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Evaluation of Gas-Stripping Methods for the Determination of Henry's Law Constants for Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls

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The objective of this research was to determine the Henry's law constants for a series of PBDE and PCB congeners using three different gas-stripping methods and to assess which method was the most accurate. A mass balance approach was applied to test the assumptions of the standard gas-stripping methodology and to quantitatively determine the fate of the chemical. The mass balance calculations showed that PCBs behaved differently in the gas-stripping systems as compared to PBDEs. The PCBs and mono- to tri-brominated PBDEs behaved ideally in the gas-stripping system while the tetra- and penta-brominated PBDEs showed extensive adsorption that invalidated the standard gas-stripping method. Also, as the number of PBDE bromine substitution increased, differences between the two classes of compounds increased. Henry's law constants for PCBs were effectively independent of the degree of chlorination, although there was a slight increase in Henry's law constants with increasing chlorination. In contrast, the PBDEs showed declining Henry's law constants with increasing bromination, from 20 Pa·m^3/mol for mono-PBDEs to 1.6 Pa·m^3/mol for penta-PBDEs.

Introduction

Polybrominated diphenyl ethers (PBDEs) are an important class of flame retardants used in a variety of commercial products. These compounds are physically blended into plastic polymers found in computers, television sets, furniture upholstery, and textiles.[1] Their extensive use in consumer products has resulted in widespread environmental distribution.[1] Since PBDEs are structurally similar to polychlorinated biphenyls (PCBs), they are expected to have similar toxicities and bioaccumulation tendencies.[2,3] Environmental concentrations have increased exponentially in the past (20 to 30) years,[4,5] thus raising concern about these chemicals. Recent studies have found high concentrations in indoor air dust particles and in common food items.[6−8]

Predicting the fate and transport of these compounds remains tenuous due to the lack of physical−chemical property data.[9,10] In particular, Henry's law constants (K_H) are essential for assessing long-range transport in environmental modeling since they describe the partitioning of chemicals between the key phases of air and water. For example, K_H values are used to determine the flux of chemical to/from large bodies of water that may act as a source or sink for semivolatile organic compounds (SOCs).[11−13]

Although Henry's law constants can be estimated from vapor pressure and water solubility data, these values are often less reliable since the errors incurred in separate measurements of two physical properties are compounded in calculating K_H.[14] Estimation methods based on quantitative structure−activity relationships (QSARs) require accurate experimental data in order to be successful.[15] Hence, experimentally determined data are indispensable for generating K_H values.

The traditional method for determining K_H for semivolatile organic compounds is the gas-stripping method (GSM), which bubbles a known volume of air through a column of water enriched with the chemical of interest.[16] The Henry's law constant is then calculated from the rate of loss of the chemical from the water column. This method has the advantage of not relying on absolute concentrations, which can be prone to analytical errors. It also requires measurement of only one phase of the system, namely water. However, this approach makes several critical assumptions, such as the absence of adsorption to the column walls and negligible chemical degradation. Also, the decrease in aqueous concentration over time must be sufficiently large since sensitivity of the method depends on the slope of the decrease of aqueous concentrations. Although PCB K_H determination by the GSM is well-documented, it is unclear whether this approach is applicable to PBDEs that have lower vapor pressures. The modified gas-stripping method (MGSM) was developed to circumvent the dependence on the decrease of aqueous concentration used by the GSM; however, the assumption of the lack of adsorption still remains unanswered.[17]

The objective of this research was to evaluate three different K_H determination methods, namely, the GSM,[16] MGSM,[17] and integrated gas-stripping method (IGSM), to identify the most accurate approach for quantifying K_H for PCBs and PBDEs. In addition, we applied a mass balance approach to K_H determination, which had not been previously conducted. The mass balance approach is the most rigorous quality control tool utilized so far that both proves the ultimate disposition of the chemical added to the system and provides new insight into the potential biases of the GSM methods. The K_H values for a series of PBDE and PCB congeners with identical substitution patterns were determined to investigate the differences in Henry's law measurements.

Materials and Methods

Calculations. Henry's law constant is defined as the partial pressure of a compound divided by its chemical concentration

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in an aqueous phase at equilibrium. Typically, it is expressed as

$$K_H = p_g/C_W \tag{1}$$

where p_g is the partial pressure of the compound in the gas phase and C_W is the concentration in the aqueous phase. The air−water distribution of a chemical can also be expressed as the dimensionless air−water partition coefficient (K_{AW}), which is related to K_H by

$$K_{AW} = C_A/C_W = K_H/RT \tag{2}$$

where C_A is the concentration of the compound in the gas phase; R is the ideal gas constant; and T is the absolute temperature.

The procedures for calculating K_H from the GSM and MGSM are already described in the literature,[16,17] so they are only summarized here. Briefly, the GSM determines K_H by the decrease in aqueous concentration of the test chemical over time as air is purged through the aqueous phase.[16] The K_H is given by

$$\ln(C_{Wt}/C_{Wo}) = -(K_H G/VRT)t \tag{3}$$

where G is the flow rate of the purge gas; V is the total volume of the liquid in the column; C_{Wt} is the aqueous concentration at time t; and C_{Wo} is the aqueous concentration at time zero. This method makes several assumptions that (1) air bubbles reach equilibrium with the aqueous phase before getting to the top of the water column, (2) chemical adhesion to the walls of the apparatus is negligible, and (3) the chemical does not undergo significant degradation in the test system.

The MGSM[17] uses the same experimental apparatus as the GSM, but both aqueous and gaseous phases are collected to obtain the time-integrated concentrations over a number of time intervals during each experiment where

$$K_{AW} = K_H/RT = C_A/[(C_{W(n)} + C_{W(n+1)})/2] \tag{4}$$

where C_A is the average gas-phase concentration for one time-interval; and $C_{W(n)}$ and $C_{W(n+1)}$ are the dissolved aqueous concentrations before and after that particular air sampling interval, respectively. One advantage of this procedure is that several measurements of K_H are obtained for each experiment, which provides greater statistical power. Since the method does not rely on the long-term decline of aqueous concentrations of the chemical, it is less sensitive to adsorption buffering effects and chemical degradation during the experiment. The disadvantage of this approach is that it requires more time and effort compared to the standard GSM since the volatilized chemical must be collected and quantified.

The last method is the IGSM, which is a new approach to calculating Henry's law constants and provides greater insight to the processes involved in chemical loss from the column. The IGSM utilizes the rate of decline in both the air and water concentrations of to determine K_{AW}. This calculation method plots the natural logarithm of the air and water concentrations against time (Figure 1). The regression line from this plot, which corresponds to a first-order decay process, provides the rate constant (k_i) of the concentration decline and the initial concentrations (C_o) for both the gas and aqueous phases. Since the gas and aqueous phases are at equilibrium at any given time, the decline rate constant for the aqueous phase (k_W) should equal the decline rate constant for the gas phase (k_A). Once the decline rate constant and initial chemical concentrations are known, then the concentrations in the aqueous and gas phases can be calculated at any given time during the experiment by

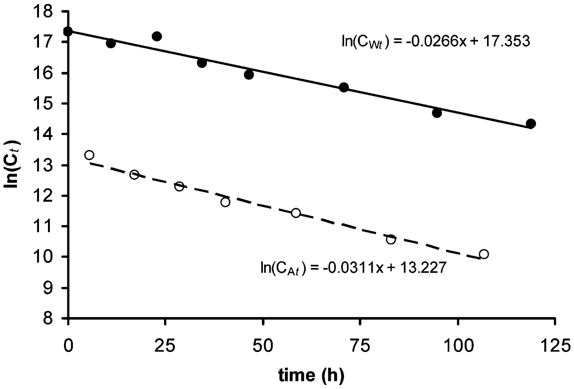

Figure 1. Plot of the natural logarithm of the air (open circles) and water (black circles) concentrations as a function of time during the experiment for PCB-3, which was an ideally behaving chemical. The decline rate constants (k/h^{-1}) are determined as the slope of the regression line, while the initial concentrations are $e^{(\text{intercept})}$.

$$C_{Wt} = C_{Wo} \cdot e^{(-k_W) \cdot t} \text{ and } C_{At} = C_{Ao} \cdot e^{(-k_A) \cdot t} \tag{5}$$

Therefore

$$K_{AW} = C_A/C_W = C_{At}/C_{Wt} = (C_{Ao} \cdot e^{(-k_A) \cdot t})/(C_{Wo} \cdot e^{(-k_W) \cdot t}) \tag{6}$$

Since the uncertainty about regression lines are the least in the middle of the line, the midpoint time of the experiment is used to calculate the air and water concentrations. The midpoint was also selected since it avoids difficulties associated with adsorptive losses in the early time periods and quantification problems in the later time periods due to very low concentrations near the limit of quantification that might bias the data. The K_{AW} is then converted into K_H.

This method can be applied in two fashions. Since k_A should equal k_W, the two k values can be kept separate in the calculation ("individual k" analysis) or they can be averaged to obtain a single value for k ("averaged k" analysis) that is used in both the air and water concentration determination. The individual k approach better matches the empirical data compared to the averaged k analysis. The advantage of the averaged k analysis combines both the air and water data to obtain a single k value, which is supported by more data points. This allows the more accurate calculation of k when the rate of change is low and the slope is near zero.

This method also allows for the inclusion of chemical adsorbed to the apparatus from the gas phase ($m_{A-\text{ads}}$) that is measured at the end of the experiment. The average concentration that adhered to the apparatus from the gas phase during the experiment ($C_{A-\text{ads}}$) is equal to the total mass adsorbed to the apparatus ($m_{A-\text{ads}}$) divided by the total volume of gas passes through the experiment ($V_{A-\text{total}}$). Therefore

$$(C_{A-\text{ads}}) = (m_{A-\text{ads}})/(V_{A-\text{total}}) \tag{7}$$

and

$$K_{AW} = [(C_{Ao} \cdot e^{(-k_A) \cdot t}) + (C_{A-\text{ads}})]/(C_{Wo} \cdot e^{(-k_W) \cdot t}) \tag{8}$$

This calculation method utilizes all the available data—namely, water concentrations, air concentration, and adsorption data—to calculate K_H. It ensures the system is behaving optimally where k_A/k_W should be equal to unity. The use of the regression lines also averages some of the sample-to-sample variability that

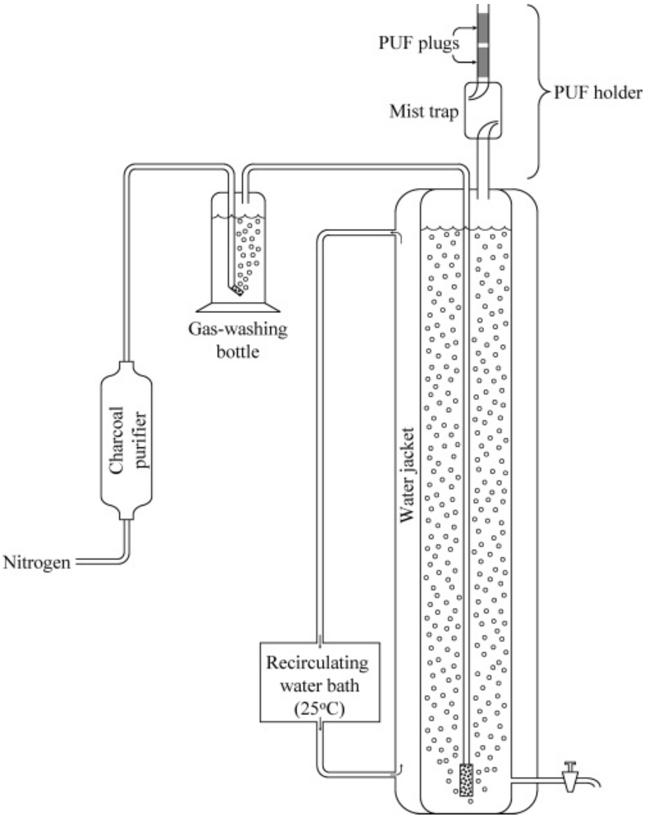

Figure 2. Schematic figure of the modified gas-stripping apparatus. A stream of nitrogen gas was purified by a charcoal filter and then saturated with water by a gas-washing bottle before being bubbled through a gas-stripping column maintained at 25 °C. The figure is not drawn to scale.

would appear in the MGSM. Furthermore, the intercept determined by the regression equation helps to obtain a more representative initial concentration of the chemical so it is not vulnerable to errors in the initial sample concentrations. The regression-estimate initial concentration can be compared to the measured initial concentration as a further quality control measure.

Chemicals. Seven PBDE and nine PCB congeners were investigated in this research. For simplicity, the IUPAC congener numbering system is used herein. PBDE 3 and 15 were purchased from Aldrich (St. Louis, MO). PBDE 28, 47, and 118 were obtained from Cambridge Isotope Laboratories (Andover, MA). PBDE 99 and 100 were purchased from Chiron AS (Trondheim, Norway). PCB congeners 1, 3, 8, 15, 28, 30, 47, 77, 99, 118, and 209 were all purchased from AccuStandard (New Haven, CT). Granular anhydrous sodium sulfate and HPLC grade water were purchased from Fisher Scientific (Hampton, NH). Dichloromethane, acetone, and isooctane were all capillary GC/GC-MS grade from Burdick & Jackson (Muskegon, MI).

Experimental Procedure. Measurements were performed using the experimental setup of MGS method (Figure 2).[17] The analytes were dissolved in HPLC grade water contained inside the gas-stripping column where they were purged from solution by a stream of nitrogen. To ensure that analytes were dissolved in the water, the analyte solutions were prepared in acetone and added to water in a 2 L volumetric flask such that acetone volume comprised only 0.025 % of the total volume. The target aqueous concentrations were 5 % or lower than the reported or estimated water solubility for each chemical. This flask was covered with aluminum foil and allowed to equilibrate at room temperature for 3 days before transferring the solution into the gas-stripping column so that only chemical that was truly dissolved was transferred into the column.

The gas-stripping columns were 1 m high and 51 mm i.d. The columns were operated at their maximum effective height of 89 cm. Two columns were operated side-by-side under the same experimental conditions to provide duplicate measurements. The columns were insulated and wrapped in aluminum foil to protect the chemicals from ambient light. The purge gas consisted of (50 to 60) mL/min of 99.997 % pure nitrogen. The low flow rate gave the smallest bubble size which aids in achieving equilibrium between the gas and aqueous phases. The nitrogen gas was passed through a charcoal purifier and then saturated with water by passing it through a gas-washing bottle containing HPLC grade water before entering the columns. Temperature of the system was controlled at 25 °C by a constant-temperature water bath that circulated through the water jacket that enveloped the column. Flame-retardant-free polyurethane foam (PUF) plugs (25 mm by 75 mm, Shawnee Instruments Inc., OH) were used to collect analytes in the gaseous phase. Each PUF had less than 1 % breakthrough. However, two PUF plugs in series were still used to collect the gas phase. Previous researchers[18] have suggested that the creation of aerosol droplets from the bubble bursting at the surface can bias K_H estimation, so a mist trap was installed between the water surface in the column and the PUF plugs to reduce aerosols from reaching the PUF and being erroneously accounted as volatilized chemical. The mist trap condenses water droplets by impaction and then allows the water to drain back into the column through a small hole in the mist trap. The mist trap and the PUF holder was a single piece of glassware. Aqueous samples (8 mL) were drawn from the column via a Teflon stopcock on the bottom of the column before and after each PUF sample time interval. During the course of an experiment, the total volume of water removed was less than 3 % of the initial water volume. We considered this change in volume to be negligible, so no correction factor was applied to account for the changing water volume as was done by Sahsuvar et al.[19] Samples were taken every 12 h during the first 2 days and then every 24 h for the last 5 days. As a precaution, the first 12 h of column operation was not used for K_H estimation to avoid any rapid decrease in aqueous concentration due to potential adsorption of the analytes to the walls of the column.

Aqueous samples were extracted by liquid−liquid extraction with 5 mL of dichloromethane (DCM) three times. The extracts were dried with anhydrous sodium sulfate, concentrated by nitrogen evaporation, and solvent-exchanged into isooctane. The internal standards of PCB 30 and 209 were added to the extract before analysis. All aqueous samples were processed without storage. PUF samples were extracted by Soxhlet in DCM for 24 h. The extracts were then reduced in volume and analyzed in the same fashion as the aqueous samples.

Sample quantification was conducted using an Agilent 6890N Network gas chromatograph with a 5973 Network mass selective detector and a 5 % phenyl-substituted capillary column (DB-5MS, 0.25 i.d. × 30 m × 0.25 μm film thickness, J&W Scientific, Folsom, CA). The oven temperature program was started at 60 °C and held for 1 min, then ramped at 12 °C/min to 155 °C, 2 °C/min to 215 °C, 3 °C/min to 268 °C, and finally 30 °C/min to 300 °C. Electron-capture negative chemical ionization was used with 50 % methane at 5 mL/min. Single ion monitoring was used for maximum sensitivity where the bromide ions were mainly used for quantification of the PBDEs. Both chloride and molecular ions were used for PCB quantification depending on which ion was the most abundant for the particular congener. If a value in a sample fell below the minimum quantifiable limit, defined as mean blank + 6 × (standard deviation) of the blank, then the data was excluded from the K_H estimation calculation.

Quality Assurance/Quality Control. All glassware, except the columns, was baked at 550 °C before each experiment to minimize contamination. The PUF plugs were cleaned by Soxhlet extraction in DCM for 24 h. For each PUF and water sample extraction set, a blank and a matrix spike were extracted simultaneously along with the samples. All samples were extracted immediately upon collection to avoid any storage stability problems.

Forty-eight hours before the experiment, blank HPLC grade water was added to the columns and then purged with nitrogen for 48 h in the columns with clean PUF plugs to collect the gas phase. The PUF plugs were then extracted in the identical fashion as the samples to determine the background contamination in the gas phase. Aqueous samples were taken and extracted to determine the amount of contaminants present in the column.

Mass Balance Approach. The most novel aspect of this research was the application of a mass balance approach where we attempted to recover all of the chemical mass originally added to the columns. After the last aqueous sample was collected, the remaining aqueous solution was drained from the column. The walls of the column and the mist trap/PUF holder were rinsed with DCM to remove any PBDEs and PCBs that adhered to the experimental apparatus. These apparatus rinse samples were dried on sodium sulfate, reduced in volume, and quantified. If there was no degradation or other unexplained loss, then the mass of chemical initially added to the columns should total the mass of chemical recovered from (1) the final aqueous solution, (2) the mass of chemical adsorbed to the apparatus, and (3) the sum of the mass volatilized. Therefore, the mass balance calculation is given by

$$m_{\text{initial}} = m_{\text{total final}} \tag{9}$$

$$m_{\text{aqueous initial}} = m_{\text{aqueous final}} + m_{\text{volatilization}} + m_{\text{column adhesion}} \tag{10}$$

$$= m_{\text{aqueous final}} + (\Sigma m_{\text{PUF}} + m_{\text{PUF holder}}) + m_{\text{column adhesion}} \tag{11}$$

where $m_{\text{aqueous initial}}$ is the initial mass added to the column (= $V_W \times C_{Wi}$); $m_{\text{aqueous final}}$ is the final mass in solution (= $V_W \times C_{Wf}$); $m_{\text{column adhesion}}$ is the mass recovered from the walls of the column from the solvent rinse; and $m_{\text{volatilization}}$ is the total mass of chemical lost from the column by volatilization during the whole experiment. The volatilization term consists of the sum of all vapor samples collected on the PUF plugs (Σm_{PUF}) plus the chemical that adhered to the PUF holder and mist trap apparatus ($m_{\text{PUF holder}}$). The mass balance is presented as the percentage of mass recovered at the end of the experiment:

$$\text{overall mass recovery} = (m_{\text{final}}/m_{\text{initial}}) \times 100 \tag{12}$$

The experiment was deemed acceptable if the overall mass recovery was between 70 % and 130 %.

The mass balance calculation is a powerful quality control mechanism since it reveals the ultimate disposition of the chemical added to the system and therefore provides a quantitative account of the fate of the chemical. Information obtained from the mass balance also tests the assumptions of the simpler GS methods, such as adhesion to column walls and chemical loss by degradation. Without such measures, quality of the resulting data would be uncertain. For example, chemical degradation can be mistaken for volatilization in the simpler GS systems, thus resulting in an overestimate of K_H.

Table 1. Average (± SD, $n = 2$) of Mass Recoveries[a] (%) of PBDE and PCB Congeners

compd	mass recovery/%	compd	mass recovery/%
	PBDE Congeners (IUPAC No.)		
3	104 ± 9.9	99	69 ± 11
15	99 ± 2.9	100	75 ± 10
28	95 ± 0.49	118	64 ± 8.7
47	76 ± 12		
	PCB Congeners (IUPAC No.)		
1	69 ± 6.2	47	89 ± 4.0
3	51 ± 26	77	76 ± 35
8	92 ± 6.2	99	103 ± 13
15	85 ± 5.1	118	98 ± 25
28	115 ± 13		

[a] Mass recovery was calculated as (the total recovered mass/initial mass added) × 100.

Table 2. Example of the Mass Balance Calculation for a PCB and PBDE K_H Determination Experiment at 25 °C[a]

	initial mass	column blank	PUF blank	final dissolved mass	total air mass	mist trap/ PUF holder rinse	column wall rinse
compd	ng	%	%	%	%	%	%
				PCB Congener			
1	38 000	<0.1	<0.1	0.7	74	<0.1	<0.1
3	83 000	<0.1	<0.1	1.8	67	<0.1	<0.1
8	17 000	<0.1	<0.1	0.8	94	<0.1	<0.1
15	12 000	<0.1	<0.1	7.7	81	<0.1	0.3
28	5 500	<0.1	<0.1	0.5	104	<0.1	0.4
47	1 100	<0.1	0.1	8.7	75	0.1	0.6
77	490	<0.1	<0.1	4.1	90	0.4	5.9
99	150	<0.1	<0.1	2.5	107	0.1	1.7
118	210	0.10	0.6	2.9	105	0.5	5.2
				PBDE Congener			
3	28 000	<0.1	<0.1	8.6	89	<0.1	0.1
15	11 000	<0.1	<0.1	17	78	0.1	2.0
28	2 000	<0.1	<0.1	20	65	0.4	11
47	92	<0.1	3.2	15	28	0.8	41
99	98	<0.1	4.3	4.2	3.7	<0.1	67
100	73	<0.1	2.6	6.2	7.4	0.7	68
118	75	<0.1	4.0	2.4	1.6	0.4	65

[a] The initial chemical added to the column is presented as nanograms of chemical while all blanks and chemical disposition measures are expressed as percent of initial mass added to the column.

Results

Mass Balance in the Experimental System. For both PCBs and PBDEs, the background levels of contaminants established before the beginning of each experiment were insignificant (less than 1 % of the spiking concentration). Therefore, the experimental results were not affected by contamination.

Mass closure was achieved for almost all experiments with the average mass recovery ranging from (51 ± 26) % to (115 ± 13) % (Table 1). The overall recovery values also demonstrated that chemical degradation was minor since the majority of the chemical was recovered. Furthermore, the overall mass recovery was similar between the PCBs, which are known to be stable, and the PBDE congeners investigated. This suggests that the PBDE congeners investigated were also stable in the experimental apparatus. Therefore, the mass balance approach was able to prove quantitatively the lack of significant chemical degradation, which is a critical assumption in the simpler GSMs.

Mass balance can also provided insight into the ultimate fate of the chemical in the experimental system (Table 2). In particular, the extent of chemical adsorption to the columns was quantitatively determined. For PCBs, adsorption to apparatus

Table 3. Comparison between Literature Values for Henry's Law Constants K_H/(Pa·m^3·mol^{-1}) of PCB Congeners and Those Determined at 25 °C by the Gas-Stripping Method (GSM), Modified Gas-Stripping Method (MGSM), and Integrated Gas-Stripping Method (IGSM) Using the "Averaged *k*" Approach

PCB congener	GSM ($n = 2$)	MGSM ($n = 10-12$)	IGSM ($n = 2$)	literature values
1	39 ± 3.8	33 ± 5.7	44 ± 12	20.43 ± 0.52[a,17]; 30.2[b,27]; 28.9[b,28]
3	30 ± 8.1	28 ± 3.7	34 ± 8.3	27.8[b,27]
8	39 ± 3.8	39 ± 5.2	52 ± 9.6	24.89 ± 0.29[a,17]; 32.1[c,27]; 30.7[b,27]; 24.9[b,28]; 31.3[b,29]; 28.4[d,30]
15	21 ± 4.0	20 ± 3.6	30 ± 2.8	18.9[c,27]; 22.7[b,27]
28	42 ± 7.9	44 ± 6.5	70 ± 9.3	38.14 ± 0.37[a,17]; 32[c,27]; 28.9[b,27]; 22.8[b,28]; 26.7[d,30]; 19.6 ± 2.97[e,31]
47	na	4.7 ± 5.1	110 ± 16	37.3[2,27]; 44.5[b,29]; 19.1 ± 4.71[e,31]
77	18 ± 0.21	32 ± 6.2	55 ± 4.2	16.20 ± 0.41[a,17]; 8.41[c,27]; 10.4[b,27]; 4.37[b,28]
99	24 ± 0.21	45 ± 27	240 ± 24	25.3[b,27]; 30.5[b,29]; 21.7[d,30]; 7.93 ± 2.73[e,31]
118	21 ± 13	88 ± 40	180 ± 41	36.2 ± 1.0[a,17]; 12.7[b,27]; 9.35[b,28]; 11.8[b,29]; 8.61[d,30]

[a] Modified gas-stripping method. [b] Calculated. [c] Gas-stripping method. [d] Bulk equilibrium. [e] Wetted-wall column.

Table 4. Comparison of Henry's Law Constants K_H/(Pa·m^3·mol^{-1}) of PBDE Congeners Determined at 25 °C by the Gas-Stripping Method (GSM), Modified Gas-Stripping Method (MGSM), and Integrated Gas-Stripping Method (IGSM) Using the "Averaged *k*" Approach

PBDE congener	GSM ($n = 2$)	MGSM ($n = 12$)	IGSM ($n = 2$)	literature values (25 °C)
3	18 ± 0.21	20 ± 2.7	23 ± 5.7	45.8 ± 9.25[24] (GSM)
15	8.9 ± 4.1	12 ± 2.6	14 ± 1.5	39.7 ± 16.1[24] (GSM), 21[14] (calcd), 4.11[9]
28	8.6 ± 4.5	9.5 ± 2.0[a]	13 ± 1.6	17.2 ± 8.55[24] (GSM), 5.1[14] (calcd), 1.92,[9] 4.83 ± 0.67[25]
47	5.3	6.4 ± 0.18	5.8 ± 1.2	42.4 ± 4.39[24] (GSM), 1.5[14] (calcd), 1.11,[9] 0.85 ± 0.35[25]
99	12	1.6 ± 0.41	3.0 ± 0.2	0.23[14] (calcd), 0.530,[9] 0.60 ± 0.11[25]
100	8.3 ± 4.9	3.0 ± 0.71	3.1 ± 0.4	0.069[14] (calcd), 0.384,[9] 0.24 ± 0.06[25]
118	21 ± 4.0	1.6 ± 1.7	1.3 ± 0.1	17.7 ± 14.9[24] (GSM)

[a] $n = 11$ due to rejection of outlier by the *Q*-test at 90 % confidence level.

was minor with the heaviest measured congeners having less than 6 % of the spiking mass adsorbed to the column wall. The vast majority (67 to 107) % of the chemical was volatilized from the column over the course of the experiment; therefore, small quantities of the PCBs remained in the aqueous phase. In contrast, the PBDEs had extensive adsorption to the column walls with as much as 68 % of the initial mass being recovered from the column wall rinse. The percentage adsorption increased with the level of bromination, which is probably due to decreasing water solubility. For example, results showed that up to only 2 % of the mono- and di-brominated congeners adsorbed to the column while tri-brominated congener showed 11 % adsorption and tetra- and penta-brominated congeners showed (41 to 68) % adsorption to the column surface. Furthermore, the amount of chemical volatilized from the column dramatically decreased for the penta-brominated congeners with only (1.6 to 7.4) % of the chemical mass being collected on the PUF plugs. For all chemicals, the amount of mass recovered on the mist trap/PUF holder apparatus was less than 1 % of the initial spiking mass. Thus, the trap had effectively prevented aerosols from reaching the gas phase. Previous reports have speculated about the influence and likelihood of chemical adsorption biasing K_H determinations, but the mass balance approach employed here quantitatively demonstrated the extent of chemical adsorption and hence disproved the validity of the "no adsorption" assumption made by the GSM.[16,17,20−23]

Method Comparison and K_H Values. The three different calculation methods gave similar results for the determination of K_H for PCBs that agreed well with the literature (Table 3). The most notable deviations were that the MGSM approach gave a low estimate for PCB 47 while the simple GSM could not calculate K_H since the rate of decline of the aqueous concentration was too low for reliable quantification. The other exception was that the IGSM using the averaged *k* approach overestimated K_H, as compared to the literature values, for the more chlorinated compounds of PCB 77, 99, and 118. In this case, the estimated values were up to an order of magnitude greater than the literature values. Generally, PCB K_H values were within the same order of magnitude for all five levels of chlorination with the exception of PCB 47, which was anomalous. These results agreed with Bamford et al.[17] where the MGSM was used. As previously mentioned, most of the PCB congeners showed very little adsorption to glass and the largest portion of the spiked mass was purged into the gas phase. The heaviest congeners (PCB 77, 99, and 118) did show sorption to column walls that were higher than all other congeners. Therefore, PCBs were behaving ideally in the gas-stripping system. Since the three methods gave reasonably consistent results, all three methods could be applied for the measurement of PCB K_H at 25 °C, although the IGSM may give higher values for the more chlorinated PCBs.

For PBDEs, the three calculation methods gave comparable results for PBDE 3, 15, 28, and 47 (Table 4). The penta-brominated PBDEs revealed differences between the methods where the simple GSM approach yielded higher values of K_H than either the MGSM or the IGSM using the averaged *k* approach. For mono-, di-, and tri-brominated congeners, the variability between the methods was negligible since they were effectively purged into the gas phase (≥ 65 % mass lost by volatilization) and very little adsorption occurred (≤ 11 % mass adsorption to column). However, as the degree of bromination increased, the difference between the three methods became increasingly pronounced. This difference was mostly due to the extensive adsorption of the PBDEs to the walls of the column. For the penta-BDEs, over 60 % of the initial mass was recovered from the walls of the column at the end of the experiment, hence extensive buffering of the aqueous concentrations would be expected to bias the GSM results. Additionally, the GSM depends on the magnitude of the slope, so it may not have the sensitivity needed for compounds of low volatility like the higher brominated PBDE congeners where the rates of decrease are more subtle. Therefore, we conclude that the GSM is not applicable for the determination of extensively brominated compounds that might have strong adsorption tendencies.

Table 5. Comparison of Utilizing the "Individual *k*" and "Averaged *k*" Approaches in the Integrated Gas-Stripping Method for the Determination of K_H/(Pa·m^3·mol^{-1})[a]

compd	replicate	k_A h^{-1}	k_W h^{-1}	k_A/k_W ratio	individual k K_H Pa·m^3·mol^{-1}	averaged k K_H Pa·m^3·mol^{-1}
			PBDEs			
PBDE 3	1	−0.019	−0.015	1.24	22	27
PBDE 3	2	−0.018	−0.020	0.92	21	19
PBDE 15	1	−0.012	−0.009	1.42	12	15
PBDE 15	2	−0.012	−0.014	0.92	14	13
PBDE 28	1	−0.011	−0.005	2.10	8.5	12
PBDE 28	2	−0.014	−0.011	1.24	12	14
PBDE 47	1	−0.004	−0.004	0.90	5.1	5.0
PBDE 47	2	−0.003	−0.008	0.32	9.2	6.6
PBDE 99	1	−0.021	−0.004	5.16	1.2	3.2
PBDE 99	2	−0.017	−0.016	1.10	2.6	2.9
PBDE 100	1	−0.004	−0.006	0.70	3.0	2.7
PBDE 100	2	−0.002	−0.013	0.14	6.5	3.4
PBDE 118	1	−0.015	−0.005	3.15	0.74	1.3
PBDE 118	2	−0.009	−0.022	0.41	2.5	1.2
			PCBs			
PCB 1	1	−0.041	−0.035	1.16	37	52
PCB 1	2	−0.041	−0.041	1.01	34	35
PCB 3	1	−0.031	−0.027	1.17	31	40
PCB 3	2	−0.030	−0.031	0.98	30	28
PCB 8	1	−0.040	−0.035	1.15	43	58
PCB 8	2	−0.041	−0.040	1.02	42	45
PCB 15	1	−0.024	−0.015	1.68	18	32
PCB 15	2	−0.023	−0.019	1.21	22	28
PCB 28	1	−0.045	−0.038	1.17	51	76
PCB 28	2	−0.048	−0.044	1.11	47	63
PCB 47	1	−0.072	−0.009	7.65	2.8	120
PCB 47	2	−0.065	−0.009	7.18	3.3	96
PCB 77	1	−0.023	−0.016	1.46	34	52
PCB 77	2	−0.027	−0.019	1.40	36	58
PCB 99	1	−0.047	−0.022	2.09	58	250
PCB 99	2	−0.053	−0.022	2.44	34	220
PCB 118	1	−0.031	−0.028	1.13	120	150
PCB 118	2	−0.034	−0.014	2.40	64	210

[a] k_A is the rate constant for the decline in the gas-phase concentrations. k_W is the rate constant for the decline of aqueous concentrations. The two replicates are shown individually to present a more accurate representation in the values of the rate constants.

Comparison between the PBDE K_H values determined here and the literature are more difficult compared to PCBs since there are fewer reported K_H values. Lau et al.[24] had previously used the GSM to measure PBDE K_H without implementing mass balance. Also, the aqueous concentrations used were based on reported solubility which was found to be too high in this study.[14] These reported K_H values were generally higher than the results of this study, which was probably caused by buffering effects in the gas-stripping apparatus and the excessively high aqueous concentration used based on published water solubility data. Most of the other literature values [9,14,25] were lower than those observed in this study by as much as a factor of 5. Additional K_H determinations should be conducted to reach a consensus of the K_H values for this important class of chemicals.

The comparison between the individual *k* and the averaged *k* formulations of the IGSM provided a better understanding of the processes involved in chemical loss (Table 5). The first observation was that the ratio of the air decline rate constant to the aqueous decline rate constant (k_A/k_W) was near 1 for most PCBs and the mono-, di-, and tri-PBDEs. Theoretically, this ratio should be unity if the chemical in the system is behaving perfectly. The exceptions for the PCBs were PCB 47, which had a ratio above 7 for both replicates and PCB 99 and 118 with ratios of approximately 2. These results indicate a decline in the gas-phase concentrations over time were greater than the decline in the aqueous concentrations. The reason for these differences in the rate constants are not completely clear, but they may be the result of buffering effects or partitioning of the chemical to the air−water surface in the column. For PBDEs, the k_A/k_W ratio was more erratic for the highly brominated compounds ranging from a low of 0.14 to a high of 5.2. This variation was probably due to the slower loss of chemical from the columns that resulted in smaller rate constants that were more difficult to measure accurately.

The second observation from the comparison of the two formulations of the IGSMs is that the averaged *k* method typically provided greater consistency between replicate measurements. For PBDEs, the numerical values were similar between the two approaches, but the averaged *k* approach provided greater consistency. For PCBs, the improvement in consistency was not as important since the data was reasonably consistent, but the averaged *k* approach gave a far higher estimation value of the K_H of PCB 47, which was anomalously low in both the MGSM and the individual *k* approaches. The rate of decline of PCB 47 from the aqueous phase was so slow that it was difficult to measure, but the rate of decline in the gas phase was relatively rapid. Averaging these two rate constants helped compensate for the slow rate of loss from the aqueous phase, which resulted in a K_H estimate that was more similar to other PCB values. Interestingly, the averaged *k* method consistently provided higher K_H values for the highly chlorinated PCB species compared to the literature.

Lastly, the IGSM can also account for chemical adsorption in the mist trap and PUF holder by taking into account the amount of chemical that was volatilized or aerosolized from the column but adsorbed to the apparatus before reaching the PUF. This adsorbed mass along with the total volume of gas passing through the system is used to calculate an "average" concentration in the gas phase that was adsorbed. Since very little of the PCBs was adsorbed to the PUF holder (Table 2), this adsorption correction factor was minor being less that 1 % of the K_H value for all PCB species investigated. The adsorption correction factor was also minor (< 1 %) for the mono-, di-, and tri-PBDEs. The PBDE 47 had a correction factor of 3.6 % while the penta-brominated PBDEs had correction factors that ranged from (9.1 to 21) %. Given the degree of variability in the replicate measures, the maximum bias due to gas-phase apparatus adsorption of 21 % is relatively minor, so we did not correct the data for this potential bias. It should be noted that this correction may need to be applied to chemicals that have low volatilites and may adsorb to glassware.

PBDE and PCB K_H Comparisons. A comparison of the K_H results for PCBs and PBDEs illustrate several differences between these two classes of chemicals that are frequently assumed to be similar. The first observation is that the K_H values were similar between the PCB congeners with different degrees of chlorination, although there is a slight increase in K_H with increasing chlorination (Figure 3). In contrast, PBDEs showed a strong declining trend in K_H values with increasing bromination (Figure 4). This implies that increasing bromination lowers the vapor pressure of the compounds faster than it lowers the water solubility. If this trend continues, we would expect the highly brominated compounds to have fairly low K_H values. Secondly, the K_H values for PBDEs are generally similar to PCBs for the mono- and di-halogenation species but they are significantly lower, from 40- to 100-fold depending on calculation method, than the corresponding PCB K_H values for the penta-halogenated species such as PCB/PBDE 118. The third observation, which has been previously noted, was that the

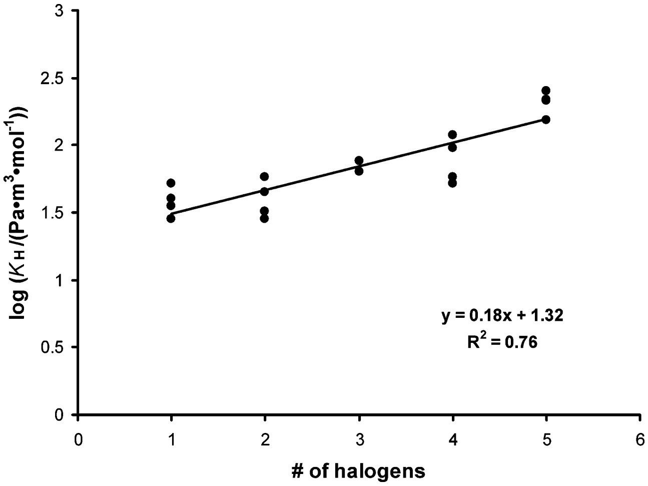

Figure 3. Correlation of log K_H, as determined by the "averaged k" IGSM at 25 °C, with PCB homologue group with increasing chlorination. The regression equation between log K_H and chlorine number is $y = 0.18x + 1.32$, and the R^2 is 0.76.

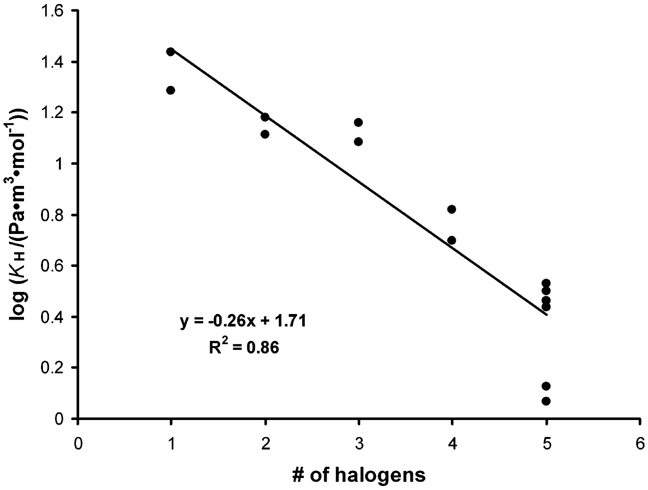

Figure 4. Correlation of log K_H, as determined by the "averaged k" IGSM at 25 °C, with PBDE homologue group with increasing bromination. The regression equation between log K_H and number of bromines is $y = -0.26x + 1.71$, and the R^2 is 0.86.

heavier PBDEs were far more prone to adhere to surfaces than the PCBs. The tendency of heavier PBDEs to adhere to surfaces will affect the environmental fate of the compounds by favoring adsorption to solid phases. The high degree of adsorption of the heavier PBDE congeners may also indicate that the effective water solubility of these compounds is lower than anticipated. Additionally, the tendency for the heavier PBDEs to absorb to surfaces may also favor their partitioning to the air−water interfaces, which could result in greater fraction of the chemical associated with aerosol formed by bubble bursting. This assertion is partially supported by the observation that the fraction of chemical mass recovered on the mist trap/PUF holder relative to the mass collected on the PUF plugs was greatest for the three penta-brominated PBDEs (Table 2).

Discussion

This research was designed to evaluate the three different gas-stripping methods for their ability to accurately determine K_H for PBDEs and PCBs. However, an objective assessment of accuracy is needed to compare the methods. Consistency between experimentally determined and reported literature values is one measure of a method's performance, but consistency does not always equate to accuracy. Furthermore, this approach can only be applied to assess properties that have already been measured by other researchers, which makes it difficult to evaluate new measurements such as the Henry's Law constants of PBDEs.

The standard used for assessing method performance adopted was a mass balance approach, which has not been conducted in previous gas-stripping experiments. The mass balance calculations directly test two of the assumptions made by the gas-stripping methodology. First, it proves the lack of chemical degradation or other unexplained loss that may be misinterpreted as volatilization in the gas-stripping system. Second, it quantitatively determines the extent of chemical adsorption to the experimental apparatus, which can buffer changes in aqueous concentrations. Furthermore, the parameter of "overall mass recovery" is similar to a "spike-recovery" experiment typical of analytical chemistry method validation. This also provides a quantitative measure of the fate of the chemical added to the system. We strongly recommend that future K_H determinations adopt a mass balance approach as a quality control measure.

All three measurement methods were acceptable for the PCBs and the lighter PBDEs with three bromines or less. These chemicals behaved in an ideal fashion in the experimental system with limited adsorption and extensive chemical loss to volatilization. The heavier PBDEs with four or five bromines, however, showed extensive adsorption that would buffer aqueous concentrations and, thus, invalidated the standard GSM. Consequently, we recommend that the MGSM and the IGSM be utilized for K_H determination of the heavier PBDEs and other chemicals that are relatively insoluble in water. It should be re-iterated that MGSM and IGSM are mainly two different approaches to interpret the results obtained from a MGS experiment, although the IGSM can use additional data from a mass balance calculation. This new calculation method provided greater consistency, particularly when using the averaged k approach, for the high congeners that have very low vapor pressures and are prone to condense on the experimental apparatus. It also provides a "double check" on the results obtained from the MGS experiment.

Although PBDEs were expected to have similar physical−chemical properties as PCBs, these results indicated they are quite different. The PBDE K_H values showed that they would be more likely to reside in the aqueous phase as compared to PCBs, which suggests that PBDEs are not as prone to volatilization from water bodies as PCBs. In addition, the heavier PBDEs were shown to partition to surfaces, which may predispose them to reside in soils, sediments and biota. These results have provided a crucial piece in understanding the behavior of PBDEs, but further research is still needed in understanding how PBDEs are transported in the environment.

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