March 11, 1960

To the Graduate Council:

I am submitting herewith a thesis written by D. John Durairaj entitled "Solubility Measurements as a Means of Studying the Reaction of Phosphorus Compounds With Soils at Different pH Levels." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agronomy.

Lloyd T. Seaty
Major Professor

We have read this thesis
and recommend its acceptance:

W. L. Parks

Robert L. Olson

Accepted for the Council:

Dale Wantling
Dean of the Graduate School

SOLUBILITY MEASUREMENTS AS A MEANS OF STUDYING THE REACTION OF PHOSPHORUS COMPOUNDS WITH SOILS AT DIFFERENT pH LEVELS

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

---

by

D. John Durairaj

March 1960

28.
33

ACKNOWLEDGEMENTS

The author wishes to express his appreciation and indebtedness to:

Dr. L. F. Seatz, for planning and directing the present investigation, helpful suggestions and useful criticisms.

Professor L. N. Skold, for his interest in the investigation and for kindly scrutinizing the manuscript and giving useful suggestions.

Dr. W. L. Parks and Dr. R. S. Dotson for serving on the graduate committee, perusing the thesis and offering useful criticisms and suggestions.

Mr. K. B. Sanders and other members of the Agronomy staff for their kind cooperation and constant help.

Mrs. Georgia C. Troglen, for typing and multilithing copies of the thesis.

445404

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION	1
II.	REVIEW OF LITERATURE	4
	A. Reactions of Soluble Phosphates in Acid Soils	4
	1. Early Work	4
	2. Recent Work	4
	a. Precipitation of phosphates from solution	5
	b. Interaction with hydrated sesquioxides	7
	c. Interactions with clay	7
	d. Phosphate movements in soils	8
	e. Physical chemistry of soluble phosphate reactions in soils	9
	f. Soluble phosphate reactions in soils	10
	B. Determination of Phosphate Availability Through Soil Extractions	11
III.	EXPERIMENTAL PROCEDURE	15
	A. Preparation of Soil Samples	15
	B. Treatment of Soils With Phosphorus Materials	16
	C. Reaction of Soil With Phosphorus Materials	18
	D. Extractions	19
	E. Chemical Analysis of Soil Extracts	20
IV.	RESULTS	25
	A. Extraction of Untreated Soils With Different Extractants	25

CHAPTER PAGE

IV. (Continued)

B. Extractions of Soils Treated With Phosphorus Materials. 27

1. First Extraction: 2 Days. 27

2. Second Extraction: 9 Days 33

3. Third Extraction: 43 Days 36

4. Fourth Extraction: 137 Days 43

C. pH Variations. 51

D. Comparison of Trends of Values at the End of the Four Reaction Periods. 51

1. Phosphorus 51

2. Iron 56

3. Aluminum 57

4. Calcium. 58

E. Statistical Analysis For Study of Relationships. . 59

1. Different Extractants, Same Constituent (Phosphorus), All Soils. 59

2. Time of Reaction 60

3. Multiple Correlation 61

V. DISCUSSION 65

VI. CONCLUSIONS. 71

VII. SUMMARY. 74

LITERATURE CITED. 76

APPENDIX (Table XIX). 80

LIST OF TABLES

TABLE PAGE

I. Phosphorus, iron, aluminum and calcium extracted by water, ammonium fluoride, hydrochloric acid-ammonium fluoride and five treatments with dilute sulfuric acid from three soil series 26

II. Extraction I: Phosphorus extracted by water, ammonium fluoride, hydrochloric acid-ammonium fluoride solutions and dilute sulfuric acid (two extractions) from soils receiving different phosphorus treatments. 28

III. Extraction I: Iron extracted by dilute sulfuric acid from soils receiving different phosphorus treatments (two extractions). 30

IV. Extraction I: Aluminum extracted by dilute sulfuric acid from soils receiving different phosphorus treatments (two extractions). 31

V. Extraction I: Calcium extracted by water and dilute sulfuric acid from soils receiving different phosphorus treatments (two acid extractions) 32

VI. Extraction II: Phosphorus extracted by water, ammonium fluoride, hydrochloric acid-ammonium fluoride solutions and dilute sulfuric acid (two extractions) from soils receiving different phosphorus treatments. . . 34

TABLE PAGE

VII. Extraction II: Iron extracted by dilute sulfuric acid from soils receiving different phosphorus treatments (two extractions) 35

VIII. Extraction II: Aluminum extracted by dilute sulfuric acid from soils receiving different phosphorus treatments (two extractions) 37

IX. Extraction II: Calcium extracted by water and dilute sulfuric acid from soils receiving different phosphorus treatments (two acid extractions) 38

X. Extraction III: Phosphorus extracted by water, ammonium fluoride, hydrochloric acid-ammonium fluoride solutions and dilute sulfuric acid (two extractions) from soils receiving different phosphorus treatments. . . 39

XI. Extraction III: Iron extracted by dilute sulfuric acid from soils receiving different phosphorus treatments (two extractions). 41

XII. Extraction III: Aluminum extracted by dilute sulfuric acid from soils receiving different phosphorus treatments (two extractions). 42

XIII. Extraction III: Calcium extracted by water and dilute sulfuric acid from soils receiving different phosphorus treatments (two acid extractions) 44

XIV. Extraction IV: Phosphorus extracted by water, ammonium fluoride, hydrochloric acid-ammonium fluoride solutions and dilute sulfuric acid (two extractions) from soils receiving different phosphorus treatments. . . 45

TABLE PAGE

XV. Extraction IV: Iron extracted by dilute sulfuric acid from soils receiving different phosphorus treatments (two extractions) 47

XVI. Extraction IV: Aluminum extracted by dilute sulfuric acid from soils receiving different phosphorus treatments (two extractions) 49

XVII. Extraction IV: Calcium extracted by water and dilute sulfuric acid from soils receiving different phosphorus treatments (two acid extractions) 50

XVIII. pH values observed for different soils, phosphorus materials and reaction time intervals. 52

XIX. Results of statistical analysis for correlation. . . . 81

LIST OF FIGURES

FIGURE PAGE

1. pH variations with time in Grenada soil treated with monocalcium phosphate. 53
2. Variations with time of P, Al, Fe and Ca extracted by 0.05 N H_2SO_4 (first extraction) for MCP-treated Grenada soil of original pH about 6. 54
3. Regression of iron extracted by 0.05 N H_2SO_4: Extraction III on corresponding value for Extraction IV 62
4. Effect of liming on pH of Dewey, Grenada and Hartsells soils. 69

CHAPTER I

INTRODUCTION

When a method was devised more than a century ago for the preparation of superphosphate from rock phosphate by treatment with sulfuric acid, an important stage in the production of phosphatic fertilizers was reached. But, although an increase in phosphate availability was thereby brought about, the problem of preventing the phosphate from reacting into unavailable forms in soils has remained unsolved and still remains one of the most difficult problems confronting soil chemists.

Numerous attempts have been made to study the exact mechanism of phosphate fixation by acid soils, for devising effective methods for prevention of fixation, and many general conclusions have been made. Reaction of applied soluble phosphate with iron or aluminum either in the soluble form in the soil or in the form of hydrated oxides, to form relatively insoluble phosphates, adsorption by clay, and anion exchange involving the exchange of phosphate for the hydroxyls of clay have been some of the mechanisms suggested.

Many of the old theories overlooked the fact that a concentration gradient is bound to be set up starting with a high phosphate concentration in the immediate vicinity of phosphate fertilizer particles and passing through decreasing levels of phosphate concentration. A recognition of this phenomenon in recent times has opened the way for a better understanding of phosphate reactions in soils.

The chain of events which occurs includes the movement of water in the vapor phase toward the superphosphate particle in soil; the hydrolysis of the monocalcium phosphate (superphosphate) with the formation of a solution of high acidity and phosphate concentration; the moving out of this solution to meet increments of soil; the dissolution of iron and aluminum from soil by this solution; the precipitation of phosphate as one or more compounds forming an isomorphous series; the leaving behind of a shell of slowly available dicalcium phosphate; and the progressive dimunition of the phosphate concentration of the outward-moving solution, have all been elucidated only recently.

Modern views on the subject include the visualization of a number of phosphate compounds occurring together simultaneously. Variscite, strengite, octacalcium phosphate, hydroxyapatite and fluorapartite have been recognized as some of the possible forms into which applied soluble phosphate may eventually pass. A whole spectrum of solubilities is thus possible and the determination of the solubility at any stage will give only the resultant solubility for the compounds present. The familiar tendency of all chemical equilibria to shift toward the state of greatest stability has also been found to operate in the formation of the phosphate of the greatest stability under a given set of conditions. The great length of time taken in certain cases for equilibrium to be reached is a factor. The existence of metastable conditions and supersaturation complicate matters further.

In the face of the intricacies involved in the problem, it is difficult to study phosphate reactions in soils with a high degree of def-

initeness. But the present study was made for obtaining more specific information on the following points:

The reactions taking place between the products of the initial reaction of monocalcium phosphate with water, i.e., (1) metastable triple-point solution (MTPS), which is in metastable equilibrium with monocalcium phosphate monohydrate and dicalcium phosphate dihydrate, (2) triple-point solution (TPS), which is in stable equilibrium with monocalcium phosphate monohydrate and anhydrous dicalcium phosphate and (3) anhydrous dicalcium phosphate, and three different soils, with different pH levels, with various periods of reaction in the air-dry and wet conditions;

The various forms into which applied soluble phosphate is converted over different periods of time under different pH conditions, as indicated by the use of various extractants;

Relationships, if any, between the various forms of phosphate formed, either among themselves or with extractable iron, aluminum and calcium; and the

Relative availability of the different forms of phosphate under the various conditions of study.

CHAPTER II

REVIEW OF LITERATURE

A. Reactions of Soluble Phosphates in Acid Soils

1. Early Work

Several reviews on this subject have been described by Kurtz (22). Early workers associated the fixation of phosphate in acid soils with acid conditions, hydrated iron and aluminum oxides and, to a smaller extent, with clay.

It was generally accepted that the sesquioxides in solution reacted with the soluble phosphates to form insoluble compounds. But some workers (Ford and Heck) felt that iron and aluminum phosphates could form in soils by reaction of soluble phosphate with hydrated iron and aluminum, even though the latter were not in solution. It appeared likely that the phosphate formed complex addition compounds with the hydrated sesquioxides, because the fixation was too slow for a gradual solution of the sesquioxides and their reprecipitation as phosphates.

Early workers emphasized stoichiometric relationships between the reacting compounds and their reaction products. Thus, it was speculated that the products formed with the sesquioxides were one or more of the known iron and aluminum phosphates.

2. Recent Work

Modern workers have studied the precipitation of phosphates from solution, interaction of soluble phosphates with hydrated sesquioxides,

interaction of phosphate with clay, and the physical chemistry of reactions of soluble phosphates in the soil.

a. Precipitation of phosphates from solution. Metzger (33) mentioned that precipitation from solution could very largely account for phosphate fixation, under field conditions, by acid soils of the prairie group, and probably other groups of acid soils.

Kittrick and Jackson (19) found that the rate of phosphate reaction was high to start with, but decreased rapidly in a few minutes. Colloidal ferric oxide and aluminum hydroxide, analogous to reactive surfaces responsible for the rapid phosphate precipitation, formed, in a few minutes separate-phase phosphate crystals by the mechanism of solution-precipitation. They followed these reactions by using the electron microscope.

Haseman et al. (15) treated goethite, gibbsite, illite, kaolinite and montmorillonite with phosphate solutions, and different bases. By this process they were able to isolate and identify, through optical examination and other means, crystals of palmerite-like phosphate minerals in which iron and aluminum could be present in widely varying proportions. In a subsequent work, Haseman et al. (16) described non-soil systems showing that taranakite and three other groups of similar minerals were formed under conditions resembling those in soils. The formulae of the minerals suggest extensive isomorphous substitution and provide for an extended series of solubilities, proportions and compositions.

Lindsay and Stephenson (28) found by X-ray analysis that the solids precipitating out of TPS which had first reacted with soil were mostly crystalline iron, aluminum and calcium phosphates.

Cole and Jackson (7) studied the solubility products of variscite and strengite systems. The formation of this series of phosphates in acid soils containing reactive aluminum or iron seemed possible since the solubility equilibrium constant was of such magnitude as to cause the formation of minerals in this series.

The precipitation of phosphate as discrete crystals was held possible by Cole and Jackson, as well as Haseman et al. The latter, however, discussed the possibility of the phosphate ions combining during the initial stages, with superficial ions of iron and aluminum, held at the extremities of the lattice or by exchange attachment on both clays, and the hydrous oxides of iron and aluminum.

Very recently Lindsay et al. (27) determined the pKsp of the phosphate occurring in six soils taken from Mount Pleasant Experimental Farm in New York which had been treated with ordinary doses of phosphate fertilizers or lime or both. They found that the solubility product closely agreed with that of variscite after a long time.

These solubility criteria indicated that the immediate reaction products of applied phosphate in acid soils were much more soluble than variscite. But, upon aging, these intermediate reaction products were slowly transformed into variscite, which might coexist with gibbsite as stable solid phases.

This would suggest that the mineral formed ultimately by phosphate reaction in these widely different soils was identical.

Lindsay and Moreno (26) developed the use of a solubility diagram, plotting pH_2PO_4 against pH for the common soil phosphate compounds

strengite, variscite, fluorapatite, dicalcium phosphate dihydrate, octacalcium phosphate and hydroxyapatite. Curves were drawn for these phosphate compounds. These curves show what the most stable phosphorus bearing compound would be at any soil pH value.

b. Interaction with hydrated sesquioxides. Metzger (34) observed that phosphate fixing capacity was closely related to the amount of iron in easily soluble form. Aluminum was not so effective in this respect. Iron in the silicate form also was observed to participate in phosphate fixation.

Hemwall (17) noted that the fixation of phosphate in acid soils was due to the formation of insoluble hydrated basic phosphates of iron and aluminum. The formation of these products was governed by the solubility product, the common ion and the salt effect principles. Under different conditions precipitation or compound-formation occurred.

c. Interactions with clay. Dean and Rubins (11,12) demonstrated that phosphate and arsenate could be alternately adsorbed and then mutually replaced; but equivalence of replacement was not observed. These workers thought that the adsorption was an exchange of hydroxyls at the edges of the lattice, and showed a general relationship between anion exchange capacity and specific surface.

McAuliffe et al. (32) using tracer technique, and Low and Black (31) observed two types of reactions between the clay particles and the phosphate solution: (1) in concentrated solutions, phosphatalysis of kaolinite occurred through a preliminary exchange of phosphate in solution for silicate ions in the outer layer of the lattice, followed by a

decomposition of the lattice, and precipitation of an aluminum phosphate; (2) in dilute solutions, the adsorption of phosphate on clay followed the Freundlich isotherm, and increased with temperature.

Coleman (10) studied phosphate fixation in the case of kaolinite and montmorillonite and concluded little or no phosphate was fixed by these clay minerals, but that all of the phosphate was fixed by the free iron and aluminum oxides on the clay. He recognized the occurrence of anion exchange but attributed it to the hydroxyls from the free sesquioxides rather than to those from the clays.

Black (1) found that finely ground kaolinite showed a maximum phosphate fixation at pH 3 to 4 regardless of the concentration of phosphate at the time of contact.

d. Phosphate movements in soils. Lawton and Vomocil (23) studied the rate of dissolution and migration of phosphorus from granular superphosphate under different conditions. Laboratory tests, performed with fertilizer tablets in soils for different periods indicated that at field capacity, 50 to 80% of the water soluble phosphate moved out of the granules in 24 hours. Even in soils with a low moisture content of 2 to 4%, about 20 to 50% of phosphate moved out into the soil during the same period of time. Superphosphate had a pronounced tendency to absorb moisture when placed in a saturated atmosphere and to draw moisture from the soil, forming a moist shell around the granules.

Migration studies with radio-active phosphorus for three soils indicated a movement as low as 1 inch at a soil moisture level approaching field capacity.

Lehr et al. (24) observed that the diffusion of phosphorus from superphosphate into soil was governed conjointly by soil type, soil moisture and humus content, capillarity of soil, time and temperature.

Bouldin and Black (2) studied phosphorus diffusion in soils using radio-active phosphorus and observed that peaks of phosphorus concentration were found at 4 cm. intervals for MCP in Miami and Muscatine silt loams. The distribution of the diffused calcium was similar to that of diffused phosphorus.

e. Physical chemistry of soluble phosphate reactions in soils. Brown and Lehr (5) applied the phase rule to monocalcium phosphate monohydrate in a soil system and indicated its usefulness in the calculation of the fraction of phosphate left at the site of the MCP granule in the form of dicalcium phosphate.

Clark and Peech (6) found that the solubility of calcium phosphate could be represented on a single solubility diagram in which functions of the chemical potentials of calcium hydroxide and monocalcium phosphate were used as coordinates. The addition of phosphate to the soil system had little effect on the chemical potential of lime, but increased that of MCP.

Kittrick and Jackson (20) applied the solubility product principle to the reaction of variscite and kaolinite in water suspensions, and observed that an increase of kaolinite concentration increased the aluminum concentration and decreased the phosphate concentration in solution in quantities predictable from solubility product principles. The same authors (21) suggested that the observed difference between the concen-

tration of phosphate in solution originating from various precipitated phosphate compounds in pure water, and the concentration of phosphate in soil solutions could be explained on the basis of solubility product principles, taking into account the great excess of iron, aluminum and calcium ions in the system.

Indications given by the solubility product principle that the solution phosphate concentration would be negligibly affected by addition of phosphate fertilizer, because of the common ion buffering capacity of soils, were borne out since addition of even 1000 pounds of 0-20-0 fertilizer per acre failed to alter the concentration of phosphate in the soil solution after reaction for 10 days.

f. Soluble phosphate reactions in soils. Lindsay and Stephenson (29) studied the nature of the reactions of MCP monohydrate in soils and found that the solution sampled at the fertilizer band closely resembled MTPS in composition. They pointed out that the concentration of the reacting phosphate solution was high and that a relatively small fraction of the total soil determined the reactants in the initial chemical reaction of phosphate fertilizers with soil. Lindsay et al. (25) worked with MTPS on Rosebud loam and concluded that $CaHPO_4 \cdot 2H_2O$ was an important initial product formed when MCP granules reacted with the soil. Lindsay and Stephenson (30) studied the effect of repeated reactions of MTPS with soil. They hypothesized that after all the MCP had dissolved, water vapor continued to move into the reaction zone. Its condensation there caused dilution and further expansion of the zone, and also precipitation of phosphates from solution.

B. Determination of Phosphate Availability Through Soil Extractions

Seatz (35) worked with 32 soils containing from 25 to 50% kaolinite in the clay fraction and compared a number of extracting solutions regarding their efficiency in dissolving phosphorus. Results showed that neutral 0.1 N ammonium fluoride dissolved the least amount and that 0.03 N ammonium fluoride in 0.1 N sulfuric acid released the highest amount. The Bray extracting solution was found to release less phosphorus than 0.1 N sulfuric acid, but more than 0.1 N hydrochloric acid. Seatz also studied the relative efficiency of some of the extracting reagents on laboratory preparations of iron and aluminum phosphates. There was little difference in extracting capacity between hydrochloric and sulfuric acids in the case of aluminum phosphate. With iron phosphate, however, sulfuric acid was the more effective of the two.

Bray and Kurtz (4) stated that when acid-soluble forms of phosphate were first dissolved in acid, without extraction, and then extraction with ammonium fluoride made, both forms were extracted, and that the acid-soluble form could be calculated by difference. Working on cornbelt soils, they recognized the presence of both the adsorbed and acid-soluble forms in those soils. In untreated soils below pH 6.0, the adsorbed forms were observed to be relatively more abundant than at higher pH values. Added soluble phosphate was changed into the adsorbed form, whereas added acid-soluble forms such as rock-phosphate were gradually dissolved and also increased the adsorbed forms. Above pH 6.0, the trend was the reverse of the above, and the adsorbed forms tended to change to acid-soluble forms.

Dickman and Bray (13) presented quantitative evidence to demonstrate the stoichiometric replacement of hydroxyl ions by fluoride ions. It was found that complete recovery of added phosphate was obtained by shaking 1 g. of kaolinite with 0.1 N ammonium fluoride for 1 minute. Ammonium fluoride was observed to extract only a part of the phosphate included in the easily acid-soluble form.

Bray and Dickman (3) observed that the initial immediate reaction between a potassium or ammonium-saturated kaolinite or soil clay and dilute phosphate solutions resulted in the adsorption of limited amounts of phosphate. The phosphate so adsorbed was completely removed in a short time by 0.1 N neutral ammonium fluoride or successive water extractions. These observations were characteristic of exchange reactions. With an increase in time, temperature or concentration, further amounts of phosphate were adsorbed. This adsorbed phosphate was not so easily removed and required longer extraction times or stronger reagents for extraction. Such reactions were characteristic of chemosorption. Ammonium fluoride in neutral and acid solutions provided a means of fractionating phosphates reacting with soil, by applying the above reactions.

Jackson (18) stated that in neutral or alkaline solutions the fluoride complex of aluminum forms, but that the fluoride of iron does not form to any appreciable extent. Neither is calcium phosphate appreciably soluble in this reagent. Thus, the phosphate extracted by neutral 0.5 N ammonium fluoride is mainly aluminum phosphate and the method of using this fluoride is an important step in the soil phosphorus frac-

tionation system. By using Bray and Kurtz reagent No. 4, that is, the solution which is 0.1 N to hydrochloric acid and 0.5 N to ammonium fluoride, calcium phosphate and some of the iron phosphate is included with the aluminum phosphate.

Cole and Olsen (8) developed a theoretical background for the study of phosphorus solubility in calcareous soils. They used the mean activity of DCP to express phosphorus solubility. By calculating this function, they found that differences in pH values, calcium concentrations and ionic strengths met with while comparing a number of soil solutions could be corrected for. This was possible because the product of calcium and hydrogen phosphate ion activities in various equilibrium solutions for soils was constant over a range of pH, calcium concentration and ionic strength values.

The same authors (9) found that phosphorus solubility expressed as the mean activity of dicalcium phosphate in equilibrium solutions increased regularly with the amounts of phosphorus adsorbed in the monolayer region on the surfaces of various materials in soils. Values of the mean activity of DCP in equilibrium soil solutions increased as a direct function of the amount of phosphate added as concentrated superphosphate.

Shapiro and Fried (37) derived a kinetic equation in terms of reaction products assuming a pseudo-first order displacement of soil phosphorus by hydroxyl ion. Application of this equation to a Bridger silt loam by means of a non-equilibrium leaching system indicated the presence of at least two forms of soil phosphorus based on rate of re-

lease: (1) a rapidly released and quickly exhausted form and (2) a slowly released, but steadily supplied form. When a few other soils were also equilibrated with solutions of varying phosphorus concentrations at constant volume, similar indications for a loosely-held and a tightly-held form of phosphorus were obtained.

CHAPTER III

EXPERIMENTAL PROCEDURE

The general plan of experiments for the present study consisted in (1) the preparation of soil samples of different pH levels out of three bulk soil samples representing the Dewey silt loam, Grenada silt loam, and Hartsells loam soil series, (2) treating each of the soil samples with metatriple point solution, triple point solution, monocalcium phosphate, and dicalcium phosphate and triple point solution together, (3) allowing reaction times of 2, 9, 43, and 137 days, respectively, (4) extracting the soil samples with water, ammonium fluoride solution, Bray and Kurtz's No. 4 extractant and dilute sulfuric acid and (5) analyzing all the extracts for phosphorus, and the sulfuric acid extract for iron, aluminum and calcium also.

A., Preparation of Soil Samples

Bulk samples of Dewey, Grenada, and Hartsells soils were obtained, passed through a 2 mm. sieve, and portions were treated with c.p. calcium oxide required to give pH increases of about 3 units in stages. The original pH values of these soils were 4.5, 4.9, and 4.6 respectively. Mixing with calcium oxide was done in stages, so as to insure good mixing and to see that the calcium oxide was distributed fairly uniformly in the soil.

Enough water was added to the soil taken in large beakers to bring the moisture content of soil roughly to field capacity and the

mixture stirred well. This process was repeated whenever necessary to maintain the moisture at approximately the same level and the soil kept in this condition for about a week. After this period, it was air-dried and powdered gently to pass completely through a 2 mm. sieve.

pH was determined once more on the lime-treated soil samples. Two samples from each of the three soil series, which had attained pH values of about 6 and 8, respectively were chosen for further experimentation and taken up along with one sample each of the original untreated soil. This gave a total number of nine samples for detailed studies.

B. Treatment of Soils With Phosphorus Materials

The phosphorus materials used in the study were metatriple point solution, (MTPS), triple point solution, (TPS), monocalcium phosphate monohydrate, (MCP), and equivalent amounts of dicalcium phosphate, (DCP), and TPS added successively. The amount of material taken was such as to give a final concentration of 1.5% phosphorus pentoxide on weight of soil when mixed. This high concentration was decided upon for simulating the conditions prevailing in the soil when the concentrated solution formed by the reaction of MCP with water moves out to react with the soil. In the case of the last treatment, the soil was first mixed with the calculated amount of dicalcium phosphate and then the TPS added and mixed once more.

1. Phosphorus Materials

a. MTPS. This was prepared according to the procedure mentioned by Lindsay et al. (25). Equal amounts by weight of monocalcium phosphate

monohydrate and water were mixed and kept stirred intermittently for about 24 hours at room temperature. Then the residue was filtered and the filtrate taken as MTPS. As MTPS is supersaturated with respect to dicalcium phosphate, it is metastable, and hence the above preparation was done immediately before treatment of soils with MTPS. The pH, density, calcium and phosphorus compositions were checked by analysis.

b. TPS. This was prepared according to the procedure given by Lindsay and Stephenson (29). The following materials were stirred together at room temperature for 3 days: 300 g. of reagent-grade monocalcium phosphate monohydrate, 25 g. crystalline anhydrous dicalcium phosphate, 90 ml. of 90% orthophosphoric acid, and 588 ml. of water. The suspension was filtered and the filtrate taken as TPS for reacting with soils. The pH, density, calcium and phosphorus compositions were checked against standard ones by actually performing these determinations on the sample of TPS obtained.

c. MCP. Reagent-grade monocalcium phosphate monohydrate was used.

d. DCP. Anhydrous dicalcium phosphate, reagent grade, was used.

2. Mixing of Phosphorus Materials With Soil

Eighty-g. lots of soil sample, each representing 3 pH levels for the 3 soil series examined were taken in 150 ml. tall form beakers for the reactions. In the case of MTPS and TPS, the soil was spread as a thin layer on a plastic sheet and the required quantities transferred with a graduated pipet uniformly on to the spread soil. When the

solution had been completely absorbed, the soil was mixed thoroughly and the lumps formed on reaction of the solutions with the soil were broken between the fingers. Finally the mass was transferred to a plastic bottle and churned up thoroughly with a stirrer with fairly sharp blades. The stirred soil was then transferred to the beakers.

In the case of the MCP and DCP, which were available in the form of fine powder, a small amount of soil was mixed intimately with the weighed powder in a mortar, taking care not to grind the soil particles. The remaining soil was added in small amounts to this preliminary mix and the process of mixing completed.

C. Reaction of Soil With Phosphorus Materials

The reaction was allowed to proceed at the original moisture level of the air-dry soils which was of the order of 2% for Dewey and Grenada, and 1.5% for Hartsells, before the first three sets of extraction and chemical analysis. These extractions were done at the end of 2 days, 9 days and 43 days after the original mixing.

After the third set of extractions and analysis of extracts, the soil samples contained in the beaker were wetted roughly to field capacity. This was done 57 days after the original reaction of the soil samples with phosphorus materials. The moisture was kept nearly constant by periodically replenishing what was lost by evaporation. The soils, however, were not stirred or disturbed otherwise.

About 70 days after the first wetting, the addition of water was stopped and the soil allowed to air dry in the beaker itself. The

fourth and final round of extraction was made after 137 days from the original reaction day and chemical analysis of the extracts performed.

D. Extractions

The extractants used in the study were water, neutral 0.5 N ammonium fluoride solution (for displacing adsorbed phosphate), a solution which was 0.1 N with respect to hydrochloric acid and 0.5 N to ammonium fluoride (Bray and Kurtz's No. 4 solution, for extracting phosphate in the adsorbed form, all of the calcium phosphates, most of the aluminum phosphates and part of the iron phosphates), and 0.05 N sulfuric acid.

1. Water Extraction

Five g. of the well-mixed and sampled soil was weighed out into an Erlenmeyer flask. Twenty-five ml. of water was added and the flask shaken in a shaking machine for 1 hour. The suspension was filtered, using a Buchner funnel, and the filtrate collected and preserved.

2. Neutral 0.5 N Ammonium Fluoride Solution Extraction

See ref. (30). The extraction process was the same as for water, except that 1.0 g. of soil, previously leached with about 50 ml. of N ammonium chloride solution was used and that the volume of fluoride solution used was 50 ml.

3. Acid Ammonium Fluoride Solution Extraction

One g. of soil was shaken for $\frac{1}{2}$ hour with 50 ml. of 0.1 N to hydrochloric acid. One g. of solid ammonium fluoride was added to make

the solution roughly 0.5 N with reference to the fluoride and the shaking continued for an additional period of 1 hour. Filtration was done as for water extraction.

4. 0.05 N Sulfuric Acid Extraction

The process employed was exactly the same as for water with the acid solution substituted for water.

In the case of the untreated original soils, an experiment was performed to study the progressive extraction of some of the soil constituents, namely phosphorus, iron, aluminum, and calcium by repeated extraction of the same soil with the sulfuric acid. In this case, the residue from the first filtration was transferred back to the same flask as was used for the first extraction, the same amount of acid solution added, and shaken for an additional period of 1 hour. Filtration was done at this stage and the filtrate collected and preserved. The experiment was repeated until five acid extracts had been collected. With the soils used for reacting with the phosphorus materials, the sulfuric acid extraction was done consecutively only two times.

pH was determined on a 1:1 water suspension of the soil samples after keeping the suspension stirred continually for 1 hour. This was done along with each of the four rounds of extraction, using the glass and calomel electrodes.

E. Chemical Analysis of Soil Extracts

Phosphorus was estimated in all the extracts. Calcium was estimated in the water extract and the two consecutive sulfuric acid extracts.

Iron and aluminum were estimated in the two sulfuric acid extracts only.

1. Phosphorus

This was estimated, employing the method described by Bray and Kurtz (4). This consisted in developing the reduced chloro-phosphomolybdic acid blue color using stannous chloride, and measuring transmittance in a Beckman Model "B" spectrophotometer.

In the case of the water extract, a suitable preliminary dilution was made. One ml. of diluted solution was mixed with 6 ml. of water, 3 ml. of Bray's ammonium molybdate-hydrochloric acid reagent added and mixed. One ml. of a diluted solution of stannous chloride in concentrated hydrochloric acid was then added and mixed.

The transmittance of the blue color developed was measured at 650 mμ in a Beckman Model "B" spectrophotometer between 6 and 15 minutes after the addition of stannous chloride.

Standards of phosphate solution containing from 0.1 to 2 p.p.m. were similarly treated and the transmittance measured. The transmittance was plotted against concentration of phosphorus on semilog paper and a standard curve drawn.

For the ammonium fluoride and hydrochloric acid-ammonium fluoride extracts, an aliquot of the diluted extract was mixed with 3 ml. of water, 3 ml. of roughly 0.9 M boric acid and the same amounts of acid ammonium molybdate and stannous chloride solutions as were used for the analysis of the water extract. (See reference 4.) Standard were treated similarly and the same concentrations of fluoride or hydrochloric acid-fluoride maintained in the standards as in the test solutions. Trans-

mittance measurements, concentration readings from curve and calculation of phosphorus were the same as for water extract analysis.

In the case of the sulfuric acid extract, the procedure was exactly the same as for water extract except that the standards were made to contain the same amount of sulfuric acid as the test solutions.

2. Iron

This constituent was determined by the method of Fortune and Mellon (14) mentioned by Lindsay and Stephenson (28).

A suitably diluted aliquot of the sulfuric acid extract was treated with 1 ml. of 10% hydroxylamine hydrochloride solution in a volumetric flask and mixed. The mixture was then diluted to about 35 ml. with water and 5 ml. of a 0.10% solution of ortho-phenanthroline added and mixed. Two drops of 6 N ammonium hydroxide were added and the solution made up to 50 ml. and mixed.

The pH of the above solution was measured with the glass and calomel electrodes and adjusted to 5 using 6 N ammonium hydroxide or hydrochloric acid.

The transmittance of the colored solution was measured in a Beckman Model "B" spectrophotometer at 508 mμ. Standard iron solutions, containing the same amount of sulfuric acid as that present in the test solutions were treated similarly and the standard curve drawn. Reading of iron concentrations from this curve and calculation of iron concentration on soil basis were done as for phosphorus.

3. Aluminum

This element was determined by the method of Shapiro and Brannock (36).

An aliquot of the suitably diluted sulfuric acid extract was taken in a 50 ml. volumetric flask, and 0.5 ml. of a roughly 1.5% solution of calcium chloride was added. One-half ml. of 10% hydroxylamine hydrochloride was then added and mixed.

One-half ml. of freshly prepared 1% potassium ferricyanide was added, mixed and allowed to stand for 5 minutes. After this, 5 ml. of buffer solution containing 70 g. sodium acetate and 30 ml. acetic acid in 500 ml. of water were added, mixed, and allowed to stand for 10 minutes. Then 2.5 ml. of a 0.1% solution of alizarin red-S solution was added, the solution made up to volume, mixed and allowed to stand for at least 2 hours.

The perfectly clear supernatant liquid was pipeted out and diluted four times with water, and the transmittance measured at 475 mμ in a Beckman Model "B" spectrophotometer. Standards of aluminum solution containing the same concentration of sulfuric acid as the test solution were treated similarly, and the transmittance measured as before. The rest of the determination was the same as for phosphorus.

4. Calcium

This was determined by measuring the emission at 422.7 mμ of the suitably diluted extract aspirated into an oxy-acetylene flame, with a Beckman Model DU Quartz spectrophotometer with flame photometric attach-

ment.

The water or sulfuric acid extract was suitably diluted so as to give a measurable emission and aspirated into the oxy-acetylene flame in the flame photometer. Oxygen pressure of 10 p.s.i. and acetylene pressure of 3 p.s.i. were used. The 100% transmission reading on the dial was set with the 20 p.p.m. calcium standard solution.

Standards containing concentrations of calcium intermediate between 0 and 20 p.p.m. were then introduced into the flame and the dial readings noted. These were used for constructing the standard curve. Standards for water extract calcium determinations were prepared in water and those for sulfuric acid extracts were adjusted to have the same concentration of sulfuric acid as the test solutions.

Calcium concentrations in test solutions were read off the standard curve and the percentage of calcium was calculated on soil basis.

CHAPTER IV

RESULTS

The results of chemical analysis of the various extracts obtained during the extraction experiments are presented in tables I to XVII. The following are the inferences that could be made after a study of the data contained in the tables.

A. Extraction of Untreated Soils With Different Extractants (Table I)

No water-soluble phosphorus could be detected in any of the three soils. Acid fluoride extractable phosphorus was higher than neutral fluoride extractable phosphorus in the case of Dewey and Grenada soils. These forms were not extracted in the case of Hartsells soil.

Sulfuric Acid Extractions

1. Phosphorus

Phosphorus extracted showed a gradual decrease over the five successive acid extractions in the case of Dewey and Hartsells, but was steady for Grenada. For the first extraction, the phosphorus content of Dewey was greater than for Grenada or Hartsells, which had similar contents.

2. Iron

Iron extracted for Dewey and Grenada increased for the second extraction, but was steady for the remaining two extractions. In the case of Hartsells, there was an increase for the second extraction and a

TABLE I

PHOSPHORUS, IRON, ALUMINUM AND CALCIUM EXTRACTED BY WATER, AMMONIUM FLUORIDE, HYDROCHLORIC ACID-AMMONIUM FLUORIDE AND FIVE TREATMENTS WITH DILUTE SULFURIC ACID FROM THREE SOIL SERIES

Extractants		Dewey				Grenada				Hartsells			
		Parts Per 100,000 of Soil											
		P	Fe	Al	Ca	P	Fe	Al	Ca	P	Fe	Al	Ca
Water		Nil				Nil				Nil			
Ammonium fluoride, Neutral, 0.5 N.		5.5				5.5				Nil			
Hydrochloric acid + ammonium fluoride, 0.1 N and 0.5 N		10.0				11.0				Trace			
Sulfuric acid 0.05 N	Extraction 1	0.6	0.9	2.5	0.9	0.2	4.9	2.4		0.2	5.0	2.4	0.5
	Extraction 2	0.6	3.0	2.8	0.2	0.3	7.3	2.6	0.9	0.2	15.8	2.9	Nil
	Extraction 3	0.5	3.0	2.3	Nil	0.3	6.8	2.3	0.3	0.1	10.0	2.8	Nil
	Extraction 4	0.5	4.6	2.1	Nil	0.3	6.8	2.3	0.2	0.1	7.0	2.3	Nil
	Extraction 5	0.3	3.3	2.4	Nil	0.2	9.5	3.5	0.2	0.2	5.0	3.0	Nil

gradual decrease thereafter.

3. Aluminum

Aluminum values were almost equal for all three soils for each of the first three acid extractions. There were slight increases for the second extraction.

4. Calcium

Calcium was almost completely extracted out in the first acid extraction itself in the case of Dewey and Hartsells. For Grenada, there was a decrease at the third acid extraction and a very slight constant extraction thereafter.

B. Extractions of Soils Treated With Phosphorus Materials

1. First Extraction: 2 Days

a. Phosphorus (Table II)

(i) Water extract. Generally, phosphorus increased for the second pH level and decreased thereafter. This observation held good generally for all the four phosphorus materials used and for the three soils.

(ii) Fluoride extract and (iii) Acid fluoride extract. No regularity of behavior could be observed.

(iv) Sulfuric acid extract I. The observation was the same as that for (ii) and (iii) above.

(v) Sulfuric acid extract II. Phosphorus content increased with increase of soil pH in all cases.

TABLE II

EXTRACTION I: PHOSPHORUS EXTRACTED BY WATER, AMMONIUM FLUORIDE, HYDROCHLORIC ACID-AMMONIUM FLUORIDE SOLUTIONS AND DILUTE SULFURIC ACID (TWO EXTRACTIONS) FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	86	157	84	148	168	150	83	148	94
	2	25	43	70	65	35	60	30	68	33
	3	25	40	55	65	35	33	35	80	28
	4	300	350	290	420	320	380	240	310	290
	5	50	75	84	60	75	86	44	70	84
Triple-point solution	1	151	150	180	151	152	143	148	166	157
	2	185	185	225	105	133	105	173	143	185
	3	83	70	143	55	70	55	98	83	113
	4	320	360	410	220	430	260	410	380	410
	5	75	84	143	46	62	98	76	110	118
Monocalcium phosphate	1	266	370	300	416	472	420	260	344	316
	2	75	133	145	133	133	178	90	140	168
	3	48	95	68	58	55	105	48	65	70
	4	300	370	400	420	430	420	260	400	360
	5	70	110	114	118	110	148	100	90	126
Dicalcium phosphate + triple-point solution	1	99	62	92	69	80	67	85	78	76
	2	153	130	150	85	120	78	128	125	165
	3	118	83	93	48	90	33	100	83	155
	4	360	260	300	230	320	260	320	260	380
	5	165	158	203	91	138	161	180	203	195

* a, b, c: Low, medium and high pH levels, respectively.

1: Water extraction; 2: 0.5 N, neutral ammonium fluoride extraction; 3: 0.1 N hydrochloric acid + 0.5 N ammonium fluoride extraction; 4: 0.05 N sulfuric acid, first extraction; 5: 0.05 N sulfuric acid, second extraction.

b. Iron (Table III)

(i) Sulfuric acid extract I. Marked decreases of iron for increase in soil pH, especially for the highest soil pH value were found.

(ii) Sulfuric acid extract II. Iron increased with soil pH in most instances. Iron content of Dewey was low, while those of Grenada and Hartsell were higher and nearly the same.

c. Aluminum (Table IV)

(i) Sulfuric acid extract I. Aluminum generally increased with pH of soil.

(ii) Sulfuric acid extract II. Aluminum changed little with soil pH. Almost similar amounts of aluminum were extracted for corresponding lime and phosphorus treatments for the three soils.

d. Calcium (Table V)

(i) Water extract. Some decrease of calcium was noticed for the second pH level and an appreciable one for the third one. Corresponding values of calcium for the three soils were similar.

(ii) Sulfuric acid extract I. Calcium increased markedly with pH levels and corresponding values of calcium for the three soils were almost the same.

(iii) Sulfuric acid extract II. Calcium did not increase appreciably at the second pH level but increased perceptibly at the third level.

Calcium values for Hartsells were generally lower than for the other two soils.

TABLE III

EXTRACTION I: IRON EXTRACTED BY DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	8.3	6.3	2.8	17.5	17.5	15.3	19.8	20.3	17.5
	2	4.5	4.0	6.8	12.3	17.8	18.3	12.5	13.5	13.3
Triple-point solution	1	11.8	10.0	4.5	23.7	23.7	20.5	26.0	26.0	16.3
	2	5.2	5.2	8.5	14.5	20.0	29.0	15.3	17.3	17.3
Monocalcium phosphate	1	7.0	6.0	3.8	13.0	15.3	15.8	19.3	19.3	10.5
	2	5.0	6.3	7.8	8.5	10.0	15.8	10.5	12.5	12.5
Dicalcium phosphate + triple-point solution	1	2.5	2.0	1.0	5.5	5.5	3.0	7.0	7.5	2.0
	2	5.8	5.3	7.8	11.8	13.0	19.5	14.8	20.0	16.3

* a, b, c: Low, medium and high pH levels, respectively.

1: 0.05 N sulfuric acid, first extraction.
2: 0.05 N sulfuric acid, second extraction.

TABLE IV

EXTRACTION I: ALUMINUM EXTRACTED BY DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	3.3	4.0	7.0	9.6	7.3	7.1	2.5	3.0	9.6
	2	4.2	4.0	2.9	6.1	4.9	6.3	4.5	4.5	4.3
Triple-point solution	1	2.1	1.8	3.4	4.1	4.3	5.2	1.5	2.1	3.3
	2	3.5	3.3	2.4	5.6	6.1	5.6	4.5	5.0	4.4
Monocalcium phosphate	1	3.0	6.8	4.6	5.7	4.2	8.0	4.0	4.0	4.0
	2	3.5	3.2	2.9	6.3	6.1	6.3	4.4	3.9	4.5
Dicalcium phosphate + triple-point solution	1	6.8	7.3	6.0	8.2	6.0	7.0	5.1	5.4	7.5
	2	2.7	2.7	2.1	4.7	4.1	4.5	2.6	3.0	2.6

* a, b, c: Low, medium and high pH levels, respectively.

1: 0.05 N sulfuric acid, first extraction.
2: 0.05 N sulfuric acid, second extraction.

TABLE V

EXTRACTION I: CALCIUM EXTRACTED BY WATER AND DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO ACID EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	81	82	53	77	82	61	81	66	71
	2	148	200	288	178	195	250	153	160	285
	3	18	15	23	18	18	30	8	5	13
Triple-point solution	1	80	91	78	73	66	69	78	89	85
	2	115	140	228	125	145	203	108	135	230
	3	8	8	15	13	15	25	3	3	13
Monocalcium phosphate	1	186	196	172	176	184	152	176	180	168
	2	170	213	300	188	203	268	163	208	288
	3	28	35	55	55	60	68	33	40	33
Dicalcium phosphate + triple-point solution	1	56	44	29	34	29	21	44	34	29
	2	315	355	455	355	365	455	340	375	450
	3	45	45	83	78	73	88	40	48	75

* a, b, c: Low, medium and high pH levels, respectively.

1: Water extraction.
2: 0.05 N sulfuric acid, first extraction.
3: 0.05 N sulfuric acid, second extraction.

2. Second Extraction: 9 Days

a. Phosphorus (Table VI)

(i) Water extract. Phosphorus values for MTPS and TPS treatments increased with pH level. For the other two phosphorus materials, they increased for the second pH level and decreased for the third one.

(ii) Fluoride extract. Phosphorus values increased for the second and third pH levels in the case of MCP treatment only. No regularity was observed for the other phosphorus materials.

(iii) Acid fluoride extract. The observations were the same as for the fluoride extract.

(iv) Sulfuric acid extract I. In the case of TPS treatment only, there was an increase of phosphorus extracted for the second pH level and a fall for the third one. There was no regularity for the others. Corresponding values of phosphorus were similar for Dewey and Hartsells soils.

(v) Sulfuric acid extract II. Phosphorus mostly increased with pH of soil.

b. Iron (Table VII)

(i) Sulfuric acid extract I. Iron mostly decreased with pH, this decrease being highest for the third pH level.

(ii) Sulfuric acid extract II. Iron did not increase for second pH level but increased for the third pH level in the case of Dewey. It increased regularly for Grenada, but changed little in the case of Hartsells.

TABLE VI

EXTRACTION II: PHOSPHORUS EXTRACTED BY WATER, AMMONIUM FLUORIDE, HYDROCHLORIC ACID-AMMONIUM FLUORIDE SOLUTIONS AND DILUTE SULFURIC ACID (TWO EXTRACTIONS) FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	50	93	63	140	110	193	90	100	110
	2	128	136	118	122	105	120	112	143	124
	3	58	53	55	55	48	73	25	61	46
	4	190	185	143	163	200	227	113	227	160
	5	103	148	125	133	139	148	135	141	141
Triple-point solution	1	100	123	183	108	103	75	108	130	203
	2	161	143	160	116	143	106	151	139	165
	3	45	53	81	26	58	53	56	46	54
	4	227	253	210	185	207	180	223	263	233
	5	135	148	210	135	141	135	156	148	183
Monocalcium phosphate	1	232	327	207	370	455	340	268	355	290
	2	83	124	123	68	78	118	83	93	143
	3	36	60	69	46	50	73	40	70	75
	4	263	328	250	415	347	335	283	350	350
	5	110	125	128	111	112	148	121	112	129
Dicalcium phosphate	1	66	68	58	48	67	41	49	73	36
	2	123	108	124	69	104	64	105	113	120
	3	58	55	65	35	70	53	55	66	89
	4	228	263	285	230	328	263	285	285	298
	5	149	158	191	131	148	150	174	185	200

* a, b, c: Low, medium and high pH levels, respectively.

1: Water extraction; 2: 0.5 N, neutral ammonium fluoride extraction; 3: 0.1 N, hydrochloric acid + 0.5 N ammonium fluoride extraction; 4: 0.05 N sulfuric acid, first extraction; 5: 0.05 N sulfuric acid, second extraction.

TABLE VII

EXTRACTION II: IRON EXTRACTED BY DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	5.4	4.3	1.9	11.5	9.1	8.0	12.4	13.4	6.1
	2	7.8	7.5	10.3	17.1	18.4	21.3	18.8	18.1	17.4
Triple-point solution	1	7.8	6.4	1.1	13.1	12.1	10.1	14.9	16.0	9.3
	2	7.6	8.8	12.9	19.9	20.8	24.0	20.4	22.9	22.0
Monocalcium phosphate	1	5.8	4.6	1.9	11.4	11.9	13.1	13.5	14.3	9.1
	2	4.3	3.0	6.8	6.4	8.5	14.9	11.8	12.4	11.8
Dicalcium phosphate + triple-point solution	1	2.1	2.1	0.7	6.3	5.0	4.9	5.0	6.5	3.6
	2	5.6	5.6	8.4	12.5	16.3	20.8	18.1	20.0	18.1

* a, b, c: Low, medium and high pH levels, respectively.

1: 0.05 N sulfuric acid, first extraction.
2: 0.05 N sulfuric acid, second extraction.

c. Aluminum (Table VIII)

(i) Sulfuric acid extract I. The values increased only slightly for the greater part. Corresponding values were similar.

(ii) Sulfuric acid extract II. The values changed little with pH changes of soil.

d. Calcium (Table IX)

(i) Water extract. Calcium content remained almost unchanged for the second pH level, but decreased markedly for the third pH level. Corresponding values of calcium were much alike. These observations were very similar to those for the first extraction.

(ii) Sulfuric acid extraction I. Calcium increased appreciably, especially for the highest pH level. Corresponding values were alike.

(iii) Sulfuric acid extraction II. The observations were the same as for the first sulfuric acid extraction, but corresponding values of Dewey and Hartsells were alike and lower than those for Grenada.

3. Third Extraction: 43 Days

a. Phosphorus (Table X)

(i) Water extract. Values decreased with pH in the case of Dewey. They were slightly lower for MCP-treated Dewey soils than for Grenada or Hartsells.

(ii) Fluoride extract. Phosphorus decreased with pH for all treatments except MCP, for which the values were steady. Phosphorus values for Grenada were generally lower than the corresponding values for Dewey and Hartsells.

TABLE VIII

EXTRACTION II: ALUMINUM EXTRACTED BY DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	3.5	3.0	5.2	3.8	4.4	4.5	3.5	2.8	4.5
	2	1.0	3.1	3.8	3.0	3.3	3.3	2.5	2.5	2.2
Triple-point solution	1	2.8	3.5	4.4	4.0	4.1	3.8	2.9	3.0	3.6
	2	2.2	2.2	2.0	2.4	2.8	3.5	2.3	2.5	2.4
Monocalcium phosphate	1	3.9	3.3	3.3	4.5	4.0	3.7	3.1	4.0	3.8
	2	2.6	2.8	2.8	4.0	4.3	4.0	3.3	3.3	2.9
Dicalcium phosphate + triple-point solution	1	3.5	4.6	4.4	4.1	4.5	5.0	3.1	3.3	4.6
	2	2.3	2.4	2.2	3.2	3.2	3.6	2.5	2.2	2.0

* a, b, c: Low, medium and high pH levels, respectively.

1: 0.05 N sulfuric acid, first extraction.
2: 0.05 N sulfuric acid, second extraction.

TABLE IX

EXTRACTION II: CALCIUM EXTRACTED BY WATER AND DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO ACID EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	53	61	44	47	45	42	55	46	50
	2	148	198	275	160	193	235	153	165	275
	3	10	12	19	15	18	28	9	9	17
Triple-point solution	1	52	57	60	49	50	45	60	61	57
	2	115	145	240	128	145	210	118	145	248
	3	6	8	16	10	13	22	6	7	13
Monocalcium phosphate	1	182	172	122	166	172	142	178	178	158
	2	190	248	325	213	238	293	193	215	320
	3	13	20	27	32	43	54	19	17	29
Dicalcium phosphate + triple-point solution	1	36	33	21	21	17	15	29	20	19
	2	315	355	455	335	348	410	313	353	428
	3	20	24	42	42	50	63	21	22	32

* a, b, c: Low, medium and high pH levels, respectively.

1: Water extraction.
2: 0.05 N sulfuric acid, first extraction.
3: 0.05 N sulfuric acid, second extraction.

TABLE X

EXTRACTION III: PHOSPHORUS EXTRACTED BY WATER, AMMONIUM FLUORIDE, HYDROCHLORIC ACID-AMMONIUM FLUORIDE SOLUTIONS AND DILUTE SULFURIC ACID (TWO EXTRACTIONS) FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	34	46	40	66	56	59	46	41	35
	2	34	44	34	36	38	34	55	44	33
	3	48	54	53	60	60	44	54	58	46
	4	208	268	265	285	243	270	285	295	253
	5	178	158	210	145	150	155	160	163	193
Triple-point solution	1	65	61	38	49	58	48	51	59	61
	2	186	188	141	129	146	115	184	163	169
	3	84	96	84	74	85	84	110	118	124
	4	310	305	220	225	253	220	278	213	253
	5	180	160	250	153	163	153	188	180	198
Monocalcium phosphate	1	317	375	300	395	430	385	353	358	363
	2	114	114	141	74	75	71	118	114	123
	3	74	63	66	46	55	60	54	61	65
	4	248	290	275	290	283	265	283	250	268
	5	123	113	140	120	115	90	118	100	128
Dicalcium phosphate + triple-point solution	1	54	40	23	35	45	46	44	45	24
	2	118	118	66	100	86	85	124	113	103
	3	58	54	59	54	46	50	49	54	56
	4	330	275	275	350	350	293	330	308	293
	5	170	198	165	155	180	153	193	198	215

* a, b, c: Low, medium and high pH levels, respectively.

1: Water extraction; 2: 0.5 N, neutral ammonium fluoride extraction; 3: 0.1 N hydrochloric acid + 0.5 N ammonium fluoride extraction; 4: 0.05 N sulfuric acid, first extraction; 5: 0.05 N sulfuric acid, second extraction.

(iii) Acid fluoride extract. For MTPS phosphorus contents for the first and second pH levels were higher in the case of Grenada and Hartsells. But values for Dewey remained steady. For TPS phosphorus increased only for the second pH value; thereafter, it did not increase. Dewey values, however, were steady as before, In the case of MCP and DCP-TPS treatments, phosphorus values were almost alike.

(iv) Sulfuric acid extract I. Phosphorus values decreased slightly at the third pH level. There was not much difference between the soils. Values for DCP-TPS were greater than those for the rest.

(v) Sulfuric acid extract II. Generally, the values for the first and second pH levels were almost the same and those for the third level showed increases. For MCP the values were lower than for the rest.

b. Iron (Table XI)

(i) Sulfuric acid extract I. Iron values for the first and second pH levels were almost the same, but decreased considerably for the third pH level. Values for Dewey were lower than those for the other two soils. Iron values were lowest for the DCP-TPS treatment.

(ii) Sulfuric acid extract II. For Dewey and Grenada, iron values were almost the same for the first two pH levels, but increased for the third level. For Hartsells, all the values were almost the same. Values for MCP treatment were lower than for the rest.

c. Aluminum (Table XII)

(i) Sulfuric acid extract I. Aluminum values generally tended to increase with pH levels, the increases being more for the third pH level. Values of aluminum for MCP and DCP-TPS were higher than those for the other treatments.

TABLE XI

EXTRACTION III: IRON EXTRACTED BY DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	10.0	9.0	2.5	16.0	14.0	10.8	18.5	17.3	9.0
	2	11.0	10.8	13.5	24.5	26.0	29.0	24.8	24.5	23.0
Triple-point solution	1	11.5	8.5	2.3	15.5	14.3	12.5	18.8	18.0	10.5
	2	11.8	11.5	15.0	24.3	28.0	30.3	23.0	26.5	24.3
Monocalcium phosphate	1	8.3	5.8	3.3	13.3	14.8	14.3	15.3	16.5	10.3
	2	2.5	0.5	4.5	6.3	8.3	15.5	10.0	12.5	10.0
Dicalcium phosphate + triple-point solution	1	3.8	1.8	1.0	5.5	5.3	3.5	7.5	6.0	2.3
	2	8.0	6.5	8.3	13.8	13.5	19.5	19.0	21.0	17.8

* a, b, c: Low, medium and high pH levels, respectively.

1: 0.05 N sulfuric acid, first extraction.
2: 0.05 N sulfuric acid, second extraction.

TABLE XII

EXTRACTION III: ALUMINUM EXTRACTED BY DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	1.6	2.0	4.8	3.6	4.2	5.0	2.4	2.5	3.8
	2	2.2	0.9	1.7	2.5	3.9	4.0	2.7	1.4	2.2
Triple-point solution	1	1.4	2.0	4.4	2.6	3.5	4.6	2.0	2.7	3.5
	2	1.5	1.2	2.6	3.6	2.3	4.9	3.0	5.6	2.3
Monocalcium phosphate	1	2.1	4.6	4.0	4.5	4.6	4.4	4.0	3.4	4.0
	2	3.9	4.5	4.0	6.0	6.0	6.5	5.3	5.3	4.6
Dicalcium phosphate + triple-point solution	1	4.0	4.5	5.9	4.8	5.9	5.3	3.6	4.6	6.0
	2	1.0	1.4	1.1	4.0	4.8	4.6	2.0	2.8	2.6

* a, b, c: Low, medium and high pH levels, respectively.

1: 0.05 N sulfuric acid, first extraction.
2: 0.05 N sulfuric acid, second extraction.

(ii) Sulfuric acid extract II. Aluminum values showed no change with pH levels in the case of MCP and DCP-TPS and varied irregularly for the rest. Values for Grenada and Hartsells were higher than those for Dewey. MCP values were higher than those for the other treatments.

d. Calcium (Table XIII)

(i) Water extract. Calcium contents were generally constant, except in the case of DCP-TPS treatments, where there was a decrease. Values for Grenada were generally lower than those for Dewey and Hartsell, except in the case of MCP. Values for MCP were far higher than those for the other treatments, DCP-TPS values being the least.

(ii) Sulfuric acid extract I. There were definite increases of calcium content with the pH level of the soils. Corresponding values for the three soils were almost the same. Highest values were obtained for DCP-TPS and the lowest for TPS.

(iii) Sulfuric acid extract II. Calcium values for the first and second pH levels were almost the same, but there was a considerable increase for the third pH level. Values for Grenada were higher than those for Dewey or Hartsells. Values for DCP-TPS were generally higher than those for the rest; those for TPS were the lowest.

4. Fourth Extraction: 137 Days

a. Phosphorus (Table XIV)

(i) Water extract. For all treatments, except DCP-TPS, the values of phosphorus were constant for the three pH levels. Values for DCP-TPS generally increased. Corresponding values were almost the same for the three soils.

TABLE XIII

EXTRACTION III: CALCIUM EXTRACTED BY WATER AND DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO ACID EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	48	50	48	35	31	31	44	35	38
	2	113	170	275	133	195	233	133	138	250
	3	8	8	15	11	14	21	6	7	13
Triple-point solution	1	38	38	38	29	25	25	44	38	44
	2	88	113	158	100	113	178	63	88	163
	3	5	6	13	8	12	18	5	6	8
Monocalcium phosphate	1	196	212	158	182	182	182	162	200	188
	2	150	200	263	163	188	238	163	163	270
	3	8	15	17	28	31	39	11	15	24
Dicalcium phosphate + triple-point solution	1	44	31	29	25	25	25	35	31	25
	2	315	350	475	300	375	415	365	350	540
	3	17	20	35	30	37	51	30	20	17

* a, b, c: Low, medium and high pH levels, respectively.

1: Water extraction.
2: 0.05 N sulfuric acid, first extraction.
3: 0.05 N sulfuric acid, second extraction.

TABLE XIV

EXTRACTION IV: PHOSPHORUS EXTRACTED BY WATER, AMMONIUM FLUORIDE, HYDROCHLORIC ACID-AMMONIUM FLUORIDE SOLUTIONS AND DILUTE SULFURIC ACID (TWO EXTRACTIONS) FROM SOIL RECEIVING DIFFERENT PHOSPHORUS TREATMENTS

Soils Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	48	43	48	55	50	48	35	33	33
	2	163	178	165	133	80	75	138	105	125
	3	110	115	110	83	80	75	113	130	110
	4	320	190	240	250	210	240	210	240	210
	5	130	210	200	170	180	160	250	220	230
Triple-point solution	1	50	40	50	60	55	55	35	55	33
	2	158	115	140	128	108	110	150	160	143
	3	123	110	135	113	83	100	110	113	120
	4	230	210	250	200	190	200	220	240	180
	5	250	210	270	210	200	210	280	290	240
Monocalcium phosphate	1	75	95	65	80	75	90	85	100	65
	2	163	175	163	102	127	120	135	138	130
	3	110	130	85	90	95	90	115	105	100
	4	270	320	270	290	250	300	270	310	250
	5	220	210	190	230	200	210	280	200	230
Dicalcium phosphate + triple-point solution	1	20	23	10	15	13	23	25	10	10
	2	143	100	90	103	85	80	98	120	110
	3	98	75	83	88	75	75	85	100	95
	4	320	290	320	300	350	300	320	320	250
	5	190	250	240	210	170	200	210	250	230

* a, b, c: Low, medium and high pH levels, respectively.

1: Water extraction; 2: 0.5 N, neutral ammonium fluoride extraction; 3: 0.1 N hydrochloric acid + 0.5 N ammonium fluoride extraction; 4: 0.05 N sulfuric acid, first extraction; 5: 0.05 N sulfuric acid, second extraction.

(ii) Fluoride extract. Decreases of phosphorus with increasing soil pH were observed for MTPS and DCP-TPS. Values for Grenada were slightly lower than for the other soils.

(iii) Acid fluoride extract. The values generally did not change with soil pH. Grenada values were lower than those of Dewey or Hartsells. DCP-TPS gave values that were lower than the others.

(iv) Sulfuric acid extract I. Values were independent of pH or type of soils. DCP-TPS gave slightly higher values.

(v) Sulfuric acid extract II. Phosphorus values were independent of pH. Values for Hartsells were slightly higher than those for Dewey or Grenada. In the case of the latter soils, values for MTPS and DCP-TPS were slightly lower than for the other treatments.

b. Iron (Table XV)

(i) Sulfuric acid extract I. Iron values for the first and second pH levels were the same, but decreased appreciably for the highest pH level. Values for Grenada and Hartsells were higher than those for Dewey. DCP-TPS values were lower than those for the other treatments, which had the same values.

(ii) Sulfuric acid extract II. Iron content changed very little with soil pH. In the case of DCP-TPS there were slight decreases for Dewey and Hartsells and increases for Grenada. Grenada and Hartsells values were higher than those for Dewey. Values for MTPS and TPS treatments were similar and higher than those for MCP, which, in turn, were higher than those for DCP-TPS.

TABLE XV

EXTRACTION IV: IRON EXTRACTED BY DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	5.5	3.8	0.8	7.5	6.3	5.0	7.8	9.0	4.0
	2	10.8	10.8	10.8	22.0	23.0	23.0	23.0	23.0	20.0
Triple-point solution	1	4.8	4.0	1.3	7.8	7.5	5.3	9.8	9.8	5.5
	2	13.5	12.8	12.8	23.0	23.0	23.0	26.3	24.3	22.3
Monocalcium phosphate	1	4.8	2.5	Trace	5.8	6.5	5.5	8.3	8.8	3.8
	2	7.0	7.0	8.3	18.5	19.3	20.5	17.5	18.0	14.3
Dicalcium phosphate + triple-point solution	1	0.5	0.3	Nil	3.0	3.0	1.5	3.5	3.3	1.3
	2	5.8	4.8	4.5	11.5	14.0	14.8	14.0	15.0	11.5

* a, b, c: Low, medium and high pH levels, respectively.

1: 0.05 N sulfuric acid, first extraction.
2: 0.05 N sulfuric acid, second extraction.

c. Aluminum (Table XVI)

(i) Sulfuric acid extract I. For the first three treatments, the aluminum content was the same for the two lowest pH levels, but increased for the highest pH level. For DCP-TPS, however, there was no perceptible change. Corresponding values for the three soils were similar. Generally, values for MTPS and TPS were higher than those for MCP and DCP-TPS.

(ii) Sulfuric acid extract II. Values increased with soil pH. Aluminum values for Grenada and Hartsells were higher than those for Dewey. Those for MCP and DCP-TPS were generally higher than those for MTPS and TPS.

d. Calcium (Table XVII)

(i) Water extract. Calcium content generally did not vary, especially for Grenada. Corresponding values for the three soils were about the same. Values for TPS and MTPS were similar; less than those for MCP, and greater than those for DCP-TPS.

(ii) Sulfuric acid extract I. Calcium values increased with pH especially for the highest pH level. Corresponding values for each soil were almost the same. The four treatments gave values in the descending order of magnitude, DCP-TPS, MCP, MTPS, TPS.

(iii) Sulfuric acid extract II. Dependence on pH was similar to that for acid extract I. Generally, values for DCP-TPS were greater than for the rest, which had almost similar ones.

TABLE XVI

EXTRACTION IV: ALUMINUM EXTRACTED BY DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	0.4	1.0	2.4	1.6	1.6	2.8	0.6	0.9	2.1
	2	0.2	0.6	0.2	2.1	0.7	1.6	1.0	1.9	1.5
Triple-point solution	1	0.6	0.8	2.3	1.0	1.9	2.3	1.4	0.7	2.3
	2	0.5	1.0	1.4	0.5	1.4	1.4	1.0	1.4	1.5
Monocalcium phosphate	1	1.1	3.0	2.3	2.5	1.9	2.7	1.2	2.0	2.7
	2	1.3	1.1	1.0	2.2	1.8	3.0	2.0	1.4	2.0
Dicalcium phosphate + triple-point solution	1	3.0	2.3	2.2	2.5	2.2	1.8	2.2	2.2	2.9
	2	1.6	Nil	0.8	2.2	2.4	3.0	0.7	1.9	3.1

* a, b, c: Low, medium and high pH levels, respectively.

1: 0.05 N sulfuric acid, first extraction.
2: 0.05 N sulfuric acid, second extraction.

TABLE XVII

EXTRACTION IV: CALCIUM EXTRACTED BY WATER AND DILUTE SULFURIC ACID FROM SOILS RECEIVING DIFFERENT PHOSPHORUS TREATMENTS (TWO ACID EXTRACTIONS)

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
		Parts Per 100,000 of Soil								
Metastable triple-point solution	1	23	31	25	23	23	31	31	25	38
	2	125	163	250	150	158	213	123	133	250
	3	18	13	18	14	17	26	10	9	18
Triple-point solution	1	25	31	31	23	23	23	25	25	25
	2	95	125	225	125	133	170	83	120	188
	3	8	10	15	11	14	23	10	8	15
Monocalcium phosphate	1	45	63	45	45	45	45	70	50	50
	2	158	195	280	188	175	258	150	163	288
	3	10	11	19	18	18	35	10	13	21
Dicalcium phosphate + triple-point solution	1	23	23	19	13	13	13	23	13	16
	2	300	340	425	300	325	390	300	325	465
	3	23	26	53	41	43	53	19	26	44

* a, b, c: Low, medium and high pH levels, respectively.

1: Water extraction.
2: 0.05 N sulfuric acid, first extraction.
3: 0.05 N sulfuric acid, second extraction.

C. pH Variations (Table XVIII)

For all four time intervals pH values determined after the time intervals dropped sharply in the case of the two highest lime levels. There was a gradual increase in pH in these cases after the initial sharp drop. For the original soil, however, there was not much variation, even on treatment with the phosphorus materials. (Refer to Figure 1.)

pH values obtained after treatment of the soil with the four phosphorus materials were almost the same for the first two soil lime levels, but increased considerably for the third lime level.

Corresponding values for all three soils were similar. Values for MTPS and TPS were similar, less than those for DCP-TPS, but more than those for MCP.

Maximum effect on pH produced by wetting the soil was observed for MCP, especially for the two lower pH levels. The effect of wetting was negligible in the case of the other phosphorus materials.

D. Comparison of Trends of Values at the End of the Four Reaction Periods (Refer to Figure 2)

1. Phosphorus

a. MTPS. Water extraction values decreased up to the third reaction period and remained steady thereafter. For fluoride extraction there was a general increase throughout the period of study. Acid fluoride extraction showed a general increase for Extraction II, no

TABLE XVIII

pH VALUES OBSERVED FOR DIFFERENT SOILS, PHOSPHORUS MATERIALS AND REACTION TIME INTERVALS

Soil Treated With	*	Dewey			Grenada			Hartsells		
		a	b	c	a	b	c	a	b	c
Metastable triple-point solution	1	4.5	6.0	7.9	4.9	6.0	7.8	4.6	5.9	7.8
	2	4.4	4.5	5.3	4.3	4.5	4.9	4.2	4.4	4.9
	3	4.2	4.7	5.3	4.5	4.7	5.1	4.3	4.5	5.2
	4	4.7	4.9	5.6	5.0	5.0	5.3	4.8	4.8	5.2
	5	4.8	4.9	5.4	4.9	5.0	5.3	4.5	4.8	5.2
Triple-point solution	1	4.5	6.0	7.9	4.9	6.0	7.8	4.6	5.9	7.8
	2	3.9	4.2	4.9	4.0	4.1	4.7	3.8	4.0	4.5
	3	4.1	4.5	5.2	4.4	4.5	4.9	4.1	4.2	4.9
	4	4.6	4.7	5.3	4.9	4.9	5.2	4.5	4.5	4.9
	5	4.7	4.8	5.4	4.6	4.9	5.1	4.4	4.6	5.1
Monocalcium phosphate	1	4.5	6.0	7.9	4.9	6.0	7.8	4.6	5.9	7.8
	2	3.7	3.9	4.4	3.5	3.8	4.2	3.6	3.9	4.4
	3	3.7	4.0	4.5	3.6	3.8	4.2	3.7	4.0	4.5
	4	3.7	3.9	4.5	3.6	3.8	4.3	3.7	4.0	4.5
	5	4.7	4.9	5.1	4.9	5.0	5.1	4.5	4.6	4.9
Dicalcium phosphate + triple-point solution	1	4.5	6.0	7.9	4.9	6.0	7.8	4.6	5.9	7.8
	2	4.3	4.6	5.5	4.3	4.6	5.4	4.4	4.6	5.5
	3	4.4	4.8	5.9	4.5	4.7	5.5	4.4	4.8	5.6
	4	4.5	5.0	6.1	4.8	5.0	5.8	4.7	4.9	5.9
	5	4.8	5.0	6.0	5.1	5.2	5.7	4.8	5.1	5.8

* a, b, c: Low, medium and high pH levels, respectively.

1: Before treatment.
2: After 2 days.
3: After 9 days.
4: After 43 days.
5: After 137 days.

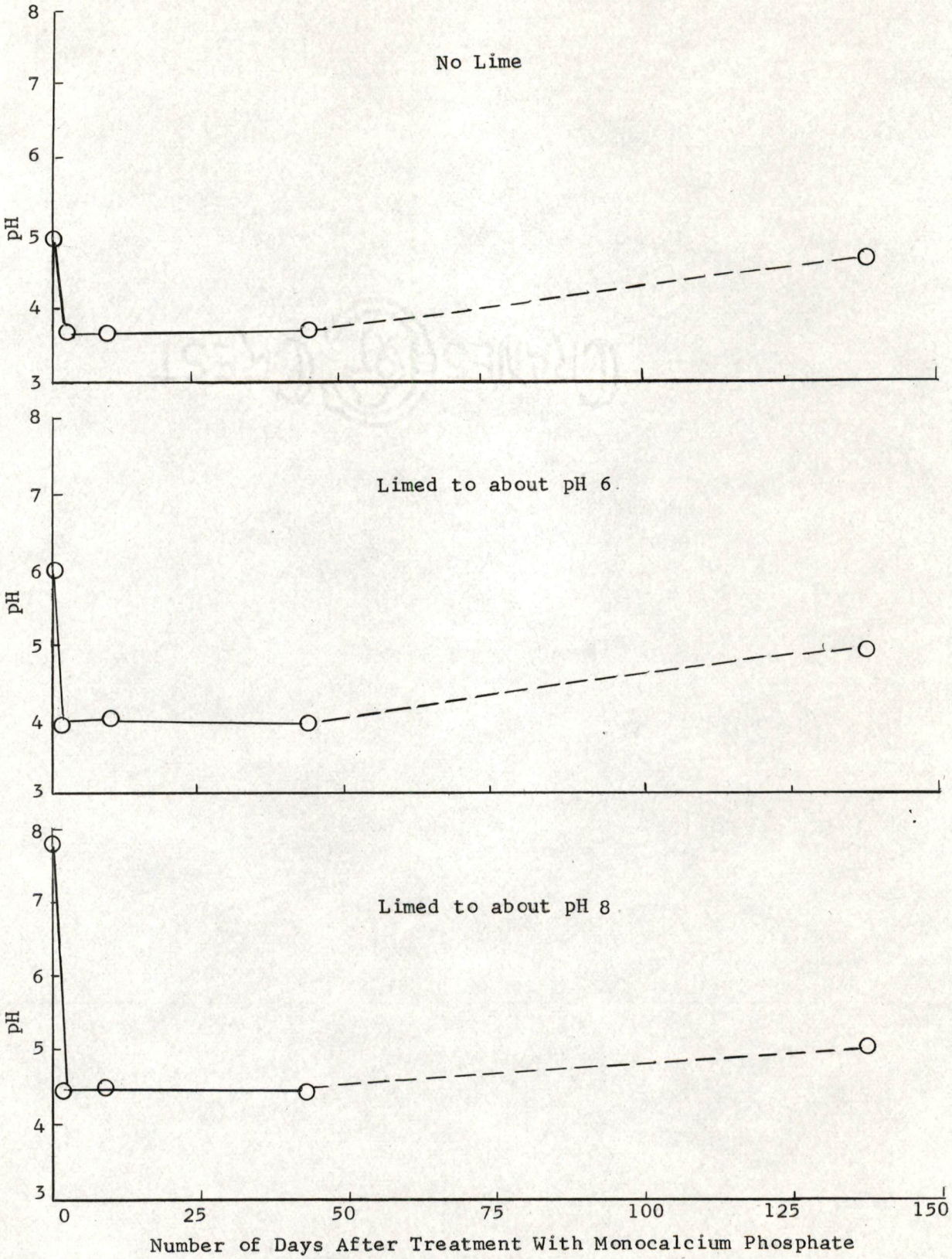

Figure 1--pH variations with time in Grenada soil treated with monocalcium phosphate.

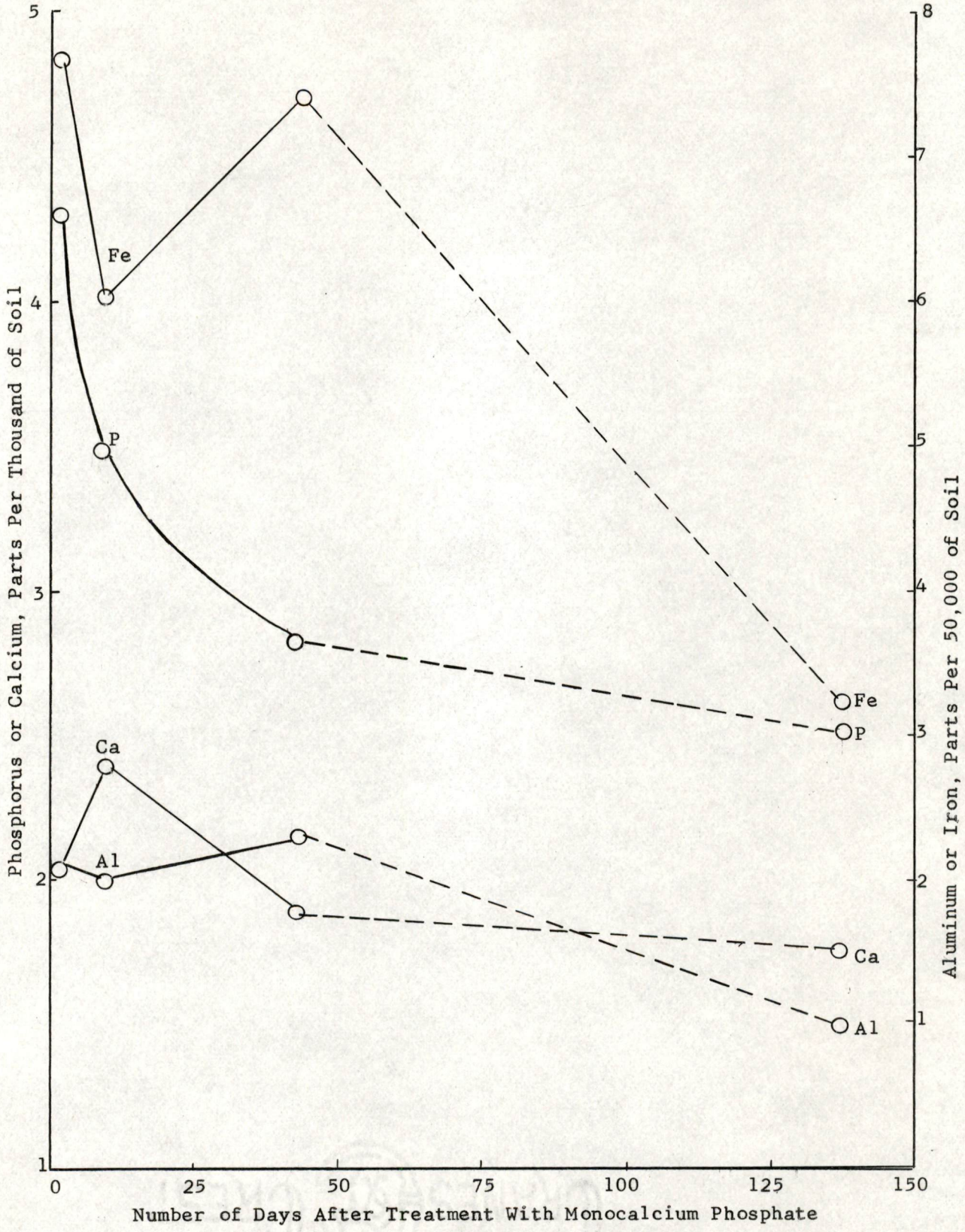

Figure 2--Variations with time of P, Al, Fe and Ca extracted by 0.05 N H_2SO_4 (first extraction) for MCP-treated Grenada soil of original pH about 6.

increase for the next extraction, but some increase for Extraction IV, especially for Dewey and Hartsells. There was a decrease for Extraction II for sulfuric acid extraction I, after which the values were steady. Second sulfuric acid extraction values showed a considerable increase for Extraction II, but only a slight increase thereafter.

b. TPS. Decreases from initial values were considerable for Extractions III and IV for water extraction. Values for fluoride extraction changed very little. In the case of acid fluoride, there was some decrease for Extraction II, increase for III, after which there was no change. For sulfuric acid extraction I, there was a decrease for Extraction II, and no change thereafter. For the second acid extraction there was a considerable increase for the second round, but only slight increases thereafter.

c. MCP. There was not much change for water extraction up to Extraction III, after which there was considerable decrease. Fluoride values were almost steady, while acid fluoride values were almost steady up to Extraction III and increased thereafter. The first sulfuric acid extraction gave a slight decrease for Extraction II, but none thereafter. For the second acid extraction, no change was observed up to Extraction III, but a considerable increase was observed for the last extraction.

d. DCP-TPS. Values mostly decreased in the case of water extraction. For fluoride extraction the values alternately decreased and increased up to Extraction III, with no change thereafter. In the case of acid fluoride extraction, they decreased for Extraction II with no change thereafter. Values were almost steady in all cases except

for Grenada, in the case of the first sulfuric acid extraction and slightly increased for the second acid extraction.

Values for water and fluoride extractions were almost the same for the first two extractions. Phosphorus extracted by acid fluoride was greater than that extracted by neutral fluoride in all cases. For MCP, values for water extraction were much higher than those for fluoride extraction, except for the last extraction, where the reverse was observed. In the case of DCP-TPS fluoride values were greater than water values in all cases.

Phosphorus extracted in the second acid extraction was about a fourth of that extracted in the first acid extraction, for the first three phosphorus materials in the first Extraction. In all the other cases, they were one-half to two-thirds the value of the phosphorus for the first extraction, except for TPS and MCP of extraction IV where the values for the second acid extraction were nearly equal to or slightly more than the values for the first acid extraction.

2. Iron

a. MTPS. For sulfuric acid extraction I there were alternating decreases and increases for the four Extractions. For the second acid extraction, there were increases up to Extraction III and no change thereafter.

b. TPS. For sulfuric acid extraction I there were alternating decreases and increases as for MTPS. The second acid extraction figures also had the same trend as for MTPS.

c. MCP. The observations for first sulfuric acid extraction were similar to those of MTPS and TPS. For the second acid extraction there was decrease up to Extraction III and a considerable increase for Extraction IV.

d. DCP-TPS. For both acid extractions there was no change up to Extraction III, after which there was a decrease.

Iron extracted in second acid extraction was less than that for the first acid extraction, for Extraction I, except for DCP-TPS. For the remaining extractions this was reversed, except in the case of MCP, Extraction II, for the two lower pH levels.

3. Aluminum

a. MTPS. Aluminum values decreased generally for both first and second acid extractions.

b. TPS. There was no regularity in the change of aluminum content.

c. MCP. For sulfuric acid extraction I there was no change up to Extraction III, after which there was a considerable decrease. For the second acid extraction there was a decrease for Extraction II, and increase for Extraction III and a considerable decrease thereafter.

d. DCP-TPS. For the first acid extraction the observation was the same as for the second extraction for MCP; for the second extraction it was the same as the first one for MCP. Among the values for the first acid extraction, there was not much variation for the four phosphorus materials and for the first three Extractions. There was not much difference between corresponding values for Extractions I and II,

but there were such differences for the other Extractions.

4. Calcium

a. MTPS. Water-extractable calcium decreased progressively throughout. For sulfuric acid extraction I there was no change for Extraction II, but there was a slight decrease up to Extraction III and increase for Extraction IV.

b. TPS. As for MTPS water-extractable calcium decreased progressively. For acid extraction I there was increase for Extraction IV, especially for the two lower pH levels. As for MTPS there was decrease up to Extraction III for the second extraction and increase for Extraction IV.

c. MCP. Water-extractable calcium did not change much up to Extraction III, after which there was a considerable decrease, and no change, respectively, for the last three Extractions. For the second acid extraction there was decrease up to Extraction III, and no change for IV.

d. DCP-TPS. Changes were irregular for water extraction. There was no change up to Extraction III and a slight decrease thereafter for acid extraction I and the opposite observation for Extraction IV.

Calcium extracted in first acid extraction was higher than that for the second extraction, in all cases. About half the amount extracted by the first acid extraction was extracted by water, except in the case of Extraction IV, where water-extractable calcium was considerably lower. Moreover, for MCP, water-extractable calcium and that extracted

by first acid extraction were nearly equal except for Extraction IV, where the former was about a third of the latter.

Calcium extracted in the first acid extraction was highest for DCP-TPS. For the second extraction the absolute values were far lower than for first extraction, but those for DCP-TPS were slightly higher than those for the other phosphorus materials.

E. Statistical Analysis for Study of Relationships

In an attempt to determine the relationships, if any, between the several constituents extracted during the four Extractions, and to see if soil properties influenced these, correlation coefficients were worked out for simple correlation. As a preliminary, the data were scrutinized for possible relationships and promising data plotted on graph paper to bring out the degree and nature of relationships more clearly. Statistical correlations were worked out only for the more promising ones. Results are presented in Table XIX. In some cases only a few pairs of data were used. Calculation of correlations with such few data may not be satisfactory, but the data do give an idea of the degree of correlation between the factors studied. In isolated instances one or more points which departed markedly from the general trend of relationships were omitted, for the sake of bringing out the general trend more clearly.

1. Different Extractants, Same Constituent (Phosphorus), All Soils (Table XIX)

Fluoride-extractable phosphorus was correlated with acid fluoride-extractable phosphorus. Fair correlations were observed for

TPS, Extraction I, for MCP, Extractions I to III, and for DCP-TPS, Extractions I and IV separately. There was poor or no relationship in other cases. An attempt was also made to separate out the three soils to see if there were a better relationship. There was a slight improvement for Dewey soil.

Other possible relationships between the phosphorus extracted by the various extractants were studied (Table XIX). There was no perceptible relationship in most cases, but in the case of the first to second sulfuric acid extraction for DCP, Extraction II, and for fluoride-extractable phosphorus to acid fluoride-extractable phosphorus for the first three phosphate treatments in Extraction I, there were fair correlations. It was interesting to note that this type of correlations was confined to the earlier experiments only.

2. Time of Reaction

The regularity of decrease in the extraction of the soil constituents with time was investigated by working out correlations between values for these constituents obtained in the earlier Extractions, and the corresponding values in the later Extractions. (Table XIX.)

a. Phosphorus. Fairly high correlations were obtained for the relationship of fluoride-extractable phosphorus for DCP between Extractions I and II, and phosphorus extracted in second sulfuric acid extraction for MTPS, TPS, and DCP-TPS, except highest pH levels for MTPS and DCP-TPS between Extractions II and III. The corresponding sulfuric acid-phosphorus correlation for Extractions III and IV was considerably lower.

b. Iron. Fair correlations were obtained for iron-phosphorus extracted by first sulfuric acid extraction comparing Extraction I and II, II and III, and III and IV. (Refer to Figure 3.) For I and II, however, MCP had a different correlation pattern from the rest. Similar relationships in the case of the second sulfuric acid extractions were obtained for MTPS and TPS only, comparing Extractions I and II and II and III.

c. Aluminum. A fair relationship was observed between aluminum extracted by the first sulfuric acid extraction in Extraction III and in Extraction IV, taking all phosphorus materials and all soils together.

d. Calcium. Fair correlations were obtained comparing water-soluble calcium for all treatments except MCP, Extraction I with Extraction II, and the second sulfuric acid extract calcium, Extraction II with Extraction III (all samples). Other relationships are indicated in Table XIX.

3. Multiple Correlation

The simultaneous effect, if any, of two or more constituents on another constituent was studied by the use of multiple correlation. In a few instances it was found that the use of this type of correlation was superior to the simple correlations described in the previous section. Results are presented in Table XIX. Only simple correlation coefficients and the multiple correlation coefficient are given, omitting the coefficients of partial correlation.

Multiple correlation coefficient was worked out for the correlation of iron and aluminum on phosphorus, for the second sulfuric acid

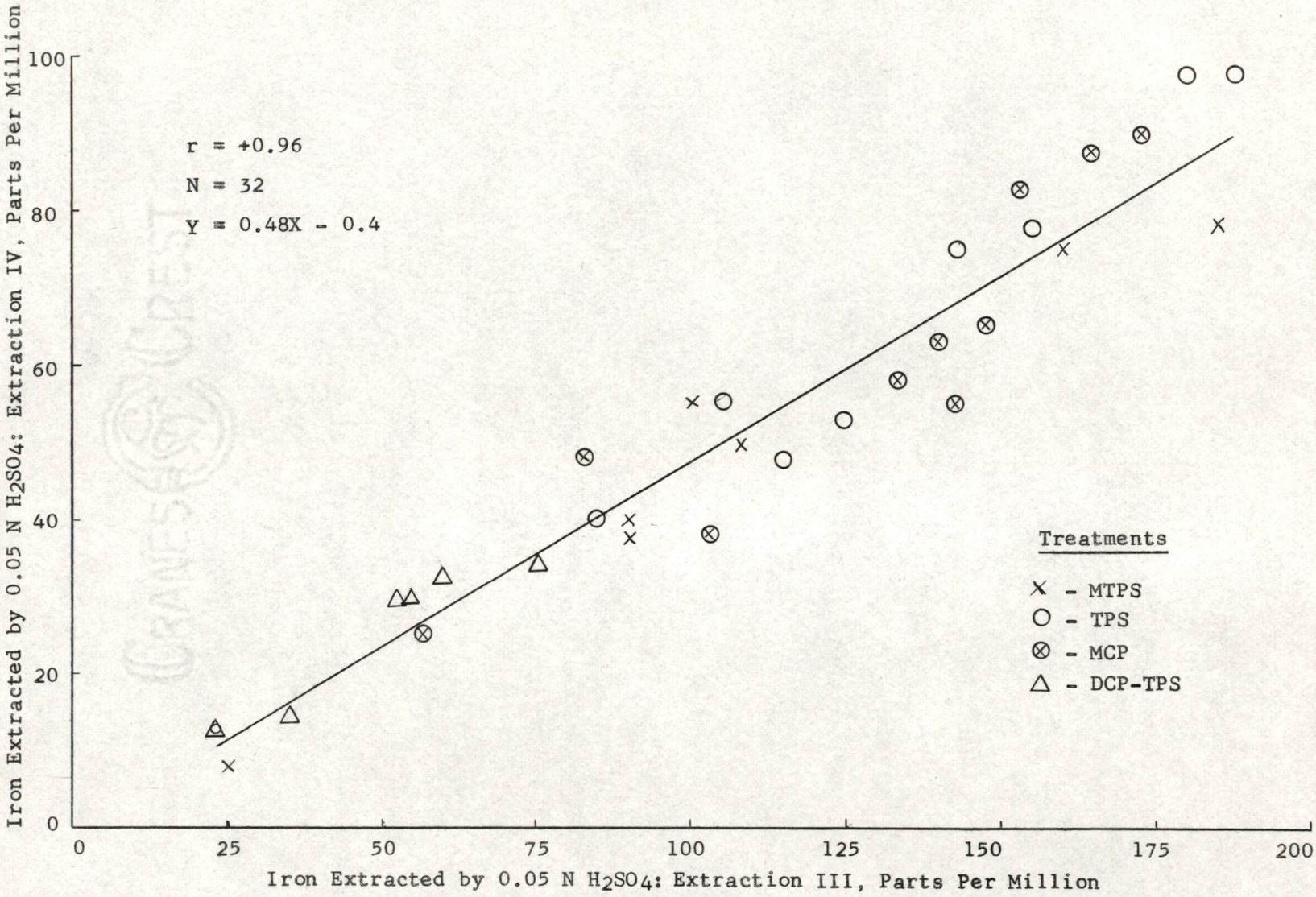

Figure 3--Regression of iron extracted by 0.05 N H_2SO_4: Extraction III on corresponding value for Extraction IV.

extraction, for MTPS and TPS of Dewey soil. But the coefficient was not better than the simple correlations of iron and aluminum compared individually with phosphorus.

Multiple correlation was worked out also for calcium and iron on phosphorus, Extraction I, for the three soils, as reported in Table XIX. The indications were that this was more useful than the simple individual correlations only in the case of Hartsells soil. In the case of Dewey the simple iron-phosphorus correlation coefficient, and in the case of Grenada, the simple calcium-phosphorus correlation coefficient were fairly high and comparable to the multiple correlation coefficients for these cases.

The above process was repeated for Extraction II also. Here the multiple correlation coefficients for the individual soils were definitely superior to the simple correlation coefficients. The magnitude of the multiple correlation coefficient increased in the order Dewey, Grenada, Hartsells. It was of interest to note that even with the four different phosphorus materials and the three levels of pH, this multiple correlation was marked in the case of Hartsells soil ($R = 0.93$).

The multiple regression equation for Hartsells soil, sulfuric acid extraction II, was $Y = 2.65X_1 + 7.55X_2 - 25$ where X_1 and X_2 were calcium and iron, respectively and Y was phosphorus, all concentrations being expressed in parts per 100,000 of air-dry soil.

To see if this multiple correlation could be improved still further by the inclusion of another variable, aluminum, the calculations were repeated, taking aluminum also together with the other constituents. But

there was no improvement, as indicated by the absence of change in the coefficient of multiple correlation, which remained at the same value ($R = 0.93$).

To observe if Hartsells soils behaved similarly for Extractions I and II, all the data were taken together and multiple correlation worked out. The R was 0.90 in this case, indicating that they were nearly so. The corresponding equation for Hartsells, for Extraction I and II taken together was $Y = 2.06\ X_1 + 10.0\ X_2 - 69$, using the same symbols and units as for Extraction II. It was interesting to observe that the iron-phosphorus simple correlation observed for Extraction I for Dewey, and the calcium-phosphorus simple correlation for Extraction I, Grenada and Hartsells had decreased considerably for Extraction II.

Multiple correlation worked out for all 36 samples for Extraction I for the same constituents (calcium and iron on phosphorus) gave a low R (0.71) which was almost equal to the simple correlation coefficient for calcium-phosphorus (0.69). This indicated that the pattern of relationship was different for the three soils, calcium-phosphorus being fairly close. When this was repeated for Extraction II, R came to 0.41, and the simple coefficients also were very low and not significant. This indicated that the divergence of the individual relationship patterns for individual soils was even greater for Extraction II, although taken individually the soils gave fair multiple correlations.

An attempt was made to correlate the sum of equivalent concentrations for calcium and iron with phosphorus in the case of Extractions I and II, individually for second sulfuric acid extraction, but the correlation was observed to be poor.

CHAPTER V

DISCUSSION

Water-extractable phosphorus increased for the second pH level (about pH 6) and decreased for the highest pH level studied (about pH 8). This finding was in accordance with the generally established relationship between pH and phosphate availability in acid soils. This relation was marked during the early stages of the reaction of the phosphorus materials with the soil. Treatment with water levelled off these differences. Similar observations were made for the phosphorus extracted by the first and second sulfuric acid extractions.

The decrease of fluoride-extractable phosphorus with increase in pH level in the third extraction period appeared to indicate that the formation of adsorbed phosphate (which was measured by fluoride extraction) was prevented by liming. The absence of this reaction in the case of MCP, which was the only material applied in solid form seemed to show that the water-dissolved phosphorus materials brought about adsorption more rapidly. There was a similar, but less pronounced observation for Extraction IV, which was the one conducted after water-treatment.

Iron extracted by the first sulfuric acid extraction decreased with an increase in pH level, but this decrease was more marked for the highest pH level. This was in contrast to the increases noted for both higher levels in the case of water-soluble phosphorus. Iron extracted by the second acid extraction was higher in amount than the first extraction, except for Extraction I. This probably was associated with the

extraction of calcium, which was removed in large amounts during the first acid extraction.

Aluminum extracted by first sulfuric acid extraction generally increased with pH, while the iron extracted simultaneously decreased. This was probably due to the pronounced amphoteric character of aluminum, which might have formed an aluminate ion at the higher pH levels.

Water-extractable calcium decreased with the increase of pH for the first two Extractions. This suggests that raising the pH fixed the calcium somehow in a form which made it difficult to extract. The water-soluble calcium was far higher for MCP than for the other phosphorus materials for the first three Extractions. But after treatment with water, the water-soluble calcium decreased considerably. This appeared to indicate that the calcium was rendered water-insoluble by the water-treatment.

Water-soluble phosphorus was much higher than the neutral fluoride-extractable form for the MCP treatment. This probably was due to the unreacted lime reacting with the fluoride extractant and lowering its effective fluoride concentration. The presence of water-extractable calcium in large amounts before water treatment was indicated.

Some relationship was noticed between the neutral fluoride and acid fluoride extractable phosphorus. This was more pronounced for MCP (the only solid phosphorus material used) before wetting the soil. This appeared to indicate that the treatment with water or the use of phosphorus materials in solution (MTPS or TPS) prevented regularity of the relationship.

In the study of regularity of decrease in the extractable forms of the constituents, fluoride-extractable phosphorus and the second sulfuric acid-extractable phosphorus showed fair regularity. This observation was striking, as this appeared to be applicable even for the different soils, pH levels, and the different phosphorus materials. This kind of relationship was observed clearly for all four extractions in the case of iron extracted by the second acid extraction and to a fair extent for aluminum, when comparing Extractions III and IV. The regression coefficients for the relationship for iron at different phases of the whole period of experimentation were similar, indicating that the acid-extractable iron almost uniformly decreased with time. For water-extractable calcium and phosphorus in the second sulfuric acid extraction, this regularity appeared to be confined to the initial stages.

Relationship of calcium and iron with phosphorus extracted in the second sulfuric acid extraction was observed for the second Extraction. The closeness of this relationship increased in the order Dewey, Grenada, and Hartsells soils. The individual soils had different patterns for this relationship and the Hartsells soil had almost the same patterns for Extractions I and II. Assuming that the second sulfuric acid extraction removed the more strongly adsorbed constituents, this may be interpreted to mean that the adsorption had taken place in such a manner as to exhibit a definite relationship between calcium, iron and phosphorus.

During the preparation of the soils for obtaining different pH levels by the addition of lime, it was observed that above about pH

6.7 Dewey and Grenada continued to show increases in pH with addition of lime, while with Hartsells the pH rose more slowly with addition of lime. (Refer to Figure 4.) The variation in buffering capacity indicated by this observation probably accounts for the differences in behavior indicated in the case of the relationship of calcium and iron to phosphorus.

The relationship appeared to disappear with time, as it was not observed for Extraction III to a marked extent.

Aluminum extracted by sulfuric acid was not observed to figure prominently in the relationships studied statistically. This may be due to the smaller fixing capacity of hydrated aluminum oxides, compared to the corresponding iron oxides, as pointed out by Metzger (34). Moreover, as observed by Seatz (36), the lower solubility of aluminum phosphate in sulfuric acid, compared to iron phosphate may account for a poor relationship between aluminum and phosphorus in most of the cases studied.

Although the soils studied had less than 2 per cent moisture, at the start, there were indications that the soil had reacted with MCP even at this low moisture level. The movement of considerable phosphorus from superphosphate granules into the soil even under low moisture levels, as observed by Lawton and Vomocil (23), may probably explain the observations mentioned above.

The treatment with water tended to level out the differences, in extractable phosphorus or basic ions, between the soils, pH levels, and phosphorus materials observed for air-dry soil. This was much

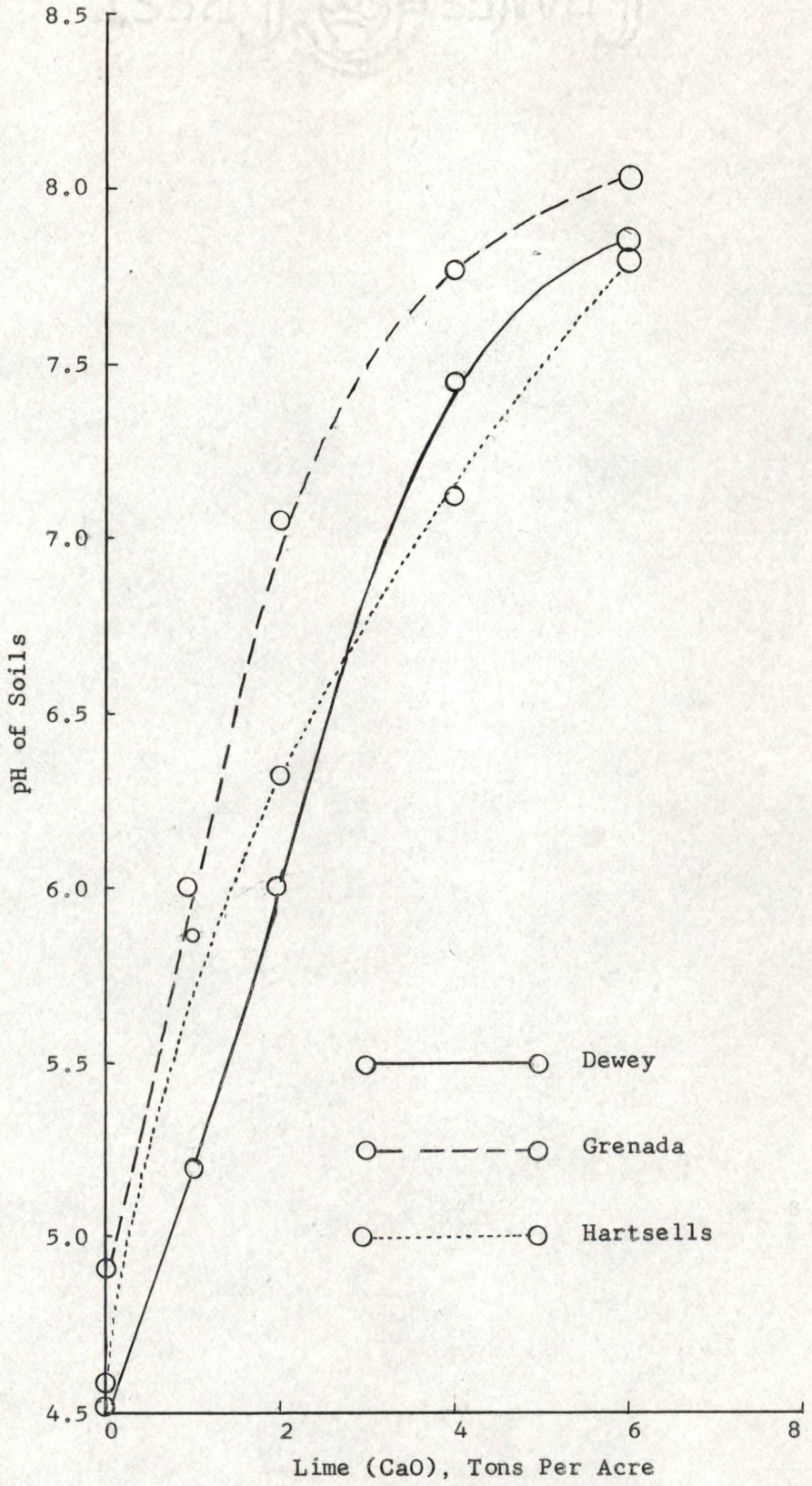

Figure 4--Effect of liming on pH of Dewey, Grenada and Hartsells soils.

pronounced for MCP. Probably the solution of MCP on treatment with water resulted in this phosphorus material reacting with the soil and in the decrease of the phosphorus in the water-soluble form.

pH values for soils treated with MCP were lower than corresponding values for the other phosphorus materials. These pH values were probably not the true pH values for the soil after reaction with the MCP, but represented in part the low pH that would have been produced by the solution, of unreacted MCP in the soils, in the water added for the preparation of the 1:1 soil suspension for pH measurements.

A comparison of the three soils indicated that Grenada and Hartsells had similar sulfuric acid-extractable iron and aluminum, which were greater than those for Dewey. In the course of the four extractions made during the study the relative proportions of these sesquioxides extracted from the original soils were reflected in the relative proportions of these constituents appearing in the acid extracts obtained during the course of the study after the addition of the phosphorus materials. But in view of the fact that large amounts of phosphorus were added and remained in the acid-extractable form, the phosphorus extracted during the study did not bear a relationship to the original phosphorus content.

The calcium content of the original soils was negligibly small. During the treatment of the soils with phosphorus materials, a large amount of calcium was added concomitantly. But it was observed that the corresponding values for calcium for the various treatments were similar for all the three soils studied.

CHAPTER VI

CONCLUSIONS

1. Reaction of phosphorus materials proceeded even in an air-dry soil, resulting in the phosphorus becoming more difficultly-extractable with time. With the phosphorus materials in the solution form fully or partly (MTPS, TPS and DCP-TPS), the decrease in the extractability of applied phosphorus was more pronounced. Wetting the systems tended to equalize the differences in the behavior of the different phosphorus materials.

2. During the initial stages of the study, water-soluble phosphorus increased for the second pH level (about pH 6) and decreased for the third (about pH 8).

3. Increasing the pH of the soils by lime application decreased the amount of iron extracted in first sulfuric acid extraction. The iron in the second acid extraction, however, increased with pH.

4. Calcium extracted by water decreased with increasing soil pH. The calcium extracted in the first sulfuric acid extraction increased progressively with an increase in soil pH.

5. Phosphorus extracted by all extractants decreased with passage of time, except the fluoride-soluble phosphorus for MTPS, which increased with time. For MCP water-extractable phosphorus was much higher than fluoride-extractable phosphorus before treatment with water, but the situation was reversed after water-treatment.

Iron extracted in the second sulfuric acid extraction was less than that extracted in the first extraction for the last three extractions. For the first extraction the reverse was true. Water-soluble calcium for MCP remained high as long as the soil was kept dry, but decreased sharply after treatment of soil with water.

6. pH levels decreased abruptly in the case of soil samples with the higher pH levels, on treatment with the phosphorus materials, but increased gradually with passage of time. The original pH, however, was not reached even after about four and a half months, with the water-treatment toward the end of the period.

7. A fair degree of relationship was observed between neutral- and acid-fluoride-extractable phosphorus in the case of MCP.

8. Regularity of decrease in extractability of the constituents was marked for iron extracted in second sulfuric acid extraction, and fair for fluoride- and the second sulfuric-acid-extractable phosphorus.

9. Calcium and iron were observed to be related to phosphorus in the second sulfuric acid extraction. This relationship was pronounced in the case of Hartsells soil for the first two Extractions and fair for Grenada and Dewey for the second Extraction only.

10. The original Dewey soil contained less acid-extractable iron and aluminum than Grenada or Hartsells, which had similar contents. These values were in this order for all the four Extractions. Phosphorus extracted by acid varied considerably with phosphate treatment or lime level. Relationship of calcium and iron on one hand and phosphorus on the other was more pronounced for Hartsells soil than for the

other two soils and this too was greater in the second extraction. Corresponding values for calcium were generally similar.

CHAPTER VII

SUMMARY

Samples of Dewey, Grenada and Hartsells soils were limed to obtain three pH levels and mixed with metastable triple-point solution, triple-point solution, monocalcium phosphate and dicalcium phosphate-triple-point solution of equivalent phosphorus concentration. The samples were allowed to react with the phosphorus materials for 2, 9, 43 and 137 days. At the end of these periods of time portions of the soil samples were removed and analyzed for phosphorus extractable by different solvents capable of dissolving out different forms of soil phosphorus and also for iron, aluminum and calcium extracted by dilute sulfuric acid. The pH of the soil samples at the end of the different time intervals was determined. The soils were kept air-dry during the first three periods, but were treated periodically with water between the third and last periods.

The original Dewey soil contained low amounts of acid-extractable iron and aluminum and fair amounts of acid-extractable phosphorus. Compared with Dewey soil, Grenada and Hartsells soils had higher amounts of acid-extractable sesquioxides, but lower amounts of acid-extractable phosphorus in the untreated condition. Calcium content was negligible for all the three untreated soils. After treatment with the phosphorus materials, the relationship of the acid-extractable calcium and iron to the phosphorus was pronounced for Hartsells soil in the case of the second extraction and was less so for the other two soils and the other extractions.

Results indicated that the water-soluble phosphorus was highest for about pH 6 and lower for the highest pH studied (about 8). Iron extracted in the first sulfuric acid extraction decreased with increase in soil pH, but the reverse was true for the second acid extraction. Water-soluble calcium decreased with soil pH. For the monocalcium phosphate treatment, the water-soluble calcium content remained at a high level until the soil was wetted.

Iron extracted by the second sulfuric acid extraction showed a regularity of decrease with time for all cases taken together. Calcium and iron were related to phosphorus extracted, in the case of second sulfuric acid extraction for Extraction II. This relationship was marked for Hartsells, which morever had the same relationship for Extractions I and II. The pH of soil samples at the higher initial pH levels decreased abruptly on treatment with phosphorus materials, but increased gradually with time.

LITERATURE CITED

LITERATURE CITED

1. Black, C. A. Phosphate fixation by kaolinite and other clays as affected by pH, phosphate concentration and time of contact. Soil Sci. Soc. Am. Proc. 7:123-133. 1942.

2. Bouldin, D. R. and Black, C. A. Phosphorus diffusion in soils. Soil Sci. Soc. Am. Proc. 18:255-259. 1954.

3. Bray, R. H. and Dickman, S. R. Adsorbed phosphates in soils and their relationship to crop responses. Soil Sci. Soc. Am. Proc. 6:312-320. 1941.

4. _____ and Kurtz, L. T. Determination of total, organic and available forms of phosphorus in soils. Soil Sci. 59:39-45. 1945.

5. Brown, W. E. and Lehr, J. R. Application of phase rule to the chemical behavior of monocalcium phosphate monohydrate in soils. Soil Sci. Soc. Am. Proc. 23:7-11. 1959.

6. Clark, J. S. and Peech, M. Solubility criteria for the existence of calcium and aluminium phosphates in soils. Soil Sci. Soc. Am. Proc. 19:171-174. 1955.

7. Cole, C. V. and Jackson, M. L. Solubility equilibrium constant of dihydroxy aluminum dihydrogen phosphate relating to a mechanism of phosphate fixation in soils. Soil Sci. Soc. Am. Proc. 15:84-89. 1950.

8. _____ and Olsen, S. R. Phosphorus solubility in calcareous soils: I. Dicalcium phosphate activities in equilibrium solutions. Soil Sci. Soc. Am. Proc. 23:116-118. 1959.

9. _____ and _____. Phosphorus solubility in calcareous soils: II. Effects of exchangeable phosphorus and soil texture on phosphorus solubility. Soil Sci. Soc. Am. Proc. 23:119-121. 1959.

10. Coleman, R. The mechanism of phosphate fixation by montmorillonitic and kaolinitic clays. Soil Sci. Soc. Am. Proc. 9:72-78. 1944.

11. Dean, L. A. and Rubins, E. J. Anion exchange in soils. I. Exchangeable phosphorus and anion exchange capacity. Soil Sci. 63:377-387. 1947.

12. _____ and _____. Anion exchange in soils. III. Applicability to problems in soil fertility. Soil Sci. 63:399-406. 1947.

13. Dickman, S. R. and Bray, R. H. Replacement of adsorbed phosphate from kaolinite by fluoride. Soil Sci. 52:263-273. 1941.

14. Fortune, W. B. and Mellon, M. G. Determination of iron with ortho-phenanthroline. Ind. Eng. Chem. Anal. Ed. 10:60-64. 1938.

15. Haseman, J. F., Brown, E. H. and Whitt, C. D. Some reactions of phosphates with clays and hydrous oxides of iron and aluminum. Soil Sci. 70:257-271. 1950.

16. _____, Lehr, J. R. and Smith, J. P. Mineralogical character of some iron and aluminum phosphates containing potassium and ammonium. Soil Sci. Soc. Am. Proc. 15:76-84. 1950.

17. Hemwall, J. A. The fixation of phosphorus by soils. Advances in Agronomy. 9:95-112. 1957.

18. Jackson, M. L. Soil Chemical Analysis. Prentice Hall, Inc., N. J. pp. 161 and 162, 1958.

19. Kittrick, J. A. and Jackson, M. L. Rate of phosphate reactions with soil minerals, and electron microscope observations on the reaction mechanism. Soil Sci. Soc. Am. Proc. 19:292-295. 1955.

20. _____ and _____. Applicability of solubility product principles to the variscite-kaolinite systems. Soil Sci. Soc. Am. Proc. 19:455-457. 1955.

21. _____ and _____. Common ion effect on phosphate solubility. Soil Sci. 79:415-421. 1955.

22. Kurtz, L. T. Inorganic phosphorus in acid and neutral soils. Soil and Fertilizer Phosphorus in Crop Nutrition, Agronomy, 4:59-88. 1953.

23. Lawton, K. and Vomocil, J. A. The distribution and migration of phosphorus from granular super in some Michigan soils. Soil Sci. Soc. Am. Proc. 18:26-32. 1954.

24. Lehr, J. R., Brown, W. E. and Brown, E. H. Chemical behavior of monocalcium phosphate monohydrate in soils. Soil Sci. Soc. Am. Proc. 23:3-7. 1959.

25. Lindsay, W. L., Lehr, J. R. and Stephenson, H. F. Nature of the reactions of monocalcium phosphate monohydrate in soils. III. Studies with metastable triple-point solution. Soil Sci. Soc. Am. Proc. 23:342-345. 1959.

26. _____ and Moreno, E. C. Application of thermodynamics to phosphate reactions in soils. Soil Sci. Soc. Am. Proc. In press.

27. _____, Peech, M. and Clark, J. S. Solubility criteria for the existence of variscite in soils. Soil Sci. Soc. Am. Proc. 23: 357-360. 1959.

28. _____ and Stephenson, H. F. Nature of the reactions of monocalcium phosphate monohydrate in soils. I. The solution that reacts with the soil. Soil Sci. Soc. Am. Proc. 23:12-17. 1959.

29. _____ and _____. Nature of the reactions of monocalcium phosphate monohydrate in soils. IV. Repeated reactions with metastable triple-point solution. Soil Sci. Soc. Am. Proc. 23:440-445. 1959.

31. Low, P. F. and Black, C. A. Phosphate induced decomposition of kaolinite. Soil Sci. Soc. Am. Proc. 12:180-184. 1947.

32. McCauliffe, C. D., Hall, N. S., Dean, L. A. and Hendricks, S. B. Exchange reactions between phosphates and soils: Hydroxylic surfaces of soil minerals. Soil Sci. Soc. Am. Proc. 12:119-123. 1947.

33. Metzger, W. H. Significance of adsorption or surface fixation of phosphorus by some soils of the Prairie group. J. Am. Soc. Agron. 32:513-526. 1940.

34. _____. Phosphorus fixation in relation to the iron and aluminum of the soil. J. Am. Soc. Agron. 33:1093-1099. 1941.

35. Seatz, L. F. Phosphate activity measurement in soils. Soc. Sci. 77:43-51. 1954.

36. Shapiro, L. and Brannock, W. W. A contribution to geochemistry: Rapid analysis of silicate rocks. Geological Survey Bulletin 1036-C, revised from Circular 165, U. S. Govt. Printing Office, Washington, pp. 34-35. 1956.

37. _____ and Fried, M. Relative release and retentiveness of soil phosphorus. Soil Sci. Soc. Am. Proc. 23:195-198. 1959.

APPENDIX

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRELATION

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
A. Extractants				
1. Different extractants, same constituent, all soils				
(a) Fluoride-extractable phosphorus for TPS, Extraction I	Acid fluoride-extractable phosphorus	9	0.85	**
(b) Fluoride-extractable phosphorus for MCP, Extraction I to III	Acid fluoride-extractable phosphorus	27	0.76	**
(c) Fluoride-extractable phosphorus for MCP, Extraction IV	Acid fluoride-extractable phosphorus	9	0.55	N. S.
(d) Fluoride-extractable phosphorus for DCP-TPS, Extraction I	Acid fluoride-extractable phosphorus	9	0.93	**
(e) Fluoride-extractable phosphorus for DCP-TPS, Extraction II	Acid fluoride-extractable phosphorus	9	0.66	*
(f) Fluoride-extractable phosphorus for DCP-TPS, Extraction IV	Acid fluoride-extractable phosphorus	9	0.84	**

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRELATION (Continued)

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
2. Different extractants, same constituents, same soils				
(a) Fluoride-extractable phosphorus for MCP, Dewey, Extraction I to IV	Acid fluoride-extractable phosphorus	12	0.89	**
(b) Fluoride-extractable phosphorus for DCP-TPS, Dewey, Extractions I, II and IV	Acid fluoride-extractable phosphorus	9	0.66	*
(c) Fluoride-extractable phosphorus for DCP-TPS, Grenada, Extractions I, II and IV	Acid fluoride-extractable phosphorus	9	0.75	*
(d) Fluoride-extractable phosphorus for DCP-TPS, Hartsells, Extractions I, II and IV	Acid fluoride-extractable phosphorus	9	0.80	**
3. Different extractants, same constituents, all soils				
(a) First sulfuric acid-extractable phosphorus, DCP, II Extraction II	Second sulfuric acid-extractable phosphorus	8	0.90	**
(b) Fluoride-extractable phosphorus for TPS, MCP and DCP-TPS, Extraction I	First sulfuric acid-extractable phosphorus	27	0.64	**

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRELATION (Continued)

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
(c) Acid fluoride-extractable phosphorus for TPS, MCP and DCP-TPS, Extraction I	First sulfuric acid-extractable phosphorus	27	0.42	*
(d) Acid fluoride-extractable phosphorus for TPS, MCP and DCP-TPS, Extraction I	Fluoride-extractable phosphorus	27	0.73	**
(e) Fluoride-extractable phosphorus, for MTP, TPS and MCP, Extraction II	First sulfuric acid-extractable phosphorus	36	0.34	*
B. Time of Reaction				
1. Phosphorus				
(a) Water-extractable phosphorus, for DCP, Extraction III	Same for Extraction IV	9	0.71	*
(b) Fluoride-extractable phosphorus, for DCP, Extraction I	Same for Extraction II	9	0.96	**
(c) Acid fluoride-extractable phosphorus, for TPS and DCP-TPS, Extraction I	Same for Extraction II	18	0.74	**
(d) Second sulfuric acid-extractable phosphorus, for MTPS, TPS and DCP-TPS (except highest pH levels for MTPS and DCP-TPS) Extraction II	Same for Extraction III	17	0.92	**

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRELATION (Continued)

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
(e) Second sulfuric acid-extractable phosphorus for MTPS, TPS and DCP-TPS (except highest pH levels for MTPS), Extraction III	Same for Extraction IV	22	0.63	**
2. Iron				
(a) First sulfuric acid-extractable iron, for MTPS, TPS and Dewey of DCP-TPS, Extraction I	Same for Extraction II	19	0.98	**
(b) First sulfuric acid-extractable iron, for MCP, Extraction I	Same for Extraction II	9	0.97	**
(c) First sulfuric acid-extractable iron, for MTPS, TPS and MCP, Extraction II	Same for Extraction III	27	0.95	**
(d) First sulfuric acid-extractable iron, all treatments, Extraction III	Same for Extraction IV	32	0.96	**
(e) Second sulfuric acid-extractable iron, for MTPS and TPS, Extraction I	Same for Extraction II	18	0.97	**
(f) Second sulfuric acid-extractable iron, for MTPS and TPS, Extraction II	Same for Extraction III	18	0.96	**

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRELATION (Continued)

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
3. Aluminum				
First sulfuric acid-extractable aluminum, Extraction III	Same for Extraction IV	36	0.78	**
4. Calcium				
(a) Water-extractable calcium, for MTPS, TPS, and DCP-TPS, Extraction I	Same for Extraction II	27	0.95	**
(b) First sulfuric acid-extractable calcium, for TPS and MCP, Extraction II	Same for Extraction III	18	0.97	**
(c) Second sulfuric acid-extractable calcium, Extraction II	Same for Extraction III	36	0.96	**
(d) Second sulfuric acid-extractable calcium, for MTPS and TPS, Extraction III	Same for Extraction IV	18	0.94	**
C. Multiple Correlations				
1. Iron and aluminum vs. phosphorus				
(a) Second sulfuric acid extractable iron, for MTPS and TPS, for Dewey and Hartsells, Extraction IV	Same for phosphorus	12	0.69	*

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRELATION (Continued)

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
Above for aluminum	Same for phosphorus	12	0.62	*
Above for iron	Same for aluminum	12	0.72	**
Above for iron and aluminum	Same for phosphorus	12	0.72	**
2. Calcium and iron vs. phosphorus				
(a) Second sulfuric acid-extractable calcium, for MTPS, TPS and MCP, for Dewey, Extraction I	Same for phosphorus	9	0.35	N. S.
Above for iron	Same for phosphorus	9	0.93	**
Above for calcium	Same for iron	9	0.48	N. S.
Above for calcium and iron	Same for phosphorus	9	0.93	**
(b) Second sulfuric acid extractable calcium, for all four treatments, for Grenada, Extraction I	Same for phosphorus	12	0.86	**
Above for iron	Same for phosphorus	12	-0.04	N. S.
Above for calcium	Same for iron	12	-0.33	N. S.
Above for calcium and iron	Same for phosphorus	12	0.81	**

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRELATION (Continued)

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
(c) Second sulfuric acid-extractable calcium, for all four treatments, for Hartsells, Extraction I	Same for phosphorus	11	0.72	*
Above for iron	Same for phosphorus	11	-0.59	N. S.
Above for calcium	Same for iron	11	-0.02	N. S.
Above for calcium and iron	Same for phosphorus	11	0.92	**
(d) Second sulfuric acid-extractable calcium, for all four treatments, for Dewey, Extraction II	Same for phosphorus	12	0.42	N. S.
Above for iron	Same for phosphorus	12	0.55	N. S.
Above for calcium	Same for iron	12	-0.06	N. S.
Above for calcium and iron	Same for phosphorus	12	0.72	*
(e) Second sulfuric acid-extractable calcium, for all four treatments, for Grenada, Extraction II	Same for phosphorus	12	0.19	N. S.
Above for iron	Same for phosphorus	12	0.74	**
Above for calcium	Same for iron	12	-0.32	N. S.
Above for calcium and iron	Same for phosphorus	12	0.86	**

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRELATION (Continued)

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
(f) Second sulfuric acid-extractable calcium, for all four treatments, for Hartsells, Extraction II	Same for phosphorus	11	0.33	N. S.
Above for iron	Same for phosphorus	11	0.55	N. S.
Above for calcium	Same for iron	11	-0.54	N. S.
Above for aluminum	Same for phosphorus	11	-0.73	**
Above for calcium	Same for aluminum	11	-0.01	N. S.
Above for aluminum	Same for iron	11	-0.69	*
Above for calcium and iron	Same for phosphorus	11	0.93	**
Above for calcium, iron and aluminum	Same for phosphorus	11	0.93	**
(g) Second sulfuric acid-extractable calcium, for all four treatments, for Hartsells, Extractions I and II	Same for phosphorus	22	0.42	*
Above for iron	Same for phosphorus	22	0.66	**
Above for calcium	Same for iron	22	-0.26	N. S.
Above for calcium and iron	Same for phosphorus	22	0.90	**
(h) Second sulfuric acid-extractable calcium, for all four treatments, for all soils, Extraction I	Same for phosphorus	36	0.69	**

TABLE XIX

RESULTS OF STATISTICAL ANALYSIS FOR CORRECTION (Continued)

Soil Constituent Studied (X)	Correlated With (Y)	No. of Observation Pairs	Correlation Coefficient	Significance
Above for iron	Same for phosphorus	36	0.13	N. S.
Above for calcium	Same for iron	36	0.06	N. S.
Above for calcium and iron	Same for phosphorus	36	<u>0.71</u>	**
(i) Second sulfuric acid-extractable calcium, for all four treatments, for all soils, Extraction II	Same for phosphorus	36	0.15	N. S.
Above for iron	Same for phosphorus	36	0.35	*
Above for calcium	Same for iron	36	-0.08	N. S.
Above for calcium and iron	Same for phosphorus	36	<u>0.41</u>	*

Underscored figures are coefficients of multiple correlation.

Significance: * : At 95% level.
**: At 99% level.
N. S. Not significant at 95% level.