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SULFATE ADSORPTION BY SOME SOILS OF THE TROPICS

A Thesis

Presented to the Faculty of the Graduate School

of Cornell University for the Degree of

Doctor of Philosophy

by

Walter Couto

January 1976

Walter Couto was born in Montevideo, Uruguay, on January 29, 1932. He pursued studies at the Facultad de Agronomia of the Universidad de la Republica, in Montevideo, and graduated as Ingeniero Agronomo in 1961. In 1970 he earned a M.S. degree in Soil Science at Colegio de Postgraduados, Escuela Nacional de Agricultura, Chapingo, Mexico.

Since graduation he has been involved in field experiments in relation to fertilizer use and other aspects of soil fertility, working for private enterprises and research organizations in Uruguay and Argentina. He received also training in France in this area and participated in several international meetings. He is a member of the Sociedad Argentina de la Ciencia del Suelo, the American Society of Agronomy and the Soil Science Society of America.

He married Rosa Loreley in 1962 and they have two children, Guillermo Manuel and Maria Gabriela.

To Rosa, Guillermo and Maria.

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I. INTRODUCTION.

Sulfur is an important nutrient for plants, the amount required being often as high as that of phosphorus.

The importance of sulfur in fertilization has been disregarded for many years probably as a result of the high amount of sulfur contained in some common fertilizers widely used in the past, such as ordinary superphosphate and ammonium sulfate. The use of more concentrated nitrogen or phosphate fertilizers led to a lower amount of sulfur applied to soils, the possibility of sulfur deficiencies becoming more important.

In soils of the temperate regions sulfur deficiencies have been reported in many countries. In the United States responses to sulfur have been found in some areas of Oregon, California, Washington, Idaho, and Montana (Chao et al., 1962). Occurrence of sulfur deficiencies in field crops and grasslands have been reported in France, Norway, Sweden, and Japan (Freney et al., 1962). In Australia, sulfur deficiencies have been reported by Williams and Steinbergs (1959), Williams (1973) and McLachlan (1974). Similar reports have been published by Walker (1955) for soils of New Zealand. In Uruguay, response to sulfur has been observed in field and pot experiments in shallow soils developed from basaltic rocks.*

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* Technical report by the author to the Direction of C.I.A. "Alberto Boerger", La Estanzuela, Uruguay.

In tropical soils, sulfur deficiency is considered widespread, mainly in wet areas and also in subhumid regions with heavy rainy seasons (Bornemisza and Llanos, 1967).

Large areas of Central Africa, the Brazilian Plateau area, and Central America are reported as low or deficient in sulfur (Olson and Engelstad, 1972; Kamprath, 1973; Richard, 1972).

In soils of the humid regions, organic sulfur represents a large proportion of soil sulfur and it is the main reservoir of sulfur for plants (Evans and Rost, 1945).

Plants absorb almost all their sulfur as sulfate, this form accounting for most of the inorganic sulfur in soils. Sulfates are fairly soluble and move fairly easy in soils and losses in the leachate may occur if they are not retained by soil, incorporated into the organic matter fraction, or adsorbed at positive charge sites.

In tropical soils and soils of the temperate regions with high amounts of 1:1 type clay minerals and hydrous oxides of iron and aluminum, a large proportion of sulfur may be retained as adsorbed sulfate (Harward and Reisenauer, 1966).

Besides the ability of the soil to supply sulfate sulfur to plants from the mineralized organic matter, the amount of sulfate retained by soils as well as the strength with which it is retained may determine the availability of sulfate for plants (Barrow, 1972).

According to some authors, adsorbed sulfate provides a ready reserve of sulfur for plants (Williams and Steinberg, Kamprath, Nelson and Fitts, Ensminger, Anderson and Webster, cited by Elkins and Esminger, 1971).

Other researchers concluded that adsorbed sulfate is lower in availability than soluble sulfate (Hasan et al., 1970). Fox et al., (1971) indicates that soils with large adsorption capability may develop sulfur deficiencies at levels of sorbed sulfate that are adequate for soils with a lower capacity to sorb sulfate.

Beyond the importance of sulfate adsorption from the point of view of sulfate supply to plants, the adsorption of sulfate by soils can also affect some properties of the soil material, such as the capacity of the soil to retain cations. Different from perchlorate, nitrate, and chloride, sulfate adsorption is considered to affect the surface of adsorbing oxides, increasing the negative charges on it (Parks, 1965; Breewsma, 1973; Hingston et al., 1968).

According to Hingston et al. (1968), sulfate anions are specifically adsorbed and are bound to a greater extent than would be expected from its proportion in the solution. When sulfate or other specifically adsorbed anions are adsorbed on the surface of iron oxides, the negative charge on the surface increases at the same time that hydroxyl ions are released.

The practical importance of these aspects of sulfate adsorption as well as those of other specifically adsorbed anions is not known, but they indicate that a better understanding of sulfate behaviour in soils is essential for developing techniques of increasing sulfate availability to plants or using sulfates as soil amendements.

The purpose of this study was to describe sulfate adsorption by some tropical soils. An estimation of pH dependence of sulfate adsorption at varying sulfate concentrations of the equilibrium solution was made also. Finally, the strength with which adsorbed sulfate is retained was studied and the effect of sulfate adsorption on the ability of the soils to retain cations was considered.

II. LITERATURE REVIEW.

1. Soil mineralogy and sulfate adsorption.

Harward and Reisenauer (1966) summarized some of the factors affecting sulfate adsorption by soils and indicated that the amount of sulfate that the soils can adsorb is higher in soils high in kaolinite than in soils with other types of clay minerals. They also pointed out that soils containing aluminum and iron oxides show a marked tendency to retain sulfate.

Chao et al. (1963) working with fifteen soils of Oregon observed that four soils showed much higher adsorption of sulfate. Soil pH was similar to other soils that did not show sulfate adsorption, the principal difference being the free sesquioxides and exchangeable aluminum contents.

Studying the sulfate adsorption of various soils before and after treatment to remove some soil constituents, the removal of organic matter reduced remarkably sulfate adsorption in two soils. Six other soils of similar organic matter content showed no similar reduction. The removal of aluminum after organic matter removal reduced adsorption up to 15% of the original adsorption. Removal of free iron oxides after organic matter removal reduced sulfate adsorption to that of some low sulfate adsorbing soils. The amount reduced was larger than that due to aluminum removal but they indicated that free aluminum oxides may have been removed also during

the removal of the free iron.

Chao et al. (1964) demonstrated that non-retentive soils showed curves for sulfate adsorption typical of retentive soils after a treatment coating the soils with Al or Fe oxides. When the amount of Fe oxides from the coating reached that of natural retentive soils, the amount of sulfate adsorbed was similar to that of retentive soils. The amount of sulfate adsorbed was higher at high Fe_2O_3 content and decreased with increasing soil pH.

Kamprath et al. (1956) working with several soils and a H-Al and Na bentonite clay found that two soils with clay minerals of the 1:1 type adsorbed higher amounts of sulfate than other soils. They emphacized that this type of clay mineral is generally associated with a high iron and aluminum content. The H-Al bentonite adsorbed some sulfate but none was adsorbed by the Na bentonite. They attributed the difference to the exchangeable Al of the H-Al bentonite and the higher pH of the Na bentonite.

Chao et al. (1962) studying the effect of different clay minerals observed that kaolinite adsorbed much more sulfate than bentonite. Al saturated clay adsorbed more than H saturated clay and the adsorption increased with increasing percent saturation.

According to Fox et al. (1971), the intensity of anion retention by soils according to their mineralogy is: amorphous hydrated oxides > goethite-gibbsite > kaolinite > 2:1

clays.

2. Effect of pH on sulfate adsorption.

Schofield (1949) observed that positive charges developed at low pH values in subsoil samples of Rothamsted soils, up to 3 me/100 g of soil. When the samples were treated with oxalic acid to remove the Fe_2O_3 the positive charges of the soil were reduced. The reduction was equivalent to 60 me/100 g of Fe_2O_3 removed by the oxalic acid. He attributed the reaction to the transfer of a proton from H_3O^+ ion to an oxigen of the hydrous ferric oxide. He also indicated that an oxygen capable of accepting an additional proton might occur at the edge of a regular crystal or as a result of imperfect crystalization.

The effect of pH on sulfate adsorption has been observed by several authors. Kamprath et al. (1956) observed that the two soils that adsorbed the greatest amount of sulfate showed greater adsorption at low pH values. A marked reduction of sulfate adsorption was observed when pH was increased from 5 to 6. Similar effects were observed by Bhardwaj and Pathak (1970) and Gebhardt and Coleman (1974). The later authors reported that the amount of sulfate adsorbed by San Gregorio soil was extremely pH dependent, the amount adsorbed ranging from 60 me/100 g to less than 5 me/100 g when pH of the solution changed from less than 4.1 to 6.3.

Sumner (1963) working with kaolinite-iron oxide complex found that positive charges decreased with increasing pH until a point is reached in the region 6 - 7 pH values for goethite or hematite where negative adsorption of anions takes place.

3. Reversibility of adsorption.

The ability of the soil to adsorb sulfate represents an important factor from the point of view of possible losses of sulfate from the profile and as a reservoir for sulfate supply to plants. The ease with which sulfate can be desorbed could indicate the relative availability of adsorbed sulfate.

Soils having high sulfate sorption characteristics, to which sulfur was applied, had no sulfate movement below 45 cm depth after five years with heavy excess in water balance through the profile (During and Cooper, 1974). On the other hand, phosphate fertilization has been showed to produce downward movement of adsorbed sulfate in yelow-brown earth of New Zealand (Bayley, 1974). Koter, Panak and Wojnowska (1973) found that 73-78% of adsorbed sulfate was leached with water from lowmoor peat, clay, kaolin, and clayey soil but only 11-32% was desorbed from Al_2O_3 and Fe_2O_3. Chao et al. (1963) observed 70-85% recovery of adsorbed sulfate with four extractions with water in four sulfate retentive soils.

Similar results were reported by Hague and Walmsley (1973)

Using a solution containing 500 ppm P as KH_2PO_4 they extracted only 32.7% of adsorbed sulfate in four extractions in a soil containing 15% kaolinite, 13% goethite, and 20% amorphous materials. In another soil with 7% kaolinite, 7% free iron oxide, 47% montmorillonite and high proportion of amorphous material (allophanoid) the amount desorbed was 76.4%. Both soils showed similar capacity for sulfate adsorption.

Aylmore et al. (1967) showed that for hematite and pseudoboehmite the adsorption isotherms were almost completely irreversible with respect to equilibrium concentration. For kaolinite, instead, they were completely reversible. They suggested that sulfate adsorbed on kaolinite, being weakly held and easily released would be less resistant to leaching and probably more available for plants than that adsorbed on Fe or Al oxides.

Considerable amounts of adsorbed sulfate could be desorbed from highly weathered soils through liming according to Fox et al. (1971).

In adsorption studies, negative fixation has been observed at pH higher than 6.0 (Bhardwaj and Pathak, 1970).

4. Mechanism of anion adsorption.

Positive charges may be present at the edges of clay particles due to proton association on octahedral and tetrahedral hydroxyl groups. Acceptance of protons may also occur on $R\text{-}NH_2$ groups on the organic matter, with consequent deve-

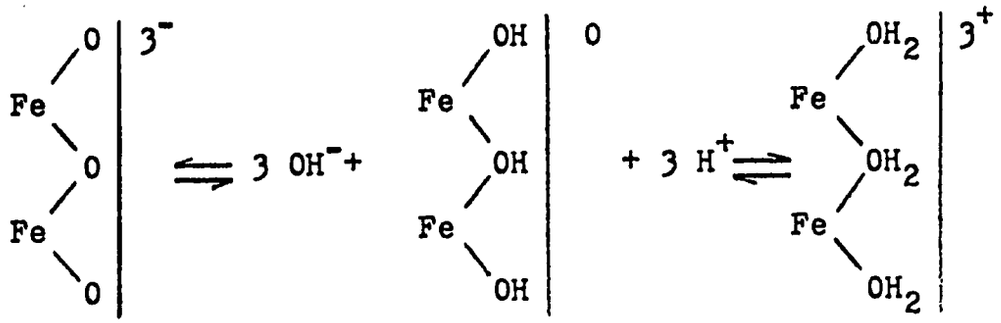
lopment of positive charges.

Iron and aluminum oxides were found to be responsible for most of the sulfate adsorption in soils with high capacity for sulfate adsorption (Harward and Reisenauer, 1966; Sumner, 1963; Breeuwsma, 1973).

Hematite (α-Fe_2O_3) and goethite (α-FeOOH) are the most frequently occurring crystalline iron oxides in soils, hematite being the dominant iron oxide in tropical soils. α-hematite crystals are formed by a ferric ion surrounded by six oxygens forming an octahedron. At the surface, in aqueous suspension, the coordinated species may be oxygen ions, hydroxyl ions, or water molecules (Atkinson, Posner, and Quirk, 1967). When solid oxide particles are inmersed in aqueous electrolyte solutions the surface of the particles develop positive or negative charges by adsorption of H^+ or desorption of OH^-.

According to Parks and deBruyn (1962), the process of positive charge development on the surface of iron oxides may be seen as H^+ adsorption. Negative charges are more likely to occur as a result of removal of H^+ from the surface rather than adsorption of OH^-.

The mechanism has been schematically represented as a reversible process as follows:



From potentiometric titrations the amount of H^+ or OH^- adsorbed by some iron oxides or soil suspensions at different pH values and ionic strength have been measured (Parks and deBruyn, 1962; Atkinson, Posner and Quirck, 1967; Hingston et al., 1967; Van Raij and Peech, 1970; Breewsma, 1973).

For ferric oxides, H^+ and OH^- are potential determining ions, since transfer of ferric hydroxocomplex ions from the surface are considered negligeable at the pH usually encountered in soils (Atkinson, Posner and Quirk, 1967).

The transfer of potential determining ions across the bounderies of the interphase results in a reversible double layer (Parks and de Bruyn, 1962). The surface charge of a reversible double layer may be expressed by:

$$\sigma_s = F\ (Z_+\Gamma_+ + Z_-\Gamma_-) \qquad (1)$$

where F is the Faraday constant, Z_+ and Z_- are the valences of ions and Γ_+ and Γ_- are the adsorption density of the potential determining ions (Parks and deBruyn, 1962).

As a result of charge development ions can be adsorbed on

the surface of iron, aluminum, and other oxides, as well as on other materials. Two mechanisms have been proposed for anion adsorption on the surface of iron oxides.

4.1 Non specific adsorption.

In absence of specific interaction between the solid surface and ions derived from the electrolyte, the potential difference across the double layer of free charges is given by

$$\psi_o = \frac{R\,T}{Z_+F} \ln\left(\frac{a_+}{a_{+o}}\right) = \frac{R\,T}{Z_-F} \ln\left(\frac{a_{-o}}{a_-}\right) \qquad (2)$$

where a_{+o} and a_{-o} are the activities of the potential determining ions in the solution phase when the net surface charge is equal to zero. Knowing the pH of the equilibrium solution and the pH at which the net surface charge is zero, the potential on the surface may be calculated (Van Raij and Peech, 1972).

The surface potential and the net charges on the surface are related according to the Gouy-Chapman theory by the following relationship (deBruyn and Agar, 1962; Overbeek, 1952):

$$\sigma = \left(\frac{2n\,\varepsilon KT}{\pi}\right)^{\frac{1}{2}} \sinh\left(\frac{z\,e\,\psi_o}{2\,K\,T}\right) \qquad (3)$$

where n is the concentration of the equilibrium solution in number of ions per cm^3, ε is the dielectric constant of the medium, z is the valence of the counter ions, K is the Boltzmann constant, T is the absolute temperature and ψ_o is the

surface potential as given by equation 2.

According to equation 3 the net surface charge, in absence of specific adsorption is a function of the electrolyte concentration, temperature, and pH.

4.2 Specific adsorption.

According to Hingston et al. (1967), the adsorption of anions such as orthophosphate, pyrophosphate, tripolyphosphate, selenite, silicate, fluoride, and sulfate on the surface of iron oxides is not determined by properties of the diffuse double layer or the outer Helmholtz layer. Studying the adsorption of silicate and orthophosphate at different pH values they observed that when plotting adsorption maximum at each pH against pH (adsorption envelope curves), the curves obtained for these two anions did not follow the theoretical adsorption curve expected from composition of the equilibrium solution. For silicate and fluoride ions there was an adsorption maximum at the pK values while a change in slope occurred at each pK value for orthophosphate.

Extending the study to other ions they found a good linear correlation between the pK values and the pH at which maximum adsorption occurs on the adsorption envelope. They concluded that the presence of a proton donor and a proton aceptor is required for adsorption of those anions behaving as weak monobasic acids.

Obihara and Russell (1972) studying the adsorption of si-

licate and phosphate by soils confirmed the results obtained by Hingston et al. with goethite for phosphorus. They observed a maximum silicate adsorption at about pH 9.2 and that the phosphate adsorption envelope breaks at about pH 6.5 and pH 11.0. That would be in accordance with the hypothesis that both a hydrogen donor and a hydrogen acceptor are required and that the maximum adsorption occurs when they are present in equal concentration.

In a later paper Hingston et al. (1968) suggested that the protons associated with the adsorbed species lower the average negative charge on the bonding atom of the anion allowing a coordinate link between the anion and an iron atom in preference to a link between OH^- and Fe^{+++}. Thus, at pH values near pK the fully charged species would be able to accept a proton from the surface lowering the negative charge on the bonding atom to be adsorbed.

The mechanism would involve the exchange of a hydroxyl from the surface and occupation of the coordination site by the adsorbed anion. As a result, contrasting with the non-specific adsorption, when specific adsorption occurs the adsorbed anion forms part of the first coordination shell of the iron atom.

The reaction proposed by the authors for fluoride at a positive site is the following:

$$\begin{array}{l} OH_2^{+.5} \\ OH_2^{+.5} \end{array}\Bigg| \begin{array}{l} +1 \\ \ldots Cl \end{array} + NaF \rightleftharpoons \begin{array}{l} F^{-.5} \\ OH_2^{+.5} \end{array}\Bigg| \begin{array}{l} 0 \\ \\ \end{array} + NaCl$$

where the brackets indicate the ions coordinated octahedrally with iron.

For phosphate at a pH value greater than the 3rd pK they suggest:

$$\begin{array}{l} OH_2^{+.5} \\ OH^{-.5} \end{array}\Bigg| \begin{array}{l} 0 \\ \\ \end{array} + Na_3PO_4 \rightleftharpoons \begin{array}{l} PO_4H^{-1.5} \\ OH^{-.5} \end{array}\Bigg| \begin{array}{l} -2 \\ \ldots 2Na + NaOH \end{array}$$

$$\begin{array}{l} PO_4H^{-1.5} \\ OH^{-.5} \end{array}\Bigg| \begin{array}{l} -2 \\ \ldots 2Na + NaOH \end{array} \rightleftharpoons \begin{array}{l} PO_4^{-2.5} \\ OH^{-.5} \end{array}\Bigg| \begin{array}{l} -3 \\ \ldots 3Na + H_2O \end{array}$$

The result is an increasing negative charge on the surface after adsorption and a shifting of the zero point of charge to more acid values.

This was confirmed through titration curves and measurements of adsorption where surface charges were determined by the authors in presence and absence of specifically adsorbed anions (Hingston et al., 1967). According to them anions specifically adsorbed are not displaced by chloride or nitrate at the same pH and ionic strength. Desorption of sulfate, orthophosphate, and other specifically adsorbed anions could

be possible only by other anions able to increase the negative charge of the surface. This occurs when a competitor can occupy sites in adition to those already occuped by specifically adsorbed anions, rendering the surface more negative and allowing in this way the hydrolysis of the previously specifically adsorbed anion.

III. MATERIALS AND METHODS.

1. Soil samples.

The six soil samples used in this study correspond to the Ap and B2 horizons of three soils of the State of São Paulo, Brazil. The soils were classified as Acrorthox, Acrohumox, and Tropudalf and are the same ones described and used by Van Raij and Peech (1972) in their study. Some of the characteristics of the soils as presented by these authors are summarized in table 1:

Table 1: Selected characteristics of the soils used in this study.

Sample #	Soil-horizon	Organic C (%)	pH H_2O	pH 1N KCl	Mineralogical Composition (%) Fe_2O_3	Gibbsite	Kaolinite
1	Acrohumox-Ap	1.9	4.9	4.1	4	3	25
2	Acrohumox-B2	0.3	4.9	4.3	6	6	37
3	Acrorthox-Ap	2.5	5.3	4.7	19	37	9
4	Acrorthox-B2	0.7	5.9	6.0	18	33	11
5	Tropudalf-Ap	2.3	6.3	5.4	16	8	33
6	Tropudalf-B2	1.0	6.7	5.9	17	10	43

The samples were air dried, crushed to pass a 2 mm sieve and stored in plastic containers.

2. Sulfate adsorption, unadjusted pH.

The amount of air dried soil equivalent to 10 g of oven dried soil was equilibrated with 50 ml of solution containing 0, 0.3, 0.6, 0.9, 1.2, 1.5, 1.8, 2.1, and 2.4 mM of $SO_4^{=}$ per liter. All solutions contained also 20 mM of KCl per liter as supporting electrolyte. The equilibration was made in 250 ml erlenmeyer flasks by shaking for 24 hours.

After this period the final pH was measured potentiometrically using combined glass-calomel electrodes, the suspension filtered through Whattman filter paper No. 42, and the amount of $SO_4^{=}$ remaining in solution was determined turbidimetricaly as described below. The amount of $SO_4^{=}$ adsorbed was estimated from the amount initially present in the equilibrium solution.

Precipitation of $CaSO_4$ was avoided by using $SO_4^{=}$ concentrations of the equilibrating solutions low enought to keep the product of concentrations of Ca^{++} and $SO_4^{=}$ below the solubility product constant of $CaSO_4$ at maximum possible concentrations. The maximum possible concentration for Ca^{++} was estimated by assuming complete desorption of exchangeable Ca^{++}.

3. Sulfate adsorption, adjusted pH.

For $SO_4^{=}$ adsorption estimation at different pH values the procedure was essentially the same but HCl or KOH were added to adjust the pH to some desired value. Soil samples suspended in solutions containing differents amounts of $SO_4^{=}$ as des-

cribed above were adjusted to four or five pH values within the range 3.5 to 7.0, according to the soils. The suspensions were let stand for three hours and the pH was measured and adjusted several times during this period. After adjusting pH again at the end of this period, the flasks were shaken overnight. The following day the pH was measured again and adjusted to the desired value. Shaking was continued to complete 24 hours. All samples were shaken for at least four hours after the last addition of HCl or KOH. No attempt to reach the desired pH value was made during the last four hours of shaking. As in the unadjusted pH studies, the sulfate adsorbed was estimated from sulfate remaining in solution after 24 hours shaking. The final pH was measured and recorded as indicated on the suspensions before filtering. Six additional equilibration and $SO_4^{=}$ adsorption estimations were made for each sample for estimation of the experimental error.

4. Sulfate and potassium desorption.

The equivalent amount of 10 g of oven dried soil was equilibrated with 50 ml of solutions containing 0, 1.2 and 2.4 mM of $SO_4^{=}$ as K_2SO_4 and 20 mM of KCl per liter.

Two samples were treated, one with the unadjusted solution pH observed after equilibration and the other adjusted several times to pH 4.0 with additions of HCl under the conditions described above. The actual value of the final pH was recorded after equilibration.

The equilibration was made in 250 ml plastic bottles. The samples were centrifuged previous to each pH measurement and before filtering.

When the 24 hour period of shaking was completed the bottles were centriguged again, the supernatant was separated and filtered. This solution (Solution A) was analyzed for $SO_4^{=}$ and K^+ and the amount of $SO_4^{=}$ adsorbed by the soil calculated from the amount remaining in solution. Potassium was determined by flame photometry and $SO_4^{=}$ by turbidimetry as described below.

After separating Solution A the bottles were weighed immediately to estimate the amount of solution occluded by soil. The soils were then washed five times with 50 ml portions of 0.5 N NH_4NO_3 and the washings collected in a volumetric flask. After the final washing the volume was made up to 250 ml with 0.5 N NH_4NO_3. This solution (Solution B) was analyzed for $SO_4^{=}$ and K^+ and the amount of $SO_4^{=}$ and K^+ desorbed calculated after correction for the amount of these ions remaining in the solution occluded by the soil.

All equilibrations and desorptions were performed twice for each sample.

5. <u>Sulfate determination.</u>

The amount of $SO_4^{=}$ remaining in solution after equilibration and the determination of $SO_4^{=}$ in solution after desorption was made by turbidimetry, following a standardized pro-

cedure developed by Thomas Greweling for the Agronomy Service Laboratories at Cornell University. It is an adaption of a standard method approved by American Public Health Association Inc. (1965) for water, sewage and industrial wastes. The method as used was the following:

Reagents:

1. Barium chloride crystals, $BaCl_2.2H_2O$, reagent grade, 40 mesh.
2. Standard sulfate solution. Weigh and dissolve 1.3585 g of K_2SO_4 into a one liter volumetric flask, dilute to volume with distilled water, and mix. This solution contains 250 micrograms of S per ml. Prepare a calibration curve by pipetting aliquots of this solution containing 125 to 1000 micrograms of S into a series of 150 ml beakers. Dilute to 50 ml with distilled water and carry these solutions through the procedure described below.
3. Conditioning reagent. Dissolve 75 g of NaCl in 300 ml of distilled water, add 100 ml of ethyl or isopropyl alcohol, 30 ml of concentrated hydrochloric acid, mix and then add 50 ml of glycerol and mix again.

Procedure:

Pipet an aliquot of solution containing 100 - 1000 micrograms of S into a 150 ml beaker and dilute to 50 ml with distilled water. Add 2.5 ml of the conditioning reagent and mix. (If the solution is visibly colored

or turbid at this time, measure the apparent $SO_4^{=}$ at 420 nm and subtract this value from the $SO_4^{=}$ concentration determined later). Begin mixing with a magnetic mixer and add about 1 g of $BaCl_2$ crystals using a small scoop or spoon so that the same amount of crystals may be added each time. Continue mixing for exactly 60 seconds, let stand for exactly four minutes and then measure the transmittancy vs. H_2O at 420 nm. Compare the results to a calibration curve established as directed under reagent 2.

IV. RESULTS AND DISCUSSION.

1. Sulfate adsorption in unadjusted pH conditions.

The actual amount of $SO_4^{=}$ remaining in solution after equilibration and the estimated adsorbed $SO_4^{=}$ are presented separately for each soil and horizon in the appendix.

Two aspect of the results are presented separately.

a) Langmuir adsorption isotherms.

Although the Langmuir equation has been developed for adsorption of gases in a monolayer on solid surfaces, the equation has been used succesfully for other adsorbates and adsorbent sustances. A fundamental assumption is implied in the Langmuir equation: adsorption is completely reversible and depends only on the final concentration of the equilibrium solution. In other words, if the amount adsorbed depends only on the final concentration of the equilibrium solution, the process has to be reversible. This aspect of the process is examined here in relation to sulfate adsorption.

From $SO_4^{=}$ adsorption values and final concentration of the equilibrium solution observed in uncontrolled pH conditions, the parameters of the Langmuir equation were estimated. The form of the Langmuir equation is:

$$\theta = \frac{K\,c}{1 + K\,c} \qquad (4)$$

where θ is the fraction of available adsorption sites occupied by the adsorbate, c is $SO_4^{=}$ concentration of the equili-

brium solution in mM/l and K is a constant. The value of K was estimated for each sample from the linear form of the equation:

$$\frac{1}{m} = \frac{1}{b} + \frac{1}{b\,K\,c} \qquad (5)$$

in which m is the amount of $SO_4^{=}$ adsorbed in me/100 g of soil and b is a constant relating θ and m as follows:

$$m = b\,\theta \qquad (6)$$

The values of the intercept and slope of the linear regressions represented by equation 5 were estimated by least squares procedure. The corresponding values of b and K are presented in table 2:

Table 2: Estimated values of intercept and slope of linear form of Langmuir's equation and b and K parameters.

Sample	Intercept	Reg. Coeff.	R^2	b	K
1	4.05120	6.37197*	0.82	0.2468	0.6359
2	0.88305*	0.08993*	0.99	1.1324	9.8193
3	3.76875*	0.37272*	0.51	0.2653	10.1130
4	1.33250*	0.12188*	0.99	0.7505	10.9327
5	9.33778*	3.48708	0.20	0.1071	2.6776
6	2.65243*	0.30178*	0.90	0.3770	8.7897

* Significant ($P \leq 0.05$)

It can be seen in table 2 that all linear regression coefficients are significantly different from zero for all samples but sample 5. The best fit was observed in samples 2, 4, and 6 in which more adsorption occurs as showed by b values which are estimates of the adsorption maximum.

From the estimated K values and equation 4, the fraction of adsorption sites occupied by adsorbed $SO_4^{=}$ was calculated for the maximum concentrations actually observed in the experiment. The results are shown in table 3.

Table 3: Estimated fraction of maximum adsorption, at highest observed concentration of the equilibrium solution.

Sample	Max. Final conc. $SO_4^{=}$ mM/l	θ
1	2.2	0.58
2	1.3	0.93
3	2.0	0.95
4	1.7	0.95
5	2.2	0.86
6	2.0	0.95

The results suggest that in samples 2, 3, 4, and 6 almost all possible adsorption took place (between 93 and 96 % of adsorption maximum) although $SO_4^{=}$ concentration of the equili-

brium solution varied considerably for different samples. Sample 2 in which highest adsorption was observed shows high values of adsorption at very low concentration of the equilibrium solution. This indicates a great ability for $SO_4^{=}$ adsorption in this sample, which is almost saturated at very low concentration of the equilibrium solution. Sample 1, however, shows low capacity for $SO_4^{=}$ adsorption and is not saturated even at higher concentration of the equilibrium solution.

This contradictory behaviour of samples 1 and 2 occured after equilibration with solutions initially higher in $SO_4^{=}$ concentration. The maximum concentrations indicated in table 3 correspond to solutions initially containing 2.4 mM $SO_4^{=}$/l for all samples, the maximum concentration included in the experiment. The low values of final concentration of the equilibrium solution in sample 2 (1.3 mM $SO_4^{=}$/l) is due to a high level of $SO_4^{=}$ adsorption of this sample in the conditions of this part of the experiment.

It can be seen in the appendix (Table 1) that for sample 2 similar amounts of adsorbed $SO_4^{=}$ were found after equilibration with solutions which reached final concentrations of 0.5, 0.7, 1.0, and 1.3 mM $SO_4^{=}$/l. This indicates that $SO_4^{=}$ adsorption is not dependent only on final concentration of the equilibrium solution as assumed in a true adsorption isotherm as described by the Langmuir equation.

The same observation is valid for sample 4 that adsorbed 0.8, 1.1, 1.4 and 1.7 me $SO_4^{=}$/100 g of soil from different solutions that reached a final concentration of approximately 0.7 mM $SO_4^{=}$/l after equilibration. Similar results are observed in sample 6.

This situation suggests that in the conditions of the experiment the initial concentration of the solution affects the amount of $SO_4^{=}$ adsorbed. A regression model including initial concentration of the equilibrium solution instead of final concentration of the equilibrium solution could fit the experimental results better than an equation such as the Langmuir that considers only final concentration.

The observed values of $SO_4^{=}$ adsorption are shown graphically in figures 1 to 3. The continuous lines on the graphs show the amount of $SO_4^{=}$ adsorbed as predicted by the Langmuir equation. The quantitative relationship between the amount of $SO_4^{=}$ adsorbed and the final concentration of the equilibrium solution as predicted by the Langmuir equation and the observed values are in close agreement but there is an apparent trend of overestimation of $SO_4^{=}$ adsorption at low concentrations and underestimation at high $SO_4^{=}$ concentrations for some of the samples. There is also an increase in pH of the equilibrium solution at increasing values of $SO_4^{=}$ adsorption in those samples that adsorb more $SO_4^{=}$. This fact and its possible effects on $SO_4^{=}$ adsorption are considered in detail in

Fig. 1: Sulfate adsorption in conditions of unadjusted pH, Langmuir's equation. Acrohumox.

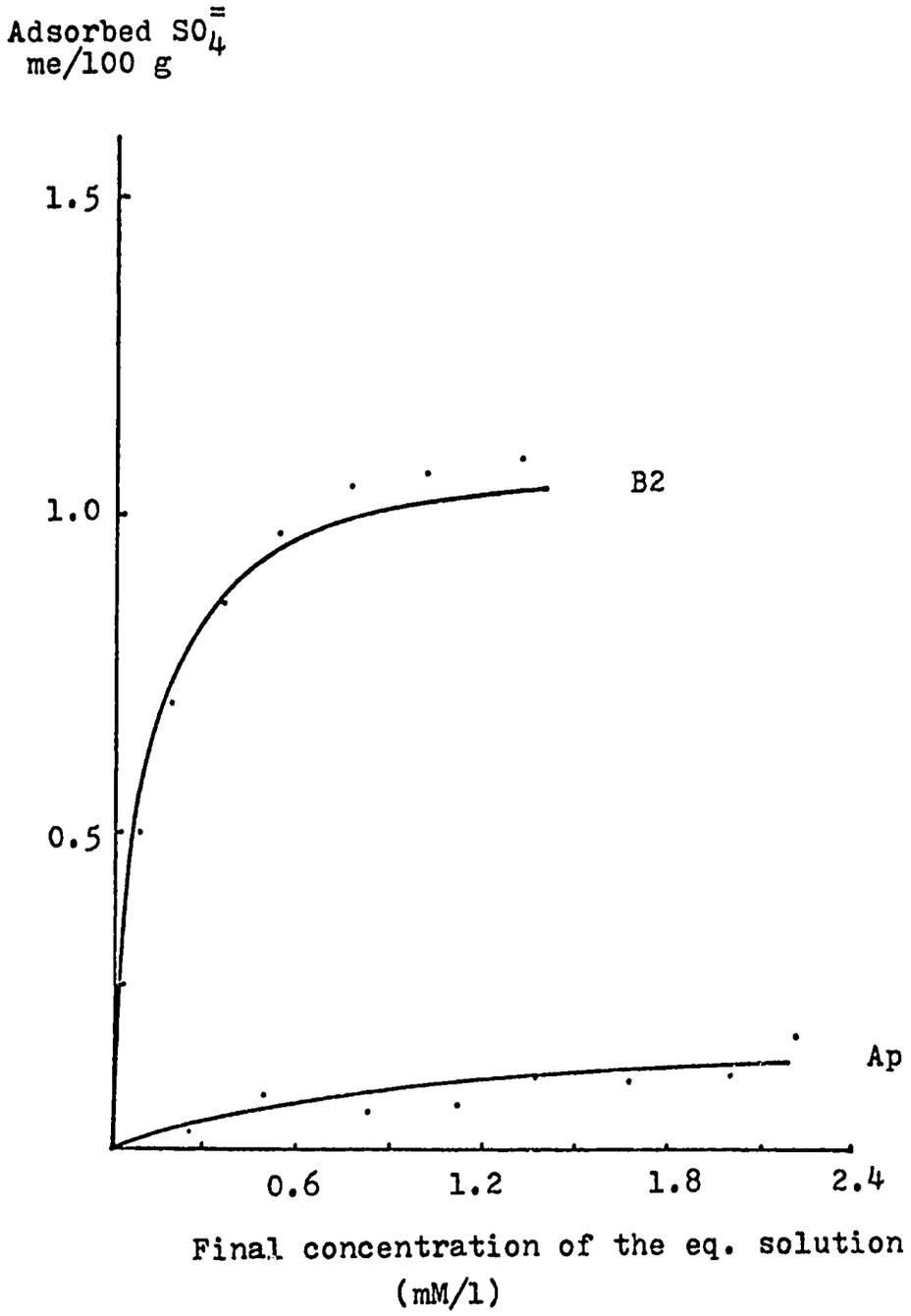


Fig. 2: Sulfate adsorption in conditions of unadjusted pH, Langmuir's equation. Acrorthox.

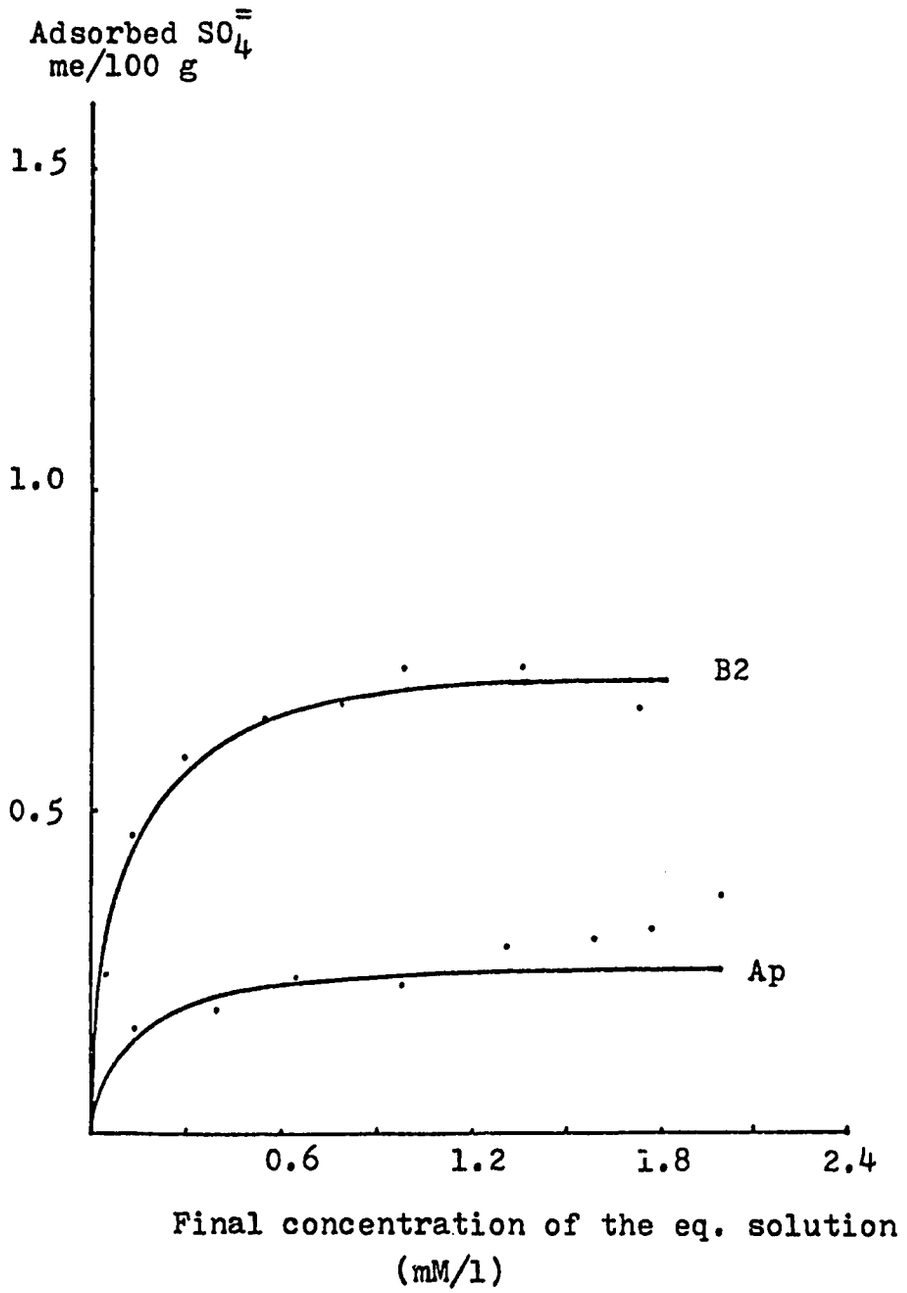
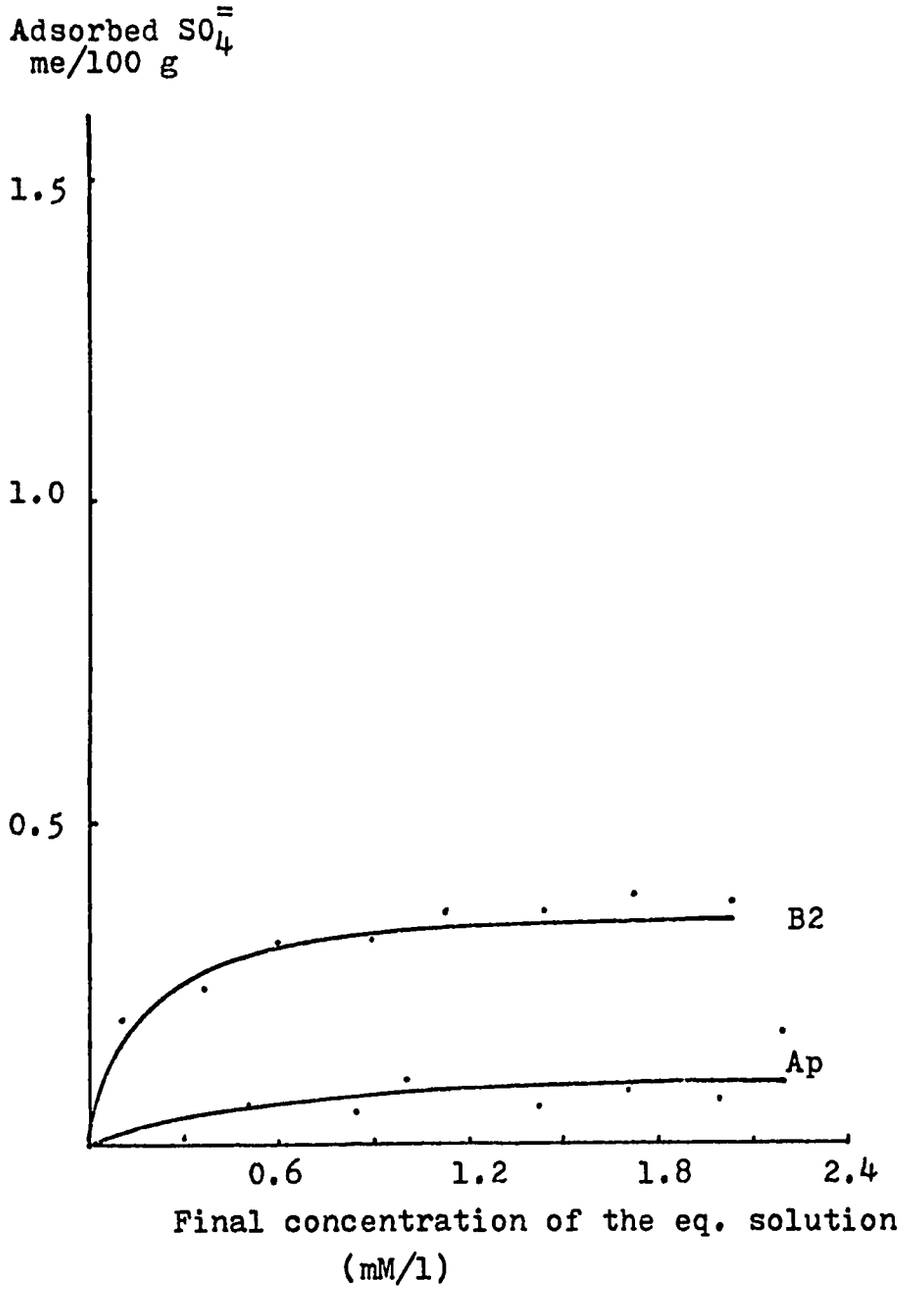


Fig. 3: Sulfate adsorption in conditions of unadjusted pH, Langmuir's equation. Tropudalf.



another part of the experiment.

b) Sulfate adsorption as described by an empirical model.

In addition to using the Langmuir equation, an empirical model using initial concentration of the equilibrium solution instead of final concentration was developed. The following model was fitted to the observed values:

$$Y = \beta_0 + \beta_1 (SO_4) + \beta_{11} (SO_4)^{\frac{1}{2}} \qquad (7)$$

where Y is the amount of adsorbed $SO_4^{=}$ in me/100 g of soil, β_0 is the intercept, SO_4 is the amount of sulfate originally present in the equilibrium solution expressed in mM $SO_4^{=}$/l and β_1 and β_{11} are constants as estimated by least squares procedure. This square root model was chosen because a function with continuously increasing values of adsorbed $SO_4^{=}$ at a decreasing rate, within the range of $SO_4^{=}$ concentrations in the equilibrium solutions, was required and a reasonable fit to the data was found.

The observed values of $SO_4^{=}$ adsorption and the resulting pH values of the equilibrium solution are shown graphically in figures 4 to 6. The continuous lines on the graphs show the amount of $SO_4^{=}$ adsorbed as predicted by the regression equation.

In the three soils studied there is a large difference in the amount of $SO_4^{=}$ adsorbed for the Ap and B2 horizons, the amount adsorbed being larger in the B2 horizons. The differen-

Fig. 4: Sulfate adsorption in conditions of unadjusted pH, empirical model. Acrohumox.

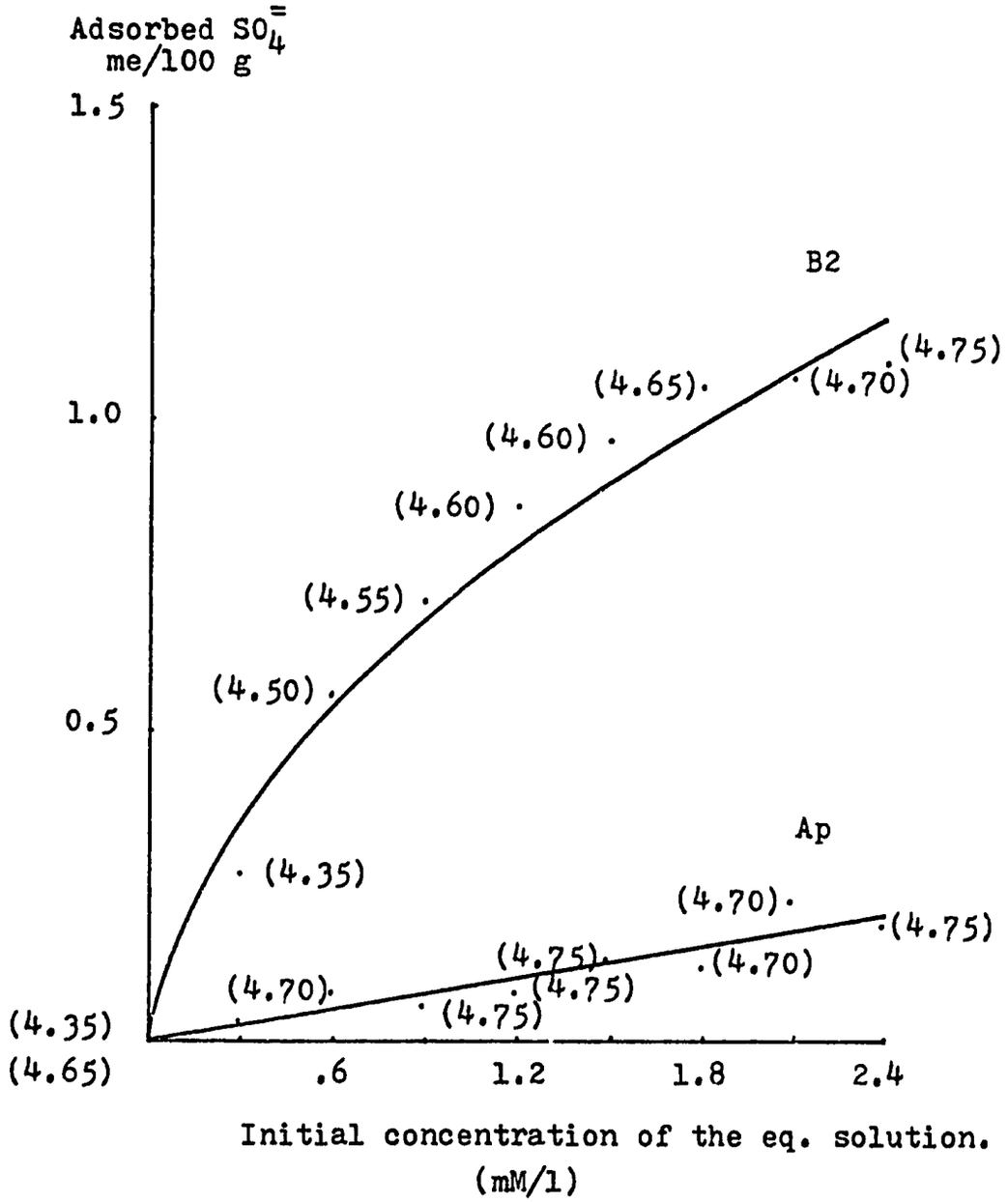


Fig. 5: Sulfate adsorption in conditions of unadjusted pH, empirical model. Acrorthox.

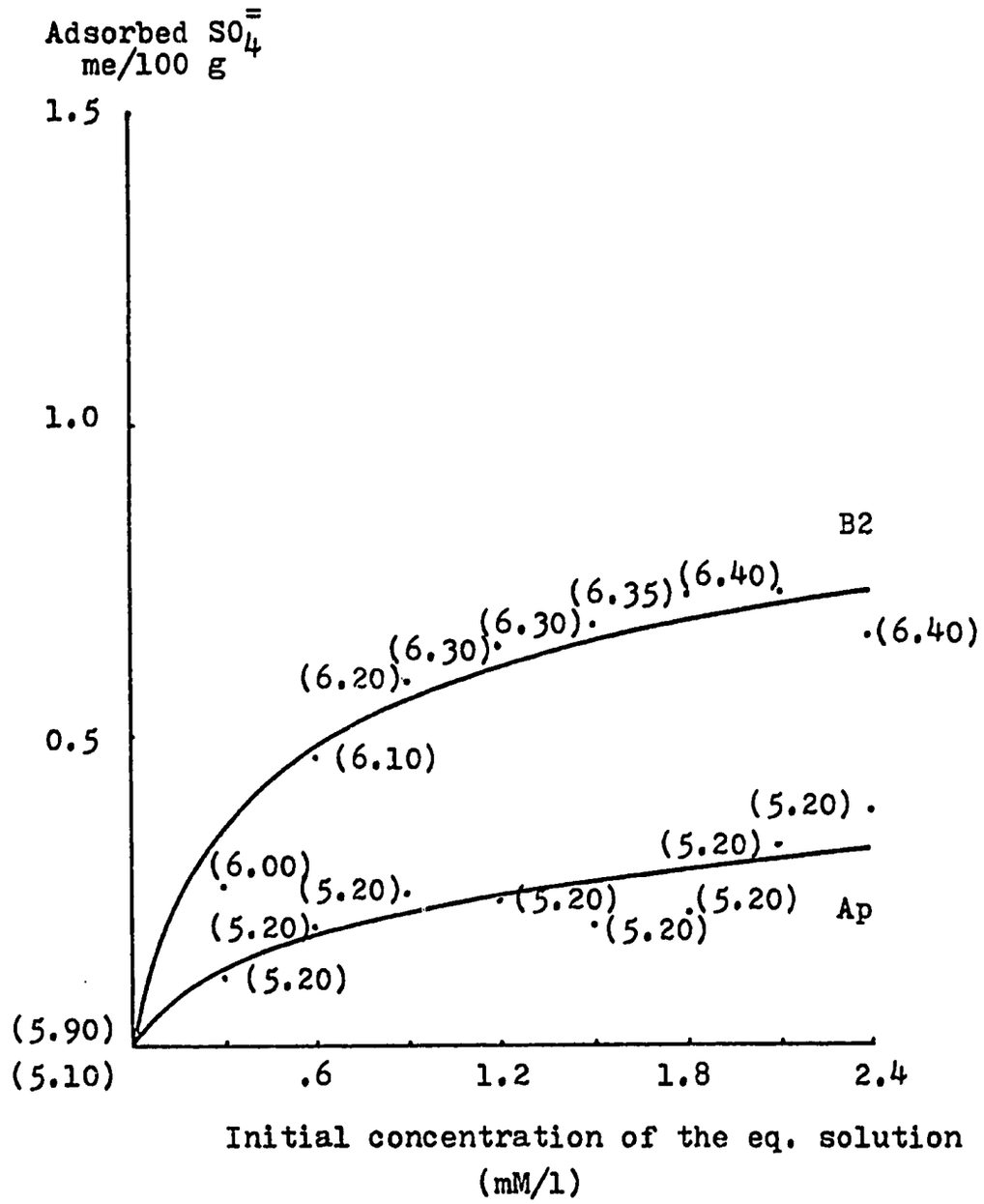
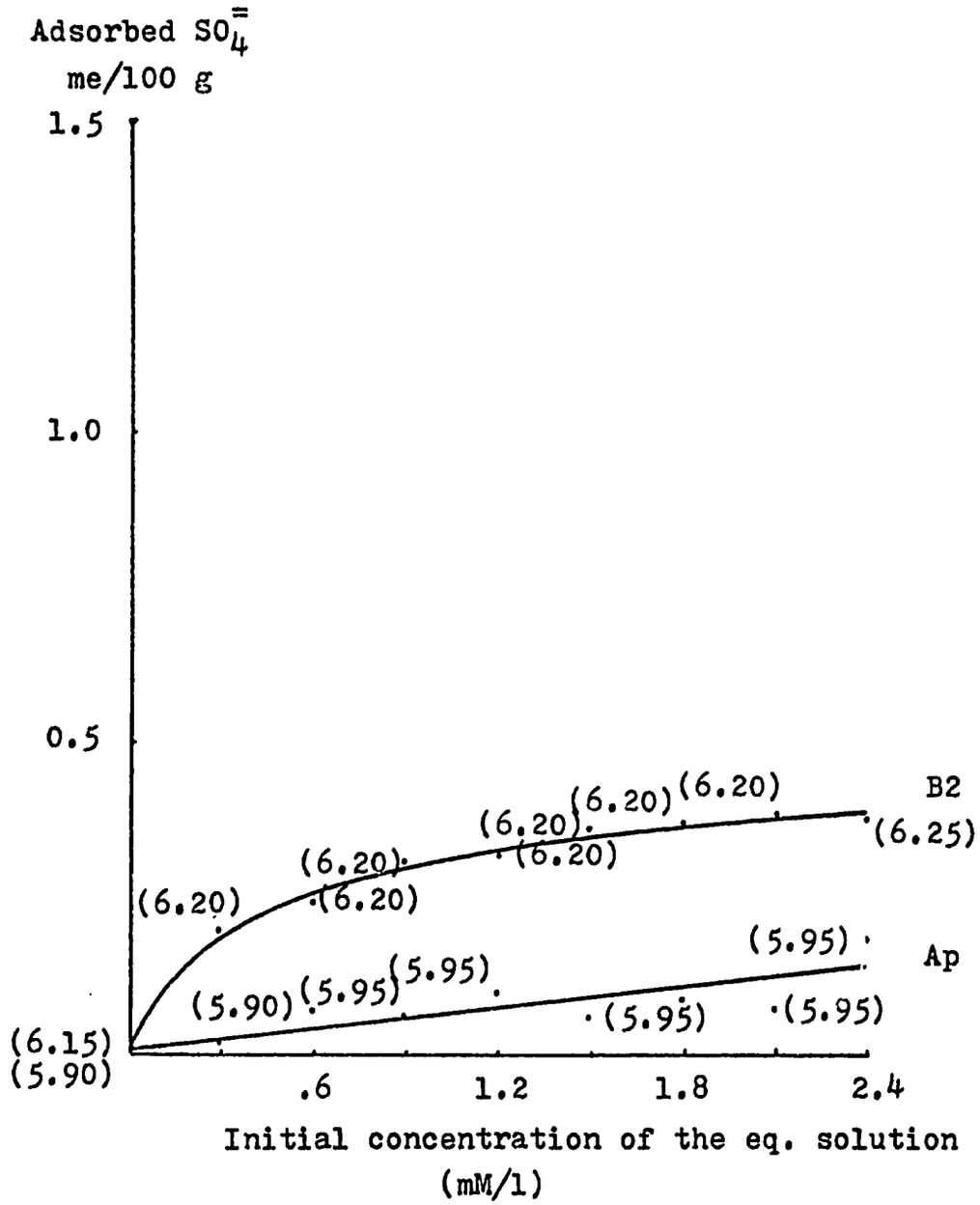


Fig. 6: Sulfate adsorption in conditions of unadjusted pH, empirical model. Tropudalf.



ce in the amount of $SO_4^{=}$ adsorbed by the three B2 horizons is clear too.

The values indicated close to the points representing the observations in the figures, correspond to the measured pH values of the equilibrium solution after equilibration. The increase in pH with increasing $SO_4^{=}$ adsorption pointed out earlier should affect the charges on the surface of the soil particles as a result of its effects on the potential of the surface of the oxides. The observed amount of $SO_4^{=}$ adsorbed is in these conditions affected by pH as well as by $SO_4^{=}$ concentration of the equilibrium solution.

Correction for pH was made by including a linear term for pH of the equilibrium solution in the proposed model. The inclusion of this term contributed significantly to the sum of squares of regression in one out of the six samples, sample 4 corresponding to Acrothox - B2 sample in which the increase in pH as result of $SO_4^{=}$ adsorption was more evident. More detailed discussion of the effect of pH on $SO_4^{=}$ adsorption is presented in section IV - 3.

2. <u>Effect of sulfate adsorption on pH of the equilibrium solution.</u>

It can be seen in graphs 4 to 6 and in tables 1 to 3 in the appendix that there is an increase in the final pH value of the equilibrium solution with increasing $SO_4^{=}$ adsorption. The effect is clear with samples 2 and 4 corresponding to the

B2 horizon of the Acrohumox and Acrorthox soils in which more $SO_4^{=}$ adsorption was observed. In other samples there is a trend of the same nature but the effect was not so strong.

If $SO_4^{=}$ adsorption occurs as a result of non-specific adsorption an exchange with some other anion already adsorbed on the surface must occur and no change in pH would be observed. On the other hand, if $SO_4^{=}$ is specifically adsorbed according to the mechanism proposed by Hingston et al. (1967), a hydroxyl coordinated to an iron atom of the crystal structure should be displaced with the consequent increase in pH of the equilibrium solution.

A constant increase in pH per unit of $SO_4^{=}$ adsorbed was not observed for different samples used in this study. Since aluminum and iron oxides as well as kaolinite were present in these soils more than one mechanism of $SO_4^{=}$ adsorption likely existed. In addition, other factors such as different buffer capacity of the soils may affect $SO_4^{=}$ adsorption-pH relationships.

3. <u>Effect of pH and sulfate concentration of the equilibrium solution on sulfate adsorption.</u>

The amount of $SO_4^{=}$ adsorbed at several $SO_4^{=}$ concentrations and pH values of the equilibrium solution is shown in tables 4 to 9 of the Appendix.

The number of observations provide a wide range of pH values for each sample. The observations considered in this

part of the study include those collected in the former part at unadjusted pH and new observations made at different pH values. The same analysis was performed first with these last observations only and no difference was observed in the results when all observations were included.

To have an estimation of the effect of pH and $SO_4^{=}$ concentration on $SO_4^{=}$ adsorption separately and their interactions, the amount of adsorbed $SO_4^{=}$ was regressed on pH values and $SO_4^{=}$ concentrations according to the following model:

$$Y = \beta_0 + \beta_1(SO_4) + \beta_2(pH) + \beta_{11}(SO_4)^{\frac{1}{2}} + \beta_{12}(SO_4)(pH)$$

where Y is $SO_4^{=}$ adsorbed in me/100 g of soil, SO_4 is the concentration in the equilibrium solution originally present, pH is the observed value of final pH of the equilibrium solution and β_0, β_1, β_2, and β_{12} are constants.

The model was choosen after examining plots of $SO_4^{=}$ adsorption values against initial $SO_4^{=}$ concentration in the equilibrium solution and adsorbed $SO_4^{=}$ against pH values. In addition, an approximate ramdom distribution of deviations from the regression was considered, as shown by plotting the residuals against adsorbed $SO_4^{=}$ values.

The variable initial $SO_4^{=}$ concentration of the equilibrium solution was included for the reasons pointed out earlier when discussing adsorption at uncontrolled pH conditions. It can be observed in the tables of the appendix (tables 4 to 9) with some samples that equilibration with solutions contain-

ing different initial $SO_4^{=}$ concentration results in the same final equilibrium $SO_4^{=}$ concentration. The amount adsorbed is obviously different in these samples, for the same final equilibrium $SO_4^{=}$ concentration. Correlation studies showed that initial $SO_4^{=}$ concentration was better correlated with $SO_4^{=}$ adsorption than the final concentration. This was observed when all values of a given sample were included in the computation of correlation coefficients. It was even more evident when the same study was made for observations falling within a narrow range of pH.

In samples 3 and 4 (Acrorthox Ap and B2 respectively), the inclusion of a term of the form $(pH)^{\frac{1}{2}}$ increased significantly the sum of squares due to regression. In these two cases the model was modified accordingly.

The regression coefficients, their standard errors, and coefficients of multiple determination are shown in tables 10 to 15 in the appendix. Table 3 presents the analysis of variance of regressions.

A similar model in which final concentration of the equilibrium solution substitutes for initial concentration of the equilibrium solution was also considered. Table 4 giving the R^2 values of both regression models shows that a larger part of the total sum of squares was explained by the model including initial concentration of the equilibrium solution.

Table 3: Analysis of variance of regressions.

Source of variation	D.F.	S.S.	M.S.	F
Acrohumox-Ap				
Regression	4	0.35823386	0.08955846	24.75*
Lack of fit	31	0.14405293	0.00464687	1.28
Error	6	0.02170992	0.00361832	
Acrohumox-B2				
Regression	4	17.06831899	4.26707975	303.26*
Lack of fit	40	1.36053322	0.03401333	2.42
Error	6	0.08442271	0.01407045	
Acrorthox-Ap				
Regression	5	2.10375337	0.42075067	70.50*
Lack of fit	30	0.21195798	0.00706527	1.18
Error	6	0.03580877	0.00596813	
Acrorthox-B2				
Regression	5	16.78613149	3.35722630	890.73*
Lack of fit	39	0.51242724	0.01313916	3.49
Error	6	0.02261453	0.00376909	
Tropudalf-Ap				
Regression	4	1.27210033	0.31802508	37.78*
Lack of fit	31	0.27015724	0.00871475	1.03
Error	6	0.05050092	0.00841682	
Tropudalf-B2				
Regression	4	6.67874686	1.66968671	195.46*
Lack of fit	31	0.25600765	0.00825831	<1.00
Error	6	0.12128622	0.02021437	

* Significant ($P \mp 0.05$)

Table 4: Multiple determination coefficients of regression equations containing the variables initial or final $SO_4^{=}$ concentration of the equilibrium solution.

Sample	Initial concentration		Final concentration	
	Number of variables	R^2	Number of variables	R^2
1	4	0.68	4	0.59
2	4	0.92	5	0.87
3	5	0.89	5	0.80
4	5	0.97	5	0.68
5	4	0.80	4	0.73
6	4	0.95	5	0.82

a) Sulfate adsorption at constant pH values.

From the regression equations, $SO_4^{=}$ adsorption at selected constant pH values were estimated for each sample. The results are shown graphically in Fig. 7 to 9.

It can be seen easily in figure 7 that the amount of sulfate adsorbed by sample 1 (Acrohumox Ap) was small and increased linearly sith $SO_4^{=}$ concentration. The effect of pH on $SO_4^{=}$ adsorption was small as shown by a slight change in the slope.

Contrasting with these observations, the amount of $SO_4^{=}$ adsorbed by sample 2 (Acrohumox B2) was considerably higher and very sensitive to pH. The adsorption maximum was not reached

Fig. 7: Sulfate adsorption as a function of concentration at some selected pH values. Acrohumox.

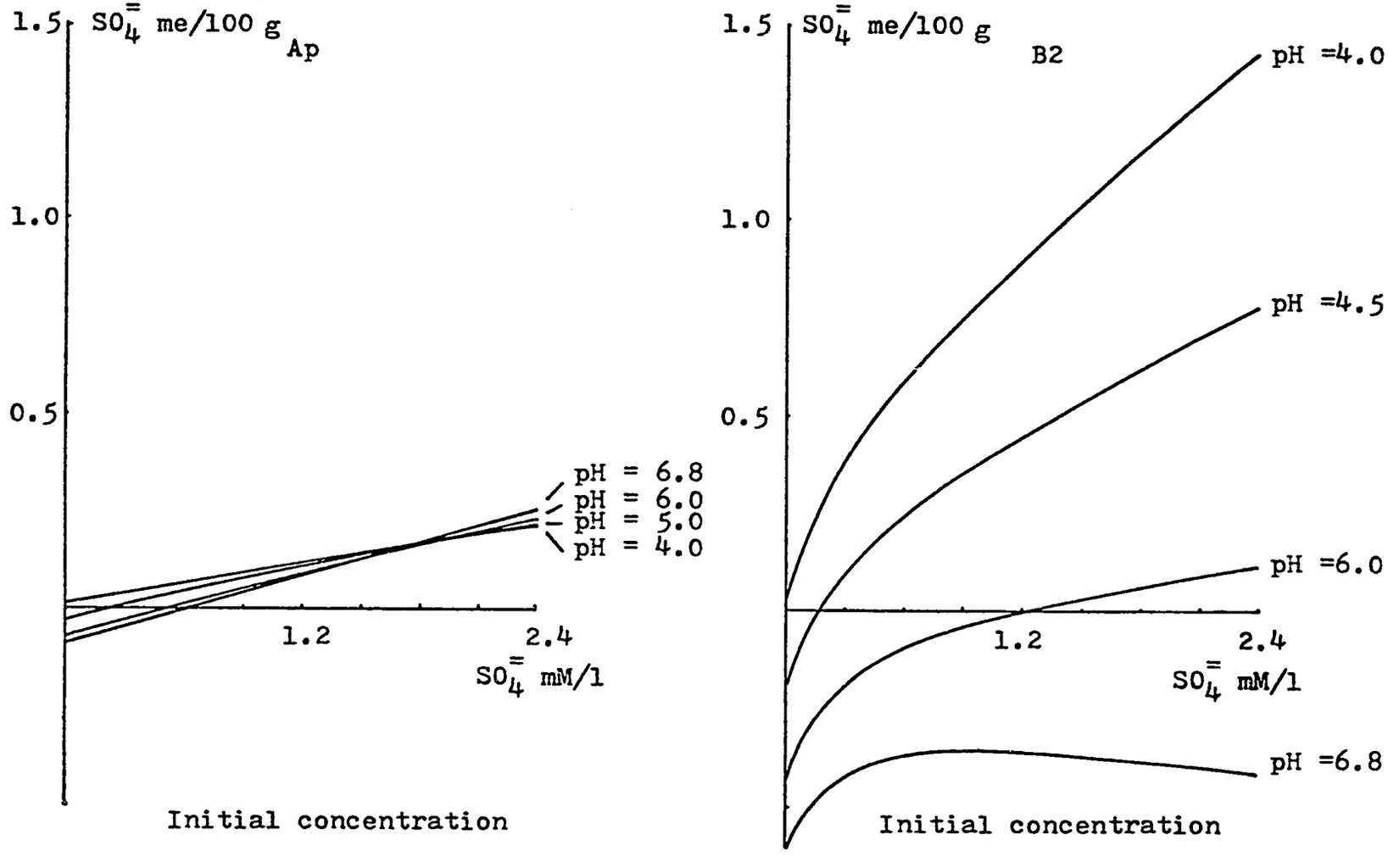


Fig. 8: Sulfate adsorption as a function of concentration at some selected pH values. Acrorthox.

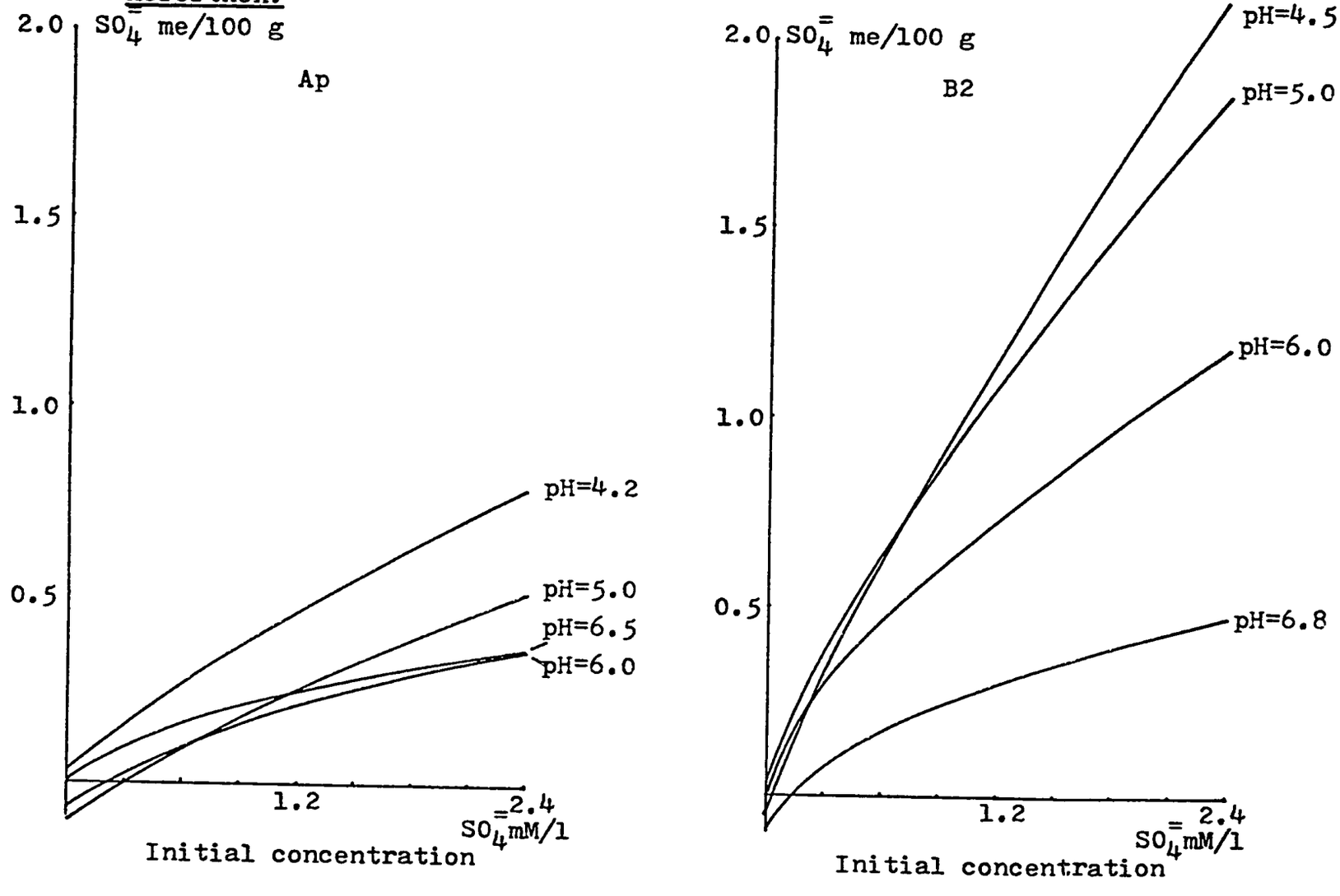
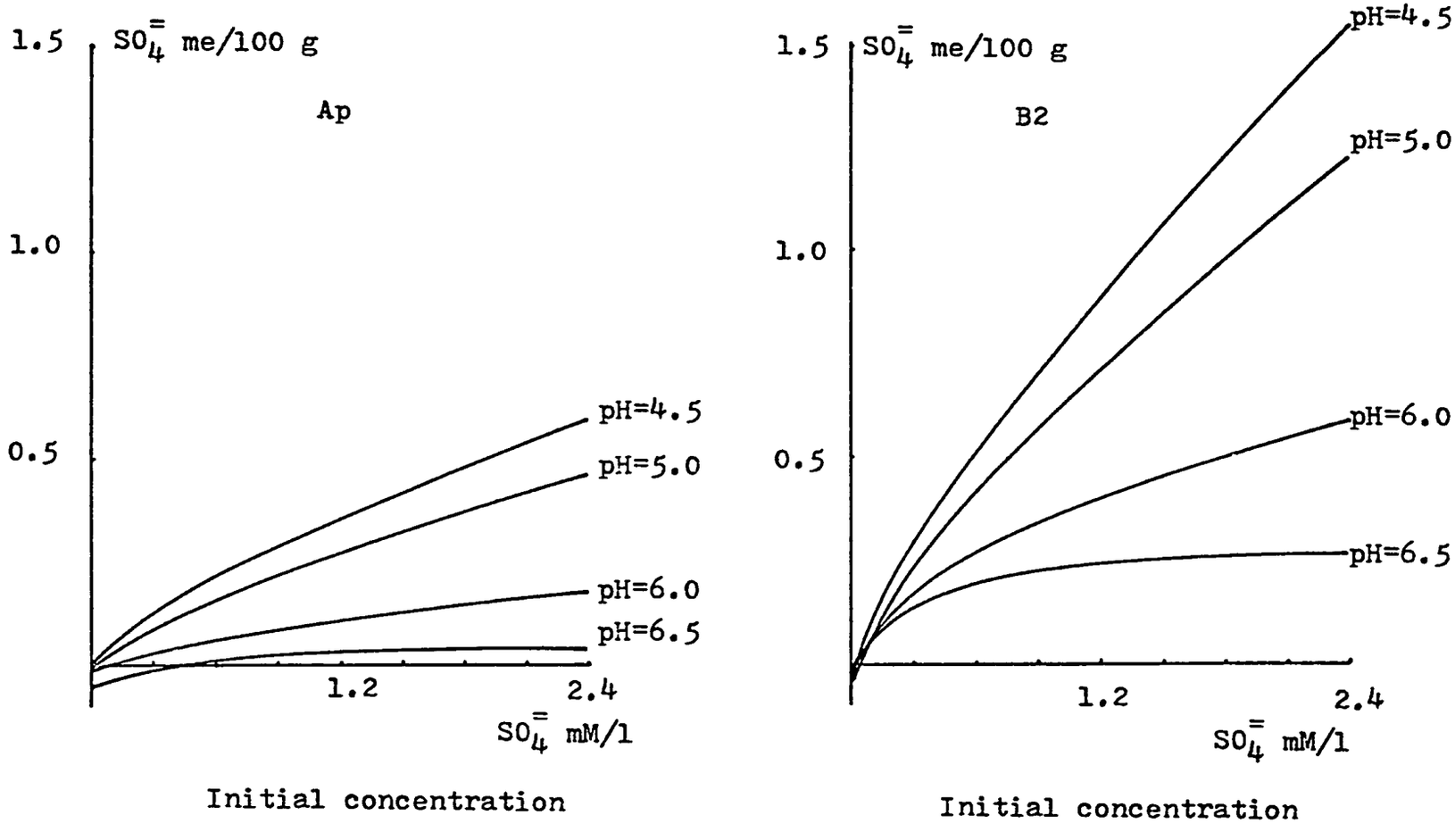


Fig.9: Sulfate adsorption as a function of concentration at some selected pH values. Tropudalf.



within the range of $SO_4^{=}$ concentration and pH values studied. It is interesting to note that at pH values 5.0 and 6.0 desorption of $SO_4^{=}$ occurred at low levels of $SO_4^{=}$ concentration. At pH 6.8 desorption occurred through the whole range of concentrations. The maximum desorption occurred obviously at zero $SO_4^{=}$ concentration and decreased at higher $SO_4^{=}$ concentration. The slight increase in $SO_4^{=}$ desorption observed beyond 1.5 mM/l should be attributed to a failure of the regression model to represent the actual observed values at limiting levels of pH and concentration. The observed values shown in table 5 of the appendix supports this interpretation.

Considering now the Acrorthox, it is clear from figure 8 that there was a sharp increase in $SO_4^{=}$ adsorption when pH was reduced for both topsoil and subsoil. The maximum $SO_4^{=}$ adsorption was 0.3 and 0.7 me/100 g of soil under conditions of unadjusted pH for the topsoil and subsoil respectively. The maximum amount adsorbed, however, was 0.8 and more than 2.0 me/100 g of soil when the pH was as low as 4.2 and 4.5 for topsoil and subsoil, respectively. At high pH values maximum adsorption was observed within the range of $SO_4^{=}$ concentration studied but not at lower pH values.

The same features can be observed in the case of the Tropudalf (figure 9). In the Ap horizon little $SO_4^{=}$ adsorption was measured when pH was not controlled (approximately pH 6.0). At pH 4.5 $SO_4^{=}$ adsorption as high as 0.6 me/100 g of

soil was found without approaching an adsorption maximum within the range of concentrations studied. The B2 horizon that adsorbed only 0.4 me/100 g of soil at pH 6.2 adsorbed more than 1.5 me/100 g of soil when the pH was lowered to 4.5.

The difference in $SO_4^{=}$ adsorption observed for Ap and B2 horizons in each soil is not attributable to differences in oxides or kaolinite content of either horizon since no significant differences in composition of either horizon is observed as shown in table 1. The difference is due probably to the higher organic matter content of the Ap horizons. Blocking of positive charge sites may occur as a result of occupation of these sites by organic anions or coating of oxide particles by the organic matter. This effect is more noticeable in the Ap horizon of the Acrohumox soil where there is also a smaller content of iron and aluminum oxides. In other soils, in which the amount of iron and aluminum oxides is higher, the effect of organic matter is also marked but the Ap horizons show still the effect of pH on $SO_4^{=}$ adsorption.

The high capacity for $SO_4^{=}$ adsorption developed by the B2 horizons at low pH values could be explained by both non-specific and specific adsorption mechanisms summarized earlier. The low pH would favour the development of positive charges by protonation of hydroxyl groups on the broken edges of kaolinite particles, the NH_2 groups of organic matter, or hydroxyl groups on the surface of iron and aluminum oxides as

well as other oxides. When non-specific adsorption occurs, $SO_4^{=}$ would be attached to positive charge sites generated in this way. Where specific adsorption occurs, an OH^- would be displaced by a $SO_4^{=}$ after protonation according to the mecchanism proposed by Hingston et al. (1967). At low pH values more H^+ are available for protonation of OH^- and more posibilities for specific adsorption occurs.

The desorption of $SO_4^{=}$ observed in the B2 horizon of Acrohumox at high pH values implies the presence of $SO_4^{=}$ already adsorbed (native $SO_4^{=}$) in this horizon. The desorption occurred easily at high pH values even at the low salt concentration used in this part of the study. If this $SO_4^{=}$ were specifically adsorbed as proposed by Hingston et al., it could be desorbed at the same salt concentration only by an anion able to render the surface more negative. They also suggested that the surface may became more negatively charged by adsorption of OH^- or, more likely, by ionization of H^+ from hydroxyl groups at higher pH. In the conditions of this experiment the latter would be the mechanism of desorption if specific adsorption is accepted.

b) <u>Adsorption isotherms at constant pH values.</u>

From the empirical model describing $SO_4^{=}$ adsorption as a function of $SO_4^{=}$ concentration and pH values, $SO_4^{=}$ adsorption and the resulting final concentration of the equilibrium so-

lutions were estimated for some selected pH values.

The values 1/m were plotted against 1/c values as indicated by equation 5. The graphical examination performed for the estimated values at several pH values showed a deviation from linearity in almost all cases. 1/m values were then regressed on 1/c values. The linear coefficients, their significance, and R^2 values for regressions are shown in table 5. In all cases the linear coefficients are significant and a moderately high R^2 value was observed. To test for deviation from linearity a $(1/m)^2$ term was included in the regression as an extended version of the linear form of the Langmuir equation. In all cases the increase in the sum of squares of regression due to the inclusion of this quadratic term was significant and a higher R^2 value was found.

These results show clearly that the amount of $SO_4^=$ adsorbed at constant pH values as predicted by the empirical model do not conform the Langmuir equation. Most of quadratic coefficients in the extended version of the linear form of the Langmuir equation were negative showing a decrease in slope at increasing 1/c values. This indicates that the amount of $SO_4^=$ adsorbed per unit change in concentration of the equilibrium solution was less than the amount predicted by the Langmuir equation at low levels of $SO_4^=$ concentration. This observation is in agreement with the actual observed values of adsorbed $SO_4^=$ in non-controlled pH conditions dis-

Table 5: Significance of regression coefficients and R^2 values for linear form of Langmuir's equation.

Sample	pH	Linear	Quadratic	R^2	Number of observations
1	4.0	6.11121*		0.98	8
1	4.0	10.20009*	-0.95346*	0.99	8
1	5.0	52.58754*		0.90	8
1	5.0	-28.85597*	21.21736*	0.99	8
1	6.0	72.36126*		0.83	7
1	6.0	-120.96276*	90.13036*	0.99	7
2	4.0	0.01567*		0.72	7
2	4.0	0.12772*	-0.00198*	0.98	7
2	4.5	0.16934*		0.94	8
2	4.5	0.40907*	-0.01220*	0.99	8
2	5.0	1.84504*		0.98	8
2	5.0	0.55070*	0.23094*	0.99	8
3	4.0	0.17003*		0.83	8
3	4.0	0.67041*	-0.02792*	0.99	8
3	5.0	15.99622*		0.89	8
3	5.0	-10.95849*	6.66915*	0.99	8
3	6.0	10.37032*		0.96	8
3	6.0	0.07589*	2.49576*	0.99	8
4	4.5	0.01021*		0.84	6
4	4.5	0.03839*	-0.00042*	0.99	6
4	5.0	0.02955*		0.86	6
4	5.0	0.09736*	-0.00281*	0.99	6
4	6.0	0.20744*		0.93	7
4	6.0	0.48671*	-0.03517*	0.99	7
5	4.5	0.06059*		0.72	7
5	4.5	0.29618*	-0.01783*	0.97	7
5	5.0	0.08518*		0.75	7
5	5.0	0.35701*	-0.02869*	0.97	7
5	6.0	0.09996*		0.80	7
5	6.0	0.35114*	-0.04171*	0.98	7

(Continued on next page)

Table 5: Significance of regression coefficients and R^2 values for linear form of Langmuir's equation.

Sample	pH	Linear	Quadratic	R^2	Number of observations
(Continued)					
6	4.5	0.02840*		0.85	8
6	4.5	0.16939*	-0.00152*	0.99	8
6	5.0	-0.76229*		0.57	9
6	5.0	2.31511*	-0.10414*	0.95	9
6	6.0	0.50915*		0.95	8
6	6.0	1.08098*	-0.06557*	0.99	8

* Significant (P = 0.05).

cussed in the first part of the experiement. Thus, the Langmuir equation predicts higher than observed values of $SO_4^{=}$ adsorption at low levels of $SO_4^{=}$ concentration in the equilibrium solution.

4. Desorption of adsorbed sulfate.

Sulfate desorbed by 0.5 N NH_4NO_3 solution includes $SO_4^{=}$ adsorbed from the equilibrium solution and $SO_4^{=}$ already adsorbed before equilibration (native $SO_4^{=}$). The amount of $SO_4^{=}$ desorbed after equilibration with solutions containing no $SO_4^{=}$ is a measure of the amount of $SO_4^{=}$ already adsorbed that can be desorbed by 0.5 N NH_4NO_3. It can be seen in tables 16 and 17 of the appendix that the amounts of $SO_4^{=}$ recovered under these conditions were small, ranging from 0 to 0.4 me/100 g of soil. The highest amount was from sample 2 (Acrohumox B2) which was also the only one in which desorption of $SO_4^{=}$ was actually ob-

served at high pH in the pH and concentration effect study.

Table 6 summarizes the $SO_4^{=}$ adsorption and desorption values for those samples equilibrated with solutions containing two levels of $SO_4^{=}$, at pH approximately 4.0. The highest amount recovered after equilibration was 1.81 me/100 g of soil. This amount, from sample 2 (Acrohumox B2), is 122 percent of the amount adsorbed by the soil showing that desorption of native $SO_4^{=}$ took place.

The fraction of desorbed $SO_4^{=}$ in other samples was close to one in almost all samples but samples 4 (Acrorthox B2) and 6 (Tropudalf B2). Samples 1, 3 and 5 (Ap horizons) show values below and above unit fraction for desorption after equilibration with solutions containing 1.2 and 2.4 mM/l respectively. The lack of consistence in the trend of fraction desorbed at these two levels of adsorbed $SO_4^{=}$ probably is the result of low levels of adsorption in these three samples.

On the other hand, samples 4 and 6 (Acrorthox B2 and Tropudalf B2) show consistently $SO_4^{=}$ desorption below unit fraction for all levels of adsorbed $SO_4^{=}$. These values are 0.46 and 0.64 for sample 4 and 0.57 and 0.73 for sample 6 for the lowest and highest level of adsorbed $SO_4^{=}$ respectively. Considering that the procedure followed for desorption was washing five times with 0.5 N NH_4NO_3, the reduced amount of $SO_4^{=}$ desorbed in relation to adsorbed $SO_4^{=}$ indicates a strong retention of adsorbed $SO_4^{=}$ by the B2 horizons of these two soils.

Table 6: Desorption of adsorbed sulfate by 0.5 N Ammonium Nitrate.*

SAMPLE	SOLUTION $SO_4^{=}$ mM/l	$SO_4^{=}$ ADSORBED me/100 g of soil	$SO_4^{=}$ DESORBED me/100 g of soil	$SO_4^{=}$ DESORBED PER UNIT AD'ED
1	1.2	.32	.25	.77
1	2.4	.40	.47	1.17
2	1.2	1.02	1.31	1.28
2	2.4	1.48	1.81	1.22
3	1.2	.71	.67	.95
3	2.4	.92	.98	1.06
4	1.2	1.12	.51	.46
4	2.4	2.31	1.47	.64
5	1.2	.50	.46	.91
5	2.4	.63	.83	1.31
6	1.2	1.14	.65	.57
6	2.4	1.94	1.42	.73

* Sulfate desorbed after equilibration with solutions containing the indicated amount of $SO_4^{=}$ at pH approximately 4.0. Average of two observations.

If the adsorption of $SO_4^=$ were not specific, washing five times with 0.5 N NH_4NO_3 should desorb most of the adsorbed $SO_4^=$. The results suggest a strong retention of adsorbed $SO_4^=$ following the mechanism proposed by Hingston et al., in which specifically adsorbed $SO_4^=$ can not be desorbed by Cl^- or NO_3^-.

There was also an apparent difference in the percent $SO_4^=$ desorbed in sample 2 compared to samples 4 and 6. The higher percent desorption observed in sample 2 suggests a high amount of native $SO_4^=$ in this sample and probably a difference in the mechanism of $SO_4^=$ adsorption. Samples 4 and 6 desorbed between 57 and 73 percent of adsorbed $SO_4^=$ while sample 2 desorbed all the adsorbed $SO_4^=$ plus some native $SO_4^=$.

Looking at the mineralogical composition of these three samples it can be observed (Table 1) that the sample 2 (Acrohumox B2) is relatively lower in Fe_2O_3 and higher in kaolinite with respect to other B2 horizons (Samples 4 and 6). This could explain the weaker retention of adsorbed $SO_4^=$ on sample 2 in agreement with the results presented by Aylmore et al., (1967), Koter et al.,(1973), and Hague and Walmsley (1974).

5. <u>Desorption of adsorbed potassium.</u>

The amount of K^+ initially present in the equilibrium solutions varied from 20 to 24.8 mM/l when the $SO_4^=$ concentration increased from 0 to 2.4 mM/l. Under these conditions a comparatively large proportion of the negative sites on the

surface of soil particles will be occupied by K^+.

The amount of K^+ desorbed by 0.5 N NH_4NO_3 after equilibration with solutions containing 0, 1.2, and 2.4 mM of $SO_4^=$ per liter can be considered as an index for estimation of negative charges already present in the soil material as well as those developed as a result of $SO_4^=$ adsorption, if any.

The amounts of K^+ and $SO_4^=$ desorbed by 0.5 N NH_4NO_3 after correction for the respective amounts contained in the occluded solution are shown in the appendix. Table 7 summarizes the average values of desorbed K^+ for each level of adsorbed $SO_4^=$ and the final pH values of the equilibrium solutions. There is a trend for increasing K^+ desorbed with increasing $SO_4^=$ adsorption within each sample except for samples 1 and 6. The trend is clearer in samples 2 and 4 corresponding to B2 horizons of the Acrohumox and Acrorthox, respectively. It can be seen also that in these samples the final pH of the equilibrium solution increased when $SO_4^=$ adsorption increased, as noted in the previous part of the experiment.

Under these conditions the apparent increase in adsorbed K^+ could be the result of $SO_4^=$ adsorption directly or the result of the increase in pH of the equilibrium solution and its effects on charge development.

To determine if the apparent increases in K^+ retained by the soils were directly related to increasing levels of adsorbed $SO_4^=$, the same experiment was performed at a constant

level of pH, approximately 4.0. The results included in table 17 of the appendix are summarized in table 8.

When pH was controlled there also was an increase in K^+ retained by the soil with increasing levels of adsorbed $SO_4^=$. The amount of K^+ desorbed by 0.5 N NH_4NO_3 however, was smaller in all cases showing a high pH dependence of cation retention in all samples. With pH controlled at approximately 4.0 the amount of desorbed K^+ expressed as percent of the amount desorbed at zero level of adsorbed $SO_4^=$ was considerably higher when compared to the results observed at higher pH values. This is due to higher absolute increases in K^+ desorbed at increasing levels of adsorbed $SO_4^=$ as well as to the lower amount of K^+ desorbed at zero level of $SO_4^=$ adsorption.

In order to determine the significance of these changes in K^+ desorption, an analysis of variance was performed. The individual estimated values of error variance (among duplicates within samples) are given for each sample in table 9.

The hypothesis of homogeneity of variances was not rejected according to Barttlet's test, showing that all mean squares can be considered estimates of the same error variance.

The analysis of variance for the group of 36 observations corresponding to K^+ desorption at low pH values is shown in table 10. All variance ratios performed in this analysis were computed using the pooled experimental error.

The results show that most of the variation is due to di-

Table 7: Potassium desorbed at each level of adsorbed sulfate in non-adjusted pH conditions. Averages of two observations.

SAMPLE	SOLUTION $SO_4^{=}$ mM/l	FINAL pH	ADSORBED $SO_4^{=}$ me/100 g	DESORBED K^+ me/100 g	RELATIVE DESORPTION
1	0.0	4.65	-0.04	1.16	100
1	1.2	4.65	0.10	1.15	99
1	2.4	4.70	0.60	1.25	108
2	0.0	4.32	-0.02	0.86	100
2	1.2	4.50	0.85	1.04	121
2	2.4	4.65	1.01	1.16	135
3	0.0	5.10	-0.04	1.42	100
3	1.2	5.17	0.39	1.55	109
3	2.4	5.15	0.77	1.65	116
4	0.0	5.77	-0.03	0.60	100
4	1.2	6.07	0.60	0.73	122
4	2.4	6.27	0.79	0.86	143
5	0.0	5.70	-0.08	3.15	100
5	1.2	5.77	0.16	3.44	109
5	2.4	5.75	0.57	3.64	116
6	0.0	6.10	-0.04	3.10	100
6	1.2	6.10	0.30	3.20	103
6	2.4	6.10	0.51	3.28	106

Table 8: Potassium desorbed at each level of adsorbed sulfate at pH values approximately constant. Averages of two observations.

SAMPLE	SOLUTION $SO_4^{=}$ mM/l	FINAL pH	ADSORBED $SO_4^{=}$ me/100 g	DESORBED K^+ me/100 g	RELATIVE DESORPTION
1	0.0	4.00	-0.10	0.88	100
1	1.2	4.00	0.33	1.02	116
1	2.4	4.02	0.41	1.05	119
2	0.0	4.07	-0.13	0.69	100
2	1.2	4.04	1.02	0.72	104
2	2.4	4.03	1.49	0.88	127
3	0.0	4.02	-0.04	0.59	100
3	1.2	4.00	0.71	0.77	130
3	2.4	4.08	0.92	1.00	169
4	0.0	4.01	-0.06	0.07	100
4	1.2	4.00	1.11	0.13	186
4	2.4	4.07	2.28	0.24	342
5	0.0	4.21	-0.08	2.20	100
5	1.2	4.20	0.50	2.35	107
5	2.4	4.30	0.63	2.67	121
6	0.0	4.06	-0.14	2.01	100
6	1.2	3.99	1.14	2.09	104
6	2.4	4.05	1.94	2.39	119

Table 9: Error variance estimates for potassium desorption values at constant pH.

SAMPLE	ERROR MEAN SQUARE	MEAN	C.V.
1	0.008433	0.98	0.09
2	0.013750	0.76	0.15
3	0.008416	0.78	0.12
4	0.004133	0.15	0.43
5	0.006833	2.40	0.03
6	0.052817	2.16	0.11

fferences in levels of desorbed K^+ among soils and between horizons within soils. Significant differences in desorbed K^+ are also observed among levels of adsorbed $SO_4^=$ within samples 3, 5, and 6.

Single comparisons between amounts of desorbed K^+ at different levels of adsorbed $SO_4^=$ are shown in table 11.

Considering the amount of K^+ desorbed after equilibration at low pH and at higher unadjusted pH, for some samples there is an increase in the amount of K^+ retained by the soil at increasing values of adsorbed $SO_4^=$.

The increase in K^+ retained is relatively high at low pH values where significant $SO_4^=$ adsorption occurs. Low amounts of K^+ are retained in some samples at pH 4.0. At higher pH

Table 10: Analysis of Variance of desorbed Potassium with 0.5 N NH_4NO_3, after equilibration with $SO_4^{=}$ solutions.

Source of variation	D.F.	S.S.	M.S.	F
Among Samples	5	23.3690	4.6738	297.17*
Among Soils	2	21.8284	10.9142	693.94*
Among Horizons/Soils	3	1.5406	0.5135	32.65*
Among Levels of $SO_4^{=}$/Samples	12	0.6568	0.0547	3.48*
Among Levels /Samp. 1	2	0.0343	0.0172	1.09
" " / " 2	2	0.0426	0.0213	1.35
" " / " 3	2	0.1647	0.0824	5.24*
" " / " 4	2	0.0297	0.0149	1.00
" " / " 5	2	0.2294	0.1147	7.29*
" " / " 6	2	0.1560	0.0780	4.96*
Among Duplicates	18	0.2831	0.0157	
Total (corrected)	35	24.3090		

* Significant ($P \leq 0.05$).

Table 11: Single degree of freedom comparisons for desorbed Potassium at three levels of adsorbed $SO_4^{=}$.

Source of Variation	SAMPLES					
	1	2	3	4	5	6
S_0 vs S_1+S_2	0.0331	0.0154	0.1141	0.0176	0.1302	0.0690
S_1 vs S_2	0.0012	0.0272	0.0506	0.0121	0.0992	0.0870
TOTALS	0.0343	0.0426	0.1647	0.0297	0.2294	0.1560
ERROR M.S.			0.0157			
			F Ratios			
S_0 vs S_1+S_2	2.10	<1.00	7.25*	1.12	8.28*	4.39
S_1 vs S_2	<1.00	1.73	3.22	<1.00	6.31*	5.53*

* Significant ($P \leq 0.05$).

the amount of K^+ retained is considerably higher and increases with $SO_4^{=}$ adsorption in all samples. Under these conditions the increase in K^+ retained by soils is due probably to both an increase in pH of the equilibrium solution and the effect of adsorbed $SO_4^{=}$ on increased negative charge development.

V. CONCLUSIONS.

Sulfate adsorption was studied in six samples corresponding to two Oxisols and one Tropudalf of São Paulo State, Brazil. The results obtained through equilibration studies as well as after desorption of adsorbed $SO_4^{=}$ can be summarized as follows:

1. The amount of $SO_4^{=}$ adsorbed by the soils was significant, specially in subsoil samples. At a pH of about 4.0 the amount adsorbed reached more than 2 me/100 of soil, an amount that can be considered high in relation to the low cation exchange capacity of these tropical soils.

2. It was observed that $SO_4^{=}$ adsorption was clearly dependent on pH of the equilibrium solution, the amount adsorbed increasing at lower pH values. In the surface horizons with relatively high organic matter content $SO_4^{=}$ adsorption capacity of the soils was smaller and the pH effect was less evident.

3. When $SO_4^{=}$ adsorption occurred, the pH of the equilibrium solution increased, probably as a result of $SO_4^{=}$ substitution for OH^- groups on the surface of oxides in these soils.

4. Sulfate adsorption at constant pH values did not follow the Langmuir adsorption isotherm equation. The amount of $SO_4^{=}$ adsorbed was affected by the initial concentration of the equilibrium solution. It was observed also that different amounts of $SO_4^{=}$ were adsorbed at similar final $SO_4^{=}$ concentrations of the equilibrium solutions.

5. Adsorbed $SO_4^{=}$ was strongly retained by some soils but easily desorbed from other soils depending probably on the nature of the adsorbent surface.

6. Increased $SO_4^{=}$ adsorption resulted in increased cation retention capacity of these soils as measured by K^+ adsorption and desorption. This was specially apparent in the B2 horizon of the Acrorthox which at low soil pH was near the zero-point-of-charge.

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APPENDIX.

Explanation of the abbreviations used in the tables:

OBS : Observation number.

SAMPLE : Sample number.

SOLUTION : Initial concentration of the equilibrium solution in $SO_4^{=}$ mM/l

FINAL_PH : Measured final pH of the equilibrium solution.

ADJD_PH : Intended adjusted pH of the equilibrium solution.

S_UGML : Final concentration of the equilibrium solution in S ug/ml.

SO4_MMOL : Final concentration of the equilibrium solution in $SO_4^{=}$ mM/l.

SO4_ABD : Adsorbed $SO_4^{=}$ in me/100 g of soil.

K_BSOL : Potassium concentration in Solution B in ug/ml.

K_ASOL : Potassium concentration in Solution A in ug/ml.

S_BSOL : Sulfate concentration in Solution B in S ug/ml.

S_ASOL : Sulfate concentration in Solution A in S ug/ml.

DESD_SO4 : Sulfate desorbed by 0.5 N NH_4NO_3 in me/100 g of soil.

DESD_K : Potassium desorbed by 0.5 N NH_4NO_3 in me/100 g of soil.

Appendix, Table 1:

SULFATE ADSORPTION AT FREE PH, ACROHUMOX AP

OBS	SAMPLE	SOLUTION	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
10	1	0.0	4.65	0.0	0.00000	.000000
11	1	0.3	4.75	8.5	0.26509	.034905
12	1	0.6	4.70	16.5	0.51460	.085404
13	1	0.9	4.75	27.0	0.84207	.057934
14	1	1.2	4.75	36.0	1.12275	.077246
15	1	1.5	4.75	44.0	1.37226	.127745
16	1	1.8	4.70	54.0	1.68413	.115668
17	1	2.1	4.70	60.0	1.87126	.228743
18	1	2.4	4.75	71.0	2.21432	.185679

N=9

SULFATE ADSORPTION AT FREE PH, ACROHUMOX B2

OBS	SAMPLE	SOLUTION	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
19	2	0.0	4.35	0	0.00000	0.00000
20	2	0.3	4.35	1	0.03119	0.26881
21	2	0.6	4.50	3	0.09356	0.50644
22	2	0.9	4.55	6	0.18713	0.71287
23	2	1.2	4.60	11	0.34306	0.85694
24	2	1.5	4.60	17	0.53019	0.96981
25	2	1.8	4.65	24	0.74850	1.05150
26	2	2.1	4.70	33	1.02919	1.07081
27	2	2.4	4.75	42	1.30988	1.09012

N=9

Appendix, Table 2:

SULFATE ADSORPTION AT FREE PH, ACRORTHOX AP

OBS	SAMP E	SOLUTION	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
28	3	0.0	5.1	0.0	0.00000	.000000
29	3	0.3	5.2	4.5	0.14034	.159656
30	3	0.6	5.2	13.0	0.40544	.194561
31	3	0.9	5.2	21.0	0.65494	.245060
32	3	1.2	5.2	31.0	0.96682	.233184
33	3	1.5	5.2	42.0	1.30988	.190120
34	3	1.8	5.2	51.0	1.59057	.209431
35	3	2.1	5.2	57.0	1.77769	.322305
36	3	2.4	5.2	65.0	2.02720	.372804

N=9

SULFATE ADSORPTION AT FREE PH, ACRORTHOX B2

OBS	SAMPLE	SOLUTION	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
37	4	0.0	5.90	0.0	0.00000	.000000
38	4	0.3	6.00	1.5	0.04678	.253219
39	4	0.6	6.10	4.5	0.14034	.459656
40	4	0.9	6.20	10.0	0.31188	.588124
41	4	1.2	6.30	18.0	0.56138	.638623
42	4	1.5	6.30	26.5	0.82647	.673528
43	4	1.8	6.35	34.5	1.07597	.724027
44	4	2.1	6.40	44.0	1.37226	.727745
45	4	2.4	6.40	56.0	1.74651	.653493

N=9

Appendix, Table 3:

SULFATE ADSORPTION AT FREE PH, TROPUDALF AP

OBS	SAMPLE	SOLUTION	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
46	5	0.0	5.90	0.0	0.00000	.000000
47	5	0.3	6.00	9.8	0.30564	-.005639
48	5	0.6	5.90	17.0	0.53019	.069610
49	5	0.9	5.95	27.0	0.84207	.057934
50	5	1.2	5.95	35.0	1.09157	.108433
51	5	1.5	5.95	46.0	1.43463	.065369
52	5	1.8	5.95	55.0	1.71532	.084681
53	5	2.1	5.95	65.0	2.02720	.072804
54	5	2.4	5.95	71.0	2.21432	.185679

N=9

SULFATE ADSORPTION AT FREE PH, TROPUDALF B2

OBS	SAMPLE	SOLUTION	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
55	6	0.0	6.15	0.0	0.00000	.000000
56	6	0.3	6.20	3.5	0.10916	.190843
57	6	0.6	6.20	11.5	0.35866	.241342
58	6	0.9	6.20	19.0	0.59256	.307435
59	6	1.2	6.20	28.0	0.87325	.326747
60	6	1.5	6.20	36.5	1.13835	.361652
61	6	1.8	6.20	46.0	1.43463	.365369
62	6	2.1	6.20	55.0	1.71532	.384681
63	6	2.4	6.25	65.0	2.02720	.372804

N=9

Appendix, Table 4:

SULFATE ADSORPTION AT DIFFERENT PH VALUES, ACROHUMOX AP

OBS	SAMPLE	SOLUTION	ADJD_PH	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
10	1	0.0	0	4.65	0.0	0.00000	.000000
11	1	0.3	0	4.75	8.5	0.26509	.034905
12	1	0.6	0	4.70	16.5	0.51460	.085404
13	1	0.9	0	4.75	27.0	0.84207	.057934
14	1	1.2	0	4.75	36.0	1.12275	.077246
15	1	1.5	0	4.75	44.0	1.37226	.127745
16	1	1.8	0	4.70	54.0	1.68413	.115868
17	1	2.1	0	4.70	60.0	1.87126	.228743
18	1	2.4	0	4.75	71.0	2.21432	.185679
64	1	0.0	6	5.80	0.0	0.00000	.000000
65	1	0.3	6	5.75	9.5	0.29628	.003718
66	1	0.6	6	5.80	18.5	0.57697	.023029
67	1	0.9	6	5.75	27.5	0.85766	.042340
68	1	1.2	6	5.75	36.0	1.12275	.077246
69	1	1.5	6	5.85	44.0	1.37226	.127745
70	1	1.8	6	5.80	54.0	1.68413	.115868
71	1	2.1	6	5.75	58.0	1.80888	.291118
72	1	2.4	6	5.80	68.0	2.12076	.279242
118	1	0.0	7	6.80	0.0	0.00000	.000000
119	1	0.3	7	6.80	18.0	0.56138	-.261377
120	1	0.6	7	6.85	18.5	0.57697	.023029
121	1	0.9	7	6.85	27.8	0.86702	.032984
122	1	1.2	7	6.85	39.0	1.21632	-.016317
123	1	1.5	7	6.85	44.0	1.37226	.127745
124	1	1.8	7	6.80	48.5	1.51260	.287400
125	1	2.1	7	6.85	61.0	1.90245	.197555
126	1	2.4	7	6.85	69.5	2.16754	.232460
172	1	0.0	4	3.92	1.3	0.04054	-.040544
173	1	0.3	4	3.97	10.5	0.32747	-.027470
174	1	0.6	4	4.02	18.0	0.56138	.038623
175	1	0.9	4	4.02	24.0	0.74850	.151497
176	1	1.2	4	4.00	31.5	0.98241	.217590
177	1	1.5	4	4.00	44.0	1.37226	.127745
178	1	1.8	4	4.00	55.0	1.71532	.084681
179	1	2.1	4	4.10	60.0	1.87126	.228743
180	1	2.4	4	4.00	68.5	2.13635	.263648
253	1	0.3	4	4.00	9.0	0.28069	.019311
254	1	1.2	4	4.08	32.0	0.99800	.201996
255	1	2.4	4	4.08	72.0	2.24551	.154491
256	1	0.3	6	5.75	10.3	0.32123	-.021233
257	1	1.2	6	5.70	31.5	0.98241	.217590
258	1	2.4	6	5.80	71.0	2.21432	.185679

N=42

Appendix, Table 5:

SULFATE ADSORPTION AT DIFFERENT PH VALUES, ACROHUMOX B2

OBS	SAMPLE	SOLUTION	ADJD_PH	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
19	2	0.0	0.0	4.35	0.0	0.00000	0.00000
20	2	0.3	0.0	4.35	1.0	0.03119	0.26881
21	2	0.6	0.0	4.50	3.0	0.09356	0.50644
22	2	0.9	0.0	4.55	6.0	0.18713	0.71287
23	2	1.2	0.0	4.60	11.0	0.34306	0.85694
24	2	1.5	0.0	4.60	17.0	0.53019	0.96981
25	2	1.8	0.0	4.65	24.0	0.74850	1.05150
26	2	2.1	0.0	4.70	33.0	1.02919	1.07081
27	2	2.4	0.0	4.75	42.0	1.30988	1.09012
73	2	0.0	4.3	4.40	0.0	0.00000	0.00000
74	2	0.3	4.3	4.40	2.0	0.06238	0.23762
75	2	0.6	4.3	4.35	2.0	0.06238	0.53762
76	2	0.9	4.3	4.30	5.0	0.15594	0.74406
77	2	1.2	4.3	4.35	9.5	0.29628	0.90372
78	2	1.5	4.3	4.40	14.0	0.43663	1.06337
79	2	1.8	4.3	4.35	19.0	0.59256	1.20744
80	2	2.1	4.3	4.35	25.0	0.77969	1.32031
81	2	2.4	4.3	4.45	58.0	1.80888	0.59112
127	2	0.0	7.0	6.75	15.5	0.48341	-0.48341
128	2	0.3	7.0	6.80	24.5	0.76410	-0.46410
129	2	0.6	7.0	6.85	34.3	1.06974	-0.46974
130	2	0.9	7.0	6.85	42.5	1.32547	-0.42547
131	2	1.2	7.0	6.85	50.5	1.57498	-0.37498
132	2	1.5	7.0	6.90	60.5	1.88685	-0.38685
133	2	1.8	7.0	7.05	69.0	2.15195	-0.35195
134	2	2.1	7.0	6.95	79.0	2.46382	-0.36382
135	2	2.4	7.0	6.85	83.0	2.58857	-0.18857
181	2	0.0	3.5	3.70	1.0	0.03119	-0.03119
182	2	0.3	3.5	3.75	2.5	0.07797	0.22203
183	2	0.6	3.5	3.75	5.0	0.15594	0.44406
184	2	0.9	3.5	3.70	5.0	0.15594	0.74406
185	2	1.2	3.5	3.70	7.0	0.21831	0.98169
186	2	1.5	3.5	3.77	8.0	0.24950	1.25050
187	2	1.8	3.5	3.62	12.0	0.37425	1.42575
188	2	2.1	3.5	3.70	24.0	0.74850	1.35150
189	2	2.4	3.5	3.65	25.0	0.77969	1.62031
226	2	0.0	6.0	5.50	5.5	0.17153	-0.17153
227	2	0.3	6.0	5.70	14.0	0.43663	-0.13663
228	2	0.6	6.0	5.60	19.5	0.60816	-0.00816
229	2	0.9	6.0	5.75	30.0	0.93563	-0.03563
230	2	1.2	6.0	5.95	47.0	1.46582	-0.26582
231	2	1.5	6.0	5.90	47.0	1.46582	0.03418
232	2	1.8	6.0	6.05	64.0	1.99601	-0.19601
233	2	2.1	6.0	6.00	65.0	2.02720	0.07280
234	2	2.4	6.0	5.90	81.0	2.52620	-0.12620
259	2	0.3	6.0	5.70	16.8	0.52395	-0.22395
260	2	1.2	6.0	6.05	42.0	1.30988	-0.10988
261	2	2.4	6.0	5.80	73.5	2.29229	0.10771
262	2	0.3	0.0	4.32	1.0	0.03119	0.26881
263	2	1.2	0.0	4.50	14.5	0.45222	0.74778
264	2	2.4	0.0	4.58	50.5	1.57496	0.82502

N=51

Appendix, Table 6:

SULFATE ADSORPTION AT DIFFERENT PH VALUES, ACRORTHOX AP

OBS	SAMPLE	SOLUTION	ADJD_PH	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
28	3	0.0	0	5.10	0.0	0.00000	.000000
29	3	0.3	0	5.20	4.5	0.14034	.159656
30	3	0.6	0	5.20	13.0	0.40544	.194561
31	3	0.9	0	5.20	21.0	0.65494	.245060
32	3	1.2	0	5.20	31.0	0.96682	.233184
33	3	1.5	0	5.20	42.0	1.30988	.190120
34	3	1.8	0	5.20	51.0	1.59057	.209431
35	3	2.1	0	5.20	57.0	1.77769	.322305
36	3	2.4	0	5.20	65.0	2.02720	.372804
82	3	0.0	6	5.90	0.0	0.00000	.000000
83	3	0.3	6	5.80	8.5	0.26509	.034905
84	3	0.6	6	5.80	17.0	0.53019	.069810
85	3	0.9	6	5.80	25.5	0.79528	.104716
86	3	1.2	6	5.80	33.0	1.02919	.170808
87	3	1.5	6	5.80	42.0	1.30988	.190120
88	3	1.8	6	5.80	48.0	1.49701	.302994
89	3	2.1	6	5.70	58.0	1.80888	.291118
90	3	2.4	6	5.80	64.0	1.99601	.403992
136	3	0.0	7	6.70	0.0	0.00000	.000000
137	3	0.3	7	6.70	6.3	0.19648	.103518
138	3	0.6	7	6.70	14.3	0.44598	.154017
139	3	0.9	7	6.70	22.0	0.68613	.213972
140	3	1.2	7	6.70	31.0	0.96682	.233184
141	3	1.5	7	6.65	39.0	1.21632	.283683
142	3	1.8	7	6.60	48.0	1.49701	.302994
143	3	2.1	7	6.60	55.3	1.72468	.375324
144	3	2.4	7	6.70	60.8	1.89621	.503792
235	3	0.0	4	4.00	1.5	0.04678	-.046781
236	3	0.3	4	4.10	8.0	0.24950	.050499
237	3	0.6	4	4.12	8.0	0.24950	.350499
238	3	0.9	4	4.10	13.0	0.40544	.494561
239	3	1.2	4	4.10	24.0	0.74850	.451497
240	3	1.5	4	4.15	32.0	0.99800	.501996
241	3	1.8	4	4.10	38.0	1.18513	.614870
242	3	2.1	4	4.05	39.5	1.23191	.868089
243	3	2.4	4	4.05	47.0	1.46582	.934182
265	3	0.3	4	4.10	2.5	0.07797	.222031
266	3	1.2	4	4.18	19.8	0.61751	.582485
267	3	2.4	4	4.15	49.0	1.52819	.871806
268	3	0.3	6	5.78	13.0	0.40544	-.105439
269	3	1.2	6	5.82	32.3	1.00736	.192640
270	3	2.4	6	5.90	65.0	2.02720	.372604

N=42

Appendix, Table 7:

SULFATE ADSORPTION AT DIFFERENT PH VALUES, ACRORTHOX B2

OBS	SAMPLE	SOLUTION	ADJD_PH	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
37	4	0.0	0	5.90	0.0	0.00000	0.00000
38	4	0.3	0	6.00	1.5	0.04678	0.25322
39	4	0.6	0	6.10	4.5	0.14034	0.45966
40	4	0.9	0	6.20	10.0	0.31188	0.58812
41	4	1.2	0	6.30	18.0	0.56138	0.63862
42	4	1.5	0	6.30	26.5	0.82647	0.67353
43	4	1.8	0	6.35	34.5	1.07597	0.72403
44	4	2.1	0	6.40	44.0	1.37226	0.72774
45	4	2.4	0	6.40	56.0	1.74651	0.65349
91	4	0.0	6	6.00	0.0	0.00000	0.00000
92	4	0.3	6	5.90	0.0	0.00000	0.30000
93	4	0.6	6	6.10	4.5	0.14034	0.45966
94	4	0.9	6	6.10	9.0	0.28069	0.61931
95	4	1.2	6	6.10	15.0	0.46781	0.73219
96	4	1.5	6	6.10	19.0	0.59256	0.90744
97	4	1.8	6	6.10	24.0	0.74850	1.05150
98	4	2.1	6	6.20	35.0	1.09157	1.00843
99	4	2.4	6	6.10	39.0	1.21632	1.18368
145	4	0.0	7	6.90	1.8	0.05614	-0.05614
146	4	0.3	7	6.90	10.0	0.31188	-0.01188
147	4	0.6	7	6.90	14.5	0.45222	0.14778
148	4	0.9	7	6.95	24.3	0.75786	0.14214
149	4	1.2	7	6.95	31.8	0.99177	0.20823
150	4	1.5	7	7.00	42.5	1.32547	0.17453
151	4	1.8	7	6.95	49.0	1.52819	0.27181
152	4	2.1	7	6.90	56.0	1.74651	0.35349
153	4	2.4	7	6.95	62.5	1.94923	0.45077
190	4	0.0	2	4.60	1.5	0.04678	-0.04678
191	4	0.3	5	4.85	3.0	0.09356	0.20644
192	4	0.6	5	5.00	1.5	0.04678	0.55322
193	4	0.9	5	5.05	1.5	0.04678	0.85322
194	4	1.2	5	5.10	6.5	0.20272	0.99728
195	4	1.5	5	5.25	5.0	0.15594	1.34406
196	4	1.8	5	5.20	10.0	0.31188	1.48812
197	4	2.1	5	5.25	16.0	0.49900	1.60100
198	4	2.4	5	5.25	15.0	0.46781	1.93219
244	4	0.0	4	4.12	0.0	0.00000	0.00000
245	4	0.3	4	4.20	0.0	0.00000	0.30000
246	4	0.6	4	4.15	0.0	0.00000	0.60000
247	4	0.9	4	4.15	0.0	0.00000	0.90000
248	4	1.2	4	4.10	4.0	0.12475	1.07525
249	4	1.5	4	4.15	4.0	0.12475	1.37525
250	4	1.8	4	4.15	4.0	0.12475	1.67525
251	4	2.1	4	4.35	4.0	0.12475	1.97525
252	4	2.4	4	4.40	10.0	0.31188	2.08812
271	4	0.3	4	4.25	3.0	0.09356	0.20644
272	4	1.2	4	4.02	2.5	0.07797	1.12203
273	4	2.4	4	4.45	10.0	0.31188	2.08812
274	4	0.3	0	5.90	3.5	0.10916	0.19084
275	4	1.2	0	6.20	20.5	0.63935	0.56065
276	4	2.4	0	6.30	61.0	1.90245	0.49755

N=51

Appendix, Table 8:

SULFATE ADSORPTION AT DIFFERENT PH VALUES, TROPUDALF AP

OBS	SAMPLE	SOLUTION	ADJD_PH	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
46	5	0.0	0	5.90	0.0	0.00000	.000000
47	5	0.3	0	6.00	9.8	0.30564	-.005639
48	5	0.6	0	5.90	17.0	0.53019	.069810
49	5	0.9	0	5.95	27.0	0.84207	.057934
50	5	1.2	0	5.95	35.0	1.09157	.108433
51	5	1.5	0	5.95	46.0	1.43463	.065369
52	5	1.8	0	5.95	55.0	1.71532	.084681
53	5	2.1	0	5.95	65.0	2.02720	.072804
54	5	2.4	0	5.95	71.0	2.21432	.185679
100	5	0.0	7	6.50	1.8	0.05614	-.056138
101	5	0.3	7	6.45	9.0	0.28069	.019311
102	5	0.6	7	6.45	18.5	0.57697	.023029
103	5	0.9	7	6.50	28.5	0.88885	.011153
104	5	1.2	7	6.50	36.5	1.13835	.061652
105	5	1.5	7	6.50	46.0	1.43463	.065369
106	5	1.8	7	6.50	56.5	1.76210	.037899
107	5	2.1	7	6.50	66.0	2.05838	.041617
108	5	2.4	7	6.50	72.0	2.24551	.154491
154	5	0.0	5	5.20	0.0	0.00000	.000000
155	5	0.3	5	5.20	6.3	0.19648	.103518
156	5	0.6	5	5.15	12.8	0.39920	.200798
157	5	0.9	5	5.25	18.8	0.58633	.313673
158	5	1.2	5	5.25	28.0	0.87325	.326747
159	5	1.5	5	5.20	37.0	1.15394	.346058
160	5	1.8	5	5.20	44.0	1.37226	.427745
161	5	2.1	5	5.20	50.0	1.55938	.540619
162	5	2.4	5	5.25	58.0	1.80888	.591118
199	5	0.0	4	4.50	2.0	0.06238	-.062375
200	5	0.3	4	4.45	5.5	0.17153	.128468
201	5	0.6	4	4.45	11.5	0.35866	.241342
202	5	0.9	4	4.45	20.0	0.62375	.276248
203	5	1.2	4	4.40	25.3	0.78905	.410953
204	5	1.5	4	4.40	39.0	1.21632	.283683
205	5	1.8	4	4.47	38.0	1.18513	.614870
206	5	2.1	4	4.50	53.0	1.65294	.447056
207	5	2.4	4	4.55	57.0	1.77769	.622305
277	5	0.3	4	4.50	5.5	0.17153	.128468
278	5	1.2	4	4.50	28.3	0.88261	.317390
279	5	2.4	4	4.60	64.0	1.99601	.403992
280	5	0.3	0	5.80	12.0	0.37425	-.074251
281	5	1.2	0	5.80	39.0	1.21632	-.016317
282	5	2.4	0	5.85	76.0	2.37026	.029741

N=42

Appendix, Table 9:

SULFATE ADSORPTION AT DIFFERENT PH VALUES, TROPUDALF B2

OBS	SAMPLE	SOLUTION	ADJD_PH	FINAL_PH	S_UGML	SO4_MMOL	SO4_ABD
55	6	0.0	0	6.15	0.0	0.00000	0.00000
56	6	0.3	0	6.20	3.5	0.10916	0.19084
57	6	0.6	0	6.20	11.5	0.35866	0.24134
58	6	0.9	0	6.20	19.0	0.59256	0.30744
59	6	1.2	0	6.20	28.0	0.87325	0.32675
60	6	1.5	0	6.20	36.5	1.13835	0.36165
61	6	1.8	0	6.20	46.0	1.43463	0.36537
62	6	2.1	0	6.20	55.0	1.71532	0.38468
63	6	2.4	0	6.25	65.0	2.02720	0.37280
109	6	0.0	7	6.95	0.5	0.01559	-0.01559
110	6	0.3	7	6.80	6.0	0.18713	0.11287
111	6	0.6	7	6.85	16.0	0.49900	0.10100
112	6	0.9	7	6.80	25.0	0.77969	0.12031
113	6	1.2	7	6.80	34.5	1.07597	0.12403
114	6	1.5	7	6.90	44.0	1.37226	0.12774
115	6	1.8	7	6.90	53.0	1.65294	0.14706
116	6	2.1	7	6.70	59.5	1.85566	0.24434
117	6	2.4	7	6.80	68.5	2.13635	0.26365
163	6	0.0	5	5.15	0.0	0.00000	0.00000
164	6	0.3	5	5.10	1.5	0.04678	0.25322
165	6	0.6	5	5.20	4.5	0.14034	0.45966
166	6	0.9	5	5.25	8.8	0.27445	0.62555
167	6	1.2	5	5.25	13.8	0.43039	0.76961
168	6	1.5	5	5.15	20.5	0.63935	0.86065
169	6	1.8	5	5.25	26.0	0.81068	0.98912
170	6	2.1	5	5.20	32.0	0.99800	1.10200
171	6	2.4	5	5.35	42.0	1.30988	1.09012
208	6	0.0	4	4.50	0.0	0.00000	0.00000
209	6	0.3	4	4.40	5.0	0.15594	0.14406
210	6	0.6	4	4.45	5.5	0.17153	0.42847
211	6	0.9	4	4.40	7.0	0.21831	0.68169
212	6	1.2	4	4.35	8.0	0.24950	0.95050
213	6	1.5	4	4.45	12.0	0.37425	1.12575
214	6	1.8	4	4.50	15.0	0.46781	1.33219
215	6	2.1	4	4.52	23.0	0.71732	1.38268
216	6	2.4	4	4.60	31.0	0.96682	1.43318
283	6	0.3	5	5.25	4.0	0.12475	0.17525
284	6	1.2	5	5.30	20.5	0.63935	0.56065
285	6	2.4	5	5.35	54.0	1.68413	0.71587
286	6	0.3	0	6.05	6.5	0.20272	0.09728
287	6	1.2	0	6.12	32.5	1.01360	0.18640
288	6	2.4	0	6.20	70.0	2.18313	0.21687

N=42

Appendix, Table 10:

ACROHUMOX - AP

ANALYSIS OF VARIANCE TABLE , REGRESSION COEFFICIENTS , AND STATISTICS OF FIT FOR DEPENDENT VARIABLE SO4_ABD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB > F	R-SQUARE	C.V.
REGRESSION	4	0.35823386	0.08955846	19.99038	0.0001	0.68365669	65.38210 %
ERROR	37	0.16576286	0.00448008				
CORRECTED TOTAL	41	0.52399671				STD DEV	SO4_ABD MEAN
						0.06693338	0.10237

SOURCE	DF	SEQUENTIAL SS	F VALUE	PROB > F	PARTIAL SS	F VALUE	PROB > F
SOLUTION	1	0.33472586	74.71431	0.0001	0.00007686	0.01716	0.8965
FINAL_PH	1	0.00848125	1.89310	0.1771	0.02295878	5.12463	0.0295
SOLSQRT	1	0.00042974	0.09592	0.7585	0.00051641	0.11527	0.7361
SOLXPH	1	0.01459699	3.25820	0.0792	0.01459699	3.25820	0.0792

SOURCE	B VALUES	T FOR H0:B=0	PROB > |T|	STD ERR B	STD B VALUES
INTERCEPT	0.18602783	1.87002	0.0694	0.09947887	0.0
SOLUTION	0.01037588	0.13098	0.8965	0.07921143	0.07321097
FINAL_PH	-0.04042922	-2.26377	0.0295	0.01785928	-0.38164092
SOLSQRT	-0.02681660	-0.33951	0.7361	0.07898562	-0.10977673
SOLXPH	0.02243783	1.80505	0.0792	0.01243059	0.88817645

Appendix, Table 11:

ACROHUMOX - B2

ANALYSIS OF VARIANCE TABLE , REGRESSION COEFFICIENTS , AND STATISTICS OF FIT FOR DEPENDENT VARIABLE SO4_ABD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB > F	R-SQUARE	C.V.
REGRESSION	4	17.06831899	4.26707975	135.84198	0.0001	0.92195028	49.00506 %
ERROR	46	1.44495592	0.03141209				
CORRECTED TOTAL	50	18.51327491				STD DEV	SO4_ABD MEAN
						0.17723455	0.36108

SOURCE	DF	SEQUENTIAL SS	F VALUE	PROB > F	PARTIAL SS	F VALUE	PROB > F
SOLUTION	1	3.10863570	98.96305	0.0001	0.81909461	26.07578	0.0001
FINAL_PH	1	12.54464577	399.35731	0.0001	0.91713130	29.19677	0.0001
SOLSORCT	1	0.27918813	8.88792	0.0046	0.22511926	7.16664	0.0103
SOLXPH	1	1.13584939	36.15963	0.0001	1.13584939	36.15963	0.0001

SOURCE	B VALUES	T FOR H0:B=0	PROB > |T|	STD ERR B	STD B VALUES
INTERCEPT	0.96891823	4.28406	0.0001	0.22616818	0.0
SOLUTION	0.97057999	5.10644	0.0001	0.19006961	1.26589102
FINAL_PH	-0.23333487	-5.40340	0.0001	0.04318295	-0.42458643
SOLSORCT	0.50511822	2.67706	0.0103	0.18868401	0.38434933
SOLXPH	-0.17814538	-6.01329	0.0001	0.02962529	-1.28828176

Appendix, Table 12:

ACRORTHOX - AP

ANALYSIS OF VARIANCE TABLE , REGRESSION COEFFICIENTS , AND STATISTICS OF FIT FOR DEPENDENT VARIABLE SO4_ABD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB > F	R-SQUARE	C.V.
REGRESSION	5	2.10375337	0.42075067	61.13421	0.0001	0.89463549	28.98367 %
ERROR	36	0.24776676	0.00688241				
CORRECTED TOTAL	41	2.35152013				STD DEV	SO4_ABD MEAN
						0.08296029	0.28623

SOURCE	DF	SEQUENTIAL SS	F VALUE	PROB > F	PARTIAL SS	F VALUE	PROB > F
SOLUTION	1	1.25281151	182.03093	0.0001	0.18784465	27.29344	0.0001
FINAL_PH	1	0.44082986	64.05167	0.0001	0.25405823	36.91414	0.0001
SOLSQROT	1	0.00532126	0.77317	0.3851	0.01186064	1.72333	0.1976
PHSQROT	1	0.26952618	39.16160	0.0001	0.25875400	37.59642	0.0001
SOLXPH	1	0.13526455	19.65366	0.0001	0.13526455	19.65366	0.0001

SOURCE	B VALUES	T FOR H0:B=0	PROB > |T|	STD ERR B	STD B VALUES
INTERCEPT	11.63552192	6.15303	0.0001	1.89102464	0.0
SOLUTION	0.55268361	5.22431	0.0001	0.10579073	1.84093956
FINAL_PH	2.20291735	6.07573	0.0001	0.36257832	8.77344560
SOLSQROT	0.12870610	1.31275	0.1976	0.09804271	0.24871140
PHSQROT	-10.17607949	-6.13159	0.0001	1.65961450	-8.85405279
SOLXPH	-0.07535244	-4.43324	0.0001	0.01699713	-1.40831691

Appendix, Table 13:

ACRORTHOX - 82

ANALYSIS OF VARIANCE TABLE , REGRESSION COEFFICIENTS , AND STATISTICS OF FIT FOR DEPENDENT VARIABLE SO4_ABD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB > F	R-SQUARE	C.V.
REGRESSION	5	16.78613149	3.35722630	282.36147	0.0001	0.96911053	15.34304 %
ERROR	45	0.53504178	0.01188982				
CORRECTED TOTAL	50	17.32117327				STD DEV	SO4_ABD MEAN
						0.10904044	0.71068

SOURCE	DF	SEQUENTIAL SS	F VALUE	PROB > F	PARTIAL SS	F VALUE	PROB > F
SOLUTION	1	8.51371415	716.05088	0.0001	2.55564054	214.94363	0.0001
FINAL_PH	1	5.04660998	424.44806	0.0001	0.41228082	34.67512	0.0001
SOLSQROT	1	0.14175722	11.92257	0.0012	0.09453153	7.95063	0.0071
PHSQRGT	1	0.69791859	58.69885	0.0001	0.42597736	35.82707	0.0001
SOLXPH	1	2.38613155	200.68698	0.0001	2.38613155	200.68698	0.0001

SOURCE	B VALUES	T FOR HO:B=0	PROB > |T|	STD ERR B	STD B VALUES
INTERCEPT	-14.43164194	-6.07684	0.0001	2.37485880	0.0
SOLUTION	2.00392662	14.66096	0.0001	0.13668472	2.70209246
FINAL_PH	-2.63896533	-5.88856	0.0001	0.44815135	-4.44442040
SOLSQROT	0.32755192	2.81969	0.0071	0.11615897	0.25765559
PHSQROT	12.37448711	5.98557	0.0001	2.06738536	4.48315710
SOLXPH	-0.28983716	-14.16542	0.0001	0.02045947	-2.35504010

Appendix, Table 14:

TROPUDALF - AP

ANALYSIS OF VARIANCE TABLE , REGRESSION COEFFICIENTS , AND STATISTICS OF FIT FOR DEPENDENT VARIABLE SO4_ABD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB > F	R-SQUARE	C.V.
REGRESSION	4	1.27210033	0.31802508	36.69618	0.0001	0.79867748	51.45125 %
ERROR	37	0.32065815	0.00866644				
						STD DEV	SO4_ABD MEAN
CORRECTED TOTAL	41	1.59275849				0.09309370	0.18094

SOURCE	DF	SEQUENTIAL SS	F VALUE	PROB > F	PARTIAL SS	F VALUE	PROB > F
SOLUTION	1	0.48274460	55.70278	0.0001	0.14880325	17.17006	0.0002
FINAL_PH	1	0.63112333	72.82386	0.0001	0.01134187	1.30871	0.2600
SOLSUROT	1	0.01217335	1.40465	0.2435	0.01499620	1.73038	0.1965
SOLXPH	1	0.14605906	16.85342	0.0002	0.14605906	16.85342	0.0002

SOURCE	B VALUES	T FOR H0:B=0	PROB > |T|	STD ERR B	STD B VALUES
INTERCEPT	0.18676024	0.94198	0.3523	0.19826371	0.0
SOLUTION	0.60852396	4.14368	0.0002	0.14685602	2.46292762
FINAL_PH	-0.04012874	-1.14399	0.2600	0.03507790	-0.15619388
SOLSUROT	0.14459041	1.31544	0.1965	0.10991808	0.33949661
SOLXPH	-0.10063626	-4.10529	0.0002	0.02451428	-2.30510989

Appendix, Table 15:

TROPUDALF - B2

ANALYSIS OF VARIANCE TABLE , REGRESSION COEFFICIENTS , AND STATISTICS OF FIT FOR DEPENDENT VARIABLE SO4_ABD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB > F	R-SQUARE	C.V.
REGRESSION	4	6.67874686	1.66968671	163.74082	0.0001	0.94652896	21.91036 %
ERROR	37	0.37729387	0.01019713				
CORRECTED TOTAL	41	7.05604073				STD DEV	SO4_ABD MEAN
						0.10098085	0.46088

SOURCE	DF	SEQUENTIAL SS	F VALUE	PROB > F	PARTIAL SS	F VALUE	PROB > F
SOLUTION	1	2.31004639	226.53884	0.0001	1.19480040	117.17024	0.0001
FINAL_PH	1	2.94771430	289.07239	0.0001	0.00036982	0.03627	0.8500
SOLSQROT	1	0.09727286	9.53924	0.0038	0.09083412	8.90781	0.0050
SOLXPH	1	1.32371329	129.81232	0.0001	1.32371329	129.81232	0.0001

SOURCE	B VALUES	T FOR HO:B=0	PROB > |T|	STD ERR B	STD B VALUES
INTERCEPT	-0.06415521	-0.33137	0.7422	0.19360676	0.0
SOLUTION	1.64944955	10.82452	0.0001	0.15238084	3.17181192
FINAL_PH	0.00629153	0.19044	0.8500	0.03303689	0.01316284
SOLSQROT	0.35568571	2.98460	0.0050	0.11917284	0.39678641
SOLXPH	-0.27032833	-11.39452	0.0001	0.02372647	-3.08243400

Appendix, Table 16:

POTASSIUM AND SULFATE DESORPTION, UNADJUSTED PH

OBS	SAMPLE	SOLUTION	FINAL_PH	K_BSOL	S_BSOL	K_ASOL	S_ASOL	OCCL_SOL	DESD_SO4	DESD_K
310	1	0.0	4.60	48.6	0.3	750	1.0	9.5501	0.04082	1.27556
311	1	1.2	4.60	47.0	0.3	830	33.5	9.4497	-0.15068	0.99917
312	1	2.4	4.70	48.6	0.3	910	55.0	8.5979	-0.24818	1.10637
346	1	0.0	4.70	40.0	0.3	760	2.0	7.8835	0.03695	1.02520
347	1	1.2	4.70	47.0	0.3	810	37.0	8.2354	-0.14328	1.29906
348	1	2.4	4.70	54.0	0.3	890	60.0	9.0749	-0.29285	1.38704
292	2	0.0	4.30	56.6	2.0	720	1.0	14.2884	0.30296	0.98781
293	2	1.2	4.50	64.4	7.0	800	9.3	15.2102	1.00333	1.00559
294	2	2.4	4.70	74.6	11.0	840	41.5	16.5025	1.28814	1.22453
328	2	0.0	4.35	58.0	3.3	760	0.0	15.3853	0.51459	0.71795
329	2	1.2	4.50	64.0	9.2	800	13.0	14.8414	1.31428	1.05547
330	2	2.4	4.60	78.0	14.0	880	47.5	17.2655	1.67059	1.09687
316	3	0.0	5.10	52.0	0.3	730	1.2	11.0651	0.03850	1.25895
317	3	1.2	5.15	56.0	0.3	770	28.0	11.1771	-0.14843	1.37945
318	3	2.4	5.15	60.4	2.0	870	55.0	10.4167	-0.04548	1.54411
352	3	0.0	5.10	53.0	0.3	680	1.0	10.5662	0.04019	1.55115
353	3	1.2	5.20	57.0	0.3	760	24.5	9.9196	-0.10481	1.71639
354	3	2.4	5.15	63.0	0.3	840	49.5	10.5972	-0.23041	1.75150
298	4	0.0	5.80	44.0	0.3	740	1.0	11.6603	0.03951	0.60649
299	4	1.2	6.10	52.0	3.5	800	18.0	12.5686	0.40467	0.75323
300	4	2.4	6.30	61.6	7.0	920	46.7	13.2369	0.70598	0.82405
334	4	0.0	5.75	46.0	0.3	770	0.6	12.5006	0.04210	0.47942
335	4	1.2	6.05	51.0	5.0	830	20.5	12.0540	0.62556	0.70209
336	4	2.4	6.25	56.0	9.0	910	56.5	11.4838	0.99873	0.90766
322	5	0.0	5.70	76.0	0.3	600	2.2	11.7304	0.03068	3.05927
323	5	1.2	5.80	84.4	0.3	640	34.5	11.8323	-0.20784	3.45967
324	5	2.4	5.75	86.0	2.0	760	57.5	10.0820	-0.04972	3.53905
358	5	0.0	5.70	76.0	0.3	590	3.0	10.7849	0.02660	3.23195
359	5	1.2	5.75	83.0	0.3	670	32.3	11.0722	-0.17629	3.40962
360	5	2.4	5.75	92.0	0.3	740	60.0	11.5696	-0.38621	3.69271
304	6	0.0	6.10	79.6	0.3	560	1.5	14.2964	0.03341	3.04195
305	6	1.2	6.10	88.0	1.5	630	26.7	15.6107	-0.02608	3.11132
306	6	2.4	6.10	95.0	5.0	690	60.7	15.4653	0.19415	3.34500
340	6	0.0	6.10	84.0	0.3	540	0.6	16.0941	0.04076	3.14813
341	6	1.2	6.10	96.0	2.7	610	31.0	18.2389	0.06836	3.29265
342	6	2.4	6.10	100.0	7.7	680	60.5	17.0865	0.55593	3.42230

N=36

Appendix, Table 17:

POTASSIUM AND SULFATE DESORPTION, ADJUSTED PH

OBS	SAMPLE	SOLUTION	FINAL_PH	K_BSOL	S_BSOL	K_ASOL	S_ASOL	OCCL_SOL	DESD_SO4	DESD_K
370	1	0.0	4.00	35.0	1.25	740	2.00	7.7141	0.18530	0.77789
371	1	1.2	4.00	41.0	1.80	832	27.50	7.7812	0.14722	0.96574
372	1	2.4	4.00	42.0	4.80	920	63.00	7.1057	0.46927	1.01349
388	1	0.0	4.00	36.0	0.75	720	4.50	7.2053	0.09673	0.97498
389	1	1.2	4.00	40.0	3.13	776	28.50	7.5638	0.35362	1.05639
390	1	2.4	4.03	43.0	5.00	888	65.25	7.2880	0.48307	1.09418
373	2	0.0	4.07	54.0	2.80	740	3.00	14.5610	0.40938	0.69690
374	2	1.2	4.02	57.0	8.75	820	6.00	13.3838	1.31437	0.83767
375	2	2.4	4.00	62.0	13.20	920	27.50	13.4178	1.82822	0.80706
391	2	0.0	4.08	53.0	3.13	758	5.00	13.9749	0.44450	0.67955
392	2	1.2	4.05	62.0	8.75	854	5.50	15.4699	1.31138	0.58535
393	2	2.4	4.05	62.0	13.20	888	31.00	13.2712	1.60176	0.95017
376	3	0.0	4.03	36.0	0.25	800	1.50	8.6099	0.03374	0.49925
377	3	1.2	3.97	43.0	5.00	800	13.38	9.9374	0.69675	0.71613
378	3	2.4	4.10	49.0	7.80	888	44.25	9.5962	0.95145	0.95360
394	3	0.0	4.02	40.0	0.00	758	1.00	9.7101	-0.00606	0.67513
395	3	1.2	4.02	42.0	4.75	854	18.00	8.5225	0.64502	0.82399
396	3	2.4	4.07	47.0	8.20	888	50.25	8.6486	1.00761	1.04093
295	4	0.0	3.98	42.6	0.30	780	1.50	13.0437	0.03458	0.12172
296	4	1.2	3.90	46.0	2.50	860	4.30	12.8298	0.35543	0.11928
297	4	2.4	4.05	48.6	8.00	940	4.00	11.6729	1.21838	0.30114
331	4	0.0	4.05	45.0	0.30	810	1.90	13.7702	0.03046	0.02459
332	4	1.2	4.10	46.0	4.30	870	1.50	12.5987	0.65874	0.13789
333	4	2.4	4.10	54.0	11.30	950	4.00	13.4660	1.72850	0.18090
382	5	0.0	4.22	64.0	0.25	684	2.00	10.5109	0.02587	2.25334
383	5	1.2	4.20	66.0	3.75	780	21.50	9.5830	0.45625	2.30825
384	5	2.4	4.27	73.0	7.60	784	58.50	9.6031	0.83471	2.74199
400	5	0.0	4.20	60.0	0.00	666	3.50	9.9604	-0.02174	2.13974
401	5	1.2	4.20	64.0	3.75	740	23.25	8.9948	0.45432	2.36973
402	5	2.4	4.32	75.0	7.60	814	55.25	10.5812	0.82047	2.59256
385	6	0.0	4.02	66.0	0.00	684	5.00	14.0296	-0.04375	1.76567
386	6	1.2	4.00	75.0	4.50	740	2.25	15.0473	0.68060	1.94757
387	6	2.4	4.00	86.0	10.20	768	13.50	15.5993	1.45921	2.43472
403	6	0.0	4.10	68.0	0.00	616	3.50	13.2883	-0.02901	2.25432
404	6	1.2	3.98	73.0	4.00	720	1.75	13.2622	0.60927	2.22537
405	6	2.4	4.10	82.0	9.70	800	16.00	14.1684	1.37119	2.34406

N=36