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ABSTRACT

Henry's law constants (K_H) for seven polybrominated diphenyl ether (PBDE) congeners and nine polychlorinated biphenyl (PCB) congeners were determined using three variations of the gas stripping method. A modified gas stripping and an integrated gas stripping method were compared with the standard gas stripping method to identify the most accurate approach for PCB and PBDE K_H determination between 5°C and 35°C. All three methods were equivalent for PCB measurements while the modified gas stripping method was more appropriate for PBDEs at or below 25°C and the integrated gas stripping method was preferred for temperatures above 25°C. Mass balance was achieved for the first time, providing a quantitative account of buffering effects and verifying the lack of degradation of the analytes during the experiment. Furthermore, the mass balance approach provided a deeper understanding of the quality of results and of the behaviour of individual compounds that cannot be achieved otherwise.

The measured Henry's Law constants for PBDE ranged from 0.18 ± 0.34 $Pa{\cdot}m^3{\cdot}mol^{-1}$ (5°C) for 2,4,4'-tribromodiphenyl ether to 29 ± 5.7 $Pa{\cdot}m^3{\cdot}mol^{-1}$ (35°C) for 4-bromodiphenyl ether. For PCBs, Henry's law constants ranged between 0.60 ± 0.45 $Pa{\cdot}m^3{\cdot}mol^{-1}$ (5°C) for 2,4,4'-trichlorobiphenyl to 123 ± 12 $Pa{\cdot}m^3{\cdot}mol^{-1}$ (35°C) for 2,2',4,4',5-pentachlorobiphenyl. K_H values were generally higher for the PCBs since they were more readily volatilized from water into the air than the corresponding PBDE congeners. Although PCB K_H values were not correlated to the degree of chlorine substitution, PCB K_H values increased with *ortho*-chlorine substitution. In contrast, PBDE K_H values decreased with the increasing bromine substitution and *ortho*-bromine substitution. The enthalpies of phase change (ΔH_H) for PBDEs varied from –2.3 kJ mol^{-1} for 2,2',4,4',6-pentabromodiphenyl ether to 105 kJ mol^{-1} for 2,4,4'-tribromodiphenyl ether. For PCBs, ΔH_H values varied from –53 $kJ{\cdot}mol^{-1}$ for 2,2',4,4'-tetrachlorobiphenyl to 114 $kJ{\cdot}mol^{-1}$ for 2,3',4,4',5-pentachlorobiphenyl. According to the ΔH_H values, temperature dependence of PBDE and PCB were similar.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are an important class of flame retardants that are used in a large variety of everyday commercial products. These compounds are physically blended into plastic polymers found in computers, television sets, furniture upholstery, paints, packaging and textiles [1]. Since the PBDEs are physically blended into the polymers rather than chemically bonded, they can leach or volatilize from the host polymers. In addition, the amount of PBDEs in plastics can be as high as 30% of the total weight of the polymer formulation; thus, the amount of PBDEs in consumer products can be very high. Their worldwide application in consumer products has resulted in their widespread environmental distribution [1]. Recent studies have also found high concentrations in indoor air dust particles and in common food items [2-5].

PBDEs are highly hydrophobic and structurally similar to polychlorinated biphenyls (PCBs), so these compounds are expected to bioaccumulate and have similar toxicities [6, 7]. Furthermore, concentrations found in the environment have increased exponentially in the past 20-30 years [4, 8]. Although the pentaBDE and octaBDE formulations were banned by the European Union (EU) in 2003, PBDEs are still unregulated in North America, which may be the reason why PBDE levels found in North American populations are approximately 17 times higher than those in Europe [9]. Consequently, the state of California will follow the EU's decision to phase out the pentaBDE and octaBDE formulations by 2008. Currently, the decaBDE formula is still in use in both Europe and North America.

PROBLEM STATEMENT

Attempts to predict the fate and transport of these compounds are still tenuous due to the lack of physical-chemical property data [10, 11]. Henry's law constants (K_H), in particular, are essential for environmental modelling of these chemical since they describe the partitioning of chemicals between key environmental phases of air and water. For example, these values are needed to determine the flux of a chemical to/from large bodies of water which may act as a source or sink for semivolatile organic compounds (SOCs) [12-14]. Air-water partitioning is an important process for the delivery and removal of SOCs to/from the atmosphere, which controls the long range transport potential of these chemicals.

Although PBDE K_H values can be estimated from vapour pressure and water solubility measurements, the errors incurred in separate measurements of two physical properties are compounded in calculating K_H, making the results less reliable [15]. Other estimation methods based on quantitative-structure property relationships (QSPRs) lack sensitivity for congeners with similar halogenation patterns. Hence, the experimentally determined data is still the best method for determining K_H. Furthermore, temperature changes can have significant effects K_H, which have been found to range from 12% to 255% per 10ºC increase [16, 17]. Since temperature effects are compound-specific, it is very important to measure temperature dependence of environmental interest.

Furthermore, the quality of measured K_H varies with experimental design. Most SOCs are measured by using the gas stripping method developed by Mackay et al. [18], but several assumptions of this method needed to be examined more closely for compounds with very low vapour pressures, such as the PBDEs. First, the decrease in aqueous concentration over time must be sufficiently large since sensitivity of the method depends on the slope of the decrease. Second, buffering effects due to compounds absorbing and desorbing from the apparatus surfaces are assumed to be negligible. Although the measurement of PCB K_H values using the gas stripping method is well-documented, the question remains whether PBDEs would behave in the same way.

OBJECTIVES

The objectives of this research were to determine the most accurate method for the determination of K_H for a variety of PBDEs and PCBs and then to determine the temperature dependence of K_H from 5°C to 35°C. Three different methods, namely the gas stripping [18], modified gas stripping [19], and integrated gas stripping methods (newly developed by this study), were evaluated to determine the most accurate method for a series of PBDE and PCB congeners. K_H values of both PBDE and PCB were compared in evaluating the partitioning of these chemicals between the air and gas phase. Also, trends in the degree and position of halogen substitution were investigated.

In order to achieve the highest accuracy in these experiments, mass balance was established for each experiment where individual components of the gas-stripping apparatus were analysed. This was the most rigorous quality control tool for K_H measurements, which had not been implemented in previous experiments. This procedure provided a deeper insight into the nature of the gas stripping method and its potential biases. The second part of the research determined the temperature dependence of K_H for a series of PBDE and PCB congeners. To our knowledge, this is the first study where temperature dependence of PBDE K_H values is reported.

THEORY

Calculations for K_H and its Temperature Dependence

Henry's law constant is defined as the partial pressure of a compound divided by its chemical concentration in an aqueous phase at equilibrium. Typically, it is expressed as:

$$K_H = p_g / C_w \qquad (1)$$

where p_g is the partial pressure of the compound in the gas phase (Pa) and C_w is the concentration of the compound in the aqueous phase ($mol \cdot m^{-3}$). Therefore, K_H has units of $Pa \cdot m^3 \cdot mol^{-1}$. However, K_H can also be expressed as the dimensionless air-water partition coefficient:

$$K_{AW} = C_g / C_w \qquad (2)$$

where C_g is the concentration of the compound in the gas phase ($mol \cdot m^{-3}$). K_H can be converted to K_{AW} by:

$$K_{AW} = K_H / RT \qquad (3)$$

where R is the ideal gas constant (8.314 Pa m^3/K mol) and T is the absolute temperature (K). Furthermore, temperature dependence of K_{AW} is described by the Gibbs-Helmholtz equation:

$$\ln K_{AW} = -\Delta H_H/(RT) + \Delta S_H/R \qquad (4)$$

where ΔH_H and ΔS_H are changes in enthalpies and entropies from the aqueous to the gas phase, respectively. ΔH_H can be obtained from the slope of the linear regression of ln K_{AW} vs. T^{-1} while ΔS_H can be obtained from the y-intercept, which is assumed to be constant between 5°C and 35°C.

Calculations for the Gas Stripping Method

Derivations for the calculations involved in the gas stripping method and the modified gas stripping method are already presented in the literature [18, 19], so they will only be summarised here. Briefly, K_H obtained from the gas stripping method is determined by the decrease in aqueous concentration over time as air is purged through the aqueous phase. K_H is thus given by:

$$\ln (C_{w(t)}/C_{w(t=0)}) = - (K_H G/VRT)t \qquad (5)$$

where G is the flow rate of the purge gas (L·min^{-1}); V is the total volume of the liquid in the column (L); $C_{w(t)}$ is the aqueous concentration at time t and $C_{w(t=0)}$ is the aqueous concentration at time zero. Therefore, K_H is in units of Pa·m^3·mol^{-1}.

Calculations for the Modified Gas Stripping Method

The modified gas stripping method uses the same experimental apparatus as the gas stripping method. However, both aqueous and gaseous phases are collected to obtain the time-integrated concentrations over a number of time intervals for each experiment where:

$$K_{AW} = K_H / RT = C_g / [(C_{w(n)} + C_{w(n+1)})/2] \qquad (6)$$

where C_g (pg·L^{-1}) is the average gas-phase concentration for one time interval and $C_{w(n)}$ and $C_{w(n+1)}$ are the dissolved aqueous concentration before and after that particular air sampling interval, respectively. The primary advantage of this procedure is that several measurements of K_H are obtained during the time course of an experiment. These multiple estimations of K_H provide more statistical power and thus greater confidence in the results. The disadvantage of this approach is that collection and analysis of gas-phase chemical adds considerable time and effort to the experiment.

Calculations for the Integrated Gas Stripping Method

The integrated gas stripping method is a new procedure devised in this study for measuring K_H. This method is complementary to the modified gas stripping method, in which the average concentration over the entire experiment was used, therefore

$$K_{AW} = K_H / RT = [(m_{g\ total} + m_{PUF\ holder})/V_{g\ total}] / [(C_{w(0)} + C_{w(end)})/2] \qquad (7)$$

where $m_{g\ total}$ is the total mass of a compound purged into the gas phase and $m_{PUF\ holder}$ is the total mass adhered to the PUF holder surface. $V_{g\ total}$ is the total volume of gas used for purging over the course of the experiment. $C_{w(0)}$ is the aqueous concentration before the start of the experiment and $C_{w(end)}$ is the aqueous concentration at the end of the experiment. The inherent assumption in this approach is that the aqueous concentration does not change appreciably during the experiment. Therefore, this approach is valuable for relatively non-volatile chemicals that slowly partition into the gas phase. It is also valuable when the aqueous concentration is buffered by adsorption and desorption from the walls of the column. The disadvantage of this approach is that it only yields a single estimate for K_H for each experiment, but it involves very little additional effort beyond the modified gas stripping method. Therefore, modified gas stripping and the integrated gas stripping approaches can be conducted in the same experiment, although the integrated gas stripping approach requires the additional solvent rinse and analysis of the apparatus at the end of the experiment.

PROCEDURE

Chemicals

4-Monobromodiphenyl ether (IUPAC Congener No. 3) and 4,4'-dibromodiphenyl ether (IUPAC Congener No. 15) were purchased from Aldrich (St. Louis, MO). 2,4,4'-tribromodiphenyl ether (IUPAC Congener No. 28), 2,2',4,4'-tetrabromodiphenyl ether (IUPAC Congener No. 47), and 2,3,',4,4',5-pentabromodiphenyl ether (IUPAC Congener No. 118) were obtained from Cambridge Isotope Laboratories (Andover, MA). 2,2,'4,4',5-pentabromodiphenyl ether (IUPAC Congener No. 99) and 2,2',4,4',6–pentabromodiphenyl ether (IUPAC Congener No. 100) were purchased from Chiron AS (Norway). 2-chlorobiphenyl (IUPAC Congener No. 1), 4-monochlorobiphenyl (IUPAC Congener No. 3), 2,4'-dichlorobiphenyl (IUPAC Congener No. 8), 4,4'-dichlorobiphenyl (IUPAC Congener No. 15), 2,4,4'-trichlorobiphenyl (IUPAC Congener No. 28), 2,2',4,4'-tetrachlorobiphenyl (IUPAC Congener No. 47), 3,3'4,4'-tetrachlorobiphenyl (IUPAC Congener No. 77), 2,2,'4,4',5-pentachlorobiphenyl (IUPAC Congener No. 99), and 2,3,',4,4',5-pentachlorobiphenyl (IUPAC Congener No. 118) were all purchased from AccuStandard (New Haven, CT). Granular anhydrous sodium sulfate and HPLC grade water were purchased from Fisher Scientific (Fair Lawn, NJ). Dichloromethane, acetone, and hexane were all capillary GC/GC-MS grade from Burdick & Jackson (Muskegon, MI)

Experimental Methods

Measurements were performed by using the experimental set-up of the modified gas stripping method (Figure 1) [18-20]. Basically, the analytes were dissolved in HPLC grade water contained inside the gas-stripping column where they were purged out of solution by a stream of nitrogen. To ensure that analytes were dissolved in the water, the analyte solutions were prepared in an acetone and added to water in a 2-liter volumetric flask such that acetone volume comprised only 0.025% of the total volume of the flask. Furthermore, the resulting aqueous concentrations were lower than 5% of the reported water solubility. This solution was covered by aluminium foil and allowed to equilibrate at room temperature for 3 days before transferring the solution into the gas-stripping column, thus only chemical that was truly dissolved was transferred into the column. For experiments below 25°C, solutions were stored at 4°C for 3 days to ensure that the chemicals would be truly dissolved in the gas-stripping column at low temperatures.

Two 1 m high gas-stripping columns, with inner diameters of 5.1 cm, were operated side-by-side under the same experimental conditions to provide duplicate measurements. Temperature of the system was controlled by a constant-temperature water bath that circulated through the water jacket surrounding the column. The purge gas was 99.997% pure nitrogen (50-60 $mL \cdot min^{-1}$), which was further passed through a charcoal purifier. 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. Breakthrough experiments found less than 1% breakthrough for each PUF. However, two PUF plugs in series were still used to collect the gas phase. 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. Samples were taken every 12 hr during the first 2 days and then every 24 hr for the last 5 days.

Aqueous samples were extracted by liquid-liquid extraction with 5 mL of dichloromethane (DCM) three times. The extracts were combined and dried by adding anhydrous sodium sulphate and rinsed with DCM. The extract was then reduced in volume by nitrogen evaporation and solvent-exchanged into isooctane by nitrogen evaporation to a final volume of 100 μL. The internal standards 2,4,6-trichlorobiphenyl (IUPAC Congener No. 30) and decachlorobiphenyl (IUPAC Congener No. 209) were added to the samples. All aqueous samples were processed without storage. PUF samples were extracted by Soxhlet extraction in DCM for 24 hours. The extracts were then reduced in volume in the same fashion as the aqueous samples. The final volume was 500 μL and the same internal standards were added prior to analysis.

Sample analyses were performed by a Hewlett-Packard 6890N Network gas chromatograph with a 5973 Network mass selective detector and a 5% diphenyl-methyl-polysiloxane capillary column (0.25 i.d. x 30 m x 0.25 μm film thickness, DB-5MS, J&W Scientific). Oven temperature program started at 60ºC and holds for 1 minute, then ramped at 12°C/min to 155°C, 2°C/min to 215°C, 3°C/min to 268, and finally 30°C/min to 300°C. Electron-capture negative chemical ionization was used with 50% methane at 5 $mL{\cdot}min^{-1}$. Electron energy was set at 130eV. Quadrupole and source temperature were set at 150°C. Single ion monitoring was used for quantification for maximum sensitivity. For PBDEs, the bromine isotopes (amu 79 and 81) were mainly used for quantification because of their high abundance. Both chlorine isotopes (amu 35 and 37) and molecular ions were used for PCB quantification depending on the abundance of the particular congener.

Quality Assurance/Quality Control and Mass Balance

Since PBDEs are common indoor air contaminants, several procedures were used to reduce possible contamination of the samples and the gas-stripping columns. All glassware was baked at 550°C before each experiment to minimize contamination. PUF plugs were cleaned by Soxhlet extraction in DCM for 24 hours. Clean PUFs were stored inside baked glass jars and sealed with Teflon tape. After each experiment, the apparatus was disassembled and cleaned by rinsing with solvents. For each PUF and water sample, a blank and a matrix spike were extracted along with the sample simultaneously.

In order to obtain mass balance for each experiment, background levels must be established before each experiment. To ascertain background levels for the aqueous phase, blank HPLC grade water was purged for 48 hr in the columns with clean PUF plugs to collect the gas phase. After 48 hr, the PUF plugs were extracted by Soxhlet extraction in the identical fashion as the samples to determine the background levels in the gas phase. Aqueous samples were taken and extracted to determine the amount of contaminants that might still have remained in the column. After each experiment, the spiked solution was drained from the column. Both the PUF holder and the column were rinsed with DCM, which was subsequently dried by sodium sulfate, reduced in volume and analysed. These solutions established the amount of analytes that adhered to the surface of the column and the PUF holder. Therefore, the amount of chemical present before and after each experiment can be compared so that any degradation, contamination, or other losses could be accounted for.

RESULTS

An assumption of both the gas stripping and modified gas stripping method is that the compounds of interest reached equilibrium between the gas and dissolved phase. Experiments were performed at different column heights to ensure that equilibrium was reached. All experiments used to calculate K_H were conducted at the maximum column height of 89 cm to ensure equilibrium conditions. Various flow rates were also investigated and the lowest flow rates (50-60 mL/min) were used to produce the smallest bubbles which had the greatest total surface area (or the greatest surface area to volume ratio). These conditions were chosen so that equilibrium was achieved for the experiments.

Different trends in the decrease of dissolved concentrations were observed (Figure 2). One trend showed a linear log concentration decline over time (e.g. BDE-3 at 35°C). Another showed high dissolved concentration at time zero but decreased dramatically at 12 hr and remained constant at this level over time (e.g. BDE-118 at 5°C) (Figure 2). The first case indicated that no sorption effects were observed over the course of the experiment. The latter showed that the compounds needed 12 hr to establish equilibrium with the surface of the column. The constant concentration that remained after the first 12 hr indicated compounds were being adsorbed and desorbed from the glass surface at approximately equal rates. Thus, even though the target initial aqueous concentrations of the PBDEs and PCBs were less than 5% of the reported water solubility, adsorption effects were still observed for some of the PBDE congeners, particularly so for those of lowest water solubility.

Considering the above observations, dissolved concentrations at time zero were not used for calculations since equilibrium between the dissolved phase and the glass surfaces might not have been reached at time zero. It was assumed that all compounds required 12 hr to equilibrate in the columns. Also, aqueous concentrations of heavy PBDE congeners (with 4 or more bromine substitutions) started to fall below the limit of quantification towards the end of the experiment, so these values were not included in the calculations. Assuming data were under normal distribution, the Q-test was used to reject suspected outliers at 90% confidence level.

Mass Balance and QA/QC

Mass closure was achieved for almost all experiments with the average mass balance of all compounds ranging from 74.5% to 94.7% (Table 1), which attested to the quality of the results. An example of the mass balance of both PCBs and PBDEs from the 25°C experiment is shown in Table 2. By analyzing each part of the apparatus separately, the extent that each congener adsorbed to particular parts of the apparatus was revealed. For both PCBs and PBDEs, blank water and PUF samples taken before the beginning of each experiment contained negligible contamination. For PCBs, adsorption to apparatus was not as extensive as PBDEs. Adsorption of PBDEs increased with the level of bromination due to decreasing water solubility. Less than 2% of the mono- and di-brominated congeners adsorbed to the column while tri-brominated congener showed 10% adsorption and tetra- and penta-brominated congeners showed more than 60% adsorption to the column surface. PCBs did not show such a tendency. Even the most chlorinated PCB congeners had less than 6% adsorption to the column glass surface while the largest portion was purged into the gas phase. This mass balance analysis revealed how much these two types of compounds differ in their sorption characteristics even though their molecular structures were similar.

The gas stripping method is the standard methodology for K_H measurements of SOCs such as PCBs, which behaved ideally in the gas stripping system. Such success, however, relied on the assumption that adsorption/desorption from the apparatus surfaces were negligible. Unfortunately, not all compounds possess these characteristics, particularly those that have low volatility and high hydrophobicity. PBDEs demonstrated the potential biases incurred by such an assumption. Being less volatile then the PCBs and equally hydrophobic, the PBDEs had such a strong tendency to adsorb to glassware that it could not be discounted in obtaining experimental results. In addition, strong sorption characteristics reduced the slope of decline in the aqueous concentration. Since the gas stripping method depends on this decrease, it may not have the sensitivity needed for compounds of low volatility, like the higher brominated PBDE congeners.

These results clearly showed that having mass closure of K_H measurements is important to assuring accurate data, especially when more and more emerging pollutants are less volatile and more hydrophobic than most SOCs. By having a quantitative account of where each compound resides in the system, buffering effects can be accurately assessed so that potential sources of errors are avoided. Also, potential losses due to degradation can be investigated and accounted for by using the mass balance approach.

K_H at 25°C and Method Comparison

At 25°C, PCB K_H values measured in this study ranged from 16 ± 0.91 $Pa \cdot m^3 \cdot mol^{-1}$ for PCB-15 to 92 ± 85 $Pa \cdot m^3 \cdot mol^{-1}$ for PCB-118 (Table 3). Overall, PCB K_H values were within the same order of magnitude for all five levels of chlorination. The results agreed with Bamford et al. where the modified gas stripping method was used to determine the K_H of PCBs [19]. On the whole, the three methods had very good agreement amongst themselves and with the literature. An exception was PCB-99, this could have been caused by a combination of its high hydrophobicity and low detection sensitivity. As mentioned above, PCB congeners showed very little adsorption to glass and the largest portion was purged into the gas phase; hence, PCBs seemed to be behaving ideally in the gas stripping system. Since values from all three methods were self-consistent, they were equivalent for the measurement of PCB K_H.

PBDE K_H values measured at 25°C ranged from 4.68 ± 5.14 $Pa \cdot m^3 \cdot mol^{-1}$ for BDE-47 to 21 ± 4.0 $Pa \cdot m^3 \cdot mol^{-1}$ for BDE-118 (Table 4). Evaluation of PBDE results was complicated by the scarcity of published values. Lau et al. [21] had previously used the gas stripping method to measure PBDE K_H without implementing the same QA/QC technique used here for mass balance. These previous values were generally higher than the results in this study, which was probably the result of adsorption/desorption for the glassware in this simple gas stripping apparatus and the aqueous concentrations used were also higher based on published water solubilities [15]. Conversely, calculated K_H values obtained from separate vapour pressure and aqueous solubility measurements from Tittlemier et al. were lower than those reported here [15].

Although K_H values of PBDEs measured by the three methods were similar at 25°C, this consistency no long held true as temperature decreased (Table 5), which was different than the trends observed with the PCBs. For mono- and di-brominated congeners, this inconsistency was negligible since they were purged in the same way as PCBs and very little adsorption occurred. However, as the degree of bromination increased, the difference in the three methods became very prominent. In fact, the gas stripping method yielded the highest values followed by the modified gas stripping method, and the integrated gas stripping method yielded the lowest values. In order to avoid buffering effects from desorption from the column glass surface, the modified gas stripping method was preferred because of its independence in the decrease of dissolved concentration over time.

Adsorption/desorption from the surface of the column was only one aspect of the problem. The other potential sorption site was the glass surface of the PUF holder. If a significant amount of the compounds purged onto the PUF plugs also adsorbed to the surface of the holder, measured values would be underestimated if this amount was not included in the gaseous phase concentration. This was particularly significant at high temperatures where more of the compounds were purged into the gas phase than at lower temperatures. If a larger amount is in the gas phase, a bigger portion of it can adhere to the holder surface; therefore, the integrated gas stripping method would be necessary to correct for the adsorption of the compounds onto the holder surface. For example, the amount of BDE-118 sorbed onto the PUF holder at 35°C was an order of magnitude higher than 5°C. Consequently, the integrated gas stripping method would yield more accurate results at temperatures higher than 25°C.

PBDE results had relative standard deviations that ranged from 13 to 184%. The higher the temperature at which the measurement was made, the better the precision. A number of factors could have affected the precision of the results. At higher temperatures, solubility of the compounds was higher and the solution would be closer to an ideal system so the quality of the results was generally improved. Relative standard deviation of PCB results generally ranged between 10-75% (with the exception of PCB-47 at 35°C). Precision of PCBs results was generally better than PBDEs. Larger variation in the measurements of PBDEs might have been caused by strong sorption characteristics.

PBDE K_H values were generally lower than the PCBs, particularly at higher levels of bromination. This showed that they were either less volatile or more water soluble than PCBs. In general, the vapour pressures of PCBs are generally one to two orders of magnitude higher than their corresponding PBDE congeners [15, 22]. When solubility data from Tittlemier et al. were compared to the range of values available for PCBs, PBDE values were well within the range found for PCBs [15, 22]. Therefore, PBDEs had a tendency of residing in the aqueous phase and might be more readily available to aquatic life than PCBs.

Different molecular trends were observed for PCB and PBDE K_H values. For PCB homologues, no correlation was found for increasing chlorine substitution (Figure 3). However, For PCBs K_H values were found to increase with *ortho*-chlorine substitution (Figure 5). Both of these results were already established in the literature, but the replication of the results for PCBs shows that the analytical procedure was functioning properly. In contrast, PBDE K_H values decreased with the level of bromination (Figure 4) and with increasing *ortho* substitution (Figure 6). The former could be mainly due to increase in molecular weight which resulted in decrease in volatility. Also, the presence of oxygen in the ether group also increases the polarity of the compound which may increase the residence time in water; thus, increasing availability for bioaccumulation. Since PBDE K_H values decreased both with degree of bromine substitution and substitution on the *ortho* position, heavy congeners with a high number of *ortho* substitutions should reside in the aquatic environment more readily and therefore, may be more easily available for aquatic organisms. A study on the toxicity of *ortho*-chlorinated diphenyl ethers (CDEs) revealed that CDEs with *ortho*-chlorine substitution may have enhanced dioxin-like effects compared to their biphenyl counterparts [23]. The ether oxygen causes the two phenyls to be almost perpendicular to one another when *ortho*-chlorines are present which makes the phenyl rings readily available to active sites [23]. Since CDEs have such similar structure to PBDEs, similar effects can be occurring as well. With the decrease of K_H of PBDEs with increasing *ortho*-bromine substitution, the possible increased bioavailability of these compounds necessitates further investigation on possible enhanced toxicity.

Temperature Dependence of K_H

K_H of PCBs, measured between 5°C and 35°C, varied from less than an order to three orders of magnitude depending on the congener (Table 6). At 5°C, K_H values ranged from 0.60 ± 0.45 $Pa{\cdot}m^3{\cdot}mol^{-1}$ for PCB- 28 to 39 ± 12 $Pa{\cdot}m^3{\cdot}mol^{-1}$ for PCB-118; while at 35°C, values ranged from 2.8 ± 3.7 $Pa{\cdot}m^3{\cdot}mol^{-1}$ for PCB-47 to 123 ± 12 $Pa{\cdot}m^3{\cdot}mol^{-1}$ for PCB-99. A typical temperature dependence plot is shown for PCB-3 (Figure 7). Good linearity ($r^2 > 0.8$) was observed for all mono- and di-chlorinated congeners with little difference between the two columns. However, as chlorination increased, linearity of temperature dependence relationships deteriorated. K_H values of mono- to tetra-chlorinated congeners usually increased between by approximately one order of magnitude as the temperature increased while the penta-chlorinated congeners could increase up to three orders of magnitude with temperature.

In contrast, PBDE congeners did not show such large variation between different temperatures (Table 7). At 5°C, PBDE K_H values ranged from 0.18 ± 0.34 $Pa{\cdot}m^3{\cdot}mol^{-1}$ for BDE-28 to 48 ± 25 $Pa{\cdot}m^3\ {\cdot}mol^{-1}$ for BDE-99; while at 35°C, values ranged from 2.5 ± 0.74 $Pa{\cdot}m^3{\cdot}mol^{-1}$ for BDE-118 to 29 ± 5.7 $Pa{\cdot}m^3{\cdot}mol^{-1}$ for BDE-3. Temperature dependence plots had the same level of linearity as PCBs up to 3 bromine substitutions (Figure 8). As observed for PCB congeners, as the level of bromination increased, linearity decreased. For all PBDE congeners, with the exception of BDE-28, K_H only varied within an order of magnitude. Therefore, within the range of temperature used here, PCBs were volatilized much more rapidly at higher temperatures than PBDEs at the same temperatures, which was also shown by the mass of the chemical collected from the gas phase.

There was very little variation in PCB ΔH_H and ΔS_H within the temperature range that they were measured (Table 8). ΔH_H values varied from -53 $kJ{\cdot}mol^{-1}$ for PCB-47 to 114 $kJ{\cdot}mol^{-1}$ for PCB-118. ΔS_H values varied from -0.23 $kJ{\cdot}mol^{-1}{\cdot}K^{-1}$ for PCB-47 to 0.35 $kJ{\cdot}mol^{-1}$ for PCB-118. Both ΔH_H and ΔS_H values were in good agreement with reported values, especially the mono- to tri-chlorinated congeners results. Literature values for PCB-15 and PCB-47 were not available. ΔH_H values for the three penta-chlorinated congeners were about 2-times greater than reported by Bamford et al. [19].

PBDE ΔH_H values varied from –2.3 kJ·mol^{-1} for BDE-100 to 105 kJ·mol^{-1} for BDE-28 (Table 9). PBDE ΔH_H values were similar in magnitude to their corresponding PCB congeners except tetra- and penta-chlorinated congeners where the PCB ΔH_H values were larger than the tetra- and penta-brominated congeners. These congeners were particularly difficult to measure because of the extensive amount of sorption to glass which made quantification problematic. ΔS_H values varied from –0.058 kJ·mol^{-1}·K^{-1} for BDE-100 to 0.31 kJ·mol^{-1} for BDE-28. PBDE ΔS_H values were in similar order of magnitude compared to those of PCBs. BDE-47 and BDE-99 had a very unusual type of temperature relationship where the slope was positive instead of negative; hence, the ΔH_H and ΔS_H values were negative. These two congeners were very difficult to measure because of the variable background levels, low water solubility and tendency to adsorb to glass surfaces. Overall, PCBs had better temperature dependence correlations than PBDEs. However, both obtained good correlation for congeners with lower degree of halogenation.

CONCLUSIONS

K_H values of PCBs and PBDEs were measured using three different gas stripping methods: gas stripping, modified gas stripping and integrated gas stripping. In comparing the results of these three methods, no significant differences were found for the PCBs, but PBDEs showed distinctive differences due to the buffering effect of chemical adsorption/desorption from the glassware. However, if buffering effects were to be avoided, the modified gas stripping method would be the most reliable method since it did not depend on the decrease of aqueous dissolved concentration over time. Two different methods were necessary for PBDEs. For temperatures at 25°C or lower, the modified gas stripping method was the most suitable. However, at temperatures higher than 25°C, the amount of analyte adhered to the PUF holder glass was significant enough that it must also be included; therefore, the integrated gas stripping method was more appropriate. Temperature dependence of PCBs and PBDEs K_H were determined. Enthalpy ΔH_H and entropy ΔS_H values obtained can now be used for determining K_H at temperatures other than those reported here.

This research also proved the power of mass balance to both better understand the system and provide an excellent quality control feature of the experiment. This rigorous approach gave a different understanding of how the gas stripping method worked for different compounds and how this method could be modified to get more accurate results. Since all of the compounds that were introduced into the system in the beginning of the experiment were accounted for at the end of the experiment, these results were not affected by degradation and contamination processes that would produce significant errors. In addition, buffering effects are no longer a qualitative speculation in having a quantitative account of where each compound resides in the system. All these factors allowed a more confident interpretation of the data.

Although PBDEs had been expected to have similar physical-chemical behaviour to PCBs due to their structural similarities, these results clearly showed the opposite. PBDEs were not as volatile as the PCBs. K_H values showed that they resided in the aqueous phase more readily than the gas phase. Also, PBDEs were shown, by mass balance, to be a lot more adsorbent. This could mean strong adsorption to solids. Measurements of watersediment partition coefficient can be used to assess the extent to which these compounds are available in the dissolved phase so that the amount of exposure to aquatic organisms can be known. Although the number of congeners where K_{H} could be measured was limited, K_{H} values for other congeners can be obtained using the reported data as a basis to develop a model that uses molecular parameters. Other important aspects of the fate of PBDEs, e.g. degradation of PBDEs in different environmental compartments, are still needed for accurate modelling of fate and transport. Environmental modelling will provide important understanding of the impact these chemicals will have in the environment.

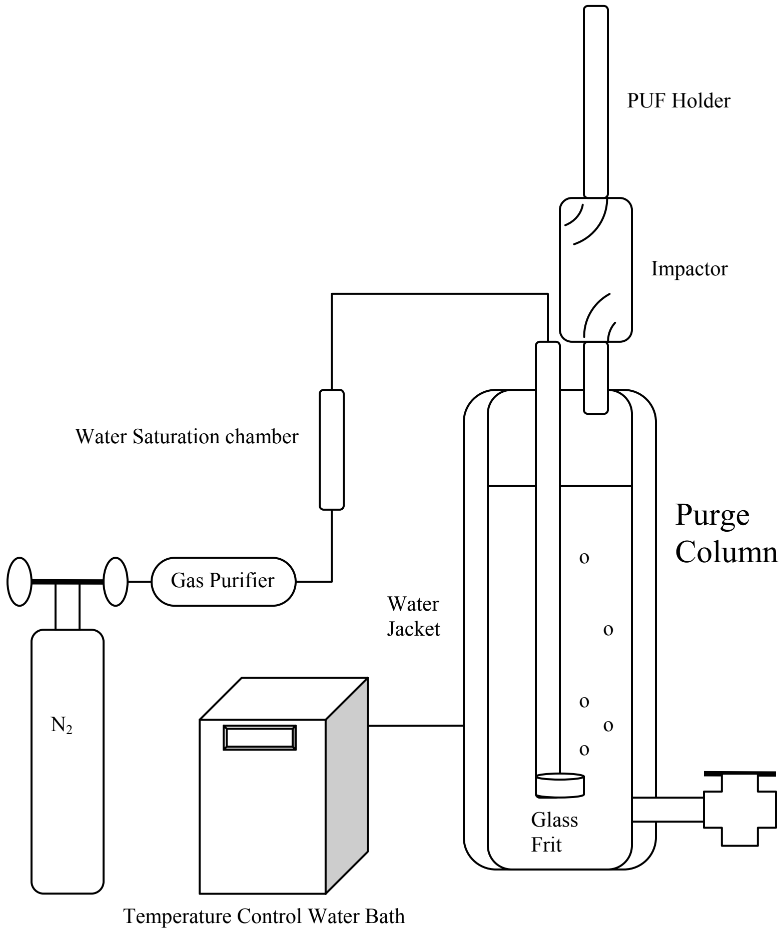

Figure 1. Modified gas stripping apparatus.

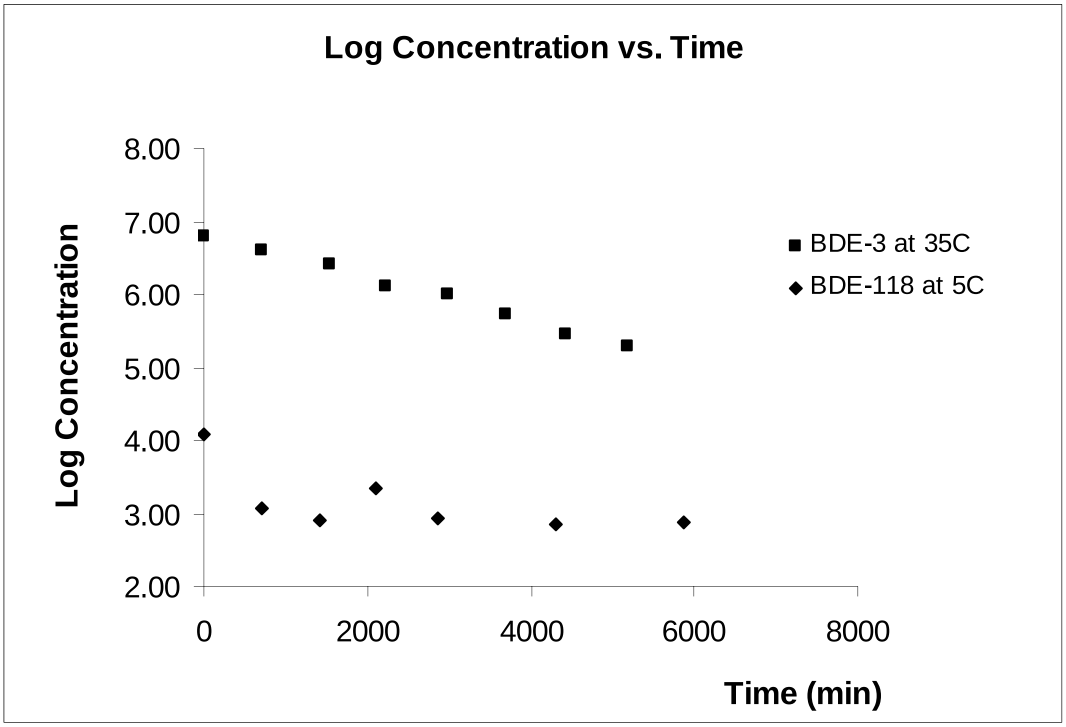

Figure 2. Decrease of log aqueous concentration over time of the experiment for BDE-3 (at 35ºC) and BDE-118 (at 35ºC).

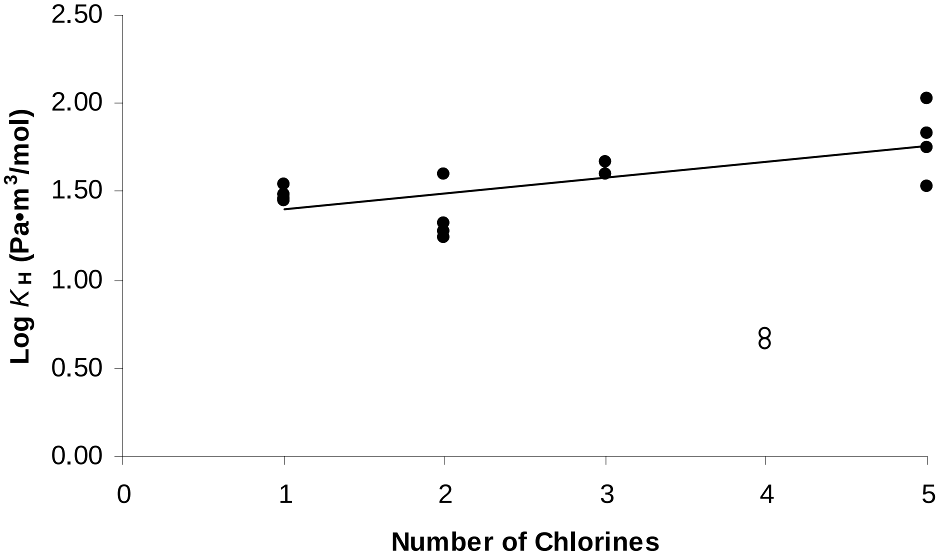

Figure 3. Correlation of log K_H (at 25°C) with PCB homologue group with increasing chlorination. With the exception of PCB-47 which appears to be anomalous, the regression equation between log K_H and chlorine number is $y = 0.091x + 1.31$ and the R^2 is 0.47.

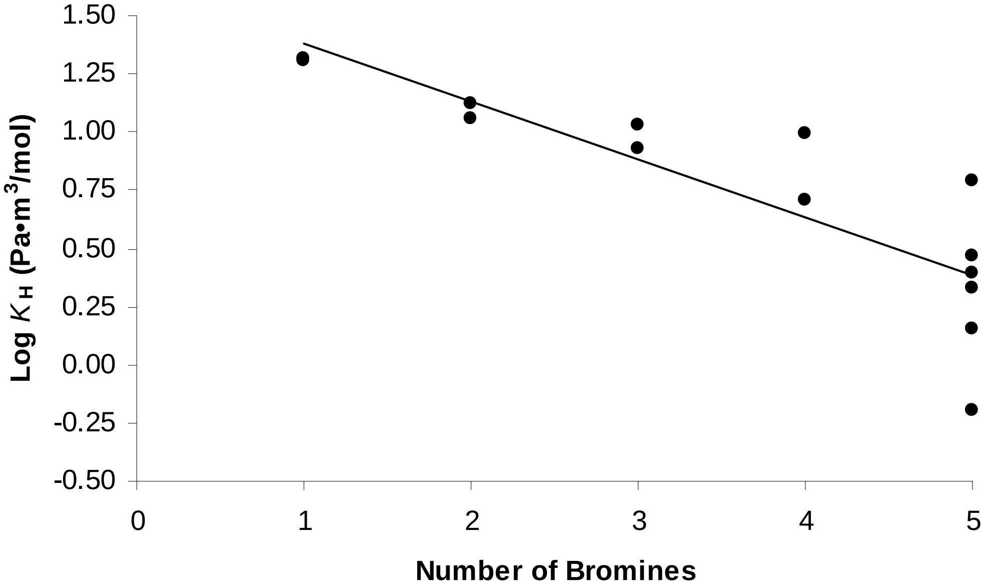

Figure 4. Correlation of log K_H (at 25°C) with PBDE homologue group with increasing bromination. The regression equation between log K_H and number of bromines is $y = -0.25x + 1.63$ and the R^2 is 0.72.

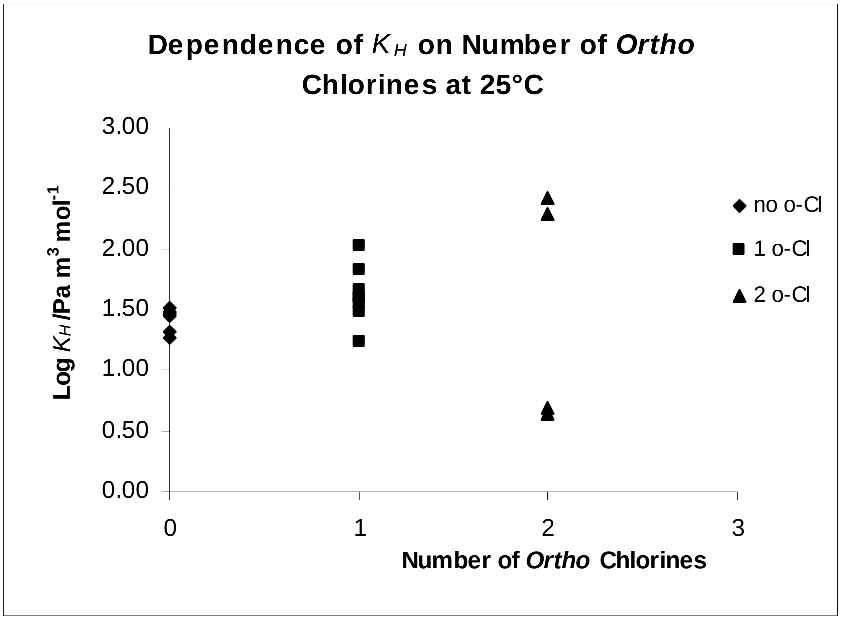

Figure 5. Correlation of PCB log K_H (at 25°C) with number of *ortho*-chlorine substitutions.

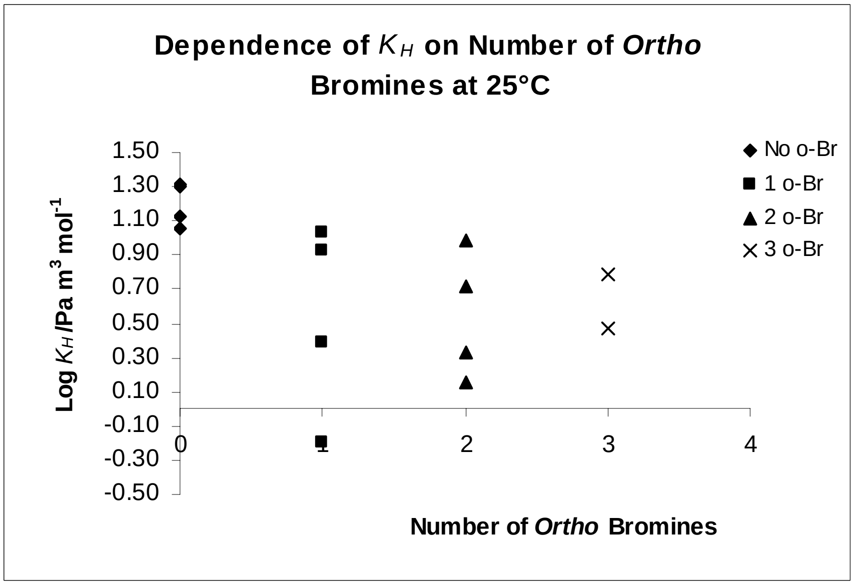

Figure 6. Correlation of PBDE log K_H (at 25°C) with number of *ortho*-bromine substitutions.

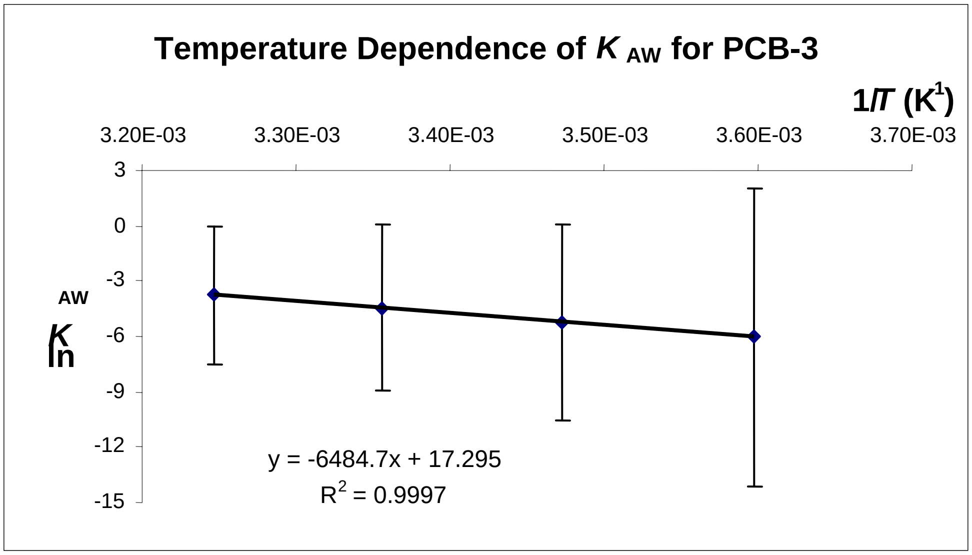

Figure 7. Duplicate temperature dependence relationships of PCB-3.

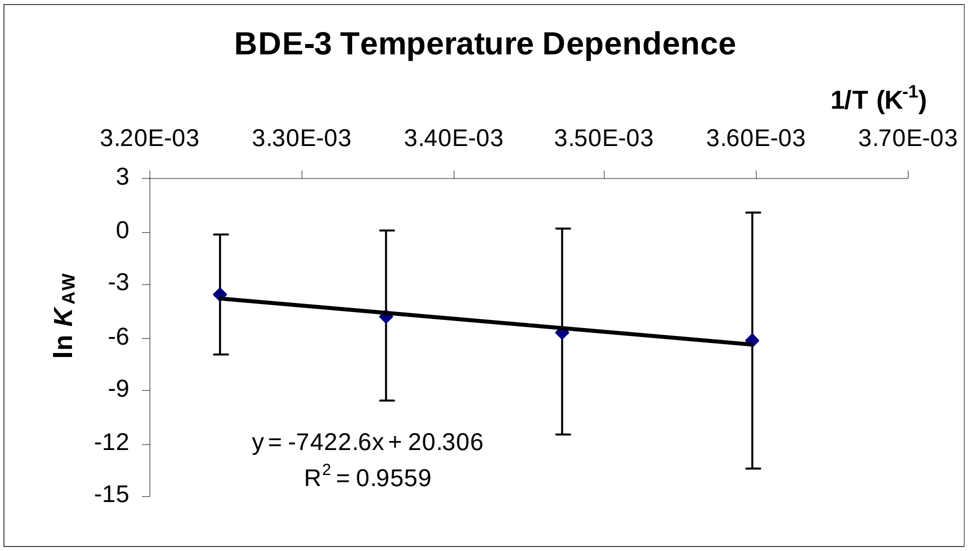

Figure 8. Duplicate temperature dependence relationships for BDE-3.

Table 1. Average of Mass Balances of PBDE and PCB congeners.

BDE Congener (IUPAC No.)	Average % (Total Mass Measured/Total Mass Spiked) ± Standard Deviation
3	95 ± 27
15	90 ± 28
28	75 ± 25
47	87 ± 21
99	93 ± 27
100	87 ± 22
118	83 ± 23
PCB Congener (IUPAC No.)	
1	82 ± 24
3	79 ± 31
8	83 ± 22
15	86 ± 25
28	87 ± 29
47	80 ± 25
77	78 ± 31
99	80 ± 26
118	76 ± 26

Table 2. Breakdown of PCB and PBDE mass balance for 25ºC experiment.

PCB	Total Mass added to column (pg)	Column Blank (pg)	PUF Blank (pg)	Dissolved Mass (pg)	Total Air Mass (pg)	PUF Holder Rinse (pg)	Column Wall Rinse (pg)
1	3.8E+07	0	0	2.6E+05	2.8E+07	0	3.9E+03
3	8.3E+07	0	0	1.5E+06	5.6E+07	0	2.1E+04
8	1.7E+07	0	0	1.3E+05	1.6E+07	2.1E+02	1.3E+04
15	1.2E+07	0	0	9.2E+05	9.7E+06	0	3.4E+04
28	5.5E+06	0	0	2.5E+04	5.7E+06	2.7E+02	2.2E+04
47	1.1E+06	8.4E+02	1.2E+03	9.6E+04	8.3E+05	1.3E+03	6.9E+03
77	4.9E+05	4.3E+01	2.3E+02	2.0E+04	4.4E+05	2.0E+03	2.9E+04
99	1.5E+05	1.2E+01	0	3.7E+03	1.6E+05	2.1E+02	2.5E+03
118	2.1E+05	2.2E+02	1.2E+03	6.0E+03	2.2E+05	1.1E+03	1.1E+04
BDE							
3	2.8E+07	1.4E+02	0	2.4E+06	2.5E+07	8.9E+02	3.7E+04
15	1.1E+07	6.0E+01	2.4E+03	1.9E+06	8.6E+06	1.1E+04	2.2E+05
28	2.0E+06	1.8E+01	1.8E+03	3.9E+05	1.3E+06	8.8E+03	2.2E+05
47	9.2E+04	1.7E+01	2.9E+03	1.4E+04	2.6E+04	7.6E+02	3.8E+04
99	9.8E+04	2.9E+1	4.2E+03	4.1E+03	3.6E+03	5.4E+01	6.6E+04
100	7.3E+04	2.3E+01	1.9E+03	4.5E+03	5.4E+03	4.9E+02	5.0E+04
118	7.5E+04	5.7E+01	3.0E+03	1.8E+03	1.2E+03	2.6E+02	4.9E+04

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

PCB	MGSM This study (IGSM)	MGSM [19]	GSM This study	GSM [24]	Calculated	Bulk Equilibrium [25]	Wetted-Wall Column [26]
1	33 ± 5.7 (18 ± 5.7)	20.43 ± 0.52	39 ± 3.8		30.2 [24] 28.9 [27]		
3	28 ± 3.7 (18 ± 4.7)		30 ± 8.1		27.8 [24]		
8	39 ± 5.2 (22 ± 6.0)	24.89 ± 0.29	39 ± 3.8	32.1	30.7 [24] 24.9 [27] 31.3 [28]	28.4	
15	20 ± 3.6 (16 ± 0.91)		21 ± 4.0	18.9	22.7 [24]		
28	44 ± 6.5 (25 ± 6.7)	38.14 ± 0.37	42 ± 7.9	32	28.9 [24] 22.8 [27]	26.7	19.6 ± 2.97
47	4.7 ± 5.1 (19 ± 2.0)		N/A		37.3 [24] 44.5 [28]		19.1 ± 4.71
77	32 ± 6.2 (29 ± 8.8)	16.20 ± 0.41	18 ± 0.21	8.41	10.4 [24] 4.37 [27]		
99	231 ± 47 (36 ± 9.7)		24 ± 0.21		25.3 [24] 30.5 [28]	21.7	7.93 ± 2.73
118	88 ± 40 (92 ± 85)	36.2 ± 1.0	21 ± 13		12.7 [24] 9.35 [27] 11.8 [28]	8.61	

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

BDE	GSM	MGSM	IGSM	Literature Values (25°C)
3	18 ± 0.21	20 ± 2.7	17 ± 4.1	45.8 ± 9.25 [21] (GSM)
15	8.9 ± 4.1	12 ± 2.6	12 ± 1.3	39.7 ± 16.1[21] (GSM) 21[15] (calc'd)
28	8.6 ± 4.5	9.5 ± 2.0	9.9 ± 0.87	17.2 ± 8.55 [21] (GSM) 5.1[15] (calc'd)
47	5.3	6.4 ± 0.18	7.5 ± 2.5	42.4 ± 4.39 [21] (GSM) 1.5 [15] (calc'd)
99	12	1.6 ± 0.41	1.8 ± 1.3	0.23 [15] (calc'd)
100	8.3 ± 4.9	3.0 ± 0.71	4.6 ± 2.6	0.069 [15] (calc'd)
118	21 ± 4.0	1.6 ± 1.7	1.1 ± 0.50	17.7 ± 14.9 [21] (GSM)

Table 5. Comparison of Henry's Law Constants K_{H} (Pa·m^3·mol^{-1}) of BDE Congeners Determined at 5°C by the Gas-Stripping Method (GSM), Modified Gas-Stripping Method (MGSM) and Integrated Gas-Stripping Method (IGSM).

BDE	GSM	MGSM	IGSM
3	5.4 ± 0.74	4.7 ± 1.7	4.7 ± 0.38
15	9.0 ± 3.9	4.6 ± 2.0	3.9 ± 2.5
28	13 ± 1.5	0.18 ± 0.34	0.34 ± 0.21
47	16 ± 2.7	9.6 ± 4.5	1.6 ± 0.28
99	25 ± 6.2	48 ± 25	4.7 ± 0.88
100	89	16 ± 2.5	1.9 ± 0.36
118	12 ± 7.6	1.1 ± 0.70	0.12 ± 0.016

Table 6. Henry's Law Constants (K_{H}/Pa·m^3·mol^{-1}) of PCBs at Temperatures between 5ºC and 35ºC

PCB	5ºC	15ºC	25ºC	35ºC
1	9.0 ± 2.2	19 ± 5.5	33 ± 5.7	58 ± 16
3	5.7 ± 0.88	13 ± 3.3	28 ± 3.7	60 ± 13
8	14 ± 4.8	20 ± 5.4	39 ± 5.2	88 ± 23
15	10 ± 2.8	13 ± 3.2	20 ± 3.6	70 ± 30
28	39 ± 12	32 ± 14	44 ± 6.5	88 ± 12
47	20 ± 14	15 ± 15	4.7 ± 5.1	2.8 ± 3.7
77	0.74 ± 0.56	24 ± 8.1	32 ± 6.2	96 ± 67
99	5.7 ± 3.0	117 ± 75	231 ± 47	123 ± 12
118	0.60 ± 0.45	48 ± 33	88 ± 40	104 ± 65

Table 7. Henry's Law Constants (K_{H}/Pa·m^3·mol^{-1}) of PBDEs at Temperatures between 5ºC and 35ºC

BDE	5ºC	15ºC	25ºC	35ºC
3	4.7 ± 1.7	8.1 ± 3.6	20 ± 2.7	29 ± 5.7
15	4.6 ± 2.0	8.5 ± 3.7	12 ± 2.6	24 ± 3.2
28	0.18 ± 0.34	9.6 ± 10	9.5 ± 2.0	16 ± 3.3
47	9.6 ± 4.5	2.1 ± 2.2	6.4 ± 0.18	8.8 ± 1.4
99	48 ± 25	2.7 ± 2.4	1.6 ± 0.41	4.7 ± 1.2
100	16 ± 2.5	1.2 ± 0.91	3.0 ± 0.71	13 ± 10
118	1.1 ± 0.70	0.14 ± 0.17	1.6 ± 1.7	2.5 ± 0.74

Table 8. Measured Enthalpy (ΔH_H) and Entropy (ΔS_H) of K_H of PCBs, and Literature Values.					
PCB	r^2	ΔH_H(kJ·mol^{-1})	ΔH_H(kJ·mol^{-1}) [Literature]	ΔS_H(kJ·mol^{-1}·K^{-1})	ΔS_H(kJ·mol^{-1}·K^{-1}) [Literature]
1	0.99	41	42.7 ± 5.8 [19]	0.10	0.104 ± 0.020 [19]
3	1.0	54	56 ± 27 [29]	0.14	0.15 ± 0.10 [29]
8	0.96	41	44.1 ± 2.6 [19]	0.10	0.110 ± 0.010 [19]
15	0.84	41	-	0.10	-
28	0.54	16	32.5 ± 1.9 [19] 50 ± 6 [30]	0.023	0.074 ± 0.006 [19] 0.191 ± 0.0205 [30]
47	0.95	-53	-	-0.23	-
77	0.84	104	39.8 ± 6.0 [19]	0.31	0.092 ± 0.020 [19]
99	0.61	70	35.4 ± 3.5 [29]	0.21	0.02 ± 0.02 [29]
118	0.74	114	49.8 ± 5.8 [19]	0.35	0.132 ± 0.018 [19]

Table 9. Measured Enthalpy (ΔH_H) and Entropy (ΔS_H) of K_H of PBDEs.			
BDE	r^2	ΔH_H(kJ·mol^{-1})	ΔS_H(kJ·mol^{-1}·K^{-1})
3	0.96	62	0.17
15	0.96	48	0.12
28	0.77	105	0.31
47	0.087	13	-0.0044
99	0.31	46	-0.21
100	0.0015	-2.3	-0.058
118	0.27	36	0.058

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