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Colored dissolved organic matter and dissolved organic carbon exclusion from lake ice: Implications for irradiance transmission and carbon cycling

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Abstract

Thick ice cover is a feature of cold-temperate, polar, and alpine lakes and rivers throughout much of the year. Our observations from Canadian lakes and rivers across the latitudinal gradient 46–80°N show that their overlying ice contains low concentrations of dissolved organic carbon (DOC) and colored dissolved organic matter (CDOM) relative to the underlying waters. The CDOM exclusion factor (water/ice) ranged from 1.4 to 114 and was typically greater than twice the exclusion factor for inorganic solutes. Application of synchronous fluorescence analysis to lake ice samples and experimentally frozen lakewater indicated that only less complex, lower molecular weight molecules were retained within the ice. Consistent with this analysis, DOC-specific absorption showed that the DOC in the ice was generally less colored than that in the underlying waters. The reduced CDOM absorption within the ice allowed relatively high ultraviolet (UV) transmission despite the elevated scattering within the ice and resulted in UV diffuse attenuation coefficients up to eight times lower in the ice than in the underlying waters. This relatively low attenuation by the ice would cause organisms trapped near the surface by inverse stratification to experience high UV exposure prior to ice breakup. The ice exclusion effect gives rise to a concentrated zone of CDOM and DOC that is likely to favor heterotrophic and mixotrophic processes and influence biogeochemical interactions.

Colored dissolved organic matter (CDOM) plays a central role in a broad range of processes in the aquatic environment. Absorption by CDOM is often responsible for most of the ultraviolet (UV, 280–400 nm) attenuation in lakes, rivers, and coastal environments (Morris et al. 1995; Laurion et al. 1997; Gibson et al. 2000). CDOM also attenuates photosynthetically available radiation (PAR, 400–700 nm), thereby affecting primary production by the plankton and benthos (Arrigo and Brown 1996; Carpenter et al. 1998; Markager and Vincent 2000) and heat exchange and buoyancy fluxes in the upper water column (Fee et al. 1996). CDOM and its correlate, dissolved organic carbon (DOC), are substrates for heterotrophic growth. In oligotrophic and mesotrophic lakes, DOC is usually the largest pool of organic carbon and represents an important constituent of the biogeochemical carbon cycle. Moreover, CDOM is photochemically active and can be photodegraded to lower molecular weight components that are then available to the microbial food web (Moran and Zepp 1997; Reche et al. 1998; Bertilsson et al. 1999). CDOM also alters contaminant toxicity and nutrient availability (reviewed in Williamson et al. 1999). Factors that affect CDOM or DOC in aquatic ecosystems such as climate effects on vegetation thus indirectly modify a wide range of aquatic processes and ultimately affect water quality and ecosystem productivity (e.g., Pienitz and Vincent 2000).

CDOM absorption or fluorescence has now been measured in samples from the water column of many types of aquatic ecosystem. Much less is known, however, about the CDOM properties of ice. Lakes and rivers in the polar and subpolar regions are covered by ice for >6 months of the year, and several months of ice cover are also characteristic of freshwater environments in several other ecoregions, including the boreal forest and alpine zones. Two types of ice form over freshwaters: clear ice and white ice. Clear ice is formed from accretion at the ice-water interface, whereas white ice results from freezing of flooded snow on the ice surface. White ice is much more opaque to irradiance penetration than clear ice and, like snow, exerts a major control on irradiance penetration (Welch et al. 1987). A third type of ice, brackish ice, is found over saline lakes throughout the cold regions, especially the Arctic and Antarctica. It is known that gases, ions, and nutrients are excluded from the ice during freeze-up and that this exclusion is generally more effective when ice growth is slow (Adams 1981; Schmidt et al. 1991; Wharton et al. 1993). Sea ice is often enriched in CDOM or DOC through ice algae production and the release of algal exudates (Perovich et al. 1998; Belzile et al. 2000). To our knowledge, however, the only account of DOC in lake ice is from Lake Bonney, McMurdo Dry Valleys, from which Priscu et al. (1999) reported that DOC concentration in bottom accretion ice was 58% of that of the underlying waters.

The objectives of the present study were to measure the partitioning of CDOM between ice and water under a wide range of ice conditions, to compare the relative exclusion of CDOM with inorganic solutes, to characterize CDOM from absorption and fluorescence measurements in lake ice and

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water, and to evaluate the effect of CDOM exclusion on spectral irradiance attenuation in ice. To address these objectives, we sampled the ice and water column of seven aquatic ecosystems (six lakes and one river) that were selected to cover the broadest range of ice and CDOM conditions. The sites were distributed across the vegetation gradient (thus CDOM gradient, Vincent and Pienitz 1996) of North America, from latitude 46°N (mixed broadleaf-conifer forest) to 80°N (polar desert).

Materials and methods

Ice cores and water column sampling—Lakes were sampled at the time of maximum ice thickness, with the exception of Lac Bédard, at which we sampled newly formed, thin ice in November. Ice cores were taken by use of a MARK II corer (9-cm internal diameter; Kovacs Entreprise). The ice cores were obtained from the central part of the lake, except at Lac Saint-Jean (stations at 2–12 km from the shore of this 1,050 km^2 lake); 10–50 cm ice sections were slowly melted in the dark in Ziploc bags. The first ~10 ml of meltwater were discarded, to eliminate contamination that might occur during coring and handling. Water samples were taken by use of a 2-liter Kemmerer sampling bottle. Samples were transferred to dark Nalgene bottles and kept cold until processing (within 6 h of collection). Water column profiles of temperature and conductivity were measured by use of a Hydrolab Surveyor III profiler. The conductivity of the melted ice samples was measured by use of the same Hydrolab. CDOM, DOC, and ion exclusion factors were calculated as the ratio of the value in the water column to that in the ice cover. The ion exclusion factors were calculated on the basis of conductivity. These exclusion factors should be viewed as ''apparent'' exclusion factors, because the concentrations in water at the time of ice formation are unknown and because subsequent DOC photodegradation may have affected the value observed in ice. Values measured in ice sections were weighted by each section thickness to calculate the value integrated over the full ice cover or mean value.

CDOM and DOC characterization—CDOM absorption coefficients, a_{CDOM} (m^{-1}), were measured for each melted ice sample and for one–three depths in the underlying water column. Samples were filtered through 0.22-μm Sartorius cellulose acetate filters and stored at 4°C in amber glass bottles until analysis (within 1 month). a_{CDOM} was measured every 2 nm over the wavelength range 250–820 nm by use of a 1 cm, acid-cleaned, quartz cuvette in a Hewlett Packard 8452A spectrophotometer. DOC concentrations were determined by use of the infrared detection and UV digestion method (for Romulus Lake and Char Lake; Environment Canada, National Laboratory for Environmental Testing) or high-temperature oxidation with a Shimadzu 5050 total organic carbon analyzer (for Lake Kachishayoot and Great Whale River). The CDOM samples were further analyzed by synchronous fluorescence spectroscopy (Senesi et al. 1991; Ferrari and Mingazzini 1995; Pullin and Cabaniss 1997; Lu and Jaffe 2001). Synchronous fluorescence (SF) spectra were recorded with a Shimadzu FR5000 spectrofluorometer used in the synchronous mode with a slit width of 5 nm on both sides and a wavelength difference between the excitation and emission beams ($\delta\lambda$) of 14 nm, which we have found to be optimal for resolving differences in CDOM between sources. This setting also minimizes the overlap between CDOM peaks and the Raman water peak and greatly suppresses the latter. SF spectra were recorded over the excitation wavelength range 236–600 nm. Fluorescence scans were corrected for the absorption within the sample (inner-filter effect) according to McKnight et al. (2001), except that the absorption coefficient of the sample was measured by spectrophotometry (as described above). SF spectra published elsewhere have been measured by use of many different $\delta\lambda$ values (e.g., 18 nm in Senesi et al. 1991; 25 nm in Ferrari and Mingazzini 1995; 20 nm in Pullin and Cabaniss 1997; and 30 nm in Lu and Jaffe 2001). However, our tests showed that the position of the fluorescence peaks was only weakly affected by the $\delta\lambda$, at least for $\delta\lambda < 30$ nm, and that peak positions identified in studies elsewhere are within 15 nm of the peak positions found when our instrument setup was used. At $\delta\lambda > 20$ nm, we found that water Raman fluorescence strongly interfered with the CDOM fluorescence peak at 300 nm and that CDOM peaks at longer wavelengths were much broader. Analysis of model compounds or water samples and isolated fulvic acids (FA) from a wide range of aquatic environments has shown that fluorophores with one aromatic ring that have aliphatic, alcoholic, or ester bonds usually show a strong fluorescence peak at 293–308 nm (corresponding to peak I in Lu and Jaffe 2001 and peak hA in Ferrari and Mingazzini 1995), whereas further substitutions and polyaromatic rings systems shift the SF peaks to longer wavelengths (Ferrari and Mingazzini 1995 and references therein; Lu and Jaffe 2001; see also Results section).

Laboratory freeze-up experiment—A laboratory freezing experiment was performed to verify and extend the field observations. A water sample collected in Lac Saint-Jean in March 2001 and kept at 4°C in the dark for 9 months was filtered through 0.22-μm Sartorius cellulose acetate filters. The filtered water was dispensed in three 400-ml insulated containers with an open top and placed in a −20°C freezer. The containers were removed from the freezer after 4.5, 5, and 6 h, and the ice and liquid water were separated. These different freezing times produced the freezing of 24%, 28%, and 32% of the water, and most of the ice formed at the upper water surface. Conductivity, a_{CDOM}, and SF spectra of the initial water sample and of each melted ice and water fractions were measured according to the methods described above.

Irradiance transmission and attenuation—Transmission of downwelling UV irradiance (at 320, 340, and 380 nm) and PAR through the ice was measured by use of a PUV500 radiometer (Biospherical Instruments) at two sites in the subarctic (Lake Kachishayoot and Great Whale River) where the catchments lie in the northern limit of boreal forest and generate moderate levels of CDOM (Gibson et al. 2001). The ice surfaces were carefully cleared of snow over a 12 m^2 area, to estimate irradiance transmission through the ice only. Irradiance transmitted through the ice was measured

Table 1. Description of the lakes and river sampled. Latitude, sampling date, total ice thickness (cm), white ice thickness (cm), CDOM absorption coefficient at 320 nm [(a_{CDOM}(320), m^{-1})], and specific conductivity (SCond, $\mu S\ cm^{-1}$) in the surface water and exclusion factor for a_{CDOM}(320) and ions in the ice cover.

Site	Latitude (°N)	Core no.	Date	Total ice (cm)	White ice (cm)	a_{CDOM}(320) (m^{-1})	SCond ($\mu S\ cm^{-1}$)	CDOM exclusion factor	Ion exclusion factor
Romulus Lake	79°52	1	06 May 2000	251	—	5.7	16,000	6.0	6.6
Char Lake	74°42	1	12 May 2000	240	2	0.4	273	1.4	110.1
Lake Kachishayoot	55°20	1	10 Apr 1999	105	61	15.4	66	11.1	2.7
Great Whale River	55°16	1	08 Apr 1999	99	5	9.8	26	16.9	4.4
Lac Saint-Jean	48°32	1	19 Mar 2000	55	0	38.0	31	69.6	4.3
		2	19 Mar 2000	70	28	38.8	29	67.2	4.5
		3	06 Mar 2001	89	8	38.0	33	114.4	4.9
		4	09 Mar 2001	85	5	34.0	27	63.7	2.8
Lac Bédard	47°16	1	01 Nov 1999	1	0	19.0	14	19.9	3.6
		2	22 Feb 2000	48	33	19.9	15	7.6	3.2
		3	22 Feb 2000	52	23	19.9	15	6.4	2.9
Lac Saint-Augustin	46°47	1	04 Mar 2000	51	21	8.5	532	12.4	18.2
		2	04 Mar 2000	53	17	8.5	532	12.9	27.6

just under the lower ice surface by deploying the PUV500 at 1 m from the hole in the ice by use of an articulated arm, whereas irradiance incident on the upper ice surface was measured simultaneously by use of a PUV510 radiometer (details of this procedure are given in Belzile et al. 2001). Transmittance was calculated as the ratio of under-ice irradiance to incident irradiance and was expressed as percentage. The albedo (E_u/E_d) of the ice surface was measured by use of the PUV510. Ice $K_d(\lambda)$ was calculated from Beer's Law, as in Belzile et al. (2001). For the $K_d(\lambda)$ determination, irradiance just under the ice upper surface, $E_d(0^-, \lambda)$ was estimated from the albedo. The albedo includes absorption and scattering effects occurring within the ice in addition to specular reflection; therefore, a value of 5% reflection at the ice surface was also assumed for the $E_d(0^-, \lambda)$ estimate. Water column $K_d(\lambda)$ values were calculated from under-ice irradiance profiles according to the technique described in Belzile et al. (2000).

Results

Dissolved organic matter in ice—The sampled lakes and river encompassed a wide range of limnological conditions (Table 1). Ice thickness varied from 1 to 251 cm, and the trophic status of these aquatic ecosystems varied from ultra-oligotrophic (Char Lake) to eutrophic (Lac Saint-Augustin). The CDOM absorption coefficients varied from very low (Char Lake) to very high (dark-stained Lac Saint-Jean), and ionic concentrations varied from dilute waters on the Precambrian Shield (Lac Bédard) to saline Romulus Lake, a meromictic lake in the Canadian high Arctic. In all cases, DOC concentration and CDOM absorption were lower in the ice than in the underlying waters. DOC exclusion factors (water/ice) for the four aquatic ecosystems for which data are available ranged from 2.6 to 4.3 (Table 2). DOC-specific absorption coefficients were generally much lower in the ice than in the water column (Table 2), which indicates that the DOC remaining in the ice was less colored. An exception to this is Char Lake, where water column DOC-specific absorption was very low (four–seven times lower than at the other sites), and values in the ice were comparatively high.

The CDOM exclusion factor [$a_{CDOM}(320)_{water}/(320)_{ice}$] showed considerable variation between sites, ranging from 1.4 to 114 (Table 1). There was no significant relationship between a_{CDOM} in the ice and a_{CDOM} in the water column (Fig. 1A). However, a strong exponential relationship existed between a_{CDOM} in water and the exclusion factor ($r^2 = 0.860$; Fig. 1B), resulting from the fact that low a_{CDOM} in the ice was always achieved, whatever the CDOM in the underlying water column. There was no significant relationship between the CDOM exclusion factor and total ice thickness (Fig. 1C). The ion exclusion factor varied over a range similar to that

Table 2. Dissolved organic carbon (DOC, mg L^{-1}), DOC exclusion factors, and DOC-specific a_{CDOM}(320) [(m^{-1} (mg L^{-1})$^{-1}$)] in the water column and ice cover of subarctic and high Arctic aquatic ecosystems.

	DOC in water (mg L^{-1})	DOC in ice cover (mg L^{-1})	DOC exclusion factor	DOC-specific a_{CDOM}(320) in water m^{-1} (mg L^{-1})$^{-1}$	DOC-specific a_{CDOM}(320) in ice m^{-1} (mg L^{-1})$^{-1}$
Romulus Lake	2.70	0.84	3.2	2.14	1.12
Char Lake	0.98	0.23	4.3	0.45	1.45
Lake Kachishayoot	5.24	2.04	2.6	2.94	0.55
Great Whale River	4.95	1.18	4.2	1.98	0.49

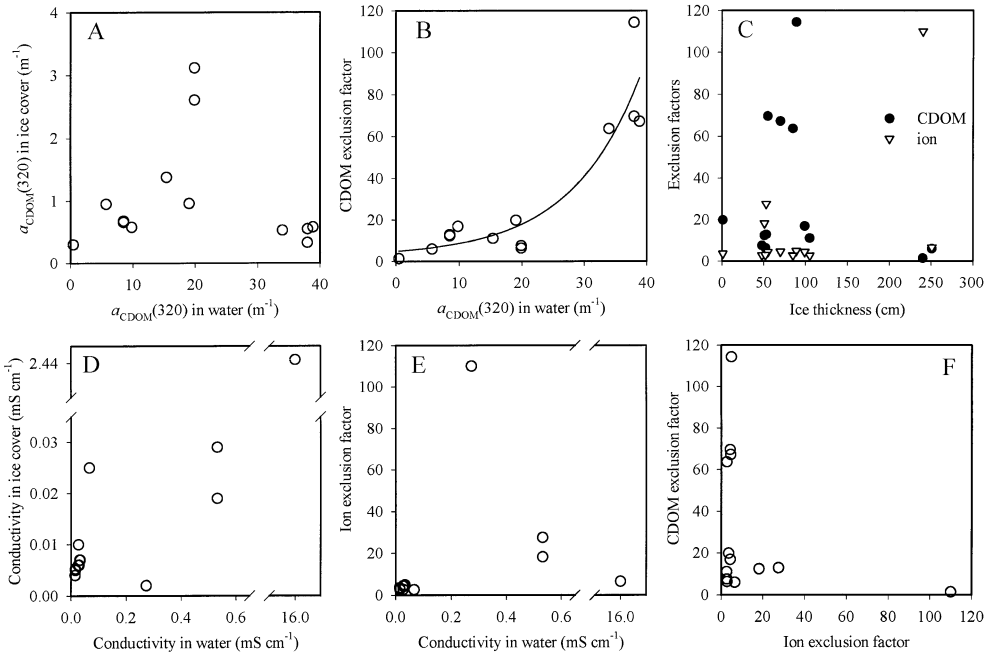

Fig. 1. Relationships between (A) the CDOM absorption coefficient at 320 nm, $a_{CDOM}(320)$, in the ice cover and water column; (B) the CDOM exclusion factor and $a_{CDOM}(320)$ in the water column; (C) CDOM and ion exclusion factors and ice thickness; (D) conductivity in the ice cover and in the water column; (E) the ion exclusion factor and conductivity in the water column; and (F) CDOM and ion exclusion factors.

of CDOM exclusion, from 2.8 to 110 (Table 1), although the CDOM exclusion factor was typically much greater at each site. Conductivity in ice was strongly correlated to water conductivity ($r^2 = 0.999$; Fig. 1D), although the high significance of this relationship is due to the poor distribution of data points (when Romulus Lake is excluded, $r^2 = 0.404$, $P = 0.026$). There was no relationship between water conductivity and the ion exclusion factor (Fig. 1E) or between the CDOM exclusion factor and the ion exclusion factor (Fig. 1F).

Figure 2 shows $a_{CDOM}(320)$ in the ice and water column of three lakes with contrasting ice types and water column CDOM. Water column $a_{CDOM}(320)$ values varied over two orders of magnitude for these three lakes, although comparatively small variations of $a_{CDOM}(320)$ in the clear ice was observed (i.e., it varied from 0.19 to 0.48 m^{-1}). Values for white ice at Lac Saint-Jean and Lake Kachishayoot were consistently higher than that in their clear ice. In the thick, clear ice cover of Char Lake, CDOM exclusion was comparatively low, although the $a_{CDOM}(320)$ values were of the same magnitude as those in the clear ice of the other two lakes.

Detailed in-ice profiles of the CDOM and ion exclusion factors revealed large differences between the exclusion behavior of organic and inorganic dissolved matter. In the lakes where white ice was present, both CDOM and ion exclusion factors tended to be higher in the clear ice (Fig. 3). Although the profiles of CDOM exclusion factors roughly paralleled that of ion exclusion, large differences in the magnitude of both exclusion factors were observed. CDOM exclusion was generally much higher than ion exclusion (Fig. 3A,B), although the opposite trend was observed at Lac Saint-Augustin (Fig. 3C). Replicated cores from a given lake (Fig. 3B,C) showed consistent trends, although a relatively high variability in exclusion factors was apparent (note that this variability partly results from the different thickness of ice sections). In the two freshwater ecosystems where snow cover was absent or negligible, the ion exclusion factors were higher near the bottom of the ice, in agreement with more effective exclusion at slow accretion rates (Fig. 4B,C). Surprisingly, CDOM exclusion factors were higher at the top of the ice at these two snow-free sites (Fig. 4B,C). In saline Romulus Lake, where snow cover was also absent from the sampled ice surface, both CDOM and ion exclusion factors were maximal in the top section of the ice cover (Fig. 4A). However, CDOM exclusion was higher than the ion exclusion in that top section, whereas it was lower than ion exclusion in the next two ice sections, down to 139 cm deep inside the ice cover. The bottom section of ice often had exclusion factors that were slightly lower than the immediately overlying clear ice sections (Figs. 3B,C, 4B,C).

Synchronous fluorescence analysis provided valuable additional information regarding CDOM characteristics of the ice and water. The well-characterized FA standards from Lake Fryxell and Suwannee River (McKnight et al. 1991, 2001) illustrate that FAs from different origins show markedly different fluorescence spectra with the instrument settings adopted in the present study (Fig. 5A). The microbially derived FA from Lake Fryxell (average molecular weight 463 Da; aromatic carbon content 13%) showed peaks centered at 300 and 360 nm and a shoulder in the 450–475 nm region. The FA from Suwannee River, mostly derived from terrestrial plants and soils (average molecular weight 840

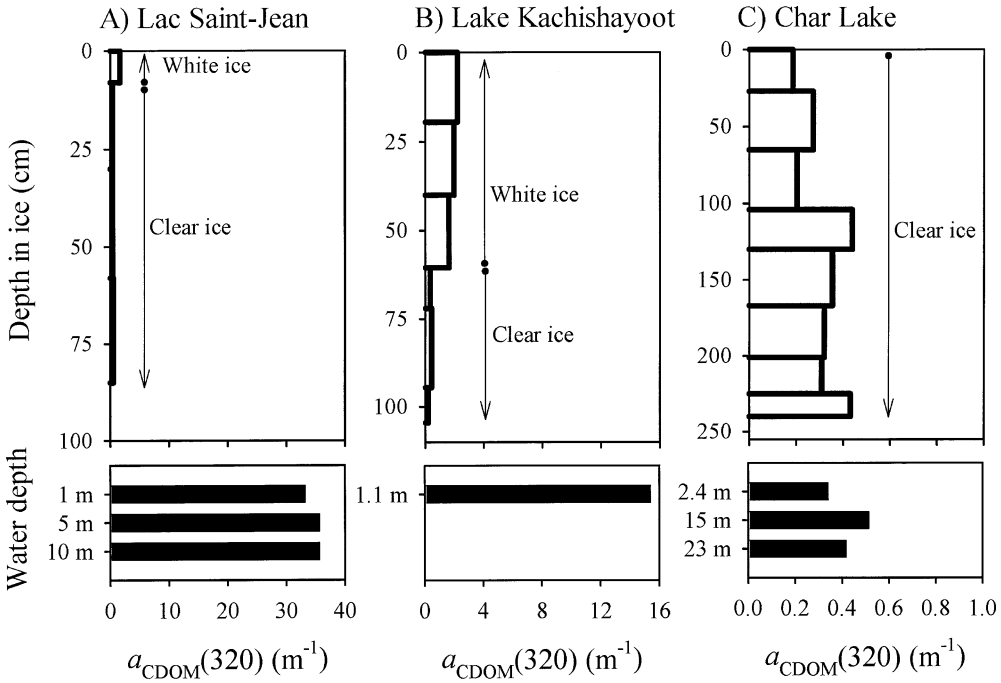

Fig. 2. CDOM absorption coefficient at 320 nm, $a_{CDOM}(320)$, in the ice and water column of three lakes with contrasting ice types and water column CDOM. (A) Lac Saint-Jean from the boreal zone; (B) subarctic Lake Kachishayoot; (C) and arctic Char Lake.

Da; aromatic carbon content 28%) fluoresced at longer wavelengths and showed peaks at 300, 400, and 450–500 nm. The 300-nm peak was less prominent for the Suwannee River FA, whereas the shoulder in the 450–475-nm region present in the Lake Fryxell FA is a major peak in the Suwannee River sample.

SF analysis of a water sample from Lake Kachishayoot that was size-fractionated by use of Vivaflow ultrafiltration modules (Vivascience Ltd., United Kingdom; nominal size fractions <0.2 μm, <30 kDa, and <5 kDa) further illustrates how larger CDOM molecules fluoresce at longer wavelengths, whereas smaller molecules show a fluorescence peak centered around 300 nm (Fig. 5B). Although the spectra for the total fraction resembled the Suwannee River FA, the smaller size fractions had a SF spectra similar to the microbially derived FA from Lake Fryxell. Note that the spectra of these fractionated samples have not been corrected for the inner-filter effect because the absorption coefficients needed for such a correction were not available. Thus, the higher 300-nm peak in the <5 kDa fraction likely results from the lower inner-filter effect in the sample.

SF spectra of the ice samples consistently lacked the peaks at wavelengths >400 nm that were present in the underlying waters (Fig. 5C–F). This indicates that most large, complex molecules were excluded from the ice, whereas smaller, less conjugated molecules were retained. The 300-nm fluorescence peak was sometimes higher in ice samples than in the water column (Fig. 5D,F).

In the laboratory experiment, CDOM and inorganic solutes were excluded from the ice during freeze-up and resulted in an increase of concentration in the unfrozen water. The CDOM exclusion factors increased as the volume of ice increased, with values (in order of increasing ice volume) of 7.6, 11.5, and 13.0. CDOM absorption [$a_{CDOM}(320)$] behaved as a conservative property—that is, the mean values in ice and unfrozen water weighted by their relative volume was within 1% of the value at T_0, which implies little flocculation. The ion exclusion factors also increased as the volume of ice increased; however, the CDOM exclusion factors were 1.4–1.7 times higher than ion exclusion factors. SF spectra of ice samples from the laboratory experiment resembled that measured on field samples (Fig. 6). As expected, the exclusion of the fluorescent material from the ice was accompanied by an increase of fluorescence in the unfrozen water. The exclusion of complex material fluorescing at longer wavelengths was much more effective than that of the smaller, less conjugated, Lake Fryxell FA–like CDOM molecules fluorescing at shorter wavelengths (Fig. 6).

Impact of CDOM exclusion on irradiance transmission—Even in snow- and ice-covered lakes, and despite the low PAR transmission through the ice and snow, phytoplankton can accumulate near the ice-water interface, as illustrated in Fig. 7 for the boreal Lac Saint-Jean. This trapping of biomass was favored by the inverse stratification (Fig. 7). In this dark-stained lake, ice K_d(PAR) (calculated under the assumption of a 5% reflection at the ice surface) was twice that in the underlying waters (3.46 m^{-1} in ice vs. 1.60 m^{-1} in the water column; Fig. 7). However, in absence of CDOM exclusion, a_{CDOM}(PAR) would have been 27 times higher in the ice, which would cause a much higher ice K_d(PAR) (Fig. 7).

Irradiance transmission through the Great Whale River ice varied from 10% (at 320 nm) to 16% (for PAR; Fig. 8A). Transmittance at Lake Kachishayoot was much lower

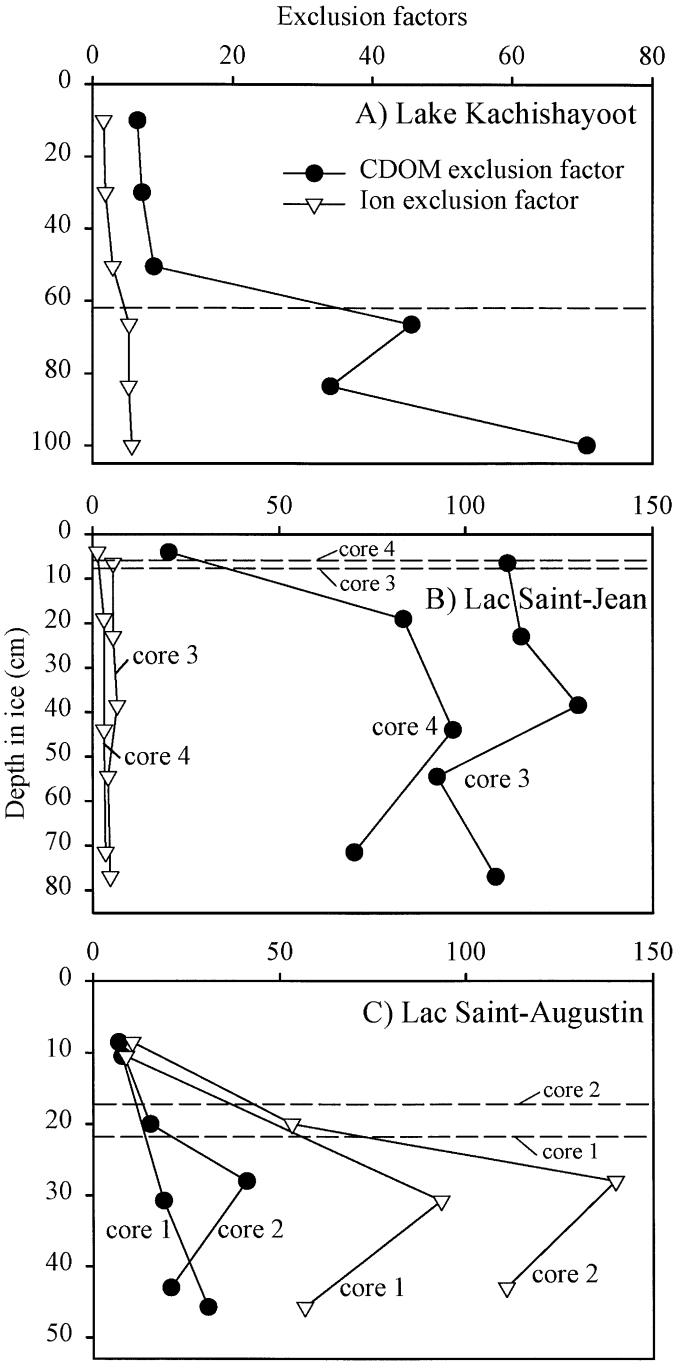

Fig. 3. In-ice profiles of CDOM and ion exclusion factors in three lakes where white ice was present. (A) Lake Kachishayoot, (B) Lac Saint-Jean, and (C) Lac Saint-Augustin. The data points correspond to the midpoint of each ice section, and the dashed lines mark the limit between white ice and clear ice (the white ice is above the dashed line). Core numbers in (B) and (C) refer to numbers used in Table 1; replicated cores in panel B were taken at sites 9 km apart, and those in panel C were taken 0.5 km apart.

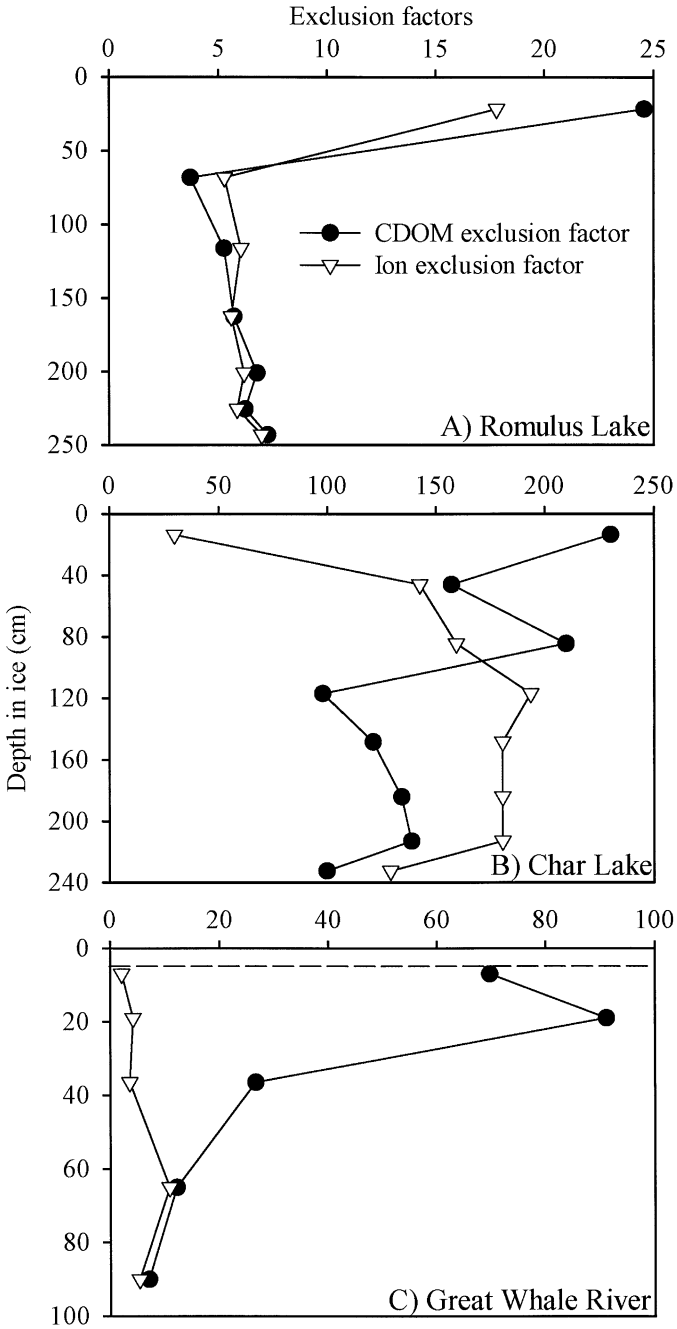

Fig. 4. In-ice profiles of CDOM and ion exclusion factors in arctic and subarctic ecosystems where snow cover was absent at the site of sampling. (A) Romulus Lake, (B) Char Lake, and (C) Great Whale River. In panel B, the CDOM exclusion factors have been multiplied by 100. The data points correspond to the midpoint of each ice section, and the dotted line in panel C marks the limit between white ice and clear ice.

(0.1%–2.9%; Fig. 8B), which likely reflects the higher scattering and higher albedo associated with the relatively thick white ice layer of this ice cover. Exclusion of CDOM from the ice caused the spectral a_{CDOM} to be one order of magnitude lower in the ice than in the underlying waters of both ice-covered ecosystems (Fig. 8C,D). This reduced CDOM absorption allowed ice K_d(UV) to be lower than in the water column (Fig. 8E,F). The higher scattering in the ice, combined with the lower influence of CDOM absorption at long-

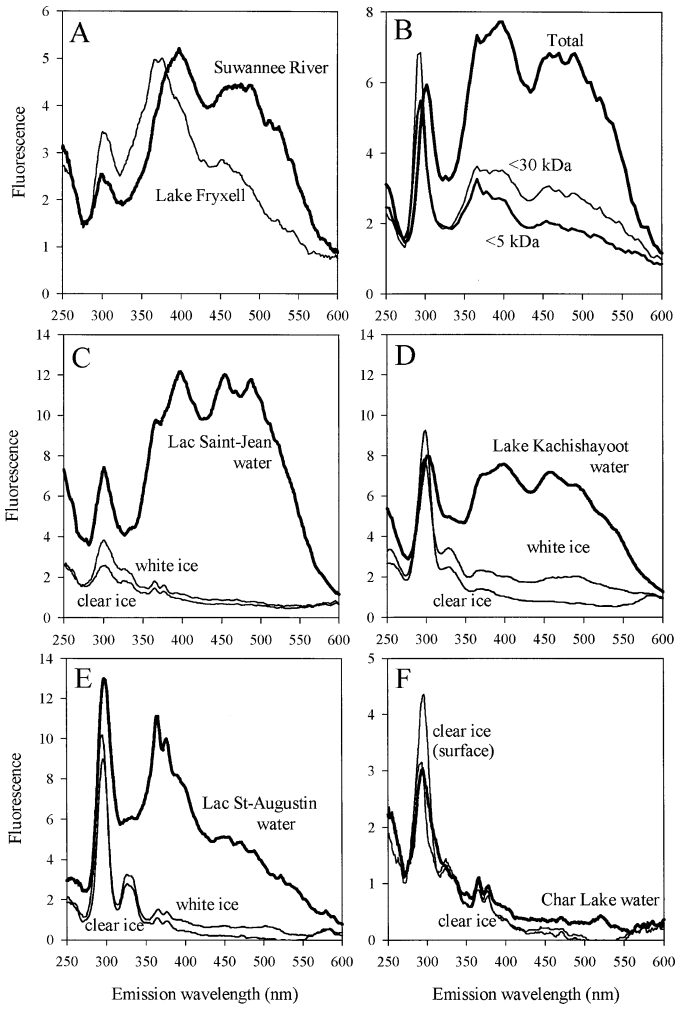

Fig. 5. CDOM synchronous fluorescence spectra. (A) Isolated fulvic acids from Lake Fryxell and Suwannee River; (B) fractionated sample from surface water of Lake Kachishayoot collected in July 1999; and ice and water column samples from (C) Lac Saint-Jean, (D) Lake Kachishayoot, (E) Lac Saint-Augustin, and (F) Char Lake. The fulvic acids solutions presented in panel A had a DOC concentration of 5 mg L^{-1}. The spectra in panel B have not been corrected for the inner-filter effect.

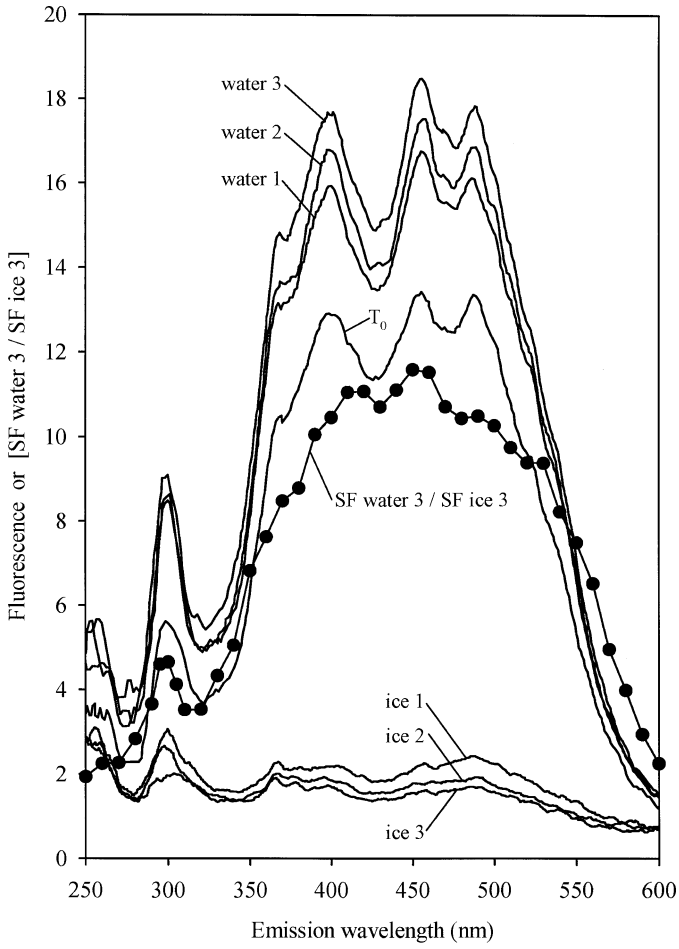

Fig. 6. CDOM synchronous fluorescence (SF) spectra of water and ice from the controlled freeze-up experiment and ratio of SF in water to SF in ice for sample 3. The sample numbers correspond to the increasing volume of ice (1 = 24%, 2 = 28%, and 3 = 32%).

er PAR wavelengths, caused K_d(PAR) to be higher in the ice than in the underlying waters.

Discussion

The results presented here show that CDOM and DOC are strongly excluded from lake and river ice. a_{CDOM} in the ice covers was always low (<3 m^{-1} at 320 nm) and showed relatively little variation, whatever the value of a_{CDOM} in the underlying water (Fig. 1A), consistent with the exponential increase in CDOM exclusion factor with increasing CDOM absorption (Fig. 1B). CDOM exclusion is very effective (up to 114 times more absorption in the water than in the ice) and is generally more effective than exclusion of inorganic solutes. Even newly formed, 1-cm-thick ice had a_{CDOM}(320) values 20 times lower than the water from which it formed (Lac Bédard on 1 November; Table 1).

CDOM exclusion likely results from the same process that affects other solutes—that is the tendency for ice to grow pure ice crystals, rejecting impurities during the process (Adams 1981; Welch and Legault 1986; Schmidt et al. 1991; Wharton et al. 1993). The lowest a_{CDOM} in the ice covers was observed in the clear ice, although the bottom section of ice often had an exclusion factor slightly lower than the remaining clear ice (Fig. 3B,C, 4B,C). a_{CDOM} in white ice was higher than in the underlying clear ice but was much lower than in the water column because of the dilution of the high CDOM water by snow during white ice formation (although there can be no exclusion of CDOM from the white ice, at least in a bulk sense). The brackish ice over Romulus Lake had one of the lowest exclusion factors for CDOM; the structure of this type of ice resembled that of sea ice (2-cm thick platelet ice was present at the bottom of the ice), and part of the CDOM was likely retained in the brine channels. CDOM is also partly excluded from sea ice, although ice algae–derived DOC can increase a_{CDOM} to values orders of magnitude higher than those in the underlying waters (Per-

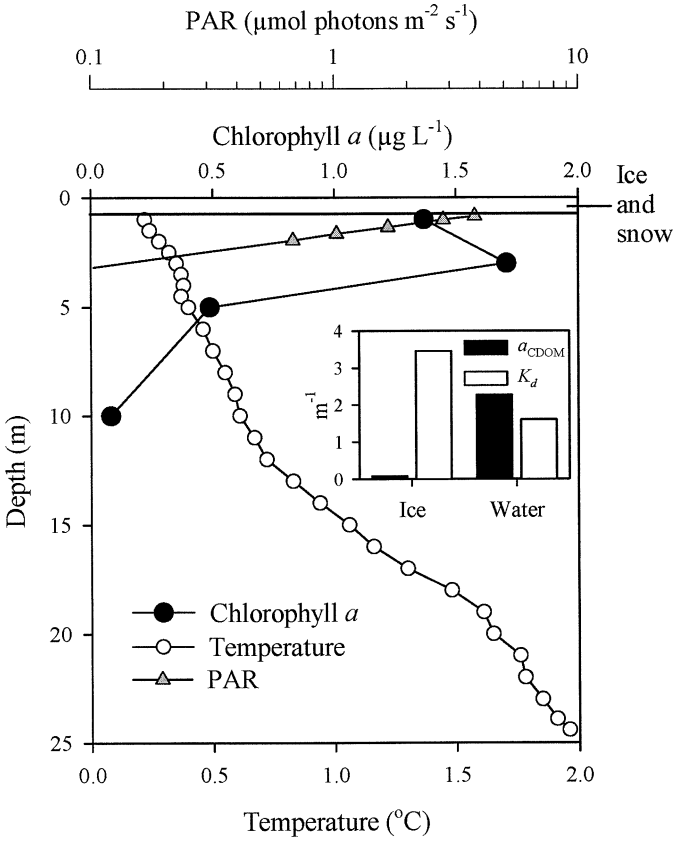

Fig. 7. Illustration of phytoplankton growing in ice- and snow-covered boreal lake, Lac Saint-Jean, 8 March 2001. The Chl *a* concentration was determined by fluorometric analysis of extracts, and the temperature profile was measured by use of a Hydrolab profiler. PAR transmission through the 85-cm-thick ice covered by 17 cm of snow was 0.46% as measured at 1200 h by use of a LiCor Li-192SA sensor positioned 2 m from the hole in the ice and with a Li-190SA reference sensor. The PAR under-ice profile was measured by use of the same LiCor sensor, also positioned 2 m from the hole in the ice, and irradiance was extrapolated downward from measured K_d(PAR). The insert shows a_{CDOM}(PAR) and K_d(PAR) in the ice and water. The K_d(PAR) of ice was calculated from transmittance measured under snow-cleared ice and under the assumption of 5% reflection at the ice surface.

ovich et al. 1998; Belzile et al. 2000). The thick, very clear ice of oligotrophic Char Lake had a CDOM exclusion factor of only 1.4, although the DOC exclusion factor was 4.3. a_{CDOM} was extremely low in the water column of Char Lake, and even background absorption in the ice gave this comparatively low exclusion factor. Also, the 1-cm cuvette used for the absorption measurements had a path length insufficient to resolve accurately such background absorption, and this may explain the relatively high DOC-specific absorption of CDOM in the ice of that lake.

Photochemical reactions may contribute to the further degradation of organic matter retained in the ice, although this effect would be limited by the presence of thick snow cover and the low UV irradiance generally prevailing during winter at mid- and high latitudes. However, the higher apparent exclusion factor observed for the top sections of ice in all three sites where snow cover was absent (Fig. 4) may be the result of photobleaching. Photochemical breakdown of CDOM retained in the ice may also explain the large synchronous fluorescence peak centered at 300 nm typical of small, simple molecules sometimes observed in the ice (Fig. 5D,F).

SF spectra suggest that only small, less conjugated molecules are retained in the ice, whereas the larger, more conjugated molecules are preferentially excluded. This fluorescence technique allows the characterization of CDOM that originates from different sources and has different aromaticity and molecular weight. The fluorescence characteristics of the well-characterized FA standards from Lake Fryxell and Suwannee River (McKnight 1991, 2001), together with results published elsewhere that used different $\delta\lambda$ (Ferrari and Mingazzini 1995; Pullin and Cabaniss 1997; Lu and Jaffe 2001), provided a valuable guide for interpreting the spectral signatures measured here. The striking resemblance of fluorescence spectra of water samples from Lac Saint-Jean and Lake Kachishayoot to that of Suwannee River FAs is in agreement with the terrestrial origin of CDOM in these boreal and subarctic lakes. The practically perfect match between Lac Saint-Augustin and Lake Fryxell FA fluorescence peaks is also in agreement with a significant fraction of CDOM originating from extensive cyanobacteria blooms that occur during summer and autumn in Lac Saint-Augustin (Belzile et al. pers. observation) and the similar dominance of autochthonous processes in Lake Fryxell. The high arctic Char Lake showed very low fluorescence at wavelengths >400 nm that are typical of large, complex molecules, as would be expected from the low input of allochthonous carbon from its barren polar desert catchment (Welch and Kalff 1974; Laurion et al. 1997; Markager and Vincent 2000). The low DOC-specific absorption coefficient measured in the water column of Char Lake also suggested a microbial origin for the CDOM (Morris et al. 1995). Factors other than CDOM characteristics and concentration affect synchronous fluorescence, notably pH and metal ion concentrations (Pullin and Cabaniss 1997; Lu and Jaffe 2001). However, even the greatest changes in SF spectra that have been attributed elsewhere to these effects (up to 50% change in SF: Pullin and Cabaniss 1997; Lu and Jaffe 2001) would be insufficient to account for the differences between most ice and water samples observed in the present study.

The CDOM and ionic composition of a given ice cover showed markedly different profiles and magnitudes of exclusion (Figs. 3, 4). The CDOM exclusion was generally much more effective than ion exclusion. Welch and Legault (1986) measured major ions and nutrient concentrations in ice and water of four arctic lakes. Inspection of their data shows that exclusion varied markedly between ions; for example, NO_3^- exclusion was 2–10 times less effective than Ca^{2+} or Mg^{2+} exclusion (other ions in the ice were at or below detection limits, which prevented calculation of the exclusion factors). Similarly, ions are excluded differentially from glacial ice, with retention increasing according to the sequence: $Cl^- > Mg^{2+} > Na^+ > NO_3^- > SO_4^{2-}$ (Davies et al. 1982). The higher exclusion factor of CDOM relative to ions generally observed, together with the observation that only the less conjugated, presumably lower molecular weight CDOM molecules were retained in the ice, suggest that larger molecules are more effectively excluded from the ice. Our results from the freeze-

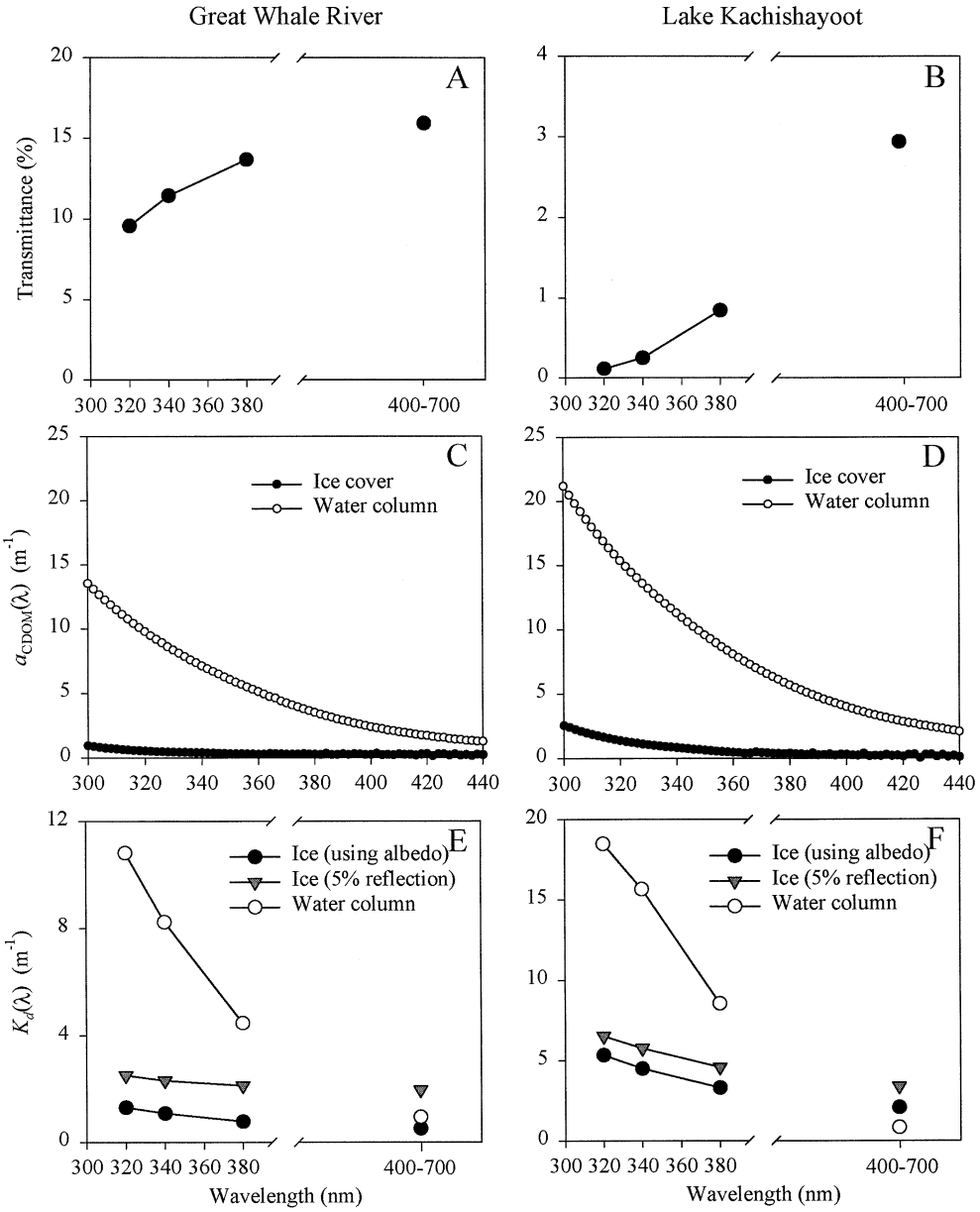

Fig. 8. (A,B) Irradiance transmission through the ice cover on 8–10 April 1999, (C,D) spectral a_{CDOM} in the ice and underlying waters, and (E,F) ice cover and water column diffuse attenuation coefficients, $K_d(\lambda)$, at the Great Whale River (A,C,D) and Lake Kachishayoot (B,D,F). Ice $K_d(\lambda)$ was calculated from the albedo and transmittance and also by assuming only 5% reflection at the ice surface.

up of Lac Saint-Jean water under controlled, experimental conditions confirmed that freezing alone can explain the field observations of CDOM exclusion. The exclusion efficiency of absorbing and fluorescing CDOM increased as the volume of ice increased, which supports the hypothesis that larger, more slowly accreted ice crystals exclude CDOM more efficiently. Consistent with our field observations, higher molecular weight CDOM appeared to be selectively excluded from the ice, and CDOM was excluded to a greater extent than inorganic solutes. Impurities not rejected into the water column are likely to be concentrated as a film at two-grain boundaries or in veins at three-grain boundaries (Mulvaney et al. 1988; Price 2000). Background concentrations of impurities are thus to be expected within bulk ice even if each ice crystal is perfectly pure. This background effect is also consistent with the exponential relationship we observed between CDOM exclusion and CDOM absorption coefficients in the underlying water.

The solute exclusion effect in ice-water systems is of considerable interest for the microbial ecology of cryoecosystems in which microorganisms live on and within ice—for example, on modern-day ice shelves and in diverse ice-habitats during major glaciation events in the past (Vincent and Howard-Williams 2000). It has been suggested that the pro-

cess of solute concentration in intercrystal veins can support microbial life—for example, even in the extreme environment of subglacial ice above Lake Vostok (Price 2000). However, unlike sea ice, the opportunities for microbial life in lake ice is likely to be limited by the minute space for colonization and limited access for microbial propagules. Two notable exceptions are the microbial communities found in slush layers within the ice cover of lakes located in regions of heavy snowfall (Felip et al. 1999) and microhabitats associated with sediment aggregates that have been discovered in the thick perennial ice of Antarctic lakes (Priscu et al. 1998). The freeze exclusion of DOC and other solutes is likely to enhance the local availability of organic carbon substrates and nutrients for such communities, as well as prolong the duration of liquid water conditions by the effects of salt concentration on the freezing point.

The exclusion of CDOM has important optical implications for high-latitude and alpine lake and river ecosystems and may affect the heat budget as well as light regime of the ice and subice environments. CDOM exclusion affects spectral irradiance transmission through the ice, particularly across the UV waveband. CDOM exclusion was sufficient to decrease K_d(UV) to values lower than those in the underlying waters despite the elevated scattering in the ice (Fig. 8; Belzile et al. 2001). Even if UV transmission through the ice should generally be lower than PAR transmission, the ratio of UV to PAR attenuation in the ice is much lower than in the underlying waters and is closer to unity (Fig. 8E,F). Thus, planktonic organisms present just under the ice would be exposed to a spectral composition of irradiance that resembles the near-surface spectrum in the absence of ice, although absolute intensities would be reduced to an extent that depends on ice characteristics. Spectral composition of the below-ice irradiance is especially important given that UV inhibition of photosynthesis may depend more on the UV : PAR ratio rather than on the absolute UV irradiance (Neale 2001). When snow or white ice is present, little UV radiation can reach the water column because of the high albedo and scattering of these media and because more CDOM absorption occurs within white ice. However, many circumstances may favor high under-ice exposure to UV. Phytoplankton blooms under newly formed, snow-free ice have been reported (e.g., Catalan 1992), and under-ice spring blooms have also been reported in Arctic lakes during years of reduced snow cover (Welch et al. 1989). In regions of low precipitation such as the high Arctic and McMurdo Dry Valleys and in basins exposed to strong winds, snow is often absent from a significant proportion of the surface (e.g., Char Lake, Romulus Lake, and Great Whale River) and significant UV penetration could occur. When snow melts, there may be a short period of time in which relatively high UV irradiance can reach the water column and the shade-adapted phytoplankton can be highly susceptible to UV photoinhibition (Neale et al. 1994). If there is a strong density gradient underneath the ice, as is often observed during winter inverse stratification (e.g., Fig. 7), then UV stress could be a factor influencing the position and activity of subice microbial populations. During spring, melting ice will be a source of UV-transparent water; if this layer is not flushed or mixed with underlying waters, it may represent a zone of high UV exposure even in ecosystems where CDOM present in the water column usually provides an effective protection against UV damage.

The exclusion of CDOM and DOC from freshwater ice also has biogeochemical implications. In lakes with a large surface-to-volume ratio and that are covered by ice, DOC released during ice formation could significantly increase DOC concentration in the water column. For example, at Lake Kachishayoot, the DOC concentration during the summer preceding our visit was 3.7–4.4 mg L^{-1} (Gibson et al. 2001). Given a mean water depth of 2 m and an ice thickness of 1 m at the end of winter, the 2 mg DOC L^{-1} measured in the ice cover of this subarctic lake (Table 2) implies a ~50% increase of DOC concentration in the water column. DOC concentration under the ice was 5.2 mg L^{-1} (Table 2), in agreement with a water column increase resulting from DOC exclusion from the ice. Flocculation of DOC after the exclusion from ice may affect the fate of this DOC in certain circumstances, although flocculation was negligible in the laboratory freeze-up experiment. The flushing of low-density and low-DOC meltwater during spring runoff may explain, by a long-term concentration process, the relatively high DOC concentration found in some high arctic lakes, despite their barren polar desert catchment (e.g., Romulus Lake; Table 2). The freeze concentration of CDOM and DOC represents a mechanism to deliver substrates for heterotrophic growth underneath the ice. It has been shown that aquatic ecosystems can switch during winter to a heterotrophic status in which carbon is consumed by bacteria and mixotrophic phytoplankton (Reitner et al. 1997; McKnight et al. 2000). It is of interest that under-ice phytoplankton communities are often dominated by motile species that can maintain their position close to the ice where light, but also DOC excluded from the ice, are maximal.

Ion exclusion during ice formation has received some limnological attention in the past in particular because it promotes under ice convection and can thereby affect the distribution of materials and biota in ice-covered ecosystems (e.g., Welch and Bergmann 1985; Ferris et al. 1991). CDOM exclusion is also likely to affect the carbon cycle in such ecosystems, and this aspect would merit further study. CDOM concentration and characteristics are highly responsive to climate change (Schindler et al. 1996; Pienitz and Vincent 2000), and changes in lake ice cover thickness and duration are characteristic climate responses (e.g., Magnuson et al. 2000). The results presented herein represent an additional pathway through which climate-induced changes in ice cover thickness and duration could significantly affect the biogeochemistry and physical properties of aquatic environments.

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