SULFUR WASTE MATERIALS FOR CALCAREOUS SOILS ACIDULATION

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SULFUR WASTE MATERIALS FOR CALCAREOUS SOILS ACIDULATION

by

Faik Ahmad Dawood

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As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Faik Ahmad Dawood

entitled Sulfur Waste Materials For Calcareous Soils Acidulation

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ABSTRACT

This study consisted of laboratory and greenhouse experiments designed to determine the effect of sulfur waste materials on acidulation and other properties of calcareous soils.

The laboratory experiment was conducted in the Soils, Water and Engineering Department, University of Arizona, for a period of nine weeks. Laveen soil (containing 6% $CaCO_3$) was treated with two levels of Morocco rock phosphate (0, 500 ppm P), and two different waste materials of sulfur, Cake S and Foam S, each with three levels (0, 5000, 10000 ppm). Treated soils were incubated for two periods (three and nine weeks) at 27°C and 66% water holding capacity. The design of the experiment was a complete randomized block with 24 treatments and two replications. Soil after each period of incubation was tested for soil pH, 0.01 M $CaCl_2$ soluble phosphorus, sulfate and phosphorus sorption isotherm. Data were evaluated by analysis of variance and multiple means comparison tests for soil pH, soluble phosphorus, and sulfate, and regression analysis for the isotherm.

Results showed that Foam sulfur had a greater effect as compared with Cake sulfur on soil pH, soluble phosphorus and sulfate and significantly shifted the isotherm to the right. Rock phosphate had no effect on soil pH and sulfate, but tended to decrease soluble phosphorus and shifted the isotherm to the left as compared with the control.

The second experiment was conducted in the greenhouse near the Agricultural Sciences Building, University of Arizona, for a period of 32 weeks starting on August 20, 1979. Two calcareous soils, Pima and Laveen, (2% and 6% $CaCO_3$, respectively) were investigated with three levels of rock phosphate (0, 250, 500 ppm P), and three sources of sulfur (Cake, Foam and pure sulfur) each at two levels (0, 8000 ppm S). Two levels of super phosphate were used as a standard treatment. The chemical treatments were mixed with the soil and transferred to plastic pots and moistened to 70% water holding capacity, then covered with plastic sheets and incubated for eight weeks. Following the incubation, tomatoes were planted and grown for a six week period. Dry weights were measured only in the Pima soil but were eliminated due to poor stand in the Laveen soil. Barley was planted after the tomato harvest. Tomato and barley plants were irrigated with distilled water until the first harvest, after which barley was irrigated with tap water and $CaSO_4$ saturated solution to eliminate sulfur deficiency detected prior to the first harvest.

Plant dry weight and plant phosphorus contents were determined following the first barley harvest, and soils were sampled for pH, EC_e, SO_4, soluble P, Zn, and P sorption isotherm. After the second barley harvest measurements were made for soluble soil P and Zn as well as plant P, Zn, and dry weight.

The experiment was a complete randomized block design with 36 treatments and three replications. Data for soils and plants were evaluated by analysis of variance, multiple means comparison test, and regression analysis.

From the results of this study the conclusions were as follows:

1. Foam sulfur tended to increase soluble P and Zn, lowered soil pH, and shifted the P isotherm to the right in the soil. Plant P and dry weight were increased more by the Foam S than Cake S and pure sulfur. However, Foam S tended to increase soluble salts more than Cake S and pure S.

2. Cake S also caused an increase in soluble P in the soil, reduced soil pH, and increased plant P and dry weight as well, although the effects were less than with Foam S.

3. Rock phosphate plus sulfur resulted in an increase in soluble P after 32 weeks of application.

4. Soils with low $CaCO_3$ content, higher organic matter content, and higher cation exchange capacity favored increased oxidation of sulfur to sulfate resulting in increased soluble P and lower soil pH.

5. Linear regression analysis of the P sorption isotherm was carried out by plotting the P remaining in the solution (ppm) on the X-axis versus P sorbed by the soil (ppm); a linear power function resulted. By this relationship, any regression equation can be used to evaluate the P status of a soil and the statistical differences between treatments.

INTRODUCTION

Soil alkalinity and its effects cause some of the main problems in some calcareous soils. The high soil pH tends to reduce the availability of several nutrients and bring about other physical and chemical properties that reduce crop production. Increasing fertilizer costs, which are due principally to the high cost of energy and a shortage of natural resources have become a great concern. With this in mind, soil scientists and agronomists must strive to improve soil conditions and use high cost fertilizers efficiently in order to obtain maximum production without waste.

Chemical amendments such as sulfur have been used widely for improvement and reclamation of sodic and alkaline soils as well as for improving soil fertility.

Waste materials containing sulfur have been produced in Iraq at a rate of about 500 ton/day as a by-product of mining and refining sulfur. Because of the high sulfur content of these materials they have a high potential as soil amendments.

This study reports two experiments designed to investigate the effects of waste materials high in sulfur, and their combinations with other factors, on different soil properties as well as plants.

The objectives of the studies reported herein were to:

1. Determine the effect of incubation period of calcareous soils treated with sulfur waste materials, on reducing soil pH, sulfate

development, available phosphorus, and on phosphorus sorption capacity of the soil.

2. Observe the benefits of sulfur waste materials as compared with pure sulfur.

3. Investigate unavailable forms of phosphorus from rock phosphate in combination with S on release of available phosphorus and plant uptake.

4. Investigate the relationship between plant uptake and release of soil phosphorus due to sulfur treatments.

5. Develop a model of phosphate sorption in calcareous soils with respect to application of sulfur waste materials.

LITERATURE REVIEW

Sulfur plays an important role in all forms of life. In plants it is a common constituent of protein and vitamins. In soil, sulfur improves physical conditions, such as soil structure and permeability, increases availability of certain plant nutrients by reducing soil pH, improves irrigation water quality, and creates a better condition in saline and alkali soils for plant growth (Chancrin and Desroit 1911; Gianitta 1913; Chauzit 1914; McGeorge and Greene 1935; Starkey 1950; Mathers 1970; Ryan et al. 1974). Waste materials which are produced in Iraq are high in sulfur can be used as a source of sulfur to improve some soil characteristics (Kadhim et al. 1976; Al-Juburi et al. 1978).

Sulfur

1. Transformation in soils.

The oxidation of sulfur or its conversion to sulfuric acid in soil is brought about either by chemical or biological agencies. The latter process is of far greater importance than the purely chemical transformation. An insignificant amount of sulfur is oxidyzed chemically, according to studies done by Demolon (1912) and MacIntyre et al. (1921). Kappen and Quensell (1915) showed that milk of sulfur will undergo oxidation to sulfuric acid in sterile soils, while flowers of sulfur is not appreciably changed. They offered the suggestion from their work that sulfur transformation was chiefly chemical rather than biological.

It is generally assumed that sulfur bacteria are responsible for oxidation of most of the inorganic sulfur in soil. Autotrophic bacteria can use sulfur compounds as specific hydrogen donors for the assimilation of carbon dioxide (CO_2). The CO_2 can meet all of their carbon requirements. Elemental sulfur undergoes relatively rapid oxidation by various micororganisms, of particular importance is Thiobacillus thiooxidans (Starkey 1950).

Sulfur oxidation in soil is a very complicated process which involves the activities of a number of species of bacteria (Brioux and Guerbet 1913). Sulfur is oxidized, but slowly, by another sulfur bacterium, Thiobacillus thioparus, whereby it is transformed to sulfate (Starkey 1935). Guittonneau (1927) observed that various microorganisms including certain bacteria, actinomycetes, and filamentous fungi, were also able to attack sulfur with the formation of thiosulfate. He found in 1932 that heterotrophic microorganisms transferred elemental sulfur to thiosulfate and polythionates, particularly tetrathionate. These products were extracted from sulfur-treated soils.

Sulfur oxidations occur in animal tissue similar to those accomplished by some bacteria. Pirie (1934) observed some tissues were able to oxidize thiosulfate and tetrathionate to sulfate, the latter at a slower rate than the former.

There are several factors affecting sulfur oxidation in soils. Brown and Kellogg (1914) reported some experiments on the so-called sulfofying power of soils. They concluded that each soil has a definite sulfofying power. Organic matter, manure, optimum moisture conditions, aeration, and the presence of bacteria are important factors of sulfate production from element sulfur. Brioux and Guerbet (1912), and Lipman and his co-workers (1916a), have demonstrated that the presence of sulfofying organisms as well as moisture relations are factors of considerable importance in the oxidation of sulfur. Nor and Tabatabai (1977) in their studies of oxidation of elemental sulfur in soils reported that thiosulfate and tetrathrionate are produced during sulfur oxidation in soil. Within the first few days of incubation $S_2O_3^{2-}$ was produced and $S_4O_6^{2-}$ accumulated in some soils. They noted that the rate of sulfur oxidation increased with increasing temperature and rate of sulfur application, it was more rapid in alkaline soils than in acid soils.

With respect to the soil texture effect on sulfur oxidation, Shedd (1914) studied the oxidation of sulfur in soil and sand. With soil to which sulfur was added in amounts varying from 100 to 7000 pounds per acre, he found by analysis, that 60 to 80% of the sulfur, regardless of the amount added, was oxidized after a period of about four months. Sulfur was oxidized also in sand, but not to the extent that it was in the soil.

2. Sulfur affecting soil pH.

Elemental sulfur undergoes relatively rapid oxidation by various microorganisms. Of particular importance in <u>Thiobacillus thiooxidans</u>, which not only oxidizes elemental sulfur but tolerates exceedingly high acidity that frequently develops in soils where sulfur is thus transformed. The reaction effected by bacteria is presented in the following equation:

$$2S + 3O_2 + 2H_2O = 2H_2SO_4$$

Some interesting data concerning the influence of sulfur on soil acidity were reported by Lint (1914) in regard to measuring the rate of oxidation of sulfur in soil. He observed that the acidity increased up to the eighth week when all the sulfur was apparently oxidized. Martin (1920) concluded that in all cases, following application of sulfur there was an increase in soil acidity as measured by the hydrogen-ion concentration of soil extract.

Jensen (1927) observed that a sandy soil from a dried marsh had a pH of 2.2. The acidity was found to be due to sulfuric acid produced by the oxidation of sulfur. A pH of 2.4 was reported by Drewes (1928) for a moor soil, and the acidity was also ascribed to development of T. thiooxidans. Sijderius (1946) observed that soil pH was dropped to 4.5 in five weeks and to 3.0 to 3.5 at the end of seven months with increasing the number of T. thiooxidans. Starkey (1966) reported a pH of 2.0 to 3.0 in soil represented acid production of as much as 1.0 mole of sulfuric acid from sulfur, under laboratory conditions.

3. Sulfur and plant nutrients.

Sulfur has a direct and indirect effect on availability of some nutrients in soil. The direct effect results from the production of sulfate which is a nutrient for plants. All plants contain some sulfur, both as organic and inorganic compounds, and many plants require more sulfur than phosphorus. On the other hand, because of the presence of sulfur in rain water, irrigation water, and as an incidental constitutent of commercial fertilizers, sulfur rarely appears in agriculture as a plant nutrient deficiency in irrigated areas.

The indirect effect of sulfur can be explained by its conversion into sulfuric acid which has a solvent action for several important plant nutrients present in the soil in insoluble or unavailable form. This is especially true of soils deficient in available phosphorus, iron, manganese, and zinc.

It was noted in the highly presence of hydrogen ions in soil, the plant has some difficulty in absorbing negatively charged ions, such as nitrate or phosphate, and therefore, will absorb an excess of positively charged ions. In the presence of an excess of hydrogen ions the opposite condition exists, namely, negatively charged ions are absorbed with greater ease (Hoagland 1917; Breazeale and McGeorge 1932).

Sulfur oxidation and soil nitrogen relationships were studied by McGeorge in calcareous soil of Arizona. He reported that the greater the amount of sulfur oxidized, the smaller the amount of nitrate found in the soil extract. It is evident that the sulfur oxidizing bacteria were withdrawing nitrate for their own nitrogen metabolism. It has been observed that nodulation of legumes is poor in case of sulfur deficiency, and from this it might be seen that deficiency of sulfur affects the process of nitrogen fixation (Nightingale et al. 1932; Anderson and Spencer 1949).

In a study of the effects of sulfur, phosphorus and molybdenum interactions on the concentration and uptake of molybdenum in soybean plants, it was reported that sulfur application significantly increased the total uptake of molybdenum in soybean and yield (Singh and Kumar 1979). Clement (1978) observed a continuous increase of P uptake with sulfur treatment for four lettuce crops harvested in the greenhouse, while H_2SO_4 tended to increase P uptake in the first and second crop, then decrease in third and fourth crops.

The application of gypsum to the alkali soil, particularly in combination with Zn (Shukla and Mukhi 1980), created conditions favorable for an increased Zn utilization by the plant by reducing the Na content in the soil.

4. Sulfur and rock phosphate role in calcareous soils.

Lipman and his co-workers (1916a, b) in their studies used a composite of sulfur and rock phosphate to release available P in a calcareous soil. They noted that the red silt loam soil, high in organic matter, was found to be more effective than the soil low in organic matter as a medium for the production of available P from a sulfur-floats (ground rock phosphate) mixture. They also observed that tricalcium phosphate, when added to soil or soil mixture in which sulfofication is active, may react with the sulfuric acid formed, and may then furnish available P to crops. The results of the greenhouse and field experiments showed that the ground phosphate rock properly composted with ground sulfur, becomes a source of available P, and may be employed to advantage as a substitute for acid phosphate.

McLean (1918) reported under certain conditions, ferrous sulfate, aluminum sulfate, and a combination of two salts exert a marked stimulating action on sulfur oxidation processes when present in small amounts in a composite composed of soil, sulfur flour, and rock phosphate. He suggested the addition of 0.4 lb of aluminum and ferrous sulfate to each ton of compost in order to obtain a maximum production of available phosphorus.

Sulfur also plays an important role in sodic or alkali soils. Lipman (1916c) reported that the change of sulfur to sulfuric acid in the soil may be employed for converting sodium carbonate into sodium sulfate, and making productive barren alkali areas. Samuels (1927) found that sulfur oxidation took place very rapidly in alkaline soils under laboratory, greenhouse, and field conditions, and most rapid in sandy soils. He also showed, in the presence of sodium carbonates, carbonates and bicarbonates were decomposed and sulfates formed during sulfur oxidation.

Kelley and Alexander (1928) concluded that the acid formed by the oxidation of sulfur, or the hydrolysis of iron sulfate and aluminum sulfate dissolves calcium carbonate, and possibly other minerals bringing calcium into solution. As a result of the exchange with calcium the sodium content of the exchange complex is decreased and the calcium content is increased.

Thorne (1944) observed that relatively large treatments of sulfur and sulfuric acid made on calcareous soils caused a considerable increase in soluble salts which might have harmful effects under greenhouse conditions. In well drained soils employed in field experiments, frequent leaching with irrigation water would prevent harmful accumulation of salts.

Prather (1977) used sulfuric acid as an amendment for reclaiming soils high in boron (B). He stated that the effect on pH of surface application of H_2SO_4 to the columns was not expected to extend below a few centimeters depth. However, the beneficial effect of the H_2SO_4 treatment in enhancing the ease of B removal by leaching extended over the entire 80 cm depth. Also, B released in the upper soil was not reabsorbed in the lower depths even though the pH was unaffected by the acid treatment.

Phosphorus

The thought that phosphorus plays a leading role in plant nutrition was further emphasized and developed by Liebig (1840). He recognized that a deficiency of this element would necessarily limit production of plants. According to many processes of plant development, phosphorus is essential for cell division, fat and albumen formation, flowering, fruit and seed formation and root development, thereby hastening crop maturation. Phosphorus increases straw strength of cereals, general crop quality and resistance to some diseases, (Black 1968; Brady 1974).

1. Soil pH and availability of P.

Soil pH has an important effect on soil P availability to plants. The percentage of the total inorganic orthophosphate present in solution as $H_2PO_4^-$ range from 99.3 at pH 5 to 50 at pH 7.2 and to

1.5 at pH 9. Corresponding figures for HPO_4^{-2} are 0.6% at pH 5, 50% at pH 7.2, and 98.4% at pH 9 (Olsen 1953). Hagen and Hopkins (1955) proposed the theory that plants absorb phosphorus as $H_2PO_4^-$ and HPO_4^{-2}. They showed a significant reduction in phosphorus uptake with an increase in pH, being less than one-fourth the amount at pH 7.7 as at pH 5.

In acid soils, iron and aluminum hydroxides and oxides account for much of the phosphate fixation (Dean 1934; Brown 1935; Toth 1937; Kittrick and Jackson 1956; Hsu 1964). Beside iron and aluminum oxides the aluminum layer silicates are also responsible for phosphate fixation (Low and Black 1950; Taylor and Gurney 1962; Taylor et al. 1964) where the edge $Al(OH)_2$ groups react with phosphate. Swenson et al. (1949) noted that in acid soil the pH of maximum precipitation of basic iron phosphate was 2.5 to 3.5; whereas for basic aluminum phosphate it was from 3.5 to 4.0. This is the pH range at which $H_2PO_4^-$ predominates and where there is relatively little HPO_4^{-2}. Haseman et al. (1950) equilibrated gibbsite, geothite, kaolinite, illite, and montnorillonite with different concentrations of P at various pH values and temperatures. They observed two distinct sorption stages occurred with time. The first stage was characterized by a rapid rate as a result of the reaction of phosphate with active iron and aluminum. The second stage was slower and occurred after aluminum and iron were released by weathering. This double stage hypothesis was also supported by Low and Black (1950). They suggested that the surface silicon tetrahedra are replaced by phosphorus tetrahedra in the first stage and precipitation of Al-phosphate occurred in the second stage as a consequence of P induced surface clay decomposition.

In calcareous and alkali soils, phosphorus fixation has been studied by several individuals. According to McGeorge and Breazeale (1931), the formation of carbonate-phosphate compounds in which one mole of calcium carbonate combined with three moles of tricalcium phosphate accounts for the low P availability in calcareous soils. They suggested that soil or rock phosphate solubility is greatly reduced when calcium carbonate is present in the solid phase. Buehrer (1932) found that phosphate solubility in calcium saturated soil is directly proportional to hydrogen ion concentration and inversely proportional to the calcium ion concentration. On the other hand, in sodium dominated soils, the solubility of phosphate is much higher than in calcium dominated soils (Gardner and Kelley 1940, Ravikovitch 1939).

Working with calcareous soils, Burd (1948) pointed out that in highly buffered soils some calcium phosphate compounds of low solubility were formed as the soil was treated with phosphate fertilizers. This occurs because calcium compounds in the soil are potentially soluble, releasing calcium ions which react with phosphate, forming less soluble Ca-phosphate compounds. He also observed that the concentration of phosphate in solution increased as that of calcium decreased. This fact can be used to explain the role of calcium in fixation of soluble native or added P to calcareous soil.

Boishot, et al. (1950) reported that soluble phosphate is fixed on the surface of calcium carbonate by a sorption phenomenon, not by precipitation. The phosphate fixed in this manner can be used by the plants as it returns to the soil solution by a desorption phenomenon.

Chang and Jackson (1958) observed that in the majority of calcareous soils, P is present as calcium phosphate although some can exist in the aluminum and iron fractions. These workers believed that when phosphate fertilizers are added to calcareous soils, P combines easily with calcium and aluminum and not with iron because those ions are more active. As iron phosphate is less soluble than calcium and aluminum phosphates, it tends to accumulate in soils.

Phosphorus Sorption Isotherm

Sorption isotherm can be defined as the relation between the amount of substance adsorbed by an adsorbant and equilibrium concentration of the substance at constant temperature (Prutton and Maron 1953).

Phosphorus sorption has been used to evaluate soil P requirements. It may predict whether or not fertilizer phosphorus is needed, it is frequently difficult to relate test values to the quantity of P required (Fox and Kamprath 1970). In highly weathered soils especially, extractable phosphate is usually low, but amounts of fertilizer P which the soil can immobilize vary greatly (Fox et al. 1962).

Several factors determine the flux of P to plant roots. Williams (1967) has discussed these as intensity, quantity, and mobility factors. In its simplest form the intensity factor can be represented as P concentration in the soil solution. For some plants 0.03 ppm P continuously supplied in nutrient solution will sustain maximum growth (Asher and Loneragan 1967). For other plants, concentrations 25 times greater are required. A value of 0.2 ppm has been suggested as one at which most plants attain near maximum growth (Beckwith 1965). In soils a value of 0.2 ppm has been used as a standard value for establishing fertilizer rates for wheat (Ozzane and Shaw 1968). However, it is recognized that the value will vary with soil moisture, since soil moisture content influences phosphate diffusion to roots (Olsen and Watanabe 1963, 1966).

Numerous workers have studied adsorption isotherm equations, to show the adsorption of liquids or ions in solutions by acid particles (Davis 1935; Boyd et al. 1947; Jackson et al. 1950; Olsen and Watanabe 1957; Hsu and Rennie 1962; Gunary 1970; Syers et al. 1973; and Rajan 1973). Fitter and Sutton (1975) observed that the slope of the logarithmic plot of P adsorbed against P concentration was correlated with exchangeable Al in acid soils, and with exchangeable Ca in neutral and calcareous soils. It also can be related to changes in the chemical potential of the adsorbed and solution phases of phosphate. So the value is proportioned to the change in the chemical potential of the adsorbed P, when that of solution P is varied by one unit. Shyan and Davey (1978) reported that the necessary parameters to derive a complete adsorption isotherm for a particular soil, from the universal isotherm, required three adsorption experiments in high concentration range (10^{-4} to 10^{-1} M P) to define the linear portion of the isotherm and the critical concentration.

Phosphate sorption by soils is influenced by conditions such as soil pH, organic matter, and Al, Fe, and $CaCO_3$. From studies of pH influence on PO_4 adsorption Lopez-Hernandes and Burnham (1978) postulated the presence of sorption sites with different energies. Harter (1969) suggests that P is adsorbed by organic matter in some anion exchange. There follows a slow reaction, probably with Al and Fe, which causes the P to become unavailable. Hsu (1964) concluded that in relatively dilute solution PO_4 is adsorbed on amorphous Al hydroxides and Fe oxides or hydroxides. He also concluded that the rapid reaction is due to reactive surface amorphous Al hydroxides and Fe oxides. Rajan and Fox (1975) also suggested that the PO_4 is adsorbed by more than two types of sites and the P at low concentration is adsorbed by ligand exchange. Ligand exchange is the displacing of H_2O or OH^- that are coordinated with the metal ions on the surface of the clay. Holford and Mattingly (1975), in their study of phosphorus adsorption by 24 calcareous soils (pH 7.2-7.6) and 0.8 to 24.2 % $CaCO_3$, found that high-energy P adsorption capacities is most closely correlated with dithionite-soluble Fe. Hydrous oxides, therefore, appear to provide the principle sites, even in calcareous soils, on which P is strongly adsorbed. The low-energy adsorption capacities is correlated with organic matter contents and the total surface area of $CaCO_3$ but not with % $CaCO_3$, pH, or dithionite-soluble Fe.

MATERIALS AND METHODS

Two calcareous soils were selected for study, Pima clay loam and Laveen loam. Pima soil is classified as fine silty, mixed, thermic, Typic Torrifluvent, while Laveen is coarse loamy, mixed, hyperthermic, Typic Calciorthid. Composite samples of the plow layer were collected from field plots at the University of Arizona Experiment Farms at Marana and Mesa, respectively. Soil tests values for both soils are shown in Table 1. Rock phosphate, an unavailable form of phosphorus (P), was obtained from IEDC (International Fertilizers Development Center), with some characteristics as described in Table 2. Waste materials of sulfur (S) of two different forms (Cake and Foam), were brought from Iraq (Table 3).

Two experiments were conducted to accomplish the objectives of this study.

Laboratory Experiment

This study was conducted in the soil fertility laboratory of Soil and Water and Engineering Department, University of Arizona. Fifty-gram-samples of Laveen soil which had been ground to pass a 2 mm seive were treated with two levels of P (0 and 500 ppm) as rock phosphate, and two sources of the sulfur materials, each at three levels (0, 5000, 10000 ppm of S). Each treatment was mixed and transferred to 250 ml wide mouth Erlenmeyer flasks. To each flask 10 ml of distilled water was added to keep moisture of 66% water holding

Table 1 Pima and Laveen Soil Analysis

Soils	Soil Depth cm	Total Sand %	Total Silt %	Total Clay %	Texture Class	pH Paste	Soil Salts EC X 10^3 in Sat. Ext. mmhos/cm	PO_4 ppm	Organic Matter %	CEC Meq/100g	$CaCO_3$ %
Laveen*	0-20	40.3	37.0	22.7	Loam	7.80	1.10	4.4	1.0	10	6
Pima**	0-30	33.7	37.9	28.4	Clay Loam	7.85	1.27	3.5	1.2	28	2.6

* Soils of The University of Arizona Experiment Station (Mesa).

** Soils of The University of Arizona Experiment Station (Marana).

Table 2 Morrocco* Rock Phosphate Analysis

P_2O_5	CaO	F	Fe_2O_3	Al_2O_3	SiO_2	CO_2
			%			
33.9	51.5	4.0	0.2	0.1	1.2	3.4

* Brought by International Fertilizer Development Center, Muscle Shoals, Alabama, U.S.A.

Table 3 Waste Material of Sulfur Analysis

Properties	Foam		Cake
		%	
Free sulfur soluble in CS_2	79.85		69.05
Sulfur insoluble in CS_2	1.57		2.38
Carbon	0.43		2.70
H_2SO_4	1.33		Trace
Ash	0.43		11.68
H_2O	14.46		13.59
Zn	20 ppm		50 ppm

Data were obtained from the sulfur-producing factory at Al-Meshrag, Mosul, IRAQ.

capacity in the soil. Flasks were covered by a plastic sheet to prevent moisture loss and yet allow air exchange. Soils were incubated at 27°C for periods of three and nine weeks. A complete randomized block design of two replication of 24 treatments was involved in the study. Soil pH, sulfate, soluble P, and P sorption was then determined. Variables were evaluated by analysis of variance, means comparison test, and regression equations.

Greenhouse Experiment

This study was conducted in the University of Arizona Greenhouse near the Agricultural Sciences Building. Two calcareous soils, Pima and Laveen, which contained about two and five percent $CaCO_3$, respectively, were used in this study. Each pot contained 1650 gm of each soil combined with the appropriate rock phosphate treatment (0, 250, 500 ppm P) and three sources of sulfur (Cake, Foam and Pure sulfur) each at two levels (0, 8000 ppm S). Treatments were prepared by mixing each combination with the soil, then placing in plastic pots. Moisture was adjusted to 70% of water holding capacity by adding distilled water. Pots were covered by a plastic sheet to reduce water evaporation for a period of eight weeks. Tomato (*Lycopersicum esculentum* Var. Floradel) were planted following the incubation period. Plant dry weights from the Pima soil were evaluated after six weeks of growth, while a poor stand and small plants in Laveen soil, probably due to salinity and sensitivity of plants, resulted in elimination of these plants from the study. Barley (*Hordeium vulgare* Var. Arivat) was planted after the tomatoes were harvested and growth for six weeks.

Tomato and first barley were irrigated by distilled water periodically, soil and barley plants sampled, and prepared for analysis following first barley harvest. Soil pH, total soluble salts, sulfate, Zn, available phosphorus, and P sorption isotherm were determined for the soil. Plant dry weight per pot and phosphorus were determined in plants.

Following the harvest of barley plants, the pots were replanted to barley which was grown for a period of 12 weeks. Irrigation was with tap water (Table 4) and a $CaSO_4$ saturated solution was added twice to eliminate the sulfur deficiency which became evident during first growth period. Soil and plants were sampled and prepared for analysis of available phosphorus and zinc in the soils and total phosphorus, dry weight and zinc in the plants.

The experiment was a complete randomized block design with 36 treatments and three replications. Results of soil and plant tests were evaluated by analysis of variance, means comparison, and regression analysis.

Separate pots of Pima and Laveen soils were treated with superphosphate (250, 500 ppm P) to compare with rock phosphate-phosphorus. The same parameters were measured on both soils and plant samples.

Soil and Plants Testing Methods

Soil pH values and total soluble salts were determined on 1:1 soil water and saturated extracts, respectively, using procedures described by Black (1965). Available P was extracted by 0.01 M $CaCl_2$, soils were equilibrated with four different concentrations of

Table 4 Tap Water Analysis

EC X 10^3	Soluble Salts	pH	Ca	Mg	Na	Cl	SO_4	HCO_3	CO_3	F	NO_3-N	Pb	Sodium Adsorption Ratio
						Milligrams per liter							
0.44	328.7	6.9	47	2.71	48.16	42	37.5	151.3	0	0.22	1.21	0.004	1.85

* Conducted by Soils, Water and Plant Tissue Testing Lab, Department of Soils, Water, and Engineering, College of Agriculture, University of Arizona.

P (1, 5, 10, 25 ppm in 0.01 M $CaCl_2$), and isotherms developed by the method described by Fox and Kamparath (1970) and modified by Bryant Gardner* (unpublished data). Phosphorus was determined by the phosphomolybdate blue method of Murphy and Riley (1962), as modified by Watanabe and Olsen (1965). Phosphorus concentration was determined using a Coleman Model 6120A spectrophotometer at 785 mu wavelength. Available Zn was extracted with the DTPA (diethyleneamine pentacetic acid) procedure of Lindsay and Norvell (1978). Atomic adsorption was used to determine the concentration of zinc. Sulfate was extracted by 0.5 M $NaHCO_3$ at pH 8.5 according to Kilmer and Nearpass (1960), and determined colorimetrically by Autoanalyzer II in Soil and Water Testing Laboratory in the Department of Soil, Water, and Engineering. Phosphorus and zinc in plant tissue was extracted by the wet digestion method as described by Toth et al. (1948). Phosphorus was determined colorimetrically as vanadomolybdophosphoric yellow method as described by Jackson (1958).

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* Soil Scientist at the Yuma Exp. Sta. Univ. of Arizona.

RESULTS AND DISCUSSION

Laboratory Study

Soil pH, phosphorus soluble in 0.01 m $CaCl_2$, sulfate, and phosphorus sorption isotherm were performed in soil after two periods of incubation. Analysis of variance, mean comparisons and regression analysis were used to evaluate the results.

Soil pH

Analysis of variance of soil pH (Table A1) indicated a highly significant difference (at 0.01) between levels of sulfur and time of incubation. Soil pH decreased slightly with application of 5,000 and 10,000 ppm of sulfur waste material, but these two levels are not significantly different. These results agree with Sijderius (1946). Time of incubation tended to increase soil pH in the second period. This could be due to increased solubilization of calcium ion in the soil then reducing the activity of H^+.

Soluble Phosphorus

The change in solubility of phosphorus due to rock phosphate, sulfur and level of sulfur interaction was significantly different at 0.01 level of probability (Table A2). The mean of the three way interactions is shown in Table 5.

Table 5 Means of soluble phosphorus in ppm as affected by rock phosphate, sulfur, and level of sulfur interaction, in Laveen soil treated with rock phosphate and sulfur waste material for two periods of incubation.

	Rock Phosphate			
	0 ppm P		500 ppm P	
Level of Sulfur	Cake	Foam	Cake	Foam
0 ppm S	0.46	0.49	0.44	0.42
5000 ppm S	0.76	0.96	0.65	0.93
10000 ppm S	0.91	1.08	0.73	1.46

LSD = 0.092 at 0.05 level of probability

Rock phosphate significantly decreased the solubility of native soil phosphorus, except when high levels of Foam S combined with the rock phosphate. Kelley and Alexander (1928) reported that the acid formed by sulfur oxidation dissolves calcium carbonate thus bringing calcium into solution. Here rock phosphate can be considered as a source of calcium which reacts with soluble phosphorus that is released from native phosphorus in soil, and caused an unavailable form of P. In high levels of Foam S the high acidity induced high solubility of phosphorus from native sources and the rock phosphate. Foam S initially has more sulfur and sulfate than Cake S, so it is more effective than Cake S in releasing phosphorus to the soil solution.

The interaction of incubation period and rock phosphate has a significant effect on solubility of phosphorus under 0.01 level of probability. Solubility of phosphorus increased with time of incubation. This was mostly due to the increase in acidity resulting from the sulfur treatment, which tended to dissolve the unavailable compounds of phosphorus in the soil (Table 6).

Table 6 Means of soluble phosphorus in ppm as affected by rock phosphate and time of incubation interaction, in Laveen soil treated with rock phosphate and waste material of sulfur for two periods of incubation.

Time of Incubation	Rock Phosphate	
	0 ppm P	500 ppm P
3 weeks	0.65	0.70
9 weeks	0.92	0.83

LSD = 0.053 at 0.05 level of probability

Soil Sulfate

Level of sulfur and time of incubation interaction has a significant effect (at the 0.01 level of probability) on releasing sulfate in soil (Table A3). The means of sulfate in ppm of this interaction is shown in Table 7.

Sulfate in soil increased with a higher rate of sulfur application and longer periods of incubation. These results agree with Lint (1914).

Table 7 Means of sulfate in ppm as affected by level of sulfur and time of incubation interaction, in Laveen soil treated with rock phosphate and waste materials of sulfur for two periods of incubation.

Time of Incubation	Level of Sulfur		
	0 ppm S	5000 ppm S	10000 ppm S
3 weeks	417	2472	5319
9 weeks	696	4356	8584

LSD = 1203 at 0.05 level of probability

Phosphorus Sorption Isotherm

Testing method of P isotherm showed that P in soil solution increased due to sulfur application and a second period of incubation and decreased with rock phosphate treatment. Foam S was more effective than Cake S in shifting the isotherm to the right, as was a higher level of sulfur, which means more phosphorus released to the soil solution. Figures 1 to 4 show the phosphorus isotherm by plotting the logarithm of P remaining in solution on the X-axis versus phosphorus sorbed by soil on the Y-axis.

A new relationship of phosphorus isotherm has been developed by plotting the phosphorus remaining in solution versus phosphorus sorbed by soil raised to power of 2.2. A straight line and a linear regression equation can be obtained from this relationship. The advantages of this plotting are:

1. By placing the phosphorus isotherm test value in the appropriate regression equation, an estimate of the amount of phosphorus fertilizer needed can be obtained.

2. Due to linear relationship the test for significance between treatments as they affected on phosphorus isotherm can be determined.

Use of this relationship can be seen in Figure 5. Rock phosphate tended to shift the isotherm to the left, indicating a greater amount of phosphorus is required to reach a specific level of phosphorus in the soil as compared to the control. A significant difference was found between Cake S and Foam S, levels of sulfur, and time of incubation in shifting the isotherm (Figures 5 to 8).

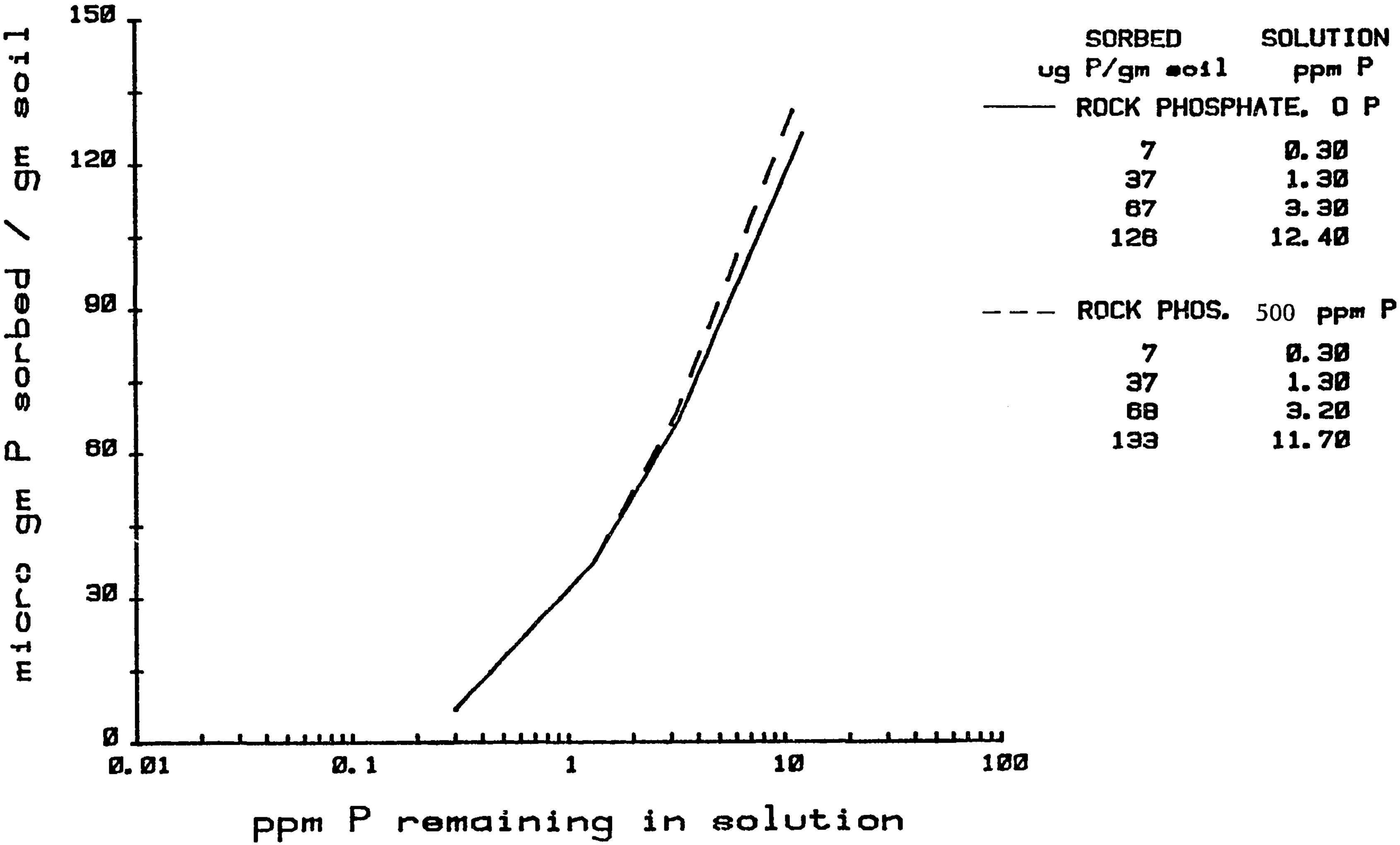

Figure 1 Phosphorus adsorption isotherms of calcareous soil (Laveen) treated with rock phosphate.

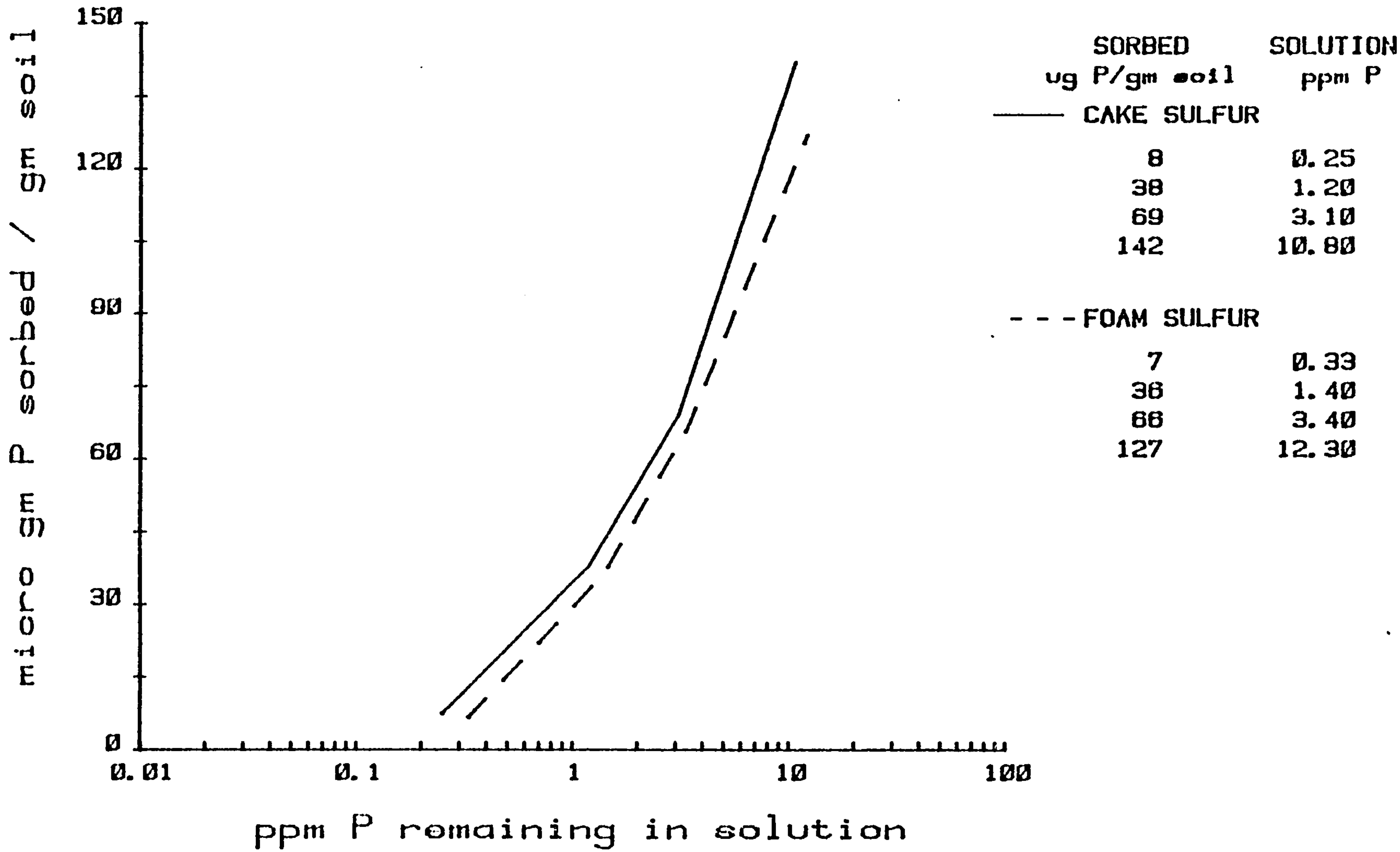

Figure 2 Phosphorus adsorption isotherms of calcareous soil (Laveen) treated with sulfur waste materials.

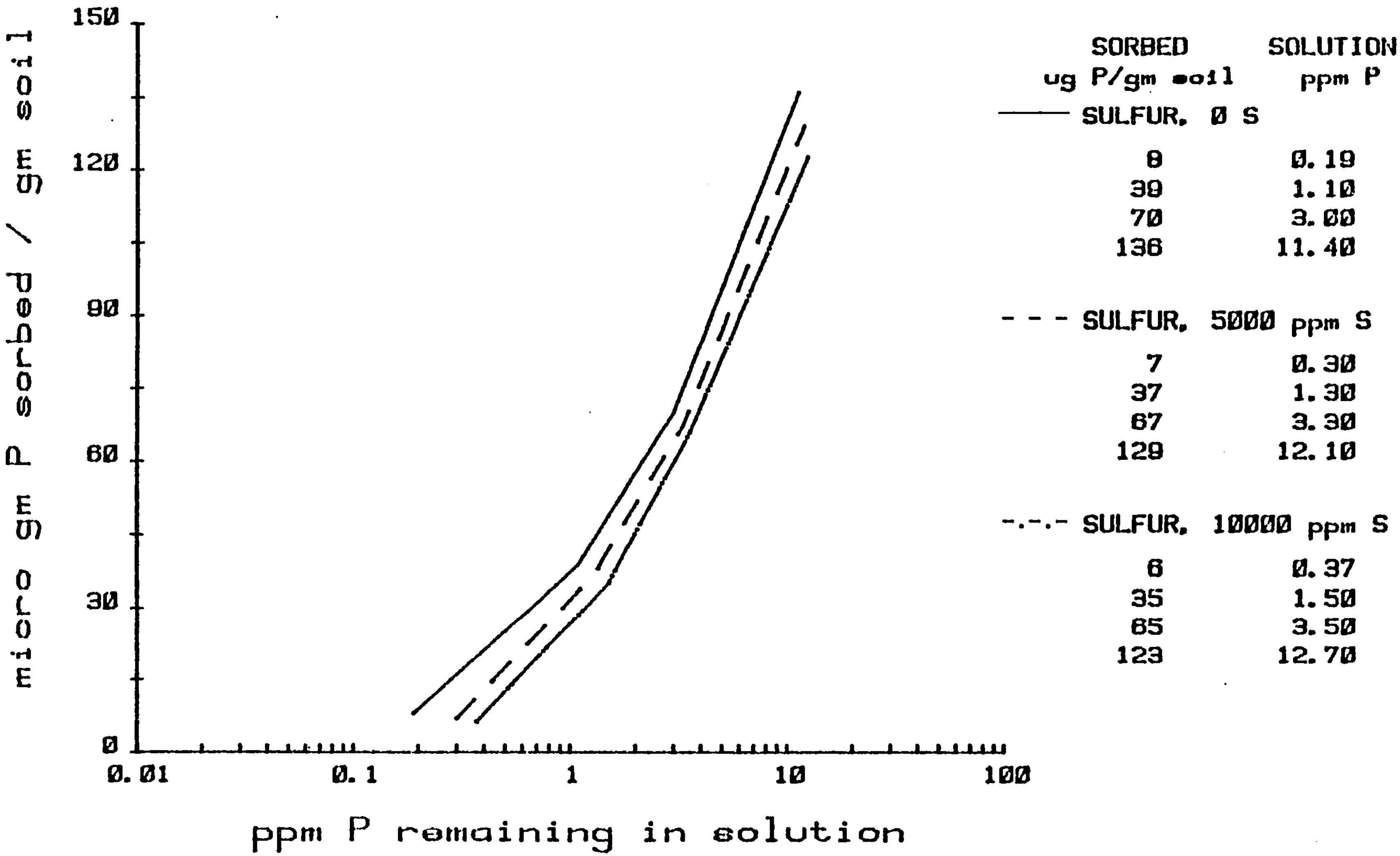

Figure 3 Phosphorus adsorption isotherms of calcareous soil (Laveen) treated with three levels of sulfur waste materials (Cake ahd Foam).

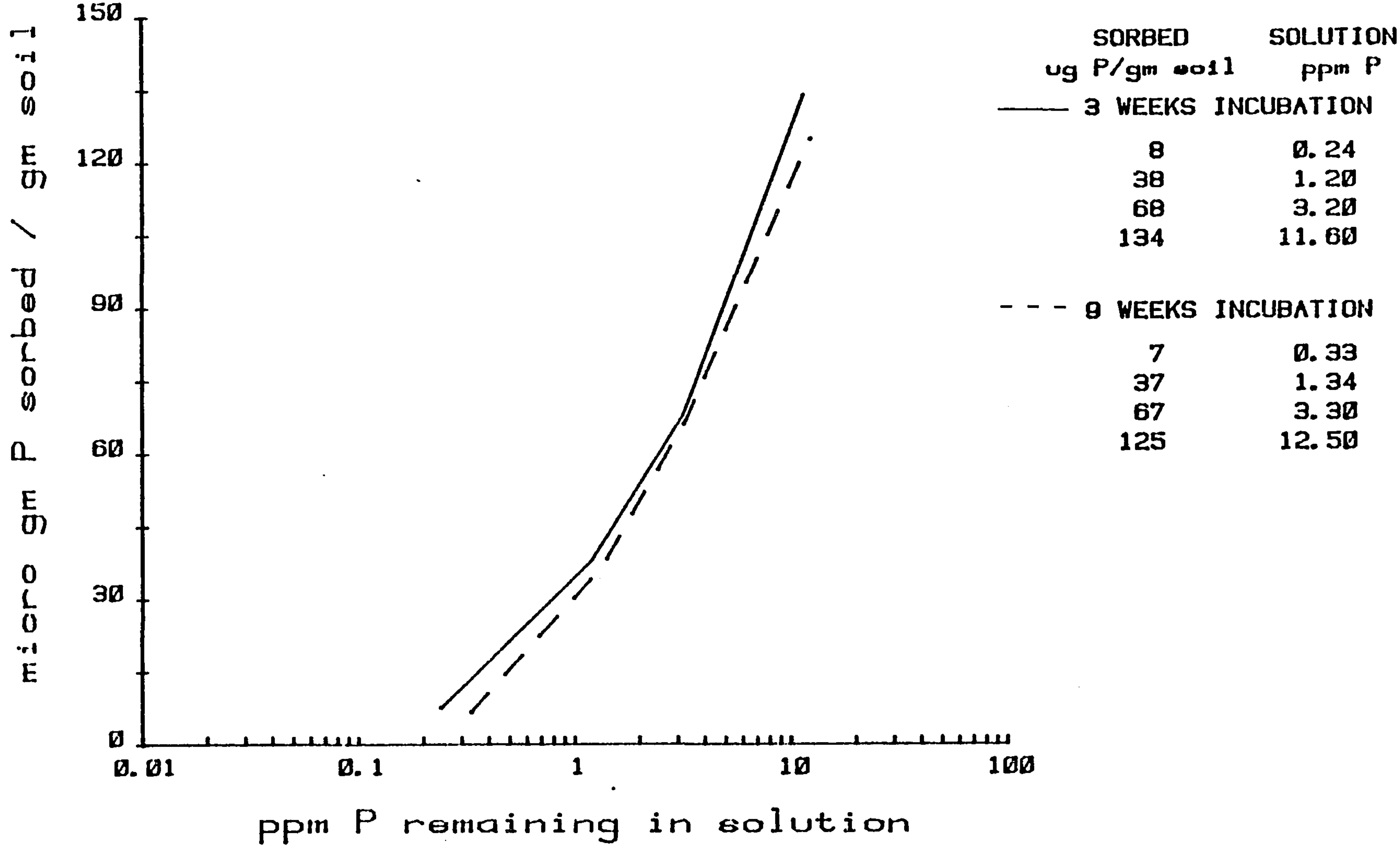

Figure 4 Phosphorus sorption isotherms of calcareous soil (Laveen) incubated with sulfur waste materials (Cake and Foam) for two periods.

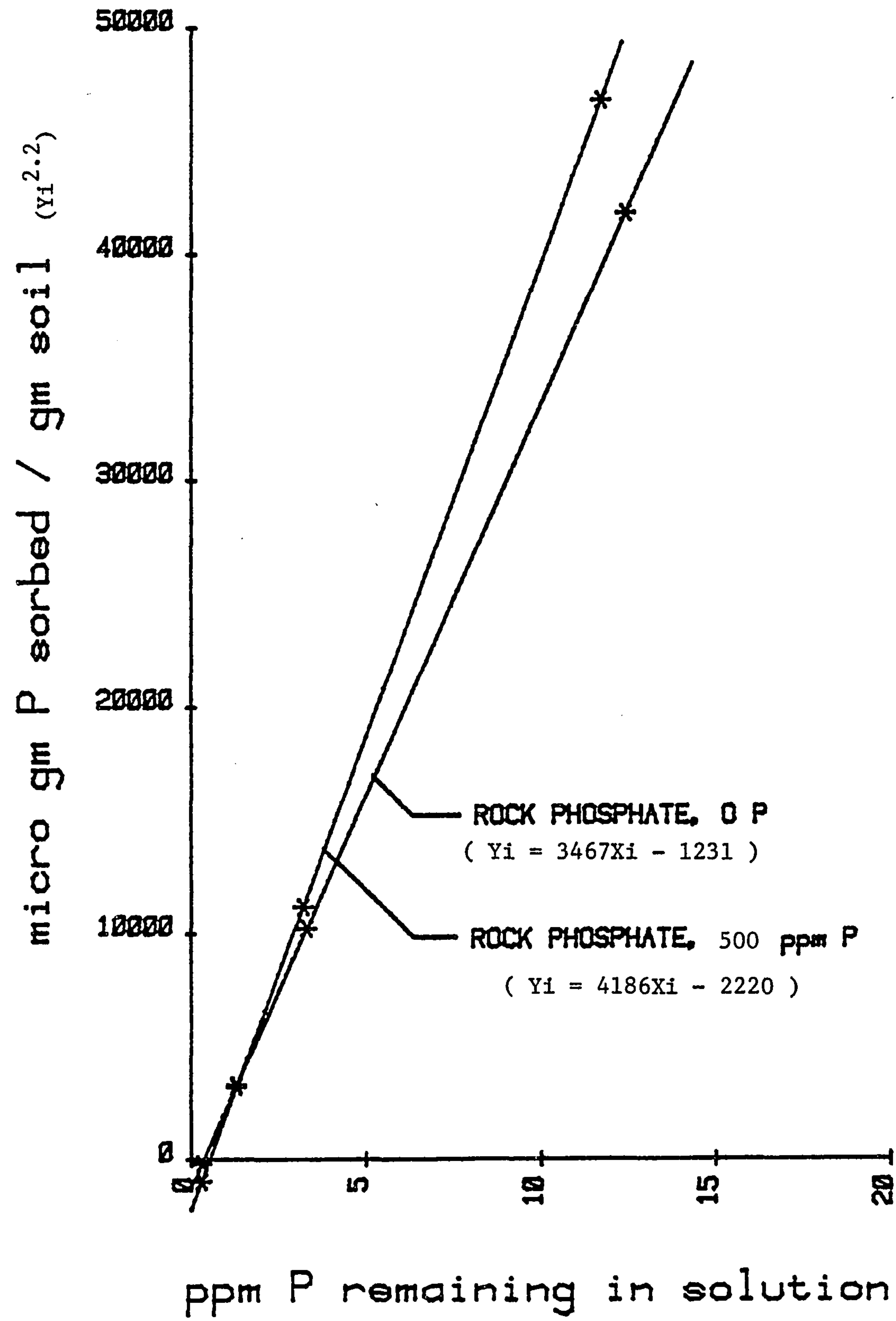

Figure 5 Linear regression of isotherms for calcareous soil (Laveen) treated with rock phosphate.

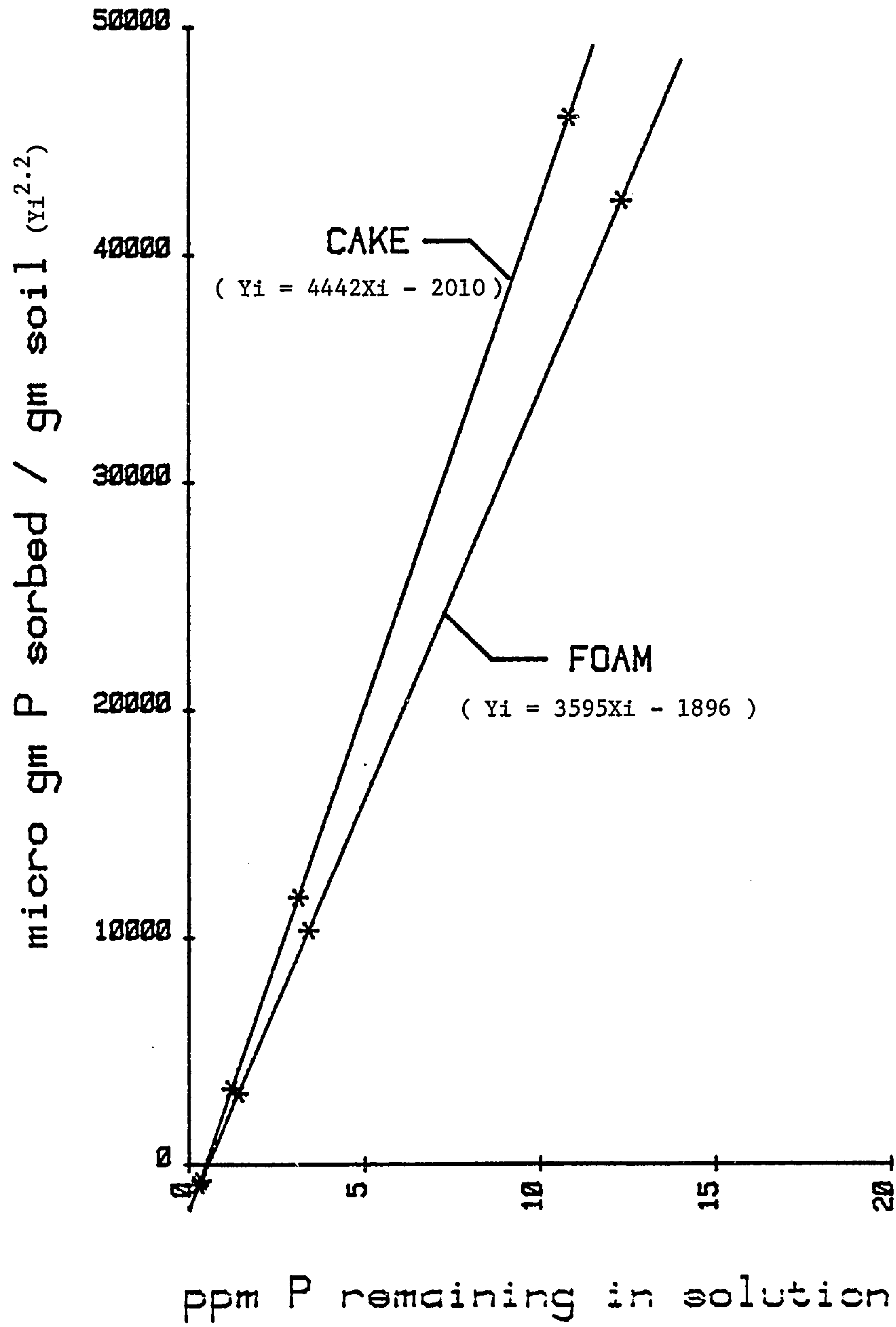

Figure 6 Linear regression of isotherms of calcareous soil (Laveen) treated with waste materials of sulfur (Cake and Foam).

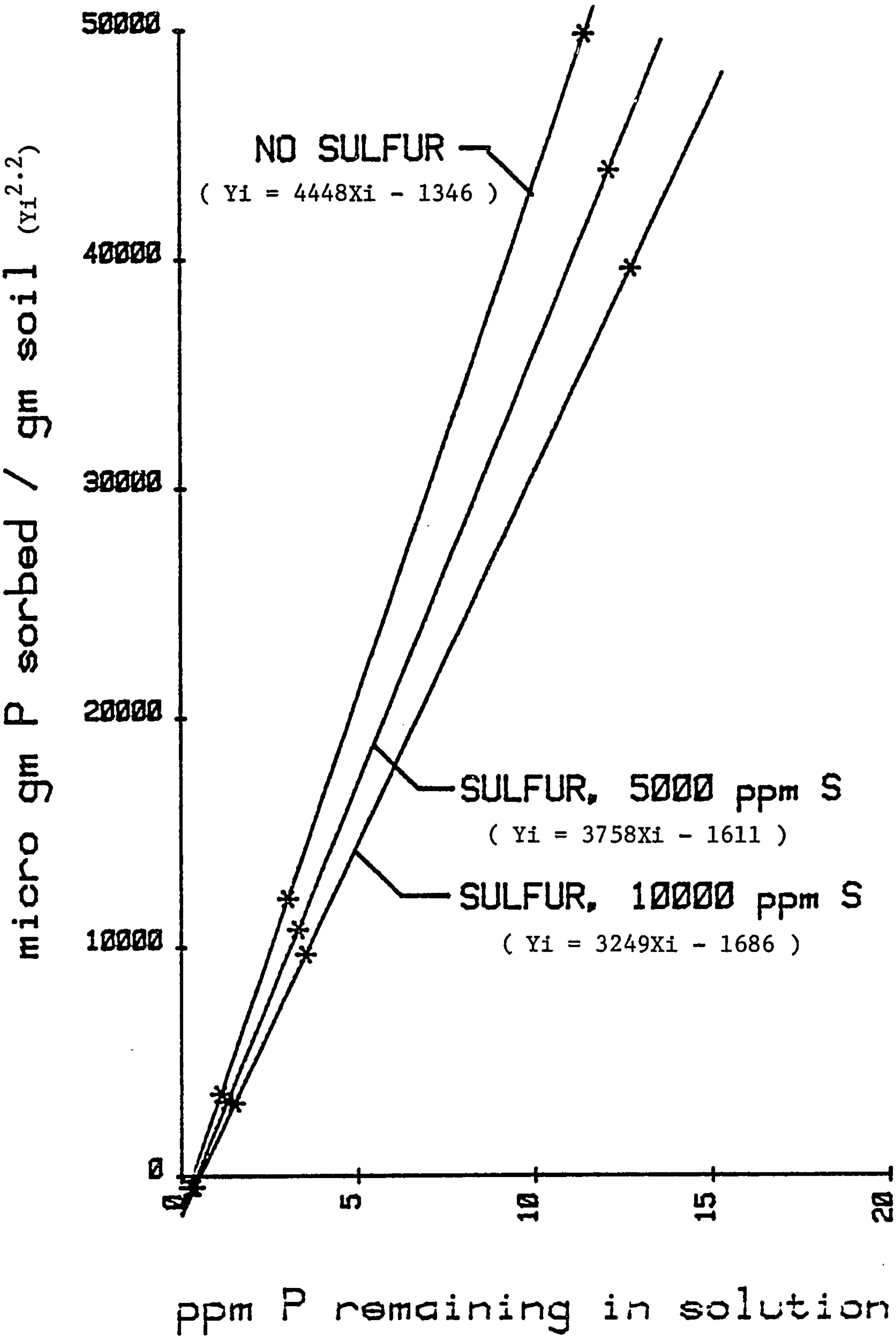

Figure 7 Linear regression of isotherms of calcareous soil (Laveen) treated with three levels of sulfur waste material (Cake and Foam).

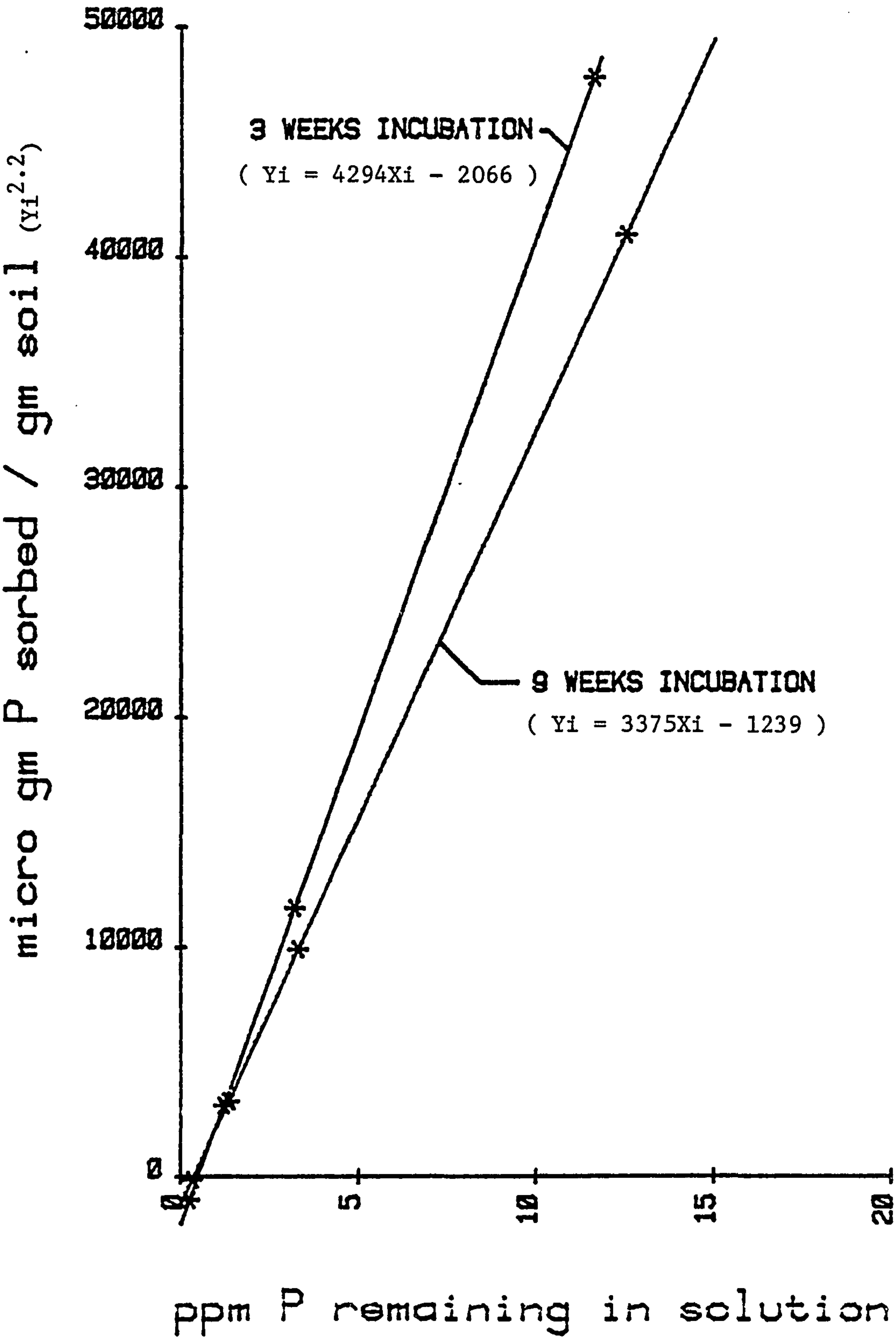

Figure 8 Linear regression of isotherms of calcareous soil (Laveen) incubated with sulfur waste materials (Cake and Foam) for two periods.

Greenhouse Experiment

Tomato and barley crops were harvested once and twice respectively. Plants and soil measurements included tomato dry weight following tomato harvest, barley dry weight and plant P following first harvest as well as soil pH, EC_e, soluble P, zinc, sulfate and phosphorus sorption isotherm, barley dry weight, plant P and Zn, then soil P and Zn following second barley harvest.

Tomato Dry Weight

Only the plants from the Pima soil were evaluated (Table B1). Plant weight was significantly increased at 0.01 level of probability as the result of sulfur treatments. Other main effects and interactions were not significantly affected on the dry weight of the tomato.

Barley First Harvest

Plants were harvested after six week growing periods; the soil was sampled at the time of harvesting. Several measurements were made and the results of each are described in the following paragraphs.

Soil pH. Analysis of variance of soil pH values (Table B2) showed a highly significant difference in soil pH due to soils, rock phosphate and level of sulfur interaction, and soil and sulfur interaction. The higher level of sulfur decreased pH in both soils as combined with rock phosphate, while higher levels of rock phosphate tended to maintain high pH (Table 8). Rock phosphate can be considered as a source of calcium which reduced the acidity that was produced by the sulfur materials in the soil solution.

Table 8 Means of soil pH as affected by soil, rock phosphate, and level of sulfur interaction after first barley harvest.

Level of Sulfur	Pima Soil			Laveen Soil		
	Rock Phosphate					
	0	250	500	0	250	500
0 ppm S	7.77	7.95	8.02	8.14	8.17	8.19
8000 ppm S	7.10	7.16	7.22	7.91	7.95	7.94

LSD = 0.166 at 0.05 level of probability

Lowered soil pH results from sulfur oxidation in soil, in which Foam S has greater effect than Cake S and pure sulfur in the Pima soil. However, they are not significantly different in Laveen soil (Table 9).

Table 9 Means of soil pH as affected by soil and sulfur interaction, after first barley harvest.

Sulfur	Pima Soil	Laveen Soil
Control	7.77	8.14
Cake S	7.63	8.03
Foam S	7.42	8.06
Pure Sulfur	7.56	8.07

LSD = 0.08 at 0.05 level of probability

Regression equation of soil pH as affected by levels of sulfur, levels of P as rock phosphate (S and P are quantitative factors), then soils and sources of sulfur as qualitative factors are shown in Table 10. High level of all sources of sulfur tended to decrease soil pH in soil, while phosphorus as rock phosphate increased soil pH at Cake S and pure sulfur in Pima soil and with Cake S at Laveen soil.

Table 10 Regression equation of soil pH as affected by two quantitative factors (level of sulfur and rock phosphate), and two qualitative factors (soils and source of sulfur).

Pima Soil	Cake S	$y = 7.74 - 6.32 \times 10^{-5}(LS) + 5.5 \times 10^{-4}(P)$
	Foam S	$y = 7.90 - 1.19 \times 10^{-4}(LS)$
	Pure S	$y = 7.89 - 10^{-4}(LS) + 3 \times 10^{-4}(P)$
Laveen Soil	Cake S	$y = 8.09 - 2.64 \times 10^{-5}(LS) + 1.83 \times 10^{-4}(P)$
	Foam S	$y = 8.183 - 3.2 \times 10^{-5}(LS)$
	Pure S	$y = 8.194 - 3.05 \times 10^{-5}(LS)$

<u>Electrical Conductivity</u>. The main effect of sulfur and level of sulfur is to significantly increase the soluble salt concentration in the soil paste (Table B3). Foam S is more effective than Cake S and significantly higher than pure sulfur on releasing salts into the soil solution. Thorne (1944) noticed a considerable increase in soluble salts due to large treatment of sulfuric acid made on calcareous soil.

Soluble Phosphorus. Analysis of variance of all combinations (Table B4) showed that the main factors and their interactions are significantly affected by the solubility of phosphorus. A separate analysis of variance for each of Pima and Laveen soil showed that the data in Table B4 agreed only with soluble phosphorus in the Pima soil, while in the Laveen soil the solubility of phosphorus was only significanlty affected by levels of sulfur. The separate analyses of variance were run because of non-homogeneous variations of soluble phosphorus found in the two soils. The means of soluble phosphorus from Pima soil as affected by rock phosphate, sulfur, and level of sulfur are shown in Table 11. The higher soluble phosphorus in Pima soil as compared with the Laveen soil might be related to its higher organic matter content, higher cation exchange capacity, and lower $CaCO_3$ content. These properties may be more important in increasing acidity in the calcareous soil, than releasing phosphorus to the soil solution, even though high level of Cake S and Foam S significantly increased the solubility of phosphorus in Pima soil, as interacted with higher level of rock phosphate. Foam S is more effective than pure sulfur in releasing soluble P at the second and third levels of rock phosphate.

Solubility of phosphorus in Pima soil had a significant linear relationship with the higher level of Cake S and pure sulfur, and a quadratic relationship with level of sulfur and rock phosphate with Foam S treatment. In the Laveen soil solubility of phosphorus has a significant relationship with the higher level of Cake S and Foam S treatments, but non-significant relationship with pure sulfur (Table 12).

Table 11 Means of soluble phosphorus in ppm as affected by rock phosphate, sulfur, and level of sulfur interaction in Pima soil, after first barley harvest.

Sulfur	Level of Sulfur	Rock Phosphate (ppm P) 0	250	500
Cake S	0	0.27	0.19	0.23
	8000	1.21	1.08	1.21
Foam S	0	0.32	0.36	0.27
	8000	3.45	4.87	6.21
Pure S	0	0.31	0.31	0.28
	8000	2.43	3.81	3.75

LSD = 0.585 at 0.05 level of probability.

Table 12 Regression equations of soluble phosphorus as affected by two quantitative factors (rock phosphate and level of sulfur) and two qualitative factors (soil and source of sulfur).

Pima Soil	Cake S	$y = 0.229 + 1.17 \times 10^{-4}(LS)$
	Foam S	$y = 0.338 + 3.9 \times 10^{-4}(LS) - 8.7 \times 10^{-5}(P) + 7 \times 10^{-7}(LS)(P)$
	Pure S	$y = 0.3 + 3.8 \times 10^{-4}(LS)$
Laveen Soil	Cake S	$y = 0.221 + 1.15 \times 10^{-5}(LS)$
	Foam S	$y = 0.251 + 2.1 \times 10^{-5}(LS)$

Soil Sulfate. Sulfate in soil was significantly affected by three way interaction of soil, sulfur and level of sulfur, and the two way interaction of rock phosphate and level of sulfur at the 0.01 level of probability (Table B5). Because of non-homogeneous of variance of the two soils the analysis of variance of each soil was run individually. The results showed that the sulfate in Pima soil was significantly different as affected by rock phosphate and level of sulfur interaction, and sulfur by level of sulfur interaction, but in the Laveen soil sulfate was only affected by rock phosphate and level of sulfur interaction. Means of sulfate in ppm as affected by rock phosphate and level of sulfur interaction of the two soils are indicated by Table 13. The data showed a significant increase in sulfate at higher levels of rock phosphate and higher level of sulfur, except there was no difference between the second and third levels of rock phosphate in the Laveen soil. Different sources of sulfur had a significant role in Pima soil when interacted with levels of sulfur (Table 14). Data in the table indicated that sulfate developed from the Foam S treatments was greater than pure sulfur treatments, and significantly higher than Cake S.

Sulfate showed a linear relationship with the level of sulfur with Cake S treatment and quadratic relationship with level of sulfur and rock phosphate with Foam S treatments on both soils. Pure sulfur has a linear relationship in Pima soil and quadratic relationship in Laveen soil (Table 15).

Table 13 Means of soil sulfate in ppm as affected by rock phosphate and level of sulfur interaction, in both soil after first barley harvest (each soil has a separate data analysis).

	Pima Soil		Laveen Soil	
	LS_1^*	LS_2	LS_1	LS_2
RP 0**	535	18168	444	16866
RP 250	548	19900	448	19050
RP 500	560	21300	446	19800

* LS = Levels of sulfur (0, 8000 ppm)
** RP = Rock phosphate
LSD = 1626 on Pima soil at 0.05 level of probability.
LSD = 1202 on Laveen soil at 0.05 level of probability.

Table 14 Means of sulfate in ppm as affected by sulfur and level of sulfur interaction, in Pima soil after first barley harvest.

	Cake	Foam	Pure Sulfur
LS_1^*	541	548	554
LS_2	16768	21600	21000

* LS = Levels of sulfur (0, 8000 ppm S)
LSD = 1626 at 0.05 level of probability.

Table 15 Regression equations of sulfate as related to the two quantitative factors (rock phosphate and level of sulfur) and two qualitative factors (soil and sources of sulfur).

Pima Soil	Cake S	$y = 541.3 + 2.0283(LS)$
	Foam S	$y = 531.1 + 2.2836(LS) + 6.9 \times 10^{-2}(LS) + 1.4 \times 10^{-3}(LS)(P)$
	Pure S	$y = 554.3 + 2.5557(LS)$
Laveen Soil	Cake S	$y = 444 + 2.24242(LS)$
	Foam S	$y = 436 + 2.0622(LS) + 3.7 \times 10^{-2}(P) + 9.95 \times 10^{-4}(LS)(P)$
	Pure S	$y = 452.7 + 1.9184(LS) - 1.33 \times 10^{-2}(P) + 1.3 \times 10^{-3}(LS)(P)$

Soil Zinc. Analysis of variance of zinc in soil (Table B6) showed a significant interaction effect on sulfur by level of sulfur, and soil by sulfur on zinc. Zinc in soil was significantly increased by Foam S as compared with the Cake S and pure sulfur treatments (Table 16). This could be caused by high zinc content in Foam S as indicated by Foam S analysis. A similar result appears in Pima soil as compared with Laveen soil (Table 17).

The higher level of pure sulfur in Pima soil tended to decrease zinc in soil, while Foam S and Cake S increased it in both soils (Table 18).

Table 16 Means of zinc in soil in ppm as affected by sulfur and level of sulfur interaction after first barley harvest.

Level of Sulfur	Cake S	Foam S	Pure Sulfur
(0 S)	3.17	3.16	3.01
(8000 ppm S)	2.86	4.99	2.52

LSD = 0.57 at 0.05 level of probability.

Table 17 Means of zinc in soil in ppm as affected by soil and level of sulfur interaction after first barley harvest.

Level of Sulfur	Pima Soil	Laveen Soil
(0 S)	5.46	0.77
(8000 ppm S)	5.24	1.67

LSD = 0.46 at 0.05 level of probability.

Table 18 Regression equation of zinc in soil as related to all treatments.

Pima Soil	Foam S	$y = 5.453 + 1.57 \times 10^{-4}(LS)$
	Pure S	$y = 5.236 - 1.5 \times 10^{-4}(LS)$
Laveen Soil	Cake S	$y = 0.649 + 1.4 \times 10^{-5}(LS)$
	Foam S	$y = 0.876 + 2 \times 10^{-4}(LS)$

Plant Phosphorus. Percent phosphorus in plant tissues was significantly different at 0.01 level of probability as a result of soil and the level of sulfur interaction (Table B7). The means of plant phosphorus in the above interaction are shown in Table 19. The greatest phosphorus uptake was found in the Pima soil containing high levels of sulfur, and the lowest uptake in the Laveen soil with lower levels of sulfur. These results correlated with the soluble phosphorus in soil as discussed previously.

Table 19 Means of percent P in plant tissue affected by soil and level of sulfur interactions, after first barley harvest.

Level of Sulfur	Pima Soil	Laveen Soil
(0 S)	0.132	0.054
(8000 ppm S)	0.253	0.066

LSD = 0.060 at 0.05 level of probability.

Plant phosphorus had a significant linear relationship with the level of sulfur under Cake S and Foam S treatment in both soils (Table 20).

Table 20 Regression equations of percent P in plant tissue as affected by all factors.

Pima Soil	Cake S	$y = 0.109 + 1.4 \times 10^{-5}(LS)$
	Foam S	$y = 0.103 + 2.1 \times 10^{-5}(LS)$
Laveen Soil	Cake S	$y = 0.0578 + 1.25 \times 10^{-6}(LS)$
	Foam S	$y = 0.05111 + 2.2 \times 10^{-6}(LS)$

Dry Weight. The interaction of soil and level of sulfur had a significant effect at the 0.01 level of probability on barley dry weight per pot as shown by the analysis of variance in Table B8. The result of soils by level of sulfur interaction affected on dry weight (Table 21) was similar to the results of percent plant phosphorus in previous discussion, it can be concluded that total content of phosphorus in plant has the same evaluation as in percent plant phosphorus and dry weight.

Table 21 Means of barley yield in grams of dry weight per pot for the first harvest.

Level of Sulfur	Pima Soil	Laveen Soil
(0 S)	1.33	0.83
(8000 ppm S)	4.07	2.56

LSD = 0.31 at 0.05 level of probability.

Pima soil when treated with Cake S, Foam S and pure sulfur treatments shows a significant linear relationship to dry weight with level of sulfur. The same relationship was found in the Laveen soil with Cake S and pure sulfur, except that a quadratic relationship existed between dry weight with level of sulfur and rock phosphate in Laveen soil when treated with Foam S (Table 22).

Table 22 Regression equation of dry weight gm per pot as related to all factors.

Pima Soil	Cake S	$y = 1.37 + 3 \times 10^{-4}(LS)$
	Foam S	$y = 1.361 + 3.6 \times 10^{-4}(LS)$
	Pure S	$y = 1.26 + 3.7 \times 10^{-4}(LS)$
Laveen Soil	Cake S	$y = 0.966 + 1.7 \times 10^{-4}(LS)$
	Foam S	$y = 0.782 + 1.8 \times 10^{-4}(LS) - 6.4 \times 10^{-4}(P) + 2 \times 10^{-6}(P)^2 + 1.2 \times 10^{-6}(LS)(P) - 2.2 \times 10^{-9}(LS)(P)^2$
	Pure S	$y = 0.692 + 2.3 \times 10^{-4}(LS)$

Phosphorus Sorption Isotherm. A shift to the right of the plotted curve for phosphorus in equilibrium solution (ppm P in soil solution) versus amounts of phosphorus sorbed (ppm P in soil) indicated an increase in soluble P, for a specific soil. A shifting of the isotherm to the right for the Pima soil, lower level of rock phosphate and super phosphate, Foam S and pure S, and higher level of sulfur as compared with Laveen soil, high level of rock phosphate and super phosphate, Cake S, and lower level of sulfur respectively (Fig. 9 to 13).

The shifting to the left by rock phosphate may be explained by converting soluble phosphorus to an unavailable form as combined with calcium which was released from the rock phosphate. Similar results were found in the super phosphate treatment, although the effect was still less than with rock phosphate. Different sources of sulfur influenced phosphorus sorption in soil, Foam S shifted the isotherm more to the right than pure sulfur and Cake S. This effect is mostly due to the release of P into the soil solution. In the same way the higher level of sulfur affected soluble P in soil. The regression equations and the linear relationship between phosphorus in soil solution and phosphorus sorbed by soil are shown in Figures 14 to 18. Significant differences were found at 0.01 level of probability between soils, rock phosphate levels, sources of sulfur, and level of sulfur. A non-significant effect was found between super phosphate levels.

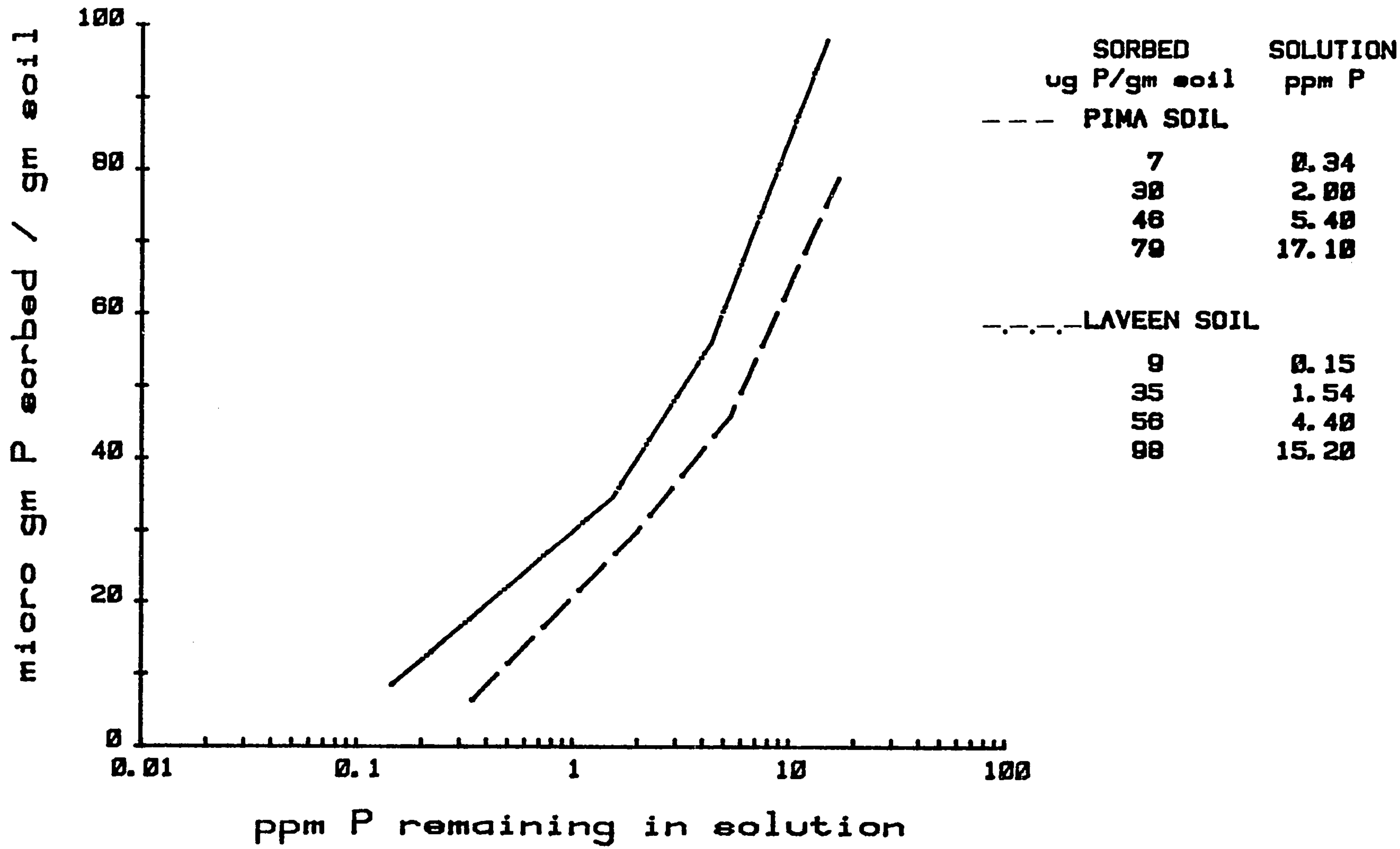

Figure 9 Means phosphorus sorption isotherms for two calcareous soils (Pima & Laveen).

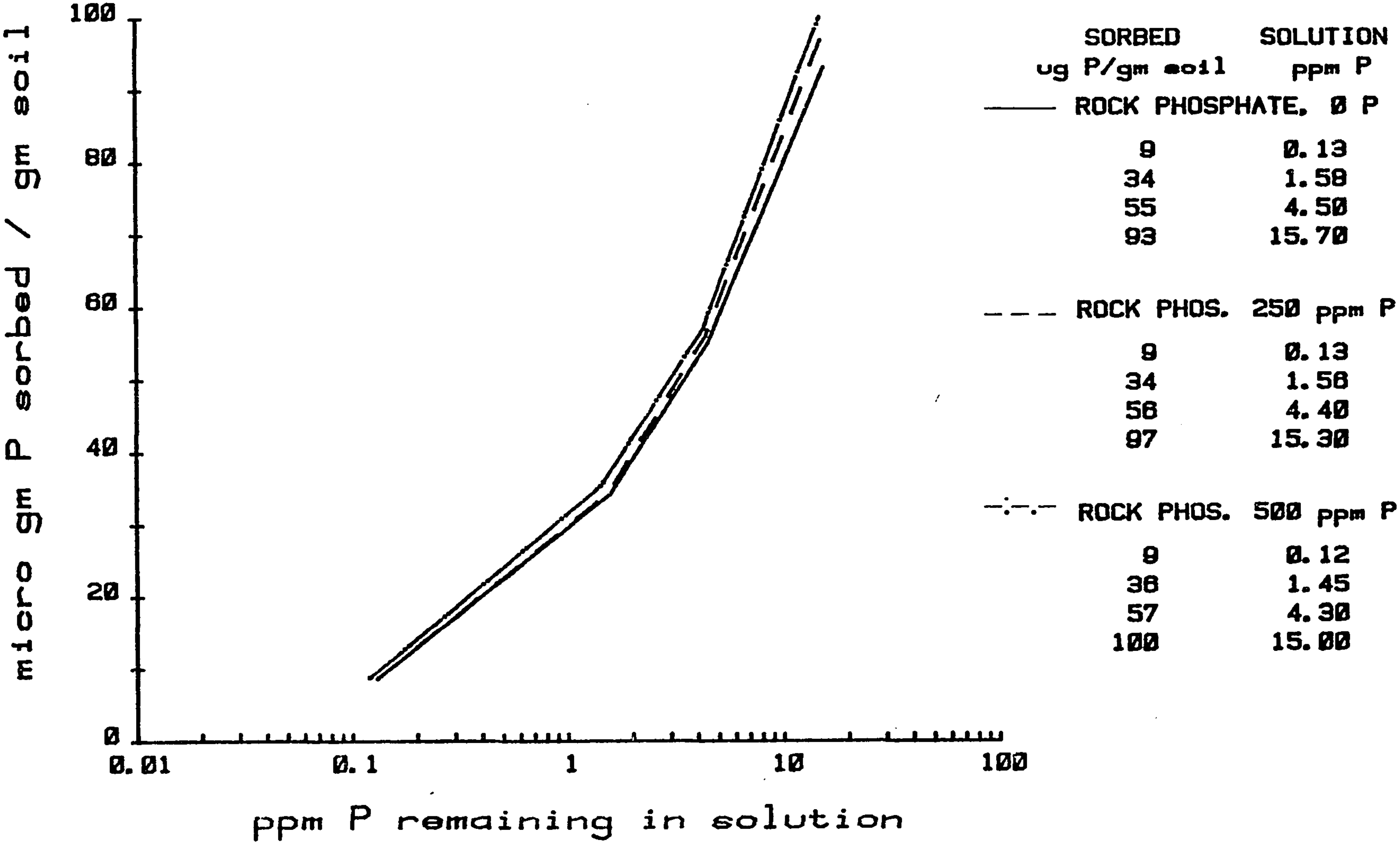

Figure 10 Mean phosphorus sorption isotherms for two calcareous soils (Pima & Laveen) treated with rock phosphate.

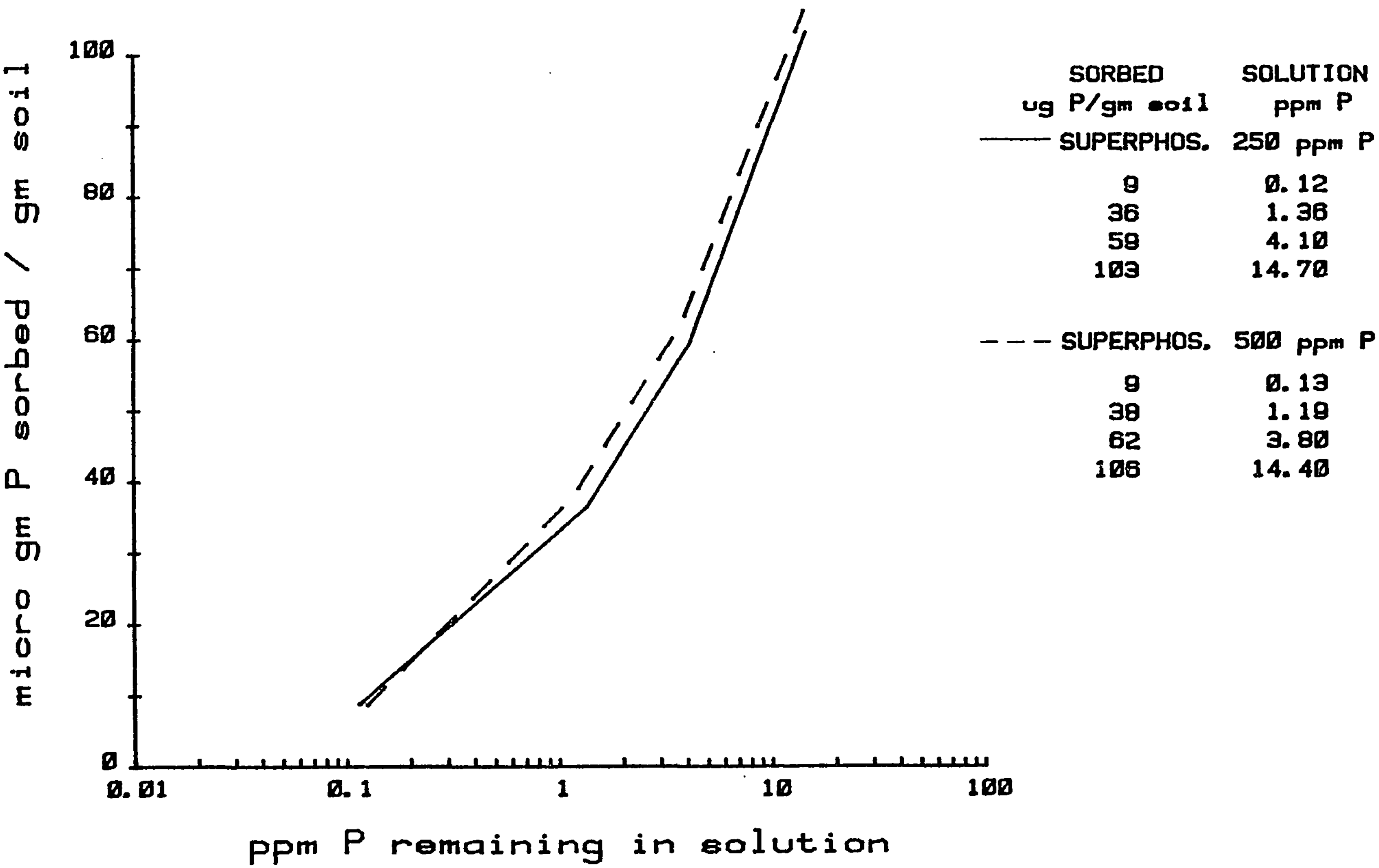

Figure 11 Mean phosphorus sorption isotherms for two calcareous soils (Pima & Laveen) treated with super phosphate.

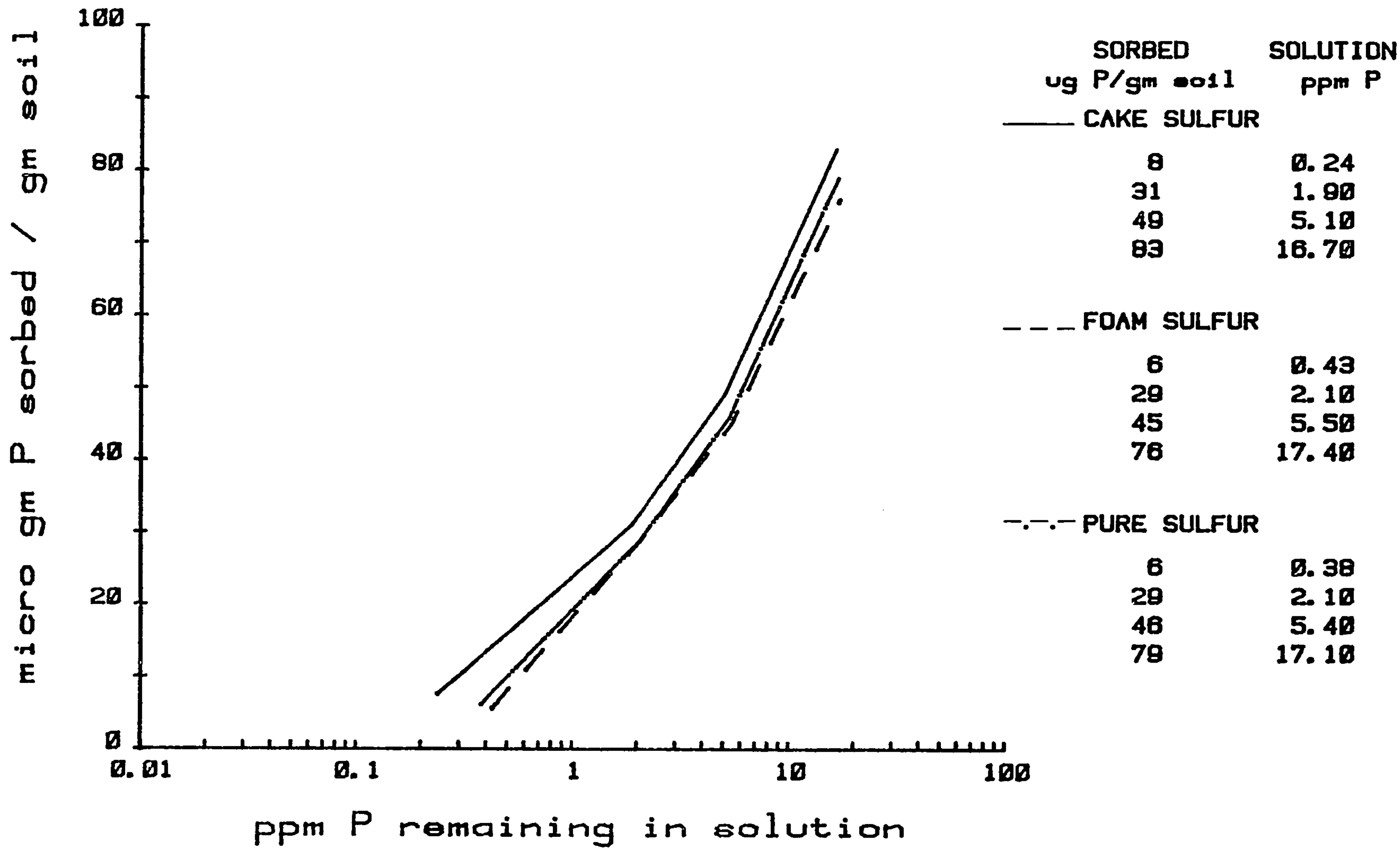

Figure 12 Means phosphorus sorption isotherms for two calcareous soils (Pima & Laveen) treated with different sources of sulfur.

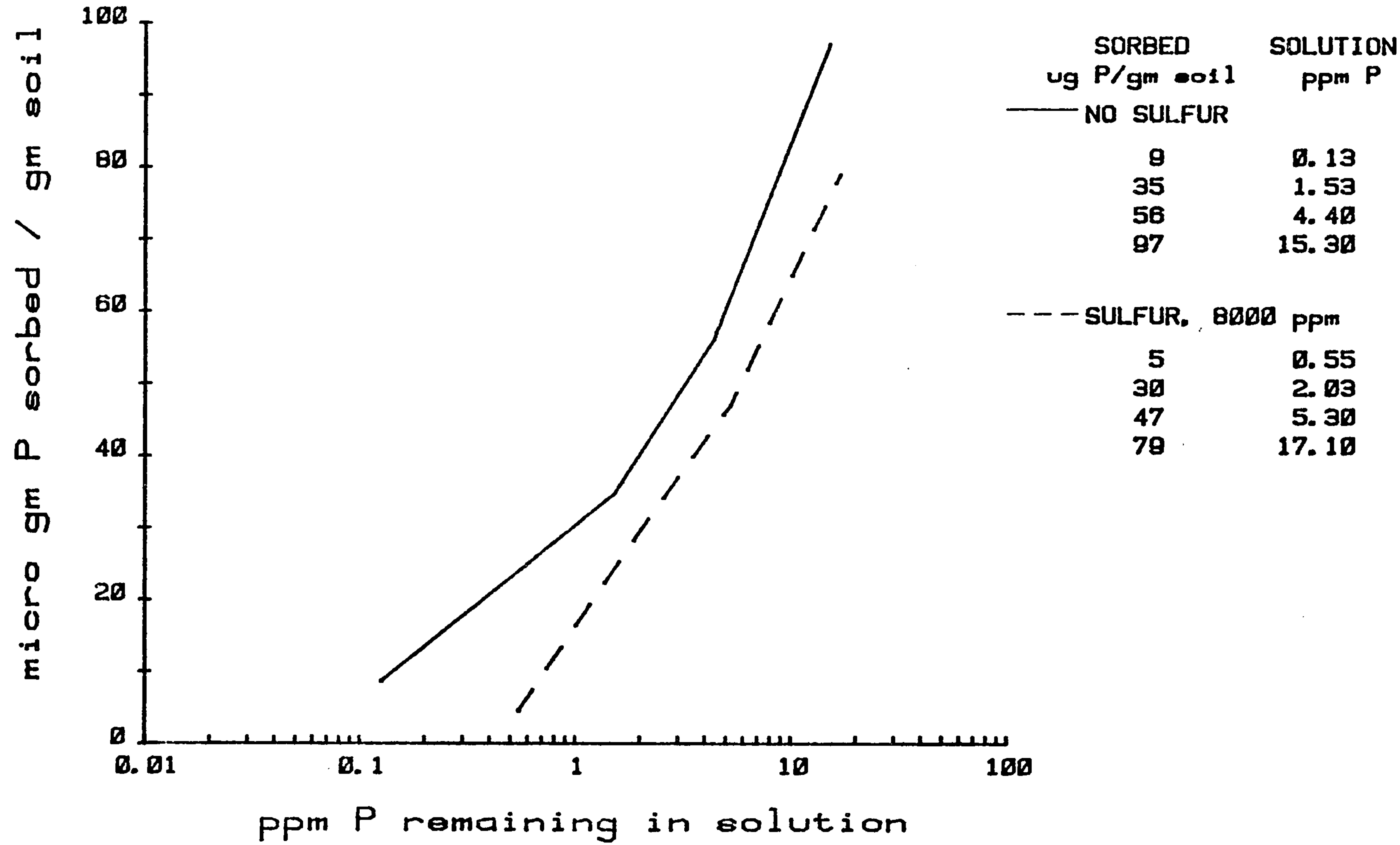

Figure 13 Mean phosphorus sorption isotherms for two calcareous soils (Pima and Laveen) as affected by sulfur treatment.

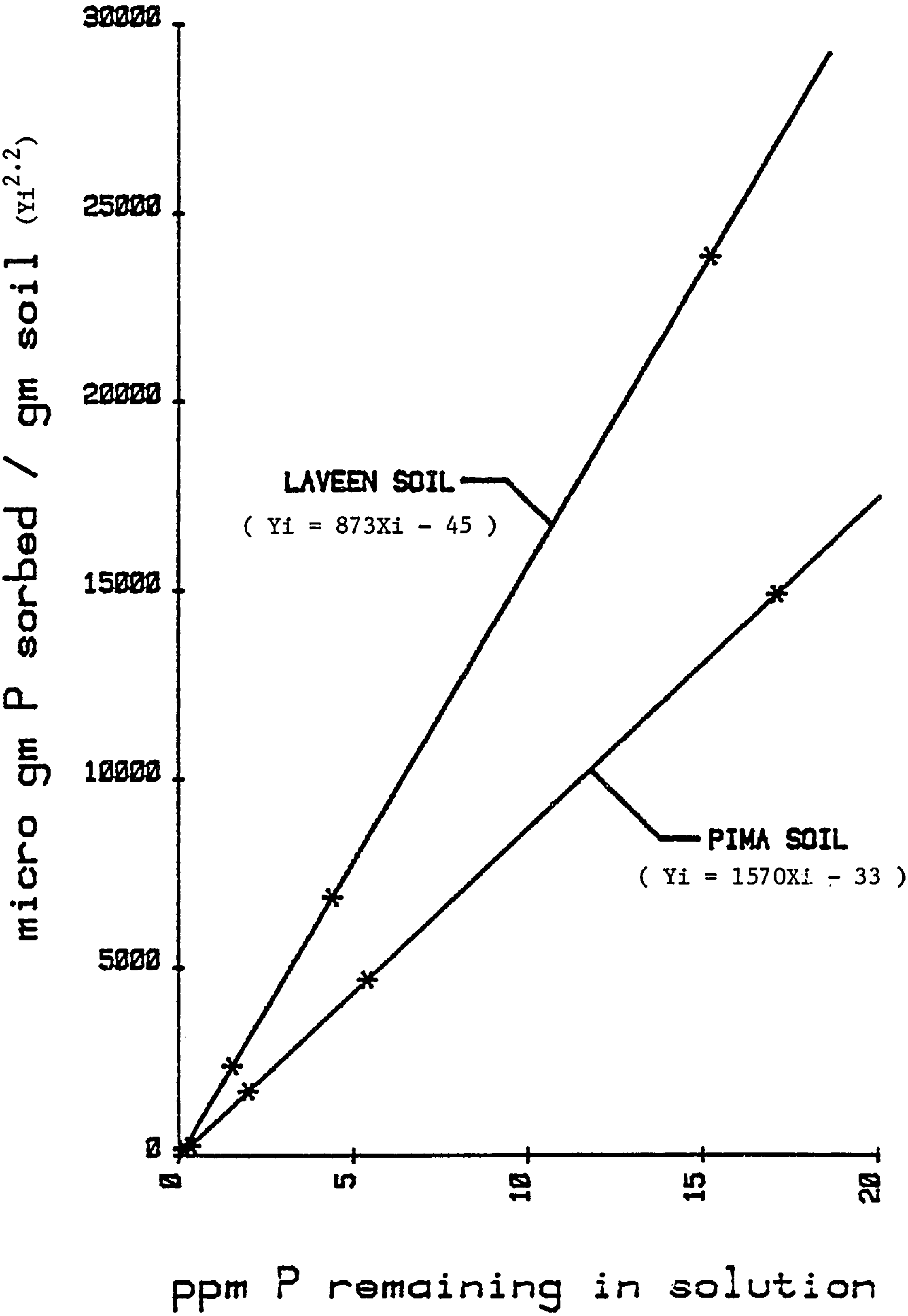

Figure 14 Linear regression of isotherms for two calcareous soils (Pima & Laveen).

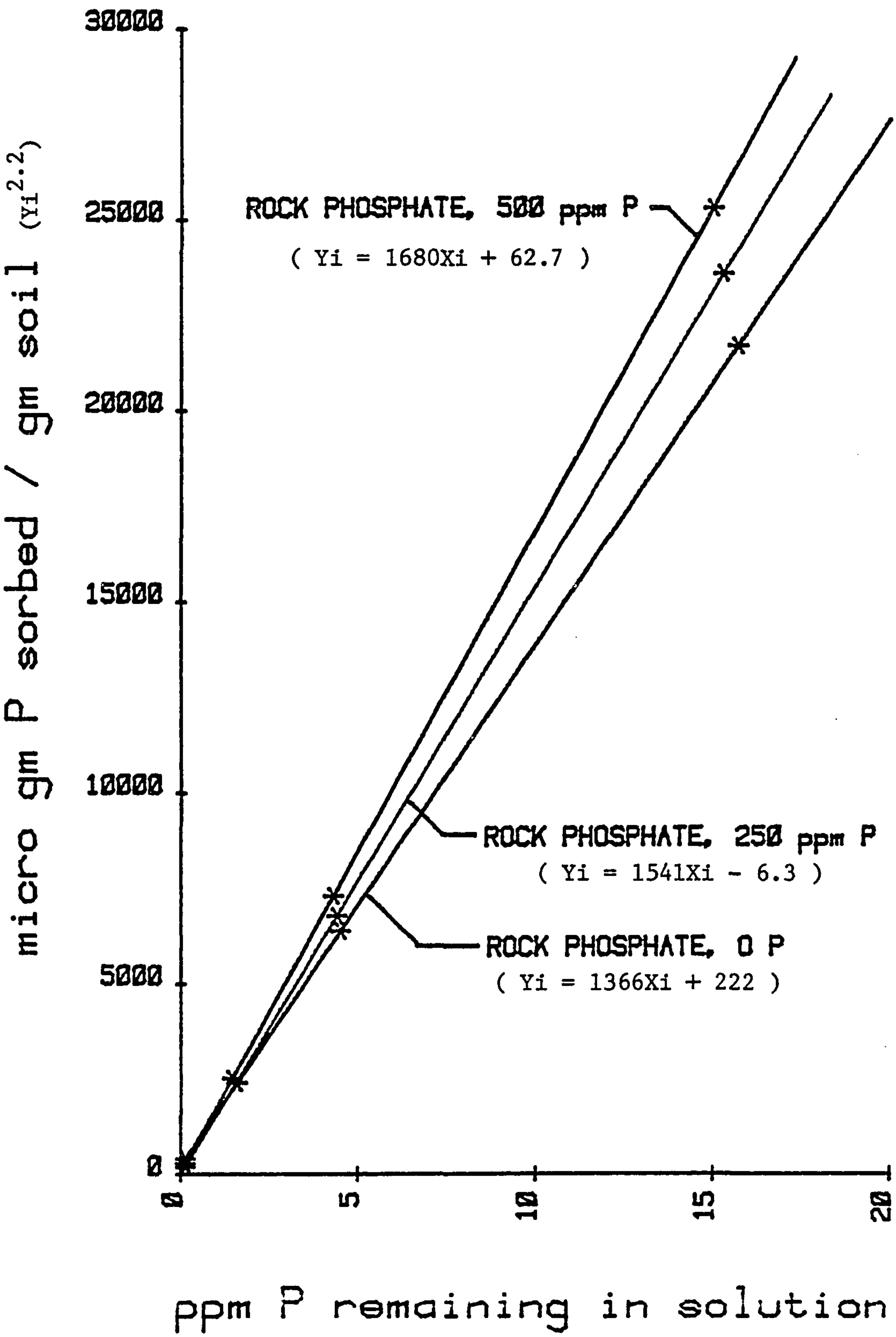

Figure 15 Linear regression of isotherms for mean of two calcareous soils (Pima & Laveen) treated with rock phosphate.

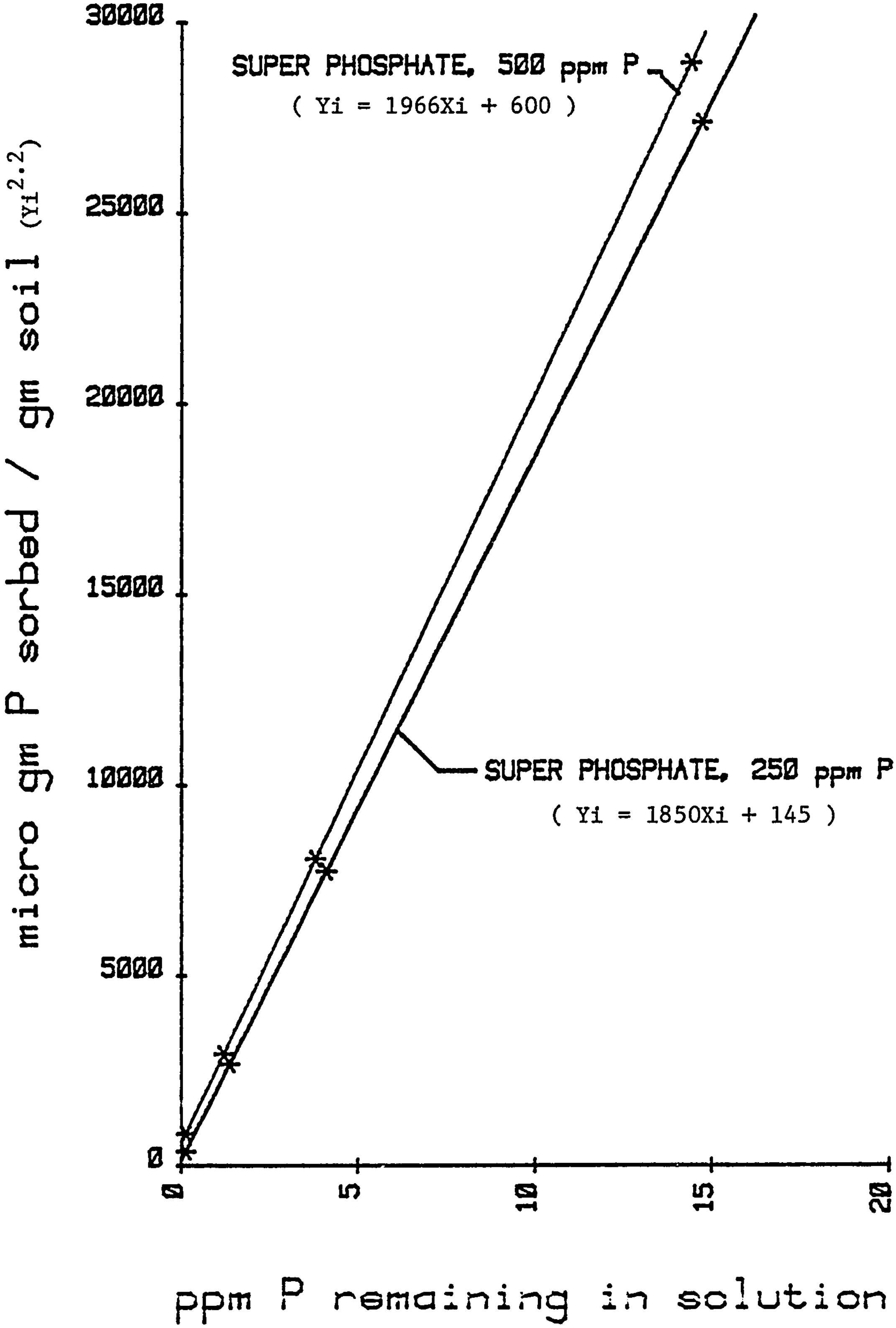

Figure 16 Linear regression of isotherms for mean of two calcareous soils (Pima & Laveen) treated with super phosphate.

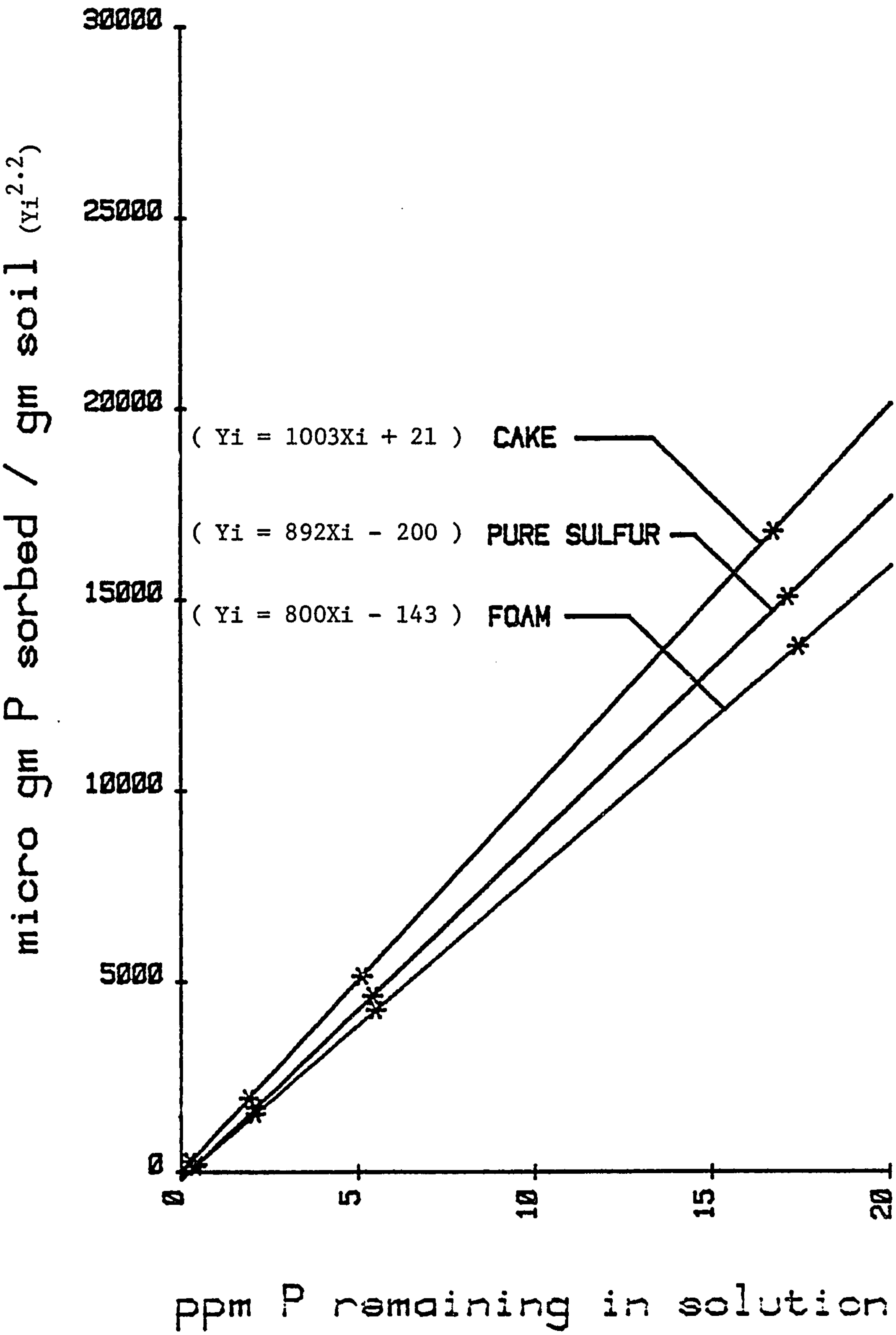

Figure 17 Linear regression of isotherms for mean of two calcareous soils (Pima & Laveen) treated with three sources of sulfur.

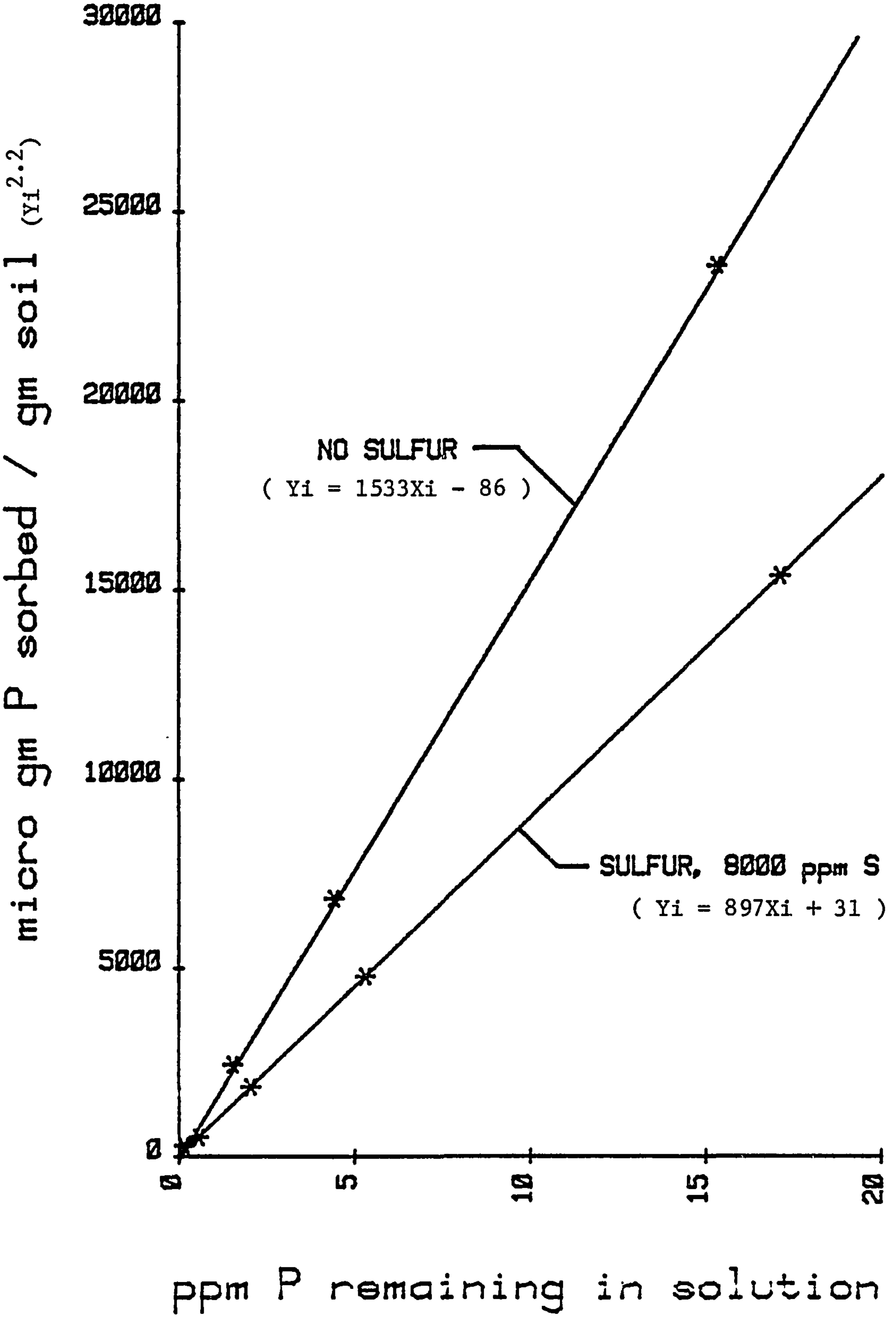

Figure 18 Linear regression of isotherms for mean of two calcareous soils (Pima & Laveen) treated with sulfur.

Second Barley Harvest

The second crop of barley plants were irrigated with tap water for all the growing period, and a saturated solution of $CaSO_4$ had been used twice, to eliminate sulfur deficiency (and find out effectiveness of sulfur as a soil amendment). The dry weight of the plants were measured and the soil and plants were analyzed for zinc and phosphorus after the 12 week growing period.

Soil Phosphorus. Analysis of variance of soluble phosphorus (Table C1) showed results similar to the first barley harvest. The means test of rock phosphate, sulfur and level of sulfur interaction were significant differences in Pima soil (Table 23) as found by separate analysis of variance. Solubility of phosphorus was increased significantly by higher level of Foam S and pure sulfur treatment and rock phosphate. However, Foam S effectiveness was significantly higher than pure sulfur. Cake S treatment had no effect on soluble P over the levels of rock phosphate. The level of sulfur significantly increased soluble phosphorus in both Pima and Laveen soils.

A significant linear relationship was found between soluble phosphorus and level of sulfur by Cake S and pure sulfur in Pima soil, and Foam S in Laveen soil. A quadratic relationship of soluble phosphorus with the level of sulfur and rock phosphate was found at Foam S in Pima soil and Cake S and pure sulfur in Laveen soil (Table 24).

Table 23 Means of soluble phosphorus in ppm as affected by rock phosphate, sulfur, and level of sulfur interaction in Pima soil after second barley harvest.

Sulfur	Level of S ppm	Rock Phosphate ppm (P) 0	250	500
Cake S	0	0.15	0.14	0.12
	8000	1.36	1.22	1.37
Foam S	0	0.13	0.18	0.14
	8000	3.18	4.03	7.77
Pure S	0	0.24	0.27	0.57
	8000	1.69	2.04	2.17

LSD = 1.48 at 0.05 level of probability.

Table 24 Regression equations of soluble phosphorus as related to the four factors (Pima or Laveen soil, Cake S, Foam S and Pure S) after second barley harvest.

Pima Soil	Cake S	$y = 0.138 + 1.47 \times 10^{-4}(LS)$
	Foam S	$y = 0.147 + 3.2 \times 10^{-4}(LS) + 1.33 \times 10^{-5}(P) + 1.14 \times 10^{-6}(LS)(P)$
	Pure S	$y = 0.359 + 2 \times 10^{-4}(LS)$
Laveen Soil	Cake S	$y = 0.195 + 6.7 \times 10^{-4}(P) - 1.5 \times 10^{-6}(P)^2$
	Foam S	$y = 0.1778 + 2.2 \times 10^{-5}(LS)$
	Pure S	$y = 0.137 + 4.3 \times 10^{-5}(LS) + 1.2 \times 10^{-4}(P) + 3.2 \times 10^{-7}(P)^2 - 3.3 \times 10^{-6}(LS)(P) - 5.5 \times 10^{-10}(LS)(P)^2$

Soil Zinc. Individual analysis of variance for each soil showed a significant effect of sulfur by level of sulfur interaction on zinc in Laveen soil. The main effect of sulfur in Pima soil was significantly increase zinc in soil in this order: Foam S > Cake S > pure sulfur, but Cake S and Foam S were not significantly different. Table 25 represents the mean value of zinc on Laveen soil as affected by the sulfur and level of sulfur interaction. Zinc increased according to the level of sulfur applied, but, was highly significant with increasing levels of the Foam S which is due to the high zinc content originally in the Foam S.

Table 25 Means of DTPA extractable zinc in soil in ppm as affected by sulfur and level of sulfur interaction in Laveen soil after second barley harvest.

Level of Sulfur	Cake S	Foam S	Pure S
(0 S)	0.68	0.57	0.63
(8000 ppm S)	0.74	2.78	1.11

LSD = 0.517 at 0.05 level of probability.

The only significant linear relationship was between soil zinc and levels of Foam S applied to Laveen soil, which indicates a linear increase of zinc in soil by Foam S treatment as shown in the following equation:

$$Y = 0.571 + 2.8 \times 10^{-4}$$

Dry Weight. Rock phosphate and the interaction of soil and the level of sulfur had a significant effect on the dry weight of the second barley harvest (Table C3). The dry weight of the barley grown in both soils was significantly increased by the level of sulfur, but it was higher in Pima than Laveen soil (Table 26). This may be attributed to the better growth conditions in Pima soil than Laveen soil.

Table 26 Means of barley dry weight in gram per pot as affected by soil and level of sulfur interaction after second barley harvest.

Level of Sulfur	Pima Soil	Laveen Soil
(0 S)	3.22	1.96
(8000 ppm S)	6.66	2.41

LSD = 0.344 at 0.05 level of probability.

Barley dry weight increased by the second and third rates of rock phosphate application in Laveen soil. This can be explained by the release of phosphorus from rock phosphate to the soil solution as correlated with the time, then reducing phosphorus deficiency in the plant.

A regression equation showed a significant increase of plant dry weight due to pure sulfur treatment in both soils, while Cake S and Foam S were significantly increased dry weight only in Pima soil (Table 27).

Table 27 Regression equation of barley dry weight in gram per pot as affected by soil, sulfur and level of sulfur, after second harvest of barley.

Pima Soil	Cake S	$y = 3.186 + 4.05 \times 10^{-4}(LS)$
	Foam S	$y = 3.338 + 4.34 \times 10^{-4}(LS)$
	Pure S	$y = 3.137 + 4.52 \times 10^{-4}(LS)$
Laveen Soil	Pure S	$y = 1.796 + 6.153 \times 10^{-5}(LS)$

Plant Phosphorus. The percent phosphorus in plant tissues was significantly increased (at 0.01 level of probability) by soil and level of sulfur interaction (Table C4). However, phosphorus in the plant was higher at the second level of sulfur in both soils, but was statistically significant only in Pima soil (Table 28).

Table 28 Means of percent phosphorus in plant tissues as affected by soil and level of sulfur interaction, after second barley harvest.

Level of Phosphorus	Pima Soil	Laveen Soil
(0 P)	0.070	0.066
(8000 P)	0.220	0.073

LSD = 0.034 at 0.05 level of probability.

In general, levels of Cake S and Foam S in Pima soil significantly increase the percent plant phosphorus as shown in Table 29.

Table 29 Regression equation for percent plant phosphorus as affected by soil, sulfur, and level of sulfur after second barley harvest.

Pima	Cake S	$y = 0.0149 + 1.93 \times 10^{-5}(LS)$
Soil	Foam S	$y = 0.049 + 2.61 \times 10^{-5}(LS)$

Plant Zinc. As represented by Table C5, zinc in plant tissues is significantly affected by soil and level of sulfur interaction. In the Pima soil increasing the level of sulfur decreased the zinc in plants, while it is increased in the Laveen soil (Table 30). This can be analyzed by negative interaction between zinc and higher solubility of phosphorus in Pima soil, which resulted in a lower uptake of zinc by plants.

The regression equations of the Pima soil with Cake S, Foam S and pure sulfur treatments show a significant linear decrease of plant zinc with level of sulfur, but in the Laveen soil only Foam S had a significant linear increase of plant zinc with increasing level of sulfur (Table 31).

Table 30 Means of zinc in plant tissue in ppm as affected by soil and level of sulfur interaction after second barley harvest.

Level of Sulfur	Pima Soil	Laveen Soil
(0 S)	133.9	62.9
(8000 ppm S)	76.2	98.8

LSD = 26.9 at 0.05 level of probability.

Table 31 Regression equation of zinc in plant tissue in ppm as affected by soil, sulfur and level of sulfur after second barley harvest.

Pima Soil	Cake S	$y = 150.11 - 7.722 \times 10^{-3}(LS)$
	Foam S	$y = 140.67 - 9.64 \times 10^{-3}(LS)$
	Pure S	$y = 125.89 - 6.167 \times 10^{-3}(LS)$
Laveen Soil	Foam S	$y = 54.33 + 1.06 \times 10^{-2}(LS)$

Rock Phosphate and Super Phosphate Comparison Experiment

Soil and plants were tested for the same measurements as in the first and second barley harvest. A multiple means comparison test was used to find the difference between rock phosphate and super phosphate effects.

First Barley Harvest. Means of different variables after the first and second harvests are shown in Table 32. Soil pH was significantly increased by applications of rock phosphate and super phosphate as compared with control. It can be explained by calcium ions being released from those materials and precipitate with sulfate ions in the soil. Soluble salts were increased by rock phosphate as well as control, and they were significantly different than higher level of super phosphate. Dry weight was significantly increased by super phosphate treatment as compared with the rock phosphate and control. This phenomenon is attributed to the higher soluble phosphorus released from super phosphate than rock phosphate, then supply available P to the plant. As a result percent P in plant is significantly higher when using super phosphate than rock phosphate treatment. Soil sulfate and zinc are not affected by rock phosphate and the super phosphate treatments.

<u>Second Barley Harvest</u>. Dry weight of the second barley harvest was the only measurement that was significantly affected by super phosphate as compared with rock phosphate. Soluble P in soil, percent P in plant, and soil and plant zinc were not significantly different due to the rock phosphate and super phosphate treatments. This may be caused by the releasing of available P from rock phosphate as treated for long period, then releasing available P in the same way as super phosphate.

Table 32 Means of different measurements as affected by rock phosphate and super phosphate, after first and second harvest.

Measurements	Control	Rock Phosphate		Super Phosphate		SNK
A - After First Barley	0	250	500	250	500	Test*
Soil pH	7.97	8.08	8.12	8.20	8.27	Sign.
EC_e mmhos/cm	2.10	2.32	2.25	1.38	0.97	Sign.
Soluble P ppm in soil	0.268	0.272	0.245	0.382	0.482	Sign.
Dry weight gm/plant	0.19	0.16	0.17	0.49	0.41	Sign.
% P in plant	0.082	0.078	0.073	0.122	0.155	Sign.
Sulfate ppm in soil	489	498	503	496	509	N. S.
Zinc ppm in soil	2.97	3.07	3.20	2.72	4.15	N. S.
B - After Second Barley						
Dry weight gm/pot	2.57	2.55	2.63	4.57	3.97	Sign.
Soluble P ppm in soil	0.17	0.21	0.24	0.32	0.28	N. S.
% P in plant	0.058	0.058	0.057	0.065	0.072	N. S.
Zinc ppm in soil	2.95	3.33	2.97	2.28	2.48	N. S.
Zinc ppm in plant	91.7	107.5	103.2	82.7	119.3	N. S.

* SNK = Student Newman Keuls' test used as multiple means comparison at 0.05 level of probability.

SUMMARY AND CONCLUSIONS

Two experiments were conducted to study the effect of waste sulfur materials on calcareous soil acidulation. Soil in the first experiment was combined with rock phosphate and waste material, then incubated for two periods in a laboratory. The second experiment was carried out in a greenhouse. Two soils were treated with rock phosphate and three sources of sulfur, then tomato and barley were planted, respectively. The soil and plants were analyzed and the data were evaluated by analysis of variance, multiple means comparison test, and regression equations.

Foam Effects

Application of Foam S at the rates of 5000 and 10000 ppm of S to the soil in the first experiment significantly reduced soil pH. Solubility of phosphorus was increased, sulfur was largely converted to the sulfate, and the phosphorus isotherm was significantly shifted to the right as compared with Cake S and pure S treatments. After the first barley harvest, the Foam S significantly reduced soil pH and increased soluble salts. Soluble phosphorus increased greatly when Foam S interacted with rock phosphate. A similar result was found with the second barley harvest. Foam S released sulfate to the soil solution to a greater extent than Cake S and pure sulfur. Foam S caused a significant increase in zinc in the Laveen soil but a decrease in the Pima soil. After the second barley harvest the zinc in plants followed a pattern to soil zinc after first barley harvest. However, soil zinc was increased in both soils. Plant phosphorus and dry weight of plants were significantly increased by Foam S treatments in both harvests of barley.

Cake Effects

In the incubation experiment Cake S treatment reduced soil pH, and increased soluble phosphorus and sulfate but to a lesser extent than Foam S. On the other hand, the isotherm was significantly shifted to the left as compared with pure sulfur and Foam S. After the first harvest of barley soil pH was reduced to a smaller extent by Cake S treatment than by pure sulfur and Foam S. Soluble salts and sulfate were increased. The dry weight and phosphorus in soil and plants after both barley harvests were increased due to the Cake S treatment. Soil zinc decreased after the first and second harvest as well as soil and plant zinc was lower after the second harvest. The P isotherm shifted to the right, although significantly less than with Foam S and pure sulfur.

Pure Sulfur Effects

In most cases the effect of pure sulfur was intermediate between the Foam S and Cake S treatments after the first and second barley harvest. Soil pH, soluble salts, and sulfate were significantly increased by pure sulfur. Similar results were found with soil and plant phosphorus and dry weight after both harvests. Zinc in the soil decreased after first harvest, and increased in the soil following second harvest. The P isotherm resulting from the pure sulfur treatment was intermediate between the Cake S and Foam S, but significantly different.

Rock Phosphate Effects

In the laboratory study rock phosphate showed no effect on soil pH and sulfate, but tended to decrease the soluble P, as it interacted with sulfur at different levels. The P isotherm shifted to the left as compared with the control which illustrates this decreased solubility of P.

Rock Phosphate and Super Phosphate

There was no significant difference between rock phosphate and super phosphate on soil pH after the first and second barley harvest, but soluble salts were increased more by rock phosphate than super phosphate. Soil and plant phosphorus after the first harvest and the plant dry weight after both harvests were significantly increased by super phosphate as compared with rock phosphate. Sulfate and soil zinc after the first harvest, and soil and plant phosphorus and zinc after second harvest were not significantly different due to treatments of rock phosphate and super phosphate.

Pima and Laveen Soil

Both soils are calcareous, but the Pima soil has less $CaCO_3$ than Laveen. As a result of sulfur and rock phosphate treatments, both soils show similar values of soluble salt content. On the Pima soil, treatments resulted in higher acidity, sulfate, soil and plant phosphorus, and barley dry weights after both harvests. The zinc levels decreased in the Pima and increased in the Laveen soil at both sampling periods. The phosphorus isotherm shifted farther to the right with the Pima soil than the Laveen soil.

In general terms, soil with less $CaCO_3$ was more affected by sulfur and rock phosphate treatments than the soil with higher content of $CaCO_3$. Rock phosphate had a similar action to super phosphate after a longer period of soil contact when applied with sulfur. A similarity between soil and plant tests values after the first and second barley harvests indicates that sulfur treatments acted as an acidifying soil amendment rather than plant nutrient. Foam S was more effective in improving the conditions of alkaline soils than Cake S and pure sulfur, and it had a greater effect when combined with rock phosphate for the longer time. Cake S, when considered as a source of sulfur lower in cost than pure sulfur, can be used as an amendment in calcareous soil.

Using Waste Materials In Iraqi Soils

Iraq is located in a semi-arid region characterized by soils high in alkalinity and lime. It is concluded from the results of this study that sulfur soil amendments can be used to ameliorate these conditions, thus reducing soil pH, increasing availability of phosphorus, and some micronutrients. In Iraq, large quantities of waste materials are available that should be beneficially utilized.

APPENDIX A

ANALYSIS OF VARIANCE TABLES FOR LABORATORY STUDY

Table A-1 Analysis of variance of pH of calcareous soil (Laveen), treated with rock phosphate, and two sources of waste material of sulfur, three levels each, for two periods of incubation during 1979.

Source of variation	Degrees of Freedom	Mean Square	F Value
Rock phosphate	1	.00005	.012
Sulfur	1	.006	1.424
Level of sulfur	2	.861	194.44**
Time of incubation	1	.49	110.70**
Rock phos. X Sulfur	1	.015	3.4
Rock phos. X Level of S	2	.003	.718
Rock phos. X Time of inc.	1	.00005	.012
Sulfur X Level of S	2	.004	.929
Sulfur X Time of inc.	1	.001	.294
Level of S X Time of inc.	2	.005	1.141
Rock phos. X S X Level of S	2	.002	.435
Rock phos. X S X Time of inc.	1	.001	.294
Rock phos. X Level of S X Time of inc.	2	.002	.506
S X Level of S X Time of inc.	2	.001	.153
Rock phos. X S X Level of S X Time of inc.	2	.005	1.212
Error	24	.004	
Total	47	.051	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table A-2 Analysis of variance of soluble P of calcareous soil (Laveen), treated with rock phosphate, and two sources of waste material of sulfur, three levels each, for two periods of incubation during 1979.

Source of variation	Degrees of Freedom	Mean Square	F Value
Rock phosphate	1	.002	.476
Sulfur	1	.656	156.034**
Level of sulfur	2	1.459	347.100**
Time of incubation	1	.482	114.710**
Rock phos. X Sulfur	1	.115	27.38**
Rock phos. X Level of S	2	.031	7.363*
Rock phos. X Time of inc.	1	.062	14.838**
Sulfur X Level of S	2	.207	49.307**
Sulfur X Time of inc.	1	.014	3.253
Level of S X Time of inc.	2	.009	2.196
Rock phos. X S X Level of S	2	.098	23.36**
Rock phos. X S X Time of inc.	1	.015	3.582
Rock phos. X Level of S X Time of inc.	2	.001	.218
S X Level of S X Time of inc.	2	.0003	.064
Rock phos. X S X Level of S X Time of inc.	2	.002	.462
Error	24	.004	
Total	47	.108	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table A-3 Analysis of variance of soil sulfate of calcareous soil (Laveen), treated with rock phosphate, and two sources of waste material of sulfur, three levels each, for two periods of incubation during 1979.

Source of variation	Degrees of Freedom	Mean Square	F Value
Rock phosphate	1	2936341	2.16
Sulfur	1	1257121	.93
Level of sulfur	2	164212970	120.9**
Time of incubation	1	39284245	28.9**
Rock phos. X Sulfur	1	3328533	2.5
Rock phos. X Level of S	2	1835854	1.35
Rock phos. X Time of inc.	1	130625	.10
Sulfur X Level of S	2	342994	.25
Sulfur X Time of inc.	1	374533	.28
Level of S X Time of inc.	2	8935684	6.67**
Rock phos. X S X Level of S	2	1543758	1.34
Rock phos. X S X Time of inc.	1	1766401	1.30
Rock phos. X Level of S X Time of inc.	2	152084	.11
S X Level of S X Time of inc.	2	218692	.16
Rock phos. X S X Level of S X Time of inc.	2	578500	.43
Error	24	1359293	
Total	47	9305147	

APPENDIX B

ANALYSIS OF VARIANCE TABLES FOR

GREENHOUSE STUDY

FIRST BARLEY HARVEST

Table B-1 Analysis of variance of tomato yield per pot from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Rock phosphate	2	.03	.14
Sulfur	2	.23	1.05
Level of sulfur	1	119.3	535.93**
Rock phos. X S	4	.06	.25
Rock phos. X Level of S	2	.03	.15
Sulfur X Level of S	2	.58	2.6
Rock phos. X S X Level of S	4	.06	.27
Error	36	.22	
Total	53	2.44	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table B-2 Analysis of variance of pH after first barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	7.182	524.1**
Rock phosphate	2	.114	8.3**
Sulfur	2	.083	6.0**
Level of Sulfur	1	6.626	483.5**
Soil X Rock phos.	2	.046	3.4*
Soil X Sulfur	2	.120	8.7**
Soil X Level of S	1	1.002	131.5**
Rock phos. X S	4	.014	1.0
Rock phos. X Level of S	2	.013	1.0
Sulfur X Level of S	2	.142	10.4**
Soil X Rock phos. X S	4	.003	.3
Soil X Rock phos. X Level of S	2	.010	.8
Soil X S X Level of S	2	.095	6.9**
Rock phos. X S X Level of S	4	.001	.1
Soil X Rock phos. X S X Level of S	4	.010	.8
Error	72	.014	
Total	107	.168	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table B-3 Analysis of variance of electrical conductivity after first barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	.43	1.12
Rock phosphate	2	.29	.75
Sulfur	2	1.31	3.4*
Level of Sulfur	1	41.32	107.8**
Soil X Rock phos.	2	.001	.002
Soil X Sulfur	2	.41	1.07
Soil X Level of S	1	1.203	3.14
Rock phos. X S	4	.167	.44
Rock phos. X Level of S	2	.015	.04
Sulfur X Level of S	2	.34	.89
Soil X Rock phos. X S	4	.18	.48
Soil X Rock phos. X Level of S	2	.086	.22
Soil X S X Level of S	2	.136	.35
Rock phos. X S X Level of S	4	.221	.58
Soil X Rock phos. X S X Level of S	4	.016	.04
Error	72	.383	
Total	107	.730	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table B-4 Analysis of variance of soluble phosphorus after the first barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	53.2	390.1**
Rock phosphate	2	1.1	7.7**
Sulfur	2	8.6	63.3**
Level of Sulfur	1	58.2	426.5**
Soil X Rock phos.	2	1.0	7.1**
Soil X Sulfur	2	7.5	55.2**
Soil X Level of S	1	50.2	368.2**
Rock phos. X S	4	.4	3.2*
Rock phos. X Level of S	2	1.2	8.7**
Sulfur X Level of S	2	7.6	55.7**
Soil X Rock phos. X S	4	.4	2.9*
Soil X Rock phos. X Level of S	2	1.1	8.0**
Soil X S X Level of S	2	7.1	51.7**
Rock phos. X S X Level of S	4	.4	2.8*
Soil X Rock phos. X S X Level of S	4	.5	3.3*
Error	72	.14	
Total	107	2.32	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table B-5 Analysis of variance of soil sulfate after first barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	11741408	5.1*
Rock phosphate	2	21475420	9.3**
Sulfur	2	18197103	7.9**
Level of Sulfur	1	9425143803	4095.7**
Soil X Rock phos.	2	256415	.1
Soil X Sulfur	2	13583264	5.9**
Soil X Level of S	1	8396787	3.7
Rock phos. X S	4	4913561	2.1
Rock phos. X Level of S	2	21080947	9.2**
Sulfur X Level of S	2	18029423	7.8**
Soil X Rock phos. X S	4	2273505	1.0
Soil X Rock phos. X Level of S	2	243376	.1
Soil X S X Level of X	2	13498558	5.9**
Rock phos. X S X Level of S	4	4897737	2.1
Soil X Rock phos. X S X Level of S	4	2305597	1.0
Error	72	2301256	
Total	107	92348253	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table B-6 Analysis of variance of soil zinc after first barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	460.2	621.6**
Rock phosphate	2	.5	.7
Sulfur	2	17.6	23.7**
Level of Sulfur	1	3.2	4.3*
Soil X Rock phos.	2	.1	.1
Soil X Sulfur	2	1.8	2.4
Soil X Level of S	1	8.5	11.5**
Rock phos. X S	4	1.3	1.8
Rock phos. X Level of S	2	.1	.1
Sulfur X Level of S	2	15.0	20.3**
Soil X Rock phos. X S	4	1.0	1.4
Soil X Rock phos. X Level of S	2	.04	.1
Soil X S X Level of S	2	.12	.2
Rock phos. X S X Level of S	4	.73	1.0
Soil X Rock phos. X S X Level of S	4	.61	.8
Error	72	.74	
Total	107	5.71	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table B-7 Analysis of variance of plant phosphorus from first barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	.469	90.5**
Rock phosphate	2	.003	.5
Sulfur	2	.007	1.4
Level of Sulfur	1	.12	23.2**
Soil X Rock phos.	2	.005	1.1
Soil X Sulfur	2	.010	1.9
Soil X Level of S	1	.080	15.4**
Rock phos. X S	4	.006	1.1
Rock phos. X Level of S	2	.008	1.6
Sulfur X Level of S	2	.005	1.0
Soil X Rock phos. X S	4	.005	1.0
Soil X Rock phos. X Level of S	2	.007	1.4
Soil X S X Level of S	2	.003	.6
Rock phos. X S X Level of S	4	.006	1.1
Soil X Rock phos. X S X Level of S	4	.007	1.4
Error	72	.005	
Total	107	.012	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table B-8 Analysis of variance of barley yields from first barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	27.15	82.6**
Rock phosphate	2	.09	.3
Sulfur	2	.47	1.4
Level of Sulfur	1	134.30	408.4**
Soil X Rock phos.	2	.67	2.1
Soil X Sulfur	2	.12	.4**
Soil X Level of S	1	6.94	21.1**
Rock phos. X S	4	.18	.6
Rock phos. X Level of S	2	.59	1.8
Sulfur X Level of S	2	.9	2.8
Soil X Rock phos. X S	4	.3	1.0
Soil X Rock phos. X Level of S	2	1.5	.5
Soil X S X Level of S	2	.05	.2
Rock phos. X S X Level of S	4	.2	.6
Soil X Rock phos. X S X Level of S	4	.24	.7
Error	72	.33	
Total	107	1.89	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

APPENDIX C

ANALYSIS OF VARIANCE TABLES FOR

GREENHOUSE STUDY

SECOND BARLEY HARVEST

Table C-1 Analysis of variance of soluble soil phosphorus after second barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	41.5	94.0**
Rock phosphate	2	2.0	4.8**
Sulfur	2	8.8	20.9**
Level of sulfur	1	47.3	112.9**
Soil X Rock phos.	2	2.0	4.8**
Soil X Sulfur	2	8.0	19.1**
Soil X Level of S	1	40.2	95.8**
Rock phos. X S	4	1.3	3.0*
Rock phos. X Level of S	2	1.54	3.7*
Sulfur X Level of S	2	9.7	23.1**
Soil X Rock phos. X S	4	1.3	3.2*
Soil X Rock phos. X Level of S	2	1.7	3.9*
Soil X S X Level of S	2	8.5	20.2**
Rock phos. X S X Level of S	4	1.5	3.6**
Soil X Rock phos. X S X Level of S	4	1.5	3.5*
Error	72	.42	
Total	107	2.48	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table C-2 Analysis of variance of soil zinc after second barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	489.5	331.3**
Rock phosphate	2	.5	.3
Sulfur	2	11.5	7.8**
Level of sulfur	1	2.1	1.4
Soil X Rock phos.	2	.8	.5
Soil X Sulfur	2	2.8	1.9
Soil X Level of S	1	11.0	7.5**
Rock phos. X S	4	.1	.1
Rock phos. X Level of S	2	.3	.2
Sulfur X Level of S	2	10.0	6.8**
Soil X Rock phos. X S	4	.2	.1
Soil X Rock phos. X Level of S	2	.1	.1
Soil X S X Level of S	2	.9	.6
Rock phos. X S X Level of S	4	.7	.5
Soil X Rock phos. X S X Level of S	4	.9	.6
Error	72	1.5	
Total	107	6.3	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table C-3 Analysis of variance of second barley yield harvested from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	205.12	512.0**
Rock phosphate	2	1.35	3.4*
Sulfur	2	.30	.7
Level of sulfur	1	102.16	255.0**
Soil X Rock phos.	2	.26	.7
Soil X Sulfur	2	.31	.8
Soil X Level of S	1	60.6	151.3**
Rock phos. X S	4	.64	1.6
Rock phos. X Level of S	2	1.16	2.9
Sulfur X Level of S	2	.19	.5
Soil X Rock phos. X S	4	.10	.2
Soil X Rock phos. X Level of S	2	.18	.5
Soil X S X Level of S	2	.15	.4
Rock phos. X S X Level of S	4	.03	.1
Soil X Rock phos. X S X Level of S	4	.02	.1
Error	72	.40	
Total	107	3.82	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table C-4 Analysis of variance of plant phosphorus percent of second barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	.154	36.00**
Rock phosphate	2	.004	1.05
Sulfur	2	.004	.89
Level of sulfur	1	.166	38.85**
Soil X Rock phos.	2	.001	.04
Soil X Sulfur	2	.001	.29
Soil X Level of S	1	.138	32.19**
Rock phos. X S	4	.003	.647
Rock phos. X Level of S	2	.002	.51
Sulfur X Level of S	2	.009	2.09
Soil X Rock phos. X S	4	.002	.56
Soil X Rock phos. X Level of S	2	.007	1.62
Soil X S X Level of X	2	.008	1.89
Rock phos. X S X Level of S	4	.005	1.13
Soil X Rock phos. X S X Level of S	4	.005	1.21
Error	72	.004	
Total	107	.008	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

Table C-5 Analysis of variance of plant zinc of second barley harvest from two calcareous soils (Pima and Laveen), treated with rock phosphate, and three sources of sulfur, each with two levels, during 1979-1980.

Source of variation	Degrees of Freedom	Mean Square	F Value
Soil	1	19280	7.8**
Rock phosphate	2	2051	.8
Sulfur	2	1647	.7
Level of sulfur	1	4866	2.0
Soil X Rock phos.	2	4148	1.7
Soil X Sulfur	2	7978	3.2
Soil X Level of S	1	65662	26.4**
Rock phos. X S	4	2171	.9
Rock phos. X Level of S	2	1198	.5
Sulfur X Level of S	2	2139	.9
Soil X Rock phos. X S	4	2301	.9
Soil X Rock phos. X Level of S	2	801	.3
Soil X S X Level of S	2	6839	2.8
Rock phos. X S X Level of S	4	1803	.7
Soil X Rock phos. X S X Level of S	4	2211	.9
Error	72	2484	
Total	107	3329	

* Significant at the 0.05 level of probability.

** Significant at the 0.01 level of probability.

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