



Linking dynamics of dissolved organic carbon in a forested lake with environmental factors

ISABEL RECHE^{1,2,*} and MICHAEL L. PACE¹

¹*Institute of Ecosystem Studies, Box AB, Millbrook, NY 12545-0129, USA;* ²*Current address: Departamento Biología Animal y Ecología Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain;* **Author for correspondence (e-mail: ireche@ugr.es; phone: +34 958246166; fax: +34 958243238)*

Received 6 August 2001; accepted in revised form 22 August 2001

Key words: Absorption, Dissolved organic carbon, Photobleaching, Seasonal dynamics

Abstract. Dynamics of dissolved organic carbon concentration (DOC) and capacity to absorb light (color) are determined by in-lake and external properties and processes. In this study, the influence of external factors such as rainfall and solar radiation on DOC and color dynamics was assessed for a small forested lake. DOC and absorption coefficients at 440 nm (a_{440}) ranged 4-fold from 0.46 to 1.62 mM and from 3.4 to 14.8 m⁻¹, respectively. DOC and a_{440} varied synchronously, but an important percentage of the variability (26%) in a_{440} was not explained by DOC. The resulting twofold variation in the molar absorption coefficient of DOC suggested significant seasonal changes in chromophoric content. Both DOC and a_{440} were positive and significantly related to cumulative rainfall. Solar radiation, however, only appeared to influence a_{440} dynamics. This influence was mediated by photobleaching. Photobleaching coefficients (k_b) were higher in fall and spring relative to the summer. This seasonal variability in k_b values was related to monthly rainfall. The influence of photobleaching on a_{440} dynamics was evaluated by comparing the half life of a_{440} in the water column with water residence time (WRT). For the study lake, photobleaching contributed notably to a_{440} dynamics during the dry periods when WRT was longer than the a_{440} half life. DOC dynamics, however, were not related to solar radiation because photomineralization was considerably slower than photobleaching.

Introduction

Dissolved organic carbon (DOC) is a heterogeneous pool of compounds with different origin (allochthonous vs. autochthonous), diagenetic condition (fresh vs. aged), chemical composition (monosaccharides, amino acids, fulvic and humic acids), and molecular size. Autochthonous DOC, derived from algae and macrophytes, is mostly composed of aliphatic molecules with low capacity to absorb light (Tipping et al. 1988; McKnight et al. 1994, 1997; Sun et al. 1997). In contrast, allochthonous DOC, derived from terrestrial sources, is enriched in aromatic compounds (mostly humic acids) with high capacity to absorb light (Meili 1992; McKnight et al. 1994, 1997; Sun et al. 1997). This capacity of DOC to absorb light has been commonly termed color (Cuthbert and del Giorgio 1992). Highly colored DOC is apparently more biorefractory (Tranvik 1990; Moran and Hodson 1990; Bano et al. 1997; Sun et al. 1997), and more efficient in PAR attenuation (Morris et al. 1995)

and phosphorus chelation (Jones 1992). Therefore, the relative contribution of humic compounds to the DOC pool is critical to determining color with consequent impacts on processes of aquatic ecosystems.

DOC and color dynamics are determined by the balance between loading, in-lake loss and production, and dilution or concentration from exchange of water directly with the atmosphere (precipitation and evaporation) (Curtis 1998). The loading of humic compounds is dominated by terrestrial inputs from catchments (at least in humid regions) (Engstrom 1987; Rasmussen et al. 1989). In-lake DOC production is mostly derived from algae and macrophyte photosynthesis (Wetzel 1992) and losses are determined by sedimentation, and microbial or photolytic mineralization. Photomineralization is the conversion of DOC to CO_2 or CO mediated by sunlight (Valentine and Zepp 1993; Granéli et al. 1996). In-lake color production depends on photohumification of algal-derived compounds (Kieber et al. 1997) and losses are mainly related to photobleaching (Morris and Hargraves 1997). Photobleaching is loss of the capacity to absorb light (i.e. color) caused by degradation of chromophoric compounds (Whipple 1914). The relative influence of in-lake (morphometry, photosynthetic DOC production, microbial DOC degradation, etc) vs. external (catchment area, soil type, environmental conditions, etc) factors on DOC and color dynamics remains to be determined.

Generally, DOC and color are closely related fluctuating synchronously (Molot and Dillon 1997a). Some authors, however, have pointed out that factors controlling DOC and color can differ (Molot and Dillon 1997b; Curtis and Schindler 1997). This divergence induces seasonal variability in molar absorption coefficients (Kortelainen 1993; Molot and Dillon 1997a). In temperate regions, environmental factors such as precipitation or incident radiation can differentially influence DOC and color (Molot and Dillon 1997b; Curtis and Schindler 1997; Curtis 1998; Lindell et al. 2000). During rainy periods, inputs of humic compounds from catchment areas can result in increases in DOC and, particularly, color. In contrast, during sunny and dry periods solar radiation can induce losses of DOC by photomineralization and color by photobleaching, but evaporation can also lead to DOC concentration and color increases. Therefore, the seasonal changes related to precipitation and incident solar radiation can be crucial in understanding DOC and color dynamics, but few studies have considered these interactions.

The goal of this paper is to assess the influence of environmental factors (rainfall and incident solar radiation) on DOC and color dynamics in a small forested lake where water residence time was relatively short. The influence of solar radiation was specifically evaluated by determining photobleaching and photomineralization and comparing the resulting estimates of half lives of DOC and color to lake water residence time.

Material and methods

Study site

Old Man McMullen Pond is located in the Great Mountain Forest of Connecticut (41° 57' N, 73° 15' W) at an elevation of 460 m a.s.l. This lake is small (7.8 ha) and shallow (1 m maximum depth). The catchment area is 29.3 ha and is primarily coniferous forest. There is a visible inlet and outlet. Macrophytes (mostly *Utricularia vulgaris*) and littoral vegetation are well represented in the lake while planktonic chlorophyll-a concentrations are low, usually $<3 \mu\text{g l}^{-1}$.

Sampling and analytical methods

The lake was sampled at a central location at least once per month from October 1995 to October 1997 including the ice-covered period from December to April. Three samples for DOC concentration and absorbance were collected on each date. DOC samples were filtered through precombusted Whatman GF/F filters, acidified (final pH < 2) and measured with a Shimadzu TOC-5050 Total Carbon Analyzer. Color samples were also filtered through Whatman GF/F filters and measured at 440 nm in 10 cm-cuvettes in a spectrophotometer. Absorbance (A_{440}) was expressed as Napierian absorption coefficient (a_{440}) in m^{-1} , commonly termed color (Cuthbert and del Giorgio 1992):

$$a_{440} = \frac{2.303A_{440}}{l} \quad (1)$$

where l is the optical pathlength in m. Molar absorption coefficient (ϵ) in $\text{m}^2 \text{mol}^{-1}$ was also calculated as:

$$\epsilon = \frac{a_{440}}{C} \quad (2)$$

where C is the concentration of DOC in mM.

Rainfall and incident photosynthetically active radiation (PAR) were monitored at the Institute of Ecosystem Studies (IES) (Millbrook NY, 41° 50' N, 73° 45' W) located within 70 km of the study lake. Total rainfall was determined using an universal recording rain gauge (Belfort Instrument Co. Series 5-780). Data for statistical analysis were expressed as cumulative (CR) and monthly (MR) rainfall. CR was obtained by additions of daily rainfall from April 1st to the day prior to sampling (the ice-covered period was not included). MR was obtained by the daily additions of rainfall for each month.

PAR was measured every two seconds using a quantum sensor (Li-Cor, Inc. Model LI-190SB). PAR data were expressed as the daily average for each month. Incident UV radiation was not monitored at the IES site prior to April, 1999. Inci-

dent ultraviolet-B radiation (UVB) and PAR are, however, significantly correlated at the IES environmental monitoring station (V. Kelly, personal comm. 2000 data). PAR data were used to estimate UV (see below).

Conductivity was measured using a Model 32 Conductance Meter and pH using an Orion digital meter with a standard Ag/AgCl triode electrode with automatic temperature compensation.

Experimental determination of photobleaching

Experiments were performed to determine photobleaching rates over the different seasons and years. These rates were obtained by measuring changes in a_{440} of GF/F filtered-water in three 300 ml-borosilicate (in 1995, 1996, and 1997) and 200 ml-quartz (in 1997) bottles with sunlight exposure. Borosilicate bottles had a mean pathlength ($2 \sin 45^\circ$ radius) of 3.25 cm and quartz bottles of 2.97 cm. Energy transmission through these experimental bottles was previously reported (Reche et al. 2000). Briefly, borosilicate bottles permitted the transmission of most UVA and PAR and quartz bottles practically the entire spectrum. Three dark bottles were used as controls. Sunlight incubations were performed on a platform and ranged from 2 days to 8 days depending on the experiments. While these bottles likely developed bacteria over the course of the incubations, we assumed consistent with the prior experience (Skoog et al. 1996; Reche et al. 1999) that bacteria would have relatively little effect on the loss of absorbance observed over the experimental time interval.

Photobleaching kinetics fit a negative exponential function (Equation 3):

$$a_{440} = a_{440o} e^{-k_b D_n} \quad (3)$$

where a_{440n} is the absorption coefficient at 440 nm (m^{-1}) after a cumulative sunlight dose of D_n , and a_{440o} is the initial absorption coefficient at 440 nm (m^{-1}). The photobleaching coefficient (k_b in $(Em^{-2})^{-1}$) is defined as the slope of the ln-linear regression between absorption coefficients (a_{440}) and cumulative sunlight dose. D_n values were obtained by the addition of incident radiation over time of exposure. PAR data were obtained from the IES environmental station (see above). The ultraviolet A (UVA) and B (UVB) radiation data were estimated by applying the PAR:UVA and PAR:UVB ratios measured in the Lake Lacawac field station ($41^\circ 23'N$, $75^\circ 18'W$) to IES data for PAR. IES and Lake Lacawac had similar atmospheric ozone concentration during sunlight exposure (based on a comparison of ozone readings at both sites on the same dates). Incident doses for the experiments using borosilicate bottles were cumulative UVA and PAR and for the experiments using quartz bottles were cumulative UVB, UVA and PAR.

To express k_b in time units (d^{-1}) sunlight doses were converted to:

$$k_b = \frac{\ln \frac{a_{440n}}{a_{440o}}}{t} \quad (4)$$

where t is $E\ m^{-2}\ d^{-1}$. Then, the time (d) to reduce color by 50% (a_{440} half life) was calculated as:

$$a_{440}\text{half life} = \frac{\ln(0.5)}{k_b} \quad (5)$$

Lake half life of a_{440} and water residence time

The experiments only represent color loss for surface waters conditions. Photobleaching coefficients for the whole water column (k_{wc}) were obtained by applying the model of Reche et al. (2000). This model assumed a completely mixed water column and a lake shaped as a truncate cone. The model variables were: incident PAR, UVA and UVB; k_b values; DOC concentration and a_{440} :DOC ratios. To assess the potential effect of photobleaching on lake a_{440} dynamics, half life of a_{440} for the whole water column was also estimated using the seasonal values of k_{wc} (d^{-1}).

Water residence times were also estimated by using data on rainfall and lake volume and assuming watershed yields typical of the region (Likens and Bormann 1995).

Experimental determination of photomineralization

Photomineralization rates were determined as DOC losses in the summer and fall of 1996. Lake water filtered through $0.2\ \mu m$ was incubated in transparent and dark-control borosilicate test tubes for 8 days in the summer experiment and for 7 days in the fall experiment. Again, we assumed little effect of bacteria on any loss of DOC observed during the experiments. Three test-tubes of each treatment were sequentially removed, and DOC concentration was measured along with the corresponding incident sunlight dose. The photomineralization coefficient (k_{ph}) is defined as the slope of the relationship between DOC concentrations and cumulative sunlight doses Equation (6):

$$DOC_n = DOC_o - k_{ph}D_n \quad (6)$$

where DOC_n and DOC_o are the concentration of DOC (mM) after a sunlight dose of D_n ($E\ m^{-2}$) and at initial conditions. Cumulative sunlight doses were obtained

by the additions of incident PAR and UVA. To express k_{ph} in time units (d^{-1}) sunlight doses were converted in days:

$$-k_{ph} = \frac{DOC_n - DOC_o}{t} \quad (7)$$

where t is $E \text{ m}^{-2} \text{ d}^{-1}$. Then, the time (d) to reduce DOC concentration by 50% (*DOC half life*) was calculated as:

$$DOChalf \text{ life} = \frac{DOC_o/2}{k_{ph}} \quad (8)$$

Statistical analysis

Data used in regression analysis were arithmetic means of the three replicates. Ordinary least-squares (OLS) or multiple ridge regressions were used when one or two independent variables were considered, respectively. Ridge regressions were used because the independent variables were collinear which can lead to unstable estimates of regression coefficients via the OLS method. Ridge regression is one method of biased estimation of coefficients that attempts to reduce or control for the effects of collinearity (Price 1977; Chatterjee and Price 1991). A small biasing factor (λ) is added during the computations, and serves to stabilize the parameter estimates. Usually, for λ values included in the range from 0 (unbiased) to 0.1 the parameter estimates are stabilized (Philippi 1993). Ridge regression artificially decreases the correlation coefficients so that more stable (yet biased) estimates of the slopes (i.e. beta coefficients) and intercept can be computed.

Results

Dynamics of DOC and a_{440}

DOC concentration varied about 4 fold from 0.46 mM to 1.62 mM over the two study years, and averaged 0.92 mM. Maximum values were reached in late summer and fall, and minimum values were observed when the lake was ice-covered (Figure 1). Values of a_{440} ranged more than 4-fold from 3.4 to 14.8 m^{-1} with maxima in fall and minima under ice-covered conditions (Figure 1). DOC concentration and a_{440} mean values were higher in 1995 and 1996 than in 1997.

DOC concentration and a_{440} were positive and significantly related ($a_{440} = -0.41 + 9.29 \text{ DOC}$; $r^2 = 0.74$; $p < 0.001$). However, an important percentage of a_{440} variance (26%) was not explained by DOC concentration. This unexplained variance was reflected in the molar absorption coefficients (ϵ) that ranged from 6.0

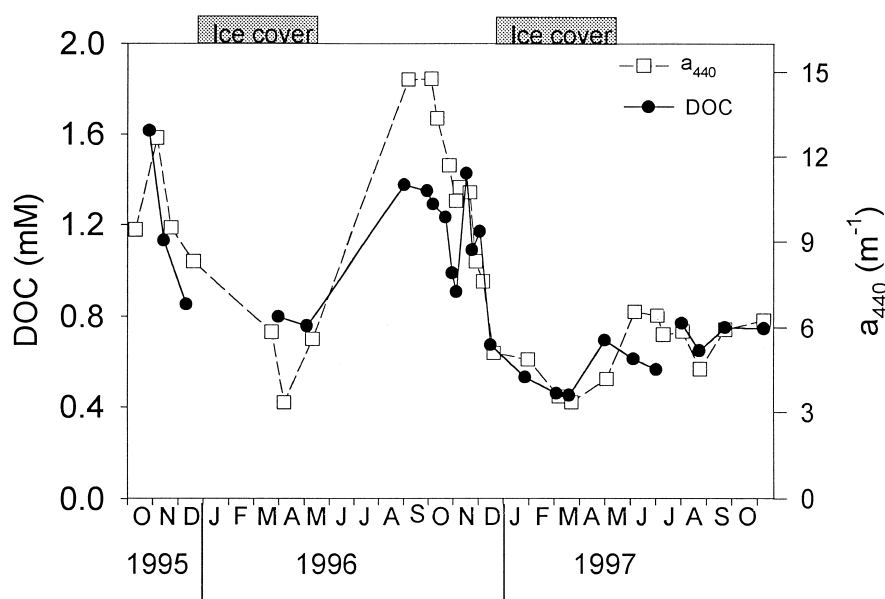


Figure 1. Seasonal changes of concentration (DOC) and absorption coefficient at 440 nm (a_{440}) of dissolved organic carbon in the study lake from October 1995 to October 1997.

$\text{m}^2 \text{mol}^{-1}$ to $12.0 \text{ m}^2 \text{mol}^{-1}$ with an average of $8.8 \text{ m}^2 \text{mol}^{-1}$. Values of ϵ above the average were observed in late fall of 1995, late summer and early fall of 1996, and in spring of 1997 (mostly rainy periods), and values markedly lower than the average were observed under ice-cover in 1996 and during the dry summer of 1997.

To examine if DOC and a_{440} dynamics were significantly related to cumulative rainfall (CR) and incident PAR, regressions analysis were performed. There was collinearity between the independent variables (CR and PAR) and so ridge regression was used to obtain stable coefficient estimates. The ridge regressions for DOC showed that β coefficients for PAR were not significant, whereas β coefficients for CR were significant for any case in the checked range. DOC dynamics appear to be primarily related to CR. In fact, the simple regression between DOC and CR is significant ($r^2 = 0.34$, $n = 21$, $p < 0.01$) although substantial unexplained variation remains (Figure 2, solid circles).

The ridge regressions performed for a_{440} showed that β coefficients for PAR were significant only for low values of λ (< 0.035), whereas β coefficients for CR were significant until $\lambda = 0.09$. In the ridge regressions for a_{440} , β coefficients for CR were always higher than for PAR. The ridge regression results suggested that a_{440} dynamics were significantly related to both CR and PAR. However, the relationship between a_{440} and CR was stronger than a_{440} and PAR. Simple regressions were also performed between a_{440} and CR and PAR, but significant results were obtained only for CR ($r^2 = 0.27$, $n = 23$, $p < 0.05$). A large fraction of the a_{440} variance (more than 70%) remained unexplained (Figure 2, open squares). There

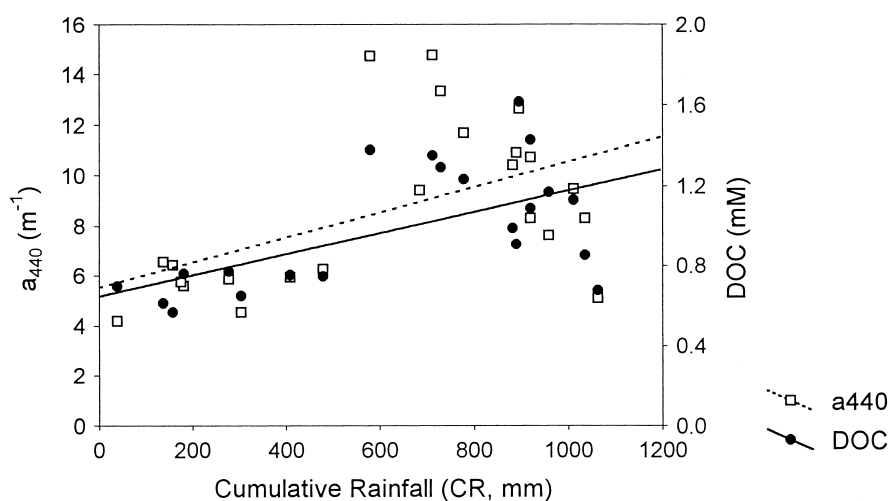


Figure 2. Simple regressions between cumulative rainfall (CR) and dissolved organic carbon concentrations (DOC) and absorption coefficients at 440 nm (a_{440}).

were no significant relationships between molar absorption coefficients (a_{440} :DOC ratios) and CR or PAR.

Photobleaching and photomineralization

Photobleaching coefficients (k_b) were determined 14 times: 11 using borosilicate bottles and 3 using quartz bottles. Values of k_b ranged from $-14.21 \times 10^{-4} \pm 1.30 \times 10^{-4}$ to $-44.40 \times 10^{-4} \pm 4.02 \times 10^{-4}$ (Em^{-2}) $^{-1}$ when borosilicate bottles were used (Figure 3, black circles) and from $25.05 \times 10^{-4} \pm 3.03 \times 10^{-4}$ to $56.09 \times 10^{-4} \pm 3.20 \times 10^{-4}$ (Em^{-2}) $^{-1}$ when quartz bottles were used (Figure 3, open square). The half life of a_{440} varied from 5 to 25 d for surface conditions.

Irrespective of the type of experimental bottles used (borosilicate vs. quartz) the slowest photobleaching (less negative k_b values) were systematically obtained in summer and the fastest photobleaching (more negative k_b values) in fall and in spring (Figure 3). To evaluate if there is a seasonal tendency in photobleaching coefficients, they were grouped by seasons and compared using t-tests. Photobleaching was significantly faster in fall ($t = 4.57$, $df = 8$, $p = 0.002$) and spring ($t = 3.58$, $df = 4$, $p = 0.023$) than in summer, but between spring and fall no significant difference was found ($t = 0.21$, $df = 6$, $p = 0.844$).

Maximum quantum yields for many photoprocesses are in the UVB range (Moran and Zepp 1997). Therefore, the photobleaching rates obtained in borosilicate bottles are underestimates. To evaluate the magnitude of this underestimation three experiments using both borosilicate (UVA+PAR transmission) and quartz (UVB+UVA+PAR transmission) bottles were performed. In the three experiments, the slopes (k_b values) obtained for the quartz bottles were significantly higher

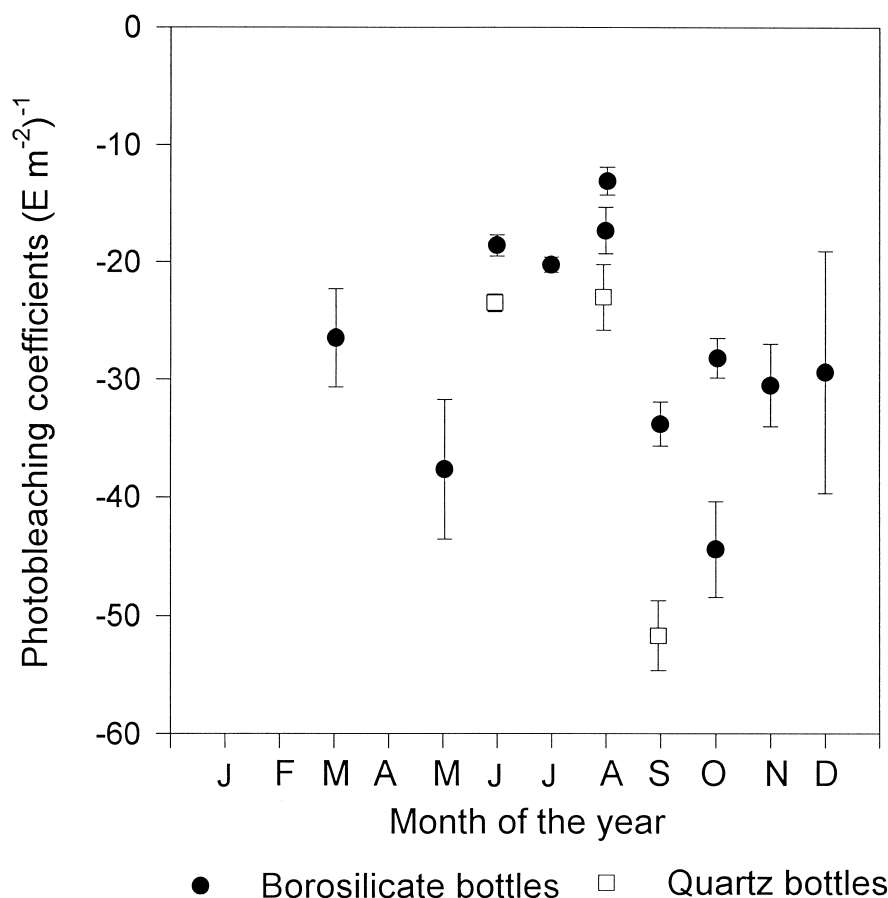


Figure 3. Photobleaching coefficients (k_b) and standard errors (error bars) for the different experiment performed. Solid circles represent k_b values obtained by using borosilicate bottles and open squares by using quartz bottles.

(faster photobleaching) than for the borosilicate bottles (Figure 4). The k_b values using borosilicate (k_{bB}) were about 75% of the k_b values using quartz (k_{bQ}).

The k_b values obtained using borosilicate varied about 3 fold over the study. The variability of photobleaching coefficients has been previously related to water chemistry and DOC optical quality (Morris and Hargraves 1997; Reche et al. 1999). Conductivity (range: 20.5–29.9 μS ; two-year average: 23.9) and pH (range: 4.2–5.7; two-year average: 4.6) varied little in the study lake. No significant relationships were found between ionic conditions (e.g. pH or conductivity) or molar absorption coefficients (DOC optical quality) and photobleaching coefficients. However, there was a negative and significant relationship between monthly rainfall (MR) and photobleaching coefficients (Figure 5). The rainier conditions were associated with faster photobleaching coefficients.

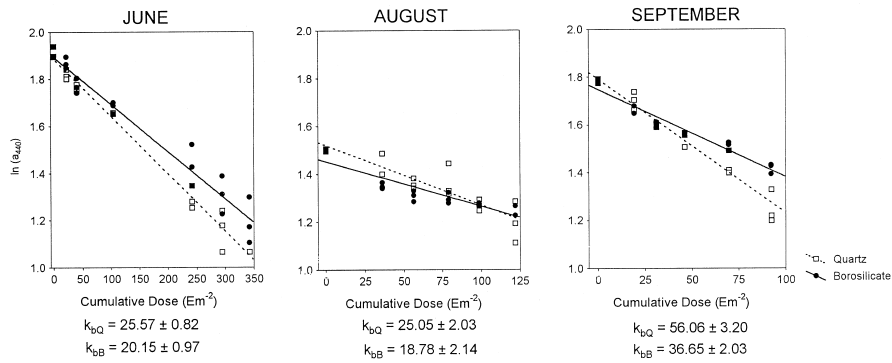


Figure 4. Changes in absorption coefficients at 440 nm (a_{440}) over sunlight exposure in the borosilicate (solid circles) and quartz (open squares) bottles in three photobleaching experiments of 1997. Incident cumulative doses for borosilicate bottles were UVA+PAR and for quartz bottles were UVB+UVA+PAR. Note k_{bQ} values ($\times 10^{-4} \text{ (Em}^{-2})^{-1}$) are photobleaching coefficients in the quartz bottles and k_{bB} values ($\times 10^{-4} \text{ (Em}^{-2})^{-1}$) are photobleaching coefficients in the borosilicate bottles.

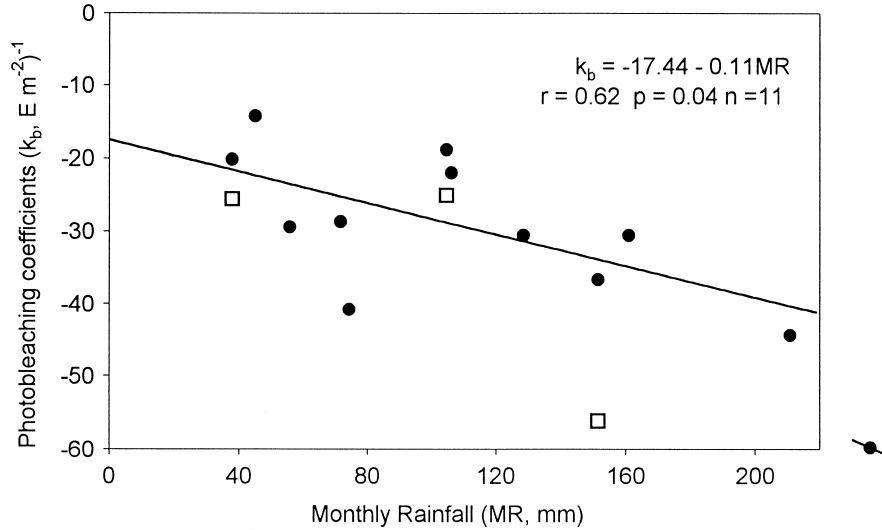


Figure 5. Relationship between photobleaching coefficients (k_b values) and monthly rainfall (MR). Note k_b values in quartz bottles (open squares) have not been included in the analysis.

Experimental photobleaching coefficients only represent surface water conditions. The estimates of a_{440} half lives for the whole water column varied from 19 d to 152 d (Figure 6). These values were close to water residence time during fall of 1995 and 1996 (particularly rainy periods) and considerably less than water residence times during spring and summer of 1996 and 1997 (particularly dry periods).

Photomineralization was quantified only in two seasons (summer and fall). Unlike the a_{440} exponential decay kinetics, photomineralization of DOC was linear. The k_{ph} value in summer was $-15.08 \times 10^{-4} \pm 0.62 \times 10^{-4} \text{ (Em}^{-2})^{-1}$ and in fall

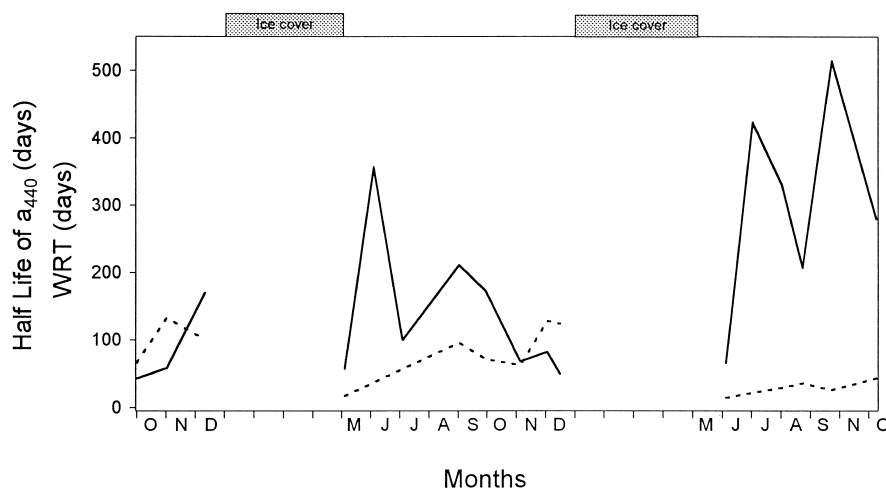


Figure 6. Seasonal changes of a_{440} half life for water column (dotted lines) and water residence time (WRT) (continuous line).

$-15.14 \times 10^{-4} \pm 1.53 \times 10^{-4} \text{ (Em}^{-2}\text{)}^{-1}$. Photomineralization coefficients were not significantly different for summer and fall experiments (Figure 7). DOC half lives were 167 d and 249 d for summer and fall conditions, respectively. These values were about 1 order of magnitude longer than a_{440} half lives.

Discussion

Seasonal changes of DOC and a_{440} in the study lake were similar to those found in other small forested lakes (Tipping and Woof 1983; Tipping et al. 1988; Meili 1992; Kortelainen 1993; Hessen et al. 1997). DOC and a_{440} mean values were higher in 1995 and 1996 than in 1997 likely related to the higher annual rainfall in 1995 (1151 mm) and 1996 (1425 mm) with respect to 1997 (965 mm).

DOC and a_{440} dynamics were significantly related to cumulative rainfall (Figure 2). These relationships may derive from the tight link between rainfall and DOC exports in humid climates (Hinton et al. 1997). It is well known that water from runoff tends to be richer in DOC and more colored than groundwater (Leenheer et al. 1974; Larson 1978). Moreover, DOC exports in coniferous forest are particularly significant (Cronan and Aiken 1985; Neff and Asner 2001). Others have also reported maxima of DOC or humic acids linked to rainy seasons (spring or fall) in northern temperate lakes (Tipping and Woof 1983; Tipping et al. 1988; Biber et al. 1996; Molot and Dillon 1997a).

DOC and a_{440} dynamics were reasonably synchronous, but there was an important percentage (26%) of a_{440} variance that was not explained by DOC. The a_{440} variance explained by DOC in this study was lower than in long-term (Molot and Dillon 1997a) or in among-systems studies (Scruton 1984; Howell 1986; Korte-

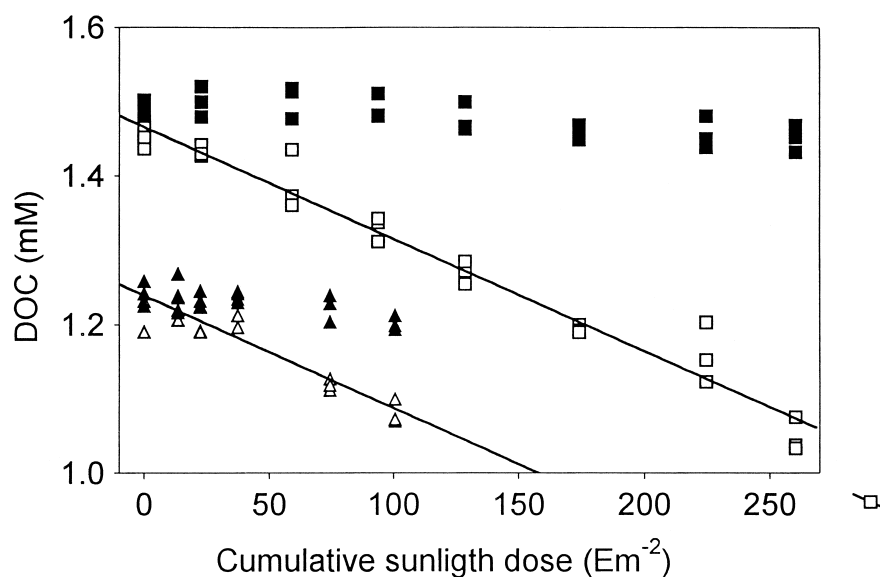


Figure 7. Changes of dissolved organic carbon concentration (DOC) as functions of cumulative sunlight doses for summer (squares) and fall (triangles) experiments. Solid symbols are DOC changes in dark controls and open symbols in transparent tubes. The slopes of the regression lines (open symbols) are the photomineralization coefficients.

lainen 1993; Curtis and Schindler 1997; Reche et al. 1999). This difference could be related to the data averaging of long-term and among-systems studies that often smooth abrupt changes typical of seasonal studies. The dispersion in the a_{440} -DOC relationship is indicated by changes in the molar absorption coefficients ($\epsilon = a_{440} \cdot \text{DOC ratio}$). These coefficients can be roughly considered as an index of the contribution of humic and fulvic acids to total DOC pool. High ϵ values indicate a greater contribution of aromatic compounds to total DOC and low ratios a greater autochthonous (less aromatic) contribution to total DOC (McKnight et al. 1994, 1997; Sun et al. 1997). If rainfall and allochthonous inputs are related, a positive and significant relationship between ϵ values and rainfall should be expected. The absence of a significant relationship between ϵ values and CR or MR in this study suggests that other factors beyond runoff are controlling ϵ values. Clair and Sayer (1997) found a clear seasonal pattern in the distribution of structural carbon (i.e. high aromatic content) in DOC related to the presence of light-sensitive chromophores.

The color loss is dependent on quantum yield and total incident energy of each waveband. Maximum quantum yield for most photochemical processes are in the UV range (Moran and Zepp 1997), but total energy is much lower in this band (Kirk 1994). In this study, the importance of UVB was assessed in three experiments using quartz (UVB+UVA+PAR transmission) and borosilicate (UVA+PAR transmission) containers (Figure 4). Photobleaching coefficients obtained in quartz containers were significantly more negative (faster photobleaching) than in boro-

silicate containers, although incident UVB represents only 4.5% of UVA and 0.1% of PAR. Since PAR and UVB radiation was correlated at our monitoring site, the seasonal trend of photobleaching coefficients measured using borosilicate containers is likely representative of those obtained when effects of the complete spectrum are included (i.e. with quartz containers).

The seasonal variability of photobleaching coefficients in this study was lower than the variability found in among-systems studies (Reche et al. 1999). Unlike the results for among-systems, k_b variability in our seasonal study was related to an environmental factor (monthly rainfall) (Figure 5). DOC during rainy months was more photoreactive (the fastest k_b values) than during dry months (the slowest k_b values). In summer, photobleaching coefficients were low probably because the humic fraction of DOC was previously subjected to high solar radiation that resulting in the degradation of chromophores. In addition summer rainfall was low decreasing new inputs of chromophores (i.e. there is proportionally less photobleachable substrate). In fall and spring, photobleaching coefficients were higher probably because DOC was subjected to lower solar radiation and recent rainfall episodes promoted new inputs of chromophore-rich DOC (i.e. there is proportionally more photobleachable substrate).

Photomineralization rates did not appear to vary seasonally. Photomineralization rates expressed as losses of carbon ($\text{mg C l}^{-1}\text{h}^{-1}$) were within the same range observed in previous studies (Salonen and Vähätalo 1994; Granéli et al. 1996; Amon and Benner 1996; Granéli et al. 1998). If these rates are normalized by their corresponding DOC concentrations, all values are remarkably close (0.0041–0.0067) even with different experimental designs and waters from very diverse areas. Some authors (Amon and Benner 1996; Granéli et al. 1998) have reported similar values of DOC-specific DIC-production under different solar radiation spectra and different DOC optical properties. These results suggest that photomineralization, probably, is a relatively constant rate of sunlight dose. In contrast, Lindell et al. (2000) found seasonal changes in the values of DOC-specific DIC-production. In this study, photomineralization coefficients were not significantly different. Therefore, photomineralization appeared less variable, whereas photobleaching showed a clear seasonal trend (probably linked to allochthonous inputs of photobleachable material).

The fact that photobleaching and photomineralization had different decay kinetics (exponential vs. linear) leads to significant differences in the experimental half lives of a_{440} and DOC. Half lives of a_{440} were shorter (about one order of magnitude) than DOC half lives. This result underlines the more severe effect of solar radiation on a_{440} than on DOC. Therefore, photobleaching and photomineralization can differentially influence on a_{440} and DOC dynamics as was also noted by Molot and Dillon (1997b); Curtis and Schindler (1997).

The net effects of photobleaching or photomineralization on a_{440} and DOC dynamics will also depend on water residence time. If a_{440} half lives for the water column due to photobleaching are shorter than water residence times then there is a greater potential for photobleaching to influence a_{440} dynamics. By contrast, if those a_{440} half lives are longer than water residence time, the effect of photobleach-

ing could be masked by new allochthonous inputs. The comparison between a_{440} half lives of water column and water residence time in the study lake (Figure 6) suggests that during dry periods (spring and summer of 1996 and 1997) photobleaching strongly influenced the changes in a_{440} . DOC half lives for water column were not estimated. However, photomineralization was not sufficient to have strong effect on DOC dynamics due to the long DOC half lives under surface conditions.

The results of this study show that external factors, such as rainfall, can drive DOC and a_{440} dynamics. Solar radiation can also have a significant influence on a_{440} when water residence times are sufficiently long. Environmental factors seem to be important in determining DOC and a_{440} dynamics in shallow, small and forested lakes with short residence times like the study system. However, more studies are necessary to characterize the relative importance of in-lake properties and processes (morphometry, DOC production via photosynthesis, microbial degradation, etc) vs. external (catchment area, soil type, environmental factors, etc) factors to forecast DOC and a_{440} dynamics and, hence, their functions in lakes.

Acknowledgements

We thank D. Thomas and D. Fisher for their assistance in the field and in the lab. Radiation and rainfall data were kindly supplied by V. Kelly. We also thank Drs. J. Cole and R. Sommaruga for valuable suggestions and Dr R. Morales-Baquero for statistical advise. This research was supported by NSF grant to MLP and by a post-doctoral fellowship from Spanish MEC to IR.

References

- Amon R.M.W. and Benner R. 1996. Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system. *Geochim. Cosmochim. Acta* 60 : 1783–1792.
- Bano N., Moran M.A. and Hodson R.E. 1997. Bacterial utilization of dissolved humic substances from freshwater swamp. *Aquat. Microb. Ecol.* 12: 233–238.
- Biber M.V., Gülaçar F.O. and Buffle J. 1996. Seasonal variation in principal groups of organic matter in a eutrophic lake using pyrolysis/GC/MS. *Environ. Sci. Technol.* 30: 3501–3507.
- Clair T.A. and Sayer B.G. 1997. Environmental variability in the reactivity of freshwater dissolved organic carbon to UV-B. *Biogeochem.* 36: 89–97.
- Chatterjee S. and Price B. 1991. *Regression Analysis by Example*. 2nd edn. Wiley, New York.
- Cronan C.S. and Aiken G.R. 1985. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. *Geochim. Cosmochim. Acta* 49: 1697–1705.
- Curtis P.J. and Schindler D.W. 1997. Hydrologic control of dissolved organic matter in low-order Precambrian Shield lakes. *Biogeochem.* 36: 125–138.
- Curtis P.J. 1998. Climatic and hydrologic control of DOM concentration and quality in lakes. In: Hessen T. (ed.), *Aquatic Humic Substances*. Springer-Verlag, Berlin, pp. 93–104.

- Cuthbert I.D. and del Giorgio P. 1992. Toward a standard method of measuring color in freshwater. *Limnol. Oceanogr.* 37: 1319–1326.
- Engstrom D.R. 1987. Influence of vegetation and hydrology on the humus budgets of Labrador lakes. *Can. J. Fish. Aquat. Sci.* 44: 1306–1314.
- Granéli W., Lindell M. and Tranvik L. 1996. Photo-oxidative production of dissolved inorganic carbon in lakes of different humic content. *Limnol. Oceanogr.* 41: 698–706.
- Granéli W., Lindell M., Marcal de Faria B. and de Assis Esteves F. 1998. Photoproduction of dissolved inorganic carbon in temperate and tropical lakes-dependence on wavelength band and dissolved organic carbon concentration. *Biogeochem.* 43: 175–195.
- Hessen D.O., Gjessing E.T., Knulst J. and Fjeld E. 1997. TOC fluctuations in a humic lake as related to catchment acidification, season and climate. *Biogeochem.* 36 : 139–151.
- Hinton M.J., Schiff S.L. and English M.C. 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. *Biogeochem.* 36: 67–88.
- Howell G. 1986. Water quality characterization of 78 acid precipitation monitoring lakes in Atlantic Canada. IWD-AR-WQB-86-109. Environment Canada, Inland Waters Directorate, Ottawa, Ont. 119p.
- Jones R.I. 1992. The influence of humic substances on lacustrine planktonic food chains. *Hydrobiol.* 229: 73–91.
- Kieber R., Hydro L. and Seaton P. 1997. Photooxidation of triglycerides and fatty acids in seawater: Implication toward the formation of marine humic substances. *Limnol. Oceanogr.* 42: 1454–1462.
- Kirk J.T.O. 1994. Optics of UV-B radiation in natural waters. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* 43: 1–16.
- Kortelainen P. 1993. Content of total organic carbon in Finnish lakes and its relationship to catchment characteristics. *Can. J. Fish. Aquat. Sci.* 50: 1477–1483.
- Larson R.A. 1978. Dissolved organic matter of a low-coloured stream. *Freshwater Biol.* 8: 91–104.
- Leenheer J.A., Malcolm R.L., McKinley P.W. and Eccles L.A. 1974. Occurrence of dissolved organic carbon in selected ground-water samples in the United States. *J. Res.* 2: 361–369.
- Likens G.E. and Bormann F.H. 1995. *Biogeochemistry of a Forested Ecosystem*. 2nd edn. Springer-Verlag New York, Inc., 159 pp.
- Lindell M.J., Granéli W. and Bertilsson S. 2000. Seasonal photoreactivity of dissolved organic matter from lakes with contrasting humic content. *Can. J. Fish. Aquat. Sci.* 57: 875–885.
- McKnight D.M., Andrews E.D., Spaulding S.A. and Aiken G.R. 1994. Aquatic fulvic acids in algal-rich antarctic ponds. *Limnol. Oceanogr.* 39: 1972–1979.
- McKnight D.M., Harnish R., Wershaw R.L., Baron J.S. and Schiff S. 1997. Chemical characteristics of particulate, colloidal, and dissolved organic material in Loch Vale Watershed, Rocky Mountain National Park. *Biogeochem.* 36: 99–124.
- Meili M. 1992. Sources, concentrations and characteristics of organic matter in softwater lakes and streams of the Swedish forest region. *Hydrobiol.* 229: 23–41.
- Molot L.A. and Dillon P.J. 1997a. Colour-mass balances and colour-dissolved organic carbon relationships in lakes and streams in central Ontario. *Can. J. Fish. Aquat. Sci.* 54: 2789–2795.
- Molot L.A. and Dillon P.J. 1997b. Photolytic regulation of dissolved organic carbon in northern lakes. *Global Biogeochem. Cy.* 11 : 357–365.
- Moran M.A. and Hodson R.E. 1990. Bacterial production on humic and nonhumic components of dissolved organic carbon. *Limnol. Oceanogr.* 35: 1744–1756.
- Moran M.A. and Zepp R.G. 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* 42: 1307–1316.
- Morris D.P. and Hargreaves B.R. 1997. The role of photochemical degradation of dissolved organic carbon in regulating the UV transparency of three lakes on the Pocono Plateau. *Limnol. Oceanogr.* 42: 239–249.
- Morris D.P., Zagarese H., Williamson C.E., Balseiro E.G., Hargreaves B.R., Mondenutti B. et al. 1995. The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. *Limnol. Oceanogr.* 40: 1381–1391.

- Neff J.C. and Asner G.P. 2001. Dissolved organic carbon in terrestrial ecosystems: synthesis and a model. *Ecosystems* 4: 29–48.
- Philippi T.E. 1993. Multiple regression: herbivory. In: Scheiner S.M. and Gurevitch J. (eds), *Design and Analysis of Ecological Experiments*. Chapman & Hall, New York, pp. 183–207.
- Price B. 1977. Ridge regression: application to nonexperimental data. *Psychological Bull.* 84: 759–766.
- Rasmussen J.B., Godbout L. and Schallenberg M. 1989. The humic content of lake water and its relationship to watershed and lake morphometry. *Limnol. Oceanogr.* 34: 1336–1343.
- Reche I., Pace M.L. and Cole J.J. 1999. Relationship of trophic and chemical conditions to photobleaching of dissolved organic matter in lake ecosystems. *Biogeochem.* 44: 259–280.
- Reche I., Pace M.L. and Cole J.J. 2000. Modeled effects of dissolved organic carbon and solar spectra on photobleaching in lake ecosystems. *Ecosystems* 3: 419–432.
- Salonen K. and Vähätalo A. 1994. Photochemical mineralisation of dissolved organic matter in lake Skjervatjern. *Environ. Int.* 20: 307–312.
- Scruton D.A. 1984. A survey of selected lakes in Labrador, with an assessment of lake status and sensitivity in relation to acid precipitation. *Can. Tech. Rep. Fish. Aquat. Sci.* 1296: 115.
- Skoog A., Wedborg M. and Fogelqvist E. 1996. Photobleaching of fluorescence and the organic carbon concentration in a coastal environment. *Mar. Chem.* 53: 333–345.
- Sun L., Perdue E.M., Meyer J.L. and Weis J. 1997. Use of elemental composition to predict bioavailability of dissolved organic matter in a Georgia river. *Limnol. Oceanogr.* 42: 714–721.
- Tipping E., Hilton J. and James B. 1988. Dissolved organic matter in Cumbrian lakes and streams. *Freshwater Biol.* 19: 371–378.
- Tipping E. and Woof C. 1983. Seasonal variation in the concentrations of humic substances in a soft-water lake. *Limnol. Oceanogr.* 28: 168–172.
- Tranvik L.J. 1990. Bacterioplankton growth on different molecular weight fractions of dissolved organic carbon from humic and clear waters. *Appl. Environ. Microbiol.* 56: 1672–1677.
- Valentine R.L. and Zepp R.G. 1993. Formation of carbon monoxide from the photodegradation of terrestrial dissolved organic carbon in natural waters. *Environ. Sci. Technol.* 27: 409–412.
- Wetzel R.G. 1992. Gradient-dominated ecosystems: sources and regulatory functions of dissolved organic matter in freshwater ecosystems. *Hydrobiol.* 229: 181–198.
- Whipple 1914. *The Microscopy of Drinking Water*. Wiley.