

## SULFUR FRACTIONS AND CARBON-NITROGEN- -PHOSPHORUS-SULFUR RELATIONSHIPS IN SOME BRAZILIAN AND IOWA SOILS \*

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### RESUMO

O atual conhecimento relativo à distribuição em percentagem das várias frações de enxofre nos solos provem principalmente dos estudos dos solos de regiões temperadas. Em vista disso, este estudo foi conduzido para determinar as frações do S e as relações C-N-P-S em alguns solos da região subtropical dos Estados de São Paulo e do Paraná, Brasil, e comparar estes valores nestes solos com aqueles nos solos do Estado de Iowa, dos Estados Unidos da América do Norte.

As análises das frações de enxofre nos solos dos dois países, indicaram que os solos do Brasil contem sulfato inorgânico adsorvido. Expressos como percentagem do S total, os solos do Brasil acusaram de 5 a 23% (média 11%) de S-sulfato inorgânico, de 20 a 65% (média 40%) de S-ester sulfato, de 5 a 12% (média 7%) de S-ligado ao Carbono e de 24 a 59% (média 42%) de S orgânico não identificado. As percentagens correspondentes nos solos de Iowa foram de 2 a 8% (média 5%) de S-sulfato inorgânico, de 43 a 60% (média 50%) de S-ester sulfato, de 7 a 18% (média 11%) de enxofre ligado ao carbono e de 30 a 39% (média 34%) de S orgânico, não identificado. Outrossim, não foi encontrado o enxofre inorgânico não-sulfato em nenhum dos solos analisados.

Houve grandes variações nas relações C, N, P e S entre solos brasileiros quando comparados com aqueles do Iowa.

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## INTRODUCTION

Although it has been shown that many of the Brazilian soils contain low levels of plant-available S, no information is available about the nature of the S compounds in these soils. MALAVOLTA (1952), noted low levels of reserve S in several Brazilian soils and indicated that use of fertilizers with low S content might lead to S deficiencies in crops. More recently, McLUNG *et al.* (1959), conducted greenhouse experiments using several representative Brazilian soils and reported that many of the soils provided a poor supply of S for millet. Most of the information reported in the literature about the S fractions in soils is derived from analysis of soils from temperate regions (FRENEY, 1961; FRENEY, 1967; LOWE & De LONG, 1963 and TABATABAI & BREMNER, 1972). These data indicate that the percentages of the various S fractions in the surface soils of temperate regions are very similar.

Current knowledge indicates that most of the S in surface soils temperate regions is organic S and that this organic S is present in two distinct forms ester sulfate S and C-bonded S. The ester sulfate S is believed to consist largely, if not entirely, of organic sulfate containing ester linkages (e.g., choline sulfate, phenolic sulfates, sulfated polysaccharides). This fraction of S in soil can be reduced to H<sub>2</sub>S with a mixture of HI, HCOOH, and H<sub>3</sub>PO<sub>2</sub>. Also, it can be readily hydrolyzed to inorganic sulfate by acid or alkali (FRENEY, 1967). The C-bonded S is believed to consist largely of S in the form of S-containing amino acids (e.g., methionine and cysteine). This fraction of S can be converted to sulfide when a soil sample is boiled with Raney Ni in alkaline medium (FRENEY, 1961; FRENEY & STEVENSON, 1966; FRENEY, MELVILLE & WILLIAMS, 1970 and LOWE & DeLONG, 1963). A large percentage (20-60%) of the organic S forms in soils, however, is still unidentified by current analytical methods. Generally, it is assumed that this unidentified S fraction in soils consists of C-bonded S, because it has been shown that the Raney Ni method used (LOWE & DeLONG, 1963) for determination of C-bonded S fraction in soils has defects; the method is not specific, and in presence of Fe and Mn, it gives low values for C-bonded S (FRENEY, MELVILLE & WILLIAMS, 1970).

The objectives of the work reported here were to characterize the S in selected subtropical soils from Brazil and to compare the values of the various S fractions in these soils with those in Iowa soils, and to compare the C, N, P, and S relationships in Brazilian soils with those in Iowa soils and, when possible, with soils from other regions.

## MATERIALS AND METHODS

The soil used (Table 1) were surface (0-15 cm) samples selected as representative of subtropical agricultural soils of Brazil and of cultivated soils of Iowa. The Brazilian soils used in this study were samples from the

States of São Paulo and Paraná. The soil samples from each state were selected to obtain a wide range in chemical and physical properties.

The classification of the Brazilian soils was taken from BRAMÃO & SIMONSON, 1956; COMISSÃO DE SOLOS DO C. N. E. P. A., 1960; BODZIAK Jr. & PAULA SOUZA, 1965; RANZANI *et al.*, 1966; MEDEIROS, 1971; EQUIPE DE PEDOLOGIA E FERTILIDADE DO SOLO, 1972.

The classification of Iowa soils was taken from RIECKEN & SMITH, 1949; OSCHWALD *et al.*, 1965; SOIL CONSERVATION SERVICE, U.S.A.D., 1966, 1972.

The Brazilian soils from numbers 1 to 6, are:

- Number 1 — described as a Podzolic Soil of Lins and Marilia, State of São Paulo (SP).
- Number 2 — Typic Tropudalf (sub-grupo), described first as Red Yellow Latosol, sandy phase (SP).
- Number 3 — Ochric Typustalf, described first as a Podzolic soil of Piracicaba, serie Pompeia (SP).
- Number 4 — Lithic Tropudalf, described first as Terra Roxa Estruturada de Jaboticabal (SP).
- Number 5 — described as Rubrozem de Curitiba, State of Paraná (PR), classified as having a textural B horizon, highly active clay (non-hidromorphic), allic, clayed, with prominent A horizon.
- Number 6 — described as a Dark Red Latosol, Virgin, serie Campos Gerais (PR).

The Iowa soils, from numbers 7 to 12, are:

- Number 7 — Alluvial — Serie Thurman or Sparta.
- Number 8 — Aquic Hapludalf — Serie Weller.
- Number 9 — Typic Hapludolls — Serie Marshall.
- Number 10 — Typic Udorthents — Serie Ida.
- Number 11 — Typic Haplaquolls — Serie Webster.
- Number 12 — Cumulic Haplaquolls — Serie Okobodji.

Before use, each sample was air-dried and crushed to pass a 2-mm screen. A small subsample of each soil was ground to pass a 100-mesh sieve for some of the analyses reported.

In the soil analyses reported in Table 1, pH was determined by a glass electrode (soil:water ratio, 1:2.5), organic C by the method of MEBIUS (1960), total N by the semimicro-Kjeldahl procedure described by BREMNER (1965), total and organic P by the procedures described by OLSEN & DEAN (1965), total S by the method of TABATABAI & BREMNER (1970). exchangeable acidity (exchangeable  $Al^{+3}$  and  $H^+$ ) by the KCl procedure

described by Mc LEAN (1965), extractable Fe by the method of JACKSON (1956), HI-reducible S and inorganic nonsulfate S by the methods of FRENEY (1961), C-bonded S by the method of LOWE & DeLONG (1963), sulfide S by the procedure described by SMITTENBERG et al. (1951), and particle-size distribution by the pipette analysis of KILMER & ALEXANDER (1949). Sulfate S was extracted by shaking 5g of soil with 50 ml of 0.1M LiCl or 500 ppm P as Ca (H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> for 30 minutes and by centrifuging (2400 rpm for 15 minutes) and filtering (Whatman N.º 42 filter paper) the resulting suspension. Sulfate S in the extract was determined by the methylene blue reduction method of JOHNSON & NISHITA (1952). The analyses for Organic C, total P, total P, organic P, total N, total S, HI-reducible S, and C-bonded S were performed on soil samples that had been ground to pass a 100-mesh sieve. The other analyses were performed on the coarser, < 2 mm, soil samples. All soil analyses reported are on a moisture-free basis, moisture being determined from loss in weight following drying at 105C for 24 hours.

## RESULTS AND DISCUSSION

The total C content of the Brazilian soils analysed ranged from 43 to 398 ppm, and the total S content of the Iowa soils ranged 55 to 580 ppm (Table 1). Total S in the Brazilian soils was significantly correlated with organic C ( $r = 0.85^*$ ) and total N ( $r = 0.88^*$ ). The corresponding correlation coefficients for the Iowa soils were  $0.98^{**}$  and  $0.99^{**}$ , respectively. Unlike the Brazilian soils, total S in the Iowa surface soils studied was also significantly correlated with organic P ( $r = 0.95^{**}$ ).

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### Forms of Sulfur

**Inorganic S.** Analyses for inorganic forms of S indicated that inorganic S in the Brazilian and Iowa soils studied occurred entirely as sulfate. Neither sulfite S nor inorganic nonsulfate S could be detected in any of the soils analyzed. The results obtained on Iowa soils in this study confirm the previous finding (TABATABAI & BREMNER, 1972), that Iowa surface soils do not contain inorganic sulfur other than sulfate S. The method used for determination of inorganic nonsulfate S is known to recover S present as

sulfides, sulfites, thiosulfates, polysulfides, or elemental S (FRENEY, 1961.)

Sulfate S extracted from the Brazilian soils by 0.1M LiCl accounted for 1 to 9 percent (average, 5 percent), and that extracted by a solution containing 500 ppm P as Ca  $(\text{H}_2\text{PO}_4)_2$  accounted for 5 to 23 percent (average, 11 percent), of the total S. The corresponding amounts of sulfate S extracted from the Iowa soils were 2 to 7 percent (average, 4 percent) and 2 to 8 percent (average, 5 percent), respectively (Table 2). The fact that more sulfate S was extracted from the Brazilian soils by the Ca  $(\text{H}_2\text{PO}_4)_2$  solution than that extracted by 0.1M LiCl indicates that the Brazilian soils contained adsorbed sulfate. No such adsorbed sulfate was found in any of the Iowa soils studied; the amounts of sulfate S extracted from the Iowa soils by the Ca  $(\text{H}_2\text{PO}_4)_2$  solution were almost identical to those extracted by the LiCl solution.

**Organic S.** Total organic S (calculated from S minus inorganic sulfate S extracted by Ca  $(\text{H}_2\text{PO}_4)_2$  solution in the Brazilian soils) analyzed ranged from 77 to 95 percent (average, 89 percent) and in the Iowa soils ranged from 93 to 98 percent (average, 96 percent).

Table 2 shows the percentage distribution of various forms of S in the Brazilian soils, HI-reducible S ranged from 36 to 70 percent (average, 51 percent), ester sulfate S (calculated from HI-reducible S minus inorganic S) from 5 to 12 percent (average, 7 percent), and unidentified organic S ranged from 20 to 65 percent (average, 40 percent), C-bonded S ranged from 24 to 59 percent (average, 42 percent). The corresponding percentages in the Iowa soils analyzed were: from 49 to 62 percent (average, 55 percent) HI-reducible S, from 43 to 60 percent (average, 50 percent) ester sulfate S, from 7 to 18 percent (average, 11 percent) C-bonded S, and from 30 to 39 percent (average, 34 percent) unidentified organic S.

The average percentage of total S as ester sulfate S in the Brazilian soils (40 percent) is much lower than that for the Iowa soils used in this work (50 percent) and those reported by FRENEY (1967) for 24 Australian surface soils (52 percent) and by LOWE & DeLONG (1963) for five Canadian soils (53 percent).

The average percentages of total S as C-bonded S in the Brazilian soils (7 percent) and Iowa soils (1 percent) are lower than those calculated from work by LOWE & DeLONG (1963) for three Canadian mineral soils (20 percent) and for two organic soils (53 percent).

The unidentified organic S fraction is assumed (FRENEY, 1967; FRENEY, MELVILLE & WILLIAMS, 1970) to consist largely, if not entirely, of S attached to C atoms. This assumption has been partly supported by recent work by FRENEY, MELVILLE & WILLIAMS (1970) showing that Fe and Mn can interfere with determination of C-bonded S in soils by the method of LOW & DeLONG (1963). FRENEY et al. (1970), however, were unable to account for a significant amount (average, 23 percent) of the organic S in 15 Australian soils even when the method of LOWE & DeLONG

was modified to reduce interference by Fe and Mn. The Brazilian soils used contained from 0.8 to 7.8 percent extractable Fe (Table 1), and there was no relationship between the C-bonded S fraction as determined by the Raney Ni method (Table 2) and the amounts of Fe extracted from these soils. Compared with the Brazilian soils analyzed, the Iowa soils contained small amounts of extractable Fe.

Also, the Raney Ni method used for determination of C-bonded S in soils does not reduce the C-bonded S of aliphatic sulfones or sulfonic acids (e.g., methionine sulfone and cysteic acid) to sulfide, and it reduces S in a range of organic S compounds (e.g., elemental S,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_3$ ) as well as C-bonded S (FRENEY, MELVILLE & WILLIAMS, 1970). Apart from elemental S added to soil as fertilizer, however, it is unlikely that appreciable quantities of these inorganic S forms will be found in soils.

The correlation coefficients for the relationships between the organic S fractions and total S, total N, organic P, and organic C in the Brazilian and Iowa soils studied are reported in Table 3. Generally, the relationships were more significantly correlated for the results obtained for the Iowa soils than those for the Brazilian soils. In the Iowa soils analyzed, there were highly significant correlations between organic S and organic P ( $r = 0.95^{**}$ ), ester sulfate S and organic C ( $r = 0.96^{**}$ ), and carbon-bonded S and total S ( $r = 0.94^{**}$ ). These relationships for the Brazilian soils were not significant at the 5% level. Carbon-bonded S was not significantly correlated with organic P in either of the two groups of soils (Table 3).

#### **Carbon-nitrogen-phosphorus-sulfur relationships**

The average C:N, N:P, N:S, P:S, and C:N:P:S ratios of the Brazilian soils analyzed were 194, 11.2, 7.2, 0.9, and 194:10:1.2:1.6, respectively. The corresponding averages for the Iowa soils analyzed were 11.1, 7.3, 7.9, 1.1, and 110:10:1.4:1.3 (Table 4). As pointed out by WHITEHEAD (1964) and WILLIAMS (1967), although the mean N:S and C:N:P:S ratios for different groups of soils are often remarkably similar, considerable variations in ratio can occur within each group. This is confirmed by the data reported in Table 4. The N:S ratio of the Brazilian soils ranged from 3.4 to 12.0. The lowest ratio (3.4) found for one of the Brazilian soils is not surprising because similar ratios have been occasionally found in surface soils from other regions (HARPER, 1959; TABATABAI & BREMNER, 1972). The highest N:S ratio (12.0) found for one Brazilian soil (Table 4), however, is higher than those found for the Iowa soils used in this study and those reported for Oklahoma soils (HARPER, 1959), Australian soils (WILLIAMS & STEINBERG, 1958), and New Zealand soils (WALKER & ADAMS, 1958).

The C:N ratio of the Brazilian soils analyzed ranged from 128 to 23.8 (TABLE 4). The averages C:N ratio (19.4) is considerably higher than 11.1 found for Iowa soils, and the averages of C:N ratios found for the Brazilian and Iowa soils are considerably different from 14.0 for Scottish soils (WIL-

LIAMS, WILLIAMS & SCOTT, 1960), 15.0 for Australian soils (WILLIAMS STEINBERG, 1958), and 14.5 for Oregon soils (HARWARD, CHAO & FANG, 1962).

The P:S ratio of the Brazilian soils analyzed ranged from 0.3 to 2.0, and those for Iowa soils ranged from 0.9 to 1.6 (Table 4). It is noteworthy that with the exception of one soil, all the Brazilian soils studied showed P:S ratio of less than 1. Excluding the P:S ratio of this soil (soil n.º 4) from the average, the average ratio of the Brazilian soils (0.65) is much lower than that for Iowa soils (1.1).

The N:P ratios for the Brazilian soils were markedly different from those for the Iowa soils. The N:P ratio of the Brazilian soils ranged from 3.3 to 18.7, and those for the Iowa soils ranged from 6.2 to 8.2, and the average N:P ratio for the Brazilian soils (11.2) was much higher than 7.3 for the Iowa soils.

The wide variations found in the ratios of C, N, and S to P for the Brazilian soils could be due to presence of variable amounts of inositol phosphates in these soils. These organic P compounds contain no N or S in their molecules, and presence of appreciable amounts of these compounds in soil could lead to lower ratios of N and S to P. The amounts of inositol phosphates present in Brazilian soils remain to be investigated.

#### **Adsorption and release of sulfate sulfur by soils**

Studies of adsorption of sulfate S by the soils used indicated that the Brazilian soils have appreciable capacities to adsorb sulfate S. Between 7 and 64 µg of the 100 µg of sulfate S added per g of soil were retained in the soils against extraction with 0.1M LiCl (Table 5). With the exception of Weller soils (soil n.º 8), none of the Iowa soils studied showed any capacity for adsorption of sulfate S. The results obtained with Iowa soils support the conclusion made by TABATABAI & BREMNER (1972) that Iowa soils do not adsorb sulfate S. The capacities of the Brazilian soils for adsorption of sulfate S was anticipated because analysis of these soils for inorganic sulfate S showed (Table 2) that they contain adsorbed sulfate S (the amounts of sulfate S extracted by Ca (H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> solution were higher than those extracted by LiCl solution). Adsorption of sulfate S by soils is affected by the amounts of hydrous oxides of Al and Fe (ENSMINGER, 1954; REISENAUER, 1967). Most of the Brazilian soils used were acid, and some these soils contained appreciable amounts of extractable Fe and Al (Table 1).

Although it has been shown (REISENAUER, 1967) that soil pH affects the retention of sulfate by soils, very little information is available in the literature concerning the effect of liming acid soils on the release of adsorbed sulfate. Because the Brazilian soils used were acid in reaction and because they contained adsorbed sulfate (Table 2), the effect of CaCO<sub>3</sub> on the release of the adsorbed sulfate in these soils was studied. Table 5 shows the amounts of sulfate S released from the Brazilian soils and one Iowa soil (soil n.º 8)

when these soils were treated with different amounts of  $\text{CaCO}_3$ , brought to 60 percent of water holding capacity, and incubated under aerobic conditions at 25C for 30 days. Increasing the amount of  $\text{CaCO}_3$  added from 50 to 200 mg per 50 g of soil (50 mg of  $\text{CaCO}_3$  per 50 g of soil is equivalent to about 1 ton of  $\text{CaCO}_3$  per acre) increased the soil pH and the amounts of sulfate S extracted by 0.1M LiCl from these soils, especially soils n.º 1, 2, 3 and 8. The results obtained from this experiment support the conclusion made by ENSMINGER (1954): liming acid soils causes a decrease in the retention of sulfate.

### LITERATURE CITED

- BODZIAK, Jr., C., and PAULA SOUZA, D. M. de. 1965 — Contribuição ao estudo dos solos de Curitiba. *Revista da Escola de Agronomia e Veterinária, Universidade Federal do Paraná*, 1(2) : 47-54.
- BRAMAO, D. àL. ;and SIMONSON, R. W., 1956 — Rubrozem — A proposed great soil group VI<sup>er</sup> *Congres de la Science du Sol. Paris*, 4 : 25-29.
- BREMNER, J. M., 1965 — Total nitrogen. In C. A. Black (ed.) *Methods of soil analysis, Part. 2. Agronomy* 9 : 1149-1178.
- COMISSÃO DE SOLOS DO C. N. E. P. A., 1960 — Levantamento de reconhecimento dos solos do Estado de São Paulo. *Boletim* 12. Serviço Nacional de Pesquisas Agrônomicas. Ministério da Agricultura, Rio de Janeiro.
- ENSMINGER, L. E., 1954 — Some factors affecting the adsorption of sulfate by Alabama soils. *Soil Sci. Soc. Amer. Proc.* 18 : 259-264.
- FRENEY, J. R., 1961 — Some observations on the nature of organic sulphur compounds in soil. *Aust. J. Agric. Res.* 12 : 424-432.
- FRENEY, J. R., and F. J. STEVENSON, 1966 — Organic sulfur transformations in soils. *Soil Sci.*, 101 : 307-316.
- FRENEY, J. R., 1967 — Sulfur-containing organics. p. 220-259. In A. D. McLaren and G. H. Peterson, (eds.) *Soil biochemistry*. Marcel Dekker, Inc. New York.
- FRENEY, J. R., G. E. MELVILLE, and C. H. WILLIAMS, 1970 — The determination of carbon bonded sulfur in soil. *Soil Sci.* 109 : 310-318.
- HARPER, H. J., 1959 — Sulfur content of Oklahoma soilse, rainfall and atmosphere. *Oklahoma Agr. Expt. Sta. Bull.* 3-536.
- HARVARD, M. E., T. T. CHAO and S. C. FANG, 1962 — The sulfur status and sulfur supplying power of Oregon soils. *Agron. J.* 54 : 101-106.
- JACKSON, M. L., 1956 — Soil chemical analysis-Advanced course. Published by the author, Department of Soil Science, University of Wisconsin, Madison, Wisconsin.
- JOHNSON, C. M., and H. NISHITA, 1952 — Microestimation of sulfur in plant materials, soils, and irrigation waters. *Anal. Chem.* 24 : 736-742.
- KILMER, V. J., and L. T. ALEXANDER, 1949 — Methods of making mechanical analyses of soils. *Soil Sci.* 68 : 15-24.
- LOWE, L. E. and W. A. DELONG, 1963 — Carbon bonded sulphur in selected Quebec soils. *Can. J. Soil Sci.* 43 : 151-155.
- MALAVOLTA, E., 1952 — Estudos químico-agrícolas sobre o enxofre .*Anais da Esc. Sup. Agric. «Luiz de Queiroz»* 9 : 40-130.

- McLEAN, E. O., 1965 — Aluminium. In C. A. Black (ed.) *Methods of soil analysis*, Part. 2. *Agronomy* 9 : 978-998.
- McLUNG, A. C., L. M. M. de FREITAS, and W. L. LOTT, 199 — Analysis of several Brazilian soils in relation to plant responses to sulfur. *Soil Sci. Soc. Amer. Proc.* 23 : 221-224.
- MEBIUS, L. J., 1960 — A rapid method for the determination of organic carbon in soil. *Anal. Chim. Acta* 22 : 120-124.
- MEDEIROS, G. B., 1971 — Genese e classificação de alguns solos da Baía do Ribeirão das Palmeiras no Município de Rio das Pedras. M. S. Thesis, Universidade de São Paulo, Piracicaba, São Paulo, Brasil.
- OLSEN, S. R., and L. A. DEAN, 1965 — Phosphorus, In C. A. Black (ed.) *Methods of soil analysis*, Part. 2. *Agronomy* 9 : 1035-1049.
- OSCHWALD, W. R., RIECKEN, F. F., DIDERIKSEN, R. I., SCHOLTES, W. H., and SCHALER, F. W., 1965 — Principal soils of Iowa. Special Report N-42. Department of Agronomy, Iowa State University of Science and Technology. Soil Conservation Service, USDA, cooperating.
- RANZANI, G. KINJO, T. and FREIRE, O., 1966 — Carta de Solos do Município de Piracicaba, Universidade de São Paulo. Escola Superior de Agricultura «Lui de Queiroz», Piracicaba, Brasil.
- REISENAUER, H. M. 1967 — Availability assays for the secondary and micro-nutrient anions. p. 71-102. In *Soil testing and plant analysis*. Part 1. Soil Testing. Soil Sci. Society of America Inc. Madison, Wisconsin.
- RIECKEN, F. F. and SMITH, G. D., 1949 — Principal upland soils of Iowa. Their occurrence and important properties. Iowa State College, Ames, Iowa. Joint contribution from the cooperative soil survey program of the Iowa Agricultural Experiment Station and the Bureau of Plant Industry, Soils and Agricultural Engineering, USDA.
- SMITTENBERG, J., G. W. HARMSSEN, A. QUISPTEL, and D. OTTEN, 1951 — Rapid Methods for determining different types of sulphur compounds in soil. *Plant and Soil* 3 : 353-360.
- SOIL CONSERVAION SERVICE. 1966 — Soil Survey Laboratory Data and Descriptions for some soils of Iowa. Soil Survey Investigations Report N-3, USDA. In cooperation with Iowa Agriculture and Home Economics Experiment Station.
- SOIL CONSERVATION SERVICE. 1972 — Soil Series of the United States, Puerto-Rico and the Virgin Islands: Their Taxonomic Classification. USDA.
- TABATABAI, M. A., and J. M. BREMNER, 1970 — An alkaline oxidation method for determination of total sulfur in soils. *Soil Sci. Soc. Amer. Proc.* 34:62-65.
- TABATABAI, M. A., and J. M. BREMNER, 1972 — Distribution of total and available sulfur in selected soils and soil profiles. *Agron. J.* 64 : 40-44.
- TABATABAI, M. A., and J. M. BREMNER, 1972 — Forms of sulfur, and carbon, nitrogen, and sulfur relationships, in Iowa soils. *Soil Sci.* 114 : 380-386.
- WALKER, T. W. and A. F. R. ADAMS, 1958 — Studies on soil organic matter: 1. Influence of phosphorus content of parent materials on accumulation of carbon, nitrogen, sulfur, and organic phosphorus in grassland soils. *Soil Sci.* 85 : 307-318.
- WHITEHEAD, D. C., 1964 — Soil and plant-nutrition aspects of the sulphur cycle. *Soils and fertilizers* 27 : 1-8.
- WILLIAMS, C. H., 1967 — Nitrogen, sulphur and phosphorus, their interactions and availability. *Intern. Soc. Soil. Sci. Trans. Comm.* II and IV : 93-111.

WILLIAMS, C. H. and A. STEINBERG, 1958 — Sulphur and phosphorus in some eastern Australian soils. *Aust. J. Agric. Res.* 9 : 483-491.

WILLIAMS, C. H., E. G. WILLIAMS, and N. M. SCOTT, 1960 — Carbon, nitrogen, sulphur, and phosphorus in some Scottish soils. *J. Soils Sci.* 11 : 334-346.

Table 1 — Analyses of soils used

Soils No.	pH	Organic	Total	P		Exch. acidity		Ext.		
		C	N	Total	Organic	Al <sup>+3</sup>	H <sup>+</sup>	Fe	Clay	Sand
		%	%	ppm	ppm	meq./100 g		%	%	%
<b>Brazilian soils</b>										
1	5.1	0.42	0.02	68	17	0.5	0.3	0.8	8	89
2	4.9	0.64	0.03	142	31	1.0	0.4	3.6	29	66
3	5.3	0.77	0.06	132	45	Tr.*	0.6	0.9	14	55
4	6.1	1.81	0.13	1,257	398	Tr.	0.2	7.3	46	36
5	4.6	5.89	0.25	300	134	4.7	1.8	6.1	48	30
6	4.6	5.96	0.25	386	245	3.2	1.1	7.8	47	27
<b>Iowa soils</b>										
7	6.3	0.47	0.05	152	81	Tr.	0.4	0.4	5	93
8	4.4	1.73	0.16	391	229	0.2	0.5	1.7	18	2
9	6.1	2.39	0.23	620	327	Tr.	0.2	3.1	33	2
10	7.6	2.57	0.25	686	311	Tr.	0.3	2.6	21	4
11	7.7	4.35	0.35	602	429	Tr.	0.3	1.7	32	18
12	7.1	5.24	0.40	802	423	Tr.	0.2	0.9	36	13

\* Tr., Trace.

**Table 2** — *Total sulfur and percentage distribution of various forms and sulfur in some Brazilian and Iowa surface soils.*

Soil no.	Total S ppm	Percentage of total soil S in form specified						Total organic S
		Inorganic sulfate S LiCl	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	HI-reducible S	Ester sulfate S	Carbon-bonded S	Unidentified organic S*	
<b>Brazilian soils</b>								
1	59	5.1	15.3	35.6	20.3	5.1	59.3	84.7
2	143	9.3	23.3	51.2	27.9	4.7	44.1	76.7
3	72	6.9	12.5	52.8	40.3	11.1	36.1	87.5
4	214	3.7	5.1	70.1	65.0	5.6	24.3	94.9
5	209	1.4	4.8	53.6	48.8	12.4	34.0	95.2
6	398	2.0	6.3	43.0	36.7	5.0	52.0	93.7
Avg	166	4.7	11.2	51.1	39.8	7.3	41.7	88.8
<b>Iowa soils</b>								
7	55	7.3	7.5	50.9	43.4	18.2	30.9	92.5
8	174	5.8	5.9	52.9	47.0	9.2	37.9	94.1
9	331	5.4	5.5	57.7	52.2	12.1	30.2	94.5
10	338	2.4	2.5	55.3	52.8	8.9	35.8	97.5
11	438	1.8	1.8	61.6	59.8	7.3	31.1	98.2
12	580	3.5	3.5	48.6	45.1	12.1	39.3	96.5
Avg	319	4.4	4.5	54.5	50.1	11.3	34.2	95.6

\* Unidentified organic S was calculated from total S — (ester sulfate S + carbon-bonded S).

**Table 3 — Simple correlation coefficiente (*r*) for paired relationships between individual organic S fractions and total S, total N, organic P, and organic C in some Brazilian and Iowa surface soils.**

Relationship	Correlaction coefficient ( <i>r</i> )	
	Brazilian soils	Iowa soils
Organic S vs total S	0,99* *	0,99* *
Organic S vs total N	0,89*	0,97* *
Organic S vs organic P	0,71	0,95* *
Organic S vs organic C	0,85*	0,98* *
Ester sulfate S vs total S	0,91*	0,97* *
Ester sulfate S vs total N	0,82*	0,98* *
Ester sulfate S vs organic P	0,91*	0,98* *
Ester sulfate S vs organic C	0,72	0,96* *
Carbon-bonded S vs total S	0,77	0,94* *
Carbon-bonded S vs total N	0,97* *	0,85*
Carbon-bonded S vs organic P	0,47	0,78
Carbon-bonded S vs organic C	0,95* *	0,86*

\* Significant at  $P < 0.05$

\* \*Significant at  $P < 0.01$

**Table 4 — Carbon, nitrogen, phosphorus, and sulfur relationships in some Brazilian and Iowa surface soils.—**

Soil no.	Ratio				
	Organic C: total N	Total:N: organic P	Total N: total S	Organic P: total S	Organic C: total N: organic P: total S (organic S)
<b>Brazilian soils</b>					
1	21.0	11.8	3.4	0.3	210:10:0.9:3.0 (2.5)
2	21.3	9.7	7.0	0.9	213:10:1.0:1.4 (1.1)
3	12.8	13.3	8.3	0.7	128:10:0.8:1.2 (1.1)
4	13.9	3.3	6.1	2.0	139:10:3.1:1.6 (1.6)
5	23.6	18.7	12.0	0.7	236:10:0.5:0.8 (0.8)
6	23.8	10.2	6.3	0.7	238:10:1.0:1.6 (1.5)
Avg	19.4	11.2	7.2	0.9	194:10:1.2:1.6 (1.4)
<b>Iowa soils</b>					
7	9.4	6.2	9.1	1.6	94:10:1.6:1.1 (1.0)
8	10.8	7.0	9.2	1.3	108:10:1.4:1.1 (1.0)
9	10.4	7.0	6.9	1.1	104:10:1.4:1.4 (1.4)
10	10.3	8.0	7.4	0.9	103:10:1.2:1.3 (1.3)
11	12.4	8.2	8.0	1.0	124:10:1.2:1.3 (1.2)
12	13.1	7.6	6.9	0.9	131:10:1.3:1.5 (1.4)
Avg	11.1	7.3	7.9	1.1	110:10:1.4:1.3 (1.2)

**Table 5** — Adsorption of sulfate by soils and the effect of  $\text{CaCO}_3$  on the LiCl extractable sulfate S and on soils pH of acid soils incubated at  $25^\circ\text{C}$  for 30 days.

Soil no.	Sulfate S adsorbed*	LiCl extractable $\text{SO}_4^-$ S as affected by $\text{CaCO}_3$ added (mg/50 g of soil)**				pH of soils as affected by $\text{CaCO}_3$ added (mg/50 g of soil)			
		0	50	100	200	0	50	100	200
		-----ug of $\text{SO}_4^-$ S/g of soil-----							
1	15	4(3)	7	8	10	5.2	7.0	7.8	7.9
2	25	5(4)	7	8	11	4.9	6.2	7.3	7.9
3	7	5(5)	11	13	14	4.9	6.6	7.5	7.8
4	31	9(8)	9	12	—	5.8	6.1	6.7	—
5	64	4(3)	3	3	5	4.8	6.0	6.5	7.4
6	45	7(8)	8	9	11	4.8	5.1	5.2	5.3
8	5	9(11)	13	18	23	4.6	6.0	6.5	7.4

\* To estimate the sulfate S adsorption capacities of soils, a 5-ml aliquot containing 500 ug of sulfate S was added to 5 g of soil (< 2 mm mesh) in a 100-ml test tube, after 10 minutes the sulfate S was extracted with 50 ml of 0.1M LiCl and determined by the methylene blue method (10).

\*\* Figure in parentheses indicates LiCl extractable sulfate S in soil before incubation.

