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## Relationship of trophic and chemical conditions to photobleaching of dissolved organic matter in lake ecosystems

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**Abstract.** Dissolved organic matter (DOM) is a major light-absorbing substance, responsible for much of the color in water bodies. When sunlight energy is absorbed by DOM, some color can be lost by the process of photobleaching. We measured rates of DOM photobleaching in thirty lakes that varied greatly in color, trophic status and ionic composition. Loss of color (measured as absorbance at 440 nm and expressed as absorption coefficients) was a first order function of sunlight dose, and rates were nearly identical for 0.2  $\mu\text{m}$ - and GF/F-filtered samples suggesting that the process was predominantly abiotic. Photobleaching rates were rapid (color loss of 1–19%  $\text{d}^{-1}$ ) and varied about seven-fold among lakes. Our method underestimated the actual rate by 15–20% based on comparisons between the glass bottles we used in the survey and quartz containers. The large variation in photobleaching rates was examined in relation to lake trophic and chemical conditions. The best predictor of this variability was acid-neutralizing capacity (ANC) ( $r^2 = 0.94$ ;  $p < 0.001$ ) such that photobleaching was most rapid in the most alkaline lakes. The relationship between ANC and photobleaching suggests that differences in ionic conditions among lakes may influence the solubility and configuration of humic and fulvic acids and hence their susceptibility to photobleaching.

### Introduction

Dissolved organic matter is one of the most important sunlight-absorbing components in aquatic ecosystems (Zepp 1988; Scully & Lean 1994; Morris et al. 1995; Schindler & Curtis 1997). This absorption of energy can result in a rich variety of photochemical processes, including photobleaching, DOC-photooxidation and humic acid polymerization (Hedges 1988; Kieber et al. 1990; Granéli et al. 1996). Generally, about half the dissolved organic matter and nearly all of the colored dissolved organic matter in freshwater consists of humic substances (Thurman 1985). Photobleaching is the loss of this color

caused directly by the absorption of solar radiation as well as the indirect effects of light-produced oxidants (e.g.  $H_2O_2$ , free radicals, etc). This energy absorption by colored DOC involves, at the same time, its partial degradation from biologically refractory DOC to lower-molecular-weight substrates that are more available to bacteria (Lindell et al. 1995; Wetzel et al. 1995; Moran & Zepp 1997). Therefore, upon photodegradation, bacteria can introduce carbon, originally refractory, into the food-web influencing carbon flux (Kieber et al. 1989; Mopper et al. 1991). In addition, the concentration of colored DOC can also control the penetration of photosynthetically active and UV-damaging radiation in the water column (Morris & Hargreaves 1997).

Photobleaching has been documented in systems ranging from the open ocean (Mopper et al. 1991) to productive wetlands (Wetzel et al. 1995), but we know little about the trends in photobleaching variability among systems. One issue, especially in developing comparisons of rates, is to determine the kinetics of the photobleaching process. In previous studies of photobleaching, absorption declined at both linear and curvilinear rates (Kieber et al. 1990; De Haan 1993; Lindell et al. 1995; Morris & Hargreaves 1997). Comparison of rate kinetics among existing studies is difficult, however, because changes in absorbance are measured at a variety of wavelengths and time is often used as a surrogate of light dose.

Variation in photobleaching should depend on both chemical composition of DOC and the trophic and chemical conditions in the water in which photobleaching occurs. Chemical composition of the DOC, its age, origin, and prior photobleaching history are likely important. Watersheds and soil types are the main determinants of the amount and quality of allochthonous DOC released, processed and transported to recipient waters (Rasmussen et al. 1989; Wetzel 1992). Usually, the biological recalcitrance of dissolved organic compounds increases as they move toward lake basins (Wetzel 1992). A fraction of this allochthonous organic carbon seems to be bioavailable but its assimilation efficiency in relation to fresh autochthonous organic carbon is typically lower (Moran & Hodson 1990; Amon & Benner 1996). However, analogous information about the photolytic recalcitrance of allochthonous versus autochthonous DOC is very limited (Thomas & Lara 1995).

Environmental conditions can also influence photobleaching. The quantity and the quality of solar radiation can modify photobleaching rates (Kieber et al. 1990). Photobleaching also involves oxygen consumption, so low  $O_2$  concentrations or anoxic conditions could reduce or inhibit the process (Zepp 1988; Lindell & Rai 1994). Further, humic substances, in addition to their light-absorbing attributes, are regarded as polyelectrolytes of high molecular weight. Ionic strength and pH affect their molecular configuration and charge (De Haan et al. 1987). The configuration of humic acids has been related to

bioavailability (De Haan 1992) and potential for enzymatic cleavage (Edling & Tranvik 1996). Therefore, we hypothesize that humic-acid configuration related to environmental conditions could also modify the susceptibility of DOC to photobleaching.

The main goal of our study was to assess the kinetics and variability of photobleaching among lakes. We experimentally determined photobleaching of DOC for thirty lakes to evaluate the magnitude of this variability. We examined the relationships between DOC-photobleaching and lake trophic and chemical conditions.

## Material and methods

### *Characterization of the lakes*

Twenty four lakes from Wisconsin (3) and Michigan's Upper Peninsula (21), most located at the University of Notre Dame Environmental Research Center (Carpenter & Kitchell 1993) and six additional lakes from the northeast U.S., 4 in New York and 2 in Connecticut (Caraco et al. 1991) were selected for this study. These lakes covered a wide range of water color, DOC concentration, total phosphorus, pH, trophic status and water hardness (Table 1).

Each lake was sampled once during the summer of 1996. Temperature and oxygen profiles were measured at 0.5 m intervals with a YSI model 58 combination electrode. Underwater PAR (photosynthetically active radiation) irradiance was measured at 0.25 m intervals with a LiCor model 193 SA spherical quantum sensor equipped with a cosine collector. Diffuse attenuation coefficients for downward irradiance in the visible spectrum ( $k_{dPAR}$ ) were determined from the slope of the linear regression of the natural logarithm of downwelling irradiance versus depth.

Samples of epilimnetic water from every lake were taken for chlorophyll-a, DOC, color, total phosphorus, pH, ANC, conductivity and cations. For chlorophyll duplicate samples were filtered through Whatman GF/F filters and frozen until extracted. Chlorophyll was extracted for 24 hours in basic methanol at 5 °C, measured by fluorometry and corrected for pheopigments by acidification (Marker et al. 1980). Triplicate samples for DOC analysis were prepared by filtering lake water through precombusted Whatman GF/F glass fiber filters, collecting the filtrate in a clean flask, and acidifying (final pH near 2) the sample until analysis. DOC concentration was then measured with a Shimadzu TOC-5050 Total Carbon Analyzer. Diffuse attenuation coefficients for UV-380 downward irradiance ( $k_{d380}$ ) were estimated from DOC concentrations using the models of Morris et al. (1995). Water color was measured by filtering lake water through Whatman GF/F

Table 1. Mean values of three replicates of chemical and trophic parameters during summer. Locations: <sup>1</sup> – Northwestern CT, <sup>2</sup> – Hudson valley NY, <sup>3</sup> – UNDERC (University of Notre Dame Environmental Research Center) WI and MI, <sup>4</sup> – LTER lake and <sup>5</sup> – Northeastern WI. O.M.M.: Old Man McMullen; N.G.B.: North Gate Bog; F.S.B.: Forest Service Bog. Lakes are ordered from fastest to slowest photobleaching rates.

Lake	$a_{440}$ ( $m^{-1}$ )	DOC ( $mg\ l^{-1}$ )	Chl-a ( $\mu g\ l^{-1}$ )	ANC ( $\mu eq\ l^{-1}$ )	TP ( $\mu g\ l^{-1}$ )	Ca <sup>++</sup> ( $mg\ l^{-1}$ )	Mg <sup>++</sup> ( $mg\ l^{-1}$ )	Conduc- tivity ( $\mu S$ )	pH
Wononscopomuc <sup>1</sup>	0.8	4.0	18.2	2788	17.0	28.6	16.6	227	8.75
Upton <sup>2</sup>	0.9	3.7	7.6	2161	11.3	28.1	10.7	230	8.43
Stissing <sup>2</sup>	1.1	4.2	16.3	2373	22.1	40.9	9.6	229	8.08
Tyrell <sup>2</sup>	1.3	4.8	9.2	901	10.9	15.7	2.6	n.d.	8.00
Chodiksee <sup>2</sup>	3.7	7.7	27.0	1233	49.3	33.2	2.7	182	7.54
Peter <sup>3</sup>	2.2	7.7	78.7	142	70.4	2.4	0.8	20.7	9.31
Inkpot <sup>3</sup>	4.9	13.3	17.8	120	31.4	12.7	3.2	82.1	7.75
Brown <sup>3</sup>	3.0	5.8	8.5	232	42.4	17.1	4.3	88.1	7.93
Kickapoo <sup>3</sup>	5.4	10.0	16.1	119	29.5	10.0	2.5	58.5	7.35
Tenderfoot <sup>3</sup>	3.6	8.5	10.1	141	33.5	11.0	2.8	74.4	7.34
Plum <sup>3</sup>	2.1	8.3	13.4	97	29.1	7.5	2.1	71.0	7.38
Morris <sup>3</sup>	11.9	14.4	14.8	137	36.0	11.0	3.0	64.9	7.28
Ward <sup>3</sup>	4.2	9.2	5.4	137	22.7	19.9	5.5	116.1	7.54
West <sup>3</sup>	5.6	8.5	3.9	68	57.3	1.0	0.4	16.4	6.0
N.G.B. <sup>3</sup>	16.9	20.6	2.7	72	16.4	1.0	0.3	19.5	4.23
Bergner <sup>3</sup>	5.3	8.9	11.7	82	15.9	0.7	0.3	11.8	5.87
O.M.M. <sup>1</sup>	14.7	16.5	4.1	n.d.	n.d.	n.d.	n.d.	26.8	4.72
Cranberry <sup>3</sup>	6.7	11.4	4.7	86	11.7	0.6	0.2	11.0	4.62
Raspberry <sup>3</sup>	2.7	5.6	6.6	68	14.2	0.8	0.3	12.0	6.07
Ed's Bog <sup>3</sup>	7.8	11.0	4.6	72	12.9	0.9	0.3	11.1	4.92
East <sup>3</sup>	12.9	15.9	8.8	72	129.3	1.2	0.5	21.7	6.05
Bolger <sup>3</sup>	9.6	13.4	19.4	84	53.6	4.2	1.2	25.7	6.85
Bog Pot <sup>3</sup>	12.6	11.6	12.1	71	25.0	1.4	0.5	14.2	5.80
Hummingbird <sup>3</sup>	19.3	20.9	13.5	56	18.8	2.0	0.5	16.4	4.77
Tuesday <sup>3</sup>	4.2	10.6	11.4	76	21.1	0.9	0.3	13.6	6.00
Trout Bog <sup>4</sup>	11.0	19.4	6.9	64	n.d.	n.d.	n.d.	14.8	4.80
Mary <sup>5</sup>	14.2	21.5	16.3	81	n.d.	n.d.	n.d.	24.4	6.10
F.S.B. <sup>3</sup>	2.3	4.8	2.2	81	8.5	0.3	0.1	9.6	5.33
Reddington <sup>3</sup>	18.4	18.0	6.9	101	24.4	3.9	1.3	23.5	6.25
Paul <sup>3</sup>	1.4	4.0	10.1	65	11.4	1.8	0.6	13.3	6.34

glass fiber filters and measuring the filtrate absorbance at 440 nm in 10 cm cells. This wavelength was selected because it provides a measure of water color especially suitable for lakes of high humic content (Cuthbert & del Giorgio 1992) and because its ecological significance relative to photosynthesis (Reche et al., unpublished data). Total phosphorus (TP) was

measured using the molybdate blue method after persulfate digestion (APHA 1985). ANC was determined with automatic potentiometric titrations (Gran 1952); pH was measured with an Orion digital meter, using a standard AG/AGCL triode electrode with automatic temperature compensation. Conductivity was measured using Model 32 Conductance Meter. Calcium and magnesium concentrations were determined on filtered samples by atomic emission spectroscopy (Perkin Elmer Plasma 400).

The 1% attenuation depths ( $Z$ , in m) were derived from the diffuse attenuation coefficient for both PAR and UV-380 downwelling radiation according to Kirk (1994) as:

$$Z = 4.605k_d^{-1} \quad (1)$$

#### *Experimental determination of photobleaching rates*

To test whether water color can be reduced by sunlight in concert with bacterial activity or if photobleaching is mainly an abiotic process, we conducted an experiment consisting of four treatments. Two treatments (light and dark) consisted of filtering water from one of the lakes (Old Man McMullen Pond, CT) through Whatman GF/F glass fiber filters. This filtration excluded bacterial predators and reduced initial bacterial abundance from 44% to 62% in this system. The three transparent (GF/F-filtered treatment) and the three dark (GF/F-filtered-aluminum foil covered treatment) borosilicate bottles were filled and incubated under natural sunlight conditions. From each bottle, three subsamples for color measurements were taken 7–10 times during the incubation. The third and fourth treatments consisted of 0.2  $\mu\text{m}$ -filtered and autoclaved water, respectively, incubated in about 30 transparent 25ml-test tubes under the same conditions as the GF/F-filtered treatments. At each sampling time we sequentially took 3 completely sealed tubes of each treatment (to insure sterility) for color measurements.

To determine the photobleaching rates, for each lake we measured water color changes at different sunlight doses in three 300 ml-transparent borosilicate bottles that were previously filled with GF/F filtered water from each lake (GF/F-filtered transparent treatment, above). To reduce the differences in the quality (UVBR:UVR:PAR ratio) of solar spectrum radiation during the incubations, bottles corresponding to groups of six lakes were incubated on a platform under the same natural sunlight conditions during summer. Bottles were mixed at sampling to avoid oxygen depletion. For these experiments we measured sunlight surface irradiance ( $\text{E m}^{-2}$ ) using a Weathertronic Mechanical Pyranograph Model 3010. Water color was determined as in lake water characterization.

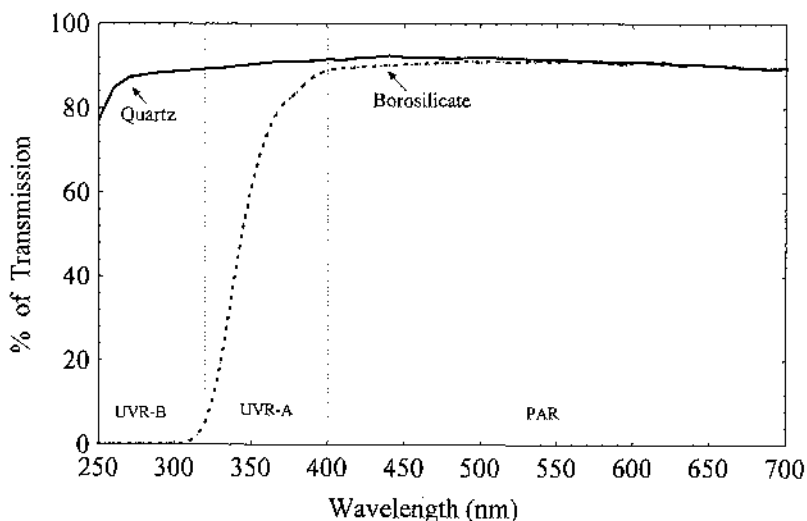


Figure 1. Percentage of energy transmission through the experimental-borosilicate and quartz bottles as a function of wavelength, measured on a spectrophotometer. Note that experimental bottles are effectively opaque to UV-B radiation.

Borosilicate bottles selectively absorb some wavelengths of incident sunlight radiation (Wetzel 1992; Wetzel et al. 1995). The transmission of the sunlight radiation through the experimental bottles was around 90% over the PAR range (>400 nm), averaged 63% for UV-A radiation (320–400 nm), was <5% for UV-B radiation (< 320 nm) (Figure 1). To evaluate the underestimation of photobleaching by using borosilicate versus quartz bottles (high transmittance in UVB range, Figure 1), we compared color loss in borosilicate bottles with quartz bottles for three of the study lakes under the same incubation conditions.

Water from the more colored lakes attenuates radiation inside the experimental bottles faster than water from clear lakes. To assess whether this differential attenuation significantly affected photobleaching variability among study lakes, we also estimated the photobleaching coefficients including the attenuation of PAR and UV-A radiation (the only wavebands that penetrate through borosilicate) inside experimental bottles. PAR and UV-A radiation attenuation were determined using  $k_d$  for PAR (from lakes profiles) and  $k_{d380}$  for UV-A radiation (at 380 nm, from DOC data using Morris et al. (1995) equations). As water in the center of the bottle receives the least light at any point in time while water on the edges receives the most light, we calculated the energy attenuation from the edges to the center (pathlength of attenuation is the radius) as well as its respective volumes at each 0.5 cm of concentric cylinders. These calculations allow us to assess the underestimation due to

attenuation of light in the bottles, and, then, to obtain the actual photobleaching rates accounting for PAR or UV-A radiation attenuation inside bottles. The pathlength of attenuation was assumed to be the radius of the bottle, because light was received from direct as well as diffuse sources and our goal was to assess the lower exposure of DOC that occurred in the center relative to the edges of the bottle.

### *Statistical analyses*

Data used in analysis are arithmetic means of two or three replicates. All independent variables, except pH, were log-transformed to meet normality assumptions. Given that we were interested in the predictive nature of the relationships analyzed, we used ordinary least-squares regression, but there is error in both dependent and independent variables. To explore the effects of colinearity among the independent variables we calculated partial correlations.

## **Results**

### *Photobleaching rates*

The lakes sampled to determine photobleaching rates varied in color absorption coefficients and DOC with ranges of 0.8 to 19.3 ( $\text{m}^{-1}$ ) and 3.7 to 21.5  $\text{mg l}^{-1}$ , respectively (Table 1). Acid neutralizing capacity and cations ranged over three orders of magnitude and  $\text{H}^+$  concentration over four orders of magnitude. Conductivity ranged from 9.6 to 230  $\mu\text{S}$ . Total phosphorus and chlorophyll-a varied from 8.5 to 129.3  $\mu\text{g l}^{-1}$  and 2.2 to 78.7  $\mu\text{g l}^{-1}$ , respectively (Table 1).

The assays performed to assess the importance of biological activity on photobleaching rates showed no significant differences between photobleaching coefficients of the 0.2  $\mu\text{m}$ -filtered and of the GF/F-filtered treatments. In the GF/F-filtered dark treatment no changes in water color during the incubation were detected (Figure 2). Similar or even, in some cases, faster photobleaching rates were obtained in the sealed autoclaved treatments than in the 0.2  $\mu\text{m}$ - or GF/F-filtered treatments (data not shown). This result could be related to changes in the DOM resulting from autoclaving. The main conclusion, however, is that photobleaching was primarily an abiotic, sunlight-mediated process and water color was not changed by bacterial activity over the time period of our measurements. The use of GF/F versus 0.2  $\mu\text{m}$  filtered water in transparent bottles did not influence the measured photobleaching coefficients, so we used GF/F filtrations for the photobleaching coefficient determinations for the rest of the study lakes.

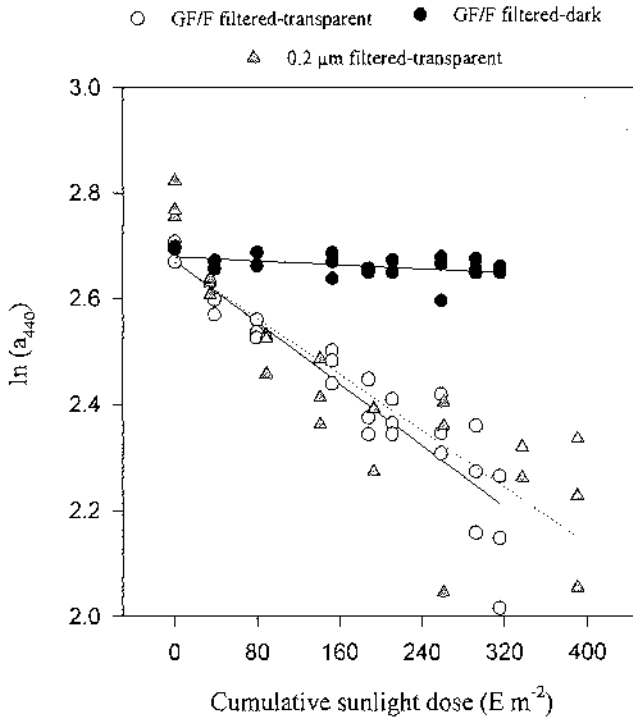


Figure 2. Changes in absorption coefficients at 440 nm ( $a_{440}$ ) under different cumulative sunlight doses in GF/F filtered-transparent treatment (open circles), GF/F filtered-dark treatment (filled circles) and 0.2  $\mu\text{m}$  filtered-transparent treatment (triangles). Note ln scale. Lines are regression lines through each treatments. In this example, water was taken from O.M.M. (see Table 1).

Water color decreased with increasing sunlight exposure for samples isolated from each lake. Photobleaching kinetics fit a negative exponential function in all cases:

$$a_{440n} = a_{440o} e^{-k_b D_n} \quad (2)$$

where  $a_{440n}$  is the absorption coefficient at 440 nm at time  $n$  (in  $\text{m}^{-1}$ );  $D_n$  is the cumulative sunlight dose ( $\text{E m}^{-2}$ );  $a_{440o}$  is the initial absorption coefficient at 440 (in  $\text{m}^{-1}$ ); and  $k_b$  is the photobleaching rate coefficient ( $(\text{E m}^{-2})^{-1}$ ).  $k_b$  is the slope of the ln-linear regression. This regression always had a negative slope; thus the more negative the value of  $k_b$ , the faster the photobleaching rate. The linearity of these plots demonstrates that photobleaching rates were a first-order function of the sunlight dose. All slopes were significantly  $< 0$  ( $p < 0.05$ ). Figure 3 illustrates several of the relationships between cumulative sunlight dose and the natural logarithm of the color absorption coefficients. Note that Forest Service Bog (F.S.B.) and Peter

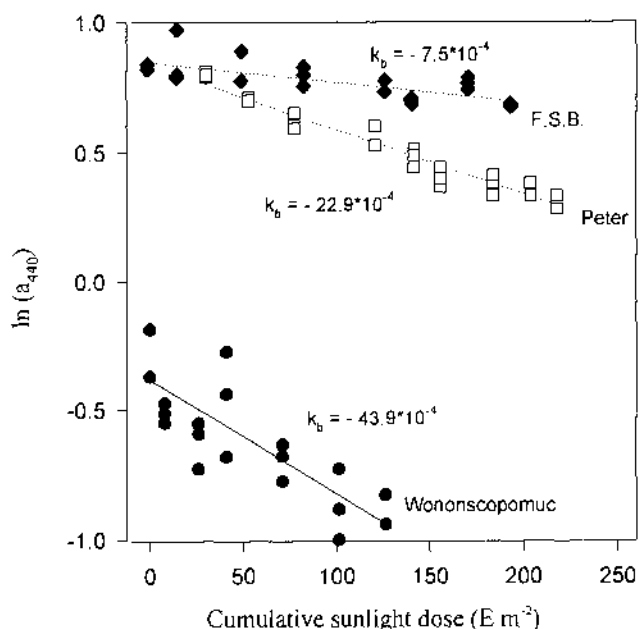


Figure 3. Regressions between absorption coefficients at 440 nm ( $a_{440}$ ) and cumulative sunlight dose for representative study lakes. Note ln scale F.S.B (Forest Service Bog; filled diamonds); Peter lake (open squares); lake Wononscopomuc (filled circles). The slopes are the photobleaching coefficients ( $k_b$ ),  $k_b$  units =  $(E\ m^{-2})^{-1}$ .

Lake have similar initial  $a_{440}$  values but very different rates of photobleaching (Figure 3). Among lakes,  $k_b$  varied from  $-7 \times 10^{-4}$  to  $-43.9 \times 10^{-4}$   $(E\ m^{-2})^{-1}$  (Figure 4).

The removal of some of the UV-radiation by our borosilicate bottles (Figure 1) caused an underestimate of photobleaching relative to UV-transparent bottles. The effect of this underestimate on the pattern of rates among lakes is illustrated in Figure 4 by comparing photobleaching coefficients obtained using quartz bottles (open circles) with the lower rates measured using borosilicate bottles (filled circles). The trend among lakes appears similar irrespective of bottle type used. The magnitude of the underestimate was 15–19% (Figure 5).

Another potential complication in our measurements could be the differential attenuation of the energy inside the experimental bottles. In Table 2 we compared the values of  $k_b$  from the experiments with  $k_b$  corrected for the attenuation of UV-A radiation at 380 nm and PAR inside the experimental bottles. These corrections were trivial in the case of  $k_b$  based on PAR attenuation; only changed slightly based on UVAR attenuation, and most importantly did not modify the magnitude of photobleaching variability (i.e.

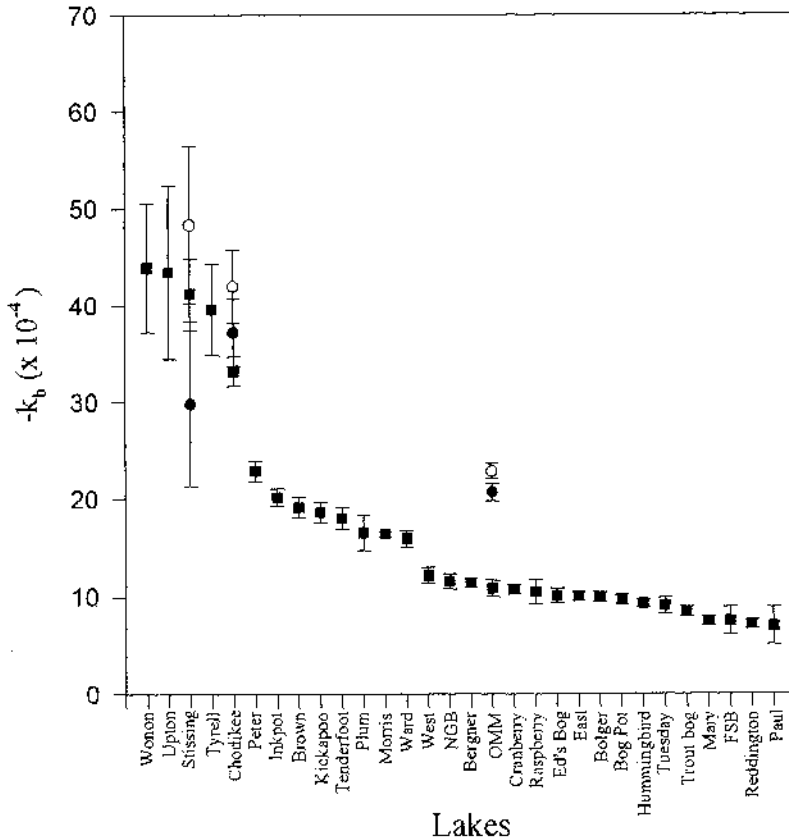


Figure 4. Photobleaching coefficients ( $k_b$ ) and standard errors for the whole set of lakes,  $k_b$  units =  $(E\ m^{-2})^{-1}$ . Each square represents a different lake. Lakes are ranked from fastest to slowest photobleaching rates. Standard errors are for slopes of the photobleaching regression lines (as in Figure 3). Circles represent photobleaching coefficients for the experiments comparing borosilicate bottles (filled circles) with quartz bottles (open circles).

range in observed rates remained large and patterns of variation among lakes consistent).

#### *Relationships of photobleaching with lake trophic and chemical conditions*

The variation in photobleaching may be related to the origin and chemical composition of DOC as well as lake chemical and trophic conditions. Spectral properties of aquatic organic matter have been used to assess origin. Allochthonous DOC is usually highly colored whereas DOC from autochthonous planktonic production contributes little to water color (Birge & Juday 1927; Hutchinson 1975; Tipping et al. 1988; Meili 1992). Color absorption coefficients, DOC and chlorophyll-a concentrations were all significantly

Table 2. Comparison of photobleaching rate coefficients obtained experimentally ( $\pm$  standard errors) and considering that experimental bottles were an optically thin system ( $k_{b1}$ ), after corrections for PAR attenuation through the pathlength of the experimental bottles ( $k_{b2}$ ), and after corrections for the attenuation of UVAR (at 380 nm) through the pathlength of the experimental bottles ( $k_{b3}$ ).

Lake	$k_{b1} (\times 10^{-4})$ ( $\text{Em}^{-2}$ ) $^{-1}$	$k_{b2} (\times 10^{-4})$ ( $\text{Em}^{-2}$ ) $^{-1}$	$k_{b3} (\times 10^{-4})$ ( $\text{Em}^{-2}$ ) $^{-1}$
Wononscopomuc	43.9 $\pm$ 6.7	44.7	45.9
Upton	43.4 $\pm$ 8.9	n.d.	45.2
Stüssing	41.2 $\pm$ 3.7	42.2	43.1
Tyrell	39.6 $\pm$ 4.7	40.4	41.8
Chodikee	33.2 $\pm$ 1.5	34.3	36.4
Peter	22.9 $\pm$ 1.1	23.4	25.1
Inkpot	20.2 $\pm$ 0.9	20.9	23.9
Brown	19.1 $\pm$ 1.1	19.6	20.5
Kickapoo	18.6 $\pm$ 1.1	19.3	21.0
Tenderfoot	18.0 $\pm$ 1.1	18.5	19.9
Plum	16.5 $\pm$ 1.8	16.9	18.2
Morris	16.4 $\pm$ 0.3	17.1	19.7
Ward	15.9 $\pm$ 0.9	16.3	17.8
West	12.2 $\pm$ 0.8	12.5	13.5
N.G.B.	11.6 $\pm$ 0.8	12.0	15.2
Bergner	11.5 $\pm$ 0.5	11.8	12.8
O.M.M.	10.9 $\pm$ 1.2	11.5	13.5
Cranberry	10.7 $\pm$ 0.5	11.1	12.4
Raspberry	10.5 $\pm$ 1.3	10.8	11.2
Ed's Bog	10.1 $\pm$ 0.8	10.6	11.6
East	10.1 $\pm$ 0.4	10.5	12.4
Bolger	9.9 $\pm$ 0.5	10.5	11.8
Bog Pot	9.7 $\pm$ 0.5	10.3	11.3
Hummingbird	9.3 $\pm$ 0.4	9.8	12.3
Tuesday	9.1 $\pm$ 0.8	9.4	10.4
Trout Bog	8.5 $\pm$ 0.5	n.d.	10.9
Mary	7.5 $\pm$ 0.5	n.d.	10.0
F.S.B.	7.5 $\pm$ 1.5	7.7	7.9
Reddington	7.2 $\pm$ 0.4	7.7	9.1
Paul	7.0 $\pm$ 1.9	7.1	7.3

n.d. - not determined.

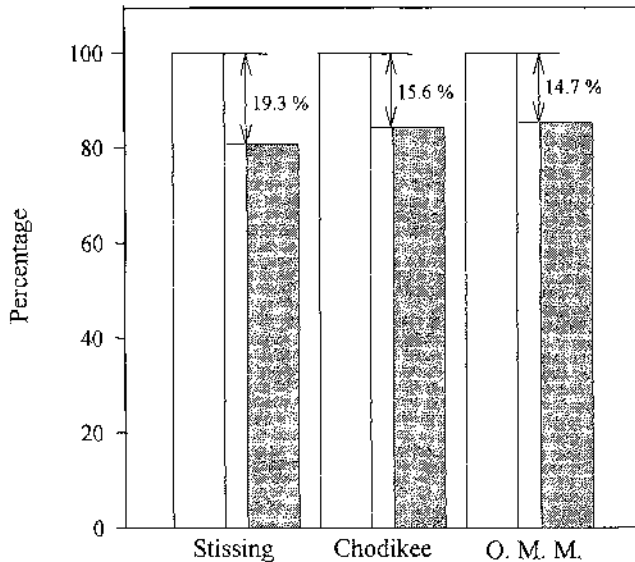


Figure 5. Percentage of color loss measured using borosilicate bottles (grey bars) relative to quartz bottles (open bars) for three of the study lakes.

related to photobleaching coefficients for the study lakes (Table 3). In order to assess the relative effects of DOC composition and trophic conditions on photobleaching we calculated two ratios. Since color is primarily determined by humic and fulvic acids, the ratio of  $a_{440}$  to DOC is an index of composition. The ratio of chlorophyll-a to DOC is an index of lake trophic normalized to DOC across the wide lakes we sampled.

There was a significant and negative relationship between  $k_b$  and the  $a_{440}$ :DOC ratio (Figure 6). The opposite relationship was obtained with the chlorophyll-a:DOC ratio (Figure 7). Lakes with more chlorophyll per unit DOC had faster photobleaching. However, regressions based either on single factors ( $a_{440}$ , chlorophyll-a, DOC) or ratios of these never explained more than about half of the variance (Table 3).

In contrast, there were stronger relationships between measures of the ionic environment and photobleaching (Table 3). Photobleaching coefficients were positively related to the sum of divalent cations ( $\text{Ca}^{++} + \text{Mg}^{++}$ ), pH, ANC, and conductivity. ANC was the best predictor of  $k_b$  explaining more than 90% of the variance among lakes (Table 3, Figure 8). The three groups of points in Figure 8 correspond to the three sets of lakes in Figure 4 and generally represent ANC classes in the range of  $<100 \mu\text{eq l}^{-1}$ ,  $100\text{--}1000 \mu\text{eq l}^{-1}$ , and  $>1000 \mu\text{eq l}^{-1}$ .

As is often the case in comparative studies, the independent variables ( $a_{440}$ :DOC ratio, chlorophyll-a:DOC ratio, cations, pH, conductivity and

Table 3. Statistical data and model equations for the relationships between photobleaching coefficients and the independent variables. Predictors, except pH, are natural log-transformed. Units as in Table 1.

	<i>n</i>	<i>r</i> <sup>2</sup>	<i>p</i>	Model equation <sup>1</sup>
<i>K<sub>b</sub> predicted by DOC composition or trophic conditions:</i>				
Color	30	0.51	<0.001	$k_b = 30.6 - 8.61 \ln a_{440}$
Chlorophyll-a (chl-a)	30	0.15	<0.05	$k_b = 3.8 + 5.9 \ln \text{chl-a}$
DOC	30	0.39	<0.001	$k_b = 46.9 - 13.3 \ln \text{DOC}$
<i>a</i> <sub>440</sub> :DOC	30	0.52	<0.001	$k_b = 5.2 - 17.7 \ln a_{440}:\text{DOC}$
Chlorophyll-a:DOC	30	0.47	<0.001	$k_b = 17.2 + 8.9 \ln \text{chl-a:DOC}$
<i>K<sub>b</sub> predicted by chemical conditions:</i>				
Cations (Ca <sup>+</sup> Mg <sup>++</sup> )	27	0.62	<0.001	$k_b = 7.6 + 6.4 \ln \text{cations}$
pH	28	0.55	<0.001	$k_b = -24.0 + 6.3 \text{pH}$
Conductivity	29	0.74	<0.001	$k_b = -15.0 + 8.9 \ln \text{conductivity}$
ANC	29	0.94	<0.001	$k_b = -30.1 + 9.4 \ln \text{ANC}$

<sup>1</sup>  $k_b$  multiplied by  $10^{-4}$ .

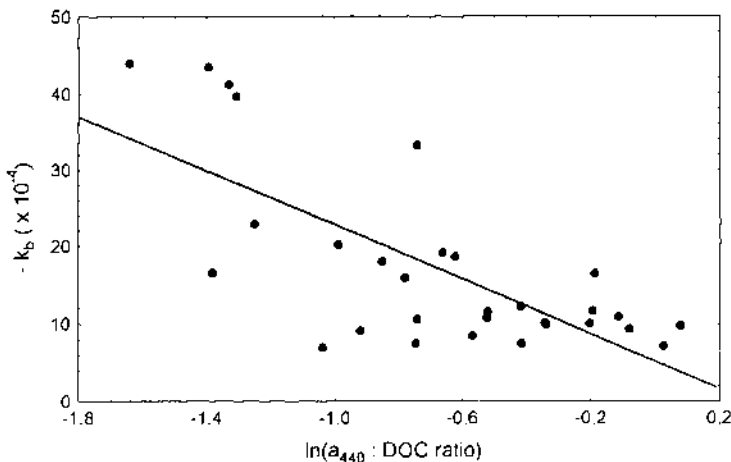


Figure 6. Relationship between photobleaching coefficients ( $k_b$ ) and  $a_{440}:\text{DOC}$  ratio. Equation as in Table 3,  $k_b$  units =  $(\text{E m}^{-2})^{-1}$  and  $a_{440}:\text{DOC}$  ratio units as in Table 1.

ANC) that we considered were co-correlated. Therefore, it is difficult to establish the most important relationships explaining variability in photobleaching rates. To assess the most important variables determining the statistical relationships, we calculated partial correlation coefficients between photobleaching and the ionic variables paired with the ratios of  $a_{440}$  or

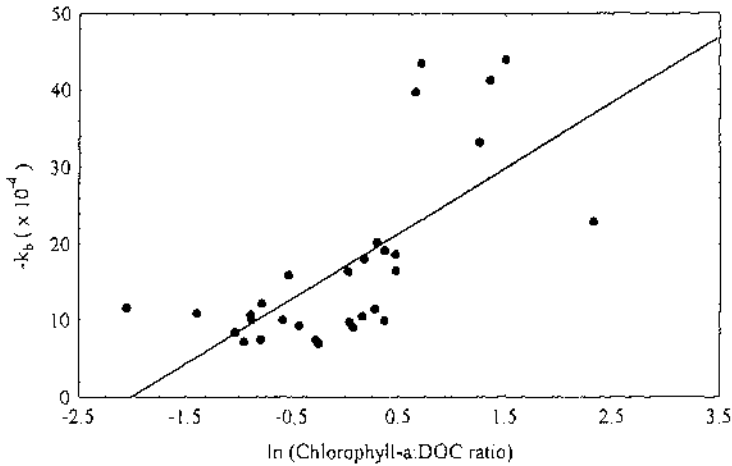


Figure 7. Relationship between photobleaching coefficients ( $k_b$ ) and chlorophyll-a:DOC ratio. Equation as in Table 3,  $k_b$  units =  $(\text{E m}^{-2})^{-1}$  and chlorophyll-a:DOC ratio units as in Table 1.

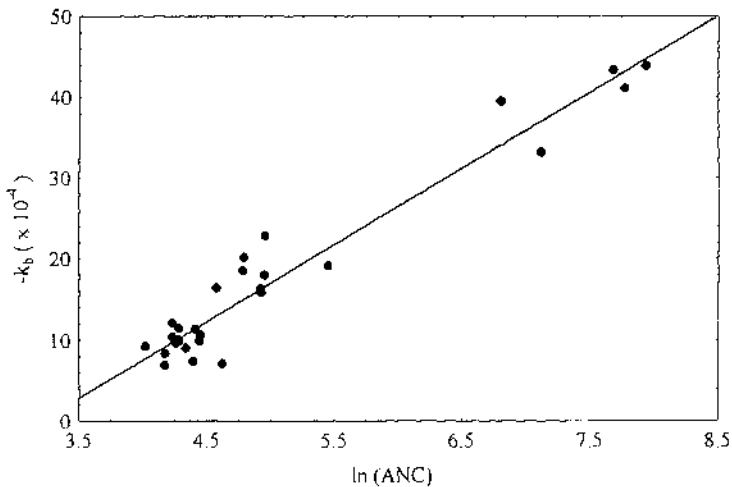


Figure 8. Relationship between photobleaching coefficients ( $k_b$ ) and acid-neutralizing capacity (ANC). Equation as in Table 3,  $k_b$  units =  $(\text{E m}^{-2})^{-1}$  and ANC units =  $\mu\text{eq l}^{-1}$ .

chlorophyll to DOC. Partial correlations for ionic variables were typically strong whereas partial correlations for the ratio variables were weak. For example, the partial correlation between ANC and photobleaching when controlling for the ratio of chlorophyll-a to DOC was 0.95 ( $p < 0.001$ ) while the partial correlation for this same ratio controlling for ANC was only marginally significant ( $r = 0.37$ ,  $p = 0.049$ ). This result suggests a stronger

and more direct relationship between ANC and photobleaching than between chlorophyll-a:DOC ratio and photobleaching.

## Discussion

### *Experimental photobleaching rates*

We observed a large amount of variation, among lakes, in measured photobleaching coefficients. Our experimental results (as percentage of color lost per day) fall within the range of previous studies (0–19%) using borosilicate bottles and measuring color a similar wavelength (Lindell et al. 1995; Molot & Dillon 1997). Previous analyses of marine and freshwater systems indicate that these rates of photobleaching lead to significant production of labile organic compounds that appear important in satisfying the carbon demands of bacteria and in making phosphorus and nitrogen biologically available (Moran & Zepp 1997; Reche et al., in press).

Photobleaching followed first order kinetics for all the lakes we studied. The generality of this result provides a basis for comparing rates among ecosystems. Further, understanding the first order kinetics of this process is necessary to accurately model photobleaching and transformation of organic matter resulting from sunlight exposure.

Our determinations of photobleaching coefficients are conservative due to the partial absorption of incident radiation, mainly in the UV-B fraction, by the glass of the bottles. The experimental bottles were effectively opaque to UV-B and impeded the penetration of an average of 37% of the radiation in the UV-A range (Figure 1). We did not make corrections for the energy absorbed by bottle walls in order to work with direct values since we were primarily interested in the magnitude and variability of photobleaching across systems and its potentially related predictors. In some studies, the UV-B band has been considered the radiation primarily responsible for the photobleaching of humic substances (Kieber et al. 1990). However, our results demonstrate that photobleaching also results from exposure to UV-A and PAR fractions of the spectrum. Geller (1986), Graneli et al. (1996), Molot and Dillon (1997), and Morris and Hargreaves (1997) also detected DOC photodegradation at longer wavelengths than UV-B radiation. Although it is well established that quantum yield of DOM photolysis decreases as wavelength increases (Kieber et al. 1990; Scully et al. 1996), weighted quantum yield (dependent on the specific quantity of energy in each wavelength that reaches Earth's surface) underlines the role of UV-A radiation in DOM photobleaching (Scully et al. 1996; Morris & Hargreaves 1997). Moreover, the low penetration of UV-B radiation into water column in study lakes (on

the order of 4 to 33 centimeters) highlights the significance of UV-A radiation and PAR in DOM photobleaching in these systems.

In spite of our measures of photobleaching are only applicable to the upper portion of the water column, a simple extrapolation of these values to the whole epilimnion (accounting for UV-A energy attenuation in water column) suggests that between 27 and 140% of water color could be lost during the summer. However, in most of the lakes we have studied, color remains relatively constant during the ice-free period. This constancy indicates that the loss of color must be balanced by new inputs of color. Color to replace photobleaching losses may come from either an input of colored water or the generation of new colored compounds within the system. Humic matter may be formed from labile monomers via microbial activity (Tranvik 1993) or via photooxidative polymerization (Hedges 1988). Hypolimnetic waters in many of the more dystrophic lakes we sampled had higher color than corresponding epilimnetic waters (Pace, unpublished data) so mixing periods, especially thermocline erosion during late summer, could provide an important source of colored water to the epilimnion.

#### *Factors involved in photobleaching variability*

We observed rapid rates of photobleaching similar to those found in other studies (e.g. Lindell et al. 1995; Molot & Dillon 1997). Some researchers, however have not found rapid rates and this may be related to differences in the age and composition of DOC. For example, Thomas and Lara (1995) irradiated autochthonous marine DOC with UV light and found little photooxidation and no change in the relative proportion of humic substances. Their experiments were performed with aged DOC and suggest especially when considered with our results that additional study is needed on the relative importance of diagenetic status (fresh vs aged), size (high vs low molecular weight) and origin (autochthonous vs allochthonous) of DOC in relation to photobleaching.

Our results suggest that chemical factors are relatively more important than either biological productivity (as reflected by chlorophyll-a) or DOC composition in explaining photobleaching variability. A possible underlying mechanism directly affecting photobleaching rates may be ionic conditions (Table 3, Figure 8) that cause variable configurations of humic substances. Acid environments promote the condensation of humic acid into larger colloids (Thurman 1985). In the same way that these colloids seem to reduce the enzymatic accessibility to active sites (Edling & Tranvik 1996), sunlight access to photoreactive bonds could be reduced. Another alternative explanation is that ANC affects the proportion of DOM that is photobleachable (fulvic vs humic acids). Therefore, in alkaline waters the higher solubility

of humic substances or the higher proportion of photobleachable DOM may lead to lower photolytic recalcitrance of the DOC.

Other environmental factors that also can modify photobleaching rates could be related to water chemistry. Sunlight-generated oxidants can accelerate photodegradation (Scully et al. 1996). Fe-III forms complexes with polycarboxylates that undergo rapid photochemical reactions in sunlight (Faust & Zepp 1993). Interactions between photochemical products such as  $H_2O_2$  and Fe-II produce hydroxyl radicals that oxidize DOM (Zepp et al. 1992). These and other reactions may be significant components of the variation in rates we observed, but there are, as yet, few studies like those of Scully et al. (1996) and Morris and Hargreaves (1997) that consider photochemical processes across a gradient of ecosystems.

#### *Ecological implications of photobleaching variability*

Photosynthetic potentials (which depend on PAR transmission in the water column) and potential UV-damage (UV-radiation transmission dependent) can be constrained by the resistance of DOC to photobleaching. Both DOC concentration and water color have been used as predictors of PAR and UV-radiation attenuation in lakes (Scully & Lean 1994; Morris et al. 1995; Williamson et al. 1996). Most of the uncertainty in predicted attenuation coefficients by these models has been related to variable DOC-specific absorbance (Morris et al. 1995). This variability may be determined by the ionic conditions of the lake which promote the potential for either greater (low ANC) or lesser (high ANC) absorption of energy by DOC without degradation.

There is a significant and positive relationship between photobleaching coefficients and the depths of 1% of PAR and UV-380 attenuation (Figure 9). A difference in photobleaching coefficients from  $10 \times 10^{-4}$  to  $40 \times 10^{-4}$  ( $Em^{-2})^{-1}$  could result in an increase in the 1% PAR attenuation depth from 2.45 to 5.06 m and in the 1% UV-380 radiation attenuation depth from 0.36 to 0.90 m. These estimates should be taken with caution because PAR or UV-380 attenuation is related to DOC and water color (Morris et al. 1995) and both parameters are related to photobleaching variability (Table 3). Nevertheless, Morris and Hargreaves (1997) have recently demonstrated that seasonal changes in DOM photobleaching affect light attenuation and the depths of 1% PAR and UV-380 attenuation in lakes.

Our study indicates that, in hardwater relative to softwater lakes, humic substances are more susceptible to photobleaching. Under natural conditions, this faster photobleaching in alkaline lakes could result in deeper PAR or UV radiation transmission in the water column as well as deeper mixing depths (Fee et al. 1996). These processes may also be important in acidified softwater

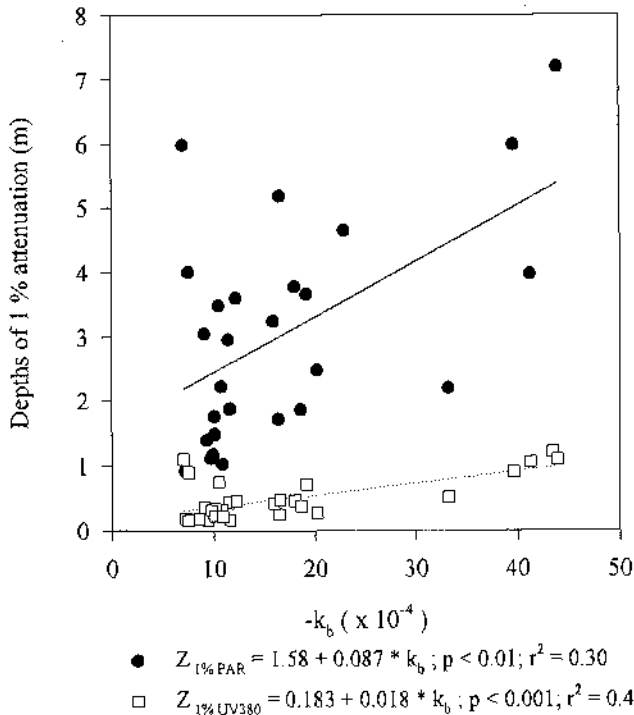


Figure 9. Relationships between depths of 1% PAR attenuation (filled circles) and UVR<sub>380</sub> attenuation (open squares) and photobleaching coefficients.  $k_b$  units =  $(E m^{-2})^{-1}$ .

lakes. Acidification can decrease solubility of humic substances (De Haan et al. 1983) and promote compensatory in-lake processes that generate alkalinity (Cook et al. 1986). Losses of DOC due to acidification may increase UV radiation transmission in lake water columns (Schindler et al. 1996a; Schindler et al. 1997). In addition, our results imply that watershed and lake processes that increase alkalinity will accelerate photobleaching and consequently the penetration of UVR. For example, liming of acidified lakes may also promote an increase in photobleaching rates and then indirectly deeper UVR transmission. Other anthropogenic factors such as climate warming (Psenner & Schmidt 1992; Schindler et al. 1996a, b) can also promote in-lake alkalinity generation.

Photobleaching is one process that regulates the color of lakes. Variability in lake water color is driven by watershed and in-lake processes and the net result has important effects on light transmission (Morris et al. 1995), photosynthesis (Jones 1992), the behavior and interactions of organisms (Williamson 1995), carbon cycling (Wetzel 1990, 1992; DeHaan 1992; Dillon & Molot 1997), and the responses of lakes to eutrophication (Carpenter &

Pace 1997; Carpenter et al., 1998). Lake color also appears to be sensitive to large scale environmental changes (Schindler et al. 1996b). These considerations suggest the need for focus on the balance between the formation and degradation of color in lakes.

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