Organic matter chemistry and dynamics in clear-cut and unmanaged hardwood forest ecosystems

K'O H. DAI, CHRIS E. JOHNSON* & CHARLES T. DRISCOLL
Department of Civil and Environmental Engineering, Syracuse University, 220 Hinds Hall, Syracuse, NY 13244-1190, U.S.A.
*(*Author for correspondence, e-mail: cejohns@mailbox.syr.edu)*

Key words: dissolved organic carbon, humic substances, nuclear magnetic resonance, soil organic matter, soil solution, Spodosol

Abstract. Forest harvesting alters the organic matter cycle by changing litter inputs and the decomposition regime. We hypothesized that these changes would result in differences in organic matter chemistry between clear-cut and uncut watershed ecosystems. We studied the chemistry of soil organic matter (SOM), and dissolved organic carbon (DOC) in soil solutions and stream samples in clear-cut and uncut sites at the Hubbard Brook Experimental Forest in New Hampshire using DOC fractionation techniques and solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

Alkyl-C (aliphatic compounds) and O-alkyl-C (carbohydrates) were the largest C fractions in soil and dissolved organic matter at Hubbard Brook. Alkyl-C ranged from 29–48% of soil C, 25–42% of soil solution C, and 22–42% of streamwater DOC. Carbohydrates comprised 32–49%, 36–43%, and 29–60% of C in soils, solutions, and streamwater, respectively. In both soils and soil solutions, the carbohydrate fraction decreased with increasing soil depth, while the aromaticity of organic matter increased with depth. There were no significant differences in the structural chemistry of SOM between clear-cut and uncut watersheds.

The aromatic-C fractions in soil solutions at the clear-cut site ranged from 12–16%, approximately 40% greater than at the uncut site (8.5–11%). Thus, clear-cutting has resulted in the leaching of more highly decomposed organic matter, and depletion of more aliphatic compounds in the soluble organic pool. Because DOC fluxes are small compared to the SOM pool, large differences in soil solution chemistry do not substantially alter the overall composition of SOM. While the organic chemistry of stream DOC varied greatly among 3 sampling dates, there were no obvious clear-cutting effects. Thus, temporal variations in flowpaths and/or in-stream processes appear to be more important than disturbance in regulating the organic carbon chemistry of these streams.

Abbreviations: CEC – cation exchange capacity; CP/MAS – cross-polarization magic-angle spinning; DOC – dissolved organic carbon; DOM – dissolved organic matter; HBEF – Hubbard Brook Experimental Forest; HPI-A – hydrophilic acid; HPI-B – hydrophilic base; HPI-N – hydrophilic neutral; HPO-A – hydrophobic acid; HPO-B – hydrophobic base; HPO-N – hydrophobic neutral; NMR – nuclear magnetic resonance; OM – organic matter; SOM – soil organic matter; W1 – watershed 1; W5 – watershed 5; W6 – watershed 6.

Introduction

Carbon and organic matter processing are central to the structure and function of biological systems. The terrestrial carbon cycle is a complex set of interactions between gaseous, aqueous, and soil phases involving both organic and inorganic forms. In forest ecosystems, photosynthetic assimilation, the conversion of gaseous inorganic carbon to structural organic carbon, is generally the principal C input. During decomposition, this organic carbon may be converted to soil organic carbon, aqueous organic and inorganic carbon, and gaseous carbon dioxide (CO_2). As the major pool of terrestrial carbon resides in soil (Schlesinger 1997), understanding the factors that govern organic matter release and retention in soils is central to both ecosystem and environmental studies. In recent years, increases in atmospheric carbon, changes in land management practices, and acute interest in the global carbon cycle have increased interest in soil organic matter (SOM) dynamics.

In addition to its role in the C cycle, soil organic matter exerts an important influence on soil fertility, soil development, and numerous soil chemical properties such as acid-base chemistry, pH, buffer capacity, cation exchange capacity (CEC), and metal complexation and transport. In Spodosols, the transport of organic matter and associated metals is the central soil-forming process (Buol et al. 1997). Both SOM and dissolved organic matter (DOM) are heterogeneous mixtures of organic compounds with a wide range of structures and functional groups (Perdue 1984; Perdue et al. 1984; Rice & MacCarthy 1991; Stevenson 1994; Vance et al. 1986). Typically, SOM and DOM are weakly acidic due to abundant carboxylic and phenolic functional groups (Perdue et al. 1984; Vance & David 1991a). The dissociation of DOM and its proton-binding properties are of major importance in the chemistry and ecology of soil solutions and stream waters.

Because SOM influences so many biogeochemical processes, any disturbance that alters the organic matter cycle may have far-reaching consequences. Forest harvesting alters the organic matter cycle through the removal of above-ground tree biomass for wood products and the alteration of the rates of a variety of other ecosystem processes. For example, inputs of litter to the forest floor decreases for several years following logging (Hughes & Fahey 1994). Other effects of clear-cutting disturbance on SOM processes are driven by changes in the soil environment. The removal of the forest canopy decreases interception of atmospheric moisture and increases solar radiation inputs at the soil surface. These conditions likely stimulate microbial activity, thereby altering rates of organic matter decomposition (Hendrickson et al. 1989; Johnson et al. 1995; Mattson & Swank 1989; Moore 1989). Covington

(1981) suggested that the organic matter content of the forest floor in northern hardwoods decreases after logging, reaching a minimum after about 15 years. Any changes in decomposition rates and patterns after clear-cutting are also likely to influence the amount or chemical structure of SOM, thereby altering important soil properties such as pH, exchangeable acidity, and CEC. Research in northern hardwood forests has suggested that changes in soil chemical properties following logging are the result of a perturbation in both the amount and character of SOM (Johnson 1995; Johnson et al. 1995, 1997; Snyder & Harter 1985).

Effects of clear-cutting on the properties of the SOM have generally been inferred from changes in critical ratios such as C:N, C:OM, N:OM, and CEC:OM (Johnson 1995; Johnson et al. 1991b, 1995, 1997). To our knowledge, little effort has been made to examine directly the chemistry of SOM and DOM in clear-cut areas. Recent advances in solid-state, ^{13}C nuclear magnetic resonance (NMR) spectroscopy have made it possible to study the structure and functionality of natural organic matter in a variety of environments, including forest soils and waters draining forested areas (Baldock & Preston 1995; Baldock et al. 1997; Kögel-Knabner 1992). Investigations of manipulated forest ecosystems, however, have been rare. David and co-workers studied SOM and DOM chemistry at sites subjected to chemical manipulations aimed at understanding acidification processes (David et al. 1989; David et al. 1992; Vance & David 1989, 1991b), but NMR techniques were not used.

We used ^{13}C-NMR spectroscopy to examine the structural chemistry of soil and dissolved organic matter collected from clear-cut and uncut northern hardwood watersheds at the Hubbard Brook Experimental Forest (HBEF), New Hampshire. Our results may be used to gain insight into biogeochemical processes in both disturbed and undisturbed areas. In this paper, we examine several research questions: (i) Did clear-cutting result in changes of concentration and composition of DOC after 15 years of forest regeneration? (ii) Did clear-cutting change the relationship between the concentration and composition of DOC in stream waters? (iii) Did clear-cutting result in preferential loss of carbohydrates and/or other aliphatic compounds from SOM, without replacement in the form of litter? (iv) What are the possible implications of these findings for the linkages among soil C, soil solution C, and stream water C?
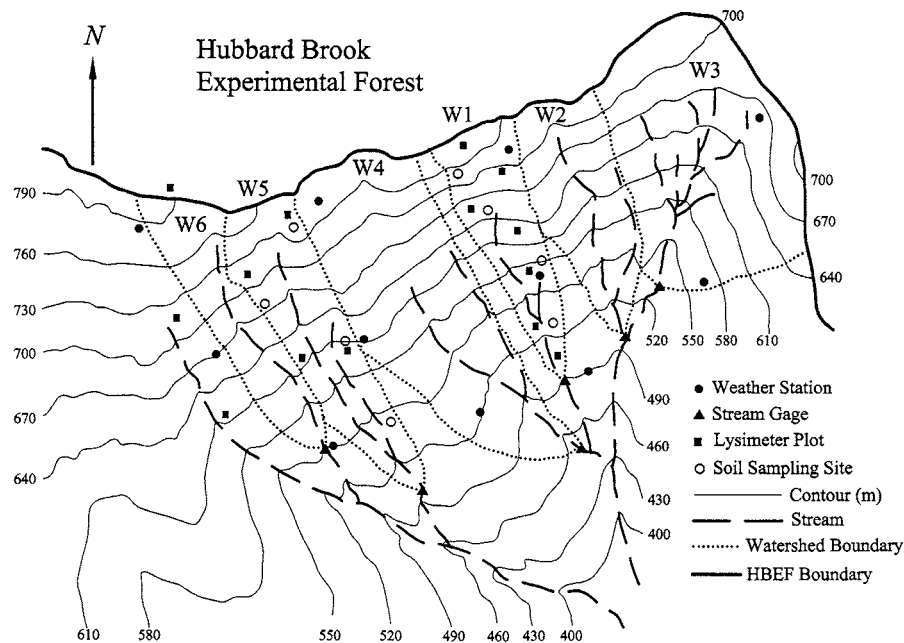
Figure 1. Map of experimental watersheds 1-6 at the Hubbard Brook Experimental Forest, New Hampshire.

Materials and methods

Soils

The HBEF lies in the southern White Mountain region of New Hampshire. Details regarding the ecology, climate, geology, and hydrology at the HBEF may be found elsewhere (Bormann & Likens 1979; Federer et al. 1990; Likens & Bormann 1995). The predominant soils are coarse-loamy, mixed, frigid Typic Haplorthods. More detailed descriptions of the soils at the HBEF have been reported elsewhere (Huntington et al 1988; Johnson et al. 1991a,b). In the autumn and winter of 1983–1984, all trees on watershed 5 (W5) which were 5 cm diameter-at-breast height (dbh) or greater were cut and the whole trees (boles & branches) were removed.

The soils used in this study were sampled from watershed 1 (W1, uncut) in 1997, and W5 (clear-cut) in 1998 (Figure 1). Soil pits were excavated at 60 sites in W5, and at 48 sites in W1. Because of the time and expense involved in solid-state NMR analyses, only a sub-set of these samples could be analyzed. Thus, the soils used in this study included samples of Oa, Bh, and Bs horizons collected from 4 of the pits in each watershed, selected to represent the range of elevation (Figure 1). The specific pits were selected

by examining soil profile descriptions; each of the pits chosen for analysis exhibited the full suite of horizons found in HBEF Spodosols (Oi, Oe, Oa, E, Bh, Bs1, Bs2). All soil samples were air-dried to constant weight and passed through a 2-mm screen. A more detailed description of the method used for sampling soils can be found in Huntington et al. (1989) and Johnson et al. (1991a). We focused our study on Oa, Bh, and Bs1 horizon samples because these horizons showed the greatest changes in chemical properties after clear-cutting (Johnson et al. 1991b, 1995, 1997).

Soil pH was determined electrometrically in deionized water and 0.01 M $CaCl_2$ on air-dried soils using a 1:2 (v/v) soil-solution ratio for Oa horizon soils, and a 1:1 (v/v) soil-solution ratio for mineral soils. The organic matter fraction was estimated by loss-on-ignition (500 °C). Loss-on-ignition has often been used as a surrogate measure of organic matter in clay-poor forest soils at the HBEF and elsewhere (Davies 1974; Huntington et al. 1989; Johnson et al. 1991a, 1997). Soil elemental content (total C, H, N) was determined by combustion-gas chromatography using methods described in Huntington et al. (1988) and Johnson et al. (1995). Site descriptions, horizon thickness, and general chemical properties of the soil samples are presented in Tables 1 and 2.

Soil solutions and stream waters

Soil solutions were collected in 1998 from tension-free lysimeters installed at 7 sites in W1 in the fall of 1997 and 6 sites in W5 in 1983 (Figure 1). Lysimeters were placed near the bottom of the Oa, and Bh horizons, and within the Bs horizon. Detailed information on lysimeter installation can be found in Driscoll et al. (1988). Due to the low yield of the soil solutions, samples were bulked by horizon and watershed for later analysis.

Stream samples were collected from three watersheds: W1, W5 and watershed 6 (W6, uncut). Watershed 6 is the biogeochemical reference watershed at the HBEF (Likens & Bormann 1995). Due to the low stream DOC concentrations ($\approx$0.1 to 0.15 mmol C L^{-1}), approximately 150 to 200 L of water was collected from each watershed in September 1997, March 1998, and October 1998 at sites just above the watershed outlet weirs (Figure 1). These solutions were concentrated using a custom-built reverse-osmosis unit with a polyamide membrane. Reverse osmosis has the advantage of utilizing ambient conditions to minimize the possibility of destructive chemical reactions, and the ability to process large volumes of water (Deinzer et al. 1975; Odegaard & Koottatep 1982; Serkiz & Perdue 1990). In our samples, approximately 85–95% of the original DOC was retained after concentration. Selected chemical characteristics of the soil solutions and stream samples are presented in Table 3.

Table 1. Site characteristics and soil horizon thickness of sampling locations used in this study

	W1 Sites (Uncut)				W5 Sites (Clear-cut)			
	W1-1	W1-2	W1-3	W1-4	W5-1	W5-2	W5-3	W5-4
Elevation (m)	715	645	565	530	740	680	610	545
Dominant Overstory Vegetation[a]	Be	Be, SM	SM, Be	Sm, Be	PC, WB	Be, WB	Be	YB, Be
Horizon Thickness (cm)								
O (Oi+Oe+Oa)	5.5	15.1	9.5	7.1	7.1	5.3	3.2	3.4
E	2.8	4.8	0.2	2.8	3.2	7.2	1.5	0.0
Bh	3.1	3.6	5.9	3.8	3.1	2.0	1.2	3.0
Bs1	5.2	3.5	7.6	5.4	5.6	3.2	3.5	5.9
Bs2	60.7	52.5	10.3	63.1	34.9	58.4	46.4	47.6
Other[b]	—	—	23.1	—	1.3	—	—	—
Total	77.5	79.5	56.6	82.3	55.3	76.0	55.8	60.0

[a]Be: American Beech; SM: Sugar Maple; PC: Pin Cherry; WB: White Birch; YB: Yellow Birch.
[b]"Other" includes buried horizons and horizons mixed by logging or other disturbance.

Table 2. Selected chemical properties of the soils used in this study. Values in parentheses are standard errors of the watershed means

Watershed	Site	Horizon	$pH_w{}^a$	$pH_s{}^b$	OM^c	Total C	Total N	Total H	C/N	C/H	N/OM
					g kg^{-1}						
W1	1	Oa	3.64	3.17	247.2	129.9	7.2	16.4	18.0	7.9	0.029
		Bh	3.68	3.20	222.4	121.7	7.0	15.4	17.3	7.9	0.031
		Bsl	4.39	3.78	159.7	76.9	3.7	11.5	20.7	6.7	0.023
W1	2	Oa	3.54	2.97	177.9	96.0	5.4	12.5	17.8	7.7	0.030
		Bh	3.64	3.08	106.6	66.8	2.3	5.9	28.6	11.4	0.022
		Bsl	3.90	3.39	135.2	61.7	2.7	7.9	23.3	7.8	0.020
W1	3	Oa	4.07	3.79	638.5	364.6	21.3	40.1	17.1	9.1	0.033
		Bh	4.38	4.15	391.4	209.2	10.6	17.3	19.7	12.1	0.027
		Bsl	4.43	4.02	209.3	99.6	4.7	13.2	21.2	7.5	0.022
W1	4	Oa	3.62	3.12	324.9	161.0	8.8	21.0	18.3	7.7	0.027
		Bh	3.85	3.44	172.7	83.8	3.7	9.5	22.7	8.8	0.021
		Bsl	3.97	3.62	174.4	84.1	3.9	6.9	21.3	12.1	0.022

Table 2. Continued

Watershed	Site	Horizon	pH_w[a]	pH_s[b]	OM^c	Total C	Total N	Total H	C/N	C/H	N/OM
						g kg^{-1}					
W1	Average	Oa	3.72	3.26	347.1	187.9	10.7	22.5	17.8	8.1	0.030
			(0.12)	(0.18)	(101.6)	(60.4)	(3.6)	(6.1)	(0.3)	(0.3)	(0.001)
		Bh	3.89	3.47	223.2	120.4	5.9	12.0	22.1	10.1	0.025
			(0.17)	(0.24)	(60.8)	(31.8)	(1.9)	(2.6)	(1.0)	(0.3)	(0.002)
		Bs1	4.17	3.70	169.7	80.6	3.8	9.9	21.6	8.5	0.022
			(0.14)	(0.13)	(15.5)	(7.9)	(0.4)	(1.5)	(1.2)	(0.3)	(0.001)
W5	1	Oa	3.44	3.14	579.9	301.6	15.7	35.1	19.2	8.6	0.027
		Bh	3.68	3.16	155.1	73.5	3.9	9.1	19.0	8.1	0.025
		Bs1	4.03	3.38	173.0	77.2	3.4	9.0	22.9	8.6	0.020
W5	2	Oa	3.25	2.66	465.0	267.1	12.9	29.9	20.6	8.9	0.028
		Bh	3.79	2.87	135.0	75.2	3.6	9.4	20.9	8.0	0.027
		Bs1	3.86	2.93	132.8	64.1	3.0	7.6	21.7	8.4	0.023

Table 2. Continued

Watershed	Site	Horizon	pHw[a]	pHs[b]	OM[c]	Total C	Total N	Total H	C/N	C/H	N/OM
						g kg^{-1}					
W5	3	Oa	3.52	2.81	429.0	221.5	10.9	25.1	20.3	8.8	0.025
		Bh	3.89	3.06	125.3	60.4	3.4	8.1	17.9	7.5	0.027
		Bs1	3.99	3.13	129.7	64.0	3.0	8.2	21.1	7.8	0.023
W5	4	Oa	3.50	2.81	492.5	248.4	12.9	31.5	19.2	7.9	0.026
		Bh	4.10	3.30	185.8	85.2	4.0	11.3	21.5	7.6	0.021
		Bs1	4.40	3.64	124.6	65.9	2.9	8.6	23.0	7.7	0.023
W5	Average	Oa	3.43	2.86	491.6	259.6	13.1	30.4	19.9	8.6	0.027
			(0.06)	(0.10)	(32.2)	(16.8)	(1.0)	(2.1)	(0.4)	(0.2)	(0.001)
		Bh	3.87	3.10	150.3	73.6	3.7	9.5	19.9	7.8	0.025
			(0.09)	(0.09)	(13.4)	(5.1)	(0.1)	(0.7)	(0.8)	(0.1)	(0.001)
		Bs1	4.07	3.27	140.0	67.8	3.1	8.4	22.2	8.1	0.022
			(0.12)	(0.15)	(11.1)	(3.2)	(0.1)	(0.3)	(0.5)	(0.2)	(0.001)

[a]pH measured in deionized water.
[b]pH measured in 0.01 M CaCl$_2$.
[c]Soil organic matter estimated by loss-on-ignition (Davies 1974).

59

Table 3. General chemical properties of soil solutions and stream waters used in this study

Watershed	Date collected	Horizon	pH	Conductivity (ms m^{-1})	I[a] (mmol L^{-1})	DOC (μmol L^{-1})
			Soil solution			
W1	3/20/98	Oa	4.24 (4.65)[b]	3.2	0.42	667 (517)[b]
	3/20/98	Bh	4.50 (4.77)[b]	1.6	0.21	558 (401)[b]
	3/20/98	Bs	4.56 (4.86)[b]	1.1	0.14	217 (317)[b]
W5	10/20/98	Oa	4.19 (4.04)[b]	4.5	0.59	878 (1879)[b]
	10/20/98	Bh	4.45 (4.41)[b]	2.7	0.35	833 (1125)[b]
	10/20/98	Bs	5.10 (4.52)[b]	1.6	0.21	800 (780)[b]
			Stream water			
W1	9/7/97		4.97 (4.94)[b]	1.8	0.23	150 (167)[b]
	3/20/98		4.92 (4.93)[b]	2.2	0.29	160 (103)[b]
	10/20/98		4.92	2.2	0.28	95
W5	9/7/97		5.82 (5.53)[b]	2.2	0.28	130 (181)[b]
	3/20/98		5.25 (5.31)[c]	1.8	0.23	170 (184)[c]
	10/20/98		5.33	1.8	0.23	75
W6	9/7/97		5.10 (4.99)[b]	2.3	0.29	130 (153)[b]
	3/20/98		5.03 (4.95)[b]	1.5	0.19	150 (114)[b]
	10/20/98		5.12	1.5	0.20	90

[a]I (mmol L^{-1}) = ionic strength = 0.13 $\times$ conductivity (ms m^{-1}) (Griffin & Jurinak 1973).
[b]Values in parentheses are annual means of monthly samples collected in 1997, independently from this study (C.T. Driscoll, unpublished data, 1999).
[c]Values in parentheses represent means of samples collected in January, February, March, and April 1998, independently from this study (C.T. Driscoll, unpublished data, 1999).

Dissolved organic carbon in subsamples of the concentrated soil solution and streamwater samples was fractionated following a modification of the method of Leenheer and Huffman (1979) and Leenheer (1981). Five fractions of DOC were characterized in this modified procedure: hydrophobic acids (HPO-A) and neutrals (HPO-N), and hydrophilic acids (HPI-A), bases (HPI-B), and neutrals (HPI-N). Detailed information on the procedure and the general characteristics of these fractions can be found in Vance and David (1991a,b). The dominant forms of DOC (HPO-A, HPI-A, and HPI-N) were also isolated for analysis using the scheme detailed in Vance and David (1991b) and Dai et al (1996).

Solid-state ^{13}C CP/MAS NMR analysis

The structural chemistry of samples of soil, soil solution, and stream water was characterized using solid-state ^{13}C NMR with cross-polarization and magic angle spinning (CP/MAS). Prior to NMR analysis, the mineral horizon (Bh & Bs) soil samples were treated with 2% HF to remove magnetic materials as suggested by Skjemstad et al. (1994), then freeze-dried and ground to pass a 400-μm screen. Oa horizon samples were freeze-dried and ground to <400 μm without HF treatment. Concentrated bulk soil solutions from the Oa, Bh, and Bs horizons in W1 and W5, as well as concentrates of the bulk stream water samples and isolated stream DOC fractions from W1, W5, and W6 were freeze-dried and stored at 5 °C prior to NMR analysis.

The structural composition of C in all samples was analyzed by semi-quantitative, solid-state CP/MAS ^{13}C NMR on a Bruker AMX 300 spectrometer at 75.47 MHz. Samples were spun at 5 kHz in a zirconia rotor within a MAS probe. All spectra were obtained with a 1 ms contact time and a 1 s recycle time. No attempt was made to remove spinning sidebands. The number of transients required for an acceptable signal-to-noise (S/N) ratio ranged from 3918 to 99224. Additional spectral conditions included: spectral width, 33112 Hz; acquisition time, 61 ms; number of decay curve, 4096. Chemical shift assignments were externally referenced to the methylene resonance of polyethylene at 38.82 ppm.

The ^{13}C-NMR spectrum was divided into four spectral regions corresponding to alkyl-C (0-50 ppm), O-alkyl-C (50–110 ppm), aromatic-C (110–160 ppm), and carbonyl-C (160–220 ppm) (Baldock & Preston 1995). Because of possible overlaps between different functional groups, these divisions should be regarded only for comparative purposes.

The aromaticity of natural organic matter has been indexed in two ways, either as the fraction of total C as aromatic-C (designated f_{a1}) or as the fraction of the total C less the carbonyl-C (i.e., carboxyl, ester, and ketone) fraction (f_{a2}) (MacCarthy et al. 1990):

$$f_{a1} = \frac{\text{Peak Area of } ^{13}\text{C} - \text{NMR Spectrum between 110–160 ppm}}{\text{Total Peak Area of } ^{13}\text{C} - \text{NMR Spectrum}} \qquad (1)$$

$$f_{a2} = \frac{\text{Peak Area of } ^{13}\text{C} - \text{NMR Spectrum between 110–160 ppm}}{\text{Peak Area of } ^{13}\text{C} - \text{Spectrum 0–160 ppm}} \qquad (2)$$

These ratios have been used to characterize the extent of humification of organic matter, under the assumption that organic matter becomes aromatic during decomposition. Baldock and Preston (1995) summarized several forest

soil ^{13}C NMR studies and concluded that aromaticity did not necessarily increase as the extent of decomposition increased. As an alternative, Baldock and Preston (1995) recommended using an alkyl/carbohydrate ratio (R) as an index of the extent of decomposition:

$$R = \frac{\text{Peak Area of } ^{13}C - \text{NMR Spectrum between 0–50 ppm}}{\text{Peak Area of } ^{13}C - \text{NMR Spectrum between 65–95 ppm}} \quad (3)$$

Results from a plant decomposition study (Hopkins et al. 1997) and a forest litter and peat study (Baldock & Preston 1995) showed increases in alkyl-C content coinciding with decreases in O-alkyl (carbohydrates) C content during decomposition, suggesting that R may be a useful indicator of degree of decomposition. For comparison purposes, we calculated and evaluated all three quantities (fa_1, fa_2, R).

Results and discussion

Soils

The four Oa horizons we analyzed from the clear-cut site had higher organic matter concentrations than those from W1, while the Bh horizons from the clear-cut site had lower average organic content (Table 2). The mean C concentrations showed similar patterns to SOM. The C/N ratios increased downward in the profile from the Oa horizon to the Bs1 horizon, and were similar in magnitude in both watersheds (Table 2).

Example CP/MAS ^{13}C NMR spectra of samples from the different soil horizons are shown in Figure 2. Integration of the major regions of ^{13}C resonance indicated that the C components in SOM were mainly alkyl (29 to 48% of total C) and O-alkyl (32 to 49% of total C) for Oa, Bh, and Bs1 horizon soils (Figure 3). Our data were consistent with forest soil ^{13}C-NMR data compiled by Mahieu et al. (1999). On average, the signal intensities for alkyl-C (0–50 ppm) increased slightly (though not statistically significantly) with depth in W5 soils but changed little in W1 soils. Increases in alkyl-C with depth are likely the result of biodegradation of forest litter, as has been reported in several studies (Dai et al. 1996; Kögel-Knabner 1992; Kögel-Knabner et al. 1988; Zech et al. 1985). In contrast, O-alkyl-C (i.e., carbohydrates; 50–110 ppm) decreased with depth in all W1 and W5 profiles. Preferential biological degradation has been suggested for the decrease in the O-alkyl C fraction with depth (Kögel-Knabner 1992, 1993). The increase of alkyl-C and the decrease of carbohydrate-C with increasing soil depth are consistent with the findings of Gressel et al. (1996), who observed similar
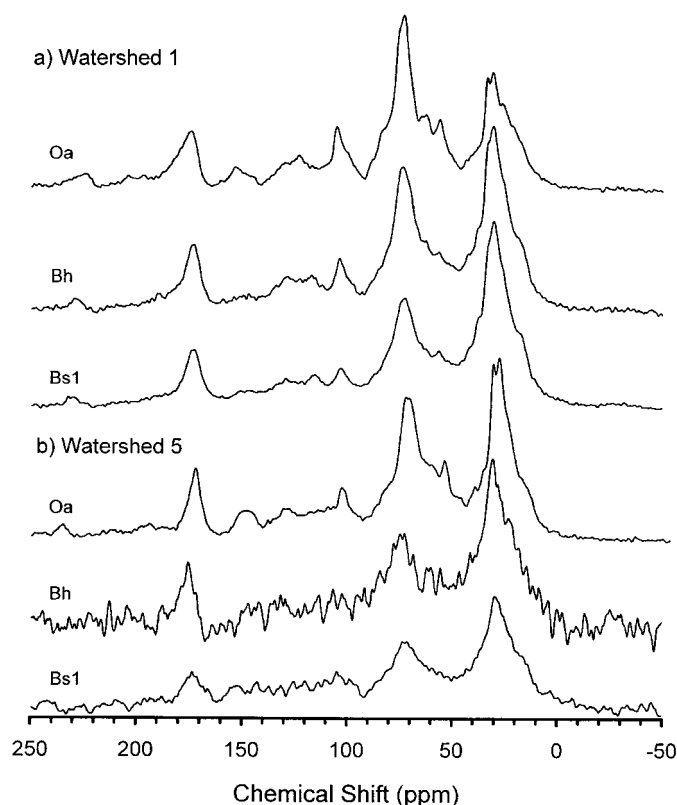
Figure 2. Solid-state CP/MAS ^{13}C NMR spectra acquired for selected soil samples from an uncut watershed (W1, site 3), and a clear-cut watershed (W5, site 1).

patterns with depth (from O to A horizons) in Alfisols underlying a conifer forest. For both W1 and W5 soils, the degree of decomposition of SOM increased with depth from the organic to the mineral horizons, and resulted in increases in the fa1, fa2, and R ratios (Figure 4). The average aromaticity of W5 soils was lower than the W1 soils (Figure 4), though the standard errors were large. The R ratios were similar between W1 and W5 samples in all horizons. Carbonyl-C (mainly carboxyl-C) changed little with soil depth (Figure 3).

The organic (Oa) horizons in W1 and W5 had relatively strong signals for lignin as suggested by chemical shifts around 54, 106, and 151 ppm (Hatcher 1987; Kögel-Knabner 1992, 1993) (Figure 2). These signals declined with depth, indicating the degradation of lignin in the mineral soil.

Decomposition rate, leaf and woody litter input, and decomposability all form a complex interaction which affects the dynamics of forest floor organic
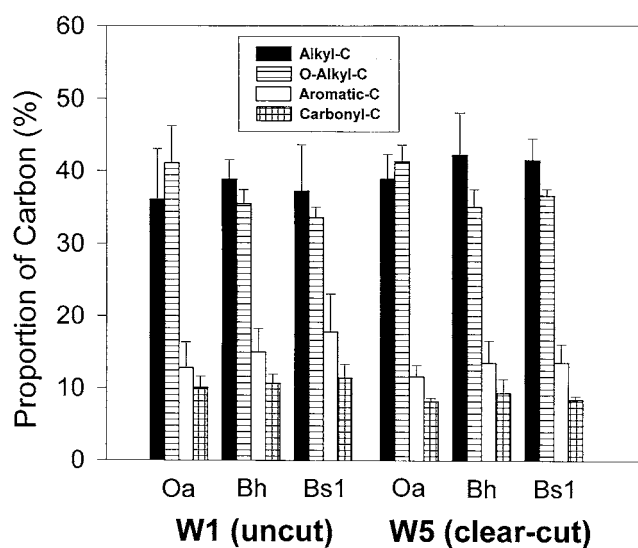
Figure 3. Distribution of C in soil organic matter, based on ^{13}C NMR analysis of soil profiles collected from a northern hardwood forest. Values are means of four profiles in both watersheds 1 and 5. Error bars represent standard errors of watershed averages.
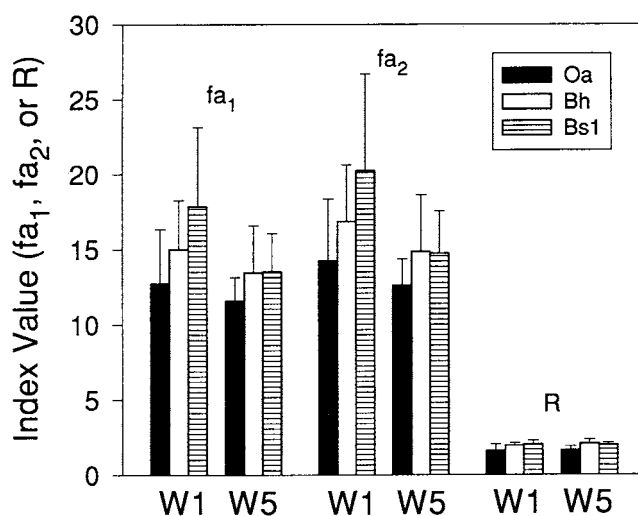

Figure 4. The alkyl/carbohydrate ratio (R) and aromaticity indices (fa_1 and fa_2) of soils collected from watersheds 1 and 5 at the Hubbard Brook Experimental Forest. Values are means and standard errors (error bars) based on four soil profiles in each watershed.

matter. The decomposition rate has been shown to accelerate in the first few years immediately after forest cutting in northern hardwood ecosystems (Marks 1974; Marks & Bormann 1972). However, once a closed canopy is attained, decomposition rates return to pre-harvest levels. Leaf and woody litter inputs recover quickly after harvesting, reaching a maximum between years 25 and 40 following cutting (Covington & Aber 1980; Hughes & Fahey 1994; Rodin & Bazilevich 1967). Finally, decomposability typically increases with increasing nutrient concentration and decreases with increasing fiber content (Covington 1981). During early succession at the HBEF, pin cherry (*Prunus pennsylvanica* L.) is the dominant tree species. Because pin cherry tissues are high in N and other nutrients, compared to other hardwood species, litterfall in the early stages of succession is likely to be more nutrient-rich compared to litter in later stages of forest development (Hughes & Fahey 1994; Marks 1974).

Covington (1981) proposed a model for the response of the O horizon to clear-cutting in northern hardwood sites. According to this model, the organic matter mass in the forest floor declines after cutting, reaching a minimum after about 15 years. After 15 years, forest floor mass increases slowly back to pre-cut levels. On W5, isolated blocks of O horizon soil experienced 20–30% mass loss 8 years after clear-cutting (Johnson et al. 1995). In addition, logging residues ("slash") and disturbance during logging caused significant redistribution of organic matter within the soil (Huntington & Ryan 1990; Johnson et al 1991a, 1995). These observations, plus changes in the chemistry of the Oa horizon (Johnson et al. 1991b, 1997) suggested that important changes in organic matter chemistry may have occurred. However, we observed no striking differences in the structural chemistry of Oa horizon samples collected from W1 and W5 fifteen years after clear-cutting (Figure 3). Thus, changes in the amount and properties of SOM on W5 after clear-cutting must be due to differences in the decomposition regime and litter chemical composition rather than changes in the structural chemistry of SOM.

Soil solutions

Johnson et al. (1995) reported elevated DOC concentrations in soil solutions up to 8 years after clear-cutting on W5. An examination of more recent data suggests that elevated DOC levels in soil solutions have persisted through post-harvest year 15. The 1997 annual average DOC concentrations ($\pm$ standard error) in soil solutions collected in W1 were 517 $\pm$ 58, 401 $\pm$ 30, and 317 $\pm$ 21 μmol L^{-1} in Oa, Bh, and Bs horizons, respectively. In the clear-cut watershed (W5), DOC concentrations in soil solutions were 1879 $\pm$ 225 (Oa), 1125 $\pm$ 81 (Bh), and 780 $\pm$ 80 (Bs) μmol L^{-1}. While the annual averages indicated that DOC concentrations were higher in W5

than W1 throughout the profile, the samples we collected showed smaller differences (Table 3). The samples we collected from W1 were similar in DOC concentration to the annual average, but the samples we collected from W5 were somewhat lower than the W5 average. The samples from W1 and W5 were collected at different times of year, which could affect the DOC concentrations and composition (McDowell et al. 1998; Qualls & Haines 1991). However, previous work at the HBEF has shown little or no seasonal variation in DOC concentrations (Johnson et al. 1995; McDowell & Wood 1984) or composition (McDowell & Likens 1988).

The elemental composition of isolated organic matter from soil solutions and stream samples are shown in Table 4. The C:N ratio of bulk solutions ranged from 11.2 to 40.9, which is comparable to soil C:N ratios, which are typically 15 to 25 at Hubbard Brook (Table 2; Huntington et al. 1988; Johnson 1995).

In both watersheds, annual average DOC concentrations decrease sharply with increasing soil depth (Johnson et al. 2000; Table 3). Previous work has shown a significant DOC adsorption capacity in mineral horizon (Bh and Bs) soils at the HBEF (McDowell & Likens 1988; McDowell & Wood 1984; Mo 1997), and spodic horizon soils at other sites (David & Driscoll 1984; David & Zech 1990; Dawson et al. 1978). High adsorption capacity of DOC in spodic horizons has been shown to be related to a high content of Fe-and/or Al-oxyhydroxides (Dawson et al. 1978; McDowell & Wood 1984; Moore 1989; Moore et al. 1992).

The mechanisms controlling DOC concentrations in soil solution are complex. A compiled data set collected from seven forested sites indicated that there was no significant relationship between concentrations of H^+ and DOC in soil solution (McDowell 1985). Increases in DOC concentrations in W5 after clear-cutting may be due to changes in microbial activity, DOC adsorption equilibria, and/or the solubility of DOM. Organic acids dominated the organic chemistry of bulk solutions collected from both watersheds. In W1, organic acids accounted for 91 to nearly 100% of the total DOC (Table 5). In W5 soil solutions, the acid fractions comprised 68 to 83% of the DOC, with a substantially higher content of hydrophilic neutrals (HPI-N) than solutions collected from W1 (Table 5). The hydrophilic acid (HPI-A) fraction in W5 soil solutions was about half the value in W1, while the hydrophobic acid (HPO-A) fractions were similar in the soil solutions of the two watersheds. Thus, the HPO-A/HPI-A ratio was uniformly higher in W5 soil solutions than in W1 soil solutions (Table 5). Other studies have also shown that elevated DOC concentrations are associated with higher HPO-A/HPI-A ratios (Dai et al. 1996; David & Vance 1991).

Table 4. Total C, H, and N in freeze-dried isolates of bulk soil solutions, stream waters, and organic matter fractions of stream samples collected from the Hubbard Brook Experimental Forest, New Hampshire. The fractions are: hydrophobic acids (HPO-A), hydrophilic acids (HPI-A), and hydrophilic neutrals (HPI-N)

Watershed	Source	Collection Date	Fraction	C	N	H	C/N	C/H
				g kg^{-1}				
W1	Oa soil solution	3/20/98	Bulk	303	14	22	21.6	13.8
W1	Bh soil solution	3/20/98	Bulk	190	17	21	11.2	9.0
W1	Bs soil solution	3/20/98	Bulk	308	15	27	20.5	11.4
W5	Oa soil solution	10/20/98	Bulk	272	17	20	16.0	13.6
W5	Bh soil solution	10/20/98	Bulk	277	11	26	13.8	10.6
W5	Bs soil solution	10/20/98	Bulk	40	1.1	3	36.4	10.8
W1	stream	9/7/97	Bulk	337	19	35	17.3	9.7
W1	stream	3/20/98	Bulk	204	5.0	23	40.9	8.7
W5	stream	9/7/97	Bulk	90	4.9	17	18.4	5.3
W5	stream	3/20/98	Bulk	210	10	30	21.0	7.0
W6	stream	9/7/97	Bulk	126	4.9	21	25.7	6.0
W6	stream	3/20/98	Bulk	190	7.2	31	26.4	6.1
W1	stream	10/20/98	HPO-A	259	3.1	16	83.5	16.5
W5	stream	10/20/98	HPO-A	333	2.3	28	144.8	11.1
W6	stream	10/20/98	HPO-A	583	2.3	24	253.5	24.3
W1	stream	10/20/98	HPI-A	304	2.2	19	138.4	15.7
W5	stream	10/20/98	HPI-A	237	11	2.1	21.5	112.8
W6	stream	10/20/98	HPI-A	354	14	21	8.4	24.4
W1	stream	10/20/98	HPI-N	22	0.5	1.5	44.0	14.6
W5	stream	10/20/98	HPI-N	56	7.0	11	8.0	5.1
W6	stream	10/20/98	HPI-N	38	3.3	11	11.4	3.5

CP/MAS ^{13}C NMR spectra of the bulk soil solution samples from W1 and W5 are presented in Figure 5. Similar to the soil samples we studied, alkyl (0–50 ppm) and O-alkyl C (50–110 ppm) were the main C forms in soil solutions. Together, they accounted for 67–78% of the C in our soil solutions (Figure 6).

Table 5. Dissolved organic carbon fractions (% of total) in stream waters and soil solutions, as determined by chromatographic fractionation and isolation

Watershed	Source	Collection Date	Fractionation					HPO-A	Isolation			
			Hydrophobic		Bases	Hydrophilic		HPI-O	Hydrophobic		Hydrophilic	
			Acids	Neutrals		Acids	Neutrals		Acids	Neutrals	Acids	Neutrals
W1	Oa soil solution	3/20/98	51.4	4.5	4.0	40.0	0.1	1.29	—	—	—	—
	Bh soil solution	3/20/98	36.7	0.1	0.2	62.9	0.1	0.58	—	—	—	—
	Bs soil solution	3/20/98	23.3	0.1	3.9	68.3	4.4	0.34	—	—	—	—
W5	Oa soil solution	10/20/98	63.4	0.2	6.4	19.1	10.9	3.32	—	—	—	—
	Bh soil solution	10/20/98	36.6	0.2	5.1	37.3	20.8	0.98	—	—	—	—
	Bs soil solution	10/20/98	32.4	0.2	2.2	35.8	29.4	0.91	—	—	—	—
W1	stream	9/7/97	39.4	2.5	14.0	44.0	0.1	0.90	31.1	0	26.5	42.4
	stream	3/20/98	50.6	2.8	7.2	15.3	24.1	3.31	41.1	0	10.0	48.9
	stream	10/20/98	24.8	3.3	17.2	40.0	14.7	0.62	20.0	2.5	30.0	47.5
W5	stream	9/7/97	41.3	0.2	0.1	40.0	18.4	1.03	36.5	2.0	24.1	37.4
	stream	3/20/98	46.4	0.2	4.7	10.8	37.9	4.30	33.1	1.5	9.3	56.1
	stream	10/20/98	20.5	18.7	0.2	34.8	25.8	0.59	17.5	5.5	26.8	50.2
W6	stream	9/7/97	39.5	3.4	0.1	35.0	22.0	1.13	—	—	—	—
	stream	3/20/98	37.4	3.3	6.4	16.4	36.5	2.28	29.9	4.0	10.1	56.0
	stream	10/20/98	18.3	14.6	7.5	38.4	21.2	0.48	16.5	5.5	25.0	53.0
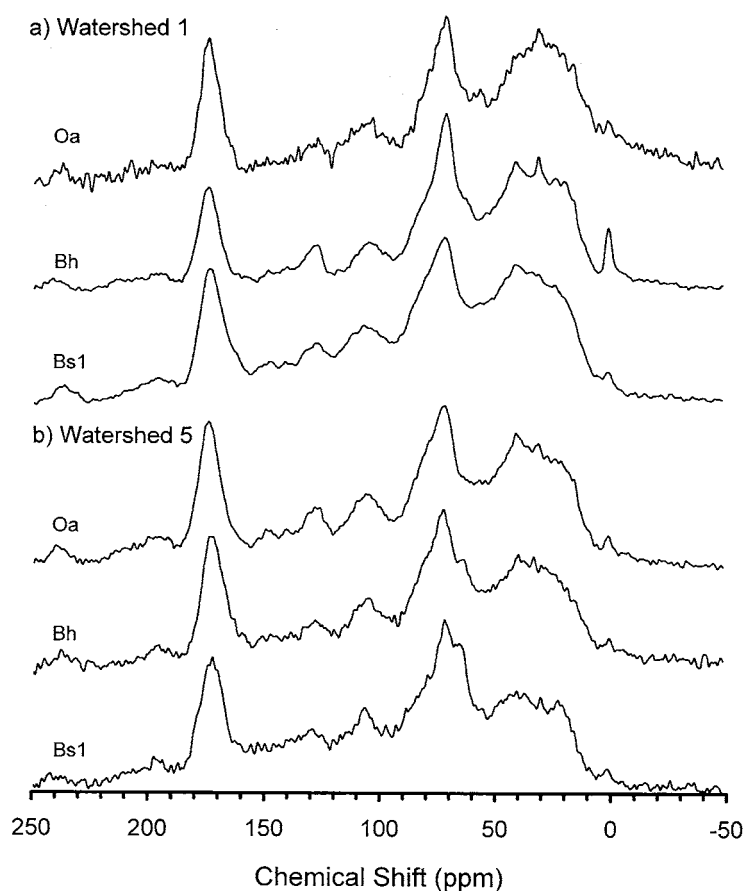
Figure 5. Solid-state CP/MAS ^{13}C NMR spectra acquired from freeze-dried soil solutions from an uncut watershed (W1) and a clear-cut watershed (W5) at the Hubbard Brook Experimental Forest, New Hampshire.

In the soil solution of all three horizons (Oa, Bh, and Bs), the proportion of alkyl C was higher in W1 than W5 (Figure 6). The fraction of aromatic C increased with depth in soil solutions from W1 and W5. Aromatic C was a greater fraction of DOC in W5 soil solutions in all horizons (Figure 6). The proportion of carbonyl C increased with depth in W1 soil solutions but changed little with depth in W5 soil solutions.

By either of the aromaticity-based decomposition indices (fa_1 or fa_2), the aromaticity of soil solutions in W5 was greater than W1 throughout the soil profile (Figure 7). The differences between the two watersheds are large, approximately 40%. Thus, it appears that soil solution organic matter represents a more highly decomposed material in the clear-cut watershed than
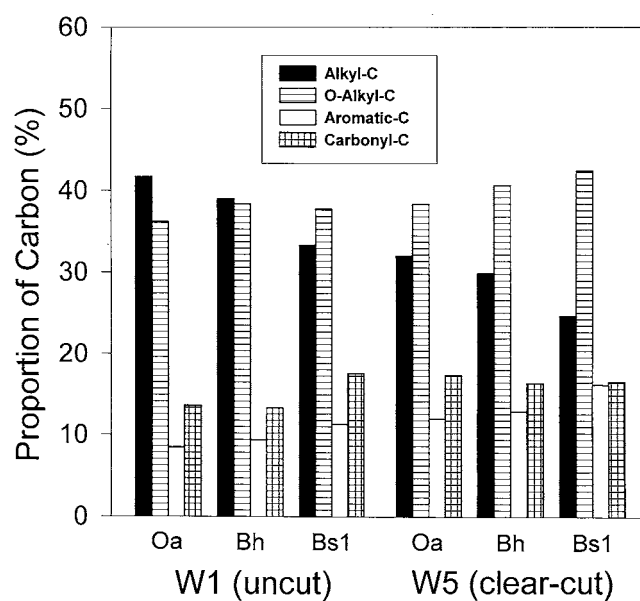
Figure 6. Distribution of C based on ^{13}C NMR analysis of organic matter isolated from soil solutions collected from an uncut (W1) and a clear-cut (W5) watershed at the Hubbard Brook Experimental Forest, New Hampshire.
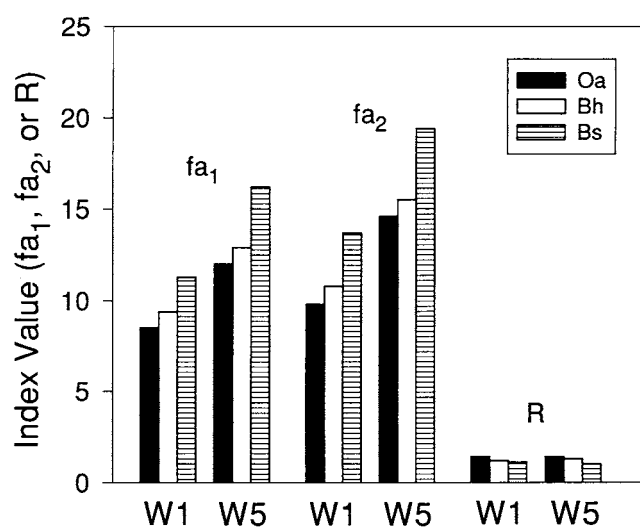
Figure 7. The alkyl/carbohydrate ratio (R) and aromaticity indices (fa_1 and fa_2) of organic matter in soil solutions collected from watersheds 1 and 5 at the Hubbard Brook Experimental Forest.

in the uncut watershed. However, when the alkyl/carbohydrate ratio (R) is compared horizon-to-horizon, there was little difference between W1 and W5 (Figure 7).

When water percolates through the soil profile, organic matter may adsorb to soil surfaces and/or be released into the soil solution. Thus, it can be difficult to infer preferential adsorption/desorption of DOC fractions from soil solution data alone. In a previous DOC study at the HBEF, McDowell and Likens (1988) suggested that, on an annual basis, the mineral soil is at steady state with respect to organic carbon transported as DOC in soil solution. Nelson et al. (1993) conducted a laboratory study on a clay-rich (50%) soil, observing little if any selective adsorption of specific types of carbon based on CP/MAS ^{13}C NMR and pyrolysis-mass spectrometry.

The sharp decrease in DOC concentration with depth indicates that all DOC fractions are adsorbed in Hubbard Brook mineral soils. However, our CP/MAS ^{13}C NMR analyses of W1 soil solutions suggest that the alkyl-C fraction is preferentially adsorbed, resulting in a lower alkyl-C contribution to DOC in the Bh and Bs1 horizons (Figure 6). In contrast, the aromatic and carbonyl-C fractions appear to be less preferentially adsorbed.

Stream samples

In all of the stream samples, fractionation analysis of DOC indicated that organic acids accounted for most of the DOC. Together, the hydrophilic and hydrophobic acid fractions accounted for 54 to 83% of DOC (Table 5). Stream samples collected in March and October 1998 contained substantial amounts of neutral compounds (Table 5). The organic C chemistry of stream samples reflect the influence of factors such as soil solution chemistry, vegetation, water flow paths, and the *in situ* abiotic/biotic environment. The most notable pattern we observed among the three sampling dates was a decrease in the fraction of HPI-A and a corresponding increase in HPI-N in the March 1998 samples. This may be indicative of slower microbial decomposition processes at the low temperature of the stream water during winter. Also, the relative decrease in the hydrophilic acid (HPI-A) fraction in March is consistent with stream water derived from shallower flow paths during late winter and early spring. Hydrophilic acid fractions are lower in Oa horizon soil solutions than in mineral horizons (Table 5). Thus, a shallower flow path would correspond to lower HPI-A fractions. Easthouse et al. (1992) conducted a DOC fractionation study in southern Norway, and observed a similar pattern, as HPO-A/HPI-A ratios decreased from 2.7 (O horizon) to 0.7 (B horizon) in soil solutions. They also observed an increased contribution from the O horizon to the stream DOC chemistry during intense storms. They

concluded that as soils became saturated during storm events, lateral transport of soil water was enhanced.

There were no consistent differences in stream DOC fractions among watersheds. Samples from W1 and W6, two uncut watersheds, were generally as different from each other as they were from the W5 samples (Table 5). Thus, our data show no obvious evidence of clear-cutting effects on DOC fractions in stream waters.

Simultaneous measurement of analytical DOC fractionation and preparative isolation has rarely been conducted (Dai et al. 1996). Our results suggest that the XAD-4 resin used in the isolation of DOC fractions resulted in lower estimates of HPI-A concentrations, and correspondingly higher estimates of HPI-N concentrations than the Duolite resin used in the fractionation procedure (Table 5). Also, hydrophilic bases were not recovered in the isolation procedure and thus were accounted for in the neutral fraction. These differences may be due to the secondary cleanup procedure used in the isolation method and the resin involved (Dai et al. 1996; Malcolm & MacCarthy 1992).

CP/MAS ^{13}C NMR spectra of selected bulk samples from the different watersheds are shown in Figure 8. Similar to soil and soil solution samples, alkyl-C (23 to 42% of total C) and O-alkyl C (29 to 60% of total C) were the main components of DOM in all but one stream sample (Figure 9). The sample collected in March 1998 from W1 had a large proportion of aromatic-C. In both collections, stream samples from W5 and W6 had very similar distribution of C among structural categories (Figure 9). In contrast, isolates from W1 exhibited somewhat different patterns. For example, W1 samples collected both in 1997 and 1998 had a higher proportion of carbonyl (mainly carboxylic) C and smaller proportions of O-alkyl C (carbohydrates) compared to bulk isolates from W5 and W6 (Figure 9). The two W1 samples had markedly different aromatic C fractions. In 1997, the W1 samples had the lowest aromatic-C fraction, whereas in March 1998, the W1 sample had more than twice the aromatic-C observed in W5 and W6 samples (Figures 9 and 10).

The similarities of C composition between W5 and W6 samples collected in both 1997 and 1998 suggest that there are no great differences in the structural chemistry of stream DOM between clear-cut and uncut watersheds fifteen years after harvest. The fact that the observed differences in the organic chemistry of soils and soil solutions are not expressed in stream water suggest that there are biotic and abiotic processes occurring in the deeper mineral soil (i.e., below the Bs lysimeters) or the stream which regulate DOM chemistry and are not sensitive to clear-cutting disturbance.
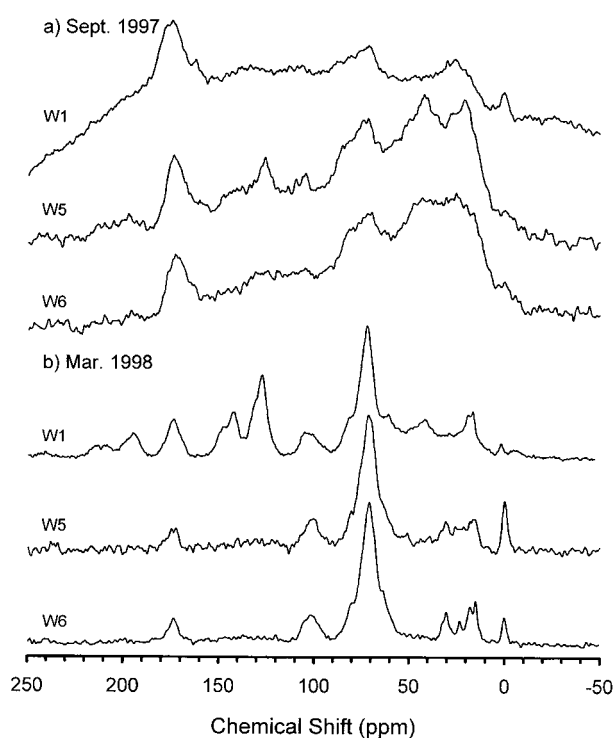
Figure 8. Solid-state CP/MAS ^{13}C NMR spectra acquired for DOC in bulk stream samples from three watersheds at the Hubbard Brook Experimental Forest. Samples were collected on (a) September 7, 1997, (b) March 20, 1998. Watershed 5 (W5) is the clear-cut site.
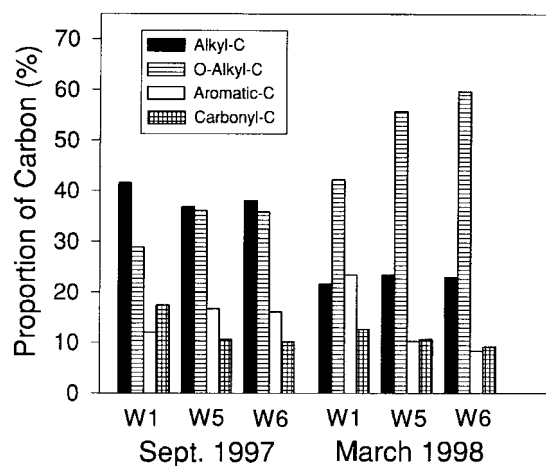

Figure 9. Distribution of C based on ^{13}C NMR analysis of organic matter isolated from bulk stream samples collected from two uncut watersheds (W1 and W6) and one clear-cut watershed (W5) at the Hubbard Brook Experimental Forest, New Hampshire.
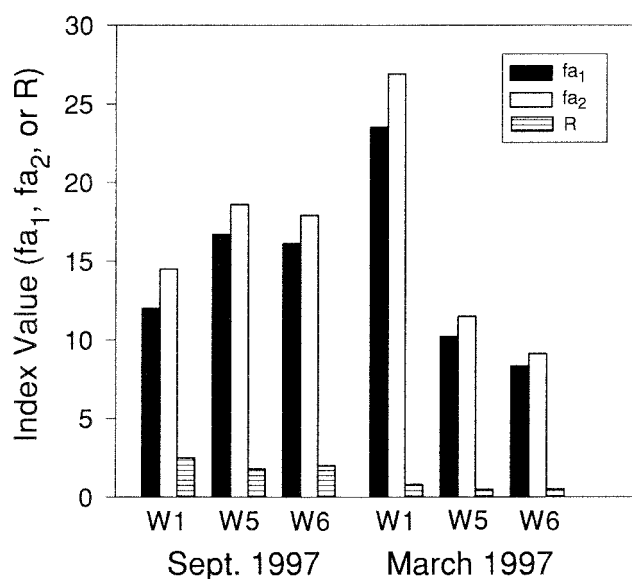
Figure 10. The alkyl/carbohydrate ratio (R) and aromaticity indices (fa$_1$ and fa$_2$) of organic matter in bulk stream samples collected from two uncut watersheds (W1 and W6) and one clear-cut watershed (W5) at the Hubbard Brook Experimental Forest, New Hampshire.

Table 6. ^{13}C NMR composition, aromaticity indices (fa$_1$ and fa$_2$), and the alkyl/carbohydrate ratio (R) of dissolved organic carbon (DOC) fractions: hydrophobic acids (HPO-A), hydrophilic acids (HPI-A), and hydrophilic neutrals (HPI-N). Samples were isolated from stream water collected from two uncut watersheds (W1 and W6) and one clear-cut (W5) watershed at the Hubbard Brook Experimental Forest, New Hampshire

Watershed	Collection Date	DOC Fraction	Fraction/chemical shift (ppm)				fa$_1$[a]	fa$_2$[b]	R[c]
			Alkyl/ 0–50	O-alkyl/ 50–110	Aromatic/ 110–160	Carbonyl/ 160–220			
W1	10/20/98	HPO-A	19.2	21.9	14.8	43.9	14.8	26.5	1.8
W5	10/20/98	HPO-A	28.0	23.1	8.6	40.2	8.6	14.4	2.3
W6	10/20/98	HPO-A	54.3	31.1	1.4	13.2	1.4	1.6	8.9
W1	10/20/98	HPI-A	12.9	20.8	24.9	41.3	24.9	42.5	1.5
W5	10/20/98	HPI-A	15.0	20.9	12.8	51.2	12.8	26.3	1.5
W6	10/20/98	HPI-A	28.1	36.5	7.3	28.1	7.3	10.2	1.3
W5	10/20/98	HPI-N	32.0	31.5	19.1	17.3	19.1	23.1	1.6
W6	10/20/98	HPI-N	35.5	28.9	24.3	11.3	24.3	27.3	1.9

[a]fa$_1$ (aromaticity), % = [(110–160) ppm/(0–220) ppm] × 100.
[b]fa$_2$ (aromaticity), % = [(110–160) ppm/(0–160) ppm] × 100.
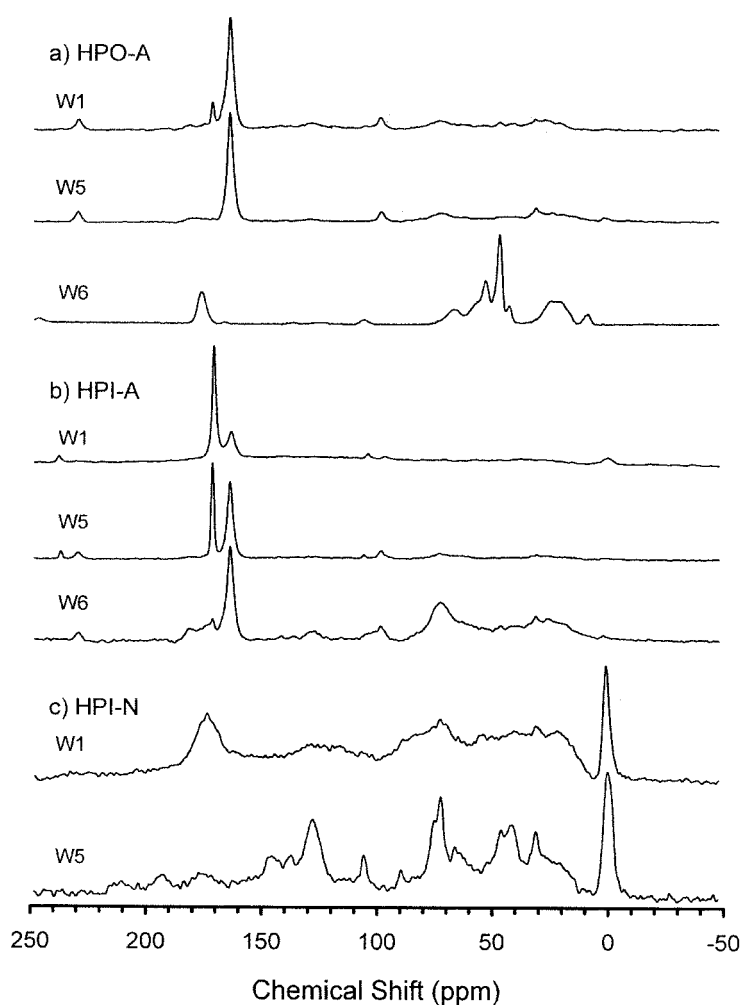[c]R= alkyl/carbohydrate ratio = [(0–50) ppm/(65–95)ppm].

Figure 11. Solid-state CP/MAS ^{13}C NMR spectra acquired for isolated DOC fractions in stream samples collected on October 20, 1998: (a) hydrophobic acid fraction (HPO-A), (b) hydrophilic acid fraction (HPI-A), and (c) hydrophilic neutral fraction (HPI-N).

The ^{13}C NMR spectra of isolated DOC fractions are presented in Figure 11. Both hydrophilic and hydrophobic acid fractions had high proportions of C as carboxylic groups, indicating the importance of carboxyl-C to organic acidity. The HPI-A fraction had the highest carboxyl-C fraction, suggesting a high degree of microbial oxidation with respect to other organic materials (Guggenberger et al. 1994). The high percentage of carboxyl-C in our hydrophilic acid isolates is consistent with other studies (Dai et al. 1996; Guggenberger et al. 1994; Vance & David 1991a). Hydrophobic acids had

high carboxylic C content, like the HPI-A fractions, but lower aromatic C content and higher alkyl C content (Table 6). Therefore, hydrophobic acids at Hubbard Brook appear to be largely aliphatic in nature, with abundant carboxyl acidity, whereas hydrophilic acids are comprised of both aliphatic and aromatic moieties. Hydrophilic neutrals had a greater aromatic character, and much lower carboxyl content than other isolates (Table 6).

Unlike the bulk stream samples, the C composition of isolated DOC fractions differed substantially among the three watersheds. For example, the HPO-A and HPI-A fractions in W6 had larger proportions of alkyl-C and much smaller proportions of aromatic-C than samples from W1 and W5 (Table 6). Compared to the acid fractions, the differences of C composition between hydrophilic neutrals isolated from W5 and W6 stream water were less significant.

Linkages among soil, soil solution, and stream carbon

The terrestrial and aquatic ecosystems of the HBEF are tightly linked by the flow of water and organic matter. Complex and ecologically important linkages between abiotic and biotic components mediate the organic chemistry of water transported through the soil.

Data from soil, soil solution, and stream samples can be used to examine the relationships between the terrestrial and aquatic ecosystems at the HBEF. The pool of carbon in O horizon soils on W5 declined in the first fifteen years after clear-cutting (Johnson et al. 1995; C.E. Johnson & S.P. Hamburg, unpublished data). Nevertheless, DOC concentrations in soil solutions collected beneath the forest floor (Oa) in W5 have been greater than or equal to concentrations in a nearby uncut area throughout the post-harvest period (Dahlgren & Driscoll 1994; Johnson et al. 1995; C.T. Driscoll, unpublished data, 1999). Concentrations of DOC in W5 stream water have also been significantly greater than in adjacent, uncut W6 for most of the post-harvest period (Johnson et al. 1995). Therefore, clear-cutting resulted in enhanced leaching of organic matter from a shrinking O horizon.

Based on our CP/MAS ^{13}C NMR data, the carbon distribution and the alkyl/carbohydrate index (R) in the soil were similar between W1 and W5 samples (Figures 3 and 4). The indices of aromaticity (fa_1 and fa_2) were somewhat greater in the W1 soils than in the W5 soils. Overall, it appears that clear-cutting has had little effect on the structural chemistry of SOM in the first fifteen years after harvesting. Therefore, the differences we observed in the composition of soil solutions and stream waters must be due to differences in organic matter processing between clear-cut and uncut areas rather than differences in SOM chemistry.
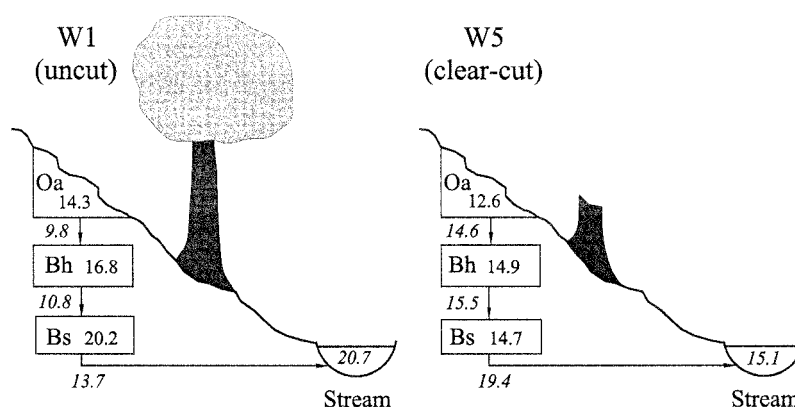
Figure 12. Patterns in the aromaticity (fa$_2$) of soils, soil solution, and stream water in uncut W1 (a) and clear-cut W5 (b) at the Hubbard Brook Experimental Forest, New Hampshire. Arrows denote soil solutions. Values in *italics* correspond to stream and soil solution samples, whereas values in the boxes correspond to soils.

In both clear-cut and uncut watersheds, the aromaticity (fa$_1$ or fa$_2$) of organic matter increased with increasing depth in soils (Figure 4) and soil solutions (Figure 7). Consequently, the aromaticity of organic matter may be a good index of degree of decomposition in these soils. The alkyl/carbohydrate ratio (R) proposed by Baldock and Preston (1995) increased with increasing depth in soil samples (Figure 4), but decreased in soil solutions (Figure 7). In both soils and soil solutions, the variation in R was small from horizon-to-horizon (Figures 4 & 7). Thus, the R ratio may not be as sensitive an indicator of decomposition status as aromaticity in HBEF soils.

Soil solutions from the clear-cut watershed (W5) were uniformly more aromatic than soil solutions from uncut W1 (Figures 6 & 7). If aromaticity is a reflection of the degree of decomposition, we conclude that the dissolved organic matter mobilized in W5 soils is more highly decomposed than DOM mobilized in W1.

In W1, soil solution organic matter has a lower aromaticity than the corresponding soil horizon (Figure 12). Indeed, the Bs horizon soil solution, which had the greatest aromaticity among W1 soil solutions, had a lower aromaticity than any of the W1 soil horizons studied. Thus, leaching of organic matter from the O horizon in W1 results in the preferential mobilization of more aliphatic compounds. As the soil water percolates downward, aliphatic constituents are preferentially adsorbed, resulting in increased aromaticity.

In contrast, soil solution organic matter in W5 was more aromatic than the corresponding soil horizons (Figure 12). Thus, it appears that preferential leaching of more aromatic compounds is occurring in the O horizon of the

clear-cut watershed. As in W1, soil solution aromaticity increases as water percolates downwards in the soil. Our observations suggest that clear-cutting may have altered the soluble organic matter pool in the soil. Removal of the forest canopy sharply reduced litter inputs immediately after clear-cutting (Hughes & Fahey 1994), but DOC levels in soil solution and stream water increased above pre-harvest levels (Johnson et al. 1995). Over time litterfall increased, but DOC losses remained elevated in W5. Thus, in comparison to the uncut watersheds, the pool of soluble organics in W5 soils was depleted after clear-cutting.

McDowell and Likens (1988) suggested that DOC mobilization in HBEF soils is approximately at steady-state. Furthermore, our W1 data suggest that soil solution organic matter generally tends to be more aliphatic than corresponding soil organic matter. Since clear-cutting results in increased DOC concentrations and reduced inputs of organic matter to replenish OM mobilized as DOC, the soluble organic pool in W5 soils should become more aromatic over time. Continued leaching of soluble organic matter from W5 would therefore be expected to result in increasing aromaticity of soil solution organic matter.

This model explains the soil solution patterns, but is inconsistent with the soil data, which indicate a greater aromaticity in W1 soils compared to W5 (Figure 12). However, the DOC lost in soil solution represents a small fraction of soil C. Using an average DOC concentration of 1000 μmol L^{-1}, and assuming 1000 mm of leaching annually, the total amount of C mobilized as DOC in the O horizon in W5 over the fifteen years since clear-cutting would be approximately 150 kg ha^{-1}. In contrast, the total C pool in the Oa horizon was about 16,000 kg ha^{-1} prior to clear-cutting (Huntington & Ryan 1990; Johnson et al. 1995). Thus, the soluble pool of organic matter in the HBEF soils is a small fraction of the total SOM. Large changes in this soluble pool would therefore not be expected to cause noticeable changes in the total SOM pool.

The C lost in respiration represents a much larger flux than DOC losses via leaching. Data from W5 suggest that C respiration increased after clear-cutting on W5 (Johnson et al. 1995). The general similarity in the chemistry of SOM in W5 and W1 (Figure 3) suggests that respired C was not preferentially drawn from any particular organic matter fraction. This is a tentative observation because the variation in organic matter chemistry among sites makes it difficult to detect subtle differences.

This study would benefit from additional analyses of soils, soil solutions, and stream waters. However, a number of impediments exist. First, solid-state ^{13}C-NMR analysis of soils, especially mineral soils, required up to 24 h of instrument time per sample. In the case of soil solutions, analysis is often

limited by the amount of solution which can be collected in the field. Low DOC concentrations in stream waters require the collection of hundreds of liters of water to isolate a sufficient amount of C for proper analysis. Despite these difficulties, our study suggests that comprehensive characterization of soils, stream waters, and soil solutions using ^{13}C-NMR can yield insight into important biogeochemical processes in forest ecosystems.

Conclusions

Clear-cutting northern hardwood ecosystems provokes complex hydrological, biogeochemical, and ecological changes. Results from this study suggest that following clear-cutting, there is a dynamic restructuring of organic matter pools, organic matter compounds, DOC, and DOC fractions in soil solutions and stream waters. We offer three general conclusions, based on our analyses of organic matter chemistry in clear-cut and uncut areas of the HBEF:

(1) Elevated DOC concentrations in soil solutions from the clear-cut site have persisted through post-harvest year 15. Using aromaticity (fa_1 or fa_2) as a decomposition index, the DOC mobilized in soil solutions in clear-cut site represented more highly decomposed organic matter than in the uncut watershed. Our data suggest that the soluble organic matter pool in the soil has become more aromatic after clear-cutting. The differences in soil solution organic matter chemistry are also likely to have implications for metal transport, nutrient availability, and acid-base chemistry.

(2) Despite evidence of clear-cutting effects on DOC chemistry in soil solutions, there were no obvious differences in DOC chemistry of watershed streams. Thus, processes in the lower mineral soil, in-stream processes, and/or variations in hydrologic flowpaths are important in regulating the organic matter chemistry of stream waters at the HBEF. Isolated DOC fractions (esp. HPO-A and HPI-A) did show substantial differences between the clear-cut and uncut systems. Additional examination of isolated DOC fractions may yield further insight into clear-cutting effects.

(3) Despite changes in soil solution DOM and the soluble pool of SOM, clear-cutting had little impact on the structural chemistry of SOM. This is not entirely surprising, since the turnover time of organic matter in the soil is much longer than in the soil solution and stream water. As a result, these more dynamic pools of organic matter are more sensitive indicators of disturbance effects, in the short- to medium-term. In the longer term (20–50 years), it may be possible to detect changes in the chemistry of SOM. Continued long-term monitoring of C concentrations and the composition of organic matter can thus be used to detect changes

in the decomposition regime and the substrate for microbial processes. From the perspective of forest and ecosystem management, such studies are useful in order to more fully understand natural biogeochemical processes and human-induced environmental changes.

Acknowledgements

References

Baldock JA, Oades JM, Nelson PN, Skene TM, Golchin A & Clarke P (1997) Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. Aust. J. Soil Res. 35: 1061–1083

Baldock JA & Preston CM (1995) Chemistry of carbon decomposition processes in forests as revealed by solid-state carbon-13 nuclear magnetic resonance. In: McFee WW & Kelly JM (Ed) Carbon Forms and Functions in Forest Soils (pp 89–117). Soil Sci. Soc. Am., Madison, Wisconsin

Bormann FH & Likens GE (1979) Pattern and Process in a Forest Ecosystem. Springer-Verlag, New York

Buol SW, Hole FD, McCracken RJ & Southard RJ (1997) Soil Genesis and Classification. 4th ed. Iowa State University Press, Ames, Iowa

Covington WW (1981) Changes in forest floor organic matter and nutrient content following clear cutting in northern hardwoods. Ecology 62: 41–48

Covington WW & Aber JD (1980) Leaf production during secondary succession in northern hardwoods. Ecology 61: 200–204

Dahlgren RA & Driscoll CT (1994) The effects of whole-tree clear-cutting on soil processes at the Hubbard Brook Experimental Forest, New Hampshire, USA. Plant & Soil 158: 239–262

Dai KH, David MB & Vance GF (1996) Characterization of solid and dissolved carbon in a spruce-fir Spodosol. Biogeochemistry 35: 339–365

David MB & Driscoll CT (1984) Aluminum speciation and equilibria in soil solutions of a Haplorthod in the Adirondack Mountains (New York, USA). Geoderma 33: 297–318

David MB & Vance GF (1991) Chemical character and origin of organic acids in streams and seepage lakes of central Maine. Biogeochemistry 12: 17–41

David MB, Vance GF & Kahl JS (1992) Chemistry of dissolved organic carbon and organic acids in two streams draining forested watersheds. Water Resour. Res. 28: 389–396

David MB, Vance GF, Rissing JM & Stevenson FJ (1989) Organic carbon fractions in extracts of O and B horizons from a New England Spodosol: effects of acid treatment. J. Environ. Qual. 18: 212–217

David MB & Zech W (1990) Adsorption of dissolved organic carbon and sulfate by acid forest soils in the Fichtelgebirge, FRG. Z. Pflanzenernähr. Bodenk. 153: 379–384

Davies BE (1974) Loss-on-ignition as an estimate of soil organic matter. Soil Sci. Soc. Am. Proc. 38: 150–151

Dawson HJ, Ugolini FC, Hrutfiord BF & Zachara J (1978) Role of soluble organics in the soil processes of a podzol, central Cascades, Washington. Soil Sci. 126: 290–296

Deinzer M, Melton R & Mitchell D (1975) Trace organic contaminants in drinking water: their concentration by reverse osmosis. Water Res. 9: 799–805

Driscoll CT, Fuller RD & Simone DM (1988) Longitudinal variations in trace metal concentrations in a northern forested ecosystem. J. Environ. Qual. 17: 101–107

Easthouse KB, Mulder J & Christophersen N (1992) Dissolved organic carbon fractions in soils and stream water during variable hydrological conditions at Birkenes, southern Norway. Water Resour. Res. 28: 1585–1596

Federer CA, Flynn LD, Martin CW, Hornbeck JW & Pierce RS (1990) Thirty years of hydro-meterological data at the Hubbard Brook Experimental Forest, New Hampshire. USDA For Serv. Gen. Tech. Rep., NE-141

Gressel N, McColl JG, Preston CM, Newman RH & Powers RF (1996) Linkages between phosphorus transformations and carbon decomposition in a forest soil. Biogeochemistry 33: 97–123

Griffin RA & Jurinak JJ (1973) Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. Soil Sci. 116: 26–30

Guggenberger G, Zech W & Schulten H-R (1994) Formation and mobilization pathways of dissolved organic matter: Evidence from chemical structural studies of organic matter fractions in acid forest floor solutions. Org. Geochem. 21: 51–66

Hatcher PG (1987) Chemical structural studies of natural lignin by dipolar dephasing solid-state C-13 nuclear magnetic resonance. Org. Geochem. 11: 31–39

Hendrickson OQ, Chatarpaul L & Burgess D (1989) Nutrient cycling following whole-tree and conventional harvest in northern mixed forest. Can. J. For. Res. 19: 725–735

Hopkins DW, Chudke JA, Webster EA & Barraclough D (1997) Following the decomposition of ryegrass labelled with ^{13}C and ^{15}N in soil by solid-state nuclear magnetic resonance spectroscopy. Euro. J. Soil Sci. 48: 623–631

Hughes JW & Fahey TJ (1994) Litterfall dynamics and ecosystem recovery during forest development. For. Ecol. Manage. 63: 181–198

Huntington TG, Johnson CE, Johnson AH, Siccama TG & Ryan DF (1989) Carbon, organic matter, and bulk density relationships in a forested Spodosol. Soil Sci. 148: 380–386

Huntington TG & Ryan DF (1990) Whole-tree harvesting effects on soil nitrogen and carbon. For. Ecol. Manage. 31: 193–204

Huntington TG, Ryan DF & Hamburg SP (1988) Estimating soil nitrogen and carbon pools in a northern hardwood forest ecosystem. Soil Sci. Soc. Am. J. 52: 1162–1167

Johnson CE (1995) Soil nitrogen status eight years after whole-tree clear-cutting. Can. J. For. Res. 25: 1346–1355

Johnson CE, Driscoll CT, Fahey TJ & Siccama TG (1995) Carbon dynamics following clear-cutting of a northern hardwood forest. In: McFee WW & Kelly JM (Ed) Carbon Forms and Functions in Forest Soils (pp 463–488). Soil Sci. Soc. Am., Madison, Wisconsin

Johnson CE, Driscoll CT, Siccama TG & Likens GE (2000) Element fluxes and landscape position in a northern hardwood forest watershed ecosystem. Ecosystems 3: 159–184

Johnson CE, Johnson AH, Huntington TG & Siccama TG (1991a) Whole-tree clear-cutting effects on soil horizons and organic-matter pools. Soil Sci. Soc. Am. J. 55: 497–502

Johnson CE, Johnson AH & Siccama TG (1991b) Whole-tree clear-cutting effects on exchangeable cations and soil acidity. Soil Sci. Soc. Am. J. 55: 502–507

Johnson CE, Romanowicz RB & Siccama TG (1997) Conservation of exchangeable cations after clear-cutting of a northern hardwood forest. Can. J. For. Res. 27: 859–868

Kögel-Knabner I (1992) Forest Soil Organic Matter: Structure and Formation. Bayreuther Bodenkundliche Berichte, University of Bayreuth, Germany

Kögel-Knabner I (1993) Biodegradation and humification processes in forest soils. In: Bollag JM & Stotsky G (Eds) Soil Biochemistry, Vol. 8 (pp 101–135), Marcel Dekker, New York, New York

Kögel-Knabner I, Zech W & Hatcher PG (1988) Chemical composition of the organic matter in forest soils: III. The humus layer. Z. Pflanzenernähr. Bodenk. 151: 331–340

Leenheer JA (1981) Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. Environ. Sci. Technol. 15: 578–587

Leenheer JA & Huffman EWD (1979) Analytical method for dissolved organic carbon fractionation. US Geological Survey Water Resources Investigations 79-4

Likens GE & Bormann FH (1995) Biogeochemistry of a Forested Ecosystem. 2nd ed. Springler-Verlag, New York, New York

MacCarthy P, Bloom PR, Clapp CE & Malcolm RL (1990) Humic substances in soil and crop sciences: an overview. In: MacCarthy et al. (Eds) Humic Subsatnces in Soil and Crop Sciences: Selected Readings (pp 261–271). American Soc. Agronomy & Soil Sci. Soc. Am., Madison, Wisconsin

Mahieu N, Powlson DS & Randall EW (1999) Statistical analysis of published carbon-13 CPMAS NMR spectra of soil organic matter. Soil Sci. Soc. Am. J. 63: 307–319

Malcolm RL & MacCarthy P (1992) Quantitative evaluation of XAD-8 and XAD-4 resins used in tandem for removing organic solutes from water. Environ. Int. 18: 597–607

Marks PL (1974) The role of pin cherry (Prunus pensylvanica L.) in the maintenance of stability in northern hardwoods ecosystems. Ecol. Monogr. 44: 73–88

Marks PL & Bormann FH (1972) Revegetation following forest cutting: mechanisms for return to steady-state nutrient cycling. Science 176: 914–915

Mattson KG & Swank WT (1989) Soil and detrital carbon dynamics following forest cutting in the southern Appalachians. Biol. Fert. Soils 7: 247–253

McDowell WH (1985) Kinetics and mechanisms of dissolved organic carbon retention in a headwater stream. Biogeochemistry 1: 329–352

McDowell WH & Likens GE (1988) Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecol. Monogr. 58: 177–195

McDowell WH & Wood T (1984) Podzolization: soil processes control dissolved organic carbon concentrations in stream water. Soil Sci. 137: 23–32

McDowell WH, Currie WS, Aber JD & Yano Y (1998) Effects of chronic nitrogen amendments on production of dissolved organic carbon and nitrogen in forest soils. Water Air Soil Pollut. 105: 175–182

Mo SS (1997) The Chemistry and Dynamics of Carbon in Forest Soils of the Hubbard Brook Experimental Forest, MS thesis, Syracuse University

Moore TR (1989) Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand. 1. Maimai. Water Resour. Res. 25: 1321–1330

Moore TR, de Souza W & Koprivnjak J-F (1992) Controls on the sorption of dissolved organic carbon by soils. Soil Sci. 154: 120–129

Nelson PN, Baldock JA & Oades JM (1993) Concentration and composition of dissolved organic carbon in streams in relation to catchment soil properties. Biogeochemistry 32: 27–50

Odegaard H & Koottatep (1982) Removal of humic substances from natural waters by reverse osmosis. Water Res. 16: 613–620

Perdue EM (1984) Analytical constraints on the structural features of humic substances. Geochim. Cosmochim. Acta. 48: 1435–1442

Perdue EM, Reuter JH & Parrish RS (1984) A statistical model of proton binding of humus. Geochim. Cosmochim. Acta. 48: 1257–1263

Qualls, RG & Haines BL (1991) Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. Soil Sci. Soc. Am. J. 55: 1112–1123

Rice JA & MacCarthy P (1991) Statistical evaluation of the elemental composition of humic substances. Org. Geochem. 17: 635–648

Rodin LE & Bazilevich (1967) Production and Mineral Cycling in Terrestrial Vegetation. Oliver & Boyd, London, England

Schlesinger WH (1997) Biogeochemistry: An Analysis of Global Change, 2nd ed. Academic Press, Inc., San Diego, Ca.

Serkiz SM & Perdue EM (1990) Isolation of dissolved organic matter from the Suwannee River using reverse osmosis. Water Res. 24: 911–916

Skjemstad JO, Clarke P, Taylor JA, Oades JM & Newman RH (1994) The removal of magnetic materials from surface soils. A solid state ^{13}C CP/MAS NMR study. Aust. J. Soil Res. 32: 1215–1229

Snyder KE & Harter RD (1985) Changes in solum chemistry following clear-cutting of northern hardwood stands. Soil Sci. Soc. Am. J. 49: 223–228

Stevenson FJ (1994) Humus Chemistry: Genesis, Composition, Reactions. 2nd ed. John Wiley & Sons, New York, New York

Vance GF & David MB (1989) Effect of acid treatment on dissolved organic carbon retention by a spodic horizon. Soil Sci. Soc. Am. J. 53: 1242–1247

Vance GF & David MB (1991a) Chemical characterization and acidity of soluble organic substances from a northern hardwood forest floor, central Maine, USA. Geochim. Cosmochim. Acta. 55: 3611–3625

Vance GF & David MB (1991b) Forest soil response to acid and salt additions of sulfate: II. Solubilization and composition of dissolved organic carbon. Soil Sci. Soc. Am. 50: 992–996

Vance GF, Mokma DL & Boyd SA (1986) Phenolic compounds in soils of hydro-sequences and developmental sequences of Spodosols. Soil Sci. Soc. Am. J. 50: 992–996

Zech W, Kögel I, Zucker A & Alt H (1985) CP-MAS-^{13}C-NMR spectren organischer lagen einer Tangelrendzina. Z. Pflanzenernähr. Bodenk. 150: 262–265