

Simulation and parameter determination of persistent organic pollutants sorption process in sediment

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1 Purposes

The distribution of persistent organic pollutants (POPs) in the ocean is affected by the sorption-desorption process of sediment particles, which is determined by the concentration of POPs in seawater, water temperature, and organic carbon content of sediment particles. Quantitative relationships between the net sorption rates and these factors have not been established and used in POPs transport models. This study aimed to accurately simulate the net sorption processes of phenanthrene, a representative POPs, in marine environments. To achieve this, the parameters of the two-compartment mass-transfer model was determined by fitting the model results to the experimental data. Quantitative relationships were then established between the model parameters and the initial concentration of phenanthrene, water temperature, as well as organic carbon content of the sediment particles.

2 Methods

2.1 Two-compartment mass-transfer model

In the two-compartment mass-transfer model, the net sorption process is divided into fast and slow processes (Ding et al., 2008). Consequently, the pollutant concentration in the solid phase (C_p , mg g⁻¹) also have two components: the concentrations of fast (C_p^f , mg g⁻¹) and slow processes (C_p^s , mg g⁻¹). The net sorption rate is the sum of the two processes and can be expressed as

$$\begin{aligned} \frac{dC_p}{dt} &= \frac{dC_p^f}{dt} + \frac{dC_p^s}{dt} \\ &= (k_a^f \cdot C_d - k_d^f \cdot C_p^f) + (k_a^s \cdot C_d - k_d^s \cdot C_p^s) \end{aligned} \quad (1)$$

where C_d (mg L⁻¹) are the concentrations of the aqueous phase. k_a^f and k_a^s (L g⁻¹ min⁻¹) are the sorption rate coefficients, and k_d^f and k_d^s (min⁻¹) are the desorption rate coefficients, $k_a^f \cdot C_d$ and $k_a^s \cdot C_d$ are sorption rates for the fast and slow processes, and $k_d^f \cdot C_p^f$ and $k_d^s \cdot C_p^s$ are desorption rates for the fast and slow processes.

2.2 Experimental data and simulations

The experimental data used in this study were obtained from the measured net sorption processes of phenanthrene between sediment particles and seawater. Three groups of experiments (Groups I, II, and III) were performed to examine the effects of the initial phenanthrene concentration in seawater, water temperature, and organic carbon content of the sediment particles on the net sorption process. These three groups of experiments can be used to determine model parameters under different phenanthrene concentrations in seawater, water temperatures, and organic carbon contents of the sediment particles. The experimental data of the three groups were the results of previous studies and the specific experimental methods are referred in the corresponding papers (Yang and Zheng, 2010; Zheng, 2010; Xu and Huang, 2011).

The parameters of the model were determined by fitting the solutions to Eq. (1) to the experimental data. The correlation coefficients (r^2) and sums of squares of error (SSE) between the model results and the experimental data were calculated to evaluate the effects of the simulation. Based on these results, the dependences of the parameters in Eq. (1) on the initial phenanthrene concentration in seawater, water temperature, and organic carbon content of the sediment particles were examined.

3 Results

3.1 Influence of the initial concentration in seawater on net sorption

The net sorption experimental data for Group I were obtained for three different initial pollutant concentrations. In the two-compartment mass-transfer model, k_a^f and k_a^s represent the migration rates of phenanthrene from seawater to sediment particles and k_d^f and k_d^s represent the migration rates from sediment particles to seawater. k_a^f and k_d^f determine the net sorption rate of the fast process, and k_a^s and k_d^s determine the net sorption rate of the slow process. k_a^f , k_a^s , k_d^f , and k_d^s showed little change at the three different initial concentrations. In other words, the initial concentration of phenanthrene in seawater had little impact on the k_a^f , k_a^s , k_d^f , and k_d^s values. Thus, a fixed set of parameters was used in all three experiments (Fig. 1). k_a^f , k_a^s , k_d^f , and k_d^s were tuned

to obtain a set of optimal values to reduce the bias between the model results and the experimental data, which were $0.0399 \text{ L g}^{-1} \text{ min}^{-1}$, $0.00331 \text{ L g}^{-1} \text{ min}^{-1}$, 0.475 min^{-1} , and 0.0766 min^{-1} , respectively, obtaining an r^2 of up to 0.9931.

The results show that the model can reproduce the experimental data using a set of parameters for different initial concentrations. Therefore, it is feasible to use a set of parameters for ocean simulations with variable phenanthrene concentrations.

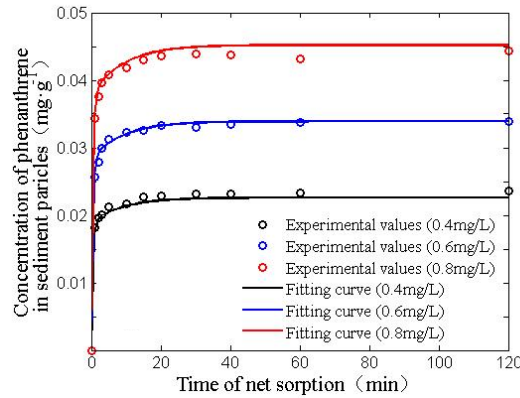


Fig. 1 Simulation curves of the two-compartment mass-transfer model for phenanthrene at different initial concentrations with the same set of parameters.

3.2 Influence of the water temperature on net sorption

The experiments in Group II tested the dependence of the net sorption curves on the water temperature. Based on the fitting results of these three experiments quantitative relationships between the parameters in the two-compartment mass-transfer model was established, which are expressed as follows:

$$k_a^f = -0.0006 \cdot T + 0.0553 \quad (2)$$

$$k_a^s = -0.0001485 \cdot T + 0.0075 \quad (3)$$

$$k_d^f = -0.0008 \cdot T + 0.4943 \quad (4)$$

$$k_d^s = 0.0022 \cdot T + 0.034 \quad (5)$$

where T is the water temperature ($^{\circ}\text{C}$).

When only one set of parameters was used, the maximum value of r^2 was 0.8903. When the linear relationship between the parameters and the water temperature in Eqs. (2-5), the mean r^2 reached up to 0.9954, with an SSE of 7.66×10^{-6} , which indicated a better performance of the model (Fig. 2).

The accuracy of the simulations was improved by considering the dependence of the model parameters on water temperature. Moreover, it has become more reasonable and feasible to apply this model to real oceans with spatially and temporally changes in the water temperature.

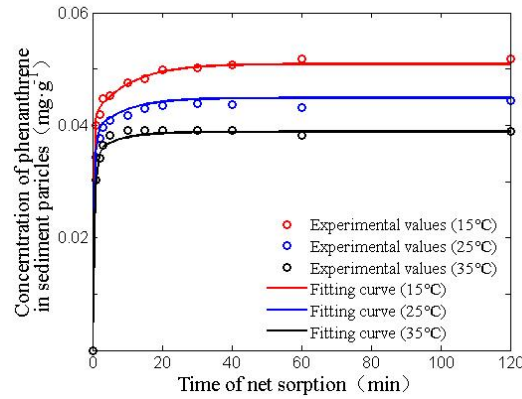


Fig. 2 Simulation curves of the two-compartment mass-transfer model considering the dependence of the parameters on the water temperature.

3.3 Influence of the organic carbon content of sediment particles on net sorption

The experiments in Group III showed the net sorption curves of the sediment particles with three different organic carbon contents. The parameters were assumed to be linear functions of the organic carbon content. In the two-compartment mass-transfer model, the linear relationships between parameters and the organic carbon content are expressed as follows:

$$k_a^f = 0.3318 \cdot f_{oc} + 0.00036445 \quad (6)$$

$$k_a^s = 0.0495 \cdot f_{oc} - 0.00016960 \quad (7)$$

$$k_d^f = 0.2554 \cdot f_{oc} + 0.0271 \quad (8)$$

$$k_d^s = -0.0258 \cdot f_{oc} + 0.0033 \quad (9)$$

where f_{oc} is the organic carbon content (%).

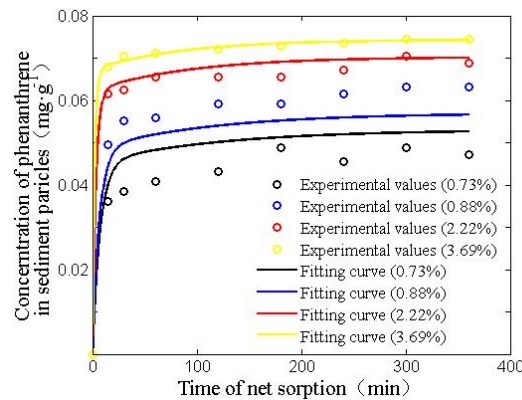


Fig. 3 Simulation curves of the two-compartment mass-transfer model considering the dependence

of the parameters on the organic carbon contents.

When considering the dependence of the parameters on the organic carbon content of the sediment particles (Fig. 3), the fitting results showed that r^2 was up to 0.9612 and SSE was 1.35×10^{-4} . However, if the dependences of the parameters on organic carbon content is ignored, the optimal r^2 was only 0.7600. The results showed that the simulation accuracy significantly improved by changing the model parameters for different organic carbon contents.

4 Future Challenges

Further improvements are required in this study. Estimations of the parameters of the two-compartment mass-transfer model largely depended on the three selected laboratory experiments. Thus, additional sorption kinetics experiments must be conducted to verify the accuracy of the parameters in the model.

In future studies, similar methods can be used to determine the sorption-desorption parameters of other POPs. In addition, the results of this study make it possible to simulate the distribution and fate of POPs in both seawater and sediment by embedding a net sorption module into the transport model of POPs, which improves the accuracy of the simulation. Moreover, the parameters can be adjusted according to the comparison between the simulated results and the observations, and the sorption-desorption parameters suitable for other POPs can be determined.

Reference

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