ANALYSIS OF SULFUR-CONTAINING COMPONENTS OF A SOIL TREATED WITH SIMULATED ACID RAIN

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Abstract. Samples of the LFH and Bfh horizons of an Orthic Humo-Ferric Podzol were analyzed for S components after irrigation with simulated acid rain solutions of pH 5.7, 3.5, and 2.0 for 720 days. Organic S was preponderant. In the LFH horizon, the mass ratio of ester sulfate: carbon-bonded S was approximately 1 : 1 for samples treated with solutions of pH 5.7 and 3.5; for the sample treated with the pH-2.0 solution, the ratio was about 2 : 1 and the concentrations of both inorganic sulfate and ester sulfate were markedly higher. In the Bfh horizon, carbon-bonded S was the major form of organic S, except in the sample subjected to the high-acid (pH 2.0) simulated rain. The organic S components were further separated into chloroform-soluble, aqueous trifluoracetic acid-soluble, and residual fractions. Significant increases in inorganic sulfate, both water soluble and adsorbed were found after the pH-2.0 treatment.

1. Introduction

The concentration of hydronium ions in the rainfall of eastern North America frequently is significantly higher than that derived from the hydrolysis of equilibrium concentrations of dissolved, atmospheric CO₂, thus giving rise to the term ‘acid rain’ (see Bubenick et al., 1983). Sulfuric acid and HNO₃, the major acidic constituents in rainfall, occur in relative proportions that are both temporally and geographically variable, the typical mass ratio of H₂SO₄ : HNO₃ being approximately 2 : 1 in eastern North America (Louckes, 1982).

After entry of rain water into the soil, the acidic components may undergo a number of processes. Geochemical adsorption accounts for the loss of a significant proportion of sulfate from soil pore water; the oxides of both Fe(III) and Al are efficient sulfate-binding agents (Johnson and Cole, 1977). In addition, the transformation of sulfate into the soil organic matter by microbial activity has been well established (Fitzgerald, 1976; Saggar et al., 1981; Strickland and Fitzgerald, 1985). A survey of the elemental composition of a broad spectrum of 54 Saskatchewan soils, ranging from semiarid grassland to grassland-forest transition zone, exhibited C:N:S ratios between 45 : 5.2 : 1 and 141 : 11.2 : 1 (ppm), with Podzols affording ratios near the upper limit of this range (Bettany et al., 1973). Typical concentrations of total S in soil horizons which are rich in organic constituents are 0.044% in the Ao horizon of a Podzol (Lowe and DeLong, 1963), 0.011 to 0.041% in the Ap horizons of a large variety of Saskatchewan soils (Bettany et al., 1973), and 0.15% in the 01 horizon of a sandy loam Ashe series (forest soil) (Strickland and Fitzgerald, 1985); the concentrations of S in mineral horizons normally are lower (Bettany et al., 1973).

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Although inorganic sulfate is present in all soils, the preponderant source of soil S is S-containing organic compounds (Melville et al., 1969; David et al., 1982), the carbon-bonded S and sulfate esters being major contributors (Lowe and DeLong, 1963; Bettany et al., 1980; David et al., 1982; Landers et al., 1983). Bettany et al. (1979) have postulated that increased concentrations of carbon-bonded S, concomitant with decreased concentrations of ester sulfate, may be attributable to microbial processes. For Podzolic B-horizons it may be anticipated (cf. Evans and Rost, 1945) that these would show a higher proportion of inorganic sulfate relative to organic sulfate in the region of accumulation of iron and aluminum sesquioxides; however, this horizon also exhibits enrichment of organic matter as compared with the Ae horizon, and consequently this process would add to the organic S present. Fitzgerald et al. (1983) have reported the adsorption of substantial quantities of exogenous sulfate at the A-horizon of sandy loam Ashe series.

Studies utilizing 6-[35S]sulfoquinovose (Fitzgerald et al., 1983) or [35S]sulfate ion (Strickland et al., 1984; Swank et al., 1984; Strickland and Fitzgerald, 1985) showed that the isotopic label was incorporated into organic S within 48 hr when incubated with forest soil at 30 °C; the first cited study indicated that the 35S was present as organic sulfate and sulfonate, whereas Strickland and Fitzgerald (1985) found it to be present in amino acids, also. The formation of ester sulfate has been found (Fitzgerald et al., 1982) to occur more rapidly and to a greater extent than carbon-bonded S.

We have had an on-going interest in the effects of acid rain on the soil of Forêt Montmorency, a boreal forest area in the Canadian Shield (vanLoon and Rutherford, 1983; Hern et al., 1983, 1985; Hay et al., 1985). In the course of our investigations soil columns were watered over a 2-yr period with 2 : 1 (w/w) H2SO4 : HNO3 solutions of pH 2.0 and 3.5, and with distilled, deionized water (pH 5.7). At the completion of this elution study the soils were removed from the columns and analyzed for S-containing constituents. We report in this paper the results of these analyses using samples of the LFH and Bfh horizons.

2. Experimental

2.1. Preparation of Soil Samples

The soil, an Orthic Humo-Ferric Podzol, collected in Forêt Montmorency, north of Quebec City, has been described by Hern et al. (1985). The soil columns were subjected to irrigation with acidic, aqueous solutions during a period of 730 days (for complete details see Hern et al., 1985). One soil column was selected from each of the sets which had been subjected to irrigation with a solution of pH 2.0, 3.5, or 5.7. The 0 to 5 cm layer, which constituted the surface LFH horizon, and the 15 to 20 cm layer, which constituted the upper portion of the Bfh horizon were homogenized and analyzed separately.