

Spectral light absorption by yellow substance in the Kattegat–Skagerrak area

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Abstract

More than 1500 water samples were taken from the Kattegat, the Skagerrak and adjacent waters. The value of the absorption coefficient of yellow substance at 310 nm was found to vary from 0.06 to 7.4 m⁻¹ in the *open* coastal waters, with a mean value of 1.3 m⁻¹. The corresponding wavelength-averaged value (250–450 nm) of the semilogarithmic spectral slope of the coefficient ranges from 0.008 to 0.042 nm⁻¹, and the mean value is 0.023 nm⁻¹. Closer to river discharges, as in the fjords, the values of the slope seem to be more constant at around 0.0175 ± 0.0015 nm⁻¹. In this area the slope must then be known in order to compare absorption at different wavelengths or to model the yellow substance absorption.

1. Introduction

The light-absorbing marine humic and fulvic acids are traditionally termed ‘yellow substance’, after the concept of ‘Gelbstoff’, introduced 50 years ago by Kalle (1949). During the last decade acronyms like CDOM for ‘coloured (or chromophoric) dissolved organic matter’ and CDOC for ‘coloured dissolved organic carbon’ have also come into use. So, as the name suggests, yellow substance is not a uniquely defined chemical mixture.

Kalle, who was the first to measure yellow substance *in vitro* by means of light absorption and fluorescence in Baltic Sea waters, demonstrated that not only these properties but also their ratio varied with water depth. This fact is of fundamental importance from a remote sensing point of view, since it implies that great changes over small time- and length-scales may be induced by vertical mixing only. Joseph (1955) and Jerlov (1953, 1955) introduced *in situ* optical measurements of yellow substance as an oceanographic tool. The usefulness of yellow substance as a natural tracer was clearly demonstrated for the Baltic and its adjacent waters, like the Sound off Copenhagen, the Belt Sea, and the Kattegat up to the Skagerrak bordering the North Sea. From the early and many later investigations it could be concluded that yellow substance was a stable quasi-conservative tracer which was easy and straightforward to measure by optical methods. It also became clear that there was a tendency to observe high yellow substance concentrations along with low salinities and vice versa in coastal waters receiving considerable freshwater discharges. At this early stage it could further be concluded that yellow substance-salinity relationships were clearly site-dependent.

Yellow substance thus has a great oceanographic potential for water mass classification in coastal waters displaying low, intermediate and high salinities. The main reason for this lies in the facts that concentrations of yellow substance may vary by several orders of magnitude in a coastal area, and that the yellow substance content is stable and apparently indifferent to phytoplankton production (Højerslev 1982, 1989). The coastal yellow substance originates mainly from land discharges, hence the source can often be identified. Aarup et al. (1996a, b) and Højerslev et al. (1996) have recently demonstrated the usefulness of yellow substance as a means for quantifying the mixing ratios of three different water masses at all depths. Their method, based on yellow substance absorption and salinity, parallels the traditional *T-S* analysis (temperature-salinity diagrams), but it has the advantage that it can also be applied to surface waters. The *T-S* method is only applicable to intermediate and deep waters because the temperature cannot be regarded as a conservative property in the surface layer.

A simple way to quantify the yellow substance content is to measure its absorption coefficient at a fixed wavelength. However, in order to compare coefficients obtained at different wavelengths it becomes necessary to know the spectral variation of the coefficient. This information is also crucial for all optical models of radiative energy transfer in coastal waters. Jerlov suggested in 1957 that the spectral light absorption of yellow substance could be approximated by an exponential function of the wavelength. It is usually expressed as

$$a_y(\lambda) = a_y(\lambda_0)e^{-\gamma(\lambda-\lambda_0)}, \quad (1)$$

where $a_y(\lambda)$ is the light absorption coefficient at wavelength λ , and λ_0 represents a reference wavelength. The quantity γ , which is the slope of $a_y(\lambda)$ as a function of λ in a semilogarithmic diagram, was first quantified by Lundgren (1976). This slope has often been treated as a physical quasi-constant, and a number of investigators have undertaken its determination. In the textbook on marine optics by Jerlov (1968, p. 56), the average slope can be calculated to equal 0.015 nm^{-1} (250–600 nm), and Lundgren (1976) found γ to vary between 0.011 and 0.017 nm^{-1} in the Baltic Sea for the spectral domain 400–725 nm. Several spectrophotometric determinations of γ for oceanic waters from the last 40 years are presented in Table 1, demonstrating a total range of 0.004 – 0.053 nm^{-1} .

The value of the spectral slope is crucial for the conversion of absorption coefficients from one wavelength to another. For example, while Kowalczyk & Kaczmarek (1996) and Kowalczyk (1999) applied the absorption coefficient at 400 nm as a measure of the yellow substance content, we chose the UVB wavelength 310 nm, since transmission of UVB daylight in the sea is more interesting from a biological point of view. A comparison of the coefficients becomes futile unless the exact value of γ is known. If $a_y(400 \text{ nm}) = 0.50 \text{ m}^{-1}$, then $a_y(310 \text{ nm}) = 0.72 \text{ m}^{-1}$ for the minimum value $\gamma = 0.004 \text{ nm}^{-1}$ (Kowalczyk & Kaczmarek 1996), but $a_y(310 \text{ nm}) = 12.8 \text{ m}^{-1}$ for the maximum value $\gamma = 0.036 \text{ nm}^{-1}$ (Kowalczyk 1999) according to eq. (1). Thus, in this extreme case the error may amount to a whole order of magnitude if the wrong slope is used.

The aim of this paper is to present the analysis of an extensive data set of $a_y(\lambda)$ and γ from the coastal waters between Denmark, Sweden and Norway, and to discuss the implications of the results.

2. Material and methods

A total of more than 1500 water samples were taken in the seawaters of the North Sea along the Danish coast, the Skagerrak, the Oslo Fjord, the Gullmar Fjord, the Kattegat, the Baltic Sea, plus a number of minor Danish fjords, straits and inlets. Several hundreds of samples were collected

Table 1. Marine observations of the spectral slope γ of yellow substance

Area	γ [nm^{-1}]			Spectral range [nm]	Baseline correction	References
	mean	min	max			
North Atlantic	0.011	–	–	420–665	–	Kalle (1961)
North Sea	0.011	–	–	420–665	–	Kalle (1961)
Baltic Sea	0.011	–	–	420–665	–	Kalle (1961)
Baltic Sea	0.015	0.011	0.017	400–725	–	Lundgren (1976)
Baltic Sea	0.026	0.018	0.031	280–310	–	Brown (1977)
Mauretanian Upwelling	0.015	–	–	375–500	$\sim \lambda^{-1}$	Bricaud et al. (1981)
Gulf of Guinea	0.014	–	–	375–500	$\sim \lambda^{-1}$	Bricaud et al. (1981)
Indian–Antarctic Ocean	0.012	–	–	375–500	$\sim \lambda^{-1}$	Bricaud et al. (1981)
Gulf of Mexico	0.014	0.012	0.017	370–440	–	Carder et al. (1989)
Gulf of Mexico	0.013	0.011	0.016	440–565	–	Carder et al. (1989)
Philippine Sea	0.017	0.015	0.018	280–490	–	Kopelevich et al. (1989)
South China Sea	0.017	0.015	0.018	270–490	–	Kopelevich et al. (1989)
Baltic Sea	0.019	0.018	0.019	280–500	–	Kopelevich et al. (1989)
Philippine Sea	0.011	0.010	0.011	500–680	–	Kopelevich et al. (1989)
South China Sea	0.011	0.011	0.011	490–670	–	Kopelevich et al. (1989)
Baltic Sea	0.012	0.011	0.013	510–650	–	Kopelevich et al. (1989)
Orinoco River – Caribbean	–	0.012	0.053	290–<700	constant	Blough et al. (1993)
South Florida	0.021	0.015	0.034	290–<700	constant	Green & Blough (1994)
South Atlantic Bight	–	0.014	0.024	300–<530	–	Nelson & Guarda (1995)

Table 1. (continued)

Area	γ [nm^{-1}]			Spectral range [nm]	Baseline correction	References
	mean	min	max			
Southern Baltic	0.019	0.004	0.034	350–<600	constant	Kowalczyk & Kaczmarek (1996)
Middle Atlantic Bight	–	0.010	0.034	290–<700	constant	Vodacek et al. (1997)
Atlantic–Pacific	0.015	–	–	412–676	–	Barnard et al. (1998)
New Zealand waters	0.015	0.011	0.018	300–460	$\sim \lambda^{-1}$	Davies-Colley (1998)
Southern Baltic	0.019	–	–	355–420	–	Ferrari & Dowell (1998)
Southern Baltic	0.019	–	–	400–600	–	Ferrari & Dowell (1998)
Sargasso Sea	0.024	–	–	325–400	–	Nelson et al. (1998)
Orinoco River – Caribbean	0.017	0.014	0.022	290–<600	constant	Del Castillo et al. (1999)
Orinoco River – Caribbean	0.014	0.010	0.016	400–500	constant	Del Castillo et al. (1999)
Southern Baltic	0.019	0.004	0.036	350–<600	constant	Kowalczyk (1999)
Southern Bight, North Sea	0.017	–	–	250–440	–	Warnock et al. (1999)
Southern Bight, North Sea	0.015	–	–	360–540	–	Warnock et al. (1999)
North Sea	0.020	0.017	0.029	350–480	–	Ferrari (2000)
European Atlantic	0.016	0.009	0.032	350–480	–	Ferrari (2000)
Western Mediterranean	0.018	0.011	0.028	350–480	–	Ferrari (2000)
Kat.–Skag.–North Sea	0.019	0.016	0.022	300–650	constant	Stedmon et al. (2000)
Danish fjord–coast. w.	0.021	0.018	0.025	300–650	constant	Stedmon et al. (2000)

Abbreviations: min – minimum value, max – maximum value.

by I. Trabjerg together with N.K. Højerslev along the coasts of Denmark and in the Gullmar Fjord. These data will be dealt with in greater detail elsewhere, but since their optical properties with respect to yellow substance are the same as for the Oslo Fjord, they should be mentioned here.

The bulk of the water samples was taken on board r/v 'Gunnar Thorson' during March and September 1992 in the open waters of the Kattegat and the Skagerrak (mainly in the eastern part of the Skagerrak, as shown by Fig. 1). The content of phytoplankton pigments in these waters covers a wide range (chlorophyll: 0.5–18 $\mu\text{g/litre}$ in March 1992, 0.5–9 $\mu\text{g/litre}$ in September 1992), as does the Secchi disc depth (7–20 m in September 1992). This area constitutes a meeting and mixing place between yellow substance-poor Atlantic waters from the North Sea and

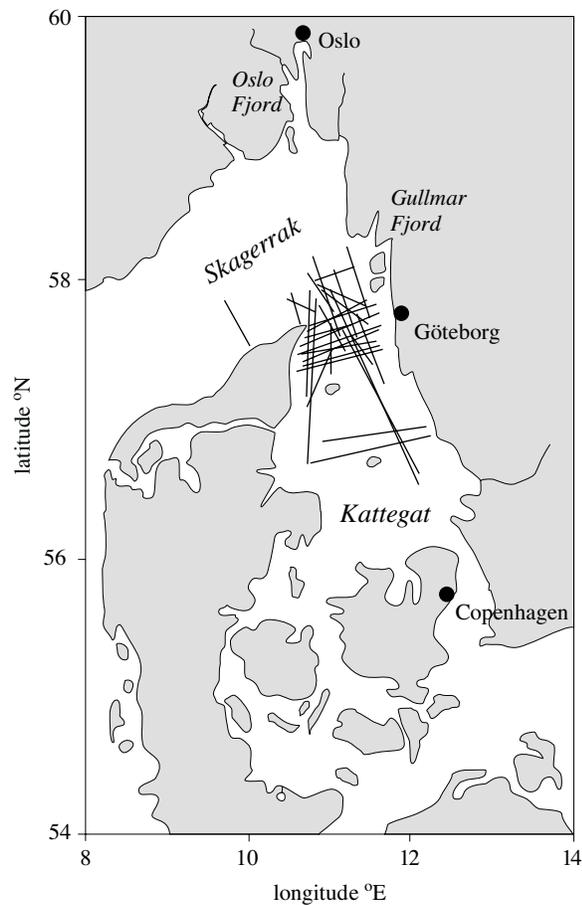


Fig. 1. The area of investigation. Sections of the 'Gunnar Thorson' cruises are marked with straight lines

yellow substance-rich waters from the German Bight, the Baltic Sea and the adjacent fjords and rivers (Karabashev et al. 1993, Aarup et al. 1996a, b, Højerslev et al. 1996). The main hydrographic characteristics are salinities from around 8 to 35.3, an almost global range.

Immediately following the hydrocasts the water samples were filtered. Various water filters had been tested, and in Copenhagen prewashed (flushed) Millipore filters of pore size $0.22 \mu\text{m}$ were found to work satisfactorily. In Oslo $0.2 \mu\text{m}$ Sartorius filters were applied. The filters were chosen as a compromise between a short filtration time and a particle-free sample. They did not clog too fast, and they were assumed to eliminate more particles than GF/C, GF/F and $0.4 \mu\text{m}$ filters. The results presented in our paper were all obtained from samples analysed after an adjustment time ranging from 0.5 to a few hours. If the water temperature is lower than the room temperature, condensation may occur on the outer walls of the cuvette (sample cell). Gas bubbles are produced in the sample by the change in pressure and temperature and can scatter the light beam entering the cuvette; some time is therefore needed to let these bubbles form and settle. They were removed by careful rotation of the sample.

The absorption coefficient $a_y(\lambda)$ of yellow substance was obtained from spectrophotometric measurements of filtered water samples, relative to a reference of pure water. It was assumed that the filtered sample was practically particle-free, so that the observed absorbance represented mainly the yellow substance content. Especially in the ultraviolet part of the spectrum, where yellow substance absorbs strongly, this assumption may be valid. According to eq. (1) the spectral curve of $a_y(\lambda)$ should appear as a straight line in a semilogarithmic diagram, but it usually flattens out towards longer wavelengths, approaching an asymptotic value.

The asymptotic absorbance may be caused by two different types of contribution. The first type is due to temporary or constant differences in optical properties between the walls of the sample and the reference cells, or due to a background signal produced by the electronics of the spectrophotometer. Most authors choose a constant value for this baseline correction, equal to an observed value of a_y in the red part of the spectrum. The other type is the result of attenuation by very small particles that have passed through the filter. According to Augedal (1978), clay particles with diameters $< 0.2 \mu\text{m}$ display a spectral attenuation $\sim \lambda^{-2.0}$ in the spectral range 380–790 nm. Kirk and Oliver (1995) found a similar spectral dependence for the scattering coefficient of clay particles in an Australian lake. The effect of small clay particles on the slope γ has been discussed by Aas (2000).

Different methods of correction for residual particles were discussed by Bricaud et al. (1981). They found that if the correction was assumed to be $\sim (\lambda_0/\lambda)^\eta$, the exponent η might theoretically attain values from 0.1 to 2.3. By comparison with measurements on seawater they adopted $\eta \approx 1$ as an average value. Høkedal (1999) applied a best-fit procedure to filtered samples from the Oslo Fjord and obtained values of η in the range 1.4–2.4. The problem is that no value of η is valid for all kinds of particles and that both these types of contribution to the absorbance may occur during field work.

The wavelength-averaged slope γ over the range $\lambda_1 - \lambda_2$ is, according to eq. (1), analytically defined as

$$\gamma = \left\{ \ln [a_y(\lambda_1)] - \ln [a_y(\lambda_2)] \right\} / (\lambda_2 - \lambda_1). \quad (2)$$

A different way of defining the slope is to determine it as the slope of the best-fit line to the function $\ln[a_y(\lambda)]$ by the least squares method. If the values of the constants C and γ that minimise the integral of $\{\ln[a_y(\lambda)] - C + \gamma\lambda\}^2$ from λ_1 to λ_2 have been determined, the slope γ for the range $\lambda_1 - \lambda_2$ becomes

$$\gamma = \frac{6(\lambda_2 + \lambda_1)}{(\lambda_2 - \lambda_1)^3} \int_{\lambda_1}^{\lambda_2} \ln [a_y(\lambda)] d\lambda - \frac{12}{(\lambda_2 - \lambda_1)^3} \int_{\lambda_1}^{\lambda_2} \lambda \ln [a_y(\lambda)] d\lambda. \quad (3)$$

The slope of eq. (3) coincides exactly with the slope of eq. (2) when $\ln[a_y(\lambda)]$ is a linear function of λ . In the present work the slope defined by eq. (2) has been applied to all samples.

On board the ‘Gunnar Thorson’ the samples were measured with a Perkin Elmer spectrophotometer in the spectral range 250–450 nm. The length of the quartz sample cell was 10 cm, relating the absorption coefficient a to the recorded absorbance A by $a = 23.026 A$. This particular spectral range was chosen because it was the only measurable and accurate range for all our open-sea stations. The detection limit of the spectrophotometer was 0.0001 for the absorbance, and the absorbance in the range 450–750 nm would often be ≤ 0.001 at these stations, as indicated by Fig. 2. Any estimate of an eventual baseline could then become very inaccurate, and in general no correction for baseline or residual particles was applied to these measurements. For those relatively few samples where the absorbance came too close to 0.0001 at wavelengths < 450 nm, the upper limit of the applied spectral range was reduced.

In a few test-runs with higher contents of yellow substance the spectral absorption was measured up to 650–750 nm. A correction of the type $a_y(650) [650/\lambda]$, where λ is in nm, was subtracted from the original curve. The resulting change in the slope in the 250–450 nm range was only a few percent

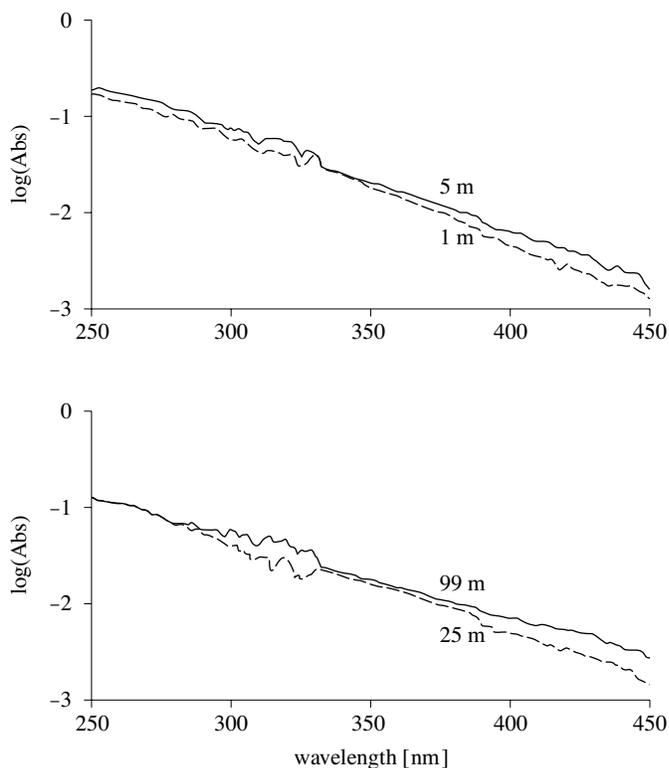


Fig. 2. Logarithm of the absorbance of yellow substance as a function of wavelength at ‘Gunnar Thorson’ Station 18, 20 March 1992, 57°55.6’N, 10°57.4’E. The length of the cuvette was 10 cm, and pure freshwater (Super-Q) was used as reference. The wavelength-averaged slopes $\gamma(250\text{--}450\text{ nm})$ for the depths 1, 5, 25, and 99 m were 0.0247, 0.0232, 0.0201 and 0.0180 nm^{-1} respectively

or less. Pure freshwater (Super-Q) was used as reference. Some unpublished tests indicate that if pure saline ocean water had been used as reference, the slopes might on average have been reduced by a few percent.

Fig. 2 presents four typical spectra from different depths at one of the open-sea stations. The curves show some noise in the region around 330 nm, where the spectrophotometer switches from one lamp to another. Otherwise the slopes are practically constant. At some stations a small shoulder or hump was observed between 260 and 280 nm. These shoulders had no influence on the wavelength-averaged slope.

A Danish intercalibration for the optical determination of yellow substance was undertaken a few years ago, in which the Chemical and Oceanographic Departments of the University of Copenhagen together with the Danish Agency for the Marine Environment took an active part. For the

three laboratories involved the overall accuracy was better than $\pm 10\%$ with respect to absorbances measured at 310, 350, 375, 400, 425 and 450 nm. The absorbances at 310 nm were in the range 0.2–0.5 for a 10 cm cuvette.

In the Oslo Fjord the spectrophotometer was a Hitachi U-1100, and Milli-Q water was used as reference. The power of resolution was 0.001 for the absorbance, which differs from the Perkin Elmer instrument in Copenhagen by a factor of 10. Even so, the applied spectral range could be extended to 650 nm owing to the higher content of yellow substance (Fig. 3). The filtered sample from the Glomma Estuary has a significant content of residual particles, and if the correction $a_y(650) [650/\lambda]$ is subtracted from the original a_y curve (Fig. 3), γ will increase from 0.012 to 0.016 nm^{-1} for the range 250–450 nm. At the border of the Skagerrak the relative content of residual particles has decreased, and by applying the same type of correction γ increases from 0.017 to 0.018 nm^{-1} . It is noteworthy that the spectral attenuation coefficient c_p of particles $> 0.2 \mu\text{m}$ has a spectral shape proportional to $\lambda^{-1.3}$ in the Glomma Estuary and to $\lambda^{-0.6}$ on the

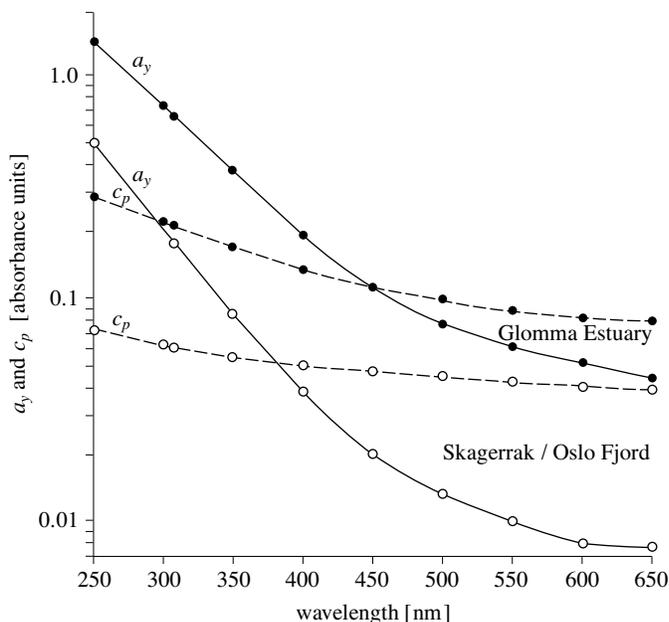


Fig. 3. Spectral absorbance of yellow substance uncorrected for baseline or residual particles (a_y , solid lines), and absorbance of particles with size $> 0.2 \mu\text{m}$ (c_p , dashed lines), for surface water of the Glomma Estuary (\bullet) in the outer Oslo Fjord and surface water close to the Færder Lighthouse (\circ) on the border between the Oslo Fjord and the Skagerrak, on 8–9 June 2000. The length of the cuvette was 10 cm, and pure freshwater (Milli-Q) was used as reference

Skagerrak border. Provided the residual particles $< 0.2 \mu\text{m}$ have a similar spectral behaviour, an average correction proportional to λ^{-1} may seem reasonable.

3. Results

The results from the ‘Gunnar Thorson’ cruises, from the Danish coastal waters, and from the Oslo Fjord are presented in Table 2 and Figs. 4–8, and their most significant features are commented on below.

3.1. Spectral slope in open-sea waters

The mean value of the slope is $\gamma = 0.023 \text{ nm}^{-1}$ for the open-sea waters of the Kattegat and the Skagerrak (Table 2) while the peak value of the frequency distribution is $\gamma = 0.021 \text{ nm}^{-1}$ (Fig. 4). The corresponding quantities calculated for the depth of observation closest to the surface only (1 m) are practically the same. No clear shift of the peak of the distribution function with depth has been found. The variation of the slope γ is considerable, with a minimum of 0.008 nm^{-1} , a maximum of 0.042 nm^{-1} , and a standard deviation of about 0.004 nm^{-1} . The range for the surface observations (1 m) becomes narrower: $0.018\text{--}0.034 \text{ nm}^{-1}$ with a standard deviation of 0.003 nm^{-1} .

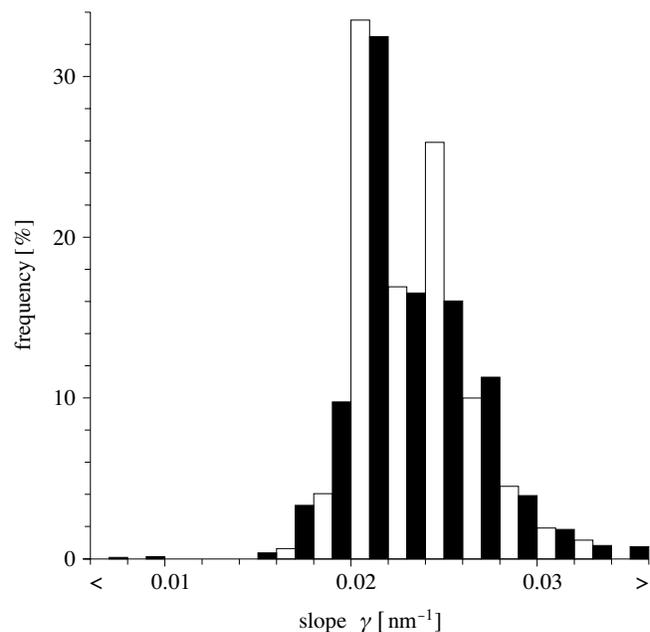


Fig. 4. Frequency distribution of the slope γ in the open-sea waters of the Kattegat and the Skagerrak. (White columns = 1 m depth, black columns = all depths)

Table 2. Optical properties of yellow substance in open Kattegat–Skagerrak waters, Danish coastal waters, and the Oslo Fjord

		Kattegat–Skagerrak		Danish coastal waters	Oslo Fjord*	River run-off
		(all depths)	(1 m depth)	(1 m depth)	(1 m depth)	to the Oslo Fjord
γ_{mean}	[nm ⁻¹]	0.0234	0.0240	0.0190	0.019	0.0177
s_{γ}^{\dagger}	[nm ⁻¹]	0.0036	0.0028	0.0015	0.001	0.0010
γ_{max}	[nm ⁻¹]	0.0420	0.0339	0.0254	0.020	0.0194
γ_{min}	[nm ⁻¹]	0.0076	0.0179	0.0145	0.018	0.0169
Range	[nm]	250–450	250–450	250–450	310–665	310–443
N^{\ddagger}		1305	146	82	11	5
$a_{y, \text{mean}}^{\S}$	[m ⁻¹]	1.28	1.67	–	3.02	9.55
s_a	[m ⁻¹]	0.70	0.67	–	0.46	2.32
$a_{y, \text{max}}$	[m ⁻¹]	7.41	4.19	–	3.98	12.21
$a_{y, \text{min}}$	[m ⁻¹]	0.06	0.20	–	2.27	6.72
N		1373	150	–	11	5
S_{mean}^{**}		31.39	27.45	8.08	26.03	0
s_S		3.39	4.21	0.96	1.32	0
S_{max}		35.28	34.61	10.50	28.96	0
S_{min}		19.00	19.00	7.31	25.16	0
N		1286	118	52	11	5

* Data from Høkedal (1999).

Symbols: $^{\dagger}s$ – standard deviation, $^{\ddagger}N$ – number of observations, $^{\S}a_y$ – absorption coefficient at 310 nm, $^{**}S$ – salinity.

3.2. Spectral slope in nearshore waters

The mean value of γ based solely on the results presented in Table 2 for the Danish coastal waters, the Oslo Fjord and its supplying rivers is 0.019 nm^{-1} , but when additional samples taken in the Danish Straits, in the fjords, inlets and interior waters along the Danish coastline facing the North Sea, and in the Gullmar Fjord are included, the mean value of the slope becomes 0.0175 nm^{-1} . This result is significantly lower than the mean slope for the open-sea stations. The standard deviations of γ for these waters, varying from 0.0010 to 0.0015 nm^{-1} , are less than half of the value for the open-sea stations. The small spread of the γ values is noteworthy and suggests that the yellow substance entering the sea directly from the land originates from the same type of degradation products in these Scandinavian sites.

3.3. Absorption coefficient in open-sea waters

The frequency distribution of absorption coefficients at 310 nm has a less distinct peak (Fig. 5) than the distribution of slopes. The mean value is $a_{y, \text{mean}}(310) = 1.28 \text{ m}^{-1}$ and the standard deviation is 0.70 m^{-1} . The total range is $0.06\text{--}7.41 \text{ m}^{-1}$. The mean value for each depth decreases with increasing depth, as illustrated by for instance $a_{y, \text{mean}}(310, 1 \text{ m}) \sim 1.7 \text{ m}^{-1}$

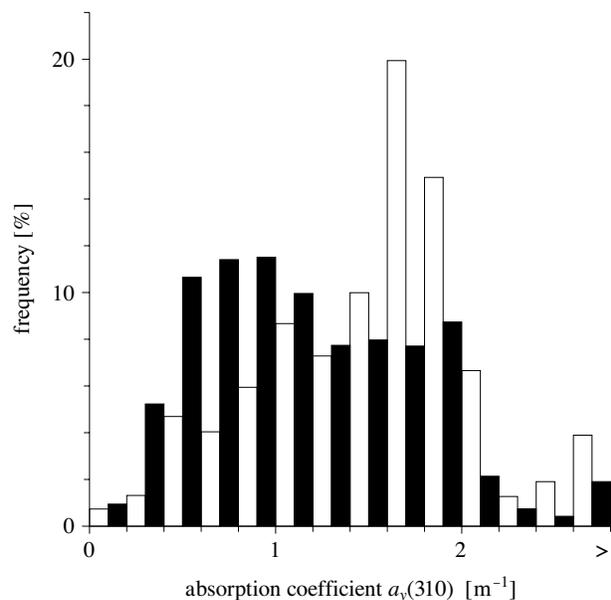


Fig. 5. Frequency distribution of the absorption coefficient $a_y(310)$ at the same stations as in Fig. 4. (White columns = 1 m depth, black columns = all depths)

and $a_{y, \text{mean}}(310, 20 \text{ m}) \sim 1.3 \text{ m}^{-1}$. An interesting result is that no significant differences between March and September can be found in our data for the Kattegat–Skagerrak area, neither for $a_y(310)$ nor for γ . In March the value of $a_{y, \text{mean}}(310)$ was 1.16 m^{-1} with a standard deviation of 0.81 m^{-1} , and in September the corresponding values were 1.37 m^{-1} and 0.59 m^{-1} respectively. The value of γ_{mean} was 0.0239 nm^{-1} with a standard deviation of 0.0038 nm^{-1} in March; the corresponding values for September were 0.0230 and 0.0033 nm^{-1} .

3.4. Absorption coefficient in nearshore waters

Table 2 demonstrates that for our data set $a_y(310)$ varies by a factor of 5 only (2.27 – 12.21 m^{-1}) for the nearshore waters, while for the open-sea stations the coefficient varies by a factor of 100. It should be noted, however, that the nearshore data consist only of samples from the surface layer and river waters, and if data from the deeper layers had been included, the range for $a_y(310)$ would have increased. For instance, Atlantic waters of salinity ≥ 35.0 may occasionally enter the Oslo Fjord below its pycnocline, thus reducing significantly the content of yellow substance in these layers.

3.5. Relations between the observed quantities

Fig. 6 presents γ as a function of $a_y(310)$ at the open-sea stations. It can be seen that on the basis of a very small percentage of the observations there seems to be a tendency for γ to decrease as the value of $a_y(310)$ increases,

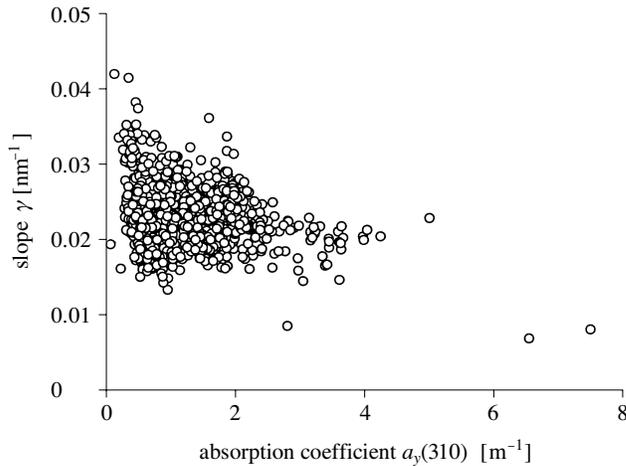


Fig. 6. The slope γ as a function of $a_y(310)$ for all stations and depths in open Kattegat–Skagerrak waters

and the lowest values of γ appear for values of $a_y(310) > 2.0 \text{ m}^{-1}$. Although the samples may have been contaminated by particles, resulting in increased a_y and decreased γ , we have no evidence to support this possibility. The two values of $\gamma > 0.040 \text{ nm}^{-1}$ appear for $a_y(310) < 0.4 \text{ m}^{-1}$, and in these cases the applied spectral ranges were narrower than 250–450 nm, implying that the spectrophotometer's power of resolution may have influenced the results. Moreover, the lack of sea salts in the freshwater reference may have contributed to the high values, but at present we are not able to quantify this contribution satisfactorily.

There is no apparent correlation between slope and salinity for the open-sea stations, as demonstrated by Fig. 7. Fig. 8 illustrates a three-source relationship between $a_y(310)$ and salinity in this area for the same data set. The sources are yellow substance-rich waters from the German Bight and the Baltic Sea and yellow substance-poor Atlantic waters. More details of the related mixing problem have been presented elsewhere by Aarup et al. (1996a, b) and Højerslev et al. (1996).

At 43 open-sea stations the salinity difference between 1 and 5 m was less than 0.01, and for these stations it was found that $a_y(310, 1 \text{ m}) - a_y(310, 5 \text{ m}) = -0.15 \text{ m}^{-1}$ on average. The estimated error of this value was $\pm 0.06 \text{ m}^{-1}$. March and September produced practically the same results. This is possibly a photo-bleaching effect. No similar result could be found for γ .

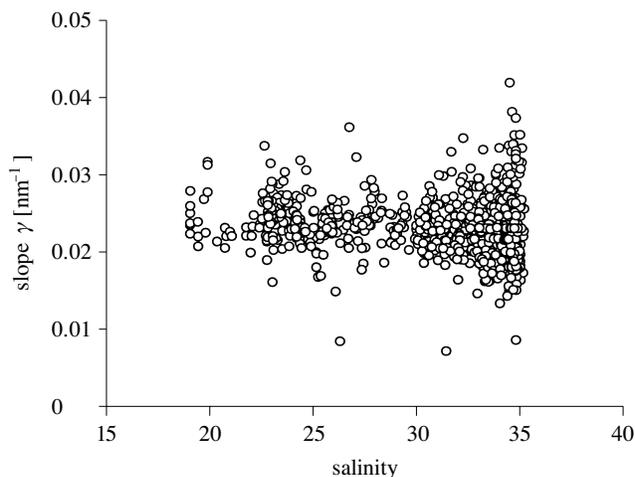


Fig. 7. The slope γ as a function of salinity in Kattegat-Skagerrak waters

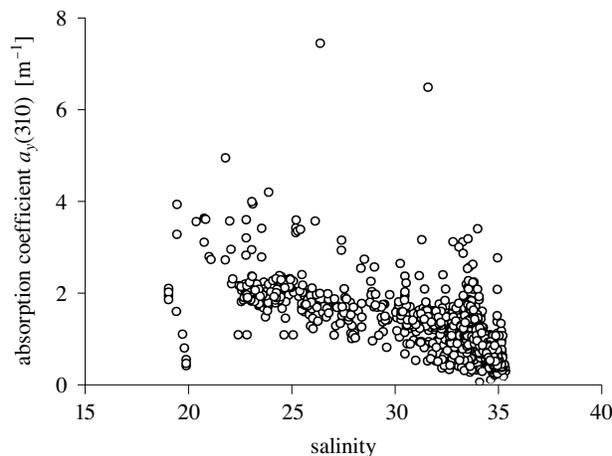


Fig. 8. The absorption coefficient $a_y(310)$ as a function of salinity in Kattegat–Skagerrak waters

4. Discussion

4.1. Uncertainty of the slope values

The dominant uncertainty of the present slope calculations is that of the absorbance at 450 nm due to the photometer’s power of resolution. If the absorbance at 450 nm for a 10 cm cuvette is 0.001 ± 0.0001 , that is $a_y(450) = 0.0230 \pm 0.0023 \text{ m}^{-1}$, the error of γ becomes $\pm 0.0005 \text{ nm}^{-1}$ according to eq. (2). Relative to the average slope of 0.0234 nm^{-1} (Table 2) this is an error of 2%, and relative to the minimum slope of 0.0076 nm^{-1} (Table 2) it constitutes 7%. If the absorbance at 450 nm decreases to 0.0005, the error of γ becomes twice as large. Although this error can contribute to the variation, it cannot explain the wide range of slope values. Fig. 6 shows that for the smallest values of a_y the range of γ is about $0.015\text{--}0.035 \text{ nm}^{-1}$, that is, an interval of 0.02 nm^{-1} , which is larger than the estimated errors by a factor of 5–10.

4.2. Influence of ‘age’ on slopes

The spectral slope for river water entering the Oslo Fjord is not as steep as that of the water of the fjord. Similarly, the slopes of nearshore Danish water are less steep than those of the open-sea stations (Table 2). It appears that the time the terrigenous yellow substance has spent in the sea (salinity being an indicator of the time) gradually leads to an increased slope. The same tendency can be seen in the observations by Blough et al. (1993) and Kowalczyk & Kaczmarek (1996). However, a possible relationship of this kind is not a simple one, as indicated by Fig. 7.

4.3. Influence of spectral range on slope

Table 1 shows that the lower limit of the spectral range applied by different authors varies from 290 to 440 nm, while the upper limit goes from 400 to 700 nm. In order to compare our slopes obtained for the range 250–450 nm with slopes obtained for different spectral ranges, we have to assume that the slopes are practically constant and independent of the applied range. There are investigations that both disprove and support this assumption. The spectral curves presented by Kalle (1961) show a much steeper slope for the range 387–420 nm than for 420–665 nm. In the textbook by Jerlov (1968, p. 56) the almost straight curve for yellow substance absorption may be divided into two spectral parts with slopes 0.0154 nm^{-1} for 250–450 nm and 0.0142 nm^{-1} for 450–600 nm, implying a ratio $\gamma(450-600)/\gamma(250-450) \sim 0.92$. Kopelevich et al. (1989) present data from which it may be deduced that $\gamma(\lambda > 500)/\gamma(\lambda < 500) \sim 0.65$. Del Castillo et al. (1999) operate with one fixed wavelength interval from 400 to 500 nm, and another interval from 290 nm to the wavelength where $a_y = 0.092 \text{ m}^{-1}$. From their results it may be estimated that the mean value of this upper limit is about 500 nm, and that the mean value of the ratio between the slopes of the intervals becomes $\gamma(400-500)/\gamma(290-500) \sim 0.85$ with a standard deviation of 0.14. Warnock et al. (1999) have presented observations from the Southern Bight of the North Sea indicating that on average $\gamma(360-540)/\lambda(250-440) \sim 0.87$. Thus there seems to be a tendency for γ to decrease with increasing wavelength, possibly by 10–15% from the UV to the visible spectral domain, provided this decrease is not due to a lack of correction for baseline or residual particles.

On the other hand, observations by Ferrari & Dowell (1998) from the southern Baltic produce a mean value of the ratio $\gamma(400-600)/\lambda(355-420)$ equal to 1.01 and a standard deviation of 0.06. We can also see that the different spectral ranges applied by the different authors in Table 1 partly overlap, and their curves for the spectral absorbance show no clear breaks. Our own measurements demonstrate that on those occasions when the absorption has been high enough to permit measurements from 250 to 700 nm and a correction of the λ^{-1} type has been applied, the slope has been almost constant (\pm a few percent) from 250 up to 550–650 nm. Thus, we cannot draw any clear conclusion, and our comparison with slopes obtained by other authors for different spectral ranges is tentative. Within the ultraviolet range our observed constancy of the slope is supported by the results of Karabashev & Zangalis (1974) who found that the slope for Baltic waters was constant between 200 and 400 nm.

4.4. Comparison of slope values with results of other authors

The present range for γ at our open-sea stations in the Kattegat and the Skagerrak is 0.008–0.042 nm⁻¹ as shown by Table 2. While Kowalczuk & Kaczmarek (1996) found $\gamma_{\min} = 0.004$ nm⁻¹, and Kowalczuk (1999) found $\gamma_{\max} = 0.036$ nm⁻¹ in open Baltic waters, our data set for all depths has 5 values > 0.036 nm⁻¹. None of them appear at a depth of 1 m, and 4 of them were obtained at 20 m and below. These properties may be brought to the surface layer by vertical convection and mixing, but their low frequency of observation indicates that their influence on the surface layer may be small. No immediate explanation for this large range of values in the open sea can be offered, but an even larger total range can be obtained from the different investigations presented in Table 1, provided we assume that the values obtained with different filters and from different spectral domains can be compared.

4.5. Implications of slope variations

The absorption coefficient is of the same order of magnitude as the vertical attenuation coefficient of downward irradiance at 310 nm in the Kattegat–Skagerrak area according to data by Højerslev (1982), implying that yellow substance is the dominant factor as regards vertical UVB attenuation. This in turn means that any estimates of UVB attenuation from coefficients at longer wavelengths require an accurate knowledge of the spectral slope γ .

It also becomes clear that the observed variation of γ in these waters will have important implications for the passive remote sensing of chlorophyll-like pigments by the channels at 412 and 443 nm. Assuming that $a_y(412 \text{ nm}) = 0.50 \text{ m}^{-1}$ for yellow substance, then $a_y(443 \text{ nm}) = 0.39 \text{ m}^{-1}$ for $\gamma_{\min} = 0.008 \text{ nm}^{-1}$, but $a_y(443 \text{ nm}) = 0.14 \text{ m}^{-1}$ for $\gamma_{\max} = 0.042 \text{ nm}^{-1}$. The first estimate of $a_y(443 \text{ nm})$ is a factor 2.8 times greater than the last estimate in this extreme case. From Fig. 4 it can be seen that 10% of the surface observations will have slopes $\leq 0.020 \text{ nm}^{-1}$ and $\geq 0.028 \text{ nm}^{-1}$, leading to values of $a_y(443 \text{ nm})$ that will differ by more than 29%. This means that satellite data concerning chlorophyll-like pigment concentrations have to be supplemented by sea-truth measurements of yellow substance in order to arrive at reliable chlorophyll retrievals. The problem of the influence of yellow substance on remote sensing of chlorophyll in the Kattegat–Skagerrak area has also been discussed by Karabashev (1992).

4.6. Fluctuations of yellow substance content

The optical behaviour of yellow substance in the surface layer may undergo substantial changes caused by dynamic processes like mixing and

advection. Wind, tides and large-scale circulation may be involved here. This implies that, practically speaking, changes can occur on all time and length scales. So far, we have not been able to estimate the time scale of the possible photo-bleaching effect mentioned earlier.

5. Conclusions

In *open* coastal sea waters the optical behaviour of yellow substance is rather unpredictable due to the wide range of values for the slope γ , as documented by the present investigation (Table 2) and the earlier findings by other authors (Table 1). In the Kattegat-Skagerrak area no useful correlations between slope, absorption and salinity could be detected. Consequently, no general spectral light absorption model for yellow substance can be established for these waters. As a result the conversion of absorption coefficients for yellow substance from one wavelength to another within the UV and blue spectral domains may be rendered inaccurate by several hundred percent if the correct value of the slope is not known. If our results for the 250–450 nm domain are valid also in the 450–600 nm domain, the retrieval of chlorophyll-like pigments by the use of remote sensing may lead to unacceptable errors during periods of low chlorophyll content when intermediate to high concentrations of yellow substance are present in open-sea coastal waters.

In *nearshore* waters the optical properties of yellow substance seem to be more constant, and here the establishment of a useful optical model for the yellow substance may represent less of a problem.

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