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Optical Properties and Signatures of Chromophoric Dissolved Organic Matter (CDOM) in Danish Coastal Waters

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The optical properties of chromophoric dissolved organic matter (CDOM) in Danish estuaries and coastal waters were investigated. A new method for estimating the spectral slope coefficient (S) was examined and found to give a closer fit for the measured absorption (92% reduction in sum of residuals) than the traditional method. The spectral pattern in residuals produced by the new technique enabled the identification of CDOM originating from areas of different land uses/types where S coefficients were similar. S values were found to behave conservatively with respect to salinity in all waters except for the off-shore North Sea region where CDOM from marine sources was suspected to have more influence. The specific absorption coefficient of CDOM did not vary significantly in Danish coastal waters. These waters are of particular interest in bio-optical studies as they allow the study of CDOM across a gradient from estuarine, brackish to near-oceanic environments. The results demonstrate that it is possible to develop regional models for the optical properties of CDOM which would then allow higher precision in remote sensing applications. \bigcirc 2000 Academic Press

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Introduction

Chromophoric Dissolved Organic Matter (CDOM) is found in all natural waters and it can make up a sizeable fraction of the DOM pool. It consists of a varied mixture of aliphatic and aromatic polymers that are derived from the degradation of terrestrial and aquatic plant matter (Kirk, 1994). CDOM is one of the major light absorbing constituents in natural waters. Its absorption is strongest in the ultraviolet region and diminishes to near zero in the red region. This behaviour can be modelled by Equation 1 (Jerlov, 1968; Lundgren, 1976; Bricaud *et al.*, 1981),

$$a_{\lambda} = a_{\lambda o} e^{S(\lambda o - \lambda)} \tag{1}$$

where a_{λ} is the absorption coefficient at a certain wavelength, λ , and $a_{\lambda o}$ is the absorption coefficient at a reference wavelength, λ_o . S is the exponential slope coefficient and is a measure of how the absorption decreases with respect to wavelength.

As a consequence of its optical behaviour CDOM has the potential to significantly effect the productivity of the water column. CDOM can enhance primary production in the upper waters via blocking out harmful UV radiation while at the same time limit production at depth due to its shading effect. Its colour signal is also an important factor in remote sensing applications where the effect of CDOM must be accounted for before reflection measurements can be utilized for phytoplankton and suspended sediment observations (Tassan, 1988; Karabashev, 1992). However as a result, this also opens the possibility of using remote sensing methods for the measurement of a sizeable fraction of the dissolved carbon pool in the surface waters (Hoge et al., 1995; Vodacek et al., 1995; Ferrari et al., 1996). In many coastal waters CDOM has been found to behave quasi-conservatively during mixing, showing considerable removal at low salinities but behaving conservatively at higher salinities (Reuter et al., 1986; Højerslev, 1988, 1989; Laane &



FIGURE 1. A contour plot showing the depth averaged salinity in the surface 10 m of Danish coastal waters. The open water stations and fjords sampled are also marked. AS=Arkona Sea, BS=Belt Sea, HB=Ho Bugt (Ho Bay), HF=Horsens Fjord, KF=Kolding Fjord, KT=Kattegat, LB=Little Belt, LF=Limfjorden, MF=Mariager Fjord, NF=Nissum Fjord, NA=Nærå Strand (Nærå Beach), NS=North Sea, NY=Nyborg Fjord, OF=Odense Fjord, RF=Roskilde Fjord, RGF=Ringkøbing Fjord, RN=Randers Fjord, SB=Great Belt, SK=Skagerrak, SO=The Sound, VF=Vejle Fjord. It should be noted that although most of the inlets are called fjords the majority of them can be considered as estuaries. T-A, T-B ... show the position of transect A, transect B ... etc. which are referred to in Figure 3.

Kramer, 1990). This property means that CDOM is a useful tool in tracing water mass movements especially in coastal regions where temperature does not behave conservatively (Højerslev, 1971; Laane & Kramer, 1990; Karabashev *et al.*, 1993; Højerslev *et al.*, 1996).

As a result of absorbing solar radiation, CDOM is broken down by photoreactions to form a variety of reactive products influencing various biogeochemical cycles in natural waters and the atmosphere (Moran & Zepp, 1997; Petterson *et al.*, 1997; Uher & Andreae, 1997). This process has been shown to cause both an increase in bioavailability of CDOM and bleaching of the CDOM pool resulting in the deeper penetration of harmful UV radiation (Moran & Zepp, 1997; Gao & Zepp, 1998).

Some of the earliest research into CDOM in open waters was carried out in the Baltic and North seas (Kalle, 1937, 1956; Jerlov, 1953, 1955). The optical

effects of CDOM are of particular interest in this area due to a large gradient from high concentration in the Baltic and German Bight waters to near oceanic conditions in the Skagerrak (see Figure 1 for locations). The importance of CDOM with respect to remote sensing applications in the region has been emphasised by many earlier studies (Højerslev, 1980; Reuter et al., 1986; Karabashev, 1992; Aarup, 1994). The aim of this study was to map the optical properties of CDOM in Danish coastal waters in order to improve the correction for its effect on water colour in remote sensing applications. A second objective was to investigate the relationship between CDOM and the concentration of total organic carbon (TOC). The work was carried out as part of the Danish Environmental Monitoring of Coastal Waters (DECO) program, which is exploring the feasibility of remote sensing techniques for monitoring purposes in Danish waters.

Materials and methods

A total of 586 CDOM samples and 89 TOC samples were collected during a number of monitoring cruises by the Danish counties (fjord samples) and the Danish National Environmental Research Institute (NERI, open water samples) during the period from February to May 1999. The exception to this were the Horsens Fjord samples taken in June 1998 during a DECO campaign. Figure 1 shows the position of the open water stations and the location of the fjords included in this study. At each station the salinity was recorded and a CDOM surface sample was taken. At the open water stations a CDOM profile and TOC measurements (from 5 m depth and 5 m above the bottom) where also taken.

CDOM samples were stored cold and in the dark in 100 ml amber glass bottles that had been rinsed three times with sample water before filling. Due to time restrictions the samples, excluding those from Horsens Fjord, could not be filtered immediately. This led samples from the county cruises being stored for 2–4 days and some samples from the NERI cruise for up to 20 days before filtration and analysis. A small study to measure any storage effects resulting from delayed filtration of the sample was carried out on water from The Sound. The spectra from triplicate samples that had been stored without filtration for 2, 10, 19 and 27 days were compared with samples that had been filtered immediately before storage.

Before analysis the samples were allowed to warm to room temperature and were then filtered through a $0.2 \,\mu\text{m}$ Minisart syringe filter, which had been prewashed with ultra pure Milli-Q water and 10 ml of sample before use. The absorption coefficients where measured in a 10 cm quartz cuvettes over the 300– 800 nm range with 0.5 nm increments, on a Shimadzu UV-2401PC UV-Vis recording spectrophotometer and referenced to ultra pure Milli-Q water. The absorption coefficients were obtained by,

$$a_{\lambda} = 2 \cdot 303 A_{\lambda} / L, \qquad (2)$$

where A_{λ} was the optical density at wavelength λ and L was the cuvette path length. A peak at 735–740 nm was seen in all the spectra and was identified as being due to a temperature effect (Pegau & Zaneveld, 1993; Trabjerg & Højerslev, 1996). As the reference cuvette remained in the spectrophotometer it was warmed above room temperature, whereas the sample water was only in the spectrophotometer for a short duration and therefore remained approximately at room temperature. In order to eliminate any temperature effects on the spectra, a Milli-Q water blank at room temperature was subtracted.

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TOC samples where taken in triplicate in 50 ml clear Nunclon[®] bottles, preserved with 0.25 ml concentrated Suprapur[®] (Merck) HCl and stored cold and in the dark. The bottles were pre-cleaned by soaking in 10% HCl overnight and then stored containing fresh acid until sampling. The bottles were rinsed with sample water three times before filling. In order to provide a blank measurement for the procedure, 16 bottles were similarly filled with ultra pure Milli-Q water. Before the analysis, sample water from each bottle was dispensed into three glass vials that had been sealed with aluminium foil and heated in an oven at 550 °C for 6 h. The vials were rinsed three times with sample water before filling. The average TOC concentration in each vial was determined from at least three simultaneous measurements on a Shimadzu TOC5000 analyser. To prevent cross contamination in the analyser between samples, a vial filled with ultra pure Milli-Q water was placed between each vial containing sample water. The analyser was calibrated with a new calibration curve ($r^2 = 1$ or 0.999) made from four standards before each batch of samples was run. All samples were analysed within a month and the mean blank value of $0.63 \text{ mg C } 1^{-1}$ (SD ± 0.16 , N=16) was subtracted from the measurements.

CDOM spectral analysis

This was carried out on the absorption spectrum between 300–650 nm using three different methods. The first (Method 1) was a linear regression of the natural logarithm of the absorption coefficient vswavelength, where the S coefficient was the slope of the line. The second method (2) was a non-linear regression of Equation 1 using the DUD iterative method in SAS/STAT software package (SAS Institute Inc., 1994). The third (Method 3) was similar to the second method but an additional background parameter (K) was added to Equation 1 to allow for any baseline shifts or attenuation not due to CDOM (Equation 3) (Markager & Vincent, 2000).

$$a_{\lambda} = a_{\lambda o} e^{S(\lambda o - \lambda)} + K \tag{3}$$

The degree of fitting that the three different methods provided was then compared by calculating the correlation coefficients and examining the residuals. The absorption at 375 nm was used as a measure of CDOM concentration.

Results

Storage test

The results from the study of storage effects of nonfiltered samples are presented in Table 1. It shows

Filtered before storage	Storage time (days)	Mean a_{375} (m ⁻¹)	$\begin{array}{c} \text{St dev } a_{375} \\ (\text{m}^{-1}) \end{array}$	Mean S (μm^{-1})	St dev S (μm^{-1})
Yes	2	0.7943	0.0093	23.3	0.1
No	2	0.8011	0.0263	23.3	0.2
No	10	0.7859	0.0142	23.1	0.2
No	19	0.7910	0.0142	23.0	0.2
No	27	0.8057	0.0176	23.0	0.3

TABLE 1. Statistics of the optical properties of CDOM after storage of unfiltered samples. a_{375} is the absorption coefficient at 375 nm and S is the spectral slope coefficient shown in Equation 3

TABLE 2. Results from the comparison of the three different methods for the estimation of S. In method 1 the S parameter is found by the linear regression of the log-transformed version of Equation 1. In method 2 S is estimated by a non-linear iterative regression of the raw absorption coefficients to Equation 1. Method 3 uses the same procedure as method 2, but applied to Equation 3

Method N		Mean S (μ m ⁻¹)	Std S (μm^{-1})	Range in S (μm^{-1})	Mean sum of absolute residuals (m ⁻¹)	Mean r ²	
1	586	17.6	6.8	2.7-39.7	126.0	0.949	
2	586	19.4	3.2	4.5-30.6	22.88	0.985	
3	586	19.9	1.9	11.0-25.2	10.01	0.998	

that storage of non-filtered samples did not have a significant impact on the absorption coefficient or the S coefficient. The values differed by less than one standard deviation from the mean of the filtered samples and no change with time was recorded. However, the standard deviations increased, so this type of storage does effect the precision of the measurement. The standard procedure is to filter the samples before storage in order to eliminate any changes in the CDOM sample as a result of particle degradation, bacterial activity or adsorption of CDOM to particles. We should emphasise that this is still the preferential method, however we have demonstrated that in the present study the absorption properties were not adversely affected by storage of non-filtered samples (Table 1).

S estimation methods

The comparison of the three different methods used to determine S was carried out by calculating S by each method on all spectra in the data set and determining the average r^2 and sum of absolute residuals for each method (Table 2). This showed that all three methods exhibited a high correlation between the observed spectra and the model. However, the third method, a non-linear regression with the background parameter (*K*), provided the best fit, exhibiting a 92% reduction in the mean sum of absolute residuals relative to method 1. This can also be seen in Figure 5 where the residuals from method 1 reveal systematic deviations whereas method 3 shows only smaller peaks between 300-500 nm.

By comparing methods 1 and 2 one can see the benefits of using a non-linear regression technique directly on the observed data rather than the natural log-transformation and linear regression method. There is an 82% decrease in absolute sum of residuals as a result of a direct application of the regression to the raw absorption data instead of using log transformed absorption data. The log transformation enhances the relative weight given to the small values, in this case at longer wavelengths, which is inappropriate in this situation because the absorption at longer wavelengths can be greatly influenced by the scattering effects of bubbles and very small particles. The non-linear fitting method on the other hand is more suitable, as it gives relatively more weight to the shorter wavelengths where the CDOM absorption signal is dominant.

The importance of including the background parameter (K) in the regression can be seen by comparing the results from method 2 and 3 (Table 2). It shows that the presence of baseline offsets due to scattering



FIGURE 2. A comparison of the different mean estimates for S obtained by applying a non-linear regression (Method 3) over different regions of the spectra. The regressions where carried out on 25 samples from the surface waters (<10 m) of The Sound. Error bars represent the standard deviations.

(Bricaud, *et al.*, 1981; Davies-Colley & Vant, 1987) or differences in refractive indices (Green & Blough, 1994), can have a significant effect on the estimation of S.

When S is calculated using method 3 instead of method 1, there is a 13% increase in its mean value and a considerable decrease in the range of values, seen by a 72% reduction in its standard deviation. For the rest of this paper the S values reported are determined by method 3 unless otherwise stated.

In order to examine the dependency of S estimation on the wavelength range used in the regression, S was estimated over six different ranges of 100 nm magnitude using Method 3. This was carried out on 25 spectra from the surface waters (<10 m) of The Sound. The results can be seen in Figure 2. It is clear that the estimated S values and the precision of the estimate decrease with increasing wavelength. The maximum and minimum values derived from the regressions were $26.4 \,\mu m^{-1}$ and $15.7 \,\mu m^{-1}$ for the wavelength ranges of 300-400 nm and 400-500 nm respectively. Although there are significant differences in S values it is impossible to say which is the most accurate estimate as this depends on the application. For example, S values estimated from 300-400 nm would be overestimates if they were to be used in remote sensing applications which are focused on longer wavelengths. In this study we have opted to use spectral data from 300-650 nm because it is within this range that CDOM has a relevant and considerable influence on aquatic optics.



FIGURE 3. Variation of salinity (∇) , a_{375} (\odot) and S (\blacksquare) at 5 m depth on a west to east transect through the major Danish water bodies (North Sea, Skagerrak, Kattegat, The Sound and Arkona Sea). Stations A–J refer to mean values from middle three stations on each of the North Sea/Skagerrak transects. Refer to Figure 1 for station and transect locations.

Variation of S and a_{375}

Table 3 shows the mean a_{375} and S coefficients for the surface waters sampled. The highest measurements of a_{375} were found in the low salinity Baltic water (mean, 0.8 m^{-1}), the south-west Jutland coastal waters close to the German Bight (mean, 0.9 m^{-1}) and within the fjords $(0.6-7.1 \text{ m}^{-1})$. The lowest was recorded in Skagerrak and open North Sea waters (mean, 0.3 m^{-1}). In general, a_{375} was found to decrease as the Baltic outflow and Jutland coastal waters mixed with the North Sea water mass in the Skagerrak and open North Sea (Figure 2). The S coefficients tended to fall linearly from c. 24–19 μ m⁻¹ as the Baltic water mixed with the more saline North Sea water (Figures 3 and 4). Data from the Skagerrak and open North Sea exhibited a wide range in S values recorded, especially in Skagerrak deep waters. Unlike the other waters sampled, there was a 'patchy' variation in S, with no apparent spatial trends.

S was lower within the fjords (mean, $19 \,\mu m^{-1}$) than in the coastal waters they discharged into and generally S showed a positive relationship with salinity in the fjords (Figure 4). Although we were not able to define the relationship in each fjord due to the limited number of samples and salinity range covered (Table 3) it was clearly evident from looking at the relationship between S and a_{375} . There was a negative linear relationship in each fjord. Since CDOM absorption (e.g. a_{375}) can be assumed to behave quasiconservatively with salinity (Reuter *et al.*, 1986; Højerslev, 1988, 1989; Laane & Kramer, 1990) this implies that S varies linearly with salinity at



FIGURE 4. Relationship between the spectral slope coefficient (S) and salinity in the different coastal waters of Denmark. The symbols represent, (\bullet) open water samples from the surface waters (≤ 10 m), (\bigcirc) open water deep samples, and (\blacksquare) fjord samples.

intermediate salinities in Danish fjords. In order to examine this more closely the relationship between S and a_{375} was determined using a model II ('reduced

TABLE 4. Results from model II regression of a_{375} and S in five Danish fjords. The equation used was, $V_{(S,a)} = \pm \sqrt{(b_{(S,a)}/b_{(a,S)})}$, where V is the slope of the relationship and b is the linear regression coefficients of S on a_{375} or a_{375} on S. These results can be used for characterizing the relationship but not for the prediction of one of the variables (Sokal & Rohlf, 1995)

Area	Ν	r^2	$V_{(S,a)}$	95% C.L. (±)
Kolding Fjord	5	0.9528	-0.0006	0.0003
Limfjorden	11	0.9209	-0.0003	0.0000
Mariager Fjord	24	0.7526	$\times 0.0010$	0.0002
Ringkøbing Fjord	8	0.8628	-0.0012	0.0005
Vejle Fjord	5	0.7372	-0.0054	0.0051

major axis' or 'geometric mean') linear regression. This regression allowed us to ascertain a relationship between two variables where neither is the dependent variable (Sokal & Rohlf, 1995). The equation and results from the regressions are shown in Table 4. There is a significant negative relationship in all the fjords tested and it appears that the slope values for the fjord waters do not differ significantly from each other (within 95% confidence levels).

TABLE 3. Average values for the optical properties of CDOM, and salinity measurements from surface waters (<10 m) in Danish coastal waters. a_{375} is the absorption coefficient at 375 nm and S is the spectral slope coefficient

Area	Ν	Mean a_{375} (m ⁻¹)	St dev a_{375} (m ⁻¹)	a_{375} range (m ⁻¹)	$\frac{\text{Mean }S}{(\mu\text{m}^{-1})}$	St dev S (μm^{-1})	S range (μm^{-1})	Salinity range
Arkona Sea	12	0.819	0.053	0.711-0.896	23.2	0.7	22.4-25.2	7.97-10.62
Belt Sea	12	0.766	0.0411	0.708 - 0.824	22.4	0.6	21.6-23.5	13.08-17.56
Great Belt	18	0.779	0.0583	0.678 - 0.954	22.4	0.5	21.3-23.3	11.60–18.91
Little Belt	18	0.800	0.0896	0.681-0.995	22.1	0.6	21.1-23.3	13.23-19.95
The Sound	25	0.806	0.0695	0.664-0.901	22.6	0.8	20.9 - 24.2	7.81-21.40
Kattegat	34	0.674	0.105	0.464-0.915	20.2	$1 \cdot 1$	17.8 - 21.8	18.59-31.77
Skagerrak	23	0.304	0.092	0.091 - 0.423	19.4	1.3	17.6 - 23.4	31.50-34.85
North Sea	46	0.644	0.436	0.164-1.51	19.0	$1 \cdot 1$	16.4-22.3	29.39-34.89
(1) Coastal North Sea	27	0.894	0.404	0.256-1.51	18.8	0.6	17.3-20.5	29.39-34.30
(2) Outer North Sea	19	0.290	0.117	0.164-0.530	19.3	1.4	16.4-22.3	32.85-34.89
Ho Bugt	3	2.32	0.646	1.93 - 3.07	18.2	0.3	18.0-18.5	19.28-25.60
Horsens Fjord	13	1.26	0.153	1.02 - 1.50	18.7	0.8	17.8 - 21.2	19.70-23.00
Kolding Fjord	5	1.75	1.79	0.830-4.94	19.4	1.0	17.7 - 20.3	5.26-23.87
Limfjorden	11	3.07	2.33	1.23 - 7.15	19.2	0.8	17.9 - 20.0	8.03-27.66
Mariager Fjord	26	2.81	0.537	1.42 - 3.43	18.7	0.4	17.9 - 19.4	13.97-21.94
Nærå Strand	2	3.06	0.106	2.98-3.13	19.3	0.1	19.2–19.3	14.04-16.30
Nissum Fjord	4	$4 \cdot 11$	0.547	3.66-4.90	18.5	0.4	17.9 - 18.9	1.17 - 6.46
Nyborg Fjord	2	4.52	1.92	3.16-5.88	18.8	0.3	18.6-19.1	0.83-8.18
Odense Fjord	3	2.30	1.49	1.08-3.96	19.3	0.7	18.9-20.1	13.05-22.47
Roskilde Fjord	8	3.73	0.098	3.53-3.385	20.0	0.1	19.8-20.2	10.06-13.55
Ringkøbing Fjord	8	3.97	0.155	3.64-4.13	18.7	0.1	18.5 - 18.8	7.01-16.00
Randers Fjord	4	3.32	1.11	1.97 - 4.65	18.2	0.6	17.5-18.9	1.91–19.64
Vejle Fjord	5	0.751	0.093	0.638–0.868	19.3	0.5	18.6–19.8	25.85-27.15



FIGURE 5. (a) The relationship between TOC and a_{375} in Danish waters. The equation of the regression line is TOC=2.89. a_{375} +0.38 (r²=0.63) and the data symbols correspond to the region where the samples were taken (see Figure 1). (b) Same as (a) but where mean TOC and a_{375} values are used for different salinity ranges. R2=5.0–9.9, R3=10–14.9, R4=15–19.9, R5=20–24.9, R6=25–29.9, R7=30–34.9 and R8– \geq 35. The error-bars show standard deviations and the equation of the line is, mean TOC=3.28. a_{375} +0.22 (r²=0.89). In both graphs the intercept does not differ significantly from zero.

TOC-CDOM relationship

The TOC concentrations ranged from a maximum of $3.79 \ (\pm 0.05) \ mg l^{-1}$ in the Arkona Sea to a minimum of $0.317 \ (\pm 0.12) \ mg l^{-1}$ at 600 m depth in the Skagerrak (no TOC measurements were taken from the fjords). A significant correlation was found between TOC and a_{375} in these waters especially if they were averaged over ranges of 5 in salinity (0–4.99, 5–9.99, 10–14.99 ... etc) (Figure 5). The specific absorption coefficients (a_{375}^*), calculated by normalising the absorption measurements to the TOC measurements, ranged from a minimum of 0.0727 m² g⁻¹ C in the Skagerrak to a maximum of 0.630 m² g⁻¹ C in the Kattegat. The data set mean

for a_{375}^* was 0.29 (± 0.11 SD) m² g⁻¹ C (N=84). The variability in a_{375}^* was tested for any variation with area, salinity range or water layer (surface/bottom) using ANOVA test (Sokal & Rohlf, 1995). However no significant patterns were found.

Residuals

The residuals resulting from the non-linear regression technique (method 3) appeared to differ depending on the water body. The results showed that there were three dominant curves shapes seen in Danish waters (Figure 6). The largest residuals were seen in the 300-400 nm range in waters where the CDOM concentration was high. As the concentration of CDOM decreased so did the residual range. The pattern in Figure 6(a) with a negative peak at 320-350 nm was typical for Baltic waters, Roskilde Fjord and the fjords on the east coast of Jutland. The twin peaked curve seen in Figure 6(b) was typical for CDOM found in fjords on the west coast of Jutland, low salinity parts of Limfjorden and the south-west Jutland coastal waters (coastal stations of TA-TD, see Figure 1). This pattern was also seen in the lowest salinity samples from both Kolding and Randers fjords. The third residual curve is actually quite similar to the first curve but found in samples with much lower concentrations, i.e. in the Skagerrak and the North Sea.

Discussion

Variation of S and a_{375}

There is clear evidence for three major sources of CDOM in Danish waters. The Baltic Sea outflow, German Bight water (south-west Jutland coast) and local coastal discharges. In the Baltic outflow a_{375} and S decreased as the water mixed with the North Sea water mass. Local point sources were easily detectable by pronounced changes in a_{375} , S and salinity (e.g. station 413 in Figure 3).

Variations in S have in the past been attributed to changes in the composition of the CDOM pool (Carder *et al.*, 1989) which can occur as a result of a number of processes. (1) The presence of multiple sources of CDOM, (2) bacterial degradation, (3) photo-degradation, and (4) physical removal of a fraction of the CDOM pool (for example via coagulation) (Brown, 1977; Gao & Zepp, 1998). The data on the variation of S coefficients in Danish waters are interesting, as it has often been assumed that a mean value of $14 \,\mu\text{m}^{-1}$ was adequate to describe most natural waters (Jerlov, 1976; Bricaud *et al.*, 1981; Reuter *et al.*, 1984; Aarup, 1994). Results from the



FIGURE 6. Residuals from the different regression techniques for the determination of S. (a) Roskilde Fjord, St. 2, 1 m depth, 11/04/99. (b) Nissum Fjord, St. 23, 1 m depth, 14/04/99. (c) Skagerrak, St. 1006, 5 m depth, 10/02/99. The dashed, thin and bold lines represent the residuals from method 1, 2 and 3 respectively. In (c) the plots for method 2 and 3 lie on top of each other.

fjords sampled appeared to agree with the findings of Kerr and Quinn (1975) that soil derived CDOM has an inverse relationship between absorption and S. As $V_{(S,a)}$ did not appear to vary significantly between the fjords sampled we can assume that similar processes

are acting on the CDOM in each fjord and causing an increase in *S* along with a decrease in concentration as water moved through the fjord. In all cases, *S* values for CDOM in the fjords were lower than those for the coastal waters in which they discharge (see Table 3).

We suggest that the observed increase is due to two processes. The removal of a 'reactive 'high molecular weight fraction of CDOM (Brown, 1975; Mayer, 1981) and the conservative mixing of the 'resistant' remainder with the CDOM from the open coastal waters.

Possible reasons for the decreases in the slope coefficients seen in the Baltic outflow are photodegradation and bacterial utilization of CDOM, as both these processes have been reported to have a flattening effect on the slope (Brown, 1977; Gao & Zepp, 1998). However, the general linear relationship between S and salinity seen during the mixing of Baltic Sea water and Skagerrak/North Sea water seems to suggest either conservative behaviour of S or that any changes in S that occur are on similar time scales as mixing processes in the region (see Figure 4). Both these are supported by the increase in standard deviation of S seen in the Kattegat, where the mixing occurs. Even though it is conceivable that solar and bacterial degradation do occur in these waters it is likely that the supply of 'new' terrestrial CDOM into the region would drown out their influence.

The high variability of S values in the Skagerrak and open North Sea cannot be explained by the mixing of CDOM from different terrestrial sources, as there is no salinity gradient. This type of wide variability in S at low CDOM concentrations has also been reported in earlier studies (Blough et al, 1993; Del Castillo et al., 1999; Markager & Vincent, 2000). Blough et al. (1993) found that it was not due to the inaccurate measurement of S at low concentrations. A possible explanation for this variability at low concentrations is that the pool is more heterogeneous in open areas compared to coastal regions where terrestrial CDOM is dominant. The occurrence of CDOM at low concentrations with high S values could be due to the presence of autochthonous DOM from algae or pelagic processes (e.g. grazing). Marine CDOM with high S values have in the past been found to be derived from algae (Doeffer & Amann, 1984) and bacterial sources (Nelson et al., 1998) and it seems feasible they could be responsible in this case. The large spatial variability in S in these waters could then be explained by patchiness in algal and bacterial populations with respect to both region and depth. Work by Gao and Zepp (1998) has shown that photodegradation processes have a decreasing effect on S values and so it is possible that this is responsible for the low values found.

It would appear that for the majority of Danish waters S seems to behave relatively predictably which is a good sign for the future of remote sensing applications in the region. Judging by the size of the

standard deviations of S reported in Table 3 one can see that the calculated regional means are reasonably precise and provide good estimates for future optical studies. However, it must be noted that possible seasonal variations still have to be studied.

TOC a_{375} relationship

The TOC- a_{375} relationship showed a degree of scattering. The statistical analysis (ANOVA and linear regression) revealed no systematic variations in the specific absorption coefficient. It can therefore be assumed to be constant in Danish coastal waters excluding fjords, where no TOC measurements were available. The data set mean for a_{375}^{\star} $(0.29 \text{ m}^2 \text{ g}^{-1} \text{ C})$ was very similar to the values found by other researchers in the Baltic Sea (0.19- $0.31 \text{ m}^2 \text{ g}^{-1} \text{ C}$, extrapolated from a_{355} (Ferrari *et al.*, 1996; Ferrari & Dowell, 1998)) and for humic acid in the Gulf of Mexico $(0.30 \text{ m}^2 \text{ g}^{-1} \text{ C}, \text{ extrapolated})$ from a_{450} (Carder *et al.*, 1989)). The fact that it is alike to those found by Ferrari et al. (1996) in the southern Baltic suggests that a_{375}^{\star} does not vary in western Baltic waters (salinity range of 5-35). It is likely that the variations seen in our data for a_{375}^{\star} can be explained by changes in the particulate fraction of TOC (POC), due to the low chlorophyll concentrations present at this time of the year. Chlorophyll measurements were in the range of $0-2 \ \mu g \ Chl \ l^{-1}$ in the open waters which means that algae could have only accounted for about 5% of the TOC in these waters (assuming a carbon-chlorophyll ratio of 50 mg C mg^{-1} Chl). A possible explanation could be the effect of photodegradation on the CDOM pool. The presence of older, ' bleached ' CDOM and newer CDOM from local sources would lead to low and high values for a_{375}^{\star} respectively due to the effects of photodegradation on CDOM absorption. However, it appears that although the CDOM pool undergoes changes in its composition in these waters, represented by changes in S values, this does not have a significant overall impact on the specific absorption coefficient. With the continued study of its behaviour in fjords and any potential seasonal fluctuations in the relationship (Ferrari et al., 1996) this will allow the use of optical measurements (e.g. remote sensing) for the estimation of dissolved carbon in different water masses and so aid the study of carbon transport in coastal waters.

Residuals

The plot of residuals verses wavelength (Figure 6) shows that the CDOM absorption spectrum can differ



FIGURE 7. A map of the different soil types found in Denmark. Based on Figure 7 in Friberg *et al.* (1998), with kind permission from Kluwer Academic Publishers.

from the exponential model at wavelengths below approximately 450 nm. A similar deviation from the model has been mentioned before (Green & Blough, 1994). The patterns allow us to distinguish between two different CDOM pools of terrestrial origin. An eastern type from the Baltic Sea water and east Denmark land run-off and a western type from the German Bight water and western coast of Jutland. This seems to correlate with the division of dominant soil types and differences in land use in Denmark. In the eastern region of Denmark the soil is predominantly sandy loam (Figure 7) and the dominant agriculture is crop growing, in the western part of Jutland, however, the soils are sandy and animal farming dominates over crop growing. The appearance of the 'west coast' type residual curve in some samples from Randers and Kolding fjords is probably due to the fact that their drainage basins include both soil types. It is interesting to note that although similar S values would suggest analogous CDOM composition in all fjords, the differing residual patterns suggest otherwise. It appears that the CDOM in the eastern waters has chromophores that absorb strongly around 300 and 315 nm whereas in the west chromophores absorbing at 318, 340 and 355 nm are present. CDOM fluorescence studies by Coble (1996) have managed to characterize the CDOM pool and distinguish between certain groups of fluorophores. As a substance needs to absorb light (excitation) before it can fluoresce (emission), the fluorescence excitation spectrum can be assumed to be similar to an absorption spectrum. This allows us to compare the excitation wavelength of the fluorescence peaks with the peaks seen in the residual plots. A fluorescence peak of particular interest is the humic-like peak C (at, ex. 350 nm) which has been found to decrease in intensity as river water mixes with seawater (Coble, 1996). As the 'west coast' samples all exhibited a strong peak at 350 nm [e.g. Figure 6(b)] which gradually disappeared during mixing with the coastal water mass it is possible that we have observed the disappearance of the same chromophore(s) as Coble (1996) via our absorption measurements. This technique has the potential to be a useful method for the characterization of different CDOM pools and further aid the use of CDOM as a water mass tracer in coastal waters. For example, from examining the residual plots one can trace the input of CDOM into coastal waters from the west coast of Jutland.

Conclusions

In this study we have made use of a new method first suggested by Markager and Vincent (2000) for the estimation of the spectral slope parameter (S). It was found to give a better description of the observed absorption spectra than previously used methods. The residuals produced from the regression provided a useful tool in the characterization of the CDOM pool and allowed the distinction between CDOM from two different land types with similar S values. The specific absorption coefficient was found to be constant in Danish coastal waters and similar to values published from other regions. S values for the coastal waters on a whole were seen to vary in a predictable, conservative fashion and we recommend the use of the regional values for S rather than an overall mean, for remote sensing applications in this area. In the offshore waters of the Skagerrak and North Sea a less precise mean for S was attained and was thought to be a result of the presence of marine sources of CDOM. The results provided here give an optimistic picture for the application of water colour remote sensing techniques in Danish coastal waters where CDOM can be a hindrance. Further work is needed however, to assess the occurrence of seasonal variations in its behaviour.

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References

- Aarup, T. 1994 Satellite imagery of Danish and neighbouring waters. University of Copenhagen Ph.D. thesis, published in Havforskning series from Miljøstyrelsen, No. 52, Danish Environmental Protection Agency. 162 pp.
- Blough, N. V. & Zafiriou, O. C. 1993 Optical absorption spectra of waters from the Orinoco River outflow: Terrestrial input of Coloured Organic Matter to the Caribbean. *Journal of Geophysical Research* 98, 2271–2278.
- Bricaud, A., Morel, A. & Prieur, L. 1981 Absorption by dissolved organic matter of the sea (yellow substance) in the UV and visible domains. *Limnology and Oceanography* 26, 43–53.
- Brown, M. 1975 High molecular-weight material in Baltic seawater. Marine Chemistry 3, 253–258.
- Brown, M. 1977 Transmission spectroscopy examinations of natural waters. C. Ultraviolet spectral characteristics of the transition from terrestrial humus to marine yellow substance. *Estuarine and Coastal Marine Science* 5, 309–317.
- Carder, K. L., Steward, R. G., Harvey, G. R. & Ortner, P. B. 1989 Marine humic and fulvic acids: Their effects on remote sensing of ocean chlorophyll. *Limnology and Oceanography* 34, 68–81.
- Coble, P. G. 1996 Characterisation of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy. *Marine Chemistry* **51**, 325–346.
- Davies-Colley, R. J. & Vant, W. N. 1987 Absorption of light by yellow substance in freshwater lakes. *Limnology and Oceanography* 32, 416–425.
- Del Castillo, C. E., Coble, P. G., Morell, J. M., Lopez, J. M. & Corredor, J. E. 1999 Analysis of the optical properties of the Orinoco River plume by absorption and fluorescence spectroscopy. *Marine Chemistry* **66**, 35–51.
- Doerffer, R. & Amann, V. 1984 The development of the horizontal distribution of a North Sea phytoplankton bloom. Special Meeting Causes, Dynamics and Effects of Exceptional Marine Blooms and Related Events, ICES, Copenhagen, 4–5 Oct. 1984, 16 pp.
- Ferrari, G. M. & Dowell, M. D. 1998 CDOM absorption characteristics with relation to fluorescence and salinity in coastal areas of the southern Baltic Sea. *Estuarine and Coastal Shelf Science* 47, 91–105.
- Ferrari, G. M., Dowell, M. D., Grossi, S. & Targa, C. 1996 Relationship between the optical properties of chromophoric dissolved organic matter and total concentration of dissolved organic carbon in the southern Baltic Sea region. *Marine Chemistry* 55, 299–316.
- Friberg, N., Rebsdorf, A. & Larsen, S. E. 1998 Effects of afforestation on acidity and invertebrates in Danish streams and implications for freshwater communities in Denmark. *Water Air and Soil Pollution* 101, 235–256.
- Gao, H. Z. & Zepp, R. G. 1998 Factors influencing photoreactions of dissolved organic matter in a coastal river of the southeastern United States. *Environmental Science & Technology* 32, 2940– 2946.
- Green, S. A. & Blough, N. V. 1994 Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. *Limnology and Oceanography* 39, 1903–1916.
- Hoge, F. E., Williams, M. E., Swift, R. N., Yungel, J. K. & Vodacek, A. 1995 Satellite retrieval of the absorption coefficient of chromophoric dissolved organic matter in continental margins. *Journal of Geophysical Research* 100, 24847–24854.
- Højerslev, N. K. 1971 Tyndall and fluorescence measurements in Danish Norwegian waters related to dynamical features. Report no. 16, 12 pp. Institute of Physical Oceanography, University of Copenhagen.
- Højerslev, N. K. 1980 Water colour and its relation to primary production. Boundary Layer Meterology 18, 203–220.
- Højerslev, N. K. 1988 Natural occurrences and optical effects of Gelbstoff. Report no. 50, 1–30. Institute of Physical Oceanography, University of Copenhagen.

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- Højerslev, N. K. 1989 Surface water quality studies in the interior marine environment of Denmark. *Limnology and Oceanography* 34, 1630–1639.
- Højerslev, N. K., Holt, N. & Aarup, T. 1996 Optical measurements in the North Sea-Baltic Sea transition zone. 1. On the origin of the deep water in the Kattegat. *Continental Shelf Research* 16, 1329–4343.
- Jerlov, N. G. 1953 Influence of suspended and dissolved matter on the transparency of seawater. *Tellus* 5, 59–65.
- Jerlov, N. G. 1955 Factors influencing the transparency of the Baltic waters. Report no. 25, Oceanographic Institute of Gothenburg, 19 pp.
- Jerlov, N. G. 1968 Optical Oceanography, Oceanography Series 5. Elsevier Pub. Co., Amsterdam.
- Jerlov, N. 1976 *Marine Optics*. Elsevier Oceanography Series 14. 231 pp.
- Kalle, K. 1937). Annln. Hydrogr. Berl., 65, 276–282. Quoted by Kalle (1966).
- Kalle, K. 1956 Dt. Hydrogr. Z., 9, 55-65. Quoted by Kalle (1966).
- Kalle, K. 1966 The problem of the gelbstoff in the sea. Oceanography Marine Biology Annual Review 4, 91–104.
- Karabashev, G. S. 1992 On the influence of dissolved organic matter on remote sensing of chlorophyll in the straits of Skagerrak and the Kattegat. *Oceanologia Acta* 15, 255–259.
- Karabashev, G. S., Khanaev, S. A. & Kuleshov, A. F. 1993 On the variability of yellow substance in the Skagerrak and the Kattegat. *Oceanologica Acta* 16, 115–125.
- Kerr, R. A. & Quinn, J. G. 1975 Chemical studies on the dissolved organic matter in sea water. Isolation and fractionation. *Deep Sea Research* 22, 107.
- Kirk, J. T. O. 1994 *Light and Photosynthesis in Aquatic Ecosystems*, 2nd edition. Cambridge University Press.
- Laane, R. W. P. M. & Kramer, K. J. M. 1990 Natural fluorescence in the North Sea and its major estuaries. *Netherlands Journal of Sea Research* 26, 1–9.
- Lundgren, B. 1976 Spectral transmittance measurements in the Baltic. Report no. 30, 38 pp. Institute of Physical Oceanography, University of Copenhagen.
- Markager, S. & Vincent, W. F. 2000 Spectral light attenuation and the absorption of UV and blue light in natural waters. *Limnology* and Oceanography 3, 642–650.

- Mayer, L. M. 1981 Geochemistry of humic substances in estuarine environments. In *Humic Substances in Soil, Sediment and Water* (Aiken, G. R., Mcknight, D. M., Wershaw, R. L. & MacCarthy, P., eds. John Wiley and Sons, New York, pp. 211–233.
- Moran, M. A. & Zepp, R. G. 1997 Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnology and Oceanography* **42**, 1307–1316.
- Nelson, N. B., Siegel, D. A. & Michaels, A. F. 1998 Seasonal dynamics of colored dissolved material in the Sargasso Sea. *Deep-Sea Research Part I—Oceanographic Research Papers* 45, 931–957.
- Pegau, W. S. & Zaneveld, J. R. 1993 Temperature dependent absorption of water in the red and near-infrared portions of the spectrum. *Limnology and Oceanography* **38**, 188–192.
- Pettersson, C., Rahm, L., Allard, B. & Boren, H. 1997 Photodegradation of aquatic humic substances: An important factor for the Baltic carbon cycle. *Boreal Environment Research* 2, 209–215.
- Reuter, R., Diebel-Langohr, D., Doerffer, R., Dorve, E., Haardt, H. & Hengstermann, T. 1986 Optical properties of gelbstoff: The influence of yellow substances on remote sensing of seawater constituents from space. Report vol. 11, 1–58. GKSS Geesthacht Research Centre, FRG.
- SAS Institute Inc 1994 SAS/STAT User's Guide, Volume 2. GLM-VARCOMP, Version 6, 4th edition.
- Sokal, R. R. & Rohlf, F. J. 1995 *Biometry*, 3rd edition. W. H. Freeman & Co., New York.
- Tassan, S. 1988 The effect of dissolved yellow substance on the quantitative retrieval of chlorophyll and total suspended sediment concentration from remote measurements of water colour. *International Journal of Remote Sensing* **9**, 787–797.
- Trabjerg, I. & Højerslev, N. K. 1996 Temperature influence on light absorption by freshwater and seawater in the visible and near-infrared spectrum. *Applied Optics* 35, 2653–2658.
- Uher, G. & Andreae, M. O. 1997 Photochemical production of carbonyl sulfide in North Sea water: A process study. *Limnology and Oceanography* **42**, 432–442.
- Vodacek, A., Hoge, F. E., Swift, R. N., Yungel, J. K., Peltzer, E. T. & Blough, N. V. 1995 The use of in situ and airborne fluorescence measurements to determine UV absorption coefficients and DOC concentrations in surface waters. *Limnology and Oceanography* 40, 411–415.