

## Air-Water Henry's Law Constants for PCB congeners: Experimental Determination and Structure-Property Relationship

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### Introduction

Polychlorinated biphenyls (PCBs) are industrial chemicals with various commercial applications and have been detected in most compartments of the ecosystem. It is a significant environmental problem because PCBs are stable, lipophilic, and toxic. Atmospheric transport has been regarded as a major global redistribution process for PCBs. Henry's law constant (HLC), a measure of PCBs' partitioning in an air-water system, is requisite in studying their transport and fate, assessing their environmental risk, and designing proper cleanup process. Yet, HLCs of many PCB congeners, especially coplanar PCBs with higher toxicity, are not available due to difficulties in analytical measurement.

The kinetic approach, based on the rate of substance loss from the aqueous phase by stripping with gas, has been widely used to determine HLCs for different chemicals. In most cases, the experiment involved large volume of aqueous solution. The first objective of this study is to design a small-scale device to directly measure HLCs for four most toxic non-*ortho* and eight moderate toxic mono-*ortho* substituted PCBs. Generator column technique was used to prepare aqueous PCB solutions that were free of any aggregates or colloidal dispersions as well as organic solvents.

It has been widely acknowledged that molecular structure holds the key to predict PCBs' physical properties, i.e. HLCs. The secondary objective is to investigate the quantitative structure-property relationship (QSPR), which relates the chlorine substitution pattern of PCBs with HLCs. HLCs of PCBs measured by the kinetic approach at 25°C (132 reported HLCs for 97 PCB congeners) were compiled by meta-analysis technique. Principal component regression (PCR) method was used to model HLCs based on pooled data for 97 PCB congeners. The remainder of the 209 PCB congeners can thus be predicted by the resulting model.

### Materials and Methods

*Preparation of PCB Aqueous Solutions.* Aqueous solutions of the PCB were prepared by a generator-column technique<sup>1</sup> to avoid the presence of micro-crystals.

*Purge Experiments.* The gas-purging system, a modification of the one used by Mackay *et al.*<sup>2</sup> and Brunner *et al.*<sup>3</sup>, used a water-jacketed column (30 cm long with a 1.1 cm i.d.) as purging vessel. The system was thermostatted at 25 ± 0.1 °C for 12 h to accomplish the adsorption equilibrium before purging. A flow rate of 50 mL/min and a sampling interval of 15 min were used. High purity nitrogen was used to strip the PCBs from the solutions. Six samples with 1 mL each of the aqueous solution were taken per column that constituted an individual HLC measurement. Recovery of PCB was calculated from the mass balance between the initial concentration of aqueous PCB solution before the experiment and the total PCB measured in both gas (collected in hexane trap) and aqueous solution after the experiment. Individual HLC determinations with recoveries of less than 75% or greater than 125% were discarded.

*Instrumental Analysis.* Surrogate standard containing PCB 61 or PCB 204 was added to aqueous sample prior to extraction. The sample including surrogate was extracted with hexane, drying over the sodium-sulfate column, and concentrated to about 50 µL under a gentle stream of nitrogen. All analyses were performed on an HP 6890 GC equipped with a split/splitless injector system and a <sup>63</sup>Ni electron capture detector (ECD), fitted with a DB-XLB column (30-m length × 0.25-mm i.d. × 0.25-mm film thickness). The GC oven temperature was programmed as follows: initial temperature of 100 °C for 2 min, then increasing to 300 °C at 10 °C/min and holding for 8 min. The PCBs in the samples were corrected by surrogate recoveries.

*HLC Calculation.* In a dilute aqueous system, HLC is given by  $H = P/C$  where  $C$  is the aqueous phase solute concentration ( $\text{mol m}^{-3}$ ), and  $P$  is the solute partial pressure (Pa). In the stripping process where the solute in the exit vapor is in equilibrium with the liquid, a mass balance for the solute gives the transfer rate as:

$$-V dC/dt = PG/RT = HGC/RT$$

where  $G$  is the gas flow rate ( $\text{m}^3\text{min}^{-1}$ ),  $V$  is the volume of the liquid ( $\text{m}^3$ ),  $R$  is the gas constant ( $\text{m}^3 \text{Pa mol}^{-1}\text{K}^{-1}$ ),  $T$  is the system temperature (K), and  $t$  is the gaseous purge time (min). This equation can be integrated from initial conditions when  $t = 0$  and  $C = C_0$  to give:

$$\ln(C_0/C_t) = (HG/VRT)t$$

A plot of log concentration against time should be linear with a slope of  $HG/VRT$  if the water volume is constant. In this small-scale stripping experiment the water volume could not be considered as constant. However, between two samplings, during the time of  $t_0$  to  $t_1$ , ...,  $t_{n-1}$  to  $t_n$ , the volume of aqueous solution is constant, and according to the above equation,

$$\ln(C_0/C_1) = [HG(t_1-t_0)]/(V_0RT)$$

.....

$$\ln(C_{n-1}/C_n) = [HG(t_n-t_{n-1})]/(V_{n-1}RT)$$

Combing all the equations above, we get the equation:

$$\ln(C_0/C_n) = [(HG \Delta t)/(RT)](\Sigma 1/V)$$

$$\ln(C_n) = \ln(C_0) - [(HG \Delta t)/(RT)](\Sigma 1/V)$$

where  $\Delta t = (t_1-t_0) = \dots = (t_n-t_{n-1}) = 15 \text{ min}$  (in this experiment) and  $\Sigma 1/V = 1/V_0 + 1/V_1 + \dots + 1/V_{n-1}$ .

A plot of  $\ln(C_n)$  versus  $(\Sigma 1/V)$  gives a straight line with slope  $HG \Delta t/RT$ , and can be used to determine Henry's law constant.

*Modeling Structure-Property Relationship.* Meta-analysis technique and principal component regression (PCR) were applied to model the relationship between experimentally determined HLCs of 97 PCB congeners (132 observations) and their structures.

## Results and Discussion

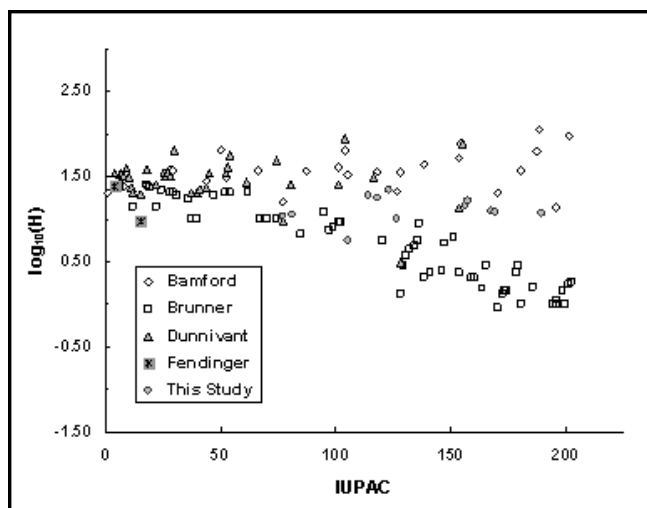
*Evaluation of Experimental Methods.* PCB77 was used to test for equilibrium conditions in the purge column. The HLC values measured at five different flow rates ranging from 50 to 110 mL/min are constant,  $12.05 \pm 0.81 \text{ Pa m}^3/\text{mol}$ , which demonstrates that equilibrium was reached in the flow-rate range of 50-110 mL/min. All the experiments for HLC determination were performed at a flow rate of 50 mL/min.

*Comparison of Experimental HLCs to Literature Values.* In this study, each HLC value is the average of 3-6 measurements as shown in Table 1. Percent variation about the mean ranged from 4.0% to 30.9%, with an average variation of 12.9%. In general, they agree well with the measured/predicted values in the literature.

Table 1. Mean HLC values (Pa m<sup>3</sup>/mol) measured by the gas-purging method

IUPAC	Structure	n	HLC	RSD (%)	Literature Values
77	34/34	6	11.04	6.1	4.36 - 16.21 (4,5,7-10)
81	345/4	3	11.35	8.9	5.17 - 50.16 (7-12)
105	234/34	4	5.57	30.9	3.24 - 33.64 (4,7-10,12)
114	2345/4	4	18.84	10.2	5.47 - 36.68 (7-12)
118	245/34	5	17.42	12.6	6.08 - 36.17 (4,7-10,12)
123	345/24	4	21.78	6.3	3.24 - 36.68 (7-12)
126	345/34	3	10.03	4.0	2.74 - 21.08 (4,7-10,12)
156	2345/34	3	14.79	6.8	1.22 - 36.98 (7-12)
157	234/345	6	16.61	25.1	2.94 - 31.61 (7-12)
167	245/345	5	12.76	10.4	2.94 - 39.21 (7-12)
169	345/345	6	12.26	8.7	1.62 - 25.13 (7-12)
189	2345/345	4	11.85	24.9	1.52 - 28.78 (7-11)

*Data Compilation and Meta-Analysis.* Meta-analysis was used to combine the results of several independent studies. There were four previous studies<sup>3-6</sup> that reported HLCs of PCBs at 25 °C measured by kinetic approach. Overall, including the data from this study, there were 132 HLC measurements for 97 PCB congeners. The results are presented in Fig. 1. There was no enough evidence<sup>13-15</sup> indicating any experimental data erroneous. Therefore, all 132 measured HLCs were used in further analysis. For PCB congeners with more than one reported HLC values, an average weighted by experimental precision was calculated.

Figure 1. Henry's law constants (H) from literature<sup>3-6</sup> and this study

*Principle Component Regression (PCR) for Quantitative Structure-Property Relationship (QSPR).* PCR is a hybrid of multivariate linear regression (MLR) and principal component analysis (PCA). PCR analysis was performed on the pooled data with chlorine substitution pattern as independent variable (X, a 97×10 indicator matrix) and log<sub>10</sub> transformation of HLC (log<sub>10</sub>(H)) as dependent variable (Y). The PCR analysis with cross-validation yields an optimum number of principal components (PCs, also called latent variables), which are associated with the higher r<sup>2</sup> value and lower root-mean-square error (RMSE) value. This procedure yielded a predictive model and was used to predict HLCs of the entire set of 209 PCB congeners.

Compared to other studies using number of *ortho*-, *meta*-, and *para*-chlorine atoms as variables, our analysis is able to isolate the effect of each chlorine substitution (10 total) position on HLCs. Results indicate that *meta*-chlorine substitution pattern is the most important factor in predicting HLCs, which has never been discussed in the literature. Results from PCR analysis provides a different QSPR compared to results from conventional linear regression.

*Predicted vs. Measured HLCs.* The scatter plots of predicted versus measured HLCs are presented in Fig. 2. The dashed lines represent 95% confidence intervals of prediction. The predicted values generally agree with the experimental data. Six HLCs measured by Bamford *et al.*<sup>4</sup> and one HLC by Dunnivant *et al.*<sup>5</sup> seem to be significantly larger than those of predicted. There might be a positive systematic bias in HLC measurement when the spiking method, that is adding the solution of PCB in isooctane into the water, was used by Bamford *et al.*<sup>4</sup> to prepare the aqueous solutions of PCBs.

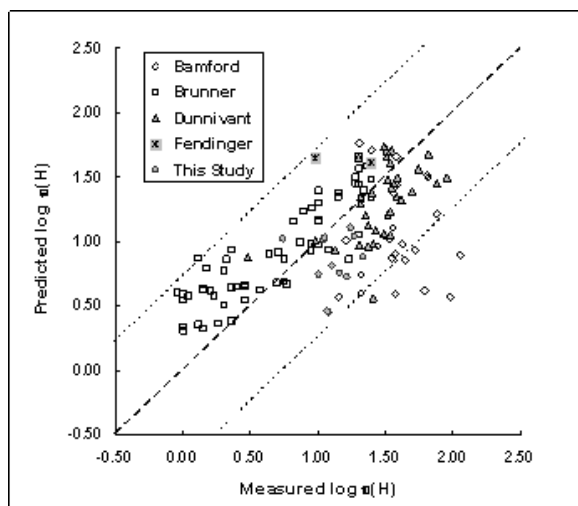


Figure 2. Predicted vs. measured HLCs (H) from literature<sup>3-6</sup> and this study

The QSPR models developed in this study can also be used to model vapor pressures and octanol-air partition coefficients, important parameters that influence estimation of mass transport in the atmosphere. It may be necessary to reassess the relationship between structure of PCBs and other physical properties such as water solubility and octanol-water partition coefficients using the advanced statistical techniques such as principal component regression analysis.

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PCB, Gas-purging technique, Henry's law constant, Quantitative structure-property relationship, Meta-analysis, Principal component regression