

Numerical simulation and flux calculation of persistent organic pollutants concentration profiles in offshore sediments

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1 Aims

persistent organic pollutants (POPs) can persist in the environment and can be harmful to organisms. Offshore sediment is a sink for many contaminants, where POPs can accumulate in large numbers. In the future, POPs emission will gradually decrease due to certain policies to prohibit the discharge of POPs, the concentration of POPs in Marine water will decrease, POPs in sediments may become a source of pollution in the ocean. Therefore, in this study, phenanthrene in polycyclic aromatic hydrocarbons (PAHs) was taken as the research object, and the sediment-water interface flux was predicted by numerical simulation according to POPs concentration profile in existing sediment, so as to provide a basis for further assessment of phenanthrene in sediments' contribution to environmental pollution in Marine. This will be achieved through the following objectives : (1) Construct a transport model for persistent organic pollutants in offshore sediments, (2) Calculation of response of sediment phenanthrene concentration profile to sediment-water interface ideal flux, and (3) invert and forecast the sediment-water interface flux of phenanthrene in offshore sediments.

2 Procedure

2.1 Model construction

A vertical one-dimensional model was constructed according to the transport process of POPs in sediment, and its governing equation was as follows:

$$\frac{\partial(1-\varphi) \cdot \rho_s \cdot C_p}{\partial t} = \frac{\partial(1-\varphi) \cdot \left[D \frac{\partial(\rho_s \cdot C_p)}{\partial z} \right]}{\partial z} - \frac{\partial(1-\varphi) \cdot [\omega_s(\rho_s \cdot C_p)]}{\partial z} + (1-\varphi) \cdot \rho_s \cdot [(K_{a1}C_w - K_{d1}C_{p1}) + (K_{a2}C_w - K_{d2}C_{p2})] \quad (1)$$

$$\frac{\partial \varphi \cdot C_w}{\partial t} = \frac{\partial \varphi \cdot \left[D \frac{\partial C_w}{\partial z} \right]}{\partial z} - (1-\varphi) \cdot \rho_s \cdot [(K_{a1}C_w - K_{d1}C_{p1}) + (K_{a2}C_w - K_{d2}C_{p2})] \quad (2)$$

where, C_p , C_w is POPs concentration in sediment particles (ng/g) and in interstitial water (ng/m³), ρ_s is dry weight density of sediment particles (g/m³), φ is sediment porosity, D is diffusion coefficient (m²/s), ω_s is deposition rate (m/s), k_{a1} (m³/g/min), k_{a2} (m³/g/min), k_{d1} (1/min), k_{d2} (1/min) are sorption-desorption rate coefficient.

2.2 Ideal experiments

Under different ideal sediment-water interface flux scenarios (different constant flux, linear flux, periodic flux, etc.), the response results of phenanthrene concentration profile in sediments simulated by the model will be obtained.

2.3 Inversion and prediction

Based on the collected vertical distribution data of phenanthrene in sediment in Bohai Sea (Figure 1), and combined with the response law of POPs concentration profile in sediments to sediment-water interface ideal flux obtained from ideal experimental results, the flux of POPs concentration profile in existing sediments was inverted. In addition, the sediment-water interface flux was predicted based on emission prohibition of POPs in the future.

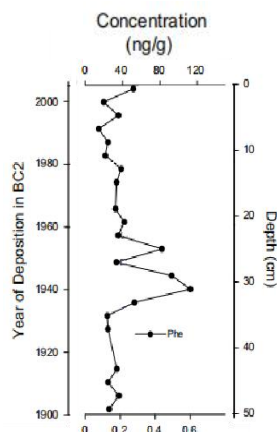


Figure 1 Profile of phenanthrene concentration in sediment particles in Bohai Sea (Hu et al., 2011).

3 Result

3.1 Response of sediment phenanthrene concentration profile to sediment-water interface ideal flux

As a first step in model studies, it is necessary to understand the response of

phenanthrene concentration profiles in sediment particles to the phenanthrene flux at the sediment-water interface (Figure 2). In this calculation, the simulated depth was 40 cm, the initial values used the observations in Figure 1. The boundary conditions of this model were as follows: the flux was given directly at the upper interface of sediment particles and interstitial water, and the flux at the lower interface was calculated using the underlying concentration.

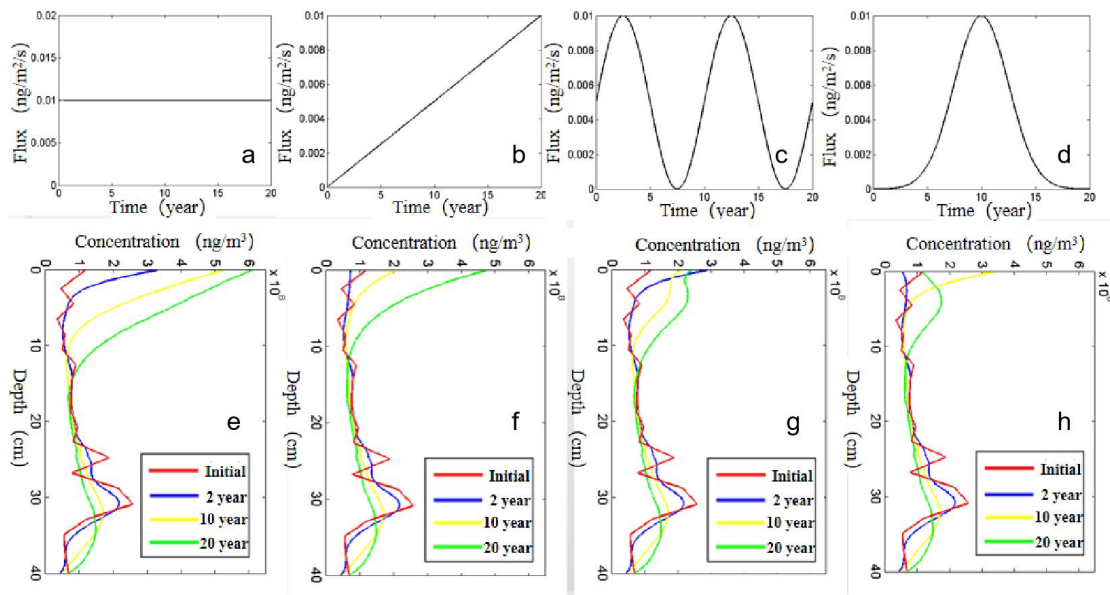


Figure 2 Response of phenanthrene concentration profiles in sediment particles to four ideal seafloor fluxes. a : the constant flux. b: the linearly increasing flux. c: the periodically changing flux. d: the normally distributed characteristic changing flux. e, f, g and h correspond to the simulation results under the four flux input scenarios a, b, c and d respectively.

The above calculations showed that different phenanthrene fluxes at the sediment-water interface could produce different phenanthrene concentration profiles in sediment.

3.2 Inversion and prediction of phenanthrene flux at sediment-water interface

The long-term phenanthrene flux at the sediment-water interface was inverted based on the response rule of the phenanthrene concentration profile in sediment in section 3.1. In this calculation, the simulated depth of sediment was 40cm, the observed values of 40-50cm in Figure 1 were used as the initial values of 0-10cm in the initial profile, and the concentrations below 30cm were the same as that at 50cm in Figure 1 (Figure 3a). The boundary conditions were similar to that of section 3.1. It was assumed that only

phenanthrene in particle was used as the input of phenanthrene in sediment. The phenanthrene fluxes in particles at the sediment-water interface were shown in Figure 3b, and the phenanthrene flux in interstitial water at the sediment-water interface was assumed to be 0. The concentration profile of phenanthrene in sediment was obtained through the simulation for 80 years (Figure 3b). The peak concentration of phenanthrene in the profile appeared at 30cm, which was not much different from the observation result, and the trend of variation was basically the same as that of the observation results. The flux peaked at $0.048 \text{ ng/m}^2/\text{s}$ around 20 years, which corresponded to the peak at 30cm of the concentration profile after 80 years.

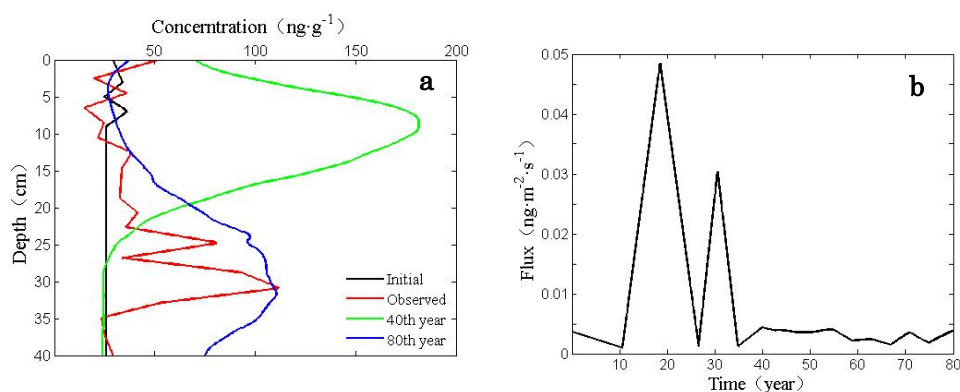


Figure 3 a: simulation of concentration profile in sediment based on inversion flux. b: inverted flux of phenanthrene at the sediment-water interface.

On this basis, if the concentration of phenanthrene in the ocean was extremely low due to control of POPs in the future, the fluxes of phenanthrene at sediment-water interface were be calculated. In this calculation, the initial values use the observations in Figure 1. The boundary conditions of this model were as follow: the phenanthrene concentration in sediment particles and in the liquid phase outside the upper interface were 0, and the upper boundary fluxes were calculated by these concentrations. And the lower boundary fluxes were calculated by using the concentration at the bottom of the interface. The concentration profile of phenanthrene in sediment was calculated through the simulation of 80 years (Figure 4a). The concentration of phenanthrene in the surface layer of sediments gradually decreased with the time. It was because part of phenanthrene in the surface layer of sediment re-entered the ocean through

re-suspension and diffusion, and some of phenanthrene in the surface layer gradually sank with the sedimentation. The peak value of phenanthrene at 30cm in sediment gradually decreased while moving down. This is because phenanthrene in interstitial water diffused into upper seawater and deeper interstitial water, resulting in a decrease in concentration. Therefore, phenanthrene in sediment particles gradually desorbed into interstitial water, and phenanthrene concentration in sediment particles also decreased gradually. In 20-40 years, the total amount of phenanthrene in the sediment can be reduced by half.

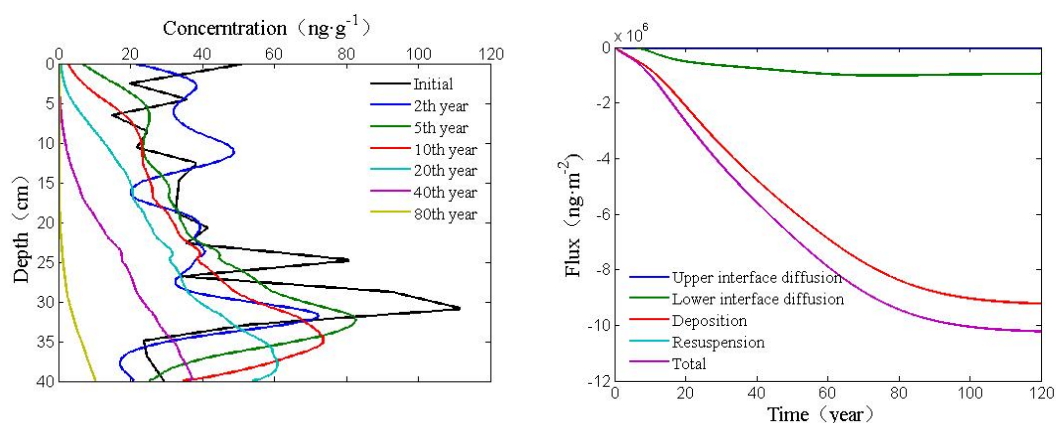


Figure 4 a: simulation of concentration profile in sediment in future scenario. b: predicted flux of phenanthrene at the sediment-water interface in future scenario.

The fluxes of phenanthrene were showed in Figure 4b (negative values represented phenanthrene leaving the sediment column). The results showed that the sedimentation of particle and interstitial water diffusion at lower interface caused most phenanthrene to enter deeper sediment, while the re-suspension of particle and interstitial water diffusion at upper interface only released a small amount of phenanthrene back into the ocean. However, the results did not consider that the high concentration of phenanthrene in deeper sediment could also re-enter the Marine environment through the diffusion of interstitial water, so the results may underestimate the phenanthrene flux at the upper interface.

Reference

Hu, L., Guo, Z., Shi, X., Qin, Y., Lei, K., and Zhang, G.. (2011). Temporal trends of aliphatic and polyaromatic hydrocarbons in the Bohai Sea, China: evidence from the sedimentary record. *Organic Geochemistry*, 42(10), 1181-1193.