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PHOSPHATE FIXATION BY TROPICAL SOILS

by

CARLOS RIVERA-HOUSE

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ACT

RIVERA-HOUSE, CARLOS. Phosphate Fixation by Tropical Soils. (Under the direction of EUGENE J. KAMPRATH).

The amounts of phosphate required to support equilibrated solution concentrations of 0.1 and 0.2 ppm were determined for a group of soils from Southeastern Mexico, Colombia and one soil from North Carolina. These quantities were related to the amount of phosphate extracted by 0.05N HCl + 0.025N H_2SO_4 and 0.5M $NaHCO_3$.

The values of phosphate extracted with the dilute acid solution appeared to be a function of the amount added. The dilute acid extraction seemed to give a measure of the capacity (Q) factor of the soil.

The alkaline solution extracted less P than the dilute acid solution. The amounts of P extracted by the $NaHCO_3$ appear to give a measure of surface P which probably is an important factor in governing P in solution.

It was concluded that in order to use extraction data to ascertain the level of P in the equilibrium soil solution, the soils have to be characterized as to the properties that determine the concentration of P in solution.

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INTRODUCTION

In many tropical areas of the world, the production of crops is often limited because of the low availability of native phosphates. The climatic conditions are commonly conducive to high rates of weathering that tend to produce high degrees of acidity with concomitant increases of the activity of aluminum and iron compounds. Under these conditions the availability of phosphates added as fertilizers is greatly decreased because reactions with soil components reduce the solubility of the phosphatic materials. The forms of phosphate of reduced solubility are spoken of as being fixed. These conditions prevail in extensive areas of the world where soils are formed on volcanic depositions of ash. The rates of weathering are frequently high in these soils because of the large degree of subdivision of the material, which, by exposing a large surface area to chemical weathering agents, bring about drastic changes in relatively short spans of time.

As a consequence of fixation reactions, rather large amounts of fertilizer phosphates often have to be applied in order to obtain a response from the growing plants. There is evidence in the literature that continued applied

applications of phosphate, or alternatively the use of massive applications of phosphate, can quench the capacity of soils to fix phosphate and at the same time provide an amount of the nutrient sufficient to meet plant needs.

Chemical methods have been used for some time to measure the so-called available phosphate, and although, when properly correlated with plant responses, have gone a long way to predict the likelihood of a response to the applied phosphate fertilizer, these methods do not provide an answer to the very important question: How much phosphate to apply to correct or prevent deficiencies?

Existing information indicates that the use of adsorption isotherms may provide a means to assess the amount of phosphate to be added to a soil so that a predetermined concentration will remain in the equilibrated soil solution and plants presumably will be able to obtain the needed phosphate. This hypothesis has been put to test and the results have been encouraging. Therefore, this work was undertaken with the following objectives in mind.

(1) To construct, for a group of soils of varying properties from Southeastern Mexico and one soil from the Llanos Orientales of Colombia, phosphate adsorption isotherms from which to determine the amounts of phosphate needed to be

applied in order to obtain a predetermined equilibrated solution concentration that was selected at 0.2 ppm P.

(2) To attempt to relate the values of added phosphate to the extraction data obtained by use of the two common extracting solutions: .05 N HCl + .025 N H_2SO_4 and 0.5 M $NaHCO_3$ at pH 8.5.

(3) To evaluate the conditions leading to fixation of phosphate by the individual soils.

REVIEW OF LITERATURE

Phosphate Fixation

It is now generally recognized that phosphate applied as a fertilizer will react readily with soluble cations as well as with the clay minerals of the soil to form compounds of reduced availability. These forms of reduced solubility phosphates are spoken of as "fixed". Various hypotheses have been advanced in the past to explain the mechanism of the reaction or reactions responsible for the fixation of phosphate, but a rather bulky body of evidence has shown that compounds of iron and aluminum are the most important factors in acid soils (Ellis and Truog, 1955). Under alkaline conditions, calcium and magnesium compounds are the primary materials reacting with phosphate (Lindsay and Moreno, 1960).

Fixation by Acid Soils

For a long time a controversy has existed among scientists regarding the nature of the fixation reaction. Some support the point of view that precipitation is the basic mechanism (Hemwall, 1957b; Low and Black, 1950), whereas others explain the observed results as originating from an adsorption reaction (Hsu, 1964; Fried and Dean, 1955)

Both mechanisms have been shown to be involved, the dominance of one over the other depending on the particular conditions (Hsu, 1965).

Low and Black (1950) have hypothesized that kaolinite is a complex salt of the weak silicic acid and the weak base aluminum hydroxide. Therefore, it would ionize in solution in accordance with solubility product principles. Phosphate by reacting with aluminum would disrupt the equilibrium causing the kaolinite to dissolve.

Hemwall (1957b) has indicated that discrete compounds with characteristic solubility products are formed when phosphorus reacts with kaolinite and montmorillonite. He concluded that phosphate is fixed by clay minerals by reacting with soluble aluminum which is released from exchange sites and from lattice dissociation of the clay to form a very insoluble phosphate of aluminum which he postulated was variscite.

Haseman et al. (1950), working with montmorillonite, illite, kaolinite, gibbsite and goethite, found a similar mechanism of fixation. One initial reaction occurred at a rapid rate and a second reaction occurred at a slower rate. The conclusion was reached that the first reaction is brought about by interaction of phosphate ions with aluminum

and iron readily available and the second one is the result of phosphate reaction with aluminum and iron originating from the decomposition of the minerals under study. These two reactions have been observed by other workers (Kittrick and Jackson, 1955; Low and Black, 1950; Hsu and Rennie, 1962a,b; Hemwall, 1957b). These results led Kittrick and Jackson (1955) to indicate, from observations made by electron microscope, that with time the surfaces of aluminum and iron in contact with the phosphate solutions dissapeared and a new, separate phase of aluminum and iron phosphate was formed. They suggested that solution-precipitation is an important process in phosphate fixation in soils. Ellis and Truog (1955) in studies with montmorillonite measured fixation before and after the removal of free aluminum and iron oxides and found that they were responsible for most of the fixation against weak acid extraction. Wey (cited by Larsen, 1967) demonstrated that hectorite does not fix phosphate. This evidence is significant because in this mineral magnesium substitutes for aluminum in the octahedral positions of montmorillonite and thus lend support to the hypothesis that aluminum is necessary for clays to fix phosphate.

The formation of crystalline aluminum phosphate, ammonium substituted or potassium taranakite has been shown to occur rapidly at pH 4 in allophane and halloysite (Wada, 1959). The reaction was slower at pH 7. It is thought that taranakite is formed by precipitation of a soluble phospho-aluminum complex anion with potassium (or ammonium) ions. This reaction has been suggested to occur under field conditions (Ling et al., 1966).

Hsu and Rennie (1962a) suggested that the mechanism of fixation basically follows the solubility product principle, but the total activity of all forms of aluminum and iron oxides should be a concern in governing the concentration of phosphate in solution. Hsu (1964) has presented evidence that the fixation of phosphate is a surface reaction when a slightly acid soil is treated with dilute solutions of phosphate of pH 7. He concluded that the adsorption occurred on the surfaces of amorphous aluminum hydroxides and iron oxides. He explained that the rapid, initial reaction which is completed in a few hours is due to the native surface reactive amorphous aluminum hydroxide and iron oxides already present in the soil. The subsequent slow reaction is due to similar surface reactive components developed during the aging process.

In further support of the concept of fixation as an adsorption reaction, Fried and Dean (1955) found that iron and aluminum saturated exchange resins had the ability to fix phosphate which was readily exchangeable with radioactive phosphate and concluded that the exchangeability observed was improbably high for a precipitate and, therefore, it was an adsorption process.

Compliance with the Freundlich isotherm has long been accepted as a criterion for an adsorption reaction. Low and Black (1950) studied the fixation of phosphate in dilute solutions by kaolinite. Their results were found to follow the Freundlich isotherm and from a study on the heat of reaction, which was found to be positive, they concluded that the nature of the adsorption reaction was chemical. However, they did not indicate whether the seat of the reaction was the clay or the sesquioxides. Fried and Shapiro (1956) made successive extractions with distilled water and from the pattern of release the interpretation was made that it was a desorption reaction. Sigurd Larsen (1967) in a review article has offered the alternative explanation that the observed pattern of extraction may have been a result of the dissolution of phosphorus compounds.

Phosphate Fixation in Alkaline Soils

The exchange complex of alkaline and calcareous soils presents a high degree of calcium and/or magnesium saturation. Chang and Sherman (1961) in fixation studies found that in alkaline soils of Hawaii phosphate fixation occurs largely by chemical precipitation by calcium and magnesium ions. Lindsay and Moreno (1960) have pointed out that these ions, among others, must be considered as potential reactants with phosphate.

In a review article, Hemwall (1957a) concluded that in alkaline and calcareous soils "the fixation of phosphate is due to the formation of a whole series of insoluble calcium compounds. These compounds form solid solutions and are rather difficult to characterize chemically, as they tend to be quite heterogenous. Further, there is evidence that phosphorus can be fixed by Al^{+++} or $Al(OH)_3$ in the clay fraction of alkaline soils, the fixation being partially a function of the other cations present".

The Adsorption Maximum

It has already been mentioned that phosphorus fixation reactions have been characterized by the Freundlich adsorption isotherm. This approach has been criticized (Hemwall, 1957a, on the grounds that many precipitation reactions also follow this isotherm.

Larsen (1967) has criticized this isotherm because it is purely empirical and the constants have no physical meaning. Hsu and Rennie (1926b) working on precipitation reactions of phosphate on a cation exchange resin found that the precipitation data conformed to the Freundlich isotherm and the Langmuir isotherms. They concluded that close agreement between phosphate fixation and the two isotherms may not necessarily imply an adsorption reaction in soils.

Onikura (1964) working with volcanic ash soils containing allophane found that the equilibrated solution in the soil-phosphate system was affected by the initial phosphorus concentration, the adsorption capacity of the soil and the pH of the system. He concluded that the equilibrium concentration was governed by the ratio of the initial phosphorus concentration to the adsorption capacity of the soil. That pH affects the adsorption capacity of soils has been reported by other investigators (Hsu and Rennie, 1962a; Woodruff and Kamprath, 1965).

The time of contact between the soil and phosphate solution affect the adsorption reaction (Hsu, 1964; Fassbender, 1969). Also, the decomposition reactions made reference to earlier make it difficult to define a sorption maximum (Rich and Thomas, 1960).

In spite of the criticisms associated with the characterization of adsorption reactions and the use of the Freundlich and Langmuir isothers, Olsen and Watanabe (1957) found that the second isotherm is useful to describe adsorption data because an adsorption maxima can be determined, whereas using the Freundlich isotherm this is not possible. A linear form of the original Langmuir formula was used:

$$C \quad x/m = \frac{1}{kb} + \frac{C}{b}$$

where:

x/m = mg P adsorbed per 100 g of soil

b = the adsorption maxima

k = a constant related to the bonding energy of the adsorbent for the adsorbate

C = the equilibrium concentration.

The adsorption maxima was found to be related to the surface area of soils as measured by ethylene glycol retention. It was further found that for a given surface area, the acid soils held 2.17 times as much phosphate as the alkaline soils.

The phosphate relations of volcanic ash soils of Central America have been described by Fassbender (1966) by means of the Langmuir isotherm.

The Residual Availability of Phosphate Fertilizers

The fertilizer phosphorus recovered by annual crops planted concurrently with the fertilizer application lies in the range of 10 to 30% (Hemwall, 1957a). Therefore, considerable interest exists in finding out the availability of the phosphorus not used by the crop planted at the same time of the application.

It is recognized that the residual effect of phosphates in soils is dependent upon the nature of the compounds formed when the fertilizer reacts with soil components (Shelton and Coleman, 1968). Lindsay and Taylor (1960) compared various phosphate compounds as sources of phosphorus for plants and concluded that amorphous iron and aluminum phosphates are moderately good sources of phosphorus. The taranakites, which form readily in volcanic ash soils in the presence of potassium and/or ammonium ions, released phosphate over a period of several months. However, the availability of ammonium taranakite was much lower than that of the potassium analog.

Ensminger and Pearson (1957) have indicated that the residual effect of phosphate fertilizers is proportional to the amounts initially applied and inversely related to the time elapsed since the last fertilizer application

(McLachlan, 1963). In soils of very high fixing properties, the residual effects are extremely low. Fox (1969) has pointed out that little or no residual effect may be expected from small rates of phosphorus application on high fixing volcanic ash soils. This observation probably may be related to the one by Onikura (1964) that in this kind of soils small applications of phosphate tends to be preferentially fixed as occluded phosphate, which is known to be of low availability.

In the cases where the residual effects of phosphorus applications have been low or non-existent, it has been observed that the phosphorus requirement of the soil has been reduced. This has been explained as being due to the blocking of fixation sites by previously applied phosphate (Hughes and Searle, 1963). Large residual effects have been recorded where large applications of phosphate have been made. This would appear to lend support to the statement of Ensminger and Pearson (1957) cited earlier. Younge and Plucknett (1966) were able to obtain satisfactory high yields in aluminous-ferruginous latosols of Hawaii six years after large applications of phosphorus. Kamprath (1967) obtained similar results in a Georgeville soil of North Carolina.

The Degree of Phosphate Saturation and Its Availability

The discussion in the previous section suggests that the availability of fertilizer phosphorus is a function of the degree of saturation of the sorbing complex. That percent of phosphate saturation of the sorbing capacity and plant uptake correlate significantly, has been shown by Fried and Dean (1955). Fox and Kamprath (1970) were able to obtain from 92 to 99 percent of the maximum yield in pot experiments using millet when they saturated the sorption capacity of the soil with an amount of phosphate sufficient to render an equilibrium concentration of 0.2 ppm P. They pointed out that this concentration may not be the optimal for plant nutrition. As will be seen later, other factors have to be considered.

Woodruff and Kamprath (1965) investigated the phosphorus adsorption maxima of several soils and its relation to phosphorus availability to plants. They found that low fixing soils required a higher degree of saturation than soils with a large fixing capacity.

The Uptake of Phosphorus by Roots and Some Factors Affecting It

Barber (1966) has presented data that strongly supports the point of view that diffusion is the most important process by which phosphate ions move toward the root surface. Within limits, the uptake of P is known to be proportional to the amount present in solution. The root acts as a pump which removes phosphate from the immediate solution, therefore, for uptake to be maintained, the soil solution has to be replenished. Many factors may affect the processes that tend to replenish the P removed, and some of them are discussed in the following paragraphs.

Intensity, Capacity and Kinetic Factors

At any given moment, the availability of phosphorus is a function of intensity, capacity and kinetic factors in equilibrium between the various solid and liquid phases in the soil (Pizer, 1965).

The concentration of P in solution is a measure of the intensity factor (Williams, 1962). As plant removal depletes the amount of P present and if uptake is to be maintained, the solution has to be replenished by the pool of labile P, the quantity of which is regarded as the capacity factor.

The kinetic factors described the rate at which the solid phase replenishes the solution.

It has been suggested that for rapidly growing crops with short duration of growth, the three parameters are important, whereas for slow growing perennial crops with extensive root systems the capacity factor may be more important than intensity or rate (Pizer, 1965).

Soil Moisture Content

As water is lost from the soil via evaporation or plant uptake, the soil solution becomes more concentrated in salts which by decreasing the activity of phosphate may lead to decreased uptake

Soil Texture

The rate of diffusion of phosphate has been found to be affected by soil texture. Slower rates have been measured in coarse textured than in fine textured soils (Olsen and Watanabe, 1963). For soils of similar P saturation but different clay contents, a higher content of clay correlated significantly with phosphorus uptake by plants (Baldovinos and Thomas, 1967). As adsorption of phosphorus generally correlates with clay content, this would lend support to the finding of Woodruff and Kamprath (1965) that lower P saturations are adequate for clay soils.

Soil Physical Conditions

Williams (1962) has pointed out that poor aereation inside aggregates may prevent root exploration which would decrease interception of phosphate which is also an important mechanism of P absorption by plants (Barber, 1962). The same result would probably be found in compacted layers of soil.

MATERIALS AND METHODS

Soils Used

The soils used in this study are considered to be representative of conditions existing in Southeastern Mexico. A description of the profiles sampled is presented in Appendix A.

Two soil samples were also obtained from the Llanos Orientales of Colombia at the region of Carimaqua. A sample of the Georgeville soil used by Woodruff and Kamprath (1965) and Kamprath (1967) was also included.

Laboratory Methods

Chemical Determinations

The results of chemical analyses performed on the soil samples of Mexico have been published (Kamprath *et al.*, 1969)[1]. For the Colombian soils, as well as the Georgeville soil, pH was determined in a 1:1 soil:water ratio using a pH meter. For the same soils, exchangeable Al was measured

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[1]Appreciation is expressed to Messrs. O. D. Philen and Ellis Edwards of the N. C. State University for assistance with X-ray diffraction analyses. Also appreciation is expressed to Dr. E. J. Kamprath of the N. C. State University faculty staff who made available the profile descriptions and for his permitting partial reproduction of Table 1 and Table 2.

by titration of N KCl leachate according to Lin and Coleman (1960). Organic matter was determined for the two Colombian samples by a modified Walkley-Black wet oxidation procedure (Allison, 1965).

The soils were prepared for X-ray diffraction studies of the clay fraction by methods described by Jackson (1956) Clay suspensions were allowed to dry on glass slides for parallel orientation. Ethylene glycol solvation and heat treatments were used in clay mineral identification. A General Electric XRD-5 diffractometer was used to obtain X-ray patterns, from which the relative amounts of clay minerals were made. Preparation of slides in this manner for samples 5, 6 and 25 was impossible. These were mounted by spreading the clay on the slide with a spatula.

For some of the soils, no data on clay contents or kind of clay was obtained due to the limited amount of sample available.

Adsorption Isotherms

To construct the adsorption isotherm, three grams of soil previously having been air dried and screened through a 1.0 mm mesh were placed in a plastic centrifuge tube of 50 ml of capacity which were previously weighed. Thirty ml of $Ca(H_2PO_4)\cdot H_2O$ solutions ranging from 0 to 100 ppm P were

added to soils which previous experience (Kamprath et al., 1969) had indicated were relatively high fixers of P and the concentrations ranged from 0 to 10 ppm P for soils of relatively low fixation capacities. All the solutions were 0.01 M with $CaCl_2 \cdot 2H_2O$. No attempt was made to adjust pH of the solutions.

At least four different P concentrations and two replicates were used for each soil. One drop of a solution of benzoic acid, made by diluting one gram of the crystals to one liter, was added to each sample to retard microbial activity.

The samples were equilibrated for six days at an approximate temperature of 25°C and were continually shaked end over end using a reciprocal shaker. After the period of equilibration had ended, the tubes were centrifuged at 12,000 rpm for 15 minutes. The clear supernatant was removed and saved for determination of P. The centrifuge tubes containing the soil samples were immediately weighed.

The determination of P was made using the method described by Murphy and Riley (1962) using a Beckman Model B spectrophotometer. The difference between the amount of P

added and that remaining in the equilibrated solution was assumed as having been adsorbed by the soils.

Extraction Methods

The more acid soils, pH less than 6.5, were extracted with .05 N HCl + .025 N H_2SO_4 in a 1:4 soil:solution ratio. The less acid group of soils, pH 6.5 and greater, were extracted using 0.5 M $NaHCO_3$ solution at pH 8.5 using a 1:5 soil:solution ratio. The tubes were in both cases shaken end over end for five minutes and then centrifuged and filtered through Whatman filter paper No. 42. Phosphorus in the extracts was determined using the method previously mentioned.

A correction had to be made to account for the P that remained in the entrapped solution from the adsorption experiment. This was done by using the differences in weight of the empty tubes plus the three grams of soil and the weight after the solutions of the first centrifugation had been drained. In this way, knowing the volume of solution and its concentration, the amount of P was calculated and subtracted from the corresponding extraction figure. During all the time of the experiment the soil samples were kept moist. All the P values reported throughout this work are in elemental P.

RESULTS AND DISCUSSION

Characteristics of the Soils Used

A description of the soils studied is given in Appendix A. The data for pH, exchangeable Al, exchangeable Ca+Mg and percent organic matter are shown in Table 1. Estimates of the clay content and relative content of the kind of clay minerals are given in Table 2. Samples 1 through 25 came from Southeastern Mexico; samples 26 and 27 came from the Llanos Orientales of Colombia and sample 28, the Georgeville soil, came from the Piedmont of North Carolina. These soils have been derived from different parent materials that may be separated into four general groups.

(1) Volcanic ash and flow rocks, samples No. 1 to No. 10.

(2) Unconsolidated alluvial and colluvial sediments, samples 11 through 21 and samples No. 26 and No. 27.

(3) Material originated from the dissolution of limestone, samples 22 to 25.

(4) The Georgeville soil derived from sericitic schist.

The groups 2 and 3 may have been influenced by additions of volcanic ash.

There were differences between soils originating from similar parent materials. The San Andres and Olotepec

Table 1. Chemical properties of the soils used

Sample No.	Location	Horizon & depth, cm	pH	Exc. cations, me/100g Al	Ca + Mg	Organic matter, %
1	San Andres Tuxtla	A, 0-10	7.1	0	22.7	1.5
2	San Andres Tuxtla	B, 10-70	7.2	0	24.1	0.46
3	San Andres Tuxtla	IIIb, 200-230	7.3	0	35.7	0.39
4	San Andres Tuxtla	IIIBb, 230-300	6.6	0	36.5	0.10
5	Olotepec	A, 0-40	6.3	0	6.9	5.9
6	Olotepec	B, 40-70	6.4	0	5.5	1.7
7	Catemaco	A, 0-25	6.6	0	13.1	6.6
8	Covarrubias	A, 0-15	6.4	0	9.0	2.3
9	Acayucan	A, 0-20	5.9	0	0.4	5.4
10	Acayucan	B, 50-120	4.9	0	5.4	1.4
11	Cardenas	A, 0-25	6.9	0	17.6	1.9
12	Subana Huimanguillo	A1, 0-25	4.6	1.5	1.2	2.5
13	Sabana Huimanguillo	A3, 30-45	5.0	.95	1.0	2.5
14	Sabana Huimanguillo	B2, 100-120	5.2	0	1.1	0.95
15	Presa Malpaso	A, 0-30	5.4	1.5	0.58	2.3
16	Presa Malpaso	B2, 40-50	5.1	3.2	0.58	
17	E. Zapata	A1, 0-20	5.9	.08	2.5	2.1
18	E. Zapata	B1, 25-50	5.2	2.7	2.4	
19	E. Zapata	B2, 100-150	4.8	4.3	2.0	
20	Uzumacinta River	A, 0-25	6.1	0	2.8	0.44
21	Uzumacinta River	B1, 25-50	7.4	0	8.4	0.24
22	Escorcega	A, 0-20	8.0	0	36.0	6.8
23	Escorcega	C, 80-100	8.5	0	37.0	
24	Kankab	A, 0-25	6.5	0	13.5	3.7
25	Tzekel-Muna	A, 0-10	7.4	0	40.5	13.3
26	Carimagua	A, 0-10	4.6	3.26	.42	4.0
27	Carimagua	10-20	4.5	3.60	.28	2.0
28	Georgeville	--	5.9	1.10	--	1.8

Table 2. Estimated clay mineral content of selected southeastern Mexico soils

Sample No.	Profile No.	Location	Horizon and depth (cm)	Clay content %	Relative abundance of clay minerals in 2u fraction[a]
1	1	San Andres-Tuxtla	A 0-70	12	Degraded 14Å, possibly allophane[b]
2	1	San Andres-Tuxtla	B 70-200	2	Amorphous material, possibly allophane
3	1	San Andres-Tuxtla	A1 200-230	28	Degraded 14Å, possibly allophane
4	1	San Andres-Tuxtla	B1 230-300	44	Degraded 14Å, 7Å, possibly allophane
5	2	Olotepec	A 0-40	11	Allophane M, vermiculite T
6	2	Olotepec	B 40-70		Allophane M, feldspar S, halloysite T
7	3	Catemaco	A 0-25	39	Kaolinite M
9	5	Acayucan	A 0-20	9	Kaolinite M, halloysite S, montmorillonite T
10	5	Cayucan	B 50-120	23	Kaolinite
11	6	Cardenas	A 0-25	27	Montmorillonite M, illite T, kaolinite-halloysite T
13	7	Huimanguillo	A2 30-45		Kaolinite M, vermiculite S
14	7	Huimanguillo	B3 100-120	11	14Å major, kaolinite, major
15	8	Presa Mal Paso	A 0-30	39	Kaolinite M-vermiculite T, gibbsite T
16	8	Presa Mal Paso	B2 40-50		Kaolinite M, vermiculite T, gibbsite T
17	9	Poblado E. Zapata	A 0-20	10	Kaolinite M, illite S, quartz T
18	9	Poblado E. Zapata	B1 25-50		Kaolinite M, illite T, quartz T
19	9	Poblado E. Zapata	B22 100-150		Kaolinite M, illite T, montmorillonite T

(continued)

Table 2. (continued)

Sample No.	Profile No.	Location	Horizon and depth (cm)	Clay content %	Relative abundance of clay minerals in 2 u fraction[a]
20	10	Uzumacinta	A 0-25		Halloysite-kaolinite M, montmorillonite T, quartz T, feldspar T
21	10	Uzumacinta	B 25-50	12	Kaolinite, major-14Å very minor
22	11	Escorcega	A 0-20	27	14Å major-10Å minor
23	12	Escorcega	- 80-100		
24	12	Yucatan (Kankab)	A 0-25	72	Kaolinite-M
25	13	Yucatan (Tzekel)	A 0-10	44	Allophane M, kaolinite S, zircon T montmorillonite T
26		Carimagua	A 0-10	36	Kaolinite M
27		Carimagua	10-20		Kaolinite M
28		Georgeville		38	Kaolinite M

[a]M = much, estimated to be 50%
S = some, 10-50%
T = trace, 1

[b]Tentative

soils which were formed from basaltic volcanic ash under conditions of identical precipitation, 2100 mm per year with a distinct dry season, differed in pH, the Olotepec soil being more acid and containing lower quantities of exchangeable Ca+Mg. It is possible that the ash materials in the San Andres soil are more basic than those in the Olotepec soil. It is also possible that the soil at San Andres may have been subjected to more frequent depositions of ash material since there was a buried soil in the profile. It is pertinent to note that the San Martin Los Tuxtlas volcano which is in this area has had eruptions in 1664, 1739, 1829 and 1922 (Aguilera, 1969).

In the Olotepec soil, allophane is the predominant mineral in the clay fraction (2u). This may indicate a young state of weathering. The X-ray diffractograms of the San Andres soil indicated degraded 14 Å reflections. Field observations showed that this soil shrinks and cracks when dry. These two factors would seem to indicate the presence of montmorillonite (Kamprath et al., 1969). The X-ray patterns indicated the presence of amorphous materials that were thought to be allophane. This material was present throughout the profile, however, field tests with NaF solution (Fieldes and Perrot, 1966) indicated

little or no allophane. It was inferred (Kamprath et al. 1969) that the dry season plus the high base status would inhibit the formation and persistence of allophane. These conditions are rather conducive to the formation of 2:1 and 2:2 minerals (Besoain, 1969). Birrell and Fieldes (1968) noted that palagonite, an amorphous mineral, formed from basaltic materials in a basic environment, may show weak XRD lines of montmorillonite and further pointed out that some properties of palogonite resemble those of montmorillonite. The soil sampled at Catemaco, sample No. 7, contained 13.1 me of exchangeable Ca+Mg, 6.6% organic matter and 39% clay. No data regarding precipitation was obtained. This soil developed in a relatively recent deposition of basalt, which may explain the high base status. The predominant clay mineral, however, was kaolinite. This would seem to indicate a more advanced degree of weathering which is generally inconsistent with the high base content. Therefore, it is possible that additions of ash can explain the presence of the high amounts of exchangeable Ca+Mg.

The soil from the Acayucan area, samples No. 9 and 10, had more red coloration than the other soils in the group. The presence of free iron is suggested, but no actual

determinations were made. Its low content of exchangeable Ca+Mg (Table 1) also may indicate a more advanced degree of weathering. The high precipitation, 2000 mm per year, and occurrence of the soil on rolling and hilly uplands may have removed soil material by geologic erosion.

The soils originated from alluvial and colluvial sediments of group No. 2 include the soils sampled at Cardenas, Sabana Huimanguillo, Presa Mal Paso, Emiliano Zapata and the depositional surfaces of the Uzumacinta River. The Cardenas soil contained more exchangeable Ca+Mg and a higher pH. Only the Uzumacinta soil had a higher pH at 7.4 but contained, however, less than half as much exchangeable Ca+Mg (Table 1) than the soil at Cardenas. All the other soils in this group were distinctly acid (pH 1:1 in water) and contained variable levels of exchangeable Al. With the exception of the soil from Cardenas in which montmorillonite was the predominant clay mineral, kaolinite was found to be the chief constituent of the clay fraction of the other soils in this group. The surface soil of the Uzumacinta River area contained in addition to kaolinite, an almost equal amount of halloysite. The percentages of clay for all the soils in this group ranged from 10 to 39 (Table 2).

The soil from Carimagua in Colombia was represented by samples No. 26 and 27. They had similar properties, both being strongly acid. The pH values were 4.6 and 4.5. Exchangeable Al was 3.26 me/100g for the surface soil and 3.60 for the subsoil. The clay content of the surface soil was 36% and kaolinite was the predominant clay mineral. No profile description was available for this soil.

The third group of soils, as already mentioned, is composed of those derived from residual material resulting from dissolution of limestone. The locations sampled were those at Escorcega, the "kankab" soil near Merida, and the Tzekel soil of Northern Yucatan. The four samples which represented these soils showed pH values above 7 with the exception of the kankab soil which was slightly acid. All the samples had a high exchangeable Ca+Mg status which ranged from 13.5 me/100g for the kankab soil to 40.5 me/100g for the Tzekel soil. The mean annual precipitation is around 800 mm with a definite dry season. Wide variations in clay content were found to occur. The values ranged from 24 to 72% (Table 2). The kind of clay found was also variable. Sample No. 22 taken at Escorcega showed very definite 14 Å peaks with the concurring presence of 10 Å minerals. For subsoil sample No. 23, which was a mixture of soil and limestone, and which showed a strong reaction to

HCl. The limited amount of sample prevented the obtainment of data on content or kind of clay minerals present. Becaus of the high base status, it was quite unexpected to find that soil No. 25 contained a high amount of clay in which allophane was the most abundant constituent. It would suggest that at some time in the formation of the soil there was a deposition of volcanic ash. This soil also contained a high amount of organic matter which typically is associated with allophane (Besoain, 1969).

The Georgeville soil used in this study was sampled near Pittsboro, N. C. It was moderately acid and contained 1.1 me/100g of exchangeable Al. The clay content was 38% with kaolinite the predominant clay mineral.

Adsorption Study

In Table 3 are presented the data obtained by plotting C/x/m versus P remaining in the equilibrium solution according to the linear form of the Langmuir equation

$$C/x/m = \frac{1}{kb} + \frac{C}{b} .$$

Table 3. Phosphate adsorption maxima of the soils used in this study

Soil No.	pH	Ads. max.	k	r	Prediction equation
			Alkaline Soils		
1	7.1	308	3.59	.997**	3.2432 + .9039
2	7.2	218	6.97	.991**	4.5864 + .6578
3	7.3	196	9.52	.998**	5.1079 + .5367
21	7.4	102	14.04	.997*	9.8328 + .7004
22	7.9	110	9.04	.987	9.1059 + 1.0068
23	8.5	112	41.64	1.000**	8.9281 + .2144
25	7.4	584	21.83	.999**	1.7135 + .0785
			Acid Soils		
4	6.6	550	1.14	.996	1.8199 + .6017
5	6.3	1050	6.52	.991	.9497 + .1456
6	6.4	1078	4.87	.995	.9274 + .1903
7	6.6	1060	7.55	.978*	.9434 + .1249
9	5.9	118	10.02	.997	8.4621 + .8444
10	4.9	600	6.35	.931	1.6676 + .2628
11	6.9	106	31.86	.990	9.4772 + .2975
13	5.0	497	18.13	.999**	2.0141 + .1111
14	5.2	551	36.26	.996	1.8164 + .0501
15	5.4	2021	9.66	.999**	.4947 + 0.512
16	5.1	1186	14.69	.994**	.8432 + .0574
17	5.9	95	31.67	.999**	10.5813 + .3341
18	5.2	572	28.17	.995	1.7468 + .0620
19	4.8	519	13.48	.996**	1.9282 + .1430
20	6.1	126	.28	.999**	7.9501 + 28.0614
24	6.5	500	13.17	.998**	2.0015 + .1520
26	4.6	531	7.04	.992	1.8836 + .2677
27	4.5	566	11.48	.992	1.7664 + .1538
28	5.9	480	16.50	.969	2.0873 + .1265

With the initial concentrations originally used for the soils with low relative fixation properties, the quantities of P remaining in solution were very large and they tended to deviate from the straight line, therefore, not adhering to the Langmuir equation. This was found to occur when the initial solutions had a concentration larger than 25 ppm P. Onikura (1964) for volcanic ash soils of Japan pointed out that the equilibrated P concentration was governed by the ratio of the initial P concentration to the P adsorption capacity of the soils. Olsen and Watanabe (1957) reported deviations from the straight line relationship when the initial P concentrations were larger than 9×10^{-4} M (28 ppm P). This was verified by Rennie and McKercher (1959) who found for four soils of Canada that the isotherms broke in the vicinity of a final solution concentration of 20 ug P/ml.

When lower initial concentrations were used, the soils adsorbed most of the P and the quantities remaining in solution were difficult to determine because the concentrations of P apparently were beyond the lower limit of detection of the method employed. Because of this, for some of the soils only three points were used to calculate the adsorption maximum.

No attempt was made to correct for surface P. It was assumed this correction to be relatively unimportant since it has been shown (Olsen and Watanabe, 1957) that for soils of low P the correction is small.

The simple regression coefficients r, see Table 3, were significant and this was accepted as evidence that the data followed the Langmuir isotherm.

The values for the adsorption maxima were found to vary widely between soils as would have been expected from the chemical analyses given in Table 1. As mentioned previously, Olsen and Watanabe (1957) found that acid soils tended to adsorb more P than alkaline soils. This was, in general, the trend followed by the soils used in this study. The average b values for alkaline soils was 232 ug P/g and 637 ug P/g for the acid soils.

The magnitude of the adsorption values was comparable to that of the values found by Fassbender (1966) for soils of Costa Rica which had a relatively high clay content. However, some of the figures were higher than the ones reported by Valverde (1970) for acid soils from Peru.

Phosphate Adsorption Maxima of Surface Soils

In Table 4 the adsorption maxima for the surface soils have been arranged in groups according to the parent material from which the soils originated. The first group, comprised of those soils originated from volcanic ashes, presents differences in pH, clay content and kind of clay composition. No exchangeable Al was detected in any of the soils. The content of exchangeable Ca+Mg was found to range from 0.4 me/100g for the Acayucan soil to 22.7 me/100g for the San Andres soil (Table 1).

The San Andres soil had an adsorption maximum of 308 ug P/g. Degraded 14 Å reflections were found in the clay fraction. In addition, amorphous material that was thought to be allophane was also present. This mineral is notorious for its P fixing properties (Fieldes and Schofield, 1960). Its presence in the clay fraction, even when the total amount was relatively low, is a factor that probably could account at least partially for the observed value of the adsorption maximum. The high base status probably also had some influence.

The Olotepec soil, sample No. 5, contained 44% clay in which allophane was the predominate constituent. The

Table 4. Phosphate adsorption maxima for surface soils grouped according to the kind of parent material from which they originated

Sample No.	Location	pH	Adsorption maxima
	Volcanic Ash Soils		ug P/g
1	San Andres-Tuxtla	7.1	308
5	Olotepec	6.3	1050
7	Catemaco	6.6	1060
9	Acayucan	5.9	118
	Sedimentary Soils		
11	Cardenas	6.9	106
15	Presa Mal Paso	5.4	2021
17	Poblado E. Zapata	5.9	95
20	Uzumacinta	6.1	126
26	Carimagua	4.5	531
	Limestone Soils		
22	Escorcega	8.0	110
24	Kankab	6.5	500
25	Tzekel	7.4	584
	Sericitic Schist Soil		
28	Georgeville	5.9	480

adsorption maximum. 1050 ug P/g, was more than three times that of the San Andres soil. The higher clay content of the Olotepec soil may probably explain the difference but, in addition, this soil was more acid, pH 6.3, as compared with the San Andres, pH 7.1. Wada and Ataka (1958) have indicated that the very large phosphate fixation found in moderately acid volcanic ash soils might be attributable in part to the fact that allophane acquires greater positive charges at lower pH's.

The Catemaco soil, sample No. 7, also had a high P adsorption maximum, 1060 ug P/g. This soil contained 39% clay with kaolinite being the chief constituent. Hsu (1965) indicated that surface reactive Al hydroxides and iron oxides are the real factors that govern the concentration of P in solution and that the surface reactivity is not a function of pH. Also, since the soil contained 13.1 me/100g of exchangeable Ca+Mg which may have arisen as a result of recent depositions of ash, there could have been reaction of P with Ca and Mg.

The Acayucan soil, sample No. 9, with 9% clay in which kaolinite predominated over halloysite and montmorillonite (2) only retained 118 ug P/g. This relatively low figure may have resulted from the low clay content, the moderate acidity, pH 5.9, and absence of exchangeable Al.

The second group of surface soils include those sampled at Cardenas, Presa Mal Paso, Poblado Emiliano Zapata, and the Plains of the Uzumacinta River, as well as the Carimagua soil from Colombia. These soils are derived from unconsolidated alluvial and colluvial materials. As in the case of the soils derived from volcanic ash, large variations in P fixation are evident (Table 4). The soil sampled at Cardenas (Sample No. 11) contained 27% clay with montmorillonite being the predominant species and only traces of kaolinite. At pH 6.9 it would not be expected that montmorillonite would fix much P (Haseman et al., 1950). The small amount of P retained, 106 ug P/g, may probably have been the result of reactions between P and kaolinite and/or the exchangeable Ca+Mg ions which were present in high amount, 17.6 me/100g.

The sample No. 15, taken at Presa Mal Paso, fixed a large amount of P. The adsorption maximum was 2021 ug P/g. It is probable that this high figure may be explained by a combination of factors which include a low pH, 5.4, 1.5 me/100g of exchangeable Al, and a relatively high clay content, 39%, with kaolinite the predominate clay mineral. The dark brown color of the soil suggested a fairly high iron oxide content.

The soil from the Pablado Emiliano Zapata, sample No. 17, was the one which fixed the smallest amount of P among all the samples. Although kaolinite predominated in the clay fraction, the total amount of clay was low, 10%. Thus, the low clay content, as well as a low content of exchangeable Al, 0.8 me/100g, probably accounted for the observed figure. The chemical properties of this soil were comparable to those of soil No. 9 previously discussed. It was found that the retention values also were comparable. The soil from the alluvial Uzumacinta area retained only 126 ug P/g soil. Halloysite and kaolinite were the main constituents of the clay fraction. Wada (1959) found that ammonium taranakite was readily formed in the presence of halloysite when exposed to ammonium phosphate solutions, but the reaction was slow at pH 7. He also reported that phosphate held between the clay sheets was readily released with water. The low fixation of the soil from the Uzumacinta region is probably related to the low clay content and a pH of 6.1 which may have reduced the reactivity of the halloysite. In a study of 14 surface soils of Costa Rica, using tracer techniques, Fassbender (1968) found that the seven alluvial soils retained less P than the andosols and latosols used.

The highly weathered Carimagua soil, from the Llanos of Colombia, had an adsorption maximum of 531 ug P/g. This high value probably can be explained by the high clay content (Table 1) in which kaolinite predominated, a pH of 4.6 and the high content of exchangeable Al, 3.26 me/100g soil.

The third group comprise those soils derived from the dissolution of limestone. The soil from Escorcega, sample No 22, contained 27% clay and 14 Å minerals predominated, although 10 Å minerals also were present. The amount of P retained was 110 ug P/g soil. The retention of P in this soil, which contained 36 me exchangeable Ca+Mg/100g soil was probably due to precipitation reactions of P with Ca and Mg (Chang and Sherman, 1961).

Sample No. 24, the Kankab soil, had an adsorption maximum of 500 ug P/g. This relatively high retention of P was probably due to the predominance of kaolinite in this soil which contained 72% clay. Another possible factor could have been reaction of P with Ca and Mg in this soil which contained 13.5 me exchangeable Ca+Mg/100g and had a pH of 6.5.

The Tzekel soil, sample No. 25, which retained 584 ug P/g soil, was fully base saturated with a content of 40.5 me/100g of exchangeable Ca+Mg and a pH of 7.4. As in

the case of sample No. 7, the high level of exchangeable Ca+Mg may constitute potential reactants (Lindsay and Moreno, 1960) with phosphate ions and would tend to decrease the solubility of the P. This soil contained 44% clay with allophane being the main constituent. The allophane undoubtedly also contributed to the P retention.

The Georgeville soil had an adsorption maximum of 480 ug P/g soil. This soil contained 38% clay, which was predominantely kaolinite, and also had a relatively high iron content as indicated by the red color. This soil represents a relatively high fixing soil on which relatively large amounts of fertilizer P are required for high crop yields (Kamprath, 1967).

Phosphate Adsorption of Surface Soils As Related to Kind of Clay

The dynamic character of soils is well recognized. The seat of the activity is the colloidal fraction of the soil where organic, as well as inorganic, components are operative. The inorganic colloids of the soil are represented by the clay minerals. The dynamic properties of the clays may vary within the types of clay but these properties are very often modified by the presence of amorphous aluminum hydroxides and/or iron oxides which possess a large degree of reactivity.

For any particular soil, the reactivity of the surfaces exposed is greatly influenced by the nature of the swarm of ions present, pH and probably other factors. The work of many investigators, a few of which have been mentioned in this paper (Ellis and Truog, 1955; Haseman et al., 1950; Hemwall, 1957b; Low and Black, 1950; Wada, 1959), has shown that clay minerals react with phosphate either by supplying Al in solution or by the surface reactivity with aluminum (and iron) compounds. The fixation of P either by precipitation with Ca or Mg ions or adsorption on the surfaces of carbonates present in calcareous and alkaloine soils is well documented.

Although in this study whole soils were used and it was recognized that factors other than kind of clay could have been instrumental in the reactions that resulted in the observed P retention values, interest was aroused to relate the kind and amount of clay to the retention of P. Also, it was realized that clay minerals other than the dominating species could have exerted some influence and modify the observed results. Nevertheless, the surface soils were grouped according to the kind of clay minerals which predominated in the clay fraction. This data is presented in Table 5.

Table 5. The retention of P as related to kind and amount of clay

Sample No.	Location	Adsorption maxima	Clay content %	ug P/g of clay	Saturation of adsorption maxima, %	Major clay mineral	pH
			Surface Soils				
1	San Andres	308	12	26	39	Allophane	7.1
5	Olotepec	1050	11	95	64	Allophane	6.3
25	Tzekel	584	44	13	80	Allophane	7.4
7	Catemaco	1060	39	27	52	Kaolinite	6.6
9	Acayucan	118	9	13	42	Kaolinite	5.9
15	Presa Mal Paso	2021	39	52	51	Kaolinite	5.4
17	Poblado E. Zapata	95	10	10	72	Kaolinite	5.9
24	Kankab	500	72	7	57	Kaolinite	6.5
26	Carimagua	531	36	15	74	Kaolinite	4.6
28	Georgeville	480	38	13	75	Kaolinite	5.9
11	Cardenas	106	27	4	78	14 Å or Montmorillonite	6.9
22	Escorcega	110	27	4	55	14 Å or Montmorillonite	8.0

In the first group, allophane was the chief constituent of the clay fraction. Samples No. 1 and 5 were derived from volcanic ash and soil No. 25 was derived from dissolution of limestone but this soil probably had been influenced by volcanic ash depositions, hence the presence of allophane. The ug P/g retained varied widely in the three soils, but it was interesting to note that retention increased with decreasing pH. Wada and Ataka (1958) presented data to support their statement that on decreasing pH the anion exchange capacity of allophane increased. This property was related to P fixation of allophane by Fieldes and Schofield (1960). It appears that at a higher pH there is a tendency to depress the ionization of OH groups from the tetrahedral Al (Wada and Ataka, 1958) and thus the affinity for P ions is decreased. This probably would explain the trend observed for these soils.

In the second group of Table 5 are presented those soils in which the predominent clay mineral was kaolinite. The ug P/g clay ranged from 7 to 52. It may be of interest to note that the soils Catemaco and Presa Mal Paso contained the same amount of clay, 39%, and yet the retention of P by the latter soil was almost double that for the Catemaco soil. The lower pH, 5.4, for the Presa Mal Paso soil as compared

with 6.6 for the Catemaco sample and the fact that no exchangeable Al was detected for the less acid soil and 1.5 me of exchangeable Al/100g of soil was present in the Presa Mal Paso soil, may furnish an explanation for the observed difference in P retention. Even when no exchangeable Al was present in the Catemaco soil and pH was relatively high the value of 27 ug P/g clay is still high. The probability remained that the relatively high P retention could be explained by reactions of P with exchangeable Ca+Mg which were present in amounts of 13.1 me/100g soil.

The clay content of the Georgeville soil was of the same magnitude as that of the soils just discussed. The amount of P retained per gram of clay was 13 ug. The pH was 5.9 and 1.10 me/100g of exchangeable Al were present. The pH, higher than that of the Presa Mal Paso soil, could explain the difference with this soil. No determinations for exchangeable Ca+Mg were made for this soil, but the content in all probability was lower than that of the Catemaco soil. This then appeared to offer an explanation for the difference in P retained when compared with the Catemaco sample.

The soil from Acayucan had the same pH value as the Georgeville soil but no exchangeable Al was detected, and, yet, the amount of P retained per gram of clay was the same for both soils at 13 ug. It may have been that the iron in the Acayucan soil, which was suggested by the red color, was more reactive toward phosphate than that in the Georgeville soil, also of red color, in spite of a lower clay content in the Acayucan soil.

The soil from Poblado Emilio Zapata also had a pH of 5.9. Clay content was 10% which is comparable to that of the Acayucan soil. The amount of retained P was 10 ug/g clay which was not far from the corresponding value of the Acayucan soil. This soil contained 0.8 me of exchangeable Al and 2.5 me of exchangeable Ca+Mg. These last two factors may probably explain the recorded figures for P retention. The Kankab soil had a pH of 6.5 and 13.5 me/100g of exchangeable Ca+Mg. These values were comparable to those of the Catemaco soil where P retention was 27 ug P/g clay but the Kankab soil only retained 7 ug P/g clay. The occurrence of the Catemaco soil in an area of volcanic ashes may suggest the presence of amorphous material not detected by SRD and this factor could probably explain the difference in P retention figures. The Carimaqua soil contained 36%

clay, pH was 4.6 with 3.26 me of exchangeable Al/100g soil. These two factors would appear to explain the figure of 15 ug P/g clay retained by this soil.

In the group of soils where montmorillonite or 14 Å minerals dominated the clay fraction, the values of P retained were lower than in the other groups. The amount of P adsorbed was 4 ug P/g clay for both samples and total contents of clay were similar, 27%. It may also be seen in Table 5 that the amounts of P retained by this group were smaller than in the other groups. The work of Haseman et al. (1950) has shown that montmorillonite fixed less P among a group of clay minerals studied and that fixation decreased with increasing pH. Thus, it appeared that the kind of clay and the relatively high pH values for these two soils have accounted for the relatively low retention figures. Also, it was thought that the activity of iron compounds probably was not very high for Ellis and Truog (1955) found that deferrated montmorillonite did not fix P.

Phosphate Adsorption Maxima of Subsoils

In Table 6 the P fixation figures have been grouped according to the parent materials from which the soils originated. In the first group, which include those soils derived from volcanic ash, the first three samples represent

Table 6. Phosphate adsorption maxima for subsoils grouped according to the kind of parent materials from which they originated

Sample No.	Location	Depth cm	pH	Adsorption maxima ug P/g
		Volcanic Ash Soils		
2	San Andres-Tuxtla	10-70	7.2	218
3	San Andres-Tuxtla	200-230	7.3	196
4	San Andres-Tuxtla	230-300	6.6	550
6	Olotepec	40-70	6.4	1078
10	Acayucan	50-120	4.9	600
		Sedimentary Soils		
13	Sabana Huimanguillo	30-45	5.0	497
14	Sabana Huimanguillo	100-120	5.2	551
16	Presa Mal Paso	40-50	5.1	1186
18	Poblado E. Zapata	25-50	5.2	572
19	Poblado E. Zapata	100-150	4.8	519
21	Uzumacinta	25-50	7.4	102
27	Carimagua	10-20	4.5	566
		Limestone Soil		
23	Escorcega	80-100	8.5	112

horizons of the San Andres soil. Phosphate fixation was relatively low for samples No. 2 and 3.

In sample No. 4 the fixation of P increased sharply. The values were: 218, 196 and 550 ug P/g for samples 2, 3 and 4, respectively. The levels of exchangeable Ca+Mg tended to increase with depth and the values were 24.1, 35.7 and 36.5 me/100g. The contents of clay were 2, 28 and 44%. Amorphous material, which was thought to be allophane, was present throughout the profile. With the exception of sample No. 2, degraded 14 Å reflections were detected in the rest of the profile. However, contrasting with the other samples of the profile, kaolinite was present in sample No. 4. The presence of the amorphous material and the level of exchangeable bases probably explain the fixation figures for samples No. 2 and 3. The large P fixation observed for sample No. 4 probably is explained by the higher clay content and the higher reactivity of the amorphous material at the lower pH.

For sample No. 6, the subsoil at Olotopec, the adsorption maximum was 1078 ug P/g soil. Allophane appeared to be the predominant clay mineral. Its presence offers a plausible explanation for the high P fixation figure. Fieldes and Schofield (1960) have associated the

high P fixation properties of allophane to the assumption that aluminum is present in tetrahedral coordination which confer to it a very strong affinity for oxygen containing anions such as phosphate.

The Acayucan subsoil, sample No. 10, fixed five times more P than the corresponding surface soil. In spite of containing a higher level of exchangeable Ca+Mg, the pH of the subsoil was one unit lower than that of the surface soil but no exchangeable Al was present. The clay content was 23% with kaolinite being the predominant clay mineral species. The moderately high content of clay, which was predominantly kaolinite, as well as the high acidity, were probably the factors responsible for the high retention of P. Furthermore, the yellowish red (5 YR 4/6) color was suggestive of a high content of free iron which could have had an influence in the fixation reactions.

In the group of sedimentary soils, samples No. 13 and 14, obtained at the Sabana Huimanguillo, represented two different depths of the same subsoil. Phosphate retention increased slightly with depth. The values were 497 and 551 ug P/g. Kaolinite was found to be the more abundant clay mineral in both samples. Clay content for sample No. 14 was 11%. This soil was distinctly acid with

pH values of 5.0 and 5.2. Exchangeable Al was .95 me/100g in sample No. 13 but none was detected in sample No. 14. The surface reactivity of aluminum hydroxides and/or iron oxides (Hsu, 1965) may have been responsible for the high P fixation recorded.

The subsoil sample No. 16 from the Presa Mal Paso area fixed a large amount of P. The adsorption maximum was 1186 ug P/g. Compared with the surface soil the subsoil was more acid, pH 5.1, and contained more exchangeable Al, 3.2 me/100g, than the surface soil where the values were 5.4 and 1.5, respectively. On the basis of only the amount of exchangeable Al one would expect a larger fixation by the subsoil (Coleman et al., 1960), however, the subsoil retained less P. The explanation for this behavior probably lies in a lower clay content. The predominant clay mineral was kaolinite, the same as in the surface soil.

The two subsoil samples No. 18 and 19 from the Pablado E. Zapata area had high fixation values, 572 and 519 ug P/g, respectively. Kaolinite was the dominating species in the clay fraction. The contents of clay were 5.2 to 4.8. Not surprisingly, exchangeable Al was found

to increase at the lower depth, from 2.7 to 4.3 me/100g. Based on these considerations one would be inclined to expect that fixation would be greater for sample No. 19. As already pointed out, this was not the case -- the difference, however, was small (Table 6). The nature of the clay minerals, plus the acidic properties of the profile, appeared to explain the high fixation properties observed.

The subsoil sample No. 21 from the Uzumacinta River plain held 102 ug P/g. The percentage of clay was 12% with kaolinite and 14 Å minerals being present. The pH was 7.4 and the soil contained 8.4 me/100g of exchangeable Ca+Mg. The low clay content and the high pH are probably the main reasons why this soil fixed relatively low amounts of P.

The subsoil sample No. 27 from the Llanos of Columbia had a high adsorption value, 566 ug P/g. This high value could have been the result of a low pH, 4.6, the presence of 3.60 me/100g of exchangeable Al and a relatively high clay content in which kaolinite appeared to dominate. The only subsoil sample for the group derived from the dissolution of limestone was the No. 23 sample taken at the Escorcega location. The amount of P retained was 112 ug P/g which is of the same magnitude as

that held by the surface soil, 110 ug P/g. This sample contained free carbonate. As in the case of the surface soil, it was thought that precipitation reactions involving exchangeable Ca+Mg and/or adsorption on the surface of the free calcium cabonate (Cole et al., 1953) accounted for the adsorption of P. The amount adsorbed, however, was relatively small.

Concentration of Soil Solution P As Related to Adsorbed P

The uptake of P by plants is from the soil solution. When the concentration of P falls below a certain level, the rate of supply becomes insufficient to meet the requirements of the plant. Thus, Aslyng (1964) reported that a soil solution concentration, at field capacity, of 0.18 ppm P was enough to avoid P deficiencies. In pot experiments, Fox and Kamprath (1970) obtained 95% of maximum yield of millet when phosphate in the soil solution was adjusted to 0.2 ppm. Therefore, interest was aroused in this work to study the relation between the degree of P saturation of the colloids and the concentration of P in the equilibrated solution. By interpolation of the P adsorption isotherms, the amounts of P to be added in order to produce equilibrium concentrations 0.1 and 0.2 ppm P were determined. As has been suggested by Ozanne and Shaw (1968), the use of

isotherms of this kind makes it possible to determine the amount of P to be added so that the level of soil solution P may be raised to a predetermined level. This was the method used by Fox and Kamprath (1970) in the pot experiments referred to earlier.

Surface Soils. The amounts of P that had to be added to produce an equilibrated solution concentration of 0.1 and 0.2 ppm for the surface soils are given in Table 7. The wide range of variation within each group of soils is evident from the table. These values are related to the slopes of the adsorption curves for the respective soils in Appendix Figures 1 to 16. Beckwith (1965) explained that soils with steep curves have a strongly buffered capacity to supply P at a given low concentration and that for soils with flat curves, the "potential" at which P is supplied decreases as P is withdrawn.

The predetermined level of P in solution is a parameter of intensity I, and the sorbed P is a parameter of capacity Q. The ratio Q/I is the buffer capacity of the soil (Ozanne and Shaw, 1968).

The difference (Table 7) between the amount of P added to support the two concentrations mentioned is then an estimate of the buffer capacity in the range in question.

Table 7. Amounts of P required to support an equilibrated solution concentration of 0.1 and 0.2 ppm P and degree of saturation of the adsorption maximum at each level. Surface soils

Sample No.	Soil location	Equilibrium solution concentration 0.1 ppm: P required ug P/g	0.1 ppm: Saturation of adsorption maxima %	0.2 ppm: P required ug P/g	0.2 ppm: Saturation of adsorption maxima %	Buffer capacity 0.1 to 0.2 ppm ug P/g
			Volcanic Ash			
1	San Andres	78	25	120	39	42
5	Olotepec	500	48	670	64	170
7	Catemaco	415	39	550	52	135
9	Acayucan	25	21	50	42	25
			Unconsolidated Alluvial and Colluvial			
11	Cardenas	65	61	83	78	18
15	Presa Mal Paso	770	38	1025	51	255
17	Poblado E. Zapata	60	63	68	72	8
20	Uzumacinta	16	13	24	19	8
26	Carimagua	310	58	395	74	85
			Limestone			
22	Escorcega	42	38	60	55	18
24	Kankab	240	48	285	57	45
25	Tzekel	380	65	470	80	90
28	Georgeville	285	59	360	75	75

It is seen from Table 7 that a high buffer capacity is directly related to the capacity factor Q (the amount of P sorbed). Mattingly (1965) found that in soils of low capacity the concentration of P in solution was reduced rapidly by cropping and succeeding crops may show deficiencies. Fried and Shapiro (1956) had previously suggested that in order to replenish the solution, as P is being withdrawn from it, the capacity factors had to be evaluated. For the soils studied, the buffer capacity probably is an indication of their ability to supply P to plants once that the capacity of the soil has been satisfied to a certain extent.

Soils that contained allophane required the largest amounts of P to give 0.2 ppm P in solution except for the soil from Presa Mal Paso. The saturation of the adsorption maxima to give a soil solution concentration of 0.2 ppm P ranged from 52 to 80%. This is an indication of the high P fixing characteristics of allophanic volcanic ash soils and why P deficiencies are often noted in this kind of soil. It also suggests why the residual effectiveness of small applications of P applications is very low. The soil from Presa Mal Paso required the largest amount of P to give 0.2 ppm P in the soil solution. This soil, as previously

discussed, had a high content of clay which was predominantly kaolinite and also was acid and rich in iron oxides. Other soils which contained kaolinite such as those from the Llanos of Colombia, the Georgeville from North Carolina, and the Kankab also required large additions of P to give 0.2 ppm P in the soil solution. The percent saturation of the adsorption maximum required for this ranged from 51 to 75%.

Relatively low rates of P applications were required on soils which had 14 Å clays, montmorillonite, halloysite or low amounts of kaolinite. The percent saturation of the adsorption maximum required to give 0.2 ppm P in the soil solution varied from 19 to 78%. The soils with a high content of clay generally required a higher percent saturation.

The amounts of P that had to be added to support an equilibrium concentration of 0.1 ppm P in the soil solution were consistently larger than the amounts of P required to raise the soil solution concentration from 0.1 to 0.2 ppm P (Tables 7 and 8). This suggests that the energy of retention of soil for the phosphate was decreasing as the amount of added P increased and probably is related to the observation of Hughes and Searle (1963) that previous additions of P decreased the availability of fixation sites.

There appeared to be no relationship between the percentage saturation of the adsorption maxima and the amount of P in the soil solution. The percent saturation of the adsorption maximum at which the soil solution contained 0.2 ppm P ranged from 19 to 80. If P is being removed from the solution, e.g., by an absorbing root, soils of low capacity would have to have their adsorption maximum saturated to a higher degree in order for plants to be able to obtain P to meet their needs. This probably would result in a higher initial soil solution P. This agrees with the work of Baldovinos and Thomas (1961) who found that for three soils of different capacity, but at the same solution concentration, the uptake of P from the high capacity soil was four and two times larger than for the other soils. On the other hand, Mattingly (1965) demonstrated that for calcareous soils of low capacity, a higher initial solution concentration was needed to obtain yields similar to those obtained on high capacity soils. Therefore, the soils with a low P adsorption maximum probably would need a soil solution concentration of 0.2 for optimum growth, while the soils with a high P adsorption maxima probably would only need a concentration of 0.1 ppm P or less.

As would be expected, the buffer capacity of the soils was related to their P adsorption maxima. After the P level of the soils has been brought up to the desired level the soils with a high buffer capacity could supply P for a considerable period of time without additions of fertilizer. Since the allophanic soils and those with a high clay content in which kaolinite and iron oxides predominate have a very high adsorption maxima, the P fertilizers should be banded, especially at low rates of application.

Subsoils. In Table 8 similar data as that given in Table 7 for the surface soils is given for the subsoils.

The subsoils in which degraded 14 Å minerals or montmorillonite were present required relatively low amounts of addition of P to reach 0.2 ppm in the soil solution. The Olotepec soil contained allophane and the required amount of P to give a solution concentration of P of 0.2 ppm was large. That amount was surpassed only by the Presa Mal Paso subsoil in which kaolinite predominated in the clay fraction. In the other soils in which kaolinite also was predominant the amounts of P required to attain a soil solution concentration of 0.2 ppm P were also markedly high. In general, the subsoils had a higher buffer capacity than the corresponding surface soils.

Table 8. Amounts of P to be added to support an equilibrated solution concentration of 0.1 and 0.2 ppm P and degree of saturation of the adsorption maximum at each level. Subsoils

Sample No.	Soil location	Equilibrium solution concentration 0.1 ppm: P added ug P/g	0.1 ppm: Saturation of adsorption maxima %	0.2 ppm: P added ug P/g	0.2 ppm: Saturation of adsorption maxima %	Buffer capacity 0.1 to 0.2 ppm ug P/g
			Volcanic Ash			
2	San Andres-Tuxtla	78	36	105	48	27
3	San Andres-Tuxtla	90	46	120	61	30
4	San Andres-Tuxtla	90	16	120	22	30
6	Olotepec	390	36	520	48	30
10	Acayucan	140	23	210	35	70
			Unconsolidated Alluvial and Colluvial			
13	Sabana Huimanguillo	187	38	262	53	75
14	Sabana Huimanguillo	390	71	495	90	05
16	Presa Mal Paso	600	51	750	63	50
18	Poblado E. Zapata	390	68	495	87	05
19	Poblado E. Zapata	240	46	300	58	60
21	Uzumacinta	16	16	66	65	50
27	Carimagua	250	44	335	59	85
			Limestone			
23	Escorcega	88	79	100	89	12

Extraction Study

Dilute Acid Extraction -- Surface Soils

The amounts of P extracted from the surface soils by 0.05N HCl+0.025 N H_2SO_4 at the levels of added P to obtain an equilibrium concentration of 0.1 and 0.2 ppm P in solution are given in Table 9. The amounts of P extracted at each level of addition of P is given in Appendix B.

The average extraction value for the dilute acid at the level of 0.1 ppm P was 45 ppm P. The amounts extracted ranged from 10 ppm P for the Uzumacinta soil to 113 ppm P for the Presa Mal Paso sample.

For acid soils of North Carolina it was observed (Woodruff, 1963) that P extracted by dilute acid appeared to be proportional to the amount added. This same tendency was observed in this work, particularly for the soils derived from sediments in which kaolinite tended to predominate. The acidic solutions of low pH have a solvent action and tend to dissolve the iron and aluminum phosphates. With soils in which the added P has reacted primarily with hydrated oxides of Fe and Al the 0.05 N HCl-0.025 N H_2SO_4 probably gives a good measure of the Q factor.

Fox and Kamprath (1970) found that on a Georgeville soil the growth of millet was linear up to a soil solution

Table 9. Phosphate extracted at the levels of added P sufficient to yield an equilibrated solution concentration of 0.07, 0.1 and 0.2 ppm P using 0.05 N HCl+0.025 N H_2SO_4 as extractant. Surface soils of pH 6.5 and less

Sample No.	Location	Phosphate equilibrium concentration ppm P 0.07 ug P/g	0.1 ug P/g	0.2 ug P/g
		Volcanic Ash		
5	Olotepec	14	20	25
9	Acayucan	9	11	20
		Unconsolidated Alluvial and Colluvial		
15	Presa Mal Paso	107	113	150
17	Poblado E. Zapata	18	20	23
20	Uzumacinta	9	10	15
26	Carimagua	60	72	100
		Sericitic Schist		
28	Georgeville	57	70	87

concentration of 0.07 ppm P and then increased only slightly up to a solution concentration of 0.2 ppm P. However, on a sandy soil growth increased up to a soil solution concentration of 0.2 ppm P. The acid soils from Acayucan, Poblado E. Zapata and Uzumacinta which had a low adsorption maxima would probably require a soil solution concentration of 0.2 ppm P. The dilute acid extraction on these soils at this soil solution concentration ranged from 15 to 23 ppm P. The adsorbed P in these soils was held quite loosely as indicated by the small amount of P required to change the amount of P in the soil solution. The soils with a high adsorption maxima could probably produce maximum growth at a lower soil solution concentration such as 0.07 ppm P. The dilute acid extractable P, which gave 0.07 ppm P in the soil solution, was 57, 60 and 107 ppm P, respectively, for the Georgeville, Carimagua and Presa Mal Paso soils. These data indicate that the dilute acid extractable P gives a good measure of the quantity factor.

Agronomic interpretation of soil tests using the dilute acid extraction would have to be correlated with field studies taking into account the chemical properties of the soils which control P availability.

The adsorption maximum for the Olotepec soil was larger than that for the Carimagua and Georgeville soils by a factor of about 2. The amounts of extracted P from these two soils at the level of 0.2 ppm P was about three times larger than that for the Olotepec soil. These data suggests that the forms of P resulting from reaction with allophane are very resistent to extraction by dilute acid solution.

Dilute Acid Extraction -- Subsoils

Extraction data similar to that presented in Table 9 for the surface soils is given for the subsoils in Table 10. Again, a wide range of values was obtained. For the 0.1 ppm P level the lowest amount of P extracted was 9 ppm P for the Acayucan soil and the largest was 106 for the Sabana Huimanguillo subsoil. The average extraction value was 57 ppm which was larger than the corresponding value for the surface soils. At the 0.2 ppm P level, the average P extracted was 81 ppm P and the individual values ranged from 28 ppm P for the Acayucan subsoil to 142 ppm P for the Sabana Huimanguillo soil. Again, it was noted that the Olotepec subsoil which contained allophane released only a relatively small amount of P to the acid solution. The wide range of variation found in the extraction figures for the dilute acid solution may

Table 10. Phosphate extracted at the levels of added P sufficient to yield an equilibrated solution concentration of 0.07, 0.1 and 0.2 ppm P using 0.05 N HCl+0.025 N H_2SO_4 as extractant. Subsoils

Sample No.	Location	Phosphate equilibrium concentration ppm P 0.07 ug P/g	0.1 ug P/g	0.2 ug P/g
		Volcanic Ash		
6	Olotepec	28	50	60
10	Acayucan	6	9	28
		Unconsolidated Alluvial and Colluvial		
13	Sabana Huimanguillo	15	21	37
14	Sabana Huimanguillo	85	106	142
16	Presa Mal Paso	68	91	126
18	Poblado E. Zapata	56	66	89
19	Poblado E. Zapata	45	54	72
27	Carimagua	40	58	90

suggest that this extractant probably is not suitable to predict from extraction data the amounts of P that could exist in solution at a predetermined level for this group of soils.

Bicarbonate Extraction -- Surface Soils

The sodium bicarbonate method was originally developed for measuring surface adsorbed P in calcareous soils. In acid soils it probably measures easily hydrolyzable P associated with hydrated oxides of Fe and Al. The P in the soil solution is probably in equilibrium with surface adsorbed P. Therefore, the sodium bicarbonate extraction might more closely be related to the solid phase P which controls the amount of P in the soil solution.

The results of P extracted by use of 0.5 M $NaHCO_3$ at the levels of P additions to yield a solution concentration of 0.07, 0.1 and 0.2 ppm P are presented in Table 11 for the surface soils.

The soils were arranged in four groups according to the kind and amount of clay content.

In the first group are those soils of relatively high clay content in which kaolinite was the predominant species. The amount of extracted P ranged from 23 to 31 ppm P. The average value was 29 ppm.

Table 11. Phosphate extracted at the levels of added P sufficient to yield an equilibrated solution concentration of 0.07, 0.1 and 0.2 ppm P using 0.5 M $NaHCO_3$ at pH 8.5. Surface soils

Sample No.	Location	Equilibrium concentration ppm P 0.07 ug P/g	0.1 ug P/g	0.2 ug P/g
Soils with high clay content, predominantly kaolinite				
7	Catemaco	13	15	23
24	Kankab	22	25	31
26	Carimagua	21	26	34
28	Georgeville	17	21	28
Soils with allophane, degraded 14 Å or montmorillonite				
1	San Andres-Tuxtla	10	12	19
11	Cardenas	15	15	19
25	Tzekel	14	16	22
Soils with low clay content				
9	Acayucan	4	5	9
17	Poblado E. Zapata	9	10	11
20	Uzumacinta	4	5	7
Calcareous				
22	Escorcega	4	4	6

When clay content was low the extracted values were even lower; the average was 9 ppm P and the range of values extended from 7 to 11 ppm P.

From the calcareous soil, sample 22, 6 ppm P were extracted when the soil solution level was 0.2 ppm P. Similar relationships existed at the other two soil solution concentrations. The data suggest that the sodium bicarbonate extraction gives a measure of surface P which determines the concentration of P in the soil solution.

To evaluate the agronomic implications of the sodium bicarbonate extraction the soils should be characterized as to properties which determine the existence of surface P. The data should also be correlated with greenhouse and field studies.

In a study conducted in Bolivia, in which various extractants were used, the bicarbonate solution was found to correlate better with yields of wheat. The critical level was set a 7 ppm P. For a similar study conducted in Peru from 1958 to 1968, it was found that the critical level was approximately 8 ppm of extracted P using the same extractant. The soil:solution ratio was 1:20.[1] The

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[1]D. L. Waugh, International Soil Testing Project, North Carolina State University, Raleigh, N. C. Personal communication.

critical level has been defined as that content of extractable P below which the likelihood of a response is large.

It is felt that for the soils used in this study a test value around the average for each group of soils (Table 11) using the bicarbonate extractant probably would be an indication of the concentration of P that these soils could support in solution at a concentration between 0.1 and 0.2 ppm and would indicate the point at which no further responses to applied P could be expected, depending on the kind of crop and if other factors were not limiting. However, more work is needed to test this hypothesis.

Bicarbonate Extraction -- Subsoils

The extraction data for the subsoils using the bicarbonate solution is given in Table 12. The first group are all samples of different depths of the same profile. The dominating clay minerals were degraded 14 A minerals and amorphous material. As already mentioned in soils in which these materials tend to predominate, the amounts of released P are relatively low.

The sample from Escorcega had a high content of calcium carbonate. The relatively high amount of P extracted may have been a reflection of the ability of this compound to adsorb P on its surface.

Table 12. Phosphate extracted at the levels of added P sufficient to yield an equilibrium concentration of 0.1 and 0.2 ppm P using 0.5 M $NaHCO_3$ at pH 8.5 as extractant. Subsoils

Sample No.	Location	Phosphate equilibrium concentration ppm P 0.1 ug P/g	0.2 ug P/g
		Volcanic Ash	
2	San Andres-Tuxtla	11	14
3	San Andres-Tuxtla	11	13
4	San Andres-Tuxtla	11	15
		Alluvial and Colluvial	
21	Uzumacinta	9	10
		Limestone	
23	Escorcega	6	40

SUMMARY AND CONCLUSIONS

The fixation of phosphate was determined using the b constant of the Langmuir isotherm as a measure of fixation for a group of soils of varying properties from Southeastern Mexico, Colombia and North Carolina. Adsorption isotherms were constructed to determine the amounts of added P which would give an equilibrated solution concentration of 0.2 ppm P which should be adequate for plant growth. The acid soils retained on the average 2.7 times as much P as the alkaline soils. The magnitude of fixation for the alkaline soils appeared to be a function of the kind and amount of clay. When these alkaline soils contained allophane the fixation was greater than when kaolinite was the dominating mineral. Also, fixation by allophanic soils tended to increase with decreasing pH.

When halloysite or montmorillonite predominated the fixation was quite low. The subsoils did not always fix more P than the corresponding surface soil but the data was insufficient.

There appeared to be no relation between the percentage saturation of the adsorption maxima and the amounts of P needed to obtain a predetermined equilibrium concentration in solution of 0.2 ppm P.

A greater amount of P was required to bring the soil solution to 0.1 ppm P than from 0.1 to 0.2 ppm indicating that as more P is added it is held less tightly.

The extraction values obtained by the use of 0.05 N HCl + 0.025 N H_2SO_4 seemed to be proportional to the amounts of P added. The extraction appeared to give a measure of the quantity factor. In the presence of allophane the amounts of P extracted were lower which suggested that P is held in a very insoluble form. The dilute acid extractant seemed unsuited to be used to predict a predetermined P concentration in solution from the amounts of P extracted. The amounts of P extracted using 0.5 M $NaHCO_3$ at pH 8.5 appeared to be a measure of surface P. The magnitude of the extraction value seemed to be related to the kind and amount of clay. It is probable that the sodium bicarbonate extractant can be used to predict the amount of P in solution at a predetermined level if the soils are well characterized as to the properties which determine the existence of surface P, however, more work, using greenhouse and field techniques, are needed to further evaluate the validity of this hypothesis.

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APPENDICES

Appendix A. Profile Description of Selected Soils of Southeastern Mexico

Profile 1

In the village of San Andres Tuxtla in southern Vera Cruz. Parent material is basaltic ash and sand from the Tuxtlas volcanoes. The profile is located on the upper part of young erosional slideslope of approximately 10% gradient. Annual rainfall is estimated to be 2100 mm with a distinct dry season.

Sample No.			
1	A1	0-24 cm	Dark brown (7.5 YR 3/3) clay loam, moderate fine blocky, slightly plastic, clear smooth boundary.
	A3	24-28	Dark brown (7.5 YR 3/3) clay loam, moderate fine and medium blocky, apparently higher in clay than horizon above, diffuse smooth boundary.
	B2t	28-43	Dark brown (7.5 YR 3/2) as coatings, dark brown (7.5 YR 3/4) inside aggregates, clay loam or silty clay loam, moderate medium blocky, prominent illuvation argillan (clay films) and a few stress cutans (pressure faces), diffuse smooth boundary.
	B3	43-68	Dark brown (7.5 YR 3/4) silt loam, weak coarse blocky, few illuviation argillans on some ped faces, clear diffuse boundary.

Sample No.			
2	C1	68-100+	Dark brown (10 YR 3/4) silt loam, massive.
3	IIA1b	200-230	Dark brown (7.5 YR 3/2) loam weak fine and medium blocky, clear smooth boundary.
4	IIBb	230-300	Dark brown (7.5 YR 3/3) clay loam or silty clay loam, weak medium blocky structure

Profile 2:

Located at the Olotepec banana plantation between San Andres Tuxtla and Catemaco in southern Vera Cruz. Parent material is basaltic volcanic ash. The profile is located on a gently sloping relatively stable but slightly modified, young depositional landform. Mean annual rainfall is approximately 2100 mm with a definite dry season.

Sample No.			
	A1	0-40 cm	Dark brown (10 YR 3/2) silt loam; weak fine blocky and coarse granular; very friable.
	B1	40-70	Dark brown (10 YR 4/3) silty clay loam, weak medium sub-angular blocky, slightly plastic; illuviation argillans (clay films) common.

Profile 3:

No profile description is available for the soil sampled (sample No. 7) at Km 502 on the Catemaco-Villahermosa

Highway. This soil has developed in a relatively recent deposit of basalt on a sloping (10%) depositional landform. The A horizon sampled is a dark brown (7.5 YR 3/2) loam.

Profile 4:

There is no profile description for the soil sampled at Ingenio Juan Diaz Covarrubias (sample No. 8). This soil has formed on a nearly level depositional landform from an earlier basaltic flow.

Profile 5:

This soil is located 5 km northwest of Acayucan in southern Vera Cruz. The parent materials is a basaltic flow of an earlier volcanic period. The profile described is located on a 5% slope, on the convex crest of an erosional landform. Though modified by geologic erosion, this is a part of the older landscape of this region apparently only slightly affected by recent ash deposits. Annual rainfall is estimated to be 2000 mm with a distinct dry season.

Sample No.			
9	A1	0-12 cm	Dark reddish brown (5 YR 3/3) loam, moderate coarse granular very friable, clear smooth boundary.

Sample No.			
	B1	12-27	Dark reddish brown (5 YR 3/3) clay loam, moderate fine and medium subangular blocky, slightly plastic, common thin illuviation argillans or peds and in voids (pores) with very few stress cutans, smooth diffuse boundary.
	B2t	27-64	Reddish brown (5 YR 4/4) clay loam or clay, moderate medium and coarse subangular blocky, plastic, cracks open to 1/2 cm width when dry, common thick illuviation cutans, clear smooth boundary.
10	B3	64-100	Yellowish red (5 YR 4/6) clay loam, weak coarse blocky, sligh plastic.
			Yellowish red, brown, yellow saprolite.

Profile 6:

No morphological description is available for this soil sampled at Campo CIASE, at Cardenas in Tabasco. The A horizon was sampled to depth of 25 cm (sample No. 11). This soil has formed from recent alluvium and lacks a B horizon.

Profile 7:

Located in Sabana Huimanguillo, Tabasco. The soil has formed from unconsolidated sediments derived from the highlands to the south. This soil is located on a gently

sloping erosional hillslope, and is a younger groundsurface than the older, more stable uplands of the area surface. Annual rainfall is approximately 1900 mm. with a distinct dry season. The profile described below is not located at the sampling site, but is of a similar profile in a nearby roadcut. Samples numbers 12, 13 and 14 correspond to horizons A1, A2, and B31.

Sample No.		
A1	0-20 cm	Dark grayish brown (10 YR 4/2) sandy loam, weak granular structure, very friable.
A2	20-45	Brown (10 YR 5/3) sandy loam, massive, very friable.
B1	40-65	Yellowish brown (10 YR 5/6) sandy loam, weak blocky, very friable.
B2	65-100	Yellowish red (5 YR 5/6) and pale brown (10 YR 6/3) sandy clay loam, weak coarse, blocky, friable.
B31	100-150	Yellowish red (5 YR 4/8), pale brown (10 YR 6/3) with a few red mottles (2.5 YR 4/6) light sandy clay loam, weak coarse blocky, friable.

Profile 8:

This soil is located near Presa Mal Paso in Tapasco. The profile has formed from alluvial and colluvial sediments which may be of Tertiary geologic age. The site is located on undulating terrain, on an erosional sideslope, thus a relatively young groundsurface.

Sample No.			
15	A1	0-30 cm	Dark brown (7.5 YR 3/2) loam or clay loam, weak fine blocky breaking to granular, very friable, clear smooth boundary.
	B1	30-40	Strong brown (7.5 YR 5/6) clay loam. Moderate fine and medium subangular blocky, friable, gradual smooth boundary.
16	B2	40-80	Red (2.5 YR 4/6) and yellowish red (5 YR 4/6) clay loam, moderate fine and medium subangular blocky, common illuviation cutans, gradual wavy boundary.
	B3	80-100+	Yellowish red (5 YR 4/6) and very pale brown (10 YR 7/3) with some red (2.5 YR 4/6) mottles, clay loam but lower in clay than horizon above.

Profile 9:

This profile is at the junction of Highway 186 and the road to Poblado Emiliano Zapata in the state of Chiapas. It has formed from alluvial and colluvial sediments from andesitic and basaltic flow rocks, volcanic ash and limestones in the highlands to the south which may be Tertiary in age. The profile is located at the edge of an older relatively stable geomorphic groundsurface -- at the point where it breaks to an erosional sideslope.

Sample No.			
17	A	0-12 cm	Dark brown (7.5 YR 3/2) loamy sand, very friable, clear smooth boundary.
	A2	12-18	Brown (7.5 YR 4/2) sandy loam, massive, very friable, clear wavy boundary.
8	B1	18-48	Brown (7.5 YR 4/4) with coatings of 7.5 YR 5/4 which are illuviation cutans and a few red (2.5 YR 4/6) mottles, sandy clay loam, weak medium subangular blocky, gradual clear boundary.
	B21t	48-100	Red (10 R 4/6) and reddish yellow (7.5 YR 6/6) in a mottled pattern with a few spots of light gray (10 YR 7/2), sandy clay loam or sandy clay, weak coarse subangular blocky, common illuviation cutans friable, gradual smooth boundary.
19	B22t	100-180	Red (10 R 4/6) with prominent coarse gray (10 YR 7/2) mottles, sandy clay loam, friable though localized areas are hard when dry (reddest areas), common illuviation cutans, few mica flakes, gradual smooth boundary.
	B3	180-210	Red (10 R 4/6), with common gray (10 YR 7/2) and light brownish gray (10 YR 6/2) mottles which tend to have vertical orientation and are also higher in clay; sandy clay loam, weak coarse blocky, friable, but red areas are hard when dry, few mica flakes, gradual wavy boundary.
	C	210+	Yellowish brown, yellowish red, red and gray sandy loam, common fine mica flakes.

Profile 10:

Located along the road from Villahermosa to Escorcega 25 km from Uzumacinta River. The profile is formed in sediments of the Uzumacinta River alluvial plain, on a young groundsurface above the flood plain. The soil is located on a level depositional surface with a high water table. Annual rainfall is estimated to be mm, with a distinct dry season. Natural vegetation appears to be savanna.

Sample No.			
20	A1	0-25 cm	Very dark grayish brown (10 YR 3/2) loam, weak fine blocky, very friable.
21	B	25-50	Very dark gray (10 YR 3/1), silty clay loam or clay loam, weak medium blocky, few illuviation cutans.

This profile is thought to be representative of the poorly drained soils of the low, young terraces just above the flood-plains of the Uzumacinta River.

Profile 11:

Located near Escorcega on Highway 186 in Campeche state. The soil has formed over Tertiary limestone on an erosional sideslope of about 5% gradient. Annual rainfall is estimated to be 800 mm, with a strong dry season. The vegetation is tropical evergreen forest approaching tropical dry forest.

Sample No.			
22	A1	0-25 cm	Black (10 YR 2/1) silty clay, moderate medium subangular blocky breaking to granular, slightly plastic, clear but wavy and irregular boundary.
23	C1	25-100+	Light gray soft powdery limestone ("sahcab" is Mayan name) with local mixtures of black and gray soil material.

This soil represents the large areas of eastern and southern Campeche, being the common soil on the rolling and hilly limestone uplands.

Profile 12:

Located on the CIAPY experimental farm near Merida, Yucatan. The soil is underlain by Eocene limestone and occupies a well drained depressional on basin area in this limestone plateau. Annual rainfall is estimated to be 800 mm per year with a distinct dry season - dry subhumid. Mean annual air temperature is about 26° C. The climate is tropical maritime. Vegetation is of the semi-deciduous tropical type. This type of soil is "kankab" in Mayan.

Sample No.			
24	A1	0-20 cm	Reddish brown (2.5 YR 4/4) silty clay loam or clay loam; weak fine blocky which breaks to moderate medium granular.

Sample No.		
B	20^+	Dusky red (10 R 3/4) silty clay loam or clay loam, friable.

A similar profile was described in detail a cut in a basin near Uxmal, Yucatan:

A1	0-10	Reddish brown (2.5 YR 4/4) silty clay loam, weak subangular blocky breaking to moderate medium granular, slightly plastic, clear smooth boundary.
B1	10-22	Dark reddish brown (2.5 YR 3/4) silty clay loam, moderate fine and medium subangular blocky, few ferriargillans (iron-rich clay films) on peds slightly plastic, gradual smooth boundary.
B2t	22-60	Dusky red (10 R 3/4) silty clay, moderate medium subangular blocky, friable, numerous ferriargillans on peds, slightly plastic, gradual smooth boundary.
B3	$60-100^+$	Dark red (10 R 3/6) silty clay loam, weak medium and coarse subangular blocky, few thin ferriargillans, slightly plastic.

This soil is representative of those occupying the basins

of the soil material is in cracks and crevices in the limestone. It is known as "tzekel" soil in Mayan. Estimated mean annual rainfall is 700-800 mm with a distinct dry season. Native vegetation is semi-deciduous tropical forest.

Sample No.			
25	A1	0-10 cm	Black (10 YR 2/1) stony clay loam; fine blocky breaking to granular; slightly plastic, very hard when dry.
	C&R	10^{+}	Limestone with cracks and crevices filled with black and dark gray soil material.

Appendix B. Phosphate Adsorption and Extraction Data at Different Levels of Addition of P

Appendix Table 1. Amounts of phosphate adsorbed by the soils at different levels of addition of phosphate

Sample No.	Location	Amounts of phosphate added, ug P/g soil					
		25	50	75	100	125	200
		Phosphate adsorbed, ug P/g soil					
1	San Andres-Tuxtla	24.8	49.6		98.9		95.2
2	San Andres-Tuxtla	24.9	49.7		98.1		91.0
3	San Andres-Tuxtla	24.8	49.8		97.9		84.2
9	Acayucan	24.8	49.9	72.4	96.0	110.7	
11	Cardenas	24.8	50.0		96.7		
17	Poblado E. Zapata	24.9	49.5		89.1		
20	Uzumacinta	22.9	49.6		92.5	115.0	
21	Uzumacinta	24.9	49.3		92.9		
22	Escorcega	[illegible]	48.8		93.9		
23	Escorcega		49.8		98.3		

(continued)

Appendix Table 1. (continued)

Sample No.	Location	Amounts of phosphate added, ug P/g soil				
		125	250	500	1000	2000
		Phosphate adsorbed, ug P/g soil				
4	San Andres-Tuxtla	123.0	241.5	457.3	795.8	
5	Olotepec	124.8	249.6	499.2	992.6	1944.5
6	Olotepec	124.9	249.4	497.1	967.5	1797.3
7	Catemaco	124.9	249.3	498.1	987.5	1467.1
9	Acayucan	110.7	248.4	241.9	307.2	
10	Acayucan	124.9	249.8	493.3	870.7	
13	Sabana Huimanguillo	124.9	249.[illegible]	482.2	860.1	
14	Sabana Huimanguillo	124.9	249.8	497.4	953.5	
15	Presa Mal Paso	124.7	249.9	499.8	998.0	1965.9
16	Presa Mal Paso	124.7	249.7	499.7	996.4	1872.9
18	Poblado E. Zapata	124.9	249.7	497.7	970.7	
19	Poblado E. Zapata	124.9	248.8	488.8	858.4	
20	Uzumacinta	--	100.5	115.4	132.1	
24	Kankab	124.9	248.7	481.1	909.2	
25	Tzekel	124.9	249.6	497.4	983.7	
26	Carimagua	124.9	249.4	495.9	945.9	
27	Carimagua	124.9	249.0	494.4	949.7	
28	Georgeville	124.9	249.6	493.4	922.9	

Appendix Table 2. Phosphate extracted at different levels of applied P, using 0.05 N HCl+0.025 N H_2SO_4 as extractant. Soil:solution ratio 1:4. Shaking time: 5 minutes

Sample No.	Location	Amount of phosphate added, ug/g soil				
		0	125	250	500	1000
5	Olotepec	2.3	4.1	8.9	19.4	56.8
6	Olotepec	5.4	16.2	29.2	66.0	158.0
9	Acayucan	1.4	47.9	52.5	117.6	182.0
10	Acayucan	.6	6.8	25.4	85.1	171.3
13	Sabana Huimanguillo	.5	9.0	32.6	114.2	226.0
14	Sabana Huimanguillo	2.0	27.2	57.5	144.0	--
16	Presa Mal Paso	0	6.0	16.3	68.0	184.1
18	Poblado E. Zapata	0	12.1	35.0	90.0	313.1
19	Poblado E. Zapata	1.2	15.2	57.0	131.8	299.0
26	Carimagua	.4	19.3	54.0	160.0	321.4
27	Carimagua	.2	19.5	58.0	128.1	284.0

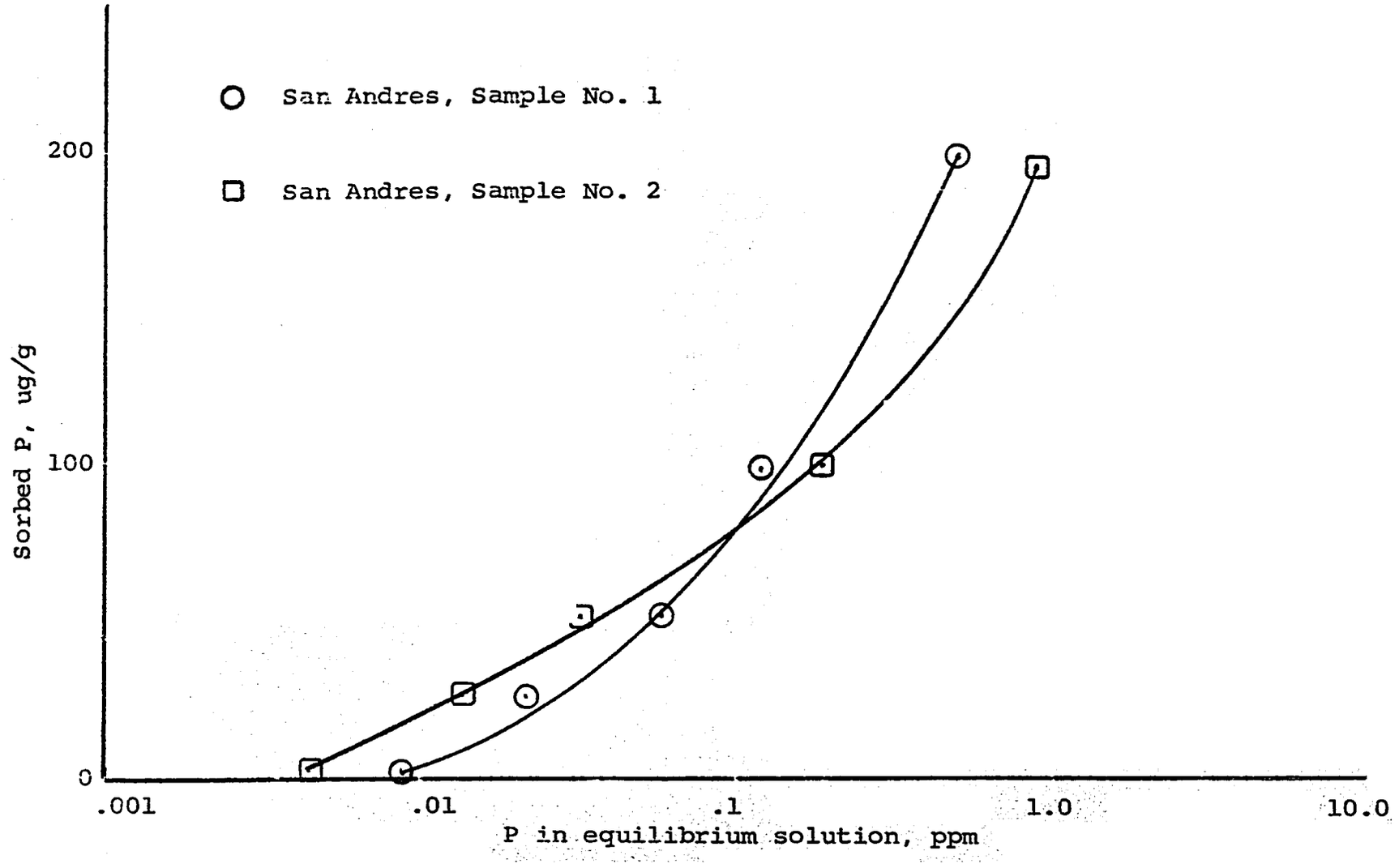
		Amounts of added P, ug/g soil						
		0	25	50	75	100	125	250
15	Presa Mal Paso	1.5	7.2	10.4	91.5	151.4		
17	Poblado E. Zapata	2.5	5.0	16.1	--	33.3		
20	Uzumacinta	1.1	15.0	29.7	43.6	57.7	76.0	
28	Georgeville	2.5	4.5	8.4	12.2	19.7	13.5	62.0

Appendix Table 3. Phosphate extracted at different levels of applied P using 0.5 M $NaHCO_3$ at pH 8.5. Soil:solution ratio 1:5. Shaking time: 5 minutes

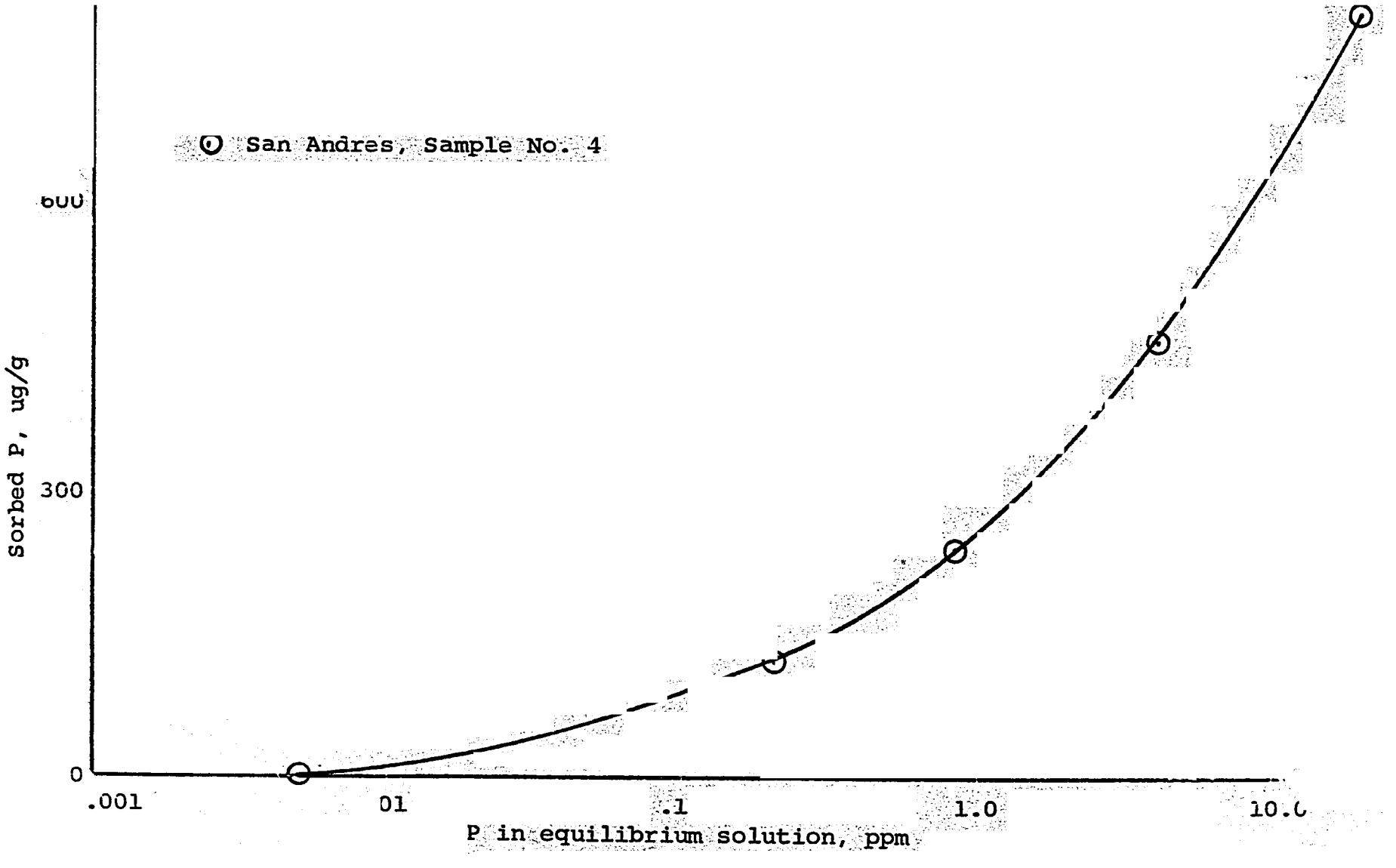
Sample No.	Location	Amounts of phosphate added, ug/g soil				
		0	125	250	500	1000
4	San Andres-Tuxtla	6	15.5	20.0	50.5	67.7
7	Catemaco	6	3.7	7.5	19.5	53.0
24	Kankab	4	8.1	26.1	60.0	68.0
25	Tzekel	6	3.3	7.6	23.8	73.7

		Amounts of phosphate added, ug/g soil						
		0	25	50	75	100	125	250
1	San Andres-Tuxtla	3.8	7.3	8.1	--	15.7	19.0	
2	San Andres-Tuxtla	.9	3.5	6.9	--	13.8	17.2	
3	San Andres-Tuxtla	1.6	3.5	5.6	--	12.0	15.2	
5	Olotepec	.7	1.2	2.2	3.5	4.0	--	13.2
9	Acayucan	.5	4.5	9.0	17.0	22.1	--	40.5
11	Cardenas	5.7	7.5	14.1	--	21.1	--	--
17	Poblado E. Zapata	.7	3.0	8.1	12.6	20.1	--	77.1
20	Uzumacinta	.2	6.6	12.1	15.7	18.1	--	40.0
21	Uzumacinta	.3	3.3	9.3	--	12.7	--	--
22	Escorcega	1.2	3.3	5.3	--	12.0	--	--
23	Escorcega	.2	9.7	19.3	--	40.0	--	--
26	Carimagua	.7	.6	1.5	2.8	5.7	--	20.0
28	Georgeville	.2	1.0	2.1	4.0	5.3	--	18.2

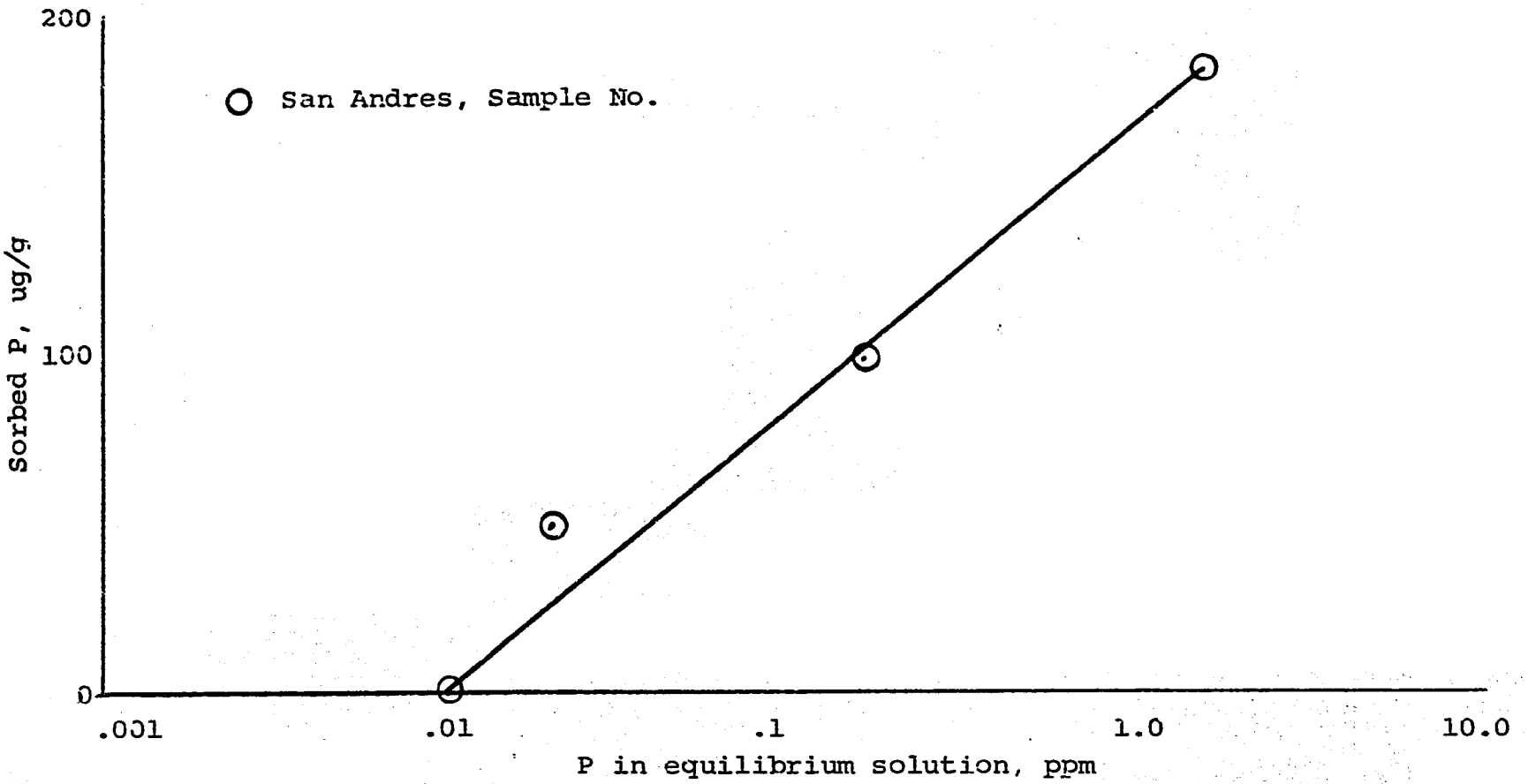
Appendix C. Phosphate Sorption Isotherms



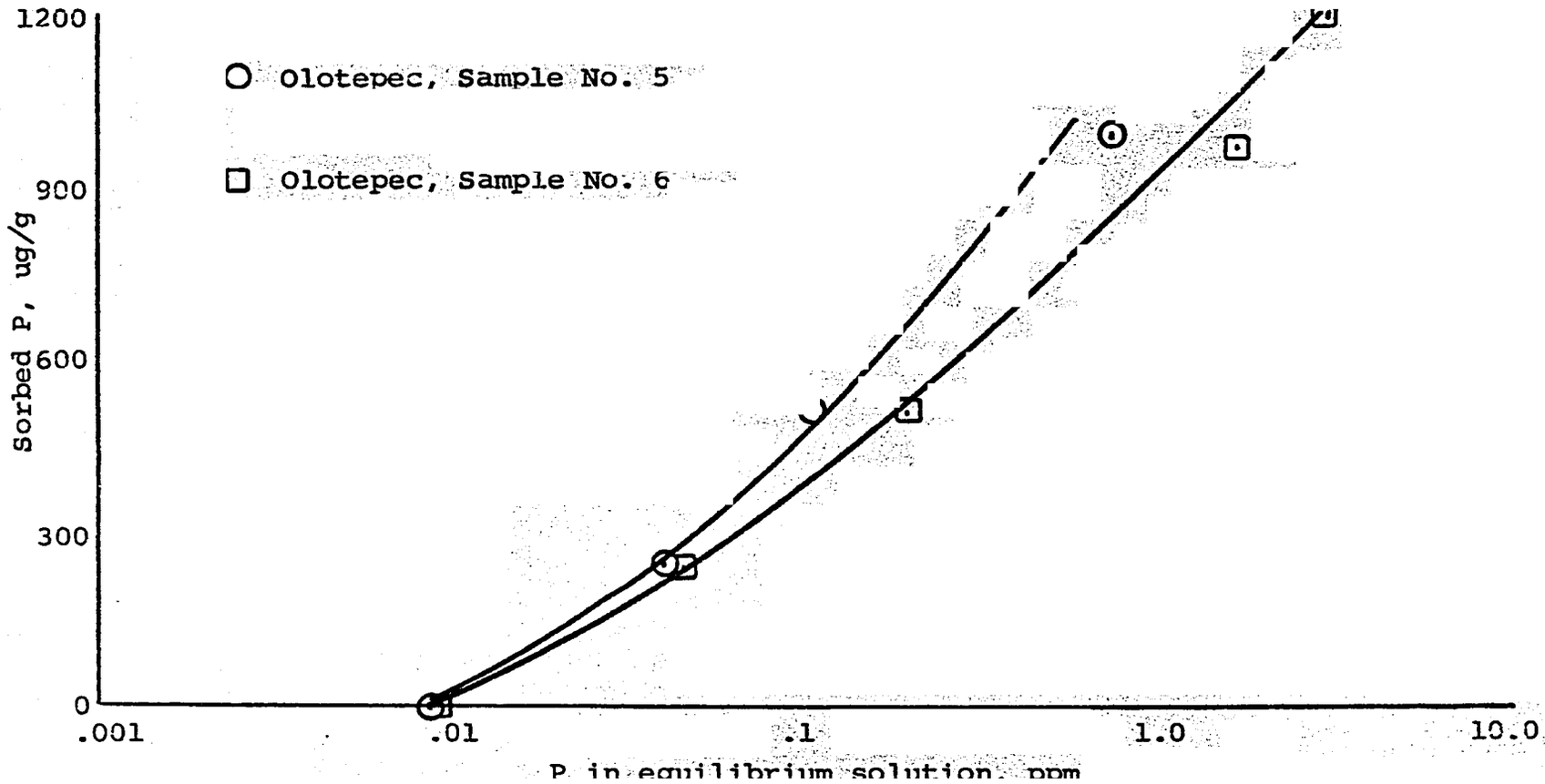
Appendix Figure 1. Phosphate sorption isotherm of the soil from San Andres, samples 1 and 2



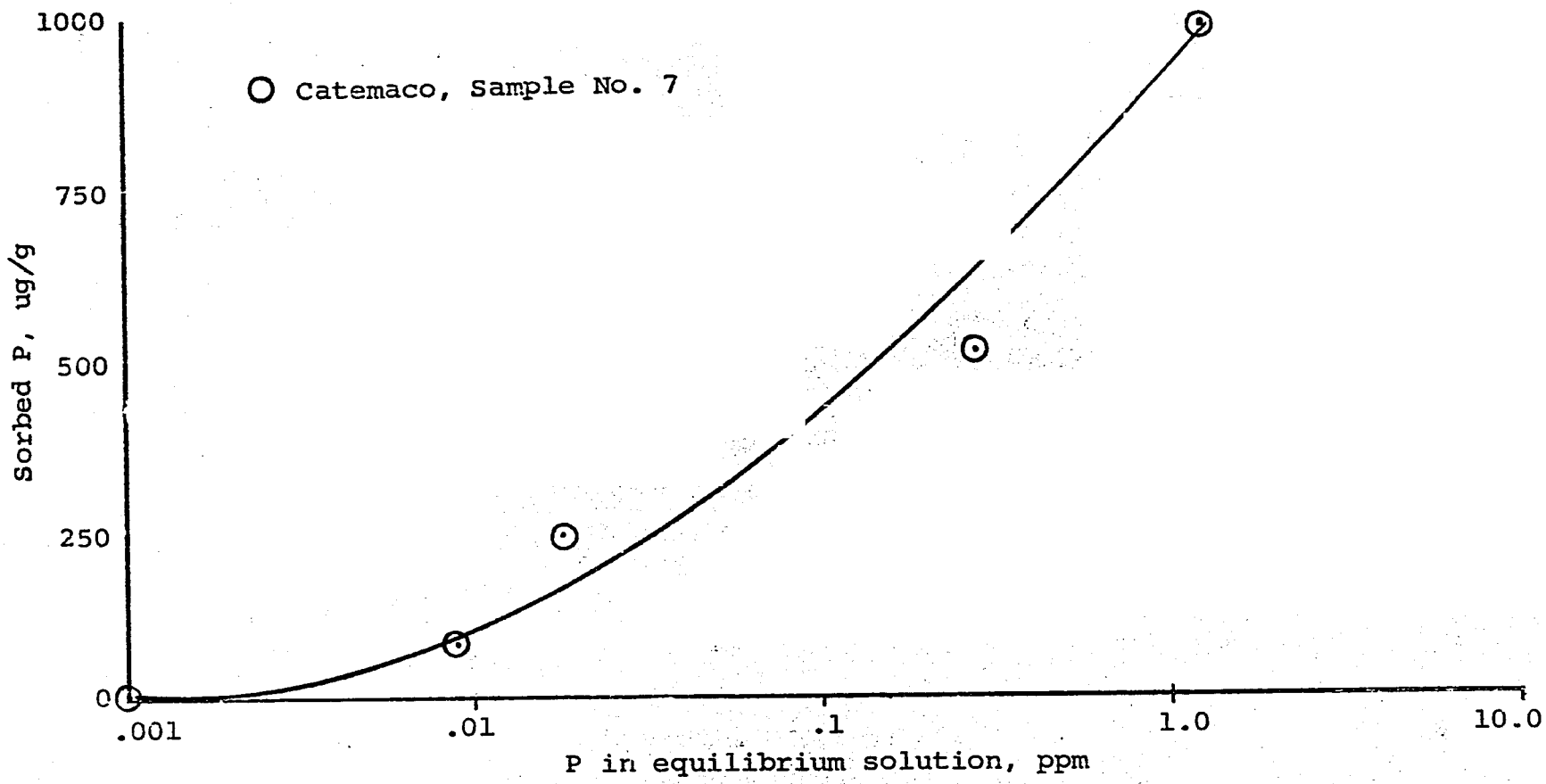
Appendix Figure 2. Phosphate sorption isotherm of the soil from San Andres, sample 4



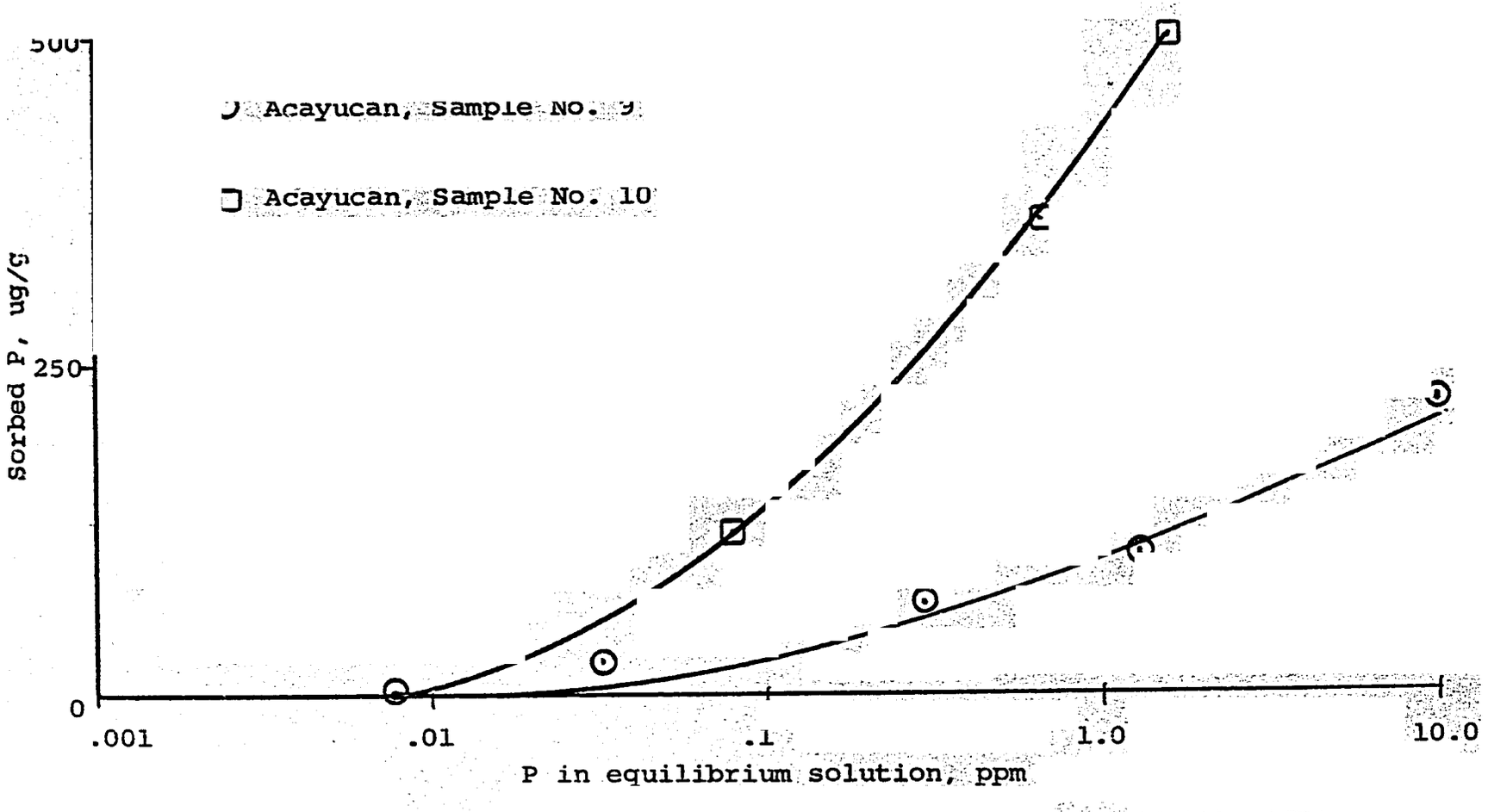
Appendix Figure 3. Phosphate sorption isotherm of the soil from San Andres, sample 3



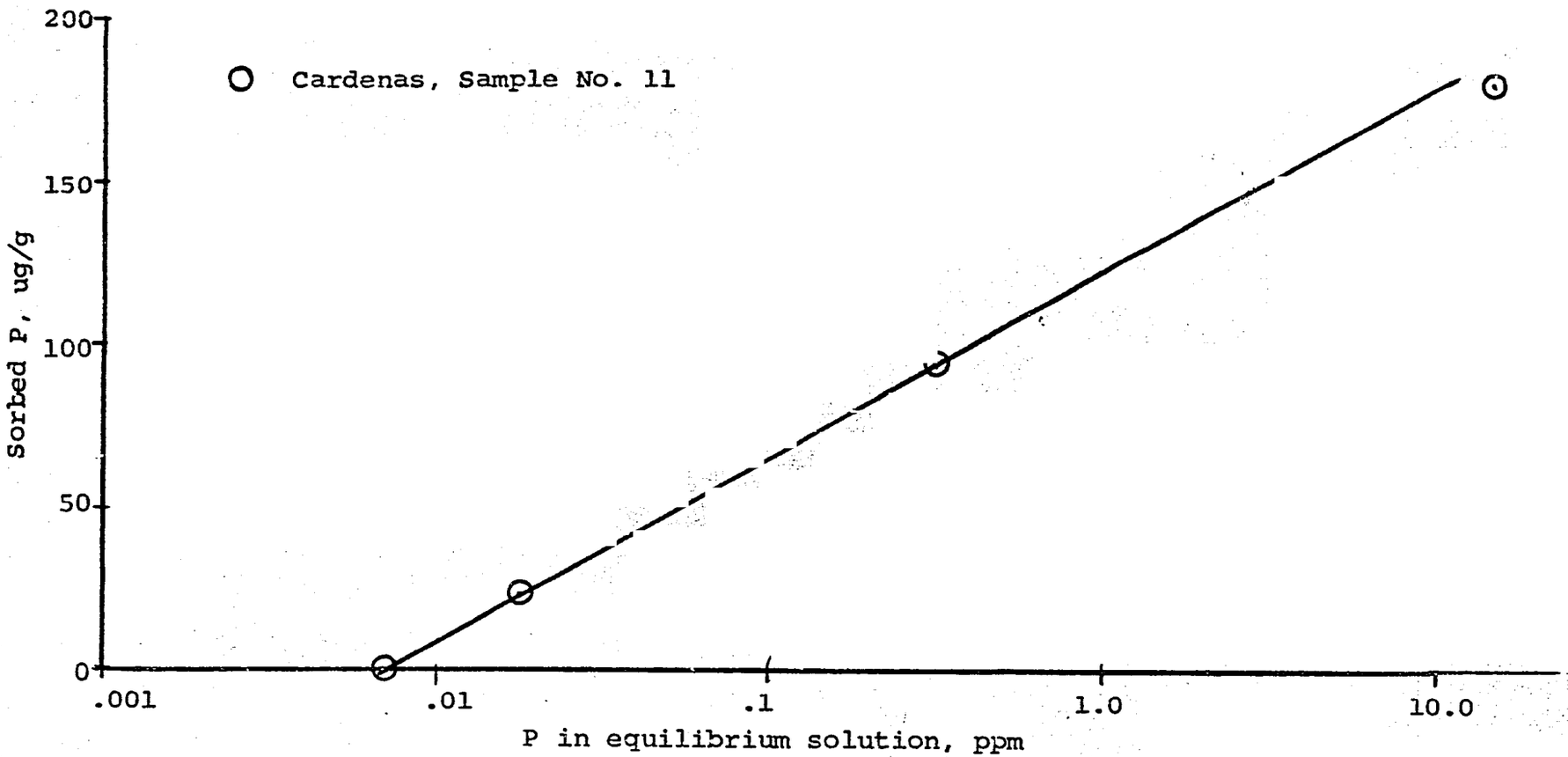
Appendix Figure 4. Phosphate sorption isotherm of the soil from Olotepec,



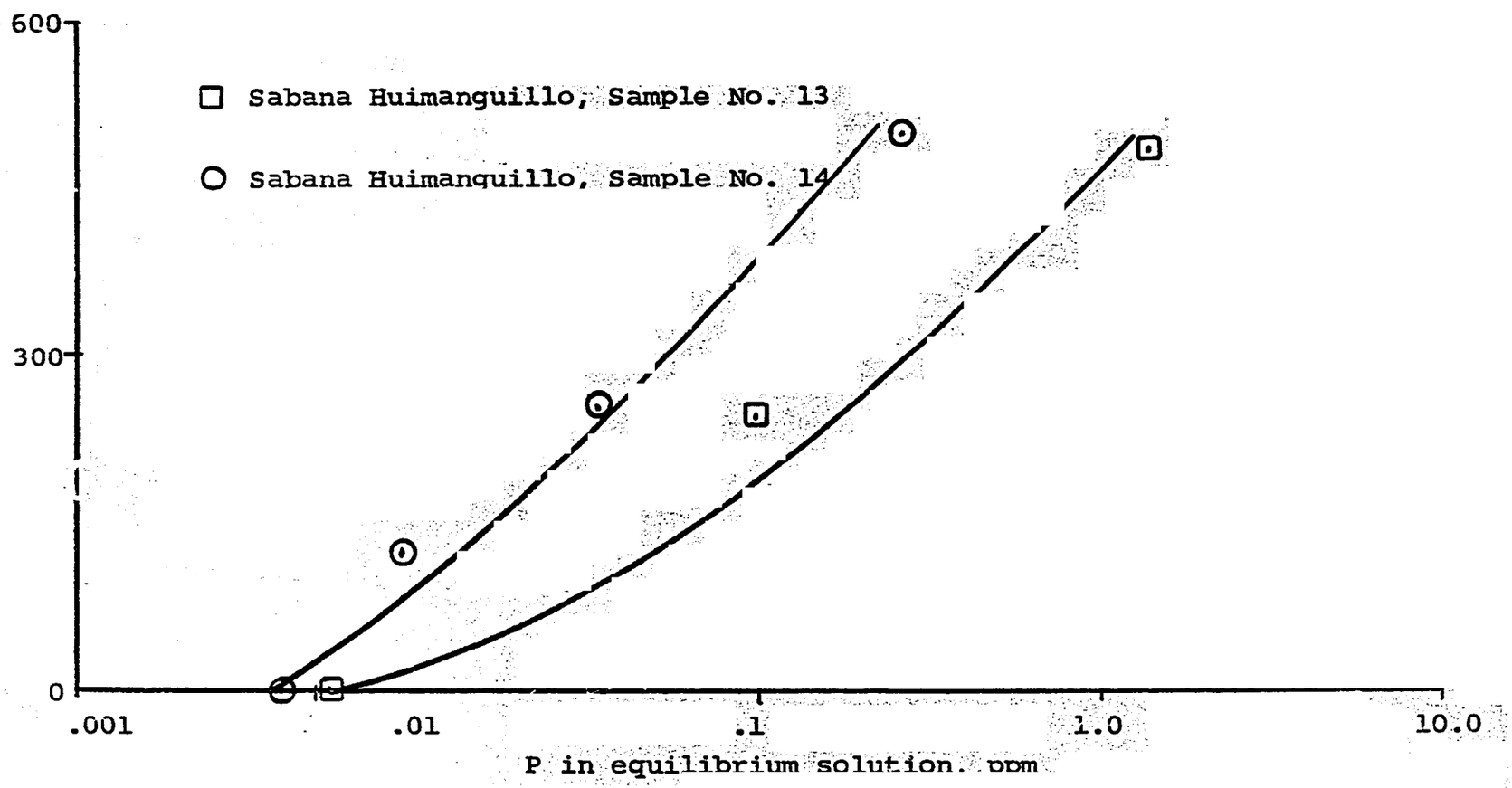
Appendix Figure 5. Phosphate sorption isotherm of the soil from Catemaco, sample 7



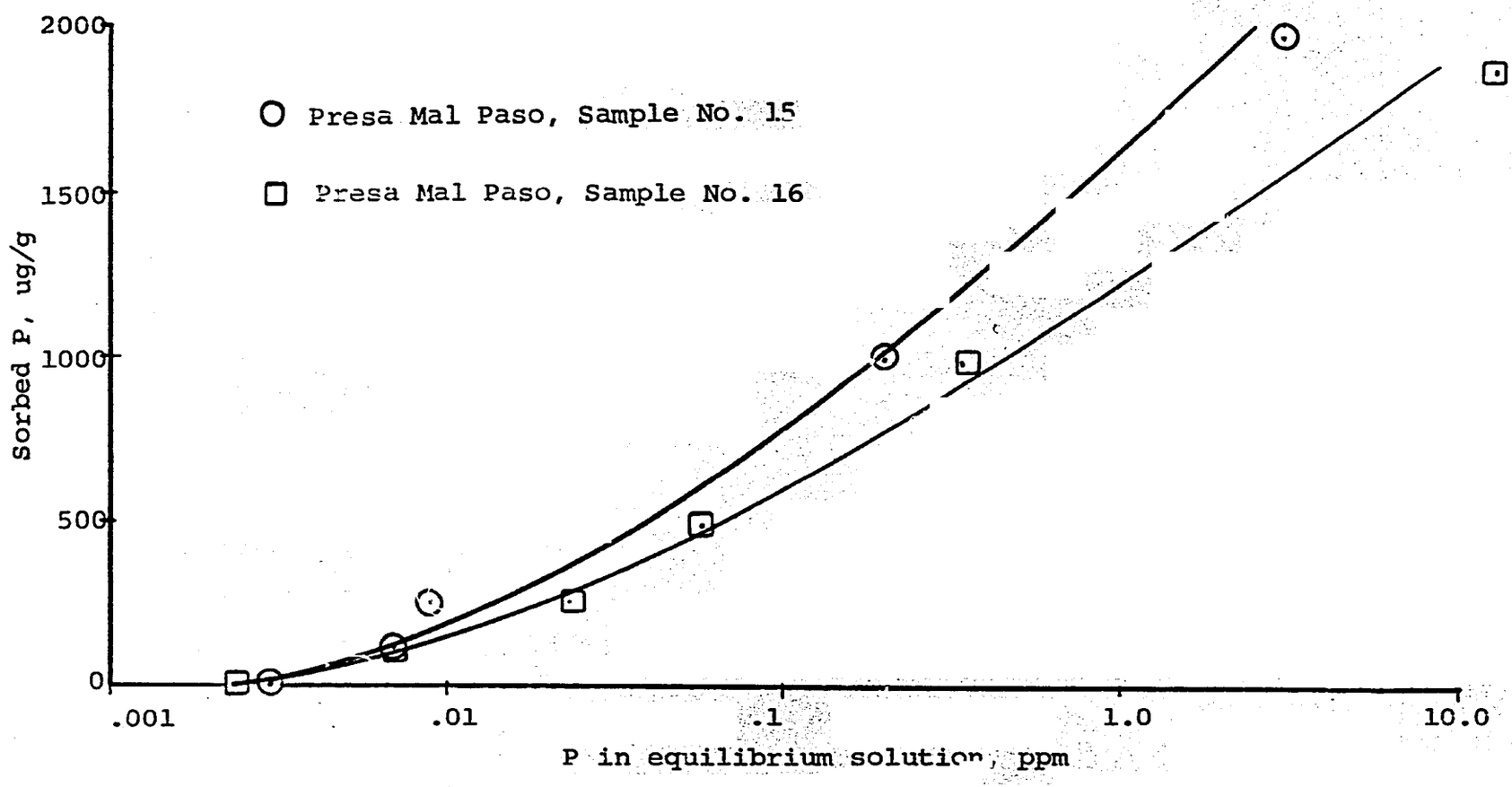
Appendix Figure 6. Phosphate sorption isotherm of the soil from Acayucan, samples 9 and 10



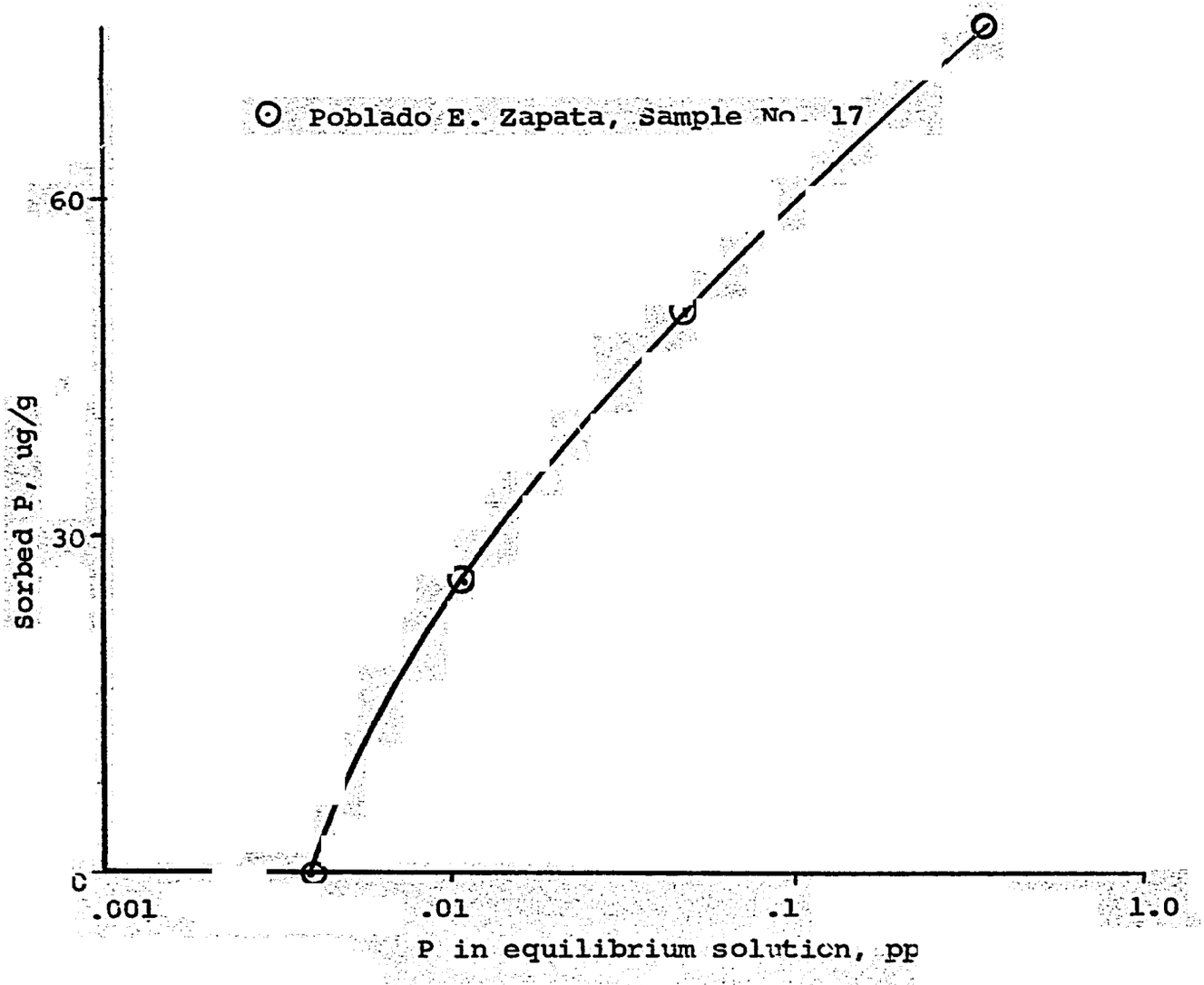
Appendix Figure 7. Phosphate sorption isotherm of the soil from Cardenas, sample 11



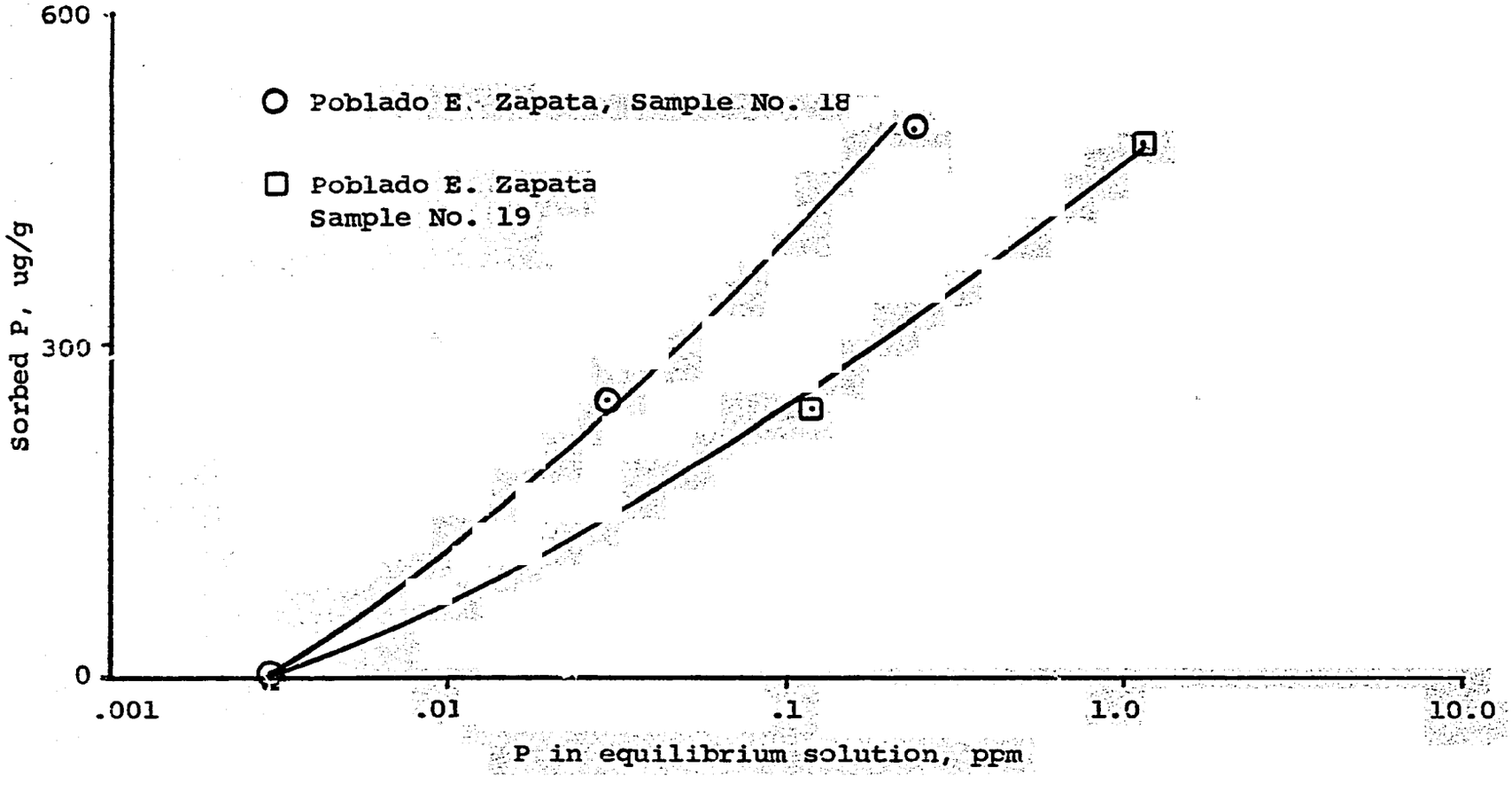
Appendix Figure 8. Phosphate sorpti... from Sabana Huimanquillo, samples 13 and 14



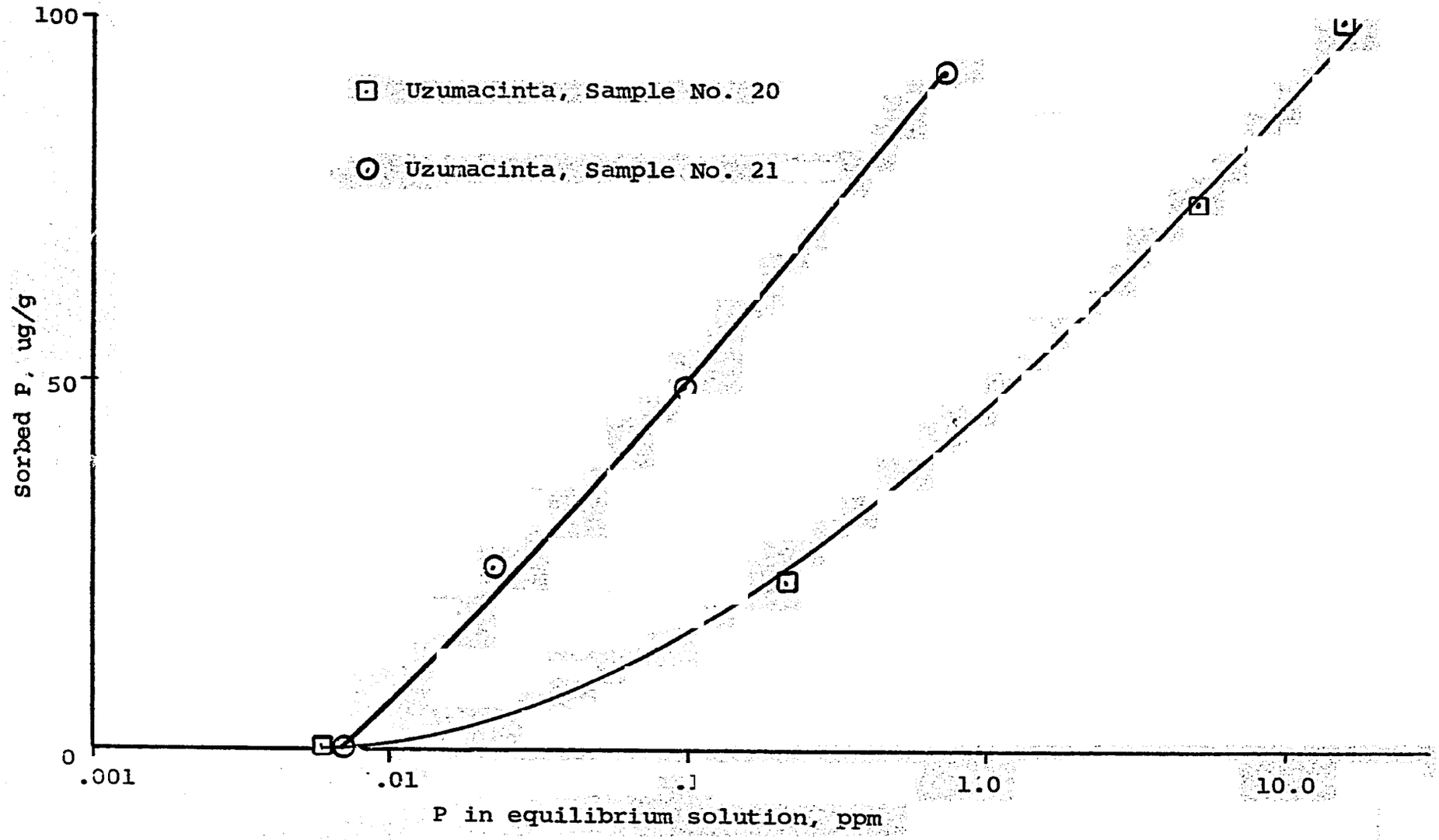
Appendix Figure 9. Phosphate sorption isotherm of the soil from Presa Mal Paso, samples 15 and 16



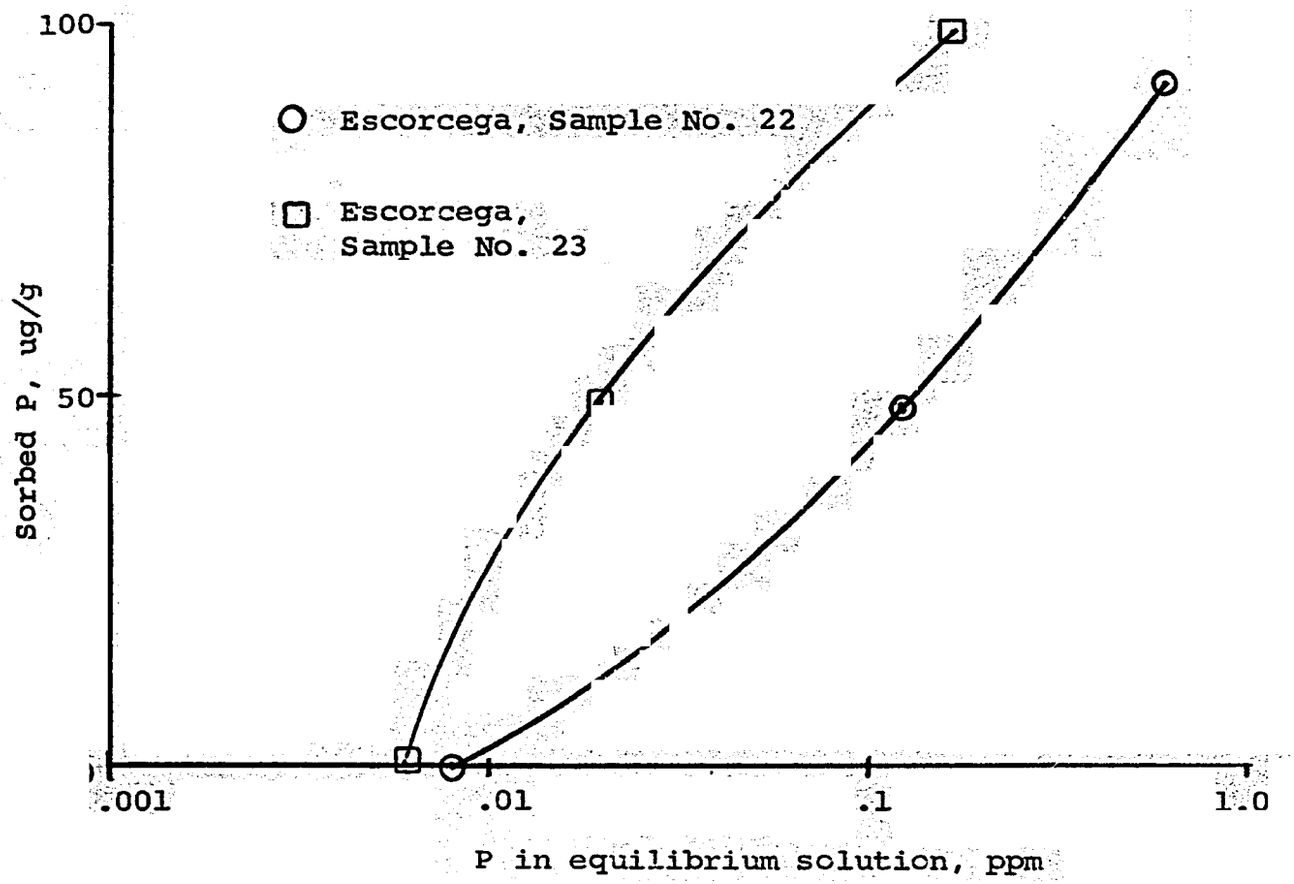
Appendix Figure 10. Phosphate sorption isotherm of the soil fro
Poblado E. Zapata, sample 17



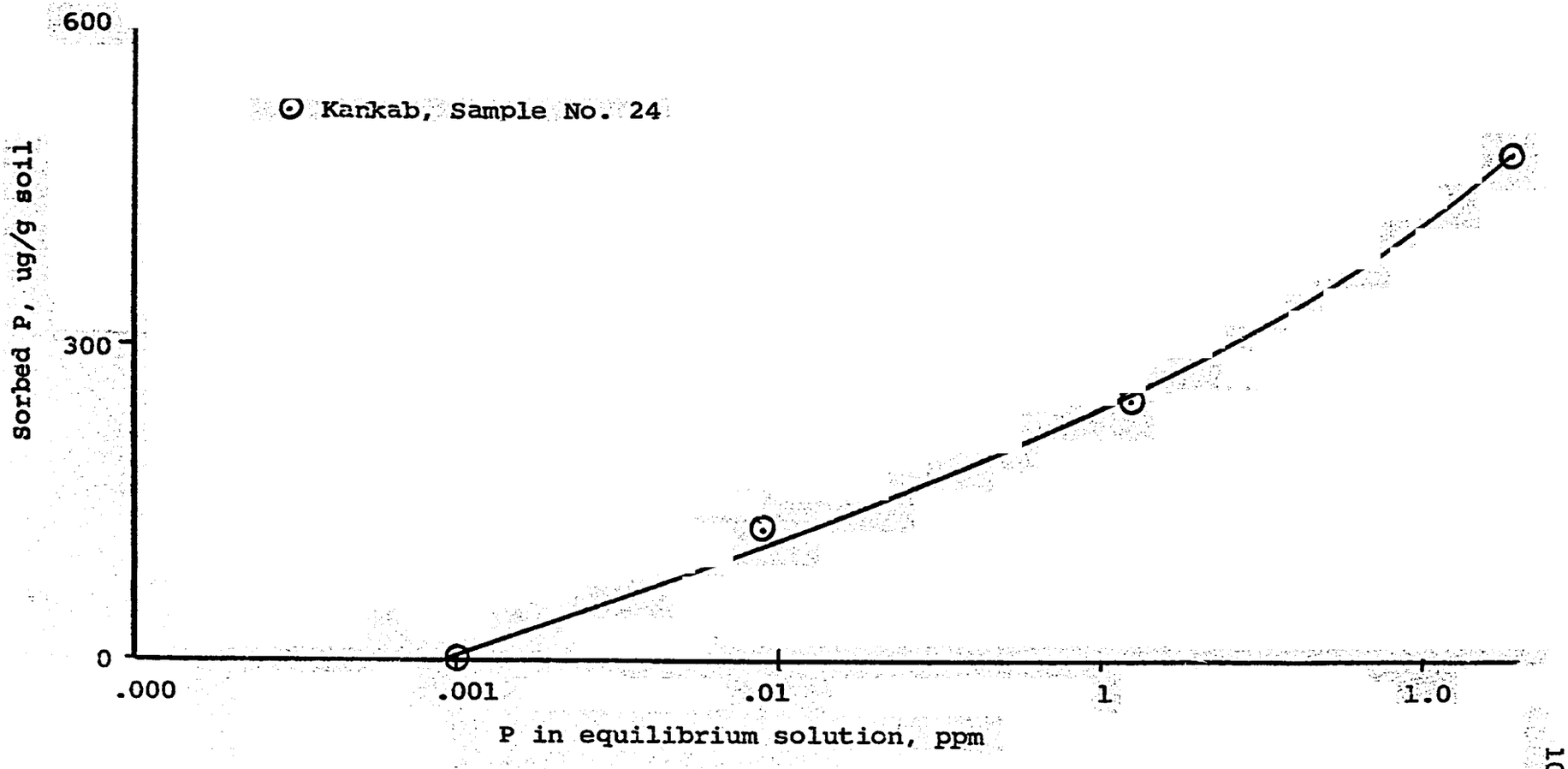
Appendix Figure 11. Phosphate sorption isotherm of the soil from Poblado E. Zapata, samples 18 and 19



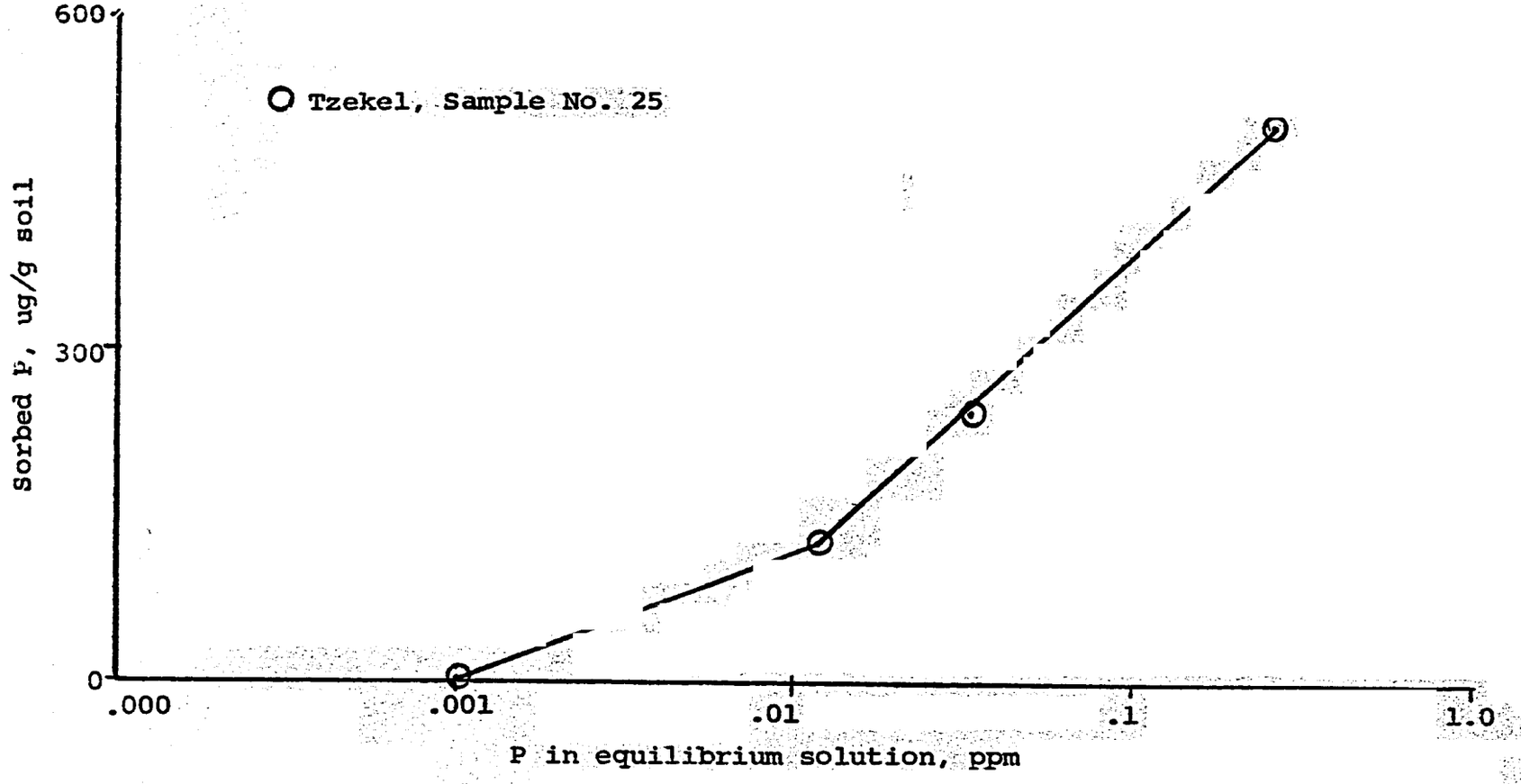
Appendix Figure 12. Phosphate sorption isotherm of the soil from Uzumacinta samples 20 and 21



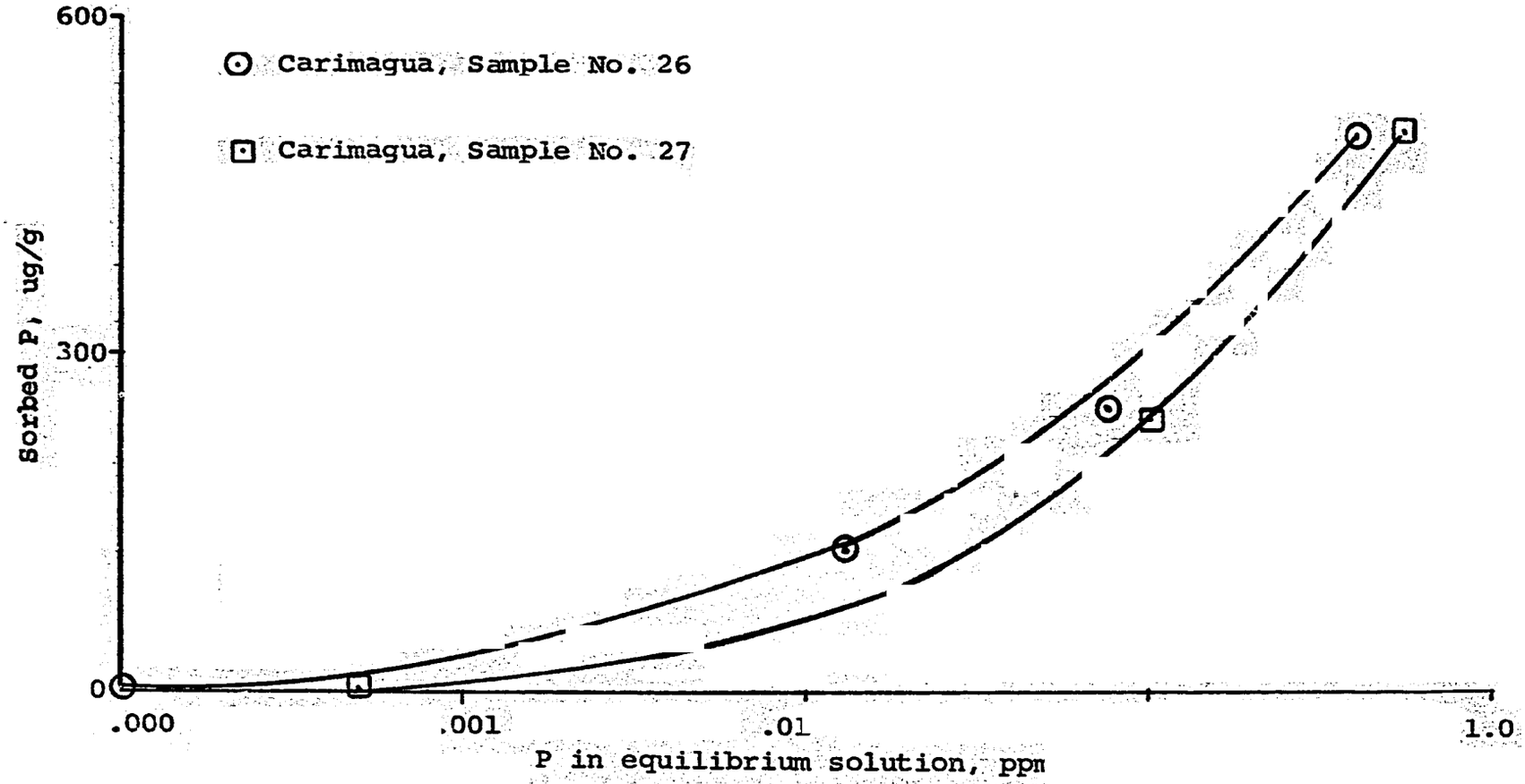
Appendix Figure 13. Phosphate sorption isotherm of the soil from Escorcega, samples 22 and 23



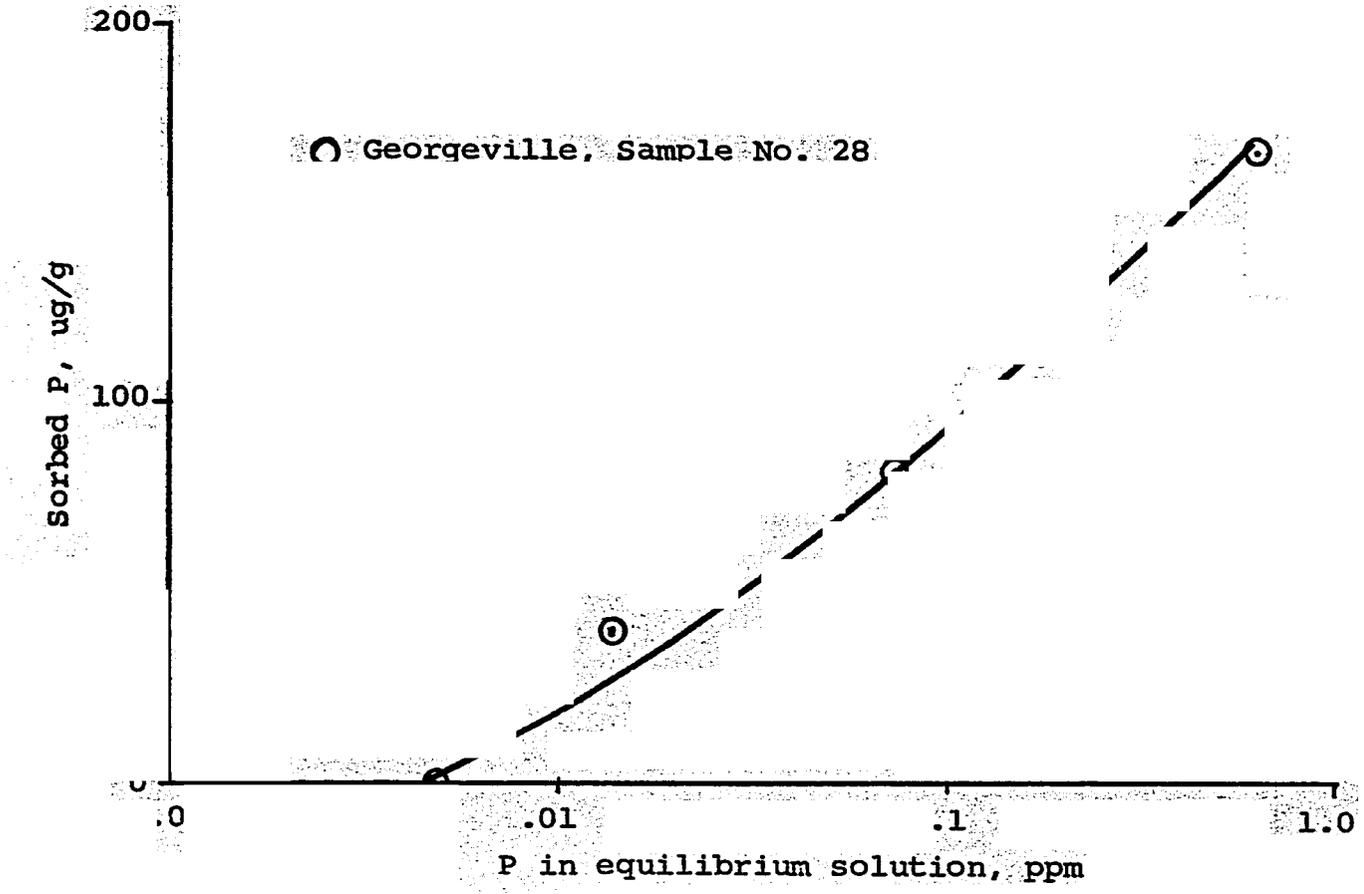
Appendix Figure 14. Phosphate sorption isotherm of the soil from Kankab sample 24



Appendix Figure 15. Phosphate sorption isotherm of the soil from Tzekel sample 25



Appendix Figure 16. Phosphate sorption isotherm of the soil from Carimagua, samples 26 and 27



Appendix Figure 17. Phosphate sorption isotherm from the Georgeville soil