

Attenuation of ultraviolet radiation in mountain lakes: Factors controlling the among- and within-lake variability

Isabelle Laurion¹

Institute of Zoology and Limnology, University of Innsbruck, A-6020 Innsbruck, Austria

Marc Ventura and Jordi Catalan

Department of Ecology, University of Barcelona, Diagonal 645, E-08028 Barcelona, Catalonia, Spain

Roland Psenner and Ruben Sommaruga²

Institute of Zoology and Limnology, University of Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria

Abstract

High-altitude lakes are exposed to high fluence rates of solar ultraviolet radiation (UVR; 290–400 nm) and contain low concentrations of dissolved organic carbon (DOC). While in most lowland lakes, DOC can be used to predict UV transparency with sufficient accuracy, current models fail to estimate UVR in clear alpine lakes. In these lakes, phytoplankton may contribute significantly to the UV attenuation either as particles or as a source of chromophoric dissolved organic matter (CDOM) with distinctive properties. We investigated a series of 26 lakes in the Alps and Pyrenees, situated at elevations ranging from 422 to 2,799 m above sea level and having DOC concentrations ranging from 0.2 to 3.5 mg L⁻¹. CDOM, as measured by the absorptivity of filtered lake water, explained most of the variability in the attenuation of underwater UVR among lakes ($r^2 = 0.94$, $P < 0.001$). However, within-lake variation in the UV attenuation revealed a significant contribution from phytoplankton in deeper waters (UV attenuation increasing with chlorophyll *a* concentration; $r^2 = 0.97$, $P = 0.002$), only apparent when DOC concentrations were low (~ 0.3 mg L⁻¹). The DOC-specific absorptivity (a_g^*) was also important for characterizing the optical conditions in this series of lakes. Epilimnetic values of a_g^* were significantly lower in lakes located at high elevations (with low allochthonous CDOM inputs from the catchment), compared to lakes surrounded by trees and meadows. Moreover, a_g^* was generally lower in surface waters than in deeper water layers, suggesting the influence of photobleaching on UV transparency. The slope *S* of the exponential regression between CDOM absorptivity and wavelength did not show clear patterns, such as found in marine systems, and often presented lower values in the epilimnetic waters (in association with lower a_g^*). Collectively, our results suggest that in transparent alpine lakes, the dynamics of the CDOM pool and phytoplankton production will have a strong effect on temporal changes in UV underwater attenuation.

Solar ultraviolet-B radiation (UVB; 290–320 nm) has increased during the last 15 yr over many Earth's locations as a consequence of the degradation of the stratospheric ozone layer. Beside Antarctica, where the increment is notorious,

some studies have demonstrated that a moderate increase in UVB also occurred in the northern hemisphere, for example, in the Arctic (Von der Gathen et al. 1995) and in the Swiss Alps (Blumthaler and Ambach 1990). Within these fragile environments, an increase in UVB radiation is an additional stress for organisms that already have to cope with high solar UV radiation (UVR; 290–400 nm), a short growing season, low temperature, and low nutrient inputs. The effects of ambient levels of UVR on the biota of alpine lakes and other aspects of UV photobiology have been recently addressed (Cabrera et al. 1997; Halac et al. 1997; Sommaruga et al. 1997, 1999*b*; Vinebrooke and Leavitt 1998; Sommaruga and Garcia-Pichel 1999). These studies have shown that UVR can alter both planktonic and benthic communities, but large differences in the sensitivity among species or groups exist. Furthermore, the impact of UVR has been related to other important environmental changes affecting high-latitude and high-altitude lakes, like acidification and climatic warming (Schindler et al. 1996; Yan et al. 1996; Vinebrooke and Leavitt 1998; Sommaruga et al. 1999*a*).

Because the biological response of aquatic organisms to UVR is highly variable and nonlinear across the UV waveband (Vincent and Roy 1993), detailed information on UV exposure as a function of wavelength and depth is needed

¹ Present address: Institut des Sciences de la Mer de Rimouski, University of Quebec at Rimouski, 310, Allée des Ursulines, Rimouski, Quebec, G5L 3A1 Canada (isabelle_laurion@uqar.quebec.ca).

² Corresponding author (ruben.sommaruga@uibk.ac.at).

Acknowledgments

We thank J. Chiapella, D. Conde, P. Indinger, A. Miro, and A. Wille for their assistance in field and laboratory work, R. Lackner for HPLC assistance, W. Vincent, M. Twardowski, I. Reche, and two anonymous reviewers for their helpful comments on the manuscript, and D. Karentz, M. Shick, and F. Garcia-Pichel for donating standards or biological material needed to analyze the MAAs. We also thank the staff from Aiguestortes i estany de Sant Maurici National Park for facilitating the sampling of most lakes in the Pyrenees. The research was supported by a grant from the Austrian Science Foundation (FWF P14153-BIO) to R.S., the Austrian Ministry of Agriculture and Forestry (BMLF 41.001/14-IVA1/98), and by a postdoctoral fellowship from FCAR (I.L.). The travel to Spain was financed by the collaborative scientific program between Austria and Spain (contract 98/17).

to estimate the effects of UVR in natural environments. In remote alpine lakes, direct measurements of UVR are sometimes difficult to accomplish. Therefore, the identification of the factors controlling the attenuation and spectral composition of UVR in these lakes must be achieved with simple though meaningful and reliable measurements.

Several authors have attempted to model the relationship between the attenuation of UVR and different optical variables measured in a variety of lakes (Scully and Lean 1994; Morris et al. 1995; Laurion et al. 1997), specifically: dissolved organic carbon (DOC) concentration, absorptivity (a_g), and fluorescence (F_g) of chromophoric dissolved organic matter (CDOM or Gelbstoff) at specific wavelengths, transmittance of a collimated beam of 660 nm light, chlorophyll *a* concentration (Chl *a*), and particulate material. Dissolved organic matter (DOM) was identified as the main factor explaining the variation in UV attenuation among those lakes, and DOC was found to be a good estimator of UV transparency. However, the uncertainty of predicting K_d with these empirical models increases in clear lakes due in part to the variable DOC-specific absorptivity (Morris et al. 1995). In the open ocean and in clear-water systems such as polar (Vincent et al. 1998b) and alpine lakes (Sommaruga and Psenner 1997) concentrations of DOM are significantly reduced. For example, a survey of 48 alpine lakes in the Austrian Alps (lakes not fed by glaciers; altitudes ranging between 1,970 and 2,890 m above sea level or a.s.l.) revealed an average DOC concentration of 0.7 mg L⁻¹ (Sommaruga et al. 1999a). Therefore, the importance of DOM on the control of UV attenuation in these ecosystems and the involvement of other UV-absorbing components deserve to be examined.

In transparent marine and freshwater systems, phytoplankton was suggested to be an important component in UV attenuation (Smith and Baker 1981; Kirk 1994). Phytoplankton can be a source of low molecular weight carbohydrates, proteins, and lipids that are transformed abiotically or microbially into DOM (Hedges 1988; Tranvik 1993). The release of organic matter by phytoplankton is considered a major source of DOM in the ocean (Lee and Henrichs 1993), and increases in DOC have often been observed following a phytoplankton bloom (e.g., Holmes et al. 1967; Norrman et al. 1995). However, organic substances produced in situ are characterized by a lower aromaticity than DOM of terrestrial origin (Carder et al. 1989; McKnight et al. 1994). Marine and lake phytoplankton can also synthesize different UV-absorbing compounds (e.g., Xiong et al. 1997; Hannach and Sigleo 1998; Sommaruga and Garcia-Pichel 1999) that may affect UV attenuation, particularly when algae are concentrated in layers or form blooms (Vernet and Whitehead 1996; Kahru and Mitchell 1998). The importance of phytoplankton cells per se for the attenuation of near-UV and blue light has been recognized (with *in vivo* spectra; Yentsch and Phinney 1989); however, measurements of *in situ* algal absorption of UVR (and its importance relative to DOM) are limited. Sommaruga and Psenner (1997) measured light attenuation in an alpine lake during the formation of the deep Chl *a* maximum and suggested that phytoplankton and/or phytoplankton-derived organic substances were important for the UV attenuation in lakes with low DOC content.

Photodegradation of DOM can also affect its optical and chemical properties (Kieber et al. 1990; Allard et al. 1994; Zepp et al. 1995), thus leading to an increase of UV transparency. Exposure of freshwater DOM to natural sunlight reduces its absorptivity of UV and visible radiation (Morris and Hargreaves 1997; Reche et al. 1999) at rates that depend on sunlight incident doses, lake chemical conditions, and mixing regime (Reche et al. 1999; Whitehead et al. 2000). Exposure of DOM to sunlight is also known to increase its lability and enhance biodegradation (Wetzel et al. 1995) that may accelerate nutrient remineralization (Moran et al. 1999 and references therein). Furthermore, formation of strong oxidants during photodegradation of DOM (singlet oxygen, superoxide, hydrogen peroxide) may have acute and chronic toxic effects on aquatic organisms (Palenik et al. 1991; Xenopoulos and Bird 1997). The spectral shape of the CDOM absorption curves (i.e., the slope *S* of the exponential regression between CDOM absorptivity and wavelength; Jerlov 1968) as well as the carbon-specific absorptivity have been used to study photodegradation processes (Morris and Hargreaves 1997; Vodacek et al. 1997; Twardowski and Donaghay 1998; Whitehead et al. 2000).

In this study, our objectives were (1) to evaluate which optical variables control the underwater UV attenuation in the water column of mountain lakes, especially the importance of phytoplankton in waters with low-DOM content, (2) to provide an empirical model to estimate the UV attenuation coefficients in these systems, and (3) to describe the optical conditions regarding altitude gradients, differences within the water-column, and seasonal changes. We addressed these objectives by means of profiles of optical parameters in a broad suite of mountain lakes from several locations in Europe.

Materials and methods

Sampling sites—A total of 26 lakes in the Tyrolian Alps (Austria and Italy) and in the Pyrenees (Spain) were sampled in 1998 (Table 1). Two lakes located in the prealpine region east of Salzburg (Mondsee and Traunsee located below 500 m a.s.l.) and two in Tyrol (Achensee and Piburgersee located at 929 and 913 m a.s.l., respectively) were sampled for comparison, all others are situated above 1,480 m a.s.l. Lake elevation in the Alps ranged from 913 to 2,799 m a.s.l. and in the Pyrenees from 1,900 to 2,400 m a.s.l. The treeline is situated approximately at 2,000 m in this region of the Alps and at 2,200 m in the Pyrenees. Most lakes in the Alps were sampled twice in July and in October (Mondsee and Traunsee sampled in November only), and lakes in the Pyrenees were sampled once in September. This series of lakes was separated in three categories according to the dominant catchment vegetation: lakes above the treeline with a poor soil cover or with less than 5% of sparse pine trees (hereafter exposed rock category; $n = 11$), lakes at high altitudes but surrounded by alpine meadows (hereafter meadows; $n = 5$), and lakes with forested catchments (hereafter trees; $n = 10$). The geology of the area is characterized by crystalline or calcareous bedrock, and the dominance of the different geological structures is reflected in the lake-water pH (range of

Table 1. Latitude, longitude, altitude, maximum lake depth, lake and catchment area, and pH (not measured at sampling; represents one to several years averages) of each lake.

Lake*	Latitude N	Longitude E	Altitude (m a.s.l.)	Maximum lake depth (m)	Lake area (ha)	Catchment area (ha)	pH
Exposed rock							
BAR p	42°36'	00°59'	2,360	13	3.5	9	6.7
DRA	47°02'	10°56'	1,874	24	4.5	188	8.2
GKS	47°13'	11°00'	2,417	9.9	1.7	30	6.9
GRA p	42°36'	00°59'	2,345	25	7	166	6.7
MPL	47°12'	11°03'	2,317	5.7	1.6	8	5.9
NEG p	42°32'	01°01'	2,320	70	32	178	7.0
OPL	47°12'	11°02'	2,344	7.5	2.1	97	6.7
RED p	42°38'	00°45'	2,240	73	24.5	155	6.5
ROT	47°14'	11°00'	2,485	5.5	0.9	33	7.6
SOS	46°57'	10°56'	2,799	18	3.5	18	5.5
TOR p	42°33'	01°03'	2,310	24	9.8	666	6.9
Meadows							
KLA	46°58'	12°07'	2,258	3	1.1	67	8.2
LIC	47°01'	11°24'	2,104	6.6	0.8	11	7.5
LLA p	42°35'	00°38'	2,125	45	28.7	736	7.3
OBR	46°53'	12°12'	2,016	26.7	12.9	210	na
PJO	46°39'	11°39'	2,231	17.2	0.6	4.2	7.3
Trees							
ACH	47°27'	11°42'	929	133	680	10,500	8.3
ANT	46°53'	12°10'	1,640	38	43.3	1,906	7.3
DUR	46°44'	11°25'	1,560	13	12.4	2,787	6.8
MON	47°48'	13°21'	481	68	1,378	24,720	7.9
OBB	46°59'	11°24'	1,590	15	12	1,163	8.2
PIB	47°11'	10°53'	913	24.6	13.4	265	7.2
PRA	46°41'	12°05'	1,489	36	31	2,664	8.2
SEE	47°21'	10°56'	1,650	14	6.4	na	na
SMA p	42°35'	01°00'	1,905	25	25	2,209	7.2
TRA	47°48'	13°26'	422	191	2,435	142,200	8.2

* ACH, Achensee; ANT, Antholzer See; BAR, Estany Barbs; DRA, Drachensee; DUR, Durnholzer See; GKS, Gossenköllesee; GRA, Estany Gran d'Amitges; KLA, Klammsee; LIC, Lichtsee; LLA, Estany Llauset; MON, Mondsee; MPL, Mittlere Plenderlesee; OPL, Oberer Plenderlesee; PJO, Pfitscher Joch See; NEG, Estany Negre; OBB, Oberbergersee; OBR, Obersee; PIB, Piburger See; PRA, Pragser Wildsee; RED, Estany Redo; ROT, Rotfelssee; SEE, Seebensee; SMA, Estany Sant Maurici; SOS, Schwarzsee ob Sölden; TOR, Estany Tort; TRA, Traunsee; p, Lakes in the Pyrenees, all others are in the tyrolian Alps, except MON and TRA that are in the pre-Alps east of Salzburg; na, not available.

5.5–8.4; Table 1). In calcareous catchments, precipitation of carbonates (whitening) was sometimes visible in lakes where photosynthetic activity raised the pH (e.g., ACH, ANT, OBB, PRA; the three-letter abbreviations represent lakes as defined in Table 1).

Optical and other water column measurements—A PUV-500A radiometer (Biospherical Instr.) provided a measure of downwelling irradiance at 305, 320, 340, and 380 nm (full bandwidth at half maximum is 8–10 nm), and of downwelling photosynthetically active radiation (PAR, 400–700 nm). The instrument also recorded depth, temperature, and upwelling radiance centered at 683 nm (naturally induced fluorescence). Profiles were made on sunny days or with stable cloud conditions, and within 3 h of solar noon. The diffuse attenuation coefficients of downwelling UVR (K_d) were calculated as the slope of an exponential regression between radiation and depth. When K_d changed through the water

column, the portion of the curve where the change occurred was excluded from calculations. Irradiance values approaching the sensor detection limit were also eliminated before calculations (using values greater than two orders of magnitude above the noise equivalent irradiance given by the manufacturer; a dark correction was not performed but the temperature effect on zero-offset values was controlled).

The lake water was sampled at one to five discrete depths with a 5-liter Schindler–Patalas sampler in the Alps or a Ruttner bottle in the Pyrenees and was kept in the dark until processed in the laboratory. The selection of sampling depths was based on profiles of light and Chl *a* fluorescence. A Backscat I-Fluorometer (Haardt, model 1101.1; excitation 380–540 nm, emission 685 nm) was used in most cases to locate the depth of the deep Chl *a* maximum. For Chl *a* measurements, 0.6–3.5 liters of lake water were filtered onto glass fiber filters (Whatman GF/F). Pigments were extracted with 90% acetone for 24 h in the dark at 4°C. Filters were

briefly sonicated with a tip sonicator (1 min) and the extracts cleared using a 0.1- μm pore size Anodisc filter (Whatman). The extracts were scanned in a spectrophotometer (double-beam Hitachi U-2000; scans between 400 and 750 nm) against an acetone reference and using 5-cm glass cuvettes. The optical density measured at 664 nm always remained above 0.03, and in most cases was more than one order of magnitude higher than the optical density at 750 nm. The equations of Jeffrey and Humphrey (1975) were used to calculate the concentration of pigments.

The direct contribution of the UV-absorbing compounds to the attenuation of UVR was estimated by measuring the total concentration of mycosporine-like amino acids (MAAs) in phytoplankton. For this, 0.8–4.85 liters of lake water were filtered onto glass fiber filters (Whatman GF/F). The filters were frozen at -80°C until subsequent extraction (within 4 months). MAAs were extracted in 20% aqueous methanol (v:v) for 24 h at 4°C , followed by a 2-h extraction in a water bath at 45°C (Sommaruga and Garcia-Pichel 1999). Filters were sonicated and the extracts cleared and scanned as above (scans between 250 and 750 nm; 5-cm Suprasil I quartz cuvette), to determine the presence of UV-absorbing compounds. The extracts were subsequently dried under vacuum in 2-ml cryovials, using a SpeedVac concentrator (Savant) at 45°C . The air in the cryovials was replaced with argon, and the samples were stored at -80°C for further characterization using high-performance liquid chromatography (HPLC).

The concentrated extracts were resuspended in 0.5–2 ml of 55% aqueous methanol (v:v). When the concentration in this solution was too high, a small portion was subsampled for further dilution. MAAs were separated by reverse-phase isocratic HPLC, injecting 30- μl aliquots in a Brownlee RP-8 column (Spheri-5; 4.6 mm inner diameter \times 25 cm) protected with an RP-8 guard column, using an aqueous mobile phase containing 55% methanol plus 0.1% acetic acid (Carefoot et al. 1998). The MAAs in the eluate were detected by online UV spectroscopy. Peak measurement was carried out at 313 and 340 nm (Karentz et al. 1991). The MAAs were identified by comparison with published retention times, by the ratio of peak areas determined at 313 and 340 nm, and by cochromatography with authenticated standards (obtained from Dr. F. Garcia-Pichel) or with secondary standards prepared from invertebrate extracts (*Aplysia dactylomela* eggs obtained from Dr. D. Karentz, and *Anthopleura* sp. and *Palythoa* sp. obtained from Dr. M. Shick). The total content of specific MAAs in each sample was calculated from HPLC peak areas using published extinction coefficients (see Sommaruga and Garcia-Pichel 1999). The extinction coefficient for asterina-330 has not been reported in the literature. The extinction coefficient of palytholol, a nearly identical chromophore, was consequently adopted for asterina-330 quantification (Dunlap et al. 1989). Total MAA concentrations were used in this paper as an additional explanatory variable for the variation in UVR attenuation; a more detailed analysis of these results will be presented elsewhere.

The DOM characteristics at each sampling site were determined by measurements of DOC concentration, spectral absorptivity (a_g), and fluorescence (F_g) of filtered lake water. In addition, the CDOM absorptivity at 320 nm was normal-

ized to the DOC concentration (a_g^*). For these analyses, the lake water was filtered on the same day (within 6 h) through glass fiber filters (Whatman GF/F; precombusted for 1 h at 450°C , rinsed with 20 ml of Milli-Q water and 10 ml of lake water) and stored in clean, precombusted glass bottles (Teflon-capped) in the dark at 4°C until subsequent analysis (within 24 h for DOC, within 48 h for a_g and within 2 weeks for F_g). Glass fiber GF/F filters were used instead of 0.2- μm filters because they can be precombusted to avoid contamination (Yoro et al. 1999). Hence, in this paper, DOM is defined as the matter passing through GF/F filters, DOC is a simple bulk measure of DOM, CDOM refers to the chromophoric fraction of DOM, and the expression "optical properties of CDOM" refers to F_g , a_g , a_g^* , and S as measured in filtered lake water. Filtration was done by hand with an acid-washed syringe and filter holder, directly over the bottle to avoid contamination. The DOC was measured with a high temperature catalytic oxidation method (Shimadzu total organic carbon [TOC] analyzer model 5000). The instrument is equipped with a Shimadzu platinumized-quartz catalyst for high sensitivity analysis (Benner and Strom 1993). Three to five injections were analyzed for each sample and blanks (Milli-Q water). Blank values (0.03–0.05 mg DOC L^{-1}) were subtracted from the average DOC values of the samples. Standardization of the instrument was done with potassium hydrogen phthalate (four points calibration curve). The TOC analyzer used participates regularly in the intercomparisons organized by the Norwegian Institute for Water Research (NIVA) for 57 laboratories.

Absorption by CDOM was determined by spectrophotometry (same instrument as above; scans between 250 and 750 nm) using an acid-cleaned 10-cm quartz cuvette (Suprasil I) prerinsed two times with the sample. These measurements were referenced against 0.22- μm membrane-filtered Milli-Q water (DOC \leq 0.05 mg L^{-1} , $F_g < 0.002 \text{ nm}^{-1}$). The absorptivity at 750 nm, which can be used to correct for the presence of particulate matter in the cuvette, was generally low and in several cases was negative. This was likely caused by the temperature dependency of pure water absorption when the sample is cooler than the reference (Pegau and Zaneveld 1993). Hence, we used a_g at 690 nm (where the temperature dependency is near zero) to correct the UV-absorptivity values. Fluorescence emission spectra were measured in a spectrofluorometer (Hitachi F-4500) at high voltage sensitivity (excitation at 355 nm, slit width of 5 nm on both monochromators) using a clean 1-cm quartz cuvette (Suprasil I) prerinsed two times with the sample. The fluorescence signal at 450 nm (peak height) was normalized to the Raman signal area to give F_g in Raman units (nm^{-1}). The fluorescence signal at 450 nm was also referred to as quinine sulfate units (QSU), where 1 QSU = 1 $\mu\text{g L}^{-1}$ of quinine sulfate dissolved in 0.1 N H_2SO_4 (Shao et al. 1993).

Calculation of the slope parameter—Irregularities on the absorption spectra of filtered lake water were found that may have important effects on the calculation of S depending on the waveband chosen (Fig. 1). First, a peak found at approximately 275 nm may affect the estimation of S if we assume the exponential model describing a_g (Jerlov 1968; the dashed line in Fig. 1 represents the exponential fit over

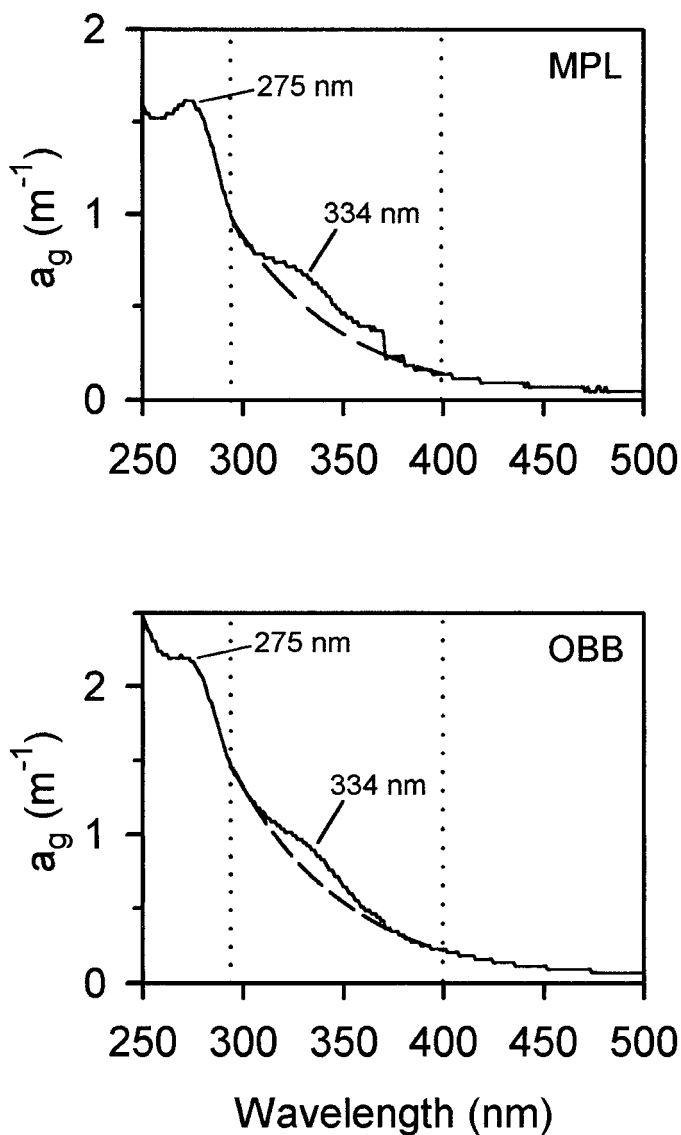


Fig. 1. Examples of CDOM absorption spectra with defined peaks at ~ 275 and 334 nm (MPL was sampled in July at 4 m depth; OBB, in October at 2 m depth). The dashed line represents the exponential fit used to get the slope parameter S . The dotted lines represent the limits of the waveband used to calculate S .

the waveband 295–400 nm used to calculate S). The presence of this peak might be associated with the absorption by proteins and nucleic acids (Bidigare 1989). In addition, in some cases, absorption by CDOM showed a peak at approximately 334 nm, representing up to 20% of a_g at this wavelength. This peak was relatively common (detectable in ca. one third of the lakes) but had small effects on the estimation of S (up to 6% difference compared to the estimation of S without the peak). Values presented in Table 2 were calculated after removing the peak (310–370 nm). This peak was likely caused by the presence of MAAs in the filtered water. In many of the lakes sampled in this study, phytoplankton showed high concentration of MAAs (Table 2) that can eventually be exuded or released during cell lysis. MAAs have already been found in the DOM pool during a

dinoflagellate bloom (Vernet and Whitehead 1996). Although care was taken in using low pressure during filtration to avoid cell damage, we cannot totally exclude the possibility of release of MAAs from fragile forms during this process.

Some authors have demonstrated the sensitivity of S on the method of calculation, the wavelength range, and the type of optical measurements (Twardowski and Donaghay 1998; Markager and Vincent 2000). As recommended by these authors, a_g values were not transformed to natural logarithms before applying the regression fit, to maintain equal weighting for each data point. Moreover, we always used the same waveband to calculate S . The slope parameter was additionally calculated between 370 and 500 nm (Table 2), a waveband that was less affected by irregularities. Although this variable does not relate directly to the waveband concerned by this study (290–400 nm), it further characterizes CDOM. Humic acids are responsible for absorption by CDOM in the visible range and present a lower slope parameter than the low molecular weight fulvic acids (Carder et al. 1989). The selection of the waveband is likely to affect the meaning of S . In agreement with previous studies (Blough et al. 1993; Green and Blough 1994), S was lower at higher wavelengths (average of $13.9 \mu\text{m}^{-1}$ compared to $16.6 \mu\text{m}^{-1}$ for the 290–400 nm waveband), but both S were correlated ($r = 0.737$, $P < 0.001$).

Data treatment—To address the first objectives of the study that were to evaluate which optical variables control the underwater UV attenuation in mountain lakes and to provide an empirical model to estimate the UV-attenuation coefficients in these systems, we selected the epilimnetic data (when possible, the value in the first meter was not selected). To investigate the relation between K_d and each variable measured in the water, simple correlations and regressions were performed using SigmaStat software. A redundancy analysis (RDA) was also performed on this data set using the CANOCO software (ter Braak 1988). The significance of the first axis and of the whole analysis was tested by means of a Monte Carlo permutation test, with 999 permutations (ter Braak 1995). To investigate the effect of catchment type, depth, and season on CDOM optical characteristics, t -tests or Pearson correlations were performed using SigmaStat.

Results

Characteristics of the lakes—The data series comprises lakes with maximum depths ranging from 3 to 191 m, lake areas from 0.6 to 2,435 ha, and catchment areas from 4 to 142,200 ha (Table 1). However, the catchment-to-lake area ratio was $<30:1$ in more than half of the lakes. The series of lakes offered a great variability in optical conditions (the epilimnetic values are presented in Table 2; the whole data set is available on request). DOC concentrations ranged from 0.2 to 3.5 mg L^{-1} (mean = 0.97 mg L^{-1}), with the lowest concentrations found in the exposed rock category, followed by meadows and trees categories (mean of 0.54, 1.08 and 1.33 mg L^{-1} , respectively). Epilimnetic Chl a concentrations

Table 2. Water optical properties: DOC, Chl *a*, total MAA concentration (MAAs), fluorescence of chromophoric dissolved organic matter (F_g ; excitation at 355 nm, emission at 450 nm, given in Raman units and quinine sulfate units), absorptivity of CDOM (a_g) at 320 and 440 nm, DOC-specific a_g (a_g^*) at 320 nm, and spectral slope S of the exponential regression of a_g calculated on the wavebands 295–400 nm and 370–500 nm.

Lake	Date (1998)	Sam-pling depth (m)	Chl <i>a</i> ($\mu\text{g L}^{-1}$)	MAAs ($\mu\text{g L}^{-1}$)	DOC (mg L^{-1})	F_g (nm^{-1} [QSU])	a_g 320 (m^{-1})	a_g 440 (m^{-1})	a_g^* 320 (L mg DOC $^{-1}$ m^{-1})	S (295–400) (μm^{-1})	S (370–500) (μm^{-1})
Exposed rock											
BAR	10 Sep	2	0.77	0.49	0.98	0.044 (3.66)	0.94	0.16	0.97	12.8	9.5
DRA	22 Jul	1	0.39	0.36	0.38	0.013 (0.92)	0.46	0.09	1.20	12.8	7.2
GKS	23 Jul	4	0.96	2.63	0.35	0.014 (1.03)	0.41	0.02	1.17	19.4	13.0
	06 Oct	2	1.96	1.31	0.52	0.009 (0.62)	0.32	0.05	0.62	17.5	14.9
GRA	10 Sep	2	0.87	0.71	0.66	0.034 (2.67)	0.58	0.07	0.88	14.8	10.4
MPL	21 Jul	1	2.40	11.46	0.56	0.020 (1.46)	0.58	0.05	1.02	13.3	13.0
	10 Oct	2	2.83	0.97	0.67	0.014 (0.96)	0.48	0.05	0.72	15.1	10.6
NEG	09 Sep	2	0.30	0.43	0.62	0.028 (2.07)	0.41	0.05	0.67	16.4	13.2
OPL	21 Jul	1	0.75	2.74	0.21	0.019 (1.34)	0.41	0.00	1.96	18.5	17.7
	10 Oct	2	1.38	0.17	0.22	0.007 (0.54)	0.21	0.00	0.95	18.0	17.3
RED	08 Sep	2	1.08	5.56	0.80	0.031 (2.43)	0.48	0.07	0.60	15.0	6.1
ROT	23 Jul	2.5	2.44	0.92	0.26	0.026 (1.94)	0.37	0.02	1.41	18.8	18.9
	06 Oct	2	2.50	5.79	0.57	0.012 (0.78)	0.28	0.02	0.48	19.2	14.9
SOS	30 Jul	2.5	1.36	4.69	0.29	0.010 (0.74)	0.25	0.02	0.88	17.1	11.3
TOR	09 Sep	2	1.35	3.00	0.97	0.048 (3.84)	1.77	0.28	1.82	14.9	13.1
Meadows											
KLA	18 Jul	1.5	1.21	0.50	0.71	0.033 (2.54)	1.01	0.21	1.43	10.8	7.1
	14 Oct	2	0.34	0.20	0.44	0.036 (2.85)	1.54	0.16	3.51	15.9	14.5
LIC	15 Jul	1	2.69	2.00	1.31	0.048 (3.96)	1.52	0.21	1.16	15.5	14.0
	09 Oct	2	3.61	0.24	1.99	0.044 (3.19)	3.13	0.46	1.57	13.6	14.8
LLA	12 Sep	2	0.58	0.04	1.05	0.042 (3.00)	1.04	0.12	0.99	15.7	12.5
OBR	17 Jul	1	0.59	0.57	0.75	0.028 (2.02)	1.17	0.09	1.57	18.0	15.5
	13 Oct	2	1.09	2.15	0.67	0.027 (2.05)	0.90	0.12	1.35	16.6	13.9
PJO	24 Jul	1.5	7.97	13.35	1.71	0.017 (1.23)	0.74	0.14	0.43	13.7	10.6
Trees											
ACH	11 Jul	3	1.10	0.33	3.50	0.060 (4.82)	2.72	0.25	0.78	18.8	17.1
	12 Oct	1	0.49	0.03	1.23	0.066 (5.17)	2.35	0.23	1.91	18.6	16.8
ANT	17 Jul	1	1.54	0.07	1.04	0.034 (2.61)	1.17	0.14	1.13	16.2	12.9
	13 Oct	2	3.30	0.52	0.53	0.036 (2.98)	0.48	0.05	0.91	15.8	13.8
DUR	19 Jul	1	0.38	Traces	0.43	0.036 (2.85)	1.11	0.18	2.59	13.7	13.2
	15 Oct	2	0.25	0.00	0.66	0.030 (2.28)	1.34	0.14	2.02	16.8	15.7
MON	05 Nov	2	3.52	0.05	2.44	0.121 (10.1)	3.62	0.44	1.48	17.8	15.5
OBB	15 Jul	1	1.08	0.03	0.42	0.032 (2.38)	0.83	0.09	1.96	17.1	13.1
	09 Oct	2	0.60	0.06	0.42	0.025 (1.83)	0.99	0.07	2.34	17.9	15.4
PIB	11 Jul	1	1.74	1.23	2.66	0.061 (5.16)	2.60	0.30	0.98	18.1	15.8
	16 Oct	2	2.03	0.37	2.36	0.063 (4.96)	2.86	0.32	1.21	17.5	15.5
PRA	18 Jul	1	1.31	1.09	1.02	0.060 (4.98)	1.06	0.09	1.04	19.9	17.1
	14 Oct	2	2.65	0.23	0.91	0.094 (8.27)	1.66	0.14	1.82	18.2	17.0
SEE	08 Oct	2	1.60	0.44	0.48	0.026 (2.00)	0.53	0.02	1.10	19.4	15.7
SMA	14 Sep	2	1.00	0.22	0.97	0.042 (3.31)	2.03	0.28	2.09	14.6	14.7
TRA	06 Nov	2	1.05	Traces	2.14	0.162 (12.6)	4.58	0.53	2.14	17.3	16.8

varied from 0.2 to 7.8 $\mu\text{g L}^{-1}$ (mean = 1.6 $\mu\text{g L}^{-1}$). In most cases, Chl *a* concentration was higher in the bottom layers (range = 0.5 to 9.9 $\mu\text{g L}^{-1}$; mean = 3.2 $\mu\text{g L}^{-1}$). Total concentration of MAAs in phytoplankton of epilimnetic waters ranged from 0 to 13.4 $\mu\text{g L}^{-1}$ (mean = 1.6 $\mu\text{g L}^{-1}$), while in deeper layers ranged from 0 to 8.6 $\mu\text{g L}^{-1}$ (mean = 1.0 $\mu\text{g L}^{-1}$).

Underwater irradiance—The study sites encompassed a broad range of transparencies in the PAR waveband with K_d

values ranging from 0.08 to 0.65 m^{-1} (epilimnetic values). More than 1% of surface irradiance at 305 nm reached the deepest part of the lake in four cases (GKS, MPL, OPL, and ROT). Moreover, OPL and ROT had the entire lake bottom exposed to more than 10% of surface UVB (at 305 nm). In six other clear water lakes (DRA, GRA, NEG, RED, SEE, and SOS), an important portion of the water body (5–13 m) was exposed to more than 1% of surface UVB radiation (at 305 nm). In these lakes, K_d at 305 nm ranged between 0.23 and 0.88 m^{-1} (Table 3). Lakes below 2,000 m had on average

Table 3. Diffuse attenuation coefficients (K_d) at 305, 320, 340, and 380 nm, and for PAR with corresponding depth ranges for calculation.

Lake	Date (1998)	Depth range (m)	K_d 305 (m ⁻¹)	K_d 320 (m ⁻¹)	K_d 340 (m ⁻¹)	K_d 380 (m ⁻¹)	K_d PAR (m ⁻¹)
Exposed rock							
BAR	10 Sep	0.1–8	1.12	0.94	0.77	0.49	0.25
DRA	22 Jul	0.5*–3.7	0.42	0.23	0.19	0.09	0.12
		5–7	0.84	0.56	0.43	0.29	0.22
GKS	23 Jul	2.1–6	0.23	0.17	na	0.05	0.08
	06 Oct	0.6*–8	0.33	0.24	0.19	0.14	0.13
GRA	10 Sep	0.1–12	0.70	0.55	0.42	0.28	0.16
		12–15	na	1.13	0.83	0.53	0.24
MPL	21 Jul	0.1–4.3	0.75	0.65	0.52	0.29	0.26
	10 Oct	0.1–2.2	0.61	0.50	0.47	0.32	0.30
NEG	09 Sep	0.1–12	0.53	0.38	0.28	0.16	0.11
		13–20	1.16	0.86	0.65	0.36	0.14
OPL	21 Jul	0.1–5.7	0.27	0.19	0.13	0.10	0.16
	10 Oct	1.5†–3	0.26	0.18	0.13	0.10	0.17
RED	08 Sep	0.1–11.4	0.34	0.28	0.22	0.15	0.13
		14–24	0.71	0.49	0.39	0.26	0.15
ROT	23 Jul	1.8–3.2	0.31	0.22	0.17	0.11	0.19
	06 Oct	1.8–3.2	0.36	0.24	0.21	0.14	0.09
SOS	30 Jul	0.1–4	0.41	0.33	0.30	0.20	0.18
		8–10	0.65	0.47	na	0.32	0.20
TOR	09 Sep	0.1–3	3.46	2.50	1.98	1.20	0.48
Meadows							
KLA	18 Jul	0.1–2.1	2.17	1.65	na	0.94	0.49
	14 Oct	0.1–2	1.86	1.50	1.21	0.77	0.10
LIC	15 Jul	0.1–5.6	3.13	2.15	1.78	1.04	0.30
	09 Oct	0.1–5.2	5.62	4.34	3.73	2.38	0.52
LLA	12 Sep	0.1–4.8	1.39	1.07	0.81	0.47	0.23
OBR	17 Jul	0.1–18.2	1.16	0.87	0.66	0.39	0.19
	13 Oct	1*–25	1.41	1.09	0.90	0.56	0.21
PJO	24 Jul	0.1–2	1.61	1.45	1.02	0.79	0.54
Trees							
ACH	11 Jul	0.1–6.5	3.69	2.64	1.93	1.07	0.37
	12 Oct	0.1–18	3.53	2.24	1.77	0.94	0.22
ANT	17 Jul	0.1–2.5	2.41	1.89	1.60	1.19	0.65
	13 Oct	0.1–5	1.24	0.97	0.82	0.60	0.36
DUR	19 Jul	0.1–8.7	2.02	1.69	0.98	0.89	0.35
	15 Oct	0.1–10.5	1.78	1.36	1.08	0.65	0.24
MON	05 Nov	0.1–8	6.32	4.41	3.08	1.82	0.43
OBB	15 Jul	0.1–1.7	2.03	1.64	1.52	1.12	0.62
	09 Oct	0.1–8.4	1.07	0.84	0.67	0.43	0.23
PIB	11 Jul	0.1–6.9	3.97	2.80	1.99	1.09	0.34
	16 Oct	0.1–6.5	4.76	3.32	2.53	1.43	0.38
PRA	18 Jul	0.1–4.8	1.90	1.37	0.95	0.56	0.32
	14 Oct	0.1–6	3.19	2.01	1.62	1.06	0.50
SEE	08 Oct	1.8*–6.5	0.88	0.60	0.43	0.22	0.12
SMA	14 Sep	0.1–8.1	2.77	2.21	1.67	0.98	0.27
TRA	06 Nov	0.2–7	na	5.73	4.22	2.31	0.49

* Data above this depth were removed from the regression because of irregularities in cloud conditions.

† Data above this depth were removed from the regression because of irregularities caused by profiling from an ice hole (ice thickness = 2–3 cm).

na, not available.

2.2 m of the water column exposed to more than 1% UVB (range of 0.7–5.2 m).

Correlation between UV attenuation and water optical properties—The attenuation coefficient of UVR at 320 nm

was chosen to illustrate the relationship between UV transparency and the optical properties of lake water. The other nominal UV wavelengths measured with the PUV radiometer lead to similar conclusions. We found a strong positive correlation between K_d and the absorptivity of CDOM at 320

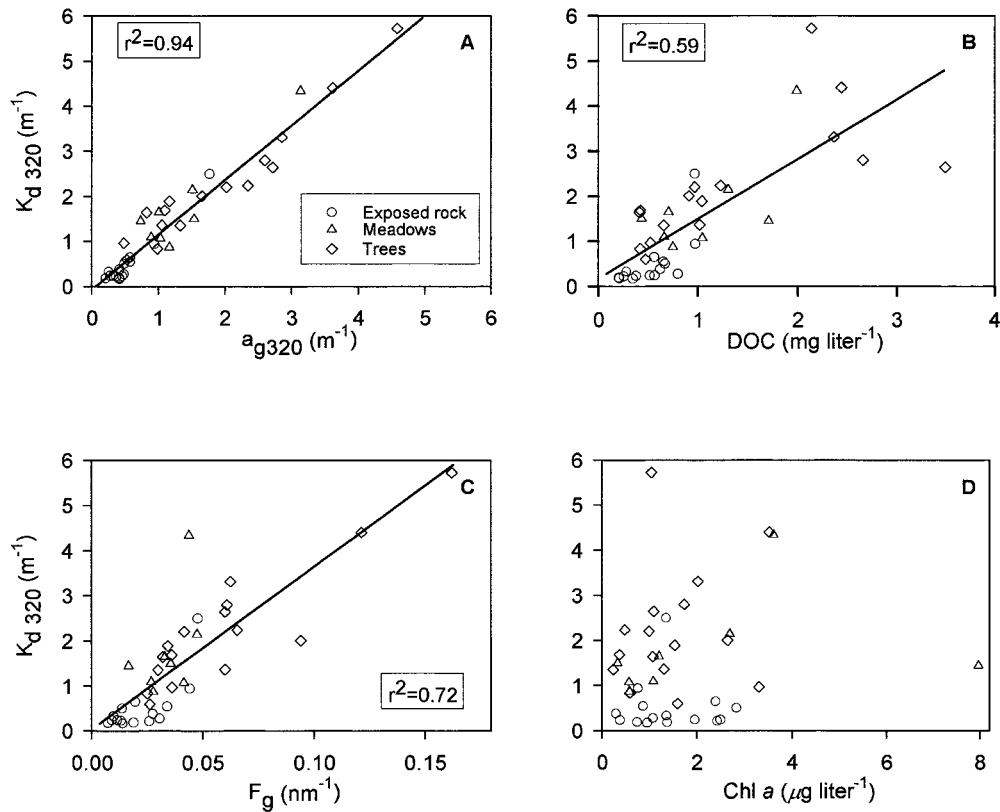


Fig. 2. Plots of diffuse attenuation coefficients measured at 320 nm (K_d 320) against (A) CDOM absorptivity at 320 nm (a_g 320), (B) DOC, (C) CDOM fluorescence (F_g), and (D) Chl *a* concentration.

nm ($r^2 = 0.94$, $P < 0.001$, $n = 39$; Fig. 2A). Other variables such as DOC (Fig. 2B) and fluorescence of CDOM (F_g ; Fig. 2C) gave weaker correlations ($r^2 = 0.59$ and 0.72 , respectively; $P < 0.001$). Chlorophyll *a* (Fig. 2D) and total MAA concentrations were not significantly correlated with the attenuation coefficients of UVR ($P > 0.05$). However, Chl *a* showed a weak but significant correlation with K_d for PAR ($r^2 = 0.174$; $P = 0.008$). Part of the residual variability in K_d might be associated with inorganic particles. For example, in Obernbergersee (OBB), DOC was only 0.4 mg L^{-1} while K_d reached 1.64 m^{-1} at 320 nm. This lake had a characteristic whitish color (like ACH, ANT, or PRA), most likely coming from precipitates of carbonates that may contribute to the elevated light attenuation (high scattering).

A redundancy analysis of the optical variables was also performed with other nonoptical variables used as explanatory variables (epilimnetic-water data set; Fig. 3, Table 4). The overall test and the first two axes were significant ($P \leq 0.002$), but most of the variability was explained by the first axis (72%) that was characterized by UV attenuation (K_d), a_g , and F_g (Table 4). The explanatory variables associated with this axis were the DOC concentration, the elevation and the categorical variable exposed rock (Table 4). A second source of variation, associated with the second axis, was characterized by a_g^* that was positively correlated with the catchment-to-lake area ratio and negatively with Chl *a*.

CDOM optical properties—The DOC-specific absorptivity (a_g^*) varied from 0.43 to $3.51 \text{ L mg}^{-1} \text{ m}^{-1}$ (at 320 nm; mean = $1.36 \text{ L mg}^{-1} \text{ m}^{-1}$). The slope parameter S ranged between 10.8 and $20.9 \mu\text{m}^{-1}$ and 6.1 and $18.9 \mu\text{m}^{-1}$ in the wavebands 295–400 nm and 370–500 nm, respectively. To test the influence of DOM sources (autochthonous versus allochthonous) on CDOM optical properties, we compared a_g^* and S in the lakes located at high elevations and having low allochthonous CDOM inputs from the catchment (exposed rock category) to the lakes influenced by allochthonous inputs (meadows and trees categories pooled). When comparing epilimnetic values, a_g^* (at 320 nm) in lakes with low allochthonous inputs were significantly lower than in lakes influenced by allochthonous inputs (average of $1.02 \text{ L mg}^{-1} \text{ m}^{-1}$ compared to $1.56 \text{ L mg}^{-1} \text{ m}^{-1}$, respectively; $P = 0.009$). However, when the deep values were compared, no significant difference was found between the two groups of lakes (average of 1.63 and $1.52 \text{ L mg}^{-1} \text{ m}^{-1}$, respectively; $P = 0.652$). On the other hand, S (range 370–500 nm) was slightly but not significantly lower ($P = 0.067$) in lakes from the exposed rock category than in lakes surrounded by meadows or with forested catchments (an average of 12.7 compared to $14.5 \mu\text{m}^{-1}$, respectively). The same comparison for S calculated in the range 295–400 nm did not yield significant differences (using epilimnetic or deeper water data sets).

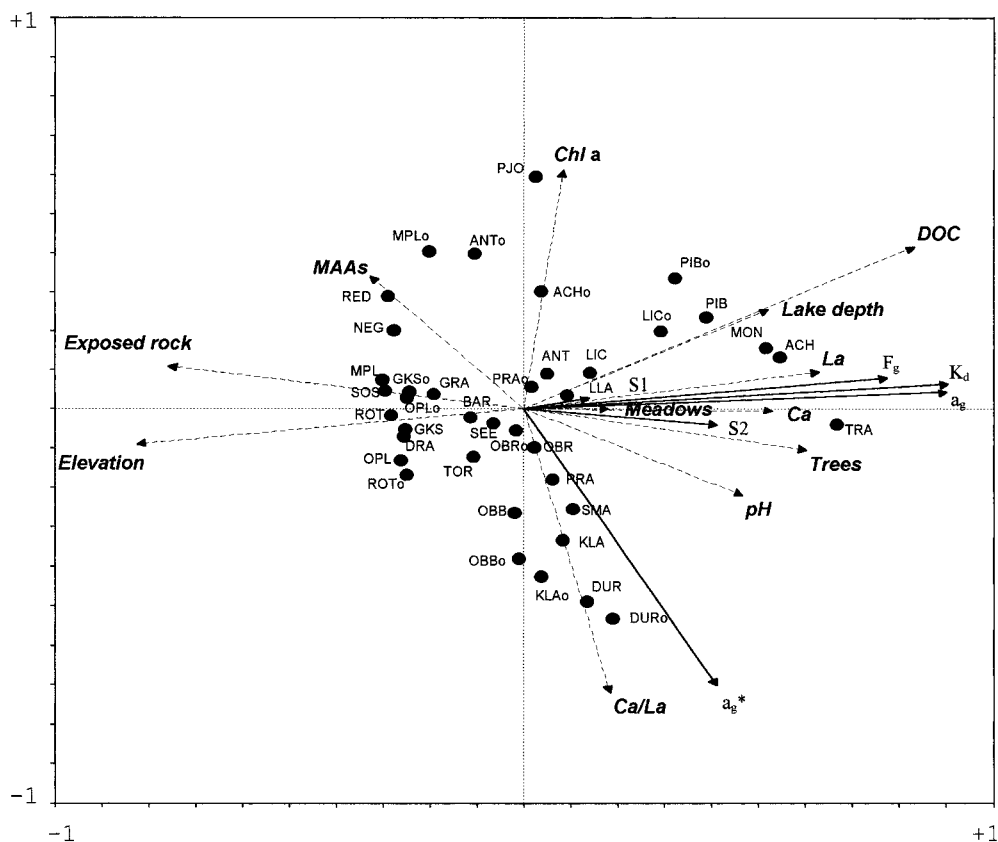


Fig. 3. RDA ordination biplot of the optical variables. The numerical results are given in Table 4. Each lake is represented by a black dot (the lakes sampled a second time in October have the letter o at the end of the abbreviation). Solid arrows represent the independent variables (or optical variables) and the dotted arrows, the explanatory variables.

To test the influence of photobleaching on UV attenuation, we examined the vertical and seasonal change in a_g^* and S . The DOC-specific absorptivity at 320 nm was found to be significantly lower in surface compared to deeper water layers (averages of 1.34 and 1.56 L mg⁻¹ m⁻¹, respectively; $P = 0.017$). When the data from July and October were analyzed separately, significant differences were found in October ($P = 0.009$) but not in July ($P = 0.432$). On the other hand, one third of the lakes showed higher S at the surface, one third lower S , and one third showed no difference. Furthermore, half of the 13 lakes sampled two times during the year showed lower S in October than in July (comparing surface values), while the other half showed no change or had higher values (Table 2).

Within-lake variation in UV attenuation—In some of the lakes studied, K_d changed significantly with depth. Deep penetration of UVR and sensitive instruments are indispensable conditions to observe such changes. These clear and deep lakes offer an opportunity to relate changes in UV attenuation coefficients with vertical gradients in phytoplankton concentration or with changes within the DOM pool (caused by autochthonous processes or photobleaching). These examples are illustrated by Schwarzsee ob Sölden (SOS) in the Alps and Estany Redo (RED) in the Pyrenees.

SOS (2,799 m a.s.l., maximum depth of 18 m) was highly

transparent to UVR, with more than 10 m of the water column exposed to more than 1% of surface radiation at 320 nm. The lake was stratified on 30 July (thermocline at 5 m; Fig. 4) with a Chl a concentration lower than 2 $\mu\text{g L}^{-1}$ in the epilimnion (Table 5). Yet, Chl a and total MAAs increased with depth (up to 8.5 and 7.1 $\mu\text{g L}^{-1}$ at 13.5 m, respectively), whereas DOC, F_g , a_g , and a_g^* showed no significant vertical changes ($P > 0.05$). However, K_d at all wavelengths significantly increased with depth (e.g., at 320 nm; $r^2 = 0.97$; $P = 0.006$).

In RED, the seasonal thermocline was found at 14 m depth (Fig. 5). The epilimnion was well mixed and the deep Chl a maximum was located at approximately 29 m, as indicated by the peak in naturally induced fluorescence (normalized to PAR and given in relative units). The lake water was sampled at 2, 10, 25, and 35 m depth (Table 6). Intense rainfall before sampling likely explains the higher DOC concentration found in surface waters (0.80 and 0.66 mg DOC L⁻¹ at 2 and 10 m, respectively; same tendency for a_g and F_g), while no significant change in K_d was found in the whole epilimnion. However, all K_d s for UVR increased significantly in the hypolimnion (an increase of 78% relative to the epilimnetic value at 320 nm), while K_d for PAR did not change. This increase in K_d s was accompanied by the increase of Chl a concentration (from ~ 1 to 2.3 $\mu\text{g L}^{-1}$) and in a_g and a_g^* (ca. two and three times higher, respectively)

Table 4. Results of the redundancy analysis: variance explained by the first two axes (eigenvalues), eigenvectors for the optical variables (solid arrows in Fig. 3), and correlations of the explanatory variables with the first two axes (dashed arrows in Fig. 3).

	Axis 1	Axis 2
Eigenvalues	0.720	0.075
Optical variables		
a_g (320 nm)	0.902	0.041
K_d (320 nm)	0.903	0.064
F_g	0.775	0.080
a_g^* (320 nm)	0.412	-0.703
S1 (295–400 nm)	0.139	0.028
S2 (370–500 nm)	0.410	-0.043
Explanatory variables		
Elevation	-0.753	-0.072
Lake depth	0.477	0.203
Ca	0.485	-0.004
La	0.576	0.076
Ca/La	0.168	-0.575
pH	0.426	-0.177
Chl <i>a</i>	0.078	0.490
MAAs	-0.300	0.272
DOC	0.761	0.331
Exposed rock	-0.693	0.088
Meadows	0.163	-0.001
Trees	0.552	-0.086

but not by significant changes in DOC or F_g (DOC actually decreased, and F_g increased at 35 m only). Finally, the total MAA concentration decreased drastically in the hypolimnion (Table 6). In lakes GRA and NEG, similar results were observed, except that the changes in DOC and F_g coincided with the changes in a_g and a_g^* (data not shown).

Discussion

Underwater irradiance—The lowest attenuation of UVR in our series of lakes (e.g., at 305 nm $K_d = 0.23 \text{ m}^{-1}$ in GKS) was comparable to the lowest values reported in the literature: 0.19 m^{-1} at Laguna Negra (Cabrera et al. 1997), 0.17 m^{-1} at Lake Schmoll (Morris et al. 1995), and 0.08 m^{-1} at Lake Vanda, in Antarctica (Vincent et al. 1998b). Almost all lakes in the exposed rock category had an important portion of the water column exposed to significant UVR (i.e.,

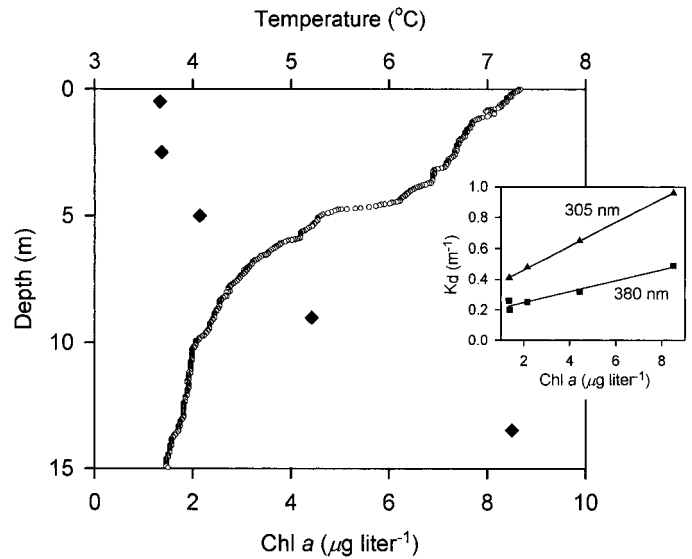


Fig. 4. Depth profile of temperature (circles) and Chl *a* concentration (diamonds) in Schwarzsee ob Sölden. Insert: plots of diffuse attenuation coefficients at 305 and 380 nm versus Chl *a* concentration in water sampled at five depths. For other water column measurements, refer to Table 5.

exposed to more than 1% of surface irradiance). Alpine lakes clearly offer reduced UV refuges for many aquatic organisms (Williamson et al. 1996; Sommaruga et al. 1999b). Understanding the factors that control the attenuation of UVR in these systems will help to estimate the consequences of ozone depletion and climatic warming.

Correlation between UV attenuation and water optical properties—Both the individual correlations obtained between UV attenuation and the measured optical properties of lake water, and the redundancy analysis integrating all measured variables clearly showed that CDOM explains most of the variability in the attenuation of UVR among lakes, even under low DOC concentrations. The estimation of UV attenuation by measurements of filtered lake-water absorption can be useful when direct measurements are not possible. DOC has often been used to estimate UV transparency in lowland lakes, but our series of data shows cases where the attenuation is higher or lower than the DOC concentration would predict. Moreover, CDOM fluorescence

Table 5. Schwarzsee ob Sölden: water optical properties (Chl *a*, MAAs, DOC, F_g , a_g , and DOC-specific a_g at 320 nm) and K_d values calculated in water slices of 1–3 m corresponding to the five depths where the water was sampled. Values in italics were calculated on irradiance values approaching the detection limit of the instrument.

Depth (m)	Chl <i>a</i> ($\mu\text{g L}^{-1}$)	MAAs ($\mu\text{g L}^{-1}$)	DOC (mg L^{-1})	F_g (nm^{-1})	a_g (m^{-1})	a_g^* (L mg DOC ⁻¹ m ⁻¹)	K_d (m^{-1})				
							305 nm	320 nm	340 nm	380 nm	PAR
0.5	1.33	3.70	0.29	0.011	0.25	0.86	0.41	0.32	0.29	0.26	0.22
2.5	1.36	4.69	0.29	0.010	0.25	0.88	0.41	0.33	0.30	0.20	0.18
5	2.14	8.75	0.28	0.013	0.21	0.75	0.48	0.42	0.39	0.25	0.20
9	4.42	8.80	0.29	0.012	0.21	0.72	0.65	0.47	0.43	0.32	0.20
13.5	8.50	7.13	0.30	0.014	0.28	0.91	0.96	0.68	0.65	0.49	0.30

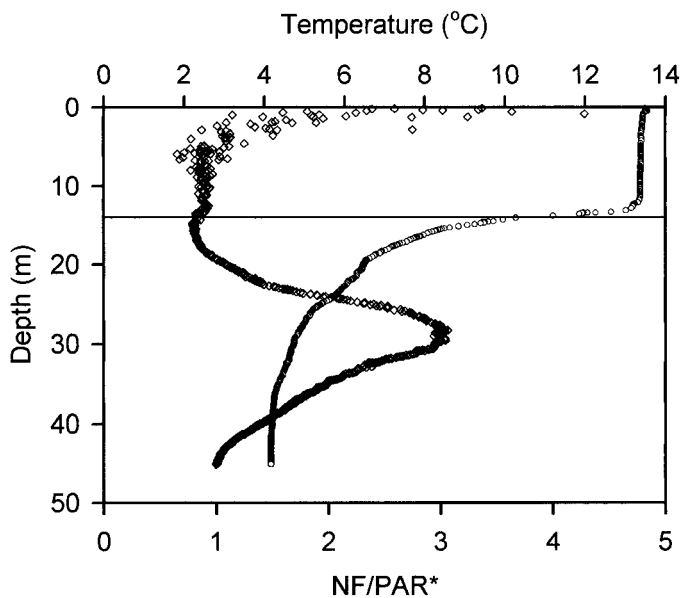


Fig. 5. Depth profile of temperature (circles) and naturally induced fluorescence (diamonds; NF/PAR^* = upwelling radiance centered at 683 nm divided by PAR and normalized to 1 at 45 m) in Estany Redo. For water column measurements, refer to Table 6.

that is known to be more sensitive than DOC measurements and that was found to predict K_d with great accuracy in a series of Canadian subarctic lakes ($r^2 = 0.98$; Laurion et al. 1997) only explained 72% of K_d variability in our study. These results suggest that the nonchromophoric fraction of DOC was variable, and that photochemical processes may have influenced the optical properties of CDOM. The fluorescence (F_g) per unit absorption (a_g at 320 nm) was highly variable (coefficient of variation of 41%) and significantly higher in lakes from the exposed rock category than in lakes from the meadows and trees categories ($P = 0.036$). This ratio has been used as an indicator for the composition and the molecular weight distribution of the DOC (Hautala et al. 2000 and references therein). Lake water pH that varies significantly in our series of lakes is known to influence the quenching of fluorescence due to metal complexation (Laane 1982) and might account for these variations (Donahue et al. 1998).

Chlorophyll *a* and total MAA concentration per se were not good predictors of UVR attenuation in epilimnetic waters

of these mountain lakes. The variability in phytoplankton composition, self-shading (cell size distribution), and acclimation state may, at least partly, explain this low correlation. Although MAAs showed a low correlation with both axes of the RDA, they were found in higher concentration in lakes with low K_d and located at high elevation (see Fig. 3), suggesting a photoprotection response to high UV exposure. On the other hand, it seems that the phytoplankton had some influence on the lake optical conditions through its influence on the DOC-specific absorptivity of CDOM (see below). Furthermore, the contribution of phytoplankton to the attenuation of UVR became apparent in clear lakes (e.g., SOS) when analyzing the changes in the water column (see *Within-lake variation in UV attenuation*).

The linear regression fit between K_d and a_g (at 320 nm) was: $K_d = 1.22 a_g - 0.06$ (SE for the slope is 0.05; for the intercept, 0.08). In a study of seasonal variations of lake UV transparency, this relationship gave similar results: $K_d = 1.27 a_g + 0.3$ (Morris and Hargreaves 1997; use of 0.2- μm pore size filters for DOM; K_d range between 0.3 and 20 m^{-1}). However, in a large data set of 65 lakes in North and South America, Morris et al. (1995) obtained the following relationship: $K_d = 1.51 a_g - 0.12$ ($r^2 = 0.84$; K_d ranges between 0.14 and 67 m^{-1}). These empirical equations are likely to differ between different types of environments and consequently should be used with caution. Moreover, the changes of K_d in the water column (e.g., caused by the presence of algal layers) can have important consequences on the estimation of UVR reaching the benthic communities. Therefore, the application of this model is limited to the epilimnetic waters. The estimation of K_d as a function of wavelength can also be obtained from empirical exponential models (as in Morris et al. 1995; Laurion et al. 1997; Markager and Vincent 2000), but such extrapolations may be subject to errors.

CDOM optical properties—To characterize CDOM optical properties, different authors have used the absorption and fluorescence of CDOM (excitation/emission matrix, fluorescence efficiency; Coble et al. 1990; Hautala et al. 2000) and the shape of the absorption spectra (the slope parameter S). The DOC-specific absorptivity provides an additional means for distinguishing the sources and types of CDOM (Blough and Green 1995 and references therein). The spectral slope parameter has been related to the source (freshwater versus marine or allochthonous versus autochthonous; Blough et al.

Table 6. Estany Redo: water optical properties (Chl *a*, total MAAs, DOC, F_g , a_g , and DOC-specific a_g at 320 nm) and K_d values calculated in water slices of 2–5 m corresponding to the four depths where the water was sampled. Values in italics were calculated on irradiance values approaching the detection limit of the instrument.

Depth (m)	Chl <i>a</i> ($\mu\text{g L}^{-1}$)	MAAs ($\mu\text{g L}^{-1}$)	DOC (mg L^{-1})	F_g (nm^{-1})	a_g (m^{-1})	a_g^* ($\text{L mg DOC}^{-1} \text{m}^{-1}$)	K_d (m^{-1})				
							305 nm	320 nm	340 nm	380 nm	PAR
2	1.08	5.56	0.80	0.031	0.48	0.60	0.34	0.27	0.25	0.15	0.16
10	0.94	4.25	0.66	0.029	0.35	0.52	0.34	0.29	0.23	0.17	0.13
25	2.11	0.20	0.53	0.028	0.92	1.75	<i>0.79</i>	0.48	0.39	0.25	0.14
35	2.57	0.16	0.49	0.051	0.71	1.47	—	—	<i>0.51</i>	0.29	0.15

1993), the composition (fulvic versus humic acids; Carder et al. 1989), and the photochemical transformation of CDOM (photobleaching; Morris and Hargreaves 1997; Vodacek et al. 1997; Whitehead et al. 2000).

The values of a_g^* found in our study fall within the range of values reported in Morris et al. (1995; a_g^* at 320 nm = 0.20–2.66 L mg⁻¹ m⁻¹) for a similar range of DOC concentrations ($n = 40$; average of 1.46 mg L⁻¹). We observed that the DOC-specific absorptivity was significantly lower in lakes influenced by autochthonous sources (as assumed for those in the exposed rock category) than in lakes influenced by allochthonous sources (meadows and trees categories). For example, the lowest value of a_g^* was found in PJO, a lake at high elevation partially surrounded by meadows, with a catchment-to-lake area ratio of 7, and showing high Chl *a* concentration (7.8–9.9 mg L⁻¹). DOM derived from autochthonous sources is known to be less aromatic and to contain a lower fraction of fulvic acids than the allochthonous DOM and consequently has lower DOC-specific absorptivity (McKnight et al. 1994; Morris et al. 1995). In the RDA, a second source of variation within this lake series was associated with a_g^* (7% of total variance) that was negatively correlated with Chl *a* and positively with the catchment-to-lake area ratio. This ratio can be considered as an index of the contribution of allochthonous material to the DOM pool, while Chl *a* represents the autochthonous contribution. On the other hand, the difference in a_g^* when deep values were compared (exposed rock category versus meadows + trees categories) was not significant. Because the Chl *a* concentration was generally higher in deeper waters, the influence of the algal CDOM source on a_g^* was expected to be larger in these layers; especially when the inputs from the catchment are not dominant. Therefore, it is difficult to attribute the differences found in surface waters exclusively to CDOM sources.

In the marine environment, the lower aromatic carbon content of DOM is associated with higher *S* values caused by decreased levels of chromophores having extended aromatic systems (i.e., absorbing at higher wavelengths; see Blough and Green 1995 for an extended discussion on these aspects). In our series of lakes, a comparison of *S* in lakes with different dominance in catchment vegetation does not support this observation, because we did not obtain significant differences between lakes with low versus high allochthonous influence (the averaged epilimnetic *S* value for the waveband 370–500 nm was actually lower in lakes with low allochthonous influence; $P = 0.067$). In our series of lakes, *S* varied greatly, a variability also reported for low-DOM systems (Markager and Vincent 2000). In addition, there were cases where *S* was particularly low at the lake surface (e.g., Estany Redo with 6.1 μm⁻¹ and Drachensee with 7.2 μm⁻¹), i.e., below the range given in the review by Markager and Vincent (2000) for lakes (9.2–36.2 μm⁻¹) or marine waters (11.5–18 μm⁻¹).

Lakes at high elevation are exposed to higher fluence rates and have deeper penetration of UVR than lowland lakes. The lower values of epilimnetic a_g^* found in lakes situated at higher elevations is in agreement with an increased role of photobleaching in these transparent systems. This is supported by the fact that the same comparison (i.e., between

exposed rock and meadows + trees) of a_g^* in deep layers, i.e., of waters less influenced by photolysis, did not show significant differences. Furthermore, for all categories merged, surface values of a_g^* were significantly lower than in deep layers. However, the same comparison for *S* did not yield any significant differences to support this hypothesis. Vodacek et al. (1997) have shown that photobleaching of marine coastal waters causes an increase in *S*, while Twardowski and Donaghay (1998) showed increases in *S* as a function of radiation dosage. These authors suggested that the increase in *S* is caused by a shift in the absorption spectrum to lower wavelengths when large humic complexes are broken down. On the other hand, Morris and Hargreaves (1997) also found a correlation between UV doses and CDOM properties in lake systems, but these authors found lower *S* values in surface waters and a declining *S* during summer (*S* was calculated over a wider range: 280–700 nm). These contrasting results underline the complexity of factors and processes involved in the accumulation and decomposition of organic matter. Most likely, the signature left by photobleaching is continually altered by the input of fresh CDOM. For example, the difference found between surface and deep a_g^* values is no longer significant when data in July are tested separately. The input of fresh CDOM to surface waters during snowmelt in July likely explains the higher values of a_g and a_g^* sometimes found in the upper first meter of the water column and the absence of a clear depth gradient caused by photobleaching. The contrasting mixing and flushing rates in such a series of lakes create a variety of scenarios that may preclude finding any consistent relationships between *S*, UV exposure, and the source of CDOM. Whitehead et al. (2000) recently demonstrated the importance of mixing rates on CDOM absorbance losses, with larger absorbance losses in fast mixing systems. Moreover, a recent study showed how the ionic conditions may influence photobleaching rates (Reche et al. 1999). Their results indicate that humic substances are more susceptible to photobleaching in alkaline lakes. The varying pH in our lake series indicates another source of variability in the relationships between a_g^* , *S*, catchment type, and UV exposure.

Within-lake variation in UV attenuation—The deep penetration of UVR in two stratified lakes gave us the opportunity to relate in-lake differences in UV attenuation with the optical water properties. These examples highlight the importance of considering phytoplankton and/or photobleaching when evaluating UV exposure in mountain lakes. For instance, phytoplankton was shown to contribute significantly to UV attenuation in SOS, a lake with very low DOM concentration. In this lake, UV attenuation and Chl *a* concentration clearly increased with depth, while no changes were observed in any of the filtered lake-water measurements (DOC, F_g , and a_g). Moreover, high concentrations of UV-absorbing compounds were found in phytoplankton of SOS (3.7–8.8 μg MAAs L⁻¹; Table 5). These results suggest that the phytoplankton biomass was responsible for this increase in UV attenuation. However, the use of total MAA concentration (as extracted in a solvent) is not appropriate to estimate K_d (the correlation between K_d and MAAs was not significant). In GKS, Sommaruga and Psenner (1997)

also observed that the increase in UV-attenuation coefficients at depth was accompanied by the formation of a deep Chl *a* maximum. A study of 48 alpine lakes of the same region showed that Chl *a* concentration was indeed correlated to total phytoplankton biomass ($r^2 = 0.94$, $P < 0.001$; Sommaruga et al. 1999a). SOS is an example where the estimation of UV attenuation using DOC (or any other filtered water properties) would lead to a large overestimation of the radiation reaching deeper waters.

We also found evidence of the importance of photobleaching on UV attenuation. In RED, the lower K_d values in the epilimnion were accompanied by lower a_g and a_g^* . The lake was sampled in September, when the whole epilimnion was well mixed and exposed to more than 1% of surface UVB (at 305 nm). Bulk measurements of DOC did not provide information on the behavior of UVR despite the large difference observed in K_d . Moreover, the lower concentration of Chl *a* in the epilimnion (a difference of $\sim 1 \mu\text{g Chl } a \text{ L}^{-1}$) seems insufficient to explain such differences in K_d . In addition, the concentration in UV-absorbing compounds (MAAs) was two orders of magnitude higher in the epilimnion. In a clear lake of northeastern Pennsylvania (Morris and Hargreaves 1997), K_d in the epilimnion decreased by midsummer to 24% of the spring value. Likewise, in the study of Vodacek et al. (1997), up to 70% of the CDOM absorption and fluorescence was lost through photobleaching from the river mouth to the outer shelf. Hence, a loss of 40–50% in UV transparency seems reasonable for a several week exposure to high fluence rates (stratification began in July). Interestingly, in our case, S was lower in the epilimnion compared to deeper water values (6.1, 10.5, 15.2, and $18.8 \mu\text{m}^{-1}$ at 2, 10, 25, and 35 m depth, respectively) that do not support the results obtained in marine waters (Vodacek et al. 1997; Twardowski and Donaghay 1998).

Implications of climatic changes for alpine lakes—The penetration of UVR in alpine lakes is comparable to values found in the open oligotrophic ocean (Smith and Baker 1981) and is among the highest reported for lake environments (Kirk 1994; Morris et al. 1995; Vincent et al. 1998b). Especially in clear water lakes, a small change in CDOM would likely lead to major changes in water column UVB and UVA radiation (Williamson et al. 1996) and in the biologically important UVR/visible spectral balance (Laurion et al. 1997). Changes in climate, lake hydrology, acid deposition, and other environmental factors can alter DOM concentrations in lakes (declining DOM; Schindler et al. 1996; Yan et al. 1996; Schindler and Curtis 1997) and may be more important than stratospheric ozone depletion in controlling UV exposure (Williamson et al. 1996; Vincent et al. 1998a; Gibson et al. 2000). However, the quantity and direction of changes in climate are expected to be site specific (Sommaruga-Wögrath et al. 1997). Alpine lakes are highly responsive to climatic warming (Sommaruga-Wögrath et al. 1997). In these systems, the export of DOM and nutrients from the catchment to the lakes is expected to increase with climatic warming (increased UV protection by CDOM, increased phytoplankton biomass), but the earlier disappearance of the lake ice and snow cover in spring may increase the accumulated UV exposure during the ice-free season

(Sommaruga et al. 1999a). The importance of CDOM in controlling the variability in UV radiation experienced by the aquatic biota emphasizes the need to better understand its sources and fate.

Conclusion

With this study, we demonstrated that the variability in UV attenuation among lakes situated on an altitudinal gradient is controlled by CDOM, despite the large variability in the source and nature of their organic carbon inputs. The absorption of filtered lake water was found to be the best predictor of UV attenuation in epilimnetic waters of alpine lakes. However, phytoplankton cells contributed significantly to the attenuation of UVR in deeper waters, when the algal biomass was important and the DOM concentration was low. However, variations in the community composition, the abundance of UV-absorbing compounds, and the photoacclimation state most likely will affect the absorption properties of phytoplankton and the relationship between UV attenuation and phytoplankton biomass.

Our results also indicate that CDOM photobleaching can become important in certain cases, and needs to be considered carefully in alpine lakes. High incident flux and deep penetration of UVR in these lakes, in combination with thermal stratification, can have profound effects on UV transparency. Especially in shallow mountain lakes (like GKS, MPL, OPL, and ROT), the impact of photobleaching on UV transparency and its positive feedback action may exacerbate the damaging effects of UVR. The differing importance of photobleaching might explain the differences between empirical models on UV attenuation found in the literature. In this study, DOC-specific absorptivity was shown to vary considerably among and within lakes. We suggest that the great variability in CDOM optical properties found in mountain lake systems depends on differing sources and biotransformation of CDOM but also on varying UV exposure, light history, lake-water pH, mixing regimes, and flushing rates.

References

- ALLARD, B., H. BORÉN, C. PETTERSSON, AND G. ZHANG. 1994. Degradation of humic substances by UV irradiation. *Environ. Int.* **20**: 97–101.
- BENNER, R., AND M. STROM. 1993. A critical evaluation of the analytic blank associated with DOC measurements by high-temperature catalytic oxidation. *Mar. Chem.* **41**: 153–160.
- BIDIGARE, R. R. 1989. Potential effects of UV-B radiation on marine organisms of the southern ocean: Distributions of phytoplankton and krill during austral spring. *Photochem. Photobiol.* **50**: 469–477.
- BLOUGH, N. V., AND S. A. GREEN. 1995. Spectroscopic characterization and remote sensing of non-living organic matter, p. 23–45. *In* R. G. Zepp and C. Sonntag [eds.], *The role of non-living organic matter in the earth's carbon cycle*. Wiley.
- , O. C. ZAFIROU, AND J. BONILLA. 1993. Optical absorption spectra of waters of the Orinoco River outflow: Terrestrial input of colored organic matter to the Caribbean. *J. Geophys. Res.* **98**: 2271–2278.
- BLUMTHALER, M., AND W. AMBACH. 1990. Indication of increasing solar ultraviolet-B radiation flux in alpine region. *Science* **248**: 206–208.

- CABRERA, S., M. LÓPEZ, AND B. TARTAROTTI. 1997. Phytoplankton and zooplankton response to ultraviolet radiation in a high-altitude Andean lake: Short- versus long-term effects. *J. Plankton Res.* **19**: 1565–1582.
- CARDER, K. L., R. G. STEWARD, G. R. HARVEY, AND P. B. ORTNER. 1989. Marine humic and fulvic acids: Their effects on remote sensing of ocean chlorophyll. *Limnol. Oceanogr.* **34**: 68–81.
- CAREFOOT, T. H., M. HARRIS, B. E. TAYLOR, D. DONOVAN, AND D. KARENTZ. 1998. Mycosporine-like amino-acids: Possible UV protection in eggs of the sea hare *Aplysia dactylomela*. *Mar. Biol.* **130**: 389–396.
- COBLE, P. G., S. A. GREEN, N. V. BLOUGH, AND R. B. GAGOSION. 1990. Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy. *Nature* **348**: 432–435.
- DONAHUE, W. F., D. W. SCHINDLER, S. J. PAGE, AND M. P. STANTON. 1998. Acid-induced changes in DOC quality in an experimental whole-lake manipulation. *Environ. Sci. Technol.* **32**: 2954–2960.
- DUNLAP, W. C., D. MCB. WILLIAMS, B. E. CHALKER, AND A. T. BANASZAK. 1989. Biochemical photoadaptations in vision: UV-absorbing pigments in fish eye tissues. *Comp. Biochem. Physiol.* **93B**: 601–607.
- GIBSON, J. A. E., W. F. VINCENT, B. NIEKE, AND R. PIENITZ. 2000. Biological exposure to UV radiation in the Arctic Ocean: The relative importance of ozone versus riverine dissolved organic carbon. *Arctic*. In press.
- GREEN, S. A., AND N. V. BLOUGH. 1994. Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. *Limnol. Oceanogr.* **39**: 1903–1916.
- HALAC, S., M. FELIP, L. CAMARERO, S. SOMMARUGA-WÖGRATH, R. PSENNER, J. CATALÁN, AND R. SOMMARUGA. 1997. An *in situ* enclosure experiment to test the solar UV-B impact on microplankton in a high-altitude mountain lake. I. Lack of effect on phytoplankton species composition and growth. *J. Plankton Res.* **19**: 1671–1686.
- HANNACH, G., AND A. C. SIGLEO. 1998. Photoinduction of UV-absorbing compounds in six species of marine phytoplankton. *Mar. Ecol. Prog. Ser.* **174**: 207–222.
- HAUTALA, K., J. PEURAVUORI, AND K. PIHLAJA. 2000. Measurement of aquatic humus content by spectroscopic analyses. *Water Res.* **34**: 246–258.
- HEDGES, J. I. 1988. Polymerization of humic substances in natural environments, p. 45–58. *In* F. H. Frimmel and R. F. Christman [eds.], *Humic substances and their role in the environment*. Wiley.
- HOLMES, R. W., P. M. WILLIAMS, AND R. W. EPPLEY. 1967. Red water in La Jolla Bay, 1964–1966. *Limnol. Oceanogr.* **12**: 503–512.
- JEFFREY, S. W., AND G. F. HUMPHREY. 1975. New spectrophotometric equations for determining chlorophylls a, b and c and c1 in higher plants, algae and natural phytoplankton. *Biochem. Physiol. Pflanz.* **167**: 191–194.
- JERLOV, N. G. 1968. *Optical oceanography*. Elsevier.
- KAHRU, M., AND B. G. MITCHELL. 1998. Spectral reflectance and absorption of a massive red tide off Southern California. *J. Geophys. Res.* **103**: 21601–21609.
- KARENTZ, D., F. S. MCEUEN, M. C. LAND, AND W. C. DUNLAP. 1991. Survey of mycosporine-like amino acid compounds in Antarctic marine organisms: Potential protection from ultraviolet exposure. *Mar. Biol.* **108**: 157–166.
- KIEBER, R. J., X. ZHOU, AND K. MOPPER. 1990. Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea. *Limnol. Oceanogr.* **35**: 1503–1515.
- KIRK, J. T. O. 1994. Optics of UV-B radiation in natural waters. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* **43**: 1–16.
- LAANE, R.W.P.M. 1982. Influence of pH on the fluorescence of dissolved organic matter. *Mar. Chem.* **11**: 395–401.
- LAURION, I., W. F. VINCENT, AND D. R. S. LEAN. 1997. Underwater ultraviolet radiation: Development of spectral models for northern high latitude lakes. *Photochem. Photobiol.* **65**: 107–114.
- LEE, C., AND S. M. HENRICH. 1993. How the nature of dissolved organic matter might affect the analysis of dissolved organic carbon. *Mar. Chem.* **41**: 105–120.
- MARKAGER, S., AND W. F. VINCENT. 2000. Spectral light attenuation and the absorption of UV and blue light in natural waters. *Limnol. Oceanogr.* **45**: 642–650.
- McKNIGHT, D. M., E. D. ANDREWS, S. A. SPAULDING, AND G. R. AIKEN. 1994. Aquatic fulvic acids in algal-rich Antarctic ponds. *Limnol. Oceanogr.* **39**: 1972–1979.
- MORAN, M. A., W. M. SHELDON, AND J. E. SHELDON. 1999. Biodegradation of riverine organic carbon in five estuaries of the southeastern United States. *Estuaries* **22**: 55–64.
- MORRIS, D. P., AND B. R. HARGREAVES. 1997. The role of photochemical degradation of dissolved organic matter in regulating UV transparency of three lakes on the Pocono Plateau. *Limnol. Oceanogr.* **42**: 239–249.
- , H. ZAGARESE, C. E. WILLIAMSON, E. G. BALSEIRO, B. R. HARGREAVES, B. MODENUTI, AND C. QUEIMALIÑOS. 1995. The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. *Limnol. Oceanogr.* **40**: 1381–1391.
- NORRMAN, B., U. L. ZWEIFEL, C. S. HOPKINSON, AND B. FRY. 1995. Production and utilization of dissolved organic carbon during an experimental diatom bloom. *Limnol. Oceanogr.* **40**: 898–907.
- PALENIK, B., N. M. PRICE, AND F. M. M. MOREL. 1991. Potential effect of UV-B on the chemical environment of marine organisms: A review. *Environ. Poll.* **70**: 117–130.
- PEGAU, W. S., AND J. R. V. ZANEVELD. 1993. Temperature-dependent absorption of water in the red and near-infrared portions of the spectrum. *Limnol. Oceanogr.* **38**: 188–192.
- RECHE, I., M. L. PACE, AND J. J. COLE. 1999. Relationship of trophic and chemical conditions to photobleaching of dissolved organic matter in lake ecosystems. *Biogeochemistry* **44**: 259–280.
- SCHINDLER, D. W., AND P. J. CURTIS. 1997. The role of DOC in protecting freshwaters subjected to climatic warming and acidification from UV exposure. *Biogeochemistry* **36**: 1–8.
- , P. J. CURTIS, B. R. PARKER, AND M. P. STANTON. 1996. Consequence of climate warming and lake acidification for UV-B penetration in North American boreal lakes. *Nature* **379**: 705–708.
- SCULLY, N. M., AND D. R. S. LEAN. 1994. The attenuation of ultraviolet radiation in temperate lakes. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* **43**: 135–144.
- SHAO, C., W. J. COOPER, AND D. R. S. LEAN. 1993. Singlet oxygen formation in lake water. *In* G. R. Helz, R. G. Zepp, and D. G. Crosby [eds.], *Aquatic and surface photochemistry*. Lewis.
- SMITH, R. C., AND K. S. BAKER. 1981. Optical properties of the clearest natural waters (200–800 nm). *Appl. Opt.* **20**: 177–184.
- SOMMARUGA, R., AND F. GARCIA-PICHEL. 1999. UV-absorbing mycosporine-like compounds in planktonic and benthic organisms from a high-mountain lake. *Arch. Hydrobiol.* **144**: 255–269.
- , AND R. PSENNER. 1997. Ultraviolet radiation in a high mountain lake of the Austrian Alps: Air and underwater measurements. *Photochem. Photobiol.* **65**: 957–963.
- , I. OBERNOSTERER, G. HERNDL, AND R. PSENNER. 1997. Inhibitory effect of solar radiation on thymidine and leucine incorporation by freshwater and marine bacterioplankton. *Appl. Environ. Microbiol.* **63**: 4178–4184.
- , R. PSENNER, E. SCHAFFERER, K. A. KOINIG, AND S. SOM-

- MARUGA-WÖGRATH. 1999a. Dissolved organic carbon concentration and phytoplankton biomass in high-mountain lakes of the Austrian Alps: Potential effects of climatic warming on UV underwater attenuation. *Arct. Antarct. Alp. Res.* **31**: 247–254.
- , B. SATTLER, A. OBERLEITER, A. WILLE, S. SOMMARUGA-WÖGRATH, R. PSENNER, M. FELIP, L. CAMARERO, S. PINA, R. GIRONÉS, AND J. CATALÁN. 1999b. An *in situ* enclosure experiment to test the solar UV-B impact on microplankton in a high-altitude mountain lake. II. Effects on the microbial food web. *J. Plankton Res.* **21**: 859–876.
- SOMMARUGA-WÖGRATH, S., K. A. KOINIG, R. SCHMIDT, R. SOMMARUGA, R. TESSADRI, AND R. PSENNER. 1997. Temperature effects on the acidity of remote alpine lakes. *Nature* **387**: 64–67.
- TER BRAAK, C. J. F. 1988. CANOCO—a FORTRAN program for canonical community ordination by [partial] [detrended] [canonical] correspondence analysis, principal components analysis and redundancy analysis (version 2.1). Report LWA-88-02, Agricultural Mathematics Group, Wageningen.
- . 1995. Ordination, p. 91–169. *In* R. H. G. Jongman, C. J. F. ter Braak, and O. F. R. Van Tongeren [eds.], *Data analysis in community and landscape ecology*. Cambridge Univ. Press.
- TRANVIK, L. J. 1993. Microbial transformations of labile dissolved organic matter into humic-like matter in seawater. *FEMS Microbiol. Ecol.* **12**: 177–183.
- TWARDOWSKI, M. S., AND P. L. DONAGHAY. 1998. The spectral signature associated with the photobleaching of CDOM absorption. *Proceedings from Ocean Optics XIV*, 10–13 November, Kona, HI. Can be obtained at: <http://argon.oce.orst.edu/web/biooptics/members/twardowski/oo1179.pdf>.
- VERNET, M., AND K. WHITEHEAD. 1996. Release of ultraviolet-absorbing compounds by the red-tide dinoflagellate *Lingulodinium polyedra*. *Mar. Biol.* **127**: 35–44.
- VINCENT, W. F., I. LAURION, AND R. PIENITZ. 1998a. Arctic and Antarctic lakes as global indicators of global change. *Ann. Glaciol.* **27**: 691–696.
- , R. RAE, I. LAURION, C. HOWARD-WILLIAMS, AND J. C. PRISCU. 1998b. Transparency of Antarctic lakes to solar UV radiation. *Limnol. Oceanogr.* **43**: 618–624.
- , AND S. ROY. 1993. Solar UV-B and aquatic primary production: Damage, protection and recovery. *Environ. Rev.* **1**: 1–12.
- VINEBROOKE, R. D., AND P. R. LEAVITT. 1998. Direct and interactive effects of allochthonous dissolved organic matter, inorganic nutrients, and ultraviolet radiation on an alpine littoral food web. *Limnol. Oceanogr.* **43**: 1065–1081.
- VODACEK, A., N. V. BLOUGH, M. D. DEGRANPRE, E. T. PELTZER, AND R. K. NELSON. 1997. Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and photooxidation. *Limnol. Oceanogr.* **42**: 674–686.
- VON DER GATHEN, P., AND OTHERS. 1995. Observational evidence for chemical ozone depletion over the Arctic in winter 1991–92. *Nature* **375**: 131–134.
- WETZEL, R. G., P. G. HATCHER, AND T. S. BIANCHI. 1995. Natural photolysis by ultraviolet irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism. *Limnol. Oceanogr.* **40**: 1369–1380.
- WHITEHEAD, R. F., S. DE MORA, S. DEMERS, M. GOSSELIN, P. MONFORT, AND B. MOSTAJIR. 2000. Interactions of UVB radiation, mixing and biological activity on photobleaching of natural CDOM: A mesocosm study. *Limnol. Oceanogr.* **45**: 278–291.
- WILLIAMSON, C. E., R. S. STEMBERGER, D. P. MORRIS, T. M. FROST, AND S. G. PAULSEN. 1996. Ultraviolet radiation in North American lakes: Attenuation estimates from DOC measurements and implications for plankton communities. *Limnol. Oceanogr.* **41**: 1024–1034.
- XENOPOULOS, M. A., AND D. F. BIRD. 1997. Effect of acute exposure to hydrogen peroxide on the production of phytoplankton and bacterioplankton in a mesohumic lake. *Photochem. Photobiol.* **66**: 471–478.
- XIONG, F., J. KOMENDA, J. KOPECKÝ, AND L. NEDBAL. 1997. Strategies of ultraviolet-B protection in microscopic algae. *Physiol. Plant.* **100**: 378–388.
- YAN, N. D., W. KELLER, N. M. SCULLY, D. R. S. LEAN, AND P. J. DILLON. 1996. Increased UV-B penetration in lake owing to drought-induced acidification. *Nature* **381**: 141–143.
- YENTSCH, C. S., AND D. A. PHINNEY. 1989. A bridge between ocean optics and microbial ecology. *Limnol. Oceanogr.* **34**: 1694–1705.
- YORO, S. C., C. PANAGIOTOPOULOS, AND R. SEMPÉRÉ. 1999. Dissolved organic carbon contamination induced by filters and storage bottles. *Water Res.* **33**: 1956–1959.
- ZEPP, R. G., T. V. CALLAGHAN, AND D. J. ERICKSON. 1995. Effects of increased solar ultraviolet radiation on biogeochemical cycles. *Ambio* **24**: 181–187.

Received: 25 August 1999

Accepted: 3 April 2000

Amended: 25 April 2000