

ABSORPTION PROPERTIES OF DISSOLVED ORGANIC MATTER IN FINNISH LAKES

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Abstract. Absorption spectra of filtered samples and concentrations of dissolved organic carbon were determined in the laboratory for ten lakes with diverse water quality characteristics. The lakes were surveyed in May and August and the absorption coefficient at 380 nm ranged from 1.9 to 20 m⁻¹. The measured absorption spectra were described by an exponential function of wavelength. The mean slope parameter of the model ranged from -0.0159 to -0.0171 nm⁻¹, depending on the correction method used for residual scattering. The mean specific absorption coefficient of aquatic humus at 380 nm was 0.98 L mg⁻¹ m⁻¹. This value is higher than most of the estimations published in the literature. The seasonal differences of the optical properties were small.

Key words: lakes, aquatic humus, dissolved organic carbon, absorption.

INTRODUCTION

The optically active fraction of the dissolved organic matter in the surface waters, often called aquatic humus, yellow substance, or coloured dissolved organic matter, is an important variable of the water ecosystems as it has an impact on the water colour and on light attenuation due to exponentially increasing absorption with decreasing wavelength. From the remote sensing point of view, coloured dissolved organic matter (CDOM), together with suspended solids and algal pigments, effects the upwelling radiance. In the interpretation of remote sensing data the spectral absorption coefficient throughout the visible range and the specific absorption coefficient of CDOM, which is used to convert the absorption coefficient into the concentration of aquatic humus, are needed.

Several researchers have measured the absorption spectra of filtered water samples in the ocean and coastal environment (e.g., Kirk, 1976; Nyquist, 1979; Højerslev, 1980; Bricaud et al., 1981; Green & Blough, 1994; Althuis et al., 1996; Mäekivi & Arst, 1996) as well as in lakes (Kirk, 1976; Davies-Colley & Vant, 1987; Bukata et al., 1991; Decker, 1993; Gallie, 1994; Mäekivi & Arst,

1996). However, only a few studies have been made with both absorption coefficient and CDOM concentration measurements required for the determination of the specific absorption coefficient.

The main objective of this study was to determine the model parameters of an exponential model for the absorption spectra in lakes with diverse water quality. In addition, specific absorption coefficients of aquatic humus were calculated from the absorption coefficients and CDOM concentrations.

MATERIAL AND METHODS

Two measurements campaigns were carried out in southern Finland in 1997. Ten lakes ranging from oligotrophic to eutrophic and from clear water to humic lakes (Table 1) were involved. Lake Lohjanjärvi and Lake Hiidenvesi consist of several sub-basins with trophic level varying from eutrophic to mesotrophic.

Table 1. Main characteristics of the lakes. Chlorophyll *a* concentration, absorption coefficient of aquatic humus at 380 nm, and Secchi disc transparency are mean values of the measurements carried out in August 1997. Eu, eutrophic; Me, mesotrophic; Ol, oligotrophic; Humic, humic lake

Lake	Area, km ²	Lake type	Chl <i>a</i> , µg L ⁻¹	<i>a</i> (380), m ⁻¹	Secchi, m
Kiskonjärvi	7	Eu	50–100	8	0.5
Enäjärvi, Vihti	5	Eu	38	4	1.0
Lohjanjärvi	94	Eu-Me	10–55	4–8	0.8–2.9
Hiidenvesi	30	Eu-Me	7–30	8	0.7–1.2
Vesijärvi	111	Me	12	2	2.9
Puujärvi	7	Ol	1.5	2	7.0
Asikkalanselkä, Päijänne	77	Ol	2.5	4	4.0
Iso-Kisko	7	Ol	2	3	4.0
Pääjärvi	13	Humic	6	11	2.7
Keravanjärvi	1	Humic	12	20	1.6

All the ten lakes were sampled in August while only six of them were surveyed in May 1997. The number of sampling stations per lake ranged from 2 to 12 and the total number of samples was 73. All the samples were taken from the surface layer of 0–0.4 m. Sampling in May was carried out on 7th and 8th, only about a week after the ice-break. Algal biomass had not yet reached the spring maximum. The weather on 7 May was windy (9 m s⁻¹), causing vertical mixing and resuspension of bottom sediment in the shallow areas. The concentrations of total suspended solids in May were higher than in August due to high river discharges. In August (sampling on 11th, 12th, and 18th) the phytoplankton biomass was at its maximum as indicated by the high chlorophyll *a* concentrations (Table 1).

Absorption spectra in May were measured at the Tvärminne Biological Station with a Shimadzu UV-PC2101 spectrophotometer using a 5 cm quartz cuvette, while in August the measurements were carried out in the Laboratory of Uusimaa Regional Environment Centre with a Perkin Elmer Lambda spectrophotometer using a 1 cm glass cuvette. The wavelength range in both measurements was 380–800 nm with an interval of 1 nm. Particulate carbon was removed from the water samples by filtering through a Nuclepore polycarbonate (pore size 0.4 μm) filter. Filtering was made within two days after sampling and absorption spectra were measured within a week after filtering.

The concentration of dissolved organic carbon (DOC) was analysed at the Laboratory of the Finnish Environment Institute. Organic carbon in the filtered water was oxidized to CO_2 and the concentration was determined by an infrared spectrometry measurement (EN1484, 1997). Before the measurement the inorganic carbon was removed by acidification and purging.

The absorption curve of CDOM was modelled by a commonly used equation assuming an exponential increase with decreasing wavelength:

$$a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0) \text{EXP}(-S(\lambda - \lambda_0)), \quad (1)$$

where $a_{\text{CDOM}}(\lambda)$ absorption coefficient of CDOM at wavelength λ ;

$a_{\text{CDOM}}(\lambda_0)$ absorption coefficient of CDOM at the reference wavelength λ_0 ;

S slope parameter.

According to Eq. (1) the absorption of CDOM is linear if the natural logarithm of the absorption coefficient is plotted as a function of wavelength.

Correction for scattering by small residual particles that are not retained on the filter was taken into account by two different methods. The method presented by Bricaud et al. (1981) is:

$$a_{\text{CDOM}}(\lambda) = X(\lambda) - X(\lambda_R) (\lambda_R/\lambda)^g, \quad (2)$$

where $a_{\text{CDOM}}(\lambda)$ absorption coefficient of CDOM at wavelength λ after correction for scattering;

$X(\lambda)$ measured coefficient;

$X(\lambda_R)$ measured coefficient at the reference wavelength λ_R ;

g exponent.

In the other correction method, suggested by Gallie (1994), the measured coefficient at the reference wavelength is subtracted throughout the measured spectra:

$$a_{\text{CDOM}}(\lambda) = X(\lambda) - X(\lambda_R). \quad (3)$$

The reference wavelength is usually selected from the longer wavelength area (e.g. 700 nm), where scattering dominates. Decker (1993) pointed out that aquatic humus may absorb light at 700 nm and beyond. In this study λ_R was set to 750 nm. The exponent g was fixed to 1 as in most of the studies where Eq. (2) has been used (Davies-Colley & Vant, 1987; Mäekivi & Arst, 1996). Thus an assumption was made that small particles scatter more light with decreasing wavelength.

RESULTS

Coloured dissolved organic carbon

Absorption coefficients at 385 nm were first plotted against DOC concentrations (Fig. 1). As can be seen, some DOC seems to be left in the water at very low absorption values ($<1.9 \text{ m}^{-1}$) if a linear relationship between DOC and absorption is assumed. This residual DOC that is not optically active (i.e. does not absorb light) can be due to (1) contamination during the analysing process or (2) colourless DOC in the original sample. One contamination source can be the Nuclepore polycarbonate filter. To find out the amount of carbon that can be leached from the filter, purified water was filtered after every 4th sample and the DOC concentration was determined. The DOC concentration of the purified water was higher than the detection limit of 0.5 mg L^{-1} only in one case. However, when filtering the actual lake samples, the filter can be a bigger source of carbon due to the lengthening of the filtering time because of the particles retained on the filter.

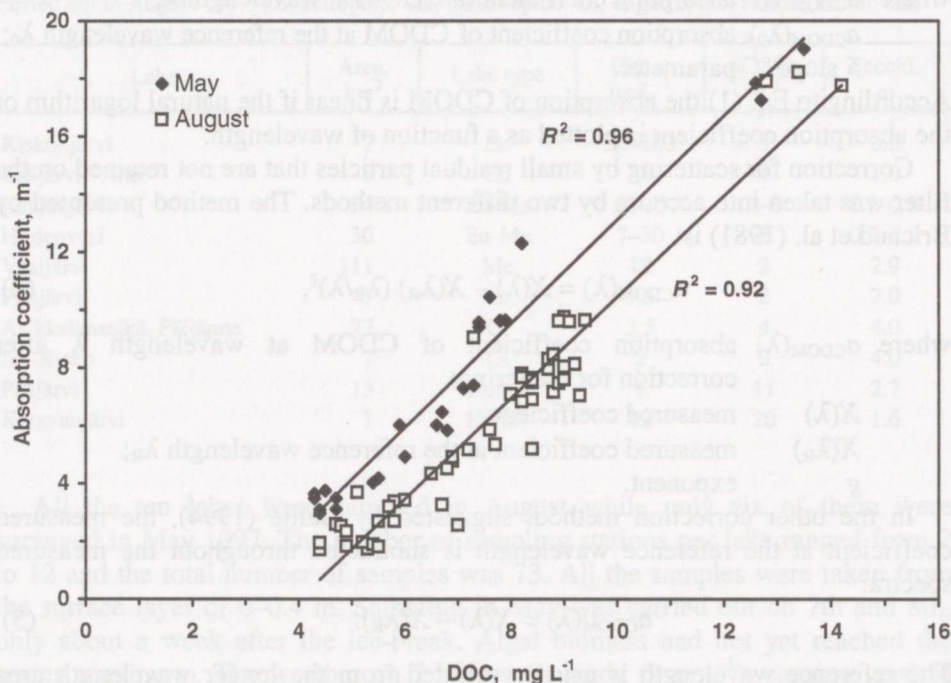


Fig. 1. Correlation between the absorption coefficient at 385 nm (uncorrected) and the concentration of dissolved organic carbon in May and August 1997.

Coloured dissolved organic carbon (CDOC) was estimated from the DOC results by:

$$\text{CDOC} = \text{DOC} - C_0, \quad (4)$$

where C_0 is the concentration of colourless dissolved organic carbon.

C_0 was obtained by calculating the intercept of the regression line on the DOC axis separately for the two seasons (Fig. 1). C_0 for May was 2.7 mg L^{-1} and for August 4.0 mg L^{-1} .

Absorption curve

The uncorrected absorbances measured with the spectrophotometer are shown in Fig. 2. As can be seen, a drop of some absorbances occurs at wavelengths shorter than 385 nm. These samples were all from August and the discontinuation of the exponential curve is probably due to the fact that a glass cuvette was used. Therefore, wavelengths shorter than 385 nm were omitted from the absorption data measured in August.

The slope parameter in Eq. (1) was obtained by taking first the natural logarithm of the absorption and then making a linear fitting by the least-square

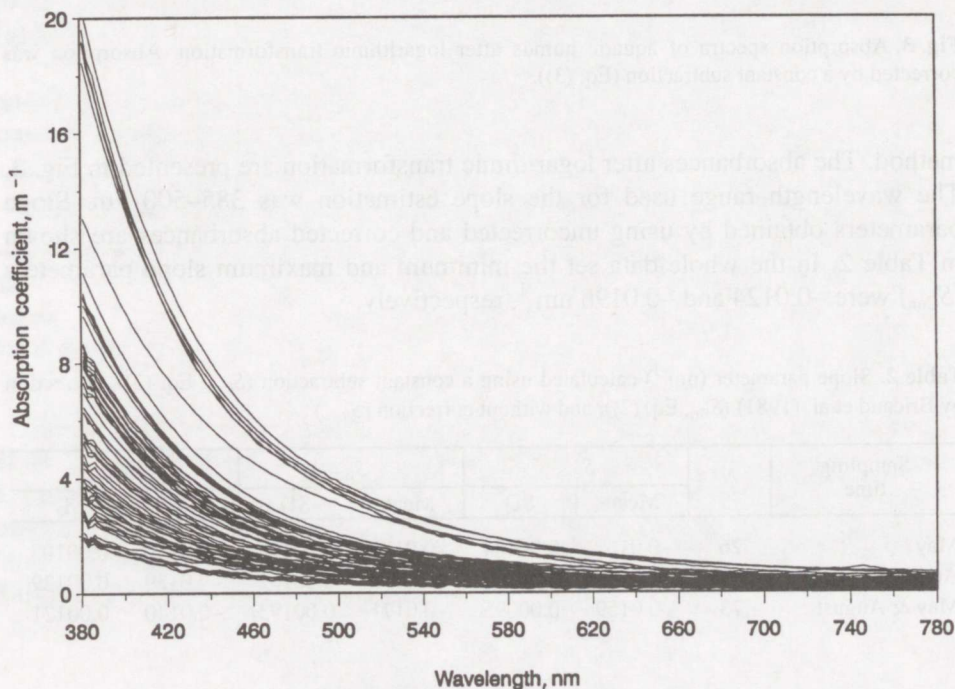


Fig. 2. Absorption spectra of aquatic humus (uncorrected).

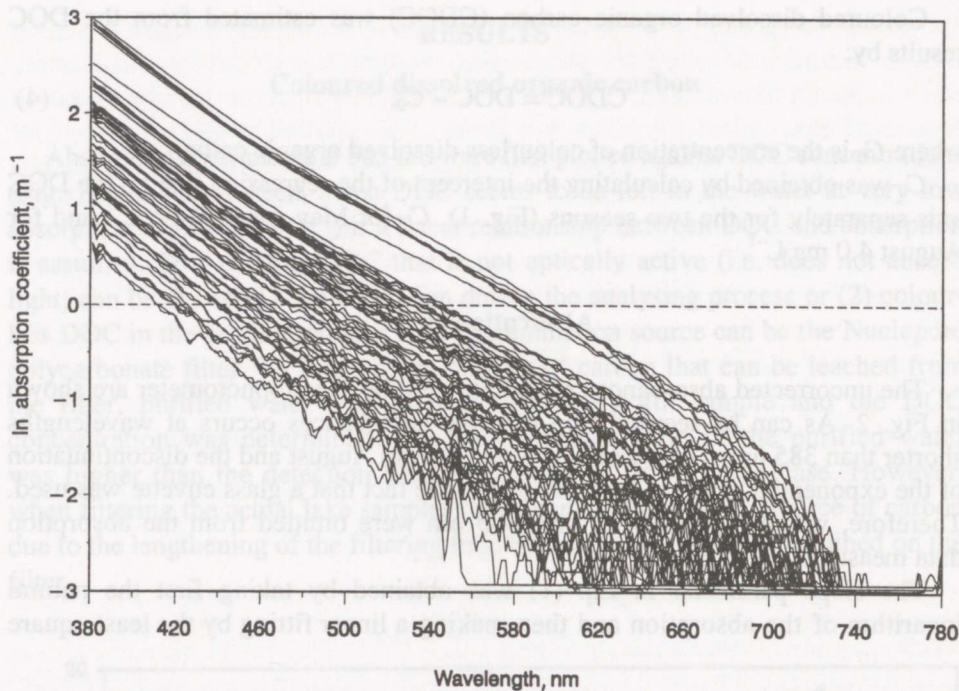


Fig. 3. Absorption spectra of aquatic humus after logarithmic transformation. Absorption was corrected by a constant subtraction (Eq. (3)).

method. The absorbances after logarithmic transformation are presented in Fig. 3. The wavelength range used for the slope estimation was 385–500 nm. Slope parameters obtained by using uncorrected and corrected absorbances are shown in Table 2. In the whole data set the minimum and maximum slope parameters (S_{Con}) were -0.0124 and -0.0196 nm^{-1} , respectively.

Table 2. Slope parameter (nm^{-1}) calculated using a constant subtraction (S_{Con} , Eq. (3)), correction by Bricaud et al. (1981) (S_{Bri} , Eq. (2)), and without correction (S_{Raw})

Sampling time	N	S_{Con}		S_{Bri}		S_{Raw}	
		Mean	SD	Mean	SD	Mean	SD
May	26	-0.0162	0.00084	-0.0177	0.00194	-0.0140	0.00108
August	47	-0.0157	0.00099	-0.0169	0.00192	-0.0139	0.00129
May & August	73	-0.0159	0.00095	-0.0171	0.00193	-0.0140	0.00121

Specific absorption coefficient

In order to be able to compare the results with other similar studies, the concentration of CDOM had to be estimated. CDOM was obtained through

multiplying CDOC by 2 (assuming that the carbon content of the organic matter is 50%).

The specific absorption coefficient $a^*_{\text{CDOM}}(\lambda_0)$ in $\text{L mg}^{-1} \text{m}^{-1}$ was calculated by:

$$a^*_{\text{CDOM}}(\lambda_0) = a_{\text{CDOM}}(\lambda_0)/\text{CDOM}, \quad (5)$$

where $a_{\text{CDOM}}(\lambda_0)$ absorption coefficient of CDOM at wavelength λ (m^{-1});

CDOM concentration of coloured dissolved organic matter (mg L^{-1}).

The reference wavelength used in the studies of optical properties of aquatic humus varies considerably; the typical values are 254, 380, 400, 420, and 440 nm. The absorptions measured at short wavelengths are more accurate as an index for the concentration of aquatic humus, because the effect of scattering in relation to absorption is small (e.g. Kortelainen et al., 1986). However, if one is interested in the absorption of the visible range, a reference wavelength close to 400 nm should be used (Althuis et al., 1996).

The reference wavelength was in this study set to 380 nm. Because of the poor quality of the absorption measurements between 380 and 385 nm in August, the absorption coefficient at 380 nm was calculated from the absorption coefficient at 385 nm using the slope parameter of -0.0159 and Eq. (1). The absorption coefficient at 380 nm, corrected by a constant subtraction, varied between 1.9 and 20 m^{-1} in the whole data set. The specific absorption coefficients are shown in Table 3.

Table 3. Specific absorption coefficient of CDOM ($\text{L mg}^{-1} \text{m}^{-1}$) at 380 nm. Absorption was corrected for scattering by a constant subtraction (Eq. (3))

Sampling time	$a^*_{\text{CDOM}}(380)$				
	<i>N</i>	Mean	SD	Min	Max
May	26	0.92	0.13	0.74	1.14
August	47	1.01	0.40	0.47	2.52
May & August	73	0.98	0.33	0.47	2.52

The minimum and maximum values of the specific absorption coefficients of all the 73 samples were 0.47 and $2.52 \text{ L mg}^{-1} \text{m}^{-1}$, respectively. If the correction is made by Eq. (2) after Bricaud et al. (1981), the mean $a^*_{\text{CDOM}}(380)$ is slightly lower ($0.93 \text{ L mg}^{-1} \text{m}^{-1}$) than in case of constant subtraction ($0.98 \text{ L mg}^{-1} \text{m}^{-1}$, Table 3). The seasonal differences of both the specific absorption coefficient (Table 3) and the slope parameter (Table 2) were small.

DISCUSSION

The mean slope parameters obtained in this study ($S_{\text{Raw}} = -0.0140$, $S_{\text{Con}} = -0.0159 \text{ nm}^{-1}$, $S_{\text{Bri}} = -0.0171 \text{ nm}^{-1}$) are within the limits of the literature

values (e.g. Bricaud et al., 1981; Baker & Smith, 1982; Davies-Colley & Vant, 1987; Althuis et al., 1996; Mäekivi & Arst, 1996). For water samples from the Baltic Sea and Estonian and Finnish lakes, Mäekivi & Arst (1996) estimated $S_{Bri} = -0.0173 \text{ nm}^{-1}$ using almost the same wavelength range (350–500 nm) as in this study. Davies-Colley & Vant (1987) reported an S_{Bri} of -0.0173 nm^{-1} for 12 lakes in New Zealand using the wavelength range of 280–460 nm. One of the problems in the comparison of the results obtained by different researchers is the sensitivity of the slope parameter to the correction method and the wavelength range used in the slope parameter calculations. The latter is due to the fact that the observations differ more or less from the assumed exponential model. For example, in this study S_{Con} was -0.0159 , -0.0149 , and -0.0143 nm^{-1} , for wavelength ranges 385–500, 385–550, and 385–600 nm, respectively.

The mean specific absorption coefficient obtained in this study ($a_{CDOM}^*(380) = 0.98 \text{ L mg}^{-1} \text{ m}^{-1}$) is higher than in most of the estimations published in the literature. In a review made by Baker & Smith (1982), including results from five different studies of the ocean and coastal waters, $a_{CDOM}^*(380)$ was in one case $2.16 \text{ L mg}^{-1} \text{ m}^{-1}$, but ranged in the rest of the cases between 0.25 and $0.565 \text{ L mg}^{-1} \text{ m}^{-1}$. The value $0.565 \text{ L mg}^{-1} \text{ m}^{-1}$ calculated by Højerslev (1980) from the data of Nyquist (1979) for the Baltic Sea is probably the most commonly applied conversion factor used (e.g. by Baker & Smith (1982) and Mäekivi & Arst (1996)) with no measurements of CDOM concentrations available. The need for the simultaneous absorption and chemical measurements of DOM in different regions, lake types, and seasons is considerable as earlier pointed out by Davies-Colley & Vant (1987) and Gallie (1994). Although this study included data measured in spring and late summer in ten lakes with diverse water quality, more data are needed particularly on humic lakes with $a_{CDOM}(380)$ higher than 12 m^{-1} and clear water lakes with $a_{CDOM}(380)$ less than 2 m^{-1} .

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SOOME JÄRVEDES LAHUSTUNUD ORGAANILISE AINE VALGUSTNEELAVAD OMADUSED

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Valguse neeldumisspektrid ja lahustunud orgaanilise aine kontsentratsioon määrati filtreeritud veeproovidest laboratooriumis. Veeproovid olid võetud kümnest Soome järvest, mis erinesid üksteisest vete omaduste poolest. Mõõtmisi tehti mais ja augustis 1997. Leiti, et neeldumiskoefitsient lainepikkusel 380 nm varieerus 1,9–20 m⁻¹. Neeldumisspektreid kirjeldati eksponentfunktsiooni abil. Saadud spektrimudeli keskmine kaldeparameeter oli vahemikus –0,0159 kuni –0,0171 nm⁻¹, sõltuvalt jääkhajumise arvestamise korrektsioonitegurist. Lahustunud orgaanilise aine keskmine erineeldumiskoefitsient lainepikkusel 380 nm oli 0,98 L mg⁻¹ m⁻¹, mis ületab enamiku teiste autorite poolt saadud väärtused. Järvede vee optiliste omaduste sesoonsed muutused olid väikesed.