AGENCY FOR INTERNATIONAL DEVELOPMENT
WASHINGTON, D. C. 20523

BIBLIOGRAPHIC INPUT SHEET

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Batch 70

1. SUBJECT CLASSIFICATION	A. PRIMARY: Food production and nutrition	AF22-0000-0000
	B. SECONDARY: Soil chemistry and physics	

2. TITLE AND SUBTITLE
Mineralogical aspects of reactivity to phosphorus among highly weathered soils

3. AUTHOR(S)
Adams, Peter

4. DOCUMENT DATE	5. NUMBER OF PAGES	6. ARC NUMBER
1977	124p.	ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS
Cornell

8. SUPPLEMENTARY NOTES *(Sponsoring Organization, Publishers, Availability)*
(Thesis M.S.--Cornell)

9. ABSTRACT
The applicability of the adsorption isotherm approach to characterizing reactivity of highly weathered soils to phosphorus was assessed for incubation periods of up to three months. Samples from 23 highly weathered soils from Puerto Rico, Brazil, Ghana, Venezuela, and Malawi were studied. Extractions of poorly ordered mineral fractions of the soils were carried out in order to establish possible relations with reactivity of the soils to phosphorus. A given isotherm was prepared by reacting subsamples of a soil with KH_2PO_4 solutions covering a range of initial concentrations, with 0.01M $CaCl_2$ used as a carrier salt. Relations between final concentrations of P and P removed from solution by soil were found to conform to Lanmuir and Freundlich isotherm treatment of the data for all incubation periods. However, evidence was found that equilibrium conditions, assumed in the Langmuir adsorption model, were not attained in short incubation periods. Estimation of poorly ordered mineral fractions in soils was attempted by extraction with 0.5M $CaCl_2$, dilute HC HCL; cold, 5% Na_2CO_3; or acid ammonium oxalate in darkness. Values of aluminum extracted by dilute HCl or 5% Na_2CO_3 were found tc correlate strongly with phosphorus sorption indices derived from isotherm data for all incubation periods. Values for iron extracted by dilute HCl or acid oxalate were found to relate poorly to reactivity indices, though correlations improved slightly for indices derived from longer term isotherms. Significant correlations were found between phosphorus reactivity indices and clay or organic matter content. The latter two factors were found to correlate strongly with Al extracted by dilute HCl or 5% Na_2CO_3.

10. CONTROL NUMBER PN-AAE-479	11. PRICE OF DOCUMENT
12. DESCRIPTORS Adsorption Phosphorus Weathering	13. PROJECT NUMBER
	14. CONTRACT NUMBER AID/ta-C-1104 Res.
	15. TYPE OF DOCUMENT

AID 590-1 (4-74)

AID/ta-C-1104 Rec
Cornell
PN AAE-479

MINERALOGICAL ASPECTS OF REACTIVITY TO PHOSPHORUS AMONG HIGHLY WEATHERED SOILS

A Thesis

Presented to the Faculty of the Graduate School

of Cornell University for the Degree of

Master of Science

by

Peter Adams

January, 1977

Biographical Sketch

Peter Adams was born on December 23, 1943 in Washington, D.C. His early education was in numerous schools in the Northeast. In February, 1967 he received a B.A. in sociology from Columbia College, N.Y.C. He worked as a cab driver and paper cutter in N.Y.C. prior to beginning his studies in agronomy at Cornell University in 1973.

Acknowledgements

The author wishes to acknowledge the major role of the chairman of his committee, Dr. R.M. Weaver, in defining the approaches to the problems studied in this thesis amd to express appreciation to Dr. Weaver for his patience and encouragement during its preparation and to Dr. R.F. Lucey for serving on the author's committee and for the influence of his practical point of view, which served as an inspiration in attempts herein to relate findings to problems of agricultural production. Thanks are due also to Nancy Hoch and Debbie Chessin for help in typing and to Paul Bloom for many useful discussions. The author wishes to express particular gratitude to Nancy Hoch for her human support and, likewise, offer warm hugs to Norma, Denny, Lew, Jake, George, Manny, Gail, Mike, Hrad, Mark, Phoeb, Dick, Sherry, Rich, J.B., Grover, Aba, Ban, Sarah, Lee, Sonny, Kate, Karen, Meg, Paul, Jill, Conga, Cheri, Marc, Claire, Debbie, Seth and Spider.

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Section I Introduction

Phosphorus has long been recognized as a factor which can be limiting for plant growth. Russell (1973) cites Liebig's insistance as early as 1840 on the importance of phosphorus as well as solid evidence accumulated by 1855 from field trials at Rothamstead for its effects on yields. The dimensions of the modern significance of phosphate fertilizer use are reflected in figures for phosphate fertilizer production for the period 1 July 1973 - 30 June 1974 expressed as metric tons P_2O_5: World, 25,490,000; U.S., 6,013,000 (Department of Economic and Social Affairs, U.N., 1975).

It has long been known that soils remove phophorus from solution often to a considerable extent, but there is disagreement about what mechanism best explains the behavior shown. It has often been argued that solubilities of crystalline reaction products control solution levels of P. Hemwall (1957) found relatively constant solubility products of solution Al and P in montmorillonite and kaolinite systems reacted with varying levels of P, which he argued constituted evidence for formation of variscite. Lindsay et al. (1959) and Wright and Peech (1960) found evidence that P reaction produacts on acid soils belonged to the variscite-strengite isomorphous series, while fluorapatite was held by Murrmann and Peech (1968) to be the ultimate reaction product on limed soils. However, later

Murrmann and Peech(1969) argued that "labile" P rather than the solubility of crystalline products controlled levels of soluble P on the basis of negligible changes in solution P levels of acid soils incubated with hydroxyapatite and of limed soils incubated with variscite or strengite. Kittrick and Jackson (1956) found x-ray diffraction evidence for the formation of taranakite at room temperature for kaolinite reacted with very high concentrations of KH_2PO_4. Norrish (1968) has found x-ray diffraction evidence for the formation of the plumbogummite family of minerals in soils. Electron microprobe analysis of soil particles by Sawhney (1973) indicated the existence of complex compounds of Al, Fe, P and Si, whose compositions varied over a wide range.

Characterization of soil-phosphorus interactions has also followed the approach of "adsorption isotherms" in which final solution levels of P are related to amounts removed from solution after incubation for a given period of time of a set of soil samples with initial solution P levels distributed through an appropiate range. Log-log plotting of such relations has often exhibited a linear form ("Freundlich" isotherm). More recently, Wantanabe and Olsen (1957) introduced the use of Langmuir's model(1918) of adsorption of gas by a solid phase to characterize soil phosphorus relations, an attraction of the model being its prediction of an adsorption maximum for a given adsorbent. They found adsorption maxima of soils from 24 hour isotherms to be highly correlated with specific surface area with different expressions for acid

and alkaline soils. Plotting by Rennie and Mc Kercher (1959) of 6 hour isotherm data for soils was found to conform to the Langmuir model below about 20ug P/ml. Syers et al. (1973) and Holford et al. (1974) were able to resolve the break in slope of Langmuir treated isotherm data extending to high equilibrium concentrations by assuming the existence of a second set of adsorption sites of sorption energy and maximum differ nt from those for the low concentration end of an isotherm. However, from the results of sorption isotherms of Al^{3+} and $Al(OH)_2^+$ saturated cation exchange resins Hsu and Rennie (1962) argued for the compatibility of precipitation reactions and conformity of isotherm data to the Langmuir adsorption expression.

Because of the success of adsorption models in characterizing quantitatively the reactivity of soils to phosphorus, attempts have been made to relate their features to plant response trials. Woodruff and Kamprath (1965) met with indifferent sucess using the Langmuir adsorption maximum as an index of reactivity. However, amounts of P sorbed by soils at 0.3 ug P/ml. after 17 hours contact were found by Ozanne and Shaw (1968) to predict very well the optimum P rates for a large number of soils. In a similiar experiment, Jones and Benson (1975) found that optimal P applications for corn on an Idaho volcanic ash soil corresponded to amounts of P removed from solution in incubation systems having solution P levels of 0.13 ug P/ml. after 6 days and found a linear

relationship between solution P levels corresponding to levels of P applications and a wide range of plant characteristics.

Because phosphorus has often been found to be a limiting factor on highly weathered soils(Olson and Engelstad,1972), the adsorption isotherm approach seems an appropiate one for quantification of reactivity of such soils to phosphorus. However, the use of adsorption isotherms has up to the present been limited to contact periods of relatively short duration. A primary intention of the present work was to test the applicability of the adsorption model approach to systems incubated for much greater periods of time using samples of highly weathered soils. A second concern has been to relate quantitative indices derived from P sorption data to other properties of the soils under study.

Section II Materials and methods

A. Soils

The soils used in the present study have been characterized by a number of workers: the Puerto Rican soils by Roberts and Weaver (1975), SCS,USDA (1967), Roberts (1942); the Brazilian soils by Weaver (1974), Cline and Buol (1973); the Ghanaian soils by Mughogho (1974); the Malawian soils by Mughogho (1975) and Brown and Young (1964); the Venezuelan soils by Daugherty (1975). Descriptions below are from these sources. All samples are from surface horizons.

Puerto Rican Soils

Catalina (B-1)

The sample was collected to a depth of 15 cm (6 in) from the vicinity of Corozal and is classified as a Tropeptic Haplorthox; clayey, oxidic, isohyperthermic and is derived from chloritized greenish black basaltic andesite flow breccia. Catalina occurs on ridges and slopes and receives an average rainfall of 198 cm (79 in).

Humatas (C-1)

A sample belonging to the Humatas series was collected at Corozal to a 15 cm(6 in) depth. The soil is classified as Typic Tropohumult, clayey, mixed isohyperthermic. The soil is derived from residuum or very local colluvium from volcanic rocks and is found on the side slopes in the uplands. Mean annual precipitation is 215 cm (86 in), mean annual temperature ranges from 22.2 to 26.1^{o} C (72-79° F).

Nipe (N-1)

This sample was collected from near Mayaguez to a depth of 30cm(12inches) and is classified as a Typic Acrorthox; clayey, oxidic, isohyperthermic. The parent material for Nipe series is serpentine rock, the land form high rounded hills and flat mesa like positions. The series is well drained and yearly rainfall is greater than 200cm(80inches), mean annual temperatures range from 25 to 26.7°C (77-80°F).

Daguey (PR-1)

The Daguey sample comes from Bayamoncito from a 0-15cm (0-6inches) depth, an Orthoxic Tropohumult; clayey, oxidic, isohyperthermic. Soils of the Daguey series are derived from fine textured residuum from very highly weathered basic volcanic rocks and occur on the more stable sloping side slopes, ridge tops and foot slopes of the volcanic uplands, having slope gradients of 12-20%. They receive a yearly average of 215cm(86inches) of rainfall. Mean annual temperature is 24.4°C(76°F).

Torres (T-1)

The Torres sample is from near Cidra, 0-15cm(0-6inches) an Orthoxic Palehummult. Soils of the Torres series are formed from material washed from Catalina, Cialitos and related soils and occur as well defined undulating or level terraces. Mean average rainfall is 198cm(79inches).

Brazilian Soils

All Brazilian samples were removed from the surface20cm (8inches) of soils situated in the central plateau of Brazil.

Br-2

This sample is from a soil classified in Brazilian soil taxonomy as Dark Red Latosol, clayey texture, cerrado phase on a slope of about 2%,13 Km south of Uberlandia, Minas Gerias. Underlying bedrock is sandstone, but the soil is believed derived from an overlying deposit.

Br-5

This sample is from a Dark Red Latosol, medium texture, cerrado-forest transition, 29 Km north of the Uberlandia-Ituiutaba road to Goiana.

Br-8

This sample is from a soil classified as a Dark Red Latosol, clayey texture, cerrado and was collected by the road from Itumbiara to Goiania 37 Km north of junction with road to Crominia on a slope of about 3%.

Br-11

The sample is from a Red-Yellow Latosol, clayey texture, cerrado, 49 Km. east of Goiania by the Goiania- Anapolis road. The site has a slope of about 2% and is near the crest of a divide.

Br-14

The sample is from a Red -Yellow Latosol, clayey texture situated 48 Km north of Sao Joao do Alianca, Goias in a region of campo cerrado vegetation. The site is representative of high level slopes of the broad divides of the Amazon basin, having a slope of 5% and at a distance of about 0.8 Km from the crest of a divide characterized by Dark-Red Latosols and about 1.6 Km. from a sharp slope break to a lower erosion surface.

Br-17

The sample is from a Red-Yellow Latosol, medium texture, on high land of the experiment station near Planaltina.

Malawian Soils

All samples from Malawi were collected to a depth of 15 cm.

M-1

The sample was collected on the Thornewood Estate near Mulanje and belongs to the Mulanje or Mimosa series, a Ferrisol (Belgian taxonomy) or Ustox (U.S. taxonomy). Mean annual temperature of the region around Mulanje is 22°C (71.5°F) and mean annual rainfall 126 cm (69.9 in) with 65% of rainfall occuring in the four wettest months.

M-2

The sample is from Bvumbwe from the Mullon series, classified as Ferrallitic Latosol or Eutrorthox. Mean annual temperature at Bvumbwe is 20.1°C (71.5°F), mean annual

rainfall 79 cm (48.3 in). There is a pronounced dry season with 85% of rainfall occuring from December through March.

M-3

The sample comes from Dedza from a series of the same name and is classed as a Ferruginous Latosol. Weathered rock lies at a depth of 100-120 cm. Dedza is in a high altitude hill zone (>4,000 ft) of central Malawi characterized by low montane grassland and single, distinct wet and dry seasons. Mean annual rainfall is 105 cm (42 in), mean annual temperature 17.8 C (64 F). As in the case of the sample from Bunda below, parent materials are from hornblende rich gneisses of basement complex rocks.

M-4

The sample was collected at Bunda and is classified as a Ferruginous Latosol of the Lilongwe series. Bunda lies in a high altitude savanna region (3400-4400ft) on a dissected plain formed during Tertiary times (Miocene or Pliocene era). The region has single, distinct wet and dry seasons, mean annual rainfall of 82.5 cm (33 in) and a mean annual temperature of 20°C (68°F).

Ghanaian Soils

All samples were collected to a depth of 20 cm (8 in) at the Soil Research Institute, Kumasi, from soils belonging to the Kumasi Series, Typic Paleudult, residual loam derived from decomposed granite. Recent analysis of base status in

subsoil control sections suggests that airborne material of the Harmattan wind may have resulted in a process of rejuvenation necessitating the reclassification of the Kumasi Series into the order, Alfisol (personal communication, R. W. Arnold). Moist semi-deciduous forest is the natural vegetation of the region, which has an average rainfall of 145 cm (58 in) and a mean annual temperature of 26.7°C (80°F). Soils of Kumasi Series are well drained, sloping about 3%.

G-1 and G-6

These are composite samples from two different parts or an area cropped for 20 years and receiving no fertilizer for more than 7 years.

G-3 and G-5

These are composite samples from two different parts of an area which was not cropped for 20 years, cleared and burned June 1973, and cleared again without burning Dec. 1973.

Venezuelan Soils

Venezuelan samples are from the Llanos region, developed from alluvial materials laid down in Quaternary times, their longer range source material being Cretaceous and Tertiary undifferentiated rocks of the northern coastal range. It is thought that the alluvial sediments may have been highly weathered when deposited. V-65, -77, -91 are Paleosols which show relic soil characteristics associated with a different climatic regime and topographical positions.

Subsoils show evidence of incipient plinthite formation associated with previous pedogenic processes.

V-47

The sample was collected southeast of Calabozo, Guarico State, to depth of 13 cm, a Typic Haplustox, clayey-skeletal, kaolinitic, isohyperthermic. Parent material is old alluvium, land form a high terrace or mesa along the Ortuco River with a slope of less than 1%. Mean annual rainfall is 130 cm (52 in), mean annual temperature, 27.5°C (81.5°F).

V-65

The sample comes from southeast of Jusepin, Monagas State and was collected to a depth of 32 cm. It is classified as a Plinthic Paleustult, clayey, kaolinitic, isohyperthermic developed from material deposited as an alluvial fan caused by an ancient river breaching its natural level and exists now as a high terrace of the Guarapiche River with a slope of less than 1%. Mean annual rainfall is 112 cm (44.8 in), mean annual temperature, 26.7°C (80°F).

V-77

The sample was collected to a depth of 43 cm northeast of Maturiu in the state of Monagas, a Paleustult, clayey, mixed, isohyperthermic. Parent material is old alluvium from an old flood plain situated between the natural levee of an old river and back water depressions but now on a high terrace of the Guarapiche River, with a slope of less than 1%. Mean annual rainfall is 122 cm (48.8 in), mean annual temperature, 25.9°C (78.5°F).

V-91

The sample was collected to a depth of 39 cm from the same area as V-77 and is a Paleaquult, clayey, mixed isohyperthermic. Parent material is old alluvium of an ancient back water depressional area now on a high terrace of the Guarapiche River and having a slope of less than 1%. Mean annual rainfall is 122 cm (48.8 in), mean annual temperature, 25.9°C (78.5°F).

B. Laboratory Methods

Particle Size Analysis

With the exception of Venezuelan samples, the soils were treated with NaOCl solution of pH 9.5 (Lavkulich and Wiens 1970) to remove organic matter and then separated into particle size fractions by wet sieving and decantation(Jackson, 1969). Particle size determinations of Venezuelan samples were done in the soils laboratory of the Ministry of Public Works Edaphology Office of the western region in Guanare, Venezuela using sodium hexametaphosphate as a dispersing agent and the pipette method of Sanchez and Abreu(1973); values are reported in Daugherty(1975).

pH Determinations of pH were carried out using a 1:10 soil-solution ratio with the glass electrode in the sediment and the calomel electrode in the supernatant in 1N KCl or 0.01M $CaCl_2$ in the case of the Malawian samples.

Organic Carbon

Organic carbon was determined by the Walkley-Black method as modified by Grewling and Peech(1965) with the exception of Venezuelan soils for which the method of Walkley-Black as modified by Allison(1965) was employed by Daugherty, (1975).

Citrate- Bicarbonate- Dithionite Extractions(CBD)

CBD extractions were performed using the method of Jackson

(1969). Iron and aluminum were determined colorimetrically after the destruction of citrate as described by Weaver et al. (1968), using orthophenanthroline method (Jackson, 1969) for the former and aluminon method for the latter (McLean, 1965). Determinations on Malawian and Ghanaian samples were done by Mughogho (1974,1975), on Venezuelan samples by Daugherty (1975).

Acid Oxalate Extractions

Acid oxalate extractions were carried out by R.M. Weaver using the method of Tamm as given by McKeague and Day(1966). 0.2M ammonium oxalate was titrated to pH 3 with oxalic acid. One gram samples were shaken in 50 ml extractant for 4 hours in the dark.

Dilute Hydrochloric Acid Extractions

Dilute acid extractions were carried out using the method of Tweneboah et al.(1967). One gram of sample was extracted twice for 6 hours with 200 ml 0.5M $CaCl_2$, pH 1.5 hydrochloric acid. Aluminum was determined using the aluminon method (McLean, 1965), silica by the reduced molybdate complex method with NHCl being substituted for NH_2SO_4 (Weaver et al., 1968), iron by the orthophenanthroline method. Determinations on Malawian soils were

carried out by Mughogho(1975).

Cold Carbonate Extractions

Al was also extracted using a modification of the procedures of Follett et al.(1965). One gram of soil was extracted sucessively three times with 70 mls of cold 5% Na_2CO_3(wt/vol.). Aluminum was determined spectrophotometrically with aluminon(McClean,1965).

Phosphorus Sorption Isotherms

A modification of Olsen and Watanabe's procedure(1957) was employed to characterize phosphorus sorption properties. A soil:solution ratio of 1:10 was used. After appropiate amounts of phosphorus had been added from phosphorus standards prepared with KH_2PO_4, systems were made 0.01M with respect to Ca Cl_2. For 2 day contact periods 2 gram sample systems in 50 ml polyethelene tubes were shaken on a reciprocating shaker. For 5, 13, and 34 day contact periods 2 gram sample systems in 90 ml polyethelene tubes were shaken for 2 days on a reciprocating shaker and thereafter briefly shaken by hand every 2 days. For 90 day contact periods 5 gram samples were used in 125 ml polyethelene bottles which were shaken 2 days on a reciprocating shaker and thereafter shaken briefly by hand every 2 days. For each soil and each contact period a number of systems differing in initial phosphorus concentrations were prepared. Several drops of toluene were added to each system and were replenished several

times for contact periods greater than 5 days. At the end of a contact period soils were centrifuged and the supernatant filtered through # 30 Whatman filters and appropiate aliquots taken upon which determinations were made spectrophotometrically, using the reduced molybdate complex method (Murphy and Riley.1962). Absorbance at 882 um was measured on a Beckman DU Spectrophotometer with 1 and 5 cm cells and on a Bausch and Lomb Spectronic 20 with 1.2 and 2.1 cm cells. Amounts of phosphorus sorbed were calculated on the basis of difference in initial and final phosphorus concentration, with native sorbed phosphorus, as measured by $NaHCO_3$ extraction, added to the figure so computed.

For 2 day contact periods, phosphorus sorption isotherms were carried out on all 23 soils. For such periods of contact, as for others of longer duration, the attempt was to have final concentrations of phosphorus fall within a range of 0.05 to 2.0 ppm P. A number of investigations have found that concentrations of phosphorus which are reasonable for plant growth fall within such a range(Jones and Benson,1975; Ozanne and Shaw 1968; Woodruff and Kamprath, 1965). Some investigation of phosphorus removal by soils have employed isotherm ranges extending to much higher values. The 1 day contact isotherms of Olson and Watanabe(1957) ranged up to 20 ppm P; Rennie and McKercher(1959) found a break in the curve of Langmuir plots of phosphorus sorption isotherms above about 20 ppm P. In recognition of this change in slope at high P con-

centrations , Syers et al. (1973) and Holford et al. (1974) have employed a 2 stage Langmuir model in which the existence of two different sets of sorption sites of differing bonding energy is posited. A soil column study by Blanchar and Caldwell (1966) on levels of water soluable phosphate fertilizer support the relevance of investigation at high equilibrium phosphorus concentration. However, in practical field conditions in which rainfall must be considered to importantly effect fertilizer soil relations, the evidence from experiments taking into account this factor suggest that P soil solution values will be more fairly represented by the range employed in the present work. Logan and McClean(1973) found, for example, that soil in a column with monocal applied as a surficial layer at rates up to 1250 kg/ha nowhere exceeded equilibrium soil solution P levels of 3.0 ppm when water filtred through the column over a 2 week period.

In formulating "sorption indices" characteristics of the soils examined and using the data obtained from phosphorus sorption isotherms two principle approaches have been tried: the Freundlich and the Langmuir. The Freundlich equation for sorption data, $y=ax^{1/n}$, where y= amount of species sorbed per unit wt. adsorbent and x=concentration of species of interest in solution, is essentialy an empirical curve fitting approach with little if any model of adsorption implied. However, it is important to note that no limiting value for adsorption is approached as $x \rightarrow \infty$. Data are readily converted by log-log plotting to a linear form. The resulting expression

is simply a power curve.

The Langmuir sorption isotherm was first developed to characterize gas-solid phase phenomena(Langmuir, 1918) and began to be used to describe interactions of ionic species and solid phases which are of interest to soil scientists in 1953 when Cole, Olsen and Scott(1953) used Langmuir's model to treat their data on sorption of phosphorus by calcium carbonate. In its simplest form the Langmuir model involves three assumptions:

1) a discrete number of adsorption sites
2) limitation of sorption to monolayer
3) constancy of affinity of sorbed species for reactive sites at different degrees of saturation of reactive sites.

With substitution of concentration units for pressure units, a derivation which closely follows that of Langmuir(1918) is presented below.

Let θ= fraction of active sites covered = y/y_m

k_1= rate of desorption per unit sorbent from sites at full saturation of active sites

k_2= rate of sorption per unit sorbent with all sites vacant

P= concentration of species of interest in solution

y= amount of species of interest sorbed per unit sorbent

y_m= maximum amount of species of interest sorbed per unit sorbent

$$k = {}^{k_1}/_{k_2}$$

At equilibrium rate of desorption = rate of sorption:

$$k_1 = k_2(1 - \theta)P \qquad (1)$$

$$\theta = \frac{kP}{1 + kP} \qquad (2)$$

$$\frac{y}{y_m} = \frac{kP}{1 + kP} \qquad (3)$$

$$\frac{P}{y} = \frac{1}{ky_m} + \frac{P}{y_m} \qquad (4)$$

The inverse of the slope of a curve formed by plotting sorption data in the linear form of equation (4) gives an adsorption maximum. For both Freundlich and Langmuir treatments of data curves have been calculated by the method of least squares.

$NaHCO_3$ Extractions

Modifications of the method of Olsen et al.(1959) were employed for the extraction of native and sorbed phosphorus. Solutions of slightly more than 0.5 moles of $NaHCO_3$ per liter were titrated to pH 8.5 with NaOH and then brought to a molarity of 0.5. Each soil was extracted at a soil:extractant ratio of 1:20 for 5 successive one hour extractions. Extractions were centrifuged and filtered and centrifuged further on a cerval centrifuge where clarification was necessary. Determination of P was performed on aliquots from the first extractions and on aliquots from a composite made from 10 ml subsamples of the 5 extractions.

Regression Analysis

Regression analysis has been carried out by computer using the program, "Statistical Analysis System (Service, 1972).

Section III Results

In an attempt to predict removal of phosphorus from solution by soils a number of soil properties have been measured or values assembled from investigations by other workers. Values for these properties are reported and relationships among them are discussed in Part A of Results Section. Quantitative indices of reactivity of soils to phosphorus have been derived from two treatments of phosphorus sorption isotherm data, raw values for which are given in Appendix . Since most studies of phosphorus sorption making use of isotherms have been restricted to relatively short contact times, isotherms have been carried out for a number of time periods in order to examine the influence of time on relationships found between phosphorus indices and soil properties. For two days contact period isotherms were carried out on 23 soils, for 90 days, on 22 of these soils and for 3 intermediate time periods a subset of 9 soils was used. Relationships between phosphorus sorption indices and soil properties for 2 day and 90 day isotherms are discussed in Parts B and C respectively. Correlates of phosphorus sorption for intermediate time period isotherms are discussed in Part D. Since simple removal of phosphorus from solution as measured in isotherms does not provide evidence on how strongly adsorbed phosphorus is withheld from solution, for the subset of 9 soils desorption extractions with 0.5M $NaHCO_3$ at pH 8.5 were carried out on the isotherm samples which had been in contact with phosphate solutions

for the 5, 13, 34, and 90 day contact periods. Results of desorption experiments are reported in Appendix and discussed in Part E of Results section.

A. Soil Properties

Table 1 lists avalible mineralogical information on soils under study and Table 2 values for a number of soil properties. In the present section particular consideration is given the question of what properties have been measured by the techniques employed to yield the values coming under the headings of Table 2 . Individual values are to greater and lesser degrees arbitrary depending on what "property" one attempts to measure, within reasonable limits the principal utility of a measurement residing in its quantification of relative differences in a population of soils.

What is subsumed under the category "soil pH" is notoriously elusive, but in the present context pH is a less arbitrary term than some others to be considered. Water, 0.01M $CaCl_2$, N KCl at varying soil solution ratios are some of the conditions under which pH measurements of soil are commonly made and which are known to frequently give divergent values for the same soil. In particular Makaru and Uehara (1972) have drawn attention to the differences in measured values of pH in water and N KCl as such differences relate to the soil materials having pH dependent charge more common in highly weathered soils. However, divergences of values between pH measurement techniques are small compared to

TABLE 1. Percentages of clay size minerals (< 0.002 mm)

Soil	Free Fe_2O_3	Vermiculite	Mica	Al-Chlorite	Kaolinite	Gibbsite
	. . . . .	% of	2 mm soil	. . . . .	. . . . .	. . . . .
B-1	n.d.	3	1	13	27	5
C-1	n.d.	5	6	5	22	-
BR-2	7.0	-	-	-	25	19
BR-5	2.9	-	-	-	6	1
BR-8	3.5	-	-	-	2	17
BR-11	3.8	-	-	-	27	16
BR-14	5.3	-	present	present	3	28
BR-17	2.7	-	present	present	11	8
M-1	5.3	-	-	-	21	1
M-2	4.2	-	-	-	18	-
M-3	3.3	-	-	-	19	2
M-4	2.2	-	present	-	10	-

Sources: B-1, C-1: Roberts and Weaver (1975)
BR-2 through BR-17: Weaver (1974)
M-1 through M-4: Mughogho (1975)

TABLE 2. Soil properties*.

Soil	pH	Sand	Silt	Clay	O.C.	--- CBD ----		----- Tamm -----			--- HCl ---		-Na_2CO_3-
						Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Al_2O_3	Al_2O_3
B-1	4.1	7	26	67	3.0	15.10	4.00	0.549	.559	.0428	.076	.448	.505
C-1	4.6	18	34	48	3.0	7.29	1.20	0.353	.439	.0147	.059	.553	.481
N-1	4.5	12	25	63	3.1	32.90	7.43	0.277	.529	.0224	.038	.529	.714
PR-1	4.6	20	13	67	3.4	10.90	1.80	1.130	.454	.0756	.158	.350	.317
T-1	4.0	12	26	62	2.6	9.87	1.89	0.925	.605	.0616	.105	.479	.485
BR-2	4.3	21	10	69	2.2	6.51	1.59	0.220	.500	.0187	.024	.283	.542
BR-5	4.2	81	3	16	0.6	3.79	0.35	0.118	.166	.0084	.013	.136	.339
BR-8	4.6	65	6	29	1.5	4.50	1.19	0.162	.416	.0129	.021	.265	.529
BR-11	4.3	12	20	68	1.9	3.22	1.97	0.197	.544	.0241	.030	.280	.528
BR-14	4.4	12	32	56	3.4	5.72	2.52	0.318	.953	.0177	.055	.442	.619
BR-17	4.2	60	9	31	1.2	4.10	1.05	0.174	.522	.0105	.030	.223	.433
M-1	4.2	42	10	48	1.5	5.28	0.05	0.277	.635	.0336	.055	.261	.562
M-2	5.2	48	14	38	2.0	4.18	0.04	0.381	.635	.0625	.041	.230	.398
M-3	4.9	49	14	36	1.1	3.31	0.04	0.260	.522	.0297	.051	.188	.264
M-4	5.6	67	11	22	1.4	2.20	0.02	0.231	.257	.0261	.038	.104	.198
G-1	5.0	64	13	23	1.2	1.61	0.62	0.091	.149	.0145	.023	.061	.183
G-3	5.4	74	10	16	1.6	1.09	0.57	0.066	.155	.0175	.010	.057	.110
G-5	5.0	75	6	19	1.6	1.12	0.39	0.058	.152	.0167	.013	.025	.136
G-6	4.8	65	15	20	1.4	1.48	0.54	0.110	.176	.0209	.020	.049	.137
V-47	3.6	56	22	22	1.3	2.70	0.52	0.093	.151	.0103	.017	.107	.081
V-65	3.6	64	18	18	0.9	0.73	0.23	0.107	.151	.0093	.033	.096	.062
V-77	3.9	38	41	21	1.1	0.36	0.33	0.214	.181	.0065	.112	.169	.147
V-91	3.6	26	38	36	1.0	0.43	0.37	0.266	.287	.0126	.052	.254	.227

O.C. = organic carbon
Na_2CO_3 = cold 5% Na_2CO_3 extraction
HCl = pH 1.5 HCl, 0.5M $CaCl_2$ extraction

CBD = citrate-dithionite-bicarbonate extraction
Tamm = acid ammonium oxalate extraction in dark

* All values except pH expressed as percentages of < 2mm soil

variations in values for poorly crystalline soil material as measured by different techniques. Measurement of soil pH in N KCl has probably been adequate to differentiate among the soils studied and values for Malawian soils, determined in 0.01M $CaCl_2$, are not likely to be seriously misleading.

Material extracted by citrate-bicarbonate-dithionite (CBD) has often been termed free sesquioxides, Mehra and Jackson (1958) claiming complete dissolution of both crystalline and amorphous iron oxides. What forms of aluminum are extracted by the procedure remain somewhat in doubt though there is agreement that well crystallized alumino-silicates (as well as nontronite) are scarcely attacked. Gorbunov et al. (1961) found that the method did not give complete dissolution of well crystallized iron oxides, whether prepared or in naturally occuring forms in a Vietnamese laterite and concretions from it. CBD treatment of concretions from a solod and a podzolic soil resulted in virtually complete dissolution of the iron oxides, this evidence taken to imply the effectiveness of CBD for amorphous forms of iron. Extraction of a bauxite with CBD yielded only about 6% Al_2O_3 of that contained in the sample of 54% total Al_2O_3. McKeague and Day (1966) also found incomplete dissolution of 300 mesh goethite and hematite and complete dissolution of iron and aluminum from prepared amorphous iron and aluminum silicates. For the present samples oxide ratios of Fe/Al for CBD extractions averaged 21 with considerable variation encountered (Table 3). The large correlation coefficient for

regression of CBD Al and Fe is surprising, such a relation not having been expected, nor found for another population of highly weathered soils (Syers et al.,1971; Table 4).

TABLE 3. Relations between values of oxides by different chemical dissolution techniques.

		Mean	Minimum Value	Maximum Value
CBD	Fe/Al	21	1.1	110
HCl	Al/Fe	6.1	1.5	13.9
	Al/Fe	1.8	0.4	3.0
Tamm	Al/Si	12	3.5	33
	Fe/Si	2.5	0.6	17
	CBD/Tamm	3.0	0.06	14.0
Al	Tamm/Na_2CO_3	1.3	0.5	2.4
	Tamm/HCl	2.0	0.8	6.1
	Na_2CO_3/HCl	1.7	0.6	5.4
Fe	CBD/Tamm	21.4	1.6	119
	Tamm/HCl	6.2	1.9	9.3

Tamm = acid ammonium oxalate extraction in dark
CBD = citrate-dithionite-bicarbonate extraction
HCl = pH 1.5, 0.5M $CaCl_2$ extraction
Na_2CO_3 = cold 5% Na_2CO_3 extraction

The iron extracted by CBD one may take to correspond to a portion of the crystalline forms in the soil samples plus the total amount of amorphous or short range ordered forms. By itself, CBD Fe may be somewhat problematical, though less so than CBD Al, but gains meaning by comparison with values for Fe by other methods. Acid ammonium oxalate extraction in darkness, originally proposed by Tamm and revived by Schwertmann (1959), is often taken as an appropriate reagent for measuring amorphous soil material (Schwertmann, 1959;

Blume and Schwertmann, 1969; McKeague and Day, 1966; McKeague, et al. ,1971; Alexander, 1974; Fey and LeRoux, 1976). CBD Fe for the soils under study averages about 20 times the amount extracted by acid oxalate(Table 4) and no relation of significance exists between the two by either simple linear regression or with CBD Fe converted to a rough surface area value by raising to 2/3 power. Blume and Schwertmann also found no re- between oxalate and CBD Fe.

Dithionite extractable aluminum is of less certain origin, claims being made for its association with iron oxides by occlusion (Weaver et al., 1968) or by isomorphous substitution in goethite(Norrish and Taylor, 1961) and lipidocrocite (de Villiers and van Rooyen, 1967). The disparity in amounts of aluminum extracted by CBD and acid oxalate is considerably less than in the case of iron, suggesting that less ordered forms constitute a large portion, if not all in some cases, of the the amount extracted by CBD. Little correlation between the values is found for aluminum by the two methods(r=.41) in contrast to the findings of Blume and Schwertman (1969); however, weak but significant correlations are found with aluminum extracted with dilute HCl and 5% Na_2CO_3.

In the present study the three extractants for which claims have been made for specificity with respect to amorphous materials are the acid oxalate in darkness, dilute HCl in 0.5M $CaCl_2$ and 5% Na_2CO_3. Schwertmann(1959) found that acid oxalate extraction in the dark of a finely ground goethite yielded hardly more iron than extraction from the less divided mat-

erial, evidence that the action of acid oxalate was not merely a function of surface area. Gorbunov et al. (1961) found that acid oxalate dissolved large portions of prepared amorphous iron and aluminum hydroxides; better crystallized metal oxides lost little to the treatment though prepared iron hydroxide lost significantly more than the aluminum hydroxide. Small amounts of aluminum were removed from halloysite. McKeague and Day(1966) extracted very little Fe from hematite and goethite, though a significant particle size effect was found especially in the case of goethite. Acid oxalate dissolved significant portions of amorphous Fe and Al silicates, much more Al extracted in the case of the latter than by CBD treatment. Al-chlorite gave x-ray diffraction patterns scarcely affected by oxalate treatment, as was also the case for CBD treatment. Oxalate extraction has also been found to remove all iron and aluminum from metal fulvate complexes(McKeague, et al., 1971) as well as to dissolve considerable portions of magnetite(Baril and Bitton, 1969; McKeague, et al., 1971). Random powder x-ray diffraction patterns from finely ground samples of the soils under study showed no peaks for magnetite; in particular, V-77 and V-91, with the narrowest oxalate/CBD Fe ratios, were found to contain no magnetic material. Deer et al. (1966) note that the normal occurance of maghemite is by supergene alteration of magnetite. With the exception of Venezuelan samples, such a process might be considered to operate in the long stable, freely draining soils of the population under study, magnetic material occuring prob-

ably being maghemite. Mc Keague and Day(1966) also found 0.1% Al_2O_3 of a 100 mesh gibbsite sample dissolved by oxalate. From Br-14, which contains the largest amount of clay size gibbsite (28% of the less than 2 mm soil), acid oxalate is found to extract somewhat less than 1% Al_2O_3. Though particle size may play an important role here, on the basis of McKeague and Day's figure the contribution from well ordered gibbsite should be negligable.

For oxalate extractions of the present population of soils only in the case of the Puerto Rican soil, Daguey, does iron on a molar basis exceed aluminum. McKeague and Day(1966) and Blume and Schwertmann(1969) found iron to constitute much larger portions of the oxides extracted; the former taking the greater preponderance of iron common in Spodosols to be a function of greater weathering intensity. By contrast, Nipe, a Typic Acrorthox, composed of about 1/3 dithionite soluble iron oxides, yields about twice as much Al_2O_3 as Fe_2O_3 with oxalate extraction.

A notable feature of the oxalate extraction of the soils under study is the strong relationship between iron and silica extracted(r=.86) and the lack of such a relationship between aluminum and silica (r=.41) McKeague and Cline(1963) report a strong affinity of freshly precipitated hydrous iron oxides for silica in solution and Follett (1965) has provided evidence that amorphous iron oxides are associated with the tetrahedral faces of kaolinite. Weaver et al. (1968) snowed that appreciable quantities of Si are associated with CBD extractable

iron oxides. As will be discussed further in a later section, the possible association of silica and amorphous iron oxides may be decisive in determining reactivity of amorphous iron oxides to phosphorus.

A second technique employed in the present study for extraction of amorphous material was the dilute HCl, 0.5M $CaCl_2$ extraction of Tweneboah et al. (1967), designed to selectively remove poorly ordered aluminum with minimal extraction of iron. The ratios of aluminum to iron oxides average about 6, close to the factor of 5 of Tweneboah et al., the procedure generally proving milder than the acid oxalate even for aluminum values, which average about half those of the oxalate extraction. Correlation of iron (r=.87) and aluminum (r=.73) between the two methods suggests similar sources of iron may be attacked, with greater variation in the sources of aluminum extracted. Some tendency exists for the ratio of aluminum by the two methods to narrow when the amounts of silica extracted per unit alumina extracted decrease. A stronger relation is the relative increase in alumina extracted by the Tweneboah procedure as the ratio of oxalate SiO_2/Fe_2O_3 decreases (r=-.68). What interactions between iron, aluminum and silica may cause the differential extractibility of aluminum are not readily apparent. Silica has a strong affinity for both iron and aluminum(McKeague and Cline, 1963; Krauskopf, 1956). The ordering of aluminous materials in the short range ordered materials of these highly weathered soils may be enhanced by silica. However, for the micro-crystalline substances in-

volved here, the affinity of silica for iron may be stronger, rendering more mobile forms of silica less available for stabilization of the short range ordered alumina. That the relationship is not expressed as straight forwardly in the data as is implied by a simple model of an amorphous material of varying degrees of solubility may be due to the more heterogeneous sources of aluminum involved. It is not unlikely that the dilute HCl treatment extracts a relatively larger portion of the total alumina extracted from the aluminum-chlorite when this is present in a sample.

Cold extraction with 5% Na_2CO_3 was also employed as a procedure for assessing poorly ordered material. Follett et al. (1965) found allophane to be almost completely dissolved by the technique with little attack on crystalline clay minerals, goethite or gibbsite. Because some of the soils under study contain large amounts of kaolinite, which Follett et al. found to release 1.6% Al_2O_3 by the procedure, values obtained may reflect a contribution from this source. However, no strong relationship between percent kaolinite on a $<$ 2mm soil basis and carbonate extractable Al_2O_3 is found and in one case (M-3) the predicted value for Al_2O_3 on the basis of kaolinite dissolution is higher than the observed value for the soil as a whole. Jorgensen et al. (1970) found little effect by the extraction method on gibbsite DTA endotherms, but found it to remove a gibbsite like component closely associated with iron oxide from the B_3 of a Podzol.

Infrared absorption spectra of untreated and cold carbonate treated clays by Follett et al. (1965) provided evidence of removal of hydrous oxides with no attack on crystalline material.

Specific surface areas by nitrogen adsorption were found to increase after Na_2CO_3 treatment, which Follett et al.(1965) concluded ruled out the possibility of the removed material existing as a finely divided separate phase. The authors argue that the material plus that extracted by hot carbonate coats surfaces of minerals, cementing them into aggregates. Support for such an interpretation of amorphous materials is provided by work of Jones and Uehara(1973) who found evidence in electronmicrographs for gel hulls around soil particles and, in the case of a Gibbsihumox, a highly hydrated gel-like mass which encased clusters of soil particles.

Sumner(1963) has argued that amorphous coatings around particles from highly weathered soils are iron oxides and it has often been assumed that free iron oxides constitute the cement aggregating soil particles(Mehra and Jackson, 1958). The possible existence of material extracted by the three procedures used for " amorphous " materials as surface active phases warrants further consideration of evidence on the nature of aggregation. Both iron and aluminum oxides have points of zero charge in the vicinity of pH 8 or greater(Kinniburgh et al. 1975) and in acid environments can be expected to have positive charges, by virtue of which an aggregating role by bridging between negatively charged clay minerals has been assigned by

some (Sumner,1963; Deshpande et al., 1968). However, some evidence suggests that Al may be more important than Fe in this connection. Saini et al.(1966) found for samples from the B horizon of 24 Spodosols that Al as extracted by citrate-dithionite at pH 4.75 was a better correlate of aggregation than Fe so extracted and was also significantly related to percent organic matter. With Fe, Al and organic matter as variables in multiple regression to predict aggregation, the importance of iron was found to be considerably less than that of Al and the role of organic matter still less so. Deshpande et al. (1968) found that treatment of a tropical red earth with citrate-bicarbonate-sulfate removed some organic matter and Al and very little Fe, but reduced aggregate stability; inclusion of dithionite rather than sulfate in the treatment did not result in greater loss of stability. Various procedures for removal of organic matter also resulted in decreases stability. Dithionite treatment was found to decrease specific surface area while extraction with 0.05N HCl, similiar to the procedure of Tweneboah et al. (1967) in removing small amounts of Fe, was found to increase it. Following the same logic as Follett et al. (1965) above, Deshpande et al. inferred an aluminous composition for the surface active material. The authors explained the lack of an aggregating role for iron oxides on the basis of neutralization of positive charges by strongly adsorbed anions, phosphate or silicate; by contrast, reaction of aluminum oxides

with such species was hypothesized to result in the separation of a new phase and exposure of fresh oxidic surfaces. The positive evidence for such a difference in reactivity is slender, but the association of positive charge with aluminous material is supported by the results of Tweneboah et al. (1967) who found that most of the material associated with positive charge in the soils they studied was removed by dilute HCl, as well as by the work of Fouche and Folcher(1975) who report that material collected at the cathode by electrophoretic treatment of highly weathered South African soil was predominantly aluminous.

Among the soils under consideration here, fairly strong relations were found between percent organic carbon and clay and between either of these two and any of the amorphous forms of aluminum(Table 4, Figure 1). Mitchell and Farmer (1962) noted such a relation between organic matter content and amounts of material(held to be amorphous also) extracted by hot 5% Na_2CO_3. Thus, the role of organic matter in aggregation may not be only a physical one as often suggested but a longer term chemical one having to do with its association with poorly ordered material. Schwertmann (1968) provided evidence that organic matter may inhibit the crystallization of iron oxides and it may be plausible to consider a similar role in the case of hydrous aluminum oxides and poorly ordered alumino-silicates. Some qualitative confirmation of an association of organic matter with amorphous forms of aluminum

TABLE 4. Correlation coefficients among soil properties*.

		pH	O.C.	Clay	Fe	Al	Fe	Al	Si	Fe	Al
					--- CBD -----		------ Tamm -------			- HCl ---	
	O.C.	.09 .70									
	Clay	-.18 .60	.79 .0001								
CBD	Fe	-.05 .81	.66 .0008	.62 .002							
	Al	-.12 .60	.69 .0006	.63 .002	.94 .0001						
	Fe	-.09 .67	.66 .0009	.64 .001	.39 .06	.28 .20					
Tamm	Al	-.04 .86	.65 .001	.76 .0001	.41 .05	.41 .05	.45 .03				
	Si	.21 .66	.54 .008	.55 .007	.31 .14	.15 .50	.86 .0001	.45 .03			
	Fe	-.22 .32	.50 .02	.49 .02	.24 .26	.16 .53	.87 .0001	.31 .14	.64 .001		
HCl	Al	-.25 .26	.81 .0001	.82 .0001	.71 .0003	.69 .0005	.60 .003	.73 .0002	.37 .08	.49 .02	
Na_2CO_3	Al	-.08 .71	.63 .002	.78 .0001	.65 .001	.65 .001	.32 .13	.83 .0001	.25 .25	.15 .52	.82 .0001

O.C. = organic carbon
Na_2CO_3 = cold 5% Na_2CO_3 extraction
HCl = pH 1.5 HCl, 0.5M $CaCl_2$ extraction

CBD = citrate-dithionite-bicarbonate extraction
Tamm = acid ammonium oxalate extraction in dark

* Correlation coefficients are the upper figure in a given cell of the matrix; lower figure is significance level

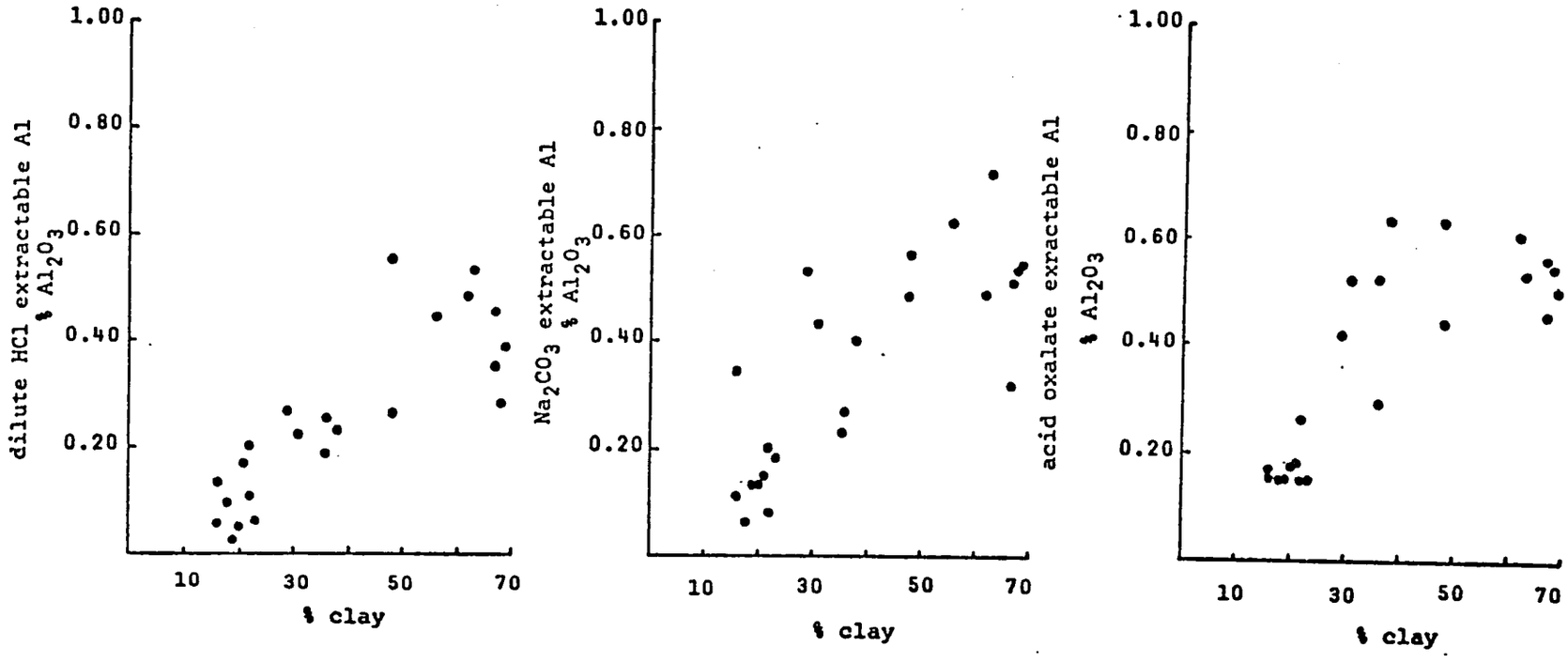

FIG. 1. Relations between clay content, organic carbon and amorphous aluminum.

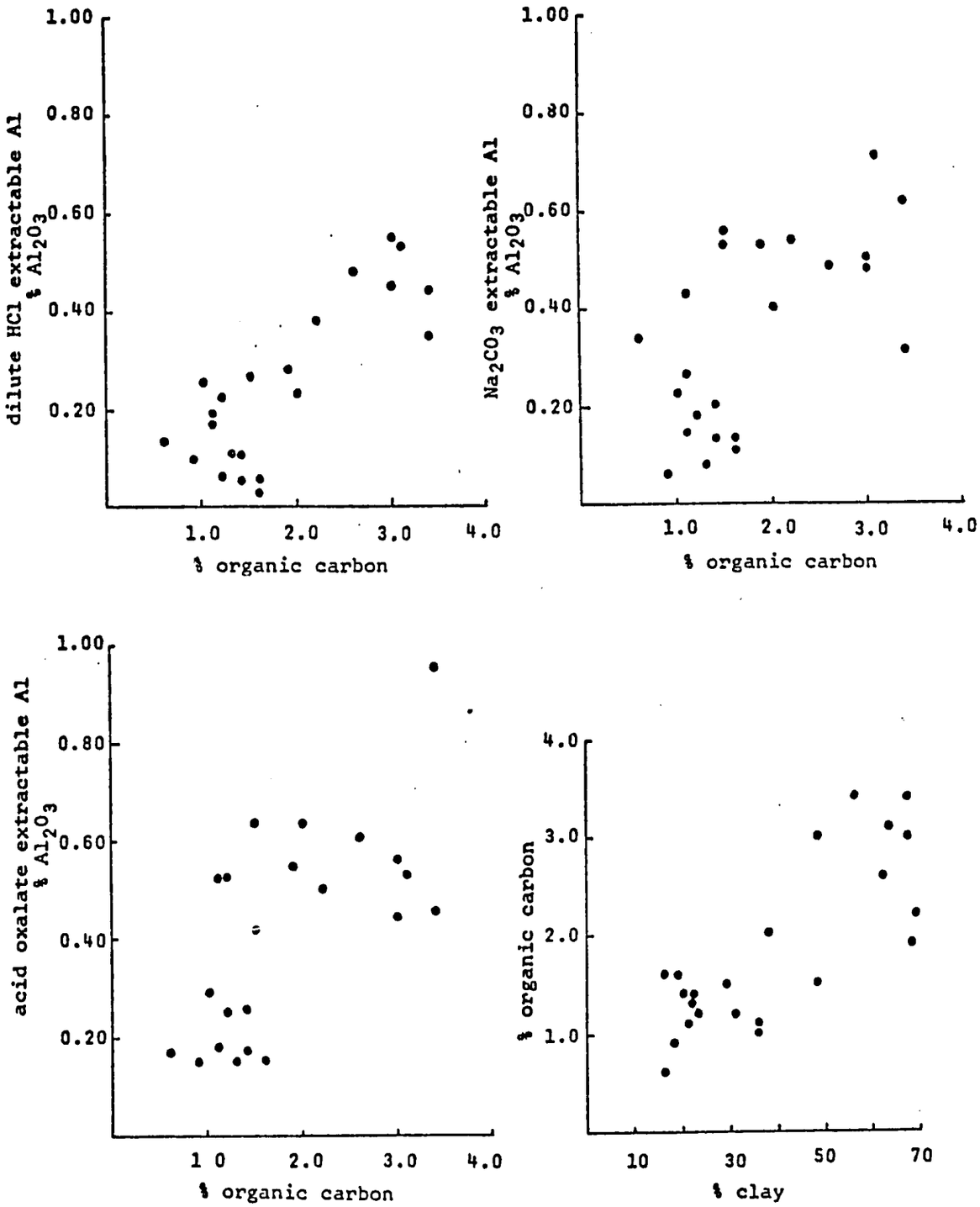
1.00
0.80
0.60
0.40
0.20
dilute HCl extractable Al
% Al_2O_3
1.0
2.0
3.0
4.0
% organic carbon
1.00
0.80
0.60
0.40
0.20
Na_2CO_3 extractable Al
% Al_2O_3
1.0
2.0
3.0
4.0
% organic carbon
1.00
0.80
0.60
0.40
0.20
acid oxalate extractable Al
% Al_2O_3
1 0
2.0
3.0
4.0
% organic carbon
4.0
3.0
2.0
1.0
% organic carbon
10
30
50
70
% clay

FIG. 1. (cont.)

may be afforded by the observation in the case of many of the soils studied of darker supernatant solution after equilibration with increasing concentration of phosphorus in contact with soil samples; values for amorphous aluminum by the various extractants have been found to be among the best predictors of reactivity of soil toward phorphorus as is discussed below. Correlation of amorphous Al by any of the three methods of extraction with clay content is consistent with the existence of such material as a surface active phase.

B. 2 Day Isotherms

Figure 2 presents sorption isotherm curves for soils for 2 day contact periods. The population of soils under study can be seen to cover a large range of differing reactivities with respect to phosphorus, including examples of soils which sorb more phosphorus than others at a low concentration but change their relative reactivities at higher concentration. Values of isotherms are given in the Appendix. Two kinds of indicies of phosphorus sorption have been listed in Table 5 , theoretical maximal sorption as given by the inverse of the slope of the curve formed by linear Langmuir transformation of isotherm data, and the amounts of phosphorus sorbed at solution concentrations of 0.1ppm by substitution of this concentration value in the expression derived from a Freundlich (power curve) treatment of isotherm data. The correlation between the two indicies is itself quite significant (r=.89) for two day contact periods on this population of 23 soils. However considerations discussed below support the meaningfulness of retaining both indicies in the discussion of the nature of phosphorus sorption to follow. Graphical representation helps to make clear the nature of the two approaches to quantifying phosphorus sorption; this is provided in Figures 3 and 4 , where the fit of least square derived Langmuir and power curves around empirical data points for several soils and times may be appreciated.

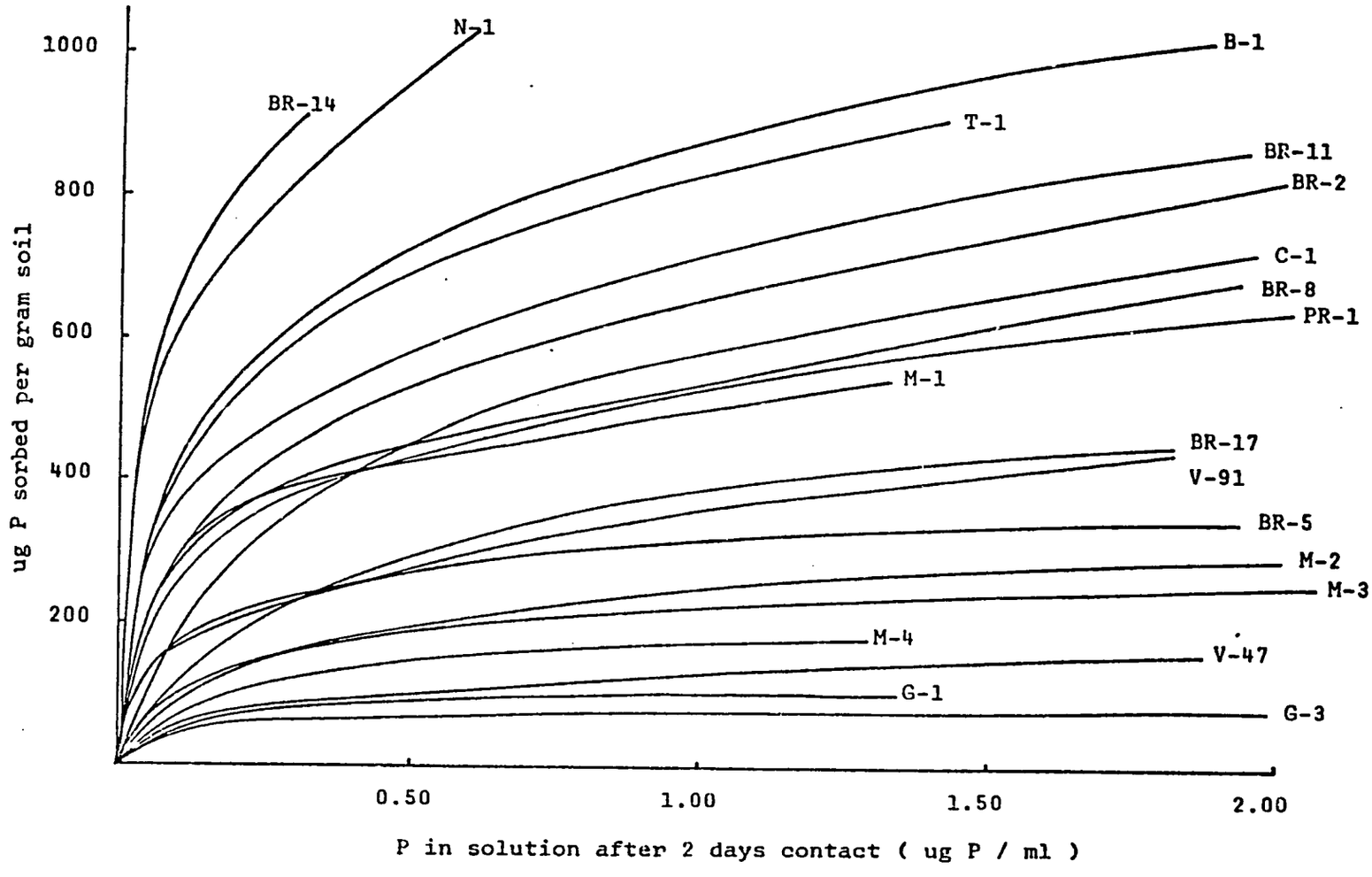

FIG. 2. 2 day phosphorus sorption isotherms

TABLE 5. 2 day phosphorus sorption indices

Soil	Langmuir adsorption maximum (ugP/g)	r value of Langmuir curves	P sorbed at 0.1ugP/ml (ugP/g)	r value of power curves
B-1	1126	.999	445	.997
C-1	886	.997	228	.995
N-1	1100	.995	616	.981
PR-1	783	.996	267	.999
T-1	993	.998	425	.996
BR-2	962	.993	315	.997
BR-5	425	.999	178	.991
BR-8	965	.940	273	.999
BR-11	930	.989	364	.997
BR-14	1020	.997	642	.990
BR-17	660	.998	137	.967
M-1	565	.996	283	.988
M-2	444	.996	111	.999
M-3	328	.999	122	.997
M-4	204	.998	92	.998
G-1	174	.998	61	.982
G-3	122	.992	35	.984
G-5	133	.995	43	.991
G-6	128	.994	50	.997
V-47	215	.999	62	.996
V-65	227	.996	66	.998
V-77	392	.999	138	.989
V-91	552	.995	149	.995

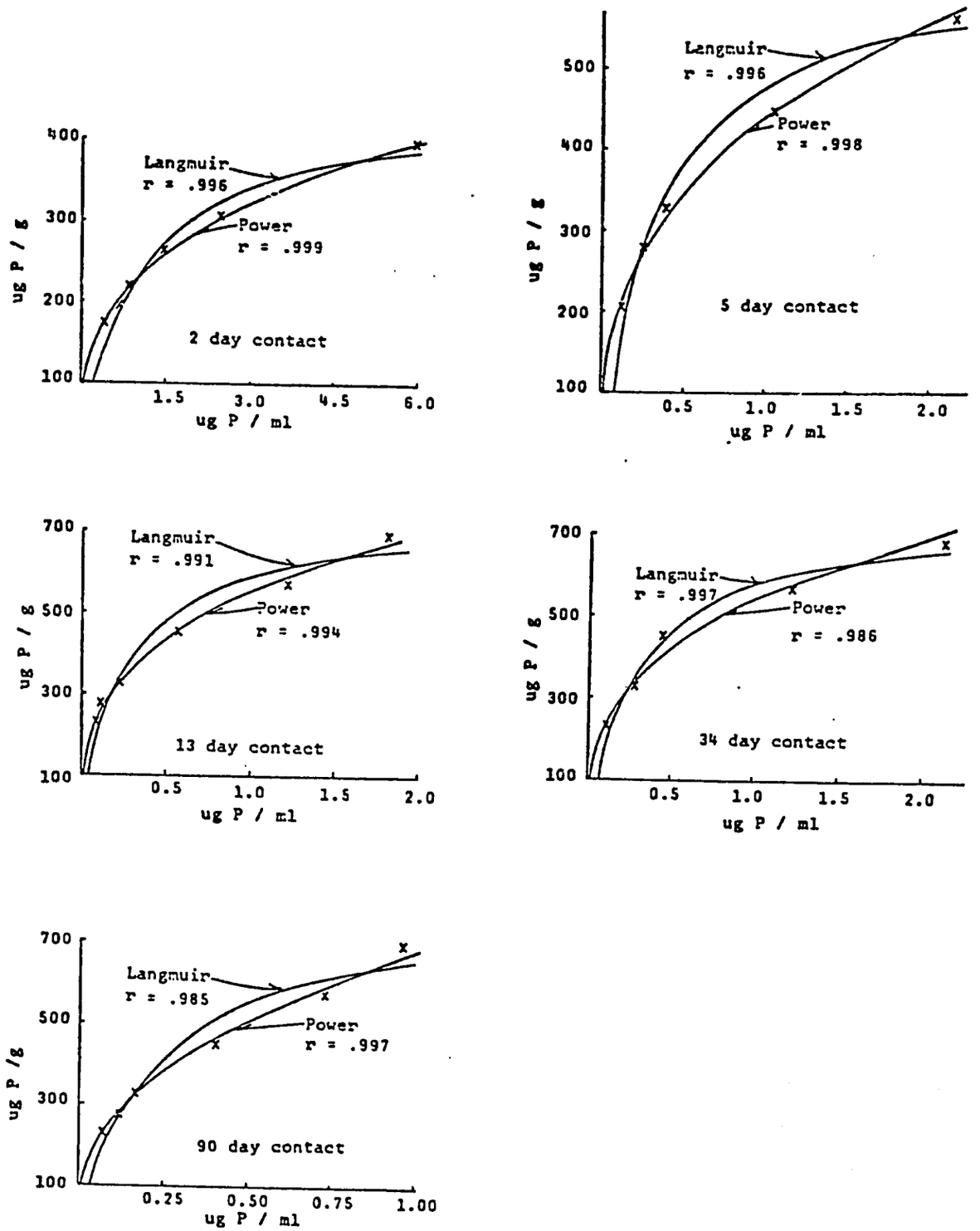

FIG. 3. P sorption isotherms of M-2, 2-90 days.

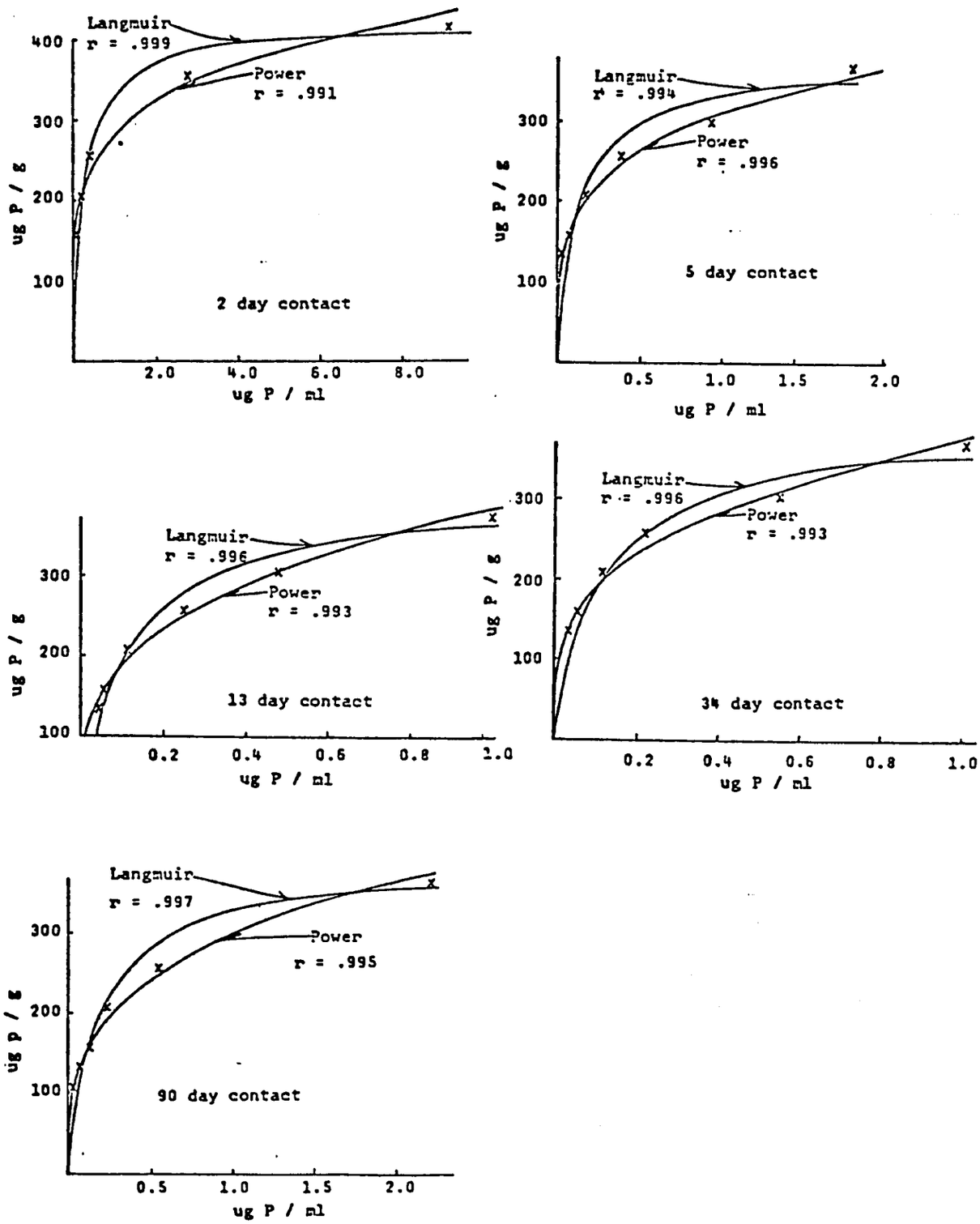

FIG. 4. P sorption isotherms of BR-5, 2-90 days.

It is apparant that the percent error in predicted values of sorption at lower solution concentration is consistantly greater in the case of Langmuir curves as opposed to Freundlich curves and in many cases rather large (e.g. 45% for Br-5 at a solution concentration of 0.07ug P/ml for 2 day contact period). Several factors conspire to mar the fit of the Langmuir curve at the low end of an isotherm. The Langmuir treatment of isotherm data involves a calculation of least square equation and correlation coefficient using concentration as the independent variable. It will be noted that values for concentration tend to cluster at the lower end of an isotherm and such a distribution tends at once to weight the fit toward higher values and to overemphasize the goodness of fit. The consistent underestimation of phosphorus sorption by derived Langmuir expressions for the isotherms shown in Figures 3 and 4 suggests a break in slope in linear Langmuir plots corresponding to different sets of sites of differing energies of adsorption or a change in energy of sites with increasing saturation, either of these possibilities occuring at much lower concentrations than those found for a break in slope by Syers et al. (1973) and Holford et al. (1974). These authors may well have overlooked such a differentiation at lower concentration values since in their experiments, final concentration values range considerably higher than those of the present work and are distributed more sparsely in the region studied here. Some Langmuir plots of isotherms given in Figure 5 suggest breaks in slope but definition of the point of change in slope is rather arbitrary, and has not been attempted as a preliminary

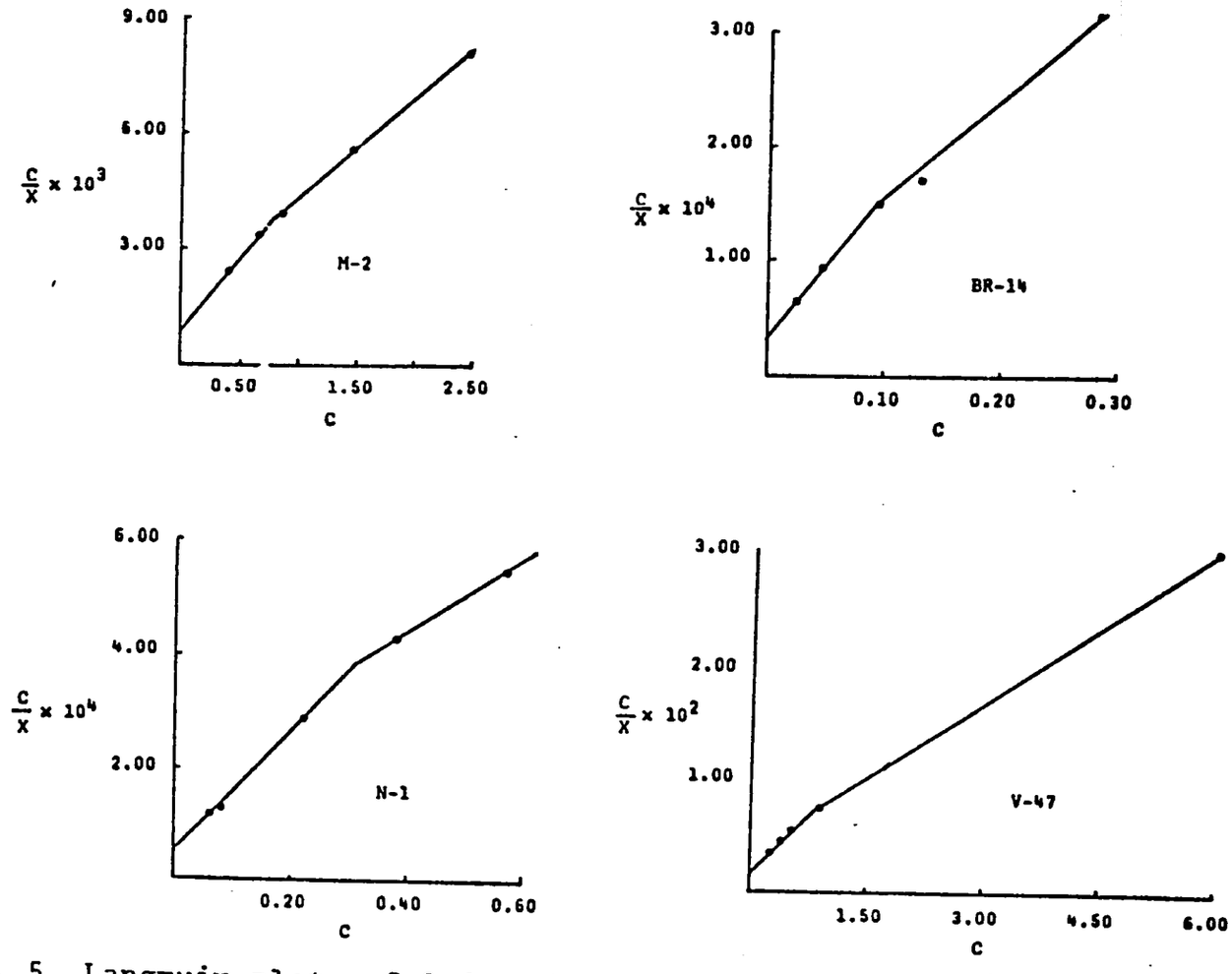

FIG. 5. Langmuir plots of 2 day phosphorus isotherm data*.

* C = concentration of P remaining in solution after 2 days (ugP/ml).
X = P removed from solution per gram soil after 2 days (ugP/g).

for construction of two surface Langmuir models for phosphorus sorption by these soils.

Avoidance of the roughly logarithmic distribution of final values in concentration requires a fairly precise knowledge of the sorption properties of a given soil before initiating an isotherm such that increasingly higher initial concentrations may be more narrowly spaced to allow for the great change in the slope of the sorption curve. The repetitions of isotherms necessary to provide a more even distribution of final concentrations were not attempted due to the size of the population of soils, the diversity of time treatments and, in many cases, an absolute constraint in the amount of soil sample.

Table 6 lists correlation coeficients and their significance levels for regressions of phosphate sorption indices against a number of soil properties. Al extracted by dilute HCl, 0.5M $CaCl_2$ or 5% Na_2CO_3 is found to predict well values for phosphorus indices; these relations are expressed graphically in Figures 6 and 7 . Sree Ramulu et al. (1967) also found dilute HCl extractable Al values to be well correlated (r=.94) with their sorption index. The authors were somewhat skeptical about the relation, citing the high P/Al molar ratio (10) of their data. Molar ratios of P sorption maximum with dilute HCl extracted Al for the present soils average about 2/5. It may be that the dilute HCl extraction procedure is selective of the material which is reactive toward phosphorus, but only removes a relatively fixed proportion of it. Other techniques, such as the acid oxalate, which are

TABLE 6. Correlation coefficients of 2 day P sorption indices and soil properties*

	ugP/g sorbed at 0.1ugP/ml	pH	clay	O.C.	- CBD - Fe	- CBD - Al	--- Tamm --- Fe	--- Tamm --- Al	--- Tamm --- Si	- HCl - Fe	- HCl - Al	Na_2CO_3 Al
Langmuir adsorption maximum	.89	-.30	.86	.72	.65	.70	.51	.74	.29	.37	.91	.90
	.0001	.17	.0001	.0002	.0011	.0004	.013	.0001	.18	.083	.0001	.0001
ugP/g sorbed at 0.1ugP/ml		-.23	.80	.75	.72	.80	.43	.77	.25	.32	.84	.87
		.29	.0001	.0001	.0002	.0001	.040	.0001	.25	.14	.0001	.0001

O.C. = organic carbon
Na_2CO_3 = cold 5% Na_2CO_3 extraction
HCl = pH 1.5 HCl, 0.5M $CaCl_2$ extraction

CBD = citrate-dithionite-bicarbonate extraction
Tamm = acid ammonium oxalate extraction in dark

* Correlation coefficients are the upper figure in a given cell of the matrix; lower figure is significance level.

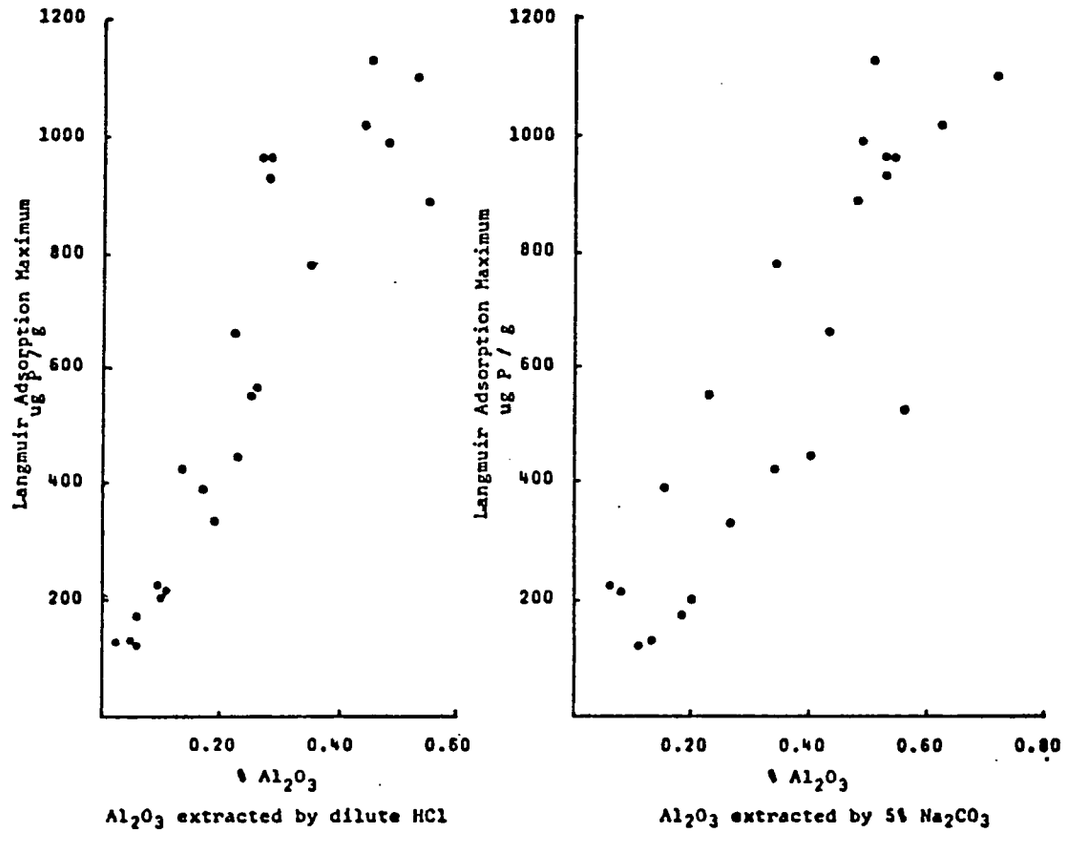

FIG. 6. Relations between 2 day Langmuir adsorption maxima and amorphous alumi. .m.

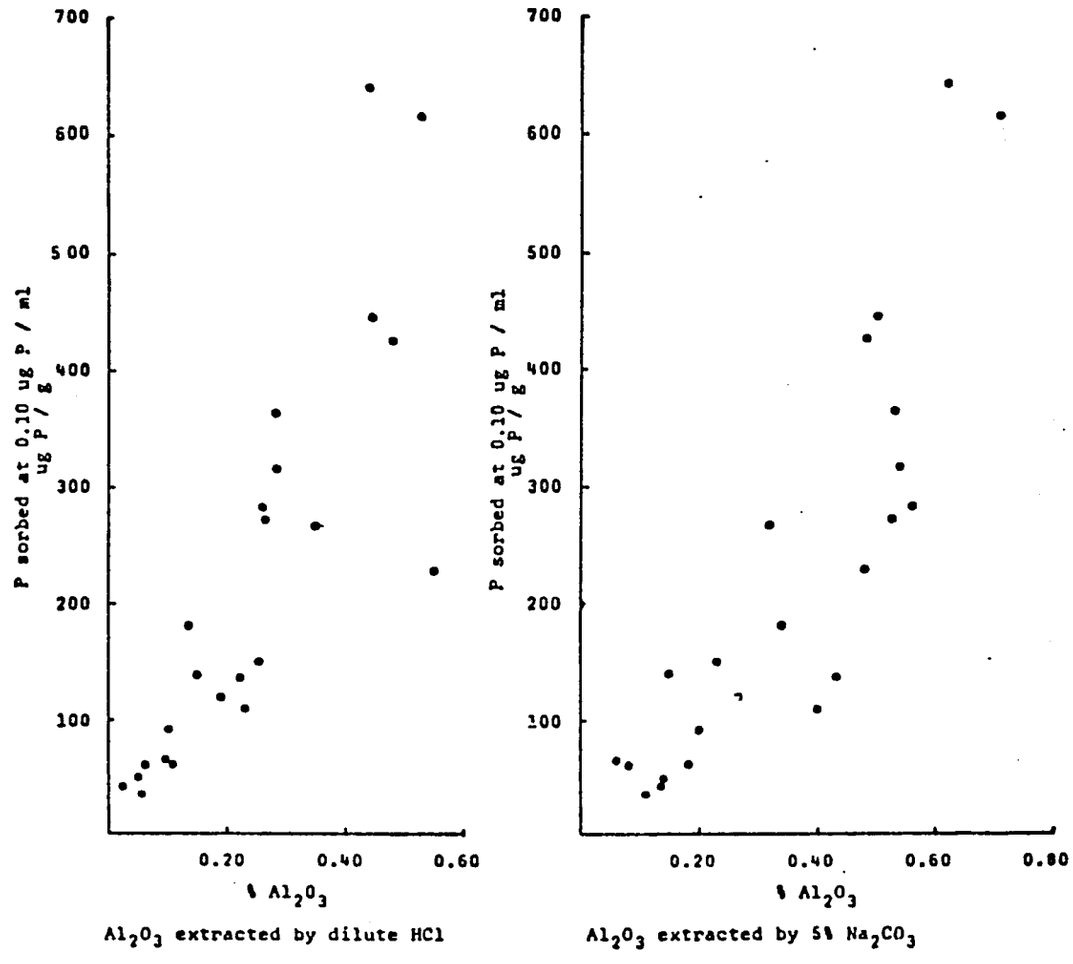

FIG. 7. Relations between P sorbed after 2 days with 0.1 ugP/ml remaining in solution and amorphous aluminum.

more vigorous in extraction of aluminum provide a basis for more reasonable P/Al ratios when very high levels of P are applied as in Sree Ramulu et al. (1967) but may be less discriminating in material extracted. By itself, acid oxalate extractable Al was found to be significantly but not strongly related to P sorption indices. This finding contrasts those of Saunders(1965) and Williams et al. (1958) who found Tamm Al to be the best correlate with P sorption using Piper's index, which involves retention against extraction of a large application of P. Ballard and Fiskell(1974) found Tamm Al to relate well to Langmuir adsorption maxima of surface samples of 42 Coastal Plains forest soils, though P correlation with Tamm Fe was slightly greater. CBD Al and dilute HCl extractable Al were also found to vary regularly with P sorption by these authors. Differences in best predictors of phosphorus reactivity may be due to differing phosphorus fixation indices in some cases as well as modal differences in the soil population. With the exception of four Venezuelan samples, soils under study herein probably exhibit effects associated with greater intensity in climatic and time factors than the studies above.

The association of phosphorus removal with the clay fraction has long been noted(Failyer et al., 1908) and may imply the concentration of reactive material in this fraction or is merely consistant with a surface active process. Saunders (1965) and Williams et al.(1958), however,found no signi-

ficant relation between phosphorus fixation and clay content. That the 5% Na_2CO_3 extractable Al is not merely a function of surface area is given support by an investigation on a B_{ir} horizon of a New York State Spodosol, Becket, which has been found to contain 1.1% clay, about 1.8% Al_2O_3 removed by the cold carbonate extraction and very high reactivity to phosphorus, comparable to the highest fixing tropical soils. A Langmuir adsorption maximum of 1675ug P/g soil was found after a 5 day contact period.

The lack of a strong relationship between oxalate extractable Fe and P sorption is notable. Findings of Ballard and Fiskell(1974) have been already noted. Sree Ramulu et al. (1967) also found Fe extracted by oxalate to correlate significantly(r=.77) with P sorption by soils, using an index formed by repeated applications of P. Here, also, significantly different methods of characterizing reactivity to phosphorus or differences in weathering intensity of the soil population may be associated with a difference in pattern of correlates. Reaction of phosphorus with amorphous iron oxides has often been held to be important in phosphorus fertility. Similarly, a number of other factors which have been associated with variation in removal of phosphorus from solution are not found here to be related simply to phosphorus sorption indices. The role of some of these factors only becomes evident through multiple correlation and is discussed below.

Correlation of CBD extractable oxides with sorption indices gives little evidence of strong relations between amounts of so called free oxides and reactivity to phosphorus, though, significantly, Al extracted is better correlated. Better correlation for Al may reflect either extraction of reactive materials or a correlation between such material and the long term pedogenic processes which involve occlusion of Al in iron oxides (Jackson, 1969).

Most evidence on the role of pH in phosphorus sorption has indicated increased adsorption with increased acidity for non-calcareous soils. Much evidence has come from experiments with systems less complex than soils but having components relevant to their study. Haseman et al.(1950) found increased removal of phosphorus from solution with decrease in pH for kaolinite, illite or montmorillonite. At a lower initial P rate (0.1M) they found for gibbsite or goethite a similar effect which was less marked at higher initial concentrations of phosphorus(1.0M). Similiar relations have been reported for kaolinite by Chen et al.(1973), and for goethite by Hingston et al.(1968). Coleman (1944) claimed an inverse pH effect for soils on the basis of differing reactivity of H+ and NH_4+ saturated clays. Though simple correlation coefficients for the present population of soils are scarcely significant, they are negative in conformity with the findings above. In multiple regressions, addition of pH to Al values for prediction of P sorption indices results in some increases in corre-

lation for a number of the extraction techniques for amorphous material. Regression coefficients for pH are in all cases negative, but F values for pH are not highly significant nor are intercepts for generated equations realistic.

Among the large number of multiple regession equations possible to predict phosphorus sorption those which were found to be of interest have been listed in Table 7 . A significant gain in predictability of adsorption maximum is apparent when carbonate extracted Al and Fe by Tamm or dilute HCl extraction are independent variables. However, the role of Fe remains secondary to that of Al in both equations when the value of the regression coefficients and the relative quantities of Fe and Al extracted by the several methods are considered. The negative sign of the regression coefficient of dilute HCl extracted Fe when this variable is added to dilute HCl extracted Al to predict adsorption maxima is surprising but the resulting equation scarcely increases precision of prediction by Al alone. Inclusion of a clay factor improves prediction by carbonate or dilute HCl extracted Al of adsorption maxima; a lesser regression coefficient is found in the case of the former and its significance by the F statistic is smaller suggesting that clay as a correction factor is more important for carbonate extracted Al. Na_2CO_3 may extract unreactive portions from kaolinite or gibbsite in addition to reactive material which is associated with surfaces, material more selectively extracted by the dilute acid proceedure. The best three variable equation for adsorption maxima has Al

TABLE 7. Regression equations*; prediction of 2 day P sorption indices

	R^2
Y_1 = 1210 Tamm Al + 99	.55
= 15.7 Clay - 30	.74
= 1639 CRB Al + 10	.80
= 2025 pH 1.5 Al + 88	.82
= 2136 pH 1.5 Al - 1000 pH 1.5 Fe + 107 (81.8,.0001) (15.7,.0008)	.83
= 1334 CRB Al + 112 O.C. - 88 (41.6,.0001) (67.0,.0001)	.85
= 1496 CRB Al + 333 Tamm Fe - 35 (82.7,.0001) (35.3,.0001)	.86
= 1575 CRB Al + 2373 pH 1.5 Fe - 79 (102,.0001) (18.9,.0003)	.86
= 1372 pH 1.5 Al + 6.5 Clay - 7 (121,.0001) (6.2,.022)	.86
= 1048 CRB Al + 7.5 Clay - 78 (19.7,.0003) (113,.0001)	.87
= 1178 pH 1.5 Al + 851 CRB Al - 2 (156,.0001) (13.7,.0014)	.89
= 1458 CRB Al + 883 Tamm Fe - 8862 Tamm Si + 43	.91

* Y_1 = Langmuir adsorption maximum.

Y_2 = P removed from solution at 0.1 ugP/ml.

F values and significance levels are in parentheses beneath relevant variable.

TABLE 7. (cont.)

	R^2
Y_2 = 609 Tamm Al - 16	.57
= 83 CBD Al + 126	.64
= 7.2 Clay - 56	.62
= 928 pH 1.5 Al - 3	.68
= 784 CRB Al - 50	.73
= 51.8 CBD Al + 4.5 Clay - 17 (59.7,.0001) (13.7,.0014)	.79
= 761 CRB Al + 947 pH 1.5 Fe - 87 (64.2,.0001) (9.3,.0063)	.79
= 554 CRB Al + 3.0 Clay - 87 (14.1,.0012) (62.1,.0001)	.79
= 622 CRB Al + 7.1 CBD Fe - 34 (26.2,.0001) (51.0)	.79
= 462 Tamm Al + 12 CBD Fe - 31 (26.6,.0001) (51.5,.0001)	.80
= 614 pH 1.5 Al + 45 CBD Al + 17 (16.2,.0007) (64.1,.0001)	.80
= 593 CRB Al + 71 O.C. - 114 (28.8,.0001) (62.7,.0001)	.82
= 544 CRB Al + 44 CBD Al - 22 (27.3,.0001) (83.9,.0001)	.85
= 62 CBD Al + 422 Tamm Al - 21 (86.3,.0001)(31.3,.0001)	.87
= 574 CRB Al + 83 CBD Al - 10 CBD Fe - 23 (32.4,.0001) (17.1,.0006)(75.7,.0001)	.87

extracted by the dilute acid and cold carbonate procedures as independent variables. The significant relation apparent where carbonate Al and O.C. predict maxima must be examined in the light of the strong correlation between O.C. and dilute HCl extractable Al. Only one model of 4 variables is of interest and is given in Table 7 . Though the r^2 value is not much increased compared to the best 3 variable model, the expression is nevertheless worth considering. The large negative regression coefficient for oxalate extractable silica more than negates the positive role of iron so extracted in a number of cases,suggesting that some of the silica so extracted is associated with some of the aluminum extracted by cold carbonate treatment possibly playing here also an inhibitory role with respect to reaction with phosphorus.

Multiple correlates of amount of P sorbed at 0.1ugP/ml(power curve P index) resemble those for adsorption maxima with some differences. As for adsorption maxima, inclusion of O. C. as a variable improves prediction by carbonate Al in this case the regression coefficient for O.C. being given relatively more weight than in prediction of maxima. Dilute HCl extractable Fe is also found to improve prediction by carbonate extractable Al, though consideration of the quantities extracted and its regression coeficient show that its role is minor and also less important than in prediction of adsorption maxima. One surprising finding is the significant role of CBD Al in multiple correlations. As noted above, CBD treatment is

more vigorous in extraction of Al than the other three techniques for almost all soils. Though a contribution of Al occluded in iron oxides confuses the picture, it is likely that the CBD Al is in some respects more precise than the other techniques. Al associated with organic matter may be mobilized by the strong chelating effect of citrate, while at the same time interlayer hydroxy Al present in some soils and and probably unreactive to phosphorus is not likely to be mobilized in the neutral environment. The other techniques, which are either acid or strongly alkaline, may differ in effectiveness in extracting O.C. associated Al or may mobilize interlayer material unreactive to P. Addition of clay content to CBD Al by itself improves prediction, and does so for CRB Al also; this effect seems to underscore the importance of surface active processes. The role of CBD Fe in improving prediction by carbonate or acid oxalate extracted aluminum is surprising and may be largely due to its strong correlation with CBD Al which may be a fortuitous association peculiar to this population of soils. Neither of the sets of Fe values for extraction techniques for amorphous material show significant relations with CBD Fe and it is unlikely that the same fixed proportion of the free iron oxides of the soils is reactive to P. The operative factor appears to be Al extracted by CBD, or a portion of it, since it is found that CBD Al improves greatly prediction by dilute HCl, acid oxalate or carbonate extractable Al

The fact that prediction by carbonate extractable Al of amounts of P sorbed at 0.1ugP/ml. is markedly improved by inclusion in regression of either O.C. or CBD Al suggests a relation between these latter two and relatively important role for Al associated with organic matter in removal of P from solution in the lower range of isotherms. It seems likely that P reacts with O.C. chelated Al and that CBD treatment removes Al bound by O.C. This should not be surprising given the strong chelation of Al by citrate(Struthers and Sieling, 1950). The relationship between CBD Al and carbonate extractable Al is relatively weak; they may differ mainly by greater efficiency in removal of organic bound aluminum by CBD treatment or by differential effects on hydroxy Al interlayer material. Al is quite stable as the aluminate ion at the high pH of 12 of the 5% Na_2CO_3 extractant and carboxyl groups of organic matter complexed with aluminum should be more stable in the ionized form at this pH. It would be surprising, therefore, if Al were not readily solubilized from organic matter complexes by the alkaline reagent. Empirical investigation of the question whether 5% Na_2CO_3 mobilizes Al from known Al-chloritized material remains to be carried out. If this were the case, then such an error by extraction of unreactive interlayer material would more readily weight the results of the relatively mild treatment afforded by the cold carbonate procedure. Less well ordered kaolinite and gibbsite may also be attacked slightly by the alkaline treatment and Al of such

material may be less reactive to P at lower concentrations than at higher. The effect of CBD Al in multiple correlation may be to emphasize factors associated with clay content(surface area) and organic matter. Addition of a third independent variable in predicting P sorbed at 0.1 ugP/ml. is only significant where CBD Fe is combined with carbonate Al and CBD Al giving a negative regression coefficient for the added variable and may be an adjustment for Al which is extracted by CBD but is occluded in iron oxides and does not react with P. In summary, Al associated with organic matter and surfaces appears to be of greater importance at the low end of 2 day isotherms though of major importance throughout the range of isotherms. Acid oxalate or dilute HCl extractable Fe is found to be of minor importance in removal of P from solution by the soils studied, especially at the low end of isotherms.

C. 90 Day Isotherms

Prediction of 2 day P isotherm values is of interest, but its relation to agronomic considerations is subject to question. Woodruff and Kamprath (1965) showed that phosphorus response of millet in greenhouse trials was related to 24 hour Langmuir P maxima in complicated ways for 5 soils studied. Relationships of isotherm characteristics to plant response have likewise been reported to be irregular by During (1968). Jones and Benson (1975), however, claimed that when P applications for corn on an Idaho Fragiorthod were related to 6 day P isotherm values, the corresponding concentrations of P remaining in isotherm solutions were found to predict well yield and plant P status. Using a reasonably large population of soils, Ozanne and Shaw (1968) claimed good prediction of P applications necessary for 95% of maximal yield in pasture land by isotherm characteristics. The situation might be improved by conducting isotherms of longer duration and, therefore, 90 day isotherms were carried out on 22 of the 23 soils studied for 2 day time periods with the aim of discovering possible mineralogical correlates. In a number of cases use of toluene to inhibit microbial activity proved inadequate as was indicated by objectionable smells. Some irregular values were obtained which were eliminated in order that remaining values might conform to reasonable patterns of increasing final concentrations corresponding to increasing initial concentrations. Such elimination biases the data

toward conformity to adsorption models and must be considered to reduce the reliability of results. However, in the majority of cases full sets of isotherm values were obtained and were found to fit very well Langmuir or Freundlich treatment; incomplete sets also fit well such treatment.

Table 8 lists the Langmuir adsorption maxima and amounts of P sorbed at 0.1ugP/ml by interpolation from power curve expressions, the correlation coefficients of the regression equations giving the indices, as well as percentage changes of these indices compared with two day values. Variations in Langmuir adsorption maxima with time, while in many cases appreciable, are much less than changes with time in amounts of phosphorus sorbed at solution concentrations of 0.1ugP/ml. The claim has often been made that "near equilibrium" conditions in P sorption isotherms exist on the basis of very little changes in amounts of phosphorus sorbed after a period of a day or so. Though for a given system changes in amounts of P sorbed become relatively small after a short period of time, solution P may change significantly.

As for two day contact periods, aluminum as measured by methods selective of more reactive forms proves to be the best correlate of phosphorus sorption by either index, Al by dilute acid or 5% Na_2CO_3 extraction, in particular, explaining much of the variation in sorption (Table 9). However, no predictors are as precise as for 2 day contact periods. Part of the increased complexity of sorption processes may be explained by the greater role which poorly crystallized iron

TABLE 8. 90 day phosphorus sorption indices

Soil	Langmuir ad-sorption maximum (ugP/g)	r value of Langmuir curve	% change of index (90-2day)	p sorbed at 0.1ugP/ml (ugP/g)	r value of power curve	% change of index (90-2day)
B-1	1110	.999	-1	893	.948	101
C-1	926	.982	5	582	.955	155
N-1	1438	.986	31	1091	.968	77
PR-1	856	.999	9	481	.987	80
T-1	1982	.979	100	1572	.989	270
BR-2	1127	.996	17	517	.997	64
BR-5	386	.997	-9	148	.995	-17
BR-8	1171	.990	21	494	.995	81
BR-11	1163	.993	25	559	.998	54
BR-14	1425	.994	39	1303	.998	103
BR-17	773	.994	17	299	.995	118
M-1	1369	.966	142	780	.985	176
M-2	810	.985	82	261	.997	135
M-3	915	.999	178	325	.999	166
G-1	139	.985	-20	94	.967	55
G-5	94	.992	-29	57	.980	31
G-6	100	.996	-21	104	.843	110
V-47	260	.997	20	81	.998	31
V-65	264	.987	16	103	.984	56
V-77	620	.997	58	234	.959	70
V-91	878	.996	59	289	.992	94

TABLE 9. Correlation coefficients of 90 day P sorption indices and soil properties*

	ugP/g sorbed at 0.1ugP/ml	pH	clay	O.C.	-- CBD -- Fe	-- CBD -- Al	--- Tamm ----- Fe	--- Tamm ----- Al	--- Tamm ----- Si	- HCl -- Fe	- HCl -- Al	Na_2CO_3 Al
Langmuir adsorption maximum	.82	-.12	.78	.59	.52	.50	.54	.82	.42	.40	.83	.84
	.0001	.60	.0001	.0054	.015	.020	.012	.0001	.053	.072	.0001	.0001
ugP/g sorbed at 0.1ugP/ml		-.11	.75	.72	.60	.62	.56	.77	.41	.40	.84	.77
		.65	.0002	.0004	.0040	.0028	.0085	.0001	.064	.069	.0001	.0001

O.C. = organic carbon
Na_2CO_3 = cold 5% Na_2CO_3 extraction
HCl = pH 1.5 HCl, 0.5M $CaCl_2$ extraction

CBD = citrate-dithionite-bicarbonate extraction
Tamm = acid ammonium oxalate extraction in dark

* Correlation coefficients are the upper figure in a given cell of the matrix; lower figure is significance level.

appears to play (Table 9). Fe extracted with dilute HCl, 0.5M $CaCl_2$ or with acid oxalate increases strongly prediction by Na_2CO_3 extracted Al of P indices especially in the case of amounts of P sorbed at 0.1ugP/ml. This finding is consistent with those of Shelton and Coleman (1968) who found that Al-P/Fe-P ratios of fractionations of soil P from fertilized fields declined with time though, as they note, uptake by plants from more available Al-P forms may in part explain their findings. For the soils under study, though the "amorphous" Fe appears to play an increased role in reactivity of the soils to phosphorus over a three month period, its effect remains decidedly secondary to that of Al. Clay as a correction factor for prediction by oxalate, dilute HCl or Na_2CO_3 extractable Al of adsorption maxima remains significant,suggesting that the dominance of surface active processes persists through time (Table 10). CBD Al is seen to play a role in increasing prediction by multiple regressions of amounts of P sorbed at 0.1ugP/ml, similar to its role for 2 day isotherms. Silica removed by acid oxalate does not appear as a negative factor to increase prediction of adsorption maxima by oxalate Fe and carbonate Al as in the case of 2 day isotherms. The role of silica so extracted may be to affect the kinetics of soil phosphorus reactions rather than to affect the equilibrium values toward which the systems tend. In regressions using carbonate Al and oxalate Fe as predictors of adsorption maxima the change in regression coefficients imply an increasing role of oxalate Fe relative to carbonate Al. However, when one compares the

TABLE 10. Regression equations; prediction of 90 day P sorption indices*

	R^2
Y_1 = 2654 pH 1.5 Al + 162	.68
= 2193 CRB Al + 45	.70
= 1788 pH 1.5 Al + 8.9 Clay + 24 (45.0,.0001) (2.7,.12)	.73
= 1225 Tamm Al + 10 Clay - 83 (47.2,.0001) (5.1,.037)	.74
= 1490 CRB Al + 9.3 Clay - 77 (44.5,.0001) (10.1,.0057)	.75
= 1950 CRB Al + 620 Tamm Fe - 51 (45.2,.0001) (25.7,.0001)	.80
= 2122 CRB Al + 4530 pH 1.5 Fe - 150 (60.2,.0001) (14.6,.0013)	.81

* Y_1 = Langmuir adsorption maximum.

Y_2 = P removed from solution at 0.1 ugP/ml.

F values and significance levels are in parentheses beneath relevant variable.

TABLE 10. (cont.)

	R^2
Y_2 = 1685 CRB Al - 128	.59
= 1488 Tamm Al - 130	.60
= 2243 pH 1.5 Al - 91	.71
= 1625 CRB Al + 3888 pH 1.5 Fe - 296 (33.8,.0001) (9.9,.0056)	.71
= 2061 pH 1.5 Al + 25 CBD Al - 77 (19.8,.0003) (24.2,.0001)	.71
= 1223 Tamm Al + 21 CBD Fe - 146 (21.4,.0002) (22.6,.0002)	.71
= 1458 CRB Al + 581 Tamm Fe - 219 (26.3,.0001) (20.0,.0003)	.72
= 1203 Tamm Al + 94 CBD Al - 137 (21.5,.0002) (25.3,.0001)	.72

90 day regression coefficients of carbonate Al and oxalate Fe with the regression coefficients of the same variables in the 4 variable model for 2 day adsorption maxima (which involves a negative effect of oxalate extracted silica) the ratios of the coefficients are found to be virtually identical. This confirms more precisely the kinetic nature of such an effect of silica.

In contrast to the case for 2 day isotherms, no 4 variable models of reactivity of soils to phosphorus are found to be significant.

It is noticeable that prediction of Langmuir adsorption maxima is more successful than of the P sorption index derived from power curves, despite the somewhat arbitrary limits set on the range of isotherms and the difficulties encountered in obtaining values across even such an arbitrary range, especially for 90 day isotherms. It seems plausible that the Langmuir adsorption maximum, even for isotherms of fairly roughly defined range, tends more strongly toward uniqueness as a soil characteristic than amounts of P sorbed at a given level of P. That is, adsorption maxima may depend more closely on actual distingishing characteristics of the soils themselves and are less a product of the particular circumstances of measurement of P sorption. The lesser significance of the power curves index is perhaps unfortuanate, since, arbitrary as it is, it may relate more closely to plant requirements. Jones and Benson (1975) reported that solution levels of isotherms correlated better than amounts of P

sorbed with response of corn in field trials. If such a relation proves to hold more generally, prediction of optimal amounts of fertilizer phosphorus from mineralogical data becomes more difficult. Nevertheless, considerable precision is still provided by the predictors listed in Table 10 and the soil properties measured may prove to be of considerable importance in interactions with soils of other species of interest. Deficiencies, in sulfate and micronutrients are often limiting factors in crop production on highly weathered soils (Drosdoff,1972) and the association of some of these with reactive Al and Fe oxides has been reported, by Chao et al. (1964) in the case of sulfate, by Reisenauer et al. (1962) in the case of molybdenum, and by Hatcher et al. (1967) and Sims and Bingham (1968, a, b) in the case of boron.

D. 2 - 90 day isotherms of a subset of 9 soils

Figures 8 and 9 represent the changes in adsorption maxima and amounts of P sorbed at final concentrations of 0.1ugP/ml for contact times ranging from 2 to 90 days for a subset of 9 soils. Values of sorption indices for intermediate time periods are presented in Table 11 .

Values for amounts of P sorbed at a final concentration of 0.1ugP/ml are seen to conform more closely than adsorption maxima to a process of increasing sorption with increase in contact time. This is partly as a result of difficulties in achieving a similar range of concentrations for all time periods, especially those of longest duration. However, problems with ranges of isotherms do not explain completely the variability encountered as is evident in Figure 10 . Figure 10 shows the change in concentration with time for a number of isotherm systems which have the same soil in contact with the same initial amounts of P in solution; removal of phosphorus from solution under the experimental system are seen to vary with time in complex ways. A number of factors may possibly be operating. As noted above microbial activity may be a factor either by virtue of removal of phosphorus from solutions by organisms themselves or by changes in redox potential. In the latter case, reduction of iron may lead ultimately to several different, opposing effects. Microbial reduction of ferric iron associated with phosphorus can lead to an increase in levels of solution phosphorus (Ponnamperuma, 1972).However,

TABLE 11. Phophorus sorption indices; 5, 13, 34 day contact *

Soil	5 day				13 day				34 day			
	X_1	r	X_2	r	X_1	r	X_2	r	X_1	r	X_2	r
N-1	1331	.996	783	.999	1897	.996	868	.999	1908	.998	950	.994
T-1	1105	.997	510	.991	1414	.993	629	.996	1451	.997	637	.979
BR-5	377	.994	181	.996	403	.996	188	.993	391	.996	191	.993
BR-14	1259	.995	904	.999	1775	.996	1034	.999	1945	.990	1097	.997
M-2	622	.996	197	.998	749	.991	247	.994	769	.997	229	.986
M-3	494	.996	191	.997	625	.997	234	.998	672	.996	235	.999
G-3	111	.994	46	.995	90	.995	61	.997	152	.993	55	.965
V-47	257	.991	80	.998	312	.918	93	.971	268	.997	94	.999
V-91	639	.994	183	.999	779	.998	211	.993	797	.997	222	.997

* X_1 = Langmuir adsorption maximum.

X_2 = P sorbed at 0.1 ugP/ml.

R values following value of index are for fit of expression from which index is derived.

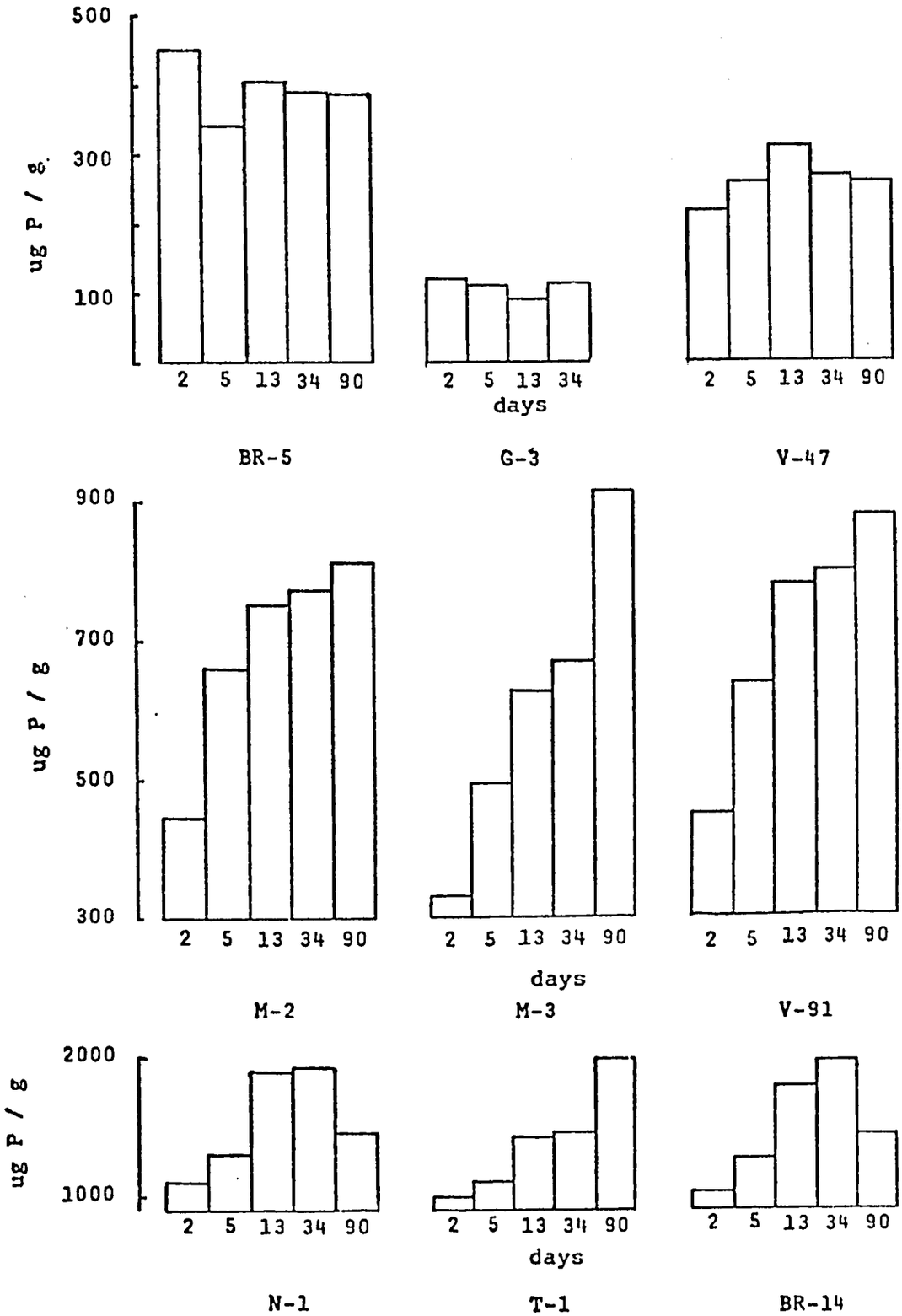

FIG. 8. Langmuir adsorption maxima, 2-90 days

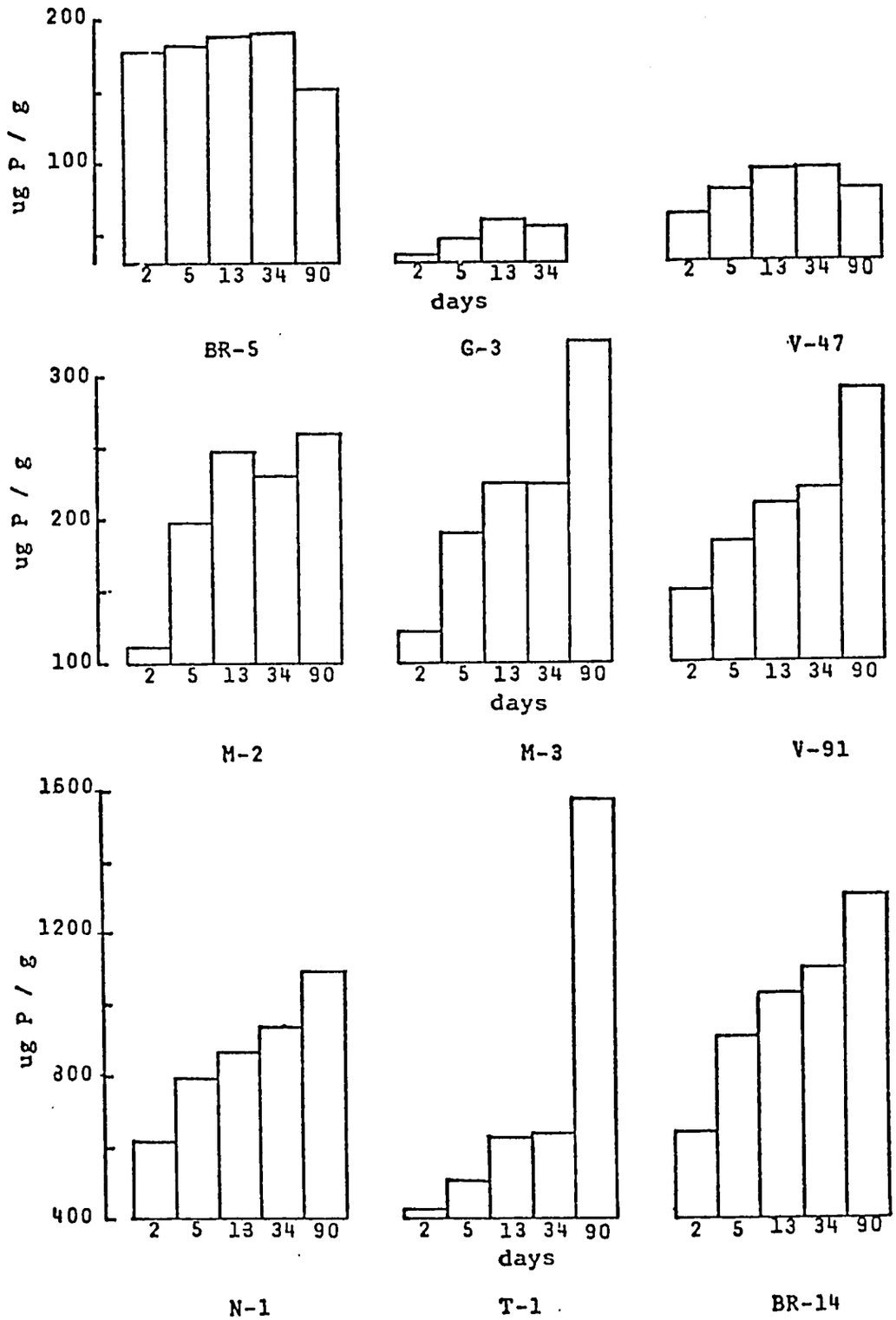

FIG. 9. Amounts of P sorbed at 0.1ugP/ml, 2-90 days

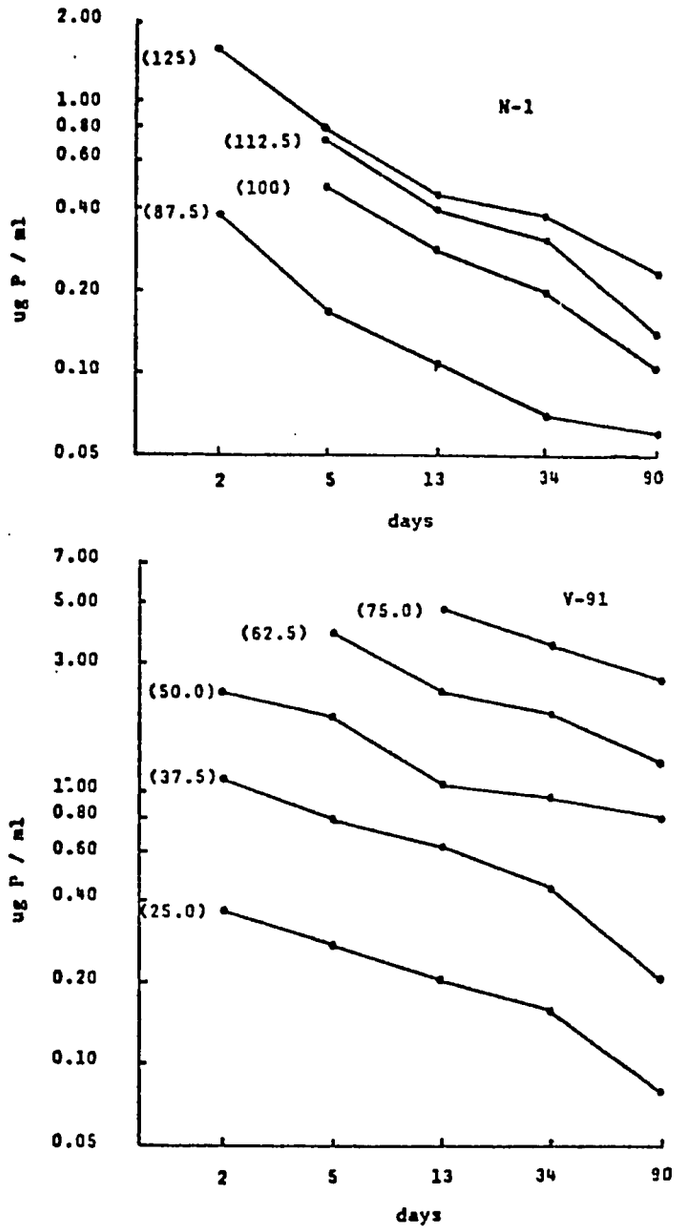

FIG. 10. P remaining in solution with increasing contact time*

* Initial concentrations of P are in parentheses

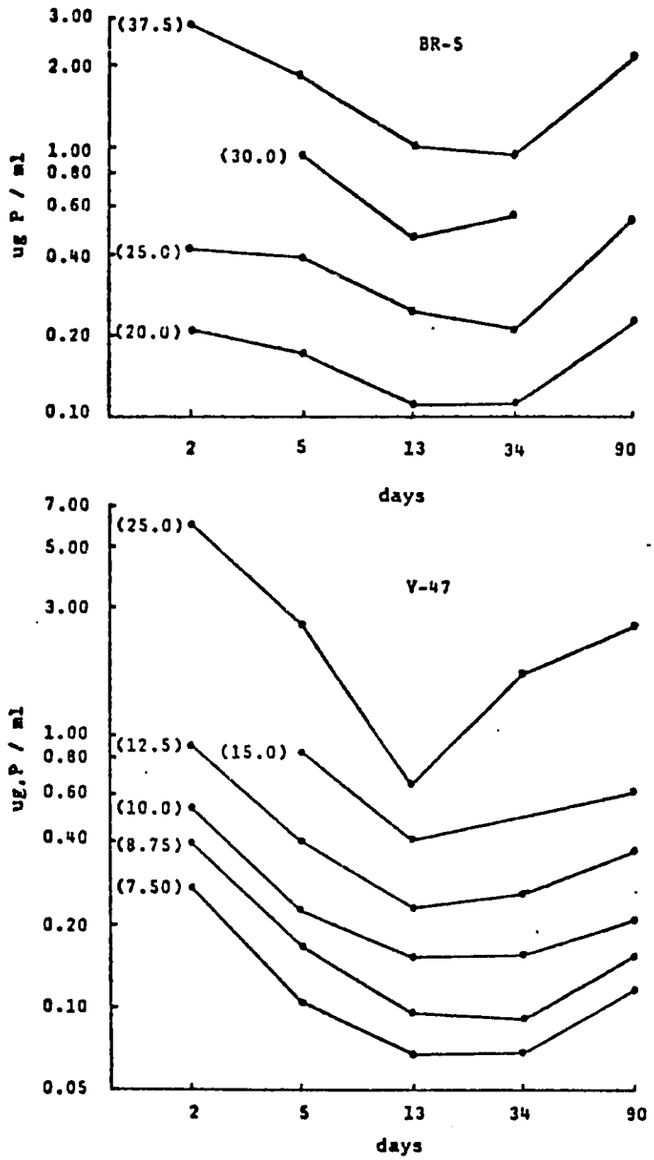
BR-5
(37.5)
(30.0)
(25.0)
(20.0)
3.00
2.00
1.00
0.80
0.60
0.40
0.20
0.10
ug P / ml
2
5
13
34
90
days
V-47
(25.0)
(12.5)
(15.0)
(10.0)
(8.75)
(7.50)
7.00
5.00
3.00
1.00
0.80
0.60
0.40
0.20
0.10
0.05
ug.P / ml
2
5
13
34
90
days

FIG. 10. (cont.)

reduced iron may be reoxidized and, since less soluble in this state, will reprecipitate forming a fresh, high sorbing surface. Hsu (1964) incubated a soil one year in a phosphorus solution and noted the development of a ring at the solution-air interface along the walls of the polyethelene container. After removal of the soil, the ring was dissolved with sulfuric acid and the material analysed and found to be composed principally of Fe and of 87% of the phosphorus removed from solution. Hsu suggested the reduction, oxidation, P fixation process referred to above as an explanation of the findings.

Munns and Fox (1976) recently reported results of investigations on 4 tropical soils in which phosphorus was incubated with soil samples for long periods of time. The authors incubated their samples without shaking at 0.1 bar moisture content and determined solution levels of P by extraction with dilute $CaCl_2$. For 3 of the soils upward fluxuations in solution P were found after contact times greater than 120 days. As the authors note, unshaken, unsuspended soils are likely to equilibrate with phosphorus more slowly than in the contrary case. Fluxuations observed over shorter time periods for the soils studied herein may reflect a difference in method of equilibration. Munns and Fox suggest that there is established after an extended period of time a steady state of slow adsorption balanced by release processes such as by mobilization from organic matter. These authors suggest that gel hulls and extent of aggregation can affect the rate at which "equilibrium" conditions are attained. It is notable that BR-5 has the lowest

content of organic matter of the soils studied and, on the basis of sorption indices related to final concentrations of 0.1ugP/ml, appears to approach the "steady state" phase more rapidly than the other soils. However, the relation between organic matter and speed of reaction is not consistent for the whole subset of soils.

Despite possible effects of microbial activity, from Table 12 it may be seen that the principal correlations between phosphorus reactivity and soil properties remained relatively constant throughout the 5 contact periods for the subset of 9 soils and strongly resemble the relations found to characterize the full sets of soils for 2 and 90 day contact periods. The higher correlation coefficients for the subset of soils as opposed to the full sets is a somewhat unfortunate circumstance resulting from a random selection of the subset from the larger group of soils such that some of the soils which were "anomalous" for correlations with the full set of soils were excluded from the subset. This selection may result in a decreased ability to identify possible changing effects of the various soil characteristics with time. The relatively higher correlation coefficients for the subset of soils must also be viewed in the light of the decreased significance of a given r value as the number of samples declines.

Clay content and Al extracted by cold Na_2CO_3 or dilute HCl show a strong relation with P sorption indices throughout the range of contact times. O.C. also varies closely with

TABLE 12. Correlation coefficients of P sorption indices and soil properties, 2-90 days *

	Day	pH	clay	O.C.	CBD Fe	CBD Al	Tamm Fe	Tamm Al	Tamm Si	HCl Fe	HCl Al	Na_2CO_3 Al
Langmuir adsorption maximum	2	-.26	.93	.80	.68	.74	.61	.71	.26	.65	.98	.93
		.51	.0006	.01	.04	.02	.08	.03	.51	.06	.0001	.0006
	5	-.15	.97	.85	.69	.74	.60	.80	.33	.65	.99	.93
		.70	.0001	.004	.04	.02	.09	.01	.61	.05	.0001	.0005
	13	-.15	.95	.86	.71	.78	.54	.79	.25	.60	.98	.94
		.70	.0002	.003	.03	.01	.14	.01	.52	.09	.0001	.0004
	34	-.12	.95	.87	.68	.76	.53	.82	.24	.60	.97	.93
		.75	.0003	.003	.04	.02	.14	.008	.53	.08	.0001	.0005
	90	.12	.95	.77	.48	.53	.83	.71	.53	.87	.92	.74
		.77	.0007	.025	.23	.17	.01	.05	.18	.005	.0016	.04
ugP sorbed at 0.1ugP/ml	2	-.14	.86	.88	.70	.80	.42	.72	.08	.47	.92	.92
		.71	.0036	.003	.04	.01	.25	.03	.83	.20	.0007	.0006
	5	-.09	.86	.89	.66	.77	.40	.79	.10	.46	.90	.92
		.82	.0035	.002	.05	.02	.29	.01	.79	.20	.0011	.0007
	13	-.08	.88	.90	.64	.75	.44	.81	.15	.51	.92	.92
		.83	.0023	.001	.06	.02	.23	.009	.70	.16	.0008	.0008
	34	-.09	.87	.89	.65	.76	.42	.79	.11	.49	.91	.92
		.81	.003	.002	.06	.02	.26	.01	.76	.18	.0009	.0008
	90	.01	.91	.85	.51	.60	.73	.71	.37	.75	.93	.78
		.97	.0019	.007	.19	.11	.04	.05	.63	.03	.0012	.0207

O.C. = organic carbon
Na_2CO_3 = cold 5% Na_2CO_3 extraction
HCl = pH 1.5 HCl, 0.5M $CaCl_2$ extraction

CBD = citrate-dithionite-bicarbonate extraction
Tamm = acid ammonium oxalate extraction in dark

* n = 8 for 90 day correlations. Correlation coefficient is in upper part of a given cell of the matrix, significance level in lower.

sorption indices, especially with amounts of P sorbed at concentrations of 0.1ugP/ml. Oxalate and CBD extractable Al are also seen to correlate significantly with reactivity to phosphorus. As for the full set of soils, Fe extracted by oxalate or dilute HCl becomes prominent as a correlate of sorption indices at the 90 day contact time. 98% of the variation in 90 day adsorption maxima is explained by a combination of two predictors, Al and Fe extracted by dilute HCl with the contribution by Al only a bit larger than that of Fe.

E. Desorption of Phosphorus

Probably in no instance can phosphorus in soil solution at a given time supply a total crop need through a growing season; some portion of solid phase P must contribute to that taken up by plants. Extraction of soil P with 0.5M $NaHCO_3$ at pH 8.5 has been suggested by Olsen et al.(1954) as a measure of plant available P. In the same manner as for Freundlich sorption indices, indices for desorption properties may be generated by power curve treatment of desorption data using as variables final adsorption isotherm P concentrations and amounts of P remaining fixed against extraction. Figure 11 represents graphically values interpolated from least square derived power curves. It may be observed that available P as measured by the sum of 5 extractions tends to remain relatively constant for a given soil over the 4 time periods measured;however, this constancy is attained by increasing initial concentrations of P for isotherms of increasing duration. Figure 12 presents relationships found at 34 days between total applied P (including"native"P as measured by 5 $NaHCO_3$extractions of untreated soil) and phosphorus remaining in the incubation solution plus that extracted by $NaHCO_3$ after incubation. A marked linearity is evident for all nine soils within the ranges represented. That linear extrapolation to the y axis does not correspond to the actual physical situation is demonstrated by the values for "native" P measured by $NaHCO_3$ of untreated soils(see Appendix). For the Nipe

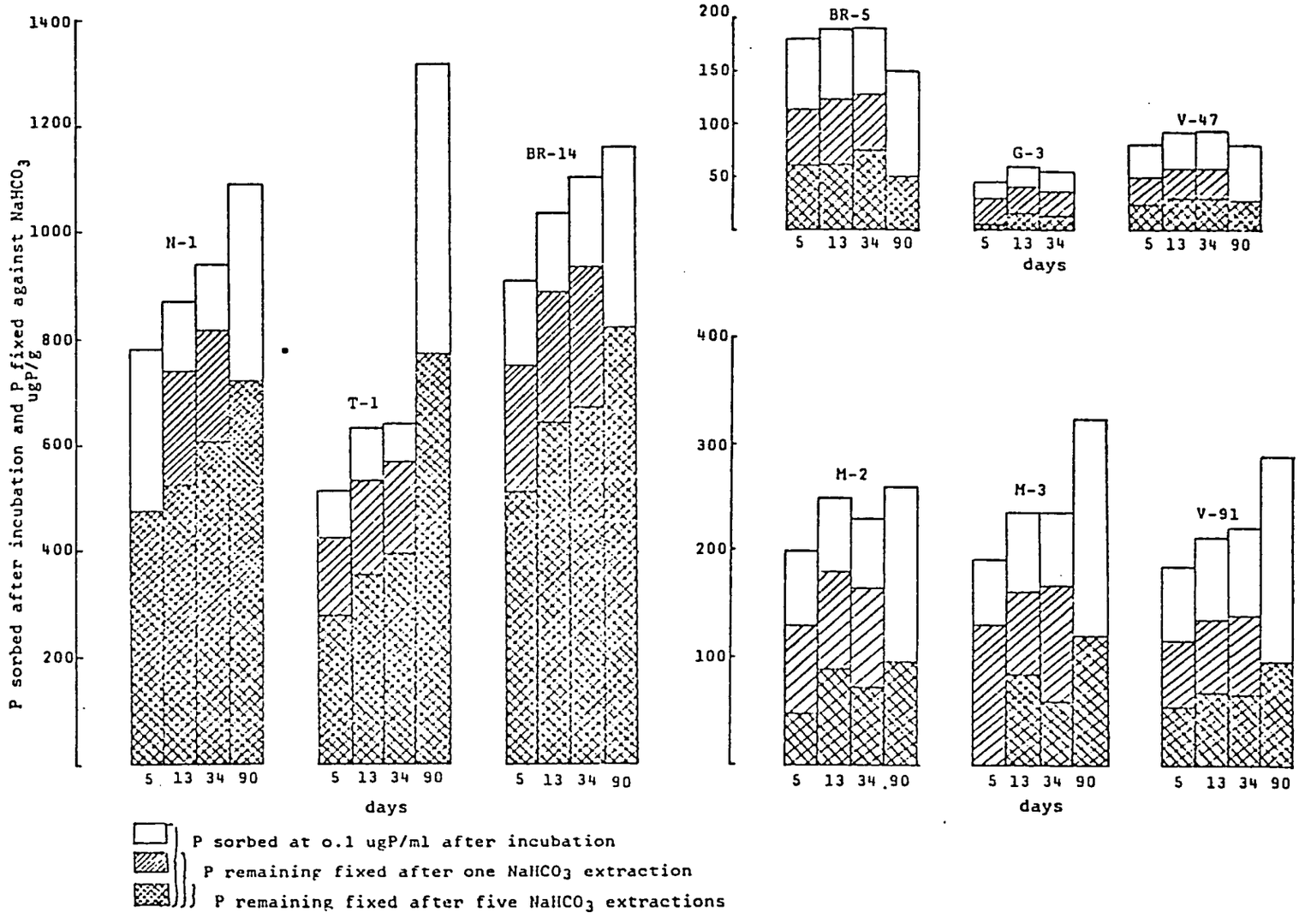

FIG. 11. Amounts of P sorbed and fixed against $NaHCO_3$ extraction, 5-90 days

sample (N-1) linear extrapolation to the y axis of the five-fold extraction data implies about 280 ugP must be per gram soil before any phosphorus becomes "available" as measured by the same extraction procedure. However, about 5ug P are released from a gram of the untreated Nipe sample by five-fold Na HCO_3 extraction. A plot of the actual physical system must approach the origin; such a plot could be generated by log-log least square statistics but would be weak quantitatively because of the lack of points in the region departing from linearity. A rough value for the amounts of "available" P needed to supply a crop of corn of 10 ton dry plant matter per acre would be 30 ug P per gram soil. For most of the soils examined for desorption characteristics the region of interest agronomically from a "capacity" standpoint is unrepresented by the data. However, the smooth curves drawn in Figure 12 may not diverge so significantly from the actual behavior of the soils at lower P applications as to preclude some useful observations being derived. For Nipe, using the five-fold extraction curve, one may observe that the P application corresponding to 30 ug P available per gram is about 120 ug P/g. However, Figure 11 shows that in order to attain a solution concentration of 0.1 ug P/ml. at 34 days, considerably greater quantities of P must be added initially, greater than 900 ug P/g. Thus, from Figure 12 and 34 day isotherm data (see Appendix) it may be inferred that solution P levels would be exeedingly low at a P application rate providing a sufficient capacity factor. Since both solution levels

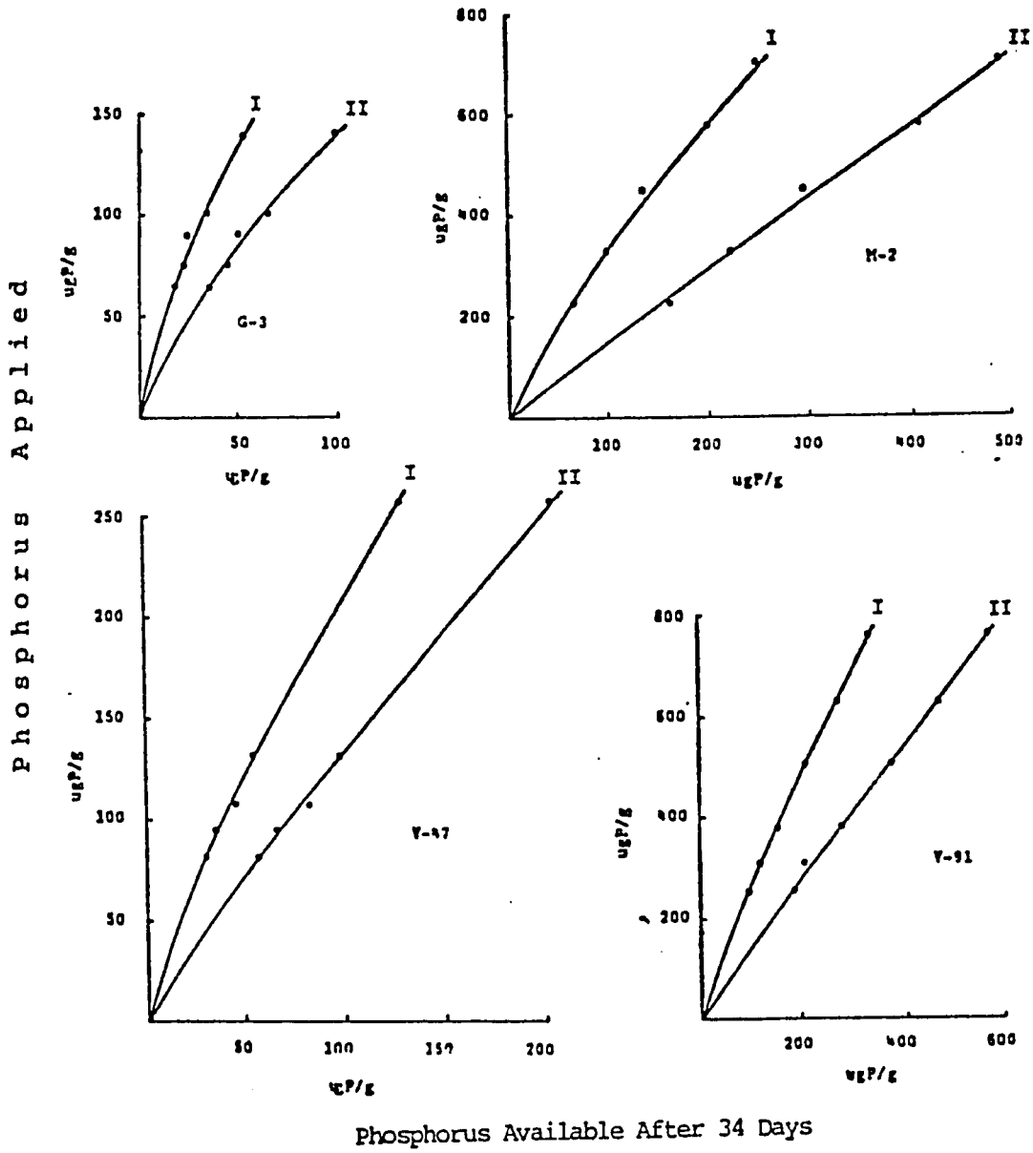

FIG. 12. Relations between applied phosphorus and phosphorus available after 34 days.*

* I corresponds to single $NaHCO_3$ extraction.
II corresponds to five-fold $NaHCO_3$ extraction.
" Phosphorus Applied " includes P extracted from untreated soil by five-fold $NaHCO_3$ extraction.
" Phosphorus Available " = P extracted by $NaCO_3$ after incubation + P remaining in solution before extraction.

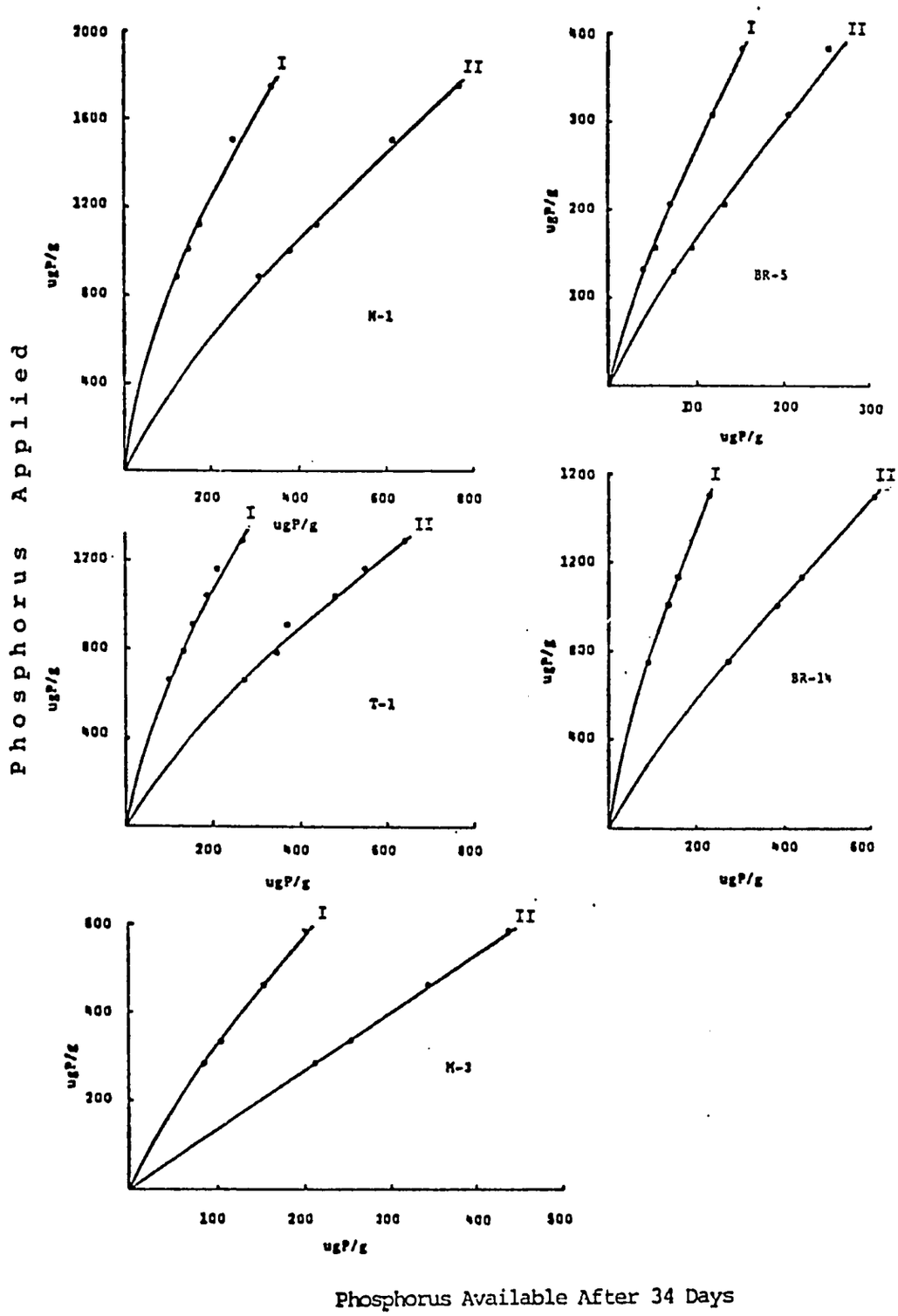
Phosphorus Applied
Phosphorus Available After 34 Days
ugP/g
I
II
M-1
BR-5
T-1
BR-14
M-3

FIG. 12. (cont.)

TABLE 13. Correlation coefficients of soil properties and P retained after single and five-fold $NaHCO_3$ extracion following incubation *

	Day	pH	clay	O.C.	CBD Fe	CBD Al	Tamm Fe	Tamm Al	Tamm Si	HCl Fe	HCl Al	Na_2CO_3 Al
P retained after one extraction	5	-.12	.81	.87	.65	.92	.50	.85	.18	.58	.87	.88
		.77	.015	.0057	.076	.0015	.21	.0077	.67	.13	.0056	.0045
	13	-.07	.87	.91	.64	.75	.44	.80	.15	.50	.91	.91
		.85	.0026	.0010	.060	.018	.24	.0097	.70	.17	.0009	.0009
	34	-.08	.87	.90	.66	.78	.42	.78	.12	.48	.91	.91
		.83	.0028	.0012	.050	.014	.26	.013	.75	.19	.0014	.0009
P retained after five extractions	5	-.04	.85	.89	.69	.81	.37	.77	.08	.46	.90	.90
		.92	.0073	.0036	.056	.016	.62	.024	.85	.25	.0031	.0026
	13	-.07	.85	.91	.64	.76	.41	.78	.11	.47	.90	.90
		.84	.0038	.0010	.063	.017	.28	.012	.77	.20	.0014	.0014
	34	-.10	.85	.91	.68	.80	.41	.74	.10	.45	.91	.91
		.80	.0038	.0011	.041	.0096	.28	.022	.80	.22	.0011	.0011
	90	-.04	.91	.91	.60	.71	.59	.72	.24	.61	.95	.85
		.92	.0002	.0021	.11	.045	.12	.043	.57	.10	.0006	.0073

O.C. = organic carbon
Na_2CO_3 = cold 5% Na_2CO_3 extraction
HCl = pH 1.5 HCl, 0.5M $CaCl_2$ extraction

CBD = citrate-dithionite-bicarbonate extraction
Tamm = acid ammonium oxalate extraction in dark

* Correlation coefficient is in upper part of a given cell of the matrix, significance level in lower.

of P and the capacity for solution P to be replenished as it is removed by plants are important for plant growth, neither can be neglected. Thus, residual effects carrying over numbers of years from large P applications necessary for good response to P on some high fixing soils may be implied by such evidence of build-up of a large capacity factor (Soil Science Dept., N.C.S.U., 1974). Though amounts of phosphorus remaining available tend to decrease slightly with time, the change in availability rate is not great. The correlation coefficients of " fixed " P at solution concentrations of 0.1 ug P/ml against other soil properties are presented in Table 13 and demonstrate that the relation of " fixed " P with soil properties closely parallels the relations found for adsorption maxima and P removed from solution at 0.1 ug P/ml.

Section III Conclusions

None of the strong correlations between phosphorus sorption indices and various soil properties demonstrates conclusively the causal role of a given soil property in removal of phosphorus from solution by soils. Two kinds of interpretations are possible from the statistical relations exhibited in the work above: simple predictions for other, sufficiently similar systems (hopefully, fertilizer P applications on highly weathered soils) and evidence for plausible mechanisms explaining the relationships found and suggesting further tests of the power of the model.

The most consistent predictors of reactivity of soils to phosphorus, as evidenced by removal of P from solution or by retention against $NaHCO_3$ extraction after incubation, have been shown to be " amorphous " Al measured by dilute HCl, acid oxalate or 5% Na_2CO_3 extraction. This finding is in marked contrast to the supposition by some that amounts of reactive iron oxides in highly weathered soils are important as predictors of reactivity to phosphorus. Buol et al. (1975) have recommended soil color as an index of iron oxides as a category of classification for soil capability. However, Weaver (1974) has provided evidence that the only mineralogical distinction between samples from some Dark Red and Red Yellow Latosols of Brazil was the presence or absence of hematite which is notably

unreactive to phosphorus. In contradiction of the assumptions of Buol et al. (1975), among Brazilian soils examined herein examples are found of very high fixing soils which are Red Yellow Latosols (e.g., BR-14) and Dark Red Latosols which are relatively moderate in fixation of P (e.g., BR-5). From the point of view of selecting a readily measurable index of reactivity to phosphorus, clay content of soils known to be on long stable, highly weathered surfaces appears to be a much more reliable variable. Better precision is gained by use of one of the three methods of evaluating " amorphous " Al, though such determinations are carried out less readily than those for soil color or clay content.

At present pedogenic factors which determine levels of " amorphous " Al in highly weathered soils have not been clearly identified. Levels of acid oxalate extractable Fe have been correlated with landscape features by Alexander (1974) and in the future genetic studies may identify more readily observable correlates of poorly organized Al such that, with clay content, more precise classification of phosphorus reactivity of highly weathered soils may be attained.

However, some uncertainty persists on the extrapolation of isotherm derived indices to field conditions. The case of the Malawian soils is instructive. Relatively high values of $NaHCO_3$ extracted native P were obtained in all four cases; further, Mughogho (personal communication) has stated that phosphorus is of secondary importance as a limiting factor on these soils. Yet, by any of the methods for extracting " amor-

phous " Al, high values were found relative to those for the whole population of soils. An association of factors may operate to make the Malawian soils distinctly different from the others; these may include the relatively more moderate temperatures, more pronounced dry seasons and more recent and violent tectonic activity of the region of provenance. Rejuvenation by air-borne material may also be a factor.

Despite some uncertainty due probably to microbial activity in some of the isotherm systems of longest duration, the present work supports the applicability of the " adsorption isotherm " approach on highly weathered soils and, in particular, the Langmuir isotherm treatment of data. However, it is clearly demonstrated that equilibrium is not attained within short periods of time. While absolute quantities of P in either the solution or the solid phase do not change greatly after 2 days for a given soil incubated at a given initial P application, concentration of P in solution does change significantly. The assumption of equilibrium implicit in the model is clearly not warranted. Further, conformity with the Langmuir model is not proof that this model accurately describes the nature of soil reaction with phosphorus. The assumption of a single or even of several adsorbing surfaces of distinctive bonding energy is questionable. While the strong correlation of P sorption indices with Al extracted by a number of mild procedures suggests strongly the participation of such Al in the removal of P from solution, the hypothesis of Jackson

(1969) that there exist in soils a continuum from crystalline forms through increasing degrees of disorder suggests that the Al with which P reacts may not be at the same chemical potential as the reaction advances. Such a condition of disequilibrium of aluminous phases implies the existence of a series of allied materials of different chemical potential and, consequently, different reactivity to phosphorus, phases existing either as discrete particles or in association. In a non-equilibrium system having Al at different potentials a given application of P may react completely with some phases of Al to form precipitates, leaving aluminous phases of lower potential to determine the equilibrium level of solution P or that level attained in the experimental period. An incubation system at a higher initial P rate may react completely with the aluminous phase which determines the " final " solution P level of a system receiving a lower initial application of P and, in consequence, an aluminous phase of lower potential may determine the solution level of P. A situation in which Al-P precipitates exist in quasi-equilibrium with aluminous phases of decreasing potential when higher initial P application rates have been made may sufficiently resemble the kinetic process of decreasing sorption with increasing saturation assumed in the Langmuir model as to give specious conformity to that model. Detection of a crystalline Al-P phase by x-ray diffraction analysis of clay fractions of 34 day reacted Nipe P isotherm samples was attempted without success. Given the insensitivity

of the technique for the small quantities of material possible even at the highest application rates and considering that possible precipitates may be poorly ordered, the results are not surprising. However, the electron microprobe technique employed by Sawhney (1973) might succeed in identifying added P distributed through a solid phase rather than merely adsorbed.

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Appendix.

Phosphate Sorption

		Initial ugP/ml	Final ugP/ml	ugP/g sorbed
Soil: B-1				
native P:				16.8
Day	2	50.0	0.18	515
		62.5	0.34	639
		75.0	0.61	761
		87.5	1.06	881
		100	1.83	999
	90	50.0	0.02	517
		75.0	0.05	767
		87.5	0.07	891
		100	0.21	1015
Soil: C-1				
native P:				11.7
Day	2	25.0	0.16	260
		37.5	0.34	384
		50.0	0.69	505
		62.5	1.34	624
		75.0	2.21	740
	90	25.0	0.02	261
		37.5	0.03	387
		50.0	0.04	512
		62.5	0.17	635
		75.0	0.24	760
		87.5	0.27	884

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: N-1						
native P:				4.9		
Day	2	50.0	0.06	504		
		62.5	0.08	629		
		75.0	0.22	753		
		87.5	0.38	876		
		100	0.57	999		
	5	62.5	0.04	630		
		75.0	0.09	754		
		87.5	0.17	878		310
		100	0.30	1002		404
		112.5	0.48	1125		448
		125	0.72	1248		527
	13	87.5	0.11	879	129	347
		100	0.16	1003	160	418
		112.5	0.28	1127	193	490
		125	0.40	1251	216	
		150	0.87	1496	283	702
		175	1.44	1741	328	825
	34	87.5	0.07	879	120	306
		100	0.14	1004	149	377
		112.5	0.20	1128	173	435
		125	0.31	1252	205	506
		150	0.50	1500	245	610
		175	1.20	1743	329	760
	90	62.5	0.02	630		175
		75.0	0.02	755		291
		87.5	0.06	879		287
		100	0.09	1004		334
		112.5	0.10	1129		378
		125	0.14	1254		431

Phosphate Sorption

		Initial ugP/ml	Final ugP/ml	ugP/g sorbed
Soil: PR-1				
native P:				15.0
Day	2	25.0	0.10	264
		37.5	0.36	386
		50.0	0.89	506
		62.5	1.89	621
		75.0	3.62	729
	90	25.0	0.02	
		37.5	0.05	
		62.5	0.18	
		75.0	0.43	

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: T-1						
native P:				36.5		
Day	2	37.5	o.10	411		
		50.0	0.20	535		
		62.5	0.41	658		
		75.0	0.81	779		
		87.5	1.44	898		
	5	37.5	0.06	411	65.3	184
		50.0	0.10	536	91.8	241
		62.5	0.23	660	116	318
		75.0	0.38	783	163	391
		87.5	0.80	904	199	471
		100	1.17	1025	237	547
	13	62.5	0.12	661	103	289
		75.0	0.22	785	136	378
		87.5	0.42	908	172	458
		100	0.69	1030	206	536
		112.5	0.90	1153	236	605
		125	1.25	1275	264	682
	34	62.5	0.12	661	101	272
		75.0	0.24	785	131	341
		87.5	0.26	909	144	367
		100	0.55	1032	187	473
		112.5	0.62	1156	207	540
		125	1.17	1275	251	630
	90	37.5	0.01	412		124
		50.0	0.02	537		164
		62.5	0.03	662		205
		75.0	0.03	787		263
		87.5	0.05	912		317
		100	0.05	1037		346

Phosphate Sorption

		Initial ugP/ml	Final ugP/ml	ugP/g sorbed
Soil: Br-2				
native P:				8.5
Day	2	37.5	0.19	382
		50.0	0.42	504
		62.5	0.85	626
		75.0	1.69	742
		87.5	2.25	862
	90	37.5	0.04	374
		50.0	0.09	508
		62.5	0.17	632
		75.0	0.30	756
		87.5	0.47	879
		100	0.74	1002

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: Br-5						
native P:				7.7		
Day	2	15.0	0.07	157		
		20.0	0.21	206		
		25.0	0.42	254		
		37.5	2.82	355		
		50.0	9.20	416		
	5	12.5	0.02	133	44.4	79.8
		15	0.07	157	57.7	106
		20	0.18	206	82.8	142
		25	0.39	254	105	179
		30	0.94	299	127	216
		37.5	1.82	365	160	269
	13	12.5	0.04	133	40.0	84.8
		15.0	0.06	157	50.8	104
		20.0	0.11	207	73.6	144
		25.0	0.24	256	93.8	182
		30.0	0.47	303	117	217
		37.5	0.99	373	150	279
	34	12.5	0.03	133	40.8	72.8
		15.0	0.06	157	53.2	95.6
		20.0	0.11	207	69.2	131
		25.0	0.22	256	89.8	163
		30.0	0.55	303	112	197
		37.5	1.10	369	140	240
	90	10.0	0.04	108		64.8
		12.5	0.08	132		84.3
		15.0	0.14	157		105
		20.0	0.23	206		137
		25.0	0.53	253		172
		37.5	2.19	361		247

Phosphate Sorption

	Day	Initial ugP/ml	Final ugP/ml	ugP/ml sorbed
Soil: Br-8				
	2	37.5	0.25	372
		50.0	1.34	487
		62.5	1.56	609
		75.0	2.19	728
		87.5	4.20	833
	90	37.5	0.05	374
		50.0	0.10	499
		62.5	0.17	623
		75.0	0.34	747
		87.5	0.41	871
		100	0.61	994
Soil: Br-11				
	2	37.5	0.11	374
		50.0	0.29	497
		62.5	0.85	616
		75.0	1.17	738
		87.5	2.10	854
	90	37.5	0.04	375
		50.0	0.07	499
		62.5	0.12	624
		75.0	0.22	748
		87.5	0.34	872
		100	0.45	996

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: Br-14						
native P:				4.6		
Day	2	37.5	0.02	380		
		50.0	0.05	505		
		62.5	0.09	629		
		75.0	0.13	754		
		87.5	0.28	877		
	5	62.5	0.03	630	92.7	256
		87.5	0.09	879	130	371
		100	0.16	1003	147	443
		112.5	0.22	1127	168	511
	13	75.0	0.04	755	97.5	266
		87.5	0.06	879	116	319
		100	0.09	1004	141	379
		112.5	0.13	1129	172	446
		125	0.18	1253	198	
		150	0.31	1500	244	
	34	75.0	0.04	755	88.9	268
		100	0.09	1004	137	382
		112.5	0.11	1129	153	436
		150	0.22	1503	223	610
	90	62.5	0.02	630		201
		75.0	0.03	755		249
		87.5	0.04	880		309
		100	0.05	1004		331

Phosphate Sorption

		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed
Soil: Br-17				
native P:				3.6
Day	2	12.5	0.13	128
		37.5	0.88	370
		50.0	2.76	476
		62.5	6.80	561
		75.0	11.6	638
	90	12.5	0.01	129
		25.0	0.05	254
		37.5	0.16	377
		50.0	0.41	500
		62.5	0.86	620
		75.0	1.62	738
Soil: M-1				
native P:				53.7
Day	2	17.5	0.05	228
		20.0	0.07	253
		25.0	0.11	303
		30.0	0.19	352
		37.5	0.59	423
		50.0	1.45	539
	90	12.5	0.01	179
		15.0	0.02	204
		25.0	0.03	304
		50.0	0.05	554
		62.5	0.06	678
		75.0	0.12	803

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: M-2						
native P:				77.7		
Day	2	10.0	0.41	174		
		12.5	0.66	196		
		15.0	0.86	219		
		20.0	1.47	263		
		25.0	2.46	303		
		37.5	5.95	394		
	5	12.5	0.11	202	68.9	156
		15.0	0.16	226	77.4	173
		20.0	0.25	276	96.6	207
		25.0	0.38	324	116	236
		37.5	1.03	443	163	331
		50.0	2.12	557	215	421
	13	15.0	0.09	227	67.0	152
		20.0	0.11	277	76.5	171
		25.0	0.23	326	99.7	215
		37.5	0.55	448	137	284
		50.0	1.22	566	188	
		62.5	1.81	685	230	447
	34	15.0	0.12	227	66.0	161
		25.0	0.26	325	96.8	218
		37.5	0.44	449	130	291
		50.0	1.21	566	188	396
		62.5	2.12	682	227	468
	90	15.0	0.07	227		148
		20.0	0.12	277		177
		25.0	0.16	326		204
		37.5	0.40	449		282
		50.0	0.73	571		351
		62.5	0.96	693		428

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: M-3						
native P:				84.9		
Day	2	8.75	0.39	169		
		10.0	0.49	180		
		12.5	0.73	203		
		15.0	1.03	225		
		20.0	2.06	264		
		25.0	3.75	298		
	5	10.0	0.09	184	60.6	
		12.5	0.15	209	72.7	
		15.0	0.17	233	85.9	
		20.0	0.32	282	120	
		25.0	0.59	329	158	
		37.5	1.58	444	228	
	13	12.5	0.08	209	65.4	
		15.0	0.10	234	71.4	156
		20.0	0.16	283	89.2	192
		25.0	0.28	332	109	234
		37.5	0.71	453	150	306
		50.0	1.68	568	207	401
	34	20.0	0.17	283	85.0	211
		25.0	0.29	332	104	251
		37.5	0.74	453	149	336
		50.0	1.43	571	188	423
	90	10.0	0.04	185		126
		12.5	0.05	209		141
		37.5	0.17	458		278

Phosphate Sorption

		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed
Soil: M-4				
native P:				89.6
Day	2	2.50	0.22	113
		5.00	0.45	136
		6.25	0.58	146
		7.50	0.75	158
		8.75	o.94	168
		10.0	1.27	177
Soil: G-1*				
native P:				33.3
Day	2	5.00	0.10	82.1
		7.50	0.25	106
		8.75	0.37	117
		12.5	0.63	152
		15.0	1.10	172
		17.5	1.57	193
	90	6.25	0.04	75.7
		7.50	0.06	85.3
		8.75	0.14	95.6
		12.5	0.25	125

* Values on basis of sample with 1-2mm fraction removed.

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: G-3*						
native P:				13.6		
Day	2	2.50	0.05	34.8		
		6.25	0.27	70.1		
		8.75	0.60	91.8		
		10.0	0.85	102		
		12.5	1.12	124		
		15.0	1.86	142		
	5	5.00	0.10	47.6	18.2	41.1
		6.25	0.20	56.3	26.4	51.7
		7.50	0.34	64.8	31.5	59.8
		8.75	0.46	73.3	28.5	64.5
		10.0	0.58	82.1	36.8	72.8
		12.5	1.14	96.5	50.4	90.5
	13	5.00	0.04	48.0	16.2	34.8
		6.25	0.07	57.3	20.2	41.6
		7.50	0.15	66.2	23.9	48.1
		8.75	0.24	75.0	29.7	57.4
		10.0	0.33	83.6	34.2	65.7
	34	5.00	0.08	47.7	17.8	36.2
		6.25	0.11	57.3	22.2	44.9
		7.50	0.13	66.3	23.8	50.3
		8.75	0.31	74.5	33.0	63.5
		12.5	0.70	100	47.0	84.7

* Values on basis of sample with 1-2mm fraction removed.

Phosphate Sorption

		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed
Soil: G-5*				
native P:				12.7
Day	2	5.00	0.10	58.1
		7.50	0.25	81.6
		10.0	0.42	105
		12.5	0.77	126
		15.0	1.22	147
		17.5	2.00	164
	90	5.00	0.05	45.1
		6.25	0.08	54.1
		7.50	0.17	63.1
		8.75	0.18	72.0
		10.0	0.32	81.4
Soil: G-6*				
native P:				9.3
Day	2	5.0	0.10	56.7
		6.25	0.13	68.9
		7.50	0.30	79.7
		10.0	0.49	103
		12.5	0.95	123
		15.0	1.77	140
	90	5.00	0.01	49.2
		6.25	0.01	59.6
		8.75	0.02	80.3
		10.0	0.07	90.5

* Values on basis of samples with 1-2mm fraction removed.

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: V-47						
native P:				7.4		
Day	2	7.50	0.27	79.7		
		8.75	0.40	90.9		
		10.0	0.54	102		
		12.5	0.92	123		
		25.0	5.96	197		
	5	7.50	0.10	81.4	29.9	58.8
		8.75	0.17	93.2	38.3	65.6
		10.0	0.23	105	45.5	76.2
		12.5	0.40	128	57.4	96.5
		15.0	0.81	149	69.9	113
		25.0	2.57	231	107	180
	13	7.50	0.07	81.7	29.5	55.3
		8.75	0.10	93.9	33.0	62.0
		10.0	0.15	106	40.6	73.6
		12.5	0.23	130	49.8	91.4
		15.0	0.41	153	61.0	108
		25.0	0.66	250	105	176
	34	7.50	0.07	81.7	30.4	56.7
		8.75	0.09	94.0	34.6	64.7
		10.0	0.16	106	44.2	81.2
		12.5	0.26	129	53.0	95.7
		25.0	1.71	240	111	186
	90	7.50	0.12	81.2		53.6
		8.75	0.15	93.4		63.1
		10.0	0.20	105		71.0
		12.5	0.38	128		89.9
		15.0	0.62	151		108
		25.0	2.54	232		168

Phosphate Sorption

		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed
Soil: V-65				
native P:				7.6
Day	2	7.50	0.20	80.6
		8.75	0.32	91.9
		10.0	0.43	103
		12.5	0.98	123
		25.0	5.08	207
	90	7.50	0.05	82.1
		8.75	0.06	94.5
		10.0	0.10	107
		12.5	0.34	130
		15.0	0.37	154
		25.0	1.60	242
Soil: V-77				
native P:				7.5
Day	2	12.5	0.11	132
		15.0	0.14	156
		20.0	0.29	205
		25.0	0.57	252
		37.5	2.47	358
	90	20.0	0.06	
		25.0	0.30	
		37.5	0.34	
		50.0	1.60	
		62.5	4.40	
		75.0	8.67	

		Phosphate Sorption			Phosphate Desorption	
		Initial ugP/ml	Final ugP/ml	ugP/ml sorbed	ugP/g extracted on first extraction	Total ugP/g extracted; sum of 5 extractions
Soil: V-91						
native P:				7.1		
Day	2	15.0	0.13	156		
		20.0	0.20	205		
		25.0	0.37	253		
		37.5	1.13	371		
		50.0	2.34	484		
	5	15.0	0.06	156	58.6	106
		25.0	0.28	254	100	188
		37.5	0.80	374	157	288
		50.0	1.90	488	213	370
		62.5	3.90	593	268	458
	13	25.0	0.20	255	93.6	176
		30.0	0.29	304	111	215
		37.5	0.64	376	144	270
		50.0	1.10	496	193	355
		62.5	2.41	608	241	449
		75.0	4.83	709	282	533
	34	25.0	0.16	255	96.6	186
		30.0	0.27	304	119	207
		37.5	0.45	378	150	275
		50.0	0.95	498	202	371
		62.5	1.96	612	255	454
		75.0	3.56	721	303	538
	90	25.0	0.08	256		166
		37.5	0.20	380		253
		50.0	0.82	499		338
		62.5	1.30	620		420
		75.0	2.62	731		459
		87.5	5.08	831		479