Sources of dissolved and particulate organic material in Loch Vale Watershed, Rocky Mountain National Park, Colorado, USA

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Abstract. The sources of both dissolved organic carbon (DOC) and particulate organic carbon (POC) to an alpine (Sky Pond) and a subalpine lake (The Loch) in Rocky Mountain National Park were explored for four years. The importance of both autochthonous and allochthonous sources of organic matter differ, not only between alpine and subalpine locations, but also seasonally. Overall, autochthonous sources dominate the organic carbon of the alpine lake, while allochthonous sources are a more significant source of organic carbon to the subalpine lake. In the alpine lake, Sky Pond, POC makes up greater than one third of the total organic matter content of the water column, and is related to phytoplankton abundance. Dissolved organic carbon is a product of within-lake activity in Sky Pond except during spring snowmelt and early summer (May—July), when stable carbon isotope ratios suggest a terrestrial source. In the subalpine lake, The Loch, DOC is a much more important constituent of water column organic material than POC, comprising greater than 90% of the spring snowmelt organic matter, and greater than 75% of the organic matter over the rest of the year. Stable carbon isotope ratios and a very strong relation of DOC with soluble $Al_{(tot)}$ indicate DOC concentrations are almost entirely related to flushing of soil water from the surrounding watershed during spring snowmelt. Stable carbon isotope ratios indicate that, for both lakes, phytoplankton is an important source of DOC in the winter, while terrestrial material of plant or microbial origin contributes DOC during snowmelt and summer.

Introduction

For most temperate lakes, two main sources of dissolved and particulate organic carbon can be identified: (1) soils and plants of the surrounding watershed, and (2) in-situ growth and decomposition of algae and macrophytes (Jordan et al. 1975; McKnight et al. 1985; Cole et al. 1989; LaZerte & Szalados 1982; LaZerte 1983; McDowell & Likens 1988;

David & Vance 1991). A third somewhat more ambiguous source of organic carbon is lake sediments, which may recycle allochthonously or autochthonously produced organic carbon back to the water column through upwelling or diffusion (Aiken et al. 1991; Ishiwatari 1985). Organic material can interact with major cations, metals, and trace anions by complexation and sorption, and can affect acid-base chemistry, so knowledge of organic carbon sources and sinks is important to understanding aquatic biogeochemical processes (Steinberg & Meunster 1985).

We explored the sources of dissolved and particulate organic carbon in an alpine and a subalpine lake in Rocky Mountain National Park. Alpine Sky Pond is located in a steep cirque basin surrounded on three sides by bedrock, a small glacier, and talus fields (Fig. 1). Spring snowmelt, which melts off three basin walls, is the major source of water to the lake (Baron 1992; Baron & Bricker 1987). Sky Pond has no clearly defined inlets. Sparse patches of alpine tundra are located above the lake. Phytoplankton are 5—10 times more abundant in Sky Pond than in The Loch. Phytoplankton are seasonally variable, and range between 20,000—30,000 cells ml^{-1} (mostly green algae and diatoms) in May and June to 180,000 cells ml^{-1} (primarily *Oscillatoria limnetica*) in late July and August (McKnight et al. 1990).
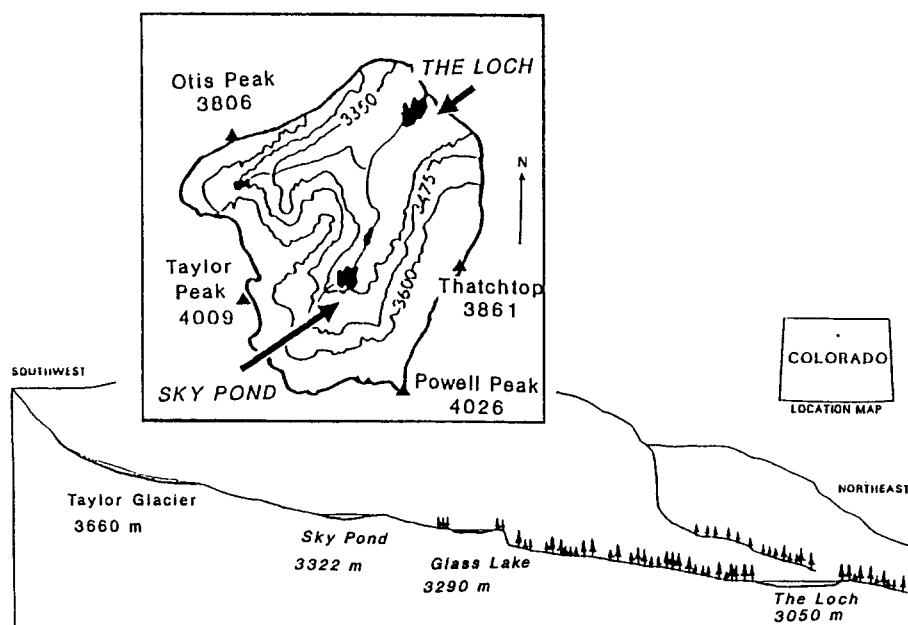

Fig. 1. Cross-sectional map of Loch Vale Watershed in Rocky Mountain National Park, Colorado. Inset shows watershed boundary (thick outer line) and contour lines (m).

In contrast, The Loch is below treeline and bordered, in part, by spruce-fir forest and wet sedge meadows. As with Sky Pond, snowmelt is the dominant hydrologic event for this lake, but most of the Loch's drainage basin (which includes Sky Pond) lies upstream and flow is channelized into The Loch by Icy Brook (Fig. 1). Phytoplankton taxa and numbers vary between seasons and years in The Loch. Diatoms and green algae range between 1,000 and 10,000 cells ml^{-1} in May, June and July, while blue-green algae range from less than 1,000 to 20,000 in August, September and October (McKnight et al. 1990).

We hypothesized the differences in alpine versus subalpine vegetation, hydrologic flowpaths, and phytoplankton abundances would cause within-lake processes to provide most of the organic carbon to Sky Pond, while organic carbon inputs to The Loch would come from mainly terrestrial sources. Possible removal mechanisms for organic material as related to our interpretation of sources were also explored.

Site description

Alpine Sky Pond and The subalpine Loch are located in Loch Vale Watershed, Rocky Mountain National Park, Colorado, USA (Fig. 1). The 660 ha Loch Vale Watershed is a steeply incised glacial valley ranging from 4000 m at the Continental Divide to 3050 m at the outlet of The Loch.

Sixty five to 80% of total annual precipitation (110 cm) is snow; the remainder is supplied by summer thunderstorms. The hydrologic year for both lakes in Loch Vale Watershed has distinct spring snowmelt, summer, and winter periods (Baron & Bricker 1987; Baron 1992). Spring snow-melt, between April 15 and July 14, carries up to 80% of total annual discharge (Fig. 2). Declining flow in summer (July 15—September 30) may be influenced by individual thunderstorms depending on antecedent soil moisture. Winter, October 1—April 14, is a period of minimal discharge. The lakes are ice-covered during this period and there is little streamflow. Sky Pond and The Loch have very short retention times: 39 and 6 days during snowmelt, and 105 and 16 days during the rest of the year for Sky Pond and The Loch, respectively (Baron 1992).

The 204 ha Sky Pond watershed lies at the headwaters of Loch Vale Watershed. Areas of soil accumulation comprise less than 2% of the total land area above Sky Pond. Those soils that do occur are immature, poorly developed Cryochrepts and Cryumbrepts (Walthall 1985). Sources of water above Sky Pond are diffuse, and most water enters Sky Pond as shallow groundwater passing under talus into the littoral zone.
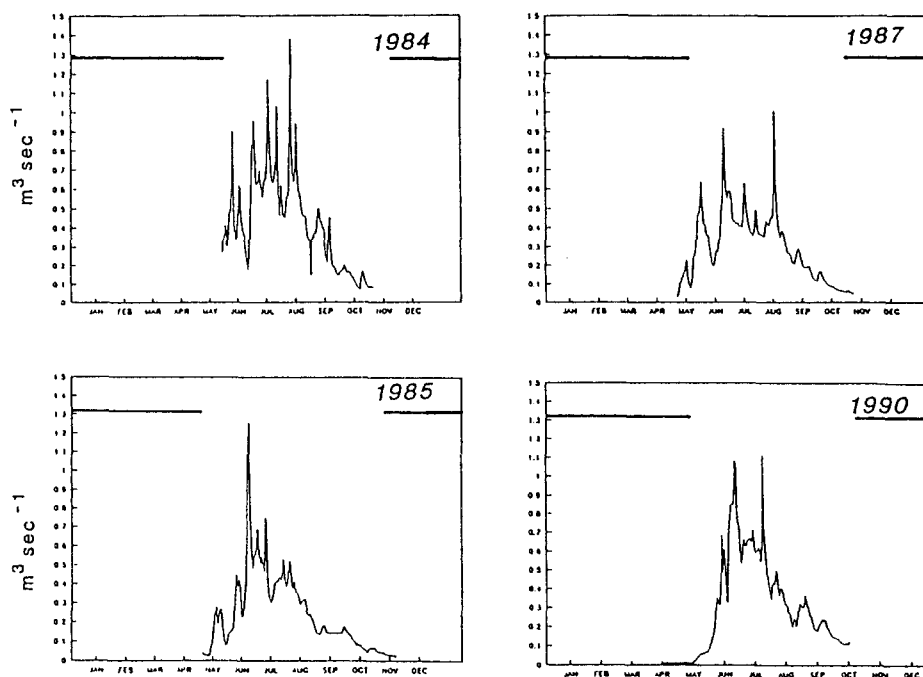
Fig. 2. Hydrographs measured at The Loch outlet for 1984, 1985, 1987 and 1990. Units are m^3 sec^{-1}. Bars indicate periods of ice cover on the lakes.

A much greater proportion of water entering The Loch is channelized, since 90% of the drainage area of The Loch lies upstream from rather than adjacent to the lake. Forested and meadow soils above and adjacent to The Loch are classified as Cryoboralfs, fluvially-deposited Cryaquents, or organic Cryohemists (Walthall 1985).

Both lakes have low concentrations of organic and inorganic solutes with specific conductances ranging from 5 to 25 μS cm^{-1} (Table 1). There are no aquatic macrophytes in these lakes.

Methods

Samples used in this study were collected in 1984, 1985, 1987 and 1990. Hydrologically, these years had 150%, 95%, 106%, and 98%, respectively, of the long-term (1961—1980) average precipitation (Colorado Climate Center records, 1984—1990). Discrete samples of surface, middle, and bottom water were collected from the deepest part of Sky Pond and The Loch using either a peristaltic pump or a van Dorn sampler. Lake inlet and outlet waters were collected as grab samples.

Table 1. Chemical and morphometric characteristics of the study lakes.

Parameter	Sky Pond				The Loch			
	Median	Min	Max	n	Median	Min	Max	n
Ca^{2+}	1.20	0.40	2.70	107	1.40	0.24	3.00	257
Mg^{2+}	0.18	0.06	2.10	107	0.22	0.10	0.50	257
Na^+	0.37	0.18	0.61	107	0.44	0.23	1.20	257
K^+	0.15	0.07	0.37	107	0.20	0.02	0.47	258
NH_4^+	0.02	0.00	0.30	136	0.02	0.00	0.15	293
NO_3^-	0.93	0.04	2.61	115	1.11	0.09	1.99	264
SO_4^{2-}	1.50	0.72	3.20	105	1.68	0.93	3.80	257
Cl^-	0.18	0.09	0.33	106	0.22	0.06	0.75	258
SiO_2	1.10	0.10	3.00	107	1.90	0.70	4.00	257
DOC	0.90	0.40	1.60	48	1.60	0.10	4.90	117
$Fe_{(tot)}(\mu g\,L^{-1})$	22.00	3.00	590.00	128	41.00	3.00	400.00	279
$Al_{(tot)}(\mu g\,L^{-1})$	23.00	1.00	220.00	107	55.00	0.00	180.00	257
$ANC(\mu eq\,L^{-1})$	30.27	9.99	133.27	104	52.00	9.90	161.40	249
pH	6.50	5.80	7.50	133	6.40	5.70	6.80	290
$cond(\mu S\,cm^{-1})$	11.00	5.90	20.10	135	13.00	5.00	131.0	289
Elev. (m)	3,320				3,050			
Area (ha)	3.0				5.0			
Volume (m^3)	122,000				61,000			
Ave. depth (m)	4.5				1.5			
Max. depth (m)	7.3				4.7			
Watershed/lake area	68				132			

Unless noted, units are mg L^{-1}. Samples are from all sample locations, including lake inlets, outlets, surface middle and bottom depths for the years 1984, 1985, 1987, and 1990.

Chlorophyll *a* concentrations were determined in 1984 and 1985 by filtration through Whatman GF/C 25 mm filters, extraction in acetone and analysis using a Turner Designs model-10 series fluorometer. Values were corrected for phaeopigments using the method described by Strickland & Parsons (1972).

Two liter samples for inorganic chemical analyses (see Table 1 for species analyzed) were filtered through 0.4-μm Nuclepore filters into acid-washed 250-mL plastic bottles within 5 h of collection. Inorganic analyses were conducted at the USGS Central Analytical Laboratory according to methods of Fishman & Friedman (1985).

Samples for dissolved and particulate organic carbon were collected in precombusted glass bottles. Samples were separated into dissolved and particulate components by filtration through precombusted Whatman GF/C filters. Particulate organic carbon was operationally defined as that

which was retained on the GF/C filter. A 100 mL aliquot (filtered either on site in 1984 and 1985, or within 5 h at the laboratory in 1987 and 1990) was stored in precombusted glass bottles for DOC analysis. Dissolved (in 1984, 1985, and 1987) and particulate organic carbon (in 1984 and 1985 only) were determined using a Dohrmann Organic Carbon Analyzer at the USGS Central Analytical Laboratory. Dissolved organic carbon samples in 1990 were analyzed by Huffman Laboratories, Golden, CO, by sealed ampoule persulfate oxidation (Coulometrics, Inc., Wheat Ridge, CO).

Additional 3 L samples were collected in precombusted glass bottles. A 60 mL aliquot was analyzed for glucose according to methods of Cavari & Phelps (1977). Hydrophobic acids were isolated from the remainder using XAD-8 resin according to methods of Thurman & Malcolm (1981). Hydrophobic acids isolated by this method are predominantly fulvic and humic acids. In Colorado mountain streams and in other rivers of the United States, humic acid is a small fraction ($< 10\%$) of the hydrophobic acids (McKnight et al., unpub.; Malcolm 1985). Therefore, we refer to the hydrophobic acids as fulvic acids for the remainder of this paper. The fulvic acid fraction of DOC was determined by the difference in total DOC between the influent and effluent of the XAD-8 resin column.

The stable carbon isotopic ratio, $\delta^{13}C$, was determined on the isolated fulvic acid by mass spectrometry at Global Geochemistry Corporation, Canoga Park, CA. $\delta^{13}C$ values are defined as the parts per thousand (or per mil) difference of the $^{13}C/^{12}C$ ratio from a standard reference material, Peedee Belemnite, a marine limestone (Craig 1957).

Precision of the measurements was estimated by collection and analysis of co-located field duplicates. Differences in inorganic and DOC concentrations between samples were generally independent of concentration, so overall precision was assessed by calculating pooled standard deviations across all sample pairs. For 24 paired DOC measurements (detection limit 0.1 mg L^{-1}), the pooled standard deviation was 0.22 mg L^{-1}. Six paired POC samples yielded a standard deviation of 0.08 mg L^{-1} (detection limit 0.1 mg L^{-1}). Chlorophyll a precision was analyzed on 14 pairs of samples and had a standard deviation of 0.35 μg L^{-1} (detection limit 0.1 μg L^{-1}). Aluminum (ICP, Fishman & Friedman 1985) precision analyses on 40 paired samples since 1983 had a standard deviation of 4.1 μg L^{-1} (Denning 1987). Two duplicate $\delta^{13}C$ analyses were within 1% of each other, and the values of the six NBS-22 standards analyzed with our samples ranged -29.70 to -29.92 against the known value of -29.80.

Sediment was collected from the center of Sky Pond on October 8, 1988 with an Ekman dredge. The sample was kept chilled and then centrifuged at 3000 rpm for 20 minutes. The supernatant was filtered through a 0.45 μm Millipore filter and analyzed for DOC by sealed

ampoule persulfate oxidation (Coulometrics, Inc., Wheat Ridge, CO). Dried sediment was analyzed for organic carbon content by Huffman Laboratories, Golden, CO.

Results

Maximum concentrations of DOC occurred in the springtime during snowmelt for all years in both The Loch and Sky Pond, and this pattern was most pronounced in The Loch (Fig. 3a shows 1985 as an example of this pattern; all other years were similar). POC was highly variable, with
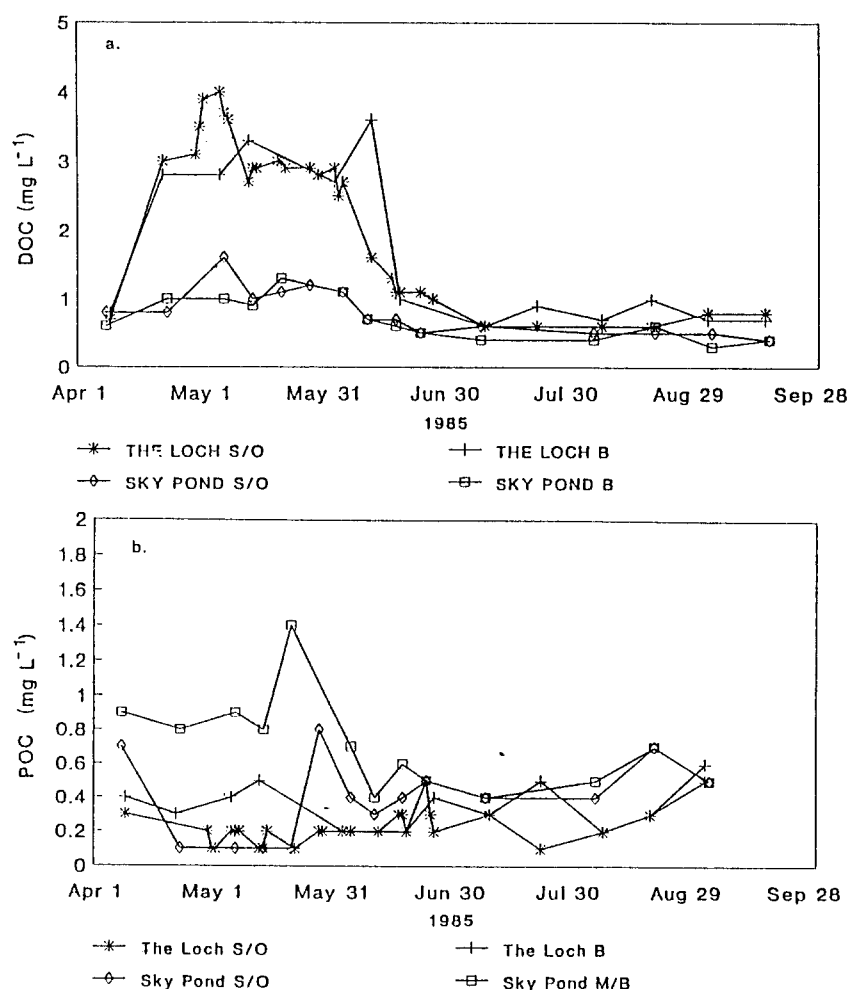

Fig. 3. Concentrations of (a) DOC and (b) POC over time in 1985 for The Loch and Sky Pond surface and outlet water (S/O) and middle and/or bottom water (M/B).

no clear temporal trend (Fig. 3b shows 1985; 1984 also did not display any temporal pattern). Average DOC was 2—3 times higher in the subalpine lake than in the alpine lake during spring snowmelt (Table 2). Concentrations were also higher for The Loch than for Sky Pond during the rest of the year, but the differences were not as pronounced. Particulate organic carbon concentrations were slightly higher in Sky Pond than in The Loch, except in May of 1985. Fifty percent or greater of the organic matter content of Sky Pond was POC, while POC comprised less than one fourth of the organic matter content in the water column of The Loch.

Glucose concentrations, measured in 1990, were very low overall, but they were markedly higher in Sky Pond than in The Loch (Table 3). No trend was observed in glucose concentrations in The Loch over time, but glucose concentrations increased in Sky Pond between mid-April and mid-July 1990.

Fulvic acids made up 14%—32% of the DOC in 1990 under the ice in The Loch. This percentage increased during snowmelt, and appeared to decrease in July (Table 3). The stable carbon isotopic ratios for the fulvic acid from The Loch surface and from The Loch outlet during the winter and snowmelt period were very similar, ranging between −26.6 and −24.9 between March 13 and May 29, 1990 (Table 3). The sample from The Loch bottom waters under ice in April, 1990 was lighter, with a value of nearly −30.0, while the sample from July was slightly heavier than the others, with a value of −24.1.

A less pronounced pattern was seen for fulvic acids in Sky Pond. The

Table 2. Mean concentrations (mg L^{-1}) of dissolved organic carbon (DOC) and particulate organic carbon (POC) in Sky Pond and The Loch by season during the years 1984, 1985, 1987, and 1990. Spring snowmelt (SPRING) is the period April 15—July 14 of each year, while the rest of the year (OTHER) is the period July 15—April 14.

	Analyte	Season	n	Mean	Std. Error
Sky Pond	DOC	Spring	19	0.9	0.09
		Other	23	0.9	0.07
	POC	Spring	30	0.5	0.05
		Other	20	0.5	0.03
The Loch	DOC	Spring	62	2.8	0.15
		Other	55	1.3	0.07
	POC	Spring	21	0.3	0.05
		Other	32	0.3	0.02

Data in this table exclude samples from lake inlets or outlets.

Table 3. Detailed dissolved organic carbon data from Sky Pond and The Loch from 1990.

Site	Date	DOC (mg L^{-1})	Glucose (μg L^{-1})	Fulvic Acid (%)	δ^{13}C
Sky S	April 17	0.98	10	30	−30.83
Sky B	April 17	1.07	15	26	−33.13
Sky O	May 15	1.10	15	45	−27.37
Sky O	June 1	1.20	20	25	−26.77
Sky O	June 12	1.00	15	30	−23.02
Sky O	July 17	0.80	20	50	−24.54
Loch S	March 13	1.97	5	32	−26.62
Loch S	April 10	1.66	<2	18	−26.41
Loch B	April 10	1.68	<2	14	−29.97
Loch O	May 1	3.46	10	48	−25.61 (−25.55)
Loch O	May 29	3.70	<2	46	−25.02 (−24.88)
Loch O	June 12	3.60	<2	69	−25.81
Loch O	July 17	1.00	3	40	−24.14

Surface (S) and bottom (B) water samples were taken from the ice-covered lakes and represent water 0.5 m below the water surface and 0.5 m above the lake bottom, respectively. All other samples were taken from the lake outlets (O). Duplicate analyses were conducted for δ^{13}C on May 1 and May 29; these values are shown in parentheses. The percentage of the total DOC that was fulvic acid percent is listed as Fulvic Acid (%).

Table 4. Correlation coefficients for chemical parameters from Sky Pond and The Loch.

Variables	Sky Pond		The Loch	
	n	r^2	n	r^2
DOC vs POC	42	0.064	40	0.105
DOC vs Al$_{(tot)}$ (spring)	19	0.001	63	0.845**
DOC vs Al$_{(tot)}$ (rest-of-year)	22	0.019	54	0.000
POC vs chlorophyll a (spring)	29	0.593**	21	0.010
POC vs chlorophyll a (rest-of-year)	20	0.555**	32	0.548**

Two stars indicate significance at the 99% confidence interval.

fulvic acid ranged 25—50% between late winter and early summer. Stable carbon isotopic ratios of the fulvic acid from Sky Pond were light in samples collected under the ice (−30.8 and −33.1 for surface and bottom, respectively), and got progressively heavier through the snowmelt season and into the summer. The July δ^{13}C value from Sky Pond (−24.5) was similar to the July δ^{13}C value from The Loch.
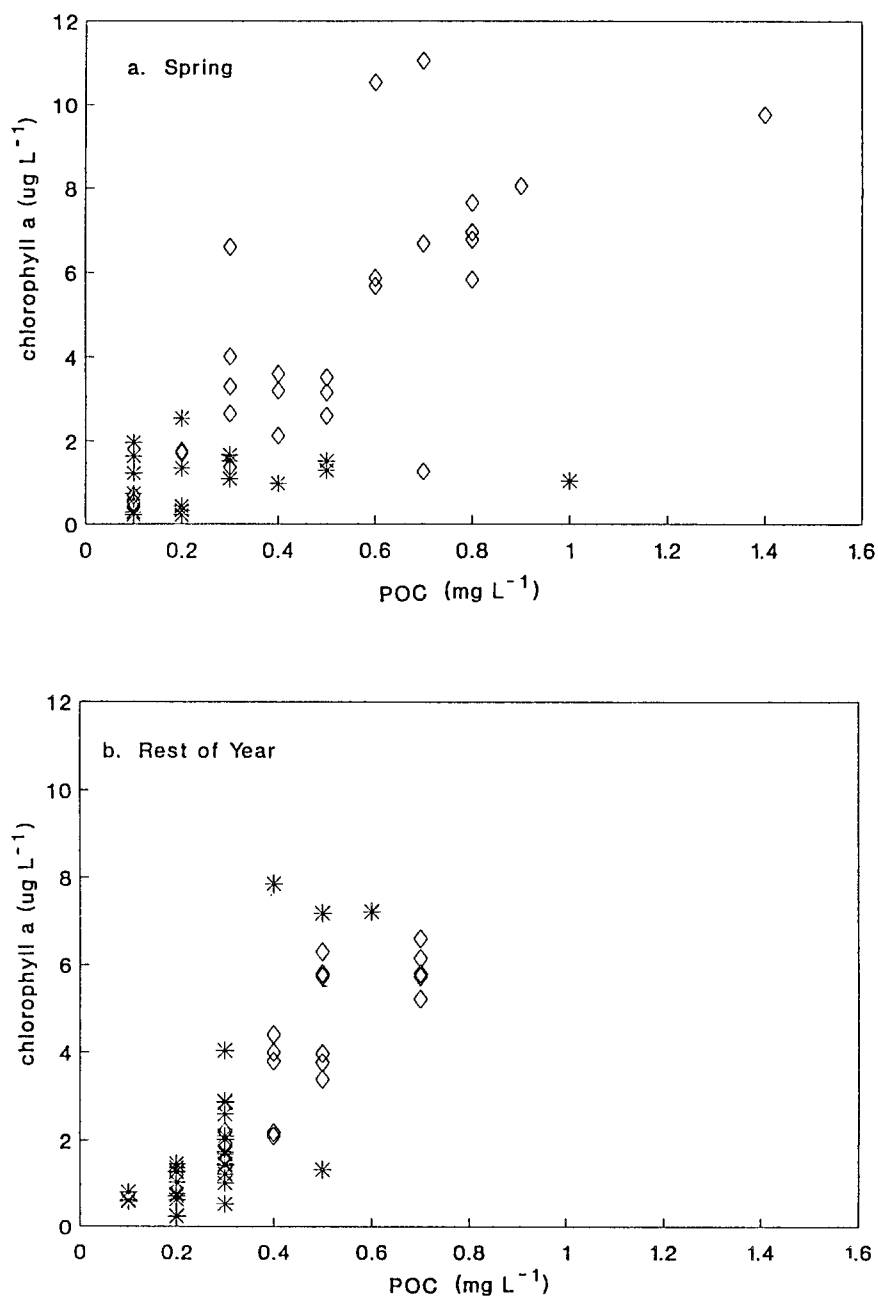
Fig. 4. Particulate organic carbon (POC) vs. chlorophyll *a* concentrations during (*a*) the spring snowmelt period, April 15—July 14; and (*b*) the rest of the water year, July 15—April 14 for Sky Pond (diamonds) and The Loch (stars).
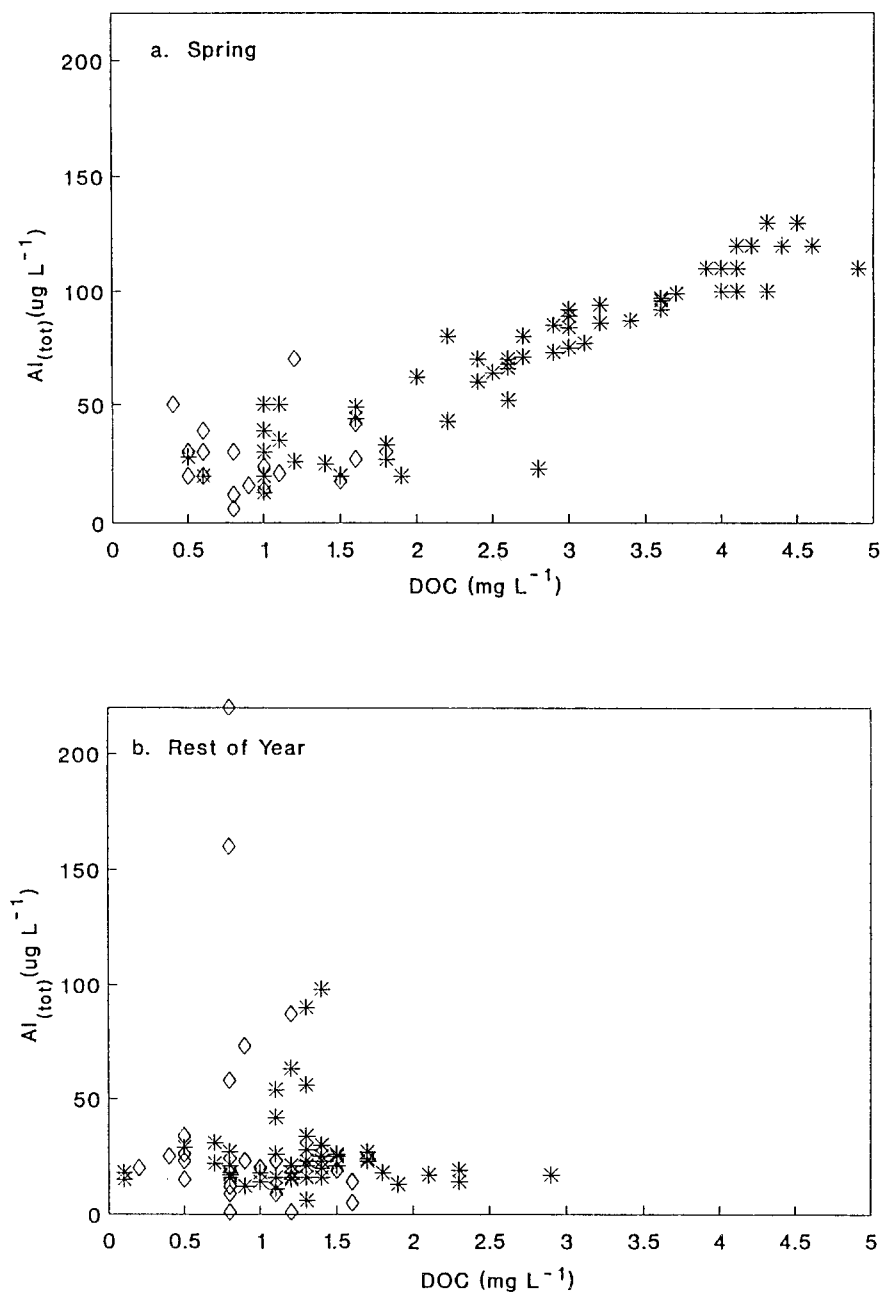
Fig. 5. Dissolved organic carbon (DOC) vs Al$_{(tot)}$ during (*a*) the spring snowmelt period, April 15—July 14; and (*b*) the rest of the water year, July 15—April 14 for Sky Pond (diamonds) and The Loch (stars).

Total soluble aluminum ($Al_{(tot)}$) was employed as an indicator for allochthonous organic carbon produced in soils, and chlorophyll a was used as a surrogate for algal standing crop (Table 4). Correlation coefficients were used to determine the association of DOC with $Al_{(tot)}$ and POC with chlorophyll a. The association of DOC with POC was also evaluated. No relation was found between DOC and chlorophyll a, or between DOC and POC. Similarly, no relation was found between POC and $Al_{(tot)}$ for either lake at any time of the year.

Chlorophyll a was strongly correlated with POC in Sky Pond all year long in 1984 and 1985, with $r^2 = 0.59$ during snowmelt (Table 4, Fig. 4a) and $r^2 = 0.56$ during the rest of the year (Table 4, Fig. 4b). The Loch POC was correlated with chlorophyll a only after the end of the melt period ($r^2 = 0.55$, Table 4, Fig. 4a, b).

Springtime correlations of DOC with $Al_{(tot)}$ were very strong for all four study years in The Loch ($r^2 = 0.85$, Table 4, Fig. 5a). The two were not correlated later in the year (Table 4, Fig. 5b). There was no correlation between DOC and $Al_{(tot)}$ for Sky Pond at any time of the year (Table 4, Figs 5a, b).

Discussion

The concentration of organic carbon in water over time is dictated by sources in the watershed and removal mechanisms. Possible sources for DOC and POC in Sky Pond and The Loch are:
(1) leaf and litter inputs from terrestrial vegetation;
(2) precipitation;
(3) soil leachates;
(4) lake sediments; and
(5) phytoplankton.
Ways by which DOC and POC can be lost from Sky Pond and The Loch include flushing downstream, settling and burial in sediments, and microbial consumption leading to respiration or transport up the food chain. At the top of the food chain are naturally-reproducing populations of trout; these long-lived fish sequester carbon and are periodically harvested by recreational fishing.

Sources of organic carbon

Leaf and litter

Many studies have shown the importance of terrestrial leaves and litter to the overall energy and carbon budgets of streams and lakes (Fisher &

Likens 1973; Cummins et al. 1983). We ruled this out as an important source for organic carbon to Loch Vale Watershed lakes because:

(1) Sky Pond is surrounded by rock material with sparse amounts of tundra, so there is little vegetation present to be transported to the lake;

(2) The Loch, and Icy Brook above it, have more of a potential vegetation source, but overhanging vegetation is not very prevalent (C. M. Tate personal communication; shading, for example, is not a factor influencing stream algal productivity), and total forest cover for Loch Vale Watershed is only 6%;

(3) elevational gradients are very steep in Loch Vale Watershed and debris dams are rare, so transport of allochthonous coarse material out of the drainage occurs rapidly; and

(4) the lakes are ice-covered more than 50% of each year, reducing the opportunity for litter input (Baron 1992; Spaulding, 1991).

Precipitation

We did not measure organic material in precipitation in this study, but Miller et al. (1989) found formate and acetate to contribute 0.03—0.05 mg C L^{-1} in two summer precipitation events at Mt. Werner, Colorado ($\sim$ 100 km NW of Loch Vale Watershed). Formate and acetate contributed 0.04 mg C L^{-1} to winter snow in an alpine lake basin in California (volume-weighted mean concentrations; Williams & Melack 1991). There will be additional DOC components in precipitation other than formate and acetate, so these measures cannot be construed as complete. Organic anions comprise at most 1 μeq L^{-1} (approx. 0.1 mg fulvic acid carbon L^{-1}) of average wet deposition based upon charge balance of major ions (Baron 1992). Since the major constituents of naturally occurring organic compounds are negatively charged, precipitation could contribute 10—20% of dissolved organic material to the study lakes (Thurman 1985; David & Vance 1991).

Soils

Soil leachates are major sources of organic material to many temperate lake ecosystems (Cole et al. 1984; McDowell & Likens 1988; Schiff et al. 1990; David & Vance 1991). The strong relation between DOC and $Al_{(tot)}$ suggests soils are the major source of DOC to The Loch. In acidic (pH range 3.5—5.0) mineral soils such as are found in the forested area around The Loch the exchange complex that controls soil solution composition is dominated by aluminum species (Reuss & Johnson 1986). Walthall

(1985) indicated that hydrolysis species in Loch Vale soils are $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3^0$, but suggested the bulk of the aluminum was tied up in organo-aluminum complexes. Organo-aluminum complexes form rapidly in soils (Planckey & Patterson 1987; Mulder et al. 1989) and persist in surface waters after flushing from the soil (Driscoll 1985; Cozzarelli et al. 1987). In Loch Vale Watershed, forest soil lysimeters had high early spring concentrations of all dissolved constituents, including DOC and $Al_{(tot)}$ (Arthur 1990). The high concentrations from the lysimeters corresponded closely in time with the highest lakewater concentrations of the year in The Loch. $Al_{(tot)}$ concentrations of $100-150$ μg L^{-1} are too high to be inorganic at pH 6.0 (Drever 1988). Concentrations of first soil, and then surface water decreased rapidly during the early stages of snowmelt, in response to replacement with snowmelt water (Mast 1989; Denning et al. 1991).

The surface and outlet waters of The Loch had fulvic acid $\delta^{13}C$ values ranging -24.14 to -26.62 (Table 3). Soil gaseous CO_2 $\delta^{13}C$ values collected from one forested and two alpine soils above The Loch in September, 1989, were -17.85, -17.60, and -18.80, respectively (M.A. Mast, pers. commun.). Other stable carbon isotopic ratios for terrestrially derived organic carbon from temperate ecosystems have been reported between -24 and -27 (Degens 1969; Rau 1980; LaZerte 1983; Schiff et al. 1990). LaZerte (1983) found that phytoplankton organic material typically has lighter organic carbon, ranging from -30 and -45, as has also been reported by Deevey et al. (1963) and Fry & Sherr (1984).

Fulvic acids in The Loch were less than a third of the total DOC ($14\%-32\%$) in late winter, when DOC was less than 2.0 mg L^{-1}. With the onset of snowmelt DOC concentrations increased and the percentage that was fulvic acids increased to nearly 70%. During this period DOC was strongly statistically associated with $Al_{(tot)}$ (Table 4). As the importance of snowmelt to lake dynamics declined in July, the proportion of fulvic acids also declined in The Loch DOC. David & Vance (1991) used a comparable XAD-8 method to measure organic acids in lakes and streams of Maine and determined that the average percentage of all fulvic acid ranged between 38% and 61%. While the winter fulvic acid values from The Loch are lower than any reported by these authors, the snowmelt and early summer (July 17) samples are similar. In the Harp Lake Watershed, Ontario, lakewater fulvic acids were similar (46% to 55%) at both summer low flow and spring high flow (Schiff et al. 1990). A seasonal difference was observed in the percentage of DOC that was fulvic acid in streams and wetlands above Harp Lake, with April values of 52% or lower, and August values 60% or greater. This pattern is the opposite of what we observed. It suggests that high flows in Harp Lake dilute existing concen-

trations of organic carbon, and during low flow there is much more interaction of surface and ground waters as compared with The Loch.

Both DOC and $Al_{(tot)}$ concentration were low in Sky Pond. The lack of a soil mantle surrounding Sky Pond and no correlation between DOC and $Al_{(tot)}$ in the lake water at any time of year rule out the possibility that soils are a major allochthonous source of organic matter. However, as the fulvic acid proportion of DOC increased during spring snowmelt (May to July 1990), samples from the outlet of Sky Pond had $\delta^{13}C$ values between −23 and −27. One explanation for these observations is that a terrestrial source of organic carbon exists above Sky Pond, and this organic matter is disjunct from mineral sources of aluminum. There are some soil pockets surrounding the outlet to Sky Pond and above the lake. These consist of organic layers up to 24 cm thick resting abruptly on granite and gneiss boulders (Walthall 1985). If decomposition products of these soils include organic matter but not $Al_{(tot)}$, then flushing of these products by snowmelt or summer thunderstorms could contribute DOC to Sky Pond.

Lake sediments and phytoplankton

An alternative explanation, which has not been explored by us, for the heavier $\delta^{13}C$ ratios observed in Sky Pond fulvic acids after snowmelt is that decomposition within the lake or its sediments preferentially consumes (and respires) lighter carbon fractions. This would result in $\delta^{13}C$ ratios that resemble those of terrestrially-derived DOC, but are, instead, a product of within-lake processes. This explanation is contrary to data presented by Schiff et al. (1990) for parts of the Harp Lake Watershed. These authors found stable carbon isotopic ratios for a beaverpond and the hypolimnion and upper sediments of Harp Lake, areas where one would expect rapid decomposition, were lighter, not heavier, than other waters that were sampled. This explanation is also contrary to other data we collected, presented below.

The fulvic acid $\delta^{13}C$ values from surface and bottom water samples of Sky Pond and bottom water samples from The Loch were very light in April, 1990. These values, −30.8, −33.1, and −30.0, respectively, are similar to $\delta^{13}C$ values reported by LaZerte (1983) from mid-lake sediment cores and phytoplankton from Lake Memphremagog in Quebec. The phytoplankton in Lake Memphremagog was dominated by diatoms and cyanobacteria. LaZerte (1983) concluded the major source of organic material to sediments in mid-lake locations (as opposed to more littoral and thus terrestrially influenced locations) was phytoplankton. Autochthonous organic matter is also well-represented in the sediments of Mirror Lake, New Hampshire (Likens & Moeller 1985), Lake Haruna, Japan

(Ishiwatari 1985), and is a postulated source for organic material in Harp Lake (Schiff et al. 1990). Based upon the fulvic acid $\delta^{13}C$ values we observed, phytoplankton in the water column or decomposition of phytoplankton in the sediments are the major sources of winter DOC in Sky Pond. The light $\delta^{13}C$ value from The Loch bottom water fulvic acids on April 10 also suggests a phytoplankton contribution to DOC in the subalpine lake in late winter. These observations are in keeping with findings of Ishiwatari (1985), who concluded that most humic substances in freshwater lake sediments originated from aquatic organisms, primarily phytoplankton.

Because there was no strong relation between chlorophyll a and DOC for either Sky Pond or The Loch during 1984 and 1985, we postulate phytoplankton remains cycle first through the sediments before diffusing or flushing DOC back into the water column. There is a bloom of blue-green algae each fall in Sky Pond, and a mid-winter and spring bloom under the ice of diatoms and green algae (McKnight et al. 1988; Spaulding 1991). Phytoplankton, mostly *Asterionella formosa*, are abundant in The Loch in the winter under the ice (Spaulding 1991). The low volume of inflow or outflow in the winter minimizes circulation. These circumstances favor deposition of algal material in lake sediments rather than removal downstream. In alpine Sky Pond, we separated interstitial sediment water from solids; the solid portion had 3.5% organic carbon. The interstitial water DOC concentration was 5.3 mg C L^{-1}, significantly greater than the median lake water DOC concentration of 0.9 mg L^{-1} (Table 1). During spring snowmelt, most of the water input to Sky Pond comes from shallow groundwater systems discharging to the lake through littoral zone sediments. The contribution of groundwater to The Loch is unknown. Upwelling from the sediments could cause flushing of high DOC sediment interstitial water and resuspension of particulate organic material into the water column. This has been observed in other studies (Wrigley & Horne 1975), and this might be responsible for input of DOC to the overlying water column. A similar process was used to explain DOC concentrations in the metalimnion and at the sediment-water interface in Lake Schöhsee, Germany, and throughout the water column of Lake Fryxell, Antarctica (Steinberg & Meunster 1985; Aiken et al. 1991).

It is possible that an organo-aluminum complex forms in lake sediments, and diffuses or is transported to the water column via upwelling. If so, this invalidates the argument presented earlier that strong correlation between DOC and $Al_{(tot)}$ represents a soil source for DOC. However, both lakes should exhibit similarly strong relations of these solutes, since $Al_{(tot)}$ and organic carbon are well represented in Rocky Mountain lake sediments (Baron et al. 1986). Since this was not observed, we think it more

likely that soil leachates are the source of the organo-aluminum complex which influences The Loch, but not Sky Pond.

The strong relation betewen chlorophyll *a* concentrations and POC supports the idea that phytoplankton constitute an important direct source of organic matter in Sky Pond throughout the year, and in The Loch after snowmelt. Chlorophyll *a* concentrations closely followed the dynamics observed in phytoplankton biomass. For example, the 1985 late summer peak in chlorophyll *a* corresponded with a bloom of *Oscillatoria limnetica* (McKnight et al. 1988). Also, the greater chlorophyll *a* and POC concentrations at depth under the ice in April—May, 1985 in Sky Pond were matched by an abundant population of the green alga *Nephrocytium limneticum* (McKnight et al. 1988). Ratios of chlorophyll *a*: POC ranged between 0.01 and 0.001 and were less than expected (0.01—0.06) should all the POC be derived from phytoplankton (Parsons et al. 1961; Strickland et al. 1969). Additional sources for POC could include resuspended particulate organic material from the sediments caused by upwelling of groundwater into littoral sediments, turbulence from snowmelt, or allochthonous inputs.

The relationship between DOC and phytoplankton was never apparent in Loch Vale Watershed lakes, although in many lakes between 5% and 70% of net primary production is released into the water as DOC (Jordan & Likens 1975; Nalewajko & Schindler 1976; Wiebe & Smith 1977). There was, however, an increase in glucose concentrations in Sky Pond in June and July 1990. Since this simple sugar is rapidly consumed in the water column, its presence implies either a die-off of the winter-time, under-ice algae, which is consistent with algal dyanmics, or a decrease in microorganisms which consume glucose, or both.

Removal mechanisms for organic carbon

While removal mechanisms within lakes can include physical, geochemical and biological processes, they are dominated by physical processes, especially snowmelt, in the Loch Vale Watershed. Of the 8160 kg DOC effluxed from Loch Vale Watershed in water year 1990 (89/10/01—90/9/30), 6480 kg were associated with the spring snowmelt period (90/4/15—90/7/14) (Baron, unpub. data).

In order for other non-hydrologic DOC or POC removal pocesses to have a significant effect, the associated rates of turnover of DOC or POC cannot be very much slower than the lake turnover rates. For DOC, the potential non-hydrologic removal processes are microbial uptake, sorption onto settling particles, and photolysis. Potentially important non-hydro-

logic POC removal processes are grazing and settling and burial in lake sediments.

In a summary of studies of several temperate lakes, bacterial respiration accounted for 10—50% of total C losses (Jordan et al. 1985). The organic compounds comprising DOC vary in their susceptibility to microbial uptake, with fulvic acid much less readily assimilated than glucose, for example. Microbial uptake could potentially influence the differences in glucose concentration between Sky Pond and The Loch, and thus shift the percent of the DOC that was fulvic acid. If the differences in glucose concentration was determined mainly by microbial uptake, the greater glucose concentration would have occurred in the lake with the shortest retention times, The Loch. However, higher glucose concentrations were found in Sky Pond.

The importance of DOC sorption onto oxide and clay surfaces of particles is dependent upon the relative concentrations of DOC and such particles. Suspended materials are not abundant in Loch Vale Watershed lakes, and are comprised to some extent of phytoplankton. Given the rapid hydrologic flushing, DOC sorption is unlikely to be a significant process.

Photolytic reactions can be important in degrading dissolving organic substances (Steinberg & Muenster 1985; Leenheer 1991). However, the rapid flushing rates in these lakes would limit the extent of a photolytic effect. Also, photolysis is not likely to directly affect the DOC characteristics upon which our interpretations are based. For example, photolysis appears to cause a decrease in the aromatic carbon content of fulvic acid but not a major decrease in fulvic acid concentration (McKnight et al. 1988).

The potential effect of grazing and settling on POC can be estimated from knowledge of phytoplankton dynamics in the lakes (McKnight et al. 1990; Spaulding 1991). During snowmelt an *Asterionella formosa* diatom bloom occurs, which indicates the phytoplankton are growing faster than the flushing rate as well as faster than the grazing and settling rates. At the end of snowmelt the die-off of *A. formosa* appears to be caused by chytrid parasites and rotifer grazing. In the late summer, when flushing rates are lower than during snowmelt, a filamentous cyanobacteria, *Oscillatoria limnetica* is abundant. Buoyancy regulation by *O. limnetica* and possibly grazing will influence POC loss. In the winter under ice retention times are greatest, and considerable fluctuations in algal abundance occur. Grazing and settling are most likely to be significant in removing POC during the winter (Spaulding 1990).

Conclusions

The results of our study support the hypothesis that soils provide the major inputs of organic matter to the subalpine lake. The strong relation of $Al_{(tot)}$ to DOC, which coincided with the flushing of soil water during the spring snowmelt period, suggests that soil water provides an important, albeit seasonal, allochthonous input of organic matter to sulalpine lakes. Statistically, DOC was strongly correlated ($r^2 = 0.845$) with dissolved $Al_{(tot)}$ during spring snowmelt in The Loch. This is consistent with stable carbon isotopic values for fulvic acid, which were representative of terrestrially-derived plant or microbial material. During the spring snowmelt, fulvic acid made up most (69%) of the DOC found in The Loch. The absence of any correlation between DOC and $Al_{(tot)}$ in Sky Pond during snowmelt also adds support to our hypothesis that the source of DOC to The Loch during the snowmelt period was soils.

In The Loch, POC showed a strong correlation with changes in chlorophyll a concentration only after snowmelt, suggesting an autochthonous source for POC in summer and fall. Elevated POC concentrations and very light $\delta^{13}C$ values of DOC present in the bottom waters of The Loch in late winter might originate from suspension or diffusion of organic material from lake sediments.

Suspended organic carbon was a major component of the Sky Pond organic carbon pool, and strongly correlated with chlorophyll a, suggesting autochthonous production. We hypothesize wintertime DOC was supplied by resuspension of autochthonously-produced organic matter from lake sediments. Summertime DOC had fulvic acid $\delta^{13}C$ values indicative of a terrestrial source, possibly flushed in from organic tundra soils as a result of late snowmelt or thunderstorms.

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Note

The use of trade or firm names in this document is for identification purposes only and does not constitute endorsement by the National Park Service or the Geological Survey.

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