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The Determination and Application of Characteristic Parameter for Spilled Oil Vertical Concentration Distribution Formula

Abstract: After analyzing and summarizing previous research, it is obvious that the characteristic parameter, surface spilled oil concentration, is the key limiting condition for the usage of the spilled oil vertical concentration distribution formula, because there are no appropriate field detection condition and measurements. However, the vertical concentration distribution should receive more attention in the environmental risk assessment in consideration of the location of the aquatic organism and the water intakes. Based on the formula of vertical concentration distribution, a mathematic calculation method of the characteristic parameter, spilled oil surface concentration, was put forward, which mainly applies to the stage of surface tension and viscous force for marine oil spill. That is to say we establish the response relationship of the vertical concentration and the surface concentration under the most unfavorable situation by integrating along the vertical direction to get the average concentration. Finally, the key characteristic parameter, surface concentration, is available and it can be used to predict the characteristics of the vertical concentration distribution, which will provide water pollution characteristic parameters for the emergency warning of sea water quality.

Keywords: oil spill, vertical concentrate distribution, surface concentration, emergency warning.

1 Introduction

Recently, accidental oil spills are more frequent and on a larger scale. Oil spills in aquatic environment have become more common because of growth in marine oil production and transport over the last few decades [1,2]. The petroleum pollutants, leak into the water body, will cause significant damage to social economy, and also bring serious harm for regional water environment and ecological environment.

Oil may be released into the marine environment as a result of oil extraction activities such as drilling, storage and transportation [3,4]. Such as, the oil tankers may cause oil spill and make significant environmental problems in the event of

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collisions or grounding [5,6]. In 1989 Exxon Valdez oil spill discharged 260 thousand barrels crude oil in Prince William Sound, Alaska through the ship's ruptured hull [7]. Some scholars found that the oil drowned into the water column could influence the water environment persistently.

Once entering into the water, the spilled oil spreads by the action of wind or currents and forms a surface slick covering a large area of the water surface [8,9]. Some light hydrocarbons and some polar components begin to go into solution in the underlying water column, even though most of these are lost through evaporation into the atmosphere [10,11]. Moreover, some of the oil is emulsified into the water column as small dispersed droplets [12-14]. These droplets may become dispersed because of the action of currents, or they may become attached to suspended particulate matter and slowly settle to the bottom. The turbulence action can also cause water to become entrained in the oil forming water-in-oil emulsion, which may eventually form dense tar balls. It is clear from these time scales that the oil undergoes significant modification during the first few hours following a spill.

Many of the oil spill models developed during the last decade only simulate the advection and spreading processes. However, what draws more attention are the trace of migration, surface distribution of oil spill and thickness of oil film [15-18]. The concentration of oil spill, especially vertical concentration, is not enough.

Several studies were performed to research the vertical oil dispersion in a wave field through experimental tests. Mackay et al. [19,20] conducted an experimental model and proposed equations to calculate the amount of spilled oil intruded into the water column due to natural oil dispersion. Otherwise, the surface oil dispersion was investigated by Delevingne and Sweeney in a small laboratory flume as well as in a test basin [21]. Their study resulted in an empirical equation to estimate the oil dispersion rate as a function of oil type and breaking wave energy. Also, an equation was proposed to predict oil droplet size distribution. In addition, an experimental program is conducted by Reza Parsa et al. [22] to investigate the vertical oil dispersion of surface oil spills in a regular wave field, and which determines the trends of oil concentration variations due to natural oil dispersion and formulate the magnitude and time of maximum oil concentration.

Based on the mechanism of oil droplets formation and diffusion, Zhao [23] established a differential equation for oil droplets turbulent diffusion and put forward spilled oil vertical concentration distribution formula. But how to determine the characteristic parameter, datum point concentration, is unknown. Blumer et al. [24,25] get a certain hydrocarbon compound concentration by computing the integral for the vertical diffusion equation. What is more, it is necessary to have the saturated solubility of this hydrocarbon compound in the sea. However, it is difficult to use this method for petroleum pollutants, as such pollutants contain so many kinds of hydrocarbon compounds. Up to now, rare equation is proposed to estimate oil concentration in the water column and most of derived equations evaluate the rate or amount of oil dispersed in the water. Furthermore, no appropriate field

measurements or experimental data is collected for numerical models validation [26]. Actually, marine biological communities located at different depths, and almost all the water intakes are set under the water surface with a certain depth. Therefore, it is significant to determine petroleum pollutants concentration distribution in the vertical direction succinctly. And the vertical concentration distribution should also receive more attention in the environmental risk assessment.

Previous research mainly focused on the total amount of oil drowned in the water column, and therefore no information was available regarding oil concentration in the water column. In particular, most of the spilled oil had dissolved and emulsified into the water in the stage of surface tension-viscous force according to some studies [27,28]. Under this premise, according to the formula of vertical concentration distribution, a mathematical method is conducted to determine the vertical oil dispersion of surface oil spills in this study. The objective is to determine the vertical oil concentration variations due to natural oil dispersion and formulate the magnitude of oil concentration. The correlation between oil concentration and some important parameters such as thickness of oil film, amount of spilled oil into the water and the vertical distance are indicated and also oil concentration variations are quantified.

After analyzing and summarizing the previous research conclusions, it is obvious that the characteristic parameter, surface spilled oil concentration, is the key limiting condition for the usage of the spilled oil vertical concentration distribution formula. However there are no appropriate field detection conditions and measurements. Therefore, this paper puts forward a mathematical calculation method for computing the surface spilled oil concentration, which is also regarded as the datum point. That is to say we establish the response relationship of the vertical concentration and the surface concentration under the most unfavorable situation by integrating along the vertical direction to get the average concentration. After a series of calculations, the surface concentration is available. Then, the petroleum concentration of different depth could be predicted so that we can evaluate the accidental influence on the marine biological communities and water intakes which are located in different depth. The characteristic parameter calculated by this mathematical method fills in the gap between theory and practice, making the usage of the spilled oil vertical concentration distribution formula possible. It will be convenient for the emergency warning of water quality and the biomass loss calculation.

2 Concentration Vertical Distribution of Oil Spill

Through analyzing the mechanism of oil droplets formation and diffusion, Zhao et al. [23] established differential equation for oil droplets turbulent diffusion and earlier proposed an opinion that this is to reduce along the depth in the water body. The variation of oil concentration with water depth due to difference droplet size and diffusion coefficients pictured in Figure 1 and Figure 2 respectively. Then, this

opinion, which the vertical concentration obeys index distribution, was further confirmed by field testing, and also expressed by Figure 3 [29]. Now, this point, the vertical concentration is exponential to reduce along the depth in the water, is widely recognized.

Figure 1: Variation of oil concentration with water depth due to difference droplet size by Zhao et al. 1990

Figure 2: Variation of oil concentration with water depth due to difference diffusion coefficients by Zhao et al. 1990

Figure 3: Vertical distribution of n-alkane in the sea by Yang et al. 1992

Assuming that the synchronous movement of oil film and water flow, and spilled oil concentration C unchanged along with time. Take the moving coordinate system. The diffusion equation of oil droplets can be simplified as follow:

$$\frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right) + \frac{\partial}{\partial z} (VC) = 0 \quad (1)$$

where C_0 is the datum point concentration (mg/L);

when $z=a$, then $C=C_0$;

when $z \rightarrow \infty$, then $C=0$.

where D_z is the vertical turbulent diffusion coefficient, taking for as a constant, then the solution of the equation (1) is:

$$C(z) = C_0 \exp \left[-\frac{V}{D_z} (z - a) \right] \quad (2)$$

This is the spilled oil concentration vertical distribution formula. Obviously, the concentration reduces exponentially.

Considering the relative motion slight between the oil droplets and water body, the oil droplets floating velocity V mentioned in the equation (2) can be calculated as follows:

$$V = \frac{(\rho_w - \rho_o) g d^2}{18 \mu_w} \quad (3)$$

where d is the oil particle diameter (m); μ_w is the coefficient of viscosity of water ($N \cdot s/m^2$), ρ_o , ρ_w present density of oil and water respectively (kg/m^3). Some studies showed that the average diameter of oil droplets is 0.250 mm and the mean square error is 0.075 mm [30].

In addition, the vertical turbulent diffusion coefficient D_z can be calculated based on the following:

$$D_z = \alpha_z h u_* \quad (4)$$

where α_z = empirical coefficient, and the suggested value is 0.067 [31]; h = water depth (m); u_* = friction velocity.

It is necessary to input datum concentration C_0 into the equation (2) to predict the vertical concentration distribution of spilled oil. Therefore it is obvious that the characteristic parameter, datum concentration C_0 , is the key limiting condition for the usage of the spilled oil vertical concentration distribution formula. However there are no appropriate field detection conditions and measurements. Obviously, it is impossible to acquire the datum concentration by actual measurement for early warning and forecasting of water quality. Therefore, it is the key technical problem

to determine the datum point and its concentration, which decides whether the petroleum pollutants vertical concentration can get practical application in marine water quality warning and forecasting or not.

3 Determination of Datum Point Concentration

On the one hand, the spilled oil extension leads to expand the scope of pollution, which makes the oil film thinner. On the other hand, it can also increase the oil-water contact area, which will make more oil dissolve and emulsify into water body, strengthen the oil-water mixed degree, increase the oil concentration of water body, exacerbate the harm of the environmental protection goals [32]. Fay divided the oil membrane diffusion process into three stages, including gravity-inertia force stage, gravity-viscous force stage and surface tension-viscous force stage, according to the dominant driving force and resistance suffered.

First, when the oil film stays in the stage of surface tension-viscous force, it is thin and most of oil disperses into water [33]. Second, although there is still less proportion of oil film on the water body surfaces in this stage, considerate the most unfavorable risk effect. Therefore, it is assumed, the spilled oil could all dissolve and emulsify into the water and disperse evenly. Finally, set the reference point on the surface of water for solving the concentration C_0 easily.

The average spilled oil concentration of per unit area water column can be predicted from the following equation under the most unfavorable saturation.

$$\bar{C} = \frac{\rho_o g D}{H} \quad (5)$$

where $\bar{C}$ = the average spilled oil concentration (mg/L); H = the depth of the water column (m); D = the oil film thickness (mm).

And then establish the response relationship of the vertical concentration and the surface concentration by integrating along the vertical direction to get the average concentration.

$$\bar{C} = \frac{\rho_o g D}{H} \quad (6)$$

So the expression of C_0 can be showed by combining the equation (5) and (6):

$$C_0 = \frac{-K \rho_o D}{e^{-KH} - 1} \quad (7)$$

Where $K = \frac{v}{D_z}$

Therefore, the concentration C_0 can be acquired by the equation (7) after inputting the corresponding data. Use the vertical distribution of concentration formula to get spilled oil concentration at different water depths.

4 Application

A petrochemical pier is located in some waters, and ships docking process may lead to oil spill accidents. The maximum credible oil spill quantity is 70t according to the source strength estimated method. Use the hydrodynamic model to simulate the hydrodynamic characteristics and take oil particle model to simulate the migration path of petroleum pollutants. Considering the risk prediction principle and adopting a conservative estimation, most spilled oil migrates into the related water column through the vertical diffusion when they stay in the stage of surface tension-viscous force. For the research waters, the coefficient of viscosity of water (μ_w) is $1.002 \times 10^{-3} \text{ N}\cdot\text{S}/\text{m}^2$; the density of oil and water (ρ_o and ρ_w) is $850 \text{ kg}/\text{m}^3$ and $1030 \text{ kg}/\text{m}^3$ respectively. And the diameter of oil particle is $250 \text{ }\mu\text{m}$. The vertical turbulent diffusion coefficient D_z is $0.002 \text{ m}^2/\text{s}$. Then, the surface concentration is available and it can be used to predict the characteristics of the vertical concentration distribution. The results are presented in Table 1 and Figure 4.

Table 1: Spilled Oil Concentration Vertical Distribution

vertical distance from water surface (m)	2	3	4	5	6	7
Concentration (mg/L)	22.1	1.7	0.13	0.01	0.0008	6.4×10^{-5}

5 Conclusions

In this paper, a mathematical calculation method for computing the surface spilled oil concentration is put forward. In a word, we establish the response relationship of the vertical concentration and the surface concentration under the most unfavorable situation by integrating the spilled oil concentration along the vertical direction. After a series of calculations, the surface concentration is available.

1. Based on the vertical concentration distribution formula of spilled oil, a calculation method of the datum point concentration, applied to the stage of surface tension-viscous force, is proposed. This method makes the usage of the vertical concentration distribution formula to analyze and forecast the possible vertical concentration distribution characteristics. Generally speaking, the characteristic parameter calculated by this mathematical method fills in the gap between theory and practice.

2. It is the application premise of this method that most of the oil has dissolved and emulsified into the water, applying for the stage of surface tension-viscous force mainly. And it can also apply for the second stage of spilled oil diffusion (stage of gravity-viscous force) after considering the safety and conservation of the risk impact assessment even though the results will be overestimated.
3. This method is not only suitable for oil spill accidents occurring in the sea, but also in the inland rivers, especially analyzing the impact from petroleum pollutants to the sensitive objects, and evaluating the accidental influence on the marine biological communities and water intakes which are located at different depths.

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