BARD

FINAL REPORT

PROJECT NO. US—689—83

Development and Verification of a Simulation Model on Phosphorus Dynamics in Soil and Uptake by Plant Roots

S.A. Barber, J. Hagin, A. Shaviv

1987

Standard BARD Cover Page for Scientific Reports

Date Nov. 3, 1987

BARD
P.O. Box 6
Bet. Dagan, ISRAEL

BARD Project No. US-689-83

Title of Research Project:

Development and verification of a simulation model on phosphorus dynamics
in soil and uptake by plant roots
Names of Investigators:

Principal Investigator: Stanley A. Barber

Cooperating Investigator(s): Josef Hagin, Avi Shaviv

Name and Address of Affiliated Institutions:

Principal Institution: Purdue University, West Lafayette, Indiana

Cooperating Institution(s): Technion Israel Institute of Technology,
Haifa

Project's starting date: October 4, 1984

Type of Report: 1st Annual 2nd Annual Final X

Signatures:

Principal Investigator

Institution's Authorizing Official

Stanley A. Barber

B. R. Baumgardt
Director
Purdue Agricultural Experiment Station

TABLE OF CONTENTS

	Page
ABSTRACT.....	1
OBJECTIVES OF THE RESEARCH.....	2
RESEARCH REPORT.....	3
1. Assessment of Phosphorus Availability as a Function of Applied Phosphorus Rates.....	5
Paper no. 1. J. L. Kovar and S. A. Barber, Phosphorus Supply Characteristics of 33 Soils as Influenced by Seven Rates of P Addition.....	6
Paper no. 2. A. Shaviv, N. Shachar, and J. Hagin, Kinetics of Phosphorus Reactions in Semi arid Calcareous Soils.....	26
Paper no. 3. A Shaviv and N. Shachar. A Kinetic-mechanistic Model of Phosphorus Sorption in Calcareous Soils.....	45
2. Phosphorus Transport from a Fertilizer Granule Into Soil and Its Transformations in It.....	61
Paper no. 4. A. Shaviv and M. Schnek. Reactions of a Granulated Superphosphate and Ammonium Sulfite Mixtures in Calcareous Soils.....	62
Paper no. 5. A. Shaviv and N. Shachar. A Model of Water Transport Into and Out of a Phosphorus Fertilizer Granule.....	78
Paper no. 6. A Shaviv and N. Shachar. A Model of Phosphorus Diffusion from a Sparingly Soluble Source and Its Transformation in Calcareous Soil.....	84
3. Influence of Phosphorus, Water and Temperature on Root Growth Rate...	107
Paper no. 7. J. Yao and S. A. Barber. Effect of One Phosphorus Rate Placed in Different Soil Volumes on P Uptake and Growth of Wheat.....	108
Paper no. 8. R. O. Kuchenbuch and S. A. Barber. Significance of Temperature and Precipitation for Maize Root Distribution in the Field.....	117
4. Modeling Phosphorus Uptake as Affected by Soil Volume Supplied With It.....	136
5. Calculation of Phosphorus Uptake from Soil Fertilized with Fertilizer Granules.....	137
DESCRIPTION OF COOPERATION.....	140
MAIN ACHIEVEMENTS OF RESEARCH.....	141
LIST OF PUBLICATIONS.....	142
APPENDIX.....	143

ABSTRACT

The objective of the cooperative research was to develop a simulation model describing soil and fertilizer phosphorus reactions and movement in the soil, and its uptake by plant roots. Models based on research at the Technion to characterize calcareous soils and at Purdue to characterize U. S. soils, were developed to predict the effect of added phosphorus on phosphorus adsorption and diffusion. Additional models developed at the Technion describe the water transport into and out of the fertilizer granule and phosphorus diffusion out of the granule into adjacent soil.

Research on phosphorus absorption by the plant root was conducted at Purdue. The effect of phosphorus placement on root stimulation in the fertilized volume was quantified and found to be the same for wheat as for maize and soybean. A verified uptake model was used to predict phosphorus uptake as related to volume of soil fertilized.

Most fertilizer phosphorus is applied to the upper 20 cm of soil. Root growth in this layer is affected by soil temperature and soil water. Measurements on maize at Lafayette, Indiana, USA over a nine year period indicated that root growth in this layer was positively correlated with precipitation during the three weeks prior to silking ($r^2 = 0.62$).

An earlier model used to calculate phosphorus uptake as affected by varying the soil volume fertilized was modified to calculate uptake due to phosphorus diffusion into soil from fertilizer granules by combining it with the Technion model predicting phosphorus distribution around fertilizer granules.

OBJECTIVES OF THE RESEARCH

The main objective of the proposed research is the development of a simulation model describing soil and fertilizer phosphorus reactions and movement and its uptake by roots. Further, the model should be tested in experiments, by detailed measurements of soil and fertilizer phosphorus parameters, root development and phosphorus uptake by plants. We believe that the model will contribute towards a better understanding of soil and fertilizer phosphorus availability to plants. Its practical use should provide means for predicting phosphorus requirements of crops and improve the efficiency of phosphorus fertilization and utilization.

This approach leads to characterizing nutrient availability by the following sub-systems:

- Chemistry of phosphorus in the soil.
- Reactions of added fertilizer phosphorus in the soil.
- Water and solute movement in the soil.
- Phosphorus uptake by plant roots.
- Plant growth and root system development.

RESEARCH REPORT

We have developed a mechanistic uptake model at Purdue University that accurately describes nutrient uptake by plant roots growing in soil. This model predicts nutrient uptake by describing the size and morphology of the root system and its change with time, the kinetics of net nutrient influx as related to the nutrient concentration in solution at the root surface and the rate of supply of nutrients to the root by the soil.

The assumptions made in this model are that roots are smooth cylinders absorbing nutrients at a rate dependent upon the solution concentration. The average nutrient flux for the root system is used, although changes with plant age or root age can be accommodated. Absorption is only from nutrients in the soil solution. Net influx vs. soil solution concentration is assumed to follow Michaelis-Menten kinetics. While the roots are assumed not to have root hairs or mycorrhizae, where they have an effect, they can be included in the model.

Nutrient supply to the root is assumed to be by mass flow and diffusion. Since roots commonly only occupy one or two percent of soil volume, many of the nutrients must move to the root before becoming positionally available for uptake. The soil is assumed homogeneous and isotropic.

Values for ten parameters are required for operation of the model. These are 1. for root size; L_0 , the initial root length, k , the rate of root length extension, and r_0 the mean root radius. 2. for influx per unit of root; $I_{\max}$, the maximal influx at high concentration, K_m , the net influx where the concentration- $C_{\min}$ is one-half $I_{\max}$ and $C_{\min}$, the concentration in solution where $I_n = 0$. 3. for nutrient supply by the soil, C_{1i} , the initial concentration of the nutrient in the soil solution; b , the buffer power of the

nutrients on the solid phase for nutrients in solution, and D_e , the effective diffusion coefficient, for diffusion of nutrients in the soil. In addition, values are needed for r_1 , the half-distance between root axes to account for potential competition between adjacent roots and v_o , the rate of water flux into the root.

The model uses radial geometry to describe the flux of nutrients to the root by mass flow and diffusion and their influx as related to the concentration that occurs at the root surface. The equations are solved numerically since they cannot be done analytically. The solution gives a description of the concentration gradient in the soil perpendicular to the root, the net influx with time of root absorption, and the uptake for the growth period selected. Further details in the model are given by Claassen and Barber (1976), Barber and Cushman (1981), and Barber (1984).

This model accurately describes nutrient uptake where the nutrient distribution is uniform throughout the soil, or when placed, where the placed nutrient is uniform throughout a known soil volume it occupies.

There are several relevant aspects which were not considered in the present uptake model. These aspects are:

- A. Assessment of phosphorus availability according to rates of application.
- B. Possible time dependent changes in phosphorus availability.
- C. Phosphorus transport from fertilizer granules and its transformation in soil.
- D. Effects of soil parameters such as phosphorus concentrations, moisture content and temperature on root distribution.
- E. Effect of soil fraction of soil volume supplied with phosphorus on its uptake by plants.

This research was aimed at providing information regarding the above mentioned aspects, which actually coincide with the original objectives in the research proposal. Part of the information attained was used to modify the uptake model, so that some of the different aspects mentioned above are taken care of. Another part of the attained information provides guidelines to possible modifications or extensions of the uptake model. This particularly relates to the time dependent distribution of phosphorus in soil as affected by the form of phosphorus fertilizer application. The achievements of this project are addressed in five chapters which are briefly presented below:

1. Assessment of Phosphorus Availability as a Function of Applied Phosphorus Rates.

This chapter includes the paper of Kovar and Barber: "Phosphorus Supply Characteristics of 33 Soils as Influenced by Seven Rates of Addition." The paper provides empirical relationships for calculating P_1 , phosphorus concentration in solution, and P_s , readily available sorbed phosphorus, as a function of the rate of phosphorus application. The chapter also presents two papers prepared by Shaviv, Shachar and Hagin and by Shaviv and Shachan. The first of the two: "Kinetics of Phosphorus Reactions in Semi Arid Calcareous Soils", presents data of sorption kinetics of four different Israeli soils with relatively large amounts of CaCO_3 . The second paper: "A Kinetic-Mechanistic Model of Phosphorus Sorption in Calcareous Soils", proposes a mathematical model for describing sorption kinetics in calcareous soils. The proposed model considers the formation of: equilibrium sorbed P; fast irreversible sorption of P; and time depending reversible and irreversible sorption of P.

PHOSPHORUS SUPPLY CHARACTERISTICS OF 33 SOILS
AS INFLUENCED BY SEVEN RATES OF P ADDITION¹

John L. Kovar and Stanley A. Barber²

ABSTRACT

Soil phosphorus supply to plant roots increases after addition of P fertilizer due to both the increase in soil solution P, P_1 , and adsorbed P, P_s , that equilibrates rapidly with P_1 . Little information is available on the effect of added P on the concurrent increase in P_1 and P_s . The objective of this research was to investigate the relation between P added and increase in P_1 and P_s of 33 soils. Surface soils collected from the U. S. and Canada were equilibrated moist for three weeks with seven rates of P ranging from 0 to 655 mg P kg⁻¹. High rates of application occur where P is placed in a small fraction of the soil.

¹Journal Paper no. 11,114 Purdue Univ. Agric. Exp. Stn., West Lafayette. IN 47907. Contribution from the Dep. of Agron. This research was supported in part by a grant from the Fluid Fertilizer Foundation and by BARD, United States-Israel Binational Agricultural Research and Development Fund.

²Graduate assistant and Professor of Agronomy, Purdue Univ., respectively.

Values for P_1 were obtained from P analysis of displaced soil solution and values for P_s from a 24-h extraction with anion exchange resin. For all soils relation of P_1 , curvilinear with P addition, x , was described by $P_1 = ax^c + d$. Values for "c", the curvilinearity, varied from 1.03 to 3.15. There was a negative correlation between "c" and exchangeable Ca ($r = -0.65^*$) and soil solution P concentration before P addition, P_{1i} , ($r = -0.61^*$). Adsorbed P increased linearly with P addition for all soils, the slope of the relation varying from 0.35 to 0.86. The slope indicates the fraction of added P extracted with the anion-exchange resin. There was a positive correlation between the slopes and the effective diffusion coefficients, D_e , for P in the soils ($r = 0.47^*$). There was no significant correlation between "c" and the adsorption line slope. Development of methods for predicting the effect of added P on P_1 and P_s will be useful in quantifying the increase in soil resulting from P addition.

Additional Index Words: Soil solution P, adsorbed P, fixed P, anion-exchangeable P.

Kovar, John L., and Stanley A. Barber. 1987. Phosphorus supply characteristics of 33 soils as influenced by seven rates of P addition. Soil Sci. Soc. Am. J.

Mechanistic models (Claassen and Barber, 1976; Barber and Cushman, 1981) have been developed that accurately predict soil P uptake by plant roots (Barber, 1984). The models relate size and morphology of the root system, kinetics of P absorption by the root and supply of soil P to the root by mass flow and diffusion to calculate P uptake. Soil P supply in the model is described with three parameters: the initial P concentration of the soil solution, C_{li} ; the buffer power of solid phase P for P in solution, b , given by the relation $\Delta C_s / \Delta C_l$ where C_s and C_l denote solid phase P and P in solution, respectively; and the effective diffusion coefficient of P in the soil, D_e . The value of D_e , together with the P concentration gradient, describes the rate of P diffusion through the soil to the root. The value of D_e can be estimated by the relation $D_e = D_l \theta f_1 b^{-1}$ (Nye and Tinker, 1977) where D_l is the diffusion coefficient for P in water, θ is the volumetric water content of the soil and f_1 is an impedance factor related to θ and soil texture. A sensitivity analysis of the model used to predict P uptake indicated that changing C_{li} , b , and D_e had a major effect on predicted P uptake (Silberbush and Barber, 1983). Measurement of C_{li} , C_{si} and their variation with P addition, together with θ and f_1 provide the soil data for calculating P supply to the plant root at several levels of P addition.

When P fertilizer is added to soil to increase P soil supply to the plant root, a fraction of the added P will increase C_{li} for P, P_l ; a fraction will increase C_{si} for P, P_s , and the remainder, P_r , will either precipitate or be adsorbed so strongly that it does not readily equilibrate with P_l . In this research, P_s is that P which moves into solution within a 24-h period of desorption, while P_r is the added P

that does not desorb within this time. The distribution of added P among P_1 , P_s , and P_r will vary with soil and rate of P applied. The distribution between P_1 and P_s will affect both D_e and b .

Limited data are available on the affect of rate of P added to a soil on the concurrent increases in P_1 and P_s . This information is needed not only for determining the rate of P to mix uniformly with a soil so that an adequate amount is supplied to the roots, but also to determine the relative effect of P placement in the soil on P uptake by the crop (Kovar and Barber, 1987). The latter requires information for a wide range of P application rates since placing the same amount of P in smaller fractions of the soil increases the rate of application per unit of fertilized soil.

The objectives of this research were to:

- (1) determine the variation in P adsorption characteristics of 33 soils by measuring the P_1 and P_s values found initially and after addition of six different rates of P.
- (2) determine if the differences among soils in their P adsorption characteristics were related to commonly measured soil physical and chemical properties.

MATERIALS AND METHODS

Soils

Moist soil samples were collected from 33 sites within the U.S. and Canada with the cooperation of soil scientists at each location. Soils were primarily from experimental sites of research supported by the Fluid Fertilizer Foundation. Ten kg samples were collected from the 0- to 20-cm layer at each site. No P fertilizer had been applied within

one year. Soils were placed in plastic bags and shipped moist. On receipt, the soils were sieved through a 2 mm sieve and stored. The soils used were Almasippi (from Manitoba, Canada. A Gleyed Rego Black soil under the Canadian system), Ayrshire (fine-loamy, mixed, mesic Aerlic Ochraqualfs), Bonifay (loamy, siliceous, thermic, grossarenic Plinthic Paleudults), Canfield (fine-loamy, mixed, mesic Aquic Fragiudalfs), Chalmers (fine-silty, mixed, mesic Typic Haplaquolls), Clarion (fine-loamy, mixed, mesic Typic Hapludolls), Clermont (fine-silty, mixed, mesic Typic Ochraqualfs), Cloquato (coarse-silty, mixed, mesic, cumulic Ultic Haploxerolls), Colby (fine-silty, mixed, mesic Ustic Torriorthents), Crosby (fine, mixed, mesic Aerlic Ochraqualfs), Decatur (clayey, kaolinitic, thermic Rhodic Paleudults), Dothan (fine-loamy, siliceous, thermic Plinthic Paleudults), Egan (fine-silty, mixed, mesic Udic Haplustolls), Flanagan (fine, montmorillonitic, mesic Aquic Argiudolls), Hubbard (sandy, mixed Udorthentic Haploborolls), Kirkland (fine, mixed, thermic Udertic Paleustolls), Malabon (fine, mixed, mesic, pachic Ultic Argixerolls), Memphis (fine-silty, mixed, thermic Typic Hapludalfs), Muscatine (fine-silty, mixed, mesic Aquic Hapludolls), Newberg (coarse-loamy, mixed, mesic Fluventic Haploxerolls), Platner (fine, montmorillonitic, mesic Aridic Paleustolls), Poinsett (fine-silty, mixed Udic Haploborolls), Pope (coarse, loamy, mixed, mesic Fluventic Dystrochrepts), Port Byron (fine-silty, mixed, mesic Typic Hapludolls), Rago/Weld (fine, montmorillonitic, mesic Pachic Argiustolls), Raub (fine-silty, mixed, mesic Aquic Argiudolls), Taintor (fine, montmorillonitic, mesic Typic Argiaquolls), Taloka (fine, mixed, thermic Mollic Albaqualfs), Tifton (fine-loamy, siliceous, thermic Plinthic Paleudults), Timula (coarse-silty, mixed, mesic Typic

Eutrochrepts), Toronto (fine-silty, mixed, mesic Udollic Ochraqualfs), and Woodburn (fine-silty, mixed, mesic Aquultic Argixerolls). The initial and -33 kPa tension water content of each soil were determined. Water held at -33 kPa tension was determined by the pressure plate method. The untreated soils were analyzed for % sand, silt and clay, % total C by combustion, NH_4Ac exchangeable Ca, Mg, Na, and K and available P by Bray P_1 on 30 soils below pH 6.6 and by Olsen for three soils with pH's between 7.3 and 7.8. The data were reported by Kovar and Barber (1987).

Treatments

Seven P treatments of 0, 11, 22, 55, 109, 218, and 655 mg P per kg of soil (O.D. basis) were prepared in duplicate. The P source was 11-37-0 clear solution containing NH_4 ortho and polyphosphates (Tisdale, Nelson, and Beaton, 1985). The fertilizer was sprayed onto the soil and the soil and fertilizer mixed thoroughly. Sufficient water was added to increase the water content to field capacity (-33 k Pa), and the soils were incubated for 3 weeks at 25°C. Moisture was maintained during incubation. After 3 weeks, the soils were air-dried to approximately -100 to -300 kPa water tension and sieved through a 2-mm sieve in preparation for determination of P_1 and P_s . Soils were never allowed to dry below wilting point water content.

Determination of Soil Solution P

Soil solutions were obtained with the displacement column procedure (Adams, 1974). A 400-g sample (oven-dry basis) of moist, incubated soil was placed into a 7.5 cm diameter Plexiglas column. The

soil surface was covered with filter paper. Deionized water was added at 4 to 8 mL per h until the soil reached field capacity water content. The columns were allowed to equilibrate for 24 h and then 40 mL of water were added (except on sandy soils where 20 mL were used) at a rate of 4 mL per h. The displaced solution was collected, filtered through a 0.45 μm filter and analyzed colorimetrically for P by the Murphy and Riley (1962) method. Analyses were performed in duplicate.

Determination of Soil Adsorbed P

Adsorbed soil P that was exchangeable with anion resin was determined with a modified method of Amer et al. (1955). A 1.0-g sample (oven-dry basis) of moist soil, 1.0 g of Dowex 2X8 Cl-saturated exchange resin >0.425 mm and 100 mL of deionized water were placed in a 400 mL plastic bottle. Duplicate soil samples were shaken continuously for 24 h at 25°C to desorb P from the soil. The resin was separated from soil by washing the soil through a 0.425 mm opening sieve. It was assumed that any sand particles retained with the resin did not adsorb P. The P was extracted from the resin by shaking with 50 mL of 1.0 M NaCl (warmed to 60°C) for 6 h. The solution was separated from the resin by filtering and analyzed colorimetrically for P by the Murphy and Riley (1962) method. This P represented P_s .

Calculation of b and D_e

The buffer power, b , describes the ability of P_s to maintain P_1 as plant roots remove P_1 from solution. The relation between P_s and P_1 is curvilinear. The value of b can be calculated from the slope of the

curve, $\partial P_s / \partial P_1$. The Freundlich equation described the relation closely for the soils used. The equation is:

$$P_s = m(P_1)^n$$

where m and n are empirical regression constants. The data for each soil were fit to this equation by non-linear regression. Since the relation is curvilinear, b is concentration dependent.

Values for D_e were calculated with the equation of Nye and Tinker (1977).

$$D_e = D_1 \theta f_1 / b$$

where D_1 is the diffusion coefficient in water, θ is the volumetric water content of the soil, and f_1 is the tortuosity or impedance factor. Values for θ were taken at field capacity. Values of f_1 were calculated from the relation $f_1 = 1.58\theta - 0.17$ of Barraclough and Tinker (1981). For soils with >75% sand and $\theta < 0.15$, the relation $f_1 = 0.25\theta$ was used. Since b is concentration dependent, values of D_e were calculated for each soil P level using $\Delta P_s / \Delta P_1$ between the observed values at each P rate.

RESULTS AND DISCUSSION

Values of P_1 and P_s were determined for seven rates of applied P , ranging from 0 to 655 mg $P \text{ kg}^{-1}$, on 33 soils. Instead of reporting all 462 values, we chose to show the differences among soils by expressing the results in terms of the coefficients of fitted regression equations for the change in P_1 and P_s with P addition and the change in P_s versus the change in P_1 . The equation for the relation of P_1 vs. P applied gives the effect of each soil on the degree of P dissociation into soil solution as added P rate increases. The relation between P_1 and P added

was curvilinear for all soils and hence, P adsorption from solution was P concentration dependent. The equation for the relation of P_s vs. P added shows the effect of rate of P addition on the level of exchangeably adsorbed P. The relation was linear for all soils. In addition to these two regressions, we investigated the relation between P_s and P_1 for each soil. This relation, which defines the buffer power of P_s for P_1 , was curvilinear for all soils. The equations apply over the range of P additions of 0 to 655 mg kg⁻¹. The coefficients for each regression equation, shown for the 33 soils in Table 1, will be discussed separately.

Effect of P added on P_1

The change of P_1 with P addition was described by the relation $P_1 = ax^c + d$, where x is the amount of P added and a, c, and d are constants. Fig. 1 gives examples of the range of fitted curves found among these soils for the relation P_1 vs. P added. The greatest increase in P_1 per unit of added P was for Bonifay sand, while the least was for Malabon silt loam. The coefficient "c" describes the degree of curvilinearity. Its value ranged from 1.03 for Port Byron, which is almost linear, to 3.15 for Decatur. The "a" coefficient describes the degree of linear increase in P with P addition. Values for "a" ranged from 2.2×10^{-7} to 2.3×10^{-2} . However, two thirds of the "a" values were between 0.13 and 4.95×10^{-4} . These values are small because only a fraction of added P ends up in the soil solution. The combined effect of "a" and "c" describes the relation between P_1 and P added. The "d" value is the intercept of the curve with the y axis and is the P concentration in solution with no P addition, i.e., the P_{1i} of the untreated soil.

Values for "d" ranged from 0.036 to 0.55 mg L⁻¹. These values reflect both intrinsic soil P and P from previous P applications.

Effect of P added on P_s

The relation between P added and P_s was linear for all soils, indicating that the proportion of added P remaining anion exchangeable was independent of rate of P added (Fig. 2). The same four soils used to illustrate the variation of P_1 with P added are used to illustrate the relation between P_s and P added. The data for all soils fit closely ($r^2 = 0.91$ to 1.00) the relation, $P_s = g + hx$, with the intercept "g" being the level of P in the untreated soil and "h" the proportion of added P that was extracted with Cl-saturated anion exchange resin in a 24-h extraction period (Table 1). The values of "g" varied from 3.5 to 190.7 mg kg⁻¹ and those of "h" from 0.34 to 0.86. There was no relation among soils between the relative rate of increase of P_s with P added and the relative rate of increase of P_1 with P added. Hence, soils which adsorbed more P in non-exchangeable positions did not necessarily hold P more tightly so that a smaller fraction of added P went into solution.

Relation Between P_s and P_1

The relation between P_s and P_1 for the seven rates of added P was curvilinear (Fig. 3), and the data were fit using the Freundlich equation, $P_s = mP_1^n$, where m and n are regression constants. The data were represented more closely by the Freundlich equation than by the Langmuir adsorption equation. The value of n, which varied from 0.34 to 0.62, indicates the degree of curvilinearity of the relation between P_s and P_1 . Values of n did not correlate closely with "c" of the relation

between P_1 and P added, because of variation among soils in the relation, P_s vs. P added.

Relation of Soil Properties to P Adsorption

Since the 33 soils differed in the degree to which added P remained in solution or was adsorbed, regression analysis was used to determine if the differences were related to soil chemical or physical properties. Coefficients describing the relation of P_s and P_1 to added P were compared with % total carbon, % clay, soil pH, volumetric moisture at -33kPa tension, exchangeable Ca, b, D_e , and initial levels of P_1 and P_s , denoted as P_{1i} and P_{si} , respectively. The data used in the regression analysis were given by Kovar and Barber (1987).

The "c" values were negatively correlated with both exchangeable Ca ($r = -0.65^*$) and P_{1i} ($r = -0.61^*$). These relations are shown in Figs. 4 and 5. The first correlation indicates that soils with greater amounts of exchangeable Ca tended to have smaller values of "c". Exchangeable Ca varied from 6.2 to 144 mmol kg⁻¹, while rate of P added varied from 0 to 19.8 mmol kg⁻¹. Soils with higher Ca levels may have provided a larger number of uniform adsorption sites for P than soils with lower Ca levels. Similarly, the second correlation indicates that the higher the P_{1i} value, the smaller the value of "c". There was a range in strengths of P adsorption sites, the extent of this range may depend on P_{1i} (Fig. 5). For soils with low P_{1i} , there may be a wide range of P adsorption strengths. For soils with high P_{1i} , the strongly adsorbed sites are filled and the range in strengths of the remaining sites may be smaller, hence "c" is smaller and the relation of P_1 versus P added is flatter. The effects of exchangeable Ca and P_{1i} on the value

of "c" were independent since no correlation existed between exchangeable Ca and P_{1i} or interaction using multiple regression.

Exchangeable Ca and P_{1i} explained 66% of the variation in "c".

The equation was:

$$"c" = 2.7 - 0.34 \text{ Ca} - 1.42 P_{1i} \quad (R^2 = 0.66^{**})$$

No other parameter significantly improved the relation.

Log "a" was linearly correlated with "c" ($r = -0.92^{**}$. Log "a" = $1.46 - 2.75 "c"$) but not with other soil properties. This relation indicates that as log "a" increases, "c" decreases, such that if "a" is larger (P_1 increases more rapidly per unit of added P) then the curvature indicated by "c" will be less.

The "h" values, the slopes of the linear relation of P_s versus P added for the 33 soils, were also used in a multiple regression analysis with soil pH, P_{1i} , P_{si} , exchangeable Ca, volumetric moisture at -33kPa tension, % clay, % total carbon, b, and D_e . The "h" values were positively correlated with D_e ($r = 0.47^*$, $h = 0.45 + 2.4 \times 10^{-11} D_e$). So as D_e increased, adsorption of P increased.

The effect of soil pH or % clay on "h" was not significant. The differences in P adsorption by the soil mineral fraction were apparently affected more by the type of minerals present in the soil than by soil pH or amount of clay.

The information on the effect of P addition on P_1 and P_s is important in determining the soil supply of P to the plant root since P supply is influenced by both P_1 and P_s through its effect on b and D_e . It is important to investigate the effect of P added on both P_1 and P_s and not just on P_1 as frequently has been done in earlier investigations

as reviewed by Sample et al. (1980) and the effect on P_s reported by McLean (1982). With both P_1 and P_s measurements, b can be calculated.

REFERENCES

- Adams, F. 1974. Soil solution. p. 441-481. In E. W. Carson (ed.) The plant root and its environment. University Press of Virginia, Charlottesville.
- Amer, F., D. R. Bouldin, C. A. Black, and F. R. Duke. 1955. Characterization of soil phosphorus by anion exchange resin absorption and ^{32}P equilibration. Plant Soil 6:391-408.
- Barber, S. A. 1984. Soil nutrient bioavailability: a mechanistic approach. John Wiley & Sons, New York.
- Barber, S. A., and J. H. Cushman. 1981. Nitrogen uptake model for agronomic crops. p. 382-409. In I. K. Iskandar (ed.) Modeling wastewater renovation-land treatment. Wiley-Interscience, New York.
- Barracough, P. B., and P. B. Tinker, 1981. The determination of ionic diffusion coefficients in field soils: I. Diffusion coefficients in sieved soils in relation to water content and bulk density. J. Soil Sci. 32:225-236.
- Claassen, N., and S. A. Barber. 1976. Simulation model for nutrient uptake from soil by a growing plant root system. Agron. J. 68:961-964.
- Kovar, J. L., and S. A. Barber. 1987. Placing phosphorus and potassium for greatest recovery. Journal of Fertilizer Issues 4:1-6.

- McLean, E. O. 1982. Chemical equilibrations with soil buffer systems as bases for future soil testing programs. *Commun. Soil Sci. Plant Anal.* 13:411-433.
- Murphy, J., and J. P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27:31-36.
- Nye, P. H., and P. B. Tinker. 1977. Solute movement in the soil-root system. Blackwell Scientific Publications, Oxford.
- Sample, E. C., R. J. Soper, and G. J. Racz. 1980. Reactions of phosphate fertilizers in soils. p. 263-310. In Khasawneh, F. E., E. C. Sample, and E. J. Kamprath (eds.) The role of phosphorus in agriculture. American Society of Agronomy, Madison, Wi.
- Silberbush, M., and S. A. Barber. 1983. Sensitivity of simulated phosphorus uptake to parameters used by a mechanistic mathematical model. *Plant Soil* 74:93-100.
- Tisdale, S. L., W. L. Nelson, and J. D. Beaton. 1985. Soil fertility and fertilizers. Forth ed. MacMillan Pub. Co., New York.

Table 1. Regression equation constants for the relation between P in solution (P_1) and P added (x), anion-exchangeable P (P_s) and P added, and P_1 and P_s . Equations are $P_1 = ax^c + d$, $P_s = mP_1^n$ and $P_s = g + hx$. The r^2 is given for the linear relation.

Soil Name	a	c	d	m	n	g	h	r^2
Almasippi	2.33 E-2	1.25	5.55 E-1	43.43	0.53	38.07	0.49	0.995
Ayrshire	2.42 E-3	1.65	4.81 E-1	69.04	0.34	51.62	0.35	0.954
Bonifay	1.95 E-4	2.22	1.04 E-1	30.68	0.41	8.09	0.38	0.999
Canfield#1	2.06 E-5	2.28	3.07 E-1	76.32	0.38	31.58	0.42	0.998
Canfield#2	3.00 E-7	2.87	4.77 E-2	65.72	0.41	7.02	0.34	0.998
Chalmers	4.93 E-4	1.85	2.75 E-1	91.84	0.41	43.26	0.68	0.999
Clarion	2.31 E-4	1.96	2.22 E-1	63.95	0.44	23.70	0.50	0.999
Clermont	1.56 E-4	2.08	1.61 E-1	59.69	0.42	20.24	0.53	0.995
Cloquato	1.93 E-4	1.67	4.94 E-1	154.52	0.41	91.75	0.37	0.998
Colby	4.60 E-3	1.23	9.59 E-2	68.59	0.57	26.41	0.37	0.987
Crosby	1.71 E-6	2.57	8.71 E-2	75.66	0.41	15.83	0.36	0.999
Decatur	1.75 E-8	3.15	9.08 E-2	138.22	0.38	30.15	0.41	0.996
Dothan	6.37 E-6	2.66	8.15 E-2	49.55	0.40	5.22	0.48	0.996
Egan	2.52 E-5	2.04	3.60 E-2	104.70	0.45	17.32	0.43	0.994
Flanagan	1.95 E-4	1.85	1.06 E-1	64.02	0.53	11.08	0.48	0.997
Hubbard	1.34 E-4	2.04	1.51 E-1	63.44	0.45	17.99	0.49	0.989
Kirkland	2.31 E-5	2.32	7.76 E-2	43.37	0.45	4.02	0.40	0.995
Malabon	8.96 E-5	1.71	1.63 E-1	202.84	0.36	85.38	0.37	0.999
Memphis	3.19 E-7	2.67	8.52 E-2	87.76	0.56	5.25	0.39	0.993
Muscatine	9.94 E-5	1.92	9.30 E-2	60.91	0.57	6.18	0.46	0.999
Newberg	1.32 E-5	2.03	1.67 E-1	175.97	0.37	67.70	0.35	0.995
Platner	3.35 E-4	1.97	1.47 E-1	37.40	0.49	10.95	0.47	0.998
Poinsett	7.18 E-5	2.14	5.73 E-2	49.44	0.48	4.47	0.50	0.999
Pope	2.22 E-7	2.61	4.17 E-2	117.68	0.58	5.13	0.35	0.998
Port Byron	6.57 E-3	1.03	4.98 E-1	299.17	0.62	190.68	0.86	0.940
Rago/Weld	4.05 E-4	2.00	6.52 E-2	38.97	0.41	34.53	0.45	0.909
Raub	4.52 E-3	1.61	4.89 E-1	84.26	0.38	66.88	0.68	0.998
Taintor	7.58 E-5	1.93	3.56 E-2	69.10	0.54	3.53	0.46	0.999
Taloka	4.53 E-5	2.18	6.09 E-2	42.21	0.42	4.84	0.38	0.998
Tifton	4.06 E-4	2.08	1.48 E-1	33.17	0.41	15.36	0.39	0.996
Timula	3.50 E-4	1.98	2.12 E-1	62.20	0.37	31.15	0.46	0.999
Toronto	6.16 E-5	2.01	9.28 E-2	66.63	0.56	8.66	0.53	0.973
Woodburn	5.26 E-5	1.86	1.83 E-1	148.88	0.38	60.39	0.35	0.998

Fig. 1. Relation between P added and P in soil solution, P_1 , for four soils representing the range found for 33 soils. Curves fit with the relation $P_1 = ax^c + d$.

Fig. 2. Relation between P added and P removed by anion-exchange resin, P_s , for four soils representing the range found for 33 soils.

Fig. 3. Relation between P_s and P_l for the four soils shown in Figs. 1 and 2. Curves calculated with the Freundlich equation.

Fig. 4. Relation between "c" value of equation $P_1 = ax^c + d$ and exchangeable Ca.

Fig. 5. Relation between "c" value of equation $P_1 = ax^c + d$ and P_{1i} , the initial P concentration in the soil solution.

Kinetics of Phosphorus Reactions in Semi Arid Calcareous Soils

A. Shaviv, N. Shachar and J. Hagin

Faculty of Agricultural Engineering

Technion, Haifa

Introduction

It is well recognized that for achieving a better description of changes with time of phosphorus reactions in soil (as nutrient or pollutant) one cannot ignore the kinetic nature of this reaction (Griffin and Jurinak, 1974; Enfield et al., 1976; Mansel et al. 1977; Enfield and Ellis, 1983; Barrow, 1985; Sparks, 1986).

Sparks (1986) presents a thorough review showing the various attempts to model phosphorus reactions in soils. It appears that by using models which include both equilibrium and nonequilibrium reactions (Enfield and Ellis, 1983; Selim et al., 1976) or by using a mechanistic multiphase model (Mansel et al., 1977), a more precise description of phosphorus transformations and transport may be obtained. Validation of the various models is done in batch experiments or in columns where in addition to the chemical transformations one needs to model the transport as well.

The present work attempts to investigate the kinetics of phosphorus sorption in four calcareous soils, by using batch experiments in which soil samples were reacted with P solutions for various time intervals. In order to be able to identify different sorbed phosphorous forms (phases?) a sequence of extractions was applied to the reacting soils. This procedure enabled the investigation of changes with time of phosphorus solution concentration, total phosphorus sorption and at the same time changes in the sorption of phosphorus "forms" defined by the sequential extractions applied.

Experimental

Four calcareous soils from different parts of Israel (Table 1) were used in this study. Two g of air-dried soil samples which passed through a 1 mm sieve were reacted with 20 ml MCP (Mono Calcium Phosphate) solutions in 35 ml centrifuge tubes. Phosphorus concentrations used in the study were: 0, 10, 50, 100 and 200 mgP/L. Three soil replicates were used for each initial concentration and reacted for: 1, 2, 4, 12 hrs and for: 1, 2, 4, 7 14 and 21 days. At the end of each reaction period the samples were centrifuged for 10 minutes at 7000 RPM and immediately after filtered. The filtrates were used for determination of P and Ca concentrations and pH. The centrifuge tube with the remaining moist soil were weighed and reacted with 30 ml of deionized water. This was followed by 1 hr shaking, 10 minutes centrifugation at 7000 RPM, decantation and filtration of the water extract. Phosphorus concentration in water extracts were determined and used for calculation of water extractable P. The centrifuge tubes with the remaining moist soil were weighed again and shaken for 1 hr with 20 ml of NaHCO_3 0.5N solutions (Olsen et al., 1954). The samples were centrifuged, decanted and filtered and the solutions used for determination of phosphorus concentration in the bicarbonate extracts. The data were used to calculate: total sorbed phosphorus at a given reaction time (P_T) by difference between initial phosphorus concentration and the one determined at the end of the given reaction time.

According to the sequence of extractions three "forms of sorbed phosphorus" were defined and calculated:

A. Water extractable phosphorus (P_{we}):

$$(2) \quad P_{we} = TP_{ex} - P_o - RP_{sol} \quad \text{mg P/g}$$

where

TP_{ex} - stands for total P extracted by water from a given sample

P_o - stands for P extracted by water from soil reacted with zero solutions

RP_{sol} - stands for residual solution P left in the moist soil.

B. Bicarbonate extractable phosphorus (P_{bic}):

$$(3) \quad P_{bic} = TP_{bic} - P'_o - RP_{we} \quad \text{mg P/g}$$

where

TP_{bic} - stands for total P extracted by bicarbonate solution from a given sample,

P'_o - stands for P extracted by bicarbonate solution from soil reacted with zero P solution, and

RP_{we} - stands for residual P left in soil solution after the water extraction.

C. Non-extractable phosphorus (P_{ns}):

$$(4) \quad P_{ns} = P_T - P_{we} - P_{bic} \quad \text{mg P/g.}$$

Results and Discussion

Results of each set of experiments obtained for a given initial phosphorus concentration were graphically presented by two figures: one showing the decrease with time of phosphorus solution concentration and the

other showing changes with time of total sorbed phosphorus (P_T) accompanied by changes in P_{we} , P_{bic} and P_{ns} . Figures 1 and 2 present a characteristic behaviour. Figure 1 shows the fast decrease in concentration from 50 to 24 mg P/L obtained within two hours followed by a much slower rate of decrease until a levelling of solution concentration is obtained after 2 to 3 weeks (15 to 16 mg P/L). The fast decrease in solution concentration is reflected in the relatively high total sorbed phosphorus (P_T) observed in Figure 2 after 2 hrs of reaction. This was then followed by a slower sorption rate, finally reaching a plateau sorption value of 0.35 mg P/g after 3 weeks of reaction.

The changes with time obtained for the three sorbed phosphorus forms P_{we} , P_{bic} and P_{ns} demonstrate profound differences between the three: The water extractable form (P_{we}) reaches an initial value of 0.09 mg P/g which is then followed by a moderate decrease with time. The bicarbonate extractable form (P_{bic}) reaches an initial sorption of 0.09 mg P/g which is followed by a relatively fast increase of phosphorus sorption until a maximum is reached after about 250 hrs and then a decrease is observed. The non-extractable form P_{ns} reaches an initial sorption value of 0.06 mg P/g which remains constant for 200 to 250 hrs after which an increase is observed. It is worth noticing that the increase in P_{ns} starts more or less at the time that P_{bic} starts to decrease, and the rates (slopes) of the decrease and the increase are of the same magnitude.

Since P_{we} slightly decrease with time but also decreased with decreasing solution concentration it was hypothesized that the sorption of the water extractable form can be regarded as an equilibrium reaction. This was checked by plotting P_{we} versus the corresponding solution concentration C as demonstrated in Figure 3. The relationship shown implies that Langmuir or Freundlich equilibrium equations can be used to relate P_{we} to solution concentration C .

The other two forms definitely seemed to be time dependent but still each was also characterized by a component of a fast sorption term. A similar kinetic pattern was offered by: Enfield et al. (1976); Mansel et al. (1977); Enfield and Ellis (1983); and Barrow (1985). According to Enfield and Ellis (1983) the reaction consisted of a fast sorption process which served as a site for a nucleation or a precipitation kinetic reaction. Such a reaction was assumed to be diffusion controlled and be driven by the difference between solution concentration C and the equilibrium concentration CE within the precipitate (or nucleation site). Accordingly it was hypothesized that two sorbed forms: P_{bic} and P_{ns} can be viewed as representing two "solubility ranges" of Ca-P precipitates each equilibrated with a respective concentration CE_1 and CE_2 . Since P_{bic} was assumed to represent a more soluble phase it was also assumed that $CE_1 > CE_2$. Thus when solution concentrations drop below CE_1 , dissolution of P_{bic} starts and P_{ns} is the only form precipitating. This may then explain the changes with time observed with P_{bic} and P_{ns} in Figure 2.

In other words it may be claimed by applying the above described sequence of extractions a chemo-physical rationale was introduced to phosphorus reactions in these soils. The water extractable phosphorus form (P_{we}) is ascribed to equilibrium sorption. The bicarbonate extractable form (P_{bic}) is ascribed to precipitation of sparingly soluble Ca-P compounds and the non-extractable form (P_{ns}) is assumed to represent the least soluble Ca-P compounds which become more dominant as reaction time increases.

Total phosphorus sorption obtained for the four soils at the different initial concentrations was characterized by two parameters: initial total sorption denoted P_{Ti} and the plateau value reached after three weeks of reaction denoted P_{Tf} . Tables 2 and 3 present P_{Tf} and P_{Ti} values obtained for

the different soils at four initial P concentrations. It is obvious that both total initial sorption (P_{Ti}) as well as the long term one (P_{Tf}) increase with increasing initial phosphorus concentrations in solution. The contribution of the kinetic reactions to total sorbed phosphorus increases too with increasing initial concentrations. For instance, reacting the soils with 10 mg P/L solutions resulted in an average increase of 27% in total sorption induced by the kinetic reactions. With 50 mg P/L solutions an increase of 65% in total sorbed phosphorus was induced by the kinetic reactions and with 100 and 200 mg P/L the observed increase was of 90 and 155% respectively. The average values obtained for P_{Tf} after three weeks had standard deviations in the range of 8 to 20% (Table 2). The standard deviations calculated for the averages of P_{Ti} were in the range of 9 to 33%. The variation in initial sorption may be explained by assuming that it depends on soil properties such as: mineralogy, cation exchange capacity, charge density, organic matter content, etc.

By considering the kinetic reaction to be dominated by Ca-P precipitation reactions one would expect it to be mainly affected by the relatively large amounts of calcium carbonate in these soils, in which case it would be expected to find smaller differences between the long term sorption values.

Initial sorption values of P_{we} , P_{bic} and P_{ns} which were obtained by extrapolating the respective fitted curves to zero reaction time (using SAS GRAPH) are presented in Table 4. The most obvious fact is the increase of the initial sorption with increasing solution concentration. This implies that the immediate sorption terms of all three forms: P_{we} , P_{bic} and P_{ns} can be related to solution concentration by using Freundlich or Langmuir type equations. Yet, it would be highly important to get a deeper insight and try to relate such values to soil properties as well. Unfortunately this could not be done with the data obtained for the soils used in the investigation.

Changes of solution pH with time were recorded but since they were moderate, it was preferred to present initial pH values obtained and averaged over 1 to 4 hrs of reaction and final pH obtained after three weeks. Table 5 demonstrates the slight pH increase with time and the differences induced within samples of a given soil by increasing MCP initial concentration. This increase induced initial pH reduction of: 0.5, 1.3, 0.9 and 0.6 units in Edden, Beerli, Lachish and Nahallal soils, respectively. The pH differences measured after three weeks were somewhat smaller, particularly for Edden and Beerli soils. The strong buffer capacity of these soils can be demonstrated by the fact that MCP solutions of 200 mg P/L which originally have a pH of 2.5 reached a pH range of 6.2 to 7.1 within a few hours of reaction with the calcareous soils.

Changes in calcium solution concentration obtained for the various soils as a function of reaction time and initial solution concentration are presented in Table 6. Calcium concentration in solution after two hrs increased with solution concentration as could be expected, ranging between 12.9 to 15.7 mg Ca/L in zero P solutions and between 65.2 to 107.7 mg Ca/L in solutions of 200 mg P/L. As reaction time progressed two important features were observed: Calcium concentration in: 0, 10 and in some of the 50 mg P/L solutions increased with time whereas in the 100 and 200 mg P/L solution it decreased. The large difference observed initially were reduced after 21 days ranging between 22 to 44 mg Ca/L for Edden, Beerli and Lachish soils. These values correspond with solution concentrations of 0.001 to 0.002 N which are characteristic of calcareous soils (Lindsay, 1979). These results indicate that calcium solubility in the soils is also affected by the calcium carbonate system.

Summary and Conclusion

Investigation of the nature of phosphorus sorption in four calcareous soils revealed the important contribution of kinetic reactions to this process. The contribution of the kinetic reactions to total sorption increased with increasing initial phosphorus concentration in solution.

Use was made of a sequence of water extractions followed by sodium bicarbonate extractions and by calculations of a non-extractable form to define three "solubility ranges" of sorbed phosphorus: water extractable form, denoted P_{we} , bicarbonate extractable form, denoted P_{bic} , and non-extractable one denoted P_{ns} . According to the extraction sequence the solubility of the three forms was rated in the following order: $P_{we} > P_{bic} > P_{ns}$.

The water extractable sorption - P_{we} was shown to be time independent and therefore could be described by Langmuir or Freundlich type equations. The two other forms were shown each to contain a fast equilibrium sorption term. These terms were attributed to nucleation sites on which a Ca-P compound precipitated. The bicarbonate extractable form (P_{bic}) which was considered the more soluble compound of the two was assumed to be equilibrated with a concentration CE_1 , characteristic of Ca-P compound. The non-extractable form P_{ns} was assumed to be equilibrated with a concentration CE_2 obeying the relation $CE_1 > CE_2$. Therefore in a system in which these two Ca-P compounds are formed a decrease of solution concentration below CE_1 should bring upon dissolution of phosphorus. This explains the maximum sorption obtained in Figure 2 which was then followed by a decrease in P_{bic} . At the time the decrease of P_{bic} started, P_{ns} became the only form precipitating in the system.

In the long

run it implies that the non-soluble form will be the major phase in these soils.

The equilibrium sorption P_{we} was found proportional to initial phosphorus concentration in solution. This was also the case with the fast sorption terms of P_{bic} and P_{ns} . Yet, more work would be needed to obtain a correlation between soil properties and the fast sorption terms.

Phosphorus extractions used in this investigation are common in practice for evaluating phosphorus plant availability. Thus, besides the contribution to a better understanding of the mechanism of P reactions in these soils, a practical approach is provided for evaluating (or modelling) changes in plant availability of P with time.

References

- Barrow, N.J. 1985. Reactions of anions and cations with variable-charge soils. *Advances in Agronomy*. 38:183-230.
- Enfield, C.G. and R. Ellis, Jr. 1983. The movement of phosphorus in soil. In: Nelson et al. (eds.). *Chemical mobility and reactivity in soil systems*. SSSA special publication no. 11. Madison, WI. Chap. 7, pp. 93-107.
- Enfield, C.G., C.C. Hardin, Jr., and B.E. Beldose. 1976. Comparison of five kinetic models for orthophosphate reactions in mineral soils. *Soil Sci. Soc. Am. J.* 210: 243-249.
- Griffin, R.A. and J. J. Jurinak. 1973. Kinetics of the phosphate interaction with calcite. *Soil Sci. Soc. Am. Proc.* 38: 75-79.
- Lindsay, W.L. 1979. *Chemical equilibria in soils*. Chap. 12. John Wiley and Sons, New York.
- Mansel, R.S., H.M. Selim, and J.G.A. Fiskell. 1977. Simulated transformations and transport of phosphorus in soil. *Soil Sci.* 124: 102-109.
- Olsen, S.R., C.V. Cole and F.S. Watanabe. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S.D.A. Circular No. 939, 1954, 19p.
- Selim, H.M., J.M. Davidson, and R.S. Mansel. 1976. Evaluation of a two-site adsorption-desorption model for describing solute transport in soils. In *Proc. 1976 Summer Computer Simulation Conf.*, Washington, D.C., 444.
- Sparks, D.L. 1986. Kinetics of reactions in pure and in mixed systems. In: D.L. Sparks (ed.): *Soil physical chemistry*. Chap. 3, p. 83-145. CRC Press, Florida.

Table 1: Some characteristic properties of the four soils reacted with phosphorus solution.

Measured Property	S O I L S			
	Edden	Beeri	Lachish	Nahallal
Texture	Clay	Sandy Loam	Clay Loam	Clay
CaCO ₃ , g/kg	345.0	176.0	217.0	106.0
EC(paste) ds/m	2.2	0.4	0.6	1.1
pH (paste)	7.7	8.1	8.1	7.8
Hygroscopic moisture, g/kg	45.0	24.0	25.0	75.0
Organic Carbon, g/kg	10.5	2.7	4.0	14.0
CEC, c mol(+)/kg	35.0	22.0	22.8	60.0

Table 2: Maximum total phosphorus sorption P_{Tf} obtained for: Edden; Beerli; Lachish and Nahallal soils after 21 reaction days.

Soil	10	<u>Initial P Concentration, mg P/L:</u>		
		50	100	200
		mg P/g		
Edden	0.082	0.35	0.70	1.50
Beerli	0.084	0.29	0.72	1.52
Lachish	0.094	0.40	--	1.32
Nahallal	0.098	0.47	0.91	1.51
Average	0.090(0.007) ^a	0.38(0.07)	0.77(0.09)	1.51(0.13)

^a Values in parenthesis are s.d.

Table 3: Initially total sorbed phosphorus - P_{Ti} obtained for: Edden; Beerli; Lachish and Nahallal soils.

Soil	10	<u>Initial P Concentration, mg P/L:</u>		
		50	100	200
		mg P/g		
Edden	0.068	0.25	0.50	0.7
Beerli	0.065	0.16	0.28	0.4
Lachish	0.072	0.22	--	0.5
Nahallal	0.080	0.28	0.45	0.8
Average	0.071(0.006) ^a	0.23(0.05)	0.41(0.09)	0.6(0.2)

^a Values in parenthesis are s.d.

Table 4: Initial sorption values of the three phosphorus forms; P_{we} ; P_{bic} and P_{ns} obtained for: Edden; Beerli; Lachish and Nahallal soils, as a function of initial P concentration in solution.

Soil	<u>Initial P Concentration, mg P/L:</u>			
	10	50	100	200
mg P/g				
Edden Soil				
P_{we}	0.022	0.09	0.15	0.23
P_{bic}	0.035	0.09	0.15	0.31
P_{ns}	0.001	0.02	0.13	0.14
Beerli Soil				
P_{we}	0.012	0.06	0.09	0.10
P_{bic}	0.027	0.06	0.10	0.17
P_{ns}	0.033	0.06	0.10	0.18
Lachish Soil				
P_{we}	0.012	0.07	—	0.17
P_{bic}	0.046	0.10	—	0.27
P_{ns}	0.026	.07	—	0.11
Nahallal Soil				
P_{we}	0.015	0.09	0.16	0.25
P_{bic}	0.016	0.08	0.14	0.26
P_{ns}	0.045	0.12	0.15	0.28

Table 5: Initial and final pH values obtained for Edden; Beeri; Lachish and Nahallal soil solution reacted with 0, 10, 50, 100 and 200 mg P/L solutions.

	0	<u>Initial P Concentration mgP/L:</u>			
		10	50	100	200
Edden Soil					
Initial pH	7.6	7.5	7.7	7.5	7.1
Final pH	7.4	7.5	7.5	7.5	7.2
Beeri Soil					
Initial pH	7.5	7.6	7.5	7.0	6.2
Final pH	7.6	7.4	7.5	7.2	6.8
Lachish Soil					
Initial pH	8.0	7.9	7.9	---	7.1
Final pH	8.3	8.3	8.2	8.0	7.3
Nahallal Soil					
Initial pH	6.8	7.2	7.2	7.0	6.6
Final pH	7.4	7.4	7.5	7.4	6.6

Table 6: Calcium solution concentrations obtained for: Edden; Beerli; Lachish and Nahallal soils reacted with: 0, 10, 50, 100 and 200 mg P/L solutions, at four reaction times.

Reaction Time	Initial P concentration, mg P/L:				
	0	10	50	100	200
mg Ca/L					
Edden Soil					
2 hrs	12.9	13.9	26.9	39.8	65.2
1 day	14.7	14.7	18.3	24.7	36.8
7 days	21.2	19.0	18.8	22.1	30.9
21 days	44.0	36.8	38.0	35.5	39.5
Beerli Soil					
2 hrs	15.7	18.9	45.1	96.4	107.7
1 day	12.0	16.8	27.8	37.5	61.5
7 days	23.9	25.0	29.0	24.3	37.9
21 days	30.8	26.4	22.9	22.0	21.9
Lachish Soil					
2 hrs	13.3	15.4	35.9	46.3	67.8
1 day	11.0	13.0	24.3	---	50.5
7 days	37.2	31.2	33.4	---	46.5
21 days	48.0	47.6	40.0	33.5	31.0
Nahallal Soil					
2 hrs	12.9	13.0	28.2	43.4	70.5
1 day	32.8	34.8	37.5	43.2	53.5
7 days	48.8	50.5	39.5	24.7	28.9
21 days	80.0	70.6	57.1	46.4	28.3

Fig. 1. Effect of time on reduction of solution P concentration where two g of Edden soil was mixed with 20 ml of monocalcium phosphate at an initial concentration of 50 mg/L.

Fig. 2. Effect of time of reaction of 2 mg of Edden soil in 20 ml of monocalcium phosphate at an initial concentration of 50 mg/L on P_T , P_{we} , P_{bic} , and P_{ns} .

Fig. 3. Relation between P_{we} and solution concentration of P using Edden soil with an initial P solution concentration of 50 mg/L.