

The role of photochemical degradation of dissolved organic carbon in regulating the UV transparency of three lakes on the Pocono Plateau

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Abstract

The role of photochemical degradation of dissolved organic carbon (DOC) on UV transparency (280–400 nm) was investigated in three Pocono Plateau lakes. Diffuse attenuation coefficients (K_{dUV}) in the epilimnia of these lakes varied seasonally (39–81% decline from maximum K_{d320nm}), with minimum K_{dUV} values occurring near summer solstice. Declines in K_{dUV} corresponded to reductions in UV absorbance by dissolved material (a_{dUV}), caused by declines in both DOC concentration and UV absorptivity (a_d : [DOC]). The seasonal decline in K_{dUV} was also accompanied by substantial increases in an absorption coefficient ratio ($a_{d250nm} : a_{d365nm}$) and decreases in spectral slopes (S).

Experimental studies of photochemical degradation were also performed using filtered lake water and natural sunlight. Exposure to solar radiation produced a number of changes in optical parameters and DOC that resembled those observed in the water column: a_{dUV} (–35 to –52%), UV absorptivity (–31 to –48%), $a_{d250nm} : a_{d365nm}$ (0 to +39%), spectral slope, S (0 to –27%), and DOC concentration (0 to –20%).

Changes in a_{dUV} were correlated with absorbed UV dose. The derived rate constants were used in a model to estimate the contribution of photochemical degradation of DOC to water column declines in K_{dUV} . Results suggest that rates of photochemical degradation were sufficient to account for the summer reductions in K_{dUV} observed in the three lakes.

Discerning the role of UV radiation (UVR; 280–400 nm) in aquatic ecosystems is of considerable interest due to its potential for profound ecosystem effects (Karentz et al. 1994; Siebeck et al. 1994). This interest has been heightened by recent evidence of increasing incident UV-B radiation in response to stratospheric ozone depletion (Tevini 1993; Young et al. 1993). This phenomenon is well documented for Antarctic ecosystems but increases in incident UV-B radiation (10–20% per decade) have also been reported for temperate latitudes (Kerr and McElroy 1993; Madronich 1992; Stolarski et al. 1992) that contain a large proportion of the world's freshwater ecosystems. The influence of UVR on Antarctic ecosystems has been well documented (Neale et al. 1994; Vincent and Quesada 1994; Smith et al. 1992). In contrast, UV effects on freshwaters are not well understood and may not be easily inferred from marine models. Lakes may be extremely susceptible to the effects of UVR due to their morphology (global mean depth <10 m; Wetzel 1990) and characteristic patterns of epilimnial circulation that limit the availability of UV refugia (Williamson 1995; Williamson et al. 1996). The heterogeneity of freshwater

ecosystems (physical, chemical, and biological) also implies that UV effects may differ substantially among lakes.

Transmission of UVR differs greatly among lakes and is largely regulated by the concentration and absorptivity of dissolved organic carbon (DOC) (Morris et al. 1995; Kirk 1994a; Scully and Lean 1994). These DOC compounds, which are primarily humic substances, contain chromophores that strongly absorb UVR. While these compounds can help to shield the water column from the direct effects of UVR, they are themselves subjected to considerable photochemical degradation (Kouassi et al. 1990; Gjessing 1980; Strome and Miller 1978). This degradation is often accompanied by changes in the optical properties of DOC (often referred to as photobleaching). Experimental evidence, mostly obtained with artificial light sources, suggests that photochemical degradation of DOC often reduces DOC absorptivity in the UV range (Lindell et al. 1995; DeHaan 1993; Mopper et al. 1991). Photochemical degradation may proceed to complete photomineralization (Miller and Zepp 1995; Allard et al. 1994; Salonen and Vahala 1994) or may result in production of low molecular weight DOC that in turn may be mineralized through microbial decomposition (Lindell et al. 1995; Amador et al. 1991). Both processes can result in a net increase in transmission of UVR through the water column.

Because DOC concentration and absorptivity strongly influence water column transparency, photochemical degradation of DOC may result in substantial temporal variability in the UV transparency of lakes and other aquatic ecosystems. This variability could occur on a variety of time scales from seasonal (driven primarily by seasonal variations in incident solar radiation and depth of the mixed layer) to interannual according to changes in climatological factors that influence incident UVR (e.g. cloud cover, particulate

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Table 1. Characteristics of the three study lakes. Chemical data are mean summer epilimnetic values measured over a 4-yr period. Data from Moeller et al. (1995, unpubl.).

Variable	Giles	Lacawac	Waynewood
Latitude	41°22'34"N	41°22'57"N	41°23'42"N
Longitude	75°05'33"W	75°17'35"W	75°21'50"W
z_{\max} (m)	24	13	12
z_{avg} (m)	10	5	6
Lake area (ha)	48	21	28
Watershed area* (ha)	183	70	728
Hydraulic detention (yr)	5.6	3.3	0.4
Chl <i>a</i> ($\mu\text{g liter}^{-1}$)	1.5	2.3	9.2
DOC (mg C liter^{-1})	1.09	4.80	5.28
pH	5.35	6.03	7.27
Alkalinity ($\mu\text{eq liter}^{-1}$)	-4.1	30	303

* Including lake area.

material, total column ozone, etc.). Recent lake surveys demonstrate variability of UV transparency among lakes (Morris et al. 1995; Scully and Lean 1994) but were not designed to identify temporal variability within lakes.

Since 1993, we have monitored water column transmission of UVR in three lakes from the Pocono Plateau of northeastern Pennsylvania and have consistently found large seasonal variations within lakes. These variations appear to be correlated with seasonal patterns of incident solar UVR and may be driven by photochemical degradation of DOC. In this study we present empirical and experimental evidence to support the hypothesis that UVR plays a critical role in regulating the UV transparency of these lakes. This process may be generally applicable to a variety of aquatic ecosystems and may influence the UV environment to an extent not previously recognized. It also demonstrates the potential influence of photochemical degradation on carbon cycling in aquatic ecosystems.

Methods

Our study was performed in summer 1994 in three lakes of the Pocono Plateau of northeastern Pennsylvania (Table 1) as part of an ongoing effort to characterize the causes and consequences of UV-A (321–400 nm) and UV-B (280–320 nm) penetration in lakes.

Light measurements were made with a Biospherical Instruments Inc. (BSI) GUV-521 atmospheric sensor and a BSI PUV-501 submersible profiling radiometer. Both radiometers measure downwelling irradiance simultaneously at four wavebands in the UV region (380, 340, 320, and 305 nm; 8–10-nm bandwidths) as well as broadband photosynthetically active radiation (PAR; 400–700 nm). Performance characteristics of these instruments were described in detail by Kirk et al. (1994). During 1994, continuous measurements of incident PAR, UV-A (380 and 340 nm), and UV-B (320 and 305 nm) radiation were made with the GUV-521 that was deployed at the Lacawac Sanctuary with a Campbell Scientific Inc. CR-10 datalogger. Estimates of total incident UV-A and UV-B radiation were obtained from these narrowband data by using an approach in which model UV

spectra (Madronich 1992, 1993) are used as end members representing different column ozone levels to generate an interpolated spectrum that matches the narrowband radiometer signal (Kirk et al. 1994). This approach has been shown to generate spectra from 280 to 400 nm with 1-nm resolution, which compare favorably with solar spectra measured by double monochromator scanning radiometers (Kirk et al. 1994). Spectra generated by this interpolation method were integrated to provide estimates of incident UV-A (321–400 nm) and UV-B (280–320 nm) radiation.

Measurements of underwater irradiance were performed using the submersible BSI PUV-501 radiometer. Diffuse attenuation coefficients (K_d) for UVR (305, 320, 340, 380 nm) and PAR were determined from the slope of the regression of the natural logarithm of downwelling irradiance (E_d) vs. depth (Morris et al. 1995). PUV data were routinely corrected for low-irradiance errors by subtracting a fixed zero offset value from each measured irradiance. The offset value, which is temperature sensitive, was determined empirically for each waveband of a given profile by adjusting it until the net irradiance formed a symmetrically expanding noise envelope at the depth corresponding to the sensor limit of detection (Kirk et al. 1994).

Water samples from the lakes and various experimental treatments were subjected to a variety of chemical and optical analyses. Particulate and dissolved fractions were separated by low vacuum pressure filtration through ashed (450°C) Whatman GF/F filters. DOC was measured by a high temperature combustion method (Shimadzu TOC-5000) following the recommendations of Sharp et al. (1993). Absorbance (D) of filtered samples was determined by spectrophotometry (Shimadzu UV 160U) using 1- or 10-cm Suprasil cuvettes and a blank consisting of low-carbon deionized water. Absorption coefficients for the dissolved fraction of lakewater (a_d) were calculated as

$$a_d = 2.303D/r,$$

where D is the spectrophotometer absorbance and r is the path length in meters (Kirk 1994b).

Photochemical degradation of dissolved absorbance and DOC was studied using samples collected from the metalimnion of lakes Lacawac and Waynewood and from the hypolimnion of Lake Giles. Surface samples were not used because of previous exposure to incident solar radiation and prior photochemical degradation in situ. Samples were gently filtered consecutively through ashed Whatman GF/F filters and prerinsed 0.2- μm Magna nylon filters and placed in 330-ml quartz bottles. Triplicate bottles were distributed into four experimental treatments designed to alter the spectral characteristics of penetrating solar radiation. In the first treatment (dark), bottles were covered with foil and placed into a sleeve of 4-mm (wall thickness) acrylic, UV-transparent tubing. The second treatment (Emco) consisted of quartz bottles in a 4-mm sleeve of extruded acrylic tubing (obtained from Emco Plastics, Inc.) that provided a cutoff at ~ 377 nm and had an average transmittance of 41% of solar UV-A and 3% of solar UV-B radiation (Fig. 1). In the third treatment (Mylar), quartz bottles were placed into a sleeve of 4-mm, acrylic UV-transparent tubing covered with 0.05-mm Mylar

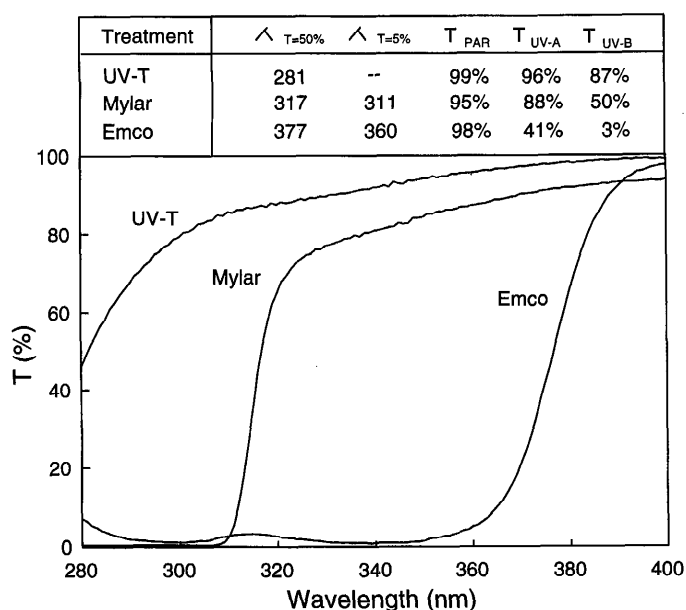


Fig. 1. Transmission characteristics (% transmittance) of optical filters used in photooxidation experiments. Values are the product of transmittance for filter materials and quartz bottles.

D. This treatment provided a cutoff at ~ 317 nm and had an average transmittance of 88% of solar UV-A and 50% of solar UV-B radiation. The final treatment (UV-T) consisted of quartz bottles in a sleeve of unaltered 4-mm, acrylic UV-transparent tubing that had an average transmittance of 96% of solar UV-A and 87% of solar UV-B radiation. Only the foil treatment significantly altered the transmission of PAR in the experimental treatments. Bottles with sleeves were submerged in a shallow pan of water designed to moderate temperature extremes and exposed to incident sunlight for up to 7 d. Subsamples were removed from each bottle at 48-h intervals and analyzed for optical absorbance (a_d) and DOC. Incident solar radiation during the photochemical degradation experiments was measured with the nearby BSI GUV-521. Exposure of each of the treatments to UV-A and UV-B radiation was estimated by multiplying the incident irradiance ($\mu\text{W cm}^{-2} \text{nm}^{-1}$ at 1-nm intervals) from the modeled solar spectrum (see above) by the transmittance (at 1-nm intervals) of the various filter-bottle combinations (Fig. 1). Resulting irradiance was summed (280–320 nm for UV-B and 321–400 nm for UV-A) to determine the UV exposure of each treatment. Exposure irradiance was converted to the dose absorbed by the DOC in each sample by using the values of a_d as an attenuation coefficient and the average pathlength of light through the quartz bottles (estimated as 50% of bottle diameter). Absorbed dose units were converted from $\mu\text{J cm}^{-2}$ to J m^{-2} .

Statistical analyses were performed using regression and ANOVA software of SPSS/PC⁺ (SPSS Inc.).

Results

Seasonal variation in epilimnial UV transparency—Diffuse attenuation coefficients for UVR showed substantial

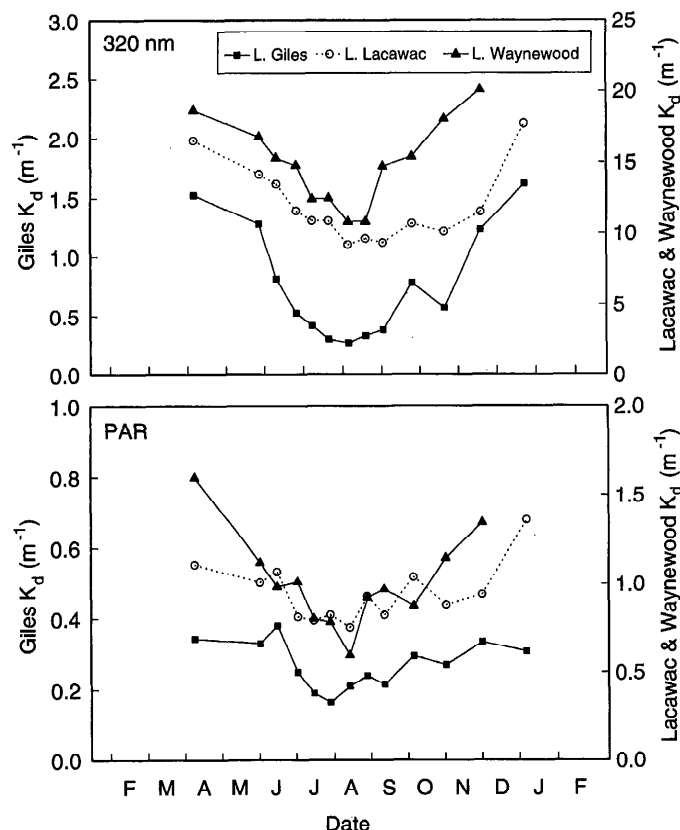


Fig. 2. The seasonal variation of near surface diffuse attenuation coefficients (K_d) measured at 320 nm and PAR (400–700 nm) for the three study lakes during 1994.

seasonal variation in the three study lakes. As illustrated by $K_{d320\text{nm}}$, the highest attenuation (lowest transparency) was observed in early spring and again in late fall (Fig. 2). Spring and early summer were characterized by progressive declines in $K_{d320\text{nm}}$, with minimum values occurring near mid-summer (July). The largest seasonal declines in attenuation occurred in the UV-B range. For instance, $K_{d320\text{nm}}$ declined 81% from spring values for Lake Giles; 47% and 39% declines occurred in Lacawac and Wayneood. Similar but less substantial seasonal variations were also observed in attenuation coefficients for UV-A radiation (340 and 380 nm not shown). The magnitude of these seasonal variations appeared to decrease at longer wavelengths as demonstrated by the contrast of K_d values for PAR and 320-nm radiation (Fig. 2).

K_d for UVR in the three study lakes was strongly correlated with absorption coefficients of the dissolved fraction of the water column (a_d , Fig. 3). This phenomenon has been noted in previous studies of lakes (Morris et al. 1995; Scully and Lean 1994) and suggests that absorption by dissolved material (principally DOC) plays a large role in regulating variations in K_d in the solar UV range.

The importance of a_d in determining the seasonal variation of UV attenuation observed in the three study lakes is illustrated in Fig. 4A. In midsummer, a_d was lowest in the epilimnion of each of the lakes and increased substantially with depth. In each instance, midsummer hypolimnetic values of a_d were similar to those observed during the previous spring

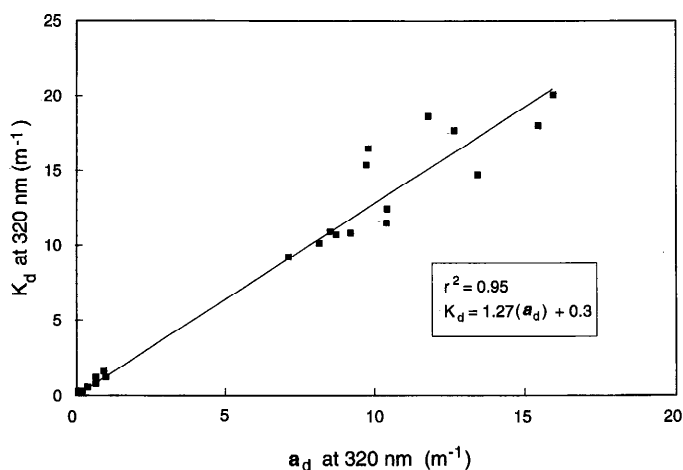


Fig. 3. Relationship between diffuse attenuation coefficients (K_d) and absorption coefficients (a_d) of 0.2- μm filtrate at 320 nm for the surface waters of the three lakes during 1994.

turnover. Decreases in a_d observed from spring turnover to midsummer (epilimnion) approximately correspond to decreases in observed K_d during the same period (Fig. 2). These data suggest that seasonal variation in K_d is essentially a surface phenomenon dependent on changes in a_d .

Photochemical degradation experiments—Exposure of lake water to various fractions of the solar spectrum produced similar changes in the optical properties of samples collected from each of the three lakes (Fig. 5). The largest declines in a_d were found in treatments exposed to the full solar spectrum (UV-T treatment). A 7-d exposure of filtered lake water to incident sunlight reduced a_d by up to 40% in the UV-B and UV-A regions but did not significantly alter absorbance of PAR. Reduction in the proportions of incident UV-B and UV-A relative to PAR caused by Mylar (317-nm cutoff) and Emco (377-nm cutoff) filters progressively reduced the photochemical effects on a_d . In samples collected from Wayne wood there was no significant reduction in a_d between initial samples and ending dark controls. However, in samples collected from Lacawac and Giles there was a small but significant difference in a_d between initial samples and dark controls ($\leq 10\%$), suggesting the presence of a non-photochemical mechanism for reduction of a_d (e.g. adsorption of DOC to bottles).

Declines in a_d during exposure to sunlight were accompanied by significant changes in DOC concentration in samples collected from Lacawac and Wayne wood (Fig. 6). The largest changes in DOC were found in UV-T treatments from Lacawac (20% decline) and Wayne wood (17% decline). Significant decreases in DOC were also noted for the Mylar (13% Lacawac; 10% Wayne wood) and Emco (11% Lacawac; 6% Wayne wood) treatments. In contrast, declines in a_d for Lake Giles were not accompanied by significant changes in DOC concentration. DOC concentrations in dark controls did not differ significantly from initial samples for any of the three lakes.

Photochemically induced reductions in a_d were often accompanied by changes in the shape of the absorbance spec-

trum that may reflect underlying changes in the composition of DOC. The $a_{d250\text{nm}}:a_{d365\text{nm}}$ ratio, which has been suggested as an index of the relative size of DOC compounds (DeHaan and De Boer 1987; DeHaan 1993; Strome and Miller 1978), changed substantially in some of the treatments exposed to full solar radiation (Fig. 7A). The mean value of this ratio increased significantly for samples from Lacawac (+39%; $P \leq 0.01$) and Wayne wood (+23%; $P \leq 0.01$), suggesting an overall reduction in average molecular weight of the DOC following irradiation. In contrast, samples from Giles did not show a significant change in this ratio, suggesting that photochemical changes did not involve a reduction in the average molecular weight of the DOC.

The spectral slope (S ; the absolute value of the slope of $\ln[a_d]$ vs. λ for 280–700 nm) also varied in a similar manner following exposure to UVR (Fig. 7B). Although this coefficient did not vary statistically for samples from Giles, significant declines in S were observed for Lacawac (14%; $P \leq 0.01$) and for Wayne wood (27%; $P \leq 0.01$). Declining values of S imply that the transmission of UVR relative to PAR increases substantially in waters subjected to photogradation.

DOC-specific absorbance (a_d : [DOC]), an index of the absorptivity of DOC, was also strongly affected by solar radiation (Fig. 7C). Following a 7-d exposure to incident solar radiation (UVT treatment), DOC-specific $a_{d320\text{nm}}$ declined by 48% for Giles, 47% for Lacawac, and by 31% for Wayne wood. Thus, photochemically induced reductions in a_d for Giles resulted from decreases in the absorptivity of DOC rather than a change in the quantity or apparent molecular weight of DOC. In contrast, photochemically induced changes in a_d for Lacawac and Wayne wood samples appeared to result from reductions in DOC concentration and apparent molecular weight, as well as from a reduction in the molar absorptivity of DOC.

Changes in the optical properties of the three lakes during summer were consistent with changes observed in photochemical degradation experiments. Values of a_d and DOC-specific a_d decreased substantially from spring turnover to midsummer in the epilimnia of each of the three lakes (Fig. 4A,B). Substantial differences between DOC-specific a_d at spring turnover and midsummer (epilimnion) suggest that much of the seasonal variations in a_d (and consequently K_d) were due to reductions in the UV absorptivity of water column DOC. The deviations between spring turnover and summer hypolimnial values of DOC-specific a_d in Lacawac and Wayne wood may be due to the production of noncolored DOC from anaerobic respiration (not specifically investigated).

Changes in the $a_{d250\text{nm}}:a_{d365\text{nm}}$ ratio (Fig. 4C) were also observed during the same time period for Lacawac and Wayne wood but not for Giles. Similar changes were also observed in values of S obtained from the lakes (Fig. 4D). In the case of Giles, this index provides some evidence for photodegradation at substantial depths in this very clear water column because values of S in the summer hypolimnion were significantly less than those observed during spring turnover ($P \leq 0.01$). In all cases, the optical indices showed substantial variation with depth during midsummer (Fig. 4),

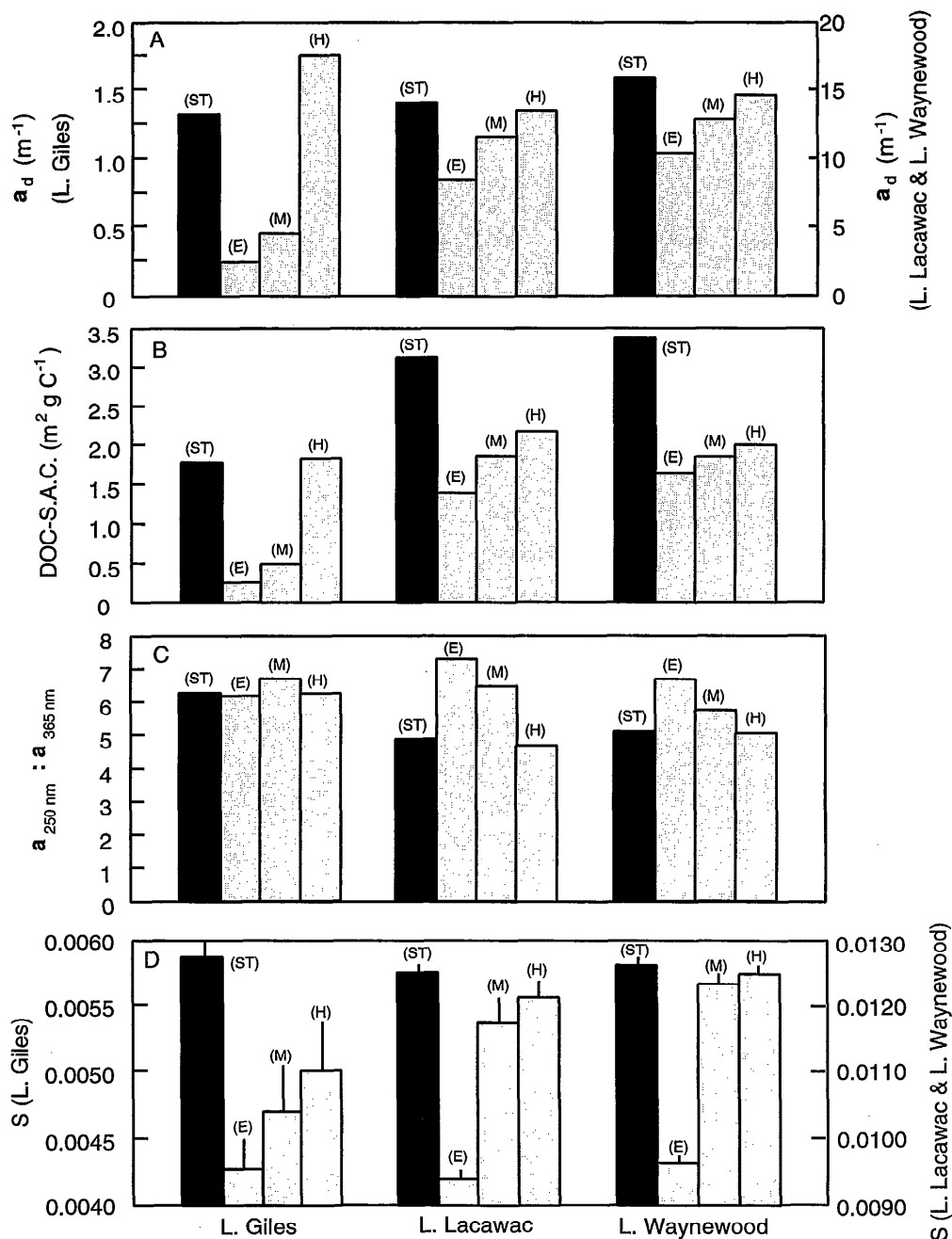


Fig. 4. Variation in four optical characteristics with depth at midsummer (14 July 1994; E—epilimnion; M—metalimnion; H—hypolimnion) contrasted with values obtained from surface waters during spring turnover (ST; 28 March 1994). A. Absorption coefficient for the dissolved fraction of lake water (a_d , m^{-1}) at 320 nm. B. DOC-specific absorption coefficient ($a_d/[DOC]$, $m^2 g C^{-1}$) at 320 nm. C. Ratio of absorption coefficients at 250 and 365 nm ($a_{d250} : a_{d365}$). D. S from slope of $\ln(a_d)$ vs. λ , 700 to 280 nm.

suggesting that the seasonal changes were primarily a photic zone phenomenon.

Modeling photochemical changes in UV transparency—Results of the photochemical degradation experiments indicate that some of the reduction in a_d was due to short wavelength UV-A as well as UV-B irradiance (Fig. 5). For this

reason, both solar UV-A and UV-B irradiance were considered in estimating rate constants for changes in a_d . A reasonable fit to the experimental data was achieved with the natural logarithm of $a_{d_final} : a_{d_initial}$ versus cumulative absorbed dose of UV energy, where the photodegradation rate constant was the negative slope (Figs. 8, 9). This equation was initially fitted separately to observed changes in a_{dUV-A}

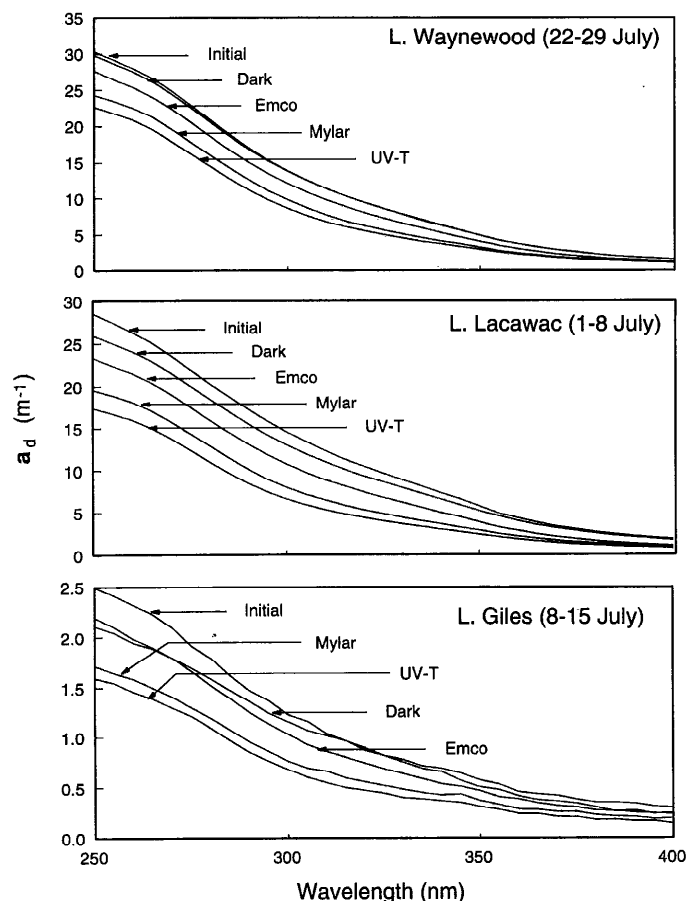


Fig. 5. Plots of filtrate absorption coefficients (a_d) vs. wavelength for initial lake water samples and samples exposed to different fractions of solar radiation for about 7 d. Each line represents the mean of three replicate samples.

and a_{dUV-B} . Photodegradation rate constants did not differ significantly for the UV-A and UV-B spectrum, hence models presented here are based on changes in average a_{dUV} (i.e. 280–400 nm).

Rate constants for water collected from Lacawac and Waynewood were initially fitted separately but photodegradation rate constants for the two lakes did not differ significantly. Thus, data for the two lakes were subsequently pooled and reanalyzed (Fig. 8). Each of the treatments (Emco, Mylar, UV-T) showed a significant relationship between decline of $a_{dUV-A+B}$ and absorbed UV dose. The highest rates of decline per unit of absorbed UVR were observed in full sunlight (UV-T treatment) for which almost 50% of $a_{dUV-A+B}$ was lost following a 7-d exposure. The rate constant for the Mylar treatment was 74% of that obtained for full sunlight, suggesting that UV-A radiation also played a significant role in photodegradation of $a_{dUV-A+B}$. The statistically significant rate constant obtained for the Emco treatment suggests that wavelengths in excess of 377 nm, or other nonphotochemical processes, may also have caused some decline in $a_{dUV-A+B}$. This effect is relatively small, accounting for 7% of the rate constant observed for full sunlight (UV-T treatment).

For samples collected from Lake Giles, the highest rate

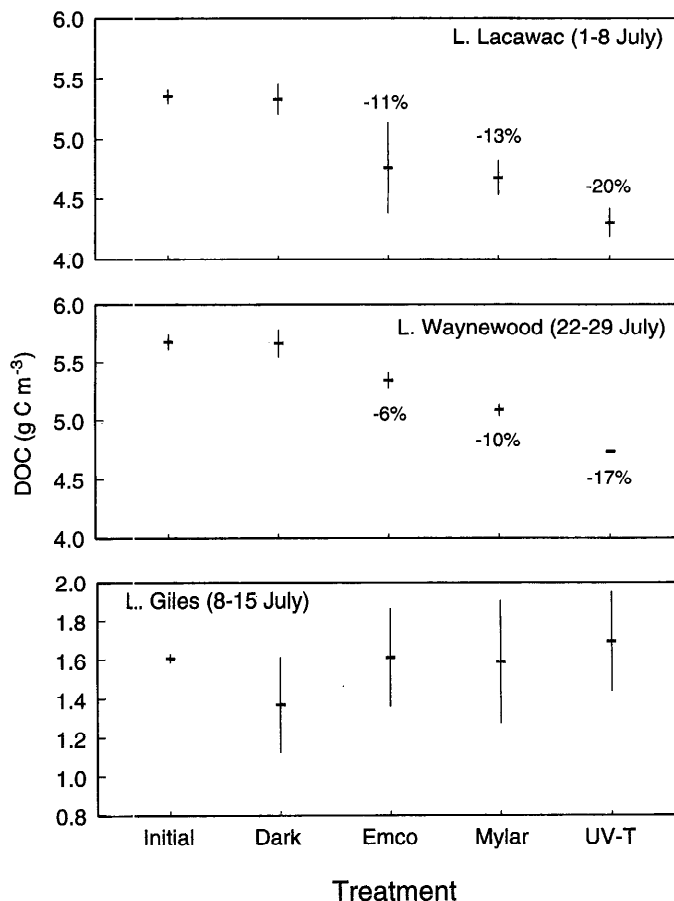


Fig. 6. Mean DOC concentration ($\text{g C m}^{-3} \pm \text{SE}$) of initial samples compared to means of samples exposed to different fractions of solar radiation for about 7 d. Percentage change from the initial value is indicated for significant ($P < 0.05$) differences between initial and sample means.

constant was also observed for full sunlight (UV-T treatment). This rate constant was more than seven times greater than that observed under similar conditions (UV-T treatments) for samples from Lacawac and Waynewood (Fig. 9). Although similar proportional reductions in $a_{dUV-A+B}$ were observed for a 7-d exposure of Giles water (45%), much less UVR was absorbed. The rate constant for the Mylar treatment was 76% of that observed for full sunlight (UV-T treatment), further suggesting an important UV-A component to photochemical degradation. In contrast to Lacawac and Waynewood, there was no significant correlation between $a_{dUV-A+B}$ and absorbed UV dose for the Emco treatment.

Discussion

Our data indicate that some lakes exhibit substantial seasonal variation in epilimnial transparency to solar UVR. Although it has recently been established that UV transparency varies widely among lakes (Morris et al. 1995; Scully and Lean 1994), temporal variability within lakes has not previously been reported in the literature. The level of seasonal variation observed in our study lakes (reductions to 19–61%

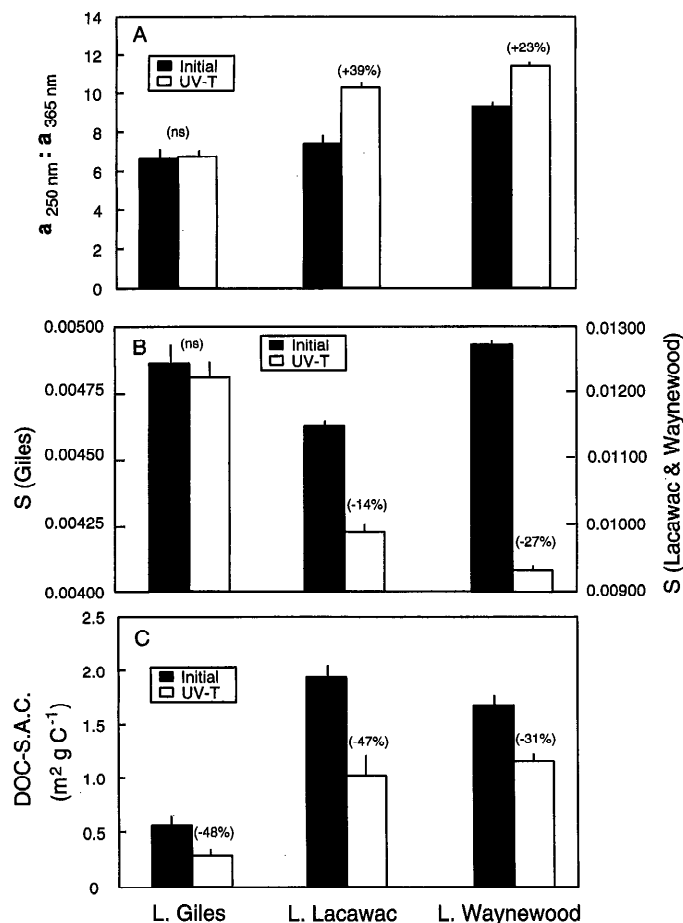


Fig. 7. A. Mean $a_{d250\text{nm}} : a_{d365\text{nm}}$ ratios (\pm SE). B. S from slope of $\ln(a_d)$ vs. λ , 700 to 280 nm. C. Mean DOC-specific absorption coefficients ($\text{m}^2 \text{g}^{-1} \pm \text{SE}$) at 320 nm before and after exposure to incident solar radiation for about 7 d (UV-T treatments). Percentage change from the initial value is indicated for significant ($P < 0.05$) differences between initial and sample means.

of spring values for epilimnial $K_{d320\text{nm}}$ may result in substantial variations in epilimnial exposure to solar UVR. For example the depth at which 10% of surface 320-nm irradiance penetrates the water column for Lake Giles varied from 1.8 m (35% of z_{mixed}) in early spring to over 7.5 m (150% of z_{mixed}) by midsummer. This degree of variability may strongly influence chemical and biological processes in the epilimnion that are affected by UVR. In less transparent Lacawac and Waynehood, seasonal variation in UV penetration was less dramatic relative to the depth of the mixed layer (seasonal variation of $z_{10\%}$ was from 4–8% of z_{mixed}).

Factors that influence variation in UV transparency among lakes also appear to influence seasonal variations within lakes. The importance of absorbance by dissolved material (a_d principally from DOC) in determining K_d for UVR was demonstrated by Morris et al. (1995) in their study of 65 lake sites in North and South America. Their data suggest that dissolved absorbance (0.2- μm filtrate), on average, contributes 65% of K_d for UV-B radiation and 40–65% for UV-A radiation. The substantial contribution of dissolved absorbance to K_d in the solar UV range is probably respon-

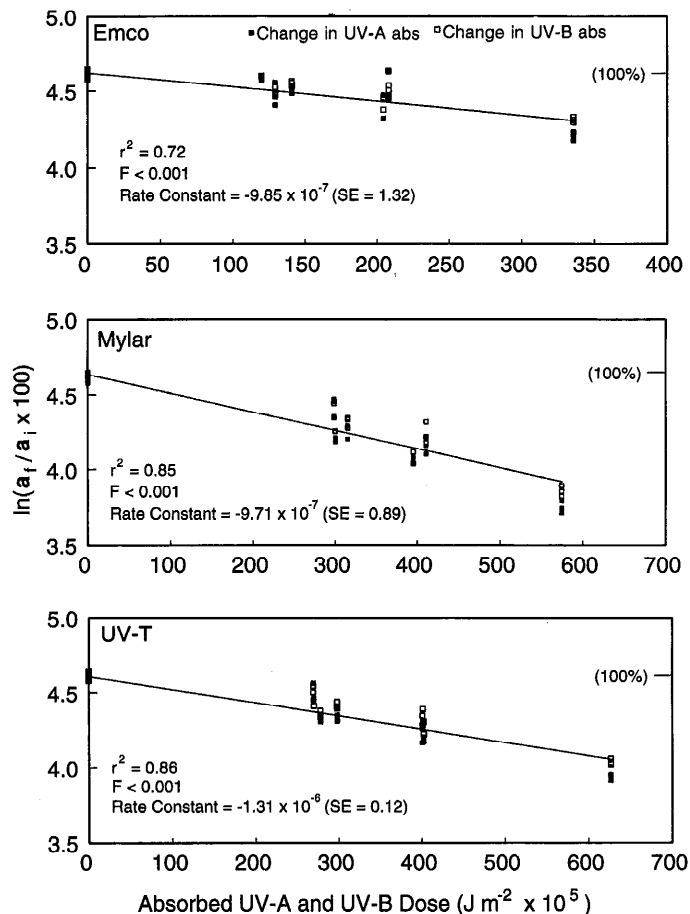


Fig. 8. Relationship between absorbed UV dose and a_d during photooxidation experiments performed on samples collected from lakes Lacawac and Waynehood. Solid squares represent a_d for UV-A while open squares represent a_d for UV-B. Data from Waynehood and Lacawac were pooled for the regression analysis shown in the figure (see text).

sible for the significant correlations between a_d and K_d observed in this (Fig. 3) and previous studies (Morris et al. 1995; Scully and Lean 1994). Evidence from our present study further supports this conclusion because seasonal changes in epilimnial K_d were closely accompanied by changes in epilimnial a_d (Fig. 4A).

As suggested by Morris et al. (1995), UV transparency of lakes is not only a function of DOC concentration but is strongly influenced by the optical properties of the DOC. Properties such as DOC-specific absorbance and the shape of the DOC absorption spectrum vary greatly among lakes and depend largely on the source and composition of DOC. Experimental evidence from our photochemical degradation studies, as well as prior evidence from the literature, suggest that many of these properties may be modified by exposure to UVR. For example, exposure to incident solar radiation reduced a_d by up to 50% in water from our study lakes (Fig. 5). Similar results have also been observed for water removed from other lakes and exposed to UV lamps (Lindell et al. 1995; Allard et al. 1994; Stewart and Wetzel 1981) or natural sunlight (Amador et al. 1991). Our photochemical

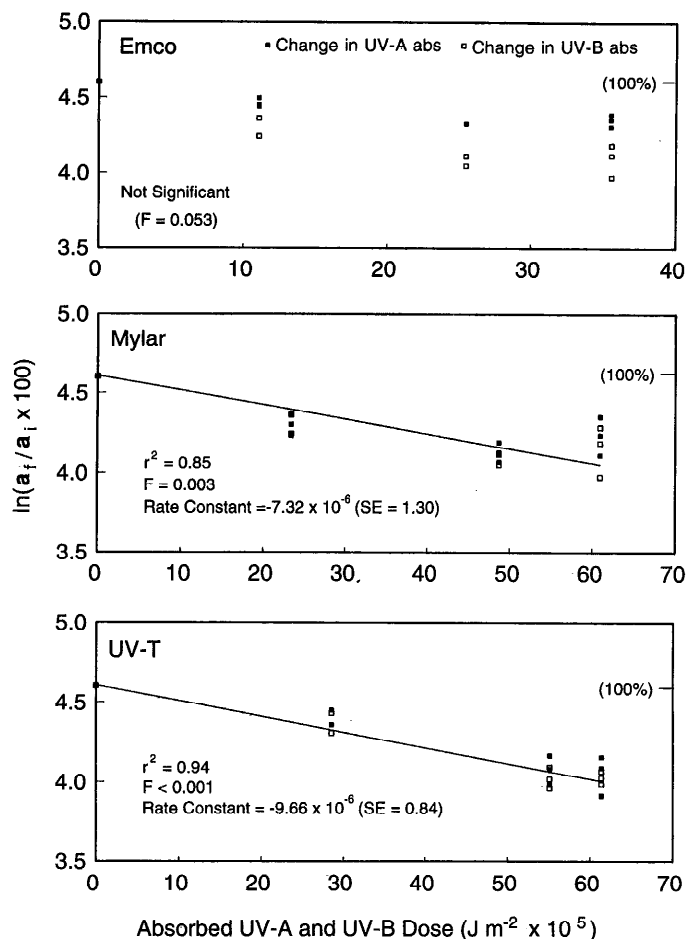


Fig. 9. Same as for Fig. 8 but for samples collected from Lake Giles.

degradation experiments further suggest that declines in a_d were closely linked with DOC photomineralization (Fig. 6), decreases in DOC-specific a_d (Fig. 7C), and changes in the shape of the DOC absorbance spectrum (Fig. 7A,B). These results are consistent with the literature on DOC photochemical degradation that suggest that UVR can mineralize humic DOC (Allard et al. 1994; Salonen and Vahatalo 1994; DeHaan 1993) and produce low molecular weight (LMW) humic compounds that exhibit different chemical and optical properties than nonirradiated DOC (Backlund 1992; Mopper et al. 1991; Strome and Miller 1978). Photochemical degradation of fulvic acids, which comprise a large fraction of humic DOC, may be responsible for many of the observed changes in optical properties of DOC in this and previous studies. Exposure to UVR can result in a marked decrease in the aromaticity of fulvic acids (Frimmel and Bauer 1987; Gjessing 1980; Chen et al. 1978), which in turn can substantially decrease the DOC-specific absorbance in the solar UV range (McKnight et al. 1996).

The effects of photochemical degradation appear to differ among lakes, possibly as a result of differences in DOC composition. For Lacawac and Wayneswood, the rate constants for UV photochemical reduction of a_d were not significantly different from each other but were significantly

lower than that determined for Lake Giles (Figs. 8, 9), indicating that Giles DOC was more susceptible to photodegradation. Differences were also observed for rates of photomineralization (Fig. 6) and rates for the apparent production of LMW DOC (as indicated by the ratio of $a_{d250\text{nm}} : a_{d365\text{nm}}$; Fig. 7A). Lake Giles DOC showed no evidence of photomineralization or photochemical production of LMW compounds following a 7-d exposure to incident sunlight. In contrast, water from Lacawac and Wayneswood showed significant rates of both photomineralization and apparent photochemical production of low molecular weight DOC. The difference between the DOC of Giles and that of Lacawac and Wayneswood may be related to differences in the source and composition of organic carbon (allochthonous vs. autochthonous) as well as differences in DOC processing in situ. For instance, lake acidity (Lake Giles is more acidic; Table 1) or the degree of prior photochemical degradation (probably significant even in the hypolimnion of Giles) may have a profound effect on DOC composition and capacity for photochemical degradation.

The surface waters of our three study lakes displayed strong seasonal variations in optical properties that were qualitatively consistent with photochemical degradation of DOC observed in our experimental studies. Decreases observed from spring turnover to midsummer in a_d , DOC-specific a_d , and S , as well as increases in the ratio of $a_{d250\text{nm}}$ to $a_{d365\text{nm}}$ (Fig. 4) were similar to trends observed in our photochemical degradation experiments. Furthermore, changes in the optical properties of these lakes appeared to coincide with summer solstice and with maximum fluxes of solar UVR (Fig. 2). At midsummer, the optical properties of our study lakes displayed substantial variation with depth (Fig. 4), suggesting that the seasonal changes were primarily a photic zone phenomenon.

This circumstantial evidence, as well as the data from photochemical degradation experiments, suggests that solar UVR plays a substantial role in degradation of DOC in situ, resulting in increased epilimnial UV transparency. In order to test whether solar UVR could potentially influence large volumes of water to the extent observed in our study lakes, we formulated a simple model to relate the results of our photochemical degradation experiments to our lake data. The model is designed to predict K_d for a mixed epilimnion based on the following parameters: first, the total daily incident UVR (E_d) derived from our GUV-521 radiometer and from the model for estimating integrated UVR from the four UV wavebands (see methods); second, the empirical relationships between absorbed UV dose and changes in a_d as determined from our photochemical degradation experiments (Figs. 8 and 9); third, the empirical relationship between a_d and K_d determined for the three study lakes (Fig. 3); and last, the observed depth of the mixed layer (z_{mixed}). The model is initially set using a K_d value observed during late spring (26 April). For each day, a light field is generated for the water column using E_d and $K_{d320\text{nm}}$. The absorbed UV dose and the percentage of remaining a_d is calculated for 5-cm strata from the surface to the bottom of the mixed layer using the appropriate degradation rate constant for each lake. The average value of a_d following photochemical degradation is then computed for the mixed layer (assuming complete mix-

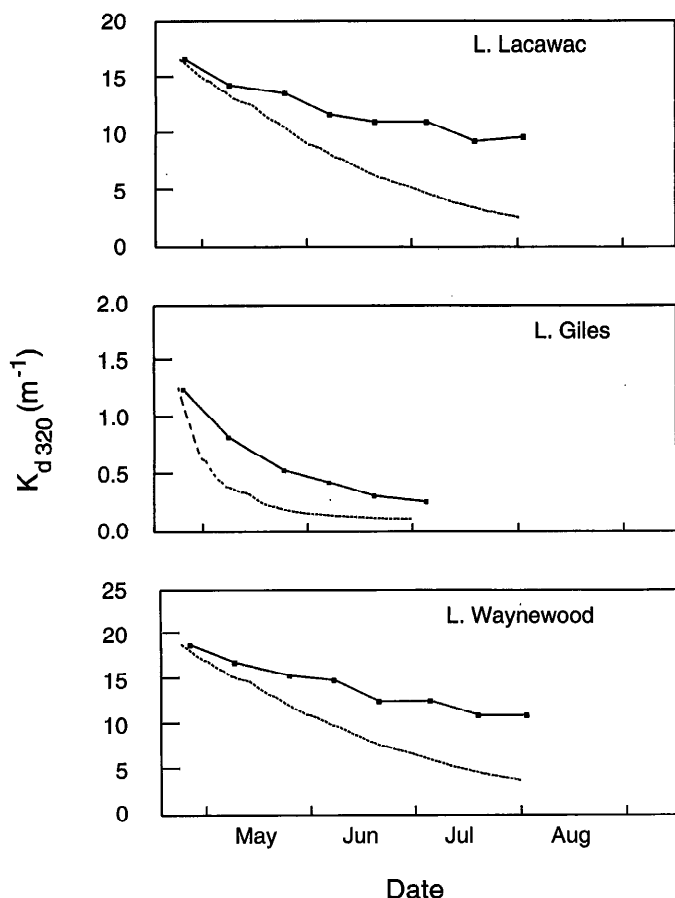


Fig. 10. Comparison of seasonal variation of measured (solid line) and modeled (dashed line) K_{d320nm} in 1994.

ing) and converted to K_d by the empirical relationship between K_d and a_d derived from the three lakes (Fig. 3). This process is repeated for each day, propagating changes in a_d and K_d through time. The value of z_{mixed} was varied over time to represent observed seasonal changes in each of the lakes.

We note that this model makes a number of simplifications that do not fully account for spectral variation of light propagated through the water column or the action spectrum of photodegradation of DOC. In addition, the model assumes that first-order degradation rate constants determined over short-term exposure experiments (7-d) are applicable for long-term exposure in situ.

The results of this model suggest that solar photochemical degradation of DOC in situ is of a magnitude sufficient to produce the large-scale changes in K_d observed in our study lakes (Fig. 10). It further suggests that photochemical degradation comprises a significant ecological "sink" for UV-absorbing DOC and may potentially affect UV transparency in a number of freshwater ecosystems.

The divergence between observed and modeled values of K_d for these lakes can be attributed to a combination of two components: unaccounted fluxes of UV-absorbing compounds through the epilimnia of the study lakes and deficiencies in model assumptions. Fluxes of UV-absorbing compounds into or out of the epilimnia were not considered

in this model and probably account for the largest portion of the deviation between modeled and observed K_d . Substantial transport of DOC from the watersheds (surface and ground water) may, in part, balance losses of DOC via photodegradation, resulting in the consistent underestimation of epilimnial K_d by our model (Fig. 10). The contention that these fluxes contribute substantially to the deviation between observed and modeled transparency is supported by differences in hydraulic detention times (HDT) and watershed characteristics among our study lakes (Table 1). Lakes Waynewood and Lacawac, which show the greatest divergence from the model, have significant hydrologic inputs (HDT 0.4 and 3.3 yr^{-1}), which include concentrated humic material from adjacent bogs. Lake Giles, which shows the least divergence, has a substantially longer HDT (5.6 yr^{-1}) and lacks significant sources of concentrated humic material (i.e. bogs) in the watershed.

A more complete model of UV transparency could be developed utilizing a mass balance approach to measuring fluxes of UV-absorbing compounds in the epilimnia of these lakes. In such a model, efflux of UV-attenuating substances (particulate and dissolved) via photodegradation, outflow, and microbial degradation would be quantified along with influx from allochthonous and autochthonous sources. During late summer and early fall, vertical transport of hypolimnial DOC may also be an important influx to the epilimnion along with declining rates of photochemical degradation (see Fig. 4) to produce the marked increases in epilimnial K_d observed at that time (Fig. 2). Because our study lakes do not lend themselves to mass transport calculations (with poorly defined groundwater exchange), we cannot yet quantitatively compare photodegradation of DOC to other environmental fluxes. However, during periods characterized by declining attenuation of UVR in the epilimnia of our study lakes (April–August; Fig. 2), losses of UV-attenuating substances via photodegradation must substantially exceed all inputs from various sources (autochthonous and allochthonous). During this period photodegradation of DOC will likely have a profound influence on the chemical and optical characteristics of the epilimnia of these lakes.

Our results suggest that solar photochemical degradation of DOC could be responsible for much of the summer decline in epilimnial UV transparency observed in our study lakes. While photochemical degradation or photobleaching have long been recognized as affecting optical properties of DOC, there have been few studies that have demonstrated the importance of this phenomenon in situ. Kouassi et al. (1990) have demonstrated and modeled the extensive effects of photodegradation on DOC fluorescence in near surface marine waters. Although their study did not specifically investigate the effects of DOC photodegradation on transparency to UVR, Kouassi et al. speculated that the process may be critical in regulating transparency in certain marine waters (i.e. Sargasso Sea). To our knowledge, similar studies do not exist that demonstrate the link between photodegradation of DOC and transparency to UVR in freshwaters.

As suggested by our optical data, photochemical degradation has a measurable effect on DOC composition in the epilimnia of our study lakes. If high rates of photomineralization and photochemical production of LMW DOC are

typical of aquatic ecosystems, then solar UVR is an integral and previously underappreciated component of carbon cycling in lakes. Recent suggestions that photochemical degradation may be a major rate-limiting process for DOC cycling in marine systems (Miller and Zepp 1995; Mopper et al. 1991) may be equally applicable to freshwater ecosystems. Photochemically produced LMW DOC compounds are biologically labile and subject to microbial mineralization (Lindell et al. 1995). Thus, stimulation of heterotrophic bacterial respiration (by generation of labile LMW DOC), photomineralization of DOC and UV inhibition of algal primary production cumulatively point to one possible ecosystem level response to high fluxes of UVR: a net reduction in the rate of carbon accumulation and a shift in the balance between ecosystem production and respiration.

In addition to these possible ecosystem level effects, we have demonstrated a positive feedback loop that may exacerbate the adverse effects of UVR on aquatic ecosystems. Solar UVR can directly influence the UV transparency of the water column and thus increase the penetration depth of potentially harmful solar radiation. The timing of this phenomenon in our study lakes was such that the water column was most transparent at or near the seasonal peak of solar UVR (summer solstice). Increased fluxes of solar UVR, due to stratospheric ozone depletion and/or seasonal variations in incident radiation, increase the rate at which UV-shielding DOC is photodegraded in the water column. This phenomenon will be most significant for clear or shallow lakes for which the penetration depth of UVR will comprise a large fraction of the mixed layer. In such instances, the UV refuge for aquatic organisms (Williamson et al. 1996; Williamson 1995) will be reduced or eliminated by photodegradation in proportion to incident UVR. Photochemical degradation of dissolved UV-absorbing substances may synergistically enhance the seasonal variability associated with solar UV radiation and must be considered when evaluating the effects of UVR on aquatic ecosystems.

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