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DETERMINATION OF KINETICS OF PHOSPHORUS MINERALIZATION IN SOILS UNDER OXIDIZING CONDITIONS

Robert S. Kerr Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Ada, Oklahoma 74820

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DETERMINATION OF KINETICS OF PHOSPHORUS MINERALIZATION IN SOILS UNDER OXIDIZING CONDITIONS

by

Y. V. Subbarao
Roscoe Ellis, Jr.
Department of Agronomy
Kansas State University
Manhattan, Kansas 66506

Grant No. R803936

Project Officer

Carl G. Enfield
Wastewater Management Branch
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma 74820

ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ADA, OKLAHOMA 74820

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

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As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in groundwater; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American public.

William C. Galegar
Director
Robert S. Kerr Environmental Research Laboratory

ABSTRACT

In search of a better approach to predict phosphorus movement in soils from applied wastewaters, reactions of added orthophosphates were studied in 9 different soils with widely varying physical and chemical properties. Information obtained on the nature and rate of P reaction will be coupled with P adsorption data to derive mathematical models for P movement in soils from applied wastewaters.

Compounds having higher solubility than variscite were formed which changed to crystalline variscite with time upon adding $Ca(H_2PO_4)_2 \cdot H_2O$ to acid soils. Monocalcium phosphate monohydrate in alkaline soils transformed to relatively insoluble $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $Ca_3(PO_4)_2$, $Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$, and $Ca_{10}(OH)_2(PO_4)_6$. The rate of transformation in both acid as well as alkaline soils was P rate dependent; slower with increased P rates.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

MCPM	--	Monocalcium phosphate monohydrate. [$Ca(H_2PO_4)_2 \cdot H_2O$]
DCPD	--	Dicalcium phosphate dihydrate. [$CaHPO_4 \cdot 2H_2O$]
DCPA	--	Dicalcium phosphate anhydrous. [$CaHPO_4$]
TCP	--	Tricalcium phosphate. [$Ca_3(PO_4)_2$]
OCP	--	Octacalcium phosphate. [$Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$]
HA	--	Hydroxyapatite. [$Ca_{10}(OH)_2(PO_4)_6$]
G	--	Gibbsite. [$Al(OH)_3$]
V	--	Variscite. [$AlPO_4 \cdot 2H_2O$]
ppm	--	parts per million

SYMBOLS

P	--	Phosphorus
Ca^{+2}	--	Calcium
Mg^{+2}	--	Magnesium
Al^{+3}	--	Aluminum
$pH - 1/3pAl$	--	Aluminum hydroxide potential
$pH - \frac{1}{2}pCa$	--	Lime potential
$\frac{1}{2}pCa + pH_2PO_4$	--	Phosphate potential
$pH + pH_2PO_4$	--	Phosphoric acid potential

SECTION 1

INTRODUCTION

Large volumes of liquid and solid industrial and municipal wastes resulting from increased urbanization and industrialization pose serious disposal problems. Land as a disposal medium is receiving widespread attention. Soil can be used as a biological and chemical filter for upgrading the wastewater prior to discharge; and, if transportation is not limiting, the wastes can be disposed onto agricultural lands. A major concern in land disposal is the accumulation in soils of certain metals in toxic quantities and movement of unacceptable levels of certain other elements such as phosphorus and nitrogen.

Excess phosphorus (P) entering lake waters increases algal bloom and eutrophication. Naturally occurring ground waters are generally in equilibrium with hydroxyapatite and hence have a P content less than the acceptable level of 0.05 ppm. Since phosphorus moves slowly in soils, its role in underground water contamination is generally ignored. However, there are instances where liberal amounts of P applied to some soils moved substantially deeper into soil profiles to cause underground water contamination. Adriano et al. (1) showed clear evidence of perched and underground water contamination by P from applying large amounts of food processing waste waters for prolonged periods. According to Fiskell and Spencer (2), P added at very high rates to a Lakeland fine sand moved as deep as 11 feet. Phosphorus contamination of high perched water tables from septic tank systems was reported by Reneau and Pettry (3). Lund et al. (4) analyzed soil cores at various depths beneath sewage sludge and effluent ponds at two treatment plant locations in California. Their data suggest that the practice of ponding liquid sewage sludge and effluent on open, porous soils can result in P contamination of underground water. They also noticed that agricultural cropland irrigated with sewage effluent for 7 years was enriched in P to a depth of at least 2 meters. From these studies it appears that unloading large volumes of wastes without knowing the physical and chemical characteristics of soils in the disposal sites can lead to P contamination of underground water.

Phosphorus in soils is immobilized by adsorption and chemical precipitation. Precipitation involves transformation of applied soluble phosphates to relatively insoluble iron, aluminum and calcium phosphates. These insoluble compounds govern the P concentration in soil solution. Efforts so far have used P adsorption capacity of soils in predicting P movement. Using the adsorption data, coupled with the solubility information for the crystalline compounds formed, to predict P movement can be a better approach than predicting from P adsorption characteristics alone.

This study was initiated to obtain information on the nature and rate of applied orthophosphate transformations for 9 soils differing widely in physical and chemical characteristics.

SECTION 2

CONCLUSIONS

* Amorphous $Al(OH)_3$ or crystalline gibbsite controlled Al^{+3} solubility in acid soils.

* Phosphorus fixation was related to pH and clay content of the soils. Soils with more clay fixed more phosphorus. Acid soils in general had more P fixation capacity than alkaline soils.

* Monocalcium phosphate monohydrate in acid soils transformed to compounds having higher solubility than variscite ($AlPO_4 \cdot 2H_2O$) which with time changed to crystalline variscite.

* Several calcium phosphate compounds $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $Ca_3(PO_4)_2$, $Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$ and $Ca_{10}(OH)_2(PO_4)_6$ controlled P solubility when $Ca(H_2PO_4)_2 \cdot H_2O$ was added to neutral and alkaline soils.

* Phosphorus when applied at higher rates approximating that found near a fertilizer granule site saturated the soil zone with $CaHPO_4 \cdot 2H_2O$ and $CaHPO_4$ in the acid as well as alkaline soils.

* The rate at which the initial and intermediary reaction products formed and transformed was P rate dependent. The conversion of intermediary compounds to crystalline variscite was relatively fast at low P rates in acid soils. Similarly in alkaline soils $CaHPO_4 \cdot 2H_2O$ formed initially converted faster to other compounds at low P rates.

SECTION 3

RECOMMENDATIONS

* Proper site selection is very important to effectively remove P from applied waste waters. Only at moderate rates of P application, sandy soils are saturated with $CaHPO_4 \cdot 2H_2O$ which has the highest solubility of all the P reaction products known. Since more P is expected to move under these conditions, sandy soils like U and AB should be avoided as waste disposal sites.

* In order to minimize the movement of P in alkaline soils it would be desirable to have hydroxyapatite present in the soils. This could be accomplished by controlling pH, rate of P application, and time intervals between applications.

* If removing P from waste waters was the only consideration it would be logical to apply waste waters to acid soils since aluminum and iron phosphates that form under acid soil conditions have very low solubilities. However, in practice, liming of waste treated acid soils may be required to immobilize heavy metals. Phosphorus solubilities in lime treated acid soils will be controlled by relatively more soluble calcium phosphate compounds.

* Applications of waste waters bring about reducing conditions and pH changes in the soil zone and the results could be different from those obtained by applying $Ca(H_2PO_4)_2 \cdot H_2O$ to these soils. Hence the P reactions should be determined by applying waste waters as such to soils.

* In this study P at a given rate was added only once, and the rate of transformation of initial and intermediary compounds formed was determined. The rates should be determined under repeated application of P to the soils.

SECTION 4

METHODS AND MATERIALS

Physical and chemical properties of soils used in this work were previously reported (5). To further characterize the chemical and physical properties, clay minerals in each soil were determined by using X-ray diffraction techniques (Table 1).

TABLE 1. CLAY MINERALOGY OF THE SOILS USED IN THIS INVESTIGATION

Soil	Clay Minerals
B	Illite, Kaolinite, and mixed layered minerals (1:1 Illite and Montmorillonite).
D	Illite, Montmorillonite, and Kaolinite
E	Illite, Kaolinite, and mixed layered minerals (1:1 Illite and Montmorillonite). 22.5% $CaCO_3$ on soil dry wt. basis.
O	Illite, Montmorillonite, Kaolinite. 6.6% $CaCO_3$ on soil dry wt. basis.
U	Chlorite
Y	Mg^{+2} rich Chlorite
AA	Mg^{+2} rich Chlorite, Kaolinite and Illite
AB	Illite, Montmorillonite, and Kaolinite. 6.6% $CaCO_3$ on soil dry wt. basis.
AC	Illite and Kaolinite

X-ray diffraction work did not show the presence of gibbsite in acid soils B, D, U, Y, or AA. For gibbsite to be detectable using X-ray diffraction, approximately 5% of the clay sized particles would have to be present as gibbsite. An alternate procedure based on solubility products can be effective in low concentrations. Identification of the specific compound can be made by comparing calculated ion activity products with solubility constants of the various crystalline forms. After measuring the Al^{+++} ion activity in soil extracts, the ion activity products (pAl + 3pOH) were calculated as listed in Table 2. The reported pK_{sp} (negative log of the ion

activity product) values ranged from 32.34 for amorphous $Al(OH)_3$(6) to 33.8 for crystalline gibbsite (7). Thus, indicating amorphous $Al(OH)_3$ in soils U and AA and crystalline gibbsite in soils B, D, and Y.

TABLE 2. CALCULATED ION ACTIVITY PRODUCTS (-LOG IAP) OF GIBBSITE IN THE ACID SOILS

Soil	-log IAP (pAl + 3pOH)
B	34.52
D	33.35
U	32.37
Y	33.54
AA	32.46

Several scientists used solubility criteria to show the existence of variscite (8), strengite (9), and several calcium phosphates as $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$, $Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$, $Ca_{10}(OH)_2(PO_4)_6$ and $Ca_{10}F_2(PO_4)_6$ (10 - 16). The same basic principles were used to obtain the solubility data in these experiments. Phosphorus was reacted with soils in two different ways. Fifty ml of 0.01 M $CaCl_2$ containing 30 and 12 ppm P was added to 15 g of soil in centrifuge tubes to give 90 and 40 ppm P on a soil basis. Reagent grade $(NH_4)_2HPO_4$ and $Ca(H_2PO_4)_2 \cdot H_2O$ were used as P sources. Adequate aeration was provided to prevent reducing conditions and CO_2 accumulation during the experiment. Sufficient replications were made to facilitate sampling at the end of 1, 3, 10, 30, 100, 300, 1000 and 3000 hours.

In the second method, desired P concentrations as $Ca(H_2PO_4)_2 \cdot H_2O$ were mixed with soil, wet to field capacity and stored in plexiglas containers. Deionized distilled water was added at regular intervals to maintain constant moisture levels. A portion of the soil sample was taken at desired time intervals and was dried immediately. Ten and 20 g of dried sample were shaken with 50 ml of 0.01 M $CaCl_2$ for two hours and the data obtained were extrapolated to Zero dilution (10).

Since method of incubation had no significant influence on the results, data from the second method of incubation are presented in this report.

pH in the suspensions was measured with a Fisher Accumet pH meter. Phosphorus in the filtered solutions was measured by the Riley Ascorbic Acid method as described in "Manual of Methods for Chemical Analysis of Water and Wastes" (18). From the total P concentrations, the values of H_3PO_4, $H_2PO_4^-$, HPO_4^{--} and PO_4^{---} were calculated by using the following equations

$$H_3PO_4 = P\left[\frac{(H)^3}{(H)^3 + K_1(H)^2 + K_2K_1(H) + K_3K_2K_1}\right]$$

$$H_2PO_4^{-1} = P\left[\frac{K_1(H)^2}{(H)^3 + K_1(H)^2 + K_2K_1(H) + K_3K_2K_1}\right]$$

$$HPO_4^{-2} = P\left[\frac{K_2K_1(H)}{(H)^3 + K_1(H)^2 + K_2K_1(H) + K_3K_2K_1}\right]$$

$$PO_4^{-3} = P\left[\frac{K_3K_2K_1}{(H)^3 + K_1(H)^2 + K_2K_1(H) + K_3K_2K_1}\right]$$

where K_1, K_2, and K_3 are 1st, 2nd and 3rd dissociation constants of phosphoric acid; 7.51×10^{-3}, 6.33×10^{-8}, and 4.73×10^{-10} respectively. Calculated P fractions at various pH values are shown in Appendix Table 1.

After measuring Al^{+3} in soil extracts on a 305B Perkin-Elmer atomic absorption spectrophotometer with a graphite furnace, aluminum activities were calculated as shown by Lindsay, Peech, and Clark (17).

Calcium and Mg^{+2} concentrations were measured with a Perkin-Elmer 303 atomic absorption spectrophotometer. The activity coefficient f_i was calculated by using the equation

$$-\log f_i = \frac{0.506\ Z_i^2 \sqrt{\mu}}{1 + 0.329\ a_i \sqrt{\mu}} + \beta\ \mu$$

where μ is the ionic strength, Z_i is the valence of the ion, a_i is 6 as given by Kielland (19), and β is -0.257 (20).

The data were interpreted by using the solubility diagrams shown in Figs. 1 and 2. Also the ion activity products -log (IAP) were calculated and compared with the known solubility product constants (pK_{sp}) of various P compounds. Table 3 gives the pK_{sp} values of various P compounds used to interpret the data.

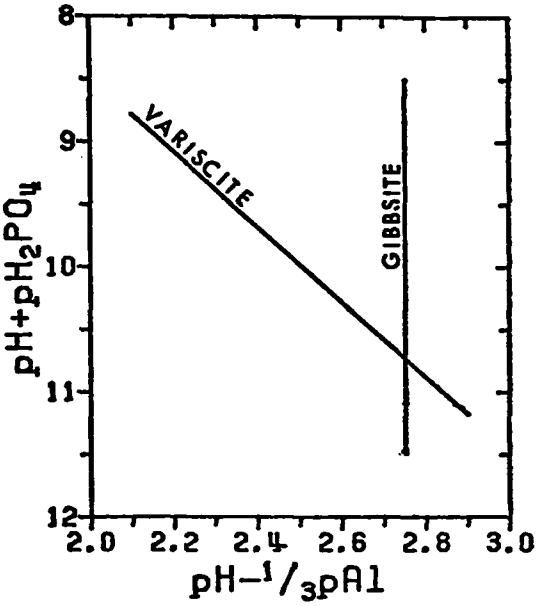


FIG. 1. SOLUBILITY DIAGRAM FOR VARISCITE AND GIBBSITE IN SOILS AT 25°C

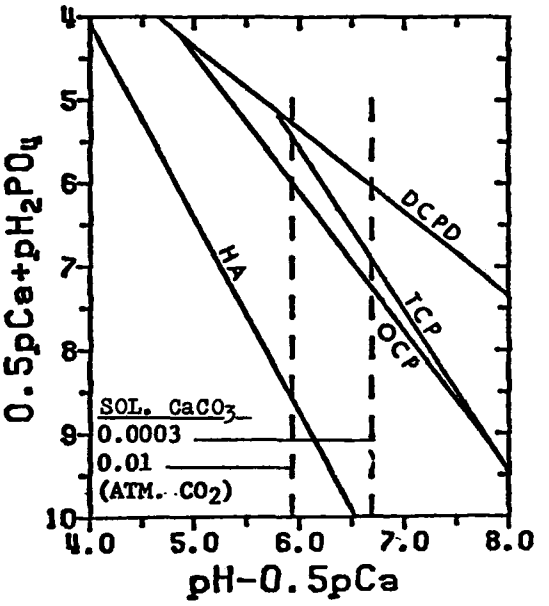


FIG. 2. SOLUBILITY DIAGRAM FOR CALCIUM PHOSPHATE COMPOUNDS IN SOILS AT 25°C

TABLE 3. REPORTED SOLUBILITY PRODUCT CONSTANTS (pK_{sp}) AND DISSOCIATION CONSTANTS AT 25°C.

Compound	Solubility Expression	pK_{sp}	Source
$CaHPO_4 \cdot 2H_2O$ (DCPD)	$pCa + pHPO_4$	6.56	20
$CaHPO_4$	$pCA + pHPO_4$	6.66	7
$Ca_3(PO_4)_2$ (TCP)	$3pCa + 2pPO_4$	26.0	6
$Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$ (OCP)	$4pCa + pH + 3pPO_4$	46.91	20
$Ca_{10}(OH)_2(PO_4)_6$ (HA)	$10\ pCa + 6pPO_4 + 2pOH$	113.7	7
$Al(OH)_3$ (Amorphous)	$pAl + 3pOH$	32.34	6
$Al(OH)_3$ (Gibbsite)	$pAl + 3pOH$	33.8	7
$AlPO_4 \cdot 2H_2O$ (Variscite)	$pAl + 2pOH + pH_2PO_4$	30.5	8
$CaCO_3$ (Calcite)	$pH - pCa + \frac{1}{2} \log P_{CO2}$	4.93	21

SECTION 5

RESULTS AND DISCUSSION

IN SITU PHOSPHORUS

In considering soil as a possible medium for P removal from applied waste waters, the fate of both applied and *in situ* phosphorus must be understood. Information obtained from analyzing the 0.01 *M* $CaCl_2$ extracts of untreated soils (Tables 4 and 5) was used to identify the compounds governing the P solubility.

TABLE 4. pH, P, Ca, Mg, Al AND ION ACTIVITY PRODUCTS (-LOG IAP VALUES) OF VARISCITE MEASURED IN 0.01 *M* $CaCl_2$ EXTRACTS OF FIVE UNTREATED ACID SOILS.

Soil	pH	P	Ca	Mg	Al	- log IAP ($pAl + 2pOH + pH_2PO_4$)
		- - - - - - - - -		ppm	- - - - - - - -	
B	4.20	0.017	279	31.8	0.710	30.98
D	4.80	0.013	242	45.7	0.206	30.53
U	4.90	0.022	345	3.4	0.663	29.68
Y	4.40	0.463	302	22.8	1.800	28.77
AA	5.15	0.087	311	11.5	0.190	29.17

Phosphorus concentrations in the equilibrium extracts of untreated acid soils ranged from 0.013 to 0.463 ppm. Ion activity products indicated crystalline variscite in Soils B and D. Equilibrium solutions of Soils U, Y, and AA were supersaturated with respect to variscite, indicating that these soils may have been treated with P prior to sample collection. Upon aging, however, these ion activity product values generally approach the solubility product of variscite.

Calculated ion activity products for alkaline soils (Table 5) indicated octacalcium phosphate (OCP) in Soils E and AB, and tricalcium phosphate in Soil O. Hydroxyapatite (HA) controlled P solubility in the untreated neutral Soil AC.

TABLE 5. SOLUBILITY DATA FOR 3 UNTREATED ALKALINE SOILS AND ONE NEUTRAL SOIL

Soil	pH	P	Ca	Mg	P Compound
E	7.70	0.124	381	3.9	$Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$ (47.2*)
O	8.10	0.216	244	19.5	$Ca_3(PO_4)_2$ (26.07)
AB	7.80	0.216	317	24.0	$Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$ (46.36)
AC	6.00	0.044	327	8.6	$Ca_{10}(OH)_2(PO_4)_6$ (119.62)

* Calculated -log IAP values for the indicated compounds.

Tricalcium phosphate and octacalcium phosphate are not stable and will be converted to less soluble hydroxyapatite.

REACTIONS IN ACID SOILS

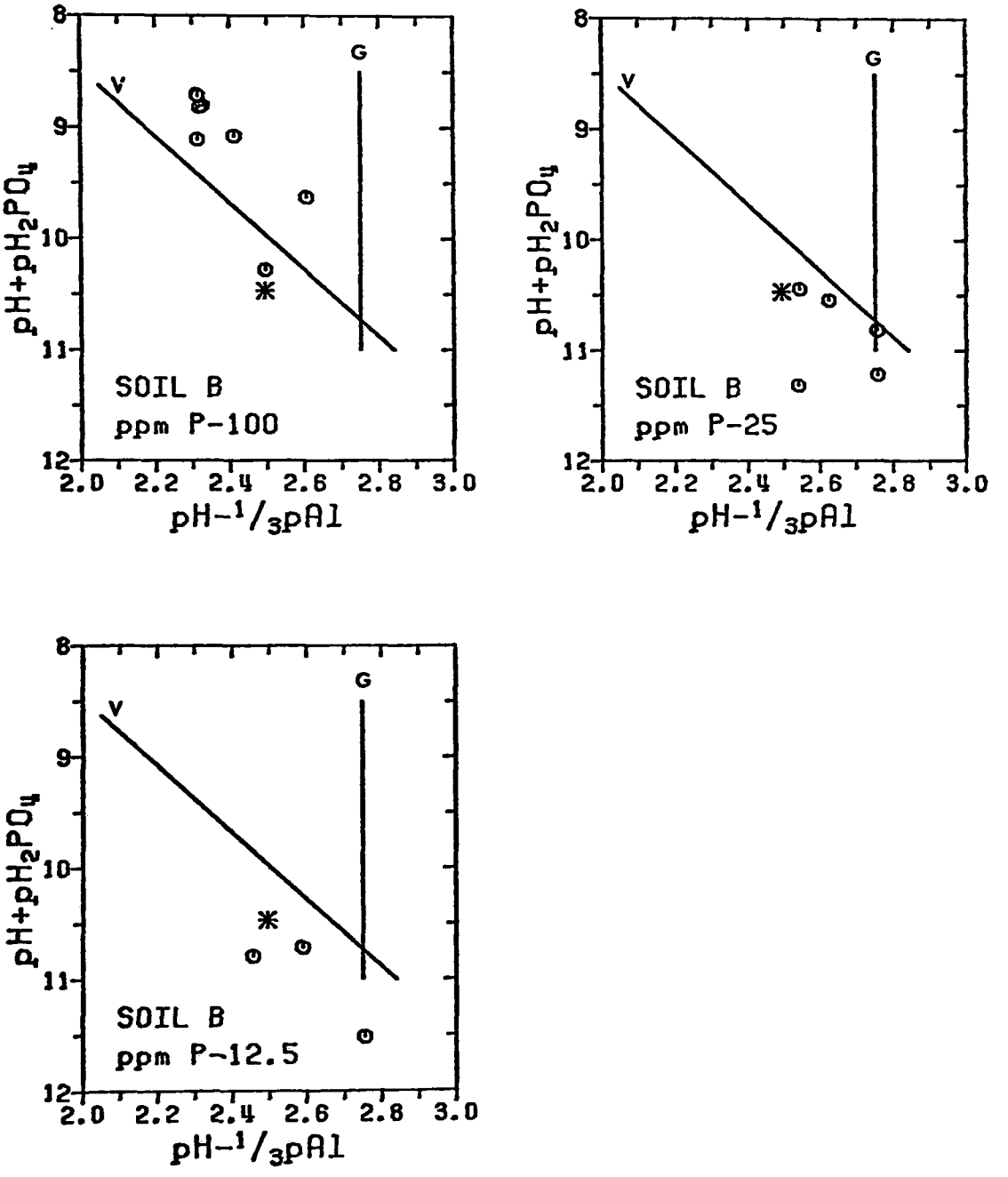
Solubility data for the phosphate treated acid Soils B, D, U, Y and AA are presented in Appendix Table 2. Soils B, D, and AA with high clay content fixed more phosphorus than U and Y, having lower amounts of clay. At 100 ppm (soil basis) rate, P in extracts of Soil B, D, and AA decreased by more than 200-fold in less than an hour compared to 50- and 6-fold decreases in Soils Y and U respectively. Phosphorus fixation rate which was rapid in the beginning decreased with time.

Aluminum hydroxide potentials (pH - 1/3 pAl) and pH values in $CaCl_2$ suspensions of the acid soils increased with time of incubation at any given rate of P application. pH of soil extracts decreased with increasing amount of applied phosphate. A decrease in the values of pH - 1/3 pAl with increased P rates was reported by Lindsay, Clark, and Peech (8). In this study, where 100, 40, 25 and 12.5 ppm P (soil basis) rates were compared, highest aluminum hydroxide potentials were noted at 40 and 25 ppm (soil basis) rates compared to 100 and 12.5 ppm P rates.

It is evident from Appendix Table 2 that the ion activity products of variscite in Soils B and D were lower in the beginning, especially at 100 ppm P rate, and approached the reported pK_{sp} value of 30.5 with time. The solubility data for Soils B and D are plotted in Figs. 3 and 4. After adding 100 ppm P Soil B yielded extracts that were supersaturated with respect to variscite and undersaturated with gibbsite. Almost immediately after adding 25 and 12.5 ppm P, variscite controlled P solubility.

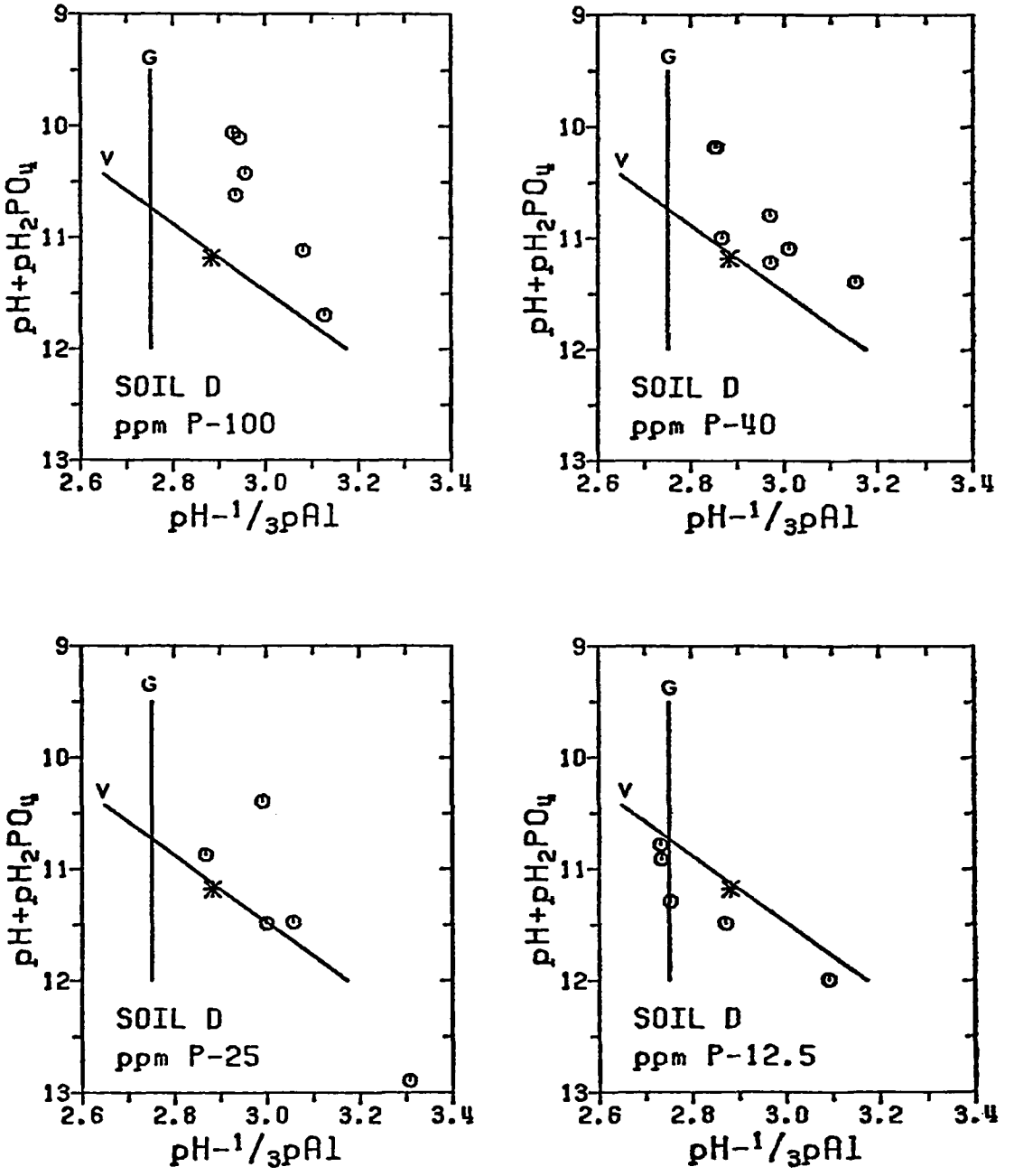
Extracts of Soil D after adding 100, 40, and 25 ppm P (soil basis) were supersaturated with both variscite and gibbsite. The soil solution was in equilibrium with variscite in less than an hour after adding 12.5 ppm P.

FIG. 3. EFFECT OF PHOSPHATE ADDITION ON THE ALUMINUM AND PHOSPHORIC ACID POTENTIALS IN SOIL - B.



* Untreated soil

FIG. 4. EFFECT OF PHOSPHATE ADDITION ON THE ALUMINUM AND PHOSPHORIC ACID POTENTIALS IN SOIL - D.



* Untreated soil

Soils U, Y and AA continued to yield extracts that were supersaturated with respect to variscite during the entire aging period. Slow rate of variscite formation is expected and reported (8). According to Wright and Peech (9), lower ion activity products of variscite may be attributed to the presence of extremely small crystals of variscite having higher solubility than particles of larger size. More complex phosphates like tarnakites, which are expected to form when orthophosphates are added to acid soils (22), have higher solubilities than variscite. So the observed low ion activity products might be due to the formation of small crystals of variscite or formation of complex phosphates like tarnakites.

Upon aging, the phosphate treated soils had higher aluminum hydroxide potentials and variscite ion activity products than the corresponding untreated soils. This is not peculiar since the data on the original soils were obtained prior to P treatments; changes in pH, P and Al concentrations of phosphate untreated soils with time of incubation were not monitored.

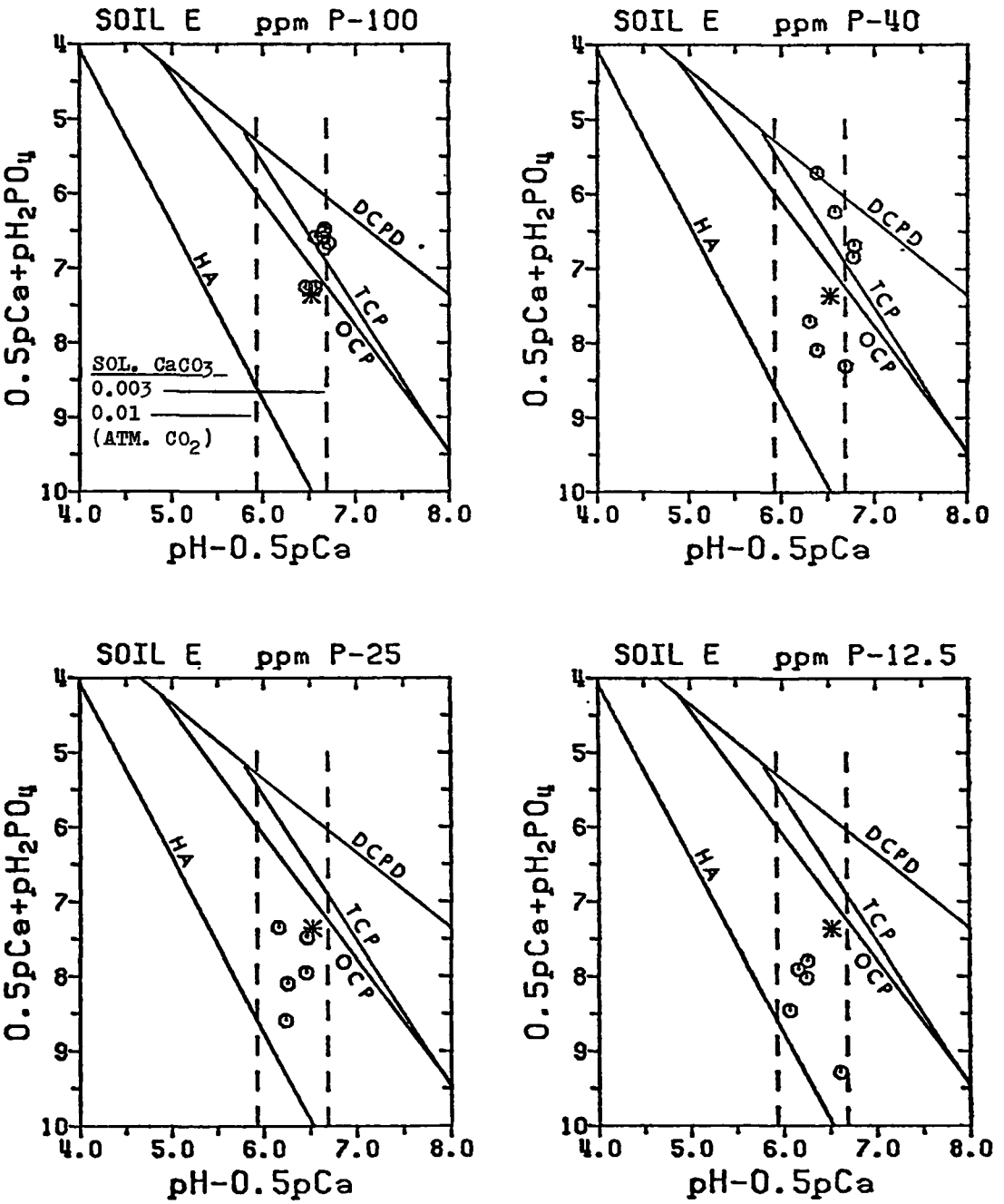
REACTIONS IN ALKALINE SOILS

Concentrations of P, Ca and Mg, and pH values in 0.01 M $CaCl_2$ extracts of alkaline soils and the calculated lime (pH - ½pCa) and phosphate (½pCa + pH_2PO_4) potentials and ion activity products are included in Appendix Table 3. In general, P applications lowered the pH_2PO_4 values which with time of incubation tended to approach those of phosphate untreated soils. pH values and lime potentials of phosphate treated soils followed no particular trend during incubation. In most cases, a gradual increase followed by a decrease in pH values was noticed with a corresponding change in the equilibrium P concentration; increased pH lowered the P concentration and vice versa. This was more so at the highest P rates. Changes in CO_2 partial pressure during incubation could have caused this kind of unusual fluctuations. Decreased suspension pH values with increased P rates was noticed by Jensen (11), in several calcareous soils. In this study, equilibrium pH values in Soil AB decreased slightly, and in Soils E and O increased slightly with increasing P rates.

Soils E and O immobilized more P in less time than Soil AB. Soil AB, with a comparatively low clay content, had a very poor P fixation capacity. One thousand hours after adding 90 ppm P, a substantial amount ($\sim$5 ppm) of P was still left in the soil solution. From the solubility data, it is evident that additions of only 100 ppm P saturated this soil with respect to $CaHPO_4 \cdot 2H_2O$. Unacceptable levels of P are likely to move down through this soil under heavy and repeated applications of waste waters.

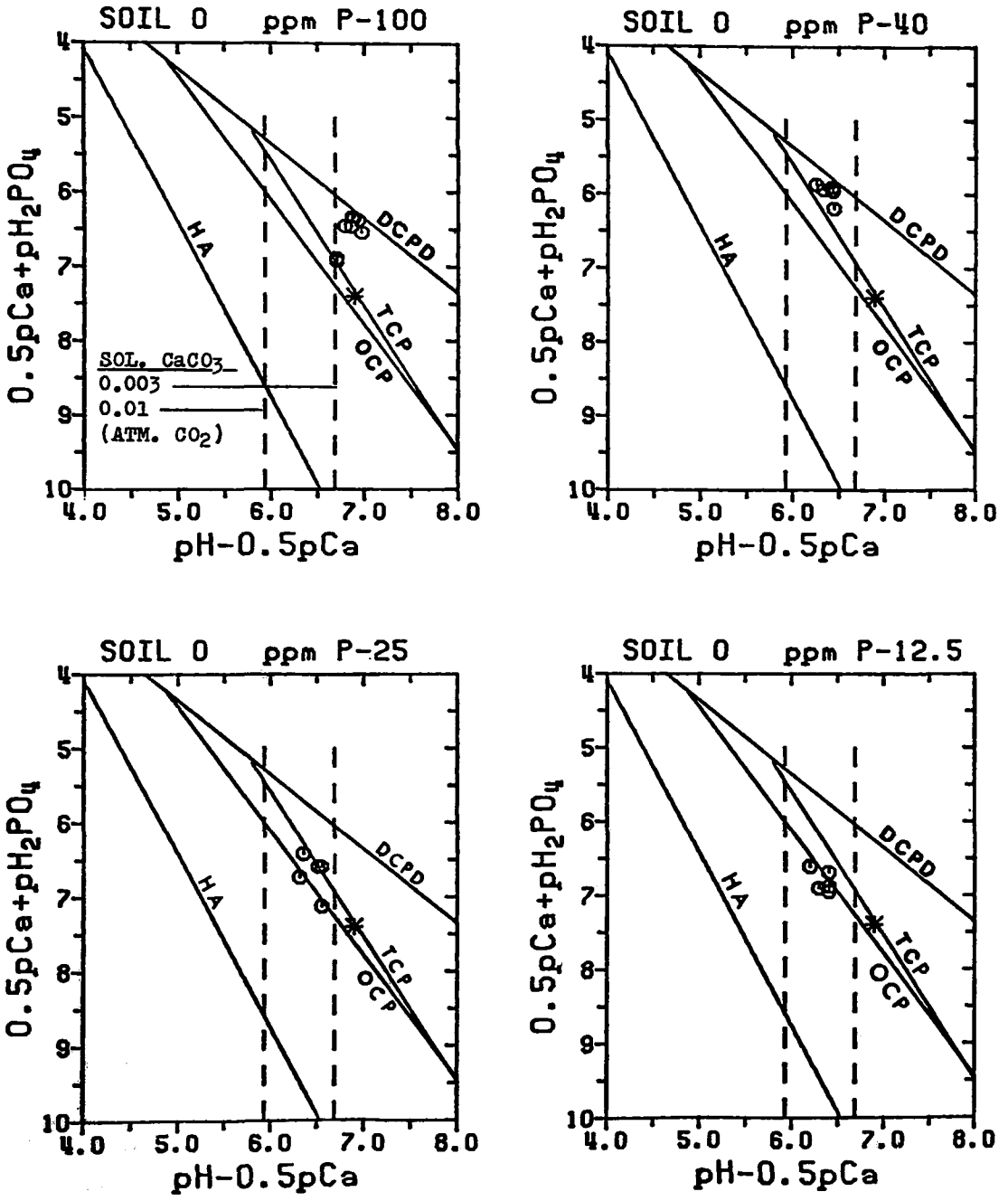
Lime and phosphate potentials obtained from the measurements made of the soil samples taken during incubation are plotted in Figs. 5, 6 and 7 for Soils E, O and AB respectively. These soils yielded extracts that were super- or undersaturated and sometimes in equilibrium, with the known calcium phosphates $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $Ca_3(PO_4)_2$, $Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$, and $Ca_{10}(OH)_2(PO_4)_6$. Soil E in the presence of 25 and 12.5 ppm added P, yielded extracts that were supersaturated with hydroxyapatite and had higher phosphate

FIG. 5. CHANGES IN LIME AND PHOSPHATE POTENTIALS IN SOIL - E BY ADDING 100, 40, 25, AND 12.5 ppm P.



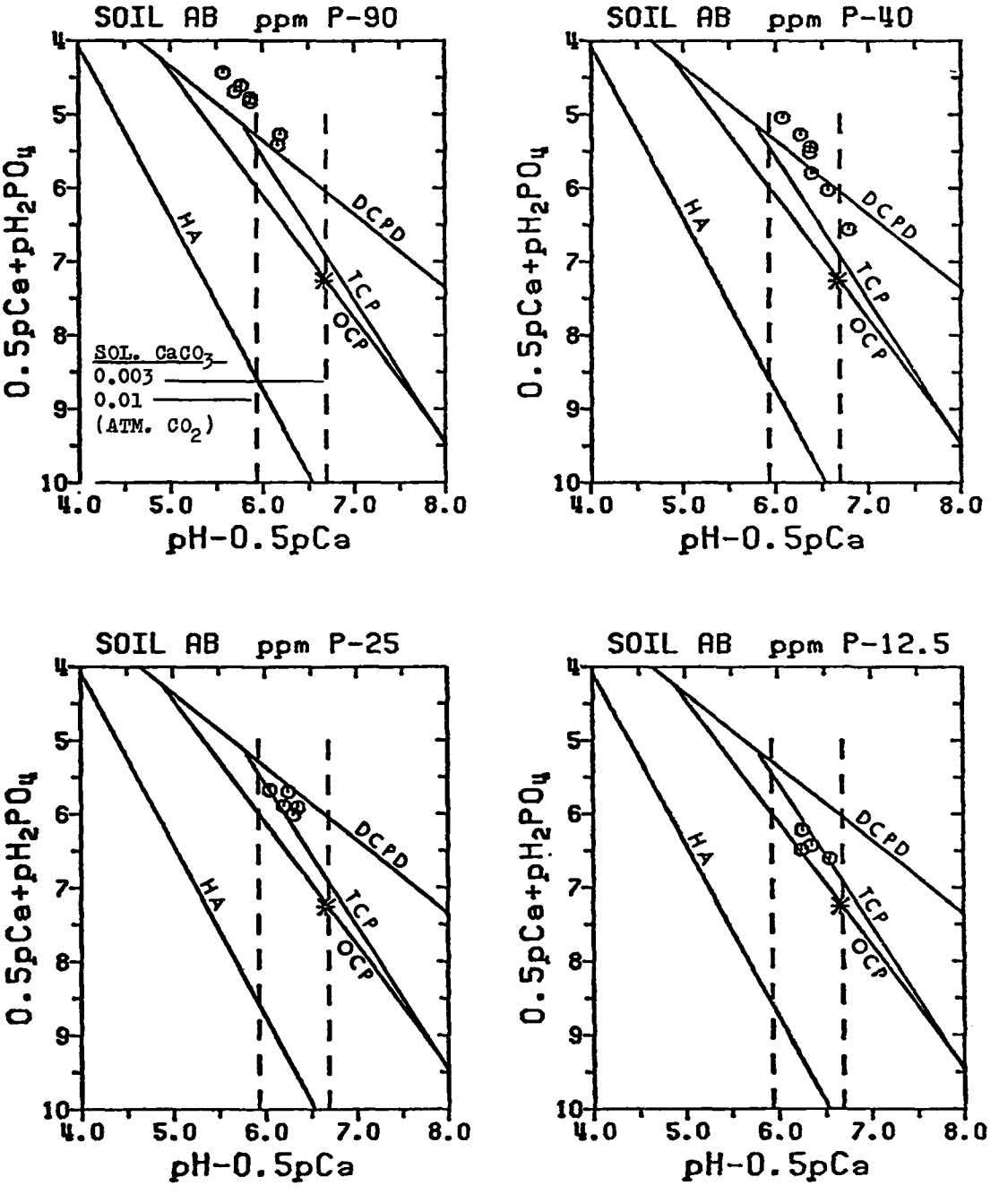
* Untreated soil

FIG. 6. CHANGES IN LIME AND PHOSPHATE POTENTIALS IN SOIL - O BY ADDING 100, 40, 25, AND 12.5 ppm P.



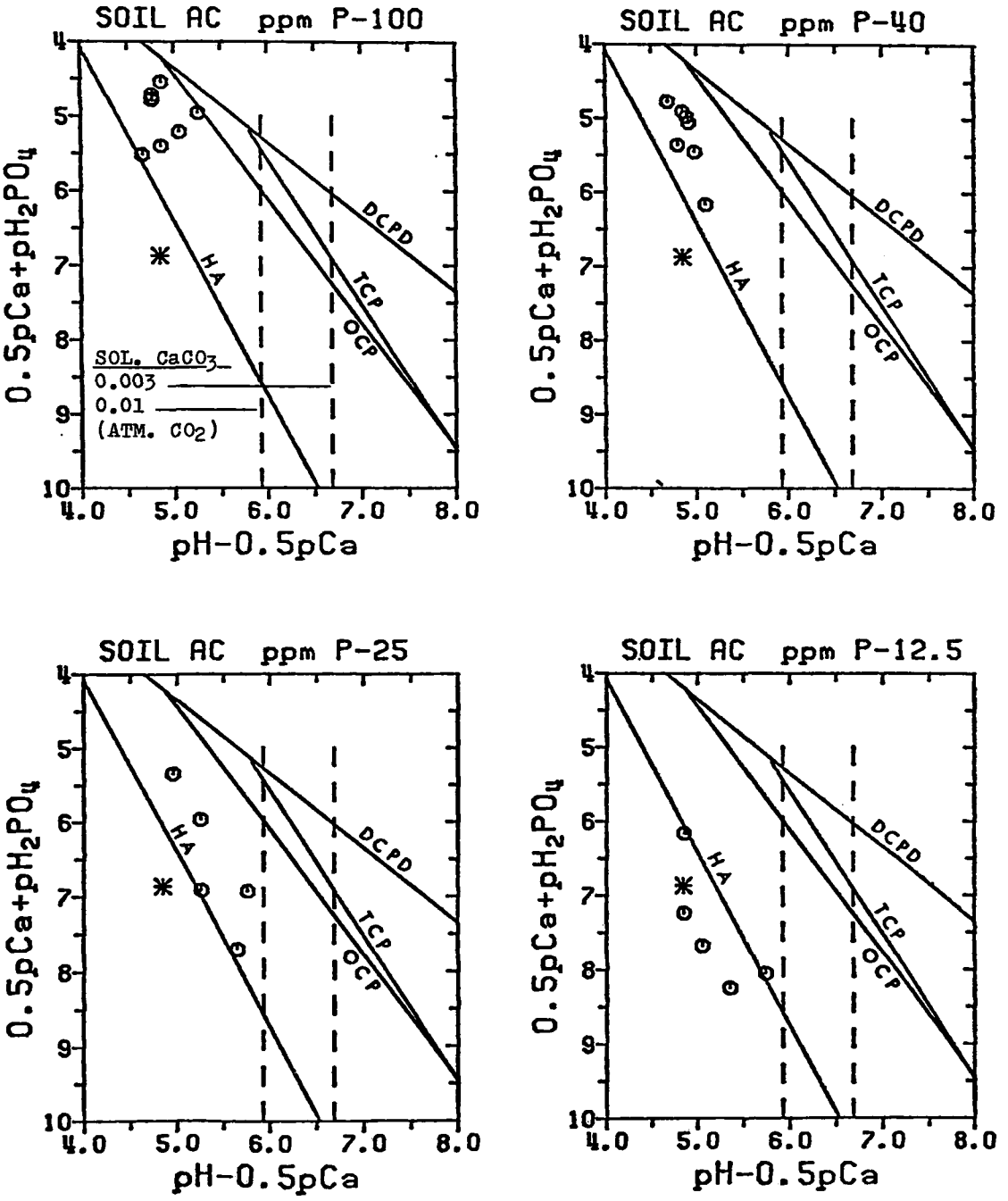
* Untreated soil

FIG. 7. CHANGES IN LIME AND PHOSPHATE POTENTIALS IN SOIL - AB BY ADDING 100, 40, 25, AND 12.5 ppm P.



* Untreated soil

FIG. 8. CHANGES IN LIME AND PHOSPHATE POTENTIALS IN SOIL - AC BY ADDING 100, 40, 25, AND 12.5 ppm P.



* Untreated soil

potentials than the original sample. This suggests a further reaction of *in situ* phosphorus along with the added P.

The phosphate potentials of Soils O and AB increased to reach those of untreated samples. The rate of transformation was P rate dependent; slower with increased P additions. Soil O when treated with 25 and 12.5 ppm P was in equilibrium with octacalcium phosphate with calculated ion activity products ranging between 46 and 47. Aslyng (10), and Weber and Mattingly (13) reported solubility data consistent with the existence of octacalcium phosphate for some Rothamsted soils.

The calculated ion activity products of $Ca_3(PO_4)_2$ at 1000 and 3000 hours after adding 100 ppm P to Soil O were 26.02 and 26.09; also the ion activity product of P untreated soil was 26.07. These ion activity products agree with the reported pK_{sp} value of 26 for $Ca_3(PO_4)_2$. It is likely that $Ca_3(PO_4)_2$ exists in soils as an unstable intermediary reaction product which with time changes to less soluble octacalcium phosphate and hydroxyapatite.

REACTIONS IN A NEUTRAL SOIL

Solubility data for Soil AC are presented in Appendix Table 4. Phosphorus applications in general lowered the pH, and lime and phosphate potentials. Depending on the rate of P application, the soil yielded extracts that were supersaturated or in equilibrium with hydroxyapatite (Fig. 8). When 100 ppm P was added the extracts were undersaturated with respect to octacalcium phosphate and supersaturated with respect to hydroxyapatite until 1000 hours. At 3000 hours the soil solution was in equilibrium with hydroxyapatite with a calculated ion activity product ($10pCa + 6pPO_4 + 2pOH$) of 113.2. Application of 40 ppm P supersaturated the soil with respect to HA until 1000 hours. Three hundred hours after adding 25 ppm P, HA controlled P solubility. Solubility data showed the existence of HA, 3 hours after adding 12.5 ppm P. According to several scientists (13, 16), acid soils limed to near neutral pH values were in equilibrium with hydroxyapatite.

X-RAY DIFFRACTION WORK

A method very similar to that of Bell and Black (23) was used to identify the reaction products of applied orthophosphates. Monocalcium phosphate monohydrate was mixed with soils and incubated in plexiglas cylinders. The cylinders were kept in a saturated atmosphere in a desiccator to prevent water loss by evaporation. Precaution was taken to provide adequate aeration at the reacting surface. X-ray diffraction patterns of the samples from the reaction surface were obtained by a Philips X-ray diffractometer using nickel-filtered Cu K α radiation with a pulse height analyzer. Identifications were made by comparing the X-ray diffraction patterns obtained with those published by Lehr et al. (24). Peak heights were used to quantitatively determine the reaction products. The quantitative data thus obtained are subject to ± 5 to 10% error.

Applied $Ca(H_2PO_4)_2 \cdot H_2O$ transformed to $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ in all the soils, which remained unchanged for more than a year. Proportions of $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ for one acid - (Soil B), and one neutral - (Soil AC), and one alkaline soil (Soil O) are presented in Appendix Table 5. These results agree well with those reported elsewhere. Bell and Black (23) identified $CaHPO_4 \cdot 2H_2O$ and $CaHPO_4$ by applying $Ca(H_2PO_4)_2 \cdot H_2O$ to slightly acid and alkaline soils. Moreno et al. (15) mixed very high concentrations of P with an acid soil and showed the soil solution was saturated with respect to $CaHPO_4 \cdot 2H_2O$ in less than an hour and remained so after one month. It is a general observation that phosphate fertilizers when banded supply more P to plants than when broadcasted; and this phenomenon is more so in the acid soils. Phosphorus concentrations are higher in the banding site and the soil zone is saturated with $CaHPO_4 \cdot 2H_2O$. Broadcasting favors aluminum and iron phosphates in acid soils and octacalcium phosphate in alkaline soils which are less soluble than $CaHPO_4 \cdot 2H_2O$.

Applied $Ca(H_2PO_4)_2 \cdot H_2O$ should transform to the next less soluble compound $CaHPO_4 \cdot 2H_2O$. However, a close look at the results in Appendix Table 5 reveals that $CaHPO_4$ precipitated earlier than $CaHPO_4 \cdot 2H_2O$. The transformation of $CaHPO_4 \cdot 2H_2O$ to $CaHPO_4$ might have occurred while drying the samples for X-ray diffraction analysis.

SECTION 6

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APPENDIX TABLE 1

Table 1. Fraction of total P as H_3PO_4, $H_2PO_4^{-1}$, HPO_4^{-2}, PO_4^{-3} at various values.

	FRACTION OF TOTAL P AS:			
PH	H3PO4	H2PO4	HPO4	PO4
4.00	0.131E-01	0.986E 00	0.624E-03	0.295E-11
4.05	0.117E-01	0.988E 00	0.701E-03	0.372E-11
4.10	0.105E-01	0.989E 00	0.788E-03	0.469E-11
4.15	0.933E-02	0.990E 00	0.885E-03	0.591E-11
4.20	0.832E-02	0.991E 00	0.994E-03	0.745E-11
4.25	0.742E-02	0.991E 00	0.112E-02	0.939E-11
4.30	0.662E-02	0.992E 00	0.125E-02	0.118E-10
4.35	0.590E-02	0.993E 00	0.141E-02	0.149E-10
4.40	0.526E-02	0.993E 00	0.158E-02	0.188E-10
4.45	0.469E-02	0.994E 00	0.177E-02	0.236E-10
4.50	0.418E-02	0.994E 00	0.199E-02	0.298E-10
4.55	0.373E-02	0.994E 00	0.223E-02	0.375E-10
4.60	0.333E-02	0.994E 00	0.251E-02	0.472E-10
4.65	0.296E-02	0.994E 00	0.281E-02	0.594E-10
4.70	0.264E-02	0.994E 00	0.315E-02	0.748E-10
4.75	0.235E-02	0.994E 00	0.354E-02	0.941E-10
4.80	0.210E-02	0.994E 00	0.397E-02	0.118E-09
4.85	0.187E-02	0.994E 00	0.445E-02	0.149E-09
4.90	0.167E-02	0.993E 00	0.499E-02	0.188E-09
4.95	0.148E-02	0.993E 00	0.560E-02	0.236E-09

	FRACTION OF TOTAL P AS:			
PH	H3PO4	H2PO4	HPO4	PO4
5.00	0.132E-02	0.992E 00	0.628E-02	0.297E-09
5.05	0.118E-02	0.992E 00	0.704E-02	0.374E-09
5.10	0.105E-02	0.991E 00	0.790E-02	0.470E-09
5.15	0.933E-03	0.990E 00	0.885E-02	0.592E-09
5.20	0.831E-03	0.989E 00	0.992E-02	0.744E-09
5.25	0.740E-03	0.988E 00	0.111E-01	0.936E-09
5.30	0.659E-03	0.987E 00	0.125E-01	0.118E-08
5.35	0.586E-03	0.985E 00	0.140E-01	0.148E-08
5.40	0.522E-03	0.984E 00	0.156E-01	0.186E-08
5.45	0.464E-03	0.982E 00	0.175E-01	0.234E-08
5.50	0.413E-03	0.980E 00	0.196E-01	0.293E-08
5.55	0.367E-03	0.978E 00	0.220E-01	0.369E-08
5.60	0.326E-03	0.975E 00	0.246E-01	0.463E-08
5.65	0.290E-03	0.972E 00	0.275E-01	0.581E-08
5.70	0.257E-03	0.969E 00	0.307E-01	0.729E-08
5.75	0.229E-03	0.965E 00	0.344E-01	0.914E-08
5.80	0.203E-03	0.961E 00	0.384E-01	0.115E-07
5.85	0.180E-03	0.957E 00	0.429E-01	0.144E-07
5.90	0.160E-03	0.952E 00	0.479E-01	0.180E-07
5.95	0.141E-03	0.946E 00	0.534E-01	0.225E-07

APPENDIX TABLE 1 (continued)

	FRACTION OF TOTAL P AS:			
PH	H3PO4	H2PO4	HPO4	PO4
6.00	0.125E-03	0.940E 00	0.595E-01	0.282E-07
6.05	0.111E-03	0.934E 00	0.663E-01	0.352E-07
6.10	0.980E-04	0.926E 00	0.738E-01	0.439E-07
6.15	0.865E-04	0.918E 00	0.821E-01	0.548E-07
6.20	0.764E-04	0.909E 00	0.912E-01	0.683E-07
6.25	0.673E-04	0.899E 00	0.101E 00	0.851E-07
6.30	0.593E-04	0.888E 00	0.112E 00	0.106E-06
6.35	0.521E-04	0.876E 00	0.124E 00	0.131E-06
6.40	0.457E-04	0.863E 00	0.137E 00	0.163E-06
6.45	0.401E-04	0.849E 00	0.151E 00	0.202E-06
6.50	0.351E-04	0.833E 00	0.167E 00	0.249E-06
6.55	0.306E-04	0.817E 00	0.183E 00	0.308E-06
6.60	0.267E-04	0.799E 00	0.201E 00	0.379E-06
6.65	0.232E-04	0.780E 00	0.220E 00	0.466E-06
6.70	0.202E-04	0.759E 00	0.241E 00	0.571E-06
6.75	0.175E-04	0.737E 00	0.262E 00	0.698E-06
6.80	0.151E-04	0.715E 00	0.285E 00	0.852E-06
6.85	0.130E-04	0.691E 00	0.309E 00	0.104E-05
6.90	0.112E-04	0.665E 00	0.335E 00	0.126E-05
6.95	0.955E-05	0.639E 00	0.361E 00	0.152E-05

APPENDIX TABLE 1 (continued)

	FRACTION OF TOTAL P AS:			
PH	H3PO4	H2PO4	HPO4	PO4
7.00	0.816E-05	0.612E 00	0.388E 00	0.183E-05
7.05	0.694E-05	0.585E 00	0.415E 00	0.220E-05
7.10	0.589E-05	0.557E 00	0.443E 00	0.264E-05
7.15	0.498E-05	0.528E 00	0.472E 00	0.315E-05
7.20	0.419E-05	0.499E 00	0.501E 00	0.375E-05
7.25	0.352E-05	0.470E 00	0.530E 00	0.445E-05
7.30	0.295E-05	0.442E 00	0.558E 00	0.527E-05
7.35	0.246E-05	0.414E 00	0.586E 00	0.621E-05
7.40	0.205E-05	0.386E 00	0.614E 00	0.729E-05
7.45	0.170E-05	0.359E 00	0.641E 00	0.854E-05
7.50	0.140E-05	0.333E 00	0.667E 00	0.997E-05
7.55	0.116E-05	0.308E 00	0.692E 00	0.116E-04
7.60	0.950E-06	0.284E 00	0.716E 00	0.135E-04
7.65	0.779E-06	0.261E 00	0.739E 00	0.156E-04
7.70	0.637E-06	0.240E 00	0.760E 00	0.180E-04
7.75	0.519E-06	0.219E 00	0.781E 00	0.208E-04
7.80	0.423E-06	0.200E 00	0.800E 00	0.239E-04
7.85	0.343E-06	0.182E 00	0.818E 00	0.274E-04
7.90	0.278E-06	0.166E 00	0.834E 00	0.313E-04
7.95	0.225E-06	0.151E 00	0.849E 00	0.358E-04

APPENDIX TABLE 1 (continued)

	FRACTION OF TOTAL P AS:			
PH	H3PO4	H2PO4	HPO4	PO4
8.00	0.182E-06	0.136E 00	0.864E 00	0.408E-04
8.05	0.146E-06	0.123E 00	0.877E 00	0.465E-04
8.10	0.118E-06	0.112E 00	0.888E 00	0.529E-04
8.15	0.948E-07	0.101E 00	0.899E 00	0.601E-04
8.20	0.762E-07	0.906E-01	0.909E 00	0.682E-04
8.25	0.611E-07	0.816E-01	0.918E 00	0.772E-04
8.30	0.490E-07	0.734E-01	0.927E 00	0.874E-04
8.35	0.392E-07	0.659E-01	0.934E 00	0.989E-04
8.40	0.314E-07	0.592E-01	0.941E 00	0.112E-03
8.45	0.251E-07	0.531E-01	0.947E 00	0.126E-03
8.50	0.200E-07	0.476E-01	0.952E 00	0.142E-03
8.55	0.160E-07	0.426E-01	0.957E 00	0.161E-03
8.60	0.128E-07	0.382E-01	0.962E 00	0.181E-03
8.65	0.102E-07	0.342E-01	0.966E 00	0.204E-03
8.70	0.812E-08	0.306E-01	0.969E 00	0.230E-03
8.75	0.647E-08	0.273E-01	0.972E 00	0.259E-03
8.80	0.515E-08	0.244E-01	0.975E 00	0.291E-03
8.85	0.411E-08	0.218E-01	0.978E 00	0.327E-03
8.90	0.327E-08	0.195E-01	0.980E 00	0.368E-03
8.95	0.260E-08	0.174E-01	0.982E 00	0.414E-03

APPENDIX TABLE 2

Table 2. Solubility data obtained from adding 100, 40, 25, and 12.5 ppm P (soil basis) to acid soils.

SOIL- B

P CONCENTRATION- 100 ppm

TIME(HRS)	pH	P(ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	4.00	0.490	6.68	4.81	8.01	16.33
3	4.00	0.620	6.58	4.70	7.90	16.23
10	4.00	0.480	6.69	4.82	8.01	16.34
30	4.00	0.600	6.59	4.72	7.92	16.24
100	4.10	0.330	6.95	4.98	8.08	16.30
300	4.30	0.146	7.51	5.33	8.23	16.25
1000	4.00	0.246	6.98	5.11	8.30	16.63
3000	4.20	0.026	8.16	6.08	9.08	17.20

TIME(HRS)	Al(ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	0.880	5.017	35.02	29.82
3	0.790	5.065	35.06	29.77
10	0.830	5.044	35.04	29.86
30	0.820	5.055	35.05	29.77
100	0.810	5.063	34.76	29.84
300	0.810	5.078	34.18	29.81
1000	0.810	5.057	35.06	30.16
3000	0.720	5.119	34.52	30.80

SOIL- B

P CONCENTRATION- 25 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	4.25	0.020	8.32	6.19	9.14	17.22
30	4.35	0.020	8.42	6.19	9.04	17.02
100	4.50	0.015	8.69	6.32	9.02	16.84
300	4.30	0.003	9.19	7.02	9.92	17.94
1000	4.50	0.006	9.09	6.72	9.41	17.24

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	0.720	5.121	34.37	30.81
30	0.650	5.174	34.12	30.67
100	0.600	5.232	33.73	30.55
300	0.500	5.283	34.38	31.70
1000	0.600	5.229	33.73	30.94

APPENDIX TABLE 2 (continued)

SOIL- B

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
30	4.30	0.012	8.59	6.42	9.31	17.34
100	4.20	0.008	8.67	6.59	9.59	17.72
1000	4.50	0.003	9.39	7.02	9.72	17.54

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
30	0.680	5.131	34.23	30.95
100	0.560	5.231	34.63	31.42
1000	0.600	5.233	33.73	31.25

APPENDIX TABLE 2 (continued)

SOIL- D

P CONCENTRATION- 100 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	4.80	0.173	7.93	5.26	7.65	15.18
10	4.80	0.155	7.98	5.30	7.70	15.23
30	4.80	0.075	8.29	5.62	8.02	15.54
100	4.90	0.060	8.49	5.72	8.01	15.44
300	5.10	0.030	8.99	6.02	8.12	15.34
3000	5.20	0.010	9.57	6.50	8.49	15.62

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	0.290	5.612	33.21	29.27
10	0.320	5.567	33.17	29.27
30	0.350	5.529	33.13	29.55
100	0.160	5.891	33.19	29.81
300	0.130	6.057	32.76	29.88
3000	0.100	6.216	32.62	30.31

APPENDIX TABLE 2 (continued)

SOIL- D

P CONCENTRATION- 40 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	4.80	0.130	8.06	5.38	7.78	15.30
3	4.80	0.130	8.06	5.38	7.78	15.30
10	4.90	0.040	8.67	5.89	8.19	15.62
30	4.90	0.020	8.97	6.19	8.49	15.92
100	4.80	0.020	8.87	6.19	8.59	16.12
300	4.90	0.015	9.09	6.32	8.62	16.04
1000	5.10	0.016	9.27	6.29	8.39	15.61

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	0.175	5.831	33.43	29.61
3	0.170	5.843	33.44	29.62
10	0.205	5.790	33.09	29.88
30	0.270	5.670	32.97	30.06
100	0.185	5.798	33.40	30.39
300	0.205	5.787	33.09	30.30
1000	0.215	5.839	32.54	29.93

APPENDIX TABLE 2 (continued)

SOIL- D

P CONCENTRATION- 25 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	4.90	0.100	8.27	5.49	7.79	15.22
30	4.90	0.033	8.75	5.98	8.27	15.70
100	5.10	0.013	9.36	6.38	8.48	15.70
300	4.90	0.008	9.37	6.59	8.89	16.31
1000	5.40	0.001	10.77	7.50	9.30	16.22

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	0.235	5.723	33.02	29.42
30	0.100	6.096	33.40	30.27
100	0.110	6.126	32.83	30.31
300	0.250	5.699	33.00	30.49
1000	0.110	6.276	32.08	30.97

APPENDIX TABLE 2 (continued)

SOIL- D

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	4.70	0.019	8.79	6.21	8.71	16.34
30	4.65	0.023	8.66	6.13	8.68	16.36
100	4.80	0.010	9.17	6.49	8.89	16.42
300	4.95	0.009	9.37	6.54	8.79	16.16
1000	5.10	0.004	9.87	6.89	8.99	16.22

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	0.140	5.897	33.80	30.71
30	0.190	5.752	33.80	30.58
100	0.085	6.136	33.74	31.03
300	0.075	6.234	33.38	30.87
1000	0.140	6.022	32.72	30.71

APPENDIX TABLE 2 (continued)

SOIL- U

P CONCENTRATION- 100 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	5.00	15.850	6.17	3.29	5.49	12.82
10	5.00	7.480	6.50	3.62	5.82	13.14
30	5.00	5.400	6.64	3.76	5.96	13.29
100	5.50	3.300	7.36	3.98	5.68	12.50
300	5.40	1.230	7.68	4.41	6.21	13.13
1000	5.40	0.630	7.97	4.70	6.50	13.42
3000	5.30	0.368	8.11	4.93	6.83	13.85

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	0.320	5.635	32.63	26.93
10	0.335	5.613	32.61	27.23
30	0.265	5.700	32.70	27.46
100	0.200	6.089	31.59	27.07
300	0.125	6.232	32.03	27.84
1000	0.195	6.039	31.84	27.94
3000	0.145	6.111	32.21	28.44

APPENDIX TABLE 2 (continued)

SOIL- U

P CONCENTRATION- 40 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	4.85	6.400	6.41	3.69	6.04	13.51
3	4.95	5.100	6.61	3.79	6.04	13.41
10	5.10	2.900	7.01	4.03	6.13	13.36
30	5.10	3.800	6.89	3.92	6.01	13.24
100	5.60	0.400	8.38	4.90	6.50	13.22
300	5.80	0.010	10.18	6.51	7.91	14.43
1000	5.30	0.010	9.67	6.50	8.40	15.42

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	0.360	5.535	32.99	27.52
3	0.235	5.759	32.91	27.65
10	0.220	5.834	32.53	27.67
30	0.230	5.801	32.50	27.52
100	0.110	6.416	31.62	28.12
300	0.175	6.362	30.96	29.27
1000	0.195	5.983	32.08	29.88

APPENDIX TABLE 2 (continued)

SOIL- U

P CONCENTRATION- 25 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	5.10	0.700	7.63	4.65	6.75	13.97
30	5.15	0.425	7.89	4.87	6.92	14.09
100	5.30	0.308	8.18	5.01	6.91	13.93
300	5.10	0.028	9.02	6.05	8.15	15.37
1000	5.20	0.034	9.04	5.96	7.96	15.09

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	0.300	5.699	32.40	28.15
30	0.265	5.775	32.33	28.34
100	0.205	5.960	32.06	28.37
300	0.205	5.867	32.57	29.72
1000	0.220	5.877	32.28	29.44

APPENDIX TABLE 2 (continued)

SOIL- U

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	4.85	0.195	7.93	5.20	7.55	15.03
30	4.90	0.115	8.21	5.43	7.73	15.16
100	5.15	0.034	8.99	5.96	8.01	15.19
300	5.15	0.026	9.11	6.08	8.13	15.30
1000	5.20	0.020	9.27	6.19	8.19	15.32

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	0.360	5.532	32.98	29.04
30	0.320	5.599	32.90	29.23
100	0.200	5.897	32.45	29.56
300	0.175	5.952	32.50	29.73
1000	0.175	5.978	32.38	29.77

APPENDIX TABLE 2 (continued)

SOIL- Y

P CONCENTRATION- 100 ppm

TIME(HRS)	pH	P(ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	4.40	2.060	6.46	4.18	6.98	14.90
3	4.40	1.960	6.48	4.20	7.00	14.93
10	4.40	2.170	6.43	4.16	6.96	14.88
30	4.40	2.010	6.47	4.19	6.99	14.91
100	4.55	1.560	6.73	4.30	6.95	14.72
300	4.60	0.710	7.12	4.64	7.24	14.97
1000	4.80	0.100	8.17	5.49	7.89	15.42
3000	4.90	0.090	8.32	5.54	7.84	15.26

TIME(HRS)	Al(ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	0.030	6.536	35.34	29.92
3	0.050	6.311	35.11	29.71
10	0.030	6.526	35.33	29.88
30	0.740	5.123	33.92	28.51
100	0.760	5.128	33.48	28.33
300	0.950	5.044	33.24	28.49
1000	1.060	5.043	32.64	28.94
3000	0.950	5.123	32.42	28.86

APPENDIX TABLE 2 (continued)

SOIL- Y

P CONCENTRATION- 40 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	4.30	1.880	6.40	4.22	7.12	15.14
3	4.40	1.580	6.57	4.30	7.09	15.02
10	4.40	1.100	6.73	4.45	7.25	15.18
30	4.40	1.200	6.69	4.41	7.21	15.14
100	4.50	0.740	7.00	4.62	7.32	15.15
300	4.80	0.320	7.66	4.99	7.39	14.91
1000	4.90	0.130	8.16	5.38	7.68	15.10

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	1.240	4.909	34.01	28.53
3	1.210	4.927	33.73	28.42
10	1.880	4.729	33.53	28.38
30	2.400	4.612	33.41	28.23
100	0.810	5.092	33.59	28.72
300	0.550	5.327	32.93	28.72
1000	0.670	5.271	32.57	28.85

APPENDIX TABLE 2 (continued)

SOIL- Y

P CONCENTRATION- 25 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	4.50	0.888	6.92	4.55	7.24	15.07
30	4.50	0.800	6.97	4.59	7.29	15.11
100	4.70	0.575	7.31	4.73	7.23	14.86
300	5.10	0.118	8.40	5.42	7.52	14.75
1000	5.30	0.089	8.72	5.55	7.45	14.47

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	1.150	4.947	33.45	28.49
30	1.280	4.897	33.40	28.49
100	0.840	5.113	33.01	28.45
300	0.550	5.417	32.12	28.64
1000	0.310	5.760	31.86	28.71

APPENDIX TABLE 2 (continued)

SOIL- Y

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	4.30	0.658	6.85	4.68	7.57	15.60
30	4.30	0.183	7.41	5.23	8.13	16.16
100	4.50	0.258	7.46	5.08	7.78	15.61
300	5.10	0.060	8.69	5.72	7.82	15.04
1000	4.60	0.078	8.08	5.60	8.20	15.93

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	1.590	4.779	33.88	28.85
30	1.500	4.807	33.91	29.44
100	0.530	5.282	33.78	29.36
300	0.350	5.615	32.32	29.13
1000	0.570	5.269	33.47	29.67

APPENDIX TABLE 2 (continued)

SOIL- AA

P CONCENTRATION- 100 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	5.20	0.170	8.34	5.27	7.26	14.39
3	5.20	0.213	8.24	5.17	7.17	14.29
10	5.20	0.220	8.23	5.15	7.15	14.28
30	5.40	0.257	8.36	5.09	6.89	13.81
100	6.10	0.092	9.54	5.56	6.66	12.88
300	5.60	0.148	8.81	5.33	6.93	13.66
1000	5.70	0.110	9.04	5.46	6.96	13.59
3000	4.90	0.019	8.99	6.22	8.51	15.94

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	0.055	6.485	32.89	29.35
3	0.205	5.911	32.31	28.68
10	0.150	6.047	32.45	28.80
30	0.088	6.380	32.18	28.67
100	0.301	6.363	30.06	27.72
300	0.175	6.208	31.41	28.34
1000	0.120	6.447	31.35	28.51
3000	0.360	5.550	32.85	29.97

APPENDIX TABLE 2 (continued)

SOIL- AA

P CONCENTRATION- 40 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	5.10	0.600	7.69	4.72	6.82	14.04
3	5.20	0.150	8.40	5.32	7.32	14.44
10	5.20	0.080	8.67	5.59	7.59	14.72
30	5.30	0.090	8.72	5.54	7.44	14.47
100	5.60	0.010	9.98	6.50	8.10	14.83
300	5.50	0.010	9.88	6.50	8.20	15.02
1000	6.70	0.020	10.89	6.31	6.81	12.43

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
1	0.240	5.801	32.50	28.32
3	0.240	5.843	32.24	28.76
10	0.180	5.968	32.37	29.16
30	0.300	5.791	31.89	28.73
100	0.105	6.421	31.62	29.72
300	0.160	6.180	31.68	29.68
1000	0.270	6.979	28.88	27.89

APPENDIX TABLE 2 (continued)

SOIL- AA

P CONCENTRATION- 25 ppm

TIME(HRS)	pH	P(ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	5.40	0.108	8.74	5.46	7.26	14.19
30	5.80	0.050	9.48	5.81	7.21	13.73
100	6.50	0.073	10.08	5.71	6.41	12.23
300	6.60	0.030	10.59	6.11	6.71	12.44
1000	6.60	0.116	10.00	5.52	6.12	11.85

TIME(HRS)	Al(ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	0.130	6.207	32.01	28.87
30	0.270	6.161	30.76	28.37
100	0.430	6.576	29.08	27.28
300	0.200	7.004	29.20	27.92
1000	0.340	6.769	28.97	27.09

APPENDIX TABLE 2 (continued)

SOIL- AA

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	5.10	0.060	8.69	5.72	7.82	15.04
30	5.50	0.007	10.03	6.65	8.35	15.18
100	6.25	0.010	10.66	6.54	7.49	13.56
300	6.60	0.025	10.67	6.19	6.79	12.51
1000	6.75	0.071	10.40	5.77	6.22	11.80

TIME (HRS)	Al (ppm)	pAl	pAl+3pOH	$pAl+2pOH+pH_2PO_4$
3	0.215	5.830	32.53	29.35
30	0.070	6.535	32.03	30.19
100	0.025	7.578	30.83	29.62
300	0.550	6.562	28.76	27.55
1000	0.180	7.191	28.94	27.46

APPENDIX TABLE 3

Table 3. Solubility data obtained from adding 100, 40, 25, and 12.5 ppm P (soil basis) to alkaline soils E, O, and AB.

SOIL- E

P CONCENTRATION- 100 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	7.80	0.400	11.26	5.59	4.99	9.51
3	7.80	0.561	11.12	5.44	4.84	9.36
10	7.80	0.661	11.04	5.37	4.77	9.29
30	7.80	0.715	11.01	5.34	4.73	9.26
100	7.85	0.510	11.25	5.52	4.87	9.35
300	7.70	0.465	11.02	5.44	4.94	9.57
1000	7.70	0.100	11.69	6.11	5.61	10.24
3000	7.60	0.085	11.58	6.11	5.71	10.43

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
1	367.	2.9	2.29	6.65	6.73
3	359.	2.9	2.30	6.65	6.59
10	359.	3.1	2.30	6.65	6.52
30	381.	2.4	2.28	6.66	6.47
100	371.	1.3	2.29	6.71	6.67
300	376.	3.4	2.28	6.56	6.58
1000	374.	2.4	2.28	6.56	7.25
3000	369.	2.6	2.29	6.46	7.25

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
1	7.28	25.89	45.50	92.37
3	7.14	25.62	45.09	91.57
10	7.07	25.48	44.87	91.14
30	7.01	25.35	44.69	90.73
100	7.16	25.56	45.04	91.27
300	7.22	25.98	45.53	92.81
1000	7.89	27.32	47.54	96.85
3000	8.00	27.73	48.05	98.28

SOIL- E

P CONCENTRATION- 40 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	7.50	2.370	9.97	4.59	4.29	9.12
3	7.70	1.000	10.69	5.11	4.61	9.24
10	7.90	0.360	11.49	5.71	5.01	9.44
30	7.90	0.500	11.35	5.57	4.87	9.30
100	7.80	0.010	12.87	7.19	6.59	11.11
300	7.40	0.020	11.88	6.60	6.40	11.33
1000	7.50	0.010	12.34	6.97	6.67	11.49

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
1	415.	2.6	2.25	6.38	5.72
3	397.	2.6	2.26	6.57	6.24
10	397.	3.1	2.26	6.77	6.85
30	421.	3.4	2.24	6.78	6.69
100	421.	4.3	2.24	6.68	8.31
300	443.	7.4	2.22	6.29	7.71
1000	405.	2.3	2.26	6.37	8.10

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
1	6.54	24.97	43.84	90.17
3	6.87	25.26	44.45	90.63
10	7.27	25.66	45.26	91.45
30	7.11	25.31	44.75	90.37
100	8.83	28.94	50.09	101.46
300	8.62	29.30	50.25	103.32
1000	8.92	29.75	51.00	104.51

APPENDIX TABLE 3 (continued)

SOIL- B

P CONCENTRATION- 25 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	7.60	0.050	11.81	6.34	5.94	10.66
30	7.30	0.044	11.38	6.20	6.10	11.13
100	7.60	0.017	12.28	6.81	6.41	11.13
300	7.40	0.009	12.23	6.95	6.75	11.67
1000	7.40	0.003	12.70	7.43	7.23	12.15

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
3	367.	2.4	2.29	6.45	7.48
30	358.	2.9	2.30	6.15	7.35
100	359.	3.3	2.30	6.45	7.96
300	358.	3.4	2.30	6.25	8.10
1000	322.	2.6	2.34	6.23	8.60

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
3	8.23	28.20	48.75	99.69
30	8.40	29.15	49.88	103.15
100	8.70	29.16	50.18	102.56
300	9.05	30.24	51.62	106.23
1000	9.56	31.32	53.21	109.50

APPENDIX TABLE 3 (continued)

SOIL- E

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	7.40	0.018	11.92	6.65	6.45	11.37
30	7.30	0.012	11.94	6.77	6.67	11.69
100	7.20	0.003	12.39	7.32	7.31	12.44
300	7.40	0.011	12.14	6.86	6.66	11.59
1000	7.75	0.001	13.78	8.15	7.60	12.17

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
3	363.	2.6	2.29	6.25	7.80
30	371.	2.2	2.29	6.16	7.91
100	374.	3.0	2.28	6.06	8.46
300	344.	3.8	2.31	6.24	8.02
1000	376.	2.2	2.28	6.61	9.29

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
3	8.74	29.63	50.70	104.39
30	8.95	30.24	51.52	106.42
100	9.60	31.73	53.65	111.07
300	8.97	30.11	51.41	105.85
1000	9.88	31.20	53.40	108.37

APPENDIX TABLE 3 (continued)

SOIL- O

P CONCZNTRATION- 100 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	8.10	1.070	11.39	5.41	4.51	8.74
3	8.10	1.700	11.19	5.21	4.31	8.54
10	8.10	2.020	11.11	5.14	4.24	8.46
30	8.10	2.160	11.08	5.11	4.21	8.43
100	8.10	1.645	11.20	5.23	4.33	8.55
300	8.00	1.280	11.12	5.25	4.45	8.77
1000	7.90	0.380	11.47	5.69	4.99	9.42
3000	7.90	0.344	11.51	5.73	5.03	9.46

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
1	367.	23.7	2.26	6.97	6.54
3	302.	18.6	2.33	6.93	6.38
10	240.	15.2	2.42	6.89	6.35
30	215.	13.3	2.46	6.87	6.34
100	211.	13.1	2.47	6.87	6.46
300	238.	16.9	2.42	6.79	6.46
1000	253.	17.2	2.40	6.70	6.89
3000	250.	21.2	2.39	6.70	6.93

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
1	6.77	24.25	43.35	86.81
3	6.64	24.07	43.04	86.34
10	6.65	24.18	43.16	86.75
30	6.67	24.25	43.24	87.01
100	6.79	24.51	43.63	87.79
300	6.86	24.80	43.98	88.80
1000	7.39	26.02	45.73	92.64
3000	7.42	26.09	45.84	92.85

APPENDIX TABLE 3 (continued)

SOIL- O

P CONCENTRATION- 40 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	7.60	1.980	10.22	4.74	4.34	9.06
3	7.60	1.800	10.26	4.78	4.38	9.11
10	7.60	1.750	10.27	4.79	4.39	9.12
30	7.60	1.920	10.23	4.75	4.35	9.08
100	7.50	1.560	10.15	4.78	4.47	9.30
300	7.40	1.500	10.00	4.73	4.53	9.45
1000	7.60	0.990	10.52	5.04	4.64	9.37

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
1	293.	20.1	2.34	6.43	5.91
3	298.	19.3	2.34	6.43	5.95
10	300.	20.1	2.33	6.43	5.96
30	312.	22.0	2.31	6.44	5.91
100	304.	21.5	2.32	6.34	5.94
300	335.	24.6	2.29	6.26	5.87
1000	317.	23.9	2.31	6.45	6.20

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
1	6.68	25.15	44.15	90.58
3	6.72	25.22	44.26	90.79
10	6.72	25.23	44.28	90.82
30	6.67	25.10	44.09	90.42
100	6.80	25.57	44.69	92.04
300	6.81	25.76	44.90	92.78
1000	6.95	25.65	44.92	92.06

APPENDIX TABLE 3 (continued)

SOIL- O

P CONCENTRATION- 25 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	7.75	0.575	11.02	5.39	4.84	9.41
30	7.55	0.610	10.64	5.22	4.87	9.64
100	7.70	0.513	10.98	5.40	4.90	9.52
300	7.50	0.268	10.92	5.54	5.24	10.06
1000	7.75	0.169	11.55	5.92	5.37	9.95

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
3	243.	17.8	2.41	6.55	6.59
30	244.	19.7	2.40	6.35	6.42
100	253.	21.6	2.39	6.51	6.59
300	252.	23.0	2.38	6.31	6.73
1000	235.	22.7	2.41	6.55	7.13

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
3	7.25	26.05	45.62	93.06
30	7.27	26.49	46.08	94.76
100	7.29	26.21	45.82	93.60
300	7.62	27.28	47.23	97.22
1000	7.78	27.11	47.22	96.25

APPENDIX TABLE 3 (continued)

SOIL- O

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	7.60	0.348	10.97	5.50	5.09	9.82
30	7.60	0.193	11.23	5.75	5.35	10.08
100	7.40	0.313	10.68	5.41	5.21	10.13
300	7.50	0.183	11.08	5.71	5.40	10.23
1000	7.60	0.224	11.16	5.69	5.29	10.01

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
3	248.	18.4	2.40	6.40	6.70
30	248.	17.9	2.40	6.40	6.95
100	241.	19.3	2.41	6.20	6.61
300	239.	21.0	2.41	6.30	6.91
1000	244.	23.2	2.39	6.40	6.88

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
3	7.49	26.84	46.66	95.71
30	7.75	27.35	47.43	97.26
100	7.61	27.49	47.42	98.06
300	7.81	27.68	47.81	98.43
1000	7.68	27.20	47.21	96.80

APPENDIX TABLE 3 (continued)

SOIL- AB

P CONCENTRATION- 90 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	6.70	20.550	7.87	3.30	3.80	9.42
3	6.90	15.680	8.25	3.47	3.77	9.20
10	7.00	10.380	8.56	3.69	3.89	9.21
30	7.30	3.750	9.45	4.27	4.17	9.20
100	7.00	11.700	8.51	3.64	3.83	9.16
300	6.80	11.350	8.26	3.58	3.98	9.51
1000	7.30	4.920	9.33	4.15	4.05	9.08

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
1	350.	20.0	2.28	5.56	4.44
3	337.	20.1	2.29	5.75	4.62
10	337.	22.1	2.29	5.86	4.83
30	332.	24.2	2.29	6.15	5.42
100	341.	22.6	2.28	5.86	4.78
300	396.	27.0	2.23	5.69	4.70
1000	378.	29.5	2.24	6.18	5.27

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
1	6.08	25.68	44.08	93.92
3	6.06	25.27	43.66	92.30
10	6.18	25.29	43.79	92.16
30	6.46	25.26	44.05	91.48
100	6.12	25.17	43.61	91.80
300	6.21	25.70	44.23	93.71
1000	6.29	24.87	43.49	90.26

APPENDIX TABLE 3 (continued)

SOIL- AB

P CONCENTRATION- 40 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	7.20	7.550	8.99	3.91	3.91	9.04
3	7.40	5.980	9.40	4.13	3.93	8.85
10	7.50	3.950	9.75	4.37	4.07	8.90
30	7.50	4.600	9.68	4.31	4.00	8.83
100	7.70	1.680	10.46	4.89	4.38	9.01
300	7.90	0.670	11.22	5.45	4.74	9.17
1000	7.50	1.940	10.06	4.68	4.38	9.20

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
1	353.	23.0	2.27	6.06	5.05
3	334.	21.6	2.29	6.25	5.27
10	334.	24.7	2.29	6.36	5.52
30	350.	24.9	2.27	6.36	5.44
100	334.	26.1	2.29	6.56	6.03
300	375.	29.5	2.24	6.78	6.57
1000	381.	28.2	2.24	6.38	5.80

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
1	6.19	24.89	43.40	90.55
3	6.22	24.58	43.12	89.23
10	6.36	24.65	43.34	89.25
30	6.28	24.47	43.08	88.69
100	6.67	24.88	43.87	89.51
300	6.99	25.06	44.38	89.64
1000	6.62	25.13	44.07	90.62

APPENDIX TABLE 3 (continued)

SOIL- AB

P CONCENTRATION- 25 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	7.40	2.260	9.83	4.55	4.35	9.27
30	7.20	1.880	9.59	4.52	4.52	9.64
100	7.50	1.600	10.14	4.76	4.46	9.29
300	7.35	1.360	9.97	4.74	4.59	9.56
1000	7.45	1.200	10.18	4.86	4.61	9.48

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
3	323.	21.7	2.30	6.25	5.70
30	321.	21.1	2.31	6.05	5.67
100	330.	22.7	2.29	6.35	5.91
300	327.	22.3	2.30	6.20	5.89
1000	324.	21.9	2.30	6.30	6.01

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
3	6.65	25.46	44.44	91.88
30	6.82	26.20	45.35	94.52
100	6.76	25.46	44.54	91.68
300	6.89	26.02	45.24	93.67
1000	6.91	25.87	45.10	93.00

APPENDIX TABLE 3 (continued)

SOIL- AB

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	7.40	0.660	10.36	5.08	4.88	9.81
30	7.40	0.688	10.34	5.07	4.87	9.79
100	7.50	0.478	10.66	5.29	4.99	9.81
300	7.40	0.370	10.61	5.34	5.13	10.06
1000	7.70	0.452	11.03	5.46	4.95	9.58

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
3	333.	21.6	2.29	6.25	6.23
30	321.	21.3	2.31	6.25	6.22
100	331.	21.8	2.30	6.35	6.44
300	316.	21.4	2.31	6.24	6.49
1000	312.	21.9	2.31	6.54	6.61

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
3	7.18	26.50	46.00	94.99
30	7.17	26.50	46.00	95.01
100	7.28	26.51	46.12	94.83
300	7.45	27.05	46.83	96.67
1000	7.27	26.10	45.70	93.23

APPENDIX TABLE 3 (continued)

APPENDIX TABLE 4

Table 4. Solubility data obtained from adding 100, 40, 25, and 12.5 ppm P (soil basis) to neutral soil - AC.

SOIL- AC

P CONCENTRATION- 100 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	5.90	7.450	7.42	3.64	4.94	11.36
3	5.90	7.850	7.39	3.62	4.92	11.34
10	5.90	8.700	7.35	3.57	4.87	11.30
30	6.00	13.150	7.27	3.40	4.60	10.92
100	6.40	5.560	8.09	3.81	4.61	10.53
300	6.20	2.980	8.13	4.06	5.06	11.18
1000	6.00	1.860	8.12	4.25	5.45	11.77
3000	5.80	1.380	8.04	4.37	5.77	12.29

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
1	360.	5.2	2.29	4.75	4.79
3	371.	5.2	2.28	4.76	4.76
10	371.	5.5	2.28	4.76	4.71
30	364.	5.9	2.29	4.86	4.54
100	353.	4.2	2.30	5.25	4.96
300	345.	6.4	2.31	5.05	5.21
1000	353.	5.3	2.30	4.85	5.40
3000	347.	4.9	2.31	4.65	5.52

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
1	7.23	29.61	49.17	107.32
3	7.20	29.53	49.05	107.07
10	7.15	29.44	48.92	106.80
30	6.89	28.71	47.92	104.42
100	6.91	27.97	47.21	101.43
300	7.36	29.29	48.97	105.76
1000	7.75	30.45	50.52	109.64
3000	8.07	31.51	51.91	113.23

SOIL- AC

P CONCENTRATION- 40 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
1	5.80	7.380	7.32	3.64	5.04	11.56
3	6.00	6.000	7.62	3.74	4.94	11.26
10	6.00	3.630	7.83	3.96	5.16	11.48
30	6.00	4.580	7.73	3.86	5.06	11.38
100	6.10	1.600	8.30	4.32	5.42	11.64
300	6.20	0.300	9.13	5.06	6.05	12.18
1000	5.90	1.890	8.01	4.24	5.53	11.96

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
1	388.	4.3	2.27	4.67	4.77
3	326.	2.7	2.33	4.83	4.91
10	462.	5.1	2.20	4.90	5.06
30	410.	4.9	2.25	4.88	4.98
100	388.	4.5	2.27	4.97	5.45
300	445.	5.4	2.22	5.09	6.16
1000	413.	4.8	2.24	4.78	5.36

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
1	7.31	29.93	49.56	108.46
3	7.27	29.53	49.13	106.92
10	7.36	29.58	49.26	106.93
30	7.30	29.50	49.13	106.75
100	7.69	30.09	50.10	108.34
300	8.27	31.01	51.61	110.85
1000	7.78	30.65	50.76	110.40

APPENDIX TABLE 4 (continued)

SOIL- AC

P CONCENTRATION- 25 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	6.10	2.130	8.17	4.20	5.29	11.52
30	6.40	0.550	9.09	4.81	5.61	11.54
100	6.90	0.075	10.57	5.79	6.09	11.52
300	6.80	0.012	11.23	6.56	6.96	12.48
1000	6.40	0.060	10.05	5.78	6.58	12.50

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
3	348.	6.0	2.30	4.95	5.35
30	334.	5.2	2.32	5.24	5.98
100	345.	6.2	2.31	5.75	6.95
300	336.	5.8	2.32	5.64	7.72
1000	349.	5.0	2.31	5.25	6.93

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
3	7.60	29.95	49.88	107.96
30	7.93	30.04	50.30	107.64
100	8.40	29.96	50.68	106.37
300	9.27	31.92	53.51	112.47
1000	8.88	31.92	53.12	113.26

APPENDIX TABLE 4 (continued)

SOIL- AC

P CONCENTRATION- 12.5 ppm

TIME (HRS)	pH	P (ppm)	pH_3PO_4	pH_2PO_4	$pHPO_4$	pPO_4
3	6.00	0.320	8.89	5.01	6.21	12.54
30	6.20	0.010	10.61	6.53	7.53	13.66
100	6.50	0.003	11.47	7.09	7.79	13.62
300	6.90	0.006	11.67	6.89	7.19	12.61
1000	6.00	0.027	9.96	6.09	7.28	13.61

TIME (HRS)	Ca (ppm)	Mg (ppm)	pCa	pH-0.5pCa	$0.5pCa+pH_2PO_4$
3	339.	5.9	2.31	4.84	6.17
30	348.	4.8	2.31	5.05	7.69
100	342.	5.8	2.31	5.34	8.25
300	327.	5.6	2.33	5.74	8.05
1000	340.	5.6	2.31	4.84	7.24

TIME (HRS)	$pCa+pHPO_4$	$3pCa+2pPO_4$	$4pCa+pH+3pPO_4$	$10pCa+6pPO_4+2pOH$
3	8.53	32.02	52.87	114.36
30	9.84	34.23	56.40	120.60
100	10.10	34.17	56.60	119.81
300	9.52	32.21	54.05	113.16
1000	9.60	34.16	56.08	120.80

APPENDIX TABLE 5

Table 5. Reaction products of applied $Ca(H_2PO_4)_2 \cdot H_2O$ as identified by X-ray diffraction analysis.

Time (hrs)	$Ca(H_2PO_4)_2 \cdot H_2O$ (∿%)	$CaHPO_4$ (∿%)	$CaHPO_4 \cdot 2H_2O$ (∿%)
SOIL - B			
1	40	60	—
3	16	53	31
10	—	37	63
30	—	30	70
100	—	35	65
300	—	40	60
600	—	49	51
1000	—	45	55
SOIL - O			
1	40	60	—
3	19	53	28
10	—	45	55
30	—	27	73
100	—	27	73
300	—	30	70
600	—	35	65
1000	—	20	80
SOIL - AC			
1	100	—	—
3	100	—	—
10	30	70	—
30	10	90	—
100	—	50	50
300	—	55	45
600	—	40	60
1000	—	50	50

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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16. ABSTRACT

In search of a better approach to predict phosphorus movement in soils from applied wastewaters, reactions of added orthophosphates were studied in 9 different soils with widely varying physical and chemical properties. Information obtained on the nature and rate of P reaction will be coupled with P adsorption data to derive mathematical models for P movement in soils from applied wastewaters.

Compounds having higher solubility than variscite were formed which changed to crystalline variscite with time upon adding $Ca(H_2PO_4)_2 \cdot H_2O$ to acid soils. Monocalcium phosphate monohydrate in alkaline soils transformed to relatively insoluble $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $Ca_3(PO_4)_2$, $Ca_4H(PO_4)_3 \cdot 2\frac{1}{2}H_2O$, and $Ca_{10}(OH)_2(PO_4)_6$. The rate of transformation in both acid as well as alkaline soils was P rate dependent; slower with increased P rates.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chemical kinetics	Phosphorus kinetics	13-B
Soil chemistry	Solubility products	02-A
Physical chemistry		07-D
Sewage treatment		08-D
Water reclamation		
Sorption		

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 72
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