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Hydrologic control of dissolved organic matter in low-order Precambrian Shield lakes

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Abstract. Concentrations of dissolved organic carbon (DOC) and color were measured as a function of time in enclosures and lakes at the Experimental Lakes Area, to calculate their net loss rates. *Loss rates in enclosures were first order for both DOC and color*, with *half-times for loss of 166 and 122 d, respectively*. Thus, *the colored, light-attenuating component of the DOC pool is lost from water more rapidly than is bulk DOC*. Loss rates in lakes, calculated from a steady state model, were similar to values for color in enclosures, but for DOC in lakes were four times slower than in enclosures. In lakes, loss rate for DOC increased rapidly with decreasing water residence time (τ_w) but was independent of τ_w when it was greater than 3 years. In lakes, the loss rate for color was independent of water residence time. The difference in losses of DOC and color between lakes and enclosures could be from release of low-color DOC from sediments.

Introduction

Dissolved organic matter, (typically measured as dissolved organic carbon and hereafter referred to as DOC) is a key factor shaping aquatic ecosystems. It transfers energy from the terrestrial catchment to the aquatic food web along with nutrients and trace and transition metals (Schindler et al. 1992; Wetzel 1992; Urban et al. 1990). DOC also attenuates visible light and ultraviolet (UV) radiation. When UV radiation is absorbed, DOC is degraded and metals are reduced or oxidized depending on the pH, and highly reactive reduced oxygen species are produced (Cooper et al. 1994). Absorbance increases with decreasing wavelength (Green & Blough 1994). UV attenuation is correlated to DOC by a power function but to organic color by a linear function (Scully & Lean 1994). Together, these observations suggest that the proportion of colored organic matter in the DOC pool is not constant and that factors which alter the proportion should be identified.

Concentrations of DOC, and the staining of water by DOC from terrestrial runoff are correlated with properties of catchments, particularly the

proportion of wetland (Urban et al. 1989). In northern oligotrophic lakes with vegetated catchments, mass balance calculations reveal that most lakes are sinks for DOC (Schindler et al. 1992, and this volume; Dillon et al. this volume). These correlations probably depend on observations that the pool of DOC, particularly colored organic matter, is dominated by external or "interfacial" inputs to the pelagial zone (Wetzel 1992). These DOC sources are characteristically highly colored relative to in-lake sources of DOC that are slightly colored or uncolored (Tipping et al. 1988). Similarly, the color of water increases directly with increasing relative drainage area and decreases directly with increasing water residence time (Schindler 1971; Engstrom 1987; Rasmussen et al. 1989; Meili 1992). Thus, properties of both lakes and their catchments can determine the concentration of bulk DOC and of the organic matter responsible for water color.

The purpose of this study was to determine the kinetics for loss of color and DOC for low-order Precambrian Shield lakes at the ELA, as part of a larger research program examining the sources and sinks of DOC in Canadian lakes. For these analyses, we assume that lakes approximate constantly-stirred tank reactors with different flushing rates. By comparing dependencies of color and DOC on the hydrologic flushing rate, we tested the hypothesis that light absorbing components of DOC are removed or transformed at rates faster than is bulk DOC. We compared these relative rates to rates measured in enclosures that contained lakewater isolated from allochthonous inputs except those from direct precipitation.

Site Description

The geography, bathymetry and chemistry of lakes in the Experimental Lakes Area (ELA) have been described elsewhere (Brunskill & Schindler 1971; Armstrong & Schindler 1971; Brunskill et al. 1971). Morphometric and chemical data for the study lakes are summarized in Table 1, and the location of the lakes within the ELA is shown in Figure 1. Briefly, the lakes are located in on the Precambrian Shield, northwestern Ontario (Figure 1), in acid granodiorite catchments with little overburden (average 0.5 m). Soils are very thin, poorly-developed orthic brunisols (Brunskill et al. 1971). The ELA occupies a divide separating catchments that drain into Lake of the Woods, and into the English River.

Sample Collection and Preparation

Closed-bottom polyethylene enclosures, 1 m^2 and 3 m long, were filled with lake water from Lake 239 on May 20 and 21, 1994. Enclosures were filled by holding the top of the enclosure open with metal bars inserted through a sewn

Table 1. Summary data for the study lakes at ELA. Ao and Ad are lake and catchment areas. Z_{mean} is the mean depth. V is lake volume. Tw is water residence time. Color is the spectrophotometric absorbance at 350 nm in a 5 cm light path. DOC is the concentration of dissolved organic carbon. Rate constants (k) and half-times, have units of d^{-1} and d, respectively. Rate constants and half-times were calculated (Equations 2, 3) assuming that lakes were at steady state for water, color and DOC for 200 ice-free days, with precipitation (P), evapotranspiration (ET) and lake evaporation (E) were 0.7, 0.55, and 0.6 m, respectively. Color and concentrations of DOC in terrestrial runoff were set to 20 mg L^{-1} and 0.9 units $(5\ cm)^{-1}$.

Lake	Ao, m^2 ($X10^4$)	Ad, m^2 ($X10^4$)	Z_{mean}, m	V, L ($X10^7$)	Tw, year	color Abs_{350}	DOC, mg L^{-1}	k(DOC) ($X10^{-3}$)	$T_{1/2}$ (DOC)	k(color) ($X10^{-3}$)	$T_{1/2}$ (color)
114	12.1	57.0	1.71	20.7	2.1	0.094	8.42	2.54	273	17.16	40
221	9.0	82.0	2.09	18.8	1.4	0.339	13.70	1.26	552	5.13	135
222	16.4	204.3	3.66	60.0	1.9	0.370	11.40	1.78	388	3.50	198
224	25.9	97.5	11.59	300.3	17.4	0.016	4.28	0.85	814	13.04	53
225	4.0	30.5	1.18	4.7	0.9	0.403	13.72	1.78	389	5.51	126
226	16.1	97.2	5.97	96.1	5.9	0.125	8.23	1.00	694	4.61	151
227	5.0	34.4	4.42	22.1	3.9	0.197	11.75	0.70	984	4.04	172
239	56.1	390.5	10.53	591.0	9.2	0.137	7.89	0.71	972	2.72	255
303	9.5	54.1	1.58	15.0	1.7	0.162	10.94	1.91	362	11.87	58
304	3.4	26.4	3.38	11.5	2.7	0.240	11.79	1.05	662	4.58	151
305	52.0	236.8	15.12	786.0	19.3	0.041	6.09	0.48	1437	4.73	147
382	37.1	204.5	5.74	212.8	6.2	0.117	8.97	0.80	868	4.74	146

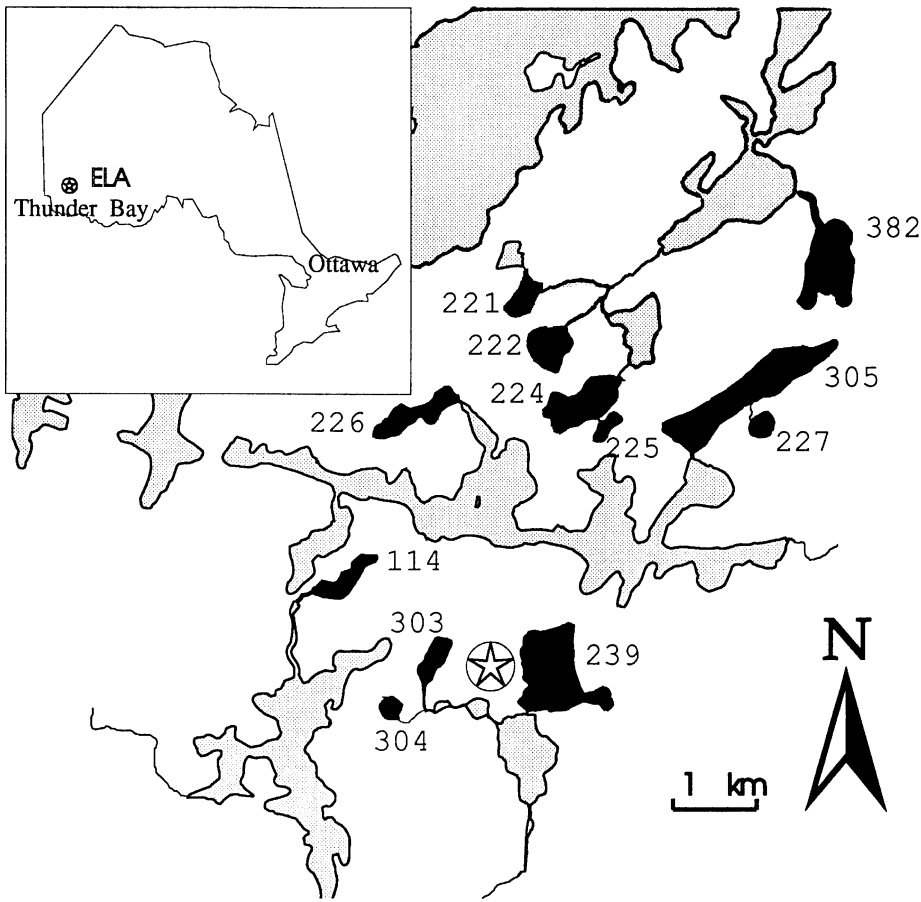

Figure 1. Map of the study site showing the location of the ELA (star), and the study (black) and other (grey) lakes with connecting drainage.

collar, collapsing the enclosures vertically, submerging the entire enclosure to about 4 m depth, and then pulling the open top of the enclosure to the surface, extending it to capture a column of water. Enclosures were suspended from floating frames and sampled weekly from 6 May until 12 August 1994 using a tygon tube to collect integrated water samples from 0–2.5 m depth.

Surface water samples were collected from 12 low-order lakes having a range of relative drainage areas and water retention times. Samples were collected in polyethylene bottles during June, July, and August 1994. Inverted bottles were immersed by hand on the leeward side of a drifting boat, and filled at a depth of about 0.3 m. Samples were returned to the field laboratory and processed within 24 hours.

Aliquots of samples were filtered through precombusted Whatman GF/F filters in the laboratory. Samples for analysis of DOC were pipetted (20 mL) into individual glass scintillation vials, acidified with 0.2 mL of 1.0 N HCl, and refrigerated in darkness until analyzed in September 1994 at the University of Alberta Water Lab.

Subsamples of filtrates were analyzed for absorbance and fluorescence in the field laboratory. Absorbance was measured at 350 nm in a 5 cm glass cuvette using a Bausch and Lomb Spectronic 70 spectrophotometer. 350 nm was chosen to conform with the wavelengths used at ELA during the 1970's. Comparison of our values to measures made at other wavelengths is simple because the slope of the absorbance vs. wavelength relationship is relatively constant (Green & Blough 1994). Fluorescence was measured on filtrates with a Turner Designs model 111 fluorometer, using a 300–400 nm excitation filter and a 340–600 nm emission filter. Values were standardized to quinine sulfate units (QSU) where 1 QSU = 1 μg L^{-1} quinine sulfate in 0.1 N H_2SO_4 (Scully & Lean 1994).

Calculations

The specific absorbance coefficient (SAC) of organic matter was calculated from Equation (1).

$$SAC = \frac{(2.303 \times Abs_{350})/(pathlength)}{[DOC]/1000} \quad (1)$$

with units of cm^2 mg^{-1} for SAC, and mg L^{-1} for the concentration of DOC, respectively. Specific fluorescence coefficients (SFC, μg QS mg^{-1} C) were calculated by normalizing fluorescence to the concentration of DOC in mg L^{-1}.

Organic carbon content was measured in subsamples of filtrate using a high temperature catalytic oxidation (HTCO) organic carbon analyzer (Ionics, 1555). The furnace temperature was 850 °C, the carrier gas was ultra high purity oxygen (Linde), and the catalyst was platinum (Ionics). Samples were acidified to pH <2 and sparged for three minutes with oxygen. Subsamples (120 μL) were injected into the furnace by an autosampler.

Rate constants for loss of color and DOC in enclosures were calculated by Equation (2).

$$k = -\ln\frac{X_t}{X_0}/t \quad (2)$$

where X is the concentration of DOC or color (absorbance), at times 0 and *t*, and *k* is the rate constant with units d^{-1}.

Rate constants for loss of color and DOC in lakes were calculated by setting the value of $X_t = X_l$ at time t = 1, substituting for X_0 the right side of Equation (3), equal to the concentration of X_l in the lake mixed with the average hydrologic inputs of water, $(P–E)A_l + (P–ET)A_d$, and X for one day,

$$X_0 = \frac{[A_d(P - ET)X_d + V_l(X_l)]}{[A_d(P - ET) + A_l(P - E) + V_l]} \tag{3}$$

to give

$$k = -\ln\left(\frac{\frac{X_l}{[A_d(P-ET)X_d+V_l(X_l)]}}{[A_d(P - ET) + A_l(P - E) + V_l]}\right) \tag{4}$$

where *X* is the concentration of DOC (mass m^{-3}) or the absorbance of a water sample (units cm^{-1}) as for Equation (2), and A is area in m^2 with the subscripts *l* and *d* indicating values for the lake and drainage area respectively. All other abbreviations are defined in Table 1. Because this is a steady state model, variation in all of the input variables are accumulated into estimation of the rate constants.

Half-times for loss of color and DOC were calculated from rate constants for enclosures and lakes by Equation (5).

$$T_{1/2} = \frac{\ln(2)}{k} \tag{5}$$

where $T_{1/2}$ is the half-time for net loss with units d, and *k* is the rate constant with units d^{-1}.

Results

Enclosures

Concentrations of dissolved organic carbon (DOC), and water color, decreased over the 100 days of the experiment (Figure 2). Loss rates were first order (Equation 2) and were significantly greater for color 0.0042 d^{-1} (cv 3.2%) than for bulk DOC 0.0031 $^{-1}$ (cv 9.5%). Half-times for loss of color and DOC were 166 and 222 d, respectively (Equation (4)). Because the color of water was lost at a rate more rapid than was DOC the specific absorbance decreased over time. Specific absorbance decreased exponentially from 8.1 to 6.8 cm^2 mg^{-1} in 100 days (data for three enclosures were pooled, r^2 = 0.54, $P < 0.01$).

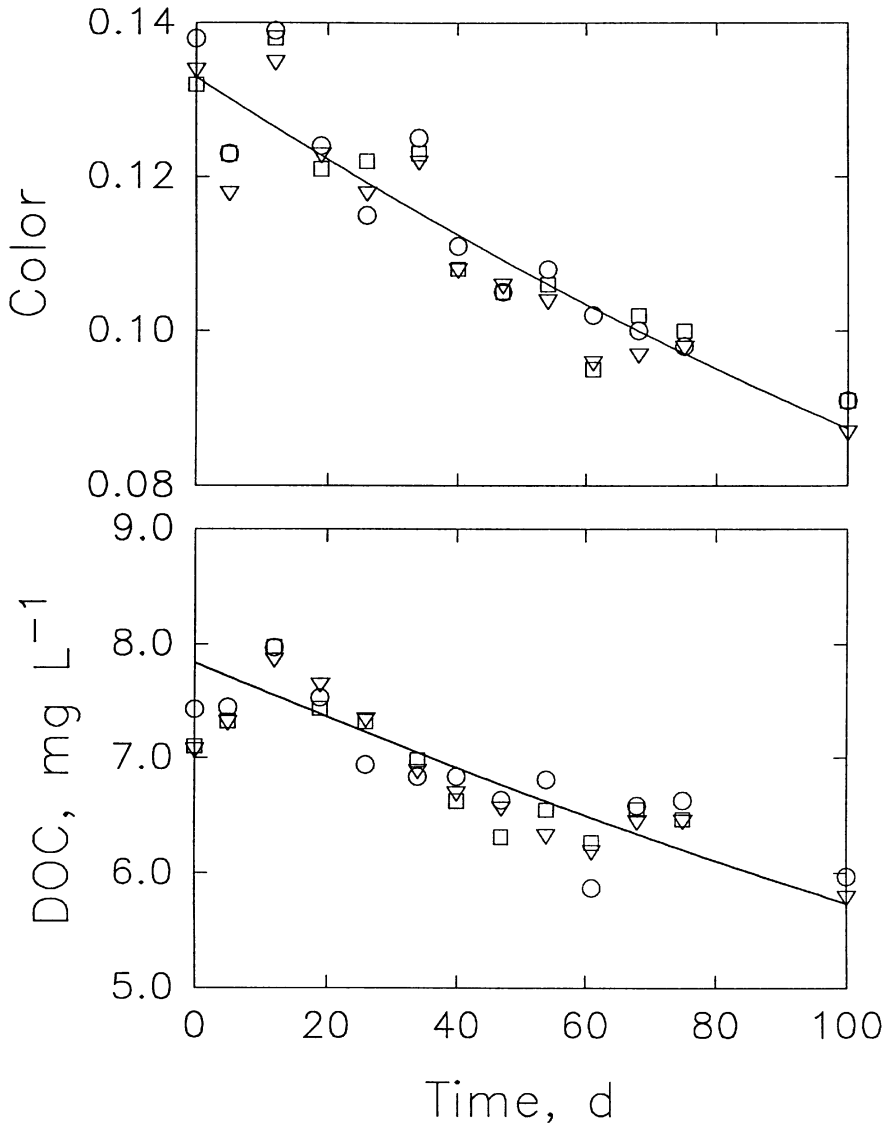

Figure 2. Color of water and concentration of DOC in three replicate enclosures (Lake 239). Lines are drawn from the mean of the three rate constants for DOC ($k = 0.0031\ d^{-1}$) and color ($k = 0.0042\ d^{-1}$) and initial concentration or color.

Lakes

Throughout the summer, concentrations of DOC, color (measured as absorbance) and fluorescence were consistently higher in lakes with high drainage

areas relative to surface areas (Ad:Ao; Figure 3a, c, e). The dependence of color and fluorescence on DOC concentration was not constant because values of specific absorbance and specific fluorescence also increased with increasing Ad:Ao. The concentration of DOC in lakewater was inversely dependent on the residence time of water in the lake basin (Figure 3b). Similarly, the color and fluorescence of water samples decreased with increasing water residence time (Figure 3d, f). The specific absorbance coefficient (SAC) and specific fluorescence coefficient (SFC) of the organic matter also decreased with increasing water residence time (Figure 3h, j). Together, these observations indicate that as water residence time increases, organic matter becomes less colored and fluoresces more weakly (Figure 3g. i).

Rate constants for removal of DOC and color from the lakes were calculated from a steady state model (Equation (4)) for removal of DOC and color (Table 1). The average values of the rate constants for DOC and color were 0.00124 d^{-1} and 0.0068 d^{-1} respectively. Half-times for loss of DOC and color were 620 and 120 days, respectively (Equation (5)). Loss rates for color among lakes were independent of the relative drainage area (Ad/Ao, Table 1), water residence time and the color of water (t-test of slope = 0). Loss rate constants for DOC were independent of Ad/Ao and DOC concentration, but decreased from 0.006 to 0.0026 with increasing water residence time ($k_{DOC} = 0.002 * \tau_W^{0.399}$, $r^2 = 0.55$, $P < 0.05$; Figure 4). Partial residence times for DOC (excluding hydrologic output, τ_{DOC}) in the lakes, calculated from rate constants by Equation 6, increased directly with the log of τ_W (Figure 5, $r^2 = 0.69$, $P < 0.05$).

$$\tau_{DOC} = \left(\frac{1}{(1 - e^{-k})} \right) / 365 \tag{6}$$

where k is the first order rate constant with units d^{-1} and 365 is a constant to convert from days to years.

Discussion

Hydrologic dependence of DOC, Color and Fluorescence

The observed relationships between the relative drainage area (Ad:Ao) and the color of water were similar to those noted previously by others (Schindler 1971; Engstrom 1987; Rasmussen et al. 1989). Similarly, Meili (1992) observed that water color decreased sharply with increasing water residence time in lakes with forested catchments. The consistency of these relationships indicate the yield of DOC from catchments and loss of colored organic matter

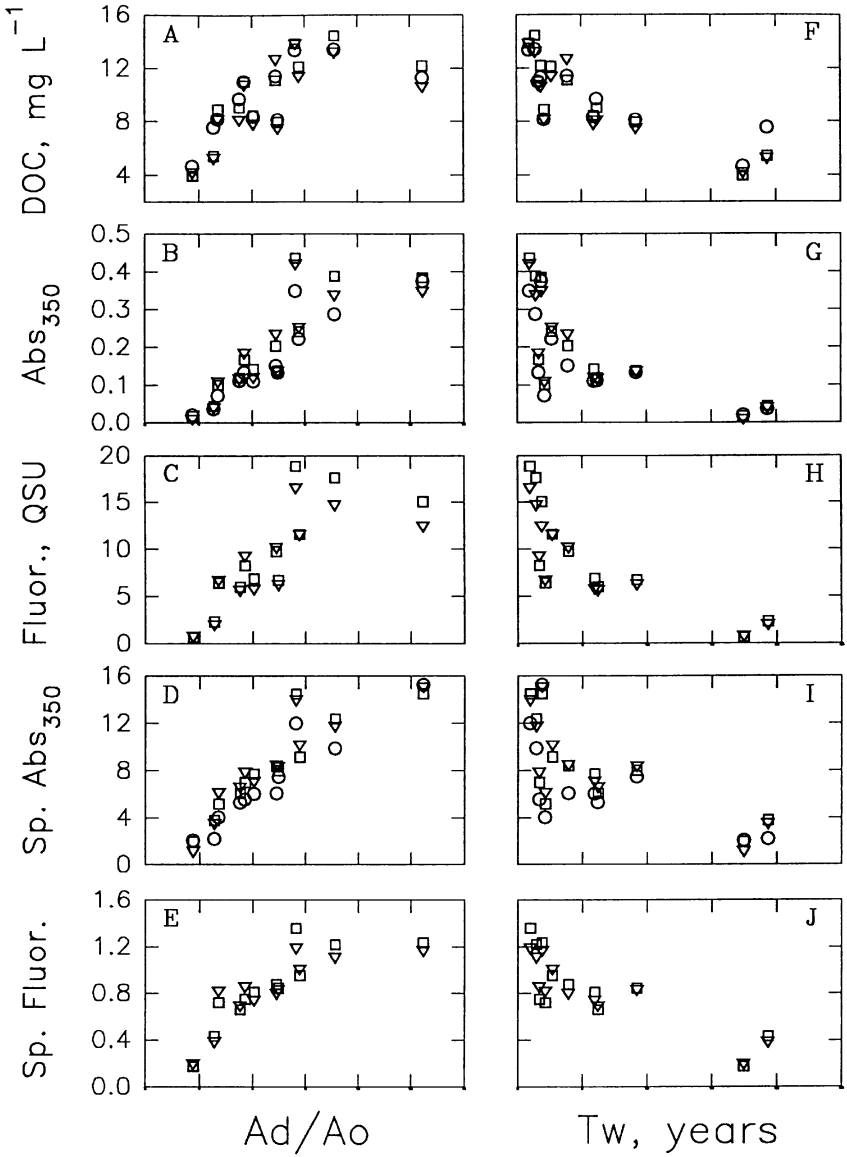

Figure 3. a) Concentrations of DOC, b) water color (measured as absorbance at 350 nm in a 5 cm cuvette), c) fluorescence in enclosures (units), d) specific absorbance coefficients (cm^2 mg-C^{-1} ÷ 1000), and e) specific fluorescence coefficients (units L mg-C^{-1}) measured in samples of lake waters (Table 1) in lakes with different relative drainage area (Ad:Ao). Figures 3 f-j are the same as described for a-e except as functions of residence times of lake water (τ_W). Circles, triangles and squares correspond to collection dates 12 June, 14 July, and 16 August, respectively.

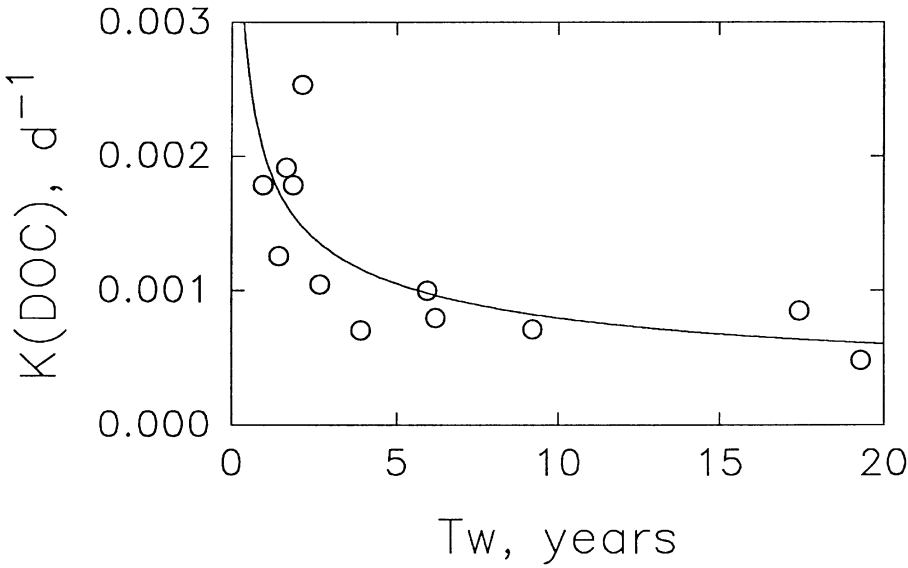

Figure 4. Rate constants for loss of DOC from the study lakes at different water retention times. Constants were calculated from Equation 3 and data in Table 1.

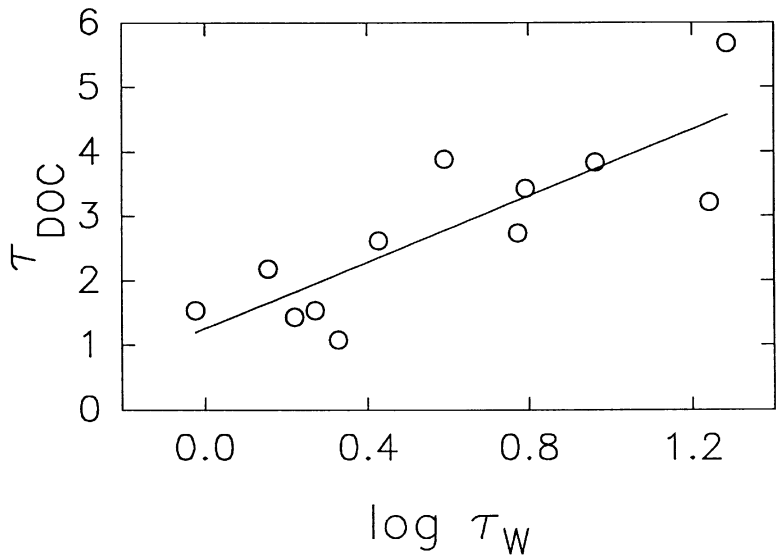

Figure 5. Partial residence times for DOC (τ_{DOC}) calculated from rate constants by Equation 5, and correlated with the log of water residence time (τ_W, $r^2 = 0.69$, $P < 0.05$).

in lakes are relatively constant within regions. Such relationships between catchment properties and the quantity and composition of organic substances in water are region-specific (Engstrom 1987).

Organic color and fluorescence appeared to be lost from lake water faster than DOC because specific color and fluorescence of organic matter decreased with decreasing Ad:Ao and increasing water residence time. Similar decreases in specific color of dissolved organic matter occurred with increasing water residence times in freshwater and saline lakes in Alberta (Curtis & Adams, 1995). Values of specific color were much lower for the saline lakes, which are endorheic basins with very long water residence times. These findings are consistent with so-called photo-bleaching of organic matter (Kieber et al. 1990) and with dilution of the DOC pool by colorless, non-fluorescing DOC, possibly released from sediments or from photosynthesis by aquatic plants.

DOC Loss rates

The loss rates of DOC from enclosures in Lake 239 ($k = 0.003$, $T_{1/2} = 222$ d) were more rapid in 1994 (this study) than for enclosures of the same dimension and material in 1987 ($k = 0.002$, $T_{1/2} = 400$ d; Curtis 1993). The difference between years was consistent with concentration-dependent loss rate, for DOC concentrations in 1987, a drought year, were 10% lower than in 1994 which followed 2 wet years. Differences in loss of DOC between years were probably not due to temperature because seasonal average surface water temperatures were within one degree between years (Schindler et al. 1995, Curtis, data not shown). Loss rates in enclosures were about three times more rapid than the average rates calculated for lakes (Table 1). The shallow mean depth of enclosures relative to lakes could have enhanced DOC loss if photochemical processes are important for DOC loss. In contrast, biodegradation and flocculation are dependent on concentration and should be independent of mean depth.

Color loss rates

The more rapid loss rates for colored organic matter than for bulk DOC in enclosures and lakes are consistent with two pools of DOC and different mechanisms for loss of organic matter – a colored component that is lost rapidly and a low-color component with slower loss rates. First, the colored portion of the DOC pool may be depleted by photolysis to less colored components (Kieber et al. 1990). Second, the colored organic matter may be flocculated or biodegraded preferentially over less colored components. And third, the bulk DOC pool could be diluted with low-color autochthonous

DOC (Tipping et al. 1988). These mechanisms are not mutually exclusive and all three may be operating.

Rapid selective loss of the colored portion of the DOC may partly explain the apparent dependence of bulk DOC loss rates on water residence time (Figure 4). Colored organic matter has a more rapid loss rate and probably composes a larger proportion of the DOC pool in rapidly flushing lakes (Figure 3i). Bulk DOC loss rates are also greatest at short water residence times but become independent of residence time at values greater than about three years (Figure 4). Rapid loss of colored organic matter has important implications for the vertical distribution of light and ultraviolet photochemical products. For example, diffuse attenuation coefficients for UV-B and UV-A radiation, and photochemical reaction rates have been correlated to spectrophotometric absorbance and fluorescence (Scully & Lean 1994).

Because color and DOC depended differently on water residence time in lakes, it may be possible to estimate empirically variables such as water residence time from simple measures of the specific absorption coefficient (SAC) for DOC in lakewater. Low-order drainage lakes, as in this study, are the simplest cases because the DOC pool is dominated by inputs from the catchments and by internal losses. Within the ELA region, the correlation between SAC and water residence time was significant ($r^2 = 0.59$, $P < 0.01$). However prediction limits are large because of real variation and small sample size. Our future studies have been designed to address these applications.

Comparison of DOC retention among lakes and over time

Retention coefficients (R = [inputs-outputs]/inputs) were calculated for the study lakes to compare with those reported for lakes in the Dorset region of Ontario (Dillon & Molot, this volume) and with estimates of DOC retention in Lake 239 (ELA, Schindler et al. 1992). Values of R were calculated for the study lakes by difference of the summed steady-state daily inputs minus outputs during a 200 d hydrologic year, using data in Table 1. Retention of DOC was dependent on water residence time for all lakes in all years (Figure 6, and Dillon & Molot, this volume) and could be described by a rectangular hyperbola. 1/R (cf. Dillon & Molot, this volume) was linearly correlated with water residence time but only for lakes with relatively short water residence times. Parameter values for the fitted rectangular hyperbola indicated that the theoretical maximum retention of DOC (R_{max}) was 0.84 (s.e. 0.044) and that half maximal retention was at about 3.2 (s.e. 0.57) years. That DOC retention does not approach 1 at infinitely long water residence times is consistent with observed evapoconcentration of DOC in saline lakes (Curtis & Adams, 1995), and with analyses of radiocarbon in DOC (Schiff et al., this volume).

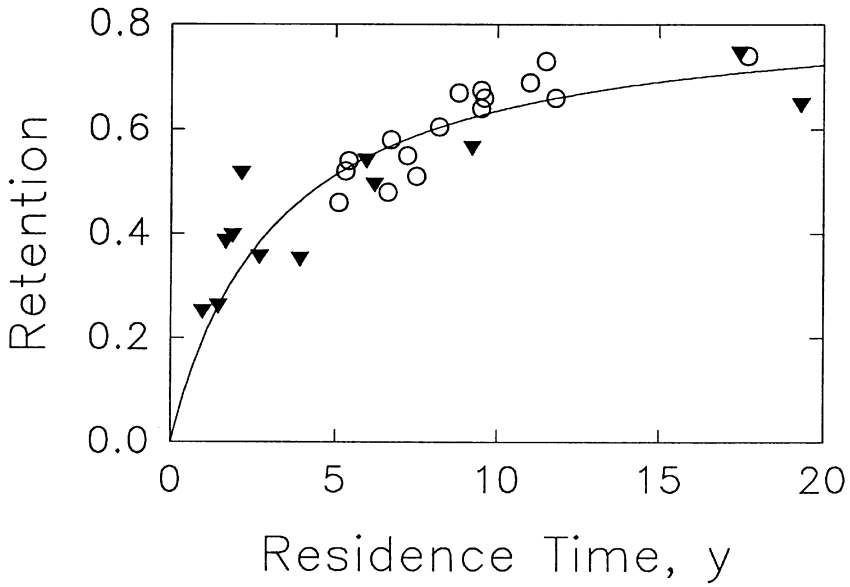

Figure 6. Retention coefficients (R) for ELA lakes (this study, closed triangles), and for Lake 239 over a 20 year period of climatic warming (Schindler et al. 1992, open circles). The line is a least squares fit to the equation $R = (R_{max} * \tau_W)/(R_{1/2} + \tau_W)$ with $r^2 = 0.86$, $P < 0.01$.

These results have two significant implications. First, DOC loss rates for boreal lakes are independent of input concentration and precipitation. Lake waters and runoff (the main source of DOC) in southcentral Ontario contain about 50% of the amount of DOC typical for ELA (Dillon & Molot, this volume; Schindler et al., this volume). Furthermore, the southcentral Ontario region receives significantly more precipitation than does ELA. Despite these differences the loss rates of DOC are similarly dependent on water renewal time. This is consistent with similar DOC quality and loss mechanisms between regions.

Secondly, the dependence of DOC retention on water residence time among lakes can be used to predict the effect of climatic change on DOC concentration for individual lakes. This extrapolation is supported because the dependence of R on water residence time was the same among lakes as it was for Lake 239 over 20 years of climatic warming (Schindler et al. 1992; Schindler et al. this volume). Formulation of this empirical relationship is important for estimating indirect effects of climate change that are mediated by DOC.

References

Armstrong FAJ & Schindler DW (1971) Preliminary chemical characterization of waters in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Board Can. 28: 171–187

Brunskill GJ & Schindler DW (1971) Geography and bathymetry of selected lake basins, Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Board Can. 28: 139–155

Brunskill GJ, Povoledo D, Graham BW & Stainton MP (1971) Chemistry of surface sediments of sixteen lakes in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Board. Can. 28: 277–294

Cooper WJ, Shao C, Lean DRS, Gordon AS & Scully FE (1994) Factors affecting the distribution of H_2O_2 in surface waters. In: Baker LA (Ed) Environmental Chemistry of Lakes and Reservoirs (pp 391–422). ACS Advances in Chemistry Series No. 237, American Chemical Society, Washington

Curtis PJ & Adams HE (1995) Dissolved organic matter quantity and quality from freshwater and saline lakes in eastcentral Alberta (Canada). Biogeochemistry 30: 59–76

Dillon PJ & Molot LA (in press) Dissolved organic and inorganic carbon mass balances in central Ontario lakes. Biogeochemistry: this volume

Engstrom DR (1987) Influence of vegetation and hydrology on the humus budgets of Labrador lakes. Can. J. Fish. Aquat. Sci. 44: 1306–1314

Green, SA & Blough, NV (1994) Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. Limnol. Oceanogr. 39: 1903–1916

Kieber RJ, Zhou X & Mopper K (1990) Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea. Limnol. Oceanogr. 35: 1505–1515

Meili M (1992) Sources, concentrations and characteristics of organic matter in softwater lakes and streams of the Swedish forest region. Hydrobiologia 229: 23–41

Rasmussen JB, Godbout L & Schallenberg M (1989) The humic content of lake water and its relationship to watershed and lake morphometry. Limnol. Oceanogr. 34: 1336–1343

Schindler DW (1971) A hypothesis to explain similarities and differences among lakes in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. 28: 295–301

Schindler DW, Bayley SE, Curtis PJ, Parker BR, Stainton MP & Kelly CA (1992) Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in precambrian shield lakes. Hydrobiologia. 229: 1–21

Scully NM & Lean DRS (1994) The attentuation of UV radiation in temperate lakes. Arch. Hydrobiol. 43: 135–144

Tipping E, Hilton J & James B (1988) Dissolved organic matter in Cumbrian lakes and streams. Freshwater Biology 19: 371–378

Urban NR, Bayley SE & Eisenreich SJ (1989) Export of dissolved orgainc carbon and acidity from peatlands. Water Resour. Res. 25: 1619–1628

Urban NR, Gorham E, Underwood JK, Martin FB & Ogden III JG (1990) Geochemical processes controlling concentrations of Al, Fe, and Mn in Nova Scotia lakes. Limnol. Oceanogr. 35: 1516–1534

Wetzel RG (1992) Gradient-dominated ecosystems: sources and regulatory functions of dissolved organic matter in freshwater ecosystems. Hydrobiologia 229: 181–198