The application of the optical classification of waters in the Baltic Sea (Case 2 Waters)

OCEANOLOGIA, No. 37 (2)
pp. 285–297, 1995.
PL ISSN 0078–3234

Bio-optical classification
of natural waters
Diffuse attenuation
coefficient for irradiance
Baltic Sea

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Abstract

In this study, the spectral values of the diffuse attenuation coefficients for downwelling irradiance $K_d(\lambda)$, which were measured in the visible spectrum in the Baltic Sea, are compared with similar spectra obtained theoretically on the basis of the classification of the optical properties of Case 1 Waters developed by Woźniak. The analysis of 481 pairs of spectra $K_d(\lambda)$ shows that in order to use this classification for a description of Baltic waters, it is necessary to introduce into it a new component $\Delta K(\lambda)$ [m^{-1}], which may be approximated by

$$\Delta K(\lambda) = 0.0716\ e^{-0.0117(\lambda-550)},$$

where λ [nm] is the wavelength.
The form of the equation approximating the $\Delta K(\lambda)$ spectrum and the value of the exponential factor suggest that the term $\Delta K(\lambda)$ is related to a high concentration of allogenic yellow substance in the Baltic Sea.

1. Introduction

The dependence of the optical properties of seawater on the composition and properties of substances found therein has been the subject of intensive study, especially as satellite images of large sea and ocean areas are obtainable. Many authors have been engaged in the classification of seawaters with respect to their optical properties. These classifications have been reviewed by Woźniak and Pelevin (1991), who also presented a new water classification developed by Woźniak, and compared it with some classifications which were well known at that time, *i.e.* those by Jerlov (1976, 1978), Baker and Smith (1982), Pelevin and Rutkovskaya (1977).

Like the others, the Woźniak classification uses the spectra of the diffuse attenuation coefficient for downwelling irradiance $K_d(\lambda)$ to describe the optical properties of water

$$K_d(\lambda) = K_w(\lambda) + K_{pl}(\lambda) + K_\Delta(\lambda), \tag{1}$$

where
$K_w(\lambda)$ – attenuation by pure seawater,
$K_{pl}(\lambda)$ – attenuation by phytoplankton pigments,
$K_\Delta(\lambda)$ – attenuation by other optically active seawater components of autogenic origin.

This classification assumes a constant $K_w(\lambda)$ spectrum determined from measurements in the Sargasso Sea, whereas $K_d(\lambda)$, $K_{pl}(\lambda)$ and $K_\Delta(\lambda)$ spectra are calculated from the equation with the variable chlorophyll *a* concentration C_a

$$K_d(\lambda) = K_w(\lambda) + C_a\{C_1(\lambda)\exp[-a_1(\lambda)C_a] + k_{d,n}(\lambda)\}, \tag{2}$$

$$K_{pl}(\lambda) = C_a\{C_2(\lambda)\exp[-a_2(\lambda)C_a] + k_{c,n}(\lambda)\}, \tag{3}$$

$$K_\Delta(\lambda) = K_d(\lambda) - [K_{pl}(\lambda) + K_w(\lambda)]. \tag{4}$$

The only variable describing the $K_d(\lambda)$, $K_{pl}(\lambda)$ and $K_\Delta(\lambda)$ spectra is C_a; all other parameters – $K_w(\lambda)$, $C_1(\lambda)$, $C_2(\lambda)$, $a_1(\lambda)$, $a_2(\lambda)$, $K_{d,n}(\lambda)$, and $K_{c,n}(\lambda)$ – are constant. Their updated values are presented in Tab. 2 of Woźniak *et al.* (1992).

In oceanology, seawaters have been divided into two groups with regard to their optical properties:

- Case 1, in which the most important processes occurring in a specific sea area are related to the phytoplankton, and the concentrations of optically active (autogenic) seawater components are closely correlated with chlorophyll concentration;
- Case 2, in which external (allogenic) components additionally appear in the ecosystem in such quantities that the relationships present in Case 1 Waters cease to be effective (Morel and Prieur, 1977). Obviously, these admixtures can influence biological processes in the area and change their parameters, including chlorophyll concentration. It was found, however, that at least some of these admixtures have a specific influence on the optical properties of seawater. For this reason, modelling using classifications based on C_a, the only variable parameter, does not yield satisfactory results. Taking this into consideration in the description of Case 2 Waters, it is necessary to add a component $\Delta K(\lambda)$ related to the presence of these additional admixtures.

This study aims to the determine of the values of $\Delta K(\lambda)$ that are characteristic of the Baltic Sea by calculating the differences between the values of $K_{d,m}(\lambda)$ obtained by measurement and the values of $K_{d,t}(\lambda)$ derived from the Woźniak classification for the simultaneously measured chlorophyll concentration.

2. Material and calculations

The material used in the calculations was taken from six cruises and complete experiments carried out between the years 1980 and 1990:

- the cruise of r/v 'Profesor Siedlecki' in July 1980 (Koblentz-Mishke *et al.*, 1985);
- the cruise of r/v 'Akademik Kurchatov' in May and June 1984 (Koblentz-Mishke and Belayeva, 1987);
- the PEX'86 experiment, in April and May 1986, observations during the spring bloom, data obtained from r/v 'Oceania' (ICES 1989)[1];
- the Sopot'87 experiment, in May 1987, also during the spring bloom, data originating from r/v 'Oceania' (Oceanologia, 28);
- the Sopot'89 experiment, in May 1989, r/v 'Oceania' (data not published);
- the cruise of r/v 'Professor Shtokman' in February 1990 (data not published).

The area covered by the investigation and the positions of the experimental study stations are shown in Fig. 1.

In all these cruises, the overall concentration of chlorophyll *a* (together with pheophytin *a*), *i.e.* C_a = chl a + *pheo.*, was determined by a standard spectrometric method (SCOR–UNESCO, 1966). The spectra of diffuse attenuation coefficients for downwelling irradiance were measured by an apparatus constructed in the Institute of Oceanology of the Polish Academy of Sciences (Woźniak and Montwiłł, 1973). During the cruise of r/v 'Profesor Siedlecki' in 1980, K_d was measured for 12 different wavelengths of light in the 400–700 nm range (425, 465, 475, 500, 525, 535, 550, 580, 600, 620, 660, 680 nm). During the other cruises the spectrophotometer had 8 interference filters for the following wavelengths: 400, 425, 465, 525, 535, 580, 620, 680 nm.

[1]Baltic Sea Patchiness Experiment PEX'86, [in:] Cooperative Research Report, ICES, 1989.

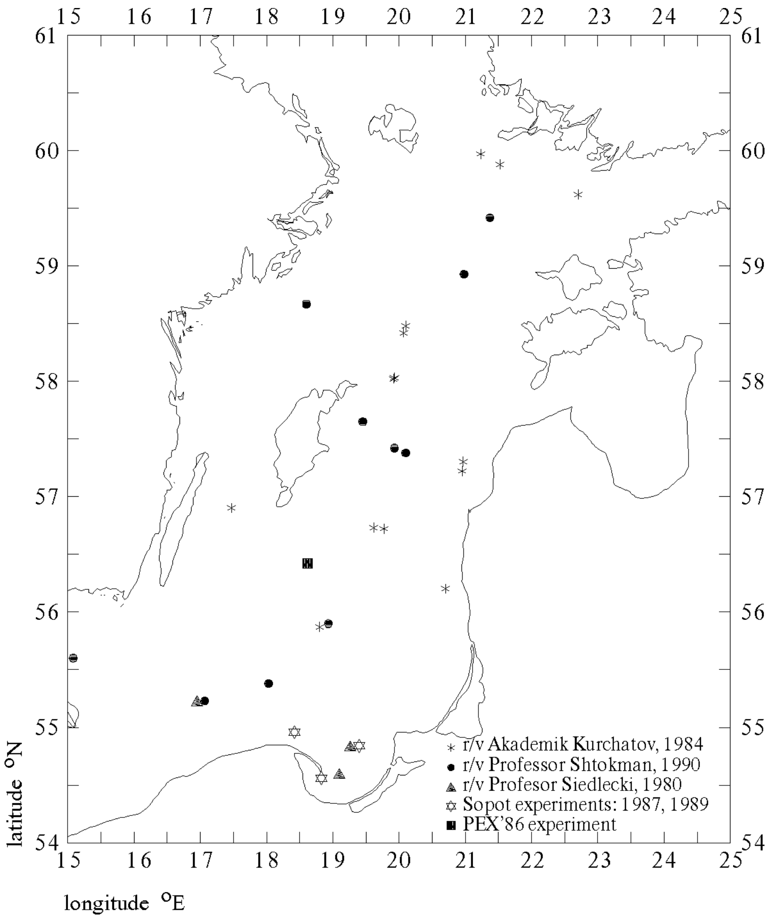


Fig. 1. Positions of the experimental stations

Because the measurements of $K_d(\lambda)$ and C_a were not usually performed simultaneously, only those samples for which the time span between the measurements was small, *i.e.* did not exceed one hour, were selected for analysis. The $K_d(\lambda)$ values measured during most of the cruises are given for 2–10 m thick layers (most often 5 m); in the case of the data from 1980 (cruise of r/v 'Profesor Siedlecki'), the average $K_d(\lambda)$ values for 0–30 m high columns of water are presented. The average chlorophyll concentration in the corresponding layer, calculated from the $C_a(z)$ profile, was applied to further calculations.

Next, the $K_{d,t}$ spectrum, corresponding to Case 1 Waters, and the difference

$$\Delta K(\lambda) = K_{d,m}(\lambda) - K_{d,t}(\lambda), \tag{5}$$

were calculated.

Each of the ΔK spectra obtained was approximated by the exponential curve

$$\Delta K(\lambda) = B\ e^{S(\lambda-\lambda_0)}, \tag{6}$$

where $\lambda_0 = 550$ nm and $B = \Delta K(\lambda_0)$.

Approximations were performed for values of λ in the spectral range 400–580 nm. $K_d(\lambda)$ measurements for red light were not taken into consideration owing to their poorer accuracy.

3. Results and discussion

Examples of discrepancies between the values of $K_d(\lambda)$ predicted by the Woźniak classification (corresponding to Case 1 Waters) and those measured in the Baltic Sea are shown in Fig. 2. They present a mean of all the

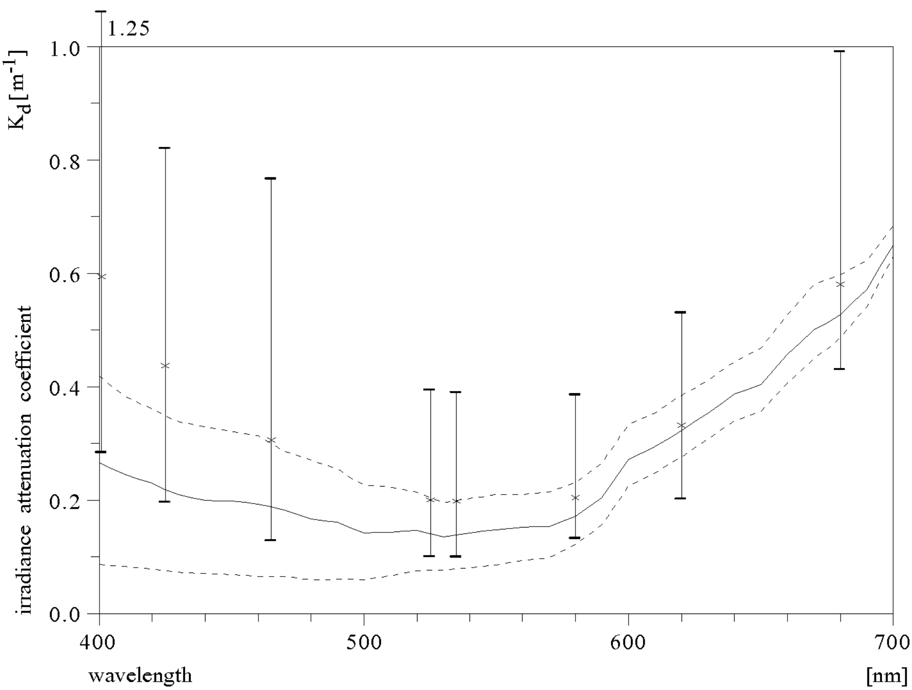


Fig. 2. The spectra of the diffuse attenuation coefficient for downwelling irradiance: solid and dashed lines: spectra calculated from the Woźniak classification (eq. (2)) for mean, maximum and minimum chlorophyll *a* concentrations respectively in the data set from the r/v 'Akademik Kurchatov' cruise in 1984; vertical lines: the variability range of measured $K_d(\lambda)$ values in the same data set; the mean value for each wavelength is indicated by a cross

measurements of $K_d(\lambda)$ taken for analysis from the cruise of r/v 'Akademik Kurchatov' in 1984 for each of eight wavelengths, and a maximum and minimum value of K_d for every wavelength in this data set. The K_d spectrum calculated from the Woźniak classification for the average chlorophyll concentration is represented by the solid line, whereas the dashed lines correspond to K_d spectra calculated for the maximum and minimum chlorophyll concentrations in this set of data. It can be seen that the discrepancies between the data compared are small in the yellow portion of the spectrum, but increase significantly towards the violet end of the spectrum.

Table 1. The mean values and standard deviations σ of parameters describing the ΔK spectra and chlorophyll a concentrations in the Baltic (the sample numbers are given in the last column)

Cruises and experiments	S	σS	B	σB	C_a	σC_a	n
'Profesor Siedlecki' July 1980	–0.01254	0.00272	0.0699	0.0206	2.72	2.03	9
'Akademik Kurchatov' May, June 1984	–0.01217	0.00406	0.0648	0.0446	1.79	0.9	58
PEX'86 April, May 1986	–0.01229	0.00371	0.0689	0.0349	3.4	1.75	185
Sopot'87 May 1987	–0.01636	0.00455	0.0772	0.0598	10.19	5.08	33
Sopot'89 May 1989	–0.01115	0.00352	0.0580	0.0333	3.88	1.78	76
'Professor Shtokman' February 1990	–0.00973	0.00244	0.0862	0.0483	0.53	0.21	120
surface layer (all cruises) z < 10 m	–0.01260	0.00341	0.0712	0.0446	3.63	3.66	232
deep waters (all cruises) z > 10 m	–0.01088	0.00413	0.0721	0.0412	2.44	2.09	240
Gulf of Gdańsk (all cruises)	–0.01158	0.00428	0.0875	0.0505	6.83	5.7	43
open sea (all cruises)	–0.01174	0.00382	0.0702	0.0413	2.63	2.27	437
all data	–0.01174	0.00387	0.0716	0.0426	3.01	3.01	481

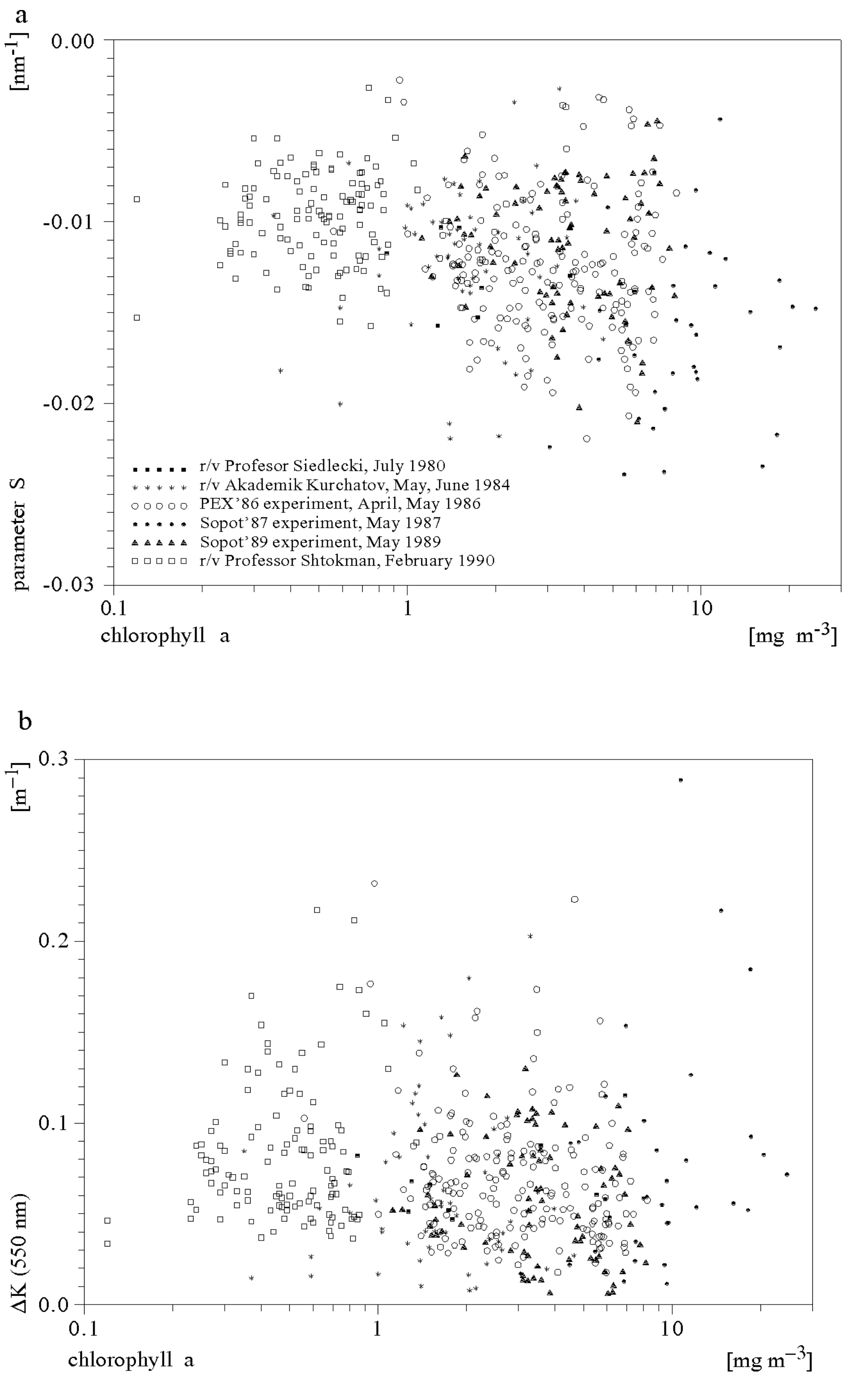
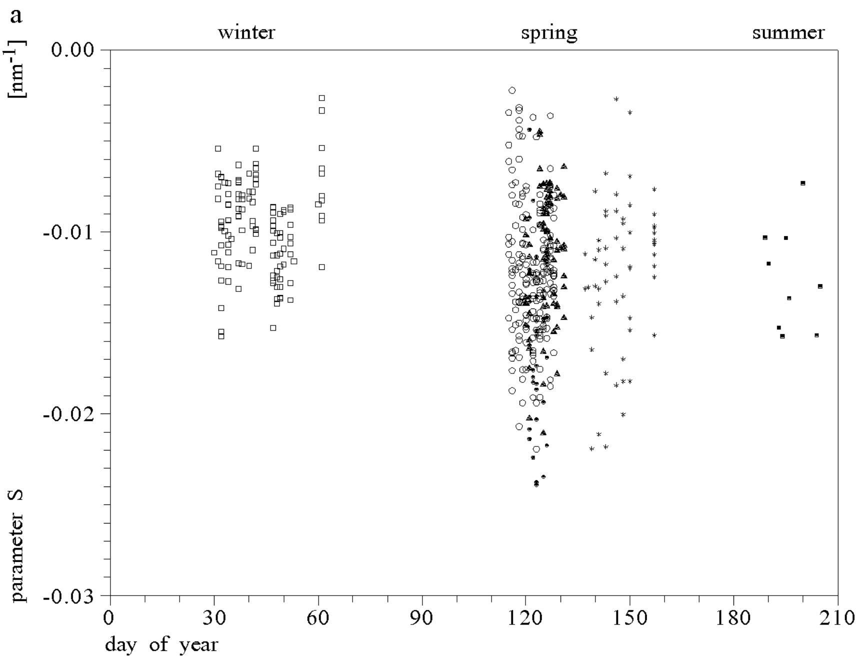


Fig. 3. The relationship between the parameters approximately describing the $\Delta K(\lambda)$ spectra and the chlorophyll *a* concentration: exponential slope S *vs.* chlorophyll *a* concentration (a), $\Delta K(550\text{ nm})$ *vs.* chlorophyll *a* concentration (b)



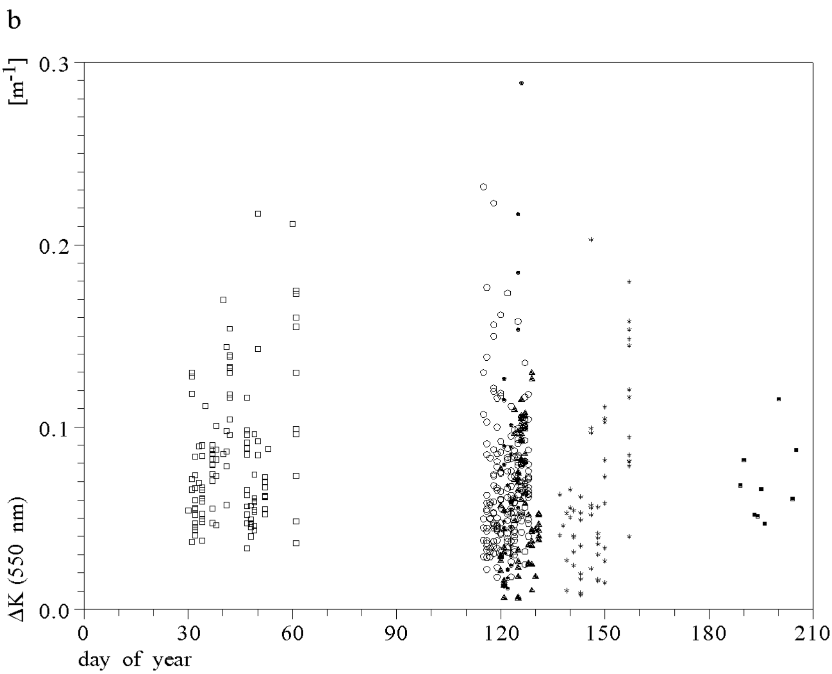


Fig. 4. Seasonal changes in the parameters describing $\Delta K(\lambda)$: exponential slope S *vs.* day of year (a), $\Delta K(550\text{ nm})$ *vs.* day of year (b)

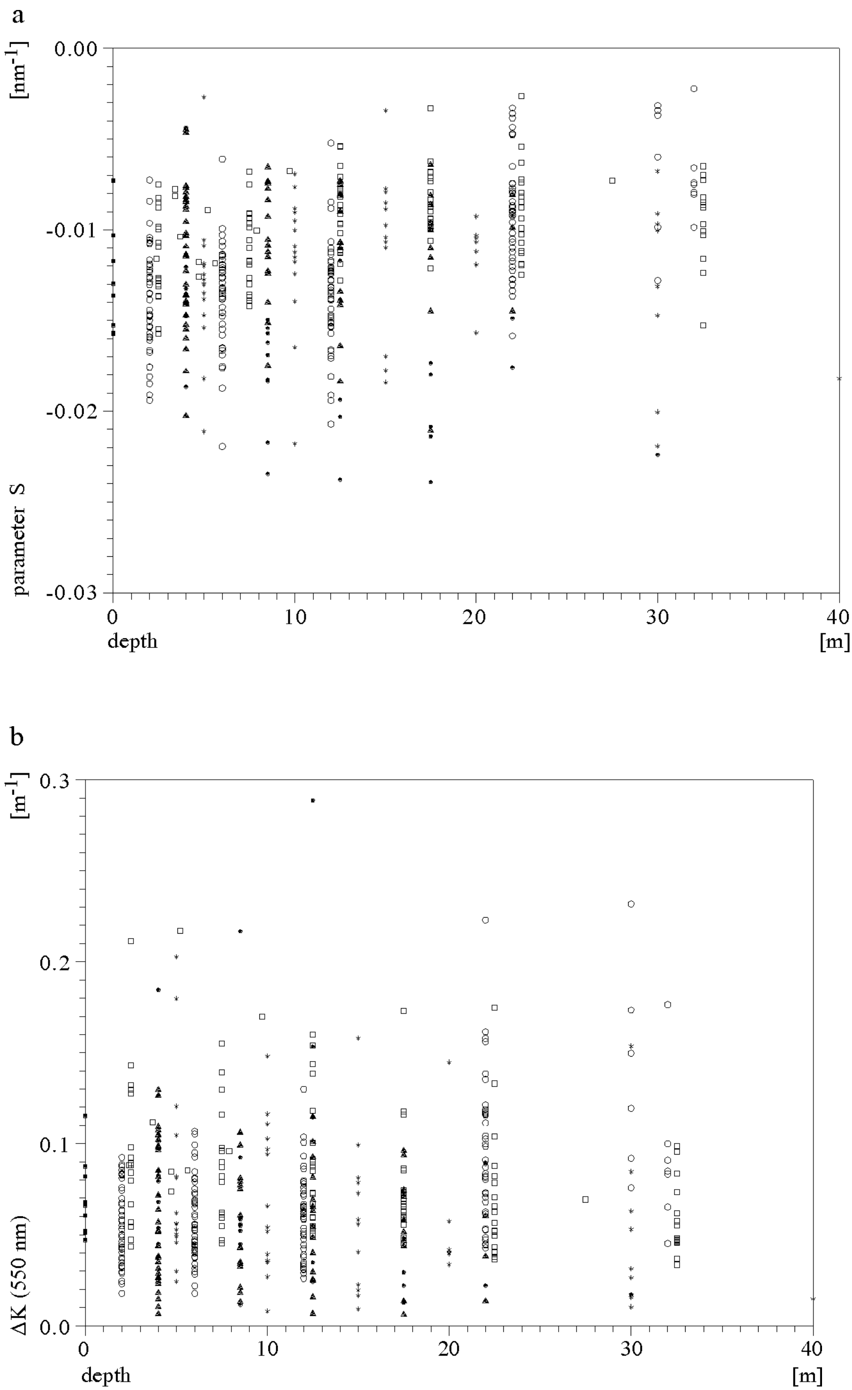


Fig. 5. The parameters of $\Delta K(\lambda)$ approximation versus depth: exponential slope S *vs.* depth (a), $\Delta K(550\text{ nm})$ *vs.* depth (b)

Table 2. Some example exponential slopes of absorption spectra of humic acids, fulvic acids and natural yellow substance from the Baltic Sea

Origin	Exponential slope S [nm^{-1}]	Literature
	isolated humic acids	
soil	–0.0090	Steumer, 1975; Zepp and Schlotzhauer, 1981
sea (Gulf of Mexico)	–0.0110 ± 0.00012	Carder *et al.*, 1989
	isolated fulvic acids	
soil	–0.011	Zepp and Schlotzhauer, 1981
river water (Mississippi mouth)	–0.0194 ± 0.00044	Carder *et al.*, 1989
sea (Gulf of Mexico)	–0.0184 ± 0.00166	Carder *et al.*, 1989
	natural yellow substances from the Baltic Sea	
Baltic and North Sea	–0.018	Kalle, 1966
coastal zone	–0.014	Nyquist, 1975
	–0.014	Lundgren, 1976
Gulf of Gdańsk	–0.00961 ± 0.00525	Samuła-Koszałka and Woźniak, 1979
	–0.018	Bricaud *et al.*, 1981

The spectral relationship of the difference ΔK may be described by the exponential curve (eq. (6)). Tab. 1 gives values of the approximation parameters B and S, which were determined and averaged for selected sub-sets of, and the whole of, the analysed material.

The graphs of both approximation parameters plotted against the chlorophyll a concentration are presented in Fig. 3. The scatter of points indicates the lack of a relationship, which tallies with the assumed meaning of the factor ΔK. The exponential factor S, however, is slightly larger for lower chlorophyll concentrations. Fig. 4 presents both parameters as a function of the season of the year. One can see here that the spectra are less steep for the data from the winter cruise (see also Tab. 1). It may be assumed that the variation in ΔK spectra is the result of the seasonal changes in the properties and concentration of allogenic factors, and the apparent relationship between chlorophyll concentration and the exponential factor S is due to the reduced chlorophyll concentrations in winter in comparison to those in spring or summer.

Fig. 5 shows both approximation parameters as a function of depth; here, too, it is difficult to observe any relationship.

Many articles on the modelling of the optical properties of seawaters assume a division of the factors influencing these properties into basic categories: pure water, phytoplankton pigments, yellow substance and suspensions (Carder *et al.*, 1991; Smith *et al.*, 1989; Sathyendranath *et al.*, 1989). Spectra of yellow substance absorption are usually described by an exponential curve (*e.g.* Kalle, 1966). Tab. 2 gives example values of the exponential approximation of yellow substance absorption spectra measured in the Baltic Sea, and also the spectra of fulvic and humic acids of various origins. As shown, the experimental slope varies depending on the sample origin. The values of the exponential factors of the ΔK spectra obtained here are quite similar to the values of the exponential factors, S, typical of terrestrial yellow substance. This suggests that allogenic yellow substance, existing in large concentrations in the Baltic Sea, is responsible for the magnitude of $\Delta K(\lambda)$ values.

4. Conclusions

It is a very complicated task to examine precisely the influence of yellow substance on the optical properties of the Baltic Sea. Because parameters describing the ΔK spectra display a small statistical scatter and are seemingly independent of depth and season, the following may be a first approximation:

$$\Delta K(\lambda) = 0.0716\ e^{-0.0117(\lambda-550)}. \tag{7}$$

At this stage, the approximation of K_d spectra for the Baltic Sea by using the Woźniak classification and $\Delta K(\lambda)$ correction may be useful in modelling over large time and space scales, *e.g.* for the determination of the annual primary production. However, further investigations are required in order to enable the variability and regionalisation of the ΔK spectra to be incorporated with precision.

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