Experimentally Determined Henry's Law Constants For Six Brominated Diphenyl Ether Congeners.

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Introduction.

Interest in the environmental fate and transport of polybrominated diphenyl ether (BDEs) flame retardants, a class of halogenated polyaromatic hydrocarbons, structurally similar to polychlorinated biphenyls (PCBs) is increasing due to their widespread use as flame retardants; their exponential increase in the environment over the past decade; and their potential toxicity to biota and humans. The fate and transport of BDEs is dependent on physico-chemical properties, such as the sub-cooled liquid vapor pressure (P_L), aqueous solubility (S), octanol-water partition coefficient (K_{ow}) and Henry's law constants (K_H). Specifically, the transfer of molecules across the air-water interface is driven by the chemical potential gradient, which in turn, is a function of the temperature dependent K_H, and the gas- and dissolved-phase concentrations of the chemicals. In aquatic ecosystems, the Henry's law constant governs air water exchange. Henry's law constant is defined as: $K_H = p/C_w$, where, p is the partial pressure of the contaminant in the air, in equilibrium with its aqueous solution of concentration C_w.

It is well recognized that in certain lakes and estuaries, volatilization of semi-volatile organics (*e.g.*, PCBs) to the atmosphere can be a significant loss mechanism of contaminants from waters. The transfer of PCBs across the air-water interface is driven by the chemical potential gradient, which in turn, is a function of the temperature dependent Henry's law constant (K_H), and the gas- and dissolved-phase concentrations of the chemicals. A paucity of data exist on the vapor pressure, aqueous solubility, and K_H to evaluate whether BDEs will behave similarly to PCBs. The data that do exist suggest that the aqueous solubilities of BDEs are similar to PCBs, but their vapor pressures are lower than their PCB analogs (Table 1). Henry law constants for BDEs estimated from aqueous solubility and vapor pressure data indicate that the K_H for BDEs are lower than for PCBs. However, given differences between predicted and experimental values, the lack of experimental data is a significant gap in understanding partitioning between atmospheric and aquatic systems. We address this gap herein by reporting the K_H at 25^{o}C for six PCB and BDE congeners.

Experimental.

We determined the $K_{H\ by}$ the inert gas stripping method. All glassware was silylated to minimize sorption of the analytes to glass walls. Initial experiments did not indicate sorption of PCBs or BDEs to the walls of the glass column. All glassware was wrapped with aluminum foil, and solutions were stored in amber vials to minimize photodegradation. Aqueous solutions of the analytes were stirred for at least twelve hours prior to the onset of the experiment to ensure complete mixing of analytes. The temperature of the glass column was maintained at 25°C. Aliquots (5 mL) of the aqueous solution were taken at time intervals: 0, 10, 30, 60, 90, 120, 180, 270, and 300 minutes. Replicate (n=2) measurements were performed in each experiment. Flow rates ranged from 200-312 mL/min. Nitrogen gas (N_2) was introduced in the bottom of a column containing an aqueous solution of the analytes, and dispersed in small bubbles at a known and constant flow rate. The gas flowed through the well-mixed aqueous solution column, ensuring that the gas exiting the column was in equilibrium with the liquid.

By measuring the decrease of the solute concentration in water, K_H are calculated from a simple mass balance for the solute. During the stripping process, the mass balance for the solute is expressed in terms of transfer rates from the liquid to the gaseous phase as: $- V\, dC/dt = p\, G / R\, T$, where, V is the volume of the liquid, C is the concentration of the solute, p is the partial pressure of the solute in equilibrium, G is the gas flow rate, R is the gas constant and T the temperature of the system. Integrating from the initial conditions t = 0 and C = C_o (the initial concentration), the expression: ln $(C/C_o) = -(K_H\ G / V\ R\ T)\ t$ was used to obtain the experimental K_H value from the slope of the linear regression of ln (C/Co) vs. time, when all other parameters are fixed.

Samples and reagent blanks were extracted three times by liquid-liquid extraction with dichloromethane. Anhydrous sodium sulfate was used to eliminate water residues from the sample. After evaporation, the solvent was exchanged to hexane. The BDEs in the sample extracts were measured by using gas chromatography/electron-capture detection (GC/ECD). Quantification was accomplished by internal standardization using PCBs 30 and 204 as internal standards. Regression equations employed for quantification were obtained by plotting the peak area of the analyte vs. the peak area of the internal standard.

Results and Discussion.

We measured the K_H for six BDEs and six PCBs substituted with one to six halogen atoms in the same position. The compounds were 4 mono- (BDE and PCB IUPAC no. 3), 4,4'di- (BDE and PCB IUPAC no. 15), 2,4,4' tri- (BDE and PCB IUPAC no. 28), 2,2',4,4' tetra- (BDE and PCB No. 47), 2,3',4,4', 5 penta- (BDE and PCB IUPAC no. 118), and 2,2',3,4,4',5' hexa- (BDE and PCB IUPAC no. 138). The values for the PCB congeners obtained in this study are compared with other studies in Table 2. They are within the range of values reported in other studies. The precision between replicate measurements ranges from 5-26%, except for PCB no. 138 (47% RSD). In contrast, the reproducibility for the BDE measurements ranges from 10-83%. Sources of error can be the method employed to measure the K_H, losses occurring in preparation of the samples, and errors in quantification of the BDEs. Measurement of the K_H using a modified gas-stripping method, as described by Bamford et al., 2000 may provide greater accuracy due to measurement of BDEs in the vapor and aqueous phases. Since the K_H for PCBs reported herein agree within a factor of two with measurements reported using similar methods (Table 3), errors associated with the analytical method may be a greater source of error. To provide an estimate of the error in this study, we calculated the ratio between the high and low values as indicated by the mean and standard deviation. For the mono-, di-, tri, and tetra BDEs, the K_H are likely within a factor of 3, whereas for the higher BDEs (penta-, and hexa-), the K_H may have an error of 10x. In spite of the limitations of the data, the measurements are important to report in view of the absence of experimental K_H data for BDEs and the environmental significance of BDEs. Additionally, the data suggest: 1) The K_H for the experimental BDEs are higher than K_H estimated from solubility and vapor pressure data. This result indicates that use of estimated K_H is a source of uncertainty in the models, 2) the K_H for the lower BDE congeners appear to be greater than the PCBs, however, these differences become smaller as the level of halogenation increases, and 3) the K_H values do not follow strict adherence to a decrease in K_H as the level of bromination increases. Based on K_H estimated from aqueous solubility and vapor pressure data, Tittlemeier et al., 2002 suggest that the value of K_H at 25°C decreases approximately fourfold with each addition of a bromine atom. This generalization needs to be further evaluated through a grater number of measurements.

References Cited.

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Table 1. Comparison of PCB and PBDE Aqueous Solubilities and Liquid Subcooled Vapor Pressures.

Compound	Aqueous Solubility @ 25°C (mol/L)		Liquid Subcooled Vapor Pressure @25°C (Pa)	
	PCB	PBDE	PCB	PBDE
4-mono (IUPAC no. 3)	4.06×10^{-6} - 7.95×10^{-6} (1,2)		0.320-0.931(1,2)	0.00984(3), 0.259(4)
4,4'-di (IUPAC no. 15)	1.08×10^{-7}- 2.75×10^{-7} (1,2)	3.99×10^{-7} (3)	0.0263-0.0837(1,2)	0.0173(4)
2,4,4'-tri (IUPAC no. 28)	1.01×10^{-6}- 5.92×10^{-7} (1,2)	1.73×10^{-7} (3)	0.027-0.034(2)	0.00160(3), 0.00219(4), 0.00017(3)
2,2',4,4'-tetra (IUPAC no. 47)	5.48×10^{-8} (1)	3.11×10^{-8} (3)	0.152-0.156(1)	0.00031(3), 0.000186(4)
2,3',4,4',5-penta (IUPAC no. 118)	4.68×10^{-8}- 6.10×10^{-9} (2)		0.000962-0.0012(2)	
2,2',3,4, 4',5'-hexa (IUPAC no. 138)	3.98×10^{-9} - 6.60×10^{-9} (2)		0.0048-0.00534	0.00000158(4), 0.0000019(4)

(1) Mackay, D., Shiu, W. Y., Ma, K. C., 1992. Illustrated Handbook of Physical Chemical Properties and Environmental Fate for Chemicals and references therein. Lewis Publishers, Ann Arbor, MI; (2) Li, N., Wania, F., Lei, Y. D., Daly, G. L. J. Phys. Chem. Ref. Data, 32:1-46; (3)Wong, A., Lei, Y. D., Alaee, M., Wania, F. 2001. *J. Chem. Eng. Data*, 46:239-242; (4)Tittlemeier, S. A., Haldorson, T., Stern, G. A., Tomy, G. T. 2002. Env. Tox. & Chem. 21(9):1804-1810.

Table 2. Comparison of PCB and PBDE Henry's Law Constants.

Compound	K_{HPCB} (Pa m^3/mol) @ 25°C		K_{HPBDE} (Pa m^3/mol)@25°C		
	This Study (n=2) Mean±S.D. (%RSD)	Other studies (estimated and measured)	This study (n=2)		Other Studies (estimated)
			Mean±S.D. (%RSD)	Range (High Value /Low Value)	
4-mono (IUPAC no. 3)	37.20±1.66 (5%)	13.07, 35.95,58.06(1,2)	45.83±9.25 (20%)	36.58-55.08 (1.6)	
4,4'-di (IUPAC no. 15)	19.97±1.66 (8%)	9.67, 11.04, 14.69, 20.16, 27,40(1,2)	39.69±16.12 (41%)	23.57-55.81 (2.4)	21(4)
2,4,4'-tri (IUPAC no. 28)	39.16±8.86 (23%)	20.27, 22.80, 28.95, 38.14, 32.0(2,3)	17.15±8.55 (50%)	8.60-25.70 (3.0)	5.1(4)
2,2',4,4'-tetra (IUPAC no. 47)	48.56±3.32 (7%)		42.37±4.39 (10%)	37.98-46.76 (1.23)	1.5(4), 5.1(5)
2,3',4,4',5-penta (IUPAC no. 118)	18.10±4.43 (26%)	9.35, 11.73, 12.73, 36.20 40.5(2,3)	17.73±14.91 (83%)	2.82-32.64 (11.57)	
2,2', 3,4,4',5'-hexa (IUPAC no. 138)	23.50±11.08 (47%)	2.13, 10.84, 11.04, 13.20, 44.6, 48.6 (1,2) 13.2(1,2,3)	25.13		

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Table 3. Comparison of PCB Henry’s Law Constants Measured by Different Methods.

Compound	**K_{HPCB} (Pa m^3/mol) @ 25°C**			
	This Study n=2) (%RSD)	**Batch-stripping**	**Wetted-Wall**	**Modified Batch Stripping**
4-mono (IUPAC no. 3)	37.20±1.66 (4.5%)	58.06, 4.14(1)	24.39(1)	
4,4’-di (IUPAC no. 15)	19.97±1.66 (8.31)	20.16(1)	9.66(1,2)	
2,4,4’-tri (IUPAC no. 28)	39.16±8.86 (23%)	32.02(1)	20.27(1)	38.14±0.37(3)
2,2’,4,4’-tetra (IUPAC no. 47)	48.56±3.32 (7%)		19.25(1)	
2,3’, 4,4’,5-penta (IUPAC no. 118)	18.10±4.43 (26%)			36.2±1.0(3)
2,2’,3,4,4’,5’-hexa (IUPAC no. 138)	23.50±11.08 (47%)		2.13(1)	44.6±1.7(3)

(1) Mackay, D., Shiu, W. Y., Ma, K. C., 1992. Illustrated Handbook of Physical Chemical Properties and Environmental Fate for Chemicals and references therein. Lewis Publishers, Ann Arbor, MI.

(2) Li, N., Wania, F., Lei, Y. D., Daly, G. L. J. Phys. Chem. Ref. Data, 32:1-46.

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