinite sink for P with an idealized instantaneous rate of adsorption, the amount of resin adsorbed P at any given time can be equated to the amount of P released by the soil. For both soils the uptake of P by the resin is rapid for the first 4 hours, then the rate of reaction noticeably decreases. If release of P were a simple first-order reaction, the plot of log C vs t should be a straight line thoughout the reaction time. This is obviously not the case for these data. The data were then plotted as log $(C_o - C)$ vs t, where C_o is the initial soil surface P (at t = 0) which is later released. If two simultaneous first-order reactions were occurring during the release of P, a plot of log $(C_o - C)$ vs t should give two distinct straight lines. Again, it was determined that this does not take place.

Since it was determined that more than two reactions were taking place at the same time during the release of P from soil, an attempt was made to describe the release phenomenon by three simultaneous first-order reactions using the equations of Amer et al (1955). Equation [29] is the general expression used with the release data for both the surface soil and subsoil. The results are shown for the surface soil at three temperatures in Figures 12, 13, and 14, and for the subsoil in Figures 15, 16, and 17. Each figure contains an insert which shows the kinetic data for the first 24 hours at a given temperature, whereas the main portion of the figures shows the kinetics of the first 4 hours of P release from soil. Indeed, these figures show that P release from soil can be described as three simultaneous first-order reactions,
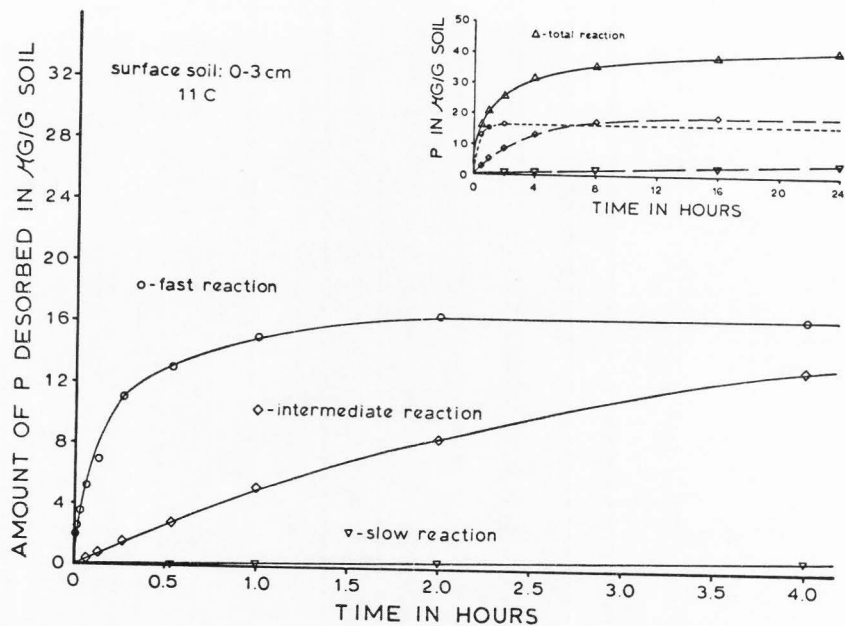
Figure 12. A plot of the three simultaneous first-order reactions occurring during the process of phosphorus release from the surface soil onto an anion-exchange resin at 11 C.

Figure 13. Simultaneous first-order rate plots for the surface soil at 25 C.

Figure 14. Simultaneous first-order rate plots for the surface soil at 40 C.

Figure 15. Simultaneous first-order rate plots for the subsoil at 11 C.

Figure 16. Simultaneous first-order rate plots for the subsoil at 25 C.

Figure 17. Simultaneous first-order rate plots for the subsoil at 40 C.

referred to as fast, intermediate, and slow. From these figures, the three reactions may be compared in rate and in intensity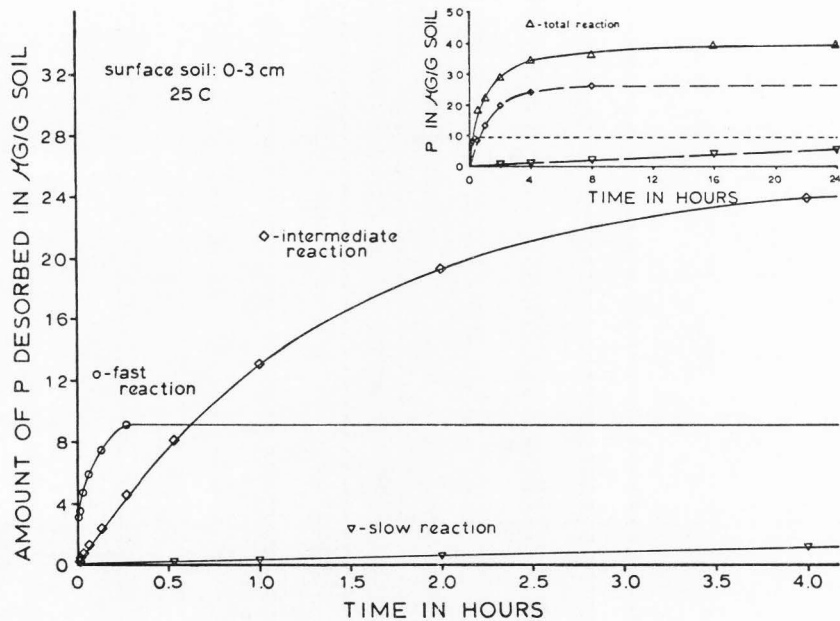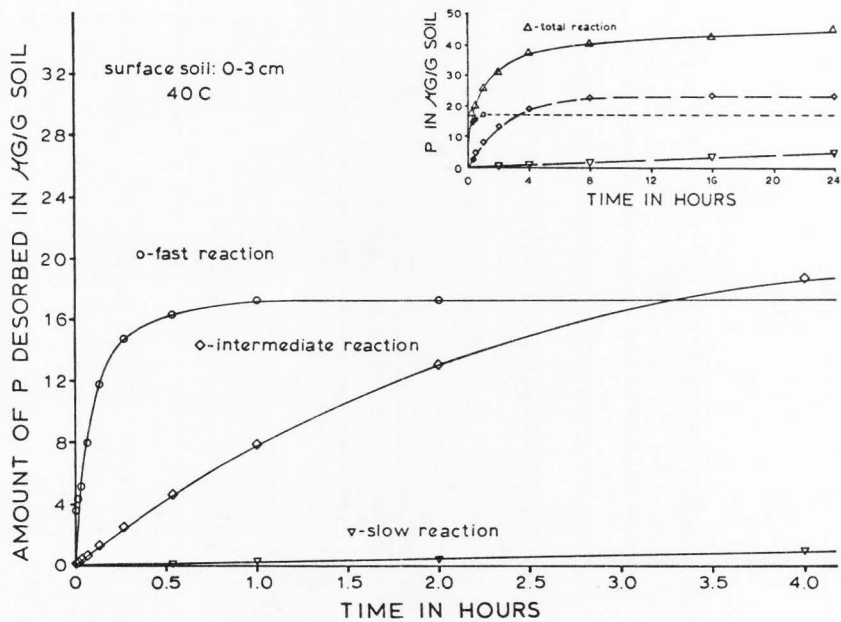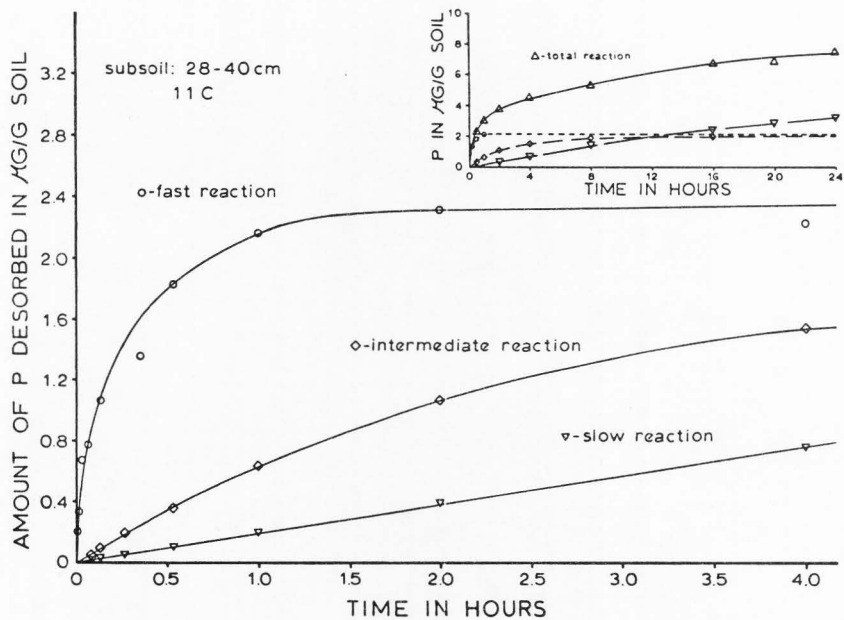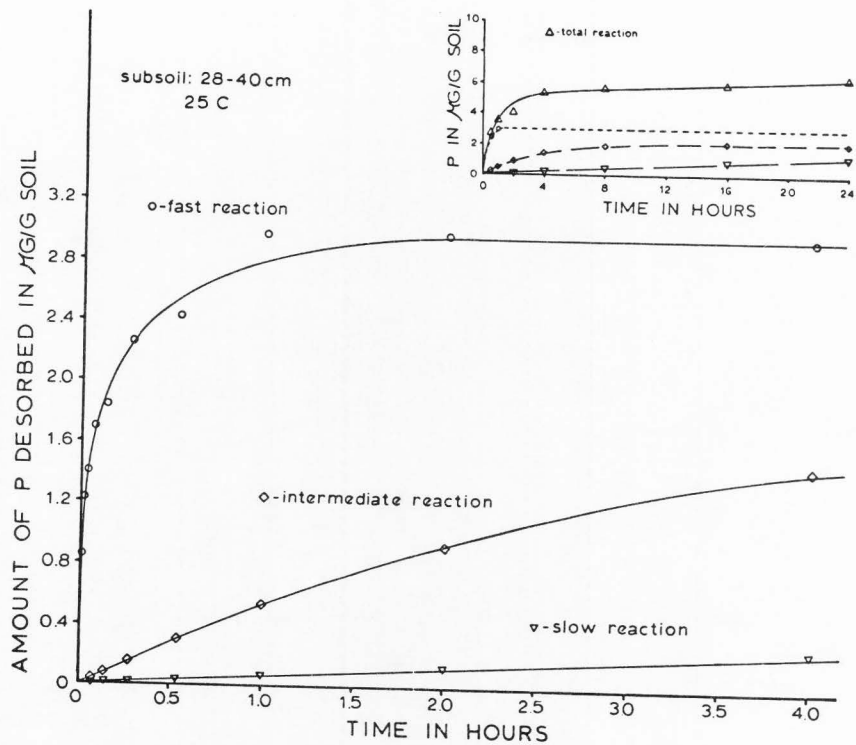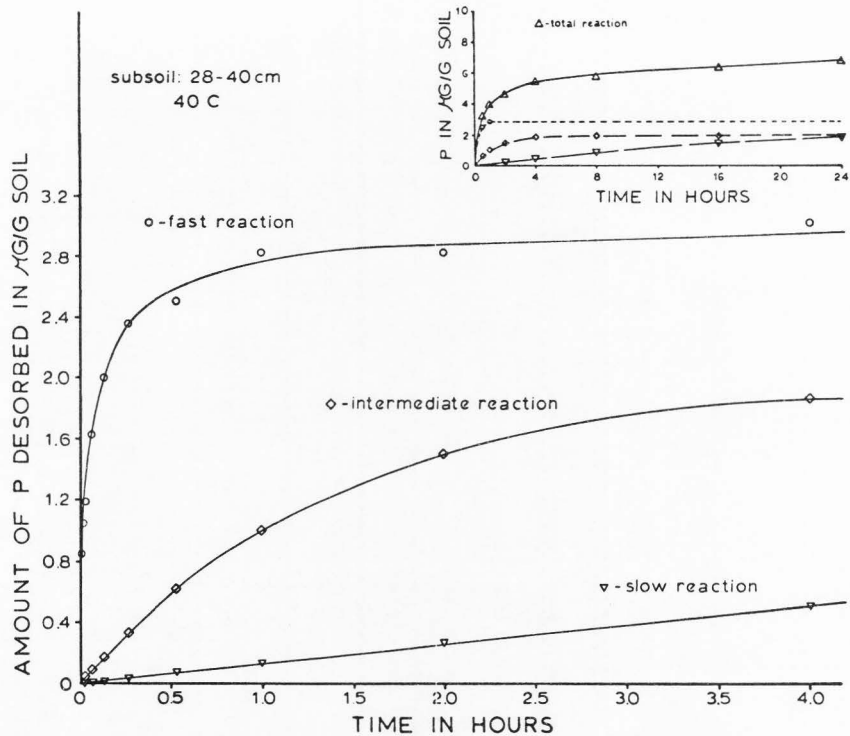. It is noted that the fast reaction terminates between 1 and 2 hours, the intermediate reaction between 8 and 16 hours, while the slow reaction is essentially complete only after 2 to 4 days have passed. Data for time periods beyond 24 hours are not shown.

Figures 18 and 19 show further analysis of the P desorption data from the surface soil and subsoil. In these figures, the "parabolic diffusion law" (expressed by equation [33]) is applied to the data. Linearity between the amount released (C) and the square root of time ($\sqrt{t}$) was demonstrated for upto 16 minutes for both soils at 40 C. This linear relationship suggests that the rate of P release is controlled by a diffusion process, possibly through the static water film surrounding the soil particles for the initial 16 minutes of the reaction. Therefore, it appears that the initial 16 minutes of P release can be described both by a diffusion rate expression or a first-order rate expression. Similar kinetic data are reported by Griffin (1973) for P desorption from calcite. Discussion in this study will be limited to describing the release of soil P by the first-order rate expression.

Table 2 shows the amount of indigenous P ($\mu g/g$ soil) released for each of the three simultaneous first-order reactions for both soil depths at the various temperatures. The value given in parentheses is the percent of the total P released which is contributed by each reaction.

An explanation of the three reactions which describe the release of P from Thiokol silt loam is necessarily speculative because of the
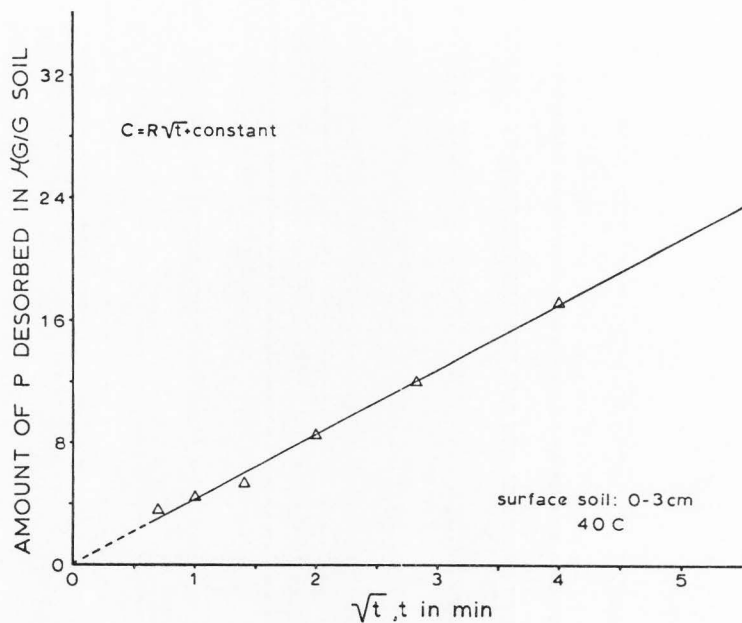
Figure 18. Phosphorus release data plotted according to the "parabolic diffusion law" for the surface soil at 40 C.
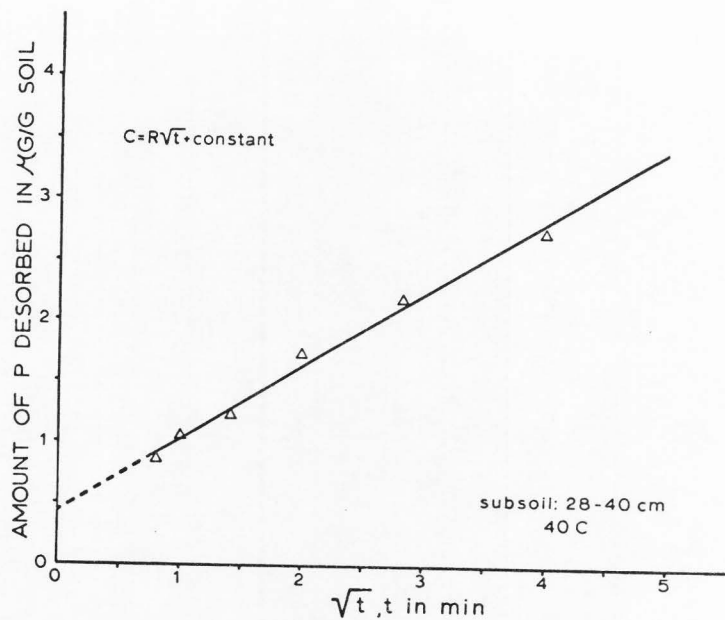
Figure 19. Phosphorus release data plotted according to the "parabolic diffusion law" for the subsoil at 40 C.

Table 2. Phosphorus Release Maxima (μg/g) for Thiokol Silt Loam

	surface soil: 0-3 cm			subsoil: 28-40 cm		
	11 C	25 C	40 C	11 C	25 C	40 C
Reaction 1	16.58 (37%)	8.98 (21%)	17.29 (35%)	2.24 (24%)	2.96 (38%)	2.83 (38%)
Reaction 2	19.02 (43%)	25.27 (59%)	23.15 (47%)	1.96 (21%)	2.14 (27%)	1.99 (26%)
Reaction 3	9.03 (20%)	8.62 (20%)	8.73 (18%)	5.26 (55%)	2.70 (35%)	2.74 (36%)
Total:	44.63	42.87	49.17	9.46	7.80	7.56

Table 3. Rate Constants and Activation Energies for Indigenous

Phosphorus Release for Thiokol Silt Loam

	surface soil: 0-3 cm			subsoil: 28-40 cm		
	11 C	25 C	40 C	11 C	25 C	40 C
k_1 (1/sec)	$.19 \times 10^{-4}$	$.51 \times 10^{-4}$	$.30 \times 10^{-4}$	$.24 \times 10^{-4}$	$.41 \times 10^{-4}$	$.41 \times 10^{-4}$
k_2 (1/sec)	$.11 \times 10^{-5}$	$.27 \times 10^{-5}$	$.16 \times 10^{-5}$	$.15 \times 10^{-5}$	$.11 \times 10^{-5}$	$.26 \times 10^{-5}$
k_3 (1/sec)	$.87 \times 10^{-7}$	$.13 \times 10^{-6}$	$.12 \times 10^{-6}$	$.15 \times 10^{-6}$	$.93 \times 10^{-7}$	$.19 \times 10^{-6}$
ΔE_{d_1} (kcal/m)		2.8			3.3	
ΔE_{d_2} (kcal/m)		2.3			3.3	
ΔE_{d_3} (kcal/m)		2.0			1.7	

lack of definitive data. It is assumed that the mechanisms are the same at both depths, although their relative importance may vary.

The fast reaction, or reaction 1, is considered to be the rapid dissolution of poorly crystalline (amorphous) calcium phosphates which are slowly converting to calcium hydroxyapatite. Calcium hydroxyapatite is the only stable form of P in the presence of calcite. Averaging over the three temperatures, reaction 1 accounts for 31% of the P released in the surface soil and 33% of the P released in the subsoil.

The intermediate reaction, or reaction 2, is attributed to the desorption of labile P (monolayer adsorbed P) from the soil and lime surface sites. Reaction 2 accounts for 50% of the desorbed P in the surface soil, but only 25% of the desorbed P in the subsoil. The greater importance of labile P in the surface soil is corroborated by the fact that the bicarbonate extractable P in the surface soil is 25.50 ppm (μg/g soil) to only 1.70 ppm (μg/g soil) in the subsoil (Jurinak and Griffin, 1972), which is nearly equivalent to the release values of reaction 2.

The slow reaction, or reaction 3, is associated with the slow dissolution of calcium hydroxyapatite, which is assumed to be the low energy form of P in the soil. From Table 2, this reaction accounts for 42% of the P released by the subsoil, while only 20% of the P released by the surface soil is associated with this reaction. This situation is considered realistic since the subsoil is a relatively undisturbed system which should be essentially in or near the equilibrium state. The surface soil, because of the P cycling by the desert vegetation, is continually in a state of flux in terms of P input and is not considered

close to equilibrium. It can be stated that hydroxyapatite is not a dominant factor in the surface soil system.

In general, P release by the soil is described by either solid phase phosphate dissolution or surface site desorption (labile P). It can be shown that both of these mechanisms have first-order rate constants.

Table 3 shows the reaction rate constants for the three proposed mechanisms. Their values were calculated using equations [30], [31], and [32]. The subscripts refer to the reaction. The release of P by the soil was converted to moles to place the rate constants in the proper units for the calculation of the activation energies. These data show that although a marked difference exists between the total amount of P released by the soil at the 2 depths, the rate constants for any given reaction is quite similar. This tends to confirm the assumption that similar reactions were occurring in both systems. Because of the procedure used to calculate the values of k_n, the confidence limits for the values are not given. The values must be regarded as first approximations.

The activation energy of desorption

It was considered of interest to compute the Arrhenius activation energy, ΔE_d, associated with the release or desorption of indigenous P from Thiokol silt loam. The data are shown on Figures 20 and 21, where ln k_n is plotted against $1/T$ in accordance with equation [35]. The values for ΔE_d, calculated by means of regression analysis, are shown in Table 3. The low values of ΔE_d for all three reactions for both the surface soil and subsoil suggest P release is not an energy consuming process. This same information can be obtained from Figures 6, 7, 8,
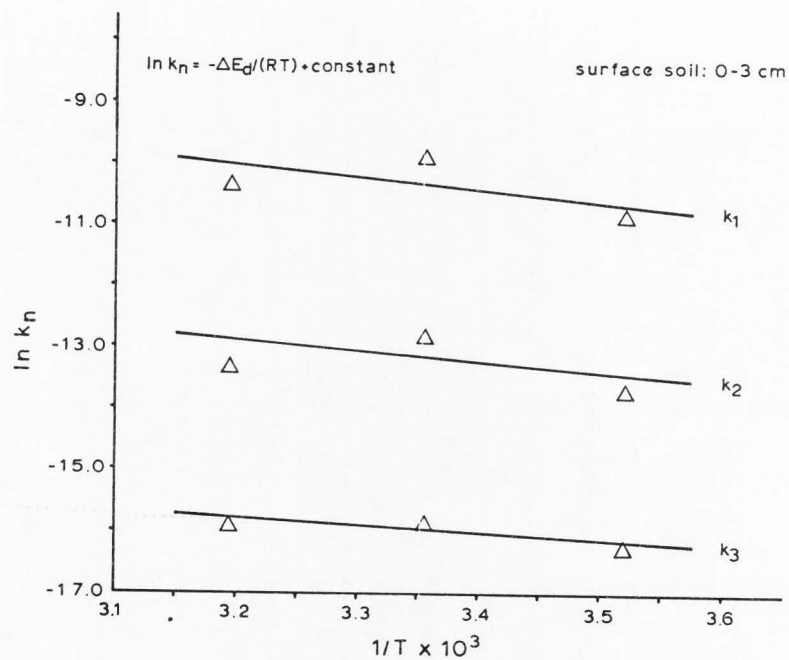
Figure 20. Arrhenius activation energy of desorption plotted for the surface soil at each of three temperatures.
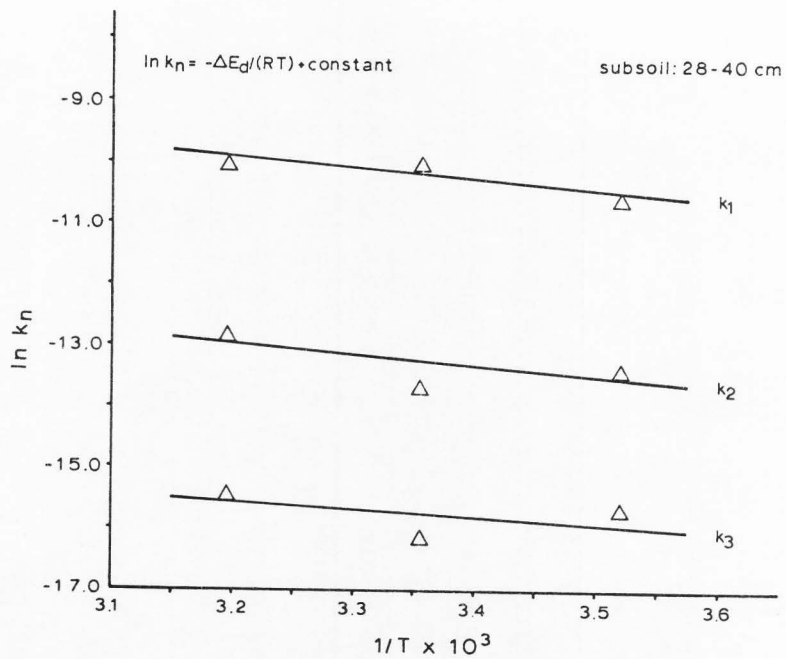
Figure 21. Arrhenius activation energy of desorption plotted for the subsoil at each of three temperatures.

and 9, which show the small temperature dependence of P release. It is difficult to say if any significant difference in ΔE_d values exist between the surface soil and subsoil for the three reactions. It necessarily follows that there is also probably not any significant difference between the k_n values for any given reaction at any given temperature between the surface soil and subsoil.

SUMMARY AND CONCLUSIONS

Summary

The primary goal of this research problem was to conduct experiments which would allow the capacity and intensity factors of soil P as orthophosphate to be evaluated for a desert soil, Thiokol silt loam. The capacity of desert soils to retain natural, as well as added, P was measured by equilibrium adsorption and evaluated using the Langmuir adsorption isotherm. From these data a hypothesis was formulated as to the nature of retention of P by the soil and a value calculated for the adsorption maximum for P with the soil at each of two soil depths and three constant temperatures within the range of biological activity. In addition to these quantitative studies, the flux of P in the soil was also investigated by means of kinetic experiments conducted to measure the nature (types or forms of P in the soil) and rate of indigenous P release from the soil. From the rate constants and release maxima calculated as a result of applying kinetic theory to the data and coupled with the adsorption maxima found for the same soil depths and temperatures in equilibrium studies, a credible, quantitative definition of the movement and saturation of the soil by P can be imposed.

The soil used for these laboratory studies was a typic calciorthid Thiokol silt loam. Two sampling depths were used: the surface soil layer and a subsoil layer. The surface areas of the two samples were measured using the ethylene glycol retention method of Bower and Gschwend (1949) and were found to be approximately 108 to 122 m^2/g for the surface soil and 102 to 115 m^2/g for the subsoil. The electrical conductivities

of saturated extracts of the soil samples were found and the ionic strengths determined from the E.C. readings using the method of Griffin and Jurinak (1973). The E.C. of the surface soil was 0.886 mmhos/cm and the subsoil 2.272 mmhos/cm, and the ionic strengths calculated from them were 0.013 moles/l and 0.034 moles/l, respectively. The pH measurements of saturated pastes were 7.8 for the surface soil and 8.2 for the subsoil. The calcium carbonate content of the surface soil was 12.0% and of the subsoil 38.7%.

The Langmuir adsorption isotherm was applied to the interaction of phosphate solutions with soil to find the capacity of the soil to retain P. Soil-K_2HPO_4 solutions were shaken to equilibrium in a constant temperature water bath at three separate temperatures, the solutions separated from the soil and organic matter by centrifuge and vacuum filtration, and the concentrations of P present in solution measured by the method of Watanabe and Olsen (1965).

The two-slope isotherms, corrected for indigenous P, were used to identify two interfacial reactions involving P. The initial reaction is considered to be surface adsorption as defined by Langmuir, where phosphate ions interact with the clay and lime mineral surfaces at definite sites. The activity of the second mechanism includes adsorption, and, in addition, the heterogeneous nucleation of metal phosphates on the lime mineral surfaces. The increase in adsorption for both soils as temperature increased suggests that the process is endothermic. The subsoil was found to have a greater adsorptive capacity for P than the surface soil, a phenomenon attributed in part to the greater percentage of calcium carbonate in the soil. The equilibrium P adsorption concentrations corresponding to the intersection of the

two slopes in the Langmuir isotherms were approximately 4.2 ppm for the surface soil and 2.5 ppm for the subsoil.

Equilibrium adsorption data are reported for two depths of Thiokol silt loam and include the linear equations of the Langmuir isotherms measured for three temperatures, the Langmuir constants (k), the adsorption maxima for adsorption according to Langmuir (first slope), and the measurements for soil indigenous P used as correction factors for the Langmuir isotherms. The latter values were found to be 45.6 µg/g soil for the surface soil and 8.3 µg/g for the subsoil.

The rate and nature of indigenous P release from the soil and its uptake by the plant root were evaluated from release data found using an anion-exchange resin. The resin was washed several times with distilled water and saturated with calcium carbonate before quantities of moist resin were equilibrated with samples of surface soil and subsoil. The soil and resin were shaken in Erlenmeyer flasks with distilled water under saturated conditions in a constant temperature water bath for various lengths of time from 0.50 minutes to 5 days, and the resin separated from the soil and solution by wet sieving and leached of adsorbed phosphate ions for colorimetric analysis. Because the resin is assumed to be an infinite sink for P with an idealized instantaneous rate of adsorption, it was possible to apply simultaneous reaction kinetics to the total raw release data to determine the rate of indigenous P removal from the soil. Ultimately, the release of indigenous P from the soil under saturated conditions was attributed to three simultaneous first-order reactions. The rates and release maxima for these three reactions were found using the equations of Amer et al (1955).

Over the three reactions identified, indigenous P release from soil can be described by both phosphate dissolution or surface site adsorption (labile or monolayer adsorbed P).

The fast reaction, or reaction 1, is believed to be the dissolution of poorly crystalline or amorphous calcium phosphates which are slowly converting in the soil system to a less available form of P, calcium hydroxyapatite.

The intermediate reaction, or reaction 2, is attributed to the desorption of surface site adsorbed or labile P. It is interesting to note that the release values calculated for this single reaction are nearly equivalent to the values for plant available ($NaHCO_3$ extractable) P reported by Jurinak and Griffin (1971). Considering the equilibrium data here as well, the adsorption maxima represent adsorption quantities which are retained by the soil according to Langmuir: monolayer surface site adsorption on soil clay and lime mineral particles. If, in all three cases, the same type of surface adsorption and P availability are being discussed, both soils appear to be unsaturated with respect to available P. The surface soil can adsorb, in a readily available form, over 300% more P than is naturally present. An emphasis on this form and percentage of P in the soil and its rate of removal by plants appears urgent for a proper analysis of the flux characteristics of the desert soil.

The slow reaction, or reaction 3, is identified as slow dissolution of calcium hydroxyapatite, a fixed, considerably less available form of P in the soil. The amount of P released due to this low energy form-- characteristic of an equilibrium soil system--from the subsoil was found

to be greater than that of the surface soil, which is considered to be in a constant state of flux with respect to P cycling by desert vegetation.

The release data was also interpreted by applying the "parabolic diffusion law" to the total data. It was found that linearity was ascribed to the data for upto the initial 16 minutes of release when plotted vs $\sqrt{t}$. Such agreement suggests that initial release of indigenous P over that period of time is controlled by a diffusion process. This information, however, was considered to be inconclusive as to the credibility of this hypothesis, largely because linearity with the data could not be proven for greater lengths of time from initiation of removal.

The activation energy of release or desorption of indigenous P was calculated from the rate constants of each reaction for both soil depths over a span of three temperatures. The values for ΔE_d were found to be similar for the surface soil and subsoil for the three reactions. This suggests that there is little significance in differences between k_n values for any given reaction at any given temperature between the surface soil and subsoil. When the kinetic parameters are added to an overall predictive model of the desert ecosystem, as is expected in accord with the Desert Biome-U.S. International Biological Program, definition of the rate of P cycling will be considerably simplified because the factors of temperature and soil depth are of little consequence.

Concluding Remarks

In practical application, possibly only nitrogen supercedes P in importance to the growth and development of plant life. Not only is the element itself a necessity, but its presence or absence regulates the availability of other plant nutrients, including nitrogen. In the desert ecosystem, for which the Curlew Valley site and soil serve as a study area, the knowledge of the capacity of a soil for orthophosphate and its ability and capacity to release indigenous phosphate, as well as the origins and rates of release of these forms, are of particular importance if sustaining the P-level in the biochemical cycle is desired. This is especially true when changes in land use occur in these desert regions, such as the introduction of irrigated forage crops and grazing. With the same concern as is expressed above for the capacity of the soil to maintain the P-cycle with desert vegetation under changing conditions, it is equally important to be concerned with the detrimental aspects of phosphate-P retention and release by desert soils, if the area is, for example, being managed as a watershed.

LITERATURE CITED

Amer, F., D. R. Bouldin, C. A. Black, and F. R. Duke. 1955. Characterization of soil phosphorus by anion–exchange resin adsorption and P32–equilibration. Plant and Soil 6:391–408.

Barrow, George M. 1966. Physical chemistry. McGraw–Hill Book Company, New York.

Bower, C. A. and F. B. Gschwend. 1952. Ethylene glycol retention by soils as a measure of the surface area and interlayer swelling. Soil Sci. Soc. Amer. Proc. 16:342–345.

Boyd, G. E., A. W. Adamson, and L. S. Myers, Jr. 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites: II. Kinetics. Jour. Amer. Chem. Soc. 69:2836–2848.

Boyd, G. E., J. Schubert, and A. W. Adamson. 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites: I. Ion-exchange equilibria. Jour. Amer. Chem. Soc. 69:2818–2829.

Brunauer, S., L. E. Copeland, and D. L. Kantro. 1967. The Langmuir and B.E.T. theories. The solid–gas interface, volume 1 (E. A. Flood, editor). Marcel Dekker, Inc., New York.

Chang, S. C. and M. L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci. 84:133–144.

Cole, C. V., S. R. Olsen, and C. O. Scott. 1953. The nature of phosphate sorption by calcium carbonate. Soil Sci. Soc. Amer. Proc. 17:352–356.

Cooke, I. J. and J. Hislop. 1963. Use of anion–exchange resin for the assessment of available soil phosphate. Soil Sci. 96:308–312.

Davis, L. E. 1935. Sorption of phosphates by non–calcareous Hawaiian soils. Soil Sci. 40:129–158.

Dyal, R. S. and S. B. Hendricks. 1949. Total surface of clays in polar liquids as a characteristic index. Soil Sci. 69:421–432.

Fried, M. and R. E. Shapiro. 1956. Phosphorus supply pattern of various soils. Soil Sci. Soc. Amer. Proc. 20:471–475.

Griffin, R. A. 1973. The kinetics and energetics of phosphate interaction with calcite. Ph.D. Dissertation, Utah State University, Logan, Utah.

Griffin, R. A. and J. J. Jurinak. 1973. Estimation of activity coeffi-
cients from the electrical conductivity of natural aquatic systems
and soil extracts. Soil Sci. (in press).

Harkins, William D., F. E. Brown, and E. C. H. Davies. 1917. The struc-
ture of the surfaces of liquids, and the solubility as related to
the work done by the attraction of two liquid surfaces as they ap-
proach each other. Jour. Amer. Chem. Soc. 39:354-364.

Harkins, William D., Earl C. H. Davies, and George L. Clark. 1917.
The orientation of molecules in the surfaces of liquids, the energy
relations at surfaces, solubility, adsorption, emulsification, mo-
lecular associations, and the effect of acids and bases on inter-
facial tension (surface energy VI). Jour. Amer. Chem. Soc. 39:541-
596.

Jurinak, J. J. and R. A. Griffin. 1972. RM 72-38, Factors affecting the
movement and distribution of anions in desert soils. Research mem-
orandum, Desert Biome, U. S. International Biological Program.

Kurtz, T., E. E. DeTurk, and R. H. Bray. 1946. Phosphate adsorption by
Illinois soil. Soil Sci. 61:111-124.

Laidler, Keith J. 1965. Chemical kinetics. McGraw-Hill Book Company,
New York.

Langmuir, I. 1918. The adsorption of gas on plane surfaces of glass,
mica, and platinum. Jour. Amer. Chem. Soc. 40:1361-1402.

Larsen, S. 1964. Some concepts on soil and fertilizer phosphate. Extr.
Bull. Docum. 37.

Larsen, S. 1967. Soil phosphorus. Advances in agronomy, volume 19.
Academic Press Inc., New York.

Li, W. C., D. E. Armstrong, J. D. H. Williams, R. F. Harris, and J. K.
Syers. 1972. Rate and extent of inorganic phosphate exchange in
lake sediments. Soil Sci. Soc. Amer. Proc. 36:279-285.

Lindsey, W. L. and E. C. Moreno. 1960. Phosphate phase equilibria in
soils. Soil Sci. Soc. Amer. Proc. 24:177-182.

McAuliffe, C. D., N. S. Hall, L. A. Dean, and S. B. Hendricks. 1948.
Exchange reactions between phosphate and soil: hydroxylic surfaces
of soil minerals. Soil Sci. Soc. Amer. Proc. 12:119-123.

Moser, U. S., W. H. Sutherland, and C. A. Black. 1959. Evaluation of
laboratory indexes of adsorption of soil phosphorus by plants: I.
Plant and Soil 10:356-374.

Murphy, J. and L. P. Riley. 1962. A modified single solution method
for the determination of phosphate in natural waters. Anal. Chim.
Acta. 27:31-36.

Olsen, S. R. and F. S. Watanabe. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci. Soc. Amer. Proc. 21:144-149.

Rennie, D. A. and R. B. McKercher. 1959. Adsorption of phosphorus by four Saskatchewan soils. Can. J. Soil Sci. 39:64-75.

Russell, G. C. and P. F. Low. 1954. Reaction of phosphate with kaolinite in dilute solution. Soil Sci. Soc. Amer. Proc. 18:22-25.

Thompson, E. J., A. L. F. Oliveira, U. S. Moser, and C. A. Black. 1960. Evaluation of laboratory indexes of absorption of soil phosphorus by plants: II. Plant and Soil 13:28-38.

Watanabe, F. S. and S. R. Olsen. 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. Soil Sci. Soc. Amer. Proc. 29:677-678.

Woodruff, J. R. and E. J. Kamprath. 1965. Phosphorus adsorption maximum as measured by the Langmuir isotherm and its relationship to phosphorus availability. Soil Sci. Soc. Amer. Proc. 29:148-158.

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