

Study on Water-Atmosphere Interface Distribution and Concentration Fluctuation Intensities of Polybrominated Diphenyl Ethers in Great Lake

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Abstract

In this study, the water-atmosphere interfaces distribution and concentration fluctuation intensities of polybrominated diphenyl ethers (PBDEs) in Great Lake were analyzed. Based on the selected significant quantum descriptors, bromination pattern descriptors (N_{PBS}) and temperature descriptors by combination of variable important for projection (VIP) and correlation analysis, 35 experimental Henry's law constants of PBDEs (transformed as $\lg H$, represented the water-atmosphere interfaces distribution) at different temperatures were divided into modeling set (25 samples) and testing set (10 samples) to establish the quantitative structure-parameter relationship (QSPR) model for $\lg H$ at different temperatures via the optimal subset method firstly. Then, the Henry's law constants of other unknown PBDEs at different temperatures were predicted and the water-atmosphere interfaces distribution regularity were analyzed from views of chemical quantum descriptors and substituent pattern respectively. At last, the concentration fluctuation intensities in Great Lake were discussed based on the correlation analysis between the detected concentration data and experimental Henry's law constants. The established optimal QSPR model has shown a good fitness and predictive ability for Henry's law constants of PBDEs, with the R^2 and R^2_{pred} of 0.985 and 0.978 respectively. From the view of chemical quantum descriptors, the $\lg H$ of PBDEs is positive correlative with E_{HOMO} , indicating the ability to provide electron of congener molecule has played a leading role in governing the exchange ability between water-atmosphere interface; from the view of bromination pattern, both number of relative positions and each position have great influence on the water-atmosphere interface distribution, especially $N_{2(6)}$ and N_o can decrease the release of PBDEs from water to atmosphere in Great Lake. The concentration fluctuation intensity is negative correlated with the $\lg H$ linearly, the bigger solubility of congener in Great Lake, and the stronger water-atmosphere interface exchange ability and fluctuation intensity.

Keywords: polybrominated diphenyl ethers, quantitative structure-parameter relationship, Henry's law constants, water-atmosphere interface distribution, concentration fluctuation intensity

Introduction

Generally added to various industrial materials and home furnishings as additive brominated flame retardants, Polybrominated diphenyl ethers (PBDEs) are physically combined with pre-produced polymer simply and do not react with them chemically, so they are more likely to leach or volatilize from products and disperse in each medium (Labunska et al., 2013; Na et al., 2013).

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The widespread use of PBDEs increased their worldwide presence in various biotic and abiotic environment, even in the remote areas of the Arctic and Antarctica, producing significant negative effect on nervous system, endocrine system and immune system of wildlife and human (Mikula and Svobodova, 2006; Möller et al., 2011).

Most of the worldwide demand for PBDEs is distributed between North American (NA, 40%), the Far East (30%), and Europe (25) (Manchester-Neesvig et al., 2001). In Great Lake, Luckey et al (2001) has found that the concentration of total PBDEs was located in 4~13pg/L in NA which composing BDE-49 and BDE-99 mostly (>90%). Following research has also found that the large usage of the PentaBDE mixture can be seen in the ubiquitous presence of the congeners BDE-47, BDE-99 and BDE-100 in freshwater and marine environments in NA (Hites 2004; Zhu and Hites 2004; Yogui and Sericano, 2009). Both the penta- and octa-BDEs have been phased out of the NA markets while the Deca-BDE will have been completely withdrawn from the market by the end of 2013 (Kemmlin et al, 2009; Ma et al., 2013). The total PBDE concentrations in Great Lakes has presented increasing trend from 1989 to 2003 (Hites 2004; Zhu and Hites 2004), but current studies has shown an obvious decreased breakpoint that in concentration after 2000-2001 for Lake Huron, Michigan and Ontario according the statistical data (Crimmins et al, 2012). However, the concentration fluctuation intensities and corresponding regularity of PBDEs in Great Lake has never been analyzed in previous studies.

Physicochemical properties, especially those partitioning properties such as Henry' law constants (H), vapor pressure and K_{OA} , play a major role in their transport and mobility in the global environment. The Henry's law constants is an important indicator that plays a fundamental role in predicting the transport, behavior and fate of organic compounds in the environment which model the chemical transfer between atmosphere and water (Cetin et al., 2006). Meanwhile, Henry's law constants obtained from the Clapeyron equation are only valid for dilute concentrations (compounds with slightly or even moderately soluble in water), approximated by the ratio of the compound's vapor pressure and its aqueous solubility, but there are large deviations from practical solutions.

PBDEs contain 209 congeners distinguished by bromine number and substitution position (Palm et al., 2002; Gu et al., 2009). Compared with other POPs such as PCDD/Fs or PCBs, physical-chemical properties of PBDEs have been measured rather scare, meanwhile only fewer than 40 PBDEs congeners have been synthesized which makes it cumbersome and expensive to detect the physical and chemical properties of each compound (Jiang et al., 2012). In order to assess overall effect and variation rules of PBDEs in Great Lake more comprehensively, it is important to develop predictive models for physicochemical properties of PBDEs from their molecular structures. Quantitative structure-property relationship (QSPR) model provides an opportunity of studying a few compounds to predict properties of other unknown homolog (Blotvogel et al., 2011). Some previous studies showed that it was indeed feasible to predict the properties or activities with QSPR models for PBDEs (Niu et al., 2006; Chen et al., 2007; Papa et al., 2011), However, this kind of studies on Henry's law constants of PBDEs is still limited. Xu et al. (2007) and Papa et al. (2009) have used different descriptors to estimate the QSPR model for Henry's law constants of 7 PBDEs congeners, however, with less data, not take temperature into consideration, most selected descriptors reflects the overall performance of PBDEs molecular, no experimental data were used for validation and not combine with the actual sea area.

Based on the existing problem, the aim in this study is to analyze the regularity of water-atmosphere interface distribution and concentration fluctuation intensities of PBDEs in Great Lake. We screen the decisive descriptors and analyze corresponding modularatory effect on water-atmosphere interface distribution of PBDEs in Great Lake firstly, and then establish the QSPR model for $\lg H$ of PBDEs at different temperatures to analyze the distribution regularity among 209 congeners. At last, the regularity of concentration fluctuation intensities in Great Lake will be discussed.

Methods and Materials

Experiment data source

Henry's law constants (transformed as $\lg H$ in this study for analysis conveniently) of seven PBDE congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-209) were measured at five different temperatures during 5-40 °C using a gas-stripping technique by Cetin and Odabasi (2005), listing in Table 1 in supporting information. The concentration values for BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154 in water of Great Lakes (Lake Erie, Lake Huron, Lake Michigan, Lake Ontario, Lake Superior) during 2004-2009 were detected by Crimmins (2012).

Descriptors for QSPR modeling

A total of 22 descriptors were obtained to establish the QSPR model, containing quantum descriptors, bromination pattern descriptors (N_{PBS}) and temperature descriptors. The molecular structures of all 209 congeners were initially optimized at the B3LYP/6-31(d) level by density function theory with Gaussian 09 software, then the frequency calculation was implemented at same level to detect whether optimized geometries were minimal on the potential energy surface (Worrall et al., 2004). Based the optimal geometries, the quantum descriptors were calculated and contained: the dipole moment (μ , debye), energy of the highest occupied molecular orbital (E_{HOMO} , eV), energy of the lowest unoccupied molecular orbital (E_{LUMO} , eV), $E_{\text{LUMO}} - E_{\text{HOMO}}$ (ΔE , eV), $E_{\text{LUMO}} + E_{\text{HOMO}}$ (E_S , eV), total energy (TE , eV), most negative atomic partial Mulliken charge in molecule (q^- , e), most positive partial Mulliken charge in hydrogen atom ($q\text{H}^+$, e), the mean polarizability (α , 10^{-30} esu) and the anisotropy polarisability ($\Delta\alpha$, 10^{-30} esu).

Eight (N_{PBS}) were presented as follow: N_T , total bromine atom number; $N_{2(6)}$, bromine atom number at positions (2, 2', 6, 6'); $N_{3(5)}$, bromine atom number at positions (3, 3', 5, 5'); $N_{(4)}$, bromine atom number at positions (4, 4'); N_o , relative *ortho*-position of bromine atom; N_m , relative *meta*-position of bromine atom; N_p , relative *para*-position of bromine atom; N_D , different number of bromine atom between two benzene rings. Five different forms of temperature descriptors (T , T^2 , $1/T$, $\lg T$, T^3) were used to establish the QSPR model.

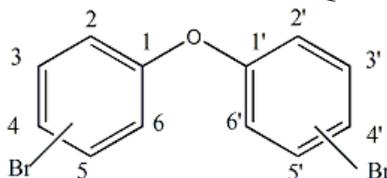


Figure 1. Atom mark number and molecular geometry of PBDEs.

Method of QSPR modeling

35 known experimental samples of $\lg H$ were divided into modeling set (25 samples) and testing set (10 samples) by interval-sampling method. Based on the modeling set, the correlation analysis between $\lg H$ and 22 descriptors was implemented firstly to eliminate uncorrelated variables in the view of statistical point which didn't have significant effect on the water-atmosphere interface distribution; the correlation among independent variables had also been obtained coinstantaneously to provide guideline for eliminating collinearity in next step. Then, the variable importance for projection (VIP) analysis for remainder descriptors on $\lg H$ was carried out by partial least square (PLS) regression to screen significant descriptors further whose VIP values were larger than 1 (Li et al., 2013).

Based on the screening significant descriptors, the best subset regression was used by Minitab software to establish a series of QSPR models. Among them, the optimal QSPR model was evaluated and decided by the comprehensive performance (fitness, robustness, predictability) of each model. For all established QSPR models, the conventional square of correlation coefficient (R^2) was used to test the fitness of the models. The robustness was evaluated during leave-one-out (LOO) cross validation (Wold, 1978), which finally gave the cross-validated correlation coefficient (q^2) and the PRESS which was defined as the sum of squared differences between the experimental (y_i) and predicted $\lg H$ (\hat{y}_i) of the excluded observation in LOO treatment. The q^2 and PRESS were calculated as follow:

$$q^2 = 1 - \frac{PRESS}{SS} = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y}_i)^2} \quad (1)$$

Where SS stood for the residual sum of squares of the experimental values around the mean value (\bar{y}_i). When q^2 was larger than 0.5, the model was considered to have well robustness. The correlation coefficient produced by testing set (R_{pre}^2) (Gramatica, 2007; Puzyn et al., 2008) was used to reflect the external predictive power of the model.

During the QSPR modeling, there was an annoying problem: more independence variables always gave rise to poorer accuracy; meanwhile too less always produced biased estimate. The parameter of C_p embedded in the best subset regression would provide help to select the best candidate regression model by weighing the balance. The smaller value of C_p always emerged the better performance of model.

Concentration fluctuation intensities calculation

In order to evaluate the concentration fluctuation intensity of each congener in Great Lake conveniently, a fluctuation intensity index was put forward in this study. For all five congeners with known experimental concentration in Great Lake during 2004-2009, the calculation process was same and presented as follow:

$$y_{ij} = x_{ij} / x_{(i-1)j} \quad (2)$$

Where x_{ij} and $x_{(i-1)j}$ were the concentration of each congener in i th year and the last year ($i=2005, 2006, 2007, 2008, 2009$) in j th lake ($j=1, 2, 3, 4, 5$), the y_{ij} was the growth rate in i th year in j th lake.

$$\sigma_j = \sum y_{ij} / 5 \quad (3)$$

Where the σ_j was the standard deviation (SD) of growth rate in j th lake during 2004-2009.

$$F = \sum \sigma_j / 5 \quad (4)$$

Where the F was the concentration fluctuation intensity index for each congener in Great Lake during 2004-2009.

Results and Discussions

Descriptors screening and effect analysis for water-atmosphere interface distribution

Before QSPR modeling, the correlation analysis was performed for modeling set to illuminate general correlation between $\lg H$ and each descriptor (Table 1). It is found that most descriptors have strong correlation with $\lg H$ (sig.<0.01), but more serious collinearity between independent variables also exists at the same time (Table 2 in supporting information). Six descriptors (T^3 , ΔE , μ , q^- , qH^+ , N_D) with less importance (sig.>0.01) and constant variable N_4 were excluded during following calculations.

Among the preliminary screening descriptors, the VIP values of all temperature descriptors, E_{HOMO} , $N_{2(6)}$, and N_o are bigger than 1 (Table 1), representing significant effect on regulating the water-atmosphere interfaces distribution of PBDEs in Great Lake for these descriptors. Combined with the symbol of correlation analysis, the $\lg H$ is positive correlated with E_{HOMO} and negative with $N_{2(6)}$ and N_o significantly.

Previous study has also found that increasing HOMO energy will result in higher reactivity (Niu et al., 2006; Fang et al, 2008). The greater the E_{HOMO} , the greater the ability of PBDE molecule to provide electrons, and the stronger the interactions between PBDE molecule and water molecule, thus the greater $\lg H$ and stronger ability of releasing from water to atmosphere, which is similar with the conclusion of Xu et al. (2007) and Papa et al. (2009).

Both the number of relative positions and substituent position has great influence on water-atmosphere interface distribution of PBDE congeners in Great Lake. The congeners with bromine atoms in *ortho*-position relative to the ether-link have lower vapor pressures compared to those with bromine atoms in the *meta/para*-positions, conducive to transport from water to gas, which may relative with the perpendicular molecular configuration, because only the congener configuration with *ortho*-position is perpendicular to each other for two benzene rings. N_o represents the pairs of bromine atoms in relative *ortho*-position in single benzene ring of molecule. The more N_o , the more concentrated distribution of bromine atoms in molecule and the more asymmetric charge distribution of molecule which is conducive to interact with water molecule and contain the release of congener to gas.

For other descriptors, the VIP values are all located in 0.90-0.1 except N_m , all showing a certain degree effect on distribution between air and water interface. In order to avoid the mission of useful information and introduction of duplicate message, all the preliminary screening descriptors were filtrated ultimately by the conjoint comparison of correlation coefficient (R^2) and VIP value, then seven descriptors: T , E_{HOMO} , ΔE , E_s , α , $N_{2,6}$ and N_o were screened for QSPR modeling at last.

Table 1 Correlation analysis and VIP value of each descriptor of PBDEs.

Descriptors	T	T^2	$1/T$	$\lg T$	T^3	TE	E_{HOMO}	E_{LUMO}	ΔE	E_s	μ
R^2	0.612**	0.541**	-	0.647**	0.472*	0.690**	0.737**	0.651**	0.471**	0.694**	0.372
sig.	0.001	0.005	0.001	0.000	0.017	0.000	0.000	0.000	0.017	0.000	0.067
VIP	1.18	1.12	1.11	1.16	-	0.93	1.14	0.90	0.94	0.94	-
Descriptors	q^-	$q\text{H}^+$	α	N_T	$N_{2(6)}$	$N_{3(5)}$	N_4	N_o	N_m	N_p	N_D
R^2	-0.188	0.431*	-	-	-	-	-	-	-	-	0.470*
sig.	0.368	0.032	0.000	0.000	0.000	0.002	-	0.002	0.007	0.001	0.018
VIP	-	-	0.92	0.93	1.09	0.92	-	1.06	0.82	0.90	-

** Correlation is significant at the 0.01 level; * Correlation is significant at the 0.05 level.

QSPR modeling and regularity analysis for water-atmosphere interface distribution

Based on the screening seven descriptors ultimately and modeling set, models (5-17) have been established by best subset regression, listing in Table 2. Through the comprehensive comparison for model performance, the model (11) has the best fitness, robustness, predictability and the smallest C_p , being selected as the optimal QSPR model with the expression as follow:

$$\lg H = 6.377 + 0.038T + 57.47E_{\text{HOMO}} - 0.021\alpha - 0.048N_o \quad (11)$$

As shown in Fig.2, for the training set and testing set, the points tends to cluster along the 45° tangent line indicating the predicted values are consistent with the corresponding determined values. Based on QSPR model (11), Henry’ law constants for other 202 PBDEs at 5 different temperatures (Table 1 in supporting information) were predicted which may be useful for exposure assessment of these compounds in Great Lake. Our results suit very well for previous efforts. Cetin and Odabasi (2005) has reported the fitted regression equation for $\lg H$ with the average R^2 0.958, which is smaller than our study (0.984).

Table 2. Modeling fitting results.

No.	R^2	C_p	$PRESS$	q^2	R^2_{pred}	T	E_{HOMO}	ΔE	E_s	α	$N_{2(6)}$	N_o
(5)	0.524	558.7	6.995	0.459	0.683		√					
(6)	0.460	636.9	8.232	0.364	0.579				√			
(7)	0.955	33.4	0.711	0.945	0.944	√	√					
(8)	0.887	112.4	1.659	0.872	0.912	√					√	
(9)	0.971	14.8	0.452	0.965	0.966	√		√	√			
(10)	0.970	16.3	0.456	0.965	0.960	√				√		√
(11)	0.984	2.1	0.093	0.984	0.978	√	√			√		√
(12)	0.982	4.4	0.297	0.977	0.980	√		√		√	√	
(13)	0.983	4.1	0.290	0.978	0.979	√	√	√		√		√
(14)	0.983	4.1	0.289	0.984	0.979	√	√			√	√	√
(15)	0.982	6	0.338	0.974	0.979	√	√	√		√	√	√
(16)	0.982	6	0.320	0.975	0.978	√	√	√	√	√		√
(17)	0.982	8	0.367	0.972	0.979	√	√	√	√	√	√	√
(18)	0.984		0.245	0.981	0.978	T^2	√			√		√
(19)	0.981		0.299	0.977	0.976	$1/T$	√			√		√
(20)	0.983		0.276	0.978	0.977	$\lg T$	√			√		√

The VIP values for four forms of temperature descriptors (T , T^2 , $1/T$, $\lg T$) are all greater than 1. Meanwhile, the last three temperature descriptors were introduced in model (11) to replace the descriptor T one by one, obtaining the QSPR model (18-20). The well performances of these models manifest that the water-atmosphere interface distribution of PBDEs in Great Lake is correlated with temperature but not with the concrete descriptor form significantly.

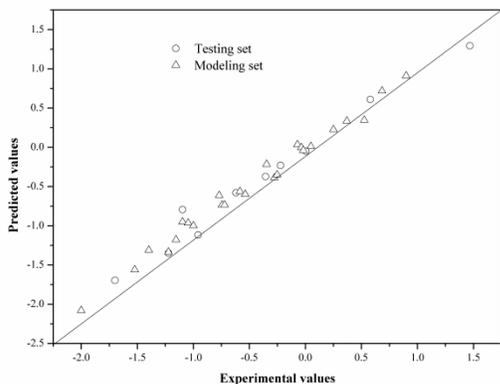


Figure 2. Plots of experimented $\lg H$ values vs. those predicted by QSPR model (11).

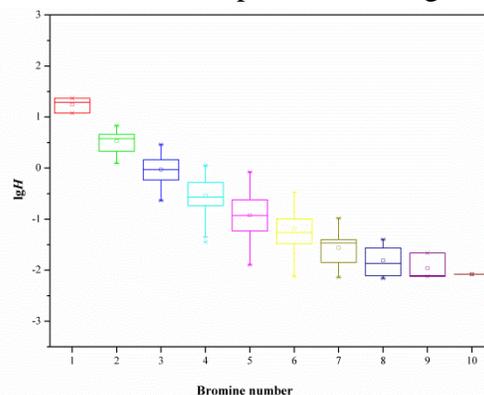


Figure 3. The correlation of $\lg H$ and total bromine number of PBDE congener

Concentration fluctuation intensities of PBDEs in Great Lake

The experimental concentration values and calculated concentration fluctuation intensity index (F) of five congeners with known experimental concentration in Great Lake during 2004-2009 were listed in Fig.1 (supporting information) Fig. 4 separately, showing the increasing trend of F along with the total number of bromine atom. Although the concentration of BDE-47 is the biggest in Great Lake, but not demonstrates the strongest concentration fluctuation intensity, presenting the water-atmosphere interface transport is not correlated with the existing concentration significantly. Due to low water temperature relatively in Great Lake (lower than $4\text{ }^{\circ}\text{C}$ in summer of central water surface), we take $5\text{ }^{\circ}\text{C}$ as the actual water temperature in Great Lake in this study because of the known detected concentration in $5\text{ }^{\circ}\text{C}$. The scatter diagram between $\lg H$ at $5\text{ }^{\circ}\text{C}$ and concentration fluctuation intensity index was shown in Fig.4, obtaining 3 different fitted lines. All the linear, exponential and polynomial fitting have shown well fitness with correlation efficiencies of 0.679, 0.721 and 0.902 separately, but the explicit correlation should be confirm further through more monitoring data.

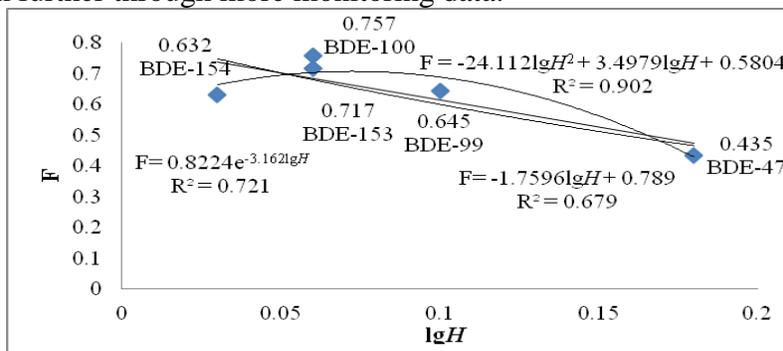


Figure 4. Scatter diagram between $\lg H$ at $5\text{ }^{\circ}\text{C}$ and concentration fluctuation intensities of five PBDE congeners in Great Lake.

Conclusions

Based on the consideration of taking Henry's law constant as index of water-atmosphere interface distribution in Great Lake, the fitness, robustness and predictive ability of optimal QSPR model of $\lg H$ at different temperatures for PBDEs have all shown well performance, with the R^2 , q^2 and R^2_{pred} of 0.985, 0.984 and 0.978 respectively. Among the selected descriptors, the water-atmosphere interface distribution of PBDEs in Great Lake are mainly regulated by temperature, E_{HOMO} , $N_{2(6)}$ and N_o , presenting the stronger ability to provide electrons of congener, perpendicular molecular configuration and asymmetric charge distribution are conducive to the releasing of PBDEs from water to atmosphere in Great Lake. Generally speaking, the concentration fluctuation intensities of five known detected congeners are negative correlated with the $\lg H$, with correlation efficiencies of 0.679, 0.721 and 0.902 for linear, exponential and polynomial fitting. The bigger solubility of congener in Great Lake, the stronger water-atmosphere interface exchange ability and fluctuation intensity

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