

## The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon

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### *Abstract*

Diffuse attenuation coefficients ( $K_d$ ) for solar UV radiation (UVR) (305, 320, 340, 380 nm, and PAR) were measured in the mixed layer of 65 lake sites in Alaska, Colorado, and Pennsylvania and the Bariloche region of Argentina. Integrated mixed layer samples of lake water were concurrently collected, and a multivariate approach was used to model  $K_d$  with a number of optical and chemical variables.

Substantial variation in transparency was observed among lakes. Attenuation depths ( $z_{1\%}$ ) for UV-B radiation ranged from several centimeters to >10 m. In some shallow, low DOC (dissolved organic C) lakes typical of high elevation ecosystems, substantial fluxes of UVR penetrated the entire water column. In deeper lakes with low DOC concentrations, high fluxes of UVR were found in a significant proportion of the mixed layer. Much of the among-lake variation in  $K_d$  (87–96%) was explained by differences in DOC concentration, which strongly influenced dissolved absorbance. On average, dissolved absorbance accounted for between 33% (for PAR) and 68% (for 305 nm) of  $K_d$  measured in situ. Throughout the solar UV-A and UV-B range,  $K_d$  was best estimated with a univariate power model based solely on DOC concentration. Models are also presented that relate absorption coefficients to  $K_d$ . These models can be used with archival DOC or color data to provide approximate estimates of UV transparency of lakes.

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Fluxes of solar ultraviolet radiation (UVR, 280–400 nm) may be a pervasive and potentially damaging influence for both aquatic and terrestrial ecosystems (e.g. Karrentz et al. 1994; Siebeck et al. 1994; Williamson and Zagarese 1994; Diffey 1991; Smith 1989). Reductions in stratospheric ozone may substantially increase fluxes of the most energetic and potentially damaging radiation at the surface of the earth (UV-B, 280–320 nm). Much emphasis has been placed on the role of UV radiation in marine ecosystems, especially those influenced by Antarctic ozone depletion (Smith et al. 1992). However, freshwater ecosystems, especially those at mid- to low latitudes, may be affected to a much higher degree by *existing* fluxes of UV radiation. Shallow depth, seasonal stratification patterns, high and seasonally variable fluxes of solar UV radiation potentially expose plankton and benthos to harsh UV environments. Unfortunately, relative to PAR, little is known about the penetration and influence of solar UVR in freshwater ecosystems.

Although attenuation of UVR in most freshwaters is poorly understood, attenuation of UVR in the solar spectrum is well characterized for pure water and is exceedingly low (Kirk 1994b; Boivin et al. 1986; Quickenden and Irvin 1980). Smith and Baker (1981) characterized some optical properties ( $a$  and  $K_d$ ) of pure freshwater, pure seawater, and some optically clear natural waters and have similarly found low values across the solar UVR spectrum. The bio-optical classification model of Baker and Smith (1982) has shown that transmission of solar UVR in offshore marine waters can be estimated from concentrations of dissolved organic matter and chlorophyll. Unfortunately, direct application of the marine bio-optical model to freshwaters is not possible because model parameters (dissolved organic matter, DOM, and Chl  $a$ ) are typically much higher in lakes (dissolved organic C, DOC, and Chl  $a$  can span 2–3 orders of magnitude across freshwaters). Differences in chemical and optical characteristics of marine and freshwater DOC can further complicate comparisons (Malcolm 1990).

Few studies have measured optical properties of natural freshwaters in situ for the UV range. A recent review by Kirk (1994b) and studies by Kirk et al. (1994) and Scully and Lean (1994) suggest that UV transmission can vary greatly between lakes and that solar UVR can penetrate to substantial depths. DOC appears to play a major role in regulating the transmission of UVR in lakes (Scully and Lean 1994) as well as in marine systems (Baker and Smith 1982). We present the results of a comparative investigation of vertical attenuation coefficients ( $K_d$ ) and absorption coefficients ( $a$ ) and model the transmission of solar UVR using a multivariate approach based on a number of chemical and optical parameters.

## Methods

We included 65 sites from 59 lakes in Alaska, Colorado, the northeastern U.S., and the Bariloche region of Argentina in our survey (Table 1). Survey sites were not

selected at random but were chosen a priori to provide a population of lakes with substantial but variable transmission of UVR as well as a gradient with respect to concentrations of DOC, Chl  $a$ , and particulate material (PM).

All lakes in the survey were sampled within 60 d of the hemispheric summer solstice and within 3 h of solar noon. Irradiance-depth profiles were obtained at 305, 320, 340, and 380 nm, and for PAR with a Biospherical PUV-500 submersible radiometer using a modification of the method described by Kirk et al. (1994). The instrument is designed to measure irradiance in 10-nm bands centered at 305, 320, 340, and 380 nm for UVR and 400–700 nm for PAR. Diffuse attenuation coefficients for downward irradiance ( $K_d$ ) were determined from the slope of the linear regression of the natural logarithm of downwelling irradiance ( $E_d$ ) vs. depth ( $z$ ). Sample size used in the determination of  $K_d$  (pairs of  $E_d$  and  $z$  values) was highly variable and depended on the depth of penetration for a specific wavelength. For PAR, 380, and 340 nm, sample size was usually large ( $n > 100$ ).  $K_d$  estimates for shorter, more rapidly attenuated wavelengths (320 and 305 nm) were often determined with fewer points ( $n = 20$ –50).  $K_d$  values are not reported for regressions with small sample size ( $n < 20$ ) or poor fit ( $r^2 < 0.95$ ). Although there was little evidence of vertical heterogeneity of  $K_d$ , the method described here provides *mean* estimates of  $K_d$  across a wavelength-specific path length (distance from the surface to the depth at which the signal falls below the detection level) in the mixed layer of the water column. Path lengths for a given lake are overlapping but become progressively shallower with decreasing  $\lambda$ .

Concurrent with the field optical data, integrated mixed-layer samples of water were also collected for chemical and optical analysis. Chl  $a$  was determined by the spectrophotometric method of Nusch (1980) and Marker et al. (1980). Samples were filtered onto Whatman GF/F filters and the pigment was extracted with hot 90% ethanol. Correction for pheophytin  $a$  was performed by acidification with HCl. Suspended PM was collected onto ashed and tared Whatman GF/F glass-fiber filters, dried to a constant weight at 60°C, and reweighed. Aliquots of filtered water were frozen and stored for analysis of DOC. DOC was measured by a high temperature Pt catalyst oxidation method (Shimadzu TOC-5000) following the recommendations of Sharp et al. (1993). Prior to measurement, samples were thawed, sonicated, acidified (HCl), and thoroughly mixed. Absorption coefficients ( $a$ ) of filtered samples (MSI Magna nylon 0.22- $\mu$ m filters) were determined every 1 nm by spectrophotometry (Shimadzu UV160U) using 1- or 10-cm Suprasil (quartz) cuvettes and a blank consisting of low carbon deionized water (also passed through MSI Magna nylon 0.22- $\mu$ m filters). Absorption coefficients were calculated as  $a = \ln(10^A)$  and reported for a 1-m path ( $m^{-1}$ ).

Statistical analyses were performed with the linear and nonlinear regression software of SPSS/PC<sup>+</sup> (SPSS Inc. 1989).

## Results

*Precision of  $K_d$  estimates*—Triplicate light profiles were obtained for 43 of the survey lakes and analyzed separately for determination of  $K_d$ . Mean coefficients of variation among triplicate determinations of  $K_d$  for each wavelength are presented in Table 2. Coefficients of variation generally indicate a small degree of analytical variability associated with measurements of  $K_d$  in situ (2–4%). Higher variability associated with  $K_d$  305 (C.V. = 6.6%) may be a function of the rapid attenuation of 305-nm light in humic lakes; determinations of  $K_d$  305 were occasionally made across very short path lengths (top 10–20 cm of the water column) and thus are subject to less precision than wavelengths which penetrate farther into the water column. Higher variability associated with estimates of  $K_d$  PAR (C.V. = 8.2%) probably resulted from wave focusing of PAR in near-surface waters. PAR is less diffuse than UVR and thus more prone to wave focusing (Kirk 1994a).

*Modeling  $K_d$  for specific UV wavebands*—Depth-irradiance profiles for survey lakes resulted in an inverse relationship between  $\lambda$  and  $K_d$  as illustrated by oligotrophic Lago Correntoso (Fig. 1A). The depth of 1% surface irradiance ( $z_{1\%}$ , depth at which  $E_d$  equals 1% of surface irradiance) decreases with decreasing wavelength. Values of  $K_d$  and  $z_{1\%}$  were highly variable across survey lakes (Table 1 and Fig. 1B). The largest values of  $K_d$  were observed in high DOC humic lakes (e.g.  $K_d$  320 = 66.8 m<sup>-1</sup> for Little Echo Lake;  $z_{1\%}$  = 0.07 m). The highest values of  $K_d$  encountered in this survey are probably substantially less than those in the most heavily stained humic waters, which were not included in this study. The lowest values of  $K_d$  were observed in ultra-oligotrophic, low DOC lakes. Values of  $K_d$  for Lago Schmoll (e.g.  $K_d$  320 = 0.14 m<sup>-1</sup>;  $z_{1\%}$  = 33 m) were similar to those obtained for the clearest natural waters and approach theoretical minimum values of  $K_d$  presented by Smith and Baker (1981).

A major goal in our study was to develop an understanding of environmental control of diffuse attenuation coefficients in lakes. Our conceptual approach was based on a variation of a multiple component model (Baker and Smith 1982; Smith and Baker 1981) in which the total measured diffuse attenuation coefficient ( $K_d$ ) is thought to be the sum of numerous partial diffuse attenuation coefficients:

$$K_{\text{total}} = K_{\text{water}} + K_{\text{DOC}} + K_{\text{pigment}} + K_{\text{PM}} + K_{\text{residual}} \quad (1)$$

We used a multivariate statistical approach to investigate the relative importance of these factors in influencing diffuse attenuation coefficients in lakes. The following models were tested: univariate linear, exponential, and power models based on DOC, Chl *a*, and PM; multivariate linear, exponential, and power models based on DOC and Chl *a*, or DOC and total pigment (Chl *a* + Pheo *a*); and multivariate linear, exponential, and power models based on DOC and PM. Since Chl *a* and PM were not independent in this data set, they could not be combined into a single multivariate model of  $K_d$ . In each of these

analyses, we treated  $K_{\text{water}}$  as a constant (estimate for pure water obtained from Smith and Baker 1981 by converting their Equation 5 into an equality) and modeled differences between measured  $K_d$  and estimated  $K_{\text{water}}$  for each wavelength.

Between-lake variations in  $K_d$  for 305, 320, 340, and 380 nm were best explained by a power model based solely on DOC concentration (Table 3). Inclusion of other variables in the model (Chl *a*, Pheo *a*, or PM) did not explain additional variation in  $K_d$ . Between-lake variations in  $K_d$  for PAR were best explained by a linear, multivariate model that included both Chl *a* and DOC. Although Chl *a* was a statistically significant model component, inclusion of Chl *a* in the model provided only a small marginal reduction in error (1–2% increase in  $r^2$ ).

$K_d$  was also modeled with laboratory measurement of absorption coefficients of filtered lake water at UV wavelengths of interest (Table 3). In addition,  $K_d$  was also related to  $a_{440}$ , which is commonly used as an index of optical color (Kirk 1994a).

*Variations in  $a$  and  $K_d$  with  $\lambda$* —In addition to describing attenuation of specific wavebands of UVR in lakes (i.e. 305, 320, 340, 380 nm), we can characterize relationships between  $K_d$  and  $a$  across the entire spectrum of solar UVR. For the population of lakes included in this survey, both  $K_d$  and  $a$  decreased sharply with increasing  $\lambda$  (Fig. 2). The mean ratio of  $a$  to  $K_d$  decreased progressively with decreasing wavelength. At 305 nm, dissolved  $a$  comprised (on average) 68% of  $K_d$  of study lakes, but this value declined to 33% for PAR (Fig. 2). This trend suggests that as  $\lambda$  decreases, absorbance by dissolved compounds comprises an increasing fraction of the total  $K_d$  relative to that contributed by scattering or particle absorbance.

Exponential increase in absorbance with decreasing  $\lambda$  was a consistent feature of these lakes and has been well documented in other aquatic systems. Absorbance data derived from scans of filtrate from each of the survey lakes was transformed to natural logarithms and regressed against wavelength (Fig. 3A). Across the solar UV-A and UV-B spectrum (280–400 nm), the mean slope ( $S_a$ ) was  $-0.0181 \text{ m}^{-1} \text{ nm}^{-1}$  (SE = 0.0004). This value is somewhat low relative to similar published estimates but falls within the range of values reported for some other lakes ( $-0.010$  to  $-0.020 \text{ m}^{-1} \text{ nm}^{-1}$ , Kirk 1994a; mean  $-0.01688 \text{ m}^{-1} \text{ nm}^{-1}$ , Cuthbert and del Giorgio 1992). No significant correlation existed between  $S_a$  and DOC for survey lakes; however, intercepts ( $I_a$ ) obtained from regressions of  $\ln(a)$  and  $\lambda$  were significantly correlated with DOC concentration (as  $\text{g C m}^{-3}$ ):

$$I_a = 6.45([\text{DOC}]^{0.13}) \quad (r^2 = 0.71, P \leq 0.01). \quad (2)$$

Although between-lake variations in  $S_a$  were insensitive to DOC, DOC had a profound effect on  $I_a$  and hence on absorbance across the entire UV range (Fig. 3A). Adjustment of absorbance for differences in DOC ( $a_\lambda / [\text{DOC}, \text{g C m}^{-3}]$ ) removed much but not all of the between-lake variation associated with absorbance- $\lambda$  relationships (Fig. 3B). Even following adjustment for DOC, humic lakes

Table 1. Chemical and optical data for the survey lakes. Chlorophyll *a* and pheophytin *a* as  $\text{mg m}^{-3}$ ; particulate material (PM) and dissolved organic C (DOC) as  $\text{g m}^{-3}$ ; absorption coefficient (*a*) and diffuse attenuation coefficient ( $K_d$ ) as  $\text{m}^{-1}$ . Data not available—na.

Lake	Chl <i>a</i>	Pheo <i>a</i>	PM	DOC	$a_{305}$	$a_{320}$	$a_{340}$	$a_{380}$	$a_{440}$	$a_{\text{PAR}}$	$K_d 305$	$K_d 320$	$K_d 340$	$K_d 380$	$K_d \text{PAR}$
Northeast U.S.															
Belle	1.74	0.89	1.38	2.52	0.90	0.67	0.41	0.23	0.12	0.09	2.43	2.25	1.90	1.24	0.44
Beltzville	4.87	1.25	2.46	1.64	2.33	1.89	1.24	0.48	0.18	0.09	3.04	2.71	2.30	1.48	0.48
Earnest	7.93	1.72	3.48	3.84	4.33	3.55	2.40	0.97	0.35	0.18	na	10.25	8.81	5.25	1.00
Fairview	1.38	2.08	1.00	2.36	2.53	1.91	1.22	0.48	0.25	0.16	na	4.18	3.09	1.78	0.55
Giles	0.64	0.31	0.13	1.16	0.35	0.23	0.14	0.07	0.07	0.05	0.40	0.32	0.26	0.16	0.13
Lacawac	2.72	0.72	1.25	4.67	6.77	5.76	3.87	1.45	0.51	0.23	na	7.78	6.26	3.22	0.65
Laura	3.57	1.38	1.29	1.75	1.34	1.01	0.96	0.32	0.18	0.09	2.18	1.90	1.51	0.95	0.40
Little Echo	5.10	3.50	na	23.5	163.1	165.1	114.2	43.6	14.3	14.6	132.9	66.9	55.7	31.7	5.21
Paupak	0.40	5.90	2.32	5.30	8.96	7.97	5.60	2.16	0.83	0.39	20.32	15.74	12.46	6.78	1.21
Penn Forest	0.68	0.25	0.54	1.34	1.59	1.29	0.85	0.37	0.21	0.12	2.21	1.63	1.26	0.82	0.32
Silver	0.86	0.90	0.60	1.79	0.74	0.48	0.25	0.14	0.09	0.09	1.63	1.21	0.92	0.56	0.27
Wallenpaupak	18.62	5.28	5.66	3.28	5.76	4.86	3.27	1.27	0.44	0.21	na	10.31	8.83	5.68	2.36
Waynewood	4.10	2.04	1.27	4.35	8.50	7.37	4.97	1.89	0.62	0.30	na	10.39	8.03	4.30	0.78
Wild Creek	1.03	1.01	0.74	1.77	2.00	1.61	1.11	0.48	0.18	0.12	2.16	1.82	1.42	0.81	0.35
Colorado															
Arvada	1.72	0.31	1.74	3.76	4.65	3.78	2.44	0.94	0.32	0.16	6.90	4.51	3.28	1.77	0.41
Boulder	2.55	0.78	7.36	3.17	4.49	3.66	3.30	0.88	0.32	0.09	9.96	7.21	5.62	3.56	1.09
Brainard	1.78	0.93	0.72	0.80	2.26	1.96	1.36	0.62	0.28	0.14	4.89	3.70	2.93	1.72	0.58
Carter	2.84	0.94	6.80	2.73	4.17	3.25	2.03	0.78	0.28	0.12	9.53	6.18	4.84	3.19	0.91
Dillon	2.90	1.02	1.76	1.89	3.89	3.25	2.12	0.83	0.27	0.14	5.43	3.79	2.80	1.57	0.38
Estes	4.26	2.28	4.39	3.01	7.46	6.56	4.54	1.86	0.71	0.32	na	9.54	7.50	4.46	0.87
Georgetown	0.16	0.12	1.81	1.46	4.17	3.66	2.69	1.17	0.46	0.02	5.55	4.81	3.89	2.35	0.58
Green	1.64	0.55	1.34	2.08	3.18	2.72	1.87	0.78	0.35	0.16	0.37	3.34	2.62	1.38	0.86
Granby	3.06	7.76	4.89	4.01	9.33	8.22	5.53	2.12	0.74	0.30	na	10.13	8.05	4.36	0.80
Grand	3.50	2.84	3.80	3.08	7.99	7.23	4.77	1.89	0.62	0.28	12.38	9.85	7.96	4.29	0.77
Green Mtn.	3.08	1.77	3.58	3.24	7.67	6.63	4.33	1.75	0.62	0.28	10.02	9.38	7.27	4.41	1.00
Left Hand	4.89	3.32	3.41	3.68	8.13	7.21	5.02	2.03	0.71	0.30	14.61	13.51	11.18	6.37	1.33
Lower Blue	1.30	1.36	1.54	1.24	2.88	2.49	1.73	0.81	0.35	0.18	4.03	3.35	2.68	1.62	0.72
Lower Cataract	0.28	1.35	0.66	1.71	4.56	4.03	2.83	1.20	0.46	0.21	7.61	6.36	5.06	2.92	0.79
Meadow Creek	0.65	0.99	1.01	5.64	16.97	17.46	11.95	4.72	1.70	0.78	35.24	23.06	17.90	9.71	0.90
Monarch	1.11	0.93	0.58	0.99	3.04	2.63	1.82	0.71	0.30	0.14	7.39	5.46	4.38	2.60	0.62
Standley	1.56	0.58	2.90	2.14	2.77	2.26	1.40	0.51	0.14	0.05	4.36	3.22	2.43	1.54	0.68
Upper Blue	1.95	0.74	0.57	1.70	2.51	2.16	1.45	0.64	0.28	0.16	3.78	2.80	2.16	1.30	0.37
Red Rock	1.84	2.06	2.58	10.11	12.80	12.11	7.65	2.95	0.97	0.37	43.07	37.47	30.13	17.40	3.12
Willow Creek	2.01	0.76	2.33	5.26	7.67	7.84	4.51	1.89	0.74	0.37	11.04	8.59	6.73	3.82	0.68

Table 1. Continued.

Lake	Chl <i>a</i>	Pheo <i>a</i>	PM	DOC	<i>a</i> <sub>305</sub>	<i>a</i> <sub>320</sub>	<i>a</i> <sub>340</sub>	<i>a</i> <sub>380</sub>	<i>a</i> <sub>440</sub>	<i>a</i> <sub>PAR</sub>	<i>K</i> <sub>d305</sub>	<i>K</i> <sub>d320</sub>	<i>K</i> <sub>d340</sub>	<i>K</i> <sub>d380</sub>	<i>K</i> <sub>dPAR</sub>
Alaska															
Camp Pond	1.68	1.04	1.28	11.06	20.70	23.42	15.80	5.96	2.14	0.92	na	29.94	22.90	13.38	2.35
Camp Pond 2	0.00	0.49	0.15	6.22	11.65	10.66	7.35	2.86	0.94	0.41	na	12.80	9.75	4.91	0.85
I1	0.36	0.85	1.00	4.60	9.49	8.50	5.87	2.30	0.81	0.35	na	9.97	8.30	4.25	0.55
I6	0.30	0.91	1.20	6.63	8.89	7.85	5.39	2.10	0.77	0.30	na	15.04	13.15	6.00	0.63
N1	2.13	6.44	9.17	6.01	8.50	7.00	4.61	1.70	0.58	0.23	na	10.08	8.34	4.88	1.68
N2A	0.12	1.00	0.70	4.82	12.57	11.58	7.92	3.06	1.08	0.51	na	10.35	8.78	4.19	0.73
N2B	0.00	1.35	0.92	5.18	10.52	7.09	2.67	0.90	0.37	0.30	na	10.51	8.61	5.69	0.74
NE2	0.71	0.58	0.85	6.27	11.54	10.52	7.09	2.67	0.90	0.37	na	7.07	8.75	4.46	0.47
NE8	1.60	1.79	1.36	5.42	6.86	5.76	3.80	1.47	0.48	0.21	na	7.08	5.40	3.40	0.49
NE9B	0.50	0.72	0.58	4.73	8.45	7.37	4.97	1.96	0.64	0.28	na	10.00	8.43	4.09	0.49
Pond S2	0.21	0.15	0.30	9.94	22.40	26.55	17.96	6.96	2.67	1.20	66.78	48.01	38.23	na	5.73
S6	0.41	0.83	0.92	4.50	8.89	7.85	5.39	2.10	0.74	0.30	na	9.35	7.39	3.74	0.68
Toolik	0.30	1.33	0.69	5.07	11.19	10.13	6.91	2.67	0.92	0.39	na	13.98	10.67	5.79	0.75
Bariloche region, Argentina															
Correntoso	0.00	0.50	0.11	0.25	0.51	0.41	0.25	0.07	0.03	0.02	0.47	0.44	0.33	0.18	0.10
Escondido	0.20	1.70	0.71	2.66	7.32	6.47	4.51	1.91	0.67	0.32	8.88	7.68	5.80	3.03	0.46
Guillelmo	0.40	0.00	0.38	0.41	0.71	0.60	0.46	0.12	0.05	0.05	1.29	1.01	0.75	0.42	0.16
Gutierrez	0.20	0.30	0.18	0.32	0.71	0.60	0.46	0.11	0.07	0.05	0.53	0.41	0.31	0.19	0.12
Los Cantaros	0.10	0.45	0.26	0.72	0.51	0.37	0.25	0.12	0.05	0.02	1.91	1.71	1.35	0.82	0.28
Mascardi	0.30	0.00	0.27	0.38	0.67	0.46	0.32	0.14	0.12	0.05	0.68	0.52	0.38	0.20	0.12
Mascardi-lower	0.20	0.00	0.68	0.36	0.71	0.53	0.39	0.12	0.04	0.02	1.07	0.87	0.70	0.41	0.22
Mascardi-upper	0.00	0.20	1.02	0.44	0.94	0.76	0.53	0.23	0.07	0.05	1.22	1.01	0.77	0.49	0.25
Moreno-east	0.25	0.90	0.20	0.65	0.62	0.51	0.35	0.14	0.05	0.02	0.69	0.52	0.39	0.23	0.16
Moreno-west	0.50	0.30	0.40	0.46	0.81	0.67	0.46	0.21	0.07	0.05	0.82	0.64	0.49	0.28	0.14
NH*, Angostura	0.10	0.20	0.02	0.44	0.67	0.64	0.51	0.09	0.05	0.03	0.43	0.31	0.22	0.13	0.12
NH*, Bahi Lopez	0.45	0.00	0.25	0.41	0.71	0.55	0.39	0.09	0.05	0.02	0.57	0.42	0.31	0.17	0.13
NH*, Blest	0.10	0.70	0.60	0.24	0.58	0.46	0.32	0.12	0.05	0.02	0.63	0.49	0.38	0.23	0.15
NH*, Frias	na	na	na	na	0.58	0.44	0.28	0.09	0.07	0.02	na	na	na	na	na
Schmoll	0.30	0.00	0.42	0.38	0.37	0.28	0.21	0.05	0.03	0.02	0.17	0.14	0.12	0.07	0.15
Toncek	0.20	0.00	0.58	0.49	0.25	0.14	0.12	0.09	0.07	0.05	0.72	0.61	0.52	0.32	0.16
Trebol	0.90	2.80	0.10	1.70	2.46	2.03	1.34	0.46	0.07	0.05	3.77	3.29	2.56	1.54	0.38
Verde	2.30	6.80	5.28	1.23	1.91	1.61	1.17	0.53	0.25	0.16	2.50	2.22	1.81	1.25	0.50

\* Lake Nahuel Huapi.

Table 2. Coefficients of variation for repeated measurements of  $K_d$ .

$\lambda$ (nm)	C.V. (%)
305	6.6
320	3.2
340	2.9
380	2.7
PAR	8.2

showed substantially higher absorption than clear lakes, especially in the UV-B range.

Relationships between  $K_d$ , DOC, and  $\lambda$  were investigated in a similar manner. The four measured values of  $K_d$  (less estimates of  $K_w$  at 305, 320, 340, and 380 nm) were transformed to natural logarithms and regressed against  $\lambda$  for each of the survey lakes (Fig. 4A). The mean slope ( $S_{Kd}$ ) of this relationship was  $-0.01347 \text{ m}^{-1} \text{ nm}^{-1}$  (SE = 0.0005), which was significantly different from  $S_a$  ( $\alpha \leq 0.05$ ). The difference in slope is a further manifestation of the wavelength dependence of  $K_d$ :  $a$  seen previously. Across survey lakes,  $S_{Kd}$  was not significantly correlated to DOC, Chl  $a$ , or PM. There was, however, a significant relationship between DOC (as  $\text{g C m}^{-3}$ ) and intercept ( $I_{Kd}$ ):

$$I_{Kd} = 4.63([\text{DOC}]^{0.25}) \quad (r^2 = 0.76, P \leq 0.01). \quad (3)$$

Regression residuals were not correlated with either Chl  $a$  or PM. Both coefficients and exponents for the models relating  $I_a$  and  $I_{Kd}$  were significantly different ( $\alpha \leq 0.05$ ).

Although  $I_{Kd}$  is of interest in modeling  $K_d$  by a slope-intercept approach, the value of  $K_d$  at the intercept ( $\lambda = 0$ ) is far from the wavelength range of interest (280–400 nm) and may be greatly influenced by small differences in slope. For this reason, we also investigated the relationship between DOC and the estimated value of  $\ln(K_d^{336.25 \text{ nm}})$  for each lake. The approach is rationalized by the fact that the line of best fit for our data must pass through  $\bar{x}$  (336.25 nm is the mean value of  $\lambda$  for which  $K_d$  was measured) and  $\bar{y}$  [ $\ln(K_d^{336.25})$ ]. Values of  $\ln(K_d^{336.25})$  were estimated from the slopes and intercepts of the plots of  $\ln(K_d)$  vs.  $\lambda$  for each lake and regressed with DOC concentration. This approach also yielded a strong correlation between DOC and estimated  $\ln(K_d^{336.25})$ , further suggesting that  $K_d$  in the solar UVR spectrum is primarily regulated by DOC concentration.

Partial adjustment of  $K_d$  for differences in DOC concentration ( $K_d/[\text{DOC}]$ ) reduced much but not all of the variation in the  $K_d$ - $\lambda$  relationship (Fig. 4B). DOC-specific  $K_d$  was much higher in humic lakes than in clear lakes (up to 16-fold), as was the pattern for  $a/\text{DOC}$ .

The mean value of  $S_{Kd}$  and the form of Eq. 3 were used to develop a slope-intercept-type model for estimating  $K_d$  at any  $\lambda$  in the solar UV spectrum. The model was fitted to the  $K_d$ ,  $\lambda$ , and DOC (as  $\text{g C m}^{-3}$ ) data obtained from the survey lakes and yielded

$$K_{d\lambda} = \exp(-0.01347\lambda + 5.36[\text{DOC}]^{0.157}) \quad (r^2 = 0.89; P \leq 0.001). \quad (4)$$

Table 3. Statistical analysis and model equations. For all instances  $P \leq 0.001$ . DOC and Chl  $a$  as  $\text{g m}^{-3}$ ;  $a$  as  $\text{m}^{-1}$ .

Predicted	$n$	$r^2$	SE*	Model equation	$K_d$ water†
$K_d$ predicted by DOC and(or) Chl $a$ concn (single $\lambda$ )					
$K_{d305}$	44	0.96	3.62	$K_{d305} = 2.76([\text{DOC}]^{1.23})$	0.13
$K_{d320}$	63	0.87	3.07	$K_{d320} = 2.09([\text{DOC}]^{1.12})$	0.09
$K_{d340}$	63	0.89	2.41	$K_{d340} = 1.64([\text{DOC}]^{1.13})$	0.06
$K_{d380}$	62	0.92	1.20	$K_{d380} = 0.83([\text{DOC}]^{1.16})$	0.02
$K_{d\text{PAR}}$	63	0.68	0.47	$K_{d\text{PAR}} = 0.22[\text{DOC}] + 0.07[\text{Chl } a] - 0.05$	—
$K_d$ predicted by chemistry (multiple $\lambda$ )					
$K_{d\lambda}$	236	0.89	3.78	$K_{d\lambda} = \exp(-0.01347\lambda + 5.36[\text{DOC}]^{0.157})$	‡
$K_d$ predicted by absorption coefficient					
$K_{d305}$	44	0.91	3.88	$K_{d305} = 2.62[a_{305}] - 2.38$	
$K_{d320}$	63	0.84	3.45	$K_{d320} = 1.51[a_{320}] - 0.12$	
$K_{d340}$	63	0.83	2.84	$K_{d340} = 1.77[a_{340}] - 0.16$	
$K_{d380}$	62	0.73	1.64	$K_{d380} = 2.28[a_{380}] + 0.25$	
$K_d$ predicted by optical color measurement ( $a_{440}$ )					
$K_{d305}$	44	0.90	4.10	$K_{d305} = 24.4[a_{440}] - 0.99$	
$K_{d320}$	63	0.83	3.62	$K_{d320} = 16.0[a_{440}] - 0.15$	
$K_{d340}$	63	0.83	2.90	$K_{d340} = 12.7[a_{440}] - 0.07$	
$K_{d380}$	62	0.87	1.71	$K_{d380} = 6.4[a_{440}] + 0.24$	
$K_{d\text{PAR}}$	63	0.58	0.55	$K_{d\text{PAR}} = 1.30[a_{440}] + 0.12$	

\* Standard error of estimate of  $K_d$ .

† Estimate of  $K_d$  for pure water by Smith and Baker (1981) to be added to model equation, see text.

‡ Add value for specific  $\lambda$  from Smith and Baker (1981).

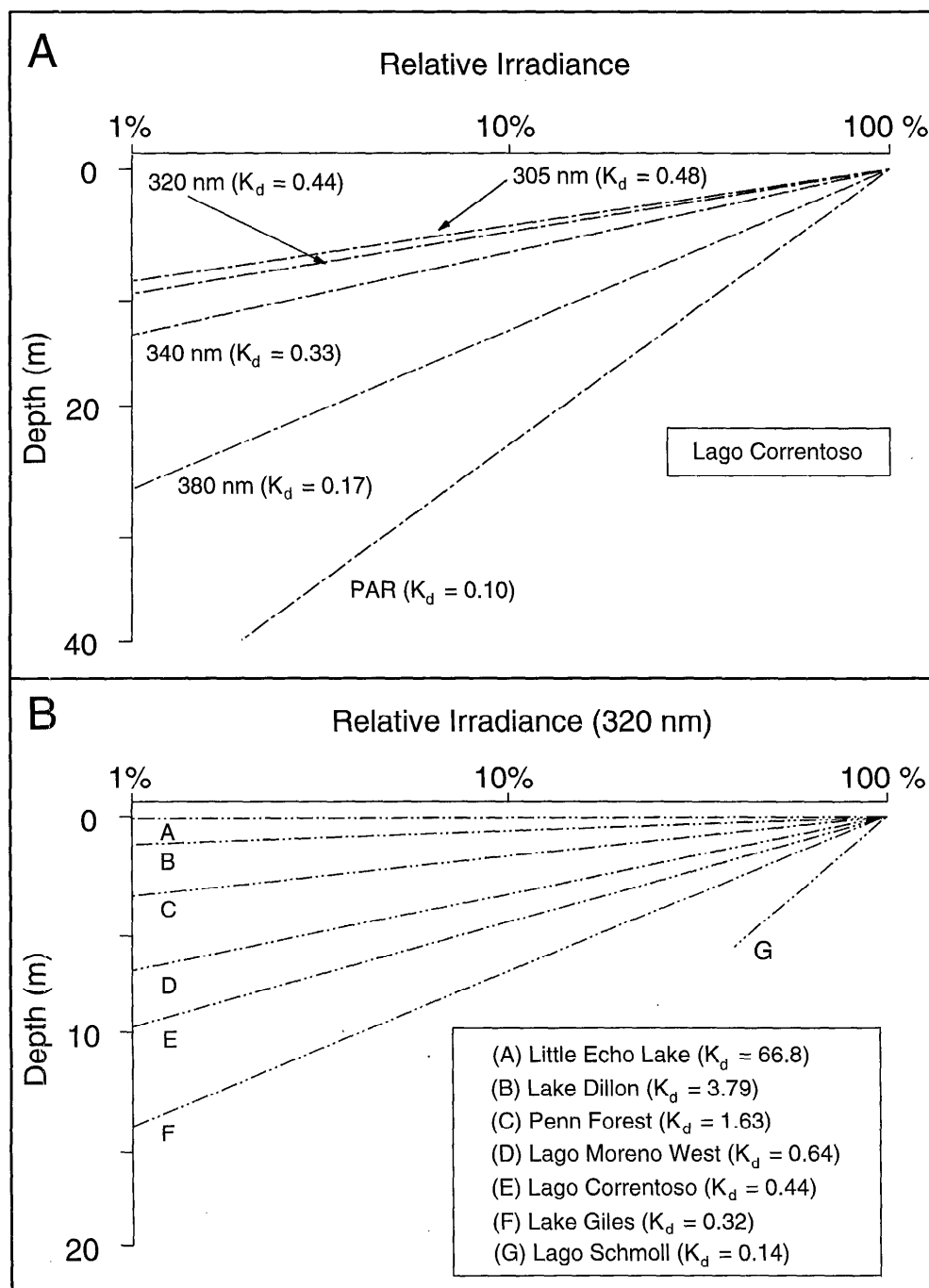


Fig. 1. A. Wavelength-specific depth-irradiance plots for Lago Correntoso, Argentina. Relative irradiance as a percentage of surface incident irradiance. The point at which each line transects the  $y$ -axis is the value of 1% surface irradiance ( $z_{1\%}$ ). B. Depth-irradiance plots for seven survey lakes illustrate between-lake variation in  $K_{d320}$  ( $m^{-1}$ ) and  $z_{1\%}$ . Similar between-lake variation was also observed at 305, 340, and 380 nm and PAR.

Again, regression residuals were not significantly correlated with either Chl  $a$  or PM.

#### Discussion

The lakes investigated show tremendous variability with respect to penetration of UVR. In low DOC lakes, trans-

parency to UVR is comparable to that of the most transparent marine ecosystems. In these lakes, substantial fluxes of the shortest, most energetic wavelengths of UV-B radiation can occur to depths in excess of 10 m. In shallow, transparent lakes such as Lago Schmoll ( $z_{\max} = 6$  m; elevation, 2,000 m), there may be little water-column attenuation of incident UVR, and the entire water column

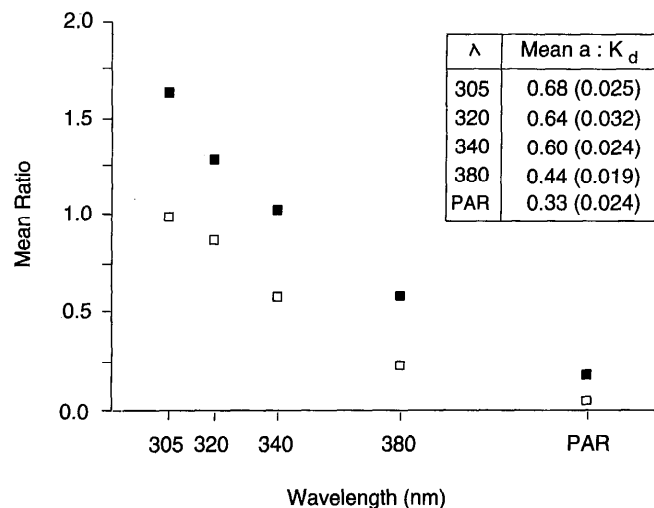


Fig. 2. Relationship between absorption coefficients ( $a$ ) and diffuse attenuation coefficients ( $K_d$ ) for survey lakes. Points represent means of  $a_\lambda : a_{305}$  ( $\square$ ) and  $K_{d\lambda} : a_{305}$  ( $\blacksquare$ ) computed for individual lakes. The value of  $a_{305}$  is arbitrarily set to 1. Tabulated values are mean (SE)  $a : K_d$  for the population of lakes for which the ratio  $< 1$ .

and sediment-water interface may be exposed to a substantial fraction of incident solar UVR. Exposure to UVR may be further enhanced for high elevation lakes because they are generally exposed to higher maximum fluxes of incident UVR due to reduced atmospheric attenuation (neglecting cloud cover, UV-B increases  $\sim 6\%$  per 1,000 m above sea level; Diffey 1991). Shallow depths and low DOC concentrations typical of many high elevation lakes combine to expose these environments to substantial fluxes of UVR.

A large fraction (85–92%) of the between-lake variation in  $K_d$  and  $a$  in the solar UV spectrum can be explained by bulk DOC concentrations. The unexplained variability was not significantly correlated with other environmental variables measured in this study but is probably explained by the variable chemical and optical properties of DOC in lakes, in particular, variability in DOC-specific  $a$  and DOC-specific  $K_d$ . This is illustrated by the fact that humic lakes consistently had higher DOC-specific values of  $a$  and  $K_d$  across the solar UV range (Figs. 2B and 3B). Absorption coefficients of common classes of DOC compounds (fulvic acids, tannic acids, and lignins) can vary by an order of magnitude across the solar UV spectrum (McKnight et al. 1994; Visser 1984; Lawrence 1980; Lewis and Tyburczy 1974). Much of the variability associated with estimates of  $K_d$  from our models may be because lake DOC tends to be a complex association of compounds with markedly different chemical and optical properties (Malcolm 1990). Given this fact, it is remarkable that DOC- $K_d$  relationships are as robust as those reported here and elsewhere (Scully and Lean 1994).

Dissolved  $a$  comprises an increasing proportion of  $K_d$  as wavelength decreases through the solar UV spectrum (Fig. 2). The mean contribution of dissolved  $a$  to  $K_d$  was

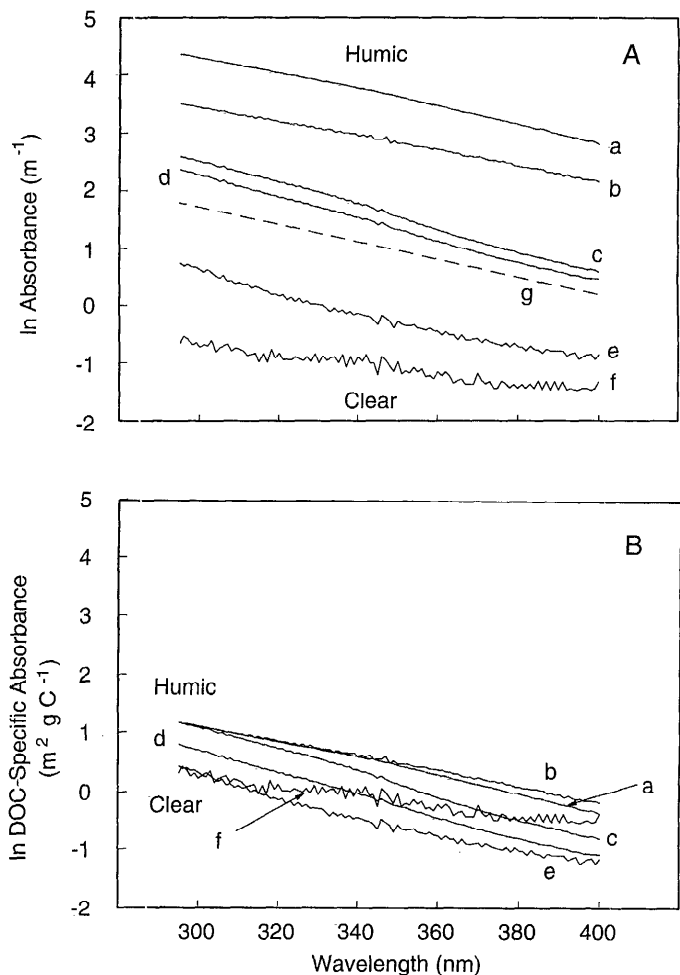


Fig. 3. A. Plots of natural log of absorbance vs.  $\lambda$  for six survey lakes showing between-lake variation in slope and intercept. B. Plots of natural log of DOC-specific absorbance,  $\ln(a/\text{[DOC]})$ , vs.  $\lambda$  a—Little Echo, [DOC] = 25.23; b—Red Rock, [DOC] = 10.11; c—Lacawac, [DOC] = 4.67; d—Granby, [DOC] = 4.01; e—Penn Forest, [DOC] = 1.34; f—Schmoll, [DOC] = 0.38; g—line with mean slope and intercept for all survey lakes. Lakes a, b, and c have highly colored (humic) DOC; lakes d, e, and f are less humic (clear).

33% for PAR, but this value increased to 68% for 305-nm radiation. It should be pointed out, however, that these values may slightly overestimate the contribution of dissolved  $a$  to  $K_d$  because our spectrophotometric technique (using cuvettes) includes some scattering in the estimates of absorbance. This analytical limitation is apparent in some clear, low DOC lakes for which values of  $a$  actually exceeded  $K_d$  (e.g. L. Schmoll). Residual contributions to  $K_d$  (not explained by dissolved  $a$ ) can be attributed to absorbance due to particulate material and to the angular distribution of the underwater light field (scattering). The second factor is wavelength-specific and is profoundly influenced by the relative contribution of sky light and direct sunlight (which was extremely variable during sampling). The relative contributions of par-

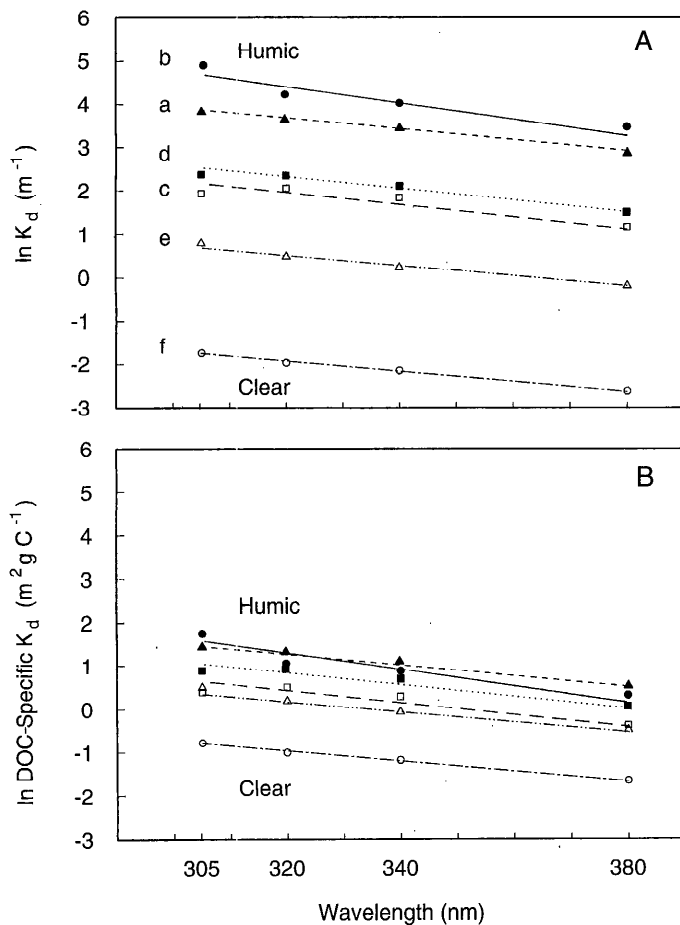


Fig. 4. A. Plots of natural log of diffuse attenuation coefficient ( $K_d$ ) vs.  $\lambda$  for six survey lakes showing between-lake variation in slopes and intercepts. B. Plots of natural log of DOC-specific  $K_d$ ,  $\ln(K_d/[\text{DOC}])$ , vs.  $\lambda$ . Lakes are the same as those identified in Fig. 3.

ticulate absorbance and scattering to  $K_d$  can vary with wavelength and sky conditions and thus cannot be separately estimated from these data.

To our knowledge, the relationships between DOC and  $S_a$ ,  $I_a$ ,  $S_{Kd}$ , or  $I_{Kd}$  have not previously been reported in the literature. While substantial variability was observed in the slope of the relationship between  $\lambda$  and  $\ln(a)$  or  $\ln(K_d)$  (range  $\pm 50\%$ ), the variability was not related to DOC concentration or to any of the other variables examined in this study. A significant relationship did exist, however, between DOC and intercepts ( $I_a$  and  $I_{Kd}$ ). This relationship reflects the strong dependence of both  $a$  and  $K_d$  on DOC concentration throughout the solar UV range and forms the basis for the slope-intercept-type model that allows estimation of  $K_d$  from DOC for any value of  $\lambda$  in the solar UV spectrum (Eq. 4).

Each of the DOC- $K_d$  models presented here takes the form of a power model. Linear models also provided a comparable fit ( $r^2$ ), but the presence of significant intercepts caused these models to return negative  $K_d$  values at

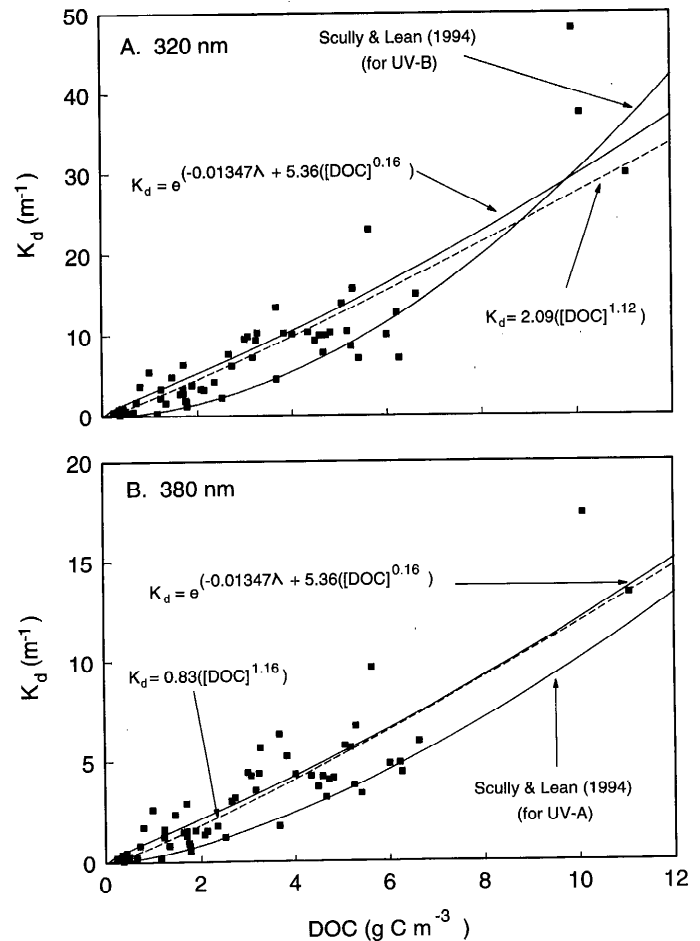


Fig. 5. A. Observed values of  $K_d$  for 320 nm plotted against DOC concentration for the survey lakes. The lines represent predicted values of  $K_d$  based on models presented in the text and by Scully and Lean (1994). B. Same but for 380 nm. Model equations for Scully and Lean:  $K_d$  UV-A =  $0.299 [\text{DOC}, \text{mg C liter}^{-1}]^{1.53}$ ;  $K_d$  UV-B =  $0.415 [\text{DOC}, \text{mg C liter}^{-1}]^{1.86}$ .

low DOC concentrations. Power models are also advantageous because they can account for increased DOC-specific absorbance, which we observed in humic lakes with higher DOC. As illustrated in Fig. 5, the single and multiwavelength models provided similar estimates of  $K_d$  at both 380 and 320 nm (as well as 305 and 340 nm, not shown). Single wavelength models developed over a narrow range of UVR provide lower standard errors for estimates of  $K_d$  (see Table 3). These models are best for estimating  $K_d$  at a single wavelength (i.e. 305, 320, 340, 380 nm) but lack the flexibility of the multiwavelength model, which can estimate  $K_d$  at any wavelength between 280 and 400 nm.

Models presented here are based primarily on data from oligotrophic and mesotrophic lakes with DOC ranges from  $\sim 0.2$  to  $23 \text{ g C m}^{-3}$  and for wavelengths from 305 to 380 nm. The models can be expected to provide valid estimates of  $K_d$  under similar conditions. However, model

performance will vary according to the specific optical characteristics of the DOC (DOC-specific absorbance), which can vary widely among lakes.

Our results generally confirm those of Scully and Lean (1994) who investigated the UV transparency at 20 lake sites (in 16 separate lakes). Their results and ours suggest that UV transparency varies greatly between lakes and that a large fraction (>85%) of the between-lake variation in  $K_d$  can be explained solely by bulk DOC concentration.

A comparison of our models with those of Scully and Lean (1994; using models for nonfluorometrically derived DOC data) is presented in Fig. 5. The Scully and Lean models for UV-A and UV-B radiation consistently provided lower estimates of  $K_d$  than ours did (also for 305 and 340 nm, not shown). Variations between our models and those Scully and Lean are probably not a result of methodological differences or performance characteristics of instruments since the methods produced similar results in a recent intercomparison (Kirk et al. 1994). More likely, each model reflects actual differences in variables controlling transparency of the particular set of lakes investigated in each study. The optical characteristics of the 16 lakes investigated by Scully and Lean (1994) fit well within the boundaries of the chemically and geographically diverse population of lakes included in our survey.

Differences between models are of little consequence in lakes with moderate to high DOC but are particularly important in low DOC lakes, where UVR may penetrate to significant depths. Our models do, however, diverge significantly from those of Scully and Lean for low DOC lakes. These differences are probably because their model is not well defined at low DOC concentrations (only 3 points below  $2 \text{ g C m}^{-3}$  DOC). In contrast, our model includes 30 points below  $2 \text{ g C m}^{-3}$  and probably provides a more accurate estimate of  $K_d$  in low DOC environments.

It should be pointed out that the models presented here are based on empirical (correlational) evidence and do not address the underlying optical basis for light attenuation in lakes. Diffuse attenuation coefficients are determined by the interaction of a number of factors, including absorbance by dissolved material ( $a_d$ ), absorbance by particulate material ( $a_p$ ), molecular and particle scattering ( $b$ ), and the angular distribution of the light field ( $\bar{\mu}$ ). The relative relationships between  $\lambda$ ,  $a_d$ ,  $a_p$ , and  $b$  are generally unknown for UVR in lakes ecosystems but are of vital importance in formulating effective optical models.

Although the models presented here are not optical models, they contribute to our understanding of the environmental control of UV penetration in freshwater ecosystems. Because of the uncertainty in predicted  $K_d$  values (due in part to variable DOC-specific absorbance), these models should not be viewed as replacements for direct measurement of UV attenuation, especially for demanding photobiological applications. However, in the absence of direct measurements, archival DOC or color data (e.g.  $a_{440}$ ) can be used to provide rough estimates of UV transmission in lakes as well as to infer seasonal or annual variations in UV transparency within individual lakes.

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