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SOLUBILITY, UPTAKE AND LEACHING OF PLANT NUTRIENTS: PHOSPHATE, SULFATE AND CALCIUM

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Nutrient availability and mobility (including leaching) is related to solubility. Phosphates and sulfates are adsorbed by highly weathered soils so that amounts in solution are small in comparison with amounts adsorbed. Except for soils with organic colloids, phosphate leaching in Hawaii soils cannot be a significant factor in any reasonable agronomic system. Sulfate leaching can be accelerated by liming and phosphate fertilization.

Calcium leaching can be demonstrated in typical agricultural situations in Hawaii. This results from the near complete lack of permanent negative charge in many soils, especially those developed from volcanic ash. This fact permits the use of small amounts of lime or calcium fertilizers to correct calcium malnutrition and it permits liming subsoils without deep mechanical placement of lime.

It now seems practical to describe soil fertility in terms of the concentration of nutrients in the soil solution and fertilizer requirements in terms of amounts of nutrients soil must to give these required concentrations.

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SOLUBILITY, UPTAKE AND LEACHING OF PLANT NUTRIENTS: PHOSPHATE, SULFATE AND CALCIUM*

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Nutrient uptake by plants and nutrient leaching in soils is a function of nutrient solubility. But nutrient solubility can be considered from at least 3 very different points of view.

First is the solubility of nutrients in an extracting solution. Many kinds of soil extractants have been developed depending on the purposes of the investigator and the chemistry of the soil. There has been a tendency to confuse "extractable" nutrients with "available" nutrients. The two are almost never the same--a point which the wise agronomist keeps firmly in mind. There is the hope--which springs eternal--that "extractable" is in some manner related to "available", which is, in turn, related to "uptake". That this hope frequently does not disappoint us has been abundantly documented. Soil testing does work--some methods much better than others. However, to hold that soil testing always works is as rash as giving no credit at all. There are those of us who think that there may be more rational approaches than those now in general use.

The second view concerning solubility is that of fertilizer solubility. This is an important topic since it is related to uptake and leaching especially during the interval of time before reactions with soil components have created entirely new compounds and complexes having solubilities unrelated to the original fertilizer materials. Usually this time interval is rather short but frequently it is long enough to make a big difference for rapidly growing crops.

The aspect of solubility which perhaps is more fundamental is solubility of nutrients in soil solutions. It is now fairly well established that plants, if they are adequately nourished, derive most of their nutrients from the soil solution. (We are eliminating from discussion "foliar feeding".) That is to say, nutrient uptake by contact exchange, whereby the root obtains nutrients directly from the solid phase without the nutrient ever really being in solution, probably does not amount to much <u>if the plant is taking up nutrients at a rapid rate</u>.

It is also well established that, within the concentration range normally encountered in soil solutions, nutrient uptake by plants is concentration dependent. Fortunately, the relationships which hold for well designed and well executed solution culture experiments (of which there are very few) generally hold for plants growing in soils as well.

Not only is nutrient absorption by plants concentration dependent, but the flux of nutrients to roots is also. The quantity of a nutrient being carried to a root system by mass flow is the product of the amount of water transpired and the concentration of that nutrient in the soil solution which moves. Likewise, leaching through a soil section is the product of concentration and volume of solution moving through that section.

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*Address presented at the 5th Hawaii Fertilizer Conference, May 5, 1972, Honolulu, Hawaii.

Nutrient movement to, or away from, roots by diffusion depends upon concentration gradients. Concentration gradients in the soil solution depend upon the solubility of nutrients at one end of the supply trail and the level of nutrient depletion by plant roots at the other end. It helps, of course, if the "trail" is as short and wide and direct as possible; but the prime mover is the concentration gradient. Without it there is no net movement by diffusion.

So, nutrient solubility is paramount in assessing the nutrient status of soils because it controls the flow of nutrients from soil to roots by both mass flow and diffusion and it controls uptake by roots.

The relationship between nutrient (phosphate) concentration in solution and phosphate uptake by plants is illustrated in Figure 1.

PHOSPHORUS SOLUBILITY IN RELATION TO PHOSPHATE ADSORBED AND OTHER FACTORS

Phosphate concentration in soil solutions is related to several factors. Amounts of labile phosphate (phosphate which equilibrates) in relation to the soils capacity of hold labile phosphate is of primary importance. The more highly saturated the soil is the greater P solubility will be. The capacity of soils to hold labile phosphate is a function of soil mineralogy and texture primarily. These are not easily manipulated but the amount of labile phosphate can be controlled by fertilization and management practices.

Phosphate fertilizer solubility, associated elements in the fertilizer, fertilizer placement and certain factors in soil chemistry such as pH and exchangeable cations are usually of secondary importance.

Figures 2 and 3 illustrate the importance of soil mineralogy and amounts of phosphate adsorbed by soils on phosphate solubility. Soils which contain much silicon-poor, amorphous material (among these are Hydrandepts formed from weathered volcanic ash) adsorb tremendous amounts of phosphate before phosphate solubility becomes appreciable. The Hydrandept of Figure 2 which had not been phosphate fertilized, had a phosphate fertilizer requirement of about 8 tons treble superphosphate per acre to adjust the soil solution to about 0.2 ppm P, which is approximately the concentration of phosphate required in solution for 95% tomato yields. When about 6 tons of treble superphosphate had been applied previously to 5 successive tomato crops, solution phosphate levels were greatly improved but were still below adequacy. A very different soil, a Haplustoll (Figure 3), which is much less weathered, is well supplied with phosphate for most crops. The amount of phosphorus this soil will adsorb to produce a shift of the adsorption curve to the right (more phosphate in solution) is an order of magnitude less than would be required for a similar shift for the Hydrandept.

There is a popular misconception abroad that liming acid soils greatly increases phosphate solubility. This concept is probably valid only over the pH range where aluminum solubility is decreasing rapidly with increasing pH (below pH 5.2). In the pH range where most agricultural crops are grown liming has little effect on phosphate solubility if calcium is held constant. Note in Figure 4 that one curve describes phosphate solubility at 3 pH levels.

There is abundant evidence that polyvalent ions, including calcium, depress phosphate solubility more than equivalent concentrations of monovalent cations. This may be one reason why fertilizers containing ammonium, bonded with phosphates, often enhances phosphate uptake by plants. A graph showing the relationships between phosphate solubility and concentrations of calcium and sodium in solution is presented in Figure 4. The fact that phosphate solubility is so sensitive to cation concentration is reason enough to avoid liming more than is required to precipitate aluminum and provide enough calcium for nutrition. This point usually occurs well on the acid side of pH 6.

PHOSPHORUS UPTAKE AND CROP YIELDS IN RELATION TO SOLUBILITY

The practical implications of the generalization we have just discussed is illustrated in Figure 1 which shows that phosphate fertilizer utilized by a crop was closely related to the amount of fertilizer phosphorus which remained in solution two days after it was applied.

The data of Figure 1 was obtained using several soils and liming rates. Recently we have been engaged in determining phosphate response curves for several crops growing on plots which are differentially fertilized so that phosphorus in solution ranges from a level the unfertilized soil will support to 1.6 ppm P. Eight to ten phosphorus levels are maintained at each of 5 locations. Figure 5 is an example of one such response curve. We have found that the external phosphate requirement (the concentration of phosphorus in solution required for 95% maximum yields) of corn is about 0.05 to 0.07 ppm and that this range seems to apply to a wide range of soil and climatic conditions.

Crops vary in their external phosphate requirement. The requirement of lettuce, for example, is about 0.3 ppm.

PHOSPHORUS LEACHING IN RELATION TO SOLUBILITY

From what has been said about low phosphorus solubility in Hawaii soils, it is obvious that phosphorus leaching does not pose a general problem. Simple arithmetic will illustrate the point. The Waialua soil of Figure 3 has high phosphate solubility by Hawaii standards. At 0.1 ppm P in solution about 4 acre feet of water would be required (as leachate) to move one pound of phosphorus into the first increment of subsoil. For most soils phosphate leaching would be much less.

This does not imply that phosphate leaching is never a problem. We have recently reported (Hawaii Farm Science 20:(4):1-4, 1971) on the hazards of over fertilization of macadamia on aa rockland. The colloidal fraction of these soils (what little there is of it) is mostly organic matter. These materials adsorbs relatively little phosphate unless aluminum saturation is very high. An example of phosphate leaching in a soil containing 10% organic matter and 90% quartz sand is presented in Figure 6. The untreated soil contained some aluminum which slowed down phosphate leaching. When the soil was aluminum saturated (Al-soil) by leaching with ammonium chloride solution there was no measurable phosphate leaching.

SULFATE SOLUBILITY AND AVAILABILITY

In some respects sulfates react with soils like phosphates. For example acid soils which contain an abundance of silicon depleted of amorphous materials high in iron and aluminum adsorb sulfate. Since Hawaii has many soils which meet these specifications sulfate adsorption is a factor influencing sulfate solubility on most soils of the state. There are some notable differences between phosphate and sulfate adsorption.

1. Sulfate is held much less tenaciously than phosphate; thus its solubility is higher. Phosphate readily displaces adsorbed sulfate.

2. Sulfate adsorption is very pH dependent. Liming will increase sulfate solubility until the sulfate so mobilized is displaced by leaching. Soils which are naturally near neutral pH adsorb little sulfate. These soils readily lose sulfate by leaching if there is excess rainfall or irrigation.

Figure 7 presents sulfate adsorption curves for two Hawaii soils. Amounts of sulfate S in solution at zero sulfate added or withdrawn is usually in the range 1 to 10 ppm although some sulfur deficient soils contain less than 1 ppm sulfate S in equilibrated solutions.

Frequently, amounts of sulfate in solution are only a small fraction of that which is soluble in phosphate extracts. Table 1 gives the distributing of sulfate sulfur in the Akaka soil of Figure 7 and compares two soils developed from basalt with the Akaka soil which was developed from volcanic ash.

Table 1

Comparison of phosphate extractable sulfate sulfur in profiles of three Hawaii soils

Depth (inches)	SO_4 -- S extracted (µg/g)*		
	Akaka	Kinau	Wahiawa
0 - 6	216	111	135
6 - 12	1,209	82	66
12 - 18	3,291	74	116
18 - 24	4,173	114	176
30 - 36	5,965	317	152
42 - 48	4,742	426	230

*Data reported for the Akaka soil are for 4 repeated extraction. The extracting solution was 500 ppm P as $Ca(H_2PO_4)_2$ using a 1:5 solution:soil ratio

The concentration of sulfur required in solutions for adequate plant nutrition has not been determined with great precision but we have some data available. Kikuyu grass growing in pots responds to increasing sulfate application until sulfate in solution is adjusted to at least 5 ppm. Young sugar cane, before shoot roots develop, respond to sulfate applications up to about 15 ppm S in solution. These external sulfur requirement apparently decreases to about 5 ppm after shoot roots develop. An example of the response of young sugar cane to increasing concentration of NO_3 and SO_4 is presented below.

Table 2

Yield of sugar cane grown in pots (soil) in relation to concentration of sulfate and nitrate in irrigation water

SO_4 - S in solution (ppm)	10	20	40	80
	---------- yield, grams ----------			
0.6	30	47	52	49
1.7	26	46	57	82
5.0	25	51	111	110
15.0	27	44	90	112
45.0	28	45	95	120

The above data are for sugar cane growing in pots in a soil with little capacity to adsorb sulfate. The external sulfur requirement is probably lower under field conditions, especially for soils which have ample reserves of adsorbed sulfate to continuously renew sulfur in soil solutions. Probably the external sulfur requirement will decrease as 'shoot roots' develop. These results are in reasonable agreement with corn data from Nebraska (Jaeger and Fox, Agronomy Journal 63:729-732, 1971) which indicates that corn being irrigated with water containing 3 ppm S was borderline S deficient.

These data suggest that the solubility of adsorbed S may be a limiting factor in sulfur uptake and yield even though total quantities of soil sulfate are great.

To correct sulfur deficiencies of equivalent intensities, we expect that initial rates of sulfate fertilization should be greater for weathered volcanic ash soils than for typical soils of the temperate zone. However, because of the buffering effects of adsorbed sulfate in highly weathered soils, leaching of sulfate from our soils may be less severe than is frequently observed elsewhere.

Liming and phosphate fertilization will solubilize adsorbed sulfate and increase its availability until it is leached into subsoil. We presume that the long term effects of liming will be to deplete the surface soil of sulfate.

SOLUBILITY, UPTAKE AND LEACHING OF CALCIUM

The chemistry of calcium in soils is very different from phosphate or sulfate. Calcium is included here to round out the discussion.

Most soil calcium is present in the ionic form adsorbed by the colloidal complex. If clay colloids are of the swelling, 2:1 type, calcium is held with a great deal of energy. This is related to the very high negative charge on these colloids. These charges arise from within the crystal structure of the clays and are not effected by external circumstances. They are permanent charges and because there is little or no positive charge these clays are said to possess a high net negative charge. Hawaii has some clays of this type; the Lualualei soil is a good example.

In contrast are those clay colloids of the 1:1 type and those which have little organization. The latter are very poorly crystalized or are amorphous although these colloids may have many charged spots they usually have both negative and positive charge at the same time. The relative proportion of negative and positive charge depends upon external conditions, especially pH. Because the positive charge (+) tend to cancel negative(-)charge, these colloids have low net negative charge and, in fact, if pH is decreased low enough a "zero point of charge" is reached. This does not imply that there is no charge but rather that positive and negative balance and net charge is zero. When conditions are extremely acid, the colloids may carry net positive charge.

Since like charges repells, it is easy to see why colloids which carry a considerable component of positive charge do not adsorb calcium ions (also positively charged) very strongly.

The highly weathered soils of Hawaii, especially those developed from volcanic ash are rich in amorphous materials which have a large component of positive charge at the pH levels normally encountered in the field. The cation exchange capacity of these soils is high but the energy of cation adsorption is low. Calcium and potassium leaching is a demonstrated problem in these soil (Mahilum, Fox and Silva. Soil Science 109:102-109. 1969).

Fortunately, because calcium is very active in these soils, calcium availability tends to be much greater than for soils containing 2:1 type clays which are similarly saturated.

We have observed that calcium deficiency in corn, on these soils, can be corrected with a nominal application of treble superphosphate which is monocalcium phosphate (Fox and Tamini, Illustrated Concepts in Tropical Agriculture, Department of Agronomy and Soil Science, University of Hawaii, 1971). This is an indication of how readily calcium is available in these soils.

The following data taken from the report by Hamilton, Fox and Silva demonstrate that calcium leaching (as indicated by extractable Ca and soil pH modification) is an important consideration in Hawaii soils.

Table 3

Influence of lime applied in 1953 on pH and "exchangeable" calcium in soil profiles in 1964

Depth (Inches)	pH				Ca (me/100 g)	
	Lime applied (Tons/Acre)				Lime applied Ton/Acre	
	0	2	5.5	17	0	17
0-6	4.3	5.3	6.1	6.9	1.5	15.3
6-12	5.0	5.1	5.9	6.3	.2	4.0
18-24	5.4	5.5	5.8	6.2	.6	2.5
30-36	5.5	5.7	6.0	6.3	.3	1.5
42-48	5.5	5.9	6.0	6.3	.3	1.2

Calcium leaching is not altogether to be avoided. We have evidence (Green, Fox and Williams, Hawaii Farm Science 14(3)6-8, 1965) that root proliferation in subsoils is inhibited when calcium is low and aluminum is high. Leaching provides the means for favorable modifying our subsoils without the expense of deep placement of lime.

SUMMARY

Nutrient availability and mobility (including leaching) is related to solubility. Phosphates and sulfates are adsorbed by highly weathered soils so that amounts in solution are small in comparison with amounts adsorbed. Except for soils with organic colloids, phosphate leaching in Hawaii soils cannot be a significant factor in any reasonable agronomic system. Sulfate leaching can be accelerated by liming and phosphate fertilization.

Calcium leaching can be demonstrated in typical agricultural situations in Hawaii. This results from the near complete lack of permanent negative charge in many soils, especially those developed from volcanic ash. This fact permits the use of small amounts of lime or calcium fertilizers to correct calcium malnutrition and it permits liming subsoils without deep mechanical placement of lime.

It now seems practical to describe soil fertility in terms of the concentration of nutrients in the soil solution and fertilizer requirements in terms of amounts of nutrients soil adsorb to give these required concentrations.

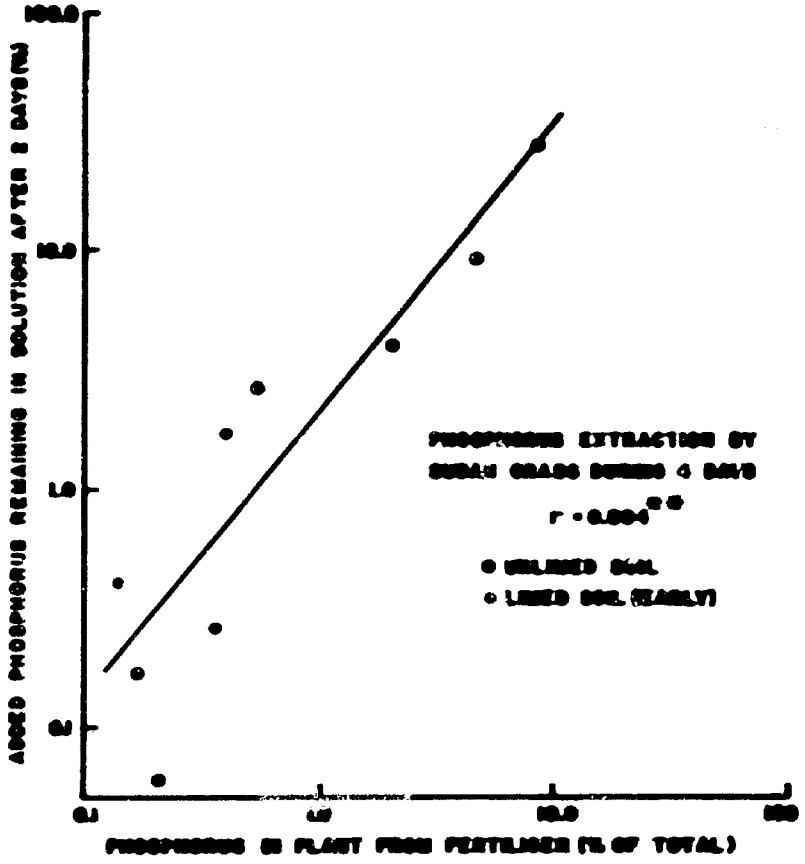

Figure 1. Relationship between phosphate solubility in a soil-water system and phosphate taken up by plants during four days.

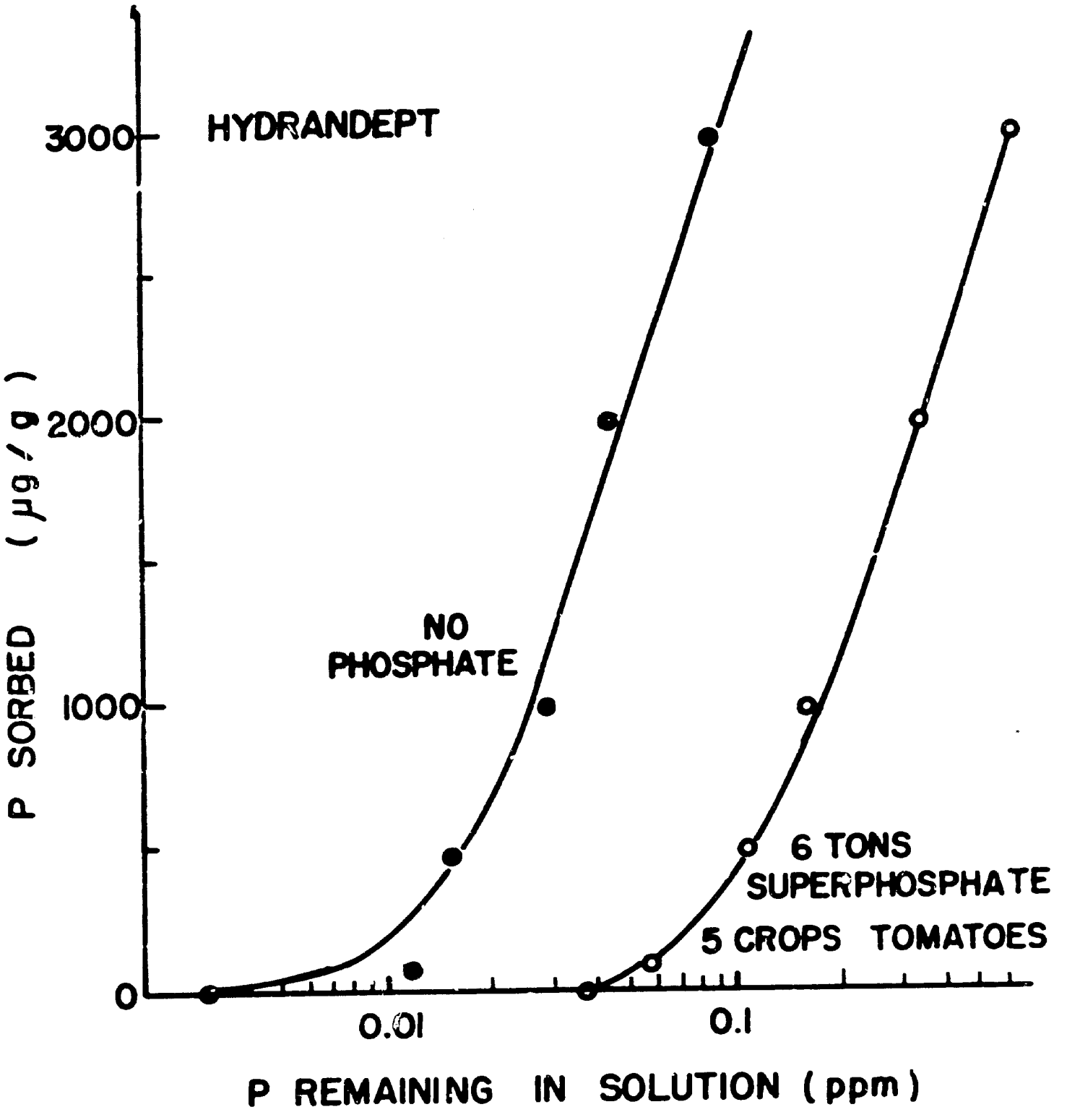

Figure 2. Phosphate in solution in relation to amount of phosphate adsorbed by a Hydrandept from Mountain View, Hawaii. Andepts are soils formed from volcanic ash.

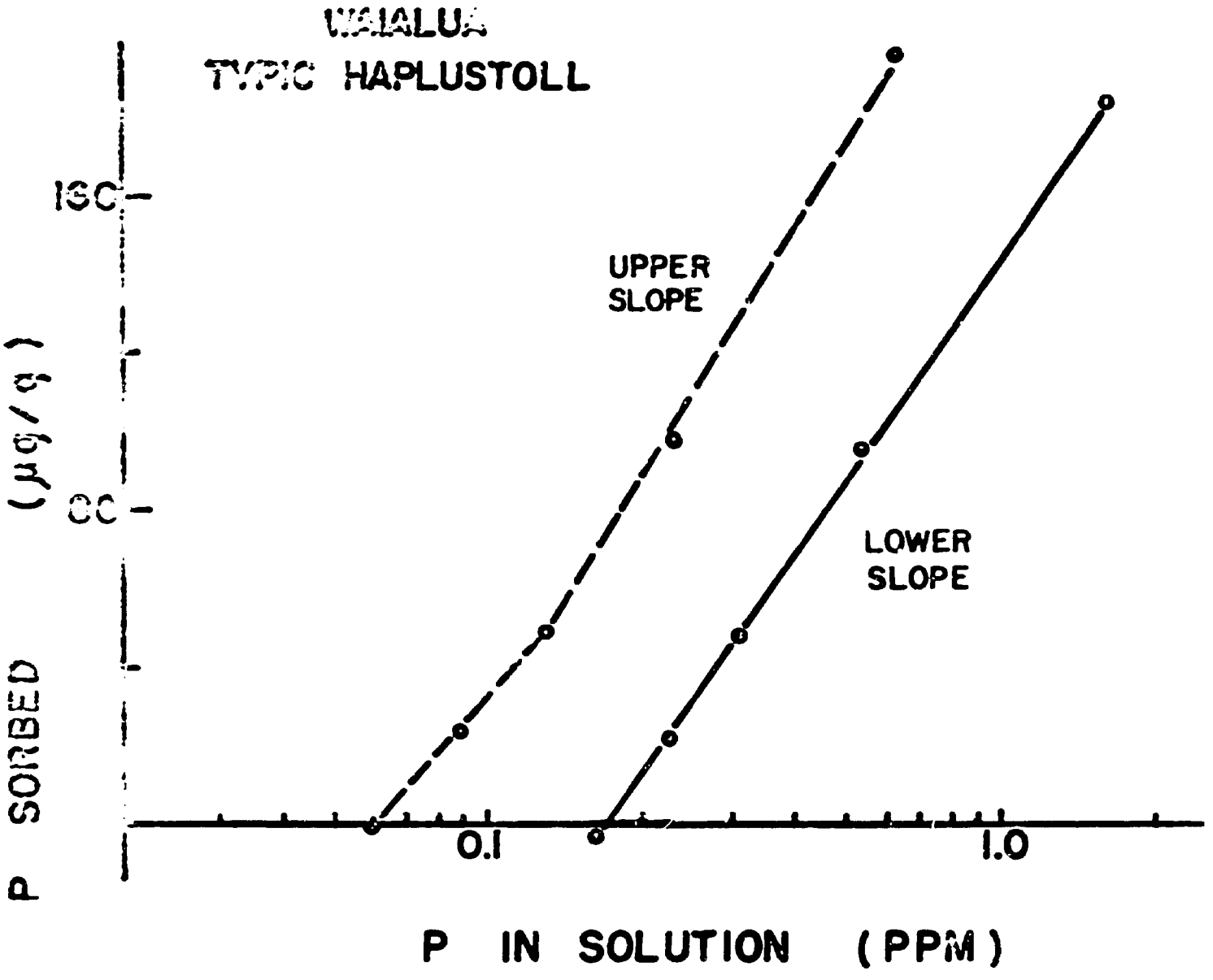

Figure 3. Phosphate in solution in relation to amounts of phosphate adsorbed by a Haplustoll, a Waialua soil, from Waimanalo, Oahu.

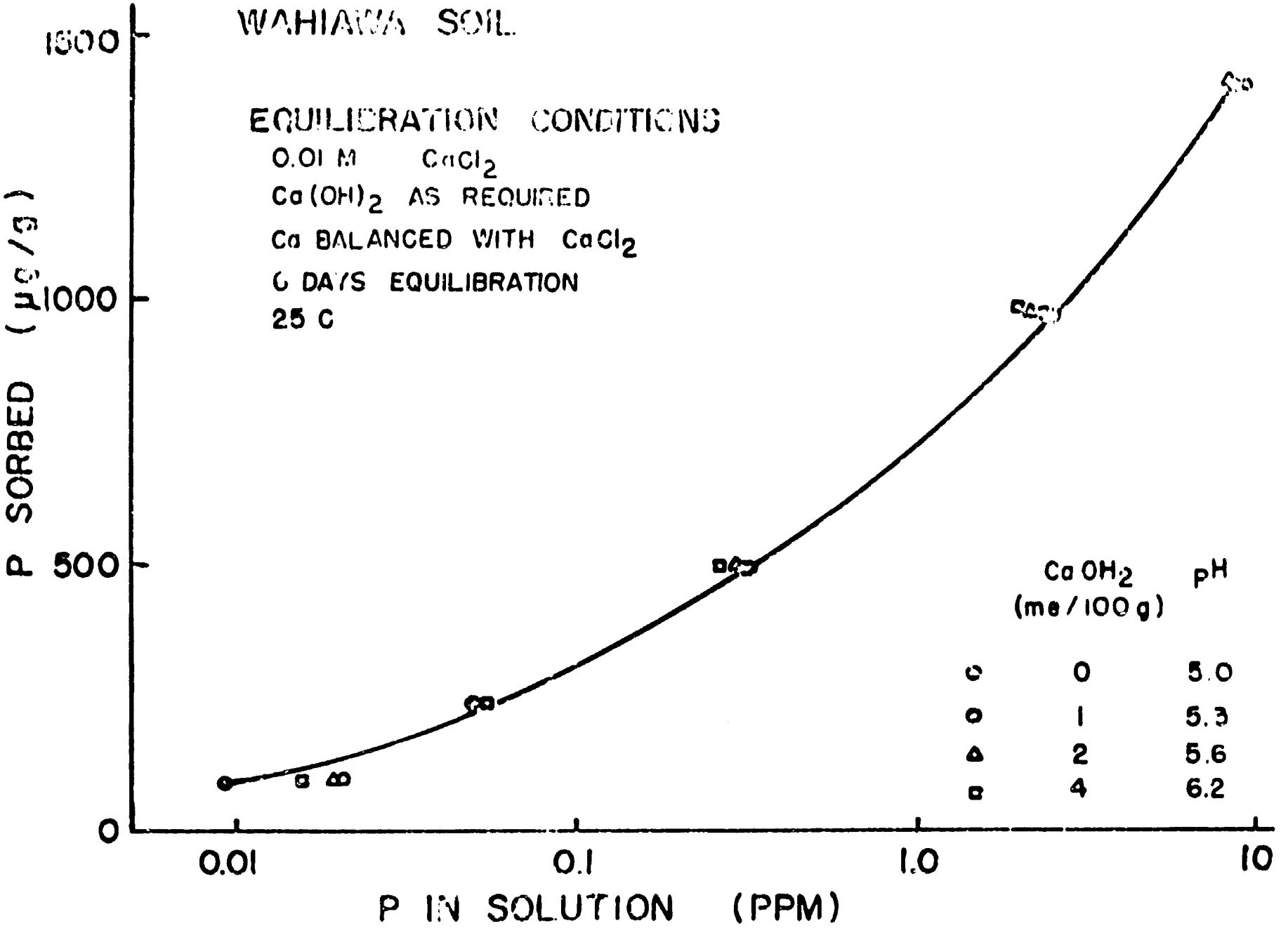

Figure 4. Phosphate in solution corresponding to varying amounts of phosphate adsorbed by a Wahiawa soil at 3 pH levels.

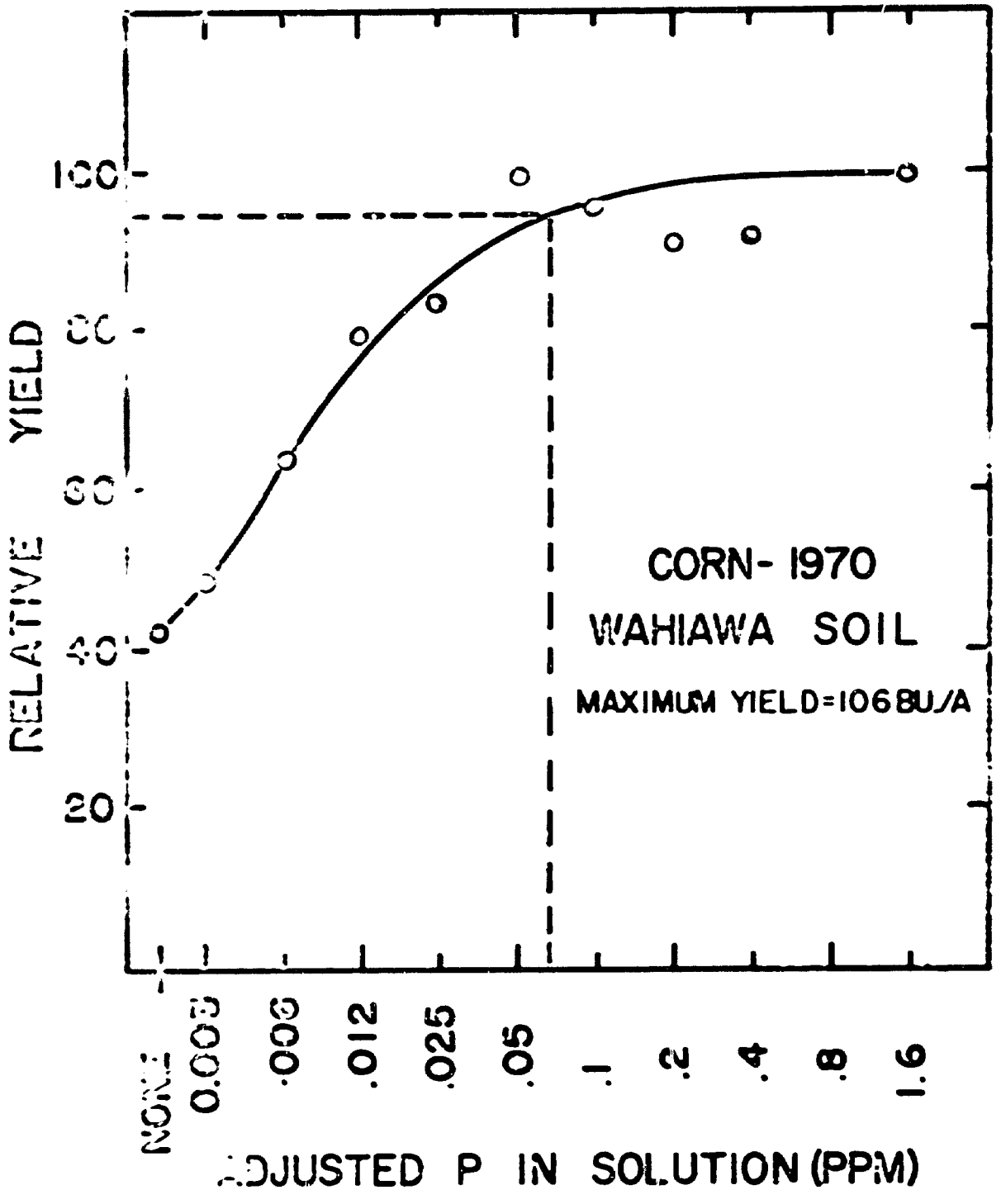

Figure 5. Yield response curve for corn growing on a phosphate deficient soil which was fertilized to adjust phosphate concentrations to the levels indicated.

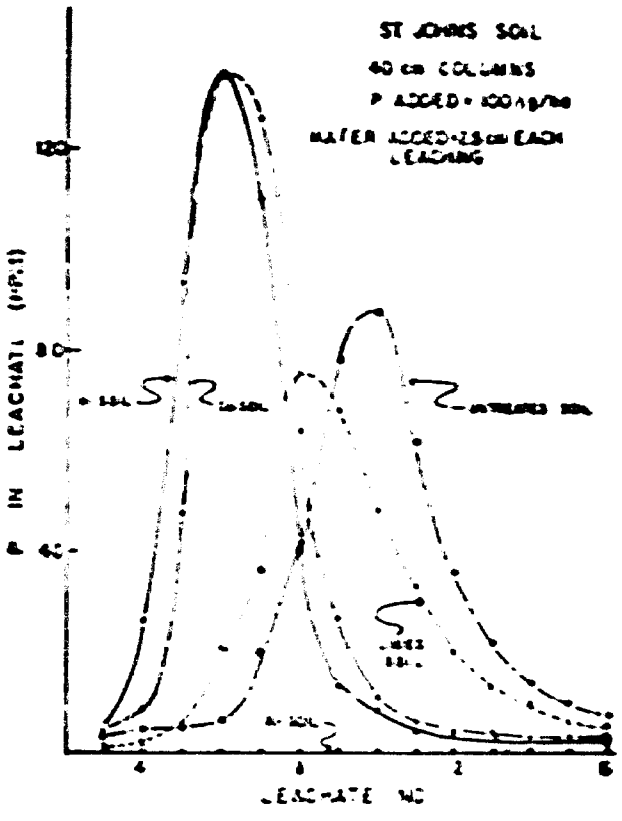

Figure 6. Phosphate leached through columns of St. John in relation to pretreatment of the soil with lime and Ca, H or Al chlorides.

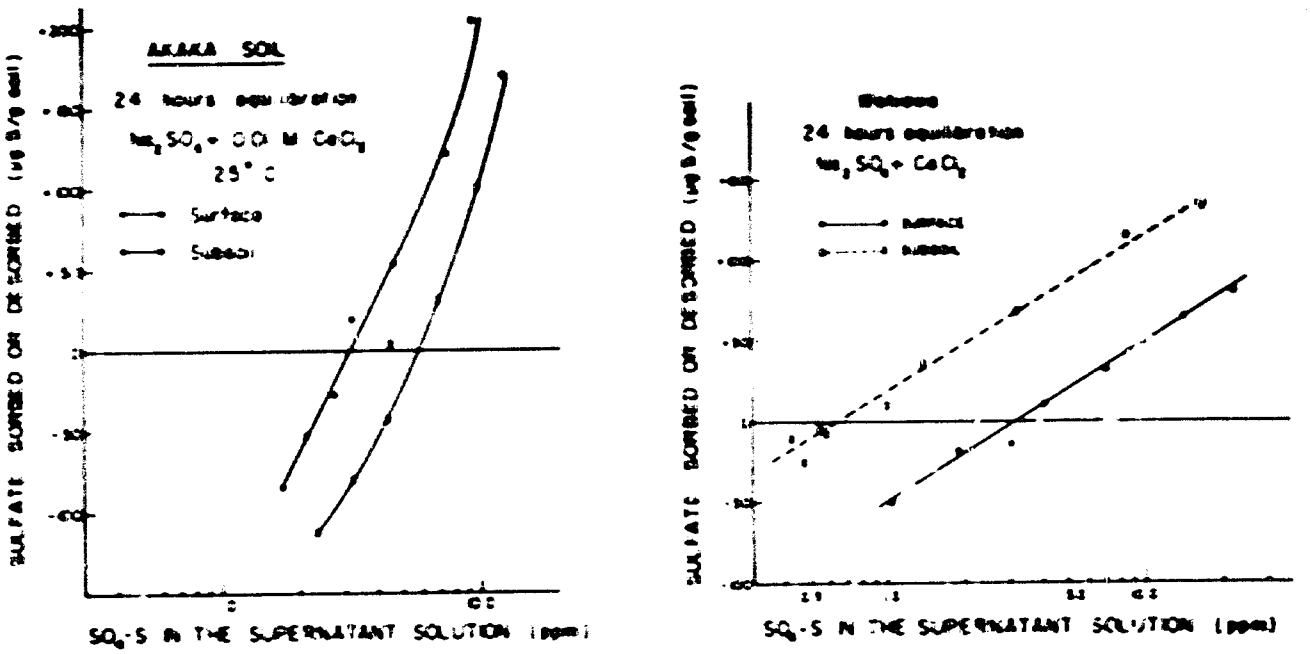

Figure 7. Sulfate adsorption curves for surface soil and subsoil of two soils show the dependence of sulfate solubility on the amount of sulfate adsorbed.