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# SULFATE RETENTION AND RELEASE IN SIX EASTERN SOILS

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By

Nancy Joan Hayden

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Civil and Environmental Engineering

#### ABSTRACT

# SULFATE RETENTION AND RELEASE IN SIX BASTERN SOILS

By

#### Nancy Joan Hayden

Adsorption/desorption experiments were conducted to determine the capability of six different eastern soils for retaining and releasing sulfate. Batch and column, adsorption and desorption experiments were used to study sulfate equilibrium in soils. Kinetic studies were also performed.

Fitting common adsorption models to batch isotherm data was explored. Nonlinear regression techniques proved superior to traditional linear transformation techniques. The use of models which accounted for native sulfate were necessary since experiments were conducted at low solution concentrations. The extended Freundlich and a new model, the extended Langmuir proved highly successful.

Equilibrium in the batch studies was comparable to equilibrium in the column studies. Kinetic studies revealed that a one hour shaking time was sufficient to reach equilibrium. Desorption was largely reversible, however in certain soils, sulfate was released more slowly.

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## INTRODUCTION

The increase in the combustion of fossil fuels in the past several decades, has led to the increased release of sulfur and nitrous oxides into the atmosphere. The problem of acid rain has been the result. Acid rain is the term used to describe precipitation that due to components such as sulfuric and nitric acid has become acid in nature. The pH of rain water in parts of the United States has been recorded below 4 (EPA Technical Report, 1980).

Rain has always been on the acid side of the pH scale due to the reaction of carbon dioxide and water in the atmosphere. This produces carbonic acid. Volcanic eruptions and forest fires are natural contributors to the acid forming components of rain. The advent of industrialization and the large increases in anthropogenic sulfur and nitrous oxides released into the atmosphere have been the main causes for the widespread problem known as acid rain.

With the concern of local air pollution problems, industry was motivated to build taller smokestacks. The acid forming components of acid rain are now sent higher into the atmosphere, changing acid rain from a local problem to one that travels over state and international

boundaries.

In mountainous areas, where soils are generally thinner and lakes are poorly buffered, the effects of acid rain have been devastating. A decrease in pH of a mountain lake can result in the killing of fish eggs, frogs eggs and other life forms of the aquatic community. It is thought that at low pH, failure occurs in the reproductive cycle of many fish and other aquatic organisms. Other contributing factors to the death of a lake may be the leaching of toxic metals, such as aluminum, from soils into the groundwater. Eventually the toxic components make their way into streams and lakes. Acidic spring thaws have resulted in large fish kills.

The extent of change in acidity is determined mainly by the buffering capability of the surrounding watershed. The soil and its characteristics are important considerations in understanding the effect of acid rain on streams and lakes. Acid rain causes additional inputs of anions, the major one being sulfate. The subsequent movement of sulfate through the soil is of major concern, since the movement of an anion must also be accompanied by an associated cation. This maintains the electroneutrality of the soil solution. Associated cations include H<sup>+</sup>, important nutrients such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and metals such as aluminum. The increased movement of H<sup>+</sup> is what causes a decrease in pH of water bodies. Movement of important nutrients from the top layers of the soil can cause

deficiencies for plants and organisms residing there. Soluble aluminum that eventually reaches lakes and streams can be toxic to fish and other aquatic organisms.

It is for these reasons that the mobility of sulfate in the soil is so very important. The retention and release of sulfate in soil may be due to different processes. Included in these, are microbial transformations, plant uptake and decomposition, and physical and chemical sorption processes. Inorganic sulfur compounds such as inorganic sulfate may accumulate in soils by means of sulfate adsorption. Some theories suggest that sulfate adsorption may provide a net sink for increased anthropogenic inputs of sulfur (Johnson et al. 1982). In order to determine if this is true, it is necessary to understand the adsorption and desorption processes of sulfate with soil. It is in this area, that this research has been conducted.

#### THEORY AND BACKGROUND

# Soil Phase

This section is provided as an introduction to some of the important characteristics of soils as they relate to sulfate adsorption and desorption.

There are four basic components to the soil. These are inorganic particles, decaying organic matter, air and water. The larger mineral particles have associated with them colloidal and fine materials. The type of soil, whether it is considered a sandy soil or clay soil depends on the ratio of the mineral particles to colloids. Mineral components, such as sand and silt, are generally quartz (SiO<sub>2</sub>) in nature. Clays are generally colloidal.

The most active part of the soil, in the physicochemical sense are those materials in the colloidal state. The organic colloids are broadly classified as humus. Organic colloids will not be discussed here.

Inorganic colloids are clays. There are two general types of clays; silicate clays are generally associated with the temperate regions, and aluminum and iron hydrous oxide clays are commonly found in the tropics and semitropics. Clays are generally characterized by large

external and often internal surface areas.

The silicate clays are broadly classified into three groups; kaolinite, montmorillonite and illite. Kaolinite clay particles are platelike. An octahedral aluminum sheet and a tetrahedral silica sheet are held together by oxygen atoms. These units are bound together by oxygen hydroxyl linkages. This makes the lattice fixed with virtually no expansion taking place upon wetting. The effective surface is the external surface only, since cations and water cannot enter between the structural units. This is called a 1:1 crystal type lattice.

Montmorillonite clay consists of two tetrahedral silica sheets and one octahedral aluminum sheet bound together by oxygen atoms. This is called a 2:1 lattice. The oxygen-oxygen linkages are fairly weak, which allows expansion upon wetting. Cations and water are also able to move in between the sheets, allowing for both internal and external surfaces.

The hydrous micas, of which illite is a member, are similar to montmorillonites except that 15% of the silicon has been replaced by aluminum. The valences that are vacated due to this replacement are satisfied by potassium. In effect, this makes a more stable crystal. In cation adsorption, swelling, hydration, and shrinkage, illite excels kaolinite, but is less than montmorillonite.

Iron and aluminum hydrous oxide clays are the other important clay group. Gibbsite is a common iron hydrous

oxide and goethite is a common aluminum hydrous oxide. Iron and aluminum oxides are the dominate clays in the tropics and semitropics. In temperate regions, they are often intermixed with the silicate clays.

Both the silicate and hydrous oxide clays carry a negative charge. The negative charge in silicate clays can be due to unsatisfied valences at broken edges of sheets, which is pH dependent, and/or ionic substitution of Al<sup>3+</sup> and Si<sup>4+</sup> by cations of lower valence. In hydrous oxides, charge is pH dependent. The zero point of charge is the pH value at which the oxide surface is electrically neutral. At pH values greater than this, the surface charge is negative and below this, the charge is positive.

The negative charges of the clay colloid particles attract cations to them. This creates a situation that is often called a diffuse double layer or electric double layer. The cations attain a state of minimum energy and maximum entropy. This means that there exists a situation of high concentration of cations near the surface of the particle which diminishes at farther distances from the particle. At low liquid content, the double diffuse layer becomes truncated. This leads to a tendency to reabsorb water until it has become fully extended. There is a large amount of water associated with this layer of cations.

A brief mention should be made at this point, of the soil profile. The layers of soil are referred to as horizons. Different soils are characterized by a certain

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sequence of horizons. The major subdivisions of the soil profile are grouped under O, A, B and C horizons.

The O group are organic horizons. The A group represents the topmost mineral horizon but still contains substantial organic matter. The B group, includes the region of maximum accumulation of materials such as iron and aluminum oxides and silicate clays. Organic matter is also present, generally in the form of humus. Horizon C is outside the zone of major biological activity and least weathering. It may contain an accumulation of calcium and magnesium carbonates. Further subgroups may occur within each horizon. Each soil has its own characteristic soil profile and not all horizons are always present.

# Adsorption Mechanisms

Hingston et al.(1967) divided anion adsorption into two types, nonspecific and specific. Nonspecific adsorption describes the binding of an anion by electrostatic forces in that area of the diffuse double layer called the outer Hemholtz plane. The anion is held as a counter ion next to cations in the diffuse double layer. The inner Helmholtz plane of the diffuse double layer is defined as that area of the layer where adsorbed ions are bound by covalent or van der Waals forces or both. These are termed ligand exchanged ions or specifically adsorbed ions. Specific adsorption involves the displacement of existing ions on the surface.

Since nonspecific adsorption is based on the charge of the particle, it is pH dependent. As the pH decreases, hydrogen ion concentration increases in the bulk solution. Increased adsorption of hydrogen ions on the colloidal surface results in a net positive charge. Sulfate adsorption is possible. Nonspecific adsorption is characterized by electrostatic forces. Because of this, sulfate is not as tightly bound as the adsorbed sulfate described by specific adsorption.

It is generally accepted that specific adsorption occurs by displacing OH- ions of iron and aluminum hydrous oxides with another anion. Chao et al.(1965), Cuoto et al.(1979), and Rajan (1978) showed that an increase in sulfate adsorption results in an increase in pH or OHconcentration. This indicates the substitution of OH- by sulfate on the surface of the oxides.

Specific adsorption mechanisms have been proposed by various researchers (Hingston et al. 1967, Hingston et al. 1974, Harward and Reisenauer 1966, Parfitt and Smart 1978). The formation of a ring with two iron or two aluminum atoms and one sulfate has been explained in detail (Rajan 1978, Parfitt and Smart 1978). The ring formations are shown on the following page.



# 2.) Parfitt and Smart 1978



Using infrared techniques, Parfitt and Smart (1978) have shown that sulfate displaces hydroxyl and aquo groups at the surface of iron oxides. They found that the reaction will not occur at pH greater than 8.0. They postulated that it must be necessary for some of the OH- groups to become protonated before an exchange with sulfate can take place.

### Soil Characteristics

I. pH

Soil pH can greatly affect the adsorption capacity of soils. As mentioned previously, pH plays an important role in nonspecific adsorption. Decreasing the pH increases the net positive charge of a soil particle, allowing anions to adsorb. As for specific adsorption, protonation of the hydroxyl groups of iron and aluminum oxides is believed to be necessary to allow specific adsorption to take place (Parfitt and Smart 1978, and Rajan 1978).

Soil pH as related to sulfate adsorption has been studied by numerous researchers (Kamprath et al. 1956, Chao et al. 1963, 1964, Harward and Reisenauer 1966, Barrow et al. 1969, Barrow 1970, Elkins and Ensminger 1971, Gebhardt and Coleman 1974, Cuoto et al. 1979, and Singh 1984c).

It is difficult to quantify the effect of pH on sulfate adsorption because of the complex nature of soil and the various ways in which pH can affect the other parameters important for sulfate adsorption to occur. However, for most soils there is at least a small increase in sulfate adsorption as a result of decreasing pH.

Chao et al. (1963) found that two less sulfate retentive soils exhibited only a gradual increase in sulfate adsorption with increasing acidity, while the more sulfate retentive soils showed a more drastic increase in sulfate adsorption with decreasing pH. The more retentive soils also had higher iron and aluminum oxides and amorphous material in the soil. Volcanic ash derived soils, all having large sulfate adsorption capacity, also showed a large increase in sulfate adsorption with decreasing pH (Gebhardt and Coleman 1974).

Conversely, there is a relationship between pH and desorption. Elkins and Ensminger (1971) saw a three fold increase in sulfate in the soil solution when the pH increased from 5.0-5.5. A 17 fold increase in desorption was observed when the pH was raised from 5.0-7.6.

# II. Iron, Aluminum, Organic Matter and Clay Content

Iron and aluminum are present in the soil in various forms. They can be present in clay and silt materials, in organic matter, as iron and aluminum oxides, as metal cations or as soluble metal species at low pH. Iron and aluminum oxide content generally increases the soils ability to adsorb sulfate (Chao et al. 1962, 1963, Parfitt and Smart 1978, Rajan 1978, Cuoto et al. 1979, Singh 1980 and Johnson and Todd 1983).

Chao et al. (1964) coated soils with aluminum and iron. He found an increase in sulfate adsorption on less sulfate retentive soils after they had been coated. In aluminum coated soils, there was a maximum adsorption point at a pH of 4.0, but there was no such maximum for iron.

Maximum adsorption points have not been observed in natural soils, possibly due to the fact that both iron and aluminum oxides are present.

Attempts have been made to determine which forms of iron and aluminum oxides have the most sulfate adsorption capacity. Non-amorphous iron oxides were most closely correlated to adsorbed sulfate in a study by Johnson and Todd (1983). Parfitt and Smart (1978) noted greater sulfate adsorption on amorphous iron oxides than on more highly crystalline forms. Dithionite citrate extractable iron and aluminum had a significant positive correlation with sulfate adsorption (Singh 1980). Fuller et al. (in press) found that crystalline iron was most highly correlated with insoluble sulfate for Adirondack soils. although only a few samples indicated its presence. They found at a New Hampshire site, that insoluble sulfate was significantly correlated with all dithionite oxalate, pyrophosphate extractable and crystalline iron and aluminum fractions. Aluminum was more highly correlated than iron.

The difficulty in determining which form has the most sulfate adsorption capacity arises not only from the differences in the soil samples but also in the analytical extraction techniques used. They are not always discriminating enough in their separations. Johnson and Todd (1983) noted there can be considerable overlap in the extractions.

High iron and aluminum oxide content in the soil does

not always mean that the adsorption capacity will be high, since other soil characteristics appear to exert an influence on adsorption. Organic matter has been negatively correlated with sulfate adsorption (Singh 1980). Surface soils high in iron and aluminum oxides, but also high in organic matter, exhibit very little sulfate adsorption capacity. Deeper subsurface layers, low in organic matter and high in iron and aluminum oxides, have a large sulfate adsorption capacity (Johnson and Henderson 1979, Johnson et al. 1979b, Singh et al. 1979, and Singh et al. 1980). The organic matter near the soil surface may be coating the iron and aluminum oxide sites, making them unavailable to sulfate (Singh 1984b). By repeated oxidation. Singh (1984b) removed the organic matter from the soil and found that there was an increase in sulfate adsorption.

The relationship between clay content and sulfate adsorption has also been studied (Aylmore et al. 1967, Kamprath et al. 1956, Chao et al. 1962). Chao et al. (1962) used relatively pure clays; a kaolinite, an illite and a montmorillonite. The results suggest that sulfate adsorption is not directly related to surface area, since the kaolinite showed greater adsorption than that of the illite or montmorillonite clays. The illite showed greater adsorption than that of the montmorillonite. This is opposite to the order of known surface area for these clays.

Kamprath et al. (1956) found that soils which contained predominately 1:1 clay types adsorbed more than those containing 2:1 types. Qualifying this, it was pointed out that soil with predominately 1:1 type clays also have associated with them larger amounts of free iron and aluminum oxides.

It is quite obvious that it is difficult to discern the effects that a certain soil characteristic has on sulfate adsorption due to interferences from other characteristics. Aylmore et al. (1967) attempted to rectify this problem by looking at pure or nearly pure substances. In this study, 2 clays were used, API-9 kaolinite and clackline kaolinite. In the laboratory, pseudoboehmite ( $\gamma$ -Al<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O) with some gibbsite and haematite  $(\alpha - Fe_3O_3)$  were synthesized. It was found for each clay that there were two distinct regions of adsorption. They concluded that there were two energetically different sites available. The amount adsorbed for the synthesized iron and aluminum oxides was much greater that that of the clay. Adsorption maxima of 84.2, 13.4, 1.86, 1.0 me/100g were noted for the pseudoboehmite, haematite, API-9 kaolinite and clackline clay respectively.

#### III. Competition among soil anions

There are many anions present in the soil besides sulfate. Phosphate, nitrate and chloride are also present

to mention a few. Competition for adsorption sites among different species is a common occurrence.

The effects of 20 different organic and inorganic anions on sulfate adsorption was investigated by Chao et al. (1964). They found with the exception of acetate, arsenite, borate, chloride, nitrate and silicate, the remaining anions depressed sulfate adsorption. This inhibition of sulfate adsorption varied depending on the anion, concentration of the anion in solution and soil properties.

Kamprath et al. (1956) noted that an increase in phosphate concentration decreased sulfate adsorption by soils. Harward and Reisenauer (1966) explained the displacement of sulfate from upper soil horizons that had recieved applications of phosphate fertilizer to be caused by the greater ability of phosphate over sulfate to replace aquo, or hydroxyl groups on the hydrous oxide surface. This is the reason that phosphate extracting solutions are used for measurement of soil sulfate.

Aylmore and Karim (1967; unpublished data from Murali and Aylmore, 1983) looked at the competition of adsorption sites on kaolinite clay and two oxides by sulfate and phosphate. By performing sulfate adsorption isotherms with different amounts of phosphate in the solutions, it was found that at all solution concentrations there was a reduction in sulfate adsorption.

Kinjo and Pratt (1971) studied anion competition of

chloride, nitrate, sulfate and phosphate in soils from Hawaii, Mexico and South America. When nitrate and sulfate solutions were added to the soils, sulfate adsorption increased and nitrate adsorption decreased. In a similar test with phosphate and nitrate, phosphate was greatly preferred over nitrate. Chloride showed only a slight preference over nitrate. This is important in understanding the effects of fertilizer applications and acid rain. If sulfate is retained in soils, it may be replacing nitrates and chlorides in the soil. These mobile anions will result in an increase in mobile cations in order to maintain the electroneutrality of the leachate (Johnson and Cole 1977). Problems with acidified ground and surface waters as well as aluminum transport may still result even if sulfate is retained.

Khanna and Beese (1978) in the laboratory, found that in undisturbed soil columns, sulfate concentration in the leachate showed a decrease when a slug of neutral salt was applied to the columns. The decrease of sulfate concentration corresponded to an increase in hydrogen ions and chloride concentration in the leachate.

Adsorption played a major role in regulating phosphate movement, a lesser role in sulfate movement and no role in nitrate or chloride movement in in a study involving wastewater-irrigated soil (Johnson et al. 1979a).

The significance of understanding the competition among anions in the study of acid rain is often overlooked.

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Although sulfate may be a stronger competitor and be retained in the soil, this may not significantly decrease the effects of the increase input of anion species into the soil. Leaching of other anions and associated cations may be the result.

# IV. Effect of soil cations

The presence and amounts of certain cations in the soil can also affect sulfate adsorption. Chao et al. (1963) found that soils saturated with different cations showed differing amounts of sulfate adsorption. Increasing sulfate adsorption in the presence of cations, followed the order of  $Al^{3+}>Ca^{2+}>K^+$ . Thus, the use of sulfate from different compounds, ie. K<sub>2</sub>SO<sub>4</sub> or MgSO<sub>4</sub>, may yield different results.

# **Experimental Considerations**

#### I. Soil preparation

For convenience, most researchers have used air dried soil, sifted through a 2mm mesh screen and stored in air tight containers (Kamprath et al. 1956, Barrow 1970, Hague and Walmsley 1973, Barrow and Shaw 1977, Cuoto et al. 1978, Johnson et al. 1979, Singh et al. 1979, Singh 1980, Johnson et al. 1982, Johnson and Todd 1983, and Singh 1984). Oven dried samples have been used by Barrow et al. (1969) and Gebhardt and Coleman (1974). Oven drying has not been used as frequently because it can drastically change the characteristics of the soil. Air drying can also cause changes in the soil. Bartlett and James (1980) studied drying and storage of soil samples. They found that air drying caused organic matter to solubilize and oxidize. It also caused changes in surface chemistry properties, which included increased surface acidity and reduced manganese. It was also found that changes continued, the longer the soil was stored. Rewetting of dried soil can cause problems resulting from increase biological effects.

Freezing can also have adverse effects, although they are probably less severe than those of drying. Whenever possible, the use of field moist samples are recommended. Hasan et al. (1970) used field moist samples in studies on sulfate sorption in Hawaiian soils.

# II. Method of mixing

Recently the question of method of mixing has come under scrutiny. In a study by Barrow and Shaw (1979), phosphate adsorption using three different mixing techniques were compared. They included a roller, reciprocating and an end-over-end shaker. Using the reciprocating shaker showed greater phosphate adsorption than the end-over-end or the roller for the same soil and experimental conditions. The conclusion reached was that more particle breakdown occurred when using the reciprocating shaker. This breakdown opened up more

adsorption sites, which increased the total amount of phosphate adsorbed. No similar study for sulfate adsorption was found but it might be reasonable to assume that similar results would occur for sulfate adsorption as well.

The method of mixing is rarely stated in the literature dealing with sulfate adsorption, with the exception of Barrow (1970), who used a reciprocating shaker and Nor (1981) who used an orbital shaker. Chao et al. (1965) used a mechanical shaker. This is a small but important detail that is very rarely considered. It appears that the method of mixing is another experimental technique that can cause a difference in results.

# III. Soil:solution ratios

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It is evident that the soil:solution ratio is an important consideration in any batch isotherm experiment. A soil:solution ratio effect or a solids effect has been noted in phosphate adsorption studies (Hope and Syers 1976, Barrow and Shaw 1979) and in other systems, such as hydrophobic pollutants in Lake Michigan sediments (Voice and Weber 1985). Generally research using sulfate adsorption isotherms has been done using a soil:solution ratio of 1:5, although no reasons have been given as to why this ratio was selected. Research on solids effect for sulfate adsorption was looked at by Barrow (1967). No solids effect was observed.

# IV. Equilibrium time

Since batch isotherms are based on the fact that equilibrium has been reached, it is necessary to insure that this is true. Chao et al. (1962) looked into equilibrium time by continuously shaking the soil for different lengths of time, up to 72 hours. It was found that equilibrium was reached in four hours, and that after one to two hours there was no difference between intermittent and continuous shaking. The scheme of shaking that was used was to shake for one hour, leave samples overnight, and shake for one hour the next day. Singh (1980) also found that this scheme gave identical results to continuous shaking for eight hours, in which time equilibrium was reached. Hague and Walmsley (1973) also used this procedure. Others have shaken continuously for 24 hours in order to reach equilibrium (Barrow et al. 1969, Cuoto et al. 1979). Gebhardt and Coleman shook samples for one hour only.

# V. Analysis method

There have been a wide variety of techniques used for sulfate analysis. This has made it difficult to compare quantitatively among different studies, since each analytical technique brings with it, its own bias.

Sulfur<sup>35</sup> tagged sulfate has been widely used by many researchers (Chao et al. 1962-1964, Barrow and Shaw 1977,

Hasan et al. 1970, Rajan 1979, Sanders and Tinker 1975, Singh 1980,1984). One of the questions arising from this method is whether there is a difference between the exchange behavior of sulfur<sup>35</sup> labelled sulfate and nonlabelled sulfate.

Other methods of sulfate analysis include bariumchloranilate colorimetry (Richter et al. 1983, Johnson and Henderson 1979, Khanna and Beese 1978), and turbidimetric determination (Kamprath et al. 1956). Johnson et al. (1979) and Johnson et al. (1980) used a Technicon Autoanalyzer for sulfate analysis. More recently, ion chromatography has been used for sulfate determination (David et al. in press). Ion chromatography is the most reliable method for analyzing sulfate over a broad range of soil solution conditions (Sawicki et al. 1978, Mulik and Sawicki 1979).

### Adsorption Models

An adsorption isotherm is the plot of the solid phase equilibrium concentration  $(q_{\bullet})$  vs. the solution equilibrium concentration  $(C_{\bullet})$ . The common method for obtaining  $q_{\bullet}$  is called the difference technique. The difference between the initial solution concentration and the solution concentration at equilibrium is used to calculate the amount of adsorption by the solid phase. By varying the original solution concentration, a number of points are obtained and plotted. This results in an adsorption

isotherm.

Numerous adsorption models have been presented over the years in an effort to describe adsorption data. Several of those pertinent to sulfate adsorption will be discussed here.

I. Freundlich model

The Freundlich equation is probably the oldest adsorption equation. It is shown below.

 $q_{\bullet} = K_f C_{\bullet}^{1/n}$ 

where:  $q_e$  is the solid phase concentration  $C_e$  is the equilibrium solution concentration  $K_f$  and 1/n are constants

Although the equation is empirical in origination, much work has been done in an attempt to relate the constants to something real. It is thought that the  $K_f$  term is related to adsorbent capacity and the exponential 1/n term is an indicator of intensity of adsorption.

The Freundlich equation has been widely used in describing adsorption data. Due to the exponential form, it does not describe an adsorption maximum. The general shape of the curve is depicted in Figure 1.

Traditionally, use of this equation has involved transforming it to a linear expression. Taking the log of both sides, reduces the equation to:

 $\log q_{\bullet} = \log K_f + 1/n \log C_{\bullet}$ 


Plotting log  $q_{\bullet}$  vs log C<sub> $\bullet$ </sub> results in a straight line, which has a slope of 1/n and a y-intercept of log K<sub>f</sub>.

Barrow (1978) discussed problems with the transformation of data in this way. Values of low concentration are given a high weighting in this method. Another problem is that the equation does not take into account any native sulfate present in the soil. Fitter and Sutton (1975) extended the Freundlich equation in their study of phosphate adsorption by including a constant which would account for native phosphate in the soils. The resulting equation is shown below.

 $q_{\bullet} + a = K_f C_{\bullet}^{1/a}$ 

This equation was used in a study by Singh (1984a) to fit various models to sulfate adsorption. He concluded that it was not as effective as the Freundlich in fitting the data. Mead (1981) used the Fitter and Sutton (1975) extended Freundlich equation for phosphate adsorption data in soil from New South Wales and found it to be the most effective in describing phosphate adsorption.

Sibbesen (1981) proposed an empirical equation, where the "shape governing" parameter, 1/n, was replaced by a "shape governing" term,  $1/nC_{\bullet}$ . It takes the form,

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 $q_{\bullet} = K_f C_{\bullet}^{1/ac_{\bullet}}$ 

He found that this equation gave a slightly closer fit than the Fitter and Sutton (1975) model.

## II. Langmuir model

The Langmuir equation was originally derived to describe adsorption of gases onto smooth solids. It may be deduced theoretically from either the kinetics or thermodynamics of adsorption. The model describes single layer adsorption. Its application to solid liquid systems, especially a solid as heterogeneous as soil, has been in question by researchers (Veith and Sposito 1977, Barrow 1978). The Langmuir equation is presented below.

$$q_{\bullet} = \frac{Q_{\bullet} b C_{\bullet}}{(1 + bC_{\bullet})}$$

where: q. is the solid phase equilibrium concentration C. is the equilibrium solution concentration Q. is the ultimate adsorption capacity b is an energy constant

Graphically, it is depicted in Figure 2.

Linear transformation of the data is also common when using the Langmuir equation. The two general transformations are the double reciprocal and the reciprocal. Both are presented on the following page.



Figure 2. General Langmuir curve.

Double reciprocal transformation

$$1/q_{\bullet} = 1/Q^{\bullet} + (1/bQ^{\bullet})(1/C_{\bullet})$$

If  $1/q_e$  is plotted vs  $1/C_e$ , the slope of the resulting line is  $1/bQ^e$  and the intercept is  $1/Q^e$ .

Reciprocal transformation

$$C_{\bullet}/q_{\bullet} = 1/bQ^{\bullet} + C_{\bullet}/Q^{\bullet}$$

If  $C/q_{\bullet}$  is plotted against  $C_{\bullet}$ , the slope of the resulting line is  $1/Q^{\bullet}$  and the intercept is  $1/bQ^{\bullet}$ . Other transformations have also been used.

Different parameter estimates will be obtained depending on the linear transformation used. The appropriate linear form may vary between data sets. Aylmore et al. (1967) found that adsorption isotherms for both aluminum and iron oxides synthesized in the laboratory obeyed a Langmuir type equation over an initial concentration range of 1 meq/l to 100 meq/l of  $K_2SO_4$ . Often times, however, the single layer adsorption model does not appear to fit the data well. Due to the fact that soil is a heterogeneous substance, it seems possible that a model describing single layer adsorption with only one energy of adsorption might not fit the data. As a result, researchers have applied two-surface equations to adsorption data (Barrow 1978, Mead 1981). The two surface equation or double Langmuir equation may be written as follows:

$$q_{\bullet} = \frac{Q_1 b_1 C_{\bullet}}{(1+b_1 C_{\bullet})} + \frac{Q_2 b_2 C_{\bullet}}{(1+b_2 C_{\bullet})}$$

where all terms have the same meaning as before, except that the different subscripts describe different adsorption energies. Barrow (1978) found that the two surface Langmuir model fit the data better than the one surface model even considering the greater number of coefficients that needed to be estimated. Mead (1981) also compared the two surface and one surface Langmuir model. He concluded that the one surface Langmuir equation was the least suitable for predicting phosphate adsorption.

Sibbesen (1981) modified the Langmuir by including another constant term, D. The proposed equation is empirical in nature.

All terms are as previously described. The Sibbesen Langmuir model was better at predicting the data than either the two surface Langmuir or the Langmuir but was not as good as the Freundlich equations previously described according to the study by Sibbesen (1981). Although the idea of a native sulfate term was discussed using the Freundlich equation, as in the Fitter and Sutton (1981) model, it could not be found for the Langmuir equation. It seems reasonable to assume that a better fit could be obtained using the Langmuir equation, if a term was added to account for the native sulfate in the soil, or whatever the species of interest is. This extended Langmuir equation is presented below.

All terms are as previously described, except the (a) term is used to describe the amount of species of interest already present in the soil.

## III. Nonlinear regression

Traditionally, fitting a model to the data was determined by transformation of the adsorption data to a linear scale. The problems of deriving constants from linearly transformed data is beginning to be discussed in the literature (Barrow 1978, Kinniburgh 1986). With the advent of computer programs that perform nonlinear regression on adsorption data, linear transformation of data is no longer necessary and in fact is often unsuitable for determining models that best fit the data.

The main problem with linear transformations is that it does not give proper weighting to each observation. The

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Langmuir transformation tends to weight low  $q_{\bullet}$  observations more than high  $q_{\bullet}$  observations (Kinniburgh 1986).

Singh (1982) used nonlinear regression to determine parameter and least squares estimates of parameters for five adsorption equations. These were the Freundlich, the extended Freundlich, the Langmuir, the Sibbesen Freundlich and the Temkin. Singh concluded that the Freundlich proved superior to all other equations for data that were uncorrected (isotopically exchangeable sulfate was included). For two of the soils in the corrected data, the Langmuir equation proved better.

In conclusion, it should probably be emphasized that there is no concensis on which model is best. The "goodness of fit" determination is often complicated by error introduced by using various curve fitting procedures. There is increased evidence to support the use of nonlinear regression analysis in fitting various models to isotherm data. Although this has not been used often in the past, this was due mostly to lack of computer algorithms that could easily perform nonlinear regression analysis. New programs are now available that allow researchers to quickly and easily use nonlinear regression analysis.

The extended models have not been considered in depth in the past literature. This is probably because many studies were carried out at high concentrations. At lower concentrations, like those that might be obtained in the field, the extended models may prove more useful.

#### **EXPERIMENTAL WORK**

As mentioned previously, the importance of sulfate retention and release in soils is crucial for the understanding of the acidification process in natural surface waters. There are numerous ways in which sulfate can be retained in the soil. These include microbial transformations of inorganic sulfate to organic sulfur compounds, plant uptake of soluble sulfates and plant decay, precipitation reactions of sulfate and physical/chemical sorption processes.

As part of the Environmental Protection Agency Direct/Delayed Response Program, the main areas of this research were the investigation of the processes involved in sulfate adsorption and desorption and determination of ways in which laboratory data can be used to best represent field data. The final goal is a predictive model of sulfate retention and release in soils. To accomplish these goals, experiments such as batch adsorption and desorption studies, kinetic studies and column studies are all required.

The EPA's final goal is an all encompassing acid rain model that predicts a given area or regions response to acid precipitation now and in the future. Important data such

as watershed size, rainfall, climate and soil characteristics are being gathered. Some of these data will include sulfate information gathered by performing batch adsorption isotherms. The use of batch isotherms has the main advantage of being easy to perform. It is not obvious, however, that data from batch isotherms can be used to accurately understand and predict processes occurring in the natural environment. This emphasizes the need for using column studies. Column studies offer the advantage of approximating a natural soil system, much more than a batch study. Necessary mass transfer terms and kinetic terms for a sulfate model can be obtained using different column experiments.

The research that this thesis describes and presents is work done using batch isotherms for the study of adsorption and desorption. Preliminary work describing kinetics and column studies is also shown.

### DESCRIPTION OF SOILS

## Collection and preparation

Six soils were collected in October and November 1985 and prepared by the U.S. Environmental Protection Agency. Preparation included air drying the soils and sifting through a 2mm mesh screen. Samples were then sealed in two heavy duty plastic bags, put in canvas bags, labelled and sent to Michigan State University, Department of Civil and Environmental Engineering Laboratory. Each soil was then given a number 1-6 for easier identification. The soils will generally be referred to by this number throughout this writing.

The EPA code, state, horizon, depth, soil series name, texture and soil order are provided for each soil in Table 1. All soils were collected from eastern states, either from B or C horizons. Textures varied and included a sand, two sandy loams, a fine sandy loam, a silty loam and a loam soil.

The six soils used for the experiments represented three different orders of soil; an ultisol, an inceptisol and a spodosol.

Soil 1 is an ultisol. The soil name is Hartleton,

|   |              |                    | SOIL              |            |                |            |
|---|--------------|--------------------|-------------------|------------|----------------|------------|
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| BPA code  | R66511650005 | R44360330005       | R339730806        | R4411337   | R223633997     | R330210906 |
| State   | VA           | NY                 | SC                | NC         | NY             | MB         |
| Horizon   | Bt           | Bsl                | BC                | U          | U              |            |
| Soil Name   | Hartleton    | Becket             | <b>Edneyt</b> own | Fannin     | Ada <b>n</b> s | Chesuncook |
| Texture   | Loan         | Fine Sandy<br>Loam | Sandy Loam        | Sandy Loam | Sand           | Silty Loam |
| Soil Order  | Ultisol      | Spodosol           | Ultisol           | Ultisol    | Spodosol       | Inceptisol |

Table 1. General properties of each soil.

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which is found in Virginia. It is a loamy-skeletal soil with a mixed clay minerology. None of the silicate clays make up more than 50 % of the clay fraction. The climate of the soil is mesic, which indicates that the average soil temperature is between 8 and 15° C and it is a typic Hapludult.

Soil 2 is a spodosol. The soil series name is Becket, from New York. It is a course loamy Fragiorthod of mixed clay minerology.

Soil 3 is an ultisol. The soil name is Edneytown from South Carolina, also of mixed clay minerology. It is a fine loamy soil, the climate is mesic and it is also a typic Hapludult.

Soil 4 is an ultisol from North Carolina. The soil series name is Fannin. It has a fine-loamy texture. It is a micaceous soil which indicates that it has more than 40 % mica by weight. It is also typic Hapludult.

Soil 5 is another spodosol from New York. The name is Adams. It is a sandy soil with mixed clay minerology. The climate is frigid with an average temperature of 5° C and below. It is typic Haplarthod.

The sixth soil that was used was an inceptisol found in Maine. The soil series name is Chesuncook. The texture is course-loam. Clay minerology is of mixed type. The climate is also frigid and it is an aquicdystrochrept. The aquic indicating that it is a poorly drained soil, one with a high water table.

Percent clay

Percent clay of each soil was estimated by reviewing information on the soil series name and by the common field technique of feel. This information provided an approximation of the clay percentage for each soil, which was believed to be adequate for these purposes. Results are shown in Table 2.

# Total carbon

Total carbon was determined using a total carbon analyzer. Approximately 4 mg sample sizes were used. Each soil was replicated 3 times. Variability between replications was low so that 4 mg was determined to be a sufficient amount of sample. Soil samples from the C horizon were treated with 4 N HCl, in order to remove carbonates. No significant difference was observed between those samples that were treated and those that were untreated, indicating that neither of the two soils from C horizon had present any appreciable amounts of carbonate.

Although this was not done for all soils, it was generally believed that carbon from carbonates did not comprise any significant amount of the total carbon. It is believed that this total carbon value is a close approximation of total organic carbon. However, for completeness, it will continue to be referred to as total carbon. Results are shown in Table 2.

General soil properties including pH, % clay, % total carbon and % moisture content. Table 2.

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|                       |       |       | SOIL  |       |      |       |
|-----------------------|-------|-------|-------|-------|------|-------|
|                       | 1     | 2     | 3     | 4     | 6    | 9     |
| рН                    | 4.09  | 4.73  | 4.65  | 4.80  | 4.72 | 4.51  |
| X clay                | 22-25 | 15-18 | 20-22 | 18-20 | 2-4  | 16-18 |
| X total<br>carbon     | 0.81  | 2.42  | 0.50  | 0.10  | 0.06 | 3.26  |
| X moisture<br>content | 1.7   | 2.5   | 1.2   | ].3   | 0.1  | 3.3   |

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Soil pH

The pH of each soil was determined using pure water. Pure water was obtained using a reverse osmosis/ion exchange combination. It will be referred to as RO/DI water from this point on. Ten milliliters of RO/DI water were added to ten grams of soil. The soil was allowed to absorb water without stirring. The soil/solution mixture was stirred with a glass rod for one minute at 15 minute intervals, up to 60 minutes. After the last stirring at 60 minutes, the suspension was allowed to settle for one minute. The pH electrode was placed in the suspension and when the reading was stable, the pH was recorded. An Orion Research digital pH/millivolt meter, #611 was used with a Fisher combination electrode. Calibration was done using pH 4 and 7 buffers. Results are shown in Table 2.

#### Moisture content

All calculations of sulfate adsorption were based on the oven dried weight. Since air dried soil was used in each experiment, it was necessary to determine the moisture content for each soil. Two samples of each soil were taken, approximately 4 grams each, and weighed on a Sartorius model 1712 MP8 electronic balance to four decimal places. Each was oven dried at 105°C for 24 hours. After baking, samples were placed in a dessicator to cool and then weighed. The moisture contents were determined from

the loss in weight. The two values were averaged and this value was used in subsequent calculations. The results for % moisture content are presented in Table 2.

After several months, this process was repeated in order to determine if any changes in moisture content existed. None were recorded.

#### Extractable iron and aluminum

Extractable aluminum and iron were determined by several extraction methods. In the first method, the extractant was a 0.01 M sodium pyrophosphate ( $Na_4P_2O_7$ ) solution. Two hundred milliliters of sodium pyrophosphate adjusted to a pH of 10, were added to 2.00 g of soil in a 250 ml centrifuge tube. This was shaken for 17 hours on a reciprocating shaker at 102 oscillations per minute. Four milliliters of a 0.2 % solution of Superfloc 16 (American Cyanamid, P.O. Box 32787, Charlotte, NC 28232) were then added. This was shaken for 15 seconds and then centrifuged at 1900 rpm for 30 minutes. The supernatant was analyzed for aluminum and iron using an Atomic Absorption Spectrophotometer. The pyrophosphate extract yields organically bound iron and aluminum (Johnson and Todd 1983).

To determine non-silicate bound iron and aluminum, a citrate-dithionite extract was used. Four (4.00) grams of air dried soil were placed in a 250 ml centrifuge tube along with 2.00 g of sodium dithionite, also known as

sodium hydrosulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>), 25 g of sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) and 125 ml of pure water. This was shaken for 17 hours on a reciprocating shaker at 102 oscillations per minute. Four milliliters of superfloc solution were then added and this was shaken for 15 seconds. This was centrifuged at 1900 rpm for 30 minutes. The supernatant was analyzed for iron and aluminum using an Atomic Absorption Spectrophotometer (Varian AA-375 series).

The third extraction involved the use of ammonium oxalate  $((NH_4)_2C_2O_4 \cdot H_2O)$  and oxalic acid  $(H_2C_2O_4 \cdot 2H_2O)$ . The acid-oxalate reagent was made by dissolving 28.4 g of ammonium oxalate in 1.0 liter of RO/DI water, and 29 g of oxalic acid in 1.0 liter of RO/DI water. Four parts of the ammonium oxalate solution were mixed with three parts of the oxalic acid solution.

A mechanical vacuum extractor (Concept Engineering, Inc., 1800 Center Park Road, P.O. Box 2555, Lincoln, Nebraska 68502) was used in this method. Balls of paper pulp, weighing approximately 1 g, were forced into the bottom of a syringe barrel with a syringe plunger. A 0.500 g sample was then added to the tube A tared extraction syringe was attached to the sample tube and 15 ml of the acid-oxalate reagent were slowly added to the sample tube. Care was taken to wash any soil that may have adhered to the side of the tube. The reservoir tube was put in place and was allowed to stand for one hour.

The sample was then extracted at a setting of one hour

until 0.5 cm of extracting solution remained above the sample. The extractor was turned off and 35 ml of the acid-oxalate reagent were added to the reservoir. Plastic bags were placed over the tubes to prevent contamination of the reservoir. This was then extracted for 11 hours. The extractant syringes were weighed and the extract was analyzed for aluminum and iron using Atomic Absorption Spectrophotometer. This extraction yields organic and amorphous oxide aluminum and iron.

All extractants were stored at 4°C until analysis. The extractant samples were analyzed within 36 hours from the time of collection. An experimental duplicate was performed for each of the three methods. The results of each extraction and duplicate are presented in Table 3 for iron and Table 4 for aluminum. Subtracting various fractions from the totals yield inorganic, amorphous and crystalline components. These are also shown in Tables 3 and 4. In some cases, subtraction of various fractions was not possible. It resulted in negative numbers. This was probably due to errors and overlap of extraction techniques. In these cases, dashes are indicated.

# Native Sulfate

Phosphate extractable sulfate was determined by placing 2.00 g of air dried soil into a 50 ml centrifuge tube. Ten milliliters of 0.016 M sodium phosphate (NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O) were added. The solution was rapidly mixed

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|---|--------------------------------|-------|-------|--------------|------|-------|-------|
| I |                                | 1     | 2     | 3            | 4    | 5     | 9     |
| T | Total Fe                       | 15.74 | 17.53 | 17.88        | 9.39 | 0.965 | 31.12 |
| 0 | Organic fe                     | 3.62  | 5.96  | 3.30         | 0.38 | 0.102 | 13.45 |
| n | Organic and<br>amorphous Fe    | 1.48  | 9.41  | 2.17         | 2.08 | 1.12  | 18.59 |
| 4 | Inorganic <b>Fe</b><br>(1-2)   | 12.12 | 11.57 | 4.58         | 9.01 | 0.863 | 7.74  |
| S | Amorphous Fe<br>(3-2)          | ł     | 3.45  | I            | 1.70 | 1.02  | 5.14  |
| 9 | <b>Crystalline Fe</b><br>(4-5) | 12.12 | 8.12  | 4.58         | 7.81 | ı     | 2.60  |

Extractable aluminum for each soil in mg/g soil. Table 4.

|   |                             |      |       | SOIL |      |      |       |
|---|-----------------------------|------|-------|------|------|------|-------|
| i |                             | 1    | 2     | e    | 4    | 5    | 9     |
|   | Total Al                    | 2.29 | 11.33 | 3.49 | 2.19 | 0.39 | 10.44 |
| 2 | Organic Al                  | 1.97 | 7.11  | 2.27 | 0.52 | 0.41 | 7.96  |
| 3 | Organic and<br>amorphous Al | 1.71 | 13.63 | 2.09 | 1.13 | 0.89 | 9.25  |
| 4 | Inorganic Al<br>(1-2)       | 0.32 | 4.22  | 1.20 | 1.67 | I    | 2.48  |
| 2 | Amorphous Al<br>(3-2)       | I    | 6.42  | I    | 0.66 | 0.48 | 1.29  |
| 9 | Crystalline Al<br>(4-5)     | 0.32 | I     | 1.20 | 1.66 | ł    | 1.19  |

using a vortex mixer and then shaken for 30 minutes using a reciprocating shaker. The speed of the shaker was the lowest possible speed that still ensured good mixing of the contents in the tube. This was approximately 102 oscillations per minute. After shaking, the tubes were centrifuged for 10 minutes at 1900 rpm. The supernatant was decanted into a 50 ml volumetric flask and diluted to 50 ml. This was filtered through a 0.2 micron membrane filter and analyzed using a Dionex 2000 i/SP ion chromatograph (Appendix). This was repeated on the same soil sample for a total of four times. Total phosphate extractable sulfate was determined by adding the results of the four extractions. Results are shown in Table 5 in row 6.

Water extractable sulfate was determined by placing 2.00 g of air dried soil into a 50 ml centrifuge tube. Forty milliliters of RO/DI water were added. The soil and water was rapidly mixed using a vortex mixer and then shaken for one hour on a reciprocating shaker. The number of oscillations per minute was the same as that in the phosphate extractable sulfate experiment. Henceforth, it will be considered a constant experimental condition.

After shaking, the samples were centrifuged at 1900 rpm for 10 minutes. The supernatant was decanted and filtered through a 0.2 micron membrane filter and analyzed using a Dionex 2000 i/SP ion chromatograph (Appendix). This procedure was continued on each sample for a total of

Extractable sulfate for each soil in mg/g soil. Table 5.

|   |   |       |       | SOIL  |       |       |       |
|---|---|-------|-------|-------|-------|-------|-------|
|   |   | 1     | 2     | S     | 4     | 9     | g     |
| - | SO4 from<br>one extraction                  | 0.042 | 0.016 | 0.037 | 0.002 | 0.005 | 0.020 |
| 2 | Total water<br>extractable SO <sub>4</sub>  | 0.120 | 0.084 | 0.187 | 0.031 | 0.020 | 0.104 |
| 3 | 804 from phosphate<br>extraction on 2       | 0.015 | 0.027 | 0.093 | 0.076 | 0.003 | 0.036 |
| 4 | WE SO <sub>4</sub> using<br>Mechanical Ext. | N/N   | 0.067 | 0.116 | 0.028 | V/N   | N/N   |
| 9 | PE SO <sub>4</sub> using<br>Mech. Ext. on 4 | V/N   | 0.020 | 0.107 | 0.075 | N/A   | N/N   |
| 9 | PE SO <sub>4</sub> on new<br>soil samples   | 0.088 | 0.067 | 0.224 | 0.088 | 0.0   | 0.101 |
| 2 | (2+3)                                       | 0.135 | 0.111 | 0.280 | 0.107 | 0.022 | 0.140 |
|   | Total soil<br>lost batch (g)                | 0.200 | 0.074 | 0.077 | 0.067 | 0.009 | 0.114 |

15 extractions. Each extraction was analyzed separately. The value for total water extractable sulfate was determined by summing all the single extraction values. Results for water extractable sulfate are presented in Table 5 in row 2. The first single water extraction is presented in row 1.

Upon completion of the water extraction experiments, the samples were extracted with 10 ml of 0.016 M NaH<sub>2</sub>PO<sub>4</sub>. A total of four extractions were done in the same manner as that of the phosphate extractable sulfate, this is shown in row 3 of Table 5. After the last extraction, the soil samples were dried and the total amount of soil lost was determined, this is presented in the last row of Table 5.

Another method involving a mechanical vacuum extractor was used to determine water extractable sulfate. For this experiment, 6.00 g of air dried soil were placed into mechanical extractor tubes with RO/DI water washed paper pulp at the bottom. It was necessary to wash the paper pulp thoroughly to remove any initial sulfate present in the pulp. The soil was saturated with RO/DI water and then extracted with a known volume of water. This was repeated for a total of 530 ml for soil 2 , 3 and for 700 ml for soil 4. Only 3 soils were tested in this manner. Total water extractable sulfate determined from this method is shown in row 4 of Table 5. After water extractions, phosphate extractions were performed using 20 ml of 0.016 M NaH<sub>2</sub>PO<sub>4</sub>. This was repeated four times and is presented in

row 5 of Table 5. The results for water extractable sulfate for each soil determined using the batch method are also depicted graphically in Figure 3. Figures 4, 5, and 6 show graphically, comparisons between the water extractable sulfate using a batch test and that of a mechanical extractor test.

Soil 3 had the largest amount of total water extractable and total phosphate extractable sulfate. Total phosphate extractable sulfate for soil 3 was 0.224 mg/g soil, which was more than twice that obtained from any other soil. Soil 5 did not show any phosphate extractable sulfate, although water extractable sulfate was found. This is probably due to the analytical method used in measuring phosphate extractable sulfate (Appendix). Very small amounts of sulfate obtained using phosphate as the extractant were difficult to quantify.

It is often assumed that phosphate extractable sulfate is representative of the total native sulfate in the soil (Singh 1984a). Johnson and Henderson (1979) divide sulfate into soluble (water extractable sulfate) and adsorbed sulfate (phosphate extractable sulfate). According to results shown in Table 5, classifying sulfate in this manner may not be feasible. There may be considerable overlap between the results of the different extracting procedures.

For example, in the case of soil 2, the value for total water extractable sulfate (row 2) was 0.084 mg/g,













0.005





e ph add which was greater than total phosphate extractable sulfate (row 6), which was 0.067 mg/g. After 15 water extractions, it was difficult to remove more sulfate. Using phosphate as the extractant after this facilitated the removal of another 0.027 mg/g (row 3). This indicates that some of the sulfate cannot be removed or is very difficult to remove by water alone. The reverse is also true. The amount removed by phosphate alone does not represent only the sulfate that can be removed by phosphate alone. Some of the sulfate extracted in the phosphate extraction (row 6) can also be removed by water. If this were not true, then the amount of sulfate removed by phosphate after 15 water extractions (row 3) should have been the same as total phosphate extractable sulfate (row 6). This was clearly not the case.

The only soil that showed some sign of phosphate extractable sulfate being separate from water extractable sulfate was soil 4. After 15 water extractions, phosphate was able to remove 0.076 mg/g (row 3). In a fresh soil 4 sample, phosphate was able to remove 0.088 mg/g (row 6). It is quite possible that a large percentage of the water extractable sulfate in soil 4 results from the dissolution of sulfate compounds in the soil. This may also be occurring in the other soils, since the total water extractable sulfate (row 2) and sulfate removed from phosphate extractions after 15 water extractions (row 3) add up to greater quantities (row 7) than the total

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phosphate extractable sulfate (row 6).

It is quite probable that four phosphate extractions remove most of the adsorbed sulfate. One water extraction initially removes sulfate that is nonspecifically adsorbed, but repeated water extractions may dissolve some of the naturally occurring sulfate compounds in the soil.

If total phosphate extractable sulfate is considered total native sulfate, both nonspecific and specifically adsorbed sulfate, then the amount of sulfate that could not be removed by water alone (row 3) was 17 % of the total for soil 1, 40 % for soil 2, 42% for soil 3, 86 % for soil 4, and 36 % for soil 6. An interesting difference is noticed between soil 1 and soil 4. They both had the same total phosphate extractable sulfate values but the manner in which it was released was quite different. In looking at the values for 1 water extraction (row 1) it is observed that very little sulfate is removed from soil 4 whereas in soil 1, sulfate removal was fast and great. This can readily be seen when looking at Figure 4. There appear to be different mechanisms at work here. Sulfate in soil 4 is difficult to remove, requiring phosphate as the extractant. Sulfate adsorption in this soil may be considered specific or ligand exchange adsorption. Sulfate in soil 1 was easily removed and sulfate retention in this soil may be considered nonspecific adsorption.

The comparison of water extraction results from the batch method and mechanical extractor are shown in Figures

4-6. The batch method appeared to give higher sulfate results than the mechanical extractor method. A higher initial release was noted when using the batch method.

It is also possible that the difference in results is due to the difference in methods. In a batch system, the solid phase concentration comes to equilibrium with the solution concentration. This is not the case in the column situation.

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## BATCH ADSORPTION STUDIES

# Introduction

Batch studies are a common method for evaluating adsorption equilibrium of different systems. An adsorption isotherm is the relationship between the solution concentration and the solid phase concentration. One method for determining the solid phase concentration is called the difference technique. The difference in the initial solution concentration and the equilibrium solution concentration is used to determine the solid phase concentration. Traditionally the equilibrium concentration, C., is plotted on the x-axis and the solid phase concentration, q., is plotted on the y-axis. This convention will be followed here.

Two general methods for determining batch isotherms are in use. One is referred to as the constant solids technique and the other is referred to as the constant initial concentration technique. The constant solids technique involves the use of a constant mass of soil added to a series of bottles. Different concentrations of solution are then added to each. The constant initial concentration technique involves varying the amount of
solids in each bottle while keeping the same initial concentration in each. The applicability of the latter technique has been in question in the light of recent research done on solids effects in batch systems. It appears that adsorption equilibrium may be dependent upon the solid phase concentration in the system (White 1966, Hope and Syer 1976, Barrow and Shaw 1979, Voice and Weber 1985). The constant solids technique was therefore the one chosen for this research.

One of the primary goals of the research involving batch adsorption isotherms was to determine an isotherm model that best represented the sulfate adsorption data. Two of the main problems that need addressing were how to treat the sulfate released from the soils at low initial concentrations and which was the best model.

A preliminary look at solids effect was also done. A general comparison of each soils ability to adsorb sulfate and its relationship to soil properties is also discussed.

## Methods

The method followed for the batch adsorption isotherms was adapted from a procedure outlined by EPA. It involved taking six, 6.00 g samples of air dried soil and placing each into separate 50 ml centrifuge tubes. Sulfate solutions were prepared using MgSO<sub>4</sub> at concentrations of 2, 4, 8, 16, 32 mg S/l. This is equivalent to 5.99, 11.98, 23.97, 47.93 and 95.97 mg SO<sub>4</sub>/l. Thirty milliliters of

each different solution were added to each tube. One tube with 30 ml of RO/DI water was also used, representing an experimental blank. The soil:solution ratio was 1:5. Each tube was immediately rapid mixed using a vortex mixer, then shaken on a reciprocating shaker at 102 oscillations per minute for one hour. After shaking, the tubes were centrifuged for 30 minutes at 1500 rpm. The supernatant was decanted and filtered through a 0.2 micron membrane filter and analyzed using ion chromatography (Appendix).

For each soil, three experiments of this nature were done. In the third experiment, two extra tubes were added. One was a tube with initial concentration high enough so that the final equilibrium concentration was close to 100 mg SO<sub>4</sub>/1. The initial concentration for this tube was estimated graphically from the 2 previous isotherms done on each soil. The other tube was designed to experimentally verify estimates of what was called the zero point. The zero point is the solution concentration that results in no net adsorption or desorption of sulfate from the soil. In this experiment, the initial concentration is selected to represent an equilibrium condition with the native sulfate, and thus the initial concentration equals the final equilibrium concentration. This results in a q. of zero.

Three experiments were conducted at a solids concentration of 0.60 g of soil for each of the six soils. The solution concentrations were decreased by the same ratio, resulting in solution concentrations of 0.599,

1.194, 2.397, 4.793, and 9.597 mg SO<sub>4</sub>/l. The soil: solution ratio was 1:50. Additional experiments were conducted on soil 3 and 4, since there was a suggestion of a possible solids effect. For these soils, higher sulfate concentrations were added in an attempt to extend the isotherm and verify any effects suspected. All other conditions remained the same.

## **Results and Discussion**

## Model Selection

The selection of a best fit model was not an easy task. The presence of native sulfate, which at low concentrations was released, resulted in equilibrium concentrations which were higher than initial concentrations. Using the standard difference technique resulted in the calculation of some negative q. values.

The Freundlich and Langmuir families of equations were the major models considered. The two parameter Freundlich and Langmuir models do not account for the presence of native sulfate. In fact, transforming negative q. values was impossible for the Freundlich and created large negative numbers for the Langmuir. By definition, both equations must go through the point (C.=0, q.=0), which makes both of them inappropriate for use with these data. Linear transformations using the Langmuir and Freundlich are shown for soil 3 in Figures 7 and 8. It is quite obvious that neither of the methods of transformation



Figure 7. Linear regression using the Langmuir transformation of 6 g data for soil 3.



Figure 8. Linear regression using the Freundlich transformation of 6 g data for soil 3.

reduce the data to a straight line.

Due to the problem of negative q. values at low solution concentrations, it was thought that the addition of a native sulfate term would alleviate this problem and thus tend to straighten the line. A model developed by Fitter and Sutton (1975) that will be referred to as the extended Freundlich in this work, employed a three parameter fit. The third parameter was a term that accounted for the native sulfate of the soil.

No mention of a three parameter Langmuir model that accounted for native sulfate could be found in the literature. It seems plausible to assume that such a model, like the extended Freundlich, would be better able to describe adsorption data, especially at low solution concentrations. This model will be referred to as the extended Langmuir model.

Neither of these extended models are limited by the necessity of going through the point (C.=0, q.=0), as are the Langmuir and Freundlich. They should therefore have the potential to better describe desorption at low solution concentrations.

The traditional method of determining the constants for isotherm models has been to transform the data to forms which linearize the model, as described in the Theory and Background section of this text. The Freundlich transformation involves taking the logarithm of both sides of the equation. The Langmuir transformation involves

taking the reciprocals of both sides of the equation. When using the extended models, it was necessary to add a native sulfate term to the solid phase concentration prior to taking logarithms or reciprocals. While it is logical to assume that this term could be estimated from the extractable sulfate results, it can be recalled that these data varied considerably for the different experimental methods employed. Thus it became necessary to decide which of the extractable sulfate terms best represented native sulfate.

The first choice was the use of the equilibrium concentration obtained in the "zero tube". This was the experimental blank used in the generation of the six point isotherm. It contained soil but an initial solution free of sulfate. This "extraction" represented the conditions of the isotherm procedure and it was thought would represent native sulfate. In actuality, the use of the "zero tube" result did little to linearize the data. The constants that were obtained were used in the models and compared to the actual data. By visual interpretation, the fit was determined to be very poor.

Other extractable sulfate terms, obtained from the batch extraction methods, were added. These included the values for one water extraction, total water extractable and total phosphate extractable sulfate. Singh (1982a) used phosphate extractable sulfate as the (a) term in the extended Freundlich model. Often the larger the (a) term

in comparison to the q. term, the greater the tendency to straighten out the line. The addition of total water extractable sulfate and total phosphate extractable sulfate resulted in transformed data that better depicted a straight line and subsequently better fits to the actual data. There was still a tendency to overestimate the extremes. This can be observed in Figures 9 and 10 which represent linear transformation of 6.00 g data for soil 3 using the extended Langmuir and extended Freundlich models. The value for the (a) term that was added to the q. term in each model was total water extractable sulfate. There is still a slight curve to the data. When putting a straight line through the majority of data points, the data points at the lower and higher concentrations fall below the line. This generally causes a poor fit at high concentrations of the model to the actual data.

The addition of a value for the native sulfate (a) term appeared to be arbitrary. No one of the extractable sulfate values was clearly superior in linearizing the data. Nor were any of the resultant models completely adequate in describing the actual data. As mentioned earlier, the main problem with the linear transformation method over such a wide range of data is that it does not give a good representation of the extremes. In almost every case, there was a tendency to overestimate the low and high concentrations. It does not appear to properly weight the extreme at the high concentration. The problem









at the low concentration is probably caused by the (a) term. When plotted against the actual data, the overestimation at the low concentration caused only a slight deviation from the data. At the high concentrations, there were large deviations between the expected values and the actual data. An example of this is shown in Figure 11, which represents the extended Freundlich and extended Langmuir models plotted against the actual data. The parameters were determined from the linear regression analysis depicted in Figures 9 and 10. The extended Freundlich seems to do a fair job in representing the data in this soil. This was not always the case when using this model for the other soils.

It seemed that linear transformation methods were not adequate in determining constants for the extended models. The transformed data using the extended models tended to form a straighter line depending on the size of the native sulfate term added. One term, however, did not consistently prove to be better for all the soils.

At this point, it was decided to use a nonlinear regression procedure to fit the models to the data. This has recently been used by other researchers (Barrow 1978, Singh 1984a, Kinniburgh 1986).

The nonlinear regression algorithm found in the ISOTHERM (Kinniburgh 1985) program was used to fit the data to the Freundlich and Langmuir family of equations. This algorithm determined the minimum residual sum of squares





using a combination of the Newton-Raphson, steepest descent and the Marquardt compromise. Two other programs were also employed for comparison with ISOTHERM. These were Plotit (Eisensmith 1985) and SAS (SAS Institute Inc. Box 8000, Cary, NC 27511), however only Plotit and ISOTHERM are currently available for microcomputers. Each nonlinear regression routine provides a method for determining the minimum RSS, and there is no universally best way. In comparing the data sets with the different programs, the results were generally similar. The results shown here, however are those determined using ISOTHERM. Figure 12 shows nonlinear regression fitting of both the Freundlich and Langmuir models for 6.00 g data for soil 3. In both cases, the models appear to fit the data better than the linear transformation techniques employed previously. The poor fit at the low concentrations was expected since the Langmuir and Freundlich models are still constrained to go through the point ( $C_{e}=0$ ,  $q_{e}=0$ ).

A number of different models were employed in analyzing the 6.00 g adsorption data for each soil, using nonlinear regression analysis methods. These included the Langmuir equation, the extended Langmuir, the Sibbesen Langmuir and the two surface Langmuir. The Freundlich, extended Freundlich and Sibbesen Freundlich models were also used.

Using this approach for the Langmuir and Freundlich models involves the determination of two unknown constants.





The extended Langmuir, extended Freundlich, Sibbesen Langmuir and Sibbesen Freundlich involve a three parameter fit. The two surface Langmuir involves a four parameter fit.

Visual inspection of these models fitted to the data, proved useful in weeding out the inappropriate models. Except for the extended Langmuir and extended Freundlich, all other models were limited at the low concentrations. This was expected since all models except those with an extended term would have to go through the origin. This would limit their application to soils with little native sulfate.

It would be possible to add a native sulfate term to the Sibbesen equations and the two surface Langmuir. This increases the number of parameters to evaluate to four in the case of the Sibbesen models and five, in the case of the two surface Langmuir. This approach was not employed since the exercise becomes more of a curve fitting technique than one for determining the best fit model to the data.

It is important to compare the fits of the various models to the data by methods other than visual observation. To do this, the coefficients of determination and the root mean square of errors values were evaluated. The correlation coefficient, referred to as r<sup>2</sup> since there is only one independent and one dependent variable, represents the proportion of variation in the y values that

can be explained by a nonlinear regression on x. It measures the strength of fit of the model. The root mean square of errors, shortened here to RMSE, is defined as the square root of the residual sum of squares divided by the degrees of freedom. The RMSE is the estimated standard deviation of the errors (Kinniburgh 1986). Residual sum of squares, correlation between parameters and standard errors of parameters were also compared, however these are not presented here.

The statistical parameters were used to describe nonlinear regression fitting of the models to the 6.00 g data. They were also necessary to compare the models determined from linear transformation methods to those obtained from nonlinear methods. The  $r^2$  and RMSE values are presented for each model in Tables 6 and 7.

These model fitting techniques were not applied to soil 5. The reason for this was that soil 5 showed virtually no adsorption capability. The adsorption data, when plotted, depicted a random scatter about the horizontal axis, y=0. The Freundlich models would not be appropriate due to the exponential term. The Langmuir model produced a near horizontal line with a correlation coefficient of near zero.

In the other soils, the models were employed. It was impossible to determine r<sup>2</sup> and RMSE values for the Langmuir and Freundlich transformed data for soil 1 due to the data itself. At low concentrations sulfate was greater than the

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| Table                 |

|   |        |        |                       |       | S(                    | 11(   |                       |        |       |        |
|---|--------|--------|-----------------------|-------|-----------------------|-------|-----------------------|--------|-------|--------|
|   |        | 1      |                       | 8     |                       | -     |                       | 4      |       | 9      |
| Model   | r2     | RMSB   | <b>r</b> <sup>2</sup> | RMSB  | <b>r</b> <sup>2</sup> | RMSE  | <b>r</b> <sup>2</sup> | RMSB   | r2    | RMSR   |
| Langmuir<br>transformed   | V/N    | N/A    | . 796                 | .0259 | -6.61                 | .1996 | .890                  | .0397  | . 549 | .0387  |
| <b>Bxtended Langmuir</b><br>transformed (0 tube)                | . 606  | . 0223 | . 666                 | .0341 | -2000                 | 3.603 | .890                  | . 0397 | .157  | .0544  |
| <b>Kxtended Langmuir</b><br>transformed (1 WB SO <sub>4</sub> ) | .675   | .0202  | -1.25                 | .0883 | . 543                 | .0538 | .874                  | .0435  | .606  | .0372  |
| Entended Langmuir $transformed (total WE SO_4)$                 | ) -276 | 0 1.86 | . 634                 | .0356 | . 903                 | .0248 | . 793                 | .0558  | .683  | . 0333 |
| <b>Extended Langmuir</b><br>transformed (PB SO <sub>4</sub> )   | .651   | . 0238 | . 636                 | .0351 | . 896                 | .030  | . 762                 | .0598  | .685  | .0333  |
| Langmuir<br>Nonlinear regression                                | . 622  | .0238  | .918                  | .0164 | . 939                 | .0192 | .972                  | .0201  | .889  | .0192  |
| Sibbeson Langmuir (NLR)   | .604   | . 0223 | .921                  | .0165 | .961                  | .0157 | .996                  | .0074  | .891  | .0195  |
| 2 Surface Langmuir (NLR)  | .513   | .0255  | . 965                 | .0129 | .956                  | .0178 | .998                  | .0061  | .938  | .0151  |
| <b>Extended Langmuir (NLR)</b>                                  | .840   | .0142  | .926                  | .0160 | .978                  | .0119 | .988                  | .0130  | . 898 | .0189  |

| Freundlich models  | 1 for                 | f1ve <b>s</b> 0 | 118.       |       |          |       |            |       |       |       |
|--|-----------------------|-----------------|------------|-------|----------|-------|------------|-------|-------|-------|
|  |                       |                 |            |       | 1103     |       |            |       |       |       |
|  |                       | 1               | 0          |       | Ċ3       | _     |            | 4     | C     | ~     |
| Model  | <b>r</b> <sup>2</sup> | RMSB            | <b>r</b> 2 | RMSB  | <b>7</b> | RMSR  | <b>F</b> 2 | RMSB  | 2     | RMSE  |
| Freundlich<br>transformed  | V/N                   | N/A             | . 893      | .0188 | . 843    | .0307 | . 909      | .0360 | . 774 | .0274 |
| <b>Extended Freundlich</b><br>tr <b>ansform</b> ed (0 tube)                    | . 834                 | .0144           | . 905      | .0181 | .878     | .0277 | . 909      | .0360 | . 336 | .0483 |
| <b>Extended Freundlich</b><br>transformed (1 WE SO <sub>4</sub> )              | . 833                 | .0145           | .916       | .0172 | .944     | .0189 | .918       | .0351 | .879  | .0206 |
| <b>Entended Freundlich</b><br>tr <b>ans</b> formed (total WE SO <sub>4</sub> ) | .796                  | .0160           | .903       | .0184 | .977     | .0121 | .973       | .0203 | .898  | .0189 |
| <b>Extended Freundlich</b><br>transformed (PE SO <sub>4</sub> )                | .805                  | .0156           | . 906      | .0181 | .969     | .016  | .973       | .0203 | .898  | .0189 |
| Preundlich<br>Nonlinear regression   | . 662                 | .0200           | .910       | .0170 | .918     | .0223 | . 977      | .0181 | .874  | .0205 |
| Sibbeson Freunclich (NLR)  | . 588                 | .0228           | . 922      | .0164 | .967     | .0145 | .997       | .0066 | . 894 | .0193 |
| <b>Extended Freundlich (NLR)</b>   | .840                  | .0142           | .928       | .0150 | .981     | .0109 | .997       | .0068 | .903  | .0185 |

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Coefficients of determination and root mean squares of error using various Table 7.

initial concentration. In most cases the nonlinear regression method proved superior to transformed methods as evidenced by the high  $r^2$  values and low RMSE values.

The individual graphs of these models fitted to the data are not shown. In fact, upon visual inspection of the models fit using nonlinear regression, it was difficult to see any differences in fit at high concentrations. As mentioned previously, the useful information was gained by providing a visual picture of what was happening at the low concentration. In the models without an extended term, the curve deviated from the actual data at low concentrations.

It is difficult to determine which model provided the best fit by using the statistical parameters also. This was because the difference in r<sup>2</sup> values and RMSE between models was often small. The distinguishing criteria for determining the better fitting models came at the low concentration. Soil 1, for instance, showed a tendency to desorb sulfate at low concentrations. In this case, the models without the extended terms proved highly inadequate. The extended models proved superior, even the extended Freundlich models, determined from transformed data gave higher r<sup>2</sup> and RMSE values than the models without the extended term.

In soil 2, 3, 4, and 6 the r<sup>2</sup> and RMSE values are often similar for the extended models determined from nonlinear regression and the Sibbesen and two surface models. The Sibbesen and two surface models tended to

misrepresent the lower concentration data. This is due to the fact that they are constrained to go through the point  $(C_{\bullet}=0,q_{\bullet}=0)$ . As mentioned previously an extended term, that would account for native sulfate would need to be added to these models also, to insure that they represent the lower concentration data. Adding another term to the Sibbesen and two surface models might make for a better fit but it becomes more of an exercise in curve fitting. It is for this reason and the fact that neither the Sibbesen nor the two surface Langmuir models were consistently superior to the extended Langmuir or extended Freundlich using nonlinear regression, that these models were excluded from further consideration.

The extended Langmuir and the extended Freundlich using nonlinear regression proved consistently superior to the extended models determined from transformation techniques. This was determined by both visual inspection of graphs and comparison of  $r^2$  and RMSE values for different data sets. Use of nonlinear regression also proved simpler to use, since only the original isotherm needed to be input into the computer. The program did the rest, easily providing an output of data, models, and relevant statistical parameters.

The extended Langmuir and extended Freundlich also proved consistently better and often times far superior to predicting the data over either the Langmuir or Freundlich. This lends some credence to the addition of a native

sulfate constant. To assess the addition of a third parameter to these two models, an F test was done. It was found in all but soil 2 and soil 6, for the extended Langmuir model, the addition of the third parameter was justified at the 90 % probability level.

The presence of native sulfate in the soils also justifies the use of a native sulfate constant in the model. The native sulfate terms (a) determined from nonlinear regression were compared to extractable sulfate data. This was done by linear regression analysis. Tables 8 and 9 show the parameter estimates for (a) using the extended Langmuir and the extended Freundlich for each soil, the water extractable and phosphate extractable values obtained for each soil, and r<sup>2</sup> values obtained by linear regression analysis.

The highest r<sup>2</sup> value was obtained when plotting the extended Langmuir (a) term against total water extractable sulfate. A good correlation was also observed using the EPA, one water extraction method and the (a) term from the extended Langmuir. This is shown graphically in Figure 13. This comparison also showed the closest similarities in value magnitudes between the (a) term determined from nonlinear regression using the extended Langmuir model and the experimental values. This might make sense in that the EPA extractable sulfate involves only one water extraction. This sulfate may represent sulfate that is easily removed at low solution concentration. Total water and phosphate

Table 8. Comparison of parameter (a) estimate from the extended Langmuir model with actual values obtained for extractable sulfate. All values in mg  $SO_4/g$  soil except r<sup>2</sup> values.

|                 | 1    | 2    | 3    | 4    | 6     | r <sup>2</sup> |
|-----------------|------|------|------|------|-------|----------------|
| (a)             | .032 | .011 | .050 | 033  | .012  | 1.0            |
| EPA<br>WE SO4   | .042 | .016 | .037 | .002 | .0198 | .852           |
| Total<br>WE SO₄ | .120 | .084 | .187 | .031 | .104  | .926           |
| PE SO4          | .088 | .067 | .224 | .088 | .101  | .392           |
| Zero<br>Tube    | .028 | .008 | .014 | 0.0  | .009  | .539           |

Soil

Table 9. Comparison of parameter (a) estimate from the extended Freundlich model with actual values obtained for extractable sulfate. All values as mg SO<sub>4</sub>/g soil except r<sup>2</sup> values.

|                 |      |      | Soil |      |      | ·              |  |
|-----------------|------|------|------|------|------|----------------|--|
|                 | 1    | 2    | 3    | 4    | 6    | r <sup>2</sup> |  |
| (a)             | .037 | .032 | .341 | .202 | .061 | 1.0            |  |
| EPA<br>WE SO4   | .042 | .016 | .037 | .002 | .020 | .004           |  |
| Total<br>WE SO4 | .120 | .084 | .187 | .031 | .104 | .173           |  |
| PE SO4          | .088 | .067 | .224 | .088 | .101 | .745           |  |
| Zero<br>Tube    | .028 | .008 | .014 | 0.0  | .009 | .057           |  |

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Langmuir equation with water extractable sulfate (one extraction). extractable sulfate may represent strongly bound or even dissolvable sulfate. With this idea in mind, it is curious why the sulfate removed in the zero tube did not correlate better than the EPA extractable since this better represents the circumstances under which the isotherm was conducted.

Although it is difficult to draw any strong conclusions when using only five soils, the approach seems to be a valid one. This being that an extended term (a) needs to be added to the solid phase concentration to account for native sulfate. It is difficult to understand why other researchers have not given more consideration to the addition of a native sulfate term. The most likely reason for this is that in most cases sulfate solution concentrations used by others have been much larger than those of this study. At high solution concentration, the effect of native sulfate is not observed. It is only at low solution concentrations and with certain soils, that the effect of native sulfate is apparent.

The comparison between the two extended models shed little light on which one is preferable. RMSE values and r<sup>2</sup> values were not consistently better for either of the two models. The parameter estimates, r<sup>2</sup> values and standard errors for the parameter estimates are summarized in Table 10 for each soil and each extended model. In this analysis, it can be seen that in most cases high standard errors are associated with each parameter estimate. High

Table 10. Statistics used for comparison of extended Langmuir and extended Freundlich for various soils.

| Soil | Model | r <sup>2</sup> | B(1) SE      | B(2) SE       | B(3) SE       |
|------|-------|----------------|--------------|---------------|---------------|
| 1    | EL    | .840           | .375 (.442)  | .0038 (.0062) | .0323 (.0086) |
| 1    | EF    | .840           | .0030(.0045) | .778 (.302)   | .0365 (.016)  |
| 2    | EL    | .926           | .330 (.085)  | .0151 (.0076) | .0106 (.0077) |
| 2    | EF    | .928           | .019 (.013)  | .545 (.138)   | .0310 (.021)  |
| 3    | EL    | .978           | .351 (.018)  | .0508 (.011   | .050 (.011)   |
| 3    | EF    | .977           | .277 (.178)  | .172 (.077)   | .341(.190)    |
| 4    | EL    | .981           | .341 (.012)  | .115 (.016)   | 033 (.006)    |
| 4    | EF    | .997           | .287 (.043)  | .153 (.018)   | .202 (.042)   |
| 6    | EL    | .898           | .253 (.048)  | .0266 (.013)  | .0123 (.010)  |
| 6    | EF    | .903           | .0452 (.038) | .368 (.154)   | .0612 (.048)  |

\* Extended Langmuir

B(1) = Q<sup>0</sup> ; ultimate adsorption capacity
B(2) = b ; energy constant
B(3) = a ; native sulfate

**\*\* Extended Freundlich** 

| B(1) | = | Kr  | ; | indicator of sorption capacity    |
|------|---|-----|---|-----------------------------------|
| B(2) | Ξ | 1/n | ; | indicator of adsorption intensity |
| B(3) | = | a   | ; | native sulfate                    |

negative correlations were also observed between the parameters of a given model. This suggests that although the models may fit the data well, the actual values of the parameters are not well defined. It is possible that over a broader range of data the models would not provide as good a fit.

Figures 14-19 show the plots of the extended Langmuir and extended Freundlich using nonlinear regression fitting techniques. Visual inspection sheds little light on the better fitting model. With the use of five soils, it is difficult to determine which model is superior. It may be equally as difficult with 50. At this point, however the extended Langmuir seems slightly preferable in that the extended term (a) correlated with native sulfate.

Soil 5 is represented graphically in Figure 18. It becomes obvious when looking at the data why the model fitting techniques were not used.

## Solids Effect Studies

Evidence of a solids effect has been reported in a wide variety of adsorption studies. Hope and Syers (1976) noted an effect due to different solution to soil ratios for phosphate experiments. It was observed that higher ratios resulted in lower phosphate adsorption but concluded that this was due to equilibrium kinetics. The conclusion being that solution to soil ratios only affected the rate at which phosphorus was removed and that given enough time



















Figure 18. Nonlinear regression using the extended Langmuir equation for 6 g data for soil 5.





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any solution to soil effects would be negated.

Barrow and Shaw (1979) also noted a solution to soil ratio effect for studies involving phosphate adsorption. They compared different methods of shaking using different soils. Using different solution to soil ratios, it was found that certain "unstable" soils showed evidence of a solids effect when a more vigorous shaking method was used but none was observed when using a less vigorous shaking method. The so called "stable" soil did not exhibit a solids effects when using either of the shaking techniques. Similar analysis to that of Hope and Syers (1979) led to the conclusion that it was not kinetics but vigor of shaking that caused the solids effect.

Other researchers (O'Connor and Connolly 1980 and Voice and Weber 1985) also noted solids effects when using hydrophobic compounds, but not always with similar results. Numerous explanations have been given to explain the solids effect phenomenon, however no sound conclusions have been made.

Barrow (1967) found that there was little difference in the amount of sulfate adsorbed at different soil:solution ratio. The ratios used varied from 1:2 to 1:50. Little evidence for or against a solids effect in sulfate literature could be found. Preliminary experiments were done to determine if this phenomena was evident in batch studies involving sulfate adsorption.

Original experiments on soil 3 and possibly soil 4

suggested some evidence for a solids effect. The equilibrium points for the 0.60 g soil at 3.2 mg S/l concentrations deviated somewhat from the 6.00 g data in this region of the curve. It was thought that by extending the 0.60 g isotherm, that any effect due to the soil:solution ratio could be detected.

Equilibrium data from both the 0.60 g isotherm studies and the 6.00 g isotherm studies were plotted on similar graphs for comparison purposes. Figure 20 represents the data obtained for soil 3. Figure 21 represents that of soil 4. Upon extension of the isotherm, no recognizable deviations from the 6.00 g data could be found. The scatter in the points had increased considerably, especially at the high end. Because of this, it makes it difficult to observe a solids effect if one does exist. At high sulfate concentrations and low solids concentrations, the amount of sulfate removed from solution may be less than 5 % of the original sulfate solution. The error associated with the calibration curve is 5 %. This causes considerable uncertainty to be associated with the calculation of the solid phase concentration.

At this point it was realized that in order to study the possibility of a solids effect, other methods would need to be employed. The heterogenity of the soil and the fact that 0.60 g is a very small sample size, and increased scatter of the 0.60 g data makes it extremely difficult to determine any significant deviation from the 6.00 g data,



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Figure 20. Comparison of batch data at solids concentrations of 6.0 g and 0.6 g for soil 3.




if one did indeed exist. The error associated with the curve, as discussed above and also the relatively low sulfate adsorption capability that the soils exhibited, made it undesirable to continue the study.

The fact that there was no clear evidence in support of a solids effect does not mean that the results clearly show that such an effect does not exist for sulfate. Using high sulfate adsorbing soils, possibly higher solids concentrations and a tighter calibration curve would be the best tact to pursue in an effort to answer this question.

#### Comparison of soils

A comparison of adsorption isotherms for each soil is presented in Figure 22. Nonlinear regression analysis using the extended Langmuir model, allows visual comparison of the six soils. Soil 4 exhibited the greatest adsorption capacity. Soil 5, as previously mentioned showed virtually no adsorption capability, this is obvious when viewing Figure 22. The other four soils exhibited adsorption capacities between these two extremes.

It is difficult to quantitatively determine which soil parameters correlate with sulfate adsorption when working with only six soils. An effort is made here to qualitatively compare sulfate adsorption with the various soil parameters measured.

In an effort to determine which soil parameters were involved, general observations were made. The most



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striking feature of soil 4 is its extremely low total carbon content. This made up 0.10 % of the soil. Soil 5 was lower, but soil 5 was almost totally sand. Soil 4 had a fair amount of inorganic aluminum and iron, but other soils had higher amounts. The significant feature of the extractable iron and aluminum tests for soil 4 were the extremely low values of organic iron and aluminum found. This also suggests low organic matter content. The extractable sulfate results for soil 4, show comparable amounts of total phosphate extractable sulfate to soils 1, 2, and 6, but a very low amount of water extractable sulfate.

The soil characteristics for soil 4 suggest that one of the reasons for its higher adsorption capacity is due to negligible organic matter. This is agreement with most research, which suggests that organic matter may bind to adsorption sites thus prohibiting sulfate adsorption. The difficulty in removing sulfate from soil 4 in the water extractable experiments suggests that sulfate may be bound tightly as in specific adsorption. Specific adsorption has been demonstrated to occur on iron and aluminum oxides (Parfitt and Smart 1978, Rajan 1979).

Soil 3 exhibited the second largest capacity for sulfate adsorption of the six soils. It also showed a low amount of total carbon. Total carbon made up 0.50 % of the soil. It showed the highest inorganic iron amount on a mg/g basis. It did show a larger amount of organic iron

that that of soil 4, which might indicate why the adsorption capacity was lower. What might be even more significant in understanding its lower sulfate adsorption capacity is the high native sulfate values. Soil 3 showed the highest native sulfate term, both for water extractable and phosphate extractable sulfate. The phosphate extractable sulfate term was more than twice that of any other soil. It was almost three times that of soil 4. Previous additions of sulfate can affect the number of adsorption sites available in the future. This might account for the decreased adsorption capacity of soil 3 as compared to soil 4.

Soil 2 and 6 had similar sulfate adsorption capabilities, as seen in Figure 22. Soil 2 was somewhat higher than soil 6. Both of these soils showed high total carbon values. Soil 2 had 2.42 % and soil 6 had 3.26 % total carbon. Both had high inorganic iron and aluminum contents, soil 6 had higher inorganic iron but soil 2 showed higher inorganic aluminum. This indicates a correlation between sulfate adsorption and iron and aluminum oxides, and organic matter. Soil 2 had less water extractable and phosphate extractable sulfate than soil 6. Both had similar % clay contents. It seems possible that due to the higher percent total carbon, soil 6 did not adsorb as much sulfate as soil 2, even though it had a higher inorganic iron content than soil 2.

Soil 1 seems to be in a category all its own. Total

carbon made up 0.81 % of the soil, which is only slightly higher than soil 3. It had a large amount of inorganic iron, only slightly lower than that of soil 3. It had quite a small amount of inorganic aluminum. The water extractable and phosphate extractable results were similar to the other soils. It had the same phosphate extractable sulfate as that of soil 4 and the second highest water extractable sulfate value of the six soils. It also had the highest percent clay content and the lowest pH.

The interesting feature of soil 1, is observed in the results for water extractable sulfate, Figure 3. There is a very rapid loss of sulfate from the soil. Desorption, it was seen, occurred at low solution concentrations. This suggests nonspecific adsorption. It is unlikely that bonding occurs on the iron and aluminum oxides. The soil characteristics measured do not seem to give any indication why this soil behaves the way that it does. In viewing the soil characteristics alone, one might think this soil would behave much as soil 3 does. This indicates the difficulty in making generalities about soils by looking only at a limited number of soil parameters. Soil 1 must possess some different characteristic that was not tested for. These unknown characteristics cause its interaction with sulfate to be very different from the other soils tested.

Conclusions

Several common isotherm models were fitted to the data using traditional linear transformation techniques and more recent nonlinear regression curve fitting methods. Nonlinear regression proved superior to the traditional methods. With the availability of nonlinear regression programs for microcomputers, it is easier and simpler to use such methods.

The extended Freundlich (Fitter and Sutton 1975) and a new model not previously discussed in the literature, which has been termed the extended Langmuir, proved superior to other models when using nonlinear regression curve fitting methods. Both were able to account for the desorption that occurred at low solution concentrations. Other models could not account for this and therefore misrepresented the data at low concentrations. They were limited due to the fact that the curves must go through the point (C.=0,  $q_{\bullet}=0$ ).

The extended Langmuir (a) term correlated better to the extractable sulfate terms and was therefore chosen as slightly preferable, however the use of both extended models is recommended until more soils are tested to confirm this.

No evidence for a solids effect was observed in preliminary studies. Comparison of adsorption capabilities of the six soils revealed that soil 4 had the greatest

sulfate adsorption capability and soil 5 had virtually none.

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#### COLUMN STUDIES

## Introduction

Preliminary column studies were performed using a mechanical vacuum extractor in order to determine if equilibrium information determined in the batch tests represents equilibrium in a flow through system. Although batch test equilibrium data is often applied to flow through systems, the validity of this step has not been determined.

Sulfate adsorption is dependent on sulfate solution concentration. Column operations offer the advantage that the experimental system is similar to the natural system of interest and the solution concentration does not vary over time. A constant solution concentration enters the column.

Most research done on sulfate adsorption has dealt with batch systems due to the relative ease in performing them. It seems apparent that the best way to study the natural system would be to exclusively use column studies. These experiments are generally more difficult and lengthier to perform and so are used less frequently than batch tests. It was thought that the use of a mechanical vacuum extractor might reduce the time involved for column studies. Its performance was also being evaluated in this

study.

Column studies have commonly been used to determine the leaching characteristics of soils. Undisturbed soil columns have been used by some investigators (Singh et al. 1980 and Khanna and Beese 1978). The difficulty in using undisturbed soil columns is in maintaining that they are truly undisturbed corings. The heterogenity of soils makes it difficult to insure that the field core represents the soil as a whole.

For these reasons and others, artificially packed soils are often used. Leaching experiments were performed using Buchner funnels for column studies done by Johnson et al. (1980), Johnson and Henderson (1978) and Johnson et al. (1979a). This method proved useful for obtaining water extractable and phosphate extractable sulfate. Johnson and Todd (1983) modified this procedure by using a mechanical vacuum extractor. Chao et al. (1962a) packed moist soil into glass tubing segments of different lengths that were taped together. They noted the movement of S<sup>35</sup> labelled sulfate throughout the soil columns after applying different amounts of water. There were large differences in sulfate movement between the soil types tested.

In the following experiments, the mechanical vacuum extractor was used to compare equilibrium determined in batch and column studies, water extractable sulfate and to evaluate the feasibility of using this device for subsequent column studies.

# Methods

To compare the equilibrium in a column to that in a batch system, it was necessary to perform an isotherm using columns. This will henceforth be called a column isotherm. To perform a column isotherm, six mechanical extractor tubes were used. Each tube was filled with approximately 1 g of paper pulp. Since the paper pulp contained a significant amount of leachable sulfate, it was first necessary to soak the paper pulp in RO/DI water. This was filtered and rinsed on the filter several times. Approximately 1 g (dry weight) was placed in the bottom of the tubes. These were then leached with 50 ml of RO/DI water twice. After this the wet paper pulp was compacted using the plastic tamper provided by the manufacturer. The second leachate was analyzed for sulfate contamination. It was found to be less than the detection limit of 0.05 mg SO<sub>4</sub>/1.

Six (6.00) grams of air dried soil were placed in the tube. Care was taken to avoid having excessive amounts of soil from sticking to the sides of the tube. The tube with soil was tapped twice to insure a uniform packing. The syringe and plunger were attached to the tube with the soil in it by using a small piece of rubber tubing. The reservoir tube was attached at the top. This setup is illustrated in Figure 23. Six sulfate solutions of the same concentrations as those in the batch experiment were



Figure 23. Mechanical vacuum extractor setup.

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used. These were 0, 2, 4, 8, 16, 32 mg S/1. An aliquot of each solution was added to one of the six reservoirs. In order to saturate the soil and allow some standing solution above the soil, the reservoir tube was tilted. This allowed air to enter which inturn allowed solution to run out. The tilting also facilitated rinsing of the sides to remove any soil that had adhered there.

The extraction time was set for one hour. After which the lower syringes were removed, samples were taken and analyzed. The empty syringe was replaced and another aliquot of solution was placed in the reservoir. Some solution was allowed to drain by tilting the reservoir. This insured that there was approximately 0.5 cm of solution above the soil.

This procedure was repeated until equilibrium was reached. Equilibrium was determined when the output solution had the same concentration as the input solution.

After equilibrium was established, aliquots of RO/DI water were added to the reservoir. This desorption part of the experiment was continued for several hundred milliliters of water.

The three soils that underwent these experiments were soil 2, 3, 4. All tubes with soil were stored at 4°C overnight between extractions. If cooled, they were allowed to come to room temperature for 1 hour before starting another extraction.

### **Results and Discussion**

An example of one breakthrough curve obtained at one solution concentration for soil 2 is shown in Figure 24. At each sulfate solution concentration, similar curves were obtained. To determine the solid phase concentration, the amount adsorbed during each extraction was determined by the difference technique. These were summed until equilibrium was obtained. Equilibrium was established when the output solution equalled the input solution within 5%.

The amount of sulfate extracted or desorbed when using the 0.00 mg S/l solution was summed. The total sulfate adsorbed for each treatment was plotted against the equilibrium or input solution concentration. These six points were then plotted against the 6.00 g batch data for that soil. These are shown in Figure 25-27.

There appears to be no significant difference in the isotherm obtained from the mechanical extractor and that of the 6.00 g batch data, although through visual observation adsorption appears to be slightly greater in the columns. In soil 2 and 3, this seems more pronounced at the high solution concentrations. There is also greater variability between experiments at the higher concentrations which might account for differences between batch and column tests.

In soil 4, there seemed to be greater adsorption at all concentrations except the highest. This could be due in part, to the fact that except at the highest











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concentration, the time to reach the equilibrium concentration took place over a period of about seven days. At the highest concentration the equilibrium experiment took only two days to complete. Its quite possible that over long periods of time, there is some conversion of the adsorbed sulfate, either due to physical/chemical means or possibly bacterial action. This would allow more sulfate to be adsorbed thereby causing an apparent increase in adsorption capacity. Since soils 2 and 3 had less overall adsorption capacity than soil 4, the adsorption experiment was completed within 2 days. Soil 4 having a higher adsorption capacity, required a greater total number of extractions in order to reach equilibrium. These extractions were spread out over several days. In the tube containing 16 mg S/l, equilibrium was reached after 2 days. Several days later, this was extracted again as a check and the soil showed more adsorption capacity. This phenomenon was not verified by further experimentation.

This raises an important consideration when conducting column experiments. Since bacterial populations can build up in a relatively short time periods, and since columns often offer optimal growing conditions for bacteria, it becomes necessary to determine if they are influencing the results. If they are, the question remains can they be eliminated or quantified. Research by Swank and Fitzgerald (1983) indicates that incorporation of sulfate per 48 hours may range from 0.0011 mg SO<sub>4</sub>/g of soil for 0 horizons to

7.84 x 10<sup>-6</sup> mg SO<sub>4</sub>/g soil for C horizons using Coweeta soils. Often such substances such as chloroform are used in an attempt to reduce the effect of bacterial population on adsorption results.

In short, preliminary column experiments suggest that the batch test should provide reasonable estimates of adsorption equilibrium in columns, especially at low solution concentrations.

The mechanical vacuum extractor was also used to determine water extractable sulfate. It was desirable to determine if the use of the mechanical extractor might give alternative results to that of the batch experiment. Results are presented in Table 5. Figures 4, 5, and 6 as discussed earlier, show the comparison of the values obtained from the mechanical extractor and batch procedure. From Table 5 and Figures 4, 5, and 6, it can be seen that the method using the mechanical extractor produced lower values of total water extractable sulfate than the batch method. The difference seems to occur in the initial release. One explanation for this may be due to the fact that the soil amounts were different in the two methods. In the column experiment, more soil was used than in the batch procedure. The smaller amount of soil would need to release more sulfate on a per gram basis to come to equilibrium in the same volume of solution, thus making it appear that it contains more sulfate. Over some time period, this would likely even out.

In an attempt to verify this, the first extraction using the mechanical vacuum extractor was compared to the 6.00 g batch data at 0.0 mg SO<sub>4</sub>/l solution concentration. There seems to be better agreement with the 0.0 tube of the 6.00 g batch data than that of the extraction procedure. This supports the assumption that differences were due to different soil amounts. However, it is difficult to determine this for sure when using only three soils.

Another explanation for the differences may be due to particle abrasion. In a batch system, and especially in the water extractable tests which continued for 15 extractions at 40 ml each, the amount of particle breakdown can be quite high. In the column, no particle abrasion takes place. The particle breakdown may allow greater amounts of sulfate to be released from the soil.

The advantages of using the mechanical vacuum extractor for equilibrium were not apparent. The extraction time was set for 1 hour. After this, it was necessary to remove the lower syringe and plunger. This was necessary to take samples. Replacing these and refilling the reservoirs took some time before the next extraction could proceed. At this rate, only four extractions could be done in one day. At lower concentrations, it took at least four extractions to reach equilibrium, if not more. This was dependent on the soil. In order to determine when equilibrium was reached, it was necessary to analyze the samples first. This also made the

procedure lengthier.

Since the experiments conducted on the three soils indicate that equilibrium determined in the columns is similar to that determined in the batch, there is no real benefit derived from using the mechanical vacuum experiments for equilibrium studies.

The use of this device for column studies was also evaluated. The difficulty arises in the fact that a given volume must be totally extracted before analysis can take place. It does not offer a continuous flow through the column, but merely incremental volumes that become tedious to collect. The fact that this device works on vacuum forces, also makes its application to natural flowing systems questionable. The extraction time of one hour became dubious when realizing the high interstitial fluid velocity this caused within the system. For example, the flowrate through the column was on the order of 50  $cm^3/hr$ . The diameter of the tube is 2.54 cm. This gives a surface area of 5.07 cm<sup>2</sup>. Dividing the flowrate by this area gives a specific velocity of 9.87 cm/hr. Assuming a porosity of 0.5, the interstitial fluid velocity becomes 19.7 cm/hr. Typical groundwater interstitial velocities are on the order of 2-7 cm/hr. In order to meet this range it would be necessary to use an extraction time of three hours, making the use of this device even more time consuming and tedious.

For leaching experiments, for which it was designed,

this device may be well suited, especially since batch systems offer such problems as particle breakdown. The question of whether this adequately represents natural systems is still in question due to high interstitial fluid velocities.

# Conclusions

Preliminary column studies using a mechanical vacuum extractor indicate that equilibrium information determined in batch systems is similar to that in column experiments. Experiments to determine water extractable sulfate using a mechanical vacuum extractor showed somewhat smaller amounts of sulfate released than in batch tests.

The use of the mechanical vacuum extractor for either equilibrium or column studies was determined to be infeasible. The question of whether it adequately describes natural systems is in doubt. The only logical method of choice are artificially packed, flow through columns, where natural groundwater interstitial velocities can be duplicated. These offer the advantage that they are continuous and unnatural vacuum forces do not come into play.

## KINETICS

## Introduction

The EPA method for conducting batch isotherms specified an equilibration time of one hour. One of the primary objectives of the research conducted for that agency is the comparison of batch systems to natural flow through systems represented by column studies. It was therefore necessary to follow their outlined procedure.

It seemed likely from extensive reviewing of the past literature, that a 1 hour equilibration time would be an insufficient amount of time to reach equilibrium between the solution concentration and solid phase concentration. Preliminary kinetics work was designed to determine if this were true for the soils used in this research.

Chao et al. (1962) used continuous shaking for different lengths of time up to 72 hours. Equilibrium was reached in 4 hours. After one to two hours there was no significant difference observed between continuous and intermittent shaking. The scheme of shaking one hour, leaving the suspension overnight and shaking again for one hour the next day was used.

Singh (1980) also found that this scheme gave identical results to continuous shaking for 8 hours upon which time equilibrium was attained. This procedure was also used by Hague and Walmsley (1973).

Equilibrium time varied among researchers. The time involved was generally several hours. Hasan et al. (1970) used 24 hours. Weaver et al. (1985) used 18 hours. It was difficult to find reference to only one hour equilibrium time, however, this was used by Gebbhardt and Coleman (1974).

# Methods

To look at the relationship between time and adsorption equilibrium, 6.00 g soil samples were used. A sulfate solution concentration of 23.967 mg/l was used. Nine soil samples were used for each of soils 2, 3, and 4. Solution concentrations were measured after 2, 5, 10, 15, 30, 60, 120, 240 and 480 minutes of shaking. The samples were filtered directly without centrifuging. Soil 6 was also tested using the same solids concentration and solution concentration. Three additional times were added to the original nine for this soil. These were 960, 1440 and 2880 minutes.

Other experiments involving soil 2 were done. The first involved rewetting the air dried soil. To rewet the soil, 3 ml of RO/DI water were added to nine, 6.00 g soil samples. These were allowed to sit for 24 hours. Twenty seven milliliters of the 23.967 mg/l sulfate solution were added to the rewet samples. This made the initial concentration 21.570 mg SO<sub>4</sub>/l in these samples. The original nine time increments were used.

Frozen, wet soil samples were also used. Frozen, unsifted wet soil 2 samples were used in the following manner. A soil sample was put in a plastic bag and allowed to thaw in the refrigerator. Another sample was thawed and allowed to air dry for several days. Although the soils were not sifted, care was taken to remove any small rocks or stones. Small clumps were crushed by hand. The end result was that the soil was close to that of the sifted soil. Three different experiments were run. The first involved taking 9 air dried samples of 6.00 g each and running the kinetic study as presented previously. Another nine, three day air dried samples of 6.00 g each were wet with 3 ml of water for 24 hours. Twenty seven milliliters of the same sulfate solution as used before were added to each and a kinetic study using the original 9 times was run.

The last experiment involved weighing 6.00 g soil samples of soil 2 that were thawed but field moist. Moisture content was determined on the wet samples so that the solids concentration could be calculated. Thirty milliliters of 23.967 mg SO<sub>4</sub>/l solution were added to each sample. The original time sequence of 2, 5, 10, 15, 30, 60, 120, 240, and 480 minutes was used.

#### **Results and Discussion**

Data for soils 2, 3, 4, and 6 are presented in Figures 28-31. Soil 3 and 4 showed only a slight increase in solid phase concentration with time after one hour. If 8 hours is taken to be the equilibrium point, then at one hour, the solid phase concentration is 95 % of that at 8 hours for soil 3 and 97 % in soil 4. Another way of looking at this might be to say that adsorption is 95 and 97 % complete after one hour in soils 3 and 4 respectively. In these 2 soils, an equilibrium time of one hour would be considered appropriate.

For soils 2 and 6, one hour appears to be inadequate. For soil 2, after one hour, adsorption was only 73 % complete, if 8 hours is used as equilibrium. The experiment involving soil 6, was continued for 48 hours. It can be seen from Figure 31, that adsorption was still taking place after 8 hours. If it is assumed that after 48 hours equilibrium was attained, the amount of the solid phase concentration at one hour was only 72 % of that at 48 hours. In the case of soil 6, adsorption was 94 % complete at eight hours when using 48 hours as the maximum.

The fact that two of the soils, 3 and 4, required only a short period of time to reach equilibrium and two of the soils, 2 and 6, needed longer periods of time in order to reach equilibrium bring several questions to mind.

The first is that could this relationship with time be

















one of the reasons for the increased variability in data when using soil 2 and 6. In an earlier discussion, it was presented that soil 1, 2 and 6 showed more variability of data points between experiments than soil 3 and 4. At that point, it was suggested that this was due to the heterogenity of the soils. Soil 2 and 6 had higher organic matter content, possibly producing a more heterogeneous soil makeup. Six grams may not have been a large enough sample size to reduce the impact of this variability.

In light of the kinetic information, it seems possible that variability between experiments may be due to slight miscalculations of shaking time, or possibly longer periods between shaking and centrifuging. A delay in taking samples from the tubes might also account for this.

This can be made clearer by looking at the differences in solid phase concentration. For example, in soil 6, if the difference in time of experiments was close to 10 minutes, perhaps one experiment was only shaken for 55 minutes while another for the same soil was shaken for 65 minutes, this could account for about a 5 % difference in solid phase concentration between the lower and higher values. This is for a 10 minute difference. This is quite possible even under careful experimental conditions.

The same 10 minute interval in soil 4 would account for an error of less than 0.4 % difference in solid phase concentration between lower and higher values. As evidenced in the isotherm data for soil 4, there was little variability between experiments.

Another question that this information brings up is whether the apparent delay in reaching equilibrium is due to the kinetics of sulfate adsorption or due to increased particle breakdown. Increased particle breakdown would facilitate increased sulfate adsorption due to opening up more active sites.

Barrow and Shaw (1977) demonstrated that using different shakers on "unstable" soils showed increased adsorption when more vigorous shaking was applied. It is quite possible that the longer the samples are shaken, the more abrasion that would occur. It was noticed after 24 and 48 hours using soil 6, filter blinding was a problem. This suggests particle breakdown, since it was not noticed at earlier times.

Soil 2 and 6 also had much higher organic carbon contents. It is quite possible that the longer the samples are shaken, the more shearing of organic matter that occurs from the surface. This organic matter may originally be bound to adsorption sites. The shearing may open up new sites for sulfate adsorption.

If this is true, the question now becomes why did the data from the column (mechanical extractor) experiments match so closely to that of the batch for soil 2? If the shaking exposes more adsorption sites, it would be expected that adsorption in the batch would be higher than that in the column. This was not the case. Since this is not the

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case, and it is assumed that adsorption is merely "slower" in certain soils, then it is peculiar that the column experiments did not show larger values than that of the batch since these experiments lasted longer than one hour. At this concentration for soil 2, there were a total of 3, one hour extractions.

The fact that equilibrium was reached after one hour in soil 3 and 4, but apparently not in soil 2 and 6, brought another possibility to mind. Perhaps there was some delay in adsorption due to a wetting problem, since soils 2 and 6 had higher total carbon content. It is possible that it takes some period of time for the solution to fully penetrate into the soil and specifically into the soil where active adsorption sites are located. For this reason, experiments involving the rewetting of soil samples were performed for soil 2.

Results for the wetting experiment are shown in Figure 32. Figure 32 shows the original kinetic data for soil 2 and kinetic data for soil 2 when it was wetted for 24 hours. There seems to be close correspondence at the earlier times. At approximately one hour, there is a slight deviation in the rewet situation compared to the original dry situation. It would be expected that if the problem with kinetics in soil 2 was a wetting problem, that at earlier times the q. values in the rewet situation would be higher than in the original situation. In other words, adsorption would be greater at earlier times and level out



Figure 32. Kinetic study comparing original, dry and original, rewet samples for soil 2.

faster than in the non-wetted situation. This was not observed and in this case, there was a decrease in adsorption after greater lengths of time. The value at 60 minutes does fall within the variability of the previous soil 2 batch experiments. Although the curve does seem to level out between 240 and 480 minutes, the solid phase concentration at 60 minutes is only 78 % of that at 480 minutes.

The evidence does not suggest that a wetting problem exists. It seems likely then that the observance of continual adsorption in soil 2 and 6 is more likely due to increased particle breakdown or shearing of organic matter from the surface of the soil. Equilibrium observed in the batch system was very similar to that in the preliminary column experiments, where no particle abrasion took place. The most likely explanation for this must be the obvious. The one hour shaking time represents some time prior to particle breakdown, or where particle breakdown is at a minimum. This would suggest that a one hour shaking period is sufficient time to reach equilibrium in the batch system for all soils. In fact, it suggests for some soils, extended shaking periods may give results which would not be representative of the natural system.

Other kinetic experiments involved using frozen soils originating from the same source as the dry soils. It is difficult to compare the results of the experiments using the frozen, dried soil to the original, since the
preparation was not the same. It might be expected that solid phase concentrations would be lower in the frozen, thawed and dried soil since small stones or other inert pieces of soil might not have been picked out. This was not the case, adsorption appeared to be faster than in the original soil as seen in Figure 33. This is evidenced by the greater q. values for the frozen, dried soil 2 at similar times. At later times, there is less adsorption. The curve seems to level out after 120 minutes. In this case, adsorption was at one hour, 83 % that at 8 hours as opposed to the 76% in the experiment using the original dry, stored soil 2 sample.

Very interesting results were obtained from the last two experiments, the frozen, dried, rewet and the frozen, thawed, field moist samples, Figure 34. Both of these two treatments acted in a similar fashion, evidenced by considerably less adsorption at all times. An explanation for this behavior may come from previous work done by Bartlett and James (1980). Their work dealt with changes in soil characteristics due to soil preparation as discussed earlier in the first section under experimental considerations. Reiterating, they found that air drying caused certain changes in the soil, which included organic matter oxidation and solubilization, increased surface acidity and other surface chemistry changes. The changes continued the longer the soils were stored. If organic matter is really oxidized and solubilized, this might allow









more adsorption sites to open up, thus increasing adsorption. A decrease in surface acidity might also aid in sulfate adsorption.

The frozen, thawed, field moist sample showed the least amount of adsorption. Drying for several days but then rewetting seemed to reduce the effects of drying. Rewetting the soil that had been stored for over a year, had little effect in decreasing adsorption. Drying the soil for only 3 days but immediately experimenting on it seemed to increase adsorption at early times but decrease it later on. No other explanation could be offered to explain this phenomenon. One method to test this, would be to do a similar set of experiments on soil 4, which had virtually no organic matter content, and see if the results were similar. If this was largely due to changes in organic matter, this phenomenon would not be expected in soil 4.

Another concern, is that frozen thawed soils do not adequately represent field moist samples. Bartlett and James (1980) concluded that fewer changes occurred in freezing than in drying, however they were not looking at sulfate adsorption. If it is assumed that the work done with frozen, thawed samples is representative of field moist soil, then the results obtained could be quite significant. Adsorption data presented using dried soils could indicate that a given soils sulfate adsorption capacity is 40 % higher than the actual field moist

situation. This would be important if one is trying to quantify a given areas response to acid rain as in the current EPA study.

### Conclusions

It appears that the increase in adsorption as time increases, as exhibited by soil 2 and 6 is not due to a wetting problem, but is more likely attributed to particle breakdown and shearing off of organic matter. This particle breakdown after long periods of shaking could be opening up new active sites for sulfate adsorption giving the appearance that adsorption equilibrium is a slow process. The one hour shaking time seems to best represent equilibrium as determined by comparison with the column data.

Soils 3 and 4 did not exhibit a similar pattern of adsorption capability in the kinetic study as did soils 2 and 6. Low organic matter content and possibly a more stable soil complex could be the reason that the solid phase concentration levelled out at an early time.

Experiments using frozen soils suggest that drying increases the adsorption capacity. Rewetting of three day dried soils reduced this capacity, however rewetting of air dried soils stored in excess of one year showed little change. Frozen, thawed soils exhibited the least sulfate adsorption capacity.

### DESORPTION

## Introduction

Sulfate adsorption cannot be properly discussed without addressing sulfate desorption. Desorption is often of interest due to its relevance to nutrient release in soils. With the concern of acid rain and its relationship with disrupting natural systems, the question of desorption has significant meaning. Knowledge of whether sulfate adsorption is a reversible or irreversible reaction is still largely unknown. The implications of this are extremely important in understanding the long term effects of acid rain. It is for this reason, that desorption has been an integral part of the adsorption studies.

Previous desorption work has dealt with using different extractants to remove adsorbed sulfate such as phosphate and nitrate solutions (Hague and Walmsley 1973, Searle 1979, Singh 1984c). Although they are interesting from a nutrient replacement point of view, they may not be as applicable for acid rain work. Water as the extractant would seem more appropriate.

Other desorption work has included looking at desorption as it relates to time (Singh 1984c, Barrow and

Shaw 1977), the type of surface (Aylmore et al. 1967, Sanders and Tinker 1975), pH (Singh 1984c, Rajan 1979) and incubation time (Sanders and Tinker 1975, Barrow 1979).

The desorption research conducted for this thesis, consisted of preliminary work looking at desorption of sulfate after the addition of different sulfate solutions. This would provide information on the reversibility of the reaction when using water as the extractant.

### Methods

Desorption experiments consisted of an extension of the adsorption experiment. Upon collection of a sample after the sulfate adsorption experiment was completed, the remaining supernatant was decanted, leaving only a small amount of sulfate solution trapped within the soil. The volume of this solution was determined by weighing the sample before the experiment started and after decanting off the liquid. The difference would be the weight of the solution trapped in the soil sample. RO/DI water was then added to bring the total solution volume to 30 ml. Thig was shaken for an hour in order to facilitate desorption. The contents were then centrifuged for 30 minutes at 1500 rpm. A sample was taken, filtered and analyzed. This was performed for each tube of the adsorption isotherm. The complete experiment was done twice, resulting in two desorption isotherms per soil. There was one exception in treatment, between the two experiments. In one treatment,

the desorption part of the experiment was conducted within 2 hours of the adsorption experiment. In the other, the desorption part of the experiment was not conducted until 11 days after the adsorption part for soils 2, 3, and 4, six days after for soil 6 and 14 days after for soil 1. In the experiments where desorption was not conducted until several days later, the adsorption solution was decanted off and the samples were capped and remained so for the entire incubation period.

Desorption experiments were also conducted on the 0.60 g adsorption experiments, within several hours of the adsorption experiment. No incubation experiments run.

Desorption experiments were also conducted using the mechanical vacuum extractor. In this case, the desorption part of the experiment started immediately upon reaching adsorption equilibrium. This continued for several hundred milliliters of RO/DI water.

# **Results and Discussion**

Results for the 6.00 g experiments for each soil are presented in Figures 35 - 39. For soils 1, 2, and 3 little difference was observed between incubated and nonincubated experiments. There is a slight difference noted at the higher concentrations. This is emphasized on the graphs by the use of arrows. Soil 4 exhibits a more dramatic difference between the two experiments. It seems possible that the soil properties of soil 4 are such that sulfate









Figure 37. Adsorption/desorption isotherm data for two experiments using soil 3.









may be more difficult to remove, once it has bound to the particle surfaces. This is also suggested by the extractable sulfate results. Soil 4 had the lowest water extractable sulfate results even though the total phosphate extractable results were similar to the other soil. Soil 1 showed virtually no difference in results from the incubated and nonincubated treatments, even though this soil was incubated for the longest period of time. This suggests that sulfate is easily removed. Soil 1 also had the greatest initial release of sulfate when determining total water extractable sulfate. In fact it was ten times that of soil 4. Phosphate extractable results were the same for both soils. The mechanisms for sulfate retention exhibited in soil 4 seem inoperative in soil 1.

It is quite possible that this phenomenon observed in soil 4 is not true irreversibility. In order to discover this, it would be necessary to continue the desorption part of the experiment by performing multiple extractions. It is possible that it is related to the kinetics of desorption, although Singh (1984c) found desorption to be virtually complete within 30 minutes with only a gradual increase with time over a period of 50 hours.

Sanders and Tinker (1975) continued desorption experiments by performing multiple extractions and found that adsorption was reversible over short periods of time but not completely reversible over days. They also found that irreversible bonding can take place upon exposure of

new adsorption sites. This was determined by grinding magnetically extracted particles. It was postulated that adsorption sites on the soil particles themselves which could bind irreversibly had already been occupied by sulfate or other ions. It is possible that irreversible bonding sites on soil 4 had not all been filled, which allowed sulfate to permanently bind to the surface.

Aylmore et al. (1967) noted irreversibility of sulfate adsorption in experiments using laboratory synthesized iron and aluminum oxides. No such irreversibility was demonstrated when using two kaolinite clays. This might also explain why soil 4 exhibited a more pronounced hysterisis than the other soils. Soil 4, it is remembered had a fair amount of inorganic iron and aluminum, but had a very low percent total carbon. In the other soils, organic matter may be bound to active adsorption sites reducing the amount of irreversible reactions that can occur.

Rajan (1979) attributed hysterisis observed in his study to pH changes during desorption. When the pH was maintained, there was an absence of hysterisis. He also noted, that regardless of the initial surface concentration of sulfate, the quantity left on the surface after desorption was about the same. This was after five extractions of a  $Ca(NO_3)_2$  solution.

The results of the 0.60 g experiments have not been included in this presentation. Large variability in the adsorption experiments led to even larger variabilities in

the desorption experiments. Little information was gained by looking at this data.

The results of the column studies proved interesting. Adsorption isotherms and successive desorption extractions are presented in Figures 40-42. In the case of soil 2, the adsorption experiments were completed after 100 ml of sulfate solution had been added in all cases but the 5.992 mg SO<sub>4</sub>/l concentration. A total of 150 ml was required in this case. Desorption started the following day. A total of 350 ml of RO/DI water extractant was used in all but the lower concentration tube. In this case, 300 ml were used. The desorption part of the experiment was conducted over several days.

For soil 3, equilibrium was attained within 150 ml of sulfate solution for all concentrations except 5.992 mg  $SO_4/l$ , in which 250 ml of solution were required. Desorption was started the following day, for a total of 300 ml RO/DI water for all concentrations except the lower one. In this case, 200 ml RO/DI water were used.

In looking at the data from the soil 2 experiment, Figure 40, adsorption appears to be reversible. In fact, with the exception of the tube with an original concentration of 47.934 mg SO<sub>4</sub>/1, removal of adsorbed sulfate was complete within 100 ml of RO/DI water. For the tube with the original concentration of 47.934 mg SO<sub>4</sub>/1, removal of adsorbed sulfate was complete within 200 ml of water. Little explanation can be offered as to why this





Figure 41. Adsorption isotherm for soil 3 using the mechanical extractor, successive desorption points for each tube are also shown.



tube required additional extractions, since it was run at the same time and under identical conditions as the other tubes. Perhaps the variability of soil samples would offer an explanation. It is also possible that desorption is more difficult when higher concentration are used in the adsorption experiment. This was not noticed in the 95.869 mg  $SO_4/l$  tube, but the method in which the desorption points were obtained might explain this. The amount of sulfate removed after each desorption extraction was subtracted from the final q. value from the adsorption part of the experiment. The amount of solution trapped in the soil was accounted for, since it was a significant amount of solution. It was between four and five milliliters in most cases. The amount of sulfate remaining on the surface of the soil as determined by the difference method just described was plotted against the solution concentration.

In soil 3, a similar phenomenon was noticed at the higher concentration. Except in the tube with an original concentration of 95.869 mg SO<sub>4</sub>/l, all desorption points fell along the adsorption curve, indicating that adsorption is reversible. At the high concentration, although the first desorption point fell within the curve, successive desorption points did not. There was an indication that they would have met that curve if several more extractions had been done. All experimental conditions remained the same. It is possible that some variability within the soil was the cause of this. Perhaps more aluminum or iron oxide

particles had been in this sample, making the release of adsorbed sulfate more difficult and slower. The other explanation is the same one as presented for soil 2. For higher concentrations, desorption may be slower or more difficult.

Soil 4 was interesting because of the longer times that were involved in both the adsorption and desorption parts of the experiment.

Equilibrium was reached within 90 ml of extractant for the 95.869 mg SO<sub>4</sub>/l and 47.934 mg SO<sub>4</sub>/l tubes. A total of 200 ml of extractant were needed for the 23.967 mg SO<sub>4</sub>/l tube, 250 ml were required for the 11.984 mg SO<sub>4</sub>/l tube, and 550 ml were required for the 5.992 mg SO<sub>4</sub>/l tube.

Six days elapsed before desorption was conducted on the two higher concentration samples. This would be similar to the case in the batch tests, in which a waiting time occurred. In the tube with the original concentration of 47.934 mg SO<sub>4</sub>/1, there does appear to be some hysterisis effect in the initial water extractions. However, after repeated water extractions, the data points end up falling on the adsorption curve. At the highest concentration, there was less total adsorption than at 47.934 mg SO<sub>4</sub>/1 concentration. This was discussed previously in the column study section dealing with adsorption. Briefly reiterating, one possibility for this, may be due to the fact that several days after equilibrium had been attained in the 47.934 mg SO<sub>4</sub>/1 tube, adsorption

extractions were run and it was found that more sulfate was being adsorbed. This was not tried at the higher concentration but it is quite possible that a similar increase in adsorption would have occurred. This would have given a higher  $q_{\bullet}$  than was subsequently recorded. If the  $q_{\bullet}$  value was higher then the desorption data points would also have been higher and would not have fallen below the adsorption curve. These data look more like that of the  $47.934 \text{ mg } SO_4/1$  desorption points than that of the other tubes, in both shape of the curve and initial slope.

It seems that repeated water extractions do remove adsorbed sulfate, although depending on the soil and total time of the experiment, the rate at which this is removed may vary.

# Conclusions

A hysterisis effect was noted in the batch tests for two of the soils after a waiting period. However, this was only done for one water extraction. In conducting desorption experiments using the mechanical vacuum extractor, it appears that upon repeated extractions, removal of adsorbed sulfate is possible. Initially, at higher concentrations, there is some evidence that adsorption is not totally reversible or at least reversibility is not as fast as that at lower concentrations. A more rigorous experimental approach to this problem should be applied before sound conclusions can be made. Looking at a waiting period after equilibrium has been attained and before desorption is started would be a the kind of experiment that could be done to look at irreversibility. It is important to note that some consideration should be given to microorganism growth within the tubes. This is necessary to determine if the retention and release of sulfate is due totally to physical/chemical sorption processes or microbiological processes or some combination of the two.

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#### CONCLUSIONS

The subject of sulfate retention and release in soils is not only complex but extremely comprehensive, and too broad to be covered in a single masters thesis. In fact only a few topics could be approached in any detail.

The majority of the work dealt with fitting isotherm models to sulfate adsorption data. Although this is the usual course of action with any adsorption study, the effort in this work dealt with comparing not only different models but different fitting techniques. The traditional method of transforming the data was to modify the equation in order to linearize the data. The model constants could be obtained by determining the slope and y-intercept. The more recent approach, made possible by programs designed for use on micro and macro computers, employs nonlinear regression curve fitting techniques. Nonlinear regression methods proved superior to the transformation techniques and required less time and effort in analysis.

In comparison of general isotherm models, it was clear that at the lower concentrations used in this research, a model was necessary that accounted for native sulfate. Only one model, the Fitter and Sutton (1975) extended Freundlich could be found in the literature. This general idea of adding an extended term was also used with the

Langmuir model. Although this was not referenced anywhere, the approach seemed very plausible. In fact the extended Langmuir as it is called, proved in many cases superior to other models presented in the literature. The extended Freundlich and extended Langmuir were determined to be the best and most consistent in describing sulfate adsorption data.

A qualitative comparison of the six soils used suggested that organic matter and its combination with iron and aluminum oxides, is extremely important in determining adsorption/desorption properties of soils. The difficulty that many researchers had in correlating iron and aluminum oxides with adsorption may be due to incomplete consideration of the organic matter present.

Column studies using a mechanical vacuum extractor gave preliminary evidence suggesting that equilibrium reached in batch tests is adequate in describing equilibrium in a flow through system. The feasibility of using a mechanical vacuum extractor as a substitute for flow through columns was also studied. It was found to be extremely time consuming and tedious, and was deemed an impractical substitute.

Kinetic studies in combination with the column data, indicated that a one hour shaking period in the batch studies was adequate in allowing equilibrium to occur. In fact a longer period of shaking led to "unnatural" breakdown and shearing of soil particles in some soils, and perhaps an overestimation of adsorption capability.

An interesting phenomenon occurred when using field moist, frozen samples of the same soil as tested dry. The dry, stored soil showed a much higher adsorption capacity than the field moist. This could lead to large overestimations of sulfate adsorption capacity and may be a serious consideration for researchers dealing with any study designed to quantify sulfate adsorption capacity of a wide variety of soils.

Desorption experiments suggested that the release of sulfate may be more difficult in some soils or after some waiting period, but is still possible.

### FUTURE RESEARCH

Much of the research conducted as part of this thesis was preliminary in nature. The success of an experiment may not just be in the questions that were answered but in the new questions that were raised and in the ideas and plans for future experiments. This section is offered as an attempt to outline further experiments that could be done in order to elucidate sulfate retention and release in soils.

- In an effort to verify if a solids effect does exist for sulfate adsorption, studies using highly sulfate retentive soils would need to be performed. Larger sample sizes should be used to eliminate variability. For example, soil samples of 4 and 40 g could be used at soil:solution ratios of 1:5 and 1:50. This could be accomplished by using larger centrifuge tubes.
- The use of pure aluminum oxide and iron oxide species at different ratios may also shed some light on this question of a solids effect. Use of these substances may also provide more information on

adsorption mechanisms and relationships between sulfate adsorption, aluminum and iron oxides and organic matter.

Adsorption experiments using column studies are the most attractive. Practical problems such as particle abrasion and breakdown could be eliminated in the column. A wide variety of combinations could be performed. As mentioned previously, determining the role of microorganisms in the column should be done, especially for experiments involving several days to complete. Suggested column experiments are presented below.

- To understand the role of pH in sulfate retention and release, it would be necessary to reduce and raise the pH of the initial solution. Looking at the release of aluminum at varying pH would also be interesting since aluminum toxicity is a major problem associated with acid rain.
- Using a solution, more typical of acid rain water including various constituents would be desirable, in order to understand the interaction of other anions on sulfate retention. Using the same soils as in these studies, a comparison of sulfate adsorption under differing solution compositions could be made.

- Performing experiments at different temperatures would be a very important area of study. Most work on sulfate adsorption has been conducted at 20° C. This does not shed light on what would happen under a wide range of temperatures, similar to those occurring naturally.
- Studies comparing field moist samples and dried, stored samples should be conducted to determine if sulfate adsorption capacity is changed by drying, to what extent and possible explanations for this.
- Desorption experiments conducted using columns are preferred to batch studies because it eliminates particle breakdown problems. Experiments comparing a waiting period between adsorption and desorption experiments and no waiting period would be an interesting place to begin.
- Desorption experiments using highly retentive soils or aluminum and iron oxide particles could also be done to provide information on whether permanent adsorption sites for sulfate exist.

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APPENDIX

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## APPENDIX

## Introduction

Ion Chromatography was developed in the mid 1970's at the Dow Chemical Company. Chromatography involves separation due to differences in equilibrium distribution between two different phases, a mobile phase and a stationary phase. Each solute molecule interacts with the column packing material, constantly moving from the mobile to stationary phase. A peak of each kind of solute molecule is now possible. The sample components which favor the stationary phase migrate slower and separation is obtained.

There are generally three separation modes; mobile phase ion chromatography, high performance ion chromatography and high performance ion chromatography with exclusion. The HPIC facilitates the separation of inorganic ions. Since this was the separation mode used in this study, it will be the one discussed hereafter. HPIC columns consist of an inert hydrophobic core, with sulfonic acid functional groups on the surface. By limiting the functional groups to the surface, the diffusion paths are shortened. This produces high efficiencies with moderately low capacities.

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The sample solution is introduced as a slug into the column. The anions in solution compete for cationic sites on the surface of the ion exchange material. The carrier solution, or eluent preserves the neutrality of the resin, by exchanging with the sample ion retained there.

Various factors affect the attraction of an ion for an exchange site. These include ionic charge, ionic size and pH to mention a few. Resin type also affects the attraction of an ion to an exchange site.

Ion chromatography utilizes a suppressor to change the concentration of the highly conductive eluent ions to species that are less conductive. In this way, a wide linear dynamic range is provided for, one with high sensitivity and high selectivity. The suppressor is a cation exchange device in hydrogen ion form. This converts carbonate eluent to weakly ionized carbonic acid, while converting solute ions into more conductive acid forms.

The suppressor operates with continuous regeneration. A dilute sulfuric acid regenerate solution flows counter current to the eluent. This makes the background conductivity dependent on both the eluent and regenerate composition and flowrate.

Ion Chromatography uses the conductivity of the solution to measure concentration of ions in solution. The ionized molecules carry electrical current, therefore the higher the concentration, the higher the conductivity. Factors such as temperature and degree of dissociation are

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important since they will affect conductivity.

## The system

The ion chromatograph used in this study was a Dionex 2000 i/sp (Dionex Corporation, 1228 Titan Way, P.O. Box 3603, Sunnyvale, CA 94088). The column type was a HPIC-AS4, which has a 3 % crosslink and an operating pressure of 700-900 psi.

The eluent consisted of 1.7 mmolar NaHCO; and 1.8 mmolar Na<sub>2</sub>CO<sub>3</sub>. The flowrate was approximately 2 ml/min, with a system operating pressure of 750 psi. The regenerate was a 0.0025 N sulfuric acid solution, with a flowrate of approximately 3 ml/min. The regenerate was under pressure by nitrogen gas, which facilitated its movement throughout the system.

The output range was normally maintained at 30 uS, however in adsorption work at low concentrations, 1 uS or 3 uS sensitivities were used. The detection limit at 1 uS was determined to be 0.05 mg/l. When working at low concentrations it was necessary to presoak filters, filter holders and centrifuge tubes in order to eliminate sulfate contamination. This soon became standard procedure at any concentration.

When determining phosphate extractable sulfate, complete separation of phosphate and sulfate could not be obtained. Because the phosphate concentration was very high, there was some overlap between peaks. For this

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reason a verifiable detection limit of 0.6 mg/l was established.

## Calibration and blank runs

As a daily start-up, a RO/DI water blank was analyzed as a check against contamination of the water supply and to insure that the system was working properly.

A standard curve was determined in the range of the samples to be tested. If a standard curve was made prior to the days start-up, several standards were run to check the accuracy of the standard curve. If the check standards matched within 5 % of the expected value, a new curve was not made for that day. If they did not, a new calibration curve was determined.

After 10 samples had been analyzed, a check standard was analyzed to insure the system was continually working properly. The final sample analyzed was also a check standard.