Size-resolved gas-particle partitioning for polybrominated diphenyl ethers

Pengtuan Hu[1, 2], Lina Qiao[1, 2], and Yi-Fan Li[1, 2, 3, *]

[1] International Research Center for Arctic Environment and Ecosystem (IRC-AEE), Academy of Environment and Ecology, Harbin Institute of Technology, Harbin, Heilongjiang, China.

[2] International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), State Key Laboratory of Urban Water Resource and Environment, Environment School, Harbin Institute of Technology, Harbin, Heilongjiang, China.

[3] IJRC-PTS-NA, Toronto, Canada.

Introduction

Polychlorinated biphenyls (PBDEs) are a class of global and ubiquitous pollutions, most of which are highly toxic and bio-accumulative, thus dam aging the health of both wildlife and human beings. Additionally, the PBDEs are general with migration moving from source regions to other remote areas determined by their gas/particle (G/P) partitioning. Meanwhile, gaseous and particulate PBDEs can entering human body with breathing and other routes, and then the G/P partitioning of PBDEs has a significant influence on human exposure.

Many researches have discussed the G/P partitioning of PBDEs for the bulk air, but only one mentioned the relation of calculated the size-resolved G/P partitioning coefficients of PBDEs with the G/P partitioning of bulk air using the PAHs pattern, which ignored verification of each size-fraction. The objectives of this study are (1) to derive an equation to predict G/P partition quotients (K_P) for PBDEs between gas-phase and particle-phase with different size particles; and (2) to verify the presently derived equation with published PBDE data.

Methods

The G/P partition quotient of SVOCs, K_P, is commonly defined as [1]:

$$K_P = (C_P / TSP) / C_G \qquad (1)$$

where C_G and C_P are concentrations of SVOCs in gas and particle phases (both in pg·m^{-3} of air), respectively, and TSP is the concentration of total suspended particle in air (μg m^{-3}).

Under the conditions of the equilibrium, Harner and Bidleman (1998) derived the following equation to predict partition quotient without the need for real monitoring data [2]:

$$\log K_{PE} = \log K_{OA} + \log f_{OM} - 11.91 \qquad (2)$$

where f_{OM} is organic matter content of the particles. The subscript "E" in K_{PE} indicates equilibrium.

An equation to predict partition quotient under steady state was developed as [3]:

$$\log K_{PS} = \log K_{PE} + \log\alpha \qquad (3)$$

In the above equation, $\log K_{PE}$ is designated the *equilibrium term*, given by Equation (2), and $\log\alpha$ is the *non-equilibrium term*, given by for PBDEs:

$$\log\alpha = -\log (1 + 4.18\text{x}10^{-11} f_{OM} K_{OA}) \qquad (4)$$

Equation (3) indicats that the equilibrium is just a special case of the *steady state* when $\log\alpha = 0$. The size-resolved G/P partition quotient of SVOCs, K_{Pi}, is commonly defined as [4]:

$$K_{Pi} = (C_{P\,i} / PM_i) / C_G \qquad (5)$$

where C_G is concentrations of SVOCs in gas phase and C_{Pi} is concentrations of SVOCs in particle phase in the range of size distribution i (both in pg·m^{-3} of air), and PM_i is the concentration of particle in air (μg m^{-3}) in the range of size distribution i. The concentrations of SVOCs in bulk TSP is given by

$$C_P = \sum C_{Pi} \quad (6)$$

and

$$TSP = \sum PM_i \quad (7)$$

Define distribution function for PBDE congener in particle-phase at different size as:

$$R_{CPi} = C_{Pi} / C_P \quad (8)$$

and distribution function for SM in particle-phase at different size as:

$$R_{PMi} = PM_i / TSP \quad (9)$$

We have

$$K_{Pi} / K_P = R_{CPi} / R_{PMi} \quad (10)$$

And finally we obtain

$$\log K_{Pi} = \log K_P + \log R_{CPi} - \log R_{PMi} \quad (11)$$

In the above equation, log K_P can be partition coefficient under equilibrium log K_{PE} given by Eq. (2) or under steady state log K_{PS} given by Eq. (3). Notably, both the log K_{PE} and log K_{PS} were the coefficient of bulk atmosphere, not each grain-size.

Result and Discussion

Case Study: Thessaloniki, northern Greece. To verify the results from Eq. (11), we use the data for Thessaloniki, northern Greece, in which six different size particle samples (S1: <0.49 μm, S2: 0.49-0.95 μm, S3: 0.95-1.5 μm, S4: 1.5-3 μm, S5: 3-7.2 μm and S6: >7.2 μm) were collected and 9 PBDEs congener (BDE-17, BDE-28, BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-183) were analyzed [5]. As shown in **Figure 1**, the values of log K_{PSi} for different sizes fluctuate up and down around the line of the log K_{PS} for the bulk particles and begin to deviated from log K_{PE} when the log K_{OA}>11.4. Additionally, it's notable that the deviation of log K_{PSi} from log K_{PS} is within 1 order of magnitudes, which caused by the R_{CPi} and R_{PMi} for the distribution of PBDE congeners among different size particles. As shown in **Figure 2**, the values of log R_{CPi}-log R_{PMi} for size 2 are higher than the other size-fraction indicating that the G/P partition coefficients of size 2 (log K_{PS2}) are higher than the other size fraction (i=1,3,4,5 and 6). The points of log K_{PS2} are mostly above the line of log K_{PS} except 1 point (only 0.10 less than the log K_{PS}).

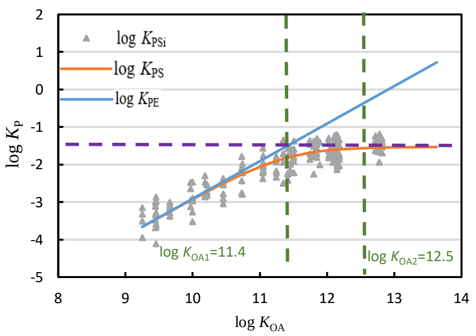

Figure 1 Size-resolved G/P partitioning coefficient of PBDEs calculated by Eq. (11) as a function of log K_{OA}.

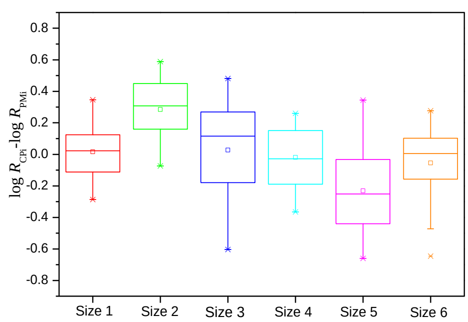

Figure 2 Size distribution of log R_{CPi} - log R_{Pmi}.

Size-resolved gas-particle partitioning quotients from monitoring data. The G/P partition quotient of PBDEs, K_{Pmi} (subscript m means the monitoring data), are calculated by Equation (5), and the result are plotted in **Figure 3**, where the log K_{Pmi} matches the log K_{PSi} well (r=0.981, p<0.01). As the calculated size-resolved G/P partition coefficient (log K_{PSi}), the monitoring partition coefficients (log K_{Pmi}) also demonstrate that the points of log K_{Pm2} are also above the lines of log K_{PS} and the values of log K_{Pm2} are higher than the other sizes, shown in **Figure 4**. Both from the calculated data and monitoring data, a tendency that gaseous PBDEs are like to be absorbed by the particle in the size 0.49-0.95 μm (size 2).

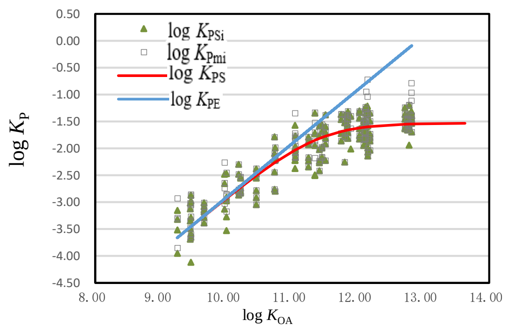

Figure 3 Size-resolved G/P partitioning coefficient of PBDEs (monitoring data) as a function of log K_{OA} with log K_{PSi}.

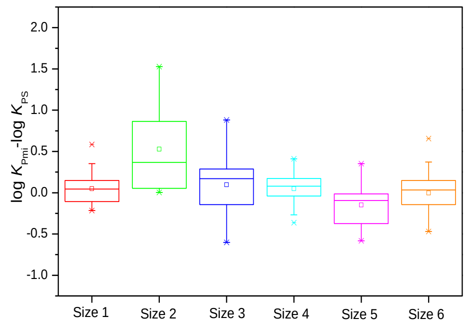

Figure 4 Size distribution of G/P partitioning for PBDEs monitoring data

Comparison to the previous equation. Basing the adsorption dominated J-P equation [6] and *equilibrium term* equation [2], Lyu et. al. calculated the different specific surface area (A) and f_{OM} varying different size of particle, and given a pair of size-resolved G/P partitioning of PBDEs. Considering the different size distribution of particle (in Greece 2015) with Lyu et. al., we adjusted A and f_{OM} as the corresponding particle size-distribution of Greece 2015 (**Table 1**) by the method given in Lyu et. al. The pair of equation were described as Eq. (12) and Eq. (13):

for adsorption

$$\log K_{P\text{-}ads} = -\log P^0_L - \log A - 8.35 = \begin{cases} -\log P^0_L - 6.65\ (<0.49\ \mu m) \\ -\log P^0_L - 7.35\ (0.49\text{-}0.95\ \mu m) \\ -\log P^0_L - 7.07\ (>0.95\ \mu m) \end{cases} \qquad (12)$$

and for absorption

$$\log K_{P\text{-}abs} = \log K_{OA} + \log f_{OM} - 11.91 = \begin{cases} \log K_{OA} - 12.26\ (<0.49\ \mu m) \\ \log K_{OA} - 12.37\ (0.49\text{-}0.95\ \mu m) \\ \log K_{OA} - 12.51\ (>0.95\ \mu m) \end{cases} \qquad (13)$$

Table 1 A and f_{OM} for different size of particle

μm	<0.49	0.9-0.95	>0.95
A ($m^2\ g^{-1}$)	50	10	19
f_{OM}	0.45	0.35	0.25

The result of log $K_{P\text{-}ads}$ and log $K_{P\text{-}abs}$ were plotted in **Figure 5** and **Figure 6**. Eq. (12) could only well describe the size-resolved G/P partitioning coefficients of PBDEs in the range of -6<log P^0_L<-4.5 and monitoring data deviated away from the line of Eq. (13) with the increasing of log K_{OA}.

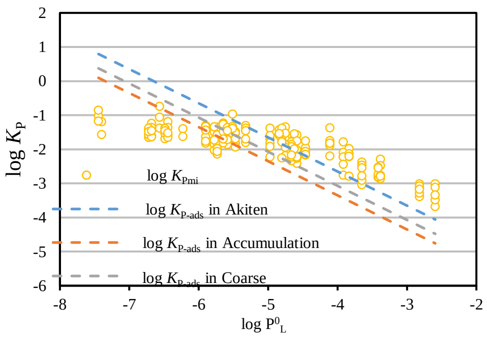

Figure 5 The relation of adsorption determined size-resolved G/P partitioning coefficients of PBDEs with bulk air.

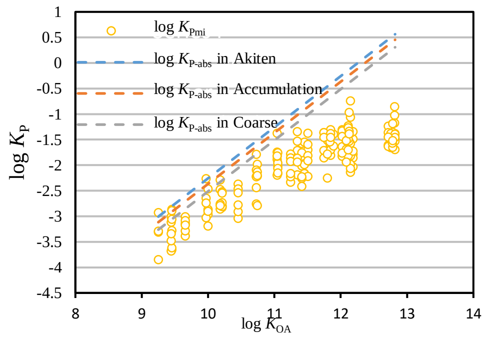

Figure 6 The relation of absorption determined size-resolved G/P partitioning coefficients of PBDEs with bulk air.

Limitation. During the verification of Eq. (11), concentration of PBDEs in gas phase was not monitoring data, but the estimated data using the steady state Eq (3). However, as shown by our published work [3,8], the results predicted using Eq (3) have matched world-wide monitoring data well. Simultaneous sampling of gaseous and size-resolved particles is crucial to the full understanding of the partitioning behavior of SVOCs between gas and particles with different sizes, and is being carried out in the IJRC-PTS. The new data is expected to be used for analyses in a near future.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21577030), and HIT Environment and Ecology Innovation Special Funds (No. HSCJ201608)

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