Biogeochemistry **34:** 157–188, 1996.

Geochemistry of aquatic humic substances in the Lake Fryxell Basin, Antarctica

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Received 29 August 1994; accepted 14 March 1996

Key words: Antarctic lakes, dissolved organic carbon, sources, fulvic acid, biogeochemical transformation, diffusion

Abstract. Dissolved organic carbon (DOC) in Lake Fryxell, 10 streams flowing into the lake, and the moat surrounding the lake was studied to determine the influence of sources and biogeochemical processes on its distribution and chemical nature. Lake Fryxell is an amictic, permanently ice-covered lake in the McMurdo Dry Valleys which contains benthic and planktonic microbial populations, but receives essentially no input of organic material from the ahumic soils of the watershed. Biological activity in the water column does not appear to influence the DOC depth profile, which is similar to the profiles for conservative inorganic constituents. DOC values for the streams varied with biomass in the stream channel, and ranged from 0.2 to 9.7 mg C/L. Fulvic acids in the streams were a lower percentage of the total DOC than in the lake. These samples contain recent carbon and appear to be simpler mixtures of compounds than the lake samples, indicating that they have undergone less humification. The fulvic acids from just above the sediments of the lake have a high sulfur content and are highly aliphatic. The main transformations occurring as these fractions diffuse upward in the water column are 1) loss of sulfur groups through the oxycline and 2) decrease in aliphatic carbon and increase in the heterogeneity of aliphatic moieties. The fraction of modern ^{14}C content of the lake fulvic acids range from a minimum of 0.68 (approximately 3000 years old) at 15m depth to 0.997 (recent material) just under the ice. The major processes controlling the DOC in the lake appear to be: 1) The transport of organic matter by the inflow streams resulting in the addition of recent organic material to the moat and upper waters of the lake; 2) The diffusion of organic matter composed of relict organic material and organic carbon resulting from the degradation of algae and bacteria from the bottom waters or sediments of the lake into overlying glacial melt water; 3) The addition of recent organic matter to the bottom waters of the lake from the moat.

Introduction

Antarctic desert lakes are unique environments for studying biogeochemical processes involving dissolved organic material (DOM) derived from algae and bacteria (Matsumoto et al. 1989; McKnight et al. 1991; Aiken et al. 1991). For most temperate lakes, DOM is derived from the soils and plants of the watershed and from microbial populations in the lake (Steinberg & Muenster 1985). Plants are essentially absent in the McMurdo Dry Valleys, and the soils are "ahumic" (Horowitz et al. 1972), containing less than 0.1% organic carbon. The watersheds of these lakes are extremely barren, greatly limiting the landscape contributions to DOC in the glacial melt water streams which feed the lakes.

Since the International Geophysical Year (1957), biological and geochemical studies have been conducted in the McMurdo Dry Valleys, especially in the lakes in the Taylor Valley and in Wright Valley. Initial studies of the organic geochemistry of these systems focused on identifiable organic compounds (Matsumoto et al. 1989) rather than on major DOM fractions. For example, Matsumoto (1989) found that the dominant phenolic acid was *p*-hydroxybenzoic acid, whereas syringic, *p*-coumaric, and ferulic acids, normally associated with the presence of vascular plants, were found to be absent. Matsumoto et al. (1989) also measured the total organic carbon (TOC) profile for Lake Fryxell and found much greater TOC concentrations in the anoxic bottom waters than in the oxic surface waters. We found a similar profile for the dissolved organic carbon (DOC) and showed that the profile could be reproduced by a model of diffusion of DOC from the lake sediments (Aiken et al. 1991). The development of such a stable DOC profile is possible because the density gradient caused by chemical statification and the permanent ice cover results in extreme stability of the water column from year to year.

Recently, Miller & Aiken (1996) have reported the appearance of tritium in the deep waters of the lake, indicating that a component of the bottom water was recently at the surface of the lake. These findings suggest that the solute profiles, including the DOC profile, are the result of the addition of dissolved solutes to the deep water of the lake via advection of modified surface water in addition to diffusion. We also have estimated the flux of DOC and humic substances from streams to the lake and found that, depending on the age of the lake, streamflow may be a significant source of organic matter in the lake (McKnight et al. 1993). In light of these findings, in this paper we examine in more detail the nature and distribution of DOC and aquatic humic substances in Lake Fryxell. Aquatic humic substances comprise heterogeneous, yellow, biogenic organic acids. This class of compounds is relatively refractory and typically accounts for a major fraction (20–80%) of dissolved organic matter. Specifically, this paper focuses on the chemical transformations occurring 1) as humic substances in the streams mix into the lake, and 2) as humic substances in the lake diffuse upward from anoxic to oxic environments.

Site description

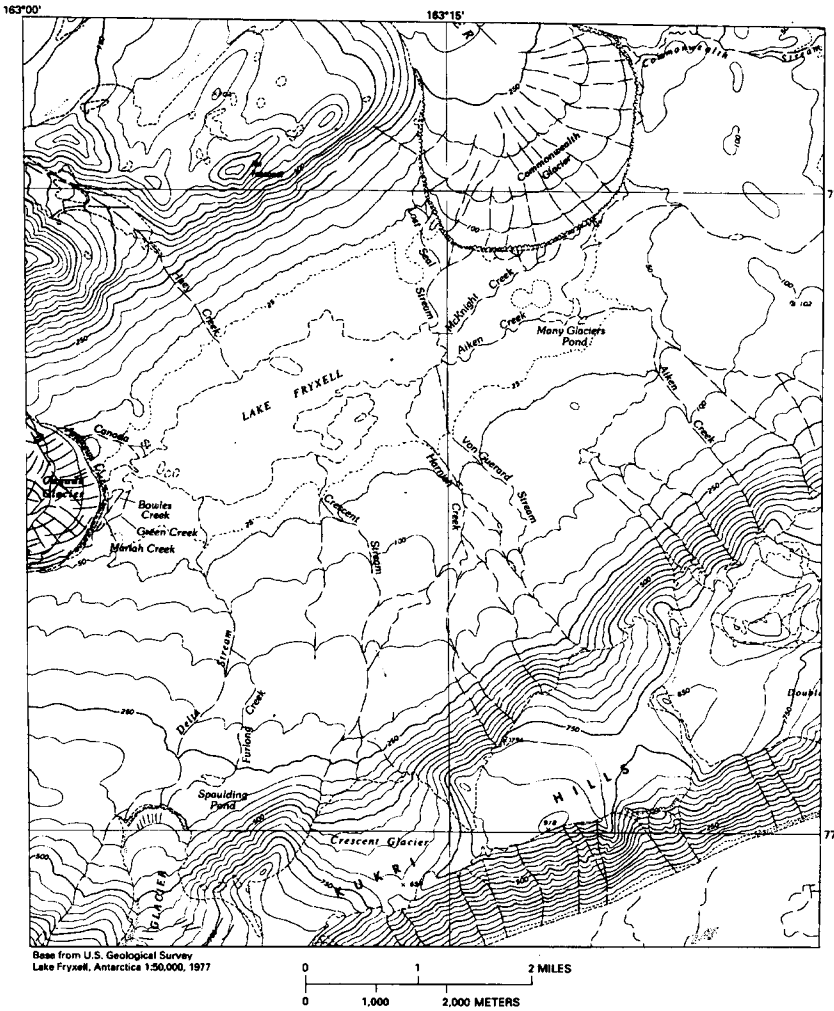
Lake Fryxell is in the lower Taylor Valley near the Ross Sea (77°37′ S, 163°11′ E) at an elevation of 16 m above sea level. The lake is approximately

5 km long and 2 km wide, and is located between the Commonwealth Glacier and the Canada Glacier (Figure 1). It has a permanent ice cover 3.8–4.6 m thick, a surface area of 7 km^2, a maximum depth of 19 m, and a mean depth of 8 m (Vincent 1981). The major source of water to the lake is melt water from alpine glaciers. Lake Fryxell does not have an outlet stream, and with no evidence for ground water discharge from the lake, the main mechanism for water loss is sublimation, with resultant ablation of the surface ice (Henderson et al. 1965; McKay et al. 1985). During the summer, an ice-free moat commonly forms as a result of stream water input and local melting of the ice cover. The water level in Lake Fryxell has risen approximately 2m since 1971 (Chinn 1993).

The history of lakes in the Dry Valleys are complex, being intimately connected to climatic shifts. Stuiver et al. (1981) proposed that the ancestral lakes were formed in the Taylor Valley when the Ross Ice Sheet, which was grounded to the floor of McMurdo Sound, moved up the valley during its latest advance, effectively forming a dam in the lower valley. Surface melt water streams from the glaciers in the valley were the sources of water to these lakes (Denton et al. 1985). ^{14}C data from remnant, nonmarine green and blue green algae in perched lacustrine deltas in the lower Taylor Valley indicate that there was a lake in the Fryxell basin between 19000 and about 8000 B.P. (Kellogg et al. 1980). Lawrence & Hendy (1985, 1989) noted 5 recognizable units in the sediments of the lake that they concluded were associated with periods of evaporation and increasing lake levels. The earliest of the units identified by Lawrence and Hendy dated from 20,000 BP. It does not appear, either from the chemical composition of the lake or from Lawrence and Hendy's sediment analyses, that the lake has gone to dryness, as has been postulated for Lake Bonney and Lake Vanda (Matsubaya 1979).

Lake Fryxell is of the Na^+-Cl^--HCO_3^- type (Table 1). It is essentially fresh water immediately below the ice cover, and increases in salinity with depth. Bottom waters have a conductance of about 14 millisiemens per centimeter, about 1/5 as salty as sea water. The chemistry and geochemical evolution of the lake have been explained in terms of the composition of the stream inflows, without invoking relict sea water or other salt sources, such as saline ground waters (Green et al. 1988).

The upper portion (to 9m depth) of the water column is aerobic with high O_2 concentrations resulting from photosynthetic processes in the euphotic zone (Vincent 1981) and from the exclusion of gases during the formation of new ice on the bottom of the ice cover (Wharton et al. 1986). The concentration of O_2 increases dramatically with depth to a maximum value at 8–9 m where the O_2 concentration is almost twice the saturation value with respect to air equilibration (Figure 2). The oxycline is very sharp with a rapid decrease in



Base from U.S. Geological Survey
Lake Fryxell, Antarctica 1:50,000, 1977

CONTOUR INTERVAL 50 METERS WITH SUPPLEMENTARY CONTOURS AT 25 METER INTERVALS
DATUM IS MEAN SEA LEVEL

Figure 1. Map of the lower Taylor Valley showing the Lake Fryxell watershed.

O_2 concentration; below 10 m depth the lake is anoxic. Below the oxycline, the HS^- concentration increases steadily and is a maximum in the anaerobic bottom waters of the lake, approaching 1.25 mM (Howes & Smith 1990). The concentration of SO_4^{2-} increases with depth to a maximum concentration of about 1.9 mM at 11 m. Below 11 m, the SO_4^{2-} concentration decreases to values near zero at the sediment-water interface.

The microflora of the lake have been studied extensively and are composed of blue-green algae, green algae, bacteria, yeasts, and fungi (Vincent

Table 1. Conductivity and major ion concentrations in Lake Fryxell.

Depth (meters)	Conductance (millisiemens)	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
		(milligrams per liter)				
5.0	0.16	285	213	22.3	47.7	25.3
5.5	1.87	354	261	24.3	53.8	31.6
6.0	2.60	486	393	24.3	58.5	40.4
6.5	3.20	609	513	32.4	62.9	50.3
7.0	3.90	771	624	42.5	58.9	59.0
7.5	4.70	944	756	54.7	69.6	80.4
7.75	5.10	–	–	–	–	–
8.0	5.60	1008	977	66.9	77.7	97.2
8.25	6.10	–	–	–	–	–
8.5	6.30	1294	1189	70.9	88.8	118.2
8.75	6.60	–	–	–	–	–
9.0	6.90	1376	1270	91.2	89.7	125.2
9.25	7.30	–	–	–	–	–
9.5	7.50	–	1434	105.4	100.4	147.8
10.0	8.20	1523	1430	113.5	90.3	144.8
10.5	9.00	1804	1588	125.6	113.3	193.2
11.0	9.80	2150	1736	145.9	115.7	204.8
11.5	10.30	–	–	–	–	–
12.0	10.70	2404	2010	131.7	122.7	232.5
12.5	11.30	–	–	–	–	–
13.0	11.70	2838	2267	166.1	136.5	274.4
13.5	12.20	–	–	–	–	–
14.0	12.30	3175	2475	176.3	142.3	303.4
14.5	12.60	–	–	–	–	–
15.0	12.80	3531	2650	190.4	141.0	319.6
15.5	12.90	–	–	–	–	–
16.0	13.00	3682	2667	190.4	135.6	329.9
16.5	13.60					–
17.0	13.60	3989	2817	202.6	126.9	334.7
17.5	13.60	–	–	–	–	
18.0	13.60	4087	2781	180.3	113.8	325.1

1988). Despite the low light intensities under the ice cover, abundant algal populations develop in the oxic zone of the lake (McKnight et al. 1993) with maximum abundance just above the oxycline (Figure 2). The populations of bacteria are also distributed according to depth. Smith & Howes (1990) reported that the bacterial abundance increased dramatically from 9 to 10.5 m, with a peak value at 10.5 m that was nearly 8 times greater than that in the overlying aerobic waters. Populations in the deeper anaerobic waters

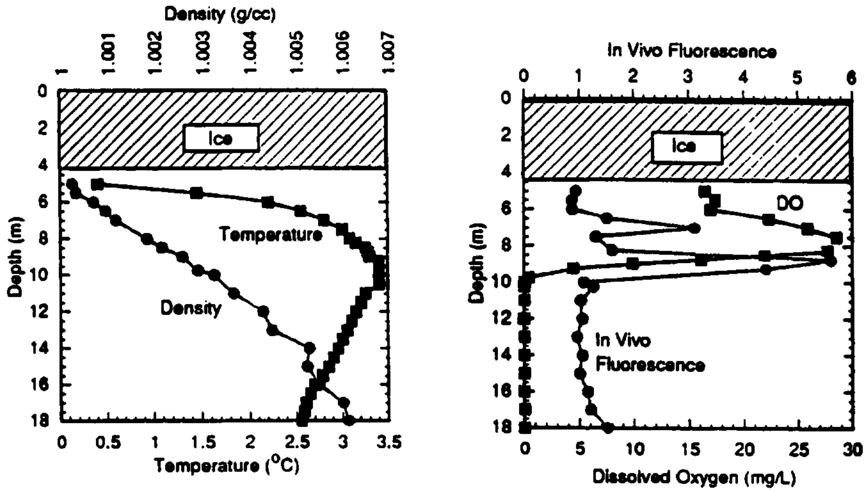


Figure 2. Temperature, density, dissolved oxygen and in-vivo fluorescence profiles for Lake Fryxell.

were found to be 2–3 times greater than those in the aerobic waters. The other important zone for bacterial activity in the lake is at the sediment-water interface. Processes occurring in this zone are responsible for the generation of HS^-, NH_4^+, and CH_4 profiles in the water column (Howes & Smith 1990), as well as the generation of dissolved organic carbon (DOC).

Thirteen glacial melt water streams flow into Lake Fryxell. Flow commences in mid-November and ends in early February. Five of the streams (Andrews, Mariah, Bowles, McKnight and Harnish Creeks) contribute substantially less flow than the other eight streams. Canada Stream generally has the greatest flows of up to 20 cfs. Flow rates are very responsive to changes in temperature and light intensity and vary both diurnally and seasonally. Several of the streams (Canada, Green, Lost Seal, and McKnight) originate from ponds at the base of the glaciers. Aiken Creek flows through Many Glaciers Pond, a large pond with several other inflow streams. The longer streams typically have higher concentrations of dissolved cations and anions as a result of weathering interactions. Green et al. (1989) reported salt compositions of the streams flowing the greatest distances (Huey Creek, Von Guerard Stream, Harnish Creek, Crescent Stream) were dominated by rock weathering while those flowing shorter distances were dominated by atmospheric inputs of marine origin (Canada Stream, Lost Seal Stream, McKnight Creek, Aiken Creek, Green Creek). Perennial algal mats and mosses are present in some of the streams. General descriptions of stream biota are presented in Table 2, based upon quantitative measurements of biomass and productivity

Table 2. Qualitative description of the major glacial melt water streams in the Lake Fryxell watershed.

Stream	Gradient	Sediment load	Biota
Canada Stream (F1)[a]	Steep	Low	Abundant algal mats and mosses in both the stream channel and pond
Huey Creek (F2)	Steep	High	Very sparse mosses in riparian zone
Lost Seal Stream (F3)	Shallow	Moderate	Sparse algal mats and mosses
McKnight Creek (F4)	Shallow	Low	Abundant algal mats and mosses
Aiken Creek (F5)	Steep/shallow	Low	Abundant algal mats and mosses in both the stream and pond
Von Guerard Stream (F6)	Steep	High	Very sparse algal mats and mosses
Harnish Creek (F7)	Steep	Moderate	Very sparse algal mats and mosses
Crescent Stream (F8)	Steep	Moderate	Very sparse algal mats and mosses
Delta Stream	Steep	Moderate	Algal mats and mosses very sparse in stream, moderate in pond
Green Creek (F9)	Shallow	Low	Algal mats and mosses moderate in stream, sparse in pond

[a] Approved names based on descriptive characteristics, commemorating events or after field party members, were given to the streams following the international guidelines for third order features. Stream designations given in parentheses are according to Green et al. (1988).

which are indicative of the DOC sources in the streams (Alger et al. 1996). In addition to the harsh winter conditions, factors controlling biomass in the streams include high suspended sediment loads which may limit or prevent the development of mats.

Methods

Sample collection

The lake was sampled during the 1987–1988, 1988–1989, and 1990–1991 austral summers through 25 cm diameter holes located above the deepest part of the lake. Water samples for analysis of dissolved ions and DOC were obtained by pumping from a measured depth through Tygon tubing. DOC samples were filtered through 0.45 μm silver membrane filters using a pressurized Gelman[1] stainless steel filtration unit and were collected in 125 mL precombusted glass bottles. Grab samples were collected from 10 streams flowing into Lake Fryxell for DOC analysis. These samples were filtered through Whatman GF/C glass fiber filters and collected in precombusted glass bottles.

Sediment pore waters from the sediment-water interface were obtained by squeezing sediment samples with a Reeburgh squeezer (Miller et al. 1993). The pore waters were filtered through 0.45 μm silver membrane filters, collected in 12 mL glass culture tubes, and acidified to pH 2 with H_3PO_4 for DOC analyses.

Large volume water samples (up to 1800 L) required for isolation of preparative quantities of the fulvic acid and syn-fulvic acid fractions of the DOC were obtained by pumping the sample from a given depth through Teflon lined stainless steel flexible tubing and two stainless steel Balston filtration units with cylindrical 1 μm and 0.3 μm glass fiber depth filters in tandem. Filtered water was collected in 38-L stainless steel milk cans.

Isolation procedures

Two operationally defined fractions of the DOC, fulvic acid and syn-fulvic acid were isolated using Amberlite XAD resins (Rohm and Haas) according to the method of Aiken et al. (1992). In brief, filtered water was acidified to pH 2 in glass carboys and 240 L of sample were then passed through 4-L columns of XAD-8 and XAD-4 resins connected in series by Teflon tubing. Fulvic acid was retained on the XAD-8 column and a fraction of the more hydrophilic acids, referred to as syn-fulvic acids, was retained on the XAD-4 resin. Each column was back eluted separately with 8 liters of 0.1M NaOH. NaOH eluates were immediately acidified with concentrated HCl to pH 2 to minimize alteration of the sample at high pH. Eluates were reconcentrated on the appropriate resin, then H^+-saturated using AG-MP 50 cation exchange resin (Biorad) and lyophilized. The term "syn-fulvic acid" is used in this manuscript to replace the term "hydrophilic acid fraction" originally used by Aiken et al. (1992) to describe the fraction of organic matter obtained from the XAD-4 resin. The original term was found to be misleading in that this fraction of the DOC is "humic-like" and does not contain all the hydrophilic organic acids in the sample.

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[1] Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Sample analyses

Temperature, conductivity and dissolved oxygen measurements were obtained from probes deployed in the water column, a YSI probe for conductivity and an Orbisphere probe for dissolved oxygen and temperature. Measurements of in-vivo fluorescence were obtained using a Turner Designs fluorimeter. Cations, with the exception of potassium, were analyzed using a plasma emission spectrometer (Thermo Jarrel Ash Corp). Samples from the bottom waters were diluted as necessary. Potassium was determined by atomic emission spectroscopy by the Central Laboratory of the United States Geological Survey, Water Resources Division, Arvada, Colorado. Chloride analyses were performed using a Lachat flow injection chloride analyzer.

Samples were analyzed for DOC concentration using an O I Analytical Model 700 Carbon Analyzer. To avoid interference from chloride ions, samples from Lake Fryxell were diluted such that the chloride concentration was below 0.02 M (Aiken 1992).

Elemental analyses were carried out by Huffman Laboratories (Golden, Colorado) according to the methods described by Huffman & Stuber (1985). Molecular weights were determined by Huffman Laboratories by vapor pressure osmometry with tetrahydrofuran (THF) as the solvent (Aiken & Malcolm 1987). ^{14}C analyses were performed by the University of Arizona NSF Accelerator Mass Spectrometry Laboratory. Inorganic sulfur species were determined by Huffman Laboratories using the following methods: sulfate was determined by ion chromatography; thiosulfate, tetrathionate and thiocyanide were determined according to the methods described by Nor & Tabatabai (1976). CS_2 extractions were carried out according to Heinrich et al. (1961).

The ^{13}C-NMR spectra were measured on solutions of approximately 100 mg/mL of the sodium salt of each of the samples dissolved in H_2O-D_2O (3 parts to 1 part) mixtures in 10 mm tubes on a Varian XL 300 spectrometer at 75.429 MHz. For the nonquantitative spectra the transmitter was set for a 45° tip angle with no pulse delay. The acquisition time was 0.2 seconds, and the sweep width was 30,000 Hz; continuous broad-band decoupling of protons by the WALTZ method was employed. All of the spectra were recorded with a line broadening of 25 Hz. The quantitative spectra were measured using inverse gated-decoupling with an 8-second delay.

Results

DOC concentrations

The DOC concentrations of the ten inflow streams to Lake Fryxell sampled throughout the 1990–1991 field season range from a high value of 9.7 mg C/L to a low value of 0.2 mg C/L (Figure 3). There is a marked temporal dependency with the greatest DOC concentrations occurring in the early part of the season when the streams first begin to flow. It is at this time that algal mats present in the stream channel are first wetted. As the season progresses, DOC concentrations drop steadily in all the streams, with the lowest values measured on samples collected in mid-January 1991.

The DOC concentrations in Lake Fryxell are significantly greater than those measured in the streams, increasing with depth to a maximum of 32 mg C/L at the bottom of the lake (Figure 4). The DOC profiles measured in the lake have been consistent over the course of this study. The impact of the stream inputs on Lake Fryxell are most apparent in the moat that surrounds the lake for a brief period during the austral summer. Samples collected near the mouth of Huey Creek in January 1991 had DOC concentrations of 0.8 mg C/L, substantially less than the DOC concentrations measured throughout the lake. The DOC concentrations of sediment pore waters obtained at the sediment-water interface from near the center of the lake range from 60–75 mg C/L.

General properties of humic substances

Two fractions of DOC, aquatic fulvic acid and syn-fulvic acid, were isolated from several depths in Lake Fryxell, from two of the streams entering the lake, and from the moat surrounding the lake (Table 3). Fulvic acid was a significant portion of the total DOC in the lake, ranging from 17% to 24% of the DOC at each location. This range is similar to that observed in another antarctic lake, Lake Hoare, and in antarctic coastal ponds (McKnight et al. 1991, 1994). This range of values is at the low end of expected values for temperate surface waters and is more similar to the range in marine environments [7–30% of the DOC, depending on whether the sample was from the open ocean or from a location near the shore (Thurman 1985)]. The percentage of the DOC that is fulvic acid in Lake Fryxell was found to be fairly constant with depth, despite the ten-fold range in DOC values. The DOC distribution was much different for the two streams sampled, Canada Stream and Aiken Creek, where fulvic acid comprised only 6% and 11% of the DOC, respectively.

Syn-fulvic acid represents a much smaller percentage of the DOC (2–6%) than does fulvic acid. Only limited data are currently available on the

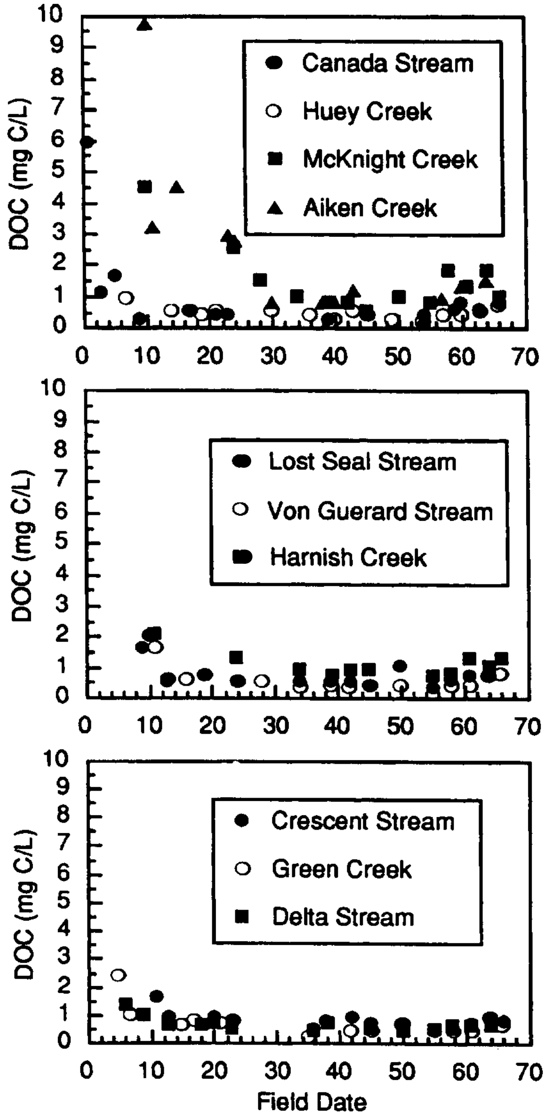

Figure 3. Temporal variation in DOC concentrations for the major melt water streams in the Lake Fryxell watershed. [Field date 1 corresponds to November 19, 1990.]

distribution of this fraction of the organic matter in other aquatic environments (Aiken et al. 1992). The percentage of syn-fulvic acid obtained from the lake is comparable to the amounts found in other aquatic samples.

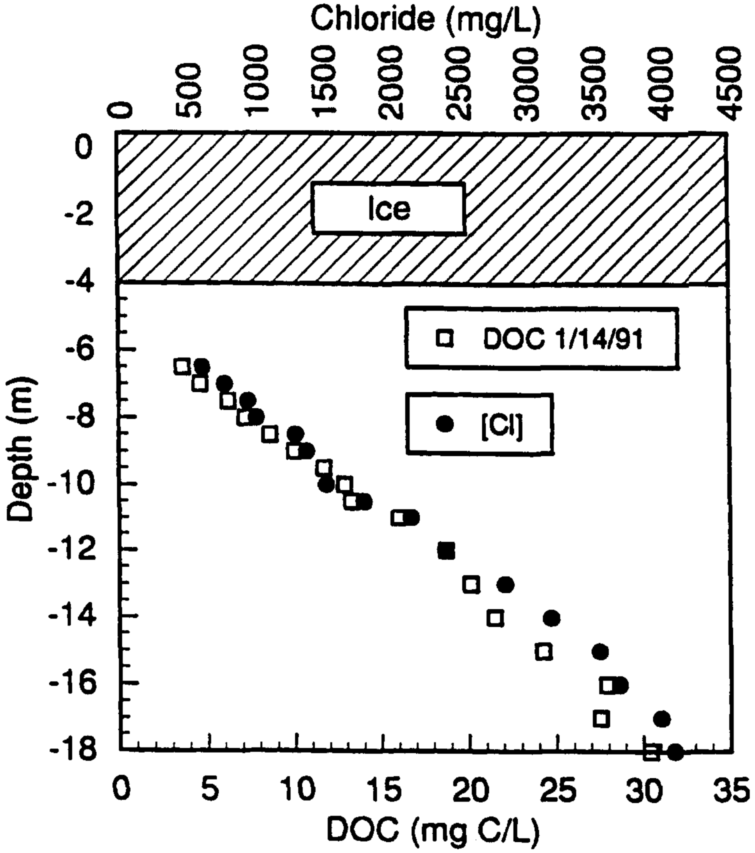

Figure 4. Dissolved organic carbon and chloride profiles for Lake Fryxell.

Table 3. Sample volumes and amounts of fulvic acid (fulvic acid) and syn-fulvic acids (syn-fulvic acid) isolated from various locations in the Lake Fryxell watershed. [Values in parentheses are percent of the DOC, nd = not determined.]

Sample site	Volume (L)	DOC (mg C/L)	Fulvic acid (grams)	Syn-fulvic acid (grams)
Lake Fryxell				
5.5 m	1588	3.7	1.917 (18%)	0.582 (5%)
7.5 m	1814	6.1	3.774 (19%)	1.311 (6%)
9 m	907	10.7	3.876 (22%)	0.416 (2%)
11 m	454	14.4	2.830 (24%)	0.71 (5%)
18 m	454	30.0	4.386 (17%)	1.135 (4%)
Moat	604	0.8	0.113 (13%)	nd
Canada Stream	1814	0.3	0.060 (6%)	nd
Aiken Creek	454	0.9	0.077 (11%)	nd

Elemental composition and molecular weight

Data for the elemental composition and molecular weight of the fulvic acid and syn-fulvic acid samples isolated from the lake, streams and moat are given in Table 4. A consistent difference in elemental composition occurs between the fulvic acid and the syn-fulvic acid isolates. The fulvic acids have lesser amounts of oxygen and nitrogen than do the corresponding syn-fulvic acids, consistent with the isolation methods employed (Aiken et al. 1992). The fulvic acids isolated from the streams have lower hydrogen contents than the fulvic acids isolated from the lake.

For the lake samples, there is systematic variation in ^{14}C and S content (Table 4, Figure 5). The ^{14}C content of the fulvic acid samples in the lake decreases with depth with a minimum value at 15m. For both the fulvic and syn-fulvic acids, S content increases with depth in the anoxic zone of the lake, although, S is a minor element of these samples based on the low S/C ratios. The greatest S contents were obtained on samples isolated from 18 m with lesser amounts obtained from the 11 m sample, just below the oxycline, and from 9 m, which is at the oxycline. Inorganic forms of sulfur (elemental S, thiosulfate, thiocyanate, sulfate, and polythionate) were found to be minor constituents of the fulvic and syn-fulvic acids. Polythionate and thiocyanate were less than 0.01% by weight for all the isolates, as were thiosulfate and sulfate for samples above the oxycline. For samples below the oxycline, the percent thiosulfate ranged from 0.2% to 0.5%, while the percent sulfate ranged from 0.1% to 1.6% by weight. Elemental sulfur was less than 0.1% by weight in all the samples analyzed.

It is possible that the high S contents for the samples isolated from sulfide rich waters are artifacts of the isolation procedures employed, resulting either from the incorporation of S into the organic matter, or from the co-isolation of inorganic S species on the resin. Francois (1987a) noted that S was incorporated into humic substances isolated from marine sediments using alkaline extraction techniques. The resin isolation methods involve elution with 0.1M NaOH; however, the contact time between the sample and the base is relatively short. Another possibility is the incorporation of S into the samples during sample processing under oxygenated conditions. The effects of storing anaerobic samples under oxic conditions on increasing S contents was studied by Francois (1987a) and found to be negligible. While co-isolation of inorganic forms of S can not be entirely ruled out, analyses of the samples for elemental S, thiosulfate, sulfate, and polythionate indicate these to be minor constituents. Polysulfides are unstable at the low pH conditions used to isolate the humic substances (LaLonde 1990) and were not analyzed for. High S contents have been reported (Francois 1987b; Ferdelman et al. 1991)

Table 4. Ash-free elemental compositions (as percents), ash contents (as percents), elemental ratios and molecular weights (MW, in daltons) data for fulvic acid (FA) and syn-fulvic acid (SFA) samples isolated from Lake Fryxell, two inflow streams and the lake moat. Standard deviations are given in parentheses [nd = not determined].

Sample	Element					Ash	Elemental Ratios				MW
	C (±0.5)	H (±0.05)	O (±0.6)	N (±0.04)	S (±0.05)	(±0.2)	H/C	O/C	N/C	S/C	(±19)
Lake Fryxell											
5.5 m SFA	49.5	5.0	38.9	4.9	1.5	0.75	1.21	0.59	0.085	0.011	
FA	54.9	5.5	34.9	3.3	1.2	2.3	1.2	0.48	0.052	0.008	468
7.5 m SFA	49.3	4.8	39.2	4.8	1.8	8.9	1.17	0.59	0.084	0.014	
FA	55.0	5.5	34.9	3.1	1.3	1.0	1.2	0.48	0.048	0.009	490
9 m SFA	51.4	5.4	36.2	4.9	2.1	13.5	1.26	0.53	0.082	0.015	
FA	55.0	5.4	35.3	2.8	1.5	1.8	1.18	0.48	0.044	0.010	483
11 m SFA	49.3	5.2	37.5	4.7	3.3	1.9	1.27	0.57	0.082	0.025	
FA	55.6	5.7	32.8	2.9	2.9	1.6	1.23	0.44	0.045	0.020	489
18 m SFA	46.5	4.9	35.5	3.8	8.9	2.8	1.26	0.57	0.070	0.072	
FA	52.4	5.3	31.7	2.4	8.0	0.1	1.21	0.45	0.039	0.057	463
Canada Stream FA	53.2	5.1	36.7	3.6	1.4	1.4	1.15	0.52	0.058	0.010	nd
Aiken Creek FA	54.1	5.2	35.9	3.1	1.7	1.5	1.15	0.50	0.049	0.012	nd
Moat FA	55.5	5.6	34.8	3.2	0.9	1.7	1.21	0.47	0.049	0.006	nd

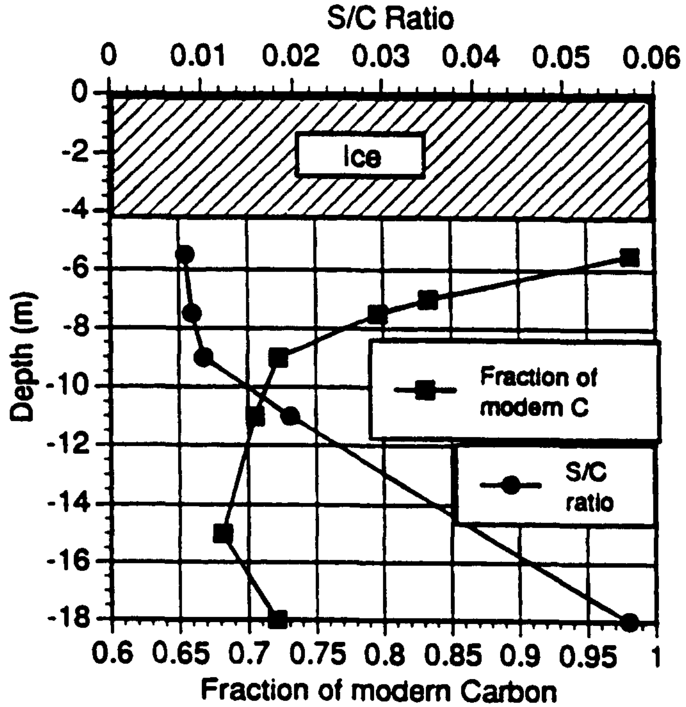

Figure 5. Depth profiles for ^{14}C age and S/C ratios for fulvic acid samples isolated from Lake Fryxell.

for samples of humic substances isolated from sediments where precautions have been taken to avoid the pitfalls noted by Francois (1987a).

Molecular weight data for each of the samples from Lake Fryxell are similar (Table 4), ranging from 463 to 490 daltons. There is no discernable trend in differences in these samples and they all lie within the analytical error of ±19 daltons of the average value of 479 daltons, suggesting that there are no differences in molecular weight of samples from the top to the bottom of the water column. The molecular weights of the antarctic samples are low compared to the range of 500–950 daltons reported by Aiken & Malcolm (1987) for fulvic acid samples isolated from a variety of aquatic systems. Molecular weight data on the samples from the streams and moat were not obtained due to insufficient sample.

^{13}C-NMR analyses

One of the most important techniques for obtaining structural information on complicated mixtures of organic compounds, such as humic substances, is

^{13}C-NMR. In recent years, there has been a dramatic increase in the use of this technique to study humic substances, and a number of review articles describing the technique and its application to environmental studies have been published (Wershaw 1985; Wershaw & Mikita 1987; Preston 1987; Steelink et al. 1990). The fact that humic substances are complex, heterogeneous mixtures limits the amount of information that can be obtained from NMR data, but this technique does provide valuable structural and functional group information.

Each ^{13}C-NMR spectrum presented here is comprised of six major bands characteristic of humic substances. General assignments (Wershaw 1985) for these major bands are as follows:

1. Aliphatic I (0–62 ppm) – primarily sp^3 hybridized carbons bonded to other carbon atoms.
2. Aliphatic II (62–90 ppm) – hetero-aliphatic carbons, primarily sp^3 hybridized carbons bonded to oxygens, including ether, alcohol, and carbohydrate carbons.
3. Acetal (90–110 ppm) – acetal and ketal carbons, and anomeric carbons of carbohydrates.
4. Aromatic (110–160 ppm) – primarily aromatic and olefinic carbons.
5. Carboxyl (160–190 ppm) – primarily sp^2 hybridized carbons bonded to oxygen, including carboxylic acids, esters and lactones.
6. Ketone (190–230 ppm) – primarily sp^2 carbons bonded to oxygen in the form of ketones and aldehydes.

In general, the broad-banded nature of the spectra presented indicate that the samples are complex organic mixtures.

Quantitative ^{13}C-NMR spectra for the fulvic acid samples isolated from 7.5 m and 18 m from Lake Fryxell are presented in Figure 6. In general, the spectra for the fulvic acid samples from all depths in the lake were found to be very similar to the spectrum for the 7.5 m sample. The exception to this similarity is the 18 m sample, which has some sharp peaks in the aliphatic I (0–62 ppm) region. The spectra all have the following characteristics:

1. Aliphatic I carbons (0–62 ppm) are more abundant than aromatic carbons, with the region representing methylene carbons ($\approx$ 20 ppm) being prominent.
2. The aromatic carbon region (110–160 ppm) is well defined with no side peaks.
3. The single, sharp carboxyl peak located at $\approx$ 180 ppm, strongly suggests that the carboxyl groups are bonded to aliphatic rather than aromatic carbons.

The largest differences in the samples are in the aliphatic I region (0–62 ppm) where deeper samples have greater amounts of aliphatic carbon than do

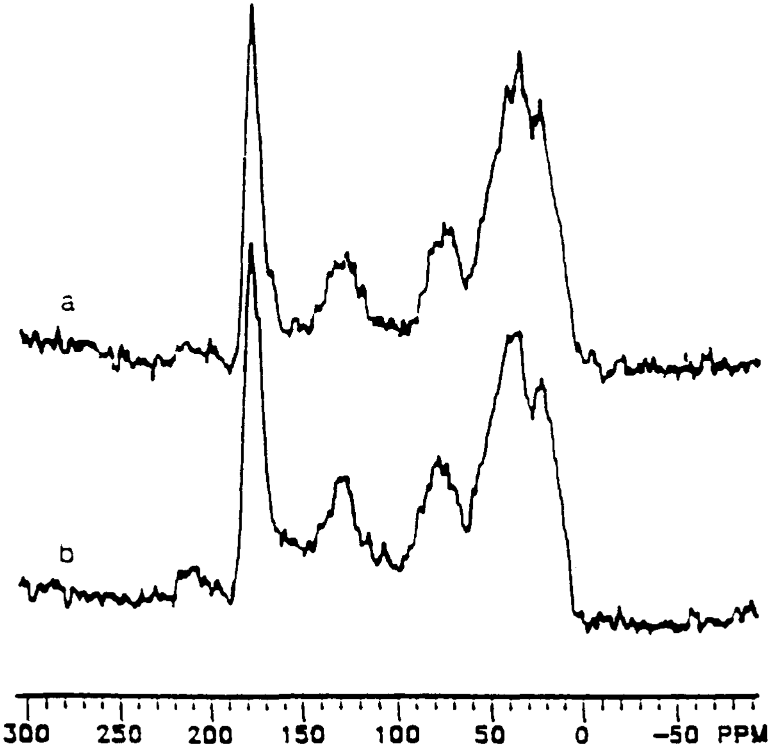

Figure 6. Quantitative ^{13}C-NMR spectra for fulvic acid samples isolated from Lake Fryxell. [18 m sample, a; 7.5 m sample, b]

samples from shallower depths (Table 5, Figure 7). These small differences are close to the value of ± 1.5% determined for the standard deviation in this region.

Nonquantitative spectra were also obtained for the Lake Fryxell 7.5 m and 18 m fulvic acid samples (Figure 8). Some qualitative information can be suppressed in ^{13}C-NMR spectra obtained under quantitative conditions (Thorn et al. 1989), and, small differences in the spectra can be accentuated by comparing the spectra collected under non-quantitative conditions. The nonquantitative spectrum of the 18 m sample has sharp peaks located at 26.2, 28.9, 37.1, and 43.3 ppm corresponding to sharp peaks in the aliphatic I region of the quantitative spectrum. These peaks are absent in the nonquantitative spectrum obtained for the 7.5 m fulvic acid sample.

NMR spectra for the synfulvic acid samples isolated from 7.5 m and 18 m are given in Figure 9. As was the case for the fulvic acid samples, the quantitative spectra for the syn-fulvic acid samples from other depths were

Table 5. Relative peak areas (in per cent) for carbon moieties in natural abundance ^{13}C-NMR spectra of fulvic acid (FA) and synfulvic acid (SFA) samples from Lake Fryxell, two inflow streams and the lake moat. Standard deviations are given in parentheses[a].

Sample	Region					
	Aliphatic-I [0–62] (±1.5)	Aliphatic-II [62–90] (±0.2)	Acetal [90–110] (±0.6)	Aromatic [110–160] (±1.2)	Carboxyl [160–190] (±0.4)	Ketone [190–230] (±1.1)
Canada Stream FA	38.2	14.4	4.3	20.8	18.5	3.7
Aiken Creek FA	41.7	13.4	3.2	20.8	17.8	3.1
Moat FA	44.6	12.1	3.9	20.1	15.4	3.9
Lake Fryxell						
5.5 m FA	46.4	14.5	4.4	15.2	19.6	0.0
7.5 m FA	47.6	12.4	3.2	13.0	20.2	3.6
9 m FA	46.9	13.0	3.7	14.4	20.3	1.7
11 m FA	50.5	11.7	2.6	12.5	19.8	2.9
18 m FA	49.9	13.5	3.5	14.0	18.2	1.0
5.5 m SFA	45.2	13.9	3.0	9.3	25.6	3.2
7.5 m SFA	44.2	13.6	3.0	9.4	26.3	3.1
11 m SFA	43.5	15.7	4.3	6.7	24.0	5.8
18 m SFA	46.2	15.3	3.8	6.4	23.1	5.1

[a] Standard deviation data were determined by triplicate analyses of the Lake Fryxell 7.5 m FA sample.

found to be similar, with the only difference occurring in the Lake Fryxell 18 m syn-fulvic acid sample. This sample contains peaks in the aliphatic I region similar to those in the 18 m fulvic acid sample. As with the 18 m fulvic acid sample, the 18 m syn-fulvic acid sample has a higher than usual S content. All the spectra are relatively simple, with sharp carboxyl peaks and the signal approaching baseline, especially in the aromatic and carboxyl regions. The syn-fulvic acid samples have less aromatic carbon, and greater amounts of aliphatic II and carboxyl carbon (Table 5).

The spectra for fulvic acid samples isolated from two inflow streams and the moat around Lake Fryxell (Figure 10) are markedly different from the lake samples. The signal-to-noise ratio for stream samples is much less than for lake samples, due to the small amount of sample available for obtaining the quantitative ^{13}C-NMR data. The integration data (Table 5, Figure 6) show that the stream and moat samples have relatively less aliphatic I and carboxyl carbon, and much greater aromatic carbon than do the lake samples. In addition, the carboxyl peak, which is narrow with no side peaks in the lake samples, is broader. The nonquantitative spectrum for the Canada

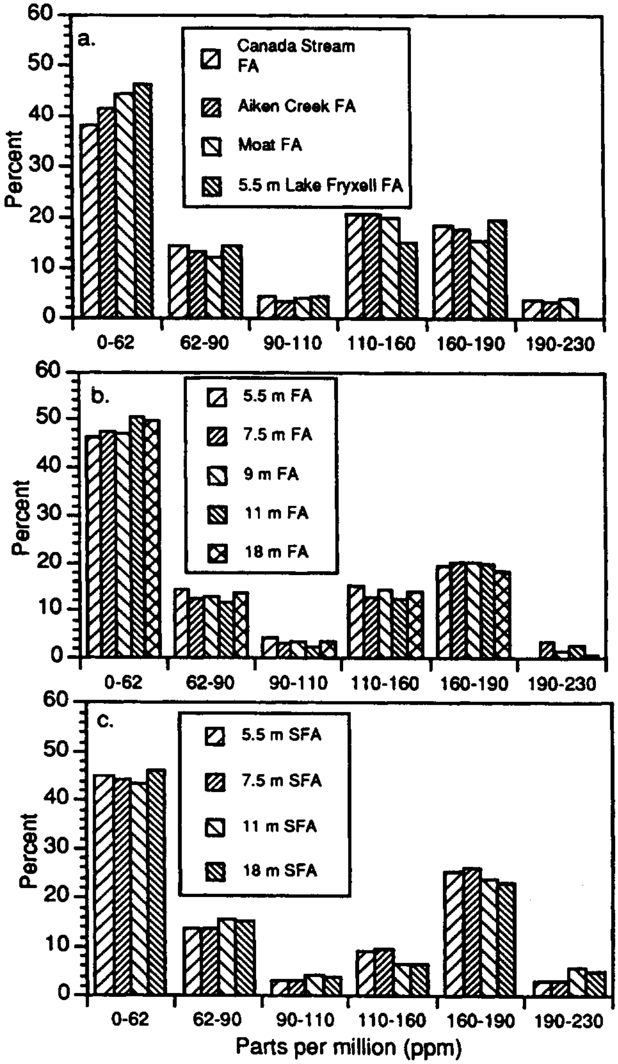

Figure 7. Bar graph comparison of the quantitative ^{13}C-NMR integration data for stream fulvic acid samples (a), lake fulvic acid samples (b), and lake syn-fulvic acid samples (c).

Stream fulvic acid shows considerably more definition than the nonquantitative spectrum for the Lake Fryxell 7.5 m fulvic acid sample (Figure 11), especially in the Aliphatic I region.

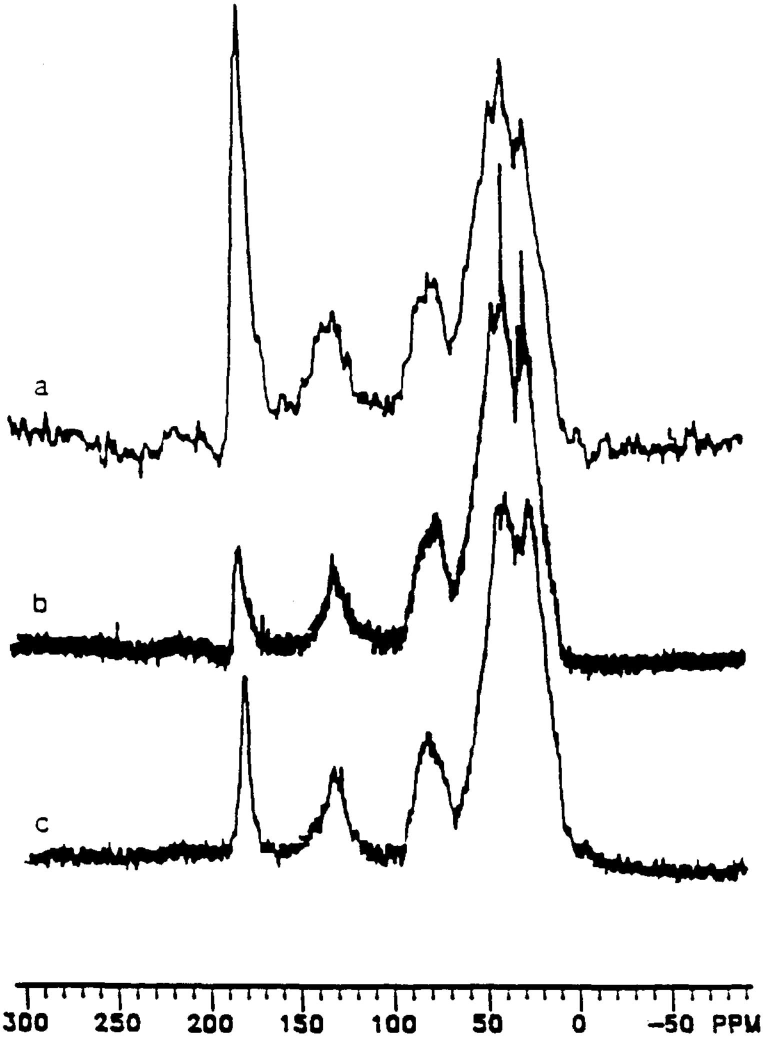

Figure 8. Quantitative and nonquantitative ^{13}C-NMR spectra of the Lake Fryxell fulvic acid samples isolated from 18 m (quantitative, a; nonquantitative, b) and 7.5 m (nonquantitative, c).

Discussion

Stream DOC

The DOC values reported for the streams in the lower Taylor Valley are low compared to DOC data obtained in streams located in temperate and especially Arctic environments. Spitzy & Leenheer (1991) reported that DOC

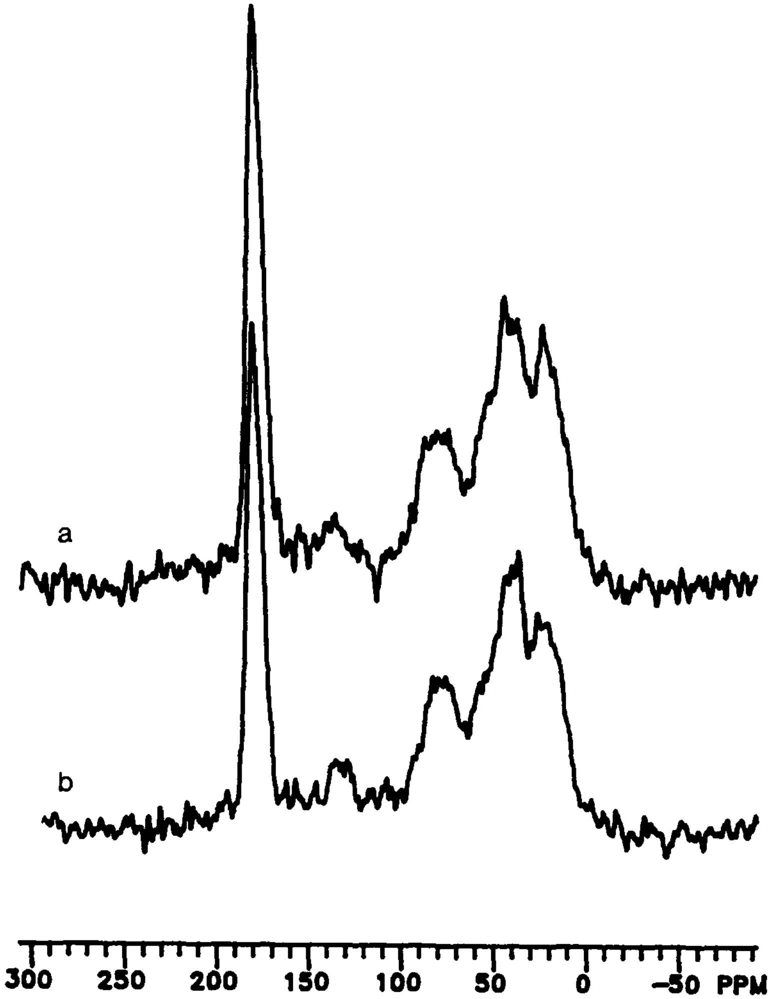

Figure 9. Quantitative ^{13}C-NMR spectra for syn-fulvic acid samples isolated from Lake Fryxell. [18 m sample, a; 7.5 m sample, b]

concentrations generally range from less than 1 mg C/L in alpine streams to more than 20 mg C/L for rivers draining swamps and wetlands, and that there is a strong soil and plant organic matter source for riverine DOC. The values reported here are similar to those determined on streams and rivers in semi-arid environments (1 mg C/L, Meybeck 1988), which is consistent with the fact that soils in the McMurdo Dry Valleys region are considered to be of the "desert" type (Ugolini 1970).

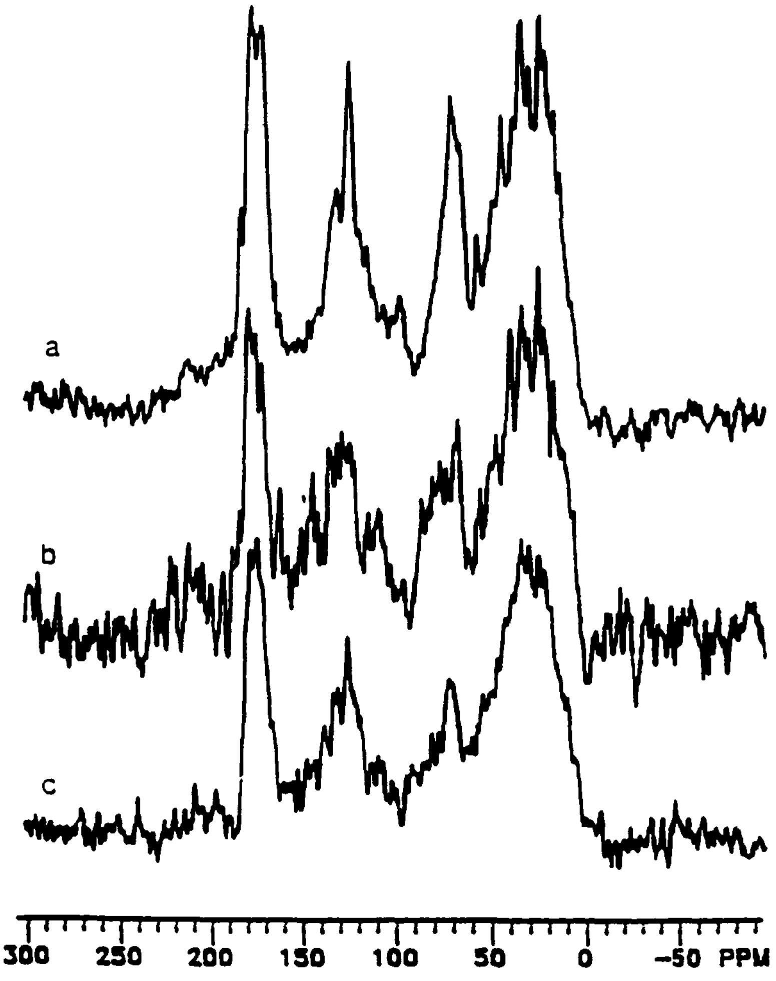

Figure 10. Quantitative ^{13}C-NMR spectra for fulvic acid samples isolated from inflow streams Canada Stream (a), Aiken Creek (b) and the moat (c) around Lake Fryxell.

The organic matter in the streams is due to leaching of the algal and bacterial mats and mosses in the stream channel and riparian zone. DOC concentrations in the streams appear to be influenced by both the abundance of the stream biota and the contact time between the stream water and the organically enriched zones associated with abundant biota (Table 2). All the stream water in Aiken Creek, which has the greatest DOC, passes through Many Glaciers Pond, the largest pond in the watershed of the lake. In addition, the stream has a shallow gradient from the Commonwealth Glacier to the lake, increasing the contact time with the biota in the channel. The stream with the

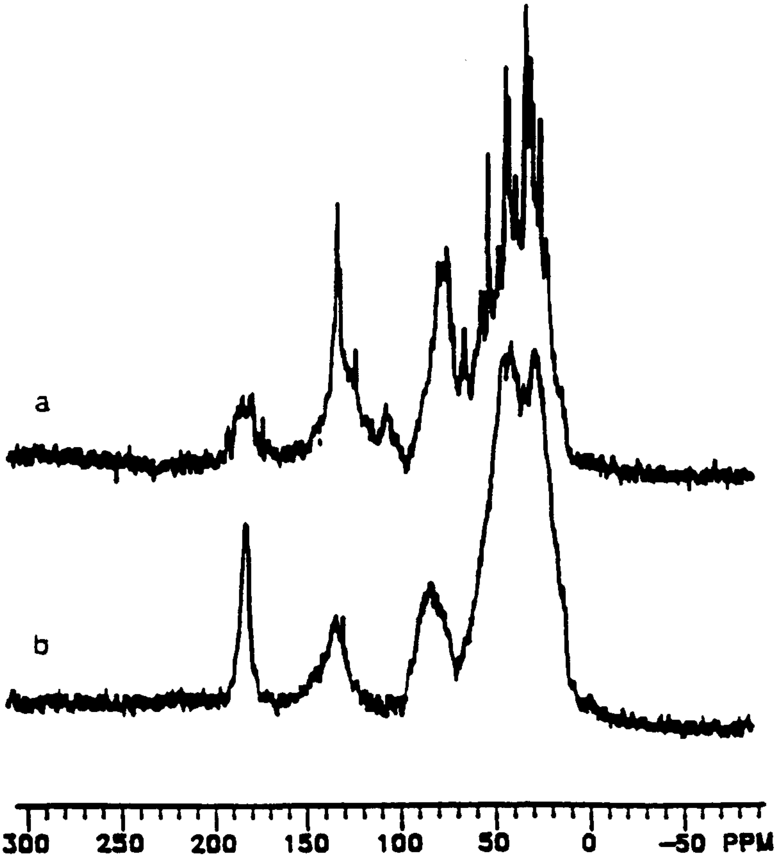

Figure 11. Nonquantitative ^{13}C-NMR spectra of the fulvic acid samples isolated from Canada Stream (a) and Lake Fryxell 7.5 m (b).

next highest DOC, McKnight Creek, also has a shallow gradient and abundant biota in the stream channel flowing from the Commonwealth Glacier. Of the three streams with the lowest DOC concentrations, Canada Stream and Green Creek are relatively short and have the highest flow rates; Huey Creek is a longer, steep gradient stream with sparse biota because of high sediment load.

It is likely that many of the compounds comprising the DOC of the streams are more biologically labile than in the samples from the lake. The fraction of modern carbon of the moat fulvic acid sample was found to be 0.997, indicating that this sample is predominantly modern carbon. There are indications that the stream fulvic acid samples have undergone less humification than the lake samples. Compared to the lake fulvic acid samples the ^{13}C-NMR spectra for the stream and moat samples have more sharp lines. This is especially apparent in the Aliphatic I region of the nonquantitative spectrum that shows considerably more definition than for the lake samples. Finally, the fulvic acid samples isolated from Canada Stream and Aiken Creek are a lower fraction of the total DOC in the streams than for the samples isolated from the lake and from other lotic systems.

The moat surrounding the lake is composed of inflowing stream water and melted lake ice from around the edges of the lake, with some mixing of lake water as the moat expands. Recent evidence (Miller & Aiken 1996) suggests that much of the new water that enters the lake is rapidly recycled through the upper water column and the overlying ice. Based on inorganic composition during mid-summer when the moat is most extensive, the density of the stream and moat water would allow it to sink to a depth of only 5m in the lake (Miller & Aiken 1996). Much of this water, therefore, moves from the moat towards the center of the lake both under and through the lake ice. The ice not only undergoes freezing at the bottom and ablation at the surface, it also exhibits a high degree of porosity near the surface during periods in the austral summer that may be related to the input of stream water through the moat. Limited data on DOC concentrations within the ice itself (0.5–2.7 mg C/L) indicate that it is not free of organic matter, as might be expected from simple freezing out of organic solutes at the bottom of the ice cover. Rather, the DOC load in the ice is similar to the inflow streams and the moat.

The DOC concentrations of the glacial melt water inflows and the moat are less than DOC concentrations in the most dilute lake water immediately below the ice cover, which may be the result of exclusion of solutes from water freezing to the bottom of the lake ice. The relative amounts of fulvic acid in the lake samples and the stream and moat samples are significantly different. The composition of the fulvic acid from the moat appears to be similar to the 5.5 m fulvic acid sample isolated from the lake with respect to elemental content and fraction of modern carbon. The fraction of modern carbon for the fulvic acid sample from the 5.5 m depth collected near the center of the lake was found to be 0.982 compared to 0.997 for the moat. This pattern is similar to that reported for tritium in the water of Lake Fryxell (Miller & Aiken 1996) and is consistent with the movement of moat water out towards the center of the lake.

Lake DOC

Within Lake Fryxell, the depth profile for DOC is generally similar to the depth profiles for specific conductance and major inorganic species such as chloride, a conservative constituent (Table 1, Figure 4), and quite different from the depth profiles for algal (Figure 2) and bacterial abundance (Smith & Howes 1990). Profiles for the most prominent conservative species (Cl^-,

Na^+, and K^+) are consistent with a lake history involving evaporation of the lake at some point in the past with subsequent concentration of dissolved constituents in the bottom waters. This event was followed by the input of less dense fresh water on top of denser bottom waters. Chemical constituents then diffused from the bottom of the lake into the surface waters, establishing both a concentration gradient and a density gradient in the lake. This phenomenon has been proposed for many of the lakes in both the Wright and Taylor Valleys (Matsubaya et al. 1979; Wilson 1981; Lawrence & Hendy 1985). Application of Fick's second law of diffusion to the DOC profile in Lake Fryxell resulted in an excellent fit with a coefficient of determination of 0.987 (Aiken et al. 1991). These results suggest that diffusion of organic matter from the sediments or bottom waters of the lake is a major process controlling organic matter in Lake Fryxell. The gradient in DOC that exists between the sediment interstitial water ($\approx$ 75 mg C/L) and the bottom water ($\approx$ 30 mg C/L) of the lake is sufficient to drive the diffusive transport of dissolved organic matter into the water column.

The shape of the DOC profile suggests that the *bulk* DOC concentrations throughout the water column are little affected by differences in the microbial processes occurring in water column. The fulvic and syn-fulvic acid samples isolated from various depths in Lake Fryxell vary little in elemental composition with the exception of S content. Although decreases in both the O/C and N/C ratios are noted with depth, the changes are small and it is difficult to determine their significance. Likewise, the ^{13}C-NMR analyses indicate few structural differences between the samples for each fraction. It is particularly significant that no compositional differences were noted for the samples collected from 7.5 m, the zone of highest algal activity, indicating that excretion of organic compounds from viable algae does not exert a strong influence on either the distribution or nature of the fulvic acid.

The amounts of sulfur present in the samples isolated from the anoxic zone of the lake are significantly greater than for similar samples from other anoxic environments. The predominant mechanisms cited for the generation of organic-S compounds in sediments are the reactions of H_2S and elemental S generated by sulfate reducing bacteria with organic matter (Vairavamurthy & Mopper 1987; Sinninghe Damste et al. 1989a). According to Sinninghe Damste et al. (1989b), the formation of organic-S compounds is second only to iron as a sink for S in the sediments. The concentration of H_2S must exceed the amount of Fe present in the system for this reaction to occur. The conditions in the bottom waters in Lake Fryxell are well suited for reactions of this type. First there are high concentrations of biologically generated HS^- (Howes & Smith 1990) in the anoxic bottom waters of the lake that greatly exceed the concentrations of iron (Green et al. 1989). Second, the pool of dissolved organic matter is greatest in the surficial sediments of the lake with DOC concentrations at the sediment-water interface ranging from 60–75 mg C/L. Microbial processes in the surficial sediments, the zone of greatest activity and biomass, are likely resulting in the formation of this organic matter.

The depth profile for S/C ratio in the fulvic acid fraction (Figure 5) suggests that, in addition to simple mixing resulting from the diffusion of S-rich organic matter from the bottom of the lake into overlying water containing organic matter with lower S content, other processes may be occurring. This profile, with a break near the oxycline, is more similar in shape to species such as NH_4^+ than to the nearly linear profile for DOC or Cl^- profile above 15 m. In addition, ^{13}C-NMR analyses may also indicate losses of organic-S moieties. The regions where sp^3 hybridized carbon bonded to S are expected to appear are 10–30 ppm for H_3C-S-, 25–45 ppm for -H_2C-S-, and 40–55 ppm for HC-S-. Sharp lines appear in all three of these regions in the nonquantitative spectrum for the 18 m fulvic acid sample, but are absent in the 7.5 m sample (Figure 8). Losses of organic-S could result from interactions with metals such as Fe and Mn. In many cases, the binding constants for organic-S ligands with metals are equivalent to or exceed those of inorganic ligands (Martell & Smith 1977). Green et al. (1989) have shown that while the reducing conditions of the bottom waters of Lake Fryxell favor the reductive dissolution of Fe and Mn, the concentrations of these species in the water column are controlled by the formation of insoluble sulfide phases. In addition, Harnish et al. (1991) reported the presence of particulate and colloidal iron throughout the water column below 10 m depth. Selective interactions of S-rich organic compounds with the particulate and colloidal iron could result in decreases of this component of the DOC with increasing distance from the sediments.

Another process leading to losses of organic-S could be metabolism of S containing moieties to compounds not comprised by the humic substance isolates. The metabolism of compounds such as dimethylsulfoniopropionate and 3-mercaptopropionate to more volatile S compounds such as dimethyl sulfide (Kiene & Taylor 1988) are examples of such a transformation. A similar process could result in losses of S from the fulvic acid. Although we present no direct evidence for the loss of organic-S by either mechanism, both processes are conceivable.

The lake DOC profile also appears to be little affected by the behavior of nonconservative species such as Ca^{2+} and Mg^{2+}. Lawrence & Hendy (1985) demonstrated that the lake is supersaturated with respect to calcite in the euphotic zone (5–9.5 m depth) due to the photosynthetic removal of CO_2 from the water column. Calcite was found to be absent in the water column above 8 m and present below 8 m (Lawrence & Hendy 1985). Interactions with precipitating calcite could possibly result in the selective removal of higher molecular weight components of the fulvic acid (Aiken & Malcolm 1987) and of aromatic components of the fulvic acid based on the strength of interactions between phenolic compounds and calcite (Reynolds 1978). Neither a decrease in molecular weight, nor an increase in the relative amount of aliphatic I to aromatic carbon was noted for the samples from the lake going from the bottom to the top of the water column.

^{14}C content

The distribution of ^{14}C in the fulvic acid samples from various depths in the lake is consistent with the diffusion of fulvic acid containing old C into the overlying waters of the lake containing recent C brought into the lake by the glacial melt water streams (Figure 5). Duplicate samples for the determination of field errors were only available for the 18m fulvic acid sample (0.704, 0.736). Analytical errors for all the measurements were determined to be ± 0.006. The fraction of carbon of the fulvic acids indicate that old C is a major component of the fulvic acid in this system. Converting the ^{14}C data into ages indicates that the fulvic acid samples throughout the water column range from a maximum of about 3000 years at a depth of 15 m to recent just under the ice. Interestingly, the fraction of modern carbon of the fulvic acid isolated from 18m is greater than that from 15 m suggesting that more recent organic matter is mixing with the old material in the bottom waters of the lake.

There is evidence for three possible sources of the DOC presently diffusing from the bottom waters of the lake. This material may be old, following a geochemical pathway that parallels the evaporative lake hypothesis used to explain the distribution of inorganic species in the lake (Matsubaya et al. 1979). In this scenario, the DOC profile results from diffusion of relict organic matter from a concentrated brine into overlying, more recently introduced, fresh water.

The second scenario is that the DOC is generated through ongoing biological activity in the sediments. The ^{14}C age of the fulvic acid isolated from 18 m is younger than the sample isolated from 15 m suggesting that younger organic matter is mixing with the old organic matter in the bottom waters of the lake. In addition, the ^{13}C-NMR analyses indicated that the 18 m sample had a slightly greater aliphatic carbon content with a number of sharp peaks in the aliphatic C region than the 7.5 m sample. Howes & Smith (1990) noted $SO_4^=$ reducing activity at the sediment water interface and in the upper few centimeters of the sediment. Several constituents, such as CH_4, NH_4^+, and HS^-, that are generated in the anaerobic degradation of organic matter in the sediments are present in the anoxic waters of the lake. The profiles for these species in the water column are consistent with diffusion from the sediments (Howes & Smith 1990; Smith et al. 1993), suggesting that DOC could be produced in the sediments.

The third scenario involves the movement of moat water to the bottom of the lake. Miller & Aiken (1996) noted the presence of tritium not only in the upper water column, but also in the bottom waters of Lake Fryxell. The presence of tritium in the bottom waters suggests that a component of this water was recently at the surface. It was hypothesized that, as the moat freezes during the fall season, dissolved constituents are excluded from the ice forming a more concentrated, denser solution that can sink as density currents to the bottom of the lake. In this process, some of the organic matter present in the moat would eventually be transported to the bottom of the lake resulting in a larger fraction of modern carbon in the mixed sample.

It is interesting to note that the average age of 3000 years for the two fulvic acid samples collected below 11m depth is similar to the estimated age of the lake of 2999 years determined by Green et al. (1988) using the chloride budget of the lake and inflow streams. The interpretation of these ages with respect to the history of the lake is quite different, however. By necessity, the chloride estimate suffers from the assumption that the input of chloride to the lake has been relatively constant over the history of the lake. Recent evidence from ice cores collected in the Asgard Range above Lake Fryxell indicates that there has been a slight increase in the chloride input from seasalt over the last 150 years. There is greater uncertainty associated with annual inputs for the discharge of melt water streams which can vary daily and annually (Chinn 1993). The average annual increase in lake elevation since 1973 for Lake Fryxell is 105 mm (Chinn 1993), indicating that the lake is in a period of active growth. Given these factors, the chloride age is likely to be an underestimate. For the purpose of interpreting the age of the lake using the fulvic acid data, we have assumed that significant mixing of old and younger organic matter occurred before the establishment of the present day diffusion cell, 600–1000 years ago, and that organic material older than 3000 years contributes to the ^{14}C age of the fulvic acid.

Summary and conclusions

Three sources of the DOC were noted in the Fryxell basin system. First, the active leaching of biomass in the stream channels of the glacial melt water streams results in the generation of relatively labile DOC. This material is transported to the lake and comprises a large amount of the DOC in the moat and upper waters of the lake. The streams were found to have relatively low DOC concentrations that may be related to the amount of instream biological activity. Second, the degradation of organic matter in the sediments and bottom waters of the lake results in the generation of organic matter that subsequently diffuses into the water column contributing to the large amount of DOC in the bottom waters of the lake. Third, relict organic matter present in the evaporated ancestral lake is diffusing into the overlying freshwater as the lake continues to increase in volume. The older DOC appears to be a major source of DOC in the water column of the present day lake.

Despite the physical, chemical, and biological differences within the lake, the composition of DOC with respect to the fulvic and syn-fulvic acid fractions was essentially constant. With the exception of sulfur content, the fulvic acid and syn-fulvic acid samples from the lake differed little in elemental content and molecular weight. Spectroscopic analyses also indicate that there are few structural differences between the samples, although subtle differences in the NMR spectra indicate that the samples of fulvic and syn-fulvic acids from the bottom waters of the lake have more sharp lines in the aliphatic carbon region. The fulvic acids in the streams and the moat were a lower fraction of the DOC than the lake, and appeared to have undergone less humification than the lake samples. The fulvic acid sample obtained from the moat was the most similar to the sample isolated from just below the ice (5.5 m) at the center of the lake, reflecting the addition of stream fulvic acid to the DOC of the upper waters of the lake. The trend in ^{14}C content for the lake and moat samples is consistent with the diffusion of older organic matter associated with the bottom waters of the lake into overlying melt waters containing recent organic matter.

The large sulfur contents for samples isolated from the bottom waters of the lake are the highest values reported for aquatic humic substances. The depth profile for the organic-S in the isolates from Lake Fryxell suggests that some of the S associated with the fulvic acid is labile due to sensitivity to changes in the redox conditions in the water column. The conditions present at the sediment-water interface are ideal for the generation of these compounds, and the stability of the water column combined with changes in the redox conditions make Lake Fryxell an ideal environment for studying the dynamics of organic-S geochemistry.

Acknowledgements

We gratefully acknowledge N. Andrews C. Bowles, M. Brooks, J. Duff, E. Furlong, L. Miller, R. Smith, and P. von Guerard for assistance in the field and laboratory and for helpful discussions. We thank B. Lyons, J. Leenheer, L. Miller, and R. Smith for valuable comments on the manuscript. This research was supported by the National Research Program of the U.S. Geological Survey and by the Division of Polar Programs, National Science Foundation through grant NSF8613607. We also thank VXE-6, U.S. Navy, for the excellent logistical support provided to us.

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