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Abstract — Résumé — Аннотация — Resumen

Soil properties and constituents in relation to mechanisms of sulphate adsorption. Studies were conducted by the use of soil column-chromatographic techniques, adsorption-desorption phenomena, and isotopic exchange procedures in order to delineate cause and effect relationships involved in the retention of sulphate by soils.

The distribution patterns of S^{35} in soil columns were found to be dependent on soil characteristics and the amounts of water applied, but were independent of the amounts of sulphate applied. Samples of Latosols, Lateritic, and Ando soils showed distinct abilities to hold sulphate against leaching. The results of adsorption-desorption equilibrium studies were in good agreement with the column studies. Both indicated that sulphate retention is dependent on the concentration of the equilibrium solution. Adsorption isotherms conformed to the Freundlich type and adsorption maxima were not indicated. Although certain soils were shown to have a marked capacity to retain sulphate, the sulphate could be easily desorbed.

The treatments of sulphate-retentive soils for the removal of organic matter, free iron and free aluminium all resulted in marked reductions in sulphate retention. The amounts of sulphate retained by reference clays were in the order kaolinite > illite > montmorillonite. Al-saturated clays retained more sulphate than H-saturated clays. Sulphate adsorption generally increased as the degree of neutralization and pH of an Al-saturated resin increased, whereas sulphate adsorption decreased with increasing pH of Al-saturated bentonite. The data suggest that two factors, the formation of reactive OH anion-exchange sites and the effect of pH on amphoteric properties of reactive groups, were operative in these systems.

Sulphate adsorption by soils from salt solutions and by soils saturated with different cations followed the order of chemical valency of cations. The influence of different cations was shown to be associated with two factors, the nature of cations and pH. Resolution of the two factors indicated that pH had the more significant influence. The influence of different cations was attributed to effects on electrokinetic potentials and anion repulsion.

The evidence indicates that sulphate retention by soils may involve several mechanisms including:

- (1) Anion exchange involving hydrous oxides of Fe and Al and crystal edges of clays at low pH's;
- (2) The retention of sulphate by co-ordination with hydroxy-aluminium complexes;
- (3) "Salt" or "molecular" adsorption resulting from attraction between the surface of soil colloids and the salt;
- (4) Retention by amphoteric organic compounds.

Propriétés et éléments constitutifs du sol eu égard aux mécanismes d'adsorption du sulfate. Pour étudier les rapports de cause à effet dans la rétention du sulfate par les sols, les auteurs ont fait appel à la chromatographie sur colonne, aux phénomènes d'adsorption-désorption et aux méthodes d'échanges isotopiques.

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Ils ont constaté que la distribution de ^{35}S dans les colonnes de sol dépendait des caractéristiques du sol et des quantités d'eau ajoutées, mais qu'elle était indépendante des quantités de sulfate appliquées. Les échantillons de latosols, de sols latéritiques et de sols ando avaient un pouvoir marqué de rétention du sulfate à la lixivation. Les résultats des études sur l'équilibre entre adsorption et désorption concordaient fort bien avec ceux des expériences au moyen de colonnes. Les uns et les autres indiquaient, en effet, que la rétention du sulfate était fonction de la concentration de la solution à l'état d'équilibre. Les isothermes d'adsorption étaient conformes au type de Freundlich, les maximums d'adsorption n'étant pas indiqués. Alors même que certains sols avaient un pouvoir marqué de rétention du sulfate, celui-ci pouvait être facilement désorbé.

Le traitement de sols à fort pouvoir de rétention du sulfate, en vue de l'élimination des matières organiques, du fer libre et de l'aluminium libre, avait toujours pour effet une réduction sensible de ce pouvoir. Les quantités de sulfate retenues par les argiles types décroissaient dans l'ordre suivant: kaolinite > illite > montmorillonite. Les argiles saturées d'ions Al retenaient plus de sulfate que les argiles saturées d'ions H. D'une manière générale, l'adsorption de sulfate augmentait en même temps que le degré de neutralisation et le pH d'une résine saturée d'ions Al, tandis que l'adsorption de sulfate diminuait avec l'augmentation du pH de la bentonite saturée d'ions Al. Les données réunies pour ces systèmes semblent indiquer l'action de deux facteurs: formation de sites d'échange d'ions OH réactifs; effet du pH sur les propriétés amphotères des groupes réactifs.

L'adsorption du sulfate par des sols à partir de solutions salines et par des sols saturés de différents cations suivait l'ordre de valence chimique des cations. On a constaté que l'influence des différents cations était liée à deux facteurs: la nature des cations et le pH. L'analyse des deux facteurs a montré que l'influence du pH était prépondérante. Les auteurs attribuent l'influence des différents cations aux effets exercés sur les potentiels électrocinétiques et à la répulsion des anions.

Il ressort des données recueillies que la rétention du sulfate par les sols peut mettre en jeu plusieurs mécanismes, notamment les suivants:

1. Echange d'anions, dans lequel interviennent l'oxyde de fer et l'alumine hydratés ainsi que les arêtes des feuillettes d'argiles à pH faible.
2. Rétention du sulfate par coordination avec des complexes à l'alumine hydratée.
3. Adsorption «saline» ou «moléculaire» résultant de l'attraction entre la surface des colloïdes de sols et le sel.
4. Rétention par des composés organiques amphotères.

Свойства и состав почвы в связи с механизмом адсорбции сульфата. Для установления причины и эффективных связей, участвующих в удержании сульфата почвой, проводились исследования с помощью методов хроматографии почвы на колонке, феномена адсорбция-десорбция и процессов изотопного обмена.

Была обнаружена зависимость распределения образцов S^{35} на колонках почвы от характеристики почвы и количества воды, но не наблюдалось никакой зависимости распределения от количества сульфата. В образцах лато-почв, латеритных почв и андо-почв обнаружена способность удерживать сульфат от вымывания. Результаты исследований равновесия адсорбции-десорбции не расходились с исследованиями на колонке. Оба вида исследований показали, что удержание сульфата зависит от концентрации равновесного раствора. Изотермы адсорбции соответствовали типу изотерм Фрейндлиха, а максимальные значения адсорбции не указывались. Несмотря на то, что некоторые виды почв показали способность удерживать сульфат, он все же легко мог десорбироваться.

Обработка почв, способных удерживать сульфат, на предмет удаления органического вещества, свободного железа и свободного алюминия, привела к заметному снижению удержания сульфата. Количество удерживаемого сульфата различными видами глинозема возрастало в порядке их перечисления: каолинит, иллит, монтмориллонит. Насыщенные алюминием глиноземы удерживали сульфата больше, нежели глиноземы, насыщенные водородом. Адсорбция сульфата вообще возрастает по мере увеличения степени нейтрализации и pH насыщенной алюминием смолы, но в то же время она понижается с повышением

pH насыщенного алюминием бентонита. Данные говорят за то, что в этих системах действительными оказались два фактора: образование реактивного OH анионообменных сторон и воздействие pH на амфотерные свойства реактивных групп.

Адсорбция сульфата почвами из соляных растворов и почвами, насыщенными различными катионами, следует порядку химической валентности катионов. Влияние различных катионов связано с двумя факторами: характером катионов и pH. Разделение двух факторов показало, что pH имеет более существенное влияние. Влияние различных катионов приписывалось воздействиям на электрокинетические потенциалы и отталкивание анионов.

Такое доказательство указывает на то, что удержание сульфата почвами может повлечь за собой несколько механизмов, включая:

1. обмен анионов, затрагивающий водные окиси железа и алюминия, а также кристаллические ребра глинозёмов при низких pH;
2. удержание сульфата координированием с окси-алюминиевыми комплексами;
3. „соляная“ или „молекулярная“ адсорбция, получающаяся в результате притяжения между поверхностью коллоидов почвы и солью;
4. удержание амфотерными органическими соединениями.

Propiedades y constituyentes del suelo que influyen en la adsorción de sulfatos. Para determinar las relaciones de causa a efecto que intervienen en la retención del sulfato por los suelos, los autores de la memoria recurrieron a técnicas cromatográficas de columnas de suelo, a fenómenos de adsorción-desorción, y a métodos de intercambio isotópico.

Se observó que los tipos de distribución del ^{35}S en columnas de suelo dependían de las características del suelo y de las cantidades de agua administradas, pero no de las cantidades de sulfato aplicadas. Las muestras de suelos "latosoles", lateríticos y "ando" acusaron diferente capacidad para impedir la lixiviación de los sulfatos. Los resultados obtenidos estudiando el equilibrio de adsorción-desorción concuerdan con los alcanzados con columnas de suelo. Ambos demuestran que la retención del sulfato depende de la concentración de la solución en equilibrio. Las isothermas de adsorción se ajustan a los de Freundlich; no se observaron máximas de adsorción. Aunque ciertos suelos tenían una marcada capacidad de retención de sulfato, este elemento podía desorberse fácilmente.

Eliminando las sustancias orgánicas, el hierro y el aluminio libre de los suelos capaces de retener el sulfato, disminuyó de manera sensible la cantidad de sulfato retenido. De las arcillas empleadas, el caolín retuvo el sulfato más que la illita y ésta más que la montmorillonita. Las arcillas saturadas de Al retuvieron más sulfato que las saturadas de H. Por lo general, la adsorción del sulfato aumentó a medida que se incrementaba el grado de neutralización y el pH de una resina saturada de Al, y disminuyó cuando se aumentaba el pH de la bentonita saturada de Al. Los resultados parecen indicar que en ambos sistemas influyen dos factores: la formación de lugares de intercambio de aniones OH reactivos, y la influencia del pH sobre las propiedades anfóteras de los grupos reactivos.

La adsorción por los suelos del sulfato contenido en soluciones salinas y la adsorción por suelos saturados de diferentes cationes correspondió al orden de valencia química de los cationes. Se demostró que la influencia de los diferentes cationes estaba asociada a dos factores: la naturaleza de los cationes y el pH. El estudio de ambos factores puso de manifiesto que el pH desempeña un papel más importante. La influencia de los diferentes cationes se atribuyó a los efectos ejercidos sobre los potenciales electrocinéticos y sobre la repulsión aniónica.

Se demostró que en la retención del sulfato por los suelos pueden intervenir varios procesos, en especial los siguientes:

1. El intercambio aniónico con óxidos hidratados de Fe y de Al y aristas de cristales de arcilla de bajo pH.
2. La retención del sulfato por coordinación con complejos de hidroxialuminio.
3. La adsorción "salina" o "molecular" resultante de la atracción entre las superficies de los coloides del suelo y la sal.
4. La retención por los compuestos orgánicos anfóteros.

Introduction

Areas of sulphur deficiency for plant growth are known to occur in different regions of the world. The soils of New Zealand, Australia, and areas of the north-western United States may be cited as examples. The occurrence of sulphur deficiency has stimulated the need for understanding the cause and effect relationships of sulphur retention and movement in soils.

The exact mechanisms of sulphate retention by soils remain an enigma in spite of recent advances in soil science. On the one hand, part of the evidence suggests that an anion-exchange mechanism is involved in sulphate adsorption. A considerable amount of data could be cited as examples. The early work of MATTSON [20] clearly indicates the importance of sesquioxide content and pH relative to isoelectric points in the retention of sulphate. The data of ENSMINGER [11] indicate that in plots having a history of liberal phosphate applications the phosphate displaced the sulphate, which moved to the heavier textural B horizons. KAMPRATH [17] showed that sulphate retention by soils and clays was decreased by the additions of phosphate to the equilibrium solution. On the other hand, some evidence suggests that molecular or salt adsorption of some type may be involved with sulphate retention. AYRES and HAGIHARA [3] leached soil columns, to which K salts had been added, and found that the amount of K eluted depended upon the anion with which it was associated. A complete retention of K in the case of some salts, without displacement of other cations, was interpreted in terms of simultaneous sorption of both cations and anions by humic and hydrol-humic latosols. WADA [30] [31] has conducted extensive studies on electrolyte uptake by halloysite. GARRETT *et al.* [12] have obtained a series of labile halloysite-salt complexes. THOMAS [28] has presented evidence of "electrolyte imbibition", a term which he used to designate the uptake of an ionic compound by soil.

It appears that in some cases an anion-exchange process may occur, while in some other cases simple anion-exchange reactions will not completely explain the retention of sulphate by soils. It is also apparent that studies to determine the relationships of soil properties and constituents should proceed or accompany investigations designed to elucidate the mechanisms of sulphate retention by soils. This paper is concerned with the results of studies involving sulphate on a range of soils from the north-western area of the United States. Much of the detailed information is published or now in the process of publication. Those parts pertaining specifically to the question posed here are brought together in this review. The objective is to delineate more clearly cause and effect relationships involved in the retention of sulphate by soils.

Materials and methods

SOILS

Soil samples from the upper 7 in of 15 important soil series of Oregon were used in this study. These series represent a wide range of soil characteristics and geographic locations in the State. Some series were selected from the areas where sulphur responses have been observed. The geographic locations, parent materials and great soil groups of these soils are presented in Table I. More detailed information on the results of chemical and physical analyses are given by CHAO *et al.* [7] [15].

TABLE I

GENERAL CHARACTERISTICS OF THE SOILS USED IN STUDIES OF SULPHATE ADSORPTION AND MOVEMENT [7]

Soils*	Geographic area	Parent material	Great soil groups
Willamette ^{a)} (Woodburn ^{b)})	Willamette Valley	Water-deposited silts	Prairie or Grey-Brown Podzolic
Chehalis ^{a) b)}	Willamette Valley	Recent alluvium	Alluvial
Aiken ^{a)} (Jory ^{b)})	Cascade, Western Oregon	Basalt colluvium and residium	Reddish-Brown Lateritic
Astoria ^{a) b)}	Coastal	Sedimentary rock, colluvium and residium	Brown Latosol ^{c)}
Quillayute ^{b)}	Coastal	Old silty alluvium	Ando
Knappa ^{b)}	Coastal	Old silty alluvium	Brown Latosol ^{c)}
Barron ^{a)}	Southern Oregon	Old alluvium from granite	Grey-Brown Podzolic
Medford ^{a)} (Central Point ^{b)})	Southern Oregon	Granitic alluvium	Prairie
Sams ^{a)}	Southern Oregon	Recent alluvium	Prairie
Deschutes ^{b)}	Eastern Oregon	Pumice	Regosol
Baker ^{a) b)}	Eastern Oregon	Old gravelly alluvium	Brown
Powder ^{a) b)}	Eastern Oregon	Recent alluvium	Alluvial
Wingville ^{a) b)}	Eastern Oregon	Recent alluvium	Humic Grey
Walla Walla ^{a) b)}	Columbia Basin	Loess	Chestnut
Athena ^{a) b)}	Columbia Basin	Loess	Chernozem

* Appreciation is expressed to Dr. E. G. Knox, Associate Soil Scientist, Oregon Agric. Exp. Sta. for his suggestions in identifying these soil series.

^{a)} According to published soil survey reports.

^{b)} According to present concepts of the national co-operative soil survey.

^{c)} A local group name not described in the literature.

COLUMN STUDIES

Glass columns were constructed by segments held together by plastic tape. The columns were prepared by systematic packing of soil material (< 2 mm) which had been adjusted to 0.5 of the moisture equivalent. The packing of columns was standardized so that the results of leaching duplicate columns agreed very closely. After packing the soil column, S³⁵-labelled gypsum (CaSO₄ · 2H₂O) with a specific activity of 1 µc/mg was uniformly distributed on the surface and then covered with a paper disc. Calculated amounts of deionized water, equivalent to 1, 2, 4 and 8 in, were applied drop-wise from a separation funnel in such a manner that a small head of water was maintained during leaching. After leaching, the columns were allowed to drain for 24 h and then dismantled into segments. The radioactivity was determined on an aliquot of the leachate and on 1-g samples from each segment of the soil column, using a G-M thin mica window (1.8 mg/cm²) counter [7].

SULPHATE ADSORPTION

Five-gram air-dry soil samples were equilibrated with S^{35} -tagged sulphate salt solutions of known concentration. Unless otherwise specified the soil:solution ratio was 1:5. A preliminary study using tagged K_2SO_4 and an adsorptive soil was conducted to determine the time for sulphate adsorption to obtain equilibrium. It was found that equilibrium was present when the suspensions were shaken for 1 h, left standing overnight and again shaken for 1 h the following morning. The solution phase was separated by centrifugation and filtration. One-milliliter aliquots of the filtrates were placed in stainless-steel planchets and dried in a forced-draft oven at 70°C. The radioactivity was measured with an Autoscaler and a G-M thin mica window counter (1.8 mg/cm²). Sulphate concentrations were calculated from the radioactivity measurement. Sulphate adsorption was obtained by differences between original and equilibrium concentrations. The effects of isotope dilution were neglected because of the low concentrations of soluble sulphates in these soils. The results are averages of duplicate determinations.

Other specific procedures are discussed in the text.

Results

FACTORS AFFECTING THE DISTRIBUTION OF $S^{35}O_4^{--}$ IN SOIL COLUMNS

Distribution patterns were obtained by counting the radioactivity in the different segments of the columns. Histograms of percentage distribution with depth were then constructed. The movement of $S^{35}O_4^{--}$ through soil columns as a function of the amounts of water applied, and the differences between soils, may best be illustrated with "secondary peak" values. Secondary-peak values represent the zone of highest concentration of S^{35} other than the first or uppermost segment. This zone, which is situated at a certain depth in the column, depending upon the treatment, represents the peak movement of the surface-applied sulphate through the soil column under the influence of water percolation.

The secondary-peak values were observed to vary with different soils in response to the amounts of water applied [7]. Consequently, the soils segregate into three groups (Fig. 1). The curve for the Walla Walla soil was typical of most of the soils studied in which sulphate moved fairly readily. Soils showing this type of phenomenon were the Barron, Powder, Medford, Sams, Athena, Deschutes, Chehalis, Baker and Wingville. Soils of this group are medium-to-coarse textured. The movement of sulphate in the Willamette soil was intermediate. The upper two curves of Fig. 1 show soils at the other extreme with respect to the movement of sulphate. There was essentially no movement of the secondary peak for the Astoria or Quillayute soils even after 8 in of water had been applied. The movement in the Aiken and Knappa soils was very slight, with the secondary peak being only slightly over 1.5 to 2.5 in deep in the column.

The following factors may be expected to influence the movement of sulphate through soil columns: the texture, amount of water applied, organic matter content, type of clay mineral, kinds and amounts of amorphous inorganic exchange materials, degree of acidity, and the presence of other anions. An examination of the distribution patterns obtained indicated that the amount of water applied is one of the primary factors. The downward movement of sulphate increased with increasing amounts of water applied, but some soils exhibited marked retention of sulphate and only little movement occurred. The texture and permeability of the soils had an effect, as is shown by the

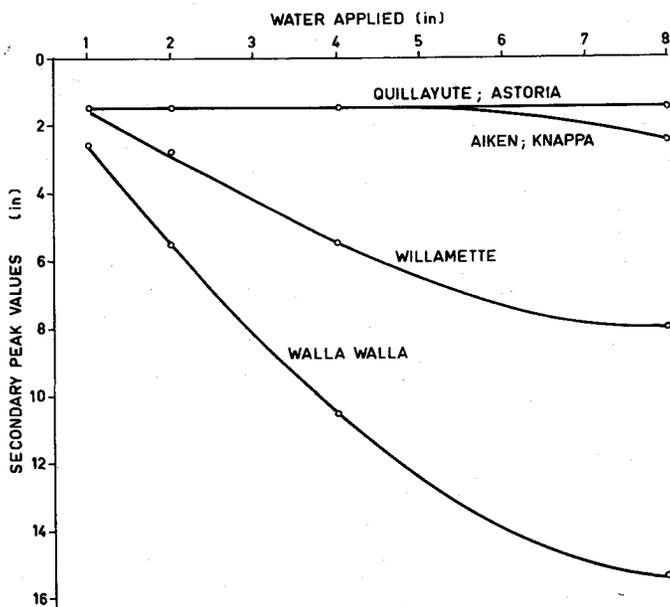


Fig. 1

Secondary peak values (depth in columns) of S^{35} and rates of water additions for different soils [7].

amount of radioactivity in the leachates from some of the sandier soils, such as Deschutes and Medford. Apparently this was not always a determining factor, since little movement occurred in the Astoria, which has a texture comparable to some of the non-retentive soils, and is known to be a permeable soil. It was shown that reference kaolin minerals adsorb more sulphate than montmorillonoids, and this may be a factor in the retention of sulphate by the different soils studied. It was apparent that this was not the only factor, since many of the soils which contained kaolin did not show strong retention of sulphate. Organic matter should have some effect, but again the results cannot be explained entirely on this basis. The Aiken soil contained 6.8% organic matter and the Knappa soil contained 18.3%, yet the movement of S^{35} was negligible in both soils. On the other hand, the movement in the Wingville and the Barron soils was much greater than in the Aiken, which has approximately the same organic-matter content. It is possible that the kind of organic matter could be of influence, that is, a qualitative rather than a quantitative factor.

The most outstanding feature from these data is the segregation of the group of soils in which only very slight movement of SO_4^{--} occurred. This group comprised the Reddish Brown Lateritic (Aiken series), Brown Latosols (Astoria and Knappa series), and the Ando (Quillayute series). It would appear that the retentive soils must have some characteristics in common which are responsible for the retention of sulphate ions. These retentive soils are generally more highly weathered than the other soils. Such soils are acid, have higher contents of free iron and aluminium oxides, higher exchangeable aluminium, and are possibly higher in amorphous inorganic compounds [7].

One of the pertinent observations made during this phase of the investigations concerns the effects of different rates of gypsum application on the distribution patterns of sulphate in the soil columns when fixed amounts of water were applied. The histograms for the Willamette soil show that the percentage distribution with depth in the Willamette soil follows a similar pattern with all four rates of sulphur addition (Fig. 2). The occurrence of the secondary-peak value was not changed by an eightfold increase in

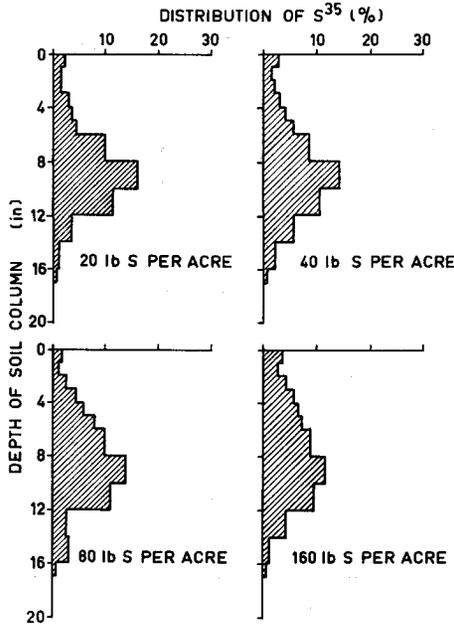


Fig. 2

Distribution of S³⁵ in columns of Willamette soil at 4 rates of gypsum (8 in water added) [7].

the rate of sulphate application. The distribution patterns for the other soils lead to the same conclusions, since the patterns for each soil were similar for the different rates of gypsum. In terms of absolute amount, a given quantity of water would move more sulphate down the columns with the higher rates of sulphur application. The percentage distribution pattern, and the location of secondary-peak value, however, were independent of the amount of gypsum applied. This clearly suggests that the movement and retention of sulphate by the soil is an equilibrium process and the amount adsorbed is increased with concentration.

ADSORPTION-DESORPTION EQUILIBRIUM STUDIES

The studies with soil columns suggested the need for information on adsorption from equilibrium solutions. Such investigations would further test the hypothesis that the retention or movement of sulphate in soil columns is associated with an equilibrium adsorption process. Such studies would also determine the adsorption-desorption behaviour of sulphate in soil systems.

Kinetic exchange

It was desirable to determine first of all whether adsorbed sulphate is in kinetic equilibrium with sulphate in the solution phase [8]. This was accomplished by equilibrating two series of soil samples for 4 h, one of which received S^{35} -tagged solution while the other received an equivalent non-tagged equilibrium solution. After shaking the suspensions, 20 ml of the S^{35} -tagged equilibrium solution were withdrawn and sulphate adsorption determined by radio-assay. An equal volume of the non-tagged equilibrium solution was then transferred to the tagged suspension. The samples were again equilibrated for different periods of time and the equilibrium solutions again analysed for radio-activity.

The exchange was virtually complete after 10 min since longer shaking did not materially increase the per cent exchange (Table II). The results also indicate that $S^{35}O_4^{2-}$, and non-tagged sulphate, have similar exchange behaviour. It was concluded that adsorbed sulphate was in kinetic equilibrium with the sulphate in solution.

TABLE II
EXCHANGE REACTION BETWEEN SO_4^{2-} AND $S^{35}O_4^{2-}$ IN TWO SOILS [8]
(Soil: solution ratio, 1:5.)

Soil	S added ($\mu\text{g/g}$ soil)	Adsorption ($\mu\text{g S/g}$ soil)	Exchange* (%)		
			1 min	10 min	30 min
Aiken	500	159	86.8	93.7	93.5
	1000	233	93.1	97.1	97.9
Astoria	500	181	86.6	90.2	91.5
	1000	304	90.1	97.2	97.1

$$* \text{ Exchange (\%)} = \frac{\text{redistribution ratio}}{\text{original distribution ratio}} \times 100,$$

where the

redistribution ratio = fraction of activity in solution after replacing a portion of labelled solution phase with otherwise identical non-labelled solution, and the
original distribution ratio = fraction of activity in solution after equilibrating with labelled sulphate solution.

Adsorption isotherms

Determinations of sulphate adsorption with 10, 20 and 50 $\mu\text{g S/ml}$ and a soil : solution ratio of 1 : 5 revealed that four soils manifested much higher adsorption of sulphate than the other soils [8]. These same soils exhibited a strong retention of sulphate in column studies. Samples of Willamette and Chehalis exhibited moderate adsorption at the higher sulphate concentrations, but all other soils showed very little adsorption. The sulphate adsorption from equilibrium solutions was thus in agreement with the column studies of all soils.

Two series of experiments were conducted in order to establish the sulphate adsorption isotherms for the four most retentive soils. The first consisted of equilibrating soil at a 1 : 5 soil : solution ratio with sulphate solution concentrations of 5, 10, 25, 50 and 100 $\mu\text{g S/ml}$. The amount of sulphate adsorbed increased with concentration. There

was no evidence that an adsorption maximum had been obtained within this range of sulphate concentrations. If the adsorption of sulphate were entirely through an anion-exchange mechanism, some evidence of an anion-exchange capacity in the form of an adsorption maximum would be expected. It was decided, therefore, to conduct a second series of experiments, using concentrations of 100, 200, 300, 400 and 500 $\mu\text{g S/ml}$. The same general trend of sulphate adsorption in relation to concentration was observed (Fig. 3) in these soils as at the lower range of concentrations. However, indications of de

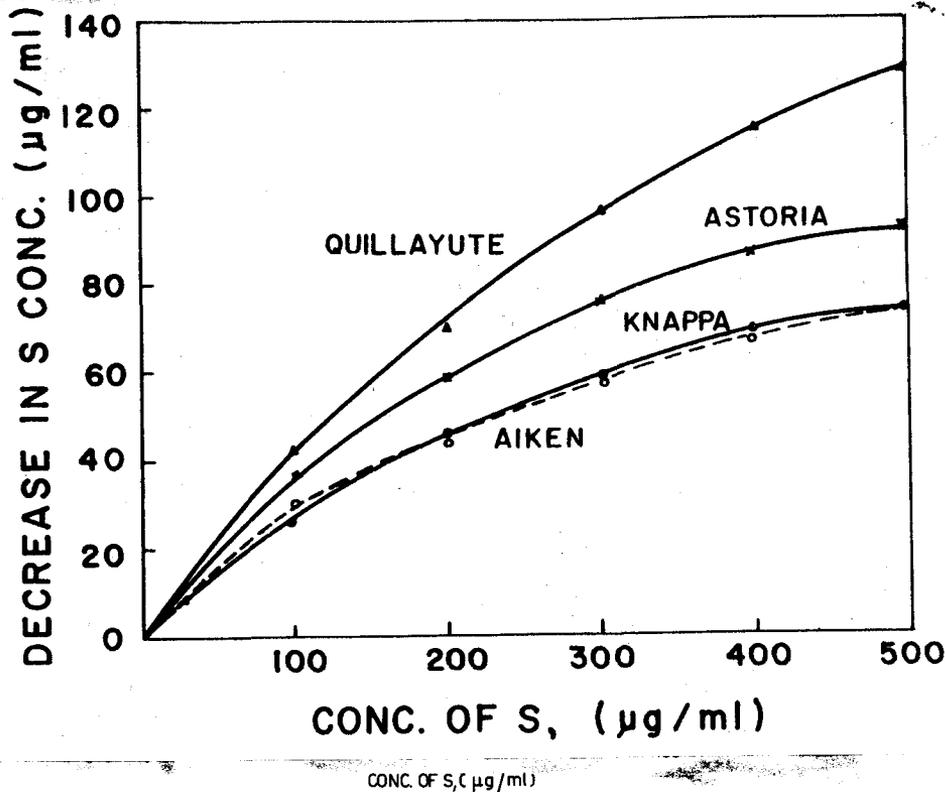


Fig. 3

Adsorption isotherms of sulphate for four sulphate-retentive soils (high-concentration series) [8].

Adsorption equations of the Langmuir and the Freundlich types have been applied to studies of soil systems. The Langmuir equation was originally derived on the basis of kinetic theory to describe the mono-molecular adsorption of a gas on a solid. It has also been frequently applied to the adsorption of ions from solutions with the general understanding that the same theoretical basis is not so fully developed in the latter case. The Freundlich equation has also been frequently applied to describe the relationship between the concentrations of an adsorbate and the amount of its adsorption by an adsorbent. It is informative to examine the sulphate adsorption data in the terms of these equations. Presumably, if the data indicate a maximum, they would best be described

by the Langmuir equation while absence of a maximum would be indicated by good conformity with the Freundlich-type equation.

The data for the two series of adsorption studies (5 to 100 and 100 to 500 $\mu\text{g S/ml}$) were plotted according to the linear forms of the Langmuir and Freundlich equations. The data were found to deviate significantly from linearity in the case of the Langmuir equation. While both sets of data could be fitted according to the Freundlich equation, only the graph for the high-concentration series is presented here (Fig. 4). It is evident that straight lines were obtained for all four soils, indicating very good conformity of data to the Freundlich-type equation. Even though the Freundlich equation indicates certain association of the adsorbate ion and the adsorbent surface, it does not give the mechanism of the reaction that takes place in the process of adsorption. Of importance is the fact that the data point to the lack of any definite sulphate-adsorption capacities of these soils, at least within the range of concentration studied here, and such as are often observed in cation-exchange studies.

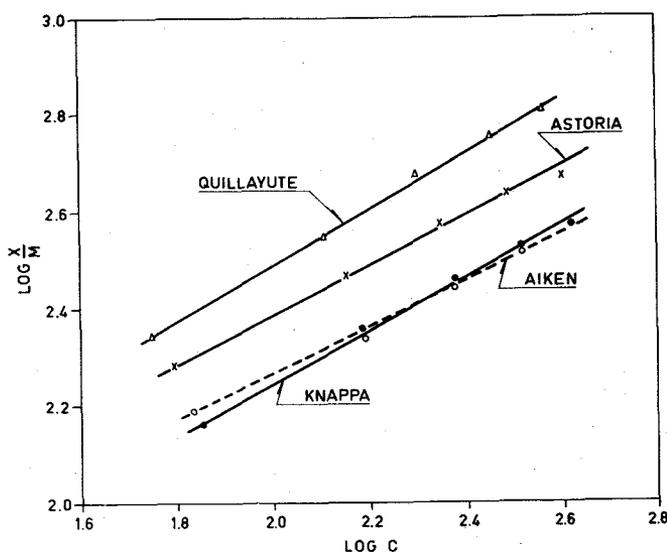


Fig. 4

Freundlich plot of sulphate adsorption data for four sulphate-retentive soils. The equilibrium concentration C is in terms of $\mu\text{g S/ml}$ while the amount of adsorption $\frac{X}{M}$ is in $\mu\text{g S/g soil}$ [8].

Desorption of sulphate

Since certain soils exhibit a marked capacity to retain sulphate, the question logically follows regarding the strength of retention. It is also of practical concern to know whether the adsorbed sulphate of soils can be easily desorbed, or how available it is to plant growth. A KH_2PO_4 solution was chosen as one of the extractors, since it has been shown to have extracting power similar to that of Morgan's solution [11]. Water was chosen as the other extractor because the water solubility of the soil nutrient is one of the important criteria for plant availability.

Two soils, Aiken and Astoria, were treated for sulphate adsorption, using two concentrations (100 and 200 $\mu\text{g S/ml}$) at a soil : solution ratio of 1 : 5. The soils were then extracted, using successive increments of either water or KH_2PO_4 solution containing 250 $\mu\text{g P/ml}$. The percentages of sulphate release relative to that initially adsorbed are presented in Table III. The amount of sulphate release decreased with the number of extractions, the first extraction removing the largest amount. Sixty-five to seventy per cent total release was effected by the first extraction with KH_2PO_4 solution, while the first water extraction removed from 35% to 45% of the total adsorbed. Three KH_2PO_4 extractions removed nearly all of the adsorbed sulphate. In four extractions, water desorbed 85% of the retained sulphate in Aiken, and more than 70% in Astoria.

TABLE III
PERCENTAGE EXTRACTION OF ADSORBED SULPHATE FROM TWO LATOSOLS
PREVIOUSLY TREATED WITH K_2SO_4 [8]

Soil	Concentration equilibrating solution ($\mu\text{g S/ml}$)	S adsorbed ($\mu\text{g/g soil}$)	Extraction of initially adsorbed sulphate (%)				
			1st	2nd	3rd	4th	Total
KH_2PO_4 solution (250 $\mu\text{g P/ml}$)							
Aiken	100	232	65.5	23.3	8.1	2.7	99.6
	200	272	68.8	24.5	5.9	2.9	102.1
Astoria	100	279	70.6	25.4	5.7	1.4	103.1
	200	436	70.0	22.7	6.0	1.4	100.1
water							
Aiken	100	225	44.2	22.7	11.6	9.1	87.6
	200	391	43.5	20.2	12.0	7.7	83.4
Astoria	100	263	36.5	17.5	10.3	6.6	70.9
	200	435	41.8	16.8	9.7	5.7	74.0

A noteworthy point is that, for a given extraction, very similar values for the percentage of adsorbed sulphate extracted were obtained, regardless of the sulphate concentration used in the initial equilibration. This applies to both KH_2PO_4 and water extractors. The data again suggest that the adsorbed sulphate was in kinetic equilibrium with that in the solution. The observations are also consistent with those of previous column studies where it was observed that the percentage distribution of sulphur in relation to depth in the column was independent of the amount added to the top of the column.

On the basis of the desorption results it may be inferred that the adsorbed sulphate is weakly held or easily released, and for this reason probably exists in highly-available form for plant growth. The relative ease with which sulphate ions were released to water suggests that sulphate retention was not due to the formation of insoluble compounds, as is the case with phosphates. The fact that KH_2PO_4 solution had higher extraction power than water may suggest that anion exchange was involved in the release of sulphate. However, this evidence is not conclusive. It is noted that evidence of definite sulphate-exchange capacities has not been obtained. It would seem that, if anion exchange is involved with sulphate retention and release, it must be accompanied by some other mechanism of sulphate retention in these soils.

SOIL CONSTITUENTS IN RELATION TO SULPHATE RETENTION

Various soil constituents, or factors, have been held responsible for sulphate adsorption, but most of the evidence has been indirect. Using three of the retentive soils, studies were conducted to measure sulphate adsorption under equilibrium conditions as affected by organic matter, free iron and aluminium oxides, types of clay minerals and the acid nature of clays [9]. Since it is not possible with present methods and knowledge to isolate the soil components of interest, the problem was approached by evaluating differences before and after the appropriate treatment to remove a given soil constituent.

Organic matter

Organic matter was removed by repeated treatments with 15% H_2O_2 until the reaction subsided on further additions of H_2O_2 . Soluble salts resulting from H_2O_2 treatment were removed by washing twice with diluted HCl and three times with water. Samples not treated with H_2O_2 were also washed with diluted HCl and water in order to provide a basis for comparison.

TABLE IV
EFFECT UPON SULPHATE ADSORPTION OF TREATMENTS FOR REMOVAL OF SOIL CONSTITUENTS [9]
($\mu\text{g S/g soil}$)

Concentration equilibrating solution ($\mu\text{g S/ml}$)	Organic matter not removed	Organic matter removed	Free Fe not removed	Free Fe removed	Free Al not removed	Free Al removed
Aiken Ap						
5	49	23	15	4	22	4
10	96	43	28	9	43	7
25	207	97	62	21	98	13
50	318	169	113	27	159	22
100	434	266	201	51	274	39
Quillayute Ap						
5	50	32	40	5	31	9
10	98	62	55	9	58	14
25	224	132	120	20	125	28
50	373	248	195	30	222	50
100	534	332	334	45	342	92

That organic matter may contribute to sulphate adsorption is shown in Table IV. Treatment with H_2O_2 resulted in reductions of sulphate adsorption by one-third to one-half. The ability of soil organic matter to retain sulphate ions has also been observed by ТИХОВА [29], who reported that organic colloids adsorbed sulphate in both the molecular and ionic form. It may appear from the data that soil organic matter contributes to sulphate adsorption. However, it was observed that some of the soils (Wingville, Barron and Athena) with organic-matter contents comparable to the Aiken soil, adsorbed

only small amounts of sulphate. There are two possible explanations. Firstly, organic matter *per se* may not have a direct effect on sulphate adsorption. It is possible that the H_2O_2 treatment affected some other soil constituents so as to decrease the capacity for adsorbing sulphate. A favoured alternative explanation is that the soil organic matter of these two retentive soils (Aiken and Quillayute) is of a different nature from that of other soils, such as the Wingville, Barron and Athena, and therefore retains much larger amounts of sulphate. It is to be expected that sulphate could be held by the positive charge of soil organic matter on the basis of its amphoteric properties. In view of the extreme complexities of soil organic matter, any present attempts to explain these phenomena and apparent contradictions must be speculative, although the latter explanation is favoured.

Iron and aluminium hydrous oxides

Samples of soil free of organic matter were used to determine the effect of the removal of free aluminium oxides on sulphate adsorption by treating with boiling NaOH for $2\frac{1}{2}$ min [16]. The pH of the soils treated with 0.5 M NaOH was adjusted to the same value as the untreated soils by adding a few drops of dilute HCl before equilibrating with sulphate solutions. The adsorption of sulphate was markedly reduced by treatment for the removal of free aluminium compounds (column 5 compared to column 4 of Table IV). About 15% only of the sulphate-adsorbing capacity remained after treatment of the Aiken soil.

Organic-matter-free soils were treated with buffered dithionite-citrate to remove free iron oxides [2]. Before equilibrating with sulphate solution, the treated and untreated soils were extracted with Morgan's solution ($CH_3COONa-CH_3COOH$ buffer at pH 4.8), and then washed with water so that soil conditions were comparable in both cases. The iron-removal treatment considerably reduced sulphate adsorption (column 7 compared to column 6 of Table IV). After Fe removal the soils exhibited magnitudes of sulphate adsorption which were close to those of some low-sulphate-adsorbing soils.

Comparing the effects of Fe and Al removal, it may appear that iron oxides are more important in sulphate adsorption than aluminium oxides. It is recognized, however, that the effects of the extracting reagents for Fe and Al are not mutually exclusive. For example, SAUNDERS [27] found that the dithionite-citrate reagent extracted appreciable quantities of Al from aluminium oxides, aluminium phosphates and soils. For this reason, the reductions in sulphate adsorption in the two cases mentioned here should not be expected to be additive. However, the data clearly indicate the importance of the hydrous oxides of Fe and Al in sulphate retention by these soils. The data obtained here support the work of other investigators who have shown that the hydrous oxides are capable of adsorbing sulphate [4] [18—21]. The sulphate ion is known to have a strong tendency to bind co-ordinatively to the Al atom [13] [14] [19] [27]. Positive charges developed in soils at low pH values, due to a transfer of a proton from H_3O^+ to an oxygen of hydrous ferric oxide, as postulated by SCHOFIELD [26], or by dissociation of OH groups as proposed by BERG [5], would result in sulphate adsorption.

Type of clay and acid nature of clays

Studies were conducted to determine the relationships between kinds of clay minerals and sulphate adsorption [9]. Variables of H- and Al-saturation were included in order

to differentiate between the relative effects of these two exchangeable cations. Two-gram samples of H- or Al-saturated clay minerals were equilibrated with 20 ml of sulphate solutions at different concentrations.

For H-saturated clays, kaolinite adsorbed much more sulphate than illite or Utah bentonite (Fig. 5). The amounts of sulphate adsorbed by Al-illite and Al-kaolinite were much higher than those adsorbed by Al-bentonite. If Al-saturation were the only direct factor associated with the increase in sulphate adsorption, Utah bentonite would show the largest sulphate adsorption as a result of the considerably greater amount of aluminium present on exchange sites. The high negative-charge density of the montmorillonoid (Utah bentonite) may be of importance in the repulsion of anions.

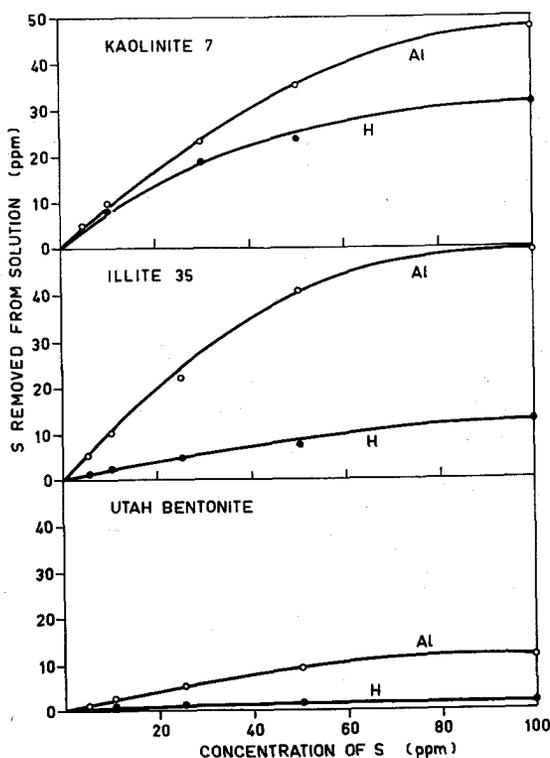


Fig. 5

Effect of type of clay mineral and nature of acid clays on the adsorption of sulphate from solution of various concentrations [10].

Aluminium probably exists in soils as hydroxy-aluminium complex [25]. The state of aluminium with respect to co-ordinated hydroxyl groups may be of importance in sulphate adsorption. If Al^{+3} were the adsorbed cation, there would appear to be no

a priori basis for expecting any increase in sulphate adsorption. On the other hand, the presence of some aluminium hydroxy complex might contribute significantly to sulphate adsorption. A study was conducted using a cation-exchange resin, Amberlite IR-120, to avoid the possible interfering effects of Al from the clay structure. For comparison a parallel experiment was carried out with Utah bentonite [9]. The samples were Al-saturated and then neutralized to different degrees with NaOH. Since the exchange capacities were not equal, different volumes of NaOH were required for comparable degrees of neutralization, and comparable solid:solution ratios could not be maintained. The samples were then equilibrated in the usual manner after adjusting the concentration to 25 $\mu\text{g S/ml}$.

TABLE V

SULPHATE ADSORPTION BY AL-AMBERLITE IR 120 AND AL-UTAH BENTONITE NEUTRALIZED TO DIFFERENT DEGREES WITH NaOH AND EQUILIBRATED WITH SULPHATE EQUIVALENT TO 25 $\mu\text{g S/ml}$ [9]

Al-Amberlite IR 120 1 g + 50 ml sulphate solution		Al-Utah bentonite 2 g + 20 ml sulphate solution	
Equilibrium pH	Adsorption $\mu\text{g S/g resin}$	Equilibrium pH	Adsorption $\mu\text{g S/g bentonite}$
4.1	0	4.2	52.5
5.7	31.5	4.9	26.0
6.2	99.0	5.4	12.5
6.9	47.5	5.7	2.5

It is evident that the effect of the pH or the degree of neutralization on sulphate adsorption was opposite in these two cases (Table V). No sulphate adsorption was measured when the IR-120 was saturated, presumably with Al^{+3} . Sulphate adsorption increased with each addition of OH, except for the greatest neutralization of the acid resin. The decrease in sulphate retention for the highest level of neutralization is interpreted to indicate a loss of reactive groups, due either to the formation of more stable compounds, such as gibbsite, or to blocking effects as the $\text{Al}(\text{OH})_3$ is precipitated. The results with resin thus offer direct experimental evidence for the importance of reactive OH groups in the phenomena of sulphate retention. For the clay system, sulphate adsorption decreased with decrease in acidity, and these results are similar to those observed with soil systems. The predominant factor appears to be the effect of pH in relation to the amphoteric nature of clays. With increasing acidity, the system behaved more as an anion exchanger. In the clay system, the formation of hydroxy groups was less important than pH. The explanation would involve the location or accessibility of Al-hydroxy anion-exchange sites. The exchangeable Al is expected to be found predominantly in interlayer spaces, and the formation of Al-hydroxy compounds, as NaOH was added, would occur in these interlayer spaces. It is logical to assume that these hydroxy groups would be relatively inaccessible because of the size of the SO_4^- ion in comparison with OH^- and as a result of anion repulsion by the negatively-charged interlayer spaces. The predominant effect would then be that of pH on other sites such as on the terminal edges of the crystal.

EFFECTS OF CATIONS AND pH

During the process of K-saturation of soil samples it was found that the amount of sulphate adsorbed from a K_2SO_4 solution was considerably reduced. This suggested the need for investigations to evaluate the relationships of sulphate adsorption to kinds of cations and variations in soil pH. The results of several studies revealed that variation in cation, either as the salt form in which sulphate was added, or in the exchangeable form, had an effect on sulphate retention [10]. The magnitudes of sulphate adsorption from sulphate solutions were in the order $CaSO_4 > K_2SO_4 > (NH_4)_2SO_4 > Na_2SO_4$. The saturation of soils with different cations gave the same general results. The amounts of sulphate adsorbed follow the order Al-soil > original soil > Ca-soil > K-soil > Na-soil.

Since samples of soil saturated with different cations also exhibit differences in pH values, it was recognized that the effect of cation saturation on sulphate adsorption was to some extent confounded with the effect of pH. In other words, the influence of different cations on sulphate adsorption may be associated with two factors, the nature of cations and pH. Studies were therefore conducted to resolve the effects of cation saturation and pH [10]. Since the pH would be adjusted with HCl or KOH, it became necessary to first determine whether chloride ions would compete with sulphate ions in the adsorption process; that chloride ions did not influence the amounts of sulphate adsorbed by these soils is shown by the data presented in Table VI. The variation of results is within the experimental error of measurements by counting radioactivity. The pH of soil suspensions was therefore adjusted by adding various amounts of 0.1 N HCl or KOH before equilibrating with a sulphate solution. The final pH was measured with a Beckman model-G pH meter after equilibration.

TABLE VI

ADSORPTION OF SULPHATE IONS BY TWO SOILS FROM A 0.005 N K_2SO_4 SOLUTION CONTAINING VARYING AMOUNTS OF KCl [10]

meq Cl^- meq SO_4^{2-} ratio	Sulphate adsorption (meq SO_4^{2-} / 100 g soil)	
	Astoria	Knappa
0.0	1.01	0.61
0.2	1.09	0.65
0.4	0.95	0.65
0.6	1.03	0.61
0.8	1.00	0.68

The relationship of equilibrium pH of the soil suspension to sulphate adsorption by the Aiken soil saturated with different cations is shown in Fig. 6. Although the effect of exchangeable cations persisted throughout the pH range studied, it appeared to be less pronounced than the effect of pH. The variation in sulphate adsorption in relation to pH changes was particularly marked in the more acid range (pH 3–5). As neutrality was approached, sulphate adsorption decreased considerably, regardless of the type of exchangeable cation.

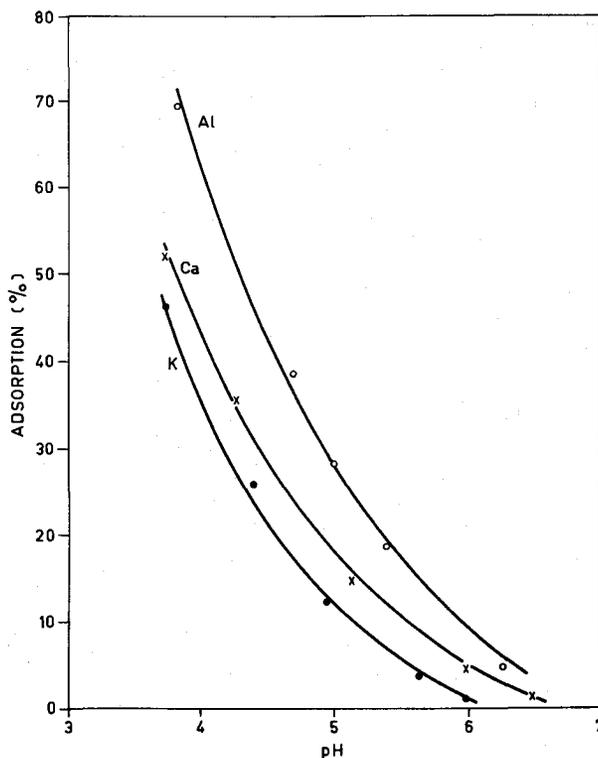


Fig. 6

Effect of pH on sulphate adsorption from a 0.005 N K_2SO_4 solution by the Aiken soil saturated with different cations [10].

It was demonstrated that Ca ions, either in the solution or on exchange sites, favour sulphate adsorption by soils in comparison to K or Na ions. Since the solubility product of $CaSO_4$ was not exceeded, the greater sulphate adsorption in the presence of Ca ions cannot be explained on the basis of the formation of insoluble precipitate. The magnitude of sulphate adsorption by soils saturated with different cations follows the order of chemical valency. Since sulphate adsorption by soil may be governed by more than one mechanism, any suggestion for this phenomenon is destined to be only partially applicable. There are, however, logical explanations for the effects of cation saturation.

The first explanation involves the possibility that di- or tri-valent exchangeable cations may act as a bridge between the sulphate ions and the soil complex. This type of micelle-cation-anion linkage has been suggested by RANIKOVITCH [22], SCARSETH [24], ALLISON [1] and BIRCH [6] to explain the adsorption of phosphate ions through exchangeable Ca. Such a mechanism would not account for the observed differences between monovalent cations. The second explanation is concerned with the effects of different exchangeable cations on the electrokinetic (zeta) potential of soil colloids and relationships to anion repulsion. It is known that the zeta potential of soil colloids decreases with the charge of the exchangeable cation and increases with the size of the hydrated cation. Since

soil colloids are, in general, negatively charged, the distribution of an anion such as SO_4^{2-} in the diffuse double layer is conditioned by electrical repulsion. As the zeta potential of soil colloids is reduced by the presence of polyvalent cations, the chances for sulphate ions to be retained are enhanced. This postulation would help to explain the regular variation caused by exchangeable cations, or cations in the equilibrating solution phase, and is favoured here. However, this does not rule out the specific affinity of individual cations for sulphate ions.

Summary and conclusions

The retention and movement of sulphate in soil systems is an equilibrium process. This was shown by the fact that the percentage distribution of sulphate in soil columns was independent of the amount of sulphate applied. A kinetic equilibrium between solid and solution phases was further verified by the exchange to solution of previously adsorbed, tagged sulphate and by adsorption-desorption equilibration procedures.

Soils were shown to differ widely in their ability to retain sulphate. The well-developed acid soils, which are high in free iron and aluminium oxides and amorphous constituents, segregate out as a group of retentive soils. Soils used in this study, which exhibited this characteristic, included the Reddish Brown Lateritic, Brown Latosol, and the Ando.

Factors which appear to be associated with sulphate adsorption include the percentage and kind of organic matter, the kind of clay, the degree and nature of acidity, the nature of cations in both the solid and solution phases, and the presence of Fe and Al hydrous oxides. The two most important factors involve the equilibrium pH and the presence of hydrous oxides. Subsequent studies (*unpublished data*) have shown that the pH effect on sulphate adsorption predominantly involves the free Fe and Al oxides. A retentive soil from which Fe and Al have been removed exhibits adsorption as a function of pH, which is characteristic of non-retentive soil. On the other hand, the addition of iron-oxide coatings to a non-retentive soil results in pH adsorption curves which are identical to those for retentive soils.

Anion exchange as a mechanism of sulphate retention is suggested by the dependence on the presence and accessibility of reactive OH groups and the dependence on the equilibrium pH. If anion exchange does occur, however, then the data suggest that other mechanisms must also be involved. The presence of other mechanisms is indicated by the lack of adsorption maximum within the range of concentrations studied and the ease with which sulphate may be desorbed or displaced with water. It is recalled that similar percentages of sulphate extracted were obtained, regardless of the sulphate concentrations used in the initial equilibration. It is clear that more critical experiments are needed to determine whether anion exchange actually does occur and, if so, the degree of its importance. Such studies are in progress at the present time.

The results to date indicate that sulphate retention by soils may involve several mechanisms, including:

- (1) Anion exchange involving hydrous oxides of Fe and Al and crystal edges of clays at low pH's;
- (2) Retention of sulphate by co-ordination with hydroxy-aluminium complexes;
- (3) "Salt" or "molecular" adsorption resulting from attraction between the surface of soil colloids and the salt;
- (4) Retention by amphoteric organic compounds.

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DISCUSSION

H. J. M. Bowen (Chairman): How were the soils coated with iron hydroxide, and could such a process be used to fix selenate in soils where selenium toxicity is a problem?

M. Harward: The procedure for coating with hydrous oxides is not described in the text of this paper. It will be dealt with in a forthcoming publication. Iron-coated samples were prepared by treatment with FeCl_3 at near boiling temperature. It has been shown that such treatment results in the hydrolysis of iron. The process could not easily be applied to soils where selenium toxicity is a problem because it was designed for laboratory conditions. In any case, the sulphate was not fixed as it could be recovered quite easily by extraction with phosphate solutions or even water.

H. W. Scharpenseel: Was the natural sequence of soil horizons maintained in your columns, or were they reconstituted from loose soil?

M. Harward: The columns were constructed under laboratory conditions, samples being taken from the Ap horizons of the different soil types. The columns were formed of disturbed samples and, consequently, the movements shown in the histograms do not represent, quantitatively speaking, the same movements as would occur under field conditions. However, we think that the general patterns are representative of the differences between soil types. This is particularly apparent when one realizes that soil texture—and thereby pore-space—is not always a determining factor in the movement of sulphate.

R. S. Mokady: How did you saturate your clay minerals with hydrogen and aluminium, and how were you able to distinguish between them? At pH 3, for example, I wonder whether aluminium clay is not actually aluminium-hydrogen clay.

M. Harward: The aluminium-saturated clays were prepared by leaching with AlCl_3 solution, followed by washing with deionized water until traces of chloride in the effluent became negligible. The hydrogen-saturated clays were prepared by leaching with normal HCl, followed by washing to remove the chloride. The samples were then equilibrated with sulphate as quickly as possible in order to keep the reversion of H-saturated to Al-saturated clays to a minimum.

H-saturated clays can be distinguished from Al-saturated clays by their acidic properties, which can be determined by potentiometric or conductimetric titrations. Alternative methods include heats of neutralization and also displacement of the exchangeable cations by a neutral salt followed by analysis of the solution phase. I think one always has a mixed hydrogen-aluminium system; the question is, which element predominates. One would certainly expect to have more hydrogen in the system at pH 3 than at pH 4, but think that even at pH 3 the system is still predominantly an aluminium one.

W. T. Spragg: In attempting to saturate your soil samples with Fe and Al, you might well produce, e. g. Fe_2O_3 and $\text{Al}(\text{OH})_3$ as separate precipitates in the solution. If that were the case, surface adsorption by these compounds would play an important role.

M. Harward: I agree that Fe and Al hydrous oxides are important in sulphate retention. The Fe-coated samples were prepared in a manner intended to produce hydrolysis and the formation of hydroxyl compounds. As the data showed, such compounds markedly increase the retention of sulphate. The same thing is demonstrated in another way by the manner in which the removal of "free" Fe and Al reduces the retention of sulphate.

The resin studies with Al also indicated the importance of OH groups, together with aluminium, for sulphate retention. However, the Al-saturated resin did not retain sulphate when OH was not added. This suggests that the aluminium did not hydrolyse under these conditions. It is also thought that the conditions by which the Al-saturated Utah Bentonite (a montmorillonite clay) was prepared did not result in any appreciable formation of Al-hydroxy compounds. This has been confirmed by the work of other investigators.

R. S. Mokady: Evidently you treated the movement of sulphate through the soil as an equilibrium process. May I ask how you knew that you were dealing with an equilibrium situation?

M. Harward: The equilibrium situation was suggested in a number of ways. In the first place, the present distribution of sulphate throughout the column was independent of the amount applied; or, to put it another way, the pattern of distribution as a function of depth remained the same so matter what the amount applied. While this does not definitely establish the equilibrium relationship, it is certainly highly suggestive of it.

We used the sulphur isotope for further equilibrium studies, by allowing sulphur-35 to be adsorbed initially, equilibrating it with unlabelled sulphur and then measuring the exchange. The fact that adsorption increases as long as the concentration is increased also suggests the same conclusion, namely that adsorption is a function of equilibrium concentration. Finally, extraction with water or phosphate compounds also suggests the existence of an equilibrium relationship, for the percentage extracted is of a similar order of magnitude with each extraction.