Source, Fate and Public Health Impact Assessments of PAHs in the Bohai Sea Region
渤海における多環芳香族炭化水素(PAHs)の排出源、環境中動態、健康影響の評価

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1. Background and objective

Polycyclic aromatic hydrocarbons (PAHs) are a group of the most important persistent organic pollutants, released through the incomplete combustion, and widely distributed in the atmospheric phase[1]. By atmospheric deposition, effluent runoff, and petroleum spill, these toxic compounds could persist in the aquatic systems, and exert a significantly negative impact on the local ecosystems and public health with carcinogenic and mutagenic activity, through the food-web and bio-accumulation effects[2].

Bohai Sea Rim (BSR, Fig.1) has witnessed an unprecedented boom in recent decades, especially in the field of economy and industry. However, with the rapid development of urbanization in BSR, the aquatic environment has been receiving large inputs of pollutants from the coastal agricultural industrial, and domestic sources, which are difficult to enumerate and characterize[3]. The relevant studies showed relatively high levels of PAHs detected in the air, water, soil vegetation, and even food items in China[1,4].

Multimedia analyses based on fugacity models[5,6] provides a useful tool for quantitatively simulating the physicochemical process of persistent organics pollutants in the environment, and even in the aquatic food web[2,5,7].

In this study, sixteen EPA priority PAHs, including naphthalene (NAP), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Dibenzo(a,h)anthracene (DahA), Indeno[1, 2, 3-cd]pyrene(IcdP), and Benzo(g,h,i)perylene(BghiP) were selected as target components, and the primary objectives of this study were: (1) to investigate the source apportionment through available data from relevant literature on Bohai Sea; (2) to establish fugacity models to simulate the historical changing and spatial distribution of these toxic components, and predict their fate in Bohai Sea Region; and (3) to assess the public health risk based on the concentration level in aquatic food consumption and the human beings' daily food intake.

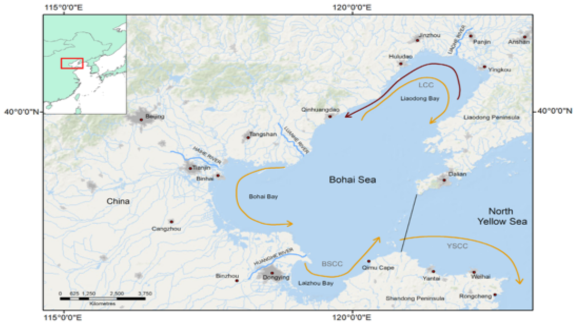

Fig.1 The Bohai Sea

2. Method

2.1 Statistical sources analyses

Data collected from the relevant literature were performed using SPSS 23.0 software. The characteristic ratios of IcdP/(IcdP+BghiP), BaA/(BaA+Chr), Fla/(Fla+Pyr), and

Ant/(Ant+Phe) were employed to identify the possible sources. Furthermore, the source contributions of PAHs congeners could be quantified by principal component analysis (PCA) combined with multivariate linear regression (MLR).

2.2 Multimedia Model

Fugacity-based multimedia model has been employed to simulate the temporal tendency of concentrations and inter-compartmental transfer fluxes of PAHs, including three main phases, air, water, and sediment, several additional phases, soil, biota (fish), atmospheric particles, suspended solids, and water in sediment. The fugacity models were subject to following the mass balance equation:

$$Z_1V_1 \times df_1/dt = E_{01t} + D_{21} \times f_2 - (D_{12} + D_{1m}) \times f_1 - E_{10t} \tag{1}$$

$$Z_2V_2 \times df_2/dt = E_{02t} + D_{12} \times f_1 + D_{42} \times f_4 - (D_{21} + D_{24} + D_{2m} + D_{bioc}) \times f_2 - E_{20t} \tag{2}$$

$$Z_4V_4 \times df_4/dt = D_{24} \times f_2 - (D_{42} + D_{4m}) \times f_4 \tag{3}$$

Where *1, 2*, and *4* means air, marine, and sediment phase; *f* is the fugacity (Pa); *0, t, m,* and *bioc* means the outside of the boundary, advection, degradation, and bioconcentration; Z_i is the capacity of fugacity (mol m^{-3} Pa^{-1}) in phase *i*; *V* means the volume (m^3), D_{ij} means the transport coefficient from phase *i* to phase *j* (mol Pa^{-1} h^{-1}).

The fugacity could unify the concentration in different phases through the fugacity capacities (Z value, Fig. 2) to established a dynamics model. Additionally, the model was programmed using Matlab2019b, and the interval was set as daily steps to start a historical progress on a long term numeric simulation from 1953 to 2053, and the major uncertainties input data would be identified through sensitivity analysis, and 1000 times Monte Carlo's simulation[8].

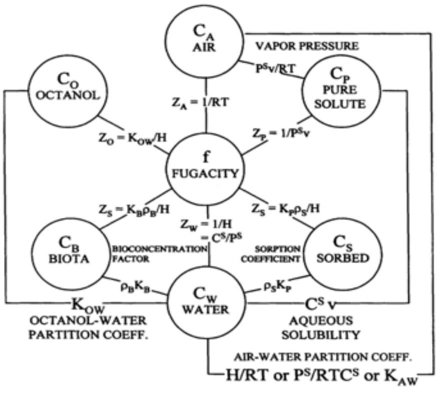

Fig.2 Definition of Fugacity Capacities

2.3 Health impact assessment

The BaP toxic equivalency factors (TEFs) were employed to estimate the carcinogenic toxicity, and combined with the behavior of human growth to estimate the concentration level in the lipid phase for a single individual over his or her entire lifetime.

3. Data source and simulation conditions

The concentration data were collected from the relevant research on PAHs in Bohai Sea Rim, and the fugacity model parameters were mainly based on Mackay's work [5].

The simulation field, Bohai Sea, is located in the northwest Pacific Ocean (37°07' N to 41°N, and 117°35'E to 121°10'E), including Liaodong Bay, Bohai Bay, Laizhou Bay, and the central Bohai Sea, with a total 7.7×10^{10} m^3, and 1.60×10^{10} m^3 in Bohai Bay, which also contains 6 compartments to reveal the geographic divergence of the PAHs fate.

The initial concentrations of air, freshwater, marine water, sediment, and soil phases in 1953 were estimated through the BETR-Global Model, which is also based on the fugacity. The boundary conditions of the emission include 3 main pathways, the direct emission in the compartment, and the pollution through the air and river advection.

4. Results and discussion

For source apportionment, the empirical results of diagnostic ratio revealed an industry and energy constructure tendency from petrogenic to pyrogenic source in the Bohai Sea region. PCA showed the source in the Bohai Sea (Fig.3) mainly consisted of mixed combustion source, with 87.81% contribution, and petrogenic source, with 8.7%. However, Bohai Bay showed 60.22% contribution for traffic source, and 20.47% for the coal and natural gas combustion, and the loading of traffic, coal, and natural gas was much higher than the other regions, like Yellow River estuary, Laizhou Bay, and Liaodong Bay.

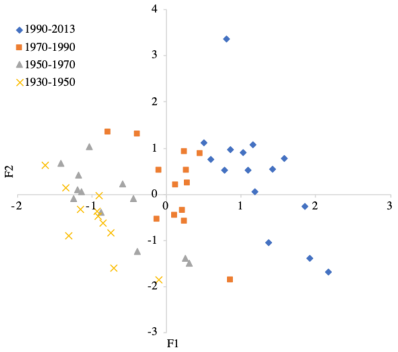

Fig.3 Loading point distribution in the Bohai Sea

The validation of the fugacity model was based on the concentration analysis from previous literature (Fig.4), including the air, particles, suspended solid, and water, and revealed a generally decent agreement with one order of magnitude with most PAHs congeners.

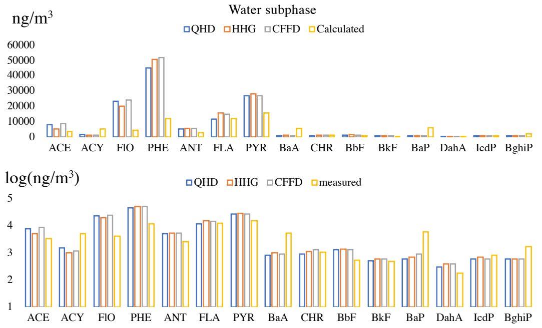

Fig.4 Concentration validation in water subphase

The concentration change could reveal the retardance of different congeners in each phase well, and the geographic divergence in the Bohai Bay region could also reveal significant concentration difference, especially for these high molecular weight PAHs. Furthermore, the scenarios of air advection and water exchange revealed the liquid media could impact the spread of these components significantly (Fig.5).

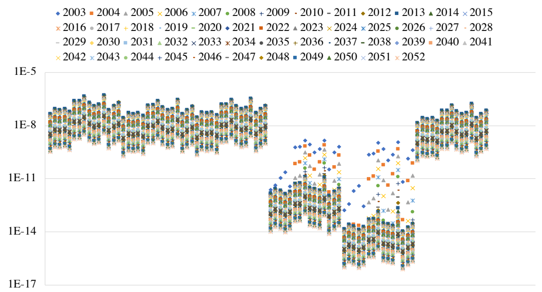

Fig5. A scenario in the water phase without water exchange (mol/m^3)

The sensitivity analysis showed several highly sensitive parameters including temperature, Henry's constant, especially in water phases, emission rate, degradation coefficient, and thickness in each phase (Fig.6). These sensitivities are also impacted by the congener structure, molecular weight, phases, and geographic divergence. The coefficient of variations for 15 congeners in the air phase is usually lower than 10%, in the liquid phase about 10%, and sediment usually higher than 20%. However, the solid phase showed a significant coefficient of variations, higher than 90% or even 100%, and for Pyr even higher than 170%. The coefficient in the biota phase (fish) is also pretty high, and higher than 70%, which could exert a significant uncertainty in environmental toxicity assessment.

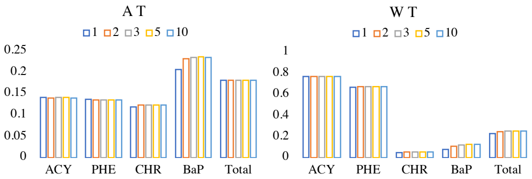

Fig.6 Sensitivity coefficient

(Temperature in Air and Water phase)

For the health assessment (Fig.7), the highest lifetime accumulation concentration per lipid weight existed in the 1960s' male, with 84.12 ng, followed by 1950s' male with 82.89 ng and 1970s' male with 79.04 ng. The highest concentration existed in the 1950s' female, with 77.83 ng. The newborn in 2010s showed the highest body burden concentration of 42.99 ng, and followed by 2020s', about 42.59 ng. However, the high uncertainty still impacted the result of health assessment, including the policy, group of the human, living environment, and aquatic species, but the results could still provide enough information to improve the environmental and health risk management systems.

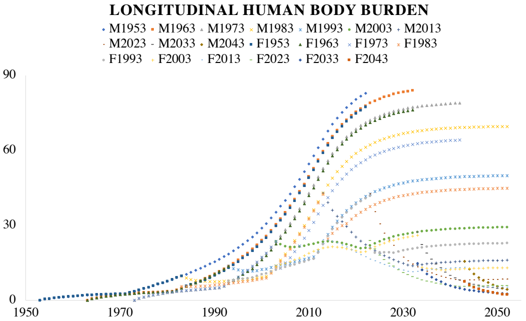

Fig.7 Longitudinal body burden of BaP TEQ (ng/lipid g)

5. Summary

In this study, the source apportionment, fate simulation, and health assessment could provide acceptable results and information for the risk management of these toxic pollutants. There is no denying that the fugacity model is under development nowadays, but could still provide available fate simulation of these organic components with complicated pathways. Though the uncertainty of the model is significantly high, fugacity is still a successful mass model in fate analysis, ecotoxicity evaluation, and health assessment.

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