

## SHORT COMMUNICATION

# ORGANOSULPHUR RECALCITRANCE IN SOIL AND LITTER FROM A HARDWOOD FOREST

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The accumulation of sulphate S in forested watersheds (Swank and Douglass, 1977) is mediated physically 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 ( $R-C-O-SO_3^-$ ) and carbon-bonded S ( $R-C-S-R$  and  $R-C-SO_3^-$ ). 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 O2 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 Dystrachrept) and the vegetation is dominated by a rhododendron understory and an oak-hickory overstory. The amount of organic S formed in the O2 and A1 horizons and the net mobilization rate for this sulphur pool was determined using a  $^{35}S$  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  $^{35}S$ -labelled sodium sulphate (0.42 mCi; 12.6 MBq) for various periods up to 437 days to allow incorporation of  $^{35}S$  into organic matter. The moisture content of the samples was maintained by the addition of deionized water weekly. Periodically, one subsample from both horizons was extracted with 1 M  $NaH_2PO_4$  to remove unincorporated  $^{35}SO_4^{2-}$ . Extracted samples were then reconstituted with a water extract from a separate untreated subsample, and held for 48 h at 30°C. The  $^{35}S$  released 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  $^{35}S$  remaining in the samples (not solubilized or mineralized during the second incubation) was recovered by acid hydro-

lysis (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  $^{35}S$  was recovered by this method, but yields were consistently > 87%. The  $^{35}S$  in each extract was quantified by liquid scintillation counting and the  $^{35}S$  mobilized (combined salt extracts from second incubation) was taken as a percent of the total  $^{35}S$  recovered i.e. combined salt extracts plus that extracted by acid and alkali (insoluble organic S).

In samples from the O2 horizon, net  $^{35}S$ -labelled insoluble organic S accumulated to a maximum of about 290 nmol  $g^{-1}$  sometime before the first determination at 31 days (Fig. 1). Thereafter, the net amount of insoluble  $^{35}S$ -labelled organic S formed in this horizon decreased by an average of about 30 nmol  $g^{-1}$  100 day $^{-1}$ . 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  $^{35}S$ -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

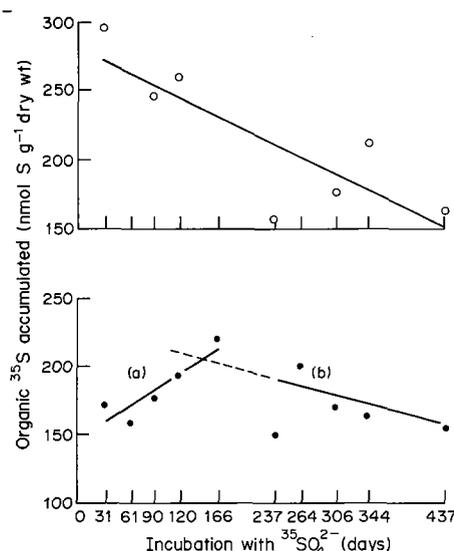


Fig. 1. Net accumulation of  $^{35}S$  in organic matter ( $^{35}S$  not extractable with phosphate). (O) O2 horizon,  $R^2 = 0.69$ , slope = -0.30, (●) A1 horizon, (a)  $R^2 = 0.76$ , slope = +0.39, (b)  $R^2 = 0.45$ , slope = -0.20.

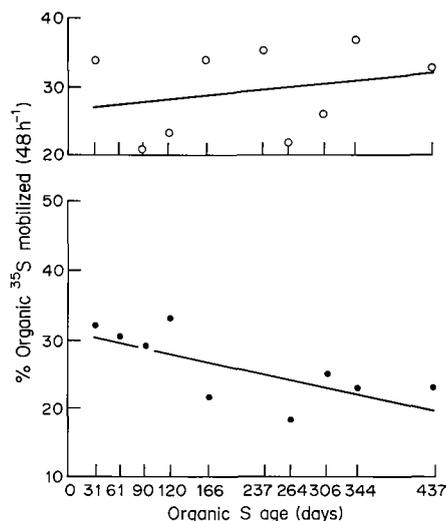


Fig. 2. Organic S mobilization capacity as a percentage of insoluble organic  $^{35}\text{S}$  accumulated. (○) O2 horizon,  $R^2 = 0.07$ , slope =  $+0.01$ , (●) A1 horizon,  $R^2 = 0.40$ , slope =  $-0.03$ .

immobilization followed by a slow linear release of sulphate in mineral soil was noted by Stevenson (1982).

The capacity of the O2 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  $3\% \text{ } 100 \text{ day}^{-1}$  throughout the 437-day experiment. It seems likely that the capacity of the O2 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; O2 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 O2 horizon (Fig. 1) may therefore be attributed in 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.

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