

## Spectral light attenuation and the absorption of UV and blue light in natural waters

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### Abstract

The spectral pattern of light attenuation in the ultraviolet (UV) and blue region (360–500 nm) was analyzed for seven high Arctic lakes. The best description of  $K_d$  versus wavelength was obtained with an exponential model similar to the model used for absorption by chromophoric dissolved organic compounds (CDOM), but with an additional parameter ( $K_{back}$ ) that accounts for background scattering:

$$K_d(\lambda) = K_d(\lambda_0)e^{S(\lambda_0-\lambda)} + K_{back},$$

where  $K_d(\lambda)$  is the diffuse vertical attenuation coefficient at wavelength  $\lambda$  and  $S$  is the exponential slope parameter that characterizes the decrease in attenuation with increasing wavelength. The inclusion of the background parameter gave a significantly better fit and eliminated the systematic deviations over the spectrum that occur in the absence of  $K_{back}$ . The resultant  $S$  values (mean =  $17.4 \mu\text{m}^{-1}$ ) were on average 47% higher than values calculated without a background parameter, and were more sensitive to between-lake differences. The same pattern was found when  $S$  was estimated from spectral  $K_d$  values in three literature data sets, so the new equation will generally increase the estimated values of  $S$  based on  $K_d$  and provide a more accurate guide to intersystem variability. A compilation of literature data for  $S$  (based on  $K_d$  and the new equation or on absorbance) showed that its mean value ( $\pm$ SE) is significantly higher in freshwaters ( $17.1 \pm 0.7 \mu\text{m}^{-1}$ ) than in the sea ( $14.0 \pm 0.4 \mu\text{m}^{-1}$ ). The variability in  $S$  was highest for low values of  $K_d$  or  $a$  (340 nm values below  $3 \text{ m}^{-1}$ ). This pattern may be due to instrument-related problems or more likely represents the real variability in the optical properties of CDOM in low colored systems. The analysis showed that  $S$  can vary significantly between and within systems (overall range =  $9.2\text{--}36.2 \mu\text{m}^{-1}$ ) and that the value obtained also depends on the method of calculation, the wavelength range, and the type of optical measurement.

Chromophoric dissolved organic matter (CDOM) is the main light-absorbing component at wavelengths below 500 nm in many natural waters, and there is often a close relationship between the optical properties of a water body and its dissolved organic carbon (DOC) content (Scully and Lean 1994; Morris et al. 1995; Laurion et al. 1997). Light absorption by CDOM overlaps the blue absorption maximum for chlorophyll, thereby affecting the availability of underwater light for photosynthesis. At lower wavelengths, CDOM is the most important bio-optical factor regulating the exposure of planktonic organisms to ultraviolet (UV) radiation (Schindler et al. 1996; Williamson et al. 1999). It also controls the ratios down through the water column of UV-B (280–320 nm) to UV-A (320–400 nm) and of total UV radiation (280–400 nm) to photosynthetically available

radiation (PAR, 400–700 nm). These ratios may influence the balance between UV damage and repair (Vincent et al. 1998, and refs therein). The DOC pool has long been thought of as a mostly refractory component of aquatic ecosystems, but recent results have shown that its photochemical degradation can contribute significantly to overall carbon fluxes (Granéli et al. 1996). This degradation is closely related to the absorption characteristics of CDOM and can result in the production of reactive oxygen species (Scully et al. 1997; Xenopoulos and Bird 1997). The spectral absorption of CDOM is also important for the upwelling light field and thus for remote sensing applications (e.g., Carder et al. 1989; Dekker 1993). There are therefore many reasons to improve our understanding of the absorption characteristics of organic compounds in water.

Within the PAR waveband, CDOM absorbs maximally in the blue region of the spectrum and, as first described by Jerlov (1968), its absorption decreases exponentially with increasing wavelength. Bricaud et al. (1981) thus proposed the equation:

$$a(\lambda) = a(\lambda_0)e^{S_a(\lambda_0-\lambda)}, \quad (1)$$

where  $a(\lambda)$  is the absorption coefficient at the wavelength  $\lambda$ ,  $\lambda_0$  is a reference wavelength and  $S_a$  a coefficient (units of  $\text{nm}^{-1}$  or, more conveniently,  $\mu\text{m}^{-1}$ ) that determines the shape of the curve. Jerlov (1968) suggested an  $S_a$  value of  $15 \mu\text{m}^{-1}$  and Bricaud et al. (1981) found that  $S_a$  varied between 10

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and  $20 \mu\text{m}^{-1}$  with a mean value of  $14 \mu\text{m}^{-1}$ . The  $S$  value is likely to be affected by the composition of the DOC pool; for example, humic acids have a lower  $S$  value than fulvic acids (Zepp and Schlotzhauer 1981; Carder et al. 1989), but little is known about how this optical parameter varies among different fractions of natural CDOM.

Given that CDOM accounts for a major fraction of the total light attenuation in natural waters, it is possible to estimate  $S$  from in situ profiles of spectral irradiance. Some authors have adopted this approach by substituting  $K_d$  (the downwelling attenuation coefficient) for the absorption coefficient in Eq. 1 (Morris et al. 1995; Laurion et al. 1997):

$$K_d(\lambda) = K_d(\lambda_0)e^{S_K(\lambda_0-\lambda)}, \quad (2)$$

where  $S_K$  denotes that  $S$  is estimated from  $K_d$ -coefficients. However, unlike the absorption coefficient, which approaches zero at longer wavelengths, the attenuation coefficient reaches a minimum value in the blue-green region that is significantly above zero in natural systems, mainly because of scattering of light by suspended particles. If this background value is not considered, the  $S$  values estimated from  $K_d$  measurements will be underestimated.

The objectives of the present paper are to examine the spectral attenuation of short wavelength radiation in natural waters, specifically: (1) to introduce an improved calculation technique for estimating  $S$  from  $K_d$  measurements; (2) to report new values of  $S$  from lakes in high Arctic Canada and from recalculation of  $S$  from literature data; and (3) to identify the extent and sources of variation in  $S$  values in the literature.

## Methods

*Bio-optical methods*—Downwelling underwater irradiance ( $E_d$ ) from 300 to 750 nm was measured with 1 nm resolution at 1–2 m intervals in seven lakes near Resolute Bay (74°N, 94°W) in high Arctic Canada with a Li-Cor 1800 underwater spectroradiometer. Two of the seven lakes were meromictic lakes with a stratified water column whereas the others had a homogeneous water column.  $K_d$  values for the meromictic lakes were calculated for the mixolimnion and the pycnocline separately, while for the other five lakes  $K_d$  spectra were determined using the full water column profiles. Further details of the lakes and measurements are given in Markager et al. (1999). Some of the  $E_d$  spectra measured close to the surface were affected by wave action and were therefore omitted from the calculations.  $K_d$  values were calculated at each nm between 300 and 700 nm from:

$$E_z(\lambda) = E_{0-}(\lambda)e^{-zK_d}, \quad (3)$$

where  $z$  is depth and  $E_{0-}$  is the irradiance just below the surface. The parameters  $K_d$  and  $E_{0-}$  in Eq. 3 were estimated at each nm with a non-linear fitting procedure (SAS 1990). Absorption by particles was measured using GF/F filters as described by Bricaud and Stramski (1990) using an integrating sphere connected to the Li-Cor spectroradiometer. The technique differed slightly from that using a spectrophotometer because in the spectroradiometer the filter was exposed to a broad irradiance spectrum (rather than individual wavelengths as in a spectrophotometer) and the trans-

mission/reflection of light was then recorded at 1 nm intervals. However, our comparison of the two methods showed that they produced identical values. The spectra were decomposed into absorption by pigments and a background absorption by non-pigmented material according to Bricaud and Stramski (1990). This technique assumes that the background absorption by non-pigmented compounds follows Eq. 1, but with the absorption at 750 nm as a background value. The relative contribution by dissolved compounds to the total absorption in the water column was calculated from the proportion of the absorption coefficients at each wavelength and averaged over the spectrum according to Kirk (1994).

*Estimation techniques for  $S$* —We first calculated  $S_K$  from the  $K_d$  spectra using Eq. 2. However, as seen in Fig. 1,  $K_d$  does not approach zero at high wavelengths and we therefore introduced a background parameter to improve the goodness-of-fit:

$$K_d(\lambda) = K_d(\lambda_0)e^{S_K'(\lambda_0-\lambda)} + K_{\text{back}}. \quad (4)$$

This gave a new value of  $S_K$ , denoted  $S_K'$ .

Estimation of  $S$  in the above equations is subject to a number of sources of error that depend on the reliability of  $K_d(\lambda)$  or  $a(\lambda)$  across the spectrum. For absorption measurements, the main problem is the low absorption at long wavelengths in combination with the limited length of the cuvette and the possible scattering effect of particles and bubbles. The larger values at short wavelengths are therefore more reliable than the values at longer wavelengths. A log-transformation of Eq. 1 will produce a straight line where  $S$  can be calculated by linear regression. However, the criterion for this technique is to minimize the sum of the squared residuals so a log-transformation will shift the weight of the observations from high to low values of  $a$  or from shorter towards longer wavelengths. Thus, the more unreliable low values at long wavelengths are given more weight. Using a direct nonlinear fitting procedure for Eq. 1 can obviate this problem. There are also various techniques to correct for errors caused by scattering and refraction (Bricaud et al. 1981; Davies-Colley and Vant 1987; Green and Blough 1994) which can help improve the reliability of data across the full spectrum.

$K_d(\lambda)$  measurements suffer from the opposite problem relative to that for  $a(\lambda)$ . Usually attenuation can be measured over several decades of irradiance and estimates of  $K_d$  are obtained even in the most transparent part of the spectrum. However, at short wavelengths an accurate determination of  $K_d$  can be difficult to achieve for the following reasons. If the surface irradiance is low then the measurements at depth may be at or below the limits of sensitivity of the instrument. In colored waters, the rapid attenuation of light with depth means that all the measurements must be done close to the surface where wave action causes large variations in spectral irradiance (e.g., Laurion et al. 1997) and also makes it more difficult to define the depth of each reading. For continuously lowered instruments, the pressure readings must be accurate and the gate-time for each radiometric channel must be sufficiently short and in synchrony with the pressure transducer to prevent the irradiance readings spilling over

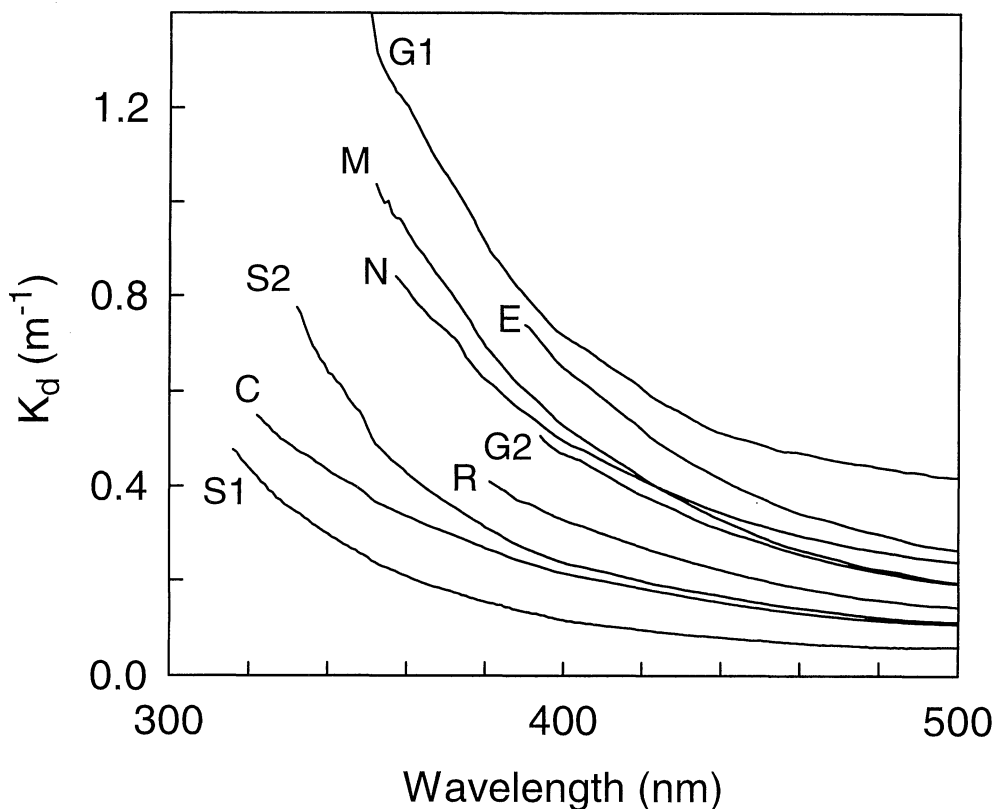


Fig. 1. Spectra for  $K_d$  for seven lakes in high Arctic Canada. C: Char Lake, E: Eleanor Lake, M: Meretta Lake, N: North Lake, G1 and G2: Lake Garrow, mixolimnion and pycnocline respectively. S1 and S2: Lake Sophia, mixolimnion and pycnocline respectively.

from adjacent depths. Finally, the UV-visible spectrum is uneven at the surface and becomes increasingly uneven down the water column, with differences in irradiance at the bottom of the euphotic zone of  $10^4$  to  $10^8$  between the blue-green and UV wavebands. This requires an extremely effective separation of the wavelengths to ensure that spillover (stray light) between wavelengths does not affect the measurements. Such a spillover effect will lead to a systematic underestimation of  $K_d$  because stray light will come from the blue-green part of the spectrum where  $K_d$  is low. One or more of these problems have been detected in the Li-Cor 1800 spectroradiometer (Markager and Vincent unpubl. data) and the Biospherical PUV-500 profiler (Laurion et al. 1997), and have previously been identified in inter-comparisons of surface UV-B radiometers (Seckmeyer et al. 1994) and of underwater UV-B profilers (Kirk et al. 1994).

As a result of the problems listed above,  $K_d$  values usually become increasingly uncertain with decreasing wavelength (also noted by Laurion et al. 1997). This is an important constraint on estimating parameters in an exponential expression such as Eq. 2 or Eq. 4. A direct fitting of the parameters  $S_K$  or  $S_K'$  and  $K_{\text{back}}$  with a nonlinear fitting procedure will put most emphasis on the values at short wavelengths, because the numerical values of the squared residuals are higher at shorter wavelengths than at longer wavelengths. This effect can be reduced by natural log-transformation. Thus Eq. 2 becomes:

$$\log(K_d(\lambda)) = \log(K_d(\lambda_0)) + S_K(\lambda_0 - \lambda). \quad (5)$$

Similarly, Eq. 4 can be transformed to:

$$\log(K_d(\lambda)) = \log(K_d(\lambda_0)e^{S_K'(\lambda_0 - \lambda)} + K_{\text{back}}). \quad (6)$$

In the present study we have compared estimates of  $S$  obtained with Eq. 5 ( $S_K$ ) and Eq. 6 ( $S_K'$ ) for our own measurements and literature data for  $K_d$ . The parameters  $S_K$  and  $K_d$  at  $\lambda_0$  (Eq. 5) were estimated with linear regression and  $S_K'$ ,  $K_d$  at  $\lambda_0$  and  $K_{\text{back}}$  (Eq. 6) using a nonlinear estimation procedure (the multivariate secant method, SAS 1989).

The value for  $K_d(\text{PAR})$  varied between 0.13 and 0.50  $\text{m}^{-1}$  for the nine spectra from the high Arctic lakes. Chlorophyll concentrations were between 0.3 and 1.24  $\mu\text{g Chl } a \text{ L}^{-1}$  except at the pycnocline of Lake Garrow, where chlorophyll was close to our detection limit (Table 1). Absorption by dissolved compounds ( $a_{380}$ ) varied 10-fold from 0.04 to 0.42  $\text{m}^{-1}$  between the lakes. Dissolved compounds dominated the light absorption between 360 and 500 nm (60–87% of the total light absorption) for four of the spectra but contributed only about 20–34% to total absorption in the surface waters of the two meromictic lakes and in Char Lake.

The  $K_d$  spectra showed the usual exponential relationship with wavelength (Fig. 1). The lowest wavelengths where reliable values for  $K_d$  could be obtained depended on wind and surface light conditions and varied between 316 and 394 nm.

Table 1. Optical data and  $S$  values for the present study and recalculated  $S$  values for three literature data sets calculated with two different estimation techniques. Values for  $K_d$ (PAR) and Chl  $a$  were obtained from Markager et al. (1999).  $S_K'$  was estimated with Eq. 6 which includes a background value for  $K_d$  ( $K_{back}$ ).  $S_K$  was estimated from Eq. 5 which assumes that  $K_d$  approaches zero at high wavelengths. The percentage difference between the two  $S$ -estimates is also given. SE values are given in brackets.  $a_{part}$  is the absorption coefficient for particles and  $S_{part}$  is equivalent to  $S_K'$  but for  $a_{part}$  calculated according to Bricaud and Stramski (1990). Abbreviations for the lakes are the same as used on Fig. 1.

Lake	$K_d$ (PAR) ( $m^{-1}$ )	$K_d$ at 500 nm ( $m^{-1}$ )	Chl $a$ ( $\mu g L^{-1}$ )	$S_K'$ ( $\mu m^{-1}$ )	$S_K$ ( $\mu m^{-1}$ )	Differ- ence %	$K_{back}$ ( $m^{-1}$ )	$a_{part}$ at 500 nm ( $m^{-1}$ )	$S_{part}$ ( $\mu m^{-1}$ )
Char Lake, (C)	0.14	0.11	0.62	15.0 (0.14)	8.4 (0.09)	44	0.07	0.044	11.6
Eleanor Lake, (E)	0.24	0.26	0.90	17.1 (0.13)	9.9 (0.10)	42	0.17	0.051	12.7
Meretta Lake, (M)	0.26	0.19	1.11	17.0 (0.08)	11.4 (0.09)	33	0.12	0.032	17.3
North Lake, (N)	0.29	0.24	0.43	16.8 (0.10)	8.8 (0.11)	48	0.18	0.048	14.1
Resolute Lake, (R)	0.16	0.14	1.19	14.3 (0.17)	9.1 (0.07)	36	0.08	0.041	11.1
Sophia Lake, mixolimnion, (S1)	0.18	0.06	0.30	20.9 (0.22)	9.1 (0.16)	56	0.05	0.037	8.9
Sophia Lake, pycnocline, (S2)	0.13	0.11	1.24	17.8 (0.23)	9.4 (0.12)	47	0.08	0.027	10.0
Garrow Lake, mixolimnion, (G1)	0.50	0.42	0.26	22.6 (0.14)	7.4 (0.16)	67	0.38	0.104	9.7
Garrow Lake, pycnocline, (G2)	0.21	0.19	0.04	15.2 (0.16)	9.3 (0.07)	39	0.11	—	—
Mean				17.4 (0.9)	9.2 (0.4)	47.1			11.9 (1.0)
(Morris et al. 1995)				16.4 (0.7)	13.4 (0.2)	22.4			
(Laurion et al. 1997)				19.2 (1.1)	15.1 (0.4)	27.2			
(Scully and Lean 1994)				19.6 (1.4)	15.3 (0.6)	28.1			

To avoid large site-to-site differences in the wavelength range, only data between 360 and 500 nm were used in the calculation of  $S$ , except for three of the spectra, for which the lowest wavelength used was between 380 and 394 nm (Fig. 1). Eq. 5 gave a reasonable description of the exponential relationship ( $r^2 = 0.938$ – $0.992$ ); however, there were systematic deviations between the data and the model. The estimated line fell below the observed values at wavelengths shorter than 385 nm and longer than 470 nm, and it produced an overestimate at intermediate wavelengths. This pattern is clearly seen in the residuals (Fig. 2B, D) and was consistent among the nine spectra. It was most pronounced in Lake Garrow (Fig. 2A, B), where the contribution to  $K_d$  from suspended particles was relatively high, and least pronounced in Char Lake (Fig. 2C, D). Eq. 6 gave a much better description of the relationship, with  $r^2$  values  $>0.9999$  for the nine spectra. Examples of the fit are shown in Fig. 2. A minor underestimation occurred between 400 and 440 nm, as expected, since the model did not account for the spectral absorption by particles, but no other systematic deviations were found. Eq. 5 and Eq. 6 gave lines that deviated substantially at wavelengths below 360 nm, showing the importance of selecting the best model when extrapolating beyond the wavelength range used to calculate  $S$ .

The values of  $S_K'$  estimated with Eq. 6 varied from 14.3 to  $22.6 \mu m^{-1}$  with a SE of about 1% for the individual estimates. The mean value was  $17.4 \pm 0.9 \mu m^{-1}$  ( $\pm$ SE). The highest values were found in the mixolimnion of the two meromictic lakes. The  $S_K$  values estimated with Eq. 5 were systematically lower by almost a factor of two, ranging from 7.4 to 11.4 (Table 1). This difference can be explained from the pattern in Fig. 2, which shows that Eq. 5 flattens out the relationship. The estimates for  $S_K$  decreased systematically when the upper bound for the wavelength range was increased over the range 400–500 nm (Table 2). In contrast, the mean of the estimates of  $S_K'$  was between 16 and  $18 \mu m^{-1}$  for all wavelength ranges tested except one (Table 2).

This means that  $S_K'$  values calculated with a background value can be compared between studies whereas  $S_K$  values are much less reliable for such comparisons because they depend strongly on the wavelength interval used for the calculation. This wavelength dependency of  $S_K$  occurs because the importance of a background value in the calculations increases when more data points with low values for  $K_d$  (longer wavelengths) are included. The  $S$  value for particles ( $S_{part}$ ) was slightly lower ( $8.9$ – $17.3 \mu m^{-1}$ ) than  $S_K'$  (Table 1).

The values for  $K_{back}$  varied 8-fold from 0.05 to 0.38 and were strongly correlated to  $K_d$  at 500 nm ( $r^2 = 0.93$ ), the region of the spectrum where  $K_d$  is minimal. There was also a positive relationship between  $K_{back}$  and  $a_{part}$  suggesting that the concentration of particles was responsible for much of the attenuation in the green waveband where absorption by CDOM and water is at a minimum.

The two calculation techniques for  $S$  (Eqs. 5, 6) were also applied to three data sets of  $K_d$  from the literature (Table 1; representative curves are given in Fig. 3). The data of Morris et al. (1995) and Laurion et al. (1997) were collected with Biospherical Inc. PUV instruments that have four channels (305, 320, 340, and 380 nm). However, the data at 305 nm are less reliable for the reasons mentioned above (*see also* Laurion et al. 1997). Therefore in cases where  $K_d(305)$  was clearly in error (i.e., below  $K_d$  at 320 nm) these values were omitted from the analysis. The data from Scully and Lean (1994) were collected with an Optronic OL752 spectroradiometer and  $K_d$  values were given at 300, 310, 320, 340, 360, 380 and 400 nm. We noticed that these data also showed cases where  $K_d(300)$  was lower than  $K_d(310)$ . We assumed that this also represented an instrumental problem and excluded such values from the calculations. The two models were fitted to a total of 79 data sets and Fig. 3 shows four examples of the results. Both models gave a reasonable fit but with very different values for  $S$ . The estimated  $S$  values increased significantly (on average by 25%) when a background parameter was introduced, consistent with our

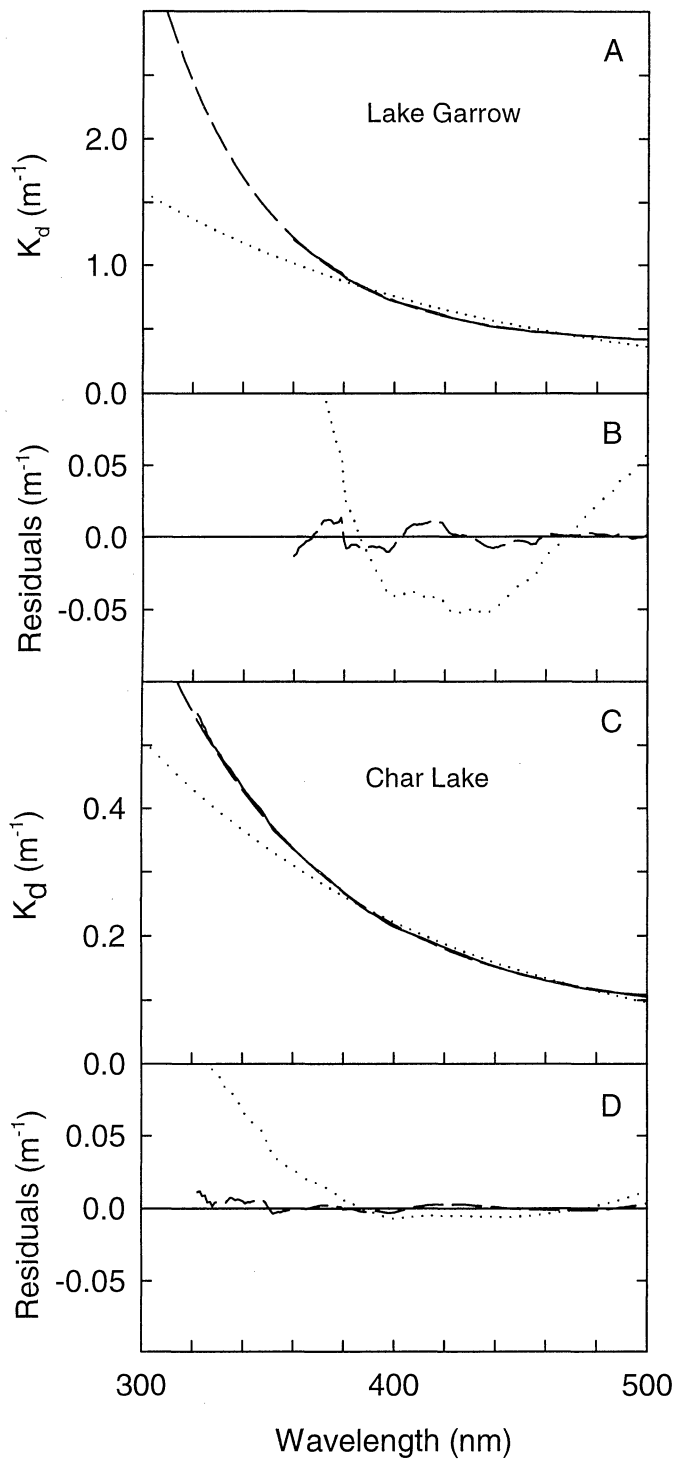


Fig. 2. Observed and estimated spectra for  $K_d$  for two optically contrasting lakes in the high Arctic: Lake Garrow, surface (A, B) and Char Lake (C, D). A and C: Observed values (solid line), the spectrum estimated with a background parameter (Eq. 6, dashed line) and the spectrum estimated without a background parameter (Eq. 5, dotted line). B and D: The spectra of residuals for the two curves given in A and C. The estimated spectra were calculated from observations between 360 and 500 nm. Note the difference in scale between A and C.

Table 2.  $S$  values estimated for a range of wavelengths without ( $S_K$ ) or with ( $S_K'$ ) a background parameter. Values are the means for eight spectra. The lower bound was 360 nm except for the spectra from Eleanor Lake (394 nm) and Resolute Lake (380 nm).

Maximum wavelength (nm)	$S_K$ ( $\mu\text{m}^{-1}$ )	$S_K'$ ( $\mu\text{m}^{-1}$ )
400	13.0	16.4
420	11.8	20.1
440	11.2	17.5
460	10.6	16.9
480	9.9	17.0
500	9.2	17.7

results from the high Arctic lakes. The use of Eq. 6 also resulted in a major increase (factor of 2) in the variation of  $S$  among lakes (Table 1). Thus much of the variation in  $S$  was hidden when Eq. 5 was applied, which may explain the low variability in this parameter that has been found in many

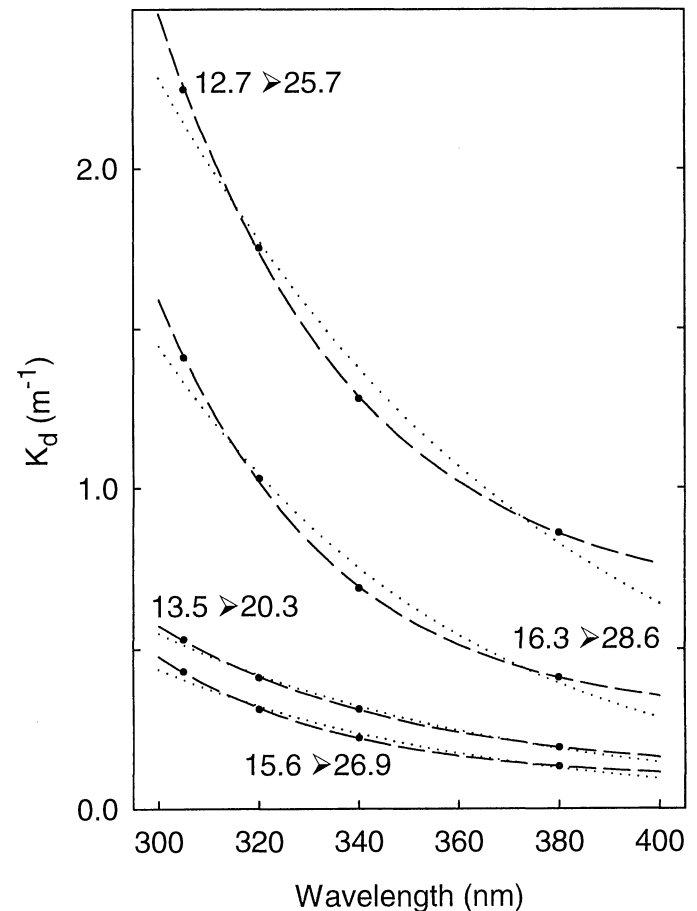


Fig. 3. Four examples of application of the  $S$  model with inclusion of a background parameter (Eq. 6, dashed line) and without (Eq. 5, dotted line). The data are from Morris et al. (1995) and Laurion et al. (1997). The effect of the inclusion of a background parameter in the model for  $K_d$  versus wavelength is shown for each line with  $S_K$  (Eq. 5) on the left side of the arrow and  $S_K'$  (Eq. 6) on the right side.

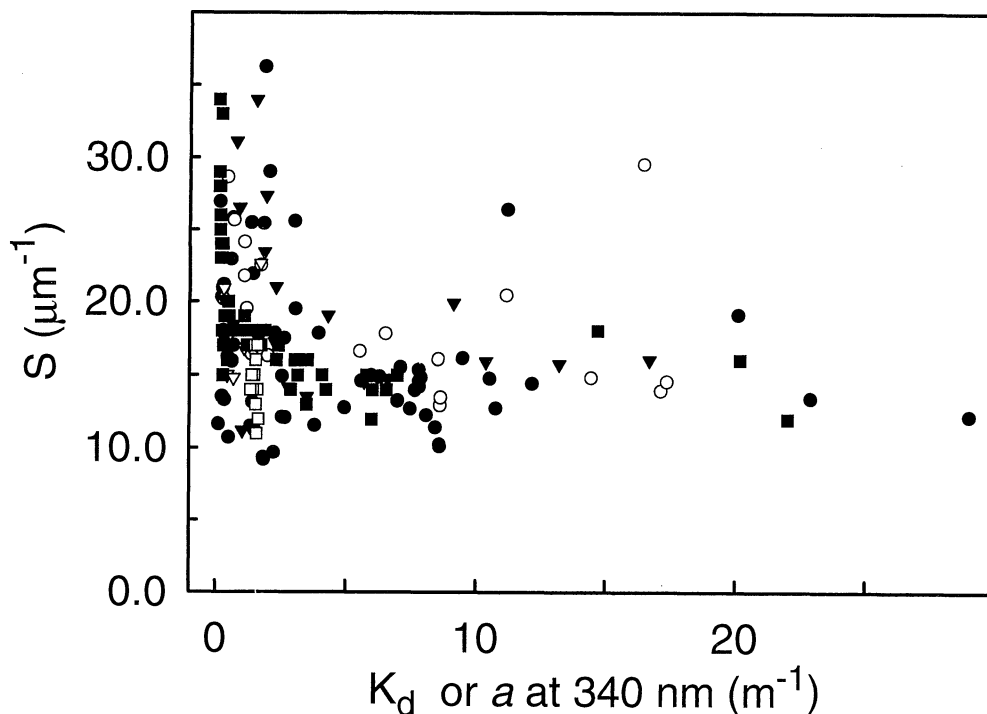


Fig. 4. Relationship between individual values of  $S$  and  $K_d$  or  $a$  at 340 nm from seven studies. Closed circles: Morris et al. (1995); open circles: Laurion et al. (1997); closed triangles: Scully and Lean (1994); open triangles: this study; closed squares: Green and Blough (1994); open squares: Lundgren (1976).  $S$  was estimated from  $K_d$  data using Eq. 6.

studies. The introduction of a background value (Eq. 6) lowered the sum of squared residuals by a factor of 2–3 compared to Eq. 5. Systematic deviations in the fit were found with Eq. 5, but not when Eq. 6 was applied (Fig. 3).

The mean  $S_K'$  values estimated from the three data sets were 16.4, 19.2, and 19.6  $\mu\text{m}^{-1}$ , respectively. This was 22–28% above the estimated mean  $S_K$  values (Table 1), which ranged from 13.4 to 15.3  $\mu\text{m}^{-1}$  and were identical to the mean values as stated by the authors. The differences between  $S_K'$  and  $S_K$  decreased with increasing  $K_d$ ; the correlation coefficient for  $[S_K' - S_K]$  versus  $K_d(340)$  was  $-0.32$ ,  $P = 0.0016$ . Thus, the largest difference between  $S_K'$  and  $S_K$  was found in lakes with low DOC concentration and high particle contents, and the lowest difference was in stained lakes with few particles. Our Arctic lake data suggest a similar pattern; for example, the difference between the two estimates of  $S$  was 67% for turbid Lake Garrow but 44% for clear Char Lake (Table 1; Fig. 2). It seems reasonable that the consequence of a background parameter is highest when the relative importance of  $a_{\text{part}}$  is high compared to  $a_{\text{dis}}$ , since there was a positive relationship between  $K_{\text{back}}$  and  $a_{\text{part}}$  as mentioned above.

The data set provided by Morris et al. (1995) also includes values for absorption (samples prefiltered through 0.22  $\mu\text{m}$  membranes) and the mean value for  $S_a$  (280–400 nm) was  $18.1 \pm 0.4 \mu\text{m}^{-1}$  ( $\pm\text{SE}$ ). This is significantly higher than the value for  $S_K'$  estimated with Eq. 6 (16.4  $\mu\text{m}^{-1}$ ,  $P = 0.036$ ); however, the agreement is better than for  $S_K$  (13.4  $\mu\text{m}^{-1}$ ). We should not expect an exact match between  $S_K'$  and  $S_a$  because  $S_K'$  is affected by the absorption by particles.

Several of the lakes in the study by Morris et al. (1995) had low values of DOC (below 1  $\text{mg L}^{-1}$ ) and absorption by particles might therefore play a significant role for the spectral shape of  $K_d$  in such lakes.

The inclusion of a background parameter has several advantages for the estimation of  $S$ . Firstly, this model provides a better fit to the optical data, particularly in low CDOM waters. Secondly, the estimate of  $S$  derived in this way is independent of the wavelength range. Finally, the values more closely resemble  $S$  for absorption. Problems with estimates of  $K_d$  at low wavelengths (high attenuation) seem to be intrinsic to bio-optical profiling in general, and the effect is an underestimation of  $K_d$  and consequently  $S$ .

The implication of an error in  $S$  for optical models depends on the specific application. If  $K_d$  is extrapolated from one wavelength to another, the magnitude of the resultant error depends on the wavelength range as well as the initial error in  $S$ . If an error of 10% for  $K_d$  is acceptable, and the uncertainty in  $S$  is  $\pm 1 \mu\text{m}^{-1}$ ,  $K_d$  can be extrapolated from one wavelength to another within 100 nm. However, if the error in  $S$  is  $\pm 3 \mu\text{m}^{-1}$  or  $\pm 5 \mu\text{m}^{-1}$  the acceptable wavelength range for extrapolation of  $K_d$  decreases to 30 nm and 20 nm, respectively. However, if one wishes to calculate the irradiance at a certain depth from data for  $K_d$  at another wavelength and a  $S$  value, the error for the estimate will be much larger given the double exponential nature of the relationship, and could amount to several orders of magnitude.

*Intersystem comparisons*—To illustrate the application of the new method and to evaluate the variability among eco-

Table 3.  $S$  values compiled or calculated from the literature and from the present study. Most values are either based on absorption measurements (Abs.) or calculated from  $K_d$  data with adjustment for a background value (Eq. 6). Values for which the calculation technique or the methodological details are unknown are placed in brackets and were not used in the calculation of mean values. Measurements indicate the type of data used to calculate  $S$ . The subscript 'yes' or 'no' indicates if a correction for a background at high wavelengths has been used.

Locality	$\lambda$ -range	Measure-ments	$N$	Mean $S$	Range	SE	CV	Source
<i>Freshwater systems</i>								
20 lakes in Québec	250–440	Abs., no	—	16.9	—	—	—	(Cuthbert and del Giorgio 1992)
9 rivers and bogs in U.S.	300–500	Abs., ?	9	(14.5)	11.6–17.5	0.5	9.1	(Zepp and Schlotzhauer 1981)
11 lakes in New Zealand	280–460	Abs., yes	139	18.7	15.1–20.5*	0.12	8.1	(Zepp and Schlotzhauer 1981)
20 lakes in North America	300–400‡	$K_d$ , yes	20	19.6	11.2–23.4	1.4	31.1	(Scully and Lean 1994)†
3 lakes in northern Quebec	305–440‡	$K_d$ , yes	15	18.3	13.0–29.6	1.2	25.6	(Laurion et al. 1997)†
3 lakes in high Arctic Canada	305–440‡	$K_d$ , yes	4	22.8	16.6–28.6	2.7	23.7	(Laurion et al. 1997)†
13 lakes in Northeast U.S.	305–440‡	$K_d$ , yes	13	14.5	9.2–25.8	1.4	34.6	(Morris et al. 1995)†
20 lakes in Colorado	305–440‡	$K_d$ , yes	20	18.6	11.6–36.2	1.6	38.2	(Morris et al. 1995)†
9 lakes in Alaska	305–440‡	$K_d$ , yes	9	14.5	10.2–17.8	0.73	15.4	(Morris et al. 1995)†
12 lakes in Argentina	305–440‡	$K_d$ , yes	16	16.1	9.3–26.9	1.2	29.2	(Morris et al. 1995)†
Rivers	Variable	Abs., no	10	(13.8)	12–17	0.47	—	(Green and Blough 1994)
7 lakes in high Arctic Canada	360  –500	$K_d$ , yes	9	17.4	14.3–22.6	1.7	29.3	This study
Statistics for the means			10	17.7	14.5–22.8	0.8	7.1	
Global range					9.2–36.2			
<i>Marine systems</i>								
Mauritanian upwelling region	375–500	Abs., yes	24	15	—	0.5	15.3	(Bricaud et al. 1981)
Indian-Antarctic Ocean	375–500	Abs., yes	7	12	—	0.9	20	(Bricaud et al. 1981)
Gulf of Guinea	375–500	Abs., yes	35	14	—	0.7	29.3	(Bricaud et al. 1981)
Villefranche Bay	375–500	Abs., yes	11	14	—	0.7	17.1	(Bricaud et al. 1981)
Mount of River Var	375–500	Abs., yes	1	15	—	—	—	(Bricaud et al. 1981)
Baltic Sea	375–500	Abs., yes	1	18	—	—	—	(Bricaud et al. 1981)
Gulf of Fos sur Mer	375–500	Abs., yes	14	13	—	0.3	9.2	(Bricaud et al. 1981)
Near the urban discharge of Marseilles	375–500	Abs., yes	12	12	—	0.2	19.2	(Bricaud et al. 1981)
Baltic Sea	400–725§	$K_d$ , yes	18	14	11–17	0.5	14.1	(Lundgren 1976)
St. Lawrence Estuary	350–750	Abs., no	—	15	—	—	—	(Nieke et al. 1997)
Gulf of Mexico	300–500	Abs., ?	2	(15.0)	14.9–15.1	—	—	(Zepp and Schlotzhauer 1981)
Mississippi plume	370–440	Abs., no	3	13.3	12.8–14.1	0.3	6.7	(Carder et al. 1989)
Gulf of Mexico	370–440	Abs., no	4	15.4	13.3–17.2	0.6	11.4	(Carder et al. 1989)
Gulf of Mexico	370–440	Abs., no	2	13.6	13.5–13.6	0.4	5.8	(Carder et al. 1989)
Gulf of Mexico	370–440	Abs., no	2	13.2	11.5–14.8	0.8	13.7	(Carder et al. 1989)
Baltic Sea	280–310	Abs., no	>100	—	15–31	—	—	(Brown 1977)
Gulf of Paria	Variable	Abs., no	8	13.7	—	0.6?	—	(Blough and Zafriou 1993)
Orinoco Estuary	Variable	Abs., no	10	13.6	—	0.4?	—	(Blough and Zafriou 1993)
New Zealand marine waters	300–460	Abs., no	—	15	—	—	—	(Davies-Colley 1998)
Amazon Estuary	Variable	Abs., yes	11	(19.2)	15–33	—	—	(Green and Blough 1994)
Gulf of Mexico	Variable	Abs., no	308	(20.6)	15–34	—	—	(Green and Blough 1994)
Statistics for the means			17	14.1	12–18	0.3	10	
Global range					11.5–34			

\* Annual mean values for the lake.

† Recalculated with Eq. 6 from  $K_d$  values in the paper.

‡ The value at 305 (300) nm was omitted from the calculations if lower than the 320 (310) nm value.

§  $S$  was calculated with a modified spectral model.

|| Lower bound was between 380 and 394 nm for three of the spectra (see Fig. 1).

systems, we compared values for  $S_{\kappa'}$  from the present study,  $S_{\kappa'}$  values calculated from the three studies mentioned above, and other literature values for  $S$  based on attenuation or absorbance. Fig. 4 shows values from studies where individual values were available. The total range is between 9.2 and 36.2  $\mu\text{m}^{-1}$  but most of the variability comes from observations in low colored systems. This pattern of greatest spread in  $S$  values at the highest water column transparencies was consistent among all six studies. It could either indicate analytical problems when absorption is low (*see below*) or that the composition and optical properties of the CDOM, and associated  $S$  values, are more variable when the DOC concentrations are low. Along with a higher variability we also observed a significantly higher mean value for  $S$  in systems with low absorption (Fig. 4). In systems where  $K_d$  at 340 nm was above 3  $\text{m}^{-1}$  most  $S$  values were between 10 and 18  $\mu\text{m}^{-1}$  with a mean value of 15.2  $\mu\text{m}^{-1}$  and a CV of 21%. In contrast, the mean  $S$  value for low-colored systems was 19.0  $\mu\text{m}^{-1}$  with a CV of 30%.

Table 3 provides a compilation of  $S$  values from the literature and from this study. Most values were either based on absorption measurements (where the background is closer to zero), or were calculated from  $K_d$  measurements with Eq. 6 or with other techniques that take a background value for  $K_d$  into account. Values were omitted from the overall calculations of means if they had not been corrected for background absorption or if details about the calculation technique were not available; these omitted values are shown in parentheses in Table 3. Most of the freshwater data had  $S$  values in the range 10–25  $\mu\text{m}^{-1}$  with an overall mean ( $\pm$ SE) of 17.7  $\pm$  0.8  $\mu\text{m}^{-1}$ . The marine values ranged from 11 to 17.2  $\mu\text{m}^{-1}$  with a mean value of 14.1  $\pm$  0.4  $\mu\text{m}^{-1}$  that was significantly lower than the mean value for freshwater systems ( $P = 0.0002$ ).

The apparent difference between marine and freshwater systems must be regarded with caution since a number of other factors seem to influence the measured  $S$ . Wavelength range is one of the more important determinants and this varies greatly among studies in the Table 3 compilation. Several studies have shown that  $S$  increases with decreasing wavelength (Kalle 1966; Howard-Williams and Vincent 1985; Table 3 in Carder et al. 1989; Fig. 2 in Blough and Zafiriou 1993; Fig. 2 in Green and Blough 1994). The relatively high values measured at 280–310 nm by Brown (1977) also support this conclusion. An increase in  $S$  with decreasing wavelength and the observation of distinct shoulders at wavelengths below 280 nm (Butler and Ladd 1969; Swift et al. 1970; Brown 1977; McKnight et al. 1994) mean that the exponential models used in this and other studies are only an approximation of the relationship between absorption and wavelength and are probably less valid at wavelengths below 280 nm.

The  $S$  value will be affected by natural sources of variability, in particular by the specific composition and aromaticity of the DOC pool. Carder et al. (1989) have shown that humic acids have a lower  $S_a$  value (11  $\mu\text{m}^{-1}$ ) than fulvic acids (18  $\mu\text{m}^{-1}$ ) and the same pattern was found by Zepp and Schlotzhauer (1981) but with lower absolute values. Other studies indicate that low molecular fractions have higher  $S_a$  than high molecular fractions (Butler and Ladd

1969; Swift et al. 1970), suggesting that natural waters with DOC pools dominated by autochthonous inputs of carbon (e.g., phytoplankton photosynthesis) will be characterized by high  $S$  values. This is consistent with the steep absorbance curves found in algal-rich geothermal lakes (Howard-Williams and Vincent 1985). Brown (1975; 1977) has suggested that coagulation of DOC with increasing salinity preferentially removes colloids and large molecules meaning that  $S$  should increase when freshwater DOC enters estuaries. However, the selective photodegradation of compounds by a greater relative absorption of photons at short wavelengths could counteract this process. Selective photodegradation was found in a study by Corin et al. (1996) where fulvic acids were degraded 30–100% faster than humic acids. This implies a decrease in  $S$  given the higher  $S$  value for fulvic acids (Carder et al. 1989). Finally, lake acidification may cause the precipitation and preferential loss of humic acids, leading to an increase in  $S$ . Consistent with this effect, changes in the CDOM fluorescence characteristics of an experimentally acidified lake indicated the preferential removal of the humic fractions and a decrease in aromaticity (Donahue et al. 1998).

## Conclusions

Our results show that an accurate estimate of  $S$  can be calculated from  $K_d$  measurements with the technique described here (Eq. 6). We can attribute some variation in  $S$  to differences between freshwater and marine systems, but systematic studies are needed to evaluate the mechanisms that control the overall variability in  $S$  between and within these two classes of aquatic ecosystems. Finally,  $S$  can deviate significantly from an overall mean value and the use of such a mean could give an erroneous picture of the spectral shape of the CDOM absorption at specific marine or freshwater sites. These problems should be addressed in studies that incorporate  $S$  in optical models, for example remote sensing algorithms for coastal waters and lakes.

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