The accumulation of sulphate S in forested watersheds (Swank and Douglass, 1977) is mediated by sulphate adsorption (Johnson and Henderson, 1979; Johnson et al., 1980) and microbially by incorporation of sulphur into covalent linkage with soil organic matter (Fitzgerald et al., 1983; Strickland and Fitzgerald, 1984). The mineralization of sulphur from organic S has been observed with agricultural (Freney et al., 1975; Bettany et al., 1980) and forested soils (Strick et al., 1982). Additional work has shown that recently-formed insoluble organic S may also be converted to soluble forms (Strickland et al., 1984, 1986). The term mobilization will therefore be used here to describe the combined effects of solubilization (depolymerization of large matrices) and mineralization.

Some evidence (Fitzgerald, 1978) indicates that organic S in humic acid occurs as ester sulphate (R–C–O–SO_4^2-) and carbon-bonded S (R–C–S–R and R–C–SO_3^2-). Carbon-bonded S may be involved in condensation reactions to form cyclic compounds as part of the humic core, and this has been postulated to contribute to the resistance of organic S to degradation (Stevenson, 1982). The recalcitrance of humic acid to mineralization is widely accepted and Nyborg (1978) postulated that organic S should be degraded at rates similar to those of the parent organic material. If such were the case, the half-life of organic S could range from hours to hundreds of years. We therefore determined the change in organic S mobilization capacity of samples as a function of the time required for organic S to be formed from sulphate.

Samples were collected during August 1982 from the 02 and A1 (0–10 cm) horizons of a mixed mature hardwood forest in the southern Appalachian mountains of North Carolina. The soil is a sandy loam Ashe (Typic Dystrochrept) and the vegetation is dominated by a rhododendron understory and an oak–hickory overstory. The amount of organic S formed in the 02 and A1 horizons and the net mobilization rate for this sulphur pool was determined using a 35S label as described by Strickland et al. (1984). Briefly, ten subsamples (2 g each) of each horizon were held at 30°C with 540 nmol of 35S-labelled sodium sulphate (0.42 mCi; 12.6 MBq) for various periods up to 437 days to allow incorporation of 35S into organic matter. The moisture content of the samples was maintained by the addition of deionized water weekly. Periodically, one subsample from each horizon was extracted with 1 m Na_2SO_4, NaH_2PO_4 and LiCl followed by deionized water. Organically-bound 35S was then reconstituted with a water extract from a separate untreated subsample, and held for 48 h at 30°C. The 35S recovered from organic S after this additional incubation was recovered by sequential extraction with 1 m Na_2SO_4, NaH_2PO_4 and LiCl followed by deionized water. Organic 35S remaining in the samples (not solubilized or mineralized during the second incubation) was recovered by acid hydrolysis (6 m HCl for 2 h at 121°C) followed by alkaline extraction (2 m NaOH, 12 h at room temperature). Not all of the added 35S was recovered by this method, but yields were consistently >87%. The 35S in each extract was quantified by liquid scintillation counting and the 35S mobilized (combined salt extracts from second incubation) was taken as a percent of the total 35S recovered i.e. combined salt extracts plus that extracted by acid and alkali (insoluble organic S).

In samples from the 02 horizon, net 35S-labelled insoluble organic S accumulated to a maximum of about 290 nmol g⁻¹ 100 day⁻¹ sometime before the first determination at 31 days (Fig. 1). Thereafter, the net amount of insoluble 35S-labelled organic S formed in this horizon decreased by an average of about 30 nmol g⁻¹ 100 day⁻¹ during the initial 166 days. The graph illustrating organic S accumulation in the A1 horizon was divided into two parts (Fig. 1a, b) because a Pearson correlation matrix indicated a strong positive correlation (+0.87) with incubation time up to 166 days. This increase was followed by an inverse correlation (−0.67) with time up to 437 days. As shown in Fig. 1, the amount of insoluble 35S-labelled organic S in this horizon increased by about 39 nmol g⁻¹ 100 day⁻¹ during the initial 166 days. Thereafter, a net decrease in accumulation of 20 nmol g⁻¹ 100 day⁻¹ was observed. A similar pattern of net sulphate

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imobilization followed by a slow linear release of sulphate in mineral soil was noted by Stevenson (1982). The capacity of the 02 horizon to mobilize organic S was not affected by the duration of the incubation (Fig. 2). However, the capacity of the A1 horizon to mobilize organic S decreased with time. While the mobilization process persisted in this latter horizon, the net amount decreased by 3% 100 day$^{-1}$ throughout the 437-day experiment. It seems likely that the capacity of the 02 horizon to mobilize increasing amounts of organic S over the entire experiment was related to the higher organic matter content of this horizon (approx. 44.5 and 3.8% total C; 02 and A1 horizons, respectively). It was noted by Burges and Latter (1960) and by Mishustin and Nikitin (1961) that metabolism of readily-degradable carbon sources by fungi and bacteria enhanced humic acid degradation. Metabolism of these carbon sources would also enhance the release of S from the humic matrix. The net decrease in insoluble organic S in the 02 horizon (Fig. 1) may therefore be attributed to part to decreases in the C:S ratio of the organic material remaining in the sample (and thus a decrease in the amount of S required by the microflora as respiration rates begin to subside). Furthermore, because the rate of organic S formation is dependent upon the amount of substrate available for carbon and energy (Strickland and Fitzgerald, 1985), S incorporation by soil microflora would decrease as the amount of organic material in the sample decreased, thus resulting in a net increase in soluble S.

Our results support the suggestions of Bettany et al. (1979, 1980) and Nyborg (1978) that condensation of S components into the humic core results in making organic S mineralization dependent to some extent upon humus degradation rates. Organic S in soil can be expected to participate in humus formation in the same way as any other organic component of the solum. Biologically-mediated cyclization and polymerization of organic material will in time increase the net recalcitrance of the organic material to microbial attack.

Fig. 2. Organic S mobilization capacity as a percentage of insoluble organic S accumulated. (O) 02 horizon, \(R^2 = 0.07, \text{slope} = +0.01, (\bullet) \text{A1 horizon, } R^2 = 0.40, \text{slope} = -0.03.

**REFERENCES**


