

Balance and distribution of sulphur in volcanic ash-derived soils in Chile

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Abstract

Sulphur distribution with an insight in S-organic fractions was studied in volcanic-ash derived soils of Chile (Typic Dystrandepts, Palehumult) by isolating each fraction and measuring S directly by instrumental elemental analysis. S-pattern followed closely C and N distribution in these soils. Light organic-S forms accounted for more than 40% of total S in soil, indicating that this S-form is the actual vehicle through which mineralization to S-SO₄ occurs. The role of this type of S-molecules, especially of those with lower molecular weight, needs to be clarified regarding its direct availability for plant roots. In younger Andisol soils, the main fraction of organic S was linked to high molecular weight humins (20–34%). In Ultisol soil, apparently a final degradation step occurs where organic soluble-S has almost disappeared and S is nearly exclusively represented by S in humic acid (HA), fulvic acid (FA) and humin (H).

Keywords: Sulphur distribution; Organic sulphur; Volcanic soils; Nutrient distribution

1. Introduction

Chemical changes in soil composition have contributed largely to the knowledge of natural edaphic systems and their corresponding modification after the intrusion of agronomic management. The non-metallic nutrients carbon, nitrogen and phosphorus are widely studied because of their fundamental role both in the chemical architecture of the soil organic systems and in plant nutrition. In the last decades, sulphur has become a frequent limiting nutrient deserving closer examination (Tabatabai and Bremner, 1972; Sorensen, 1981; Wander and Traina, 1996; Eriksen, 1997a, 1997b; Amelung et al., 1998; Zhou et al., 1999; Dail and Fitzgerald, 1999; Chowdhury et al., 2000). Soil organic matter (SOM), together with biological activity are the most important factors affecting nutrient cycling modeling, soil fertility and their associated plant nutrition processes (David et al., 1982; Aguilera et al., 1996).

The hazardous effect of sulphur emissions on the environment has led to restrictive policies for S-containing pesticides or fertilizers and SO₂-emissions. Correspondingly at present, scientists investigate more often S-cycling, S-requirement in plants and S-depletion from soil pools

(Stevenson, 1986; Miller and Donahue, 1990; Chapman, 1997). The decrease of available sources of S has led to S-deficiency symptoms in plants (Stevenson, 1986), favouring studies focusing on the distribution and availability of sulphur in soils.

Sulphur is mainly incorporated in soil as primary minerals, sulphate being liberated during aging and soil forming processes. Sulphate is readily absorbed by plant roots and becomes organic-S within plant or microbial tissue, in such forms as cistine, cisteine and methionine and other less abundant forms as vitamins, glutathionine, thiamine, biotine, ferredoxine, coenzyme A, etc. All these organic-S forms follow their own cycle in soil and, after decay, become part of the humus structure. Humus constitutes the most important S-reservoir in soil from which the plant-available sulphate is gradually liberated to rhizospheres. The mineralization rate of S is closely related to the nature of its organic form in humus and its corresponding chemical linkages; thus, further studies are necessary for a better understanding of the physico-chemical and biological conditions occurring during sulphur mineralization in soil.

Sulphur and N behave similarly in soil with regard to cycling, plant availability, soluble forms and losses by leaching. Sulphur economy is mainly affected by type of

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soil, organic matter content, microbial community and redox conditions (Miller and Donahue, 1990). Especially in humid-climate soils, 95–99% of total soil-S is in organic forms (Tabatabai, 1982) with a good correlation to C and N content leading to a C/N/S ratio of approximately 140:10:1.3 (Stevenson, 1986). In addition, the S/P ratio has been also described as a good indicator of soil fertility, especially in soils with high P-fixing capacity given the case that both elements are absorbed by plant roots through similar mechanisms (Marschner, 1995).

Sulphur distribution in soil is usually studied by measuring total-S and $\text{SO}_4\text{-S}$; organic-S is then calculated by difference. Organic-S is more specifically studied by examining S-organic molecule linkages, which may correspond to C–S linkage or ester-type bonding C–O–S. The hydriodic acid method is widely used to determine sulphur, wherein S is measured as H_2S (Williams and Steinberg, 1959; Freney, 1961; Tabatabai, 1982; Pirela and Tabatabai, 1988; Mitchell et al., 1989; Strehl and Prietzel, 1998). However, analytical studies allowed us to conclude that elemental analysis is the most reliable method for S determination in soils and plant materials (Kowalenko, 2000).

About two-third of the agricultural land in Chile, approximately 40 million ha, is derived from volcanic ash. In these volcanic soils of the Dystrandeps and Palehumult series, attention has been focused on the chemistry and biochemistry of C, N and P (Borie and Zunino, 1983; Peirano et al., 1992; Aguilera et al., 1996, 1997, 1998; Peirano et al., 1999; Borie et al., 2001). However, even though analytical procedures for total S-determination in these soils have been developed early, there is a paucity of research on S-cycling in this type of soils.

Volcanic ash-derived soils are a very unusual soil system, developed under a humid but cold climate regime. Their microbiology is dominated by fungi and actinomycetes, which provide a very high biochemical activity, especially enzymatic ones (Zunino et al., 1982a; Zunino and Borie, 1985; Peirano et al., 1992). This is supported by the very high level of organic matter interacting with a clay fraction dominated by allophane or allophane-like secondary minerals with specific surfaces characterized by high physico-chemical sorption capacity (Galindo and Escudey, 1985).

The organic-clay complexes of volcanic ash-derived soils are extremely important to sustain the coexistence of a microbial and endomycorrhizal population with the native rhizosphere, generating very unusual and complex mechanisms for nutrient-flux from the soil matrix and soil solution to the root plasmalemma of native vegetation (Borie et al., 2001). Once this type of vegetation is removed for agricultural purposes, the land tends to lose its fertility rapidly, mainly because the high P-fixing capacity of the soil emerges as a serious competitor for P with agricultural plants, which do not have the same rhizosphere biochemistry as the native ones. At present, a renewed interest to study the chemistry and biochemistry of these Chilean

volcanic soils, especially virgin soils, will permit to advance in the discovery of unknown biochemical processes involved in the availability of nutrients to plants, among them sulphur.

This paper reports an evaluation and balance of total-S, $\text{SO}_4\text{-S}$ and organic-S of volcanic soils in Chile by measuring S linked to humic acid (HA–S), fulvic acid (FA–S) and humin (H–S). In addition, a special-S fraction, corresponding to the sulphur linked to organic polymer less than 10,000 Da, solubilized by hydrolysis throughout the extraction procedure, is calculated and referred to as ‘soluble organic-S’. A sequential method to fractionate S in soils is proposed that permits to follow the actual S-changes within the SOM. Sulphur is determined directly in each isolated organic fraction by means of elemental analysis. Thus, sulphur input and output can be adequately studied in soil, covering the entire S-cycling.

2. Materials and methods

Four volcanic-ash derived soils of Chile were chosen for this study.

Andisols, Typic Dystrandeps.

1. GORBEA series, under prairie cultivation.
2. TEMUCO series, under wheat cultivation.
3. PEMEHUE series, under permanent natural grassland.

Ultisols, Palehumult.

4. METRENCO series, under wheat cultivation.

Two soil samples were taken in each plot at 0–10 and 10–20 cm depth. Each laboratory sample was composed by mixing four soil samples thoroughly.

Some general characteristics of the soils under study are shown in Table 1.

2.1. Chemical analyses

1. pH was determined in 1:2 soil–water mixture.
2. S- SO_4 was measured applying the Sadzawka et al. (2000) method developed for this type of soils. Briefly this method consist on a S- SO_4 extraction using a $\text{Ca}(\text{H}_2\text{PO}_4)_2$ 0.01 M solution, followed by a turbidimetric measurement of sulphate as BaSO_4 .
3. Total organic matter fraction was extracted using the Aguilera et al. (1997) method and fractionated to fulvic acid (FA), humic acid (HA) and humin (H). The fractionation was performed after alkaline extraction, using a technique adapted by Aguilera et al. (1997) for this type of soil rich in allophane–organic matter complexes.
4. C, N, and S were determined in each soil sample and

Table 1
Some chemical characteristics of Chilean volcanic soils (values are means of two replicates \pm s)

Series (cm)	pH	%C	%N	%S	S-SO ₄ (mg g ⁻¹)
Andisol					
Gorbea					
0–10	4.80	8.85 \pm 0.07	0.74 \pm 0.01	0.135 \pm 0.004	12
10–20	4.88	9.03 \pm 0.02	0.75 \pm 0.00	0.129 \pm 0.001	2
Temuco					
0–10	5.42	9.28 \pm 0.03	0.81 \pm 0.01	0.113 \pm 0.004	9
10–20	5.54	8.53 \pm 0.05	0.74 \pm 0.00	0.168 \pm 0.038	8
Pemehue					
0–10	4.91	5.23 \pm 0.01	0.43 \pm 0.00	0.061 \pm 0.002	16
10–20	5.10	5.07 \pm 0.05	0.41 \pm 0.00	0.055 \pm 0.000	15
Ultisol					
Metrengo					
0–10	4.81	2.98 \pm 0.01	0.25 \pm 0.01	0.046 \pm 0.000	7
10–20	5.26	2.29 \pm 0.02	0.20 \pm 0.00	0.040 \pm 0.001	4

organic fraction by elemental analysis, using an Elemental Analyzer Vario El calibrated accurately for these types of samples. Data reported in Tables 1 and 3 correspond to the mean value of two independent samples whose variability between themselves were less than 1% as shown in Table 1; for simplicity Table 3 does not include the variability which were also less than 1%.

5. S linked to small organic molecule was referred to as 'soluble organic S' and determined by balance between total soil-S – S-SO₄ – S-organic polymeric fractions.

$$\text{Soluble-organic S} = (\text{Total soil-S}) - (\text{S-SO}_4) - (\sum \text{S-organic fractions})$$

All chemical analyses were made in duplicate and the results were expressed on an oven dry weight basis. Values are mean of two replicates \pm standard deviation.

3. Results

Table 1 shows some properties of the soils studied. The pH varied from 4.8 to 5.5; total C, N and S levels were high when compared with soils from other latitudes. For the Andisol series, total C varied from 5.2 to 9.3% in the first 10 cm surface layer and was similar to the second layer (5.1–9.0%). For the Ultisol series, total-C was lower at both depths and varied from 2.3 to 3.0%. This agrees with previous studies (Zunino et al., 1982a,b) which pointed out the better capacity of Andisols to stabilize humus by interacting with allophane. Ultisols represent the oldest and most weathered volcanic-ash derived soils, wherein the allophane has already been degraded to more crystalline

Table 2
Relationship between C, N and S in Chilean volcanic soils

Series (cm)	C/N	C/S	N/S	C/N/S
Andisol				
Gorbea				
0–10	12.0	65.7	5.5	119.6:10:1.8
10–20	12.0	70.3	5.8	120.4:10:1.7
Temuco				
0–10	11.5	82.5	7.2	114.6:10:1.4
10–20	11.6	50.7	4.4	115.2:10:1.4
Pemehue				
0–10	12.1	85.7	7.1	121.6:10:1.4
10–20	12.5	91.8	7.4	123.6:10:1.3
Ultisol				
Metrengo				
0–10	11.8	64.5	5.5	119.2:10:1.8
10–20	11.3	55.6	4.9	114.5:10:2.1

clay minerals with lower specific surface activity. Total-N content was also high in both types of soils, in correlation with total-C.

S-SO₄ in Andisols ranged from 9 to 16 mg kg⁻¹ for the surface layer and from 2 to 15 mg kg⁻¹ for the 0–10 cm soil layer; in Ultisols S-SO₄ were 7 and 14 mg kg⁻¹.

Table 2 shows the ratios C/N, C/S, N/S and between all these elements. There were excellent correlations with r^2 values of 0.998, 0.902 and 0.910 for each ratio, respectively. C/N/S average value found was 119:10:1.4.

Table 3 lists the elemental analysis (C, N and S) of the isolated and purified organic fractions of all the soil samples analyzed. The lighter organic fraction corresponds to fulvic acid (FA), composed by molecules higher than 10,000 Da (given by the dialysis membrane cut-off) but lower than the second fraction, humic acid (HA). HA are high molecular weight molecules which precipitated upon neutralization and strong acidulation after alkaline extraction. The third fraction humin (H) is an organic fraction still linked to some clay mineral constituents mainly allophane, allophane-like minerals or sesquioxides of Fe and Al (Galindo and Escudey, 1985).

Figs. 1 and 2 show S behavior and its distribution in soil, both organic and inorganic forms. Fig. 1 depicts how total S is distributed in each soil fraction expressed as g 100 g⁻¹ of soil sample allowing the comparison among soils. Fig. 2 shows how the same total S (referred to 100%) is specifically distributed in each soil within its five fractions; this facilitates the evaluation of the actual grade of S stability, as a function of the molecular weight of its corresponding organic matrix.

4. Discussion

Total-S ranged from 0.04 to 0.17%, which is very high

Table 3
Carbon, nitrogen and sulphur content in humic fraction from Chilean volcanic soils

Series (cm)	Residual-Humin			Humic acid			Fulvic acid		
	%C	%N	%S	%C	%N	%S	%C	%N	%S
Andisol									
Gorbea									
0–10	3.91	0.27	0.03	50.05	4.49	0.78	35.10	2.95	2.11
10–20	3.98	0.28	0.03	50.86	4.54	0.69	35.00	2.84	1.68
Temuco									
0–10	4.27	0.32	0.04	49.61	4.42	0.80	35.55	3.13	1.37
10–20	3.60	0.28	0.04	51.16	4.39	0.76	33.14	2.85	1.14
Pemehue									
0–10	1.92	0.15	0.02	51.17	4.44	0.67	34.40	2.87	1.22
10–20	2.10	0.15	0.02	51.64	4.39	0.67	35.22	2.94	1.81
C/N/S	136	10	13	114	10	1.6	119	10	5.2
Ultisol									
Metrenco									
0–10	1.16	0.08	0.02	21.13	1.78	0.38	21.39	1.34	2.40
10–20	0.71	0.06	0.01	15.80	1.36	0.32	18.88	1.20	2.62
C/N/S	132	10	2.1	118	10	2.3	159	10	20

when compared to international standards for agricultural soils, which are of the order of 0.006–0.06% with a mean value of 0.03% (Tabatabai and Bremner, 1972; Tabatabai, 1982). However, values of 0.17–0.20% have been reported for surface soil under conifer (David et al., 1982) and hardwood forest. Stevenson (1986) reported a total-S content of 0.002 and 5.0% for leached saline and calcareous soils of arid and semiarid regions and 0.01–0.05% for

humid or semihumid agricultural soils. In conclusion, it can be stated that the total-S levels found in Chilean volcanic-ash derived soils are high and consistent with the properties sustained by their high humus content and volcanic-originated clay mineral. The higher values for total-S were found in Andisol soil (0.05–0.17%), while for Ultisol soils was around 0.05%, a similar value to that reported by David et al. (1982). The amounts of inorganic-S are similar to

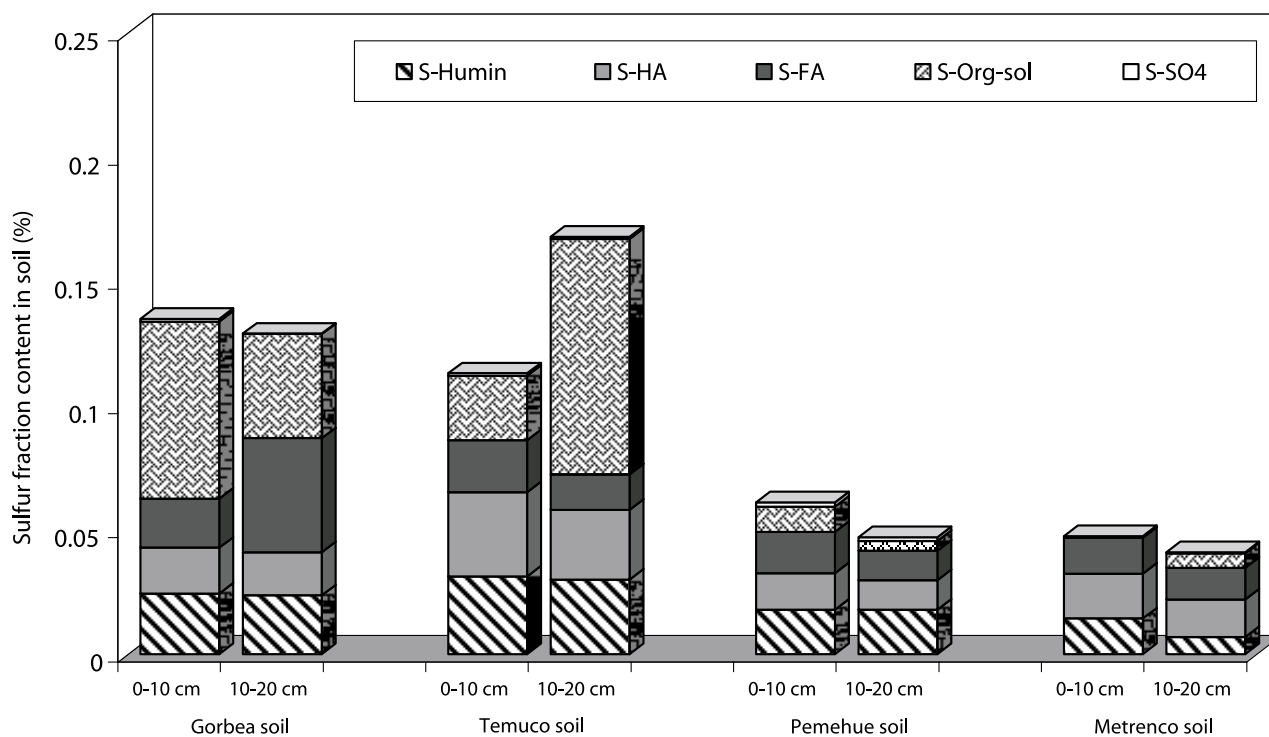


Fig. 1. Sulphur balance in volcanic Chilean soils.

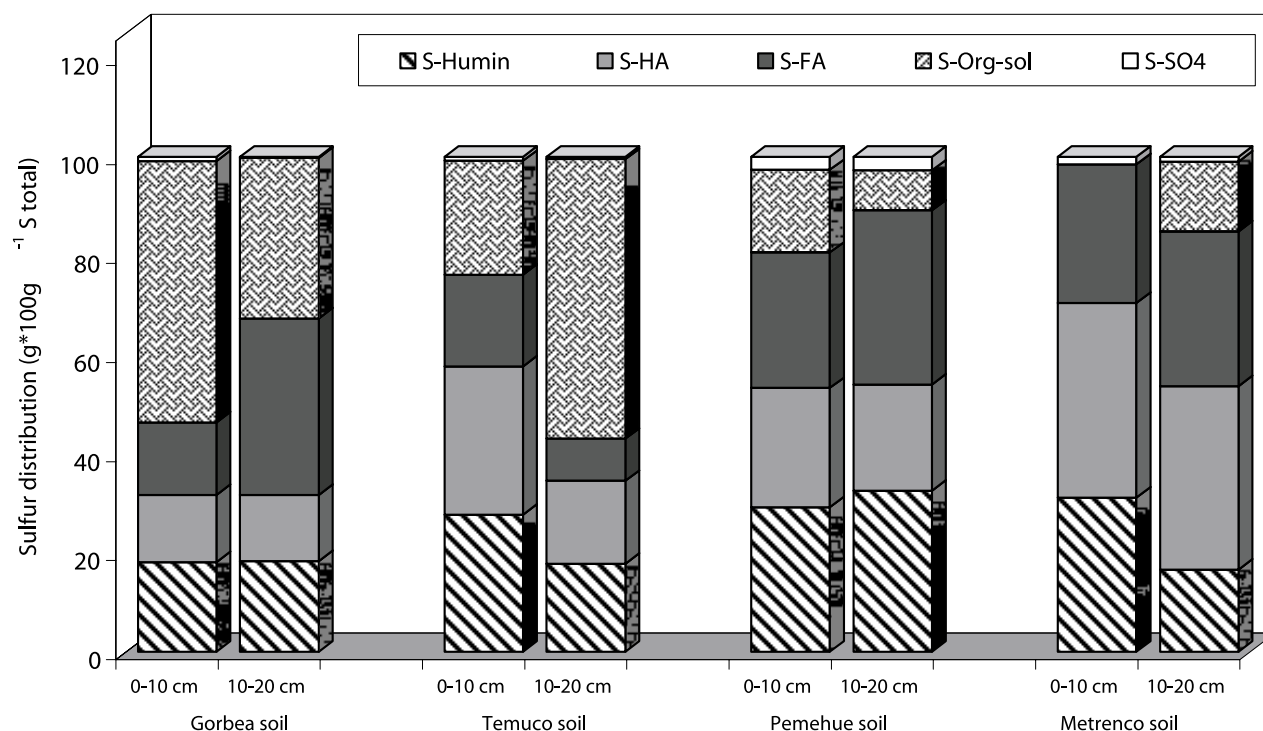


Fig. 2. Sulphur distribution in volcanic Chilean soils.

those reported in literature (Tabatabai and Bremner, 1972; Eriksen, 1997a).

The values obtained for the C/N, C/S, N/S ratios (Table 2) agree with those found by Kirchmann et al. (1996), but are much higher than those reported by Castellano and Dick (1988). Also these data for volcanic-ash derived soils under humid and cold regime confirmed that S is mainly linked to organic molecules (Stevenson, 1986; Miller and Donahue, 1990) with an N/S ratio of 6:7; C/S ratio for Andisols ranged from 65 to 92 and for Ultisol from 65 to 56. On the other hand, the C/N ratio stays around 12, which means that nitrogen is readily available for plants in these soils.

The triple ratio C/N/S was very similar in spite of the type of soil and series, their dissimilar composition, C, N, S levels and agronomic uses. The triple ratio was proposed as a good fertility indicator. Stevenson (1986) reported C/N/S ratio average values in soils 140:10:1.3 and gave figures of 91:10:1.6 and 122:10:0.9 for grassland soils and forest soils of Canada, respectively. The data shown in Table 2 confirm that total N and S status in these volcanic soils are adequate, presenting a high level, similar to the forest soils cited by Stevenson (1986).

Given the particular characteristics of these volcanic-ash derived soils, the fractionation method for each organic fraction must include strong hydrolytic processes to separate HA and FA molecules from their naturally stable associations with allophane, silicates or oxides minerals (Aguilera et al., 1997). Nevertheless, the recovery or mass balance evaluated after the whole extraction, fractionation and purification process was fairly good, therefore the analytical consistency and accuracy of the given ratio values

for each organic fractions allow to us calculate lighter organic-S (organic-soluble S) by difference with total-S as shown in Section 2. Moreover, the precision and analytical validity of this calculation was confirmed through a separate experiment with two samples with higher values of soluble organic-S.

Carbon content for Andisols were of the order of about 40–50% which agrees fairly well with the data reported for volcanic-ash-derived soils in Chile by Aguilera et al. (1997). However, for Ultisols, C contents for FA and HA were consistently lower than other kinds of volcanic soils (Aguilera et al., 1997); this must have been the consequence of humus degradation and loss of humus after intensive agronomic use of these soils, altering C-cycling.

Allophane or allophane-like minerals in Dystrandeps is one of the main factors stabilizing organic matter in soil. As pointed out by Stevenson (1986) quoting Zunino et al. (1982a) “the dynamics of organic matter in soil is strongly favoured toward C-remaining as humus in soil after incorporation of different kinds of residues like wheat straw, cellulose in comparison with the most simple organic molecule: glucose”. This behavior of Chilean Dystrandeps should have influenced the stabilization of organic forms of C, N and S, discussed in this work.

As expected, N and S contents of the organic fractions were well correlated to C; as in the case for the whole soils the organic fractions were well correlated to C. The C/N/S ratios in organic fractions were also similar to whole soils, which indicates that humus controls soil C, N and S turnover and their economy.

In Andisols the S-content in the organic fractions (HA,

FA, H) plus light organic-S were higher than the ones for Ultisol Metrenco, which followed the same pattern for C and N as discussed above. There were no major differences between layers in each soil, except for Temuco soil whose soluble organic-S was quite high in the 10–20 cm layer. In addition, the level of S linked to HA, FA and H did not change noticeably, but the S linked to high weight organic molecules does change, the highest values being for Andisol Temuco soil at 10–20 cm layer and the lowest, almost zero, for Ultisol Metrenco at 0–10 cm.

Data of Fig. 2 demonstrate that S in Chilean Dystrandepts is almost 100% (96–99%) linked to organic molecules. Again the important difference from the figure of 93% reported by David et al. (1982) must be noted.

Regarding the degree of stabilization or resistance against chemical or microbiological degradation of organic-S in soil, the S linked to HA, FA and H should represent a highly stabilized chemical state. This is reflected in the higher values of these forms in Ultisols (82–99%) over Andisols (42–92%) which would be a consequence of aging, resulting in more humified organic S-macromolecules with less chemical or microbiological availability.

The major organic-S fraction in Andisols corresponded to S–H (14–36%), while the S in the other fractions was evenly distributed. In Ultisols, the most important fraction was S–HA (40%) followed by S–FA (31%) and finally S–H (29%). Soluble, or easily hydrolyzable, organic-S and S–SO₄ may be referred to as the ‘available S-pool’. Soluble organic-S in the three Andisol soils was very high, while in the Ultisol very low. Thus, it can be concluded that in younger Dystrandepts S-availability is regulated by tight binding to these types of organic molecules, which are less complexing than the ones found in more aged Ultisol soils.

Eriksen et al. (1995a,b) presented an interesting approach to discuss the interactive forces among S-fractions in soils, applying especially developed experimental methods to extract and remove these materials. According to his hypothesis there should be some ‘more protected’ form of organic-S and another ‘less protected’ one, corresponding to the soluble ones. This degree of protection would be related to molecular weight of organic-S molecules. Thus they estimate that about 50% of the total-S in the soils studied should be stabilized under non-extractable forms.

The results given in this work for Dystrandepts clearly agree with Eriksen’s approach. In Andisols, S linked to HA and H (high molecular weight) corresponded to 32–58% while in Ultisols increased up to 70%. However, by fractionating S-forms with the methodology proposed here, a more detailed measure of S-availability can be made by measuring directly by elemental analysis of the S-linked to HA, FA and H macromolecules.

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