SHORT COMMUNICATIONS

Carbon-13 Nuclear Magnetic Resonance Spectra of Soil Water-Soluble Organic Carbon

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ABSTRACT

Water-soluble organic carbon (WSOC) was extracted from the surface horizon (0–15 cm) of a South Carolina floodplain soil (Pickney series–sandy, silicious, thermic Cumulic Humaquepts) using either 1.2-μm Whatman glass fiber type C (GF) or polycarbonate (PC) (<0.4 μm) filters. The trend in functional group C distribution for both WSOC fractions was O-alkyl > aliphatic > aromatic > carboxylic acid > carbonyl structures. Overall, the ^{13}C NMR spectra showed similar functional group C distributions for fractions obtained with both filters.

THE MEASUREMENT AND CHARACTERIZATION of dissolved organic carbon (DOC) in aquatic and soil ecosystems is an important parameter because of the involvement of DOC in many biogeochemical processes (Thurman, 1985). By convention, DOC is operationally defined as organic carbon (OC) which passes through a 0.45-μm filter (Thurman, 1985). Dissolved OC readily passes through a 0.45-μm filter, whereas most particulate material (plankton, bacteria, and solid phases) are retained. A 0.45-μm size boundary is an arbitrarily convenient dimension for separation of particulates from the DOC fraction (Thurman, 1985).

Some researchers studying the chemistry of soil solution or stream DOC filter samples through 0.45-μm polycarbonate (PC) filters and others use 1.2-μm Whatman glass fiber type C (GF) filters. The GF filters have an average pore diameter of 1.2 μm, which is appreciably larger than the 0.45-μm filter pore diameter recommended by Thurman (1985). Use of the GF filters, owing to their larger pore diameter may compromise sample quality by allowing passage of some solid-phases and/or microbes. Thus, organic geochemical interpretations of soil water-soluble organic carbon (WSOC) may be influenced by the type of filter employed. We are unaware of any ^{13}C nuclear magnetic resonance (NMR) spectroscopic studies of the effect of filter types on the qualitative nature of DOC compounds. Therefore, our objective was to investigate the effect of GF vs. PC filters on structural composition of soil WSOC by comparing functional group C distribution in filtrates as determined by ^{13}C NMR spectroscopy.

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MATERIALS AND METHODS

Collection and Analysis of Soil

Soil was collected from a floodplain area in the Upper Three Runs Creek watershed on the U.S. Department of Energy's Savannah River Site (SRS). The watershed is located on the Upper Atlantic Coastal Plain physiographic region of South Carolina (Siple, 1967) and is covered by late Eocene age (Barnwell group) sediments, underlain in places by middle age Eocene (McBean group) strata (Dennehy et al., 1989). The soil was classified as a Pickney series (sandy, silicious, thermic Cumulic Humaquepts), a typical Coastal Plain floodplain soil on the SRS (Rogers, 1990).

About 5 kg of soil were collected from the surface horizon (0–15 cm) over a 0.001–ha area and composited. The soil was air-dried, ground to pass a 2-mm sieve, and stored in the dark at 4 °C. Soil OC content was measured using a C analyzer (Carlo Erba/model NA 1500, Milan Italy). Soil sample pH was measured (Ion 85 analyzer; Radiometer Copenhagen Corp., Cleveland, OH) with a combination electrode at a water/soil ratio of 2:1. Particle size analysis was performed using the micro-pipet method of Miller and Miller (1987). The soil had an OC content of 33 g kg^{-1}, a pH of 5.3, and a texture of 91% sand, 6% silt, and 3% clay.

Isolation and Characterization of Water-Soluble Organic Carbon

Water-soluble OC was obtained by performing five sequential water extractions on 150 g of 2-mm sieved, air-dried soil using Millipore Milli-Q H_2O) at a 1:1 water/soil ratio. All centrifuge tubes were agitated using a rocking shaker (Eberbach shaker, Eberbach Corp., Ann Arbor, MI) at 1.8 Hz (8 cm stroke length) for 45 min at room temperature, and centrifuged (model Centra-7A; International Equipment Corp., Needham Hts., MA) for 20 min at 1400 × g. The supernatant was prefiltered through prerinsed Whatman no. 42 filter paper (Whatman Int., Maidston, England) and then split into two portions. One portion was filtered through precombusted Whatman GF type C filters, whereas the second portion was filtered through prerinsed, 0.4-μm PC filters (Nuclepore Corp., Pleasanton, CA). Both WSOC fractions (GF and PC) were acidified with conc. HCl to a pH <2, then eluted through a cleaned XAD-8 resin column (Rhom and Hass, Philadelphia, PA) to remove nonhumic impurities. The XAD-8 resin was cleaned according to Leenheer and Huffman (1979), except the ether step was omitted. The sorbed WSOC fraction was then removed by back eluting the column with 0.1 *M* NaOH and the eluant acidified to a pH <2. Both WSOC fractions were purified by eluting several times through a column of H^+

Abbreviations: WSOC, water-soluble organic carbon; GF, glass fiber; PC, polycarbonate; DOC, dissolved organic carbon; OC, organic carbon; NMR, nuclear magnetic resonance; SRS, Savannah River Site; CPMAS NMR, cross-polarization, magic angle spinning nuclear magnetic resonance.

Table 1. Carbon distribution† within a water-soluble organic C fraction passed through 1.2-μm pore size glass-fiber and 0.4-μm pore size polycarbonate filters.

Structural group	Water-soluble organic C passed through: Glass-fiber (1.2 μm)	Polycarbonate (0.4 μm)
	%	
Aliphatic-C	21	22
O-alkyl-C	50	44
Aromatic-C	13	16
COOH-C	12	14
Carbonyl-C	4	4

† Estimated by integration of NMR spectra

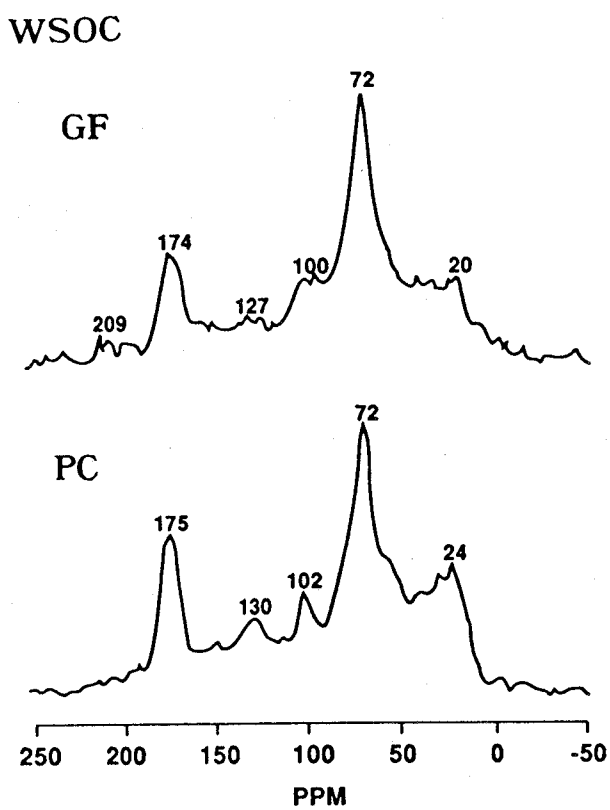

Fig. 1. Carbon-13 NMR spectra of soil water-soluble organic carbon isolated using Whatman glass-fiber (GF; 1.2 μm) and polycarbonate (PC; <0.4 μm) filters.

saturated Bio-Rad (Bio-Rad Labs, Richmond, CA) AG50W-X8 cation-exchange resin, evaporated to dryness at 40 °C, and stored in a desiccator.

Purified PC and GF filtered WSOC fractions were then analyzed using solid-state ^{13}C cross-polarization, magic angle spinning nuclear magnetic resonance (CPMAS NMR) spectroscopy by the Colorado State University Nuclear Magnetic Resonance Center. Spectra were obtained on a custom-built spectrometer (Nicolet 1180B data system, and 293B pulse programmer, General Electric, Los Angeles, CA) operating at 25.3 MHz. Hexamethylbenzene was used as an external chemical shift reference compound for spectrometer fine-tuning and optimization. Spectra based on 50 000 scans were obtained using a contact time of 1 ms, and a recycle time of 1 s. Each spectrum was divided into the following regions (Novak and Smeck, 1991): 0 to 50 (aliphatic-C), 50 to 110 (O-alkyl-C), 110 to 160 (aromatic-C), 160 to 190 (COOH-C), and 190 to 240 ppm (carbonyl-C). In each spectrum, peak area was measured with an integrator and C distribution reported as a percentage of total OC content (Table 1). Malcolm (1989) and Wilson (1989) have cautioned that data obtained using ^{13}C NMR spectroscopy are semiquantitative because of differences in C relaxation times and interferences of paramagentic species that may cause line broadening. These differences were minimized by analyzing samples using a similar cross-polarization and recycle time to ensure a relative comparison of spectral data could be made.

RESULTS AND DISCUSSION

The ^{13}C NMR spectra of both GF and PC filtered WSOC fractions are similar (Fig. 1). Each spectrum is dominated by a relatively intense signal at 72 ppm and a moderately intense signal at 174 to 175 ppm, which are attributed to C in O-alkyl and COOH structures, respectively (Malcolm, 1989). Carbon in both WSOC fractions occurs mostly as O-alkyl structures (Table 1). The large percentage of C as O-alkyl structures in both soil WSOC extracts is consistent with extracted WSOC from an Inceptisol in Germany (Candler et al., 1988). In each spectrum there are weak peaks indicative of aliphatic (20–24 ppm), aromatic (127–130) and carbonyl (209) structures, which account for 4 to 22% of the C distribution.

In comparison, the overall structural chemistry of the WSOC was unaffected by filtering solutions through GF or PC filters. Our data indicates that the use of either filter effects similar functional group C distributions within filtrates.

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