

# Influence of exchange processes in the Earth–atmosphere system on the evolution of surface oil film

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The oil outflows on water are very dangerous ecological pollutant for natural water bodies. To develop practical measures for accident elimination, it is necessary to have an information on oil film parameters, namely, its configuration, thickness, temperature, composition, etc., that can change significantly with time under impact of meteorological and hydrological processes.

Theoretical models of spreading, drift, and diffusion of spilled oil give practically reasonable accuracy under oceanic conditions,<sup>1,2</sup> where wind speeding-up is large, stratification of water–air interface layer is weakly pronounced, and variability of meteorological parameters (on the spot scale) is small. As concerning inland water bodies having limited areas, asymptotic estimations may be too rough because of neglecting such local-scale phenomena as interaction of near-surface turbulent layers with a fine vertical structure.

To reveal quantitative characteristics of light fractions diffusion to the surface and their evaporation, a description of heat and mass exchange through water – oil film – air interface is very important. In the process of oil-in-water emulsion formation, the surface shaking caused by wind waves and turbulent energy flow into water plays an essential part. The wind stresses form a vertical shear of the drift velocity in the film that results in slick elongation along the wind direction and decrease of its thickness.<sup>3</sup> The heat exchange and associated evaporation of low-polymeric fractions facilitate the film thinning and diminishing net oil mass. Eckmann velocity rotation in the water body causes deviation of the surface drift from the wind direction in the near-water layer and corresponding change of the slick trajectory. The mechanisms listed above give rise to oil-spot evolution in the water body at the turbulent diffusion stage that follows the surface tension stage.<sup>4</sup>

Below we formulate three-layer numerical model of heat and mass exchange in air, oil film, and water body with a detailed consideration of vertical processes and account for wind wave generation within a limited area. The model is used for obtaining quantitative estimates of oil spot parameters on a diurnal time scale at moderate breeze.

## Statement of the problem

Let us direct  $x$ -axis horizontally along the wind velocity,  $U_a$ ,  $z$ -axis vertically upward, and  $z = 0$  level coincides with air – oil film interface. The air flow movement we will consider in the range  $0 \leq z \leq h_{10}$ , where  $h_{10}$  is the level, at which meteorological quantities are given. In this range we isolate an intermediate layer with the thickness  $h_s$ , occupied by moving waves. To describe turbulent air motion, we consider the following system:

$$\begin{aligned} \frac{\partial}{\partial z} K_a \frac{\partial U_a}{\partial z} &= \gamma_L |U_a - C| (U_a - C), \\ \frac{\partial}{\partial z} K_a \frac{\partial \Theta}{\partial z} &= 0, \quad \frac{\partial}{\partial z} K_a \frac{\partial Q}{\partial z} = 0, \quad \frac{\partial}{\partial z} K_a \frac{\partial N_j}{\partial z} = 0, \end{aligned} \quad (1)$$

where  $K_a$  is the coefficient of vertical turbulent exchange;  $\Theta$ ,  $Q$  are the air temperature and specific air humidity;  $N_j$  ( $j = 1, \dots, J$ ) is the specific content of  $j$ th oil component vapor in air;  $C$  is the wave phase velocity;  $\gamma_L$  is the wind resistance parameter. The  $\gamma_L$  value characterizes relation between normal and tangential wind stresses and substantially influences intensity of surface heat and mass exchange because the latter is conditioned only by the tangential component. In the range where  $z > h_s$  it is accepted that  $\gamma_L = 0$ . To calculate  $\gamma_L$  in the intermediate layer, the equation of wave energy evolution in the spectral form is used<sup>4</sup>:

$$\frac{\partial S}{\partial t} + C_x \frac{\partial S}{\partial x} + C_y \frac{\partial S}{\partial y} = I - D - G_f, \quad (2)$$

where  $S(\sigma, \varphi, x, y, t)$  is the frequency-angular spectrum of wind waves;  $\sigma$  is the frequency and  $\varphi$  is the propagation direction;  $I$  is the energy flux toward waves;  $D$  is the dissipation due to wave collapse;  $G_f$  describes damping effect of the film (on a free water  $G_f = 0$ ). The following relation results from analysis of energy fluxes in the atmosphere – wind waves – water body system<sup>5</sup>:

$$\frac{1}{2} \rho_w g \int_0^\infty d\sigma \int_0^{2\pi} I d\varphi =$$

$$= \rho_a \gamma_L \int_0^{h_s} C |U_a - C| (U_a - C) dz, \quad (3)$$

which gives an explicit expression for  $\gamma_L$ . There are the following designations in the Eq. (3):  $g$  is the acceleration due to gravity;  $\rho_w$ ,  $\rho_a$  are the water and air densities.

In describing vertical exchange in the film ( $h_f < z < 0$ ), we suppose oil motion to be laminar.<sup>3</sup> Having in mind this assumption, for drift velocity components  $U_f$ ,  $V_f$ , temperature distribution  $T_f$ , and concentration of liquid mixture components  $H_j$  we can write

$$\begin{aligned} v_f \frac{\partial^2 U_f}{\partial z^2} = 0, \quad v_f \frac{\partial^2 V_f}{\partial z^2} = 0; \\ \frac{\partial T_f}{\partial t} = \lambda_f \frac{\partial^2 T_f}{\partial z^2} + \frac{1 - \delta_f}{\rho_f c_{pf}} \frac{\partial R_0}{\partial z}, \quad \frac{\partial H_j}{\partial t} = \eta_j \frac{\partial^2 H_j}{\partial z^2}, \end{aligned} \quad (4)$$

where  $R_0$  is the solar radiation flux;  $\delta_f$  is the portion of surface absorption;  $\rho_f$ ,  $v_f$ ,  $\lambda_f$  are the oil density, molecular viscosity, and thermal diffusivity;  $c_{pf}$  is the specific heat of the film at constant pressure;  $\eta_j$  is the diffusion coefficient of the  $j$ th component. In Eq. (4) a hypothesis is accepted that the ratio between vertical and horizontal film sizes is small therefore the drift velocity direction holds unchanged within the film thickness.<sup>3</sup>

Let us write equations determining current in the upper layer of the water body at  $H_w < z < h_f$ , as

$$\begin{aligned} \frac{\partial U_w}{\partial t} = lV_w + \frac{\partial}{\partial z} K_w \frac{\partial U_w}{\partial z}, \\ \frac{\partial V_w}{\partial t} = -lU_w + \frac{\partial}{\partial z} K_w \frac{\partial V_w}{\partial z}, \\ \frac{\partial T_w}{\partial t} = \frac{\partial}{\partial z} K_w \frac{\partial T_w}{\partial z} + \frac{(1 - \delta_f)(1 - \delta_w)}{\rho_w c_{fw}} \frac{\partial R_0}{\partial z}, \end{aligned} \quad (5)$$

where  $U_w$ ,  $V_w$  are the drift velocity components;  $T_w$  is the water temperature;  $l$  is the Coriolis parameter;  $K_w$  is the coefficient of vertical turbulent exchange;  $\delta_w$  characterizes the portion of solar radiation absorbed by the oil – water interface. To calculate turbulence parameters in water, the following equations are used:

$$\begin{aligned} \frac{\partial b}{\partial t} = \frac{\partial}{\partial z} K_w \frac{\partial b}{\partial z} + K_w J_w - \varepsilon, \quad K_w = c_1 \frac{b^2}{\varepsilon}, \\ \frac{\partial \varepsilon}{\partial t} = \frac{\partial}{\partial z} K_w \frac{\partial \varepsilon}{\partial z} + c_2 \frac{\varepsilon}{b} K_w J_w - c_3 \frac{\varepsilon^2}{b} = 0, \end{aligned} \quad (6)$$

where  $b$  is the kinetic turbulent energy;  $\varepsilon$  is its dissipation rate;  $J_w = (U_w)_z^2 + (V_w)_z^2 - g\beta_T T_z$ ,  $\beta_T$  is the thermal expansion coefficient for water;  $c_i$  are universal constants.<sup>6</sup>

Boundary conditions are formulated as:

$$\begin{aligned} U_a = U_{10}; \quad \Theta = \Theta_{10}; \quad Q = Q_{10}; \\ N_j = f_{10} N_{j0} \text{ at } z = h_{10}, \end{aligned} \quad (7)$$

where values with subscript “10” are considered to be given;  $f_{10}$  is the dimensionless characteristics of oil vapor concentration at the observation level relative to near-surface value  $N_{j0}$ . If we accept the assumption that profiles of oil vapor concentration above the film and humidity field above open water are similar, the value  $f_{10}$  is analogous to relative humidity in near-water layer. Since measurement of  $f_{10}$  value under field conditions is technically difficult, it is possible to estimate its value from characteristic quantity of relative humidity above the water body taking, for example,  $f_{10} = 0.85$ . For the level corresponding to the upper film boundary we write

$$\begin{aligned} U_a = U_f; \quad \rho_a K_a \frac{\partial U_a}{\partial z} = \rho_f v_f \frac{\partial U_f}{\partial z}; \quad \frac{\partial V_f}{\partial z} = 0; \\ \rho_f c_{pf} \lambda_f \frac{\partial T_f}{\partial z} = \rho_a c_{pa} K_a \frac{\partial \Theta}{\partial z} + \sum_j L_j E_j + \delta_f R_0 - R_F, \quad (8) \\ \Theta = T_f, \quad E_j = \rho_{fj} \eta_j \frac{\partial H_j}{\partial z} \text{ at } z = 0, \end{aligned}$$

where  $L_j$  is the heat of evaporation;  $E_j = \rho_a K_a \frac{\partial N_j}{\partial z}$  is the mass flow of volatile oil fractions;  $\rho_{fj}$  is the individual density of liquid fractions in the film ( $\rho_f = \sum_j \rho_{fj} H_j$ );  $R_F$  is the longwave radiation. The latter equality in Eq. (8) shows component mass balance in the air – film interface.

In describing mechanism of oil evaporation into air, it is necessary to take into account the rate limitation for diffuse transfer of liquid fractions to evaporating surface. It is important for light low-molecular polymers when its evaporation rate is limited by low rate of substance arrival from lower film layers. Let us write this condition in the form

$$\begin{cases} N_j = N_{j0}, & H_j > 0 \\ H_j = 0, & H_j < 0 \end{cases} \text{ at } z = 0, \quad (9)$$

where  $N_{j0} = e_j M_j / (p_a M_a)$  is the vapor saturation value<sup>7</sup>;  $M_a$ ,  $M_j$  are the molecular weights of air and oil components;  $e_j$  is the partial pressure of  $j$ th gas;  $p_a$  is the atmospheric pressure. The relations (9) suggest that under conditions of liquid component deficiency ( $H_j < 0$ ), on the surface  $H_j$  is forced to be equal to 0 that gives necessary conditions for calculating concentration and flow of this fraction vapor into the atmosphere.

Let us formulate the conditions at the oil – water interface in the form

$$U_f = U_w; \quad V_f = V_w; \quad T_f = T_w;$$

$$\rho_f v_f \frac{\partial U_f}{\partial z} = \rho_w K_w \frac{\partial U_w}{\partial z} - \frac{\rho_w g}{2U_w} \int_0^\infty d\sigma \int_0^{2\pi} G_f d\phi,$$

$$\rho_f v_f \frac{\partial V_f}{\partial z} = \rho_w K_w \frac{\partial V_w}{\partial z}; K_w \frac{\partial b}{\partial z} = D_1, K_w = h_s \sqrt{b}; \quad (10)$$

$$\rho_w c_{pw} K_w \frac{\partial T_w}{\partial z} = \rho_f c_{pf} \lambda_f \frac{\partial T_f}{\partial z} + \delta_f \delta_w R_0;$$

$$\frac{\partial H_j}{\partial z} = 0 \text{ at } z = h_f,$$

where  $D_1$  is the turbulent energy flux directed to water due to wave damping determined via  $D$  function.<sup>5</sup> The term with  $G_f$  in Eq. (10) is representative of the mechanism of energy transfer from waves to drift flow at viscous damping by the film. On the whole, one can show that conditions formulated at the interfaces provide an energy balance in the airflow – oil film – wind waves – water flow system.

We suppose that the motion decays at the lower boundary in the water body is:

$$U_w = V_w = 0; \frac{\partial T_w}{\partial z} = \gamma_H; b = 0, \frac{\partial \varepsilon}{\partial z} = 0 \text{ at } z = H_w, \quad (11)$$

where  $\gamma_H$  is the stable water temperature stratification along the depth.

### Numerical experiment

The problem (1)–(11) was solved by finite difference method with respect to geometric variables and time. Numerical schemes with the second approximation order have been used.

Consider results of model calculation of thermodynamic regime of oil film at  $U_{10} = 7 \text{ m/s}$ , where oil slick edge with the initial thickness  $|h_f| = 1 \text{ cm}$  is 1 km away from the shore. Figure 1 shows distribution of rough parameters along  $x$ -axis 3 hours after the start of integration. Root-mean-square

elevation of wave surface  $h_0 = \int_0^\infty d\sigma \int_0^{2\pi} S d\phi$  increases

with the distance from the shore achieving the value of 4.2 cm at the slick leading edge (curve 1), then it decreases at  $x > 1 \text{ km}$ . Distribution of water surface roughness parameter  $z_0$  has similar behavior (curve 2).

In Fig. 1 maximum value  $z_0$  is equal to 0.4 mm. It should be noted for a comparison that parametric formulas for open ocean<sup>8</sup> give the value  $z_0 = 0.9 \text{ mm}$  under the same conditions. Curve 3 (the scale is on the right) gives an idea of the drift velocity on the  $z = 0$  surface. In the range occupied by the film, motion is faster as compared with one in open water that is indicated by a step on the curve 3 at the slick boundary at  $x = 1000 \text{ m}$ . It is associated with the fact that

drift flow. Curve 4, that shows  $U_f$  distribution on the

oil – water interface, gives an idea of velocity step within the film thickness.

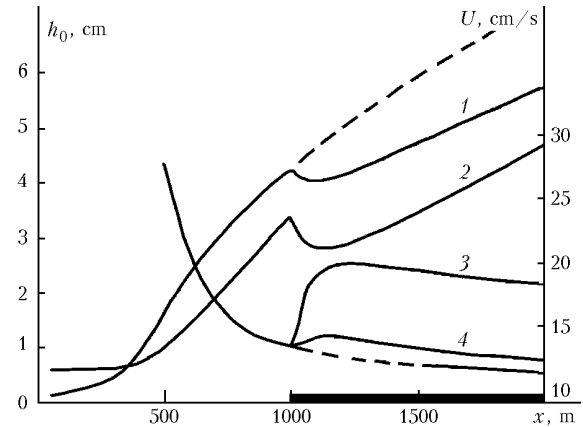


Fig. 1. Horizontal distribution of root-mean-square elevation (curve 1), roughness parameter (curve 2), and drift velocities of film (curve 3) and water (curve 4). Dashed lines correspond to the problem parameters without film.

Vertical velocity shear in the film causes oil spot elongation and decrease of its thickness.<sup>3</sup> Another one factor, resulting in  $h_f$  change, is the loss of oil mass due to evaporation. Combination of these processes weakens impact of the oil film on surface waves and wind drift, therefore regularities for oil migration within limited area are much more complicated as compared to that in taking into account only the dynamic factors.<sup>3</sup> In particular, heat and mass transfer between the film and adjacent media may be of considerable importance.

When determining thermal regime for the system, let us preset the initial moment on summer day at 10 a.m. and assume  $\Theta_{10} = 20^\circ\text{C}$ ,  $\gamma_H = 0.2^\circ\text{C/m}$ ,  $\delta_f = 1$  (null transparency of oil film). Qualitative composition of oil mixture is schematized through presetting three components from methanol hydrocarbon family (light, average, and high-molecular ones) in equal fractions and molecular weights  $M = 86, 114, 198 \text{ g/mole}$ . Boiling points for these fractions are 60, 99, 190°C, respectively. Physicochemical constants and dependences needed have been borrowed from tables.<sup>9</sup>

Heat and mass exchange in the system have been developed according to the following scheme. In insolation period the oil mass is heated that is accompanied by intense evaporation of light fractions and spending heat for evaporation. Figure 2 presents time behavior of evaporation rate for three fractions under consideration (curves 1, 2, 3), as well as the total gas flow from the surface (curve 4).

The most mobile mixture component 1 has two qualitatively different periods: at the beginning (till  $t \approx 10:10$ ) natural evaporation processes are developed because the initial liquid phase reserve provides for vapor saturation near the surface. Further evaporation

with time. Heavier fraction 2 has first period enlarged

to 40 minutes due to lower evaporation rate (curve 2 in Fig. 2), whereupon evaporation rate also decreases. Because of low vaporability of the component 3, diffuse mechanism does not hinder establishing of saturating regime on the surface. Thus, the mass flow practically does not change with time (curve 3).

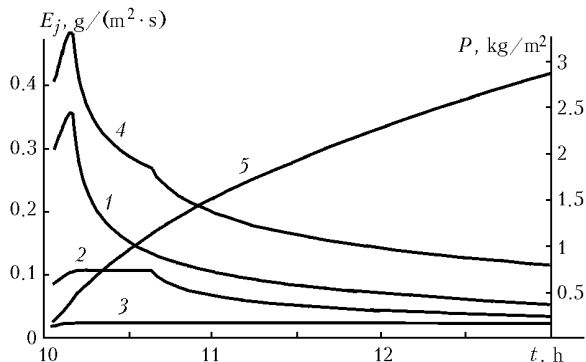


Fig. 2. Time behavior of oil vapor flows for components 1, 2, 3 (curves 1, 2, 3), their sum (curve 4), and total mass loss (curve 5).

Curve 4 in Fig. 2 demonstrates the total gas flow  $E$ . Integration of this value over time gives dependence of oil mass loss  $P$  per unit square since evaporation beginning (curve 5 in Fig. 2, right scale). On the whole 2.84  $\text{kg}/\text{m}^2$  was evaporated during 3-hour interval including 1.5  $\text{kg}/\text{m}^2$  during the first hour. Calculations show that total oil mass decreases by 4.8  $\text{kg}/\text{m}^2$  within 24 hours. Taking into account that non-volatile fractions (paraffins and resins) were not considered here, the estimation obtained is close to real values of outflowed and evaporated oil.<sup>1</sup>

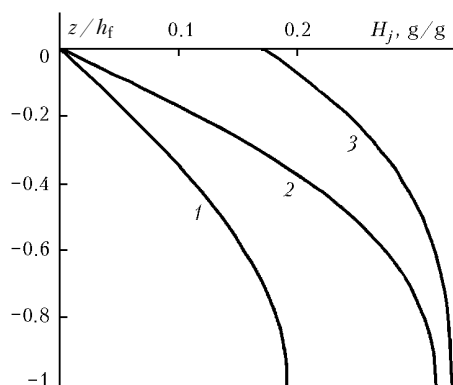


Fig. 3. Vertical profiles of concentrations for oil components 1, 2, 3 in a film at  $t = 13$  h.

Figure 3 illustrates vertical distribution of concentration within the film at  $t = 13:00$ . The lightest fraction (curve 1), having avoided the stage of maximum evaporation, is in the state of limited regime ( $H_1 = 0$  at  $z = 0$ ), and it lost 60% from the initial mass after 3 hours. The same is valid for the medium fraction (curve 2), but evaporated portion here is 34%. Diffuse transfer of the heavy fraction (curve 3) as well as low evaporation rate cause non-zero values of  $H_3$  on the

surface, thus this component is at the stage of natural evaporation.

## Conclusion

The numerical model is presented for description of basic thermodynamic mechanisms determining oil film evolution on the water body surface having limited area. In the frameworks of this model such important characteristics can be obtained as film temperature, velocity step in the oil layer, fractional mixture content, concentration of gas components near the surface. The latter parameter, for example, allows solving a problem of ecological damage elimination because an inflammation capability is related to gas phase concentration near the surface. The model does not describe explicitly a number of significant processes in the film, for example, photochemical decomposition, biodegradation, dissolution, aqueous oil dispersion, etc. At the same time a set of reproducible parameters of the physical system permits significant extending the model functional capabilities. Thus, turbulent energy flux due to surface shake ( $D_1$ ) is an important factor when forming water – oil emulsion, the coefficient of turbulent exchange determines diffusion rate for a spot and entraining of low-buoyant fractions into vertical exchange with the following oil penetration into deep water layers.

The model is functionally closed and gives physically reasonable results. So it can be applied to both calculation of one-time oil outflows and as a constituent part of an expert system in solving problems on protection and rational exploitation of water resources.

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