

Effects of moisture content on sulfate generation and retention in hardwood forest upper soil horizons

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The influence of moisture on organic S mineralization and the fate of both mineralization-derived and added sulfate were examined in A and B horizon soil samples from a hardwood forest. The sulfur-containing amino acid methionine was chosen to study organic S mineralization. ³⁵S-labelled sulfate or methionine was added to field-moist samples, which were then suction dried to contain between 2 and 80% moisture. Both added sulfate-S and sulfate-S released by methionine mineralization was incorporated into organic matter, and the highest levels of organic S formed were observed for those A and B horizon samples containing between 25 and 35% moisture. The A horizon incorporated much less added sulfate under very dry than under extremely moist conditions. The B horizon exhibited substantial decreases under both extreme moisture regimes. At moisture contents over 30%, high levels of methionine mineralization were observed, and at lower moisture contents mineralization decreased substantially. For soil moistures lower than 10 and 20% for the A and B horizons, respectively, most of the added methionine remained nonmineralized following incubation. In addition to mineralization, a portion of the added methionine was also incorporated directly into organic matter. The highest levels of this incorporation were achieved at soil moistures between 20 and 35%.

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Les auteurs ont examiné l'influence de l'humidité sur la minéralisation du S organique et le devenir du sulfate dérivé de la minéralisation et du sulfate ajouté à des échantillons d'horizons A et B du sol d'une forêt feuillue. La méthionine, acide aminé renfermant du soufre, fut choisie pour étudier la minéralisation du S organique. Le sulfate ou la méthionine marquée (^{35}S) fut ajouté aux échantillons humides du terrain qui furent subséquemment séchés par succion pour renfermer entre 2 et 80% d'humidité. Le soufre du sulfate ajouté et celui qui fut libéré par minéralisation de la méthionine furent incorporés dans la matière organique, et les plus forts niveaux de S organique formés furent observés pour chaque horizon dans les échantillons renfermant de 25 à 35% d'humidité. L'horizon A a incorporé beaucoup moins de sulfate ajouté en condition très sèche qu'en condition très humide. L'horizon B a montré des diminutions substantielles dans les deux régimes extrêmes d'humidité. Aux teneurs en humidité supérieures à 30%, on a observé des niveaux élevés de minéralisation de la méthionine alors qu'aux faibles taux d'humidité la minéralisation a diminué fortement. Aux taux d'humidité inférieurs à 10 et 20% des horizons A et B, respectivement, la majeure partie de la méthionine est demeurée non minéralisée à la fin de l'incubation. En plus de la minéralisation, une partie de la méthionine ajoutée fut aussi directement incorporée dans la matière organique. Les plus hauts niveaux de cette incorporation furent atteints aux taux d'humidité du sol compris entre 20 et 35%.

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Introduction

Sources of sulfate for forest soils include precipitation and throughfall (Swank and Douglass 1977; Shriner and Henderson 1978; Johnson et al. 1980; Stewick 1982) as well as the mineralization of S-containing organic compounds ubiquitous in litter and soil (Fitzgerald and Andrew 1984). Carbon-bonded S, consisting primarily of S-containing amino acids and sulpholipid (Harwood and Nicholls 1979), is a major component of hardwood foliage and has been shown to undergo mineralization in forest soils (Fitzgerald and Andrew 1984; Strickland and Fitzgerald 1983). Sulfate derived from either atmospheric deposition or the mineralization of S-containing organics may be retained by adsorption (Fitzgerald et al. 1984; Johnson et al. 1982) or by incorporation of S into organic matter through the formation of covalent linkages (Strick et al. 1982; Fitzgerald and Andrew 1984; McLaren et al. 1985; Fitzgerald et al. 1988). Fitzgerald and Andrew (1984) found that the S-containing amino acid methionine was mineralized in forest soil, and that some of the resulting sulfate-S was rapidly incorporated into organic matter. Direct incorporation into this organic fraction of a portion of the added methionine also occurred, and it was suggested (Fitzgerald et al. 1984) that this process might serve as a possible storage mechanism for methionine that could later be released and thus made available for mineralization. Microbial involvement has been documented for this latter process as well as for methionine mineralization and organic S formation (Fitzgerald and Andrew 1985). Thus, any environmental parameter influencing soil microbial populations would be expected to influence these processes. The effects of incubation time, temperature, antimicrobial agents, and nutritional amendments have been examined (Fitzgerald et al. 1983, 1984; Fitzgerald and Andrew 1984; Watwood et al. 1986). However, apart from the work of Singh (1984) on sulfate adsorption and that of Williams (1967) on S mineralization, there has been little work done on the effects of soil moisture content. The current study examines the influence of this variable on methionine mineralization, sulfate and methionine incorporation into organic matter, and sulfate adsorption occurring in A and B horizon forest soil. This study is especially relevant with respect to the recent drought conditions experienced in the southeastern United States, which temporarily altered forest soil moisture.

Materials and methods

Site description

Samples of A and B horizon soil were collected in April 1986 from watershed 2 within the Coweeta basin, near Otto, North Carolina. This undisturbed, mixed mature hardwood forest has been a primary control site for nutrient cycling studies at the Coweeta Hydrologic Laboratory. The catchment has a south-facing slope and soils of the sandy loam Chandler series of the Typic Dystrocrepts. The A and B horizons were sampled at approximate depths of 3 and 15 cm, respectively.

Sulfur addition and moisture manipulation

Field-moist subsamples (1 g wet weight, not sieved) were placed in open-ended, sintered glass-candlestick filters (1 cm \times 3.5 cm). Various volumes all containing 7.5 nmol S of carrier-free sodium [^{35}S]sulfate (115.2 TBq mmol^{-1} , Amersham) or L-methionine (mixture of unlabelled and ^{35}S -labelled amino acid; 51.0 TBq mmol^{-1} , Amersham) were added to separate subsamples. Some samples were then dried by applying suction to the bottom of the filter while a tube containing anhydrous CaSO_4 (8 mesh, Hammond Drierite) was attached to the top of the filter. Suction was applied for varying lengths of time and the underside of the filter was inspected periodically to ensure that none of the fluid had become suctioned through the filter. After adjustment of moisture content, samples were incubated at 20°C for 48 or 24 h with sulfate or methionine, respectively. Percent moisture content was determined by oven-drying at 50°C for 48 h following fluid addition and suction drying. We chose to express soil moisture on a percent basis in lieu of soil water potential expressions to facilitate future coupling of sulfur transformations to existing models of changes in soil water content (Helvey et al. 1972). Moisture retention curves are somewhat different between horizons; for example, at 40 kPa pressure, moisture content for A and B horizons are 32 and 27%, respectively.

Following incubation, samples were extracted as previously described by Fitzgerald et al. (1988) or Fitzgerald and Andrew (1984) to recover ^{35}S added as sulfate or methionine, respectively. After an initial water wash to remove soluble ^{35}S , reactions involving either sulfate or methionine were terminated by isotope dilution with successive washings with 1 M Na_2SO_4 or 1 M Na_2SO_4 in a saturated solution of methionine. Adsorbed ^{35}S was recovered by a series of NaH_2PO_4 , LiCl , and water washes. In previous work (Fitzgerald et al. 1984), radioactive sulfate or methionine remaining in the sample was found to be incorporated into organic matter through the formation of covalent linkages during incubation. These fractions were recovered by treatment with strong acid and base, which rupture covalent linkages.

TABLE 1. Percent moisture content of A and B horizon samples following fluid addition and suction drying

| Fluid volume added (μL) | Suction time (min) | Sulfate | | Methionine | |
|--------------------------------------|--------------------|------------|------------|------------|------------|
| | | A | B | A | B |
| 300 | 0 | 73.0 (0.6) | 67.2 (1.0) | 69.4 (0.2) | 76.2 (3.8) |
| 200 | 0 | 48.4 (0.3) | 43.5 (1.2) | 59.4 (0.6) | 62.6 (0.8) |
| 100 | 0 | 36.8 (0.2) | 31.4 (0.9) | 49.3 (0.1) | 48.5 (1.2) |
| 100 | 3 | 32.1 (0.7) | 25.0 (1.3) | 34.8 (0.3) | 34.6 (0.2) |
| 100 | 5 | 28.2 (1.1) | 22.8 (1.6) | 30.0 (0.7) | 18.5 (2.3) |
| 100 | 10 | 21.9 (3.0) | 20.7 (0.8) | 22.2 (1.8) | 12.8 (1.9) |
| 100 | 15 | 16.3 (2.5) | 12.9 (3.9) | 16.8 (2.4) | 10.8 (0.5) |
| 100 | 20 | 13.7 (1.5) | 9.6 (3.2) | 8.6 (2.0) | 6.5 (0.6) |
| 100 | 25 | 4.0 (1.5) | 2.7 (2.2) | 5.4 (1.3) | 3.6 (0.9) |

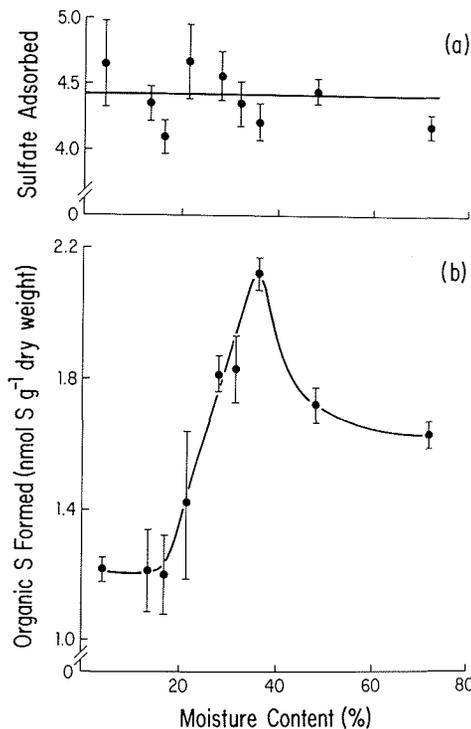
NOTE: Values are means (\pm SE), $n=4$.

FIG. 1. Influence of A horizon soil moisture on (a) sulfate adsorption and (b) organic S formation following 48 h incubation with [³⁵S]sulfate. Units for both determinations are expressed as nanomoles S adsorbed or incorporated into organic matter (per gram dry weight). Error bars indicate 1 SE ($n = 4$).

Radioactivity of each fraction was then determined by scintillation counting, and the percent of label recovered in each fraction was calculated. Total ³⁵S recoveries >91% were obtained for all samples. Extracts of samples incubated with [³⁵S]methionine were subjected to electrophoresis to separate products of the metabolism of this amino acid. Separations were carried out on Whatman No. 1 paper in 0.1 M barium acetate - acetic acid buffer or 0.1 M sodium acetate - acetic acid buffer, pH 4.5, for 2 h at 250 V (Fitzgerald and Andrew 1984). Radioactive components present in each extract were then located on strips by scanning in a Packard electrophoretogram scanner.

Results and discussion

A broad range of moisture contents was achieved by varying the amount of fluid added and the duration of suction drying (Table 1). Standard errors associated with

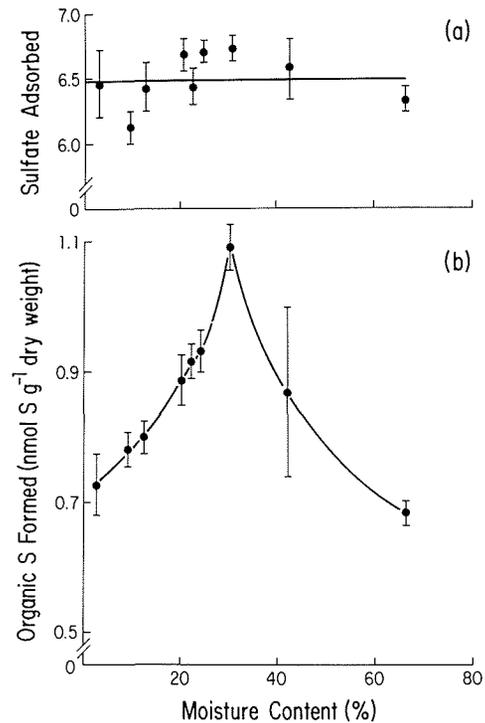


FIG. 2. Influence of B horizon soil moisture on (a) sulfate adsorption and (b) organic S formation following 48 h incubation with [³⁵S]sulfate. See legend to Fig. 1 for further details.

mean values decreased with increasing moisture content, and less than 3% variation was observed during incubation at any given moisture content.

The fate of added [³⁵S]sulfate relative to moisture content in A and B horizon samples is shown in Figs. 1 and 2, respectively. Sulfate adsorption (measured as salt-extractable ³⁵S) was not affected by moisture content. This was not unexpected because adsorption is not considered to be microbially mediated. However, results obtained by Singh (1984) indicated an inverse relationship between adsorption and moisture content in iron podzol and brown earth soils. The longer incubation period (12 days) and lower temperature (12°C) utilized in that study, together with the different soil types examined, may account for the different results. In the present study, sulfate adsorption levels were approximately 30% higher in the B than in the A horizon. This result confirms work at Coweeta by Johnson et al.

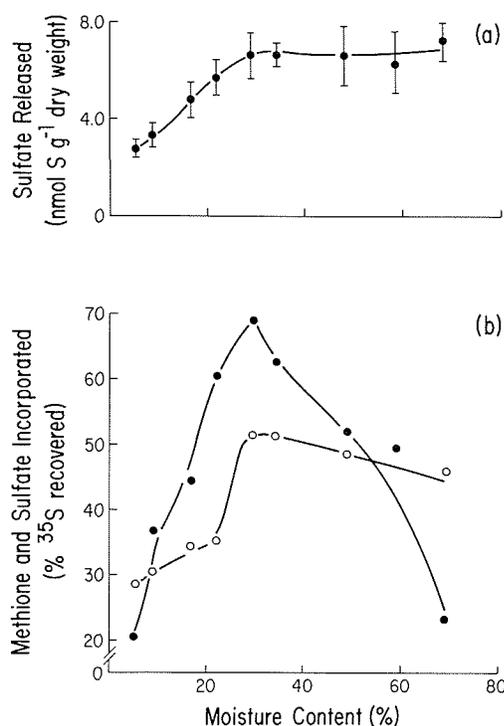


FIG. 3. Influence of A horizon soil moisture on the metabolism of methionine. (a) [³⁵S]sulfate released from methionine; (b) ●, [³⁵S]methionine incorporated into organic matter; and ○, incorporation into organic matter of [³⁵S]sulfate derived from mineralization. Incubation was for 24 h. Error bars in *a* indicate 1 SE. Standard error in *b* was <12% (*n* = 4). Values in *b* are expressed as a percentage of the total methionine or sulfate available for incorporation.

(1980) who also observed higher levels of adsorption in B horizon forest soils and attributed the increased adsorption to the presence of iron and aluminum oxides and a relative lack of organic matter in the deeper horizon.

The incorporation of sulfate-S into organic matter (measured as acid- and base-extractable ³⁵S) varied markedly with respect to moisture content. In the A horizon (Fig. 1) the highest amount of incorporation was observed with samples containing approximately 36% moisture. At higher moisture contents organic S formed by incorporation decreased by 24%, and below 18% moisture a 43% decrease was observed. With respect to the B horizon (Fig. 2) the highest levels of incorporation, which were approximately half of those obtained with the A horizon, were detected with samples containing 31% moisture. In the B horizon incorporation decreased equally under low and high moisture regimes to levels which were approximately 36% lower than the maximum levels observed. Thus it may be inferred that microbial populations in both horizons have similar moisture requirements for maximum sulfate incorporation and respond similarly to dry conditions. However, the response of these populations to high soil moisture (>30%) differs and may be due to the shift from aerobic to anaerobic redox potentials in soil microzones. Thus, elevated soil moisture may result in more widespread anaerobiosis in the B than in the A horizon because of decreased aeration and lower porosity in the B horizon (50%) compared with 65% for the A horizon. If so, then smaller incorporation of sulfate-S into organic matter could be expected because aerobic populations appear to be

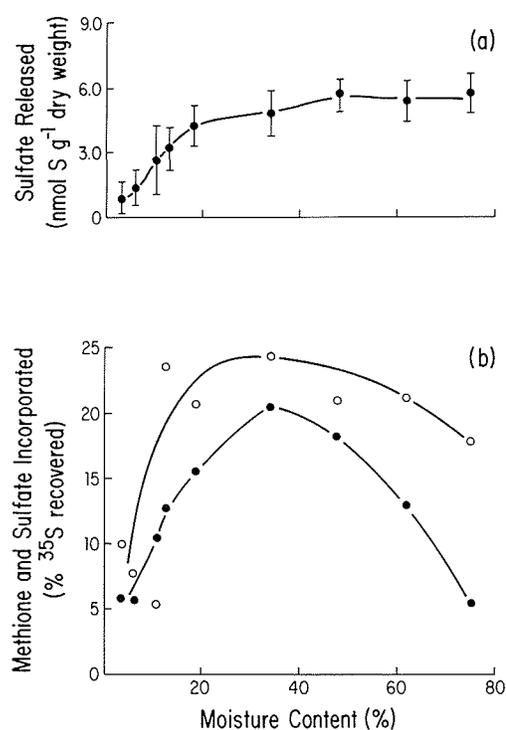


FIG. 4. Influence of B horizon soil moisture content on the metabolism of methionine. (a) [³⁵S]sulfate released from methionine; (b) ●, [³⁵S]methionine incorporated into organic matter; and ○, incorporation into organic matter of [³⁵S]sulfate derived from mineralization. See legend to Fig. 3 for further details.

primarily responsible for this process (Fitzgerald et al. 1983; Watwood et al. 1986).

The effect of moisture content on the fate of [³⁵S]methionine in the A and B horizons is shown in Figs. 3 and 4, respectively. For both horizons methionine mineralization was not influenced by moisture at contents above 30%. However, mineralization of S in the amino acid decreased sharply at lower ³⁵S moisture contents. Maximum levels of sulfate derived from mineralization were somewhat higher in the A than in the B horizon (6.5 and 5.5 nmol sulfate-S g⁻¹, respectively). At moisture contents below 10 and 16% for the A and B horizons, respectively, more than half of the ³⁵S was recovered as nonmineralized methionine after 24 h (Figs. 3a and 4a). A similar decrease in mineralization of soil organic sulfur under dry conditions was observed with yellow podzolic soils by Williams (1967). This investigation also noted a decrease in mineralization at moisture contents exceeding 50%. However, in the current study maximum levels of methionine mineralization remained constant at moisture contents up to approximately 80% in both horizons examined.

As noted previously for soil from other watersheds in the Coweeta basin (Fitzgerald et al. 1984), some of the [³⁵S]methionine, present in larger quantities under very dry conditions, was directly incorporated into organic matter (acid- and base-extractable ³⁵S) during 24 h, and this type of incorporation was also observed for a portion of the sulfate derived from mineralization. Levels of methionine incorporation were highest at 30 and 35% moisture and maximum levels of sulfate-S incorporation were observed at 30 and 20% moisture for the A and B horizons, respectively (Figs. 3 and 4). At lower moisture levels substantial

decreases in methionine incorporation occurred (70 and 75% decrease, A and B horizons, respectively). Similar decreases in this process were observed under very moist regimes (e.g., 50 to 80% moisture). With respect to the incorporation of mineralization-derived sulfate-S, the A and B horizons exhibited 45 and 65% decreases, respectively, at low moisture levels. Unlike methionine incorporation, the incorporation of sulfate-S remained constant at higher moisture values in both horizons.

Generally, maximum incorporation levels for both sulfate-S and methionine-S corresponded to very similar amounts of moisture. This indicates that microbial populations responsible for these processes have very defined moisture requirements with respect to the incorporation of these S-containing moieties. Collectively, these results suggest that under dry conditions, retention of anthropogenic or mineralization-derived sulfate-S by incorporation into organic matter may be diminished, thus leaving more of the anion available for plant uptake or leaching. Increased moisture could cause a shift favoring microbial incorporation, thereby storing sulfur as organic S for future availability. However, generation of sulfate from methionine mineralization was also maximized at moisture contents of 30% or more, so that although retention may be elevated, there is also more available sulfate under these moist conditions. Therefore, the net effect of the competing processes of sulfate generation and retention appears to depend on levels of microbial activity in moist soils. Conversely, since both sulfate generation and retention are diminished under drier conditions, the fate of the anion relative to availability or retention may be less dependent on microbial activity.

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