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Penetration of solar ultraviolet radiation into New Zealand lakes: influence of dissolved organic carbon and catchment vegetation

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Abstract Eleven lakes in the South Island of New Zealand were sampled in summer 1996. Water column profiles of ultraviolet radiation (UVR) at four wavelengths and photosynthetically available radiation (PAR) were obtained, along with analyses of dissolved organic carbon (DOC) concentration, total suspended solids (TSS), and catchment vegetation, including forest and natural grassland. Downward attenuation coefficients (K_d) and lake water transparency ($1/K_d$) for UVR were examined in relation to these variables. Consistent with other regions of the world, DOC concentration and variables related to DOC were the best predictors of UVR penetration. With our data set, we calculated ratios of water column integrals (RI) of UVR/PAR irradiance, using equations from the literature. At DOC concentrations below $4\,g\,m^{-3}$, a progressive increase in RI shows that lakes become increasingly transparent to UVR. We also normalized chromophoric dissolved organic matter (CDOM) absorption of UVR at 380 nm (a_{380}) to DOC concentration and found that the UVR-absorbing capacity per unit DOC increases with increasing percentage of forest in the catchment area. This indicates that not only DOC concentration but also DOC type or composition is important in determining the transparency of lake water to UVR, and that qualitative differences in DOC are dictated by the type and amount of vegetation present in the lake's catchment area.

Key words Climate change · Land use · Light attenuation · UVR/PAR ratio · Water clarity

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Introduction

The impact of increasing ultraviolet radiation (UVR) in the south polar region has been of particular concern due to the annual spring and summer depletion of stratospheric ozone (e.g., Bodeker 1997). Although the ozone hole itself is generally confined to latitudes higher than 60 degrees South, significant eddies of ozone-depleted atmosphere swirl into lower latitudes when the ozone hole breaks up, and have been shown to pass over New Zealand (Toon and Turco 1991). New Zealand is already exposed to high UVR levels, 50% greater than countries of similar latitudes in the Northern Hemisphere (McKenzie et al. 1996; Bodeker 1997), and significant increases in UVR over New Zealand have been observed in association with the ozone hole (National Science Strategy Committee 1998). This combination of factors means that ecosystems in New Zealand may receive significantly higher doses of UVR than would be expected on the basis of latitude alone.

The impact of UVR on aquatic, particularly planktonic, communities has been well studied in the marine environment (de Mora et al. 2000), and in the last few years reports on the role of UVR in North and South American freshwaters have been made (e.g., Morris et al. 1995; Williamson et al. 1996; Laurion et al. 1997; Vinebrooke and Leavitt 1999). Vincent and Roy (1993) and Vincent and Neale (2000) have reviewed the photobiological influences of UVR on aquatic organisms and communities, demonstrating that the ecological impacts of UVR cover a wide spectrum of life forms and processes.

The damaging effects of UVR increase steeply with decreasing wavelength, particularly in the lower UVBR wavelengths (280–320 nm). Higher wavelength UVR, termed UVAR (320–400 nm), has been shown to be implicated in both damage and repair of DNA, whereas wavelengths in the photosynthetically active part of the spectrum (PAR) are known to assist in repair of UVR damage (Karentz et al. 1991). Smith et al. (1992) have shown that the net toxicity of UVR reflects the balance between photochemical damage and biosynthetic repair. UVR is markedly attenuated as it passes through natural waters (Kirk 1994b; Scully and Lean 1994; Morris et al. 1995; Williamson et al. 1996; Laurion et al. 1997), and the differential attenuation of UVR and PAR wavelengths across the solar spectrum results in a changing potential for UVR damage with depth.

The attenuation of UVR in natural waters is affected mostly by colored or chromophoric dissolved organic matter (CDOM), often measured as dissolved organic carbon (DOC), concentrations of which are highly variable in freshwaters. For instance, Morris et al. (1995) showed that approximately 90% of the between-lake variation in the attenuation of UVR over a wide range of lakes could be explained by differences in DOC concentration. Lakes in areas with sparse catchment vegetation have low DOC concentrations and have been shown to be relatively transparent to UVR wavelengths (Vincent et al. 1998). However, underwater UVR can also be influenced by high turbidity (Smith et al. 1999) or by high concentrations of chlorophyll *a* (Hodoki and Watanabe 1998). It has been demonstrated for some high-altitude lakes with low DOC concentrations that phytoplankton within the water column can attenuate UVR, probably because of high concentrations of UVR-absorbing compounds (Laurion et al. 2000).

New Zealand has a highly varied topography and a wide range of lake types and optical properties (Howard-Williams and Vincent 1985; Davies-Colley et al. 1993). The elevated solar UVR levels experienced in New Zealand provide an interesting basis for studies of UVR in lakes. This paper provides the first data set on UVR penetration in New Zealand freshwaters. Eleven lakes in the South Island, covering a wide range of water clarities, were chosen to examine the major determinants of UVR penetration, including potential catchment vegetation effects.

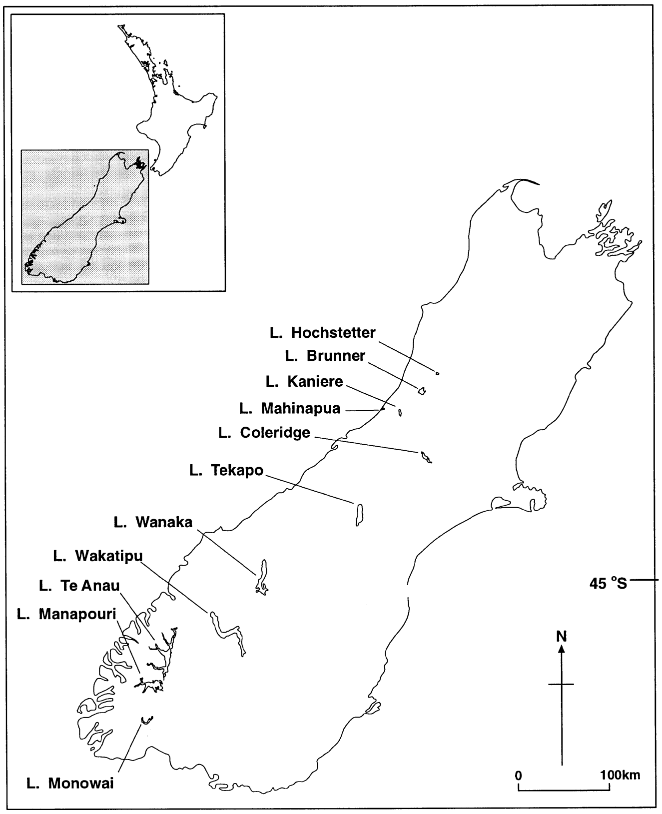


Fig. 1. Locations of the 11 lakes sampled on the South Island of New Zealand

Materials and methods

Study sites and optical measurements

Eleven lakes, ranging from very clear to turbid and spanning colors from blue or blue-green to brown, were sampled in February 1996 (Fig. 1). At an offshore site in each lake, the Secchi disk depth was measured and depth profiles of cosine-corrected downwelling irradiance were obtained using a Biospherical Instruments PUV-500 radiometer. In addition to photosynthetically available radiation (PAR; 400–700 nm), this instrument provided a measure of irradiance at 305, 320, 340, and 380 nm (half maximum bandwidth of 8–10 nm). Measurements were made from just below the water surface to a depth of 1% of surface PAR and were logged at 1-s intervals, corresponding to 10–15 measurements per metre. Incident irradiance for the duration of the profile was measured using a Li-Cor Li190SA quantum sensor attached to an Li-1000 logger. The downward attenuation coefficient for PAR ($K_{d(PAR)}$) and for the UVR wavelengths ($K_{d(UVR)}$) was calculated by log-linear regression of the irradiance values, corrected for changes in incident irradiance, against depth.

Lake water was collected at each site, and two replicate 2-l samples were filtered through pre-ashed, preweighed GF/F filters for analysis of total suspended solids (TSS) concentration. Plankton chlorophyll *a* (Chl *a*) concentration was determined by extracting filtered and ground material in 90% acetone prior to measuring fluorescence by the technique of Strickland and Parsons (1968). Calibration was done using a Chl *a* standard (Sigma Biochemical C-6144), and correction of the samples for phaeophytin was made using 1 N HCl.

Dissolved organic matter was determined at each site by measurements of DOC concentration using a Dohrman Model DC180 Low Level TOC analyzer (ESR Laboratories, Christchurch, New Zealand). DOC was also measured by fluorometry to obtain Raman DOC (DOC_{Rn}). Fluorescence emission scans were measured on a Perkin Elmer Luminescence LS-50B spectrometer, between 360 and 650 nm, with the excitation beam set to 348 nm and a slit width of 5 nm. The fluorescence signal at 450 nm (peak height) was normalized to the Raman peak height as described in Determann et al. (1994).

Spectrophotometric CDOM absorption between 300 and 700 nm was measured on 0.22-μm Millipore filtered water samples. Absorbance of samples in 100-mm quartz cuvettes was scanned and recorded against a 0.22-μm filtered distilled water blank, using a double beam JASCO spectrophotometer. The absorption coefficient, α_λ at wavelengths 305, 320, 340, 380, and 440 nm was calculated as:

$$a_\lambda = 2.303\ A_\lambda / r \quad (1)$$

where A_λ is spectrophotometric absorbance at λnm and r is the cuvette path length (m) (Davies-Colley et al. 1993).

Catchment characteristics

Vegetation as a percentage of total catchment area was obtained for each lake catchment from the New Zealand Land Resource Inventory (1997) and was separated into grassland (primarily native tussock grasses), forest (comprising both tall and short dense forest cover), cropland, and areas with alpine herbs.

Literature data set

To determine how our data for New Zealand lakes compare with and relate to DOC, TSS, UVR, and PAR relationships in other parts of the world, we extracted data from several published papers. Data were obtained from Scully and Lean (1994; Alberta, Ontario, Central Quebec), Morris et al. (1995; Argentina, Alaska, northeast USA, Colorado), Laurion et al. (1997; subarctic Quebec, Canadian high Arctic), and Vincent et al. (1998; Antarctica). Literature values were taken only from studies that had measured discrete downwelling UVR wavelengths (specifically at 320nm) and downwelling PAR across the 400–700nm range, consistent with the measurements we made in New Zealand. Published data were obtained for 110 freshwaters.

Statistical analyses

All statistical analyses were performed using STATISTICA for Windows (Statsoft).

Modeling of UVR penetration into natural waters using waveband ratios

Waveband ratios between PAR and UVR are particularly relevant to phototrophs (Vincent and Roy 1993; Quesada et al. 1995) and imply that the impacts of UVR may be offset by photosynthetic wavelengths. Laurion et al. (1997) have modeled UVR attenuation at wavelengths across the UVR spectrum from 300 to 440nm based on the equation

$$K_{d(\lambda)} = K_{d(440)} \exp[-S(\lambda - 440)] \quad (2)$$

where S is a constant that describes the slope of the exponential curve of the absorption coefficient as a function of wavelength, λ. The equation was shown to provide an accurate description of the attenuation of underwater UVR. The slope, S, of 0.0151 nm^{-1} varied little between lakes and was similar to literature values of absorbance curves for filtered natural waters (Laurion et al. 1997). For instance, Howard-Williams and Vincent (1985) found S for several New Zealand lakes to fit within the range 0.013–0.016 nm^{-1}. It should be noted, however, that more recent analyses using a background attenuation parameter in Eq. 2 indicate a much larger variability in S (Markager and Vincent 2000).

Laurion et al. (1997) showed that at any depth, the ratio of UVR to PAR is given by

$$E_{UVR}/E_{PAR} = R_{atm} \exp(-\Delta K\, z) \quad (3)$$

where R_{atm} is the incident irradiance ratio just below the water surface and is dependent on weather condition, solar angle, altitude, and atmospheric ozone concentration. ΔK is the difference between UVR and PAR diffuse attenuation coefficients. The ratio of irradiance at 320nm UVR and across the PAR waveband at a specific depth (E_{UVR}/E_{PAR}) is applicable in the description of net UVR effects on organisms that occur at fixed depths in lakes.

In the upper mixed layer of open waters, planktonic organisms circulate in the water column, and a UVR/PAR ratio based on E_{UVR}/E_{PAR} is less appropriate. In this case, an alternative computation of the spectral balance is the ratio of mixed water column integrals (RI) for the two wavebands. Laurion et al. (1997) have shown that the ratio of integrals

$$RI = \int E_{UVR} dz / \int E_{PAR} dz$$

can be reduced to the following expression:

$$RI = R_{atm}\ (K_{d(PAR)}/K_{d(UVR)}) \quad (4)$$

Results

Lake characterization

The 11 New Zealand lakes span a range of sizes (3.4 to 352 km^2) and maximum depths (9.6 to 444m) and can all be considered oligotrophic, with Chl *a* concentrations ranging from 0.39 to 4.38 $\mu g\, l^{-1}$ (Table 1). TSS ranged over more than an order of magnitude (<1 to 20.8 $g\, m^{-3}$) and DOC from <1 $g\, m^{-3}$ in lakes with predominantly grassland catchments, to highly colored lakes in forested catchments with >8 $g\, m^{-3}$ (Table 1). DOC_{Rn} showed a high correlation with DOC measured on the TOC analyzer ($r = 0.99$, $P < 0.001$). Water clarity among the lakes varied by an order of magnitude, with Secchi depth values measured at <1 to 13.5m and the downward attenuation coefficients for PAR ($K_{d(PAR)}$) varying from 0.13 to 1.92 m^{-1} (Table 2).

A high degree of variability in attenuation of the UVR wavelengths can be expected from this lake series. CDOM absorption coefficients for the wavelengths 305, 320, 340, 380, and 440nm and the downward attenuation coefficients for the UVR wavelengths and PAR confirm this (Table 2). The downward attenuation coefficient at 320nm, $K_{d(320)}$, varied by two orders of magnitude among the 11 lakes (0.36 to >60 m^{-1}), corresponding to depths of penetration for 1% of 320nm UVR between 12.94m in Lake Coleridge and 0.08m in Lake Hochstetter.

Lake Tekapo has a relatively high transparency to UVR, yet one of the greatest attenuation coefficients

Table 1. Physical dimensions, chlorophyll *a* (Chl *a*), total suspended solids (TSS), dissolved organic carbon (DOC), and Raman DOC (DOC_{Rn}) estimators of 11 New Zealand lakes

Lake	Surface area (km^2)	Maximum depth (m)	Chl *a* ($mg\,m^{-3}$)	TSS ($g\,m^{-3}$)	DOC ($g\,m^{-3}$)	DOC_{Rn} (Raman units)
Brunner	36.0	109.0	2.23	1.40	2.1	1.51
Coleridge	33.0	200.0	0.39	1.40	0.4	0.02
Hochstetter	6.6	17.0	4.38	3.06	8.6	7.29
Kaniere	13.0	198.0	0.69	0.65	1.8	1.24
Mahinapua	3.4	9.6	1.80	1.39	10.0	7.68
Manapouri	153.0	444.0	1.12	0.47	1.2	0.60
Monowai	32.0	161.0	1.80	1.93	2.2	0.86
Te Anau	352.0	414.0	1.35	0.54	1.4	0.62
Tekapo	87.0	120.0	0.74	20.86	0.3	0.01
Wakatipu	293.0	380.0	1.20	1.00	0.6	0.03
Wanaka	193.0	311.0	0.87	1.02	0.5	0.02

Table 2. Downward attenuation coefficients (K_d) for PAR and four UVR wave bands and chromophoric dissolved organic matter (CDOM) absorption coefficients (a_λ) for four UVR wavebands and 440 nm[a]

Lake	$K_{d(305)}$	a_{305}	$K_{d(320)}$	a_{320}	$K_{d(340)}$	a_{340}	$K_{d(380)}$	a_{380}	$K_{d(PAR)}$	a_{440}
Brunner	12.35	*11.23*	10.15	*8.92*	9.40	*6.62*	5.59	*3.53*	0.74	*1.30*
Coleridge	0.57	–	0.36	–	0.29	–	0.20	–	0.13	*0.06*
Hochstetter	–	*63.33*	60.54	*51.93*	53.95	*39.27*	33.91	*20.27*	1.92	*7.70*
Kaniere	12.57	*9.36*	9.14	*7.48*	6.96	*5.54*	4.20	*2.81*	0.62	*0.94*
Mahinapua	–	*64.05*	33.36	*45.34*	41.85	*31.67*	25.07	*20.15*	1.64	*6.48*
Manapouri	5.78	*4.82*	3.79	*3.71*	3.11	*2.67*	1.77	*1.33*	0.34	*0.59*
Monowai	–	*5.40*	4.52	*4.10*	3.66	*2.88*	2.25	*1.33*	0.37	*0.43*
Te Anau	8.64	*4.68*	3.46	*3.49*	3.26	*2.48*	1.82	*1.22*	0.33	*0.43*
Tekapo	4.33	–	3.22	–	3.49	–	2.62	–	1.15	*0.01*
Wakatipu	1.03	–	0.81	–	0.62	–	0.42	*0.22*	0.23	*0.16*
Wanaka	1.42	–	0.91	–	0.77	–	0.53	*0.29*	0.26	*0.17*

[a] Units for all coefficients are m^{-1}. – indicates data outside the detection limits of our instruments

for PAR (Table 2). In the following lake series: Kaniere – Brunner – Tekapo, with $K_{d(PAR)}$ values of 0.62, 0.74, and 1.15, respectively, the lake order based on $K_{d(320)}$ is Tekapo – Kaniere – Brunner. Lake Tekapo has a high TSS concentration composed of glacial flour, which attenuates PAR but has relatively little influence on UVR transparency. Because of this unusually low PAR but high UVR transparency, analyses of DOC and TSS effects on UVR penetration were carried out both with and without the inclusion of Lake Tekapo.

Influence of DOC concentration on UVR penetration

Attenuation of UVR wavelengths was highly correlated with DOC and with parameters that estimate DOC in the New Zealand lake series (Table 3). All three estimators of DOC were good predictors of $K_{d(320)}$, particularly when the highly reflective Lake Tekapo was excluded from the analysis. For example, with the complete series of 11 lakes, the prediction obtained from DOC measured on the TOC analyzer had an r^2 of 0.78 ($P < 0.001$), but when Lake Tekapo was excluded, the DOC prediction increased to 93% of the $K_{d(320)}$ variability. This also altered the slope of the line when it was plotted as transparency ($1/K_{d(320)}$) versus DOC (Fig. 2).

All lakes from the literature data set also show a general linear relationship on a log-log plot of transparency and DOC (Fig. 2). The most transparent waters are from Argentina, Antarctica, and New Zealand, with the highest variability in the relationship of UVR attenuation and DOC in these lakes with low DOC concentration. In the New Zealand lakes, UVR attenuation at 320 nm as a function of DOC is slightly higher than for lakes in other regions of the world. This is illustrated in Fig. 2, where the New Zealand data for transparency ($1/K_{d(320)}$) are at the lower side of the scatter plot (see also linear regression equations in the figure legend).

Influence of TSS on UVR penetration

We examined TSS as an additional predictor of UVR penetration in both New Zealand lakes and the literature data set. With the 11 New Zealand lakes, TSS was a significant addition to the multiple regression only when Lake Tekapo was included in the analysis (Table 3), and in this case it explained an additional 8% of the variability in $K_{d(320)}$. TSS and DOC were not correlated ($r = -0.16$, $P > 0.05$). When Lake Tekapo was excluded, TSS was no longer significant and DOC alone best described $K_{d(320)}$. In the combined literature and New Zealand data sets, TSS was not a

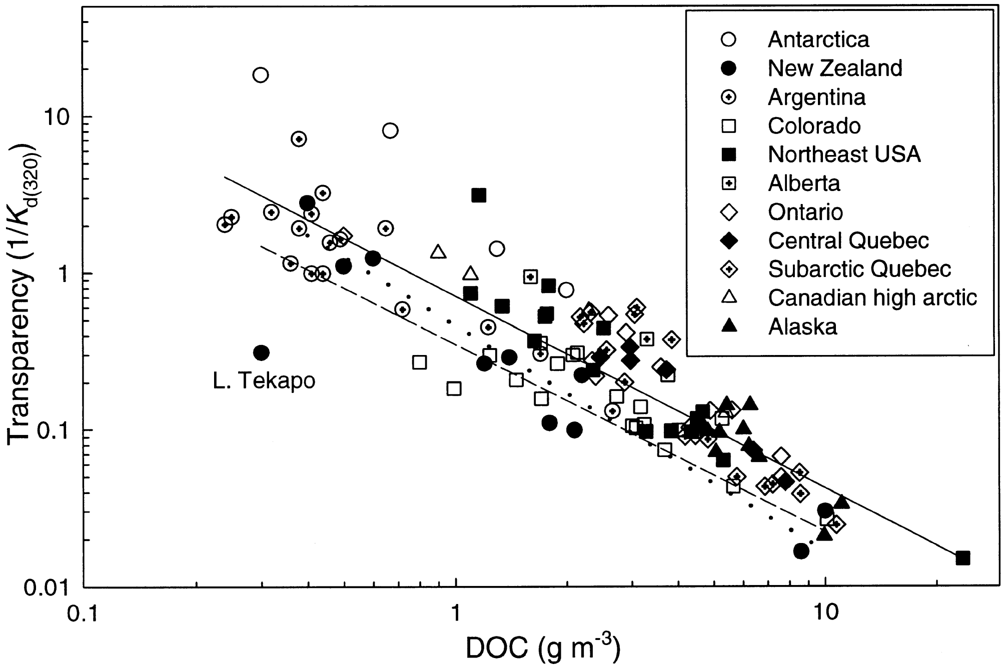


Fig. 2. A log-log plot of transparency ($1/K_{d(320)}$) as a function of dissolved organic carbon (DOC) concentration for data in the literature (n = 110) and for lakes in this study (n = 11). The *solid line* shows the linear relationship for the whole data set [$\log(1/K_{d(320)}) = -1.23 \log \text{DOC} - 0.15$, $r^2 = 0.78$, $P < 0.001$] and the *dashed line* for New Zealand lakes alone [$\log(1/K_{d(320)}) = -1.20 \log \text{DOC} - 0.46$, $r^2 = 0.80$, $P < 0.001$]. When Lake Tekapo was excluded from the New Zealand data set, the relationship denoted by the *dotted line* was obtained [$\log(1/K_{d(320)}) = -1.45 \log \text{DOC} - 0.33$, $r^2 = 0.94$, $P < 0.001$]

Table 3. Regression equations and variance explained (r^2) for predicting $K_{d(320)}$ from DOC concentration measured on a TOC analyzer (DOC, g m^{-3}), Raman DOC (DOC_{Rn}, Raman units), CDOM absorption at 440 nm (a_{440}, m^{-1}), and both DOC and total suspended solids (TSS, g m^{-3}) together[a]

Variable(s)	Lake series	Regression equation	r^2
DOC	All lakes	$\log K_{d(320)} = 1.20 \log \text{DOC} + 0.46$	0.78***
	Excluding Tekapo	$\log K_{d(320)} = 1.45 \log \text{DOC} + 0.33$	0.93***
DOC_{Rn}	All lakes	$\log K_{d(320)} = 0.62 \log \text{DOC}_{Rn} + 0.91$	0.81***
	Excluding Tekapo	$\log K_{d(320)} = 0.74 \log \text{DOC}_{Rn} + 0.88$	0.95***
a_{440}	All lakes	$\log K_{d(320)} = 0.64 \log a_{440} + 0.86$	0.59**
	Excluding Tekapo	$\log K_{d(320)} = 1.03 \log a_{440} + 0.85$	0.97***
DOC and TSS	All lakes	$\log K_{d(320)} = 1.26 \log \text{DOC} + 0.43 \log \text{TSS} + 0.38$	0.85*** DOC*** TSS*
	Excluding Tekapo	$\log K_{d(320)} = 1.51 \log \text{DOC} - 0.28 \log \text{TSS} + 0.33$	0.93** DOC*** TSS n.s.

[a] Equations are given for the full New Zealand data set and with Lake Tekapo excluded. *** $P < 0.001$; ** $P < 0.01$; * $P < 0.05$; n.s., not significant

significant predictor of $K_{d(320)}$, which was best described by the relationship $\log K_{d(320)} = 1.0 \log \text{DOC} + 0.31$ ($r^2 = 0.99$, $P < 0.001$).

Waveband ratios: benthic systems

The $E_{d(320)}/E_{d(PAR)}$ ratio, obtained from Eq. 3, is highly variable among the New Zealand lakes. Scaling problems in the presentation of this relationship, which arise from the two orders of magnitude difference between the depth of UVR penetration, have been resolved in Fig. 3 by plotting the ratio of $E_{d(320)}/E_{d(PAR)}$ against percent surface PAR as a measure of depth. The $E_{d(320)}/E_{d(PAR)}$ ratio decreases with decreasing percent surface PAR due to the selective absorption of the UVR wavelengths relative to PAR. In lakes with moderate DOC, such as Lake Brunner, the ratio declines rapidly, whereas in clear lakes with low DOC, such as Lake Coleridge, the ratio decreases more slowly (Fig. 3).

Waveband ratios: planktonic systems

The ratio RI for the New Zealand lakes data shows a strong nonlinear relationship with DOC (Fig. 4). At DOC concentrations below 4 g m^{-3}, the progressive increase in RI shows that lakes become increasingly transparent to UVR. The RI values for those New Zealand lakes with less than 4 g m^{-3} DOC do not, however, fit the curve obtained by Laurion et al. (1997), but rather are better explained using a power function. New Zealand's lakes cover a range of RI values, some being similar to those of permanently ice-capped lakes of Antarctica (Fig. 4, inset). One Argentinean lake obtained from a literature data set is at an extreme, with an RI of >0.005. Again, with the pooled literature data set, a power function provides the best fit to the data below $4\,g\,m^{-3}$.

Catchment vegetation and DOC absorption characteristics

The New Zealand lake series was representative of a wide range of catchment types (Table 4), and the effects of catchment vegetation on lake water DOC concentration were marked. The greater the proportion of forest in the catchment, the higher the DOC concentration (Fig. 5a) and the lower the RI value (figure not shown). Thus, lakes with heavily forested catchments were less transparent to UVR.

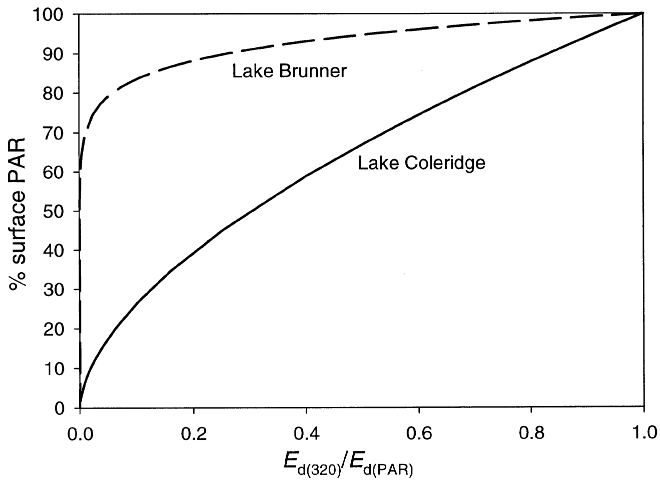


Fig. 3. Dependence of UVR/PAR ratio on depth for two lakes of contrasting DOC concentration, Lakes Coleridge and Brunner. Depth is shown as percent surface photosynlhetically available radiation (PAR) to overcome scaling problems

Given that grassland and forest together composed the majority of catchment vegetation, an inverse relationship to that of percent of forest was found with the proportion of natural grassland in the catchment. Lakes with more than 55% grassland cover in the catchment were particularly transparent to UVR (Lakes Coleridge, Tekapo, Wanaka, and Wakatipu).

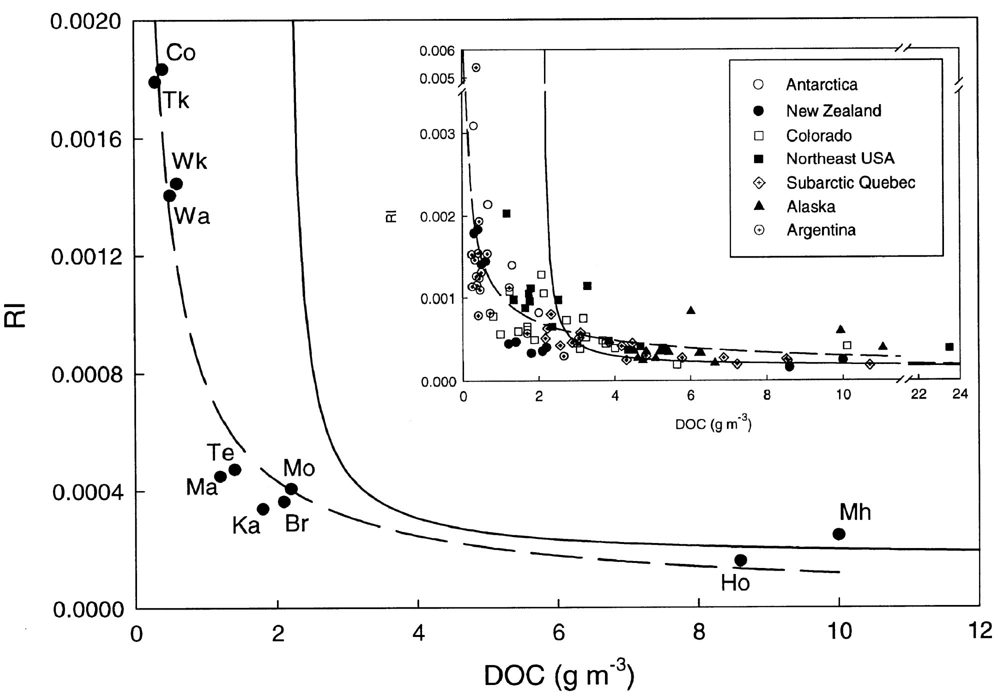
In addition to DOC concentration, the UVR-absorbing capacity per unit DOC was related to the catchment vegetation of New Zealand lakes. We normalized CDOM absorption at 380 nm (a_{380}) to DOC concentration and found that a_{380}/DOC increased with increasing forest in the catchment (Fig. 5b), and the reverse was seen with increasing grassland. For example, lakes with catchments containing 55%–65% natural grassland and <30% forest have low DOC concentration ($<1\,g\,m^{-3}$) and low relative absorption (a_{380}/DOC <0.6). Lakes in moderately forested (50%–60%) catchments have DOC concentrations of 1–$2.5\,g\,m^{-3}$ and a_{380}/DOC of 0.6–1.7, whereas those in densely forested (>70%) catchments have DOC concentrations of $>8\,g\,m^{-3}$ and relative absorption >2.

Discussion

Predicting UVR penetration

The strong relationship between lake water DOC concentration and transparency to UVR that has been demonstrated in many regions of the globe (Scully and Lean 1994; Morris et al. 1995; Laurion et al. 1997) holds true for lakes in New Zealand. Moreover, when data are pooled from several studies representing a diverse set of lakes in North and South America, Antarctica, and the current New

Fig. 4. Ratio of integrals (RI, see Eq. 4) as a function of DOC concentration in New Zealand lakes (Br: Brunner, Co: Coleridge, Ho: Hochstetter, Ka: Kaniere, Mh: Mahinapua, Ma: Manapouri, Mo: Monowai, Te: Te Anau, Tk: Tekapo, Wk: Wakatipu, Wa: Wanaka). The **inset** shows the same relationship for the lakes from the literature in addition to New Zealand (n = 86). In both figures the *solid line* represents the equation of Laurion et al. (1997), while the *dashed line* is a power function. **Main figure**: RI = $0.00076[\text{DOC}]^{-0.82}$, $r^2 = 0.93$; **inset**: RI = $0.001[\text{DOC}]^{-0.53}$, $r^2 = 0.50$



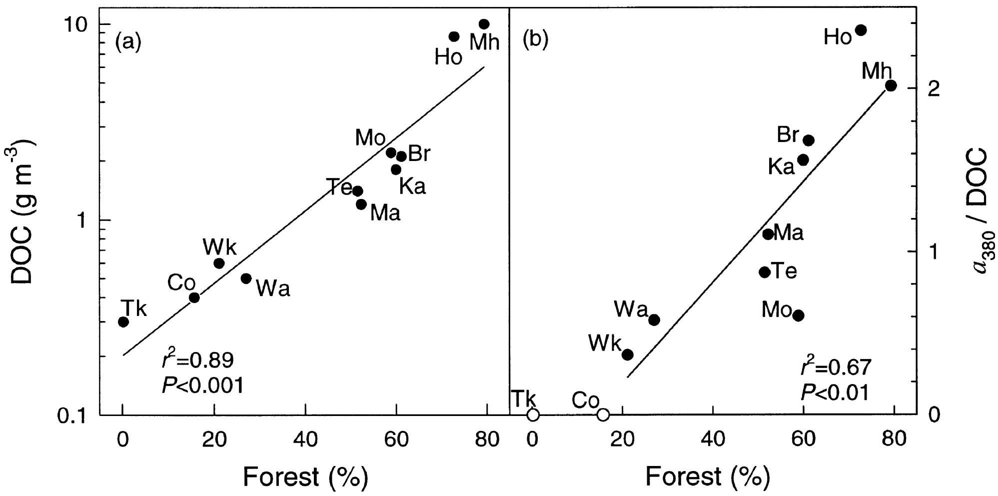


Fig. 5. **a** Relationship between DOC concentration and percent forest in the lake catchment, represented on a log-linear plot. **b** CDOM absorption at 380nm relative to DOC concentration (a_{380}/DOC) in terms of percent forest present in the lake catchment. Lakes Tekapo and Coleridge had a_{380} values below the detection limits of our instruments. Therefore they were not included in the regression analysis shown in the figure and appear as white symbols on the abscissa only to indicate the proportion of forest in their catchments. In both panels, the lakes are identified as *Br*: Brunner, *Co*: Coleridge, *Ho*: Hochstetter, *Ka*: Kaniere, *Mh*: Mahinapua, *Ma*: Manapouri, *Mo*: Monowai, *Te*: Te Anau, *Tk*: Tekapo, *Wk*: Wakatipu, *Wa*: Wanaka

Table 4. Catchment area and proportion of the total catchment covered by four classes of vegetation in the New Zealand lake series

Lake	Catchment area (km^2)	% of catchment area			
		Grassland	Cropland	Forest	Alpine herb
Brunner	379	22.1	10.5	61.2	6.3
Coleridge	200	64.4	5.5	15.7	14.3
Hochstetter	18	18.6	0.3	72.8	8.3
Kaniere	55	29.3	2.1	60.0	8.6
Mahinapua	31	8.2	4.0	79.4	8.3
Manapouri	1428	35.8	10.6	52.3	1.3
Monowai	231	26.6	14.5	58.9	0.0
Te Anau	2998	35.5	11.7	51.5	1.3
Tekapo	1391	57.7	7.1	0.2	35.0
Wakatipu	2674	60.9	9.7	21.1	8.3
Wanaka	2590	56.2	11.0	27.0	5.8

Zealand information, DOC explains approximately 80% of the variability in UVR transparency.

Ten of the 11 New Zealand lakes have UVR transparency values below the best-fit regression line for the pooled data. This suggests that the New Zealand lakes may have particular characteristics that explain the consistently negative residuals in the pooled data set, whereby transparency is lower at any particular DOC concentration than for many lakes in other regions of the world. For the whole data set, greater variability around the regression line is evident at low DOC concentration, which could be due to a higher contribution to light attenuation by other components of natural waters at low DOC levels. We examined the TSS load in each of the lakes and added it into a multiple regression model to determine if it could explain additional variation in UVR transparency.

Total suspended solids concentration was a significant but minimal contributor to UVR penetration in New Zealand lakes and became nonsignificant when Lake Tekapo, with a particularly high TSS and high UVR/PAR transparency, was removed from the analysis. In examining the intralake variability of UVR penetration in Lake Erie, Smith et al. (1999) measured a small range of DOC concentrations and a high range of TSS values and found that TSS better explained UVR attenuation than did DOC. Only with Lake Tekapo included in our data set do we have a significant TSS variable for UVR prediction. The lack of contribution by TSS toward explaining any additional variation in UVR transparency of the remaining 10 New Zealand lakes examined is consistent with the results of Morris et al. (1995), who found that DOC alone was the best predictor of UVR attenuation. Therefore, the scatter about the regression line at low DOC and the propensity of New Zealand lakes to fall on the lower side of the relationship may be explained by the DOC pool itself having differences in UVR attenuation properties (see Effects of catchment vegetation on DOC, below).

Lake Tekapo was unusual in the New Zealand data set because of high attenuation of PAR, yet relatively low attenuation of UVR. Together with several other large glacial lakes on the eastern side of the Southern Alps, Lake Tekapo receives a significant input of fine glacial flour, which markedly affects its optical properties. Glacial flour provides a highly scattering medium for light in water, and these lakes characteristically have a high reflectance coefficient, some with the major scattering wave band at the blue end of the spectrum (Howard-Williams and Vincent 1985; Davies-Colley et al. 1993). Nonetheless, Lake Tekapo should have UVR penetration to depths similar to those of Lake Coleridge, based on its DOC concentration, which is the lowest in the New Zealand lake series at $0.3\,g\,m^{-3}$. However, its UVR attenuation coefficients are more similar to those of Lakes Manapouri, Monowai, and Te Anau. In Lake Tekapo, the TSS load, dominated by glacial flour, is 20 times that in most of the other New Zealand lakes and evidently affects low wavelength attenuation through extensive scattering, but not absorption, as absorption coefficients for UVR are below detection limits.

Biological significance of UVR penetration for New Zealand lakes

The wide range of DOC concentrations in New Zealand lakes means that organisms living in these environments will be exposed to a variety of UVR climates, from very little UVR in lakes such as Brunner, to a considerable dose even at several metres depth in lakes such as Coleridge. Organisms with limited motility, such as benthic algae and rooted macrophytes, will be exposed to UVR doses at levels that have been shown to be inhibitory elsewhere (Bothwell et al. 1993; Vinebrooke and Leavitt 1999). Although periphyton have been examined for UVR effects in a number of stream and lake environments, we have little information worldwide on freshwater macrophyte responses to UVR. Early results from Lakes Coleridge, Wanaka, and Te Anau show that several macrophyte species in these lakes decrease their photosynthetic yield in response to both artificial and natural UVR exposure, although others appear to be well adjusted to their UVR environment (Hawes et al., in prep.).

In addition to potential increases in ground-level UVR due to ozone thinning, the underwater UVR environment in New Zealand lakes is altered through other mechanisms, such as human-induced and natural water level fluctuations. Several lakes experience variations of 2–3 m or greater during an average year (NIWA unpublished data). The implications for littoral zone plants are considerable, particularly for the extensive deep-water Characean meadows that appear to be physiologically adapted to low light conditions (Howard-Williams et al. 1995) and may therefore be quite sensitive to an increase of underwater UVR or change in the UVR/PAR ratio. The littoral zones of New Zealand lakes are also extensive and important habitats for a variety of invertebrate and fish species (James et al. 2000).

The ratios of UVR to PAR and of UVBR to UVAR have been shown to be important in biological systems for controlling the balance between UVR-induced damage and its biochemical repair in the presence of longer wavelengths (Smith et al. 1992; Vincent and Roy 1993; Quesada et al. 1995). Variations in the UVR/PAR ratio in lakes are dependent firstly on factors controlling incident UVR/PAR ratios, such as ozone thickness, cloud cover, and zenith angle of the sun (Madronich 1993), and secondly on characteristics of lake water that differentially attenuate and scatter UVR and PAR (Kirk 1994a). The biological significance of these ratios varies with lake habitat within the bounds of changes in UVR/PAR ratios.

Benthic plants receive a fixed ratio of UVR to PAR, depending on their depth, but planktonic organisms present a different case for UVR exposure due to their subjection to vertical mixing processes that carry them from shallow high-UVR depths to deeper low-UVR strata (Neale et al. 1998). The calculation of RI as a representation of UVR sensitivity for organisms mixed within the water column provides a way of examining the relative impact of DOC concentration over a series of lakes. Also, the potential sensitivity to changes of the underwater light environment in response to an alteration of DOC concentration can be assessed. The nonlinear upswing in RI at low DOC has been described for subarctic lakes (Laurion et al. 1997) with an equation that does not accurately fit the New Zealand or whole lake data set at very low DOC concentrations ($<2.5\,g\,m^{-3}$). In these cases, the data are best described by a power function. Regardless of the best-fit equation, it is evident that the ratio of water column UVR/PAR increases greatly at low DOC concentration, and any shift in DOC to lower levels could produce a significant increase in exposure for planktonic organisms.

The nonlinearity of the relationship between DOC and RI may be interpreted as a change in the proportion of the UVR-absorbing, or chromophoric, fraction of the DOC pool in those lakes with low DOC concentrations (Scully and Lean 1994; McKnight et al. 1994). UVR transparency in lakes is not only a function of the concentration of DOC, but also depends on the optical properties of the DOC pool itself (Waiser and Robarts 2000). Absorption coefficients for various types of DOC compounds, such as tannins, fulvic acids, and lignins, vary by an order of magnitude across the solar UVR spectrum (McKnight et al. 1994; Morris et al. 1995). Highly aromatic DOC compounds with large molecular weights, such as fulvic acids, tend to have a high specific absorbance for UVR wavelengths. Photochemical degradation of these compounds to low-molecular-weight (LMW) DOC has been shown to change the optical properties (Backlund 1992), reducing the DOC-specific absorbance of UVR. In addition, photochemically produced LMW DOC compounds are biologically labile and subject to microbial mineralization (Lindell et al. 1995), thereby increasing the effect of photodegradation. That the New Zealand data and many of the literature data are poorly represented by the Laurion et al. (1997) equation, yet the data for which the equation was developed are very well described, indicates that the properties of the DOC pool can be highly variable.

Effects of catchment vegetation on DOC

The variability in the relationship of UVR with DOC implies that DOC from different catchment sources attenuates UVR in different ways. For instance, in polar desert lakes most of the DOC is generated autochthonously by microbial processes in the water, since there is no catchment vegetation. McKnight et al. (1994) showed that this DOC differs from that in temperate latitudes by having a reduced ratio of aromatic to aliphatic residues. Low aromaticity is associated with lower UVR-absorbing ability. Although we do not have information on the molecular structure of the DOC in the lakes we sampled, the differences among lakes in absorption per unit DOC imply that transparency is not only related to DOC concentration but must also be influenced by DOC composition. In other words, the type of DOC from predominantly grassland catchments is qualitatively different in terms of its UVR attenuation properties than DOC from a mainly forested catchment. The study lakes with a high proportion of natural grassland in their catchment are all on the eastern side of the Southern Alps, where native tussock grasses are the dominant plants in the rain shadow catchments of the mountains. Where lakes occur in catchments with cultivated grasslands, such as developed sheep pasture on lands once covered by forest, the relationship of DOC to percentage of grassland may be very different.

The DOC pool itself has also been shown to vary seasonally in lakes, due mostly to photobleaching effects on the DOC at times of high incident UVR (Morris and Hargreaves 1997; Lindell et al. 2000). For example, the highest transparency to UVR in Pennsylvanian lakes was found in late summer, associated with the time of maximum incident UVR flux and corresponding with the time of minimum DOC concentration in the lakes (Morris and Hargreaves 1997). Our study took place at the height of summer, when the incident UVR flux is greatest (McKenzie et al. 1999). If seasonal variation occurs through photobleaching, presumably we measured the lakes at their period of highest transparency. However, we have no seasonal UVR data or estimates of DOC bleaching in New Zealand lakes.

Effect of climate change scenarios on DOC and UVR

Lakes on the Canadian Shield are becoming clearer as a result of reduced concentrations of DOC, attributable to changing water balances in catchments caused by global warming (Schindler et al. 1990). Acidification and photobleaching have also been implicated in contributing to greater UVR transparency of lakes (Yan et al. 1996; Schindler et al. 1996). Recently it has been shown that climate change can influence UVBR penetration into natural waters through climatic controls on the production and export of DOC from watersheds; for instance, increasing rainfall results in greater DOC runoff (Schindler et al. 1997). It has been suggested that this type of change in climate could have a greater influence on UVR penetration in lakes than would an increase of ground-level UVR due to ozone depletion (Schindler et al. 1996; Pienitz and Vincent 2000).

Whetton et al. (1996) described climate change scenarios for Australia and New Zealand over the next century. Their analysis was based on regional climate change scenarios from a Global Climate Model (GCM), which uses a number of global simulations from international laboratories. For the area that covers the New Zealand lakes presented in this paper (southern half of the South Island), the scenario for 2030 AD is for warming of 0.5°–2.0°C on the eastern side of the Southern Alps (Canterbury and Otago regions) and 0.5°–1.5°C elsewhere. The predicted changes in precipitation are for an increase of zero to +15% in South Canterbury and Otago and for a change of −10% to +10% in the remainder of the island. Newer coupled GCMs suggest a tendency for greater increases in rainfall on the already wet western side of the Southern Alps and decreases on the dry eastern plains (Watson et al. 1998). Lakes in native grassland catchments, mostly on the eastern side of the Alps (Lakes Coleridge, Tekapo, Wanaka, and Wakatipu) are in the drier areas and, hence, are subject to less cloud cover. Photochemical bleaching of the DOC pool in the lake waters can be expected (Bertilsson and Tranvik 2000), and warmer temperatures combined with less rainfall will result in a decrease in DOC generated within the catchments. The opposite may be expected for the forested lakes in the west (Lakes Kaniere, Mahinapua, and Brunner). Thus, over the next few decades, the clear lakes on the eastern side of the Southern Alps may become clearer and more transparent to UVR and the humic lakes in the west less transparent.

Conclusions

Like other ecosystems in New Zealand, lakes are subject to relatively high dosage rates of UVR at some times of the year. The penetration of UVR into the water column is controlled by DOC, as is the case with lakes elsewhere in the world. Some New Zealand lake ecosystems may be very sensitive to the short, energetic wavelengths of the solar spectrum because of deep penetration of these wavelengths in waters with low concentrations of UVR-absorbing DOC.

The type and amount of vegetation surrounding a lake dictate the concentration of DOC in the lake water. Lakes with greater than 50% grassland cover in the catchment are particularly prone to UVR penetration (Lakes Coleridge, Tekapo, Wanaka, and Wakatipu). Conversely, the greater the proportion of forest, the higher the DOC concentration and the less transparent the waters are to UVR. In addition to concentration, the chemical composition of the DOC pool is likely to be important for determining the UVR exposure of a lake environment. Land use and climate changes can therefore potentially influence DOC export from catchments and hence affect penetration of UVR into lakes. We are at an early stage in our understanding of the role of UVR in the natural waters of New Zealand, but further investigation is imperative, since many of our lakes lie at one extreme of the DOC concentration scale and therefore are among the most at risk from UVR.

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References

Backlund P (1992) Degradation of aquatic humic material by ultraviolet light. Chemosphere 25:1869–1878

Bertilsson S, Tranvik LJ (2000) Photochemical transformation of dissolved organic matter in lakes. Limnol Oceanogr 45:753–762

Bodeker G (1997) UV radiation in polar regions. In: Lyons B, Howard-Williams C, Hawes I (eds) Ecosystem processes in Antarctic ice-free landscapes. Balkema, Rotterdam, pp 23–42

Bothwell ML, Sherbot D, Roberge AC, Daley RJ (1993) Influence of natural ultraviolet radiation on lotic periphytic diatom community growth, biomass accrual, and species composition: short-term versus long-term effects. J Phycol 29:24–35

Davies-Colley RJ, Vant WN, Smith DG (1993) Colour and clarity of natural waters: science and management of optical water quality. Ellis Horwood, New York

de Mora S, Demers S, Vernet M (2000) The effects of UV radiation in the marine environment. Cambridge University Press, Cambridge

Determann SR, Reuter R, Wagner P, Willkomn R (1994) Fluorescent matter in the eastern Atlantic Ocean Part 1: Method of measurement and near-surface distribution. Deep-Sea Res 41:659–675

Hodoki Y, Watanabe Y (1998) Attenuation of solar ultraviolet radiation in eutrophic freshwater lakes and ponds. Jpn J Limnol 59:27–37

Howard-Williams C, Schwarz A-M, Vincent WF (1995) Deep-water aquatic plant communities in an oligotrophic lake: physiological responses to variable light. Freshwater Biol 33:91–102

Howard-Williams C, Vincent WF (1985) Optical properties of New Zealand lakes. II. Underwater spectral characteristics and effects on PAR attenuation. Arch Hydrobiol 104:441–457

James M, Hawes I, Weatherhead M (2000) Removal of settled sediments and periphyton from macrophytes by grazing invertebrates in the littoral zone of a large oligotrophic lake. Freshwater Biol 44:311–326

Karentz D, Cleaver JE, Mitchell DL (1991) Cell survival characteristics and molecular responses of Antarctic phytoplankton to ultraviolet-B radiation. J Phycol 27:326–341

Kirk JTO (1994a) Light and photosynthesis in aquatic ecosystems. Cambridge University Press, Cambridge

Kirk JTO (1994b) Optics of UV-B radiation in natural waters. Arch Hydrobiol 43:1–16

Laurion I, Vincent WF, Lean DR (1997) Underwater ultraviolet radiation: development of spectral models for northern high latitude lakes. Photochem Photobiol 65:107–114

Laurion I, Ventura M, Catalan J, Psenner R, Sommaruga R (2000) Attenuation of ultraviolet radiation in mountain lakes: factors controlling the among- and within-lake variability. Limnol Oceanogr 45:1274–1288

Lindell MJ, Granéli HW, Bertilsson S (2000) Seasonal photoreactivity of dissolved organic matter from lakes with contrasting humic content. Can J Fish Aquat Sci 57:875–885

Lindell M, Granéli W, Tranvik L (1995) Enhanced bacterial growth in response to photochemical transformation of dissolved organic matter. Limnol Oceanogr 40:195–199

Madronich S (1993) The atmosphere and UV-B radiation at ground level. In: Young AR, Björn LO, Moan J, Nultsch W (eds) Environmental UV photobiology. Plenum Press, New York, pp 1–40

Markager S, Vincent WF (2000) Spectral light attenuation and the absorption of UV and blue light in natural waters. Limnol Oceanogr 45:642–650

McKenzie RL, Bodeker GE, Keep DJ, Kotkamp M, Evans JH (1996) UV radiation in New Zealand: measured north to south differences, and relationship to other latitudes. Weather Climate 16:17–26

McKenzie R, Connor B, Bodeker G (1999) Increased summertime UV radiation in New Zealand in response to ozone loss. Science 285:1709–1711

McKnight DM, Andrews ED, Spaulding SA, Aiken GR (1994) Aquatic fulvic acids in algal-rich Antarctic ponds. Limnol Oceanogr 39:1972–1979

Morris DP, Hargreaves BR (1997) The role of photochemical degradation of dissolved organic carbon in regulating the UV transparency of three lakes on the Pocono Plateau. Limnol Oceanogr 42:239–249

Morris DP, Zagarese H, Williamson CE, Balseiro EG, Hargreaves BR, Modenutti B, Moeller R, Queimalinos C (1995) The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. Limnol Oceanogr 40:1381–1391

National Science Strategy Committee (1998) Annual report for 1997 of the National Science Strategy Committee for Climate Change. Royal Society of New Zealand, Wellington

Neale PJ, Davis RF, Cullen JJ (1998) Interactive effects of ozone depletion and vertical mixing on photosynthesis of Antarctic phytoplankton. Nature 392:585–589

New Zealand Land Resource Inventory (1997) Our land resources. New Zealand Land Resource Inventory Worksheets for National Water and Soil Conservation Organisation. Water and Soil Division, Ministry of Works and Development, Wellington, New Zealand

Pienitz R, Vincent WF (2000) Effect of climate change relative to ozone depletion on UV exposure in subarctic lakes. Nature 404:484–487

Quesada A, Mouget J-L, Vincent WF (1995) Growth of Antarctic cyanobacteria under ultraviolet radiation: UVA counteracts UVB inhibition. J Phycol 31:242–248

Schindler DW, Beaty KG, Fee EJ, Cruikshank DR, Debruyn ER, Findlay DL, Linsey GA, Shearer JA, Stainton MP, Turner MA (1990) Effects of climatic warming on lakes in the central boreal forest. Science 250:44–47

Schindler DW, Curtis PJ, Parker BR, Stainton MP (1996) Consequences of climate warming and lake acidification for UV-B penetration in North American boreal lakes. Nature 379:705–707

Schindler DW, Curtis PJ, Bayley SE, Parker BR, Beaty KG, Stainton MP (1997) Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. Biogeochemistry 36:9–28

Scully NM, Lean DRS (1994) The attenuation of ultraviolet light in temperate lakes. Ergeb Limnol 43:135–144

Smith RC, Prézelin BB, Baker KS, Bidigare RR, Boucher NP, Coley T, Karentz D, MacIntyre S, Matlick HA, Menzies D, Ondrusek M, Wan ZE, Waters KJ (1992) Ozone depletion: ultraviolet radiation and phytoplankton biology in Antarctic waters. Science 255:952–959

Smith REH, Furgal JA, Charlton MN, Greenberg BM, Hiriart V, Marwood C (1999) Attenuation of ultraviolet radiation in a large lake with low dissolved organic matter concentrations. Can J Fish Aquat Sci 56:1351–1361

Strickland JDH, Parsons TR (1968) A practical handbook of seawater analysis. Bull Fish Res Bd Can 167:1–311

Toon OB, Turco RP (1991) Polar stratospheric clouds and ozone depletion. Sci Am 264:40–47

Vincent WF, Neale PJ (2000) Mechanisms of UV damage to aquatic organisms. In: de Mora S, Demers S, Vernet M (eds) The effects of UV radiation in the marine environment. Cambridge University Press, Cambridge, pp 149–176

Vincent WF, Rae R, Laurion I, Howard-Williams C, Priscu JC (1998) Transparency of Antarctic ice-covered lakes to solar ultraviolet radiation. Limnol Oceanogr 43:618–624

Vincent WF, Roy S (1993) Solar ultraviolet-B radiation and aquatic primary production: damage, protection and recovery. Environ Rev 1:1–12

Vinebrooke RD, Leavitt PR (1999) Differential responses of littoral communities to ultraviolet radiation in an alpine lake. Ecology 80:223–237

Waiser MJ, Robarts RD (2000) Changes in composition and reactivity of allochthonous DOM in a prairie saline lake. Limnol Oceanogr 45:763–774

Watson RT, Zinyowera MC, Moss RH, Dokken DJ (1998) The regional impacts of climate change: an assessment of vulnerability. Cambridge University Press, Cambridge

Whetton P, Mullann AB, Pittock AB (1996) Climate change scenarios for Australia and New Zealand. In: Bouma WJ, Pearman GI, Manning MR (eds) Greenhouse: coping with climate change. CSIRO Publishing, Collingwood, pp 145–168

Williamson CE, Stemberger RS, Morris DP, Frost TM, Paulsen SG (1996) Ultraviolet radiation in North American lakes: attenuation estimates from DOC measurements and implications for plankton communities. Limnol Oceanogr 41:1024–1034

Yan ND, Keller W, Scully NM, Lean DRS, Dillon PJ (1996) Increased UV-B penetration in lakes owing to drought-induced acidification. Nature 381:141–143