The position of the seasonal thermocline in southern Baltic waters polluted with crude oil

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> Seasonal thermocline Eutrophic seawater Crude oil pollution

JADWIGA MROZEK-LEJMAN, GRAŻYNA KARBOWNICZEK-GRATKOWSKA Marine Physics Department, University of Szczecin, Szczecin

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Abstract

The paper deals with the formation of the thermocline and the mixed layer in a sea polluted with crude oil when the natural optical parameters of eutrophic seawater are seasonally variable. Differentiation of the degree of eutrophication of the seawater is expressed in terms of the concentrations of chlorophyll and yellow substances. The occurrence of crude oil pollution is taken into account by modifying the time-variable absorption coefficient of the seawater – crude oil system. The variability in the absorption spectra of natural seawater in the spring – summer season is estimated on the basis of investigations of seasonal changes in the chlorophyll concentration in the southern Baltic.

Numerical simulations were carried out for Baltic and Gulffax crude oil using the one-dimensional integral DKTz–2 model. The computations were performed for monthly average values of parameters determining the state of the southern Baltic environment collected over several years. Experimentally found crude-oil optical parameters (light refraction and absorption coefficients) were applied, as were the variability with time of these parameters and that of the crude oil layer thickness.

The results of the numerical simulations show that the increase in the volumetric concentration of crude oil in the upper sea layer causes the thermocline to be formed closer to the water surface. Simultaneously, the thickness of the mixed layer decreases but its temperature rises. If a crude oil layer appears on the water surface, the trend of the changes is the same.

1. Introduction

For both long-term weather forecasts and studies of atmosphere – hydrosphere interactions it is essential to be able to predict seasonal changes in the thermal structure of the upper sea layer. Wherever disinct seasonal changes in the temperature profiles occur, seasonal variability is found in other physical and chemical parameters, as well as in the faunal and floral dynamics (Pickard, 1979). The seasonal variability in the seawater temperature is distorted owing to pollution, especially by crude oil, both at the surface and deep water (Jarvis, 1962; Arst, 1984; Byutner and Dubov, 1985).

This paper deals with the formation of the thermocline and the mixed layer in oil-polluted seawater where the natural optical parameters of the seawater vary seasonally. The aim of these studies, which are of a predictive nature, was to carry out numerical simulations in order to demonstrate the influence of such pollution on the position of the seasonal thermocline in southern Baltic waters. The variations in the natural optical parameters of seawater resulting from changes in the concentration of substances in the water in the spring – summer season have been taken into account. The occurrence of crude oil pollution is described by a modification of the time-variable absorption coefficient of the 'natural seawater – crude oil' system.

2. Material and methods

Examination of the seasonal variability in the thermal structure of the upper layer (eutrophic regions) of the sea contaminated with crude oil was divided into several stages:

- the spectral distributions of the absorption coefficient of seawater eutrophicated to different extents were determined;
- the spectral distributions of the modified absorption coefficients of eutrophic seawater polluted with crude oil were calculated;
- numerical simulations were carried out in order to examine the influence of crude oil pollution on the absorption spectrum of natural seawater;
- the seasonal variability in the absorption coefficient of southern Baltic water was estimated;
- the influence of crude oil pollution on the seasonal variability of the absorption spectra of the seawater was determined;
- seasonal changes in the temperature and thickness of the mixed layer in eutrophic sea regions polluted with crude oil were calculated;
- numerical simulations were carried out so as to examine the influence of crude oil pollution on the position of the seasonal thermocline in the southern Baltic.

In order to perform the above tasks, a mathematical model of the absorption coefficient of eutrophic seawater polluted with crude oil was elaborated (see section 3). Owing to the lack of data in the literature, values of the absorption coefficient of natural seawater during the spring and summer were estimated theoretically on the basis of investigations into seasonal changes in the chlorophyll concentration in the southern Baltic (Kayzer *et al.*, 1984).

The temperature and mixed layer thickness were calculated using the one-dimensional integral DKTz–2 model (Karbowniczek-Gratkowska, 1991a,b). The numerical simulations were performed for monthly average values of parameters determining the state of the southern Baltic environment, collected over several years (Karbowniczek-Gratkowska, 1991a). In the calculations of radiation transmission in Baltic seawater in the 400–700 nm range, the values of the parameters given in Karbowniczek--Gratkowska and Zieliński (1990) were used.

The calculations were carried out for two different kinds of crude oil: Baltic and Gulffax. The experimentally found optical parameters of crude oil, *i.e.* light refraction and absorption coefficients, as well as the variability of these parameters and the thickness of the crude oil layer in the spring-summer season were applied (Mrozek-Lejman and Karbowniczek-Gratkowska, 1996).

3. Mathematical model

The occurrence close to the sea surface of a layer of water at almost constant temperature and with a steep temperature gradient along its borders (mixed sea layer and thermocline) is a characteristic feature of the stationary temperature field in the upper sea layer. The temperature and thickness of the mixed layer is determined by the range of potential energy changes resulting from turbulent mixing generated by wind, heat exchange between sea and atmosphere, evaporation, long-wave radiation and the radiation component of solar heat (Kraus and Turner, 1967; Turner, 1969; Denman, 1973; Thompson, 1976; Czyszek, 1985).

The mathematical model deals with the problem of thermocline formation and of the mixed layer in the sea polluted with crude oil when the natural optical parameters of eutrophic seawater are seasonally variable.

The optical properties of seawater determine the propagation of solar radiation in the ocean: the quantity and spectral content of light reaching different depths of the water depend on them. In turn, the optical characteristics are dependent on substances contained in seawater, hence they can provide quantitative and qualitative information about its content. To a good approximation they can be described as a superimposition of the optical properties of its different components. It is known from experiment that seawater absorption is adequately described with the aid of two elements – suspensions and dissolved substances. The absorbent properties of suspensions are due largely to phytoplankton pigments, yellow substances and inorganic salts. These last, together with pure water, constitute a constant component in seawater absorption (Jerlov, 1976).

Therefore, the absorption coefficient of seawater can be presented as the sum

$$a_e(\lambda) = a_w(\lambda) + a_p(\lambda) + a_y(\lambda), \tag{1}$$

where

 $a_w(\lambda)$ – pure seawater absorption coefficient,

 $a_p(\lambda)$ – phytoplankton pigment absorption coefficient,

 $a_y(\lambda)$ – yellow substance absorption coefficient.

The annual cycle of transformations of the ocean – atmosphere system is reflected in the seasonal variability of physical, chemical and biological parameters of the marine environment (Shpaer *et al.*, 1988), and in consequence in its optical properties. This has been confirmed by the results of experiments performed at the Institute of Oceanology of the Polish Academy of Sciences and at the Institute of Meteorology and Water Management.

The analysis of the results of these investigations suggests that the most important elements influencing the seasonal changes in the optical properties of waters are:

- the usually greater surface run-off in the spring summer season, containing large quantities of suspended matter;
- the spring phytoplankton bloom.

Moreover, the distribution of different optical parameters depends strongly on the hydrometeorological conditions, which are the cause of the variable circulation of waters and of such phenomena as the transport of sediment from the sea bed and beaches. The surface layer of water (0–30 m) is optically the most variable, which is related to the annual cycle of biological activity in the euphotic sea zone (Sagan, 1991).

In the numerical simulations carried out by the authors of the present paper, modified values of the seawater absorption coefficient were used. Because of the lack of literature data concerning its seasonal variability, its value was estimated theoretically. In these considerations it was assumed that the variability of the absorption coefficient in the spring – summer season is due mainly to phytoplankton growth. This can be estimated from measurements of the chlorophyll concentration, the variability of which in the waters of the Gulf of Gdańsk is illustrated in Fig. 1 (Kayzer *et al.*, 1984). The maximum chlorophyll concentrations occur in April, which coincides with the biomass maximum of the phytoplankton. The experiments show that the seasonal changes in the chlorophyll and phytoplankton content in southern Baltic waters are much the same in nature. A much higher chlorophyll concentration (more than double the usual) in the early spring (March) has been characteristic in recent years. Data from the Institute of Meteorology and Water Management on the state of southern Baltic waters indicate a marked increase in the temperature of the 0–25 m layer from 9.5°C to 11°C (annual average values) after 1989. The recent relatively mild winters and lack of ice-cover has enabled unicellular algae to appear earlier in large quantities (Wrzołek, 1994).



Fig. 1. Annual daily-average cycle of chlorophyll concentration in the sea layer 0–10 m (southern Baltic; Gulf of Gdańsk)

The differentiation of the degree of eutrophication of seawater can be expressed in terms of the changes in the chlorophyll and yellow substance concentration. The occurrence of crude oil pollution is taken into account by modifying the time-variable absorption coefficient of the 'seawater – crude oil' system (Karbowniczek-Gratkowska, 1991a).

Assuming that the seasonal variability in the absorption coefficient is related mainly to phytoplankton growth, the influence of pollution on the variability in the absorption spectra of eutrophic seawater in the spring – summer season can be assessed on the basis of seasonal changes in the chlorophyll concentration (Fig. 1).

Hence, the absorption coefficient was determined as follows:

• for eutrophic seawater (Kopyelevich, 1983):

$$a_e(\lambda, t) = a_w(\lambda) + c_{chl}(t) a_{chl}(\lambda) + c_y(t) a_y(\lambda), \qquad (2)$$

where

 $a_w(\lambda)$ – pure seawater absorption coefficient,

 $a_{chl}(\lambda)$ – specific absorption coefficient of chlorophyll,

 $c_{chl}(t)$ – chlorophyll concentration,

 $a_y(\lambda)$ – specific absorption coefficient of yellow substances,

 $c_y(t)$ – yellow substance concentration.

Since a method of extracting yellow substances from seawater has not yet been perfected and in consequence it is not known what percentage of the substances dissolved in the sea they make up, it was assumed in the calculations that their concentration was equal to that of chlorophyll $c = c_u = c_{chl}$ (Arst *et al.*, 1983).

• for eutrophic seawater polluted with crude oil:

$$a(\lambda, t) = a_e(\lambda, t) + c_r(t) a_r(\lambda, t), \tag{3}$$

where

 $a_r(\lambda, t)$ – crude oil absorption coefficient,

 $c_r(t)$ – volumetric concentration of crude oil in eutrophic seawater.

4. Results of calculations and discussion

Relationship (2) in the mathematical model was used to determine the spectral distributions of the absorption coefficients of seawaters eutrophicated to various degrees. The differentiation of the degree of seawater eutrophication is expressed in terms of the concentration changes in its main components. Example results of calculations carried out for different concentrations c are presented in Fig. 2; they show that this parameter has a marked influence on the absorption coefficient spectrum of eutrophic seawater. The absorption coefficient increases with the growth in the value of c, especially in the short-wave range (400–540 nm), which significantly alters the form of the spectrum.

In order to examine the influence of crude oil pollution on the absorption spectrum of eutrophic seawater further numerical simulations were carried out. Using eq. (3) the spectral distributions of the modified absorption coefficients of eutrophic seawater polluted with crude oil were calculated for two different kinds of crude oil – Baltic and Gulffax. The numerical simulations were performed for different volumetric crude oil concentrations ($c_r = 0$; 1.E–7; 1.E–6; 1.E–5) in waters with a different degree of eutrophication (c = 0; 1; 2; 5; 10 mg m⁻³). Example results are shown in Figs. 3 and 4. Evidently, it is not only the degree of eutrophication of the seawater, but also the concentration and type of crude oil that significantly affect the value of the absorption coefficient. The increase in crude oil concentration causes



Fig. 2. Light absorption spectra of eutrophic seawater with different concentrations of its main components $(c_{chl} = c_y = c)$

the absorption coefficient of seawater to rise. The effect is more evident when the pollution is due to Gulffax crude oil, whose absorption coefficients $a_r(\lambda)$ are much larger than those of Baltic crude oil. With the latter, striking changes become evident at a minimum volumetric concentration of the order of 1.E–5, but with the Gulffax crude oil, such changes are already apparent at 1.E–6. They are particularly large in the short-wavelength part of the spectrum, which strongly modifies its form.

The next stage of the investigation involved the determination of the influence of crude oil pollution on the seasonal variability in the absorption spectra of eutrophic seawater $a_e(\lambda, t)$. In accordance with the earlier assumption, the variability in the absorption coefficient was estimated on the basis of chlorophyll concentration changes in the spring – summer season (Fig. 1). Example results of calculations for eutrophic seawater polluted with Baltic and Gulffax crude oil at a volumetric concentration of $c_r = 1.E-6$ are shown in Figs. 5, 6 and 7.

The results obtained at this stage were then used to calculate the seasonal changes in the temperature and thickness of the mixed sea layer polluted with crude oil. Numerical simulations were carried out using the





Fig. 3. Light absorption spectra of unpolluted eutrophic seawater ($c = 2 \text{ mg m}^{-3}$), and the same water polluted with Baltic crude oil (a) and Gulffax crude oil (b)





Fig. 4. Light absorption spectra of unpolluted eutrophic seawater ($c = 10 \text{ mg m}^{-3}$), and the same water polluted with Baltic crude oil (a) and Gulffax crude oil (b)



Fig. 5. Light absorption spectra of eutrophic seawater (southern Baltic; spring – summer season)



Fig. 6. Light absorption spectra of eutrophic seawater polluted with Baltic crude oil (southern Baltic; spring – summer season; volumetric concentration of crude oil $c_r = 1.\text{E-6}$)



Fig. 7. Light absorption spectra of eutrophic seawater polluted with Gulffax crude oil (southern Baltic; spring – summer season; volumetric concentration of crude oil $c_r = 1.E-6$)

DKTz-2 model, which enables seasonal temperature distributions in the upper sea layer to be analysed and time-variable crude oil pollution to be simulated. The parameters characterising the type of crude oil (density, complex refraction coefficient) and the form of the pollution – the concentration in the case of volumetric contaminations and the thickness of the oil layer in the case of superficial pollution – are subject to changes.

The temperature structure of the sea is determined by turbulent mixing. Values of the turbulent mixing coefficient were found from numerical experiments. This coefficient is variable and depends on the dimensionless combination of numerous parameters characterising the environmental conditions, such as the stability of the atmosphere and the surface layer of the sea, state of the sea, *etc.* Calculations of temperature and mixed-layer thickness were performed for various values of this coefficient using mean long-term parameters of the Baltic environment in the spring – summer season (Karbowniczek-Gratkowska, 1991b).

The results of the numerical simulations performed for pollution with Baltic and Gulffax crude oil are illustrated in Figs. 8, 9, 10 and 11. The position of the seasonal thermocline was determined from the temperature and the mixed layer thickness calculations. These were carried out for different volumetric concentrations ($c_r = 0$; 1.E–6; 6.E–6; 1.E–5)



Fig. 5. Position of the seasonal thermocline in unpolluted eutrophic seawater and in the same water polluted with Baltic crude oil ($h = 0, c_r = \text{var.}$)



Fig. 6. Position of the seasonal thermocline in unpolluted eutrophic seawater and in the same water polluted with Baltic crude oil ($h = \text{var.}, c_r = 1.\text{E-6}$)



Fig. 7. Position of the seasonal thermocline in unpolluted eutrophic seawater and in the same water polluted with Gulffax crude oil $(h = 0, c_r = \text{var.})$



Fig. 8. Position of the seasonal thermocline in unpolluted eutrophic seawater and in the same water polluted with Gulffax crude oil ($h = \text{var.}, c_r = 1.\text{E-6}$)

(Figs. 8 and 10) and thicknesses h of the crude oil layer ($h = 0; 5; 10; 20 \ \mu m$) (Figs. 9 and 11). These figures demonstrate that both the concentration and the thickness of the crude oil layer influence the depth of appearance of the seasonal thermocline. An increase in the volumetric concentration of the oil in the upper sea layer causes the thermocline to form closer to the sea surface. The effect is more evident when the polluting oil is Gulffax crude. At the same time a decrease in the thickness of the mixed layer and an increase in its temperature are observed. Should a crude oil slick appear on the water surface, the direction of changes is the same.

Fig. 12 presents the results of computations of the effect of time-variable surface pollution with Baltic crude oil on changes in the position of the seasonal thermocline in the southern Baltic. The changes in the oil layer

No. seri	of Time [weeks]	0 - 2	2-4	4–6	6–8	8–10	10-12	12–14	14-16	16-18	18-20	20-22
0)	0	0	0	0	0	0	0	0	0	0	0
1		350	115	65	35	20	10	5	0	0	0	0
2		0	0	350	115	65	35	20	10	5	0	0
3	3	0	0	0	0	350	115	65	35	20	10	5
	time										[wee	ks]
		2	4	6	8	10	12	14	16	18	20	22
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position of seasonal thermocline	15 -						2^ ====D	<u>A</u>	<u>A</u>	- <u>A</u>	-X	-*
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Values of $h \ [\mu m]$ in particular periods

Fig. 9. Changes in position of the seasonal thermocline for a time-variable Baltic crude oil film of thickness $h \ [\mu m]$ at the seawater surface. 0, 1, 2, 3 – no. of series, as in the table; 0 – unpolluted seawater; 1, 2, 3 – pollution occurs in the first two, four and eight weeks respectively of the spring – summer season

thickness were chosen in such a way that they were in accordance with the results of measurements (Mrozek-Lejman and Karbowniczek-Gratkowska, 1996). Clearly, the time at which increased pollution occurs is significant. The greatest effect on the position of the seasonal thermocline is exerted by pollution occurring when the warming of the sea is at its most intensive. The effect of a short-lived increase in pollution when the sea is beginning to warm up is also significant, though not so pronounced.

5. Conclusions

The results of the numerical investigations presented here allow the following remarks and conclusions to be formulated:

- The differentiation of the degree of eutrophication of seawater can be expressed in terms of changes in the chlorophyll concentration, which have a marked influence on the absorption coefficient spectrum of natural seawater. As this concentration increases, so does the seawater absorption coefficient, especially in the short wavelength range, something that changes the form of the spectrum to a significant extent.
- The occurrence of crude oil pollution in eutrophic waters can be taken into account by modifying the time-variable absorption coefficient of 'the natural seawater – crude oil' system. The concentration and type of crude oil exert a significant influence on the value of the absorption coefficient. Increasing crude oil pollution causes the absorption coefficient of eutrophic seawater to rise as well. The effect is more evident in the case of pollution by Gulffax crude, which is characterised by much larger absorption coefficients $a_r(\lambda)$, than pollution by Baltic crude.
- The position of the seasonal thermocline can be determined from the temperature and calculations of the mixed layer thickness. These calculations were performed for different volumetric concentrations and different thicknesses *h* of the crude oil layer. Both the volumetric concentrations and the thickness of the crude oil layer influence the depth of appearance of the seasonal thermocline in eutrophic waters. An increase in the volumetric concentration of crude oil in the upper sea layer causes the thermocline to form closer to the sea surface. At the same time the mixed layer becomes thinner and the temperature rises. If a crude oil layer appears on the water surface, the direction of changes is the same.

• The time when increased pollution occurs is significant. The greatest effect on the position of the seasonal thermocline is caused by pollution at the moment of most intensive heating. The effect of a short-lived increase in pollution when the water is starting to warm up is still significant, though not as pronounced.

Further investigations should take into account the changes in the pollutant concentration and the eutrophic components of seawater with depth.

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