

Hydrologic control and diurnal photobleaching of CDOM in a subarctic lake

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With 7 figures and 1 table

Abstract: Changes in the concentration of chromophoric dissolved organic matter (CDOM) were determined over short (hours to days) and medium (weeks) time scales during summer in a shallow, polymictic lake in subarctic Québec, Canada. CDOM fluorescence (F_{CDOM}) decreased linearly from mid-June until early August, consistent with the zero-order kinetics expected for photodegradation of organic matter in a regularly mixed lake in which most of the photochemically-active radiation is absorbed by CDOM. A major rainfall event then resulted in a sharp increase in F_{CDOM} back to levels recorded at the start of the study. These changes showed that CDOM concentrations were controlled by the balance between catchment inputs and subsequent photodegradation processes within the lake. Shorter term changes in CDOM concentration were monitored by measuring the penetration of ultraviolet radiation (UVR) using a Sallantic TACCS system moored near the center of the lake and set to monitor downwelling 380 nm irradiance at 10 min intervals. The diffuse attenuation coefficient $K_d(380)$ decreased by 12 % during the deployment indicating increased penetration of UVR and the change paralleled the drop in F_{CDOM} over the same period. Many of the daily records showed a significant decline in $K_d(380)$ in the near-surface waters over the course of the morning and early afternoon indicating diurnal photobleaching of CDOM, and an increase later in the day consistent with the breakdown of the diurnal thermocline and entrainment of deeper waters. The results illustrate the short and medium term dynamics of CDOM, the importance of diurnal stratification and mixing for photochemical processes, and the variability that aquatic organisms must experience in UV exposure in their natural environment.

Key words: CDOM, dissolved organic carbon, mixing, stratification, UV radiation.

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Introduction

Ultraviolet (UV) radiation has a broad range of detrimental effects on the biota of aquatic ecosystems, including DNA damage and the impairment of physiological processes such as photosynthesis, nutrient uptake and respiration (KARENTZ *et al.* 1994, VINCENT & NEALE 2000). UV-induced damage of algae may subsequently impact on the grazers which rely on these organisms, and the effects may be felt throughout the entire ecosystem (HESSEN *et al.* 1997). UV exposure can also have positive effects by causing the breakdown of organic material into more biologically available forms, thereby stimulating some components of the microbial food web (MORAN & ZEPP 1997, LAURION *et al.* 1998, TRANVIK *et al.* 2000). Conversely, UV radiation may cause some loss of carbon substrates for the microbial food web by photo-oxidizing organic material to dissolved inorganic carbon (BERTILSSON & TRANVIK 2000), and by initiating condensation reactions that decrease the biological availability of some organic compounds (OBERNOSTERER *et al.* 1999).

In most non-turbid lakes, the penetration of UV-A (320–400 nm) and UV-B (290–320 nm) into the water column is controlled to a large extent by chromophoric dissolved organic matter (CDOM), the fraction of dissolved organic matter (DOM) that absorbs in both the visible and UV portions of the electromagnetic spectrum (SCULLY & LEAN 1994, WILLIAMSON *et al.* 1996, LAURION *et al.* 1997). Processes that control the concentration and the absorption characteristics of CDOM in lakes will thus also have a major influence on UV photochemistry and on the biological UV regime experienced throughout the water column.

Despite the pivotal role of CDOM in controlling underwater UV exposure and carbon supply in aquatic ecosystems, knowledge of the processes which control its concentration in lakes is still limited. Studies of intra-annual trends indicate that CDOM concentrations generally decrease with time. This is especially so in enclosures that preclude the importation of new CDOM (CURTIS & SCHINDLER 1997). More complex responses have been reported for whole lakes over the annual cycle, in which a decrease in CDOM has been observed in spring to a minimum near the summer solstice, followed by an increase in fall and early winter (CURTIS & SCHINDLER 1997, MORRIS & HARGREAVES 1997). Little attention has been given to the controls on CDOM concentration in lakes at shorter time scales.

Our objectives in the present study were to evaluate the magnitude of change in CDOM variables and UV penetration in a northern lake during summer open-water conditions, and to identify the mechanisms controlling these variations. Using a moored UV-radiometer and various measures of CDOM, we examined two time-scales of variation: short-term (hours to days) and medium-term (weeks). Our measurements were carried out in a shallow lake of a

type widely distributed throughout the Subarctic. This latitudinal zone is currently subject to increasing levels of incident UV radiation (IASC 1995) and the lakes have experienced large variations in biological UV exposure in the past associated with changes in climate, catchment vegetation and CDOM loading (VINCENT & PIENITZ 1996, PIENITZ & VINCENT 2000). The magnitude of short-term variability in CDOM and underwater UV is therefore of interest not only for understanding the natural level of variation that aquatic biota must contend with but also as a reference for assessing longer term trends.

Study site

The study was carried out at Lake Kachishayoot (local Cree name), which is located at $55^{\circ} 20.0' N$, $77^{\circ} 37.4' W$ in northern Québec, Canada, approximately 3 km from the eastern shore of Hudson Bay (Fig. 1). It has a surface area of 29.5 ha, a maximum recorded depth of 5 m, a shoreline of 2.0 km and a volume, assuming an average depth of 2 m, of $5.9 \times 10^5 \text{ m}^3$. The drainage basin of the lake is located on granite-gneiss rocks of the Precambrian Canadian Shield, and has an area (including the lake itself) of 210 ha.

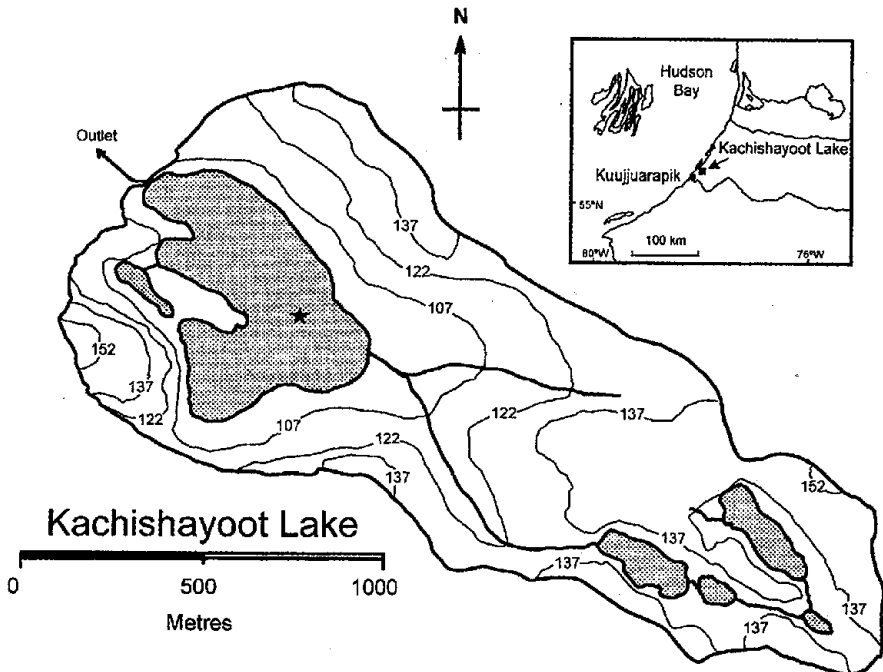


Fig. 1. Map of the drainage basin of Lake Kachishayoot (elevations in m). The star indicates the location of the sampling site in Lake Kachishayoot. The inset shows the site of the lake and Kuujuarapik, where the weather station was located.

Comparison of the ratio of lake volume to catchment area (300 km²) and the average annual precipitation (650 mm) indicates the hydraulic residence time is likely to be <1 year, and that spring snow melt probably flushes out most of the water present in the lake at the end of winter. The flora of the drainage basin includes areas of white spruce (*Picea glauca*), willow (*Salix* spp.), birch (*Betula glandulosa*) and green alder (*Alnus crispa*) scrub, and bogs. However, most of the drainage basin (70 %) is made up of bedrock covered by a thin layer of cryptogams, including mosses and lichens. Soil development has occurred mainly along the creeks and around the margins of the lake and ponds.

Materials and methods

Weather data for the closest station, Kuujjuarapik, located 10 km to the south-west of the lake (Fig. 1), were obtained from Environment Canada. The lake was visited at 5–8 day intervals from 18 June 1998 to 27 August 1998. Water temperature and conductivity profiles were measured with a Hydrolab Surveyor 3 profiler (Hydrolab Corporation). Temperature was also measured at a depth of 2 m every 12 minutes with a Tidbit recorder (Onset Corporation). Further deployments of Tidbit recorders were made at 0.2 m and 4 m during the 1999 summer.

Initial measurements of downwelling UV radiation at 320, 340 and 380 nm were made on 20 June 1998 using a Biospherical Instrument Inc. PUV-500. This instrument also recorded photosynthetically available radiation (PAR), temperature (°C) and depth, and was lowered slowly through the water column to measure all variables at 1–10 cm depth intervals. The diffuse, downwelling attenuation coefficients (K_d) were estimated by log-linear regressions of irradiance versus depth.

Temporal variations in the penetration of UV radiation were recorded between 10 July and 4 August 1998 with a Tethered Attenuation Coefficient Chain Sensor (TACCS) system (Satlantic Corporation). This instrument consisted of a series of sensors measuring downwelling radiance at 380 nm (bandwidth 10 nm), one above ($E_0(380)$) and four beneath the surface of the water. $K_d(380)$ values were calculated using the data from sensors positioned at depths of 0.18 m and 0.33 m beneath the surface. The instrument was set to collect data every 10 minutes, with an integration time of 10 seconds.

Samples for water chemistry were collected from 0, 1, 2 and 3 m using a Kemmerer bottle (Wildco), and transferred to polyethylene or glass bottles. The concentration of chlorophyll-a (Chl-a) was measured using a Sequoia-Turner 450 fluorometer after filtration of the phytoplankton onto GF/F filters and extraction with boiling 90 % ethanol (NUSCH 1980). A standard solution of Chl-a in ethanol (Aldrich) was used to calibrate the fluorometer, and corrections were made for the presence of pheopigments.

Major ions (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- and SO_4^{2-}), nitrate (NO_3^- -N), soluble reactive phosphorus (SRP), total nitrogen (TN) and total dissolved phosphorus (TP), particulate organic carbon (POC), total dissolved iron (Fe_T), Sr^{2+} and Ba^{2+} were determined at the National Laboratory for Environmental Testing (Burlington, Ontario) using methods described previously (Environment Canada 1994). The concentrations of dissolved inorganic carbon (DIC) and total carbon were measured using a Shimadzu

5050 TOC analyser. Dissolved organic carbon was calculated by difference. The data given are the average of two determinations, which in all cases had a coefficient of variation of less than 2%, equivalent to approximately 0.06 mg/L.

CDOM fluorescence (F_{CDOM}) was determined on GF/F-filtered samples using a Shimadzu RF 5000U spectrofluorometer with excitation at 348 nm and a slit width of 5 nm (LAURION et al. 1997). Emission was measured from 360 to 600 nm. All measurements were made using an acid-cleaned, 1-cm Suprasil fused silica cuvette that was rinsed four times with sample before measurement. The height of the fluorescence peak at 450 nm was normalised to the area of Raman water peak, and F_{CDOM} is reported in units of nm^{-1} (LAURION et al. 1997). The absorbance of the samples was measured against a blank of Milli-Q water using a Hewlett-Packard 440 Diode Array Spectrophotometer. Measured absorbances (unitless) were converted to absorption coefficients (units: m^{-1}) using the equation of KIRK (1994):

$$a(\lambda) = 2.303A(\lambda)/r \quad (1)$$

where $a(\lambda)$ is the absorption coefficient at wavelength (λ), $A(\lambda)$ is the measured absorbance and r is the path length of the measurement cell. Spectral absorption curves for natural water samples can typically be described by the following equation, modified slightly from BRICAUD et al. (1981) by the choice of reference wavelength and the inclusion of a constant (a_{back}) to adjust for zero offset:

$$a(\lambda) = a(380)e^{S(380-\lambda)} + a_{\text{back}} \quad (2)$$

where $a(380)$ is the absorption coefficient at 380 nm and S (units: nm^{-1}) is a constant. The measured data were fitted to Equation 2 using non-linear regression over the wavelength range 280 to 460 nm (Sigma-Plot 4.0, Jandel Corporation). Inclusion of the background term a_{back} in the regressions significantly improved the r^2 of modelled fits (MARKAGER & VINCENT 2000). The variable $a(380)$ is dependent both on the concentration of CDOM and the chemical nature of this organic material (GREEN & BLOUGH 1994), whereas S is independent of concentration and reflects the optical characteristics of the CDOM. Higher values of S are associated with waters that lack chromophores that absorb at longer wavelengths. Conversely, waters with greater concentrations of more complex organic molecules that absorb into the visible portion of the spectrum have lower S .

Results

Weather

Average daily temperatures ranged from 6.7 °C to 24.7 °C (average for the study period: 12.5 °C), and were generally cooler later in the study (Fig. 2a). There was little rainfall prior to a severe thunderstorm during the night of the 9–10 August, which resulted in a total rainfall accumulation of over 100 mm (Fig. 2b). This event caused a dramatic increase in the stream inflow to Lake Kachishayoot. Cloud cover increased during the study, resulting in a reduction

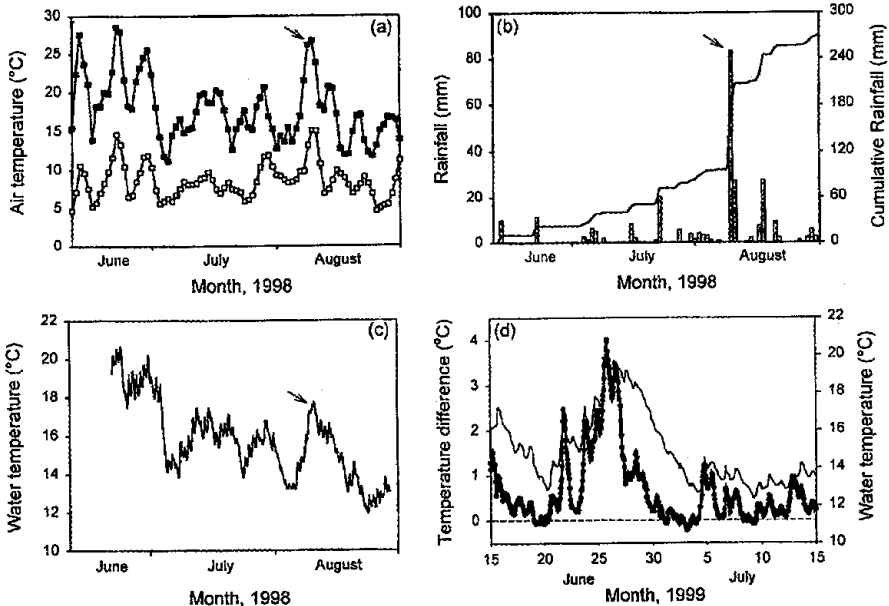


Fig. 2. Air temperature and precipitation recorded at Kuujjuarapik and water temperature in Lake Kachishayoot: (a) maximum and minimum air temperature (3-day running mean); (b) daily rainfall (bars) and cumulative rainfall (line); (c) lakewater temperature at 2 m in 1998; (d) lakewater temperature at 0.2 m (thin line) and the difference between temperatures at 0.2 m and at 4 m (dots and thick line) in 1999. The arrow in each graph identifies the date of the storm event.

in the average daily sunlight hours from 9.2 h/d in June to 4.7 h/d in August. Average wind speed increased during the study from 8 km/h in June to 17 km/h in August.

Temperature and stratification

Water temperature at 2 m reached a maximum of over 20 °C early in the study period and then declined as the season progressed (Fig. 2 c). The temperature closely tracked the three-day running average maximum air temperature. Temperature data from profiles recorded in 1998 as well as the surface and the bottom sensors in 1999 (Fig. 2 d) showed that short-term stratification occurred, with surface temperatures up to 4 °C greater than at the bottom of the water column. The lake mixed as a result of afternoon winds, surface cooling at night, or after a period of several days of more intense stratification, due to strong wind events. An example of the weak diurnal stratification of the water column is shown in Fig. 3.

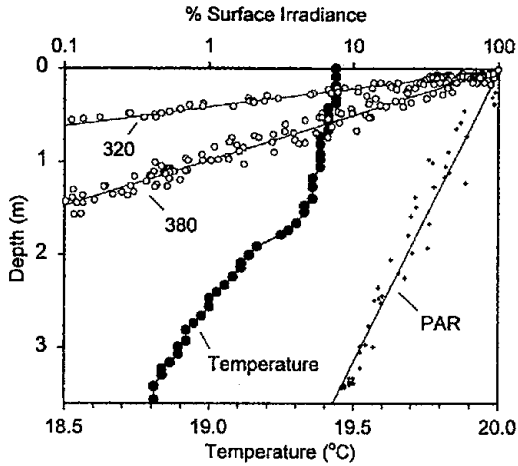


Fig. 3. Penetration of PAR and UVR at two wavelengths (320 nm and 380 nm). The measurements were made around midday on 20 June 1998. The attenuation curves are from log-linear regressions. The temperature profile recorded at the same time as the radiation profiles indicated weak thermal stratification of the water column.

Attenuation of solar radiation

Initial PUV profiles (20 June 1998, Fig. 3) of underwater solar irradiance gave K_d values of 11.4 m^{-1} (320), 8.9 m^{-1} (340), 4.6 m^{-1} (380) and 0.71 m^{-1} (PAR). By the time of installation of the TACCS system the $K_d(380)$ value had fallen by about 10%, and this decline then continued over the subsequent 26-day period of deployment of the instrument (Fig. 4). Significant declines in $K_d(380)$ were also observed during single days (Fig. 5 a), often accompanied by a subsequent increase in the late afternoon associated with increasing wind stress and mixing (Fig. 5 b).

Major ions, nutrients and carbon

Concentrations of the major cations and anions (Table 1) increased during the summer in concert with a slight increase in conductivity from 34 to $38 \mu\text{S}/\text{cm}$. The relatively high Na^+ and Cl^- concentrations and the Na^+/Cl^- molar ratio, which was similar to that in seawater, indicated that the lake is influenced by deposition of marine aerosols blown inland from nearby Hudson Bay. Nutrient concentrations were low throughout the study, although SRP, TN and TP increased slightly with time. The concentrations of Fe_T , Ba^{2+} and Sr^{2+} (Fig. 6) exhibited markedly different behaviours that highlighted the importance of the rainfall event on 9–10 August (Fig. 2). Throughout June and July, Fe_T , Ba^{2+} and Sr^{2+} were nearly constant. After the rainfall event, Fe_T dropped by more than 50%, whereas Ba^{2+} doubled in concentration and Sr^{2+} increased by over

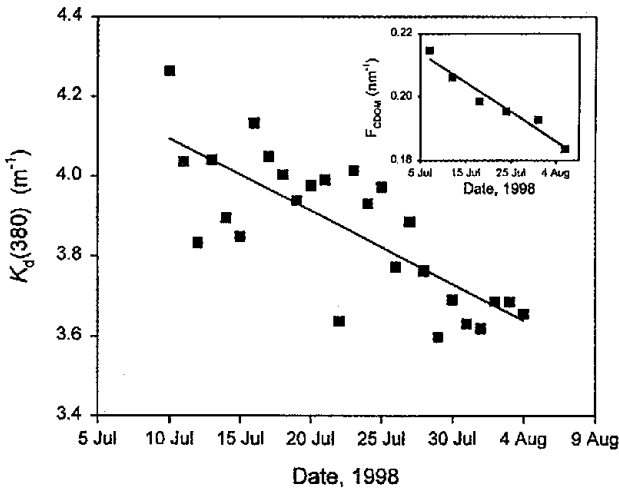


Fig. 4. Daily median $K_d(380)$ during the TACCS deployment (for the regression: $r^2 = 0.60$, $p < 0.001$). The inset shows the decrease in F_{CDOM} during the period of the deployment.

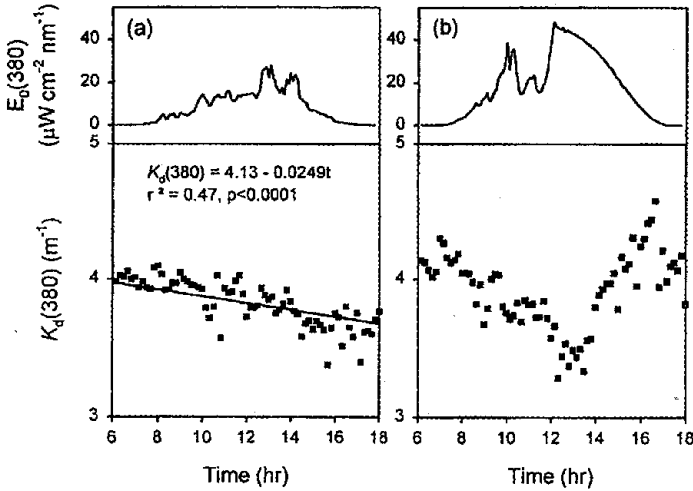


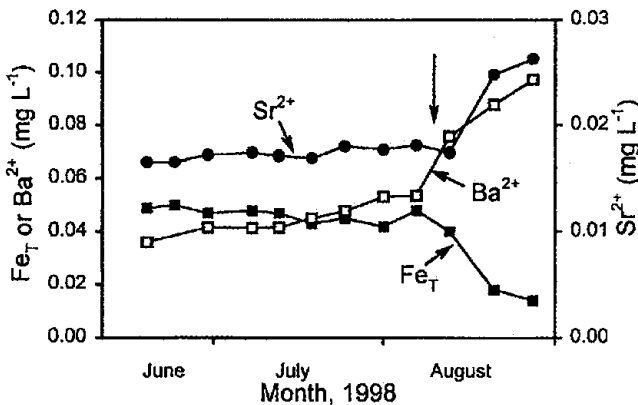
Fig. 5. Diurnal variations in $K_d(380)$ on (a) 12 July 1998 with the line of best fit; and (b) 25 July 1998 (closed squares). The upper panels (thin lines) show the surface irradiance at 380 nm measured on these two days.

50 %. The changes in concentration did not happen instantaneously with the storm, but rather occurred over a period of one or two weeks.

The concentration of POC increased throughout the period July–August to a maximum at the end of the sampling period, and Chl-a followed a similar trend, but with an initial peak in late June (Fig. 7 a). DIC also generally in-

Table 1. Range of concentrations in chemical variables (mg/L) in Lake Kachishayoot during summer 1998.

Variables	Average	Minimum	Maximum
Major ions			
Cl ⁻	5.2	5.0	5.4
SO ₄ ²⁻	2.5	2.2	2.8
Na ⁺	3.2	3.1	3.4
K ⁺	0.33	0.32	0.34
Ca ²⁺	2.5	2.3	2.7
Mg ²⁺	0.83	0.77	0.88
Nutrients			
NO ₃ ⁻ -N	<0.01	<0.01	<0.01
TN	0.21	0.18	0.25
SRP	0.0010	0.0002	0.0014
TP	0.007	0.003	0.011
SiO ₂	1.1	0.9	1.3

**Fig. 6.** Chemical constituents measured in Lake Kachishayoot in 1998. The values are mean concentrations in the water column for Fe_T (closed squares), Ba²⁺ (open squares) and Sr²⁺ (closed circles). The arrow marks the date of the storm event.

creased throughout the course of summer, with a sharp increase following the storm event (Fig. 7b). Concentrations of DOC similarly increased over summer, from 3.7 to 4.4 mg C/L (Fig. 7b).

CDOM dynamics

CDOM fluorescence (F_{CDOM}) decreased steadily from the start of the study to a minimum in early August (Fig. 7c). A sharp increase in F_{CDOM} occurred throughout the water column in the period following the storm event, and then slightly dropped at the end of the study. Measured $a(380)$ showed similar

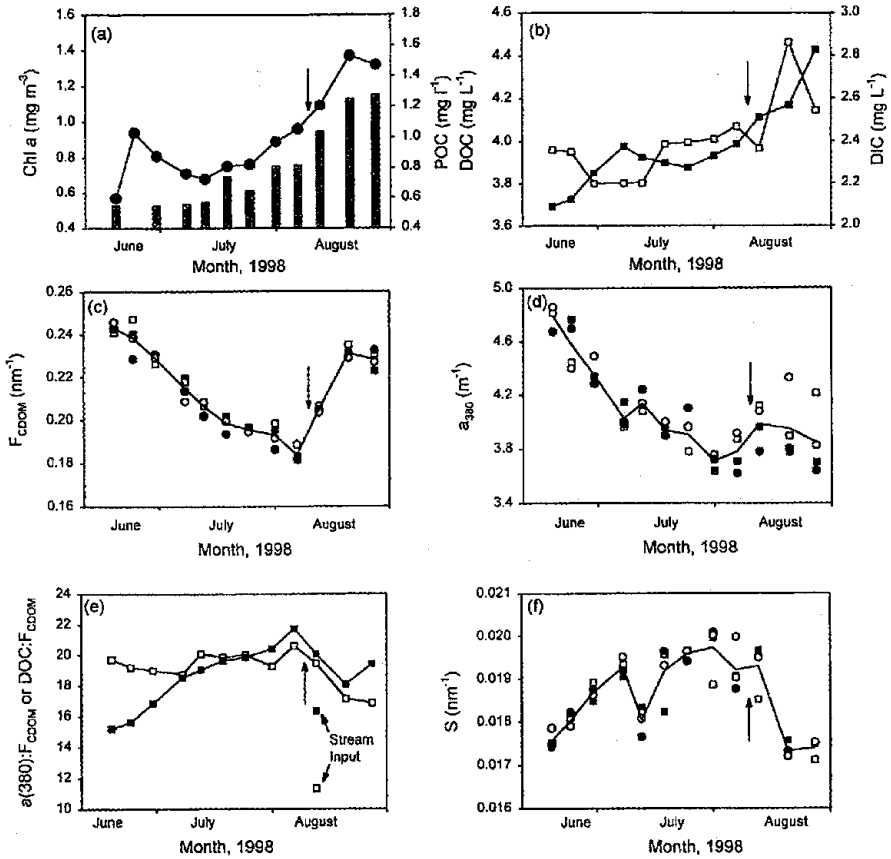


Fig. 7. Seston, carbon pools and CDOM-related variables measured in Lake Kachishayoot in 1998: (a) mean concentrations of chlorophyll-a (squares and line) and POC (bars) for the water column; (b) DOC (closed squares) and DIC (open squares) at 1 m; (c) F_{CDOM} ; (d) $a(380)$; (e) $a(380) : F_{CDOM}$ ratio (open squares) and $DOC : F_{CDOM}$ ratio (closed squares); also shown are the ratios in the major inflowing stream on the 13 August 1998; and (f) S , the slope of CDOM absorbance versus wavelength. The values for the CDOM variables are for four sampling depths: closed squares = 0 m, open squares = 1 m; closed circles = 2 m, open circles = 3 m. The arrows in each graph show the date of the storm event.

trends to F_{CDOM} early in the season (Fig. 7d), but did not increase as markedly after the rainfall. The ratios absorbance : F_{CDOM} and $DOC : F_{CDOM}$ both declined after the storm event (Fig. 7e). The parameter S in Equation 2 exhibited a pattern qualitatively opposite to both F_{CDOM} and $a(380)$ (Fig. 7f), in that it generally increased up until the rainfall event, and then dropped sharply. There was a pronounced, short-term drop in S in mid-July, accompanied by a slight increase in $a(380)$ but no change in the decreasing F_{CDOM} trend. There was little variation with depth in DOC , F_{CDOM} , $a(380)$ or S throughout the study.

The CDOM variables were measured in the main inflowing stream to Lake Kachishayoot (Fig. 1) on 14 August, four days after the major rainfall event. F_{CDOM} was 0.433 nm^{-1} , about two times higher than in the offshore lakewater. The $a(380)$ value was also higher (7.07 m^{-1}) and the S value much lower (0.0137 nm^{-1}) than in the lake. The concentration of DOC in the stream at the time of sampling was 4.9 mg/L and the DIC was 1.7 mg/L . The ratios absorbance : F_{CDOM} and DOC : F_{CDOM} were both low in the stream, consistent with the decline in these ratios in the lake caused by inflows after the storm event (Fig. 7e).

Discussion

The observed changes that occurred in Lake Kachishayoot during the study period highlight the dynamic nature of CDOM and the resultant variability in underwater UV experienced by aquatic biota over time scales of hours to months. Here we use the absorption and fluorescence characteristics of the CDOM, as well as other chemical and physical variables, to elucidate which of the possible loss and gain mechanisms were responsible for the variations in CDOM concentration. Processes which could be responsible for the loss of CDOM include bacterial degradation (MORAN & HODSON 1990, TRANVIK 1998); photochemical degradation (photobleaching; WETZEL et al. 1995, MORAN & ZEPP 1997, BERTILSSON & TRANVIK 1998); coagulation/flocculation and sedimentation (MOLOT & DILLON 1997); and export from the lake. Gains in CDOM stem mostly from input from the drainage basin (VISSER 1984, HINTON et al. 1997). Autochthonous production of DOC within the lake could also add to the CDOM budget, but such input is likely to be limited due to the less-complex, non-fluorescent nature of this organic material (THURMAN 1985, MCKNIGHT et al. 1994).

For the decrease in F_{CDOM} that occurred between the start of the study and the major rainfall event in early August to have been the result of export from the lake, it would be necessary for the inflowing stream to have lower F_{CDOM} than the lake. Measurements taken after the rainfall event in August and again during the 1999 summer (unpublished data) suggested that this was unlikely, as F_{CDOM} in the main inflowing stream was always higher than in the lake at the same time.

Flocculation is also unlikely to be the main cause for the decrease in F_{CDOM} . This process would be expected to result in a concomitant decrease in the concentration of DOC, but DOC remained steady or increased slightly during this period. This mechanism could only operate if the fluorescent material was concentrated into a very small fraction of the DOC, or if autochthonous DOC production was able to balance the loss. Particulate material collected in

sediment traps positioned in the lake throughout the study was dominated by zooplankton faecal pellets, with no evidence of flocculent material. The concentration of POC increased slightly during this period, but this was correlated with an increase in Chl-a (Fig. 7a). Similarly, bacterial degradation would decrease the concentration of DOC, but perhaps have less effect on F_{CDOM} , as the more accessible, uncoloured fraction of the DOC would be preferentially remineralised. Again, the recorded patterns were not consistent with this mechanism. The observed increase in DOC was probably the result of autochthonous production by phytoplankton and macrophytes. Alternatively, the increase in non-coloured DOC in the lake might also reflect seasonal changes in catchment vegetation and organic carbon release. For example, the release of sugars and sugar alcohols has been measured in Antarctic terrestrial environments dominated by mosses and lichens (VINCENT 1988), the vegetation-type that also dominates over most of the Lake Kachishayoot catchment.

Photodegradation of the CDOM (photobleaching) satisfactorily explained the observed variations in F_{CDOM} , $a(380)$ and S . Photo-oxidation results in the loss of fluorophores and longer wavelength chromophores, and therefore F_{CDOM} and absorbance decrease, and S increases, as was observed. Even though the other mechanisms discussed above may have played some role, it is probable that photobleaching was the dominant process controlling F_{CDOM} in the lake prior to the rainfall event. The nature of the DOC produced autochthonously was not determined, and though likely to contain little CDOM, may have had high S , and therefore led to an increase in S measured for the lake water.

The near linear decrease in F_{CDOM} was also consistent with the photo-oxidation of CDOM by UV radiation. MILLER (1998, 2000) has shown that this process should be approximately zero-order with respect to CDOM in mixed systems in which all the radiation responsible for the oxidation is absorbed, as was the case in Lake Kachishayoot:

$$dC/dt \approx k \quad (3)$$

where C is the concentration of CDOM, t is time and k is a constant. The relationship between F_{CDOM} and time in Lake Kachishayoot could be described by the equation:

$$F_{\text{CDOM}} = 0.241 - 1.23 \times 10^{-3} t_s \quad (4)$$

where t_s refers to the time in days from the start of the study. The form of this equation is that expected for the integrated zero-order rate equation, and requires that the incident radiation integrated between measurements was effectively constant. The equation implies a half-life for F_{CDOM} in the lake of 121 days, assuming an initial concentration of 0.30 nm^{-1} at the beginning of May at the time of ice-melt (determined by extrapolation of the F_{CDOM} relationship

back in time). This value is similar to half-lives estimated for colour degradation in lakes further south in the Canadian Shield as calculated by CURTIS & SCHINDLER (1997).

The results from the deployment of the TACCS unit confirmed that the decrease in CDOM resulted in an increase in clarity of the water column, and therefore increased penetration of UV radiation. This study is the first in which the relationship between these bio-optical parameters has been shown by means of a time series in a single lake; previous studies generally compared single point determinations of the penetration of UV radiation and F_{CDOM} in a range of lakes (e.g., SCULLY & LEAN 1994, LAURION et al. 1997). A linear relationship passing through zero has been reported to occur between F_{CDOM} and $K_d(\lambda)$ (LAURION et al. 1997). Therefore, the decrease in F_{CDOM} observed during the period of the TACCS deployment would be expected to result in a similar percentage decrease in $K_d(380)$. The decrease in $K_d(380)$ calculated from the data from the TACCS unit was nearly the same (12.0%) as that for F_{CDOM} (11.4%), in accordance with this relationship (Fig. 4). In contrast to F_{CDOM} , the concentration of DOC increased during this period, indicating that the production or inflow of non-fluorescent, presumably less complex organic material did not play a major role in determining $K_d(380)$. The sudden increase in DOC and F_{CDOM} in August was directly associated with the increased stream input after the major rainfall event. The characteristics of the water in the main inflowing stream four days after the rainfall were consistent with this conclusion: F_{CDOM} was considerably higher than in the lake itself, as was DOC. The organic matter in the stream had a far lower DOC : F_{CDOM} ratio (Fig. 7e) and lower S (0.0137 nm^{-1} cf. 0.0195 nm^{-1}) than the lake water immediately prior to the rainfall, suggesting that it was less bleached. The changes in the concentration of Fe_T , Ba^{2+} and Sr^{2+} after the rainfall event allow a preliminary estimate of the percentage of the volume of the lake flushed by the inflow after the storm. Fe_T decreased markedly in the weeks after the rainfall (Fig. 6). For this change in the concentration to occur, at least 60% of the lake volume must have been replaced during this period if it is assumed that the inflowing water had zero Fe_T . Higher Fe_T in the inflowing water would imply a greater percentage of the lake basin being flushed. The strong correlations between Ba^{2+} and Sr^{2+} (ions with little biological reactivity), and Fe_T imply that the inflowing water had higher concentrations of these ions than the lake water, and indicated that the decrease in Fe_T was not the result of biological processes. Assuming the volume given in the 'Study Site' section above, there is a reasonable balance between the amount of rainfall during August on the drainage basin and the volume of water entering the lake.

The changes in these chemical variables did not occur in a single event, but rather continued to change over a period of approximately 2 weeks. This resulted from the non-instantaneous nature of the input. Even though the rainfall

occurred over a 24-hour period, the filling of reservoirs within the drainage basins and slow flushing of organic material from the soils, swamps and bogs resulted in the spreading of the CDOM input into the lake over a much longer period than the rainfall event. Within-lake mixing processes are also likely to have retarded the effect of the high CDOM water at the sampling site.

The rise in $a(380)$ associated with the rainfall event was less than anticipated from changes in F_{CDOM} alone. As $a(380)$ is conservative on the mixing of waters of differing characteristics, this suggests that the incoming CDOM had different properties to that in the lake, as its fluorescence was relatively high compared to its $a(380)$. The characteristics of the stream input again supported this conclusion, in that the ratio of $a(380)$ to F_{CDOM} was much lower in the stream than in the lake (Fig. 7e). If the majority of the CDOM present in the lake at the start of the study was the result of inputs during snow melt, then the characteristics of the CDOM imported into the lake must have changed with time, especially considering that the $a(380):F_{\text{CDOM}}$ ratio was reasonably constant during the period of photodegradation. VISSER (1984) similarly found that the optical and chemical characteristics of humic substances in streams and bogs of the Canadian boreal forest changed with time, and suggested that this was due in part to the release of younger, less 'mature' humic and fulvic acids during periods of greater flushing associated with spring snow melt.

Given the correlation between $K_d(380)$ and F_{CDOM} (Fig. 4), the TACCS record also provided information regarding short term (within-day) CDOM dynamics. Changes in the structure of the water column appear to have played an important role in controlling CDOM concentrations in the near-surface waters of the lake. During periods of diurnal stratification there was a significant decline in $K_d(380)$ over the course of the day consistent with photobleaching of CDOM in the uppermost few tens of cm of the water column where the UV measurements were recorded. The rate of photodegradation was much higher than that observed over the full sampling period because the surface waters were recharged with CDOM from below the photochemical zone (*sensu* SCULLY *et al.* 2000) during nocturnal or afternoon mixing of the water column (Fig. 5b). Thus diurnal stratification and mixing influence the short-term dynamics of CDOM in the near-surface waters as well as the distribution of photochemically-produced, reactive oxygen species (SCULLY & VINCENT 1996) and the photobiology of planktonic algae (MILOT-ROY & VINCENT 1994).

The results from this study reveal a number of important factors in the CDOM dynamics of lakes. Photodegradation of CDOM proceeds at an approximately constant rate during ice-free periods when considered over weekly time scales. In the absence of significant CDOM inputs this results in a steady decrease in CDOM concentration. The input of CDOM can be a stochastic occurrence that depends to a large degree on the timing and intensity of hydrological processes, specifically snow melt and rainfall. For lakes with large

drainage area to volume ratio, snow melt would be expected to replace much of the water in the lake, and therefore the CDOM characteristics for the lake will be reset from the previous year and from processes occurring during winter to those of the meltwater input. This could result in significant variations in CDOM concentration from year-to-year, as it will depend on such variables as the amount of snowfall, the rapidity of melt, the depth of the active layer (in permafrost regions), and the efficiency of mixing of terrestrial CDOM into the snow melt. For larger, deeper lakes in which a smaller percentage of the volume is replaced, there may be a legacy (*sensu* VOGT et al. 1997) of the processes and conditions occurring in the lake during the previous summer and winter. On shorter time scales, the diurnal stratification cycle will strongly influence CDOM dynamics, especially in the near-surface zone in which photo-bleaching takes place. The biota living in the surface layer of lakes must therefore be adapted to survive in a highly variable UV environment given the fluctuations in exposure caused by intermittent stratification and mixing, and the variations in UV-screening by CDOM caused by the dynamic interplay between hydrologic processes and photodegradation.

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