

ESTIMATION OF THE CONCENTRATION OF YELLOW SUBSTANCE IN NATURAL WATERS BY BEAM ATTENUATION COEFFICIENT SPECTRA

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Abstract. Two ways for describing the influence of the yellow substance on the properties of the water environment were considered: (1) by using spectral attenuation coefficients of yellow substance measured from the samples of filtered water; and (2) by using effective concentrations of yellow substance in water estimated from optical measurements. Both ways have some positive features, but also certain shortcomings. The yellow substance concentration values determined using different numerical parameters (obtained by different investigations) in the yellow substance absorption coefficient formula are compared and analysed. The values of the slope parameter in this formula are calculated using our spectrophotometrical measurements in the Baltic Sea and in some Estonian lakes. The differences between the absorption coefficients of the yellow substance and the corresponding beam (and also diffuse) attenuation coefficients of the filtered water are discussed and estimated. In addition to the classical method, which uses for the determination of the yellow substance concentration the beam attenuation coefficient spectra of the filtered water, an alternative method based on the measurements of the beam attenuation coefficient spectra of unfiltered water is described. The reliability of the yellow substance concentration values (obtained by both methods) depends mainly on the reliability of the values of specific absorption coefficients of the yellow substance. For improving the accuracy of these results new, more authentic data on the optical properties of the yellow substance for different types of water bodies are highly necessary.

Key words: yellow substance, spectrophotometrical measurements, light attenuation coefficient.

REFERENCES

INTRODUCTION

As known, natural waters contain besides phytoplankton and inorganic matter also (different amounts of) dissolved organic matter. Their chromophore-containing components can contribute significantly to the total light absorption within the water bodies. These optically active

substances are sometimes referred to as coloured dissolved organic matter, CDOM (Hoge et al., 1993), sometimes yellow substance (Копелевич, 1983; Dera, 1992), gelbstoff (Kalle, 1938, 1966) or gilvin (Kirk, 1976, 1983). We chose the term "yellow substance", probably most familiar to scientists of many countries.

By yellow substances physicists refer to a rather indeterminate mixture of dissolved organic substances, which have an important effect on the absorption of light in the natural waters (Dera, 1992). Since they strongly absorb violet, these substances appear yellow in daylight, and hence their name. Their presence in the water in large concentrations also makes the water yellow in daylight, and this colouration is particularly apparent in bays and river estuaries (Kirk, 1976). Absorption of light by yellow substance (particularly at the blue end of the light spectrum) amounts to direct competition with phytoplankton and other aquatic plants for capture of available light energy (Davies-Colley & Vant, 1987; Kirk, 1976, 1980). Yellow substance also affects the vision of aquatic fauna. Changing the colour and also clarity of the water, yellow substance influences its quality. Remote sensing of phytoplankton or suspended matter concentration is disturbed by the optical influence of yellow substance, especially when its amount varies simultaneously (Davies-Colley & Vant, 1987; Morel & Prieur, 1977; Bukata et al., 1983).

The nature of yellow substance has not yet been finally elucidated, but we do know that it consists of complex organic compounds formed as a result of the metabolism and breakdown of organisms living in the aquatic environment or carried into it (Dera, 1992). According to Kalle (1966), some of the more important and commonly found yellow substances are melanoids. Besides substances of the melanin type, many other complex organic compounds have been found in the seawater, but their structures are for the moment somewhat hypothetical. According to Stuermer (1975) and Gagosian & Stuermer (1977) hydrocarbon fragments, amino acids, amino sugars, organic acids, and aromatic rings may be present. Davies-Colley & Vant (1987) argue that yellow substance is humic-type material similar to soil humic and fulvic acids. Note that it is by no means a simple matter to distinguish between the dissolved and suspended phases of yellow substance because of the size of many of their molecules and their ability to flocculate, that is to come out of solution and form colloids, fine suspensions, or organic clusters (Dera, 1992). This fact is especially important when interpreting the results of beam attenuation coefficient measurements.

A large fraction of the yellow substance, especially in coastal regions, may be derived from soil leaching (transported mainly by rivers). The remainder may be derived from degradation and breakdown of plankton and other aquatic organisms (Kalle, 1966; Kirk, 1983; Копелевич, 1983; Davies-Colley & Vant, 1987).

Yellow substance is typically the largest single category of components of the dissolved organic carbon (DOC) in natural waters and there is an overall correlation of DOC and light absorption (Davies-Colley & Vant, 1987). However, by Kopelevich (Копелевич, 1983) the connections

between the amounts of the yellow substance and DOC in the water are not regular (corresponding correlation coefficients are from 0.29 to 0.39).

It has been possible to develop applicable analytical methods for determining organic carbon in seawater, but it is extremely difficult to determine individual organic compounds therein (Dera, 1992). As mentioned above, yellow substance is a rather indeterminate mixture of organic substances. Investigations of numerous authors have shown that optical determination of the yellow substance has distinct advantages over chemical analytic techniques (Bricaud et al., 1981; Baker & Smith, 1982; Копелевич, 1983; Davies-Colley & Vant, 1987; Ferrari & Tassan, 1991; Dera, 1992). There are two main optical methods: (1) direct measurement of absorption with a spectrophotometer, or the so-called standard beam transmission method (Austin & Petzold, 1977); and (2) measurement of induced fluorescence (Ferrari & Tassan, 1991; Hoge et al., 1993). In using optical methods, yellow substance is referred to in order to describe the optical properties of any dissolved organic matter, regardless of its origin and chemical composition (Bricaud et al., 1981). That convention, although questionable from a chemical point of view, enables us to include in a single parameter any dissolved matter causing variations in the water colour. Consequently, in case of the beam transmission method the yellow substance influence is expressed through the absorption coefficient of the filtered water at a given wavelength in UV or visible regions.

The alternate measurement of yellow substance fluorescence induced by monochromatic radiation (Bristow et al., 1981; Ferrari & Tassan, 1991; Hoge et al., 1993) offers several advantages: it can be performed rapidly *in situ*, it does not require elaborate filtration and there is no influence of scattering by residual particulate matter. However, by Kopelevich (Копелевич, 1983), fluorescent components represent only a part of the yellow substance (all fluorescent matter also absorbs light, but not all absorbing dissolved organic matter fluoresces). This means that the absorbing and fluorescent components are not identical. Hence, also the fluorescence method is connected with some uncertainty.

In this paper we consider the beam transmission method (including some problems of its accuracy and also the variations of the corresponding calculation procedure) and its quantitative parameters for the aquatic environment from oceanic to coastal (or inland) water.

ABSORPTION SPECTRA OF YELLOW SUBSTANCE DETERMINED BY THE BEAM TRANSMISSION METHOD

A well-known characteristic of yellow substance is the monotonically increasing absorption with decreasing wavelength in the visible and ultraviolet regions of the light spectrum (Kalle, 1966; Jerlov, 1968, 1976; Stuermer, 1975; Nyquist, 1979; Takematsu et al., 1979; Bricaud et al., 1981; Baker & Smith, 1982; Davies-Colley & Vant, 1987). The corresponding absorption curve is represented by a straight line on a

semilog plot (logarithm of the absorption coefficient vs. wavelength). It demonstrates that the absorption spectrum of yellow substance, $a_y(\lambda)$, is approximately exponential in shape and can be represented by the following equation:

$$a_y(\lambda) = a_y(\lambda_0)\exp[-S(\lambda-\lambda_0)], \quad (1)$$

where S is the so-called slope parameter and $a_y(\lambda_0)$ is the absorption coefficient for yellow substance at the fixed wavelength λ_0 . Højereslev (1980), reviewing earlier work on the subject, stated that a postulated by Kalle (1966) direct proportionality between fluorescence and yellow substance can be found:

$$a_y(\lambda_0) = a'_y(\lambda_0)C_y, \quad (2)$$

where $a'_y(\lambda_0)$ is expressed in $l\text{ mg}^{-1}\text{ m}^{-1}$ and C_y (concentration of yellow substance) in mg l^{-1} . The values of S and $a'_y(\lambda_0 = 380\text{ nm})$, obtained by different investigators, are presented in Table 1.

Table 1

Component constants for yellow substance as given by investigators who measured an absolute absorption $a_y(\lambda_0)$ (from Baker & Smith, 1982)

Author	S, nm^{-1}	$a'_y(\lambda_0 = 380), l\text{ mg}^{-1}\text{ m}^{-1}$
Højereslev	0.014	0.565*
Jerlov	0.0147	0.325
Okami et al.	0.01675	0.275
Stuermer (coastal waters)	0.0175	2.160
Stuermer (Sargasso sea)	0.020	0.2456

* Originally the value of a'_y was determined by Nyquist (1979) for $\lambda_0 = 450\text{ nm}$ ($a'_y = 0.212\text{ l mg}^{-1}\text{ m}^{-1}$) and later derived for 380 nm by Højereslev (1980).

We can see that there is general agreement with respect to the exponent parameter S , but not with respect to the $a'_y(380)$ values. A discussion on the extremal $a'_y(380)$ value (2.16) in Table 1 will be presented later.

Relationship (1) gives us a possibility to determine the spectrum of $a_y(\lambda)$ on the basis of beam attenuation coefficient ($c_y(\lambda_0)$) measurements with a spectrophotometer. The main assumption is that the scattering coefficient at the reference wavelength ($b(\lambda_0)$) is negligible in comparison with the absorption coefficient, i.e. $c_y(\lambda_0) = a_y(\lambda_0)$. (Later we will see that this assumption is almost true when λ_0 lies in the UV or violet region of

the light spectrum, but definitely wrong for the red region.) Practically, the difference $c_f(\lambda_0) - c_w(\lambda_0)$ is measured, where $c_f(\lambda_0)$ is the beam attenuation coefficient of the filtered water and $c_w(\lambda_0)$ is that of the distilled water. So, as the first approximation

$$a_y(\lambda_0) = c_y(\lambda_0) = c_f(\lambda_0) - c_w(\lambda_0). \quad (3)$$

Using relationships (1) and (2) and also data from Table 1 it is possible to calculate the concentration of yellow substance, C_y (in mg l^{-1}). Note that if we choose λ_0 equal to that in Table 1 ($\lambda_0 = 380 \text{ nm}$), the value of S will not affect the value of C_y . However, $a_y(\lambda_0)$ always depends on the numerical values of $a'_y(\lambda_0)$, which, unfortunately, show no coincidence between different investigators (see Table 1).

Baker & Smith (1982), assuming that the diffuse attenuation due to yellow substance, $K_{d,y}(\lambda)$, will have a wavelength dependence similar to $a_y(\lambda)$, obtained:

$$K_{d,y} = K'_{d,y} C_y \exp[-S(\lambda - \lambda_0)]. \quad (4)$$

In their opinion this assumption is true when the contribution of scattering to $K_{d,y}$ is relatively independent of wavelength. Following this assumption they (and also Topliss et al., 1989) used in formula (4) the same numerical values of the constants as given in Table 1 (i.e., they assumed that $K'_{d,y} = a'_y$). So, formula (4) is used alongside with formulae (1) and (2) (see also Prieur & Sathyendranath, 1981; Hoge et al., 1993). However, $K_d(\lambda)$ differs from $a(\lambda)$ not only due to the contribution of scattering in the attenuation coefficient, but also due to its dependence on the illumination conditions. For describing the connection between $K_d(\lambda)$, $a(\lambda)$, and the scattering coefficient, $b(\lambda)$, Kirk (1981, 1984, 1989) has proposed the following formulae:

$$K_d(\lambda) = \frac{1}{\cos \varphi_0} [a^2(\lambda) + n_1 \cos \varphi_0 - n_2] a(\lambda) b(\lambda)]^{1/2} \quad (5)$$

for clear sky and

$$K_d(\lambda) = 1.168 [a^2(\lambda) + n_3 a(\lambda) b(\lambda)]^{1/2} \quad (6)$$

for overcast conditions. Here φ_0 is the angle of the photons in the direct solar beam to the vertical just below the water surface; n_1 , n_2 , and n_3 are constants that depend on the depth region for which $K_d(\lambda)$ is determined. Although relationship (5) was obtained for direct sunlight, in Kirk's opinion it is applicable also for real-world conditions (direct plus diffuse solar radiation), giving the best results for fairly high solar altitudes. However, a comparison of $K_d(\lambda)$ calculated using formula (5) with the corresponding model calculation results (Apct et al., 1991) shows that Kirk's formulae work fairly well up to the solar zenith angles of about 70° . Note also that the expression for totally overcast conditions (6) is similar to relationship (5).

If we consider the case where $b = 0$ (or is negligible) for all wavelengths, formulae (5) and (6) will yield respectively

$$K_d(\text{clear}) = \frac{a}{\cos \varphi_0} \quad (7)$$

and

$$K_d(\text{overcast}) = 1.168a. \quad (8)$$

For solar zenith angles $0-70^\circ$ the cosine of the direct solar beam in water varies between 1 and 0.707, the value of $1/\cos \varphi_0$ varying between 1 and 1.41. So, the mean difference between K_d and a is about 14–17%. For estimating the corresponding differences under the conditions when $b \neq 0$ we computed, using formula (5), the values of K_d varying the solar zenith angle from 0 to 70° (φ_0 varies then from 0 to 45°) and the contribution of the scattering coefficient b to the beam attenuation coefficient c from 0.1 to 0.9. Table 2 demonstrates the relative differences between K_d and a , obtained by these results. One can see that these differences vary within wide limits and grow remarkably with the increasing contribution of b in c .

So, the question is whether scattering is really negligible when we determine the beam attenuation coefficient of filtered water with a spectrophotometer and how much $K_d(\lambda)$ differs from $a(\lambda)$ when the contribution of $b(\lambda)$ is essential.

Table 2

Relative differences $2(K_d - a)/(K_d + a)$ (in per cent), computed using formula (5)

ϑ_0	0°	20°	40°	70°
$b = 0.1c$	1.3	4.6	14.3	34.8
$b = 0.5c$	8.6	11.5	20.0	38.3
$b = 0.9c$	55.3	56.5	59.9	66.5

CORRECTION OF THE BEAM ATTENUATION COEFFICIENT SPECTRA OF FILTERED WATER

As known, seawater remains a scattering medium even after filtration, because small particles pass through the filter. These scattering colloids may include fine inorganic particles as well as colloidal forms of aquatic humus which appear to coexist with yellow substance (Bricaud et al., 1981; Davies-Colley & Vant, 1987). For such a medium the coefficient actually obtained by using a conventional spectrophotometer is inter-

mediate between the beam attenuation coefficient and the absorption coefficient (the scattered light is a fraction of the total scattered light). The relationship between the true and apparent absorption is given by Bricaud et al. (1981) as

$$a_y(\lambda) = x(\lambda) - \beta(\lambda), \quad (9)$$

where $x(\lambda) = c_f(\lambda) - c_w(\lambda)$ (i.e., the spectrophotometrical measurement result) and $\beta(\lambda)$ is a correction that takes into account the residual scattering in $x(\lambda)$. The general relationship for determining $\beta(\lambda)$ is (Bricaud et al., 1981; Davies-Colley & Vant, 1987):

$$\beta(\lambda) = x(L) \left(\frac{L}{\lambda} \right)^g, \quad (10)$$

where L is some reference wavelength and $g = -1$ (Bricaud et al., 1981) or $g = 1$ (Davies-Colley & Vant, 1987). The wavelength L must be located in the red region of the light spectrum, where $a_y(L) \approx 0$ (remember that the absorption coefficient of yellow substance decreases exponentially with increasing wavelength). In that case $x(L) = \beta(L)$, which gives us a possibility to determine $\beta(L)$ by measuring x at the wavelength L .

The different values of g give different dependences of $\beta(\lambda)$ on wavelength: when $g = -1$, $\beta(\lambda)$ increases with wavelength; when $g = 1$, it decreases. For estimating the real contribution of $\beta(\lambda)$ in the values of $x(\lambda)$ at different wavelengths we carried out the computations using formula (10) and the results of our spectrophotometric measurements on the basis of water samples taken from some Estonian lakes. Four examples of these results are shown in Table 3.

Table 3

Dependence of the ratio $\beta(\lambda)/x(\lambda)$ (in per cent) on the wavelength, computed by formula (10) ($L = 700$ nm, $g = \pm 1$) for some Estonian lakes. Secchi disk depths (SD) are also shown in the table

No.	Lake and date	SD	g	λ				
				350	400	500	600	700
1	Uljaste, 5 July 1994	3.4	+1	23	49	77	95	100
			-1	6	16	40	67	100
2	Kurtna Nõmmjärv, 7 May 1995	3.0	+1	1.5	3.7	20	56	100
			-1	0.4	1.2	10	41	100
3	Nohipalu Valgejärv, 10 June 1995	5.4	+1	5.5	10.6	28	50	100
			-1	1.4	3.4	14	37	100
4	Verevi, 9 June 1995	1.5	+1	34	57	95	100	100
			-1	9	19	49	78	100

The results presented in Table 3 show that in the case of turbid water and $g = 1$ the contribution of $\beta(\lambda)$ may be remarkable even in the violet and blue regions of the light spectrum. For clear water the different values of g (i.e. +1 or -1) do not bring about very remarkable differences in the numerical values of $\beta(\lambda)/x(\lambda)$, but in the case of turbid water the value of g is important. It is more likely that we must use $g = 1$, because only small particles (or colloids) can pass through our filters with 0.45 mm pores and for these particles the scattering coefficient decreases with the increasing wavelength (Dera, 1992).

ESTIMATION OF THE YELLOW SUBSTANCE CONCENTRATION IN WATER

So, by determining $\beta(\lambda)$ we can derive from the measured apparent spectrum of filtered water, $x(\lambda)$, the real absorption spectrum of yellow substance, $a_y(\lambda)$. Using relationships (1) and (2) we can determine the concentration of yellow substance, C_y :

$$C_y = \frac{x(\lambda) - \beta(\lambda)}{a'_y(\lambda_0) \exp[-S(\lambda - \lambda_0)]} = \frac{x(\lambda) - \beta(\lambda)}{a'_y(\lambda)} \quad (11)$$

In principle λ may be any wavelength in the measured $x(\lambda)$ spectrum, but in practice it is much better to choose it in the UV, violet, or blue region: the values of $x(\lambda)$ decrease and the contribution of $\beta(\lambda)$ increases quickly with the increasing wavelength, which brings about the big relative errors in case λ is in the red region of the light spectrum.

We investigated the stability of the C_y values with λ varying from 350 to 700 nm (see also Mäekivi & Arst, 1995). The calculations were carried out on the basis of formula (11) for two variants: (1) $\beta(\lambda)$ was calculated by formula (10), where $g = 1$; and (2) $\beta(\lambda)$ was assumed to be zero. The results are shown in Fig. 1.

As one can expect, C_y is highly unstable if we use λ in the region 500–700 nm, especially in the case $\beta(\lambda) = 0$, where C_y also grows remarkably with the increasing wavelength. Taking into account the correction $\beta(\lambda)$, the differences decrease, but instability remains. The negative values of C_y (Fig. 1a) need some comments. Such values are certainly absurd and appear due to (small) measurement errors of $x(\lambda)$: in the range 600–700 nm its spectral curve varies insignificantly, but irregularly and sometimes $x(700)$ even exceeds some of its neighbouring values at smaller wavelengths. These small absolute errors bring about big errors in the yellow substance concentration values, because C_y is determined by dividing the values of $x(\lambda) - \beta(\lambda)$ to very small values of $a'_y(\lambda)$ in the range 600–700 nm (see formula (11)). So, the suitable wavelengths for determining the yellow substance concentration in the water by formula (11) are in the region 300–400 nm.

As mentioned above, the influence of yellow substance on the colour and transparency of the water environment can be described either by means of its absorption coefficients (in m^{-1}) or concentration (in $mg\ l^{-1}$) in

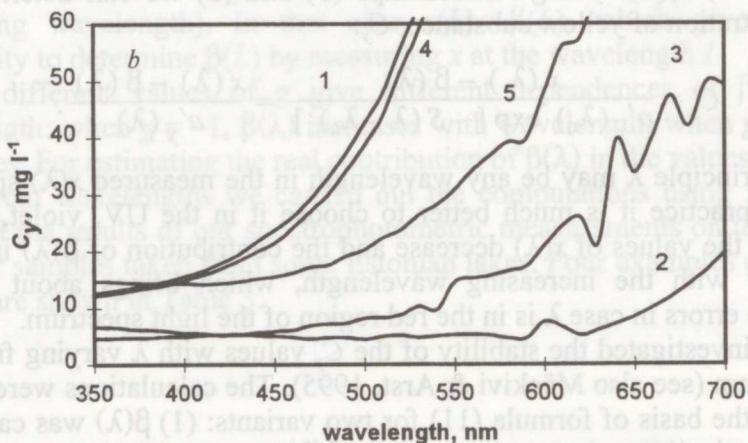
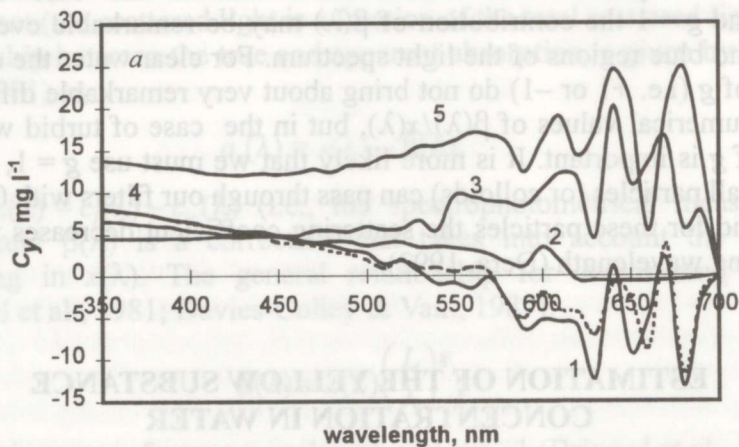


Fig. 1. Concentration of yellow substance computed by formula (11) using different values of λ : (a) $\beta(\lambda)$ was calculated assuming $g = 1$; (b) $\beta(\lambda) = 0$. Results are shown for five Estonian lakes: 1, Uljaste, June 1995; 2, Kurtna Nõmmjärv, May 1995; 3, Nohipalu Valgejärv, June 1995; 4, Verevi, June 1995; 5, Võrtsjärv, August 1995.

the water. The question which parameter is preferable is as yet not clear. The easiest way is to express the contribution of yellow substance in the underwater processes through the absorption coefficient of the filtered water. This will give us a large number of numerical results for one water sample (the values of the absorption coefficient at numerous wavelengths in the range of the measured spectrum). In order to get only one numerical result, we must choose one of these wavelengths. This means that a comparison of the results of different investigators is possible only if they

have determined the absorption coefficient of the yellow substance at the same wavelength. Taking into account that the amount of the other optically active components of the aquatic environment is usually expressed in mg m^{-3} (or mg l^{-1}), it would be convenient and more habitual to obtain the yellow substance in the same units. However, for this the specific absorption coefficient of the yellow substance, $a'_y(\lambda)$, is needed. As one can see from Table 1, the values of $a'_y(380)$ obtained by different investigators differ rather essentially from one another. Note that almost all (except one) results presented in this table are determined for open ocean waters. As $a'_y(\lambda_0)$ values for lake and coastal waters are often required, we paid special attention to the value of $a'_y(380) = 2.16 \text{ l mg}^{-1} \text{ m}^{-1}$, obtained by Stuermer (1975) for coastal waters. For estimating the dependence of C_y on the numerical values of $a'_y(\lambda_0)$ and S we calculated C_y (using formulae (1), (2), and (11)) on the basis of the beam attenuation coefficient spectra measured using water samples taken from some Estonian lakes and the Baltic Sea. Some examples of these results are given in Table 4.

Table 4

Concentration of yellow substance, C_y , in the waters of two Estonian lakes and in the Baltic Sea determined using different values of S and $a'_y(380)$

No.	S	$a'_y(380)$	$C_y, \text{mg l}^{-1}$			
			Lake Kurtna Nõmmjärvi, 5 June 1995	Lake Uljaste, 5 Aug. 1995	Open Baltic, 21 July 1995	Pärnu Bay, 3 July 1994
1	0.014	0.565	15	13	2.0	17
2	0.0147	0.325	26	22	3.4	29
3	0.01675	0.275	29	25	3.8	32
4	0.02	0.2456	30	25	3.8	32
5	0.0175	2.16	3.6	3.1	0.47	4.0

These results show that the combinations 1–4 give such values of C_y that differ from one another in some measure, but are of the same order. However, all these concentrations exceed many times the value of C_y obtained using the fifth combination of S and a'_y . Note that this combination is the only one that expresses the properties of yellow substance for coastal waters (Table 1). It seems that for open sea waters we should choose one of the combinations 1–4, but for lakes and coastal waters use combination No. 5. However, as seen from Table 4, in this case the concentration (mass per volume unit) of yellow substance in lakes and coastal waters would be equal to or even smaller than that in the open sea, which is a surprising result (as known, yellow substance is brought to the

sea essentially by river discharge). It is unlikely that significant amounts of yellow substance are formed in the sea by chemical breakdown processes of organic matter (Højereslev, 1980). So, one can expect that in lakes and coastal waters the mass of yellow substance per volume unit exceeds that in the open sea waters. Perhaps the value $a'_y(380) = 2.16$ in Table 1 (and Table 4) is not correct.

It must be remembered also that the value $a'_y(380) = 0.565$ in Table 1 was derived from $a'_y(450) = 0.212$ assuming $S = 0.014$ (for other values of $a'_y(380)$ in this table we have no information whether they are derived or determined just for $\lambda = 380$ nm). However, the derived value depends on the parameter S : on the basis $a'_y(450) = 0.212$ we get $a'_y(380) = 0.697$ if $S = 0.017$ and $a'_y(380) = 0.747$ if $S = 0.018$. When these values are used the yellow substance concentration will be respectively by 20 and 30% smaller than in case $a'_y(380) = 0.565$. To avoid the dependence of C_y on the value of S it must be calculated using the same wavelength for which the specific absorption coefficient was originally determined. However, if this wavelength is located in the green or red part of the light spectrum, where the absorption coefficient of the filtered water is small, the corresponding relative error may be high. All this implies an urgent need to carry out additional investigations for determining the optical properties of yellow substance for lake and coastal waters, especially its specific absorption coefficients in the shortwave region of the spectrum.

THE SLOPE PARAMETER OF THE YELLOW SUBSTANCE ABSORPTION SPECTRUM

There is abundant information by different investigators on the values and variability of the slope parameter S in formula (1). The main results obtained before 1981 are presented by Bricaud et al. (1981). Three groups of waters have been considered: 1) oceanic waters; 2) coastal zones; 3) highly contaminated waters, where dissolved substances are likely different in nature. Except for a few (probably erratic) values, the parameter S was found to vary from 0.010 to 0.020 with a mean value of 0.014 nm^{-1} . These data show no connections between S and the turbidity of the water. The values obtained are consistent with the absorption curve published by Jerlov (1968) ($S = 0.015$), with Lundgren's (1976) data for Baltic waters (S is between 0.011 and 0.017), and also with Kirk's (1976) data for lake waters, which lead to values of S between 0.013 and 0.016 nm^{-1} .

However, the results obtained later show somewhat higher values of S . Davies-Colley & Vant (1987), investigating the variations of S in twelve New Zealand freshwater lakes, show the mean slope of S to be equal to $0.0187 \text{ nm}^{-1} (\pm 0.0013)$. Effler et al. (1991), carrying out investigations for the waters of Lake Ontario, obtained S varying in the range 0.0159–0.0206, the average value being 0.0170 nm^{-1} . Hoge et al. (1993) obtained the mean value of 0.018 nm^{-1} , S varying from 0.015 to 0.023 nm^{-1} .

We determined the slope parameter S on the basis of the beam attenuation coefficient spectra of filtered water, measured (with a Hitachi spectrophotometer) using water samples taken from Estonian and Finnish freshwater lakes and also from the Baltic Sea. Altogether the results of 98 water samples were considered. The slope parameter was calculated using spectra corrected with formula (10) (with $g = 1$ and reference wavelength $\lambda = 700$ nm) and also uncorrected spectra of filtered water. To avoid the influence of the possible measurement errors in the red region of the spectrum the slope parameter was determined using the data for the intervals 350–450 nm (uncorrected spectra) and 350–500 nm (corrected spectra). The results are presented in Table 5.

As one can see, the slope parameter was determined for different types of water (open sea, coastal regions, lakes) and for rather different amounts of yellow substance in the water (from 1.6 to 34 mg l⁻¹). The mean value of S obtained from the whole data complex is 0.0162 nm⁻¹ (without correction)

Table 5

Minimum, maximum, and mean values of $c_f - c_d$ at the wavelength 380 nm (in m⁻¹), the concentration of yellow substance, the slope parameter S (in nm⁻¹), and correlation coefficients (R) between C_y and S . The regions of the measurements are the Baltic Sea (summer 1994 and 1995) and some Estonian and Finnish lakes (summer 1995)

Indicator		Baltic Sea		Six Estonian lakes	Five Finnish lakes
		Open sea	Coastal regions		
Number of the spectra		30	27	23	18
$c_f - c_d$	min	0.86	1.49	0.81	2.43
	max	2.28	14.7	15.1	19.3
	mean	1.48	4.64	5.87	9.24
C_y , mg l ⁻¹	min	1.56	2.86	1.58	4.44
	max	4.03	25.8	26.3	33.7
	mean	2.67	8.39	10.4	16.8
S , nm ⁻¹ uncorrected	min	0.0135	0.0157	0.0139	0.0140
	max	0.0178	0.0177	0.0180	0.0175
	mean	0.0159	0.0170	0.0162	0.0162
S , nm ⁻¹ corrected	min	0.0150	0.0163	0.0153	0.0148
	max	0.0205	0.0189	0.0184	0.0174
	mean	0.0173	0.0175	0.0170	0.0162
R	S_{uncor}	0.012	0.213	-0.293	0.560
	S_{cor}	-0.246	0.213	-0.125	0.343

and 0.0173 nm^{-1} (corrected spectra). These results coincide well with the data by the other investigators presented above. According to our results the slope parameter for corrected spectra is systematically higher than that for uncorrected spectra. The correlation coefficients C_y vs. S are mostly low and show variability between positive and negative values. No regularities were observed in the changes of the correlation coefficients when moving from sea waters to lakes. These results correspond to the conclusion made by Bricaud et al. (1981) on the lack of connections between the slope parameter and the turbidity of the water.

ESTIMATION OF THE YELLOW SUBSTANCE CONCENTRATION BY THE BEAM ATTENUATION COEFFICIENT SPECTRA OF UNFILTERED WATER

As is known, the spectral beam attenuation coefficient, $c_\lambda - c_{d,\lambda}$, measured with a Hitachi spectrophotometer, may be described as a sum of the following components:

$$c_\lambda^* = c_\lambda - c_{d,\lambda} = a'_{y,\lambda} C_y + a'_{c,\lambda} C_c + (a'_{s,\lambda} + b'_{s,\lambda}) C_s \quad (12)$$

where $c_{d,\lambda}$ is the beam attenuation coefficient of pure (in practice, distilled) water at the wavelength λ ; C_y , C_c , and C_s are the concentrations of yellow substance, chlorophyll *a*, and suspended matter (non-chlorophyll organic and inorganic particles); $a'_{i,\lambda}$ and $b'_{i,\lambda}$ are their specific absorption and scattering coefficients.

We tried to determine the concentration of yellow substance by another method, based on the data on c_λ^* spectra of unfiltered water. For this we used equation (12) for four wavelengths: 400, 450, 500, and 550 nm, and expressed the values $[a'_s(\lambda_i) + b'_s(\lambda_i)]C_s$ for these wavelengths:

$$[a'_s(\lambda_i) + b'_s(\lambda_i)]C_s = c^*(\lambda_i) - a'_y(\lambda_i)C_y - a'_c(\lambda_i)C_c \quad (13)$$

In this way we got four equations for four wavelengths. Subtracting one equation from another we got three equations for the differences, $C_s[a'_s(\lambda_i) + b'_s(\lambda_i)] - C_s[a'_s(\lambda_{i+1}) + b'_s(\lambda_{i+1})]$. Then we assumed that the specific attenuation coefficient, $a'_s + b'_s$, changes linearly in the range of 400–550 nm. Hence, the differences corresponding to equal wavelength intervals (each 50 nm) are equal and, subtracting (once more) the second equation from the first etc., we can eliminate the values connected with the suspended matter. As a result we get

$$C_c(a'_{c1} - 2a'_{c2} + a'_{c3}) = C_y(-a'_{y1} + 2a'_{y2} - a'_{y3}) + c_1^* - 2c_2^* + c_3^* \quad (14)$$

$$C_c(a'_{c2} - 2a'_{c3} + a'_{c4}) = C_y(-a'_{y2} + 2a'_{y3} - a'_{y4}) + c_2^* - 2c_3^* + c_4^*$$

where subscripts 1, 2, 3, and 4 refer to the wavelengths 400, 450, 500, and 550 nm respectively. Dividing the first equation by the second, we can eliminate the chlorophyll concentration, C_c . The final equation obtained

contains the value of C_y (which we are seeking for), the specific absorption coefficients of yellow substance, specific absorption coefficients of chlorophyll a (data from literature, e.g. Plass et al., 1978; Халтурин et al., 1983), and the values of c_λ^* obtained by our measurements. We used the value $S=0.017$ in formula (1) and the data by Plass et al. (1978) for $a'_c(\lambda_i)$. With these numerical data the final equation for determining the yellow substance concentration is:

$$C_y = 3.974(c_1^* + 0.126c_2^* - 3.252c_3^* + 2.126c_4^*). \quad (15)$$

A comparison of the C_y values determined by formula (15) and by the method of spectrophotometric measurements of filtered water ($\lambda = 350$ nm as the base wavelength) is presented in Fig. 2. The correlation coefficient between the values of C_y determined by the two different methods is 0.86. It is not very high, but good correspondence of these two methods is shown by the regression line, which is almost identical to a bisectrix.

$$C_y(I) = 0.01 + 0.99C_y(II). \quad (16)$$

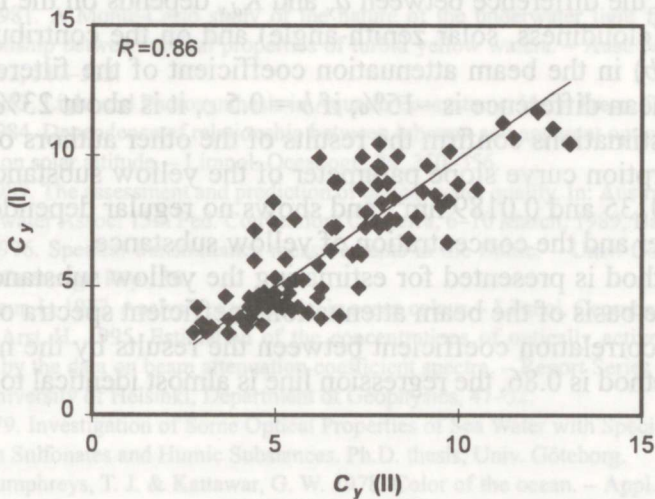


Fig. 2. Comparison of two methods for determining the yellow substance concentration in water: $C_y(I)$, by formula (11); $C_y(II)$, by formula (15).

CONCLUSIONS

1. The influence of yellow substance on the properties of the water environment can be described either by means of its absorption coefficients (in m^{-1}) or concentration (in $mg\ l^{-1}$) in the water. Which parameter from these two is preferable needs further research.

2. Yellow substance absorption coefficients determined by different investigators are comparable only if they are obtained for the same wavelengths and using the same correction formulae for taking into account the contribution of scattering in the beam attenuation coefficient of the filtered water.

3. For the estimation of the yellow substance concentration in water the value of its specific absorption coefficient at the wavelength under consideration (as a basic parameter) is necessary. To avoid the dependence of C_y on the value of the slope parameter it must be calculated using the same wavelength for which the specific absorption coefficient was originally determined. There is an urgent need to get more authentic data on the yellow substance specific absorption coefficients for different types of water.

4. It is reasonable to determine the absorption coefficient or the concentration of yellow substance using data in the UV, violet, or blue region of the spectrum. At the longer wavelengths the results may be highly unstable and the relative errors big.

5. For the description of the spectral variability of the absorption coefficient, a_y , as well as the diffuse attenuation coefficient, $K_{d,y}$, different investigators use the same formula (with the same numerical parameters). Our investigations suggest that the difference between a_y and $K_{d,y}$ depends on the illumination conditions (cloudiness, solar zenith angle) and on the contribution of the scattering (b) in the beam attenuation coefficient of the filtered water. If $b \approx 0$, the mean difference is $\sim 15\%$; if $b = 0.5 c$, it is about 23%.

6. Our estimations confirm the results of the other authors on the value of the absorption curve slope parameter of the yellow substance: it varies between 0.0135 and 0.0189 nm^{-1} and shows no regular dependence on the type of water and the concentration of yellow substance.

7. A method is presented for estimating the yellow substance concentration on the basis of the beam attenuation coefficient spectra of unfiltered water. The correlation coefficient between the results by the new and the classical method is 0.86, the regression line is almost identical to a bisectrix.

REFERENCES

- Austin, R. W. & Petzold, T. J. 1977. Considerations on the design and evaluation of oceanographic transmissometers. In: Tyler, J. E. (ed.). *Light in the Sea*. Dowden, Hutshinson and Ross, 104–120.
- Baker, K. S. & Smith, R. C. 1982. Bio-optical classification and model of natural waters. 2. – *Limnol. Oceanogr.*, 27, 3, 500–509.
- Bricaud, A., Morel, A. & Prieur, L. 1981. Absorption by dissolved organic matter of the sea (yellow substance) in the UV and visible domains. – *Limnol. Oceanogr.*, 26, 1, 43–53.
- Bristow, M., Nielsen, D., Bundy, D. & Furtek, R. 1981. Use of water Raman emission to correct airborne laser fluorosensor data for effects of water optical attenuation. – *Appl. Opt.*, 20, 2889–2905.
- Bukata, R. P., Burton, J. E. & Jerome, J. H. 1983. Use of chromaticity in remote measurements of water quality. – *Remote Sensing Environ.*, 13, 161–177.
- Davies-Colley, R. J. & Vant, W. N. 1987. Absorption of light by yellow substance in freshwater lakes. – *Limnol. Oceanogr.*, 32, 2, 416–425.

- Dera, J. 1992. *Marine Physics*. Elsevier, Warszawa.
- Effler, S. W., Perkins, M. G. & Wagner, B. A. 1991. Optics of Little Sodus Bay. – *Great Lakes Res.*, 17, 1, 109–119.
- Ferrari, G. M. & Tassan, S. 1991. On the accuracy of determining light absorption by “yellow substance” through measurements of induced fluorescence. – *Limnol. Oceanogr.*, 36, 777–786.
- Gagosian, R. B. & Stuermer, D. H. 1977. The cycling of biogenic compounds and their diagenetically transformed products in seawater. – *Marine Chemistry*, 5, 605–611.
- Hoge, F. E., Vodacek, A. & Blough, N. V. 1993. Inherent optical properties of the ocean: Retrieval of the absorption coefficient of chromophoric dissolved organic matter from fluorescence measurements. – *Limnol. Oceanogr.*, 38, 7, 1394–1402.
- Højereslev, N. K. 1980. On the origin of yellow substance in the marine environment. – *Univ. Copenhagen Inst. Phys. Oceanogr. Rep.*, 42.
- Jerlov, N. G. 1968. *Optical Oceanography*. Elsevier, Amsterdam.
- Jerlov, N. G. 1976. *Marine Optics*. 2nd ed. Elsevier, Amsterdam.
- Kalle, K. 1938. Zum Problem des Meereswasserfarbe. – *Ann. Hydrol. Mar. Mitt.*, 66, 1–13.
- Kalle, K. 1966. The problem of gelbstoff in the sea. – *Oceanogr. Mar. Biol. Annu. Rev.*, 4, 91–104.
- Kirk, J. T. 1976. Yellow substance (Gelbstoff) and its contribution to the attenuation of photosynthetically active radiation in some inland and coastal south-eastern Australian waters. – *Aust. Mar. Freshwater Res.*, 27, 61–71.
- Kirk, J. T. O. 1980. Spectral absorption properties of natural waters: Contribution of the soluble particulate fractions to light absorption in some inland waters of south-eastern Australia. – *Aust. Mar. Freshwater Res.*, 31, 287–296.
- Kirk, J. T. O. 1981. A Monte-Carlo study of the nature of the underwater light field in and the relationship between optical properties of turbid yellow waters. – *Aust. Mar. Freshwater Res.*, 32, 517–532.
- Kirk, J. T. O. 1983. *Light and Photosynthesis in Aquatic Ecosystems*. Univ. Press, Cambridge.
- Kirk, J. T. O. 1984. Dependence of relationship between inherent and apparent optical properties of water on solar altitude. – *Limnol. Oceanogr.*, 29, 350–356.
- Kirk, J. T. O. 1989. The assessment and prediction of optical water quality. In: *Australian Water and Wastewater Assoc. 13th Fed. Convention, Canberra, 6–10 March, 1989, Barton*, 504–507.
- Lundgren, B. 1976. Spectral transmittance measurements in the Baltic. – *Univ. Copenhagen Inst. Phys. Oceanogr. Rep.*, 30.
- Morel, A. & Prieur, L. 1977. Analysis of variations in ocean colour. – *Limnol. Oceanogr.*, 22, 709–722.
- Mäekivi, S. & Arst, H. 1995. Estimation of the concentrations of optically active substances in water by the data on beam attenuation coefficient spectra. – *Report Series in Geophysics*, 32, University of Helsinki, Department of Geophysics, 47–52.
- Nyquist, G. 1979. Investigation of Some Optical Properties of Sea Water with Special Reference to Lignin Sulfonates and Humic Substances. Ph.D. thesis, Univ. Göteborg.
- Plass, G. N., Humphreys, T. J. & Kattawar, G. W. 1978. Color of the ocean. – *Appl. Optics.*, 17, 9, 1432–1446.
- Prieur, L. & Sathyendranath, S. 1981. An optical classification of coastal and oceanic waters based on the specific spectral absorption curves of phytoplankton pigments, dissolved organic matter, and other particulate materials. – *Limnol. Oceanogr.*, 26, 4, 671–689.
- Stuermer, D. H. 1975. *The Characterization of Humic Substances in Sea Water*. Ph.D. thesis, Mass. Inst. Technol. Woods Hole Oceanogr. Inst.
- Takematsu, N., Kishino, M. & Okami, N. 1979. Optical properties and modelling of turbidity components in sea water. – *Bull. Soc. Fr. Jap. Oceanogr.*, 17, 9–18.
- Topliss, B. J., Miller, J. R. & Irwin, B. 1989. Ocean optical measurements. 1. Statistical analysis of data from the western North Atlantic. – *Cont. Shelf Res.*, 9, 113–131.
- Арст Х., Поздняков Д., Розенштейн А. 1991. Оптическое зондирование в океанологии. Валгус, Таллинн.
- Копелевич О. В. 1983. Факторы, определяющие оптические свойства морской воды. In: *Оптика океана*. Наука, Москва, 1, 150–166.
- Халтурин В. И. 1983. О распространении световых потоков в однородном по глубине океане. *Морской гидрофизический институт АН УССР, Севастополь*.