EVALUATION OF GAS-PARTICLE PARTITIONING OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN GLOBAL AIR BY AVAILABLE MODELS

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Introduction

The importance of gas-particle (G-P) partitioning in affecting the efficiency and scope of their long-range atmospheric transport and fate for semi-volatile organic compounds (SVOCs) has been widely recognized[1]. Several models for prediction of G-P partitioning of SVOCs, including Junge-Pankow model, Harner-Bidleman model, Dach-Eisenreich model, poly-parameter linear free energy relationship (pp-LFER) model, multi-phase poly parameter linear free energy relationship (mp-pp-LFER) model, Li-Jia empirical model, and Li-Ma-Yang model, have been developed and applied for several POPs, but not all for PBDEs. To have a better understanding of G-P partitioning of PBDEs in the study of fate, long-range transport and wet and dry deposition of PBDEs, in the present study, all these models are applied to predict the G-P partitioning of PBDEs and the predicted results by these models are compared, and the models are evaluated.

Materials and Methods

Data sources

Available concentration data of PBDEs in both gas- and particle-phases from our previous study[2-4] and also from several other international studies have been collected[5-9]. Eight PBDE congeners (-28, -47, -99, -100, -153, -154, -183, and -209) were studied on G/P partitioning behavior in this work.

Method

Junge-Pankow model. Based on the linear Langmuir isotherm, the Junge-Pankow model was originally suggested by Junge and later critically reviewed by Pankow[10]. This model assumes that the semi-volatile organic compounds are entirely adsorbed onto the surface of particle matters, and the particle fraction, Φ ($=C_P/(C_P+C_G)$, where C_G and C_P are respectively the concentrations of SVOCs in gas and particle phases (both in $pg \cdot m^{-3}$ of air)) is given by[10]

$$\Phi = C_J\Theta/(C_J\Theta + P_L^0) \quad (1)$$

where the P_L^0 (Pa) is the sub-cooled liquid vapor pressure, Θ ($cm^2_{surface}cm^{-3}_{air}$) is the particle surface area concentration. and C_J is a parameter usually assumed to be 17.2 Pa·cm.

Harner and Bidleman Model. Assuming absorption is the main processes between gas- and particle- phase, Harner and Bidleman[11] derived Equation (2) to calculate G/P partition quotient ($K_P = C_P / (TSP\ C_G)$, where *TSP* is the concentration of total suspended particle in air) in the equilibrium state, denoted by $K_{P,HB}$,

$$\log K_{P,HB} = \log K_{OA} + \log f_{OM} - 11.91 \quad (2)$$

where f_{OM} is organic matter content of the particles and K_{OA} is octanol-air partition coefficients.

Dachs and Eisenreich Model. Dachs and Eisenreich[12] suggested the use of a dual-model that, in addition to absorption into organic matter, accounts for adsorption onto soot particles. Assuming that EC is a surrogate for the soot phase, this model can be formulated as

$$K_P = 10^{-12}[f_{OM}/\rho_{OCT} \times (\gamma_{OCT} M_{OCT}/\gamma_{OM} M_{OM}) K_{OA} + f_{EC}(\alpha_{EC}/\alpha_{AC}) K_{SA}] \quad (3)$$

where f_{OM}, f_{EC} is the fraction of organic matter (OM), elemental carbon (EC) in particle matters; α_{EC} and α_{AC} are specific surface areas of elemental carbon and activated carbon, respectively. ρ_{OCT} is the density of octanol. γ_{OCT} and γ_{OM} are activity coefficients of the target compound in octanol and organic matter, respectively, M_{OCT} and M_{OM} are molecular mass of octanol and organic matter, respectively.

pp-LFER Model. The poly-parameter liner free energy relationship (pp-LFER) approach was developed by Abraham[13] and Goss[14] as

$$\log K_{P,LFER} = sS + aA + bB + vV + lL + c \quad (4)$$

where capital letters (S, A, B, V, L) are the parameters for dipolarity/polarizability, electron-acceptor and donator, non-specific interactions like cavity formation energy and the energy that comes from dispersive van der Waals interaction. The corresponding small letters are known as system parameters and reflect the matrix-specific solute-independent energetic contribution to the K_P.

GÖtz[15] applied pp-LFER sorption model to predict the G-P partitioning of SVOCs, including adsorption and absorption process. The dimensionless partition coefficient K_P* is the sum of partition coefficients to the bulk aerosol i and the aerosol surface j, which is calculated by

$$K_P^* = \sum_i C_i K_{i,bulk/air} + \sum_j C_j K_{j,surf/air} \quad (5)$$

where $K_{i,bulk/air}$ is the partition coefficients for absorption into aerosol bulk phases i, in unit of m^3 air/g aerosol; $K_{j,surf/air}$ is the partition coefficients for adsorption on the various aerosol surfaces j, in unit of m^3 air/m^2 aerosol. C_i ($\mu g/m^3$) is the mass concentration of aerosol components i and C_j (m^2/m^3) is the surface area concentration of aerosol components j in air.

Li-Jia Empirical Model. Based on a large data set of more than 700 pairs of air samples in both gas and particle phases with a wide ambient temperature range of 60 ºC from -22 to 38 ºC obtained from Chinese POPs Soil and Air Monitoring Program, Phase2 (China-SAMP-II), Li and Jia[16] derived for the first time empirical equations to predict the values of slopes and intercepts for both K_{OA}-based and P_L-based models as functions of temperature, without assuming an equilibrium status and free of artifacts. The Li-Jia empirical model is

$$\log K_{P,LJ} = (0.011A - 0.135)t - 2.74B/(t+273) + 0.263A + 0.011B - 5.006 \quad (6)$$

$$\log K_{P,LJ} = 0.011B(\log K_{OA} - 12.27)/(\log K_{OA} - A) - 2.74\log K_{OA} + 31.85 \quad (7)$$

where A and B are parameters for log K_{OA} calculation.

Li-Ma-Yang Model. By considering wet and dry deposition of particles in studying the G/P partition of PBDEs, Li et al.[3] developed equation (2) to calculate the G/P partition quotient of PBDEs under the steady state

$$\log K_{P,LMY} = \log K_{P,Eq} + \log \alpha \quad (8)$$

where $\log K_{P,Eq}$ is designated the equilibrium term, given by any equation based on the equilibrium theory, (e.g, Equation (2)), and $\log \alpha$ is the non-equilibrium term, a function of f_{OM} and K_{OA}:

$$\log\alpha = -\log (1 + G / C) \quad (9)$$

In equation (3), C equals 5 for PBDEs and $G = 2.09 \times 10^{-10} f_{OM} K_{OA}$.

The two threshold values of $\log K_{OA}$, $\log K_{OA1}$ (=11.4) and $\log K_{OA2}$ (=12.5) of PBDEs divide the log K_{OA} into equilibrium (EQ), none-equilibrium (NE) and the maximum partition (MP) domains. [3]

Results and discussion

We have compared the Li-Ma-Yang model with the Harner-Bidleman model extensively[3,4], and this comparison between these two models is not repeated here. The results predicted by the Dach-Eisenreich model are close to the Harner-Bidleman model for PBDEs. Thus, the comparison between the Li-Jia empirical model, Li-Ma-Yang model and pp-LFER and mp-pp-LFER models are discussed here.

Based on the monitoring data of China-SAMP-II (with a wide ambient temperature range from -22 to 38 ^{o}C), 91.0-94.6 % of the total data pairs for the 8 PBDEs congeners were predicted within one order of magnitude accuracy with RMSE (root mean square errors) of log K_P ranging from 0.47 to 0.61 for the Li-Ma-Yang model. And the Li-Jia empirical model has a similar performance with Li-Ma-Yang model for the PBDE congeners, with RMSE ranged from 0.52 to 0.61 (from 88.9% to 95.5% of data pairs were predicted within one 1 log unit). The pp-LFER model has good performance for BDE-47 and BDE-100, but largely under-predicted the K_P values for BDE-28, BDE-99 and largely over-predicted the K_P values for BDE-153, BDE-154, BDE-183, and BDE-209. The RMSE of log K_P for target PBDEs ranged 0.65-2.67. The mp-pp-LFER model largely over-predicted the K_P values for 7 PBDEs except BDE-28, especially for the congeners with larger K_{OA} values (the RMSE ranged 1.06-1.24).

The monitoring data form west Antarctic Peninsula, Arctic Alaska, northern Greece, Italy, Japan have been also used to compare the four models in this study. The pp-LFER model largely underpredicted the K_P values for BDE-28 (RMSE: 1.23), -47 (RMSE: 0.8), and overpredicted the K_P values for BDE-183 (RMSE: 0.93), -209 (RMSE: 3.07). This model has been found the similar performance for PAHs. The mp-pp-LFER model largely overpredicted the K_P values of target PBDEs (except BDE-28 and -47) across all sites. The RMSE ranged from 1.15 to 5.39 (0% to 55.4% of data points were predicted within 1 order of magnitude accuracy for BDE-99, -153, -154, -183, and -209). The results show a good accuracy and a minor change for all target PBDE congeners in the performance of Li-Jia empirical model (i.e. RMSE: 0.37 ~ 0.57), and Li-Ma-Yang model (i.e. 0.31 ~ 0.91). The percentage range of the monitoring data points for the eight PBDE congeners were within ± 1 log unit in comparison to the predicted results by Li-Jia empirical model and Li-Ma-Yang model are 91.9% to 100 % and 70.4% to 100%, respectively.

Li-Jia empirical model and Li-Ma-Yang model have better performance than the others on predicting the G-P partitioning of PBDEs, especially when the values of their K_{OA} values are larger than $10^{12.5}$. Each model tells a good story of G-P partitioning of PBDEs in atmosphere, while the Li-Ma-Yang model captures the most important factors affecting the G-P partitioning of PBDEs.

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