Spectral attenuation of solar ultraviolet radiation in humic lakes in Central Finland

P.S. Huovinen *,1, H. Penttilä 2, M.R. Soimasuo
Department of Biological and Environmental Science, University of Jyväskylä, Survontie 9, FIN-40500 Jyväskylä, Finland

Received 25 July 2000; accepted 13 November 2000

Importance of this paper: Increasing fluxes of solar ultraviolet-B radiation resulting from stratospheric ozone depletion pose a threat also to aquatic biota and ecosystems. Photobiological effects are not only a function of the level of irradiance, but also a function of wavelength. The penetration of UV radiation in natural waters is governed by characteristics of the water body, altering also the spectral composition of the underwater light field. Thus, when the impact of increasing UV-B radiation on aquatic environments and organisms is assessed, understanding of the patterns determining spectral underwater composition forms the basis for response evaluation.

Abstract

The attenuation of solar ultraviolet (UV) radiation in five lakes in Central Finland was evaluated through field measurements and/or by determining the optical properties of the lake water during summer 1999. Spectral UV irradiance in the air and at several depths underwater was measured in three lakes (Lake Palosjärvi, Konnevesi, and Jyväskylä) with dissolved organic carbon (DOC) ranging from 4.9 to 8.7 mg l⁻¹ and chlorophyll a ranging from 1.6 to 16 μg l⁻¹. According to the field measurements, 99% of the UV-B radiation was attenuated in approximately a half meter water column in the clearest lake. In the UV-A region at 380 nm, the corresponding attenuation occurred in the upper one meter. In a small humic lake (DOC 13.2–14.9 mg l⁻¹) UV-B radiation was attenuated to 1% of the subsurface irradiance within the top 10 cm water column, whereas UV-A radiation (at 380 nm) penetrated more than twice as deeply (maximum 25 cm), as predicted from the absorption coefficients. These results suggest the importance of the dissolved fraction of lake water in governing the UV attenuation in lakes. This was seen from the significant relationship between the vertical attenuation coefficients (Kd) based on field measurements and the absorption coefficients (a_d) derived from spectrophotometric laboratory scannings, as well as between Kd and DOC.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: UV-B; UV-A; Vertical attenuation coefficient (Kd); Absorption coefficient (a_d); Humic lakes; DOC

1. Introduction

Understanding the depth pattern of solar ultraviolet (UV) radiation (280–400 nm) and its underwater spectral composition is essential when evaluating the exposure of aquatic organisms to harmful UV dose rates in their habitats. Because of enhanced fluxes as a result of stratospheric ozone depletion (Blumthaler and Ambach, 1990; Kerr and McElroy, 1993) the penetration depth of UV-B radiation (280–315 nm) in natural waters
especially important. Although, UV-B radiation is biologically more damaging than longer wavelengths (e.g. Green and Miller, 1975), it is also more quickly attenuated in the water column (Kirk, 1994a) thus mitigating photodamage. Despite the importance of the UV-B waveband, understanding the depth profile of UV-A radiation (315–400 nm) is essential as well, e.g. because of its harmful effects and involvement in photorepair processes in aquatic organisms (Mitchell and Karentz, 1993; Vincent and Roy, 1993).

In situ studies have demonstrated that ambient solar UV radiation can inhibit primary production in lakes (Gala and Giesy, 1991; Huovinen and Goldman, 2000) and in oceans (Smith et al., 1992). Generally, the attenuation of UV-B radiation is more efficient in lakes than in oceans (Kirk, 1994a). The UV-B penetration depths may vary from only few centimeters in highly humic lakes (Kirk, 1994a) to dozens of meters in the oceans (Smith et al., 1992; Kirk, 1994a). Dissolved organic carbon (DOC) strongly governs the UV attenuation in humic lakes (e.g. Kirk, 1994a; Scully and Lean, 1994), whereas in oceans (Smith and Baker, 1979) and in clear lakes with low DOC concentration the contribution of phytoplankton to UV attenuation can be significant (Sommaruga and Psenner, 1997). Field measurements and the factors determining the attenuation of UV radiation in freshwaters have started to receive more attention in recent years (Scully and Lean, 1994; Morris et al., 1995; Williamson et al., 1996; Laurion et al., 1997; Sommaruga and Psenner, 1997; Lean, 1998; Vincent et al., 1998; Crump et al., 1999; Arts et al., 2000; Huovinen et al., 2000). The protection against UV radiation provided by dissolved humic material for aquatic biota may be diminished if photodegradation of DOC by UV radiation (Morris and Hargreaves, 1997) and acidification (Schindler et al., 1996; Yan et al., 1996) increase the UV transparency in lakes.

In this study, the spectral attenuation of solar UV radiation (UV-B and UV-A) in five lakes with different characteristics located in Central Finland (62°N, 25°–26°E) was evaluated in summer 1999 through field measurements and/or by determining the optical properties of lake water. The role of dissolved humic substances and optical properties of lake water in affecting UV attenuation was evaluated. As an extension of studies conducted in summer 1998 (Huovinen et al., 2000), this work continues to characterize the summer UV penetration depths in typical range of Finnish humic lakes.

2. Methods

2.1. Study lakes

The spectral measurements of UV irradiance in air and underwater were performed in three lakes situated in Central Finland. Lake Palosjärvi (62°03′N, 26°09′E), Lake Konnevesi (62°38′N, 26°21′E) and Lake Jyväsjärvi (62°14′N, 25°48′E) were chosen to represent varying (as DOC) and phytoplankton (as chlorophyll a) concentrations (Table 1). Samples for laboratory analyses were taken from the surface water, not only concurrent with the field measurements, but also at other

<table>
<thead>
<tr>
<th>Lakes</th>
<th>Date</th>
<th>DOC (mg l⁻¹)</th>
<th>TOC (mg l⁻¹)</th>
<th>Chl a (µg l⁻¹)</th>
<th>a₄₄₀ nm (m⁻¹)</th>
<th>a₃₈₀ (250/365 nm)</th>
<th>a₄₀₀ (315 nm)</th>
<th>a₄₀₀/K₄₀₀ (380 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palosjärvi</td>
<td>July 14¹</td>
<td>4.9</td>
<td>–</td>
<td>1.6</td>
<td>0.63</td>
<td>7.85</td>
<td>1.06</td>
<td>0.56</td>
</tr>
<tr>
<td>Konnevesi</td>
<td>June 11¹</td>
<td>5.9</td>
<td>–</td>
<td>3.1</td>
<td>1.61</td>
<td>6.53</td>
<td>0.97</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>June 29¹</td>
<td>6.5</td>
<td>–</td>
<td>1.7</td>
<td>1.45</td>
<td>7.22</td>
<td>0.99</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>August 26</td>
<td>6.9</td>
<td>–</td>
<td>2.8</td>
<td>1.83</td>
<td>7.29</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tuomiojärvi</td>
<td>August 27</td>
<td>7.6</td>
<td>7.8</td>
<td>8.9</td>
<td>2.07</td>
<td>7.40</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Jyväsjärvi</td>
<td>June 11¹</td>
<td>8.7</td>
<td>–</td>
<td>6.4</td>
<td>4.90</td>
<td>5.16</td>
<td>0.97</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>June 30¹</td>
<td>8.2</td>
<td>–</td>
<td>16.1</td>
<td>3.92</td>
<td>5.80</td>
<td>0.85</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>July 14</td>
<td>8.4</td>
<td>–</td>
<td>9.4</td>
<td>3.76</td>
<td>5.84</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>August 27</td>
<td>8.7</td>
<td>9.0</td>
<td>7.4</td>
<td>3.33</td>
<td>5.82</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Kopru</td>
<td>June 11</td>
<td>13.7</td>
<td>–</td>
<td>9.2</td>
<td>6.75</td>
<td>5.38</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>June 29</td>
<td>13.2</td>
<td>–</td>
<td>1.6</td>
<td>6.68</td>
<td>5.58</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>August 26</td>
<td>14.9</td>
<td>15.6</td>
<td>19.5</td>
<td>4.74</td>
<td>6.11</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Properties characterizing optical color (absorption coefficient at 440 nm) and molecular size of humic molecules (ratio of absorption coefficients at 250 and 365 nm) as well as the ratio of a₄₀₀ and vertical attenuation coefficient (K₄₀₀) in the UV-B (315 nm) and the UV-A (380 nm) regions are presented.  

¹ Dates of field underwater UV measurements.
times during the summer 1999 to demonstrate seasonal variation (Table 1). Water samples were also taken from two additional lakes, Lake Tuomiojärvi (62°15′N, 25°48′E) and small Lake Kopru (62°38′N, 26°21′E), where field measurements of underwater UV irradiance were not made (Table 1). During the field measurements in 1999, the ozone concentrations were 322 DU (June 11), 327 DU (June 29), 299 DU (June 30), and 321 DU (July 14) as measured at Jokioinen, Finland (60°11′), 327 DU (June 29), 299 DU (June 30), and 321 DU (July 14) as measured at Jokioinen, Finland (60°44′N, 23°30′E) (the Brewer spectrophotometer #107), being approximately 5–13% below the 1979–1998 average (TOMS satellite data; 1993 and 1995–1996 not included) (Karhu, J., FMI, Sodankylä Meteorological Observatory, Personal communication).

2.2. Spectral measurements of UV irradiance

The spectral UV measurements were carried out within 3 h of solar noon, using a Hamamatsu Photonic Multichannel Analyzer (model PMA-11) with a spectral resolution of 1.5 nm. This device consists of input optics, a reflection grid and a 25 mm long light detector array of 1024 MOS diodes. The spectra are not scanned but recorded in a single exposure. Thus, all parts of each spectrum are recorded in similar conditions, and the recording is fast and suitable for field measurements. Each exposure consists of two parts. First, the leak current of the diode array in the dark (the dark current) is measured. Then the shutter is opened, and the diode is exposed to light. The diode leak current is subtracted before digitizing the spectrum. As a result, there are statistical fluctuations in the spectra. Especially below 290 nm, the measured intensity in one diode can have a negative value since the value is statistically fluctuating around the true value zero. The standard deviation of the fluctuation for a single diode is of the order of 1 mW m⁻² nm⁻¹. When the data is binned to 1 nm per channel, standard deviation of fluctuation is reduced to one half of that. The measured spectra covered the wavelength region of 200–400 nm binned to 0.2 nm channels, but the raw data was modified to represent 1 nm channels to simplify the data handling.

The sunlight was collected with an integrating sphere (Oriel model 70451) with a diameter of 15 cm and a 38 mm diameter input port. The integrating sphere was connected to PMA-11 via a 4.5 m long quartz fiber bundle. To prevent lake water from influencing the reflecting properties of the inner surface of the integrating sphere, it was filled with distilled water, which has minimal UV absorption. To avoid mixing of lake water to distilled water in the integrating sphere, the input port was covered with a transparent polypropylene film. This causes a small discrimination of very large entering angles to the integrating sphere. However, this error is small and a correction factor derived from the measurements taken both with and without the film was used to minimize it. The system was calibrated against a NIST traceable quartz halogen calibration lamp. Because of the compactness of PMA-11 optics the measurements suffered to some extent from stray light. The level of stray light was reduced by a broadband pass filter (Oriel type 51560) whose transmission range is from 250 to 390 nm. The filter was positioned between the PMA-11 entrance slit and the end of the quartz fiber bundle. Since this filter has some 40% transmission in the wavelengths longer than 700 nm, the stray light is not totally blocked but reduced to approximately 20% level.

The measurements were made from the dock by lowering the integrating sphere using a device made of aluminum bar, which was designed to keep the upward position and to measure the depth. The exposure time for each spectrum was 3 s. The mean of three replicate readings was used. The operation of the PMA-11 was controlled and data recorded by a laptop computer.

2.3. Vertical attenuation

The attenuation of irradiance with depth in optically homogenous water follows the law \( E_d(z) = E_d(0)e^{-K_d z} \), where \( K_d \) is the vertical attenuation coefficient for downward irradiance, \( E_d(z) \) the irradiance at depth \( z \), and \( E_d(0) \) the irradiance just below the surface (Kirk, 1994a). \( K_d \) values in this study were obtained from the slope of the linear regression of the natural logarithm of measured irradiance versus depth. The log-linear part of the curve was used, and values only from fit \( r^2 \geq 0.95 \) were accepted. The number of depths (minimum of three) that was used depended on the penetration depth at each wavelength. \( K_d \) values were determined for three adjacent wavelengths (e.g. 309, 310, 311 nm) to avoid random errors, and means are presented for wavelengths 310, 315, 320, 340, 360, and 380 nm. When pooling of the data was required 310, 315, and 320 nm were included to represent UV-B, and 340, 360, and 380 nm to represent UV-A waveband. Since the distance from subsurface to the depth where the irradiance falls below the detection limit was very short, only a few centimeters at short wavelengths especially in highly humic waters, the estimates of \( K_d \) at these wavelengths are less precise, or in some cases could not be determined. Also, the depth measurements in these cases were difficult to make accurately, and were affected by even a slight breeze.

2.4. Analyses of water characteristics

For the determination of the optical properties, lake water was filtered with a 0.2 μm membrane (cellulose acetate, Lida) to remove the particulate fraction. Absorbance (200–700 nm) of the remaining dissolved
fraction of lake water was measured with a Beckman DU-640 scanning spectrophotometer in a 1 cm quartz cuvette, using 0.2 μm filtered distilled (Milli Q) water as a blank. Absorption coefficients (a_d) for the dissolved fraction of lake water were calculated as a_d = 2.303D/r, where D is the absorbance and r the path length (Kirk, 1994b). The absorption coefficient at 440 nm (a_d440 nm) was used as an indication of optical color (Kirk, 1994b). Molecular size of the humic molecules was estimated from the ratio of the absorption coefficients at 250 and 365 nm (a_d250 nm/a_d365 nm), the molecular size increasing towards smaller ratios (De Haan and De Boer, 1987; De Haan, 1972, 1993).

Organic carbon was measured at the Central Finland Regional Environment Centre from filtered (Sartorius 0.45 μm; dissolved organic carbon, DOC) and unfiltered (total organic carbon, TOC) water (preserved with 1 ml of 2 M HCl/100 ml of sample) using a high temperature combustion method (SFS-EN, 1997; ISO, 1999). For the measurement of chlorophyll a concentrations, the water samples were filtered on Whatman GF/C filters on the day of sampling. The filters were kept frozen at −20 °C until extraction in 90% ethanol at 75 °C, and spectrophotometric measurements (SFS, 1993). No acid correction for phaeophytin was made.

3. Results

3.1. Field measurements of underwater UV irradiance

The measured underwater spectra demonstrated a wavelength dependent attenuation of solar UV radiation with depth, short wavelengths attenuating more rapidly (Fig. 1). Vertical attenuation coefficients (K_d) derived from the field measurements further demonstrated the increasing of attenuation with decreasing wavelengths (Fig. 2A). Linear regression of natural logarithm of K_d as a function of wavelength gave a slope (S_{K_d}) of 0.0120 nm⁻¹ for Lake Jyväsjärvi, 0.0154 nm⁻¹ for Lake Konnevesi, and 0.0102 nm⁻¹ for Lake Palosjärvi (Fig. 2A).

The largest K_d values i.e. the strongest attenuation was observed in humic lakes with increasing DOC concentrations (Fig. 2B). The relationship between K_d and the DOC concentration in the lakes, where DOC ranged from 4.9 to 8.7 mg l⁻¹, was best described with an exponential function (r² = 0.95, Fig. 2B), although a power function also provided an almost similar fit (r² = 0.95; Table 2). DOC specific K_d (K_d/DOC) was higher towards the more humic lakes (Fig. 2A). The seasonal changes in DOC concentration within a single lake were rather small (Table 1). Adding chlorophyll to the examination of the relationship of K_d and DOC (combined data of 310, 315, and 320 nm) improved the linear regression coefficient only by 6.5%. A significant rela-
3.2. Optical properties of the lake water

The analyses of the dissolved fraction of lake water showed increasing absorption with decreasing wavelengths (Fig. 4A) as well as with higher humic concentrations (Fig. 4B). When the natural logarithm of \( a_d \) was plotted against wavelength (300–400 nm), slopes (\( S_{a_d} \)) of 0.0169 nm\(^{-1}\) (Lake Kopru and Jyväsjärvi), 0.0184 nm\(^{-1}\) (Lake Tuomiojärvi), 0.0180 nm\(^{-1}\) (Lake Konnevesi), and 0.0204 nm\(^{-1}\) (Lake Palosjärvi) were obtained (Fig. 4A). The relationship between the absorption coefficients (\( a_d \)) and DOC concentration (range 4.9–14.9 mg l\(^{-1}\)) was best described with a power function (Fig. 4B, Table 2). The DOC specific \( a_d \) (\( a_d / \text{DOC} \)) was higher in the more humic lakes and at the shorter wavelengths, and it reduced some of the variation between the lakes (Fig. 4A). According to the \( a_d / \text{DOC} \) relationship, the lakes with higher humic content had larger humic molecules as compared to the clear lakes in this study (Table 1).

3.3. Prediction of attenuation from optical properties of water

The linear relationship between the absorption coefficients (\( a_d \)) based on the spectrophotometric scannings of filtered lake water and the vertical attenuation coefficients (\( K_d \)) derived from the field measurements is presented in Table 2. In Fig. 5, the data from the present study is pooled with the data from the previous study in these lakes. In the UV-B region, a power function gave a slightly better fit (\( r^2 = 0.97 \)) compared to the linear function (\( r^2 = 0.94 \)). In the UV-A region (340–380 nm), the relationship between \( K_d \) and \( a_d \) was linear (Fig. 5, Table 2). The UV penetration depths for the lakes where field measurements were not made were estimated from the equation derived from the pooled data (Fig. 5, Table 2). The 1% UV-B penetration depths (\( z_{1\%} \)) were estimated to be 0.22–0.26 m in Lake Tuomiojärvi and only 0.07–0.11 m in Lake Kopru (Fig. 3A). The corresponding UV-A (380 nm) penetration depths were 0.61 m in Lake Tuomiojärvi and 0.19–0.25 m in Lake Kopru.

The \( a_d / K_d \) ratio indicated that the absorbance of the dissolved fraction of lake water (\( a_d \)) comprised an increasing proportion of \( K_d \) with decreasing wavelengths (Table 1). In the UV-B region at 315 nm, the dissolved fraction comprised more than 85% of the vertical attenuation (Table 1). In the UV-A region at 380 nm, the corresponding fraction was more than 56% (Table 1).

4. Discussion

According to the field measurements, 99% of the solar UV-B radiation was attenuated in approximately half a meter water column in the clearest of the study lakes with DOC concentration of 4.9 mg l\(^{-1}\). In the UV-A region at 380 nm, the corresponding attenuation occurred in the upper one meter of water. In small humic Lake Kopru (DOC 13.2–14.9 mg l\(^{-1}\)) UV-B radiation was attenuated to 1% of the subsurface irradiance within the top 10 cm water column, whereas UV-A radiation (at 380 nm) penetrated more than twice as deeply (maximum of 25 cm), as predicted from the absorption coefficients. These results suggest the importance of DOC in regulating the UV transmission in

![Fig. 2. Vertical attenuation coefficients (\( K_d \); open markers) and DOC specific \( K_d \) (solid markers) as a function of wavelength in Lakes Palosjärvi (P), Konnevesi (K), and Jyväsjärvi (J) (A). The relationship between \( K_d \) and DOC at different wavelengths in these lakes (B).](image-url)
a predicted accordingly from more frequent samplings. In order to compare equations reported in other studies as well as of the present study, fluorescence (Scully and Lean, 1994). When examining the power function of DOC and a linear function of DOC the 300–320 nm waveband has been described as a For the present study, the importance of the dissolved fraction of lake water in regulating the UV penetration (Williamson et al., 1996). Variation in the vertical attenuation coefficients (K_d) between lakes (Scully and Lean, 1994) and seasonal variation within a lake (Morris and Hargreaves, 1997) have been largely explained by DOC. K_d in the 300–320 nm waveband has been described as a power function of DOC and a linear function of DOC fluorescence (Scully and Lean, 1994). When examining the relationship between K_d and DOC, the concentration range of DOC is an important factor, which should be considered. At the DOC concentrations below 2 mg l⁻¹, UV penetration has been found to increase abruptly (Williamson et al., 1996).

In the present study, the importance of the dissolved fraction of lake water in regulating the UV penetration could be seen from the significant relationships between DOC and the vertical attenuation coefficients (K_d) as well as between K_d and the absorption coefficients (a_d). However, when predicting UV-B penetration depths on the basis of DOC concentration, higher K_d values, i.e. lower penetration depths, were obtained from the results of the present study as compared to the empirical model equations presented by Granéli et al. (1996) and Arts et al. (2000) (Table 2). Instead, the relationship between K_d and DOC was quite similar to that given by Scully and Lean (1994) and Morris et al. (1995). Although the importance of DOC in influencing the attenuation of UV radiation in natural waters is evident, the variation in the absorption properties of the dissolved organic compounds with different molecular weight and origin (Stewart and Wetzel, 1980) interferes with the evaluation and the generalization of the UV penetration as a

<table>
<thead>
<tr>
<th>Variables/waveband</th>
<th>Equation</th>
<th>r²</th>
<th>DOC (mg l⁻¹)</th>
<th>Reference</th>
<th>K_d (m⁻¹)</th>
<th>z_{1%} (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 0.10[DOC]^{2.77}</td>
<td>0.95</td>
<td>4.9–8.7</td>
<td>Present study</td>
<td>13.65</td>
<td>0.34</td>
</tr>
<tr>
<td>UV-B (300–320 nm)</td>
<td>K_d = 0.42[DOC]^{1.86}</td>
<td>0.97</td>
<td>0.5–7.8</td>
<td>Scully and Lean (1994)</td>
<td>11.40</td>
<td>0.40</td>
</tr>
<tr>
<td>UV-B (320 nm)</td>
<td>K_d = 2.09[DOC]^{1.12}</td>
<td>0.87</td>
<td>0.2–23.5</td>
<td>Morris et al. (1995)</td>
<td>15.26</td>
<td>0.30</td>
</tr>
<tr>
<td>UV-B (280–320 nm)</td>
<td>K_d = 4.14[DOC]^{−1.70}</td>
<td>0.98</td>
<td>3.9–19.4</td>
<td>Granéli et al. (1996)</td>
<td>6.73</td>
<td>0.68</td>
</tr>
<tr>
<td>UV-B (280–320 nm)</td>
<td>K_d = 0.60[DOC]^{1.29}</td>
<td>0.76</td>
<td>4.1–80.1</td>
<td>Arts et al. (2000)</td>
<td>5.92</td>
<td>0.78</td>
</tr>
<tr>
<td>UV-A (340–380 nm)</td>
<td>K_d = 0.71[DOC]^{−1.25}</td>
<td>0.84</td>
<td>–</td>
<td>Arts et al. (2000)</td>
<td>6.53</td>
<td>0.71</td>
</tr>
<tr>
<td>UV-A (340–380 nm)</td>
<td>K_d = 0.07[DOC]^{2.87}</td>
<td>0.77</td>
<td>4.9–8.7</td>
<td>Present study</td>
<td>8.00</td>
<td>0.58</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 10.95(ad_{440 nm})^{0.80}</td>
<td>0.97</td>
<td>4.9–8.7</td>
<td>Present study</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UV-B (320 nm)</td>
<td>K_d = 16.0(ad_{440 nm})^{−0.15}</td>
<td>0.83</td>
<td>0.2–23.5</td>
<td>Morris et al. (1995)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UV-A (340–380 nm)</td>
<td>K_d = 4.84(ad_{440 nm})^{1.07}</td>
<td>0.83</td>
<td>4.9–8.7</td>
<td>Present study</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 0.71(ad_{440 nm})^{1.13}</td>
<td>0.97</td>
<td>4.9–8.7</td>
<td>Present study</td>
<td>14.37</td>
<td>0.32</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 1.06(K_{d310 nm})^{0.63}</td>
<td>0.94</td>
<td>4.9–16.0</td>
<td>Present study (Fig. 5)</td>
<td>15.81</td>
<td>0.29</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 1.12(K_{d310 nm})^{0.46}</td>
<td>0.97</td>
<td>8.1–9.5</td>
<td>Huovinen et al. (2000)</td>
<td>16.50</td>
<td>0.28</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 1.23(K_{d310 nm})^{0.24}</td>
<td>0.98</td>
<td>0.5–7.8</td>
<td>Scully and Lean (1994)</td>
<td>19.44</td>
<td>0.24</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 1.51(K_{d310 nm})^{−0.12}</td>
<td>0.84</td>
<td>0.2–23.5</td>
<td>Morris et al. (1995)</td>
<td>19.65</td>
<td>0.23</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 1.27(K_{d310 nm})^{0.3}</td>
<td>0.95</td>
<td>–</td>
<td>Morris and Hargreaves (1997)</td>
<td>16.92</td>
<td>0.27</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 0.95(K_{d310 nm})^{−0.24}</td>
<td>0.82</td>
<td>6.9–20.3</td>
<td>Crump et al. (1999)</td>
<td>18.76</td>
<td>0.25</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>K_d = 1.22(K_{d310 nm})^{−0.49}</td>
<td>0.94</td>
<td>7–20</td>
<td>Lean (1998)</td>
<td>19.93</td>
<td>0.23</td>
</tr>
<tr>
<td>UV-A (340–380 nm)</td>
<td>K_d = 1.29(K_{d440 nm})^{0.70}</td>
<td>0.96</td>
<td>4.9–16.0</td>
<td>Present study (Fig. 5)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UV-B (310–320 nm)</td>
<td>a_d = 0.81[DOC]^{1.60}</td>
<td>0.85</td>
<td>4.9–14.9</td>
<td>Present study</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UV-A (340–380 nm)</td>
<td>a_d = 0.30[DOC]^{1.70}</td>
<td>0.68</td>
<td>4.9–14.9</td>
<td>Present study</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

For the present study, K_d data for UV-A waveband is pooled from separate determinations at 340, 360, and 380 nm from five field measurements (number of data points n = 15). Data from 310, 315, and 320 nm is pooled for UV-B waveband. Data for a_d is pooled accordingly from more frequent samplings. In order to compare equations reported in other studies as well as of the present study, predicted K_d and z_{1%} values are presented for Lake Konnevesi.

a Predicted K_d values using different equations for Lake Konnevesi with values DOC 5.9 mg l⁻¹, ad_{350 nm} 15.61, ad_{315 nm} 14.27, and ad_{420 nm} 13.09. Mean of ad values (14.32) was used for 310–320 nm waveband.

b Pooled with the data of Huovinen et al. (1994).

c Pooled with the data of Huovinen et al. (2000).
function of DOC. According to Lean (1998), the proportion of DOC, which absorbs UV-B radiation changes also temporally, the recent input of the fresh DOC being photochemically more active. Morris and Hargreaves (1997) found that seasonal declines in $K_d$ corresponded to the reductions in the UV absorbance of dissolved material, which were caused by declines in the DOC concentration and in the UV absorptivity ($a_d$/DOC), as well as in increased $a_{d_{250nm}}/a_{d_{365nm}}$ ratio (i.e. smaller molecules). Crump et al. (1999) concluded in their study on humic ponds that the DOC concentration was not a good predictor of the UV attenuation due to its varying absorption properties, although a general trend of a higher attenuation with a higher DOC is obvious. In addition to the optical properties, other factors can interfere with the prediction of the UV penetration from the DOC concentration. Recently Arts et al. (2000) reported that UV radiation penetrated deeper in saline prairie lakes than in freshwater systems with a similar DOC concentrations.

Conclusions on the role of chlorophyll concentration on the UV attenuation are difficult to draw, since the clear lakes with a low DOC concentration in the present study tended also to be oligotrophic and low in phytoplankton, whereas the darker humic lakes were more eutrophic having a higher phytoplankton abundance. Adding chlorophyll $a$ concentration to the examination of the linear relationship between $K_d$ and DOC indicated only a marginal impact of chlorophyll in these lakes. If the impact of the particulate material was crucial, the field measurements would not have correlated so well with the absorbance spectra of the filtered water samples. Also, the absorbance spectra of filtered and unfiltered lake water were often quite similar (data not shown) suggesting the dominant role of the dissolved material, which reflects the low proportion of the particulate fraction ($<$5%) of the total organic carbon content (Table 1). Similar conclusions were drawn by Scully and Lean (1994) from their data on north
temperate lakes. Instead of comparing different lakes, the impact of the seasonally changing chlorophyll concentration on UV attenuation could be described in a clear, low DOC alpine lake (Sommaruga and Psenner, 1997).

Rather than DOC, Crump et al. (1999) and Lean (1998) suggested that the absorption coefficients are more suitable for predicting the UV penetration in highly humic ponds. Also in the present study, the significant relationship between $K_d$ and the absorption coefficients ($a_d$) proved to be useful in predicting the UV penetration depths in lakes, corresponding quite well with several other studies (Scully and Lean, 1994; Morris et al., 1995; Morris and Hargreaves, 1997; Crump et al., 1999; Huovinen et al., 2000) (Table 2). In the present study, the penetration depths predicted from $a_d$ for Lake Tuomiojärvi and Lake Kopru, where field measurements were not made, corresponded well with the results from the actual field measurements made in these lakes in previous summer (Huovinen et al., 2000). Since the absorption measurement takes into account the varying absorption properties of dissolved material, it provides a more reliable tool to predict the UV penetration than DOC alone does. However, the spectral slope values (the slope of ln($K_d$) or ln($a_d$) vs. wavelength) for $K_d$ ($S_{K_d}$) were lower than for $a_d$ ($S_{a_d}$), which was also observed in the study by Morris et al. (1995) demonstrating the wavelength dependence of $K_d/a_d$. Although the absorption and scattering characteristics in a spectrophotometric cuvette do not represent the natural conditions, the absorption properties of natural water provide additional information and support for the actual field measurements, which are susceptible to various disturbances. Short wavelengths of the solar UV-B radiation with lower intensity than longer wavelength UV-A radiation, were attenuated the most intensely underwater and were therefore even more difficult to measure. Changing environmental conditions and a wave action during the measurement of a depth profile of UV irradiance can cause additional uncertainties, especially in highly humic lakes, where UV radiation penetrates only into the top centimeters of the water column.

Wavelength dependent attenuation of solar UV radiation modifies the underwater irradiance spectrum and thus the proportions of UV-B, UV-A and PAR with depth. Since biological effects of UV radiation are generally a function of wavelength (Green and Miller, 1975) varying photobiological effects and the effectiveness of repair processes can be expected with depth. The mixing depth and the seasonal stratification patterns, as well as the capability of an organism to move from harmful irradiance conditions finally determine the extent of exposure. In addition to the direct effects, aquatic organisms face a stress from indirect effects of UV radiation, e.g. through increased formation of photochemical reaction products, such as singlet oxygen and hydrogen peroxide, especially in low DOC lakes (Scully et al., 1997), and photoenhanced toxicity of some environmental contaminants (Huovinen et al., 2001). Also, photodegradation of organic matter can release complexed metals in the water (Hessen and Van Donk, 1994).

Although attenuation of UV radiation in the water column can mitigate its harmful effects, increased fluxes of UV-B radiation resulting from the stratospheric ozone depletion potentially also increase UV-B intensities underwater. On the other hand, UV penetration can be increased due to photodegradation of DOC by UV radiation (Morris and Hargreaves, 1997). Because of their more limited previous exposure to UV radiation, aquatic organisms in humic waters might be more sensitive to such increase in UV transparency than aquatic biota adapted to higher irradiance conditions in clear waters. When evaluating the impact of increased UV-B radiation on aquatic ecosystems as a whole, interactions and links to other environmental factors, such as acidification and climate warming, which may also increase...
UV transparency of natural waters (Schindler et al., 1996; Yan et al., 1996), can be important. Also, deleterious effects of UV radiation on marine phytoplankton impairing its role as an important sink for atmospheric CO₂ could thus promote global warming (Falkowski, 1994). Changes in temperature could again e.g. affect the effectiveness of mechanisms repairing UV induced damage (Bjørn et al., 1999). Considering the complex nature of UV radiation in natural waters, understanding the depth pattern of the UV penetration and the environmental factors affecting it are of a great importance in predicting the impact of increasing UV-B radiation on aquatic ecosystems.

Acknowledgements

We thank Dr. Esko Kyrö and Juha Karhu from Sodankylä Meteorological Observatory for kindly providing the ozone data for the days of field measurements. This study was financially supported by the Maj and Tor Nessling Foundation (grant no. 99060 to P. Huovinen).

References


Dr. Pirjo Huovinen's main research field is aquatic photo-tropy, including research on the effects of UV radiation on algae and zooplankton, and on phototoxicity of environmental contaminants, as well as characterization of underwater UV.

Dr. Heikki Penttilä's major field of research has been detection of weak and exotic radioactivities, especially developing measurement techniques for most short lived anthropogenic isotopes in laboratory and for the very weak samples of naturally occurring radioactivities e.g. in lake sediments. Recently, he has developed measurement techniques for underwater UV detection.

Dr. Markus Soimasuo's main research field is aquatic ecotoxicology. In recent years, he has been involved with UV research (biological effects and measurement techniques for underwater UV), currently studying especially effects of UV on fish larvae (development, biochemistry).