
Papers

Analysis of temporal and spatial variability of 'yellow substance' absorption in the southern Baltic

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Inherent optical properties
Absorption
Yellow substance
Southern Baltic

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Abstract

The value of the yellow substance absorption coefficient in the visible-light spectrum is a very important characteristic used in the optical classification of seawaters. The absorption of yellow substance also needs to be included in algorithms for the remote detection of optically-active seawater constituents. This paper presents the results of an analysis of yellow substance absorption coefficient data, a_y , collected during 11 cruises in the southern Baltic. The statistical distribution of the value of a_y ($\lambda = 400$ nm) and the value of the yellow substance absorption spectrum slope coefficient are analysed. The range of spatial and temporal variability of these parameters is discussed, and the auto-correlation matrix of the absorption coefficient measured at different wavelengths is analysed. Particular attention is given to selected wavelengths, essential in evaluating the influence of changes of a_y on the spectral reflectance.

1. Introduction

The absorption of light by Dissolved Organic Matter (DOM) is one of the main factors to be evaluated in algorithms for estimating the concentration of optically-active compounds in seawaters. They were constructed under the assumption that dissolved organic matter is correlated with chlorophyll concentration. This has yielded good results in Case 1 Waters, which do not receive terrigenous DOM, and where the entire DOM content is due to phytoplankton growth and decomposition. However, the application of these algorithms to Case 2 Waters has been unsuccessful, so there is an urgent

need to examine the temporal and spatial variability of the DOM absorption coefficient on different scales in various regions. This information is important in order to gain the background knowledge necessary for assessing the influence of a_y on the spectral reflectance, the key parameter in the interpretation of remotely-sensed colour data. The absorption of yellow substance is also an important element of a number of optical classifications of seawaters (Prieur and Sathyendranath, 1981; Sathyendranath *et al.*, 1988; Carder *et al.*, 1991).

The Marine Physics Division of the Institute of Oceanology PAS has been conducting experimental research into the influence of the optically active components of seawaters on the spectral reflectance (Darecki *et al.*, 1994; Darecki *et al.*, 1995). The principal aim of this study is to summarise the results of the measurements made during 11 cruises, and to describe the absolute range of variation of the yellow substance absorption coefficient and the yellow substance absorption spectrum slope coefficient, and their variability on the different temporal and spatial scales in the Baltic Sea.

2. The optical properties of DOM

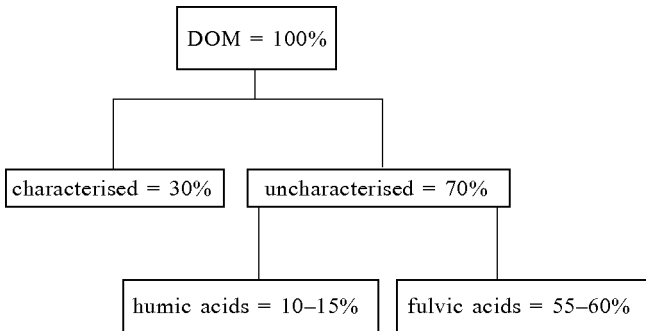


Fig. 1. The quantities of various dissolved organic matter (DOM) components (Spitzky and Ittekot, 1986)

DOM includes most of the organic matter deposited in the oceans and consists of a variety of organic compounds. So far, only about 30% of them have been analysed and classified into analytical groups – see Fig. 1 (Spitzky and Ittekot, 1986). The properties of the remainder have yet to be characterised, hence their specific optical properties are still unknown; these compounds are gathered under the general heading of ‘aquatic humus substances’ (yellow substance). As far as the visible light spectrum is concerned, the justifiable simplification is made that absorption by humic substances can account for total DOM absorption.

$$a_{\text{DOM}} = \sum_{i=1}^n a_i^* C_i = a_H = a_y,$$

where

a_{DOM} – total absorption by DOM,

a^* – specific absorption coefficient of a selected organic compound,

C_i – concentration of a selected organic compound,

a_H – absorption coefficient of the aquatic humus,

a_y – absorption coefficient of yellow substance.

The chemical and optical properties of yellow substance in the sea have already been studied (Kalle, 1966; Højerslev, 1974, 1988; Jerlov, 1976; Nyquist, 1979; Reuter, 1986; Pempkowiak, 1988; Carder, 1989; Dera, 1992). According to the results published, the molecular structure of the organic compounds determines the absorption properties of DOM. The kind of chemical bond and the type of chromophoric group related to it, as well as the number and mutual position of such groups in the molecular structure, are responsible for the spectral absorption range. Although the chemical structure of aquatic humus has not yet been described in detail, this group of organic compounds has been divided into a humic acid fraction and a fulvic acid fraction. The absorption of these two fractions generally increases monotonically and exponentially towards the UV end of the spectrum. On the semi-logarithmic scale this absorption can be expressed in the form of a two-parameter equation (valid also for aquatic humus in the visible light spectrum):

$$a_h^*(\lambda) = a_h^*(\lambda_0) e^{-S_h(\lambda_0 - \lambda)},$$

$$a_f^*(\lambda) = a_f^*(\lambda_0) e^{-S_f(\lambda_0 - \lambda)},$$

$$a_y = a_H(\lambda) = a_H(\lambda_0) e^{-S_H(\lambda_0 - \lambda)},$$

where

a_h^* , a_f^* – the respective specific absorption coefficients of the humic and fulvic acid fractions,

a_H – absorption coefficient of aquatic humus,

a_y – absorption coefficient of yellow substance,

S_h , S_f , S_H – the respective slope coefficients of humic acids, fulvic acids and aquatic humus.

The properties of the fulvic and humic acid fractions extracted from natural water in various environments have been described in detail by Carder (1989) and Dera (personal communication). For the purpose of this article, we would like to emphasise the following characteristics of the two fractions. The specific absorption coefficient of the fulvic acid fraction is low because of the aliphatic hydrocarbons it incorporates. Its slope coefficient is high in seawater (0.018–0.020) but low in freshwater and soil (0.011–0.013).

By contrast, the specific absorption coefficient of the humic acid fraction is high because of the strongly absorbing aromatic rings it contains. Its slope coefficient is low (*ca* 0.010) and remains stable in various environments. In nature the solution of organic compounds consists of a mixture of fulvic and humic acids, together with an uncharacterised fraction. The value of the yellow substance absorption spectrum slope coefficient is therefore indicative of the content of the dominant organic compound fraction. Samuła-Koszalka and Woźniak (1977) investigated the seasonal variability of the slope coefficient of the natural composition of dissolved organic compounds collected in the Gulf of Gdańsk.

3. Methods

The yellow substance absorption was measured as the UV–VIS transparency of the filtered sample *in vitro*. The samples were collected during a number of cruises on the Baltic Sea: three cruises of the ULISSE Experiment, carried out by the Institute of Oceanology PAS and the Institute of Remote Sensing Applications JRC Ispra, and eight optical cruises organised by the Institute of Oceanology PAS (see Tab. 1). In accordance with the procedure recommended by Reuter *et al.* (1986b), samples were collected in Nansen bottles and then filtered on board through 0.2 μm Sartorius cellulose membrane filters. The filtered water was stored in the dark and at a low temperature (*ca* 4°C) in 200 ml brown-glass bottles, to which 400 μl of 0.5 M HgCl_2 was added to prevent bacterial growth and DOM decomposition. Sample transparency was measured with a double-beam Perkin-Elmer spectrophotometer in a 10 cm quartz cell in the 300–700 nm spectral range. Another 10 cm quartz cell filled with doubly-distilled water was used as reference. The transparency (in units of absorbance $A_{10}(\lambda)$) was converted by means of the following relation into the absorption coefficient obeying the Lambert-Beer law:

$$a_y(\lambda) = 23.3 A_{10}(\lambda) \text{ [m}^{-1}\text{]}.$$

This procedure was applied to minimise the loss of DOM absorption properties. The effect of time, bacterial decomposition, bacterial growth, and light on DOM absorption properties has been assessed by Diebel-Langohr *et al.* (1986).

Least-square methods were used to estimate the linear parameters of the spectrum in the semi-logarithmic scale in the 350–600 nm spectral range, from which the yellow substance absorption spectrum slope coefficients were calculated. This range was chosen as it had been noticed that the spectra obtained were extremely sensitive to the high signal-to-noise ratio at wavelengths longer than 600 nm. The UV lamp of the spectrophotometer was

sometimes found to be unstable within the UV range, so the yellow substance absorption spectrum slope coefficients should be considered valid for visible light.

For further statistical analysis the absorption coefficient was set at $\lambda = 400$ nm. This wavelength has been recommended by Sathyendranath *et al.* (1989) as suitable for distinguishing phytoplankton from yellow substance. This wavelength lies between $\lambda = 380$ nm, the wavelength of the absorption coefficient frequently cited in the literature, and $\lambda = 412$ nm, the wavelength of the first band of the future SeaWiFS satellite colour sensor.

4. Results

4.1. The statistical distribution of the yellow substance absorption coefficient and the yellow substance absorption spectrum slope coefficient

The research cruises were planned in such a way that samples could be collected in different water masses: in bays, in the coastal zone and in the open southern Baltic. The locations of the stations were selected to cover as many as possible of the variety of hydrological and biological situations occurring in the Baltic. Systematic sampling was conducted along the Vistula river profile. The material collected was separated according to the site of collection, *i.e.* bay waters, coastal waters and open-sea waters. Altogether nearly 500 yellow substance absorption spectra were analysed: 225 from bay-water samples, 179 from open-sea water samples and 97 from coastal-water samples. Tab. 1 sets out the dates of each cruise and the number of samples collected in the different water types, as well as the range, mean values and standard deviation of the parameters analysed. Tab. 2 gives the values of the statistical parameters calculated for the total number of samples collected in a given water type. Figs. 2 and 3 show the respective frequency distributions of two characteristics analysed for all the samples collected in a given region.

The total magnitude of the yellow substance absorption coefficient ranged from 0.16 to 4.60 m^{-1} , an almost 30-fold amplitude. This range differs in each water body; the greatest was recorded in bay waters ($a[\lambda = 400 \text{ nm}]$, range: 0.16–4.55 m^{-1}), and the smallest in open-sea waters ($a[\lambda = 400 \text{ nm}]$, range: 0.3–1.84 m^{-1}). The amplitude of the yellow substance absorption spectrum slope coefficient was much smaller (between 0.004 and 0.034) and the extreme values differed from each other by a factor of 8. The greatest variability of this parameter was noted in bay waters (0.005–0.034) and the smallest in open-sea waters (0.012–0.028).

Table 1. Statistical values of the yellow substance absorption coefficient at $\lambda = 400$ nm and the yellow substance spectrum slope coefficient for a series of cruises during 1993–1995

Cruise	Parameter	Mean value	Maximal value	Minimal value	Standard deviation	Sample size
optical cruise 5–14 Sept. 1993	open-sea waters	0.86	1.65	0.47	0.27	38
	S_H VIS	0.016	0.020	0.011	0.0025	25
bay waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.95	1.96	0.16	0.41	30
	S_H VIS	0.012	0.020	0.006	0.004	22
ULISSE-1 cruise 10–17 April 1994	open-sea waters	1.11	1.84	0.51	0.55	25
	S_H VIS	0.019	0.20	0.017	0.001	25
coastal waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	1.51	4.60	0.62	0.97	37
	S_H VIS	0.019	0.020	0.016	0.0008	37
bay waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	2.64	4.55	1.50	0.92	30
	S_H VIS	0.020	0.021	0.019	0.0005	30

Table 1. (continued)

Cruise	Parameter	Mean value	Maximal value	Minimal value	Standard deviation	Sample size
optical cruise 6–15 May 1994	open-sea waters $a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.71	1.39	0.40	0.32	11
	S_H VIS	0.020	0.027	0.011	0.006	11
coastal waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.69	1.33	0.42	0.27	11
	S_H VIS	0.020	0.027	0.014	0.004	11
bay waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	1.28	2.35	0.51	0.56	12
	S_H VIS	0.017	0.026	0.014	0.004	12
ULISSE-2 cruise 17–25 Aug. 1994	open-sea waters $a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.57	0.70	0.48	0.05	18
	S_H VIS	0.020	0.022	0.019	0.0007	18
coastal waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.98	1.81	0.62	0.56	7
	S_H VIS	0.019	0.020	0.018	0.0008	7
bay waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.78	2.84	0.58	0.37	36
	S_H VIS	0.019	0.021	0.016	0.0009	36

Table 1. (continued)

Cruise	Parameter	Mean value	Maximal value	Minimal value	Standard deviation	Sample size
ULISSE-3 cruise 22–29 Sept. 1994	$a_y(\lambda = 400 \text{ nm}) [\text{m}^{-1}]$	0.72	0.94	0.57	0.08	41
	$S_H \text{ VIS}$	0.019	0.022	0.016	0.001	40
coastal waters	$a_y(\lambda = 400 \text{ nm}) [\text{m}^{-1}]$	0.72	1.01	0.55	0.11	33
	$S_H \text{ VIS}$	0.019	0.022	0.016	0.001	33
bay waters	$a_y(\lambda = 400 \text{ nm}) [\text{m}^{-1}]$	0.98	2.08	0.63	0.31	33
	$S_H \text{ VIS}$	0.019	0.022	0.017	0.001	29
optical cruise 10–14 Nov. 1994	$a_y(\lambda = 400 \text{ nm}) [\text{m}^{-1}]$	1.03	1.66	0.69	0.43	4
	$S_H \text{ VIS}$	0.006	0.007	0.004	0.001	4
bay waters	$a_y(\lambda = 400 \text{ nm}) [\text{m}^{-1}]$	0.96	2.11	0.71	0.41	10
	$S_H \text{ VIS}$	0.007	0.009	0.005	0.001	10
optical cruise 18–19 Feb. 1995	$a_y(\lambda = 400 \text{ nm}) [\text{m}^{-1}]$	0.52	1.99	0.25	0.47	12
	$S_H \text{ VIS}$	0.027	0.034	0.020	0.003	12

Table 1. (continued)

Cruise	Parameter	Mean value	Maximal value	Minimal value	Standard deviation	Sample size
optical cruise 23 March – 4 April 1995	open-sea waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.58	0.81	0.48	0.11
		$S_H \text{ VIS}$	0.019	0.030	0.009	0.008
	bay waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.70	1.41	0.47	0.26
		$S_H \text{ VIS}$	0.021	0.030	0.013	0.006
cruise 23–29 April 1995	open-sea waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.46	0.52	0.42	0.037
		$S_H \text{ VIS}$	0.024	0.029	0.018	0.004
	bay waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.93	1.30	0.47	0.25
		$S_H \text{ VIS}$	0.019	0.026	0.012	0.005

Table 1. (continued)

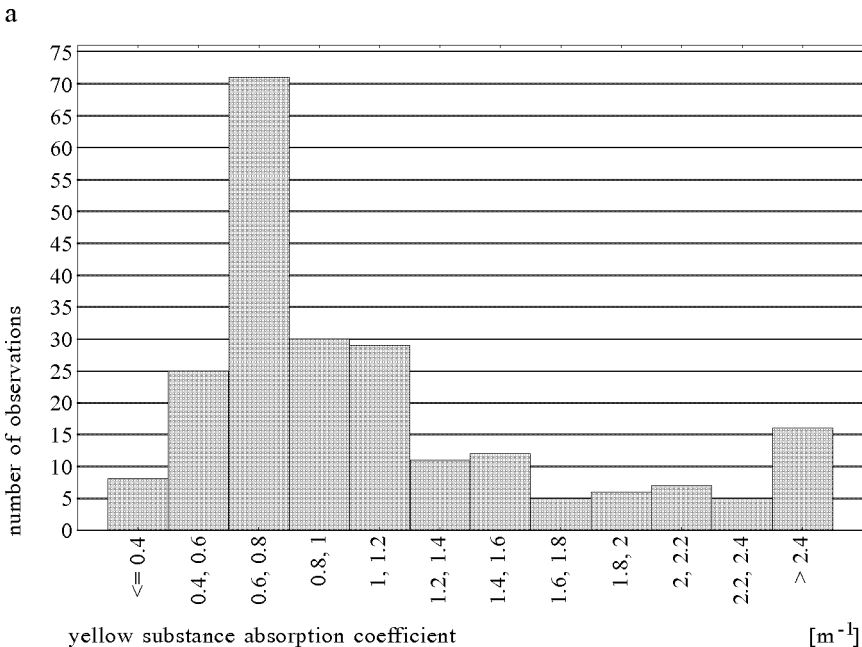
Cruise	Parameter	Mean value	Maximal value	Minimal value	Standard deviation	Sample size
cruise 16–20 May 1995	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.64	0.70	0.58	0.05	4
	S_H VIS	0.015	0.021	0.012	0.004	4
bay waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.85	1.80	0.49	0.33	27
	S_H VIS	0.019	0.027	0.011	0.005	27
optical cruise 3–11 June 1995	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.59	0.76	0.51	0.073	19
	S_H VIS	0.020	0.023	0.017	0.002	19
coastal waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	0.62	0.71	0.53	0.07	6
	S_H VIS	0.020	0.024	0.013	0.004	6
bay waters	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	1.27	3.16	0.78	0.72	9
	S_H VIS	0.016	0.021	0.014	0.002	9

Table 2. Statistical parameters calculated for the total samples collected in three different water masses

	Bay waters		Coastal waters		Open-sea waters	
	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	$S_H \text{ VIS}$	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	$S_H \text{ VIS}$	$a_y(\lambda = 400 \text{ nm})$ [m^{-1}]	$S_H \text{ VIS}$
minimal value	0.16	0.005	0.42	0.012	0.3	0.004
maximal value	4.55	0.034	4.60	0.029	1.84	0.030
mean value	1.12	0.018	1.02	0.19	0.76	0.019
median	0.84	0.019	0.71	0.19	0.67	0.019
standard deviation	0.73	0.005	0.73	0.002	0.32	0.004
sample size	225	213	97	97	179	165

The lowest values of this parameter had been noted in the study area previously (Samuła-Koszalka and Woźniak, 1979), whereas the highest ones were recorded during only one cruise at a few sampling stations in open-sea waters, and could have been due to measurement inaccuracy. Such exceptionally high values have not been published so far, but it was decided to include them in the present analysis, because they did not exert very much influence on the statistics.

The respective histograms of the absorption and slope coefficients are presented on Fig. 2 and 3. The statistical distribution of the absorption coefficient is close to the log-normal distribution in the bay and open-sea waters, but in the coastal-water distribution there are two peaks. One of them is at *ca* 0.8 m^{-1} , the second at *ca* 1.8 m^{-1} . The first of these peaks reflects the influence of open-seawater, which is dominant in the coastal zone, the second the influence of freshwater from small rivers flowing into the coastal zone. It should be noted that the presence of increased absorption has resulted from the sampling strategy, which focused on the freshwater sources. The impact of the freshwater in the coastal zone is small, because the total input of small coastal rivers is less than 5% of the total outflow from the whole territory of Poland. The first section of Fig. 2b should therefore be more representative of the coastal zone. The histograms of the absorption coefficient in the bay waters and in the open-sea waters are characterised



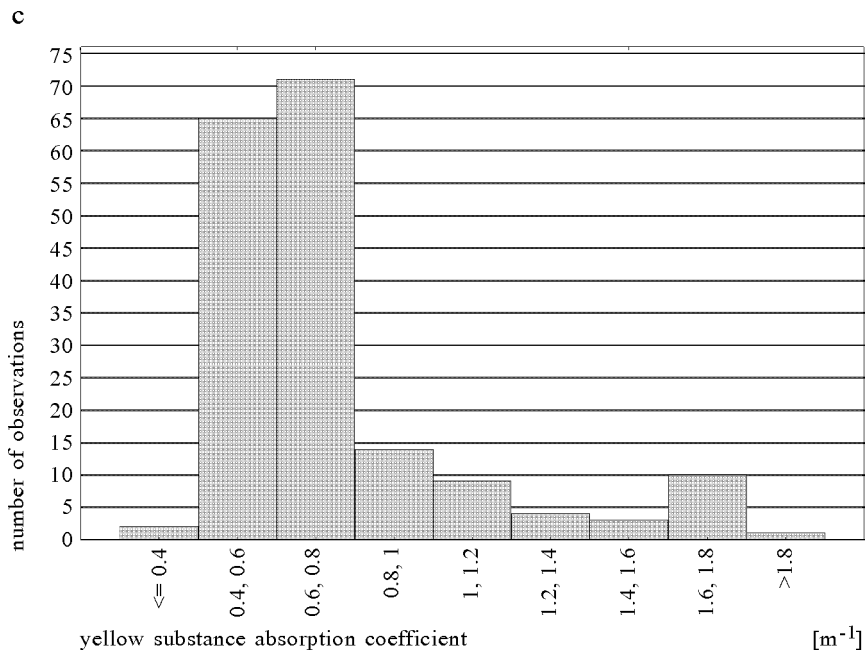
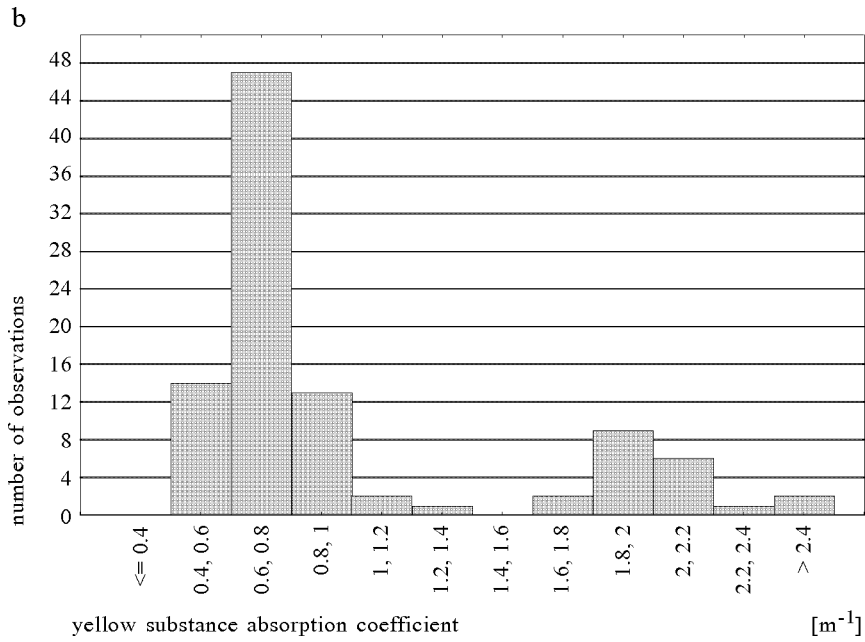
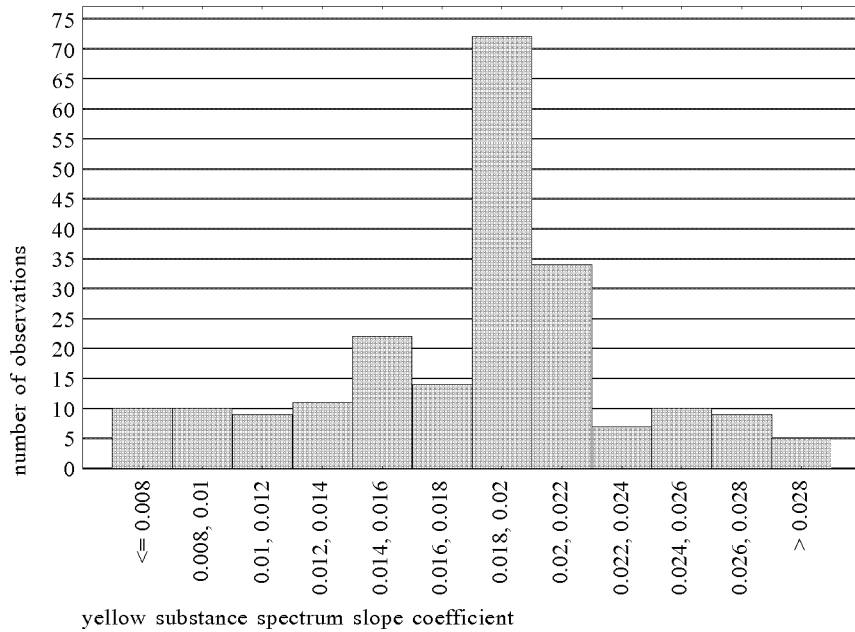
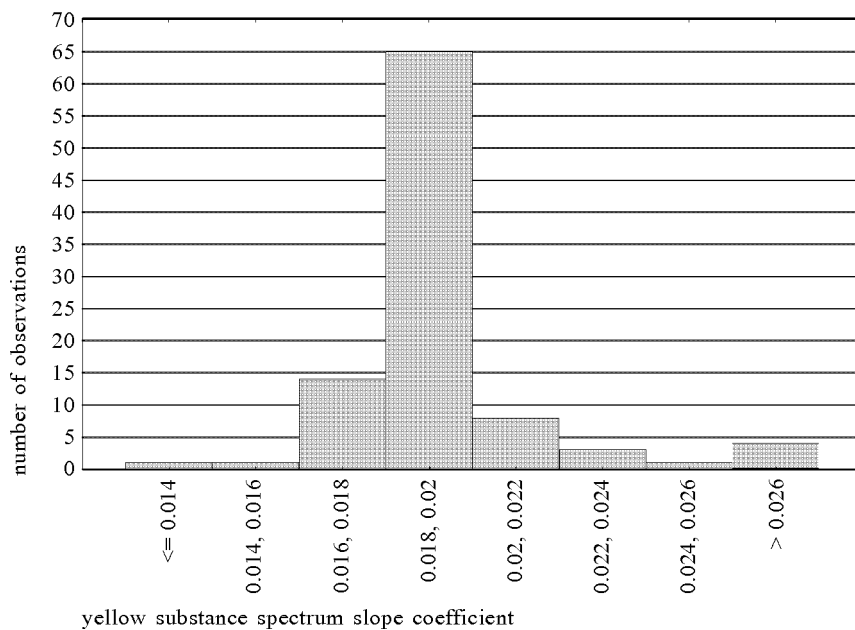


Fig. 2. The frequency distribution of the yellow substance absorption coefficient in the different water types: bay waters (a), coastal waters (b), open-sea waters (c)

a



b



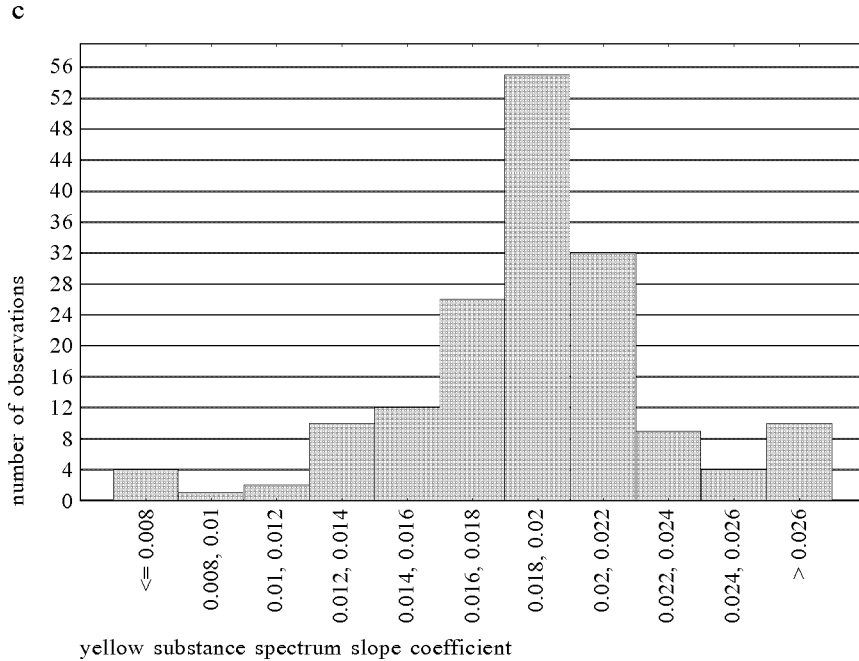


Fig. 3. The frequency distribution of the yellow substance spectrum slope coefficient in the different water types: bay waters (a), coastal waters (b), open-sea waters (c)

by very strong peaks at *ca* 0.6 m^{-1} in the open-sea waters and at 0.8 m^{-1} in the bay waters. The presence of strongly absorbing freshwater can be seen on Fig 2a. The impact of the waters of the rivers Vistula and Odra in bay waters resulted in the frequent occurrence of absorption coefficients greater than 1.4 m^{-1} . The highest mean value and standard deviation were observed in the bay waters, and the lowest in the open sea; nearly 85% of the absorption coefficients in the southern Baltic lie in the range between 0.6 and 1.4 m^{-1} .

The histograms of the slope coefficient are more regular, very close to the normal distribution, and very steep in all three water types. 75% of the slope coefficients lay within the 0.014–0.022 range. The mean values are the same and the standard deviations are similar in all three water types. In the open sea and in the bays slope coefficients < 0.008 were recorded. Such values were not recorded in the coastal zone, but most samples had been collected there in the spring and summer. So the most probable explanation of this fact is that the yellow substance absorption spectrum coefficient tends to change with time rather than space. However, another explanation, that the very low values of this parameter encountered in the open-sea waters could be due to patches of river water plume, cannot be ruled out. According to

theory the presence of low slope coefficient values in the bays could be due to the permanent presence of freshwater from river mouths. The difference in the chemical properties of the drainage area of small coastal rivers could explain the absence of low slope coefficients in the coastal zone. The relation between the properties of the drainage area and the values of the yellow substance absorption coefficient and the yellow substance spectrum slope coefficient were described by Carder (1989) and Kirk (1994). The present results show that in a region influenced by a river plume, the values of these parameters are highly sensitive to the hydrological conditions. Apart from a general explanation it is not possible to describe the fate of yellow substance in the marine environment without a detailed chemical study of yellow substance properties in the Vistula river and the drainage area of small coastal rivers.

The experimental results suggest that the DOM absorption properties which can be recorded in the southern Baltic will be characterised by an absorption coefficient lying between 0.4 and 1.6 m^{-1} , and a slope coefficient in the range between 0.014–0.022. This fact suggests that the fulvic acid fraction of marine humus is dominant in the southern Baltic. This finding was predicted by Bricaud *et al.* (1981), but generalisation of this conclusion is liable to lead to error.

As the largest data sets were collected in the open-sea waters and bay waters it was decided to examine the temporal variations in the absorption coefficient and slope coefficient in these two environments. The temporal distribution of the statistical parameters of the yellow substance absorption coefficient and the yellow substance spectrum slope coefficient in the open-sea waters and bay waters are presented in Figs. 4 and 5.

The mean values of the absorption coefficient recorded during particular cruises oscillate around a mean value, specific to the region, computed for the whole data set collected there. The highest mean absorption coefficient in the open sea and bays was noted in April 1994, the lowest in February 1995. The February 1995 data were not included in the open-sea water section; however, the few measurements that were made there also show minimal values. Data sets for both regions collected during the April 1994 cruise are scattered; the largest variability (the highest value of standard deviation) was noted during this cruise. The observed maximum can be interpreted as being due to the seasonal maximum freshwater outflow from the land. The range of the Vistula river plume (Fig. 6) was so large that its influence was observed in the open sea, which resulted in a significant increase in the mean absorption in comparison to other months. The samples collected in this area had a great influence on the mean value and standard deviation of the yellow substance absorption coefficient. In February 1995 stations in

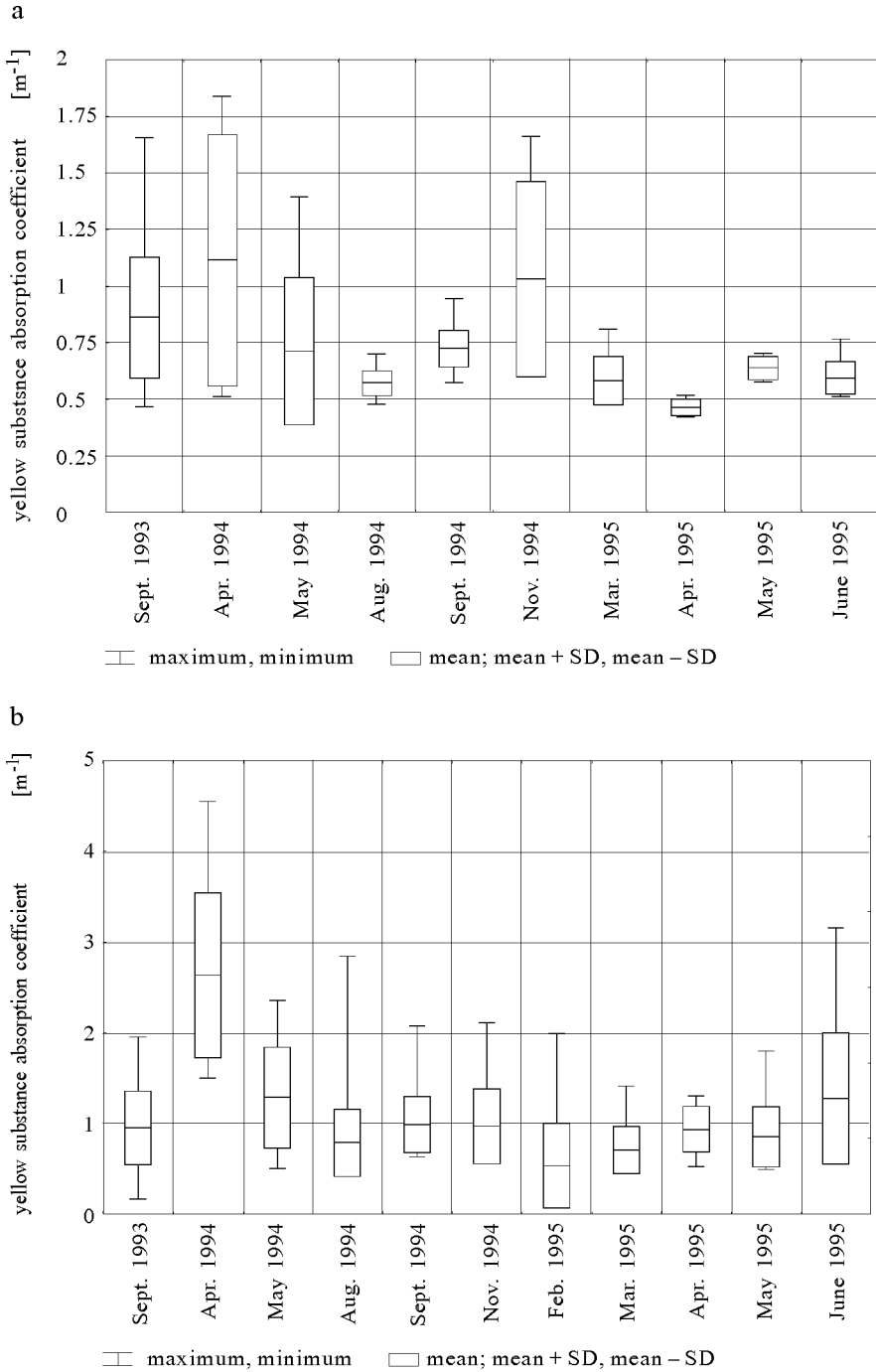


Fig. 4. Temporal distribution of yellow substance absorption coefficient in open-sea waters (a) and bay waters (b)

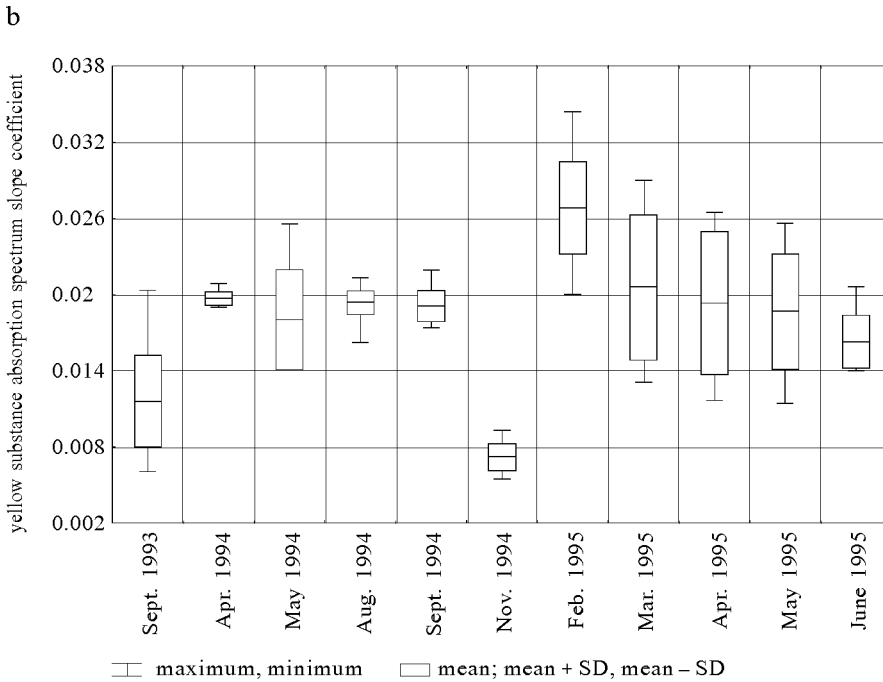
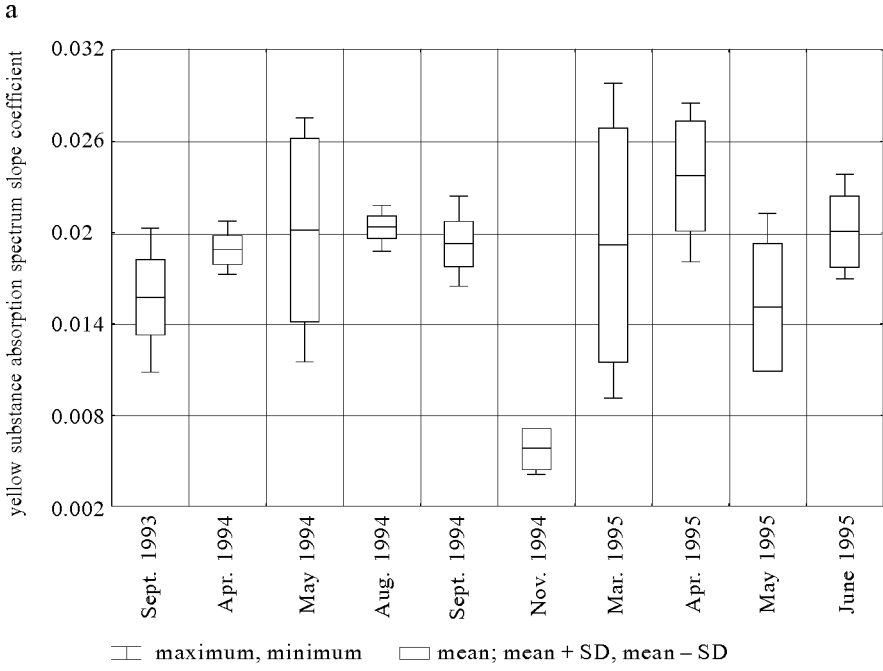


Fig. 5. Temporal distribution of yellow substance absorption spectrum slope coefficient in open-sea waters (a) and bay waters (b)

the Vistula river profile in the Gulf of Gdańsk were sampled. Most samples collected during this cruise had a small absorption (*ca* 0.6 m^{-1}), but one sample taken in the river mouth had a maximum value of *ca* 2 m^{-1} and the biggest impact on statistical parameters.

Like those of the mean absorption coefficient, the temporal distributions of the statistical parameters of the yellow substance absorption spectrum slope coefficient fluctuate. The major difference in comparison with the temporal variations in the absorption coefficient is that the range of changes of the slope coefficient is very similar in the two regions. The mean values of the slope coefficients oscillate around 0.019, which is the mean value for both regional data sets. The most important feature on this plot is that the lowest mean slope coefficient was recorded in both environments in November 1994. The maximum mean slope coefficient was recorded in the open-sea waters in May 1994 and April 1995, and in the bay waters in February 1995. During those cruises in the bay waters different hydrological situations were encountered. In November the plume of river water was extensive, owing to the high rainfall in the catchment area. In February, river outflow was low, since most of the catchment area was frozen. In November 1994 the yellow substance absorption coefficient was quite high, while values of slope coefficients were very low. In February 1995, however, the situation was reversed: absorption coefficients were very low (except in one sample collected at the Vistula mouth), but slope coefficients were very high. The presence of freshwater affected the value of the yellow substance absorption spectrum slope coefficient: low slope coefficients in November were typical of the land humus absorption spectrum slope coefficient, high values in February were close to those typical of marine humus. This example shows the influence of the freshwater plume on the absorption properties of water in the same marine basin. In open-sea waters the increase in the mean slope coefficient in the spring months could have been due to the spring activity of plankton.

4.2. The spatial distribution of the yellow substance absorption coefficient $a_y \lambda = 400 \text{ nm}$

The main sources of yellow substance in the sea are rivers. A number of maps showing the horizontal distribution of a_y ($\lambda = 400 \text{ nm}$) in the surface layer of water have been processed in order to estimate the spatial variability of this parameter. This paper presents the two most interesting examples, namely, the surface distributions of a_y ($\lambda = 400 \text{ nm}$) during two cruises – in April 1994 in the southern Baltic and in May 1995 in the Pomeranian Bay.

Analysis of the maps shows that in the open Baltic sea the variability is relatively small and varies in the range $0.5 < a_y (\lambda = 400 \text{ nm}) < 1 \text{ m}^{-1}$ throughout the year. Exceptions were recorded in April 1994, when values

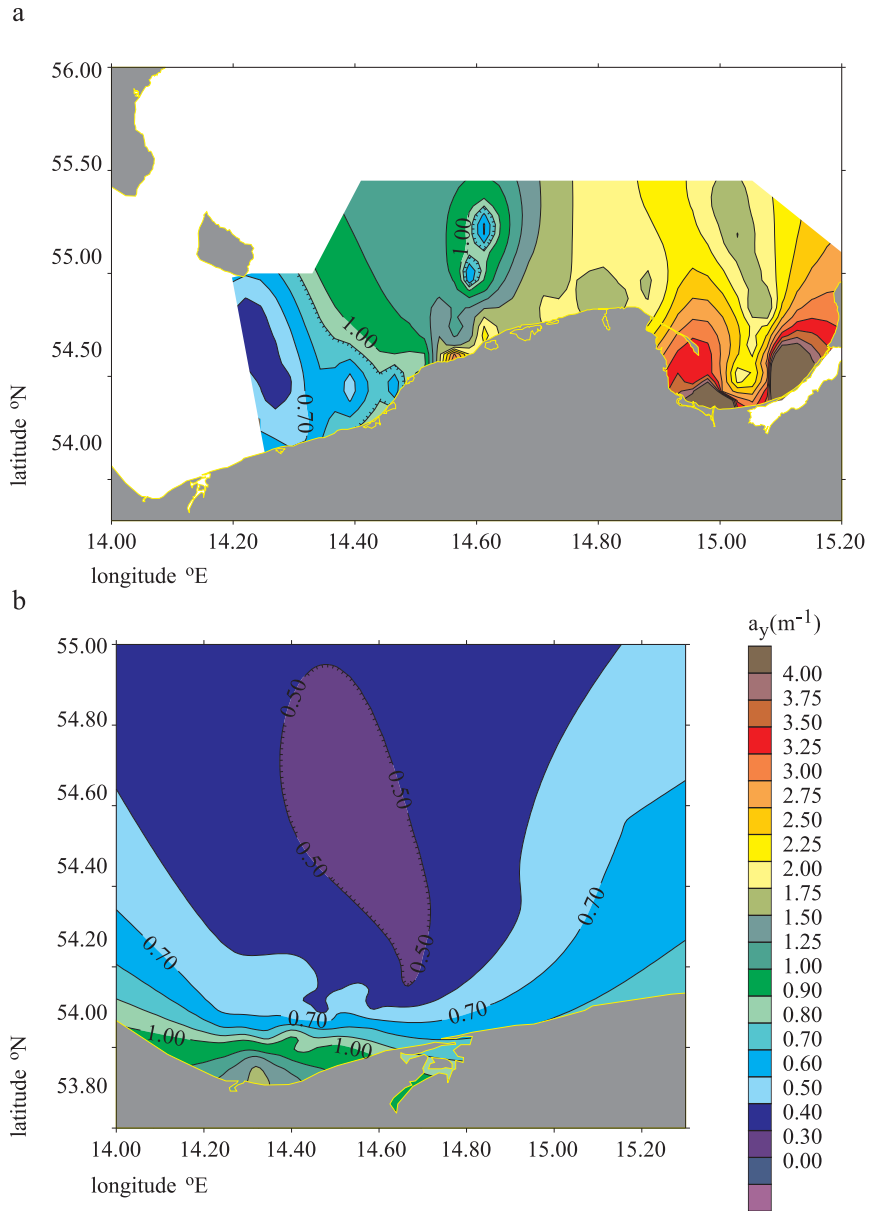


Fig. 6. The spatial distribution of the yellow substance absorption coefficient a_y at $\lambda = 400$ nm in the surface layer of Baltic Sea waters during two cruises: in April 1994 in the southern Baltic (a) and in May 1995 in the Pomeranian Bay (b). The colour scale next to the maps is scaled in physical values of a_y ($\lambda = 400$) nm [m^{-1}]

of $a_y(\lambda = 400 \text{ nm}) > 2 \text{ m}^{-1}$ were recorded offshore (see Fig. 6a), and in February 1995, when minimal values of $a_y(\lambda = 400 \text{ nm}) < 0.5 \text{ m}^{-1}$ were recorded. The high values in the open sea recorded in April are due to the exceptional penetration of the freshwater from the Vistula river plume and its associated extensive algal bloom. A significant increase in yellow substance absorption is recorded in the coastal zone near river outlets, and in the Gulf of Gdańsk and Pomeranian Bay (see Fig. 6b). In these latter two regions, where the respective mouths of the rivers Vistula and Odra are located, values of $a_y(\lambda = 400 \text{ nm})$ are usually greater than 1 m^{-1} . In these regions absolute maxima of $a_y(\lambda = 400 \text{ nm})$ were recorded, sometimes $>4 \text{ m}^{-1}$. It is very important to underline the fact that the spatial range of increase of the yellow substance absorption field is governed by the hydrological regime of those large rivers, but in most cases absorption drops radically with increasing distance from their mouths. In the coastal zone, where the mouths of small rivers are located, the influence of fresh turbid waters with an increased absorption field is only of local significance.

The spatial range of plumes of turbid freshwaters, rich in dissolved organic matter, and their influence on the yellow substance absorption field, was studied in the Vistula river profile in the Gulf of Gdańsk. The sampling stations in this profile were visited during 6 cruises, and the results of the measurements are shown in Fig. 7.

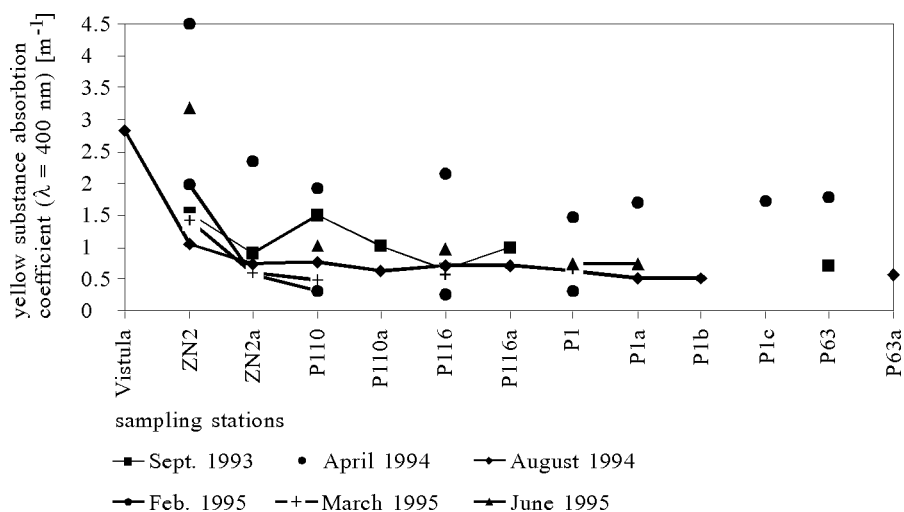


Fig. 7. The distribution of the yellow substance absorption coefficient a_y ($\lambda = 400 \text{ nm}$) measured in the surface waters along the Vistula river profile during several cruises. The distance between the mouth of the Vistula river and station P116 is 48 kilometres

The most important feature of this graph is the radical decrease in the value of a_y ($\lambda = 400$ nm) with increasing distance from the river mouth. Several kilometres offshore the absorption coefficient is half as much in value as at the river mouth. There are also visible differences between cruises. The highest values of a_y ($\lambda = 400$ nm) were noted in April 1994, the lowest in February 1995. This is the effect of the river activity, described in previous paragraphs. Flocculation and sedimentation at the hydrological front are responsible for the rapid reduction in the increased absorption field near the river mouth. This phenomenon was described by Pempkowiak (1988), and can be viewed on processed CZCS (Coastal Zone Color Scanner) images of the North Sea published by Doerffer and Fischer in 1994.

4.3. The relations between the yellow substance absorption coefficient at $\lambda = 400$ nm, and the yellow substance absorption coefficient at other wavelengths, the slope coefficient and chlorophyll concentration

The technique of remote detection is limited by the spectral properties of the spectral reflectance of the water body in question and the optical properties of the atmosphere above it (Robinson, 1985). These limitations have to be taken into consideration if the yellow substance absorption is to be estimated by means of remote sensing. The UV band provides the best accuracy of measurements, although the light in this part of the spectrum is strongly attenuated in the atmosphere. Measurements in the visible part of the spectrum are sufficiently accurate as regards yellow substance absorption properties, but chlorophyll absorption peaks appear in this region (the blue-green part of the spectrum).

Tab. 3 sets out the autocorrelation matrix of yellow substance absorption coefficients measured at different wavelengths during the same experiment. The wavelengths in the visible part of the spectrum are compatible with the CZCS wavebands. The measurement accuracy of the yellow substance absorption coefficient evidently decreases radically towards the longer wavelengths. Measurements at wavelengths longer than 490 nm are very sensitive to the noise introduced by absorption, fluorescence, and scattering by other optically-active compounds. This can be inferred directly from the yellow substance absorption properties. The measurements at 380 nm are the most useful from this point of view, but cannot be applied in remote sensing. The autocorrelation coefficients for the two wavelengths 400 and 443 nm are very good in the blue-green region of the visible-light spectrum and statistical significant at all other wavelengths. These two wavelengths are applicable

in remote sensing, but the 443 nm waveband lies within the range of the maximum absorption of chlorophyll *a*. The absorption of yellow substance at these two wavelengths and its relations with the spectral reflectance will be the subject of further research.

The present results do not provide an answer to the question of yellow substance absorption – chlorophyll concentration correlation on a local scale. It is generally assumed that in Case 2 Waters yellow substance absorption and chlorophyll concentration are not correlated because of the continuous yellow substance supply from terrigenous sources. However, some workers suggest that such a relation can be estimated for selected regions on a given spatial and time scale (Reuter *et al.*, 1986a; Tassan, 1994). The correlation matrix (see Tab. 4) of the yellow substance absorption coefficient at $\lambda = 400$ nm in the 0.25–4.6.0 m^{-1} range, the slope coefficient and the chlorophyll concentration, shows that all of these variables are independent. Nevertheless, the correlation coefficient between the absorption and the slope coefficients, and that between the absorption coefficient and the chlorophyll concentration are statistically significant.

Table 4. Correlation matrix of the yellow substance absorption coefficient, $a_y\lambda = 400$ nm, yellow substance absorption spectrum slope coefficient, S_H , and chlorophyll concentration C_a . Statistically significant values of the correlation coefficient are given in bold

Correlation matrix Sample size N = 366 Confidence level p < 0.05			
	$a_y\lambda = 400$ nm	S_H	C_a
bay waters, sample size N = 153			
$a_y\lambda = 400$ nm	1	-0.10	0.35
S_H	-0.10	1	0
C_a	0.35	0	1
coastal waters, sample size N = 82			
$a_y\lambda = 400$ nm	1	0.88	-0.44
S_H	0.88	1	-0.48
C_a	-0.44	-0.48	1
open-sea waters, sample size N = 138			
$a_y\lambda = 400$ nm	1	-0.37	0.29
S_H	-0.37	1	0.17
C_a	0.29	0.17	1

Interpreting the results of the correlation analysis presented in Tab. 4 is difficult. There is some kind of positive relation between the absorption

coefficient and the chlorophyll concentration, and a negative relation between the absorption coefficient and the slope coefficient in open-sea waters and bay waters. The results obtained for coastal waters are totally different and at the present time we are unable to explain this difference. The low values of the correlation coefficient in all the regions selected may have resulted from the analysis of data sets consisting of samples collected in different seasons. The temporal analyses of the absorption and slope coefficients suggest that seasonal changes are important. The properties of the waters encountered in the different water types differ considerably (Sagan, 1991; Olszewski *et al.*, 1992), so the results need to be classified on the basis of objective parameters, which could lead to a significant increase in the correlation coefficient. The results achieved in the preliminary classification of Baltic Sea waters based on the spectral reflectance ratio have given good correlation between the chlorophyll concentration and the total suspended matter concentration on the one hand, and the spectral reflectance ratio on the other (Darecki *et al.*, 1995). This shows the direction of further research.

5. Discussion

It is very difficult to compare our results with existing published data. First of all, the published material provides general information illustrated by examples of single measurements selected sites (Højerslev, 1974, 1988; Jerlov, 1976; Dera, 1992). Single measurements almost identical with those already published are readily found in our large data set. In the literature, authors cite absorption coefficient values at different wavelengths, usually 380, 400 or 440 nm. So for comparison the data needs to be recalculated. Yellow substance has also been measured by fluorescence; however, only a qualitative comparison of the results of this procedure with our results has been possible.

Our results are very similar to those obtained by Samuła-Koszalka and Woźniak (1979), especially where range value and temporal changes in the slope coefficient are concerned. Bricaud *et al.* (1981) present data on yellow substance absorption collected at various sites in coastal and oceanic waters, including the Baltic Sea. It is worth emphasising that their data are very close to ours. In this publication the authors have calculated the value of the slope coefficient at about 0.018, which is close to the mean value of our data set. Previous data published by Højerslev had put the slope coefficient at 0.014, and the absorption coefficient in the range of a_y ($\lambda = 400$ nm) 0.4–0.6 m^{-1} . These measurements were made in the northern Baltic Sea off the Swedish coast, the drainage area of which has different hydrological characteristics from those of the southern Baltic, so the values of a_y and S_H are lower. Reuter *et al.* (1986a) present a whole table of measurements

made in coastal waters of the North Sea and the Adriatic; some examples from the Baltic Sea (Bornholm Basin and Fehmarn Belt) are also included. The values of a_y and S_H given in this paper for the Baltic Sea sites are very close to ours. Reuter and his co-workers also present very interesting absorption coefficient data from the river Elbe: their value is greater than a_y ($\lambda = 400$ nm) 4 m^{-1} . Furthermore, the results from the Baltic Proper published by Højerslev (1988) are almost the same as ours.

In his monograph, Pempkowiak (1988) describes the chemical properties of yellow substance in the Baltic in detail, but the optical properties only briefly. The important conclusion of his work relating to the absorption properties of DOM is that the absorption coefficient in the VIS cannot be used as a measure of DOM concentration. The same problem was pointed out by Reuter *et al.* (1986a). Another very important conclusion is that nearly 50% of humic acids in Baltic Sea water are of allochthonous origin. The terrigenous humus undergoes flocculation and is very quickly removed from the water. This could explain the very high mean value of the yellow substance absorption spectrum slope coefficient and its rapid decrease in river plume waters. Another process which affects the yellow substance distribution in the sea, and which should be considered in any analysis of DOM dynamics, is bacterial decomposition and utilisation. Zweifel *et al.* (1995) noted that bacterial utilisation of DOM is a very important factor in seasonal DOM concentration dynamics in coastal systems. This process intensifies in the presence of nutrients.

A good number of papers describe the spatial and temporal variability of the yellow substance absorption field measured by fluorescence in Danish coastal waters, and in the Skagerrak and Kattegat. (Højerslev, 1989; Karabashev, 1992; Karabashev *et al.*, 1993). The conclusions reached in these papers might be misleading owing to the difference in time scale. On a short timescale (from a day to a week), the yellow substance absorption fields are very variable, by a factor of up to 6 (Karabashev), but when the timescale is several years long, the absorption field shows stability (Højerslev). Our results could support both conclusions because we observed very considerable variability during the cruise programme, but when analysed together the results oscillate around the mean values. These oscillations are due to the hydrological conditions in the southern Baltic. This is discussed by Sagan (1991) and Olszewski (1992), who describe the fluctuation in the attenuation coefficient, with its spring maximum and winter minimum.

6. Conclusions

The results of this research is of a preliminary nature. The small timescale of the observations has enabled us to reach certain conclusions about the spatial and temporal variability pattern. The results of other workers support our findings. The extensive data set has enabled a satisfactory analysis of the statistical distribution of data to be made.

The most important conclusions are:

- The statistical distribution of values of a_y ($\lambda = 400$ nm) is log-normal and the statistical distribution of the slope coefficient is nearly normal. The most probable yellow substance absorption spectrum which could be measured in the southern Baltic would be characterised by a value of a_y ($\lambda = 400$ nm) in the 0.4–1.6 m^{-1} range, and the value of the slope coefficient will lie in the 0.014–0.022 range. The lowest mean absorption coefficients were recorded in open-sea waters, intermediate values in the coastal zone, and the highest values in bay waters.
- Comparison of the statistical distribution of the slope coefficient with the absorption properties of selected fractions of marine humus shows that fulvic acids are the dominant such fraction in the southern Baltic. The humic acid fraction is present in river water plumes and can significantly change the properties of the absorption field in the region influenced by it.
- The temporal variability of this parameter tends to oscillate around the mean values. This oscillation is obvious in the case of the absorption coefficient, less so in the case of the slope coefficient. The highest values of the absorption coefficient in the surface layer of Baltic Sea water are recorded in spring and summer, the lowest in winter.
- The spatial distribution of a_y ($\lambda = 400$ nm) in the surface layer of Baltic Sea water shows that during the investigation period the lowest values of a_y were recorded offshore. A field of increased absorption was usually found near river mouths. The horizontal range of such an increased absorption field was small and decreased with distance from the source (river).

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References

- 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, 43–53.
- Carder K. L., Steward R. G., Harvey G. R., Ortner P. B., 1989, *Marine humic and fulvic acids. Their effect on remote sensing of ocean chlorophyll*, *Limnol. Oceanogr.*, 34, 68–81.
- Carder K. L., Hawkes S. K., Baker K. A., Smith R. C., Steward R. G., Mitchell G., 1991, *Reflectance model for quantifying chlorophyll a in the presence of productivity degradation products*, *J. Geophys. Res.*, 96 (C11), 20599–20611.
- Darecki M., Olszewski J., Kowalczyk P., 1994, *Spectral characteristics of the diffusive reflection coefficient in southern Baltic – the latest experimental studies*, *Proc. 19th Conf. Baltic Oceanogr.*, *Inst. Oceanol.*, Sopot, 137–148.
- Darecki M., Olszewski J., Kowalczyk P., 1995, *Preliminary study of the spectral characteristics of the upward radiance field in the surface layer of the Baltic. Empirical algorithm for remote detection of chlorophyll concentration*, *Stud. i Mater. Oceanol.*, 68, 27–49.
- Dera J., 1992, *Marine physics*, Elsevier, Amsterdam–Oxford–New York–Tokyo, 516 pp.
- Diebel-Langohr D., Doerffer R., Reuter R., Dörre F., Hengstermann T., 1986, *Long-term stability of gelbstoff concerning its optical properties*, [in:] *The influence of yellow substances on remote sensing of seawater constituents from Space*, Rep. ESA, Contract No. RFQ 3–5060/84/NL/MD, GKSS Res. Centre, Geesthacht.
- Doerffer R., Fischer J., 1994, *Concentrations of chlorophyll, suspended matter, and gelbstoff in case II waters derived from satellite coastal-zone color scanner data with inverse modeling methods*, *J. Geophys. Res.*, 99 (C4), 7457–7466.
- Højerslev N. K., 1974, *Inherent and apparent properties of the Baltic*, Rep. Inst. Phys. Oceanogr., Univ. Copenhagen, 24.
- Højerslev N. K., 1988, *Natural occurrences and optical effects of Gelbstoff*, Rep. Inst. Phys. Oceanogr., Univ. Copenhagen, 50.
- Højerslev N. K., 1989, *Surface water-quality studies in the interior marine environment of Denmark*, *Limnol. Oceanogr.*, 34, 1630–1639.
- Jerlov N. G., 1976, *Marine optics*, Elsevier, Amsterdam–Oxford–New York–Tokyo, 194 pp.

- Kalle K., 1966, *The problem of the Gelbstoff in the sea*, Mar. Biol. Ann. Rev., 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 Kattegat*, Oceanol. Acta, 15 (3), 255–259.
- Karabashev G. S., Khanaev S. A., Kuleshov A. F., 1993, *On the variability of 'yellow substance' in the Skagerrak and the Kattegat*, Oceanol. Acta, 16 (2), 115–125.
- Kirk J. T. O., 1994, *Light and photosynthesis in aquatic ecosystems*, 2nd ed., Cambridge Univ. Press, Cambridge, 509 pp.
- Nyquist G., 1979, *Investigation of some optical properties of seawater with special reference to lignin sulfonates and humic substances*, Ph. D. thesis, Dep. Ann. Mar. Chem., Göteborg Univ., Göteborg.
- Olszewski J., Sagan S., Darecki M., 1992, *Spatial and temporal changes in some optical parameters in the southern Baltic*, Oceanologia, 33, 87–103.
- Pempkowiak J., 1988, *The distribution, origin and properties of humic acids in the Baltic Sea*, Ossolineum, Wrocław, 146 pp., (in Polish).
- 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 material*, Limnol. Oceanogr., 26, 671–689.
- Reuter R., Diebel-Langohr D., Doerffer R., Dörre F., Haard H., Hengstermann T., 1986, *Optical properties of Gelbstoff*, [in:] *The influence of yellow substances on remote-sensing of seawater constituents from Space*, Rep. ESA, Contract No. RFQ 3–5060/84/NL/MD, GKSS Res. Centre, Geesthacht.
- Reuter R., Albers W., Brandt K., Diebel-Langohr D., Doerffer R., Dörre F., Hengstermann T., 1986, *Ground truth techniques and procedures for Gelbstoff measurements*, [in:] *The influence of yellow substances on remote-sensing of seawater constituents from Space*, Rep. ESA, Contract No. RFQ 3–5060/84/NL/MD, GKSS Res. Centre, Geesthacht.
- Robinson I. S., 1985, *Satellite oceanography*, Ellis Horwood Ltd. Publishers, Chichester, 455 pp.
- Sagan S., 1991, *Light transmission in the waters of the southern Baltic Sea*, Inst. Oceanol. PAN, Sopot, 149 pp., (in Polish).
- Samuła-Koszalka T., Woźniak B., 1979, *The share of particular seawater component in the light attenuation and analysis of the absorption spectra of yellow substances taking Bay of Gdańsk as an example*, Stud. i Mater. Oceanol., 26, 203–216, (in Polish).
- Sathyendranath S., Prieur L., Morel A., 1989, *A three-component model of ocean colour and its application to remote sensing of phytoplankton pigments in coastal waters*, Int. J. Remote Sens., 10 (8), 1373–1394.

- Spitzky A., Ittekkot V., 1986, *Gelbstoff: an uncharacterised fraction of dissolved organic carbon*, [in:] *The influence of yellow substances on remote-sensing of seawater constituents from Space*, Rep. ESA, Contract No. RFQ 3-5060/84/NL/MD, GKSS Res. Centre, Geesthacht.
- Tassan S., 1994, *Local algorithms using SeaWiFS data for the retrieval of phytoplankton, pigments, suspended sediments and yellow substance in coastal waters*, *Appl. Opt.*, 33 (12), 2369-2378.
- Zweifel U. L., Wikner J., Hagström Å., Lundberg E., Norrman B., 1995, *Dynamics of dissolved carbon in a coastal ecosystem*, *Limnol. Oceanogr.*, 40, 299-305.