

Seasonal Changes of Light Attenuation Coefficient in Selected Points of the Oder River in the Szczecin Region, Poland

B. Pawlak*, R. Gąsowski, A. Banaszak, A. Andrzejewska

Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland

Received: 12 July, 2002

Accepted: 13 September, 2002

Abstract

This paper contains a description of seasonal changes of light attenuation coefficient in selected points of the Oder River in the Szczecin region. It demonstrates that applying a modified and approximate formula for light attenuation coefficient is an effective method for interpreting changes. The formula was used earlier for analysis of time changes of roily oil products. In all (except two) control points and seasons it gives good approximation of empirical values.

Keywords: light attenuation coefficient

Introduction

Examination of physical processes in water environments allows searching for new methods of comprehensive application of waters for human use, and above all of a limitation of ecological threats to Earth.

Water erosion of soils is one of these threats. An average amount of suspensions taken away every year with the Vistula and Oder Rivers into the Baltic Sea is estimated to be about 10 mln tons. Fertilizer components corresponding to 100,000 tons of superphosphate and 80,000 tons of potassium salt lixiviated out of soil get into rivers together with the suspensions. Degradation of soils can be stopped, chemical contamination of waters can be lowered and water containers can be protected against filling up with gravel and slime by getting under the control water erosion. As a consequence the potential height of a flood wave can be lowered. Estimation of the amount of suspensions in a river's waters and its seasonal changes is therefore very

important from ecological, agricultural and hydrotechnical points of view.

Water suspensions affect absorption and scattering of light in water areas. Estimation of its relative content and its changes is possible by measuring light attenuation coefficient (with respect to clear water). It is also possible to apply the light attenuation coefficient as an indicator of content of dissolved substances in water areas [3] as well as for examination of content and size of suspensions [1,6]. The spectrum of light attenuation coefficient $c(\lambda)$ characterizes and discriminates waters in different areas. It also allows for estimation of effectiveness of radiation transportation as an optical signal in water in a given direction. Therefore it determines underwater visibility conditions.

The purpose of the present paper is to show that modification of the approximate formula for light attenuation coefficient used for examination of evolution of roily oil products in laboratory conditions [7] can be applied for examination of seasonal changes of level and of kind of contaminations in the dispersed form in natural water areas. The method was applied for the first time for monitoring contaminations of the Oder.

*Corresponding author; e-mail: pawlak@univ.szczecin.pl

Method of Experimental Examinations

The performed experiments consisted of collecting water samples from the Oder (its surface) every two weeks from 20.10.98 to 23.03.99. Localization of places from which samples were collected is illustrated on Figure 1. Next, the samples were analyzed spectrophotometrically using SPECORD M-40 in the range of wavelengths 260-800 nm. Quartz trays (S 50.01) 5 cm long were used for the examinations. Distilled water was a comparative medium. The period of collection of samples was divided into four seasons:

Season I	20.10.98 – 18.11.98
Season II	01.12.98 – 30.12.98
Season III	12.01.99 – 23.02.99
Season IV	09.03.99 – 23.03.99.

To calculate the light attenuation coefficient $c_z(\lambda)$ the following relation was used [2]:

$$c_z(\lambda) = c(\lambda) - c_w(\lambda) = -\frac{1}{r} \ln \frac{1}{T} \quad (\text{m}^{-1}) \quad (1)$$

where:

$c_z(\lambda)$ - contamination attenuation coefficient

$c(\lambda)$ - total light attenuation coefficient,

$c_w(\lambda)$ - water attenuation coefficient,

λ - wavelength of light,

r - length of a tray,

T - transmittance.

From (1) it follows that the measured value of light attenuation coefficient depends only on the properties of

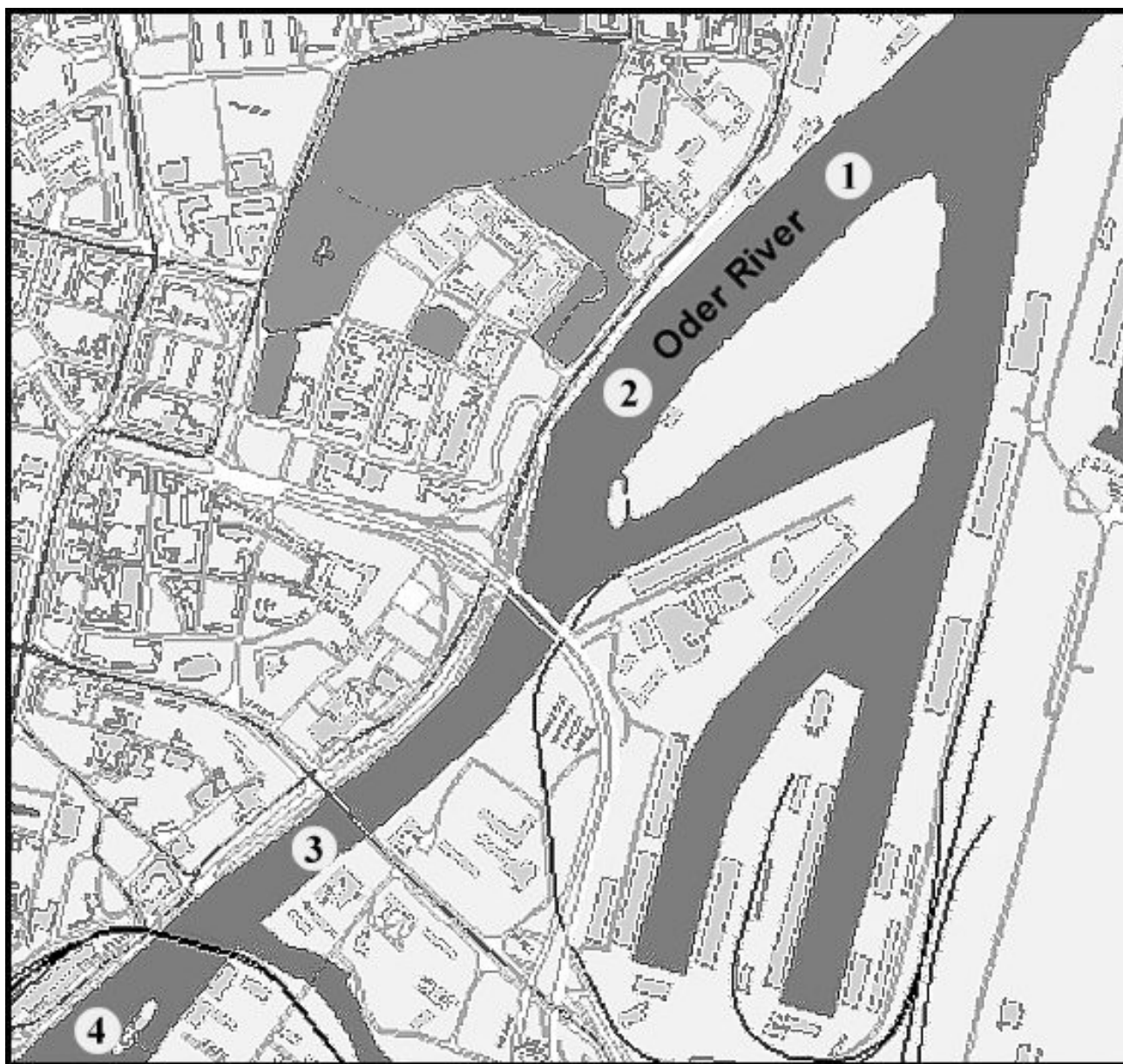


Fig. 1. Places of collection of samples in the Oder.

substances suspended or dissolved in water. Concentration, content and sizes of suspensions depend on rainfalls and snowfalls, the phenomenon of return of river waters, the structure of a river's bottom and neighbouring regions and also on location of local industry and on the structure of the whole Szczecin agglomeration. All these factors can affect the differentiation of results of measurements at the different points.

Application of Approximate Formula in the Analysis

In the papers of Dera, Pawlak [4]; Kopeć, Pawlak [7]; and Pawlak [8] for the classification of spectra of light attenuation coefficient and for the estimation of stability of population of suspensions and emulsions the approximate formula was used:

$$c(\lambda) = A \exp(-\alpha\lambda) + B|\lambda + \beta|^{-1} + D, \quad (2)$$

where λ is a light wavelenght, α , β , A , B , D are constants determined from empirical data with the help of least square method. While using these formulae different dimensions of constants A and B and different values of constants α , β are not convenient. Therefore, in this paper the formula will be used in a modified form:

$$c(\lambda) = A \exp(-\lambda/\alpha) + B \left| 1 + \frac{\lambda}{\beta} \right|^{-p} + D, \quad (3)$$

where A , B , D have dimensions the same as c and are smaller numbers, while the factors dependent on λ are dimensionless. p is usually equal to 1. Exceptionally other values are more advantageous. It turns out that the sum of squared deviations depend linearly A , B , D . The minimalization of two variables can be solved using earlier described methods [7,8]. If it is not sufficient, the optimum exponent p can be determined by testing. If the optimum parameters of the function (3) are known then usually different properties of its diagram can be determined easily. And if it approximates distribution well, then the properties of spectral distribution are also well approximated and the physical properties of population of the contaminations can be found.

In natural water areas in most cases we have

$$(I) \quad A > 0, B > 0.$$

If $\beta > 0$, then the function $C(\lambda)$ is bounded decreasing and convex in $(-\infty, \infty)$.

If $I_p = \langle \lambda_p, \lambda_k \rangle$ is a measurement interval and $-\beta < \lambda_p$, then the function $C(\lambda)$ is bounded, decreasing and convex in I_p and in $(-\infty, \lambda_p)$ has a vertical asymptote (for $\lambda = -\beta$) on the left from I_p . If $\lambda_k < -\beta$, then the function $C(\lambda)$ is convex in I_p but does not possess a minimum.

From the examinations performed in emulsions of roily oil products [7,8] it follows that this case takes

place in stable states which become established some time after stopping perturbations of the medium (strong turbulent motions) depending on the composition of dispersing medium and on the conditions of storing the sample. Appearance of an asymptote indicates that there exists a band of strong selective attenuation in ultraviolet and sometimes in infrared. For $D < 0$ one must assume for preserving physical sense of the formula (3) that $C(\lambda) = 0$ for $\lambda \geq \lambda_0$, which means that in this region of the spectrum dispersing substance has no effect on attenuation in the medium.

$$(II) \quad A, B \text{ have opposite signs, } \beta > 0.$$

The function $C(\lambda)$ remains unbounded, but may possess zeros, extrema or inflection points. In the case of emulsion such situation characterizes transient states appearing immediately after or a short time after ceasing perturbation. The extrema flatten in time and the curve becomes monotonic. In natural water areas this case happens rarely.

$$(III) \quad A, B \text{ have opposite signs, } \beta < 0.$$

In the interval $(-\infty, -\beta)$ the function $C(\lambda)$ is monotonic but it may possess zeros or an inflection point. In the interval $(-\beta, \infty)$ there may exist extrema, zeros or inflection points. There exists an asymptote (singular point) for $\lambda = -\beta$. The points may be located inside or outside the measurement interval. This case which is exceptional for roily oil products emulsions requires for natural water areas more detailed analysis applying additional information about the water area.

The accuracy of the approximation is very good in case (I), (the sum of the squared deviations for 11 measurements of the order of 5×10^{-2}), in case (III) usually much worse, especially when the asymptote lies inside the measurement interval.

The mineral suspensions are subjected to similar changes in emulsions as a result of turbulent motions. Hence we think that the above interpretation can also be applied for natural water areas with small algae contamination.

Because of the regular form of spectral curves for comparison purposes it is useful to apply a synthetic attenuation indicator being an integral mean value with respect to the distribution of light attenuation coefficient:

$$\overline{C(\lambda)} = \frac{1}{\lambda_k - \lambda_p} \int_{\lambda_p}^{\lambda_k} C(\lambda) d\lambda \approx \frac{1}{\lambda_k - \lambda_p} \sum_{i=1}^{n-1} C(\lambda_i) (\lambda_{i+1} - \lambda_i) \quad (4)$$

For equal distances between subsequent values of λ it does not differ essentially from the usual mean value.

According to the Mie theory for finite number of scattering particles with diameters D_i and number $N = \sum n_i$ in a

unit volume we have

$$C(\lambda) = K \sum n_i D_i Q(\pi D_i / \lambda) \quad (5)$$

K is a constant depending on the choice of units and the refraction index of the medium. Q is a cross-section for the scattering. With the small differentiation of the sample with respect to particle sizes $D_i \cong D$ number of particles in a unit volume, for which this mean value is the estimate (for comparison), is a main differentiating element.

Results of Measurements and Their Analysis

Diagrams of the spectrum of light attenuation for all seasons and measurement points are similar. All the curves decrease and have a large falldown at the beginning of the measurement interval ($[c(\lambda_1) - c(\lambda_2)]/(\lambda_2 - \lambda_1)$) and a small falldown at its end. However, there exist remarkable differences for the curves in the same as well as in different seasons.

Season I

Essential parameters of spectral distributions are presented in Table 1.

All the distributions are decreasing functions. In the formula (3) there is an asymptote indicating existence of a band of strong selective attenuation. Distributions at points 3 and 4 practically do not differ from one another. The spectral curves are convex, the approximation with the formula (3) is good. There exists only a slight shift of the asymptote towards the short waves, which in the diagram corresponds to smaller falldown. The mean values are almost the same, the correlation coefficient is very large (0.9998). In the interval between these points the structure of the population of the suspensions is therefore stable and practically does not change. Distribution at

point 2 is also a decreasing and convex function. An approximation with the curve (3) is very good. However, it differs significantly from the distributions at points 3 and 4. Mean values and falldown are smaller. Substantial shift of the asymptote towards short waves is a main difference. Hence there appears a change of structure of contamination. One can suppose that this is a result of increase of contamination with crude oil products possessing strong absorption bands in ultraviolet connected with intensive traffic of barges at this time of year and in this region. The curve at point 1 has a completely different character. The approximation with the formula (3) is much worse. The minimum of sum of squared deviations appears for the exponent $P=10$ (and not 1 as for remaining curves), and gives small value of the constant B.

Almost double increase of the mean value indicates remarkable increase of general number of contaminations. The curve of spectral distribution is not convex. In the formula (3) there appears an inflection ($\lambda \approx 335$ nm) which corresponds to appearance of the second negative difference in the values of measurements. The singular point and two zeros of the curve (3) lie between the second and the third measurement value. Hence, they are not visible in the diagram in which the curve is falling down with the inflection hardly remarkable. Their existence in the curve (3) allows us to conclude that in this interval there appear additionally remarkable amounts of contamination with absorption bands in visible parts of the spectrum. These can be suspensions as well as emulsions and microbes and dissolvable contamination. They probably come from harbour contamination and municipal sewage. Hence, they can contain harmful chemical contamination, e.g. salts of heavy metals and biological contamination, e.g. bacteria. This part of the Oder should be permanently monitored in this season using physical, chemical and biological methods.

Just for the illustration we presented the diagrams of spectra corresponding to points 1 and 4 (Figure 2) and Table 2 with the measured and calculated values of the light attenuation coefficient.

Table 1. Parameters of spectral distribution for four measurement points of the Oder. Season I.

Parameters	Measurement points			
	1	2	3	4
α	102.1404	54.7739	50.225	44.715
β	-375.1852	-84.61842	-178.3438	-197.4375
P	10	1	1	1
A	740.1282	4799.675	6404.326	10871.67
B	$-8.061371 \cdot 10^{-12}$	18.21305	9.850846	9.676152
D	6.511964	0.3536395	1.038819	0.6035136
$\overline{c(\lambda)}$	14.87445	7.181	9.413182	9.58609
SUK	0.7766037	$2.18626 \cdot 10^{-2}$	$3.895 \cdot 10^{-2}$	$1.141986 \cdot 10^{-2}$

α , β , A, B, D - constants, P - exponent, $\overline{c(\lambda)}$ - mean value, SUK - sum of squares.

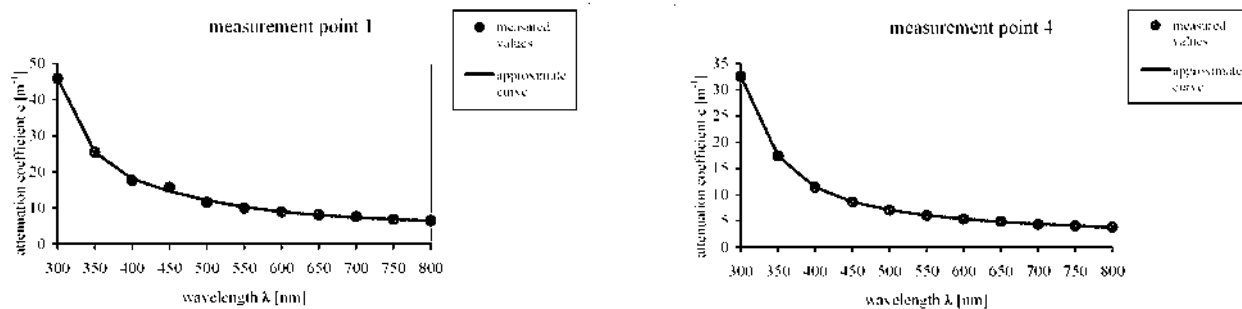


Fig. 2. Spectra of experimental and theoretical light attenuation coefficients for the first and the fourth measurement points in the Oder.

Table 2. The measured c_{zm} and calculated values c_{ob} of the light attenuation coefficient for measurement points 1 and 4.

No.	Wavelength λ (nm)	Measurement point 1		Measurement point 4	
		c_{zm} (m^{-1})	c_{ob} (m^{-1})	C_{zm} (m^{-1})	c_{ob} (m^{-1})
1	299.9	45.796	45.790	32.538	32.538
2	350.4	25.376	25.376	17.389	17.389
3	400.9	17.6	17.560	11.396	11.382
4	450	15.701	15.547	8.593	8.631
5	500.5	11.52	12.023	7.076	7.057
6	551.2	9.894	9.867	6.06	6.052
7	601.6	8.86	8.560	5.344	5.346
8	651.8	8.114	7.765	4.87	4.813
9	699.2	7.582	7.300	4.344	4.413
10	749.5	6.78	6.993	4.044	4.065
11	802.4	6.396	6.799	3.793	3.762

Season II

All measurement curves are decreasing and convex. There are no asymptotes in $(-\infty, \infty)$. The value of all parameters (except β) are similar (also mean values and the coefficient of variability are similar in spite of some differences in β parameter). This can be seen in Table 3.

One can conclude that the population of suspensions is stable with respect to the content in the whole examined interval. There are no suspensions with strong selective attenuation (crude oil products, algae). One observes neither inflow of contaminations changing optical properties of dispersion system, nor dispersion distribution of particle sizes.

Season III

Spectral distributions are very similar to the distributions in season II. Only at measurement point 1 does

there appear an asymptote in the neighbourhood of the measurement interval ($\beta = -249$ nm). It can be interpreted as an inflow of contamination with absorption band close to ultraviolet. However, in much smaller amounts than in season 1, since the spectral curve remains convex and the (mean) concentration just slightly increases.

Season IV

Now there appear similar phenomena as in season 1, however with higher intensity. The asymptotes appear for curves (3) at all measurement points. The asymptote ($\beta = -379$ nm) appears inside the measurement interval just in the second measurement point, in which the approximation of the distribution with the formula (3) is much worse. In the first measurement interval an asymptote appears close to the measurement interval in near ultraviolet ($\beta = -232$ nm), but the concentration of suspensions (mean value) increases twice. Hence there appear threats similar to the first season.

Table 3. Parameters of curves for four measurement points.

Measurement Point	Mean value $\overline{c(\lambda)}$	Variability Coefficient $v=\delta/\bar{x}$	β	Sum of squared values
1	7.22	1.07	152.38	$3.066 \cdot 10^{-2}$
2	7.19	0.94	455.84	$2.677 \cdot 10^{-2}$
3	8.8	1.11	481.14	$2.747 \cdot 10^{-2}$
4	7.98	1.09	658.31	$3.475 \cdot 10^{-2}$

δ - standard deviation, \bar{x} - mean value

Conclusions

- In the case when in the measurement interval there is no band of strong selective attenuation and the state of water area is stable, the formula (3) approximates spectral distribution of light attenuation coefficient very well not only in emulsions of crude oil products, but also in natural water areas. The curve of the spectral distribution is decreasing and convex.
- Coefficient β in formula (3) has a simple interpretation: it determines a vertical asymptote and not directly a location of a band of strong selective attenuation.
- Concentration of suspensions, an indicator of which is a usual integral mean value $c(\lambda)$, is an element which differentiates distributions with simple interpretation.
- In the examined water area the measured light attenuation coefficients varied in a wide range depending on the season, measurement point and wavelength. For example, for the first measurement point and the wavelength $\lambda = 299.8$ nm the value of $c - c_w$ was equal to: 45.8 m^{-1} (in autumn), 30.32 m^{-1} (in winter), 54.16 m^{-1} (in spring). For the wavelength $\lambda = 749.5$ nm it was equal to: 6.78 m^{-1} (in autumn), 1.99 m^{-1} (in winter), 7.38 m^{-1} (in spring).
- We showed that in the examined water area there is a close relation between changes of the spectral distributions in different seasons and measurement points and changes of coefficients in the formula (3) and other characteristics of the distributions on the basis of which one can deduce about changes of magnitudes and forms of contaminations and determine the parts of the river which are particularly threatened ecologically. These parts of the river require permanent monitoring. More advanced methods allowing for determination of the kind and amount of contaminations

are spectroscopy in infrared, mass spectroscopy and chromatography.

Acknowledgments

The authors thank prof. J.Kopeć for help in writing numerical programs for calculation of parameters of spectral distributions of the light attenuation coefficient.

References

1. BRICAUD A., MOREL A., Light Attenuation and Scattering by Phytoplanktonic Cells: A Theoretical Modeling, *Applied Optics*, **25**, (4), 571, **1986**.
2. DERA J., *Marine physics*, Elsevier, Amsterdam – Oxford – New York – Tokyo, **1992**.
3. DERA J., GOHS L., WOŹNIAK B., Experimental Study of The Composite Parts of the Light – beam Attenuation Process in the Waters of Gulf of Gdańsk, *Oceanologia*, **10**, 5, **1978**.
4. DERA J., PAWLAK B., Light Attenuation in Oil Polluted Sea Water, *Proceedings vol. 1*, CBO, Kiel, pp 340–348, **1988**.
5. DERA J., PAWLAK B., Light attenuation in oceanic water strongly contaminated with crude oil, (in Polish), *Studia i Materiały Oceanologiczne PAN*, nr **53**, Sopot, pp 77–103, **1988**.
6. JONASZ M., The Effect of Nonsphericity of Marine Particles on Light Attenuation, *J. Geophys. Res.*, **C 13**, 14637, **1987**.
7. KOPEĆ J., PAWLAK B., Application of Approximate for Analysis of Spectral Distribution of Light Attenuation Coefficient, *Oceanologica Acta*, **21/5**, 623, **1998**.
8. PAWLAK B., Influence of chosen physical factors on changes of some optical properties of emulsions and sediments in water, *Rozprawy i Studia T. (CDXL)* **366**, Uniwersytet Szczeciński, 94, **2000**.