

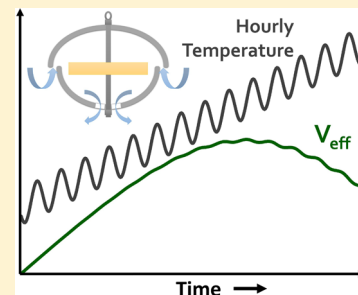
A Model Using Local Weather Data to Determine the Effective Sampling Volume for PCB Congeners Collected on Passive Air Samplers

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Supporting Information

ABSTRACT: We have developed and evaluated a mathematical model to determine the effective sampling volumes (V_{eff}) of PCBs and similar compounds captured using polyurethane foam passive air samplers (PUF-PAS). We account for the variability in wind speed, air temperature, and equilibrium partitioning over the course of the deployment of the samplers. The model, provided as an annotated Matlab script, predicts the V_{eff} as a function of physical-chemical properties of each compound and meteorology from the closest Integrated Surface Database (ISD) data set obtained through NOAA's National Centers for Environmental Information (NCEI). The model was developed to be user-friendly, only requiring basic Matlab knowledge. To illustrate the effectiveness of the model, we evaluated three independent data sets of airborne PCBs simultaneously collected using passive and active samplers: at sites in Chicago, Lancaster, UK, and Toronto, Canada. The model provides V_{eff} values comparable to those using deuration compounds and calibration against active samplers, yielding an average congener specific concentration method ratio (active/passive) of 1.1 ± 1.2 . We applied the model to PUF-PAS samples collected in Chicago and show that previous methods can underestimate concentrations of PCBs by up to 40%, especially for long deployments, deployments conducted under warming conditions, and compounds with log K_{oa} values less than 8.



INTRODUCTION

Our knowledge of the sources, exposures and toxicity of airborne persistent organic pollutants is limited by our ability to accurately and conveniently measure these compounds. Passive air sampling methods are very attractive and have been widely adopted, yet commonly suffer from a major limitation—determination of the effective sampling volume to convert the mass accumulated on the sampler to an environmental concentration.^{1–10} This problem has now reached an urgent level as researchers and governments around the world are expanding their monitoring programs to measure and reduce air concentrations of toxic chemicals.^{11,12}

Effective sampling volumes are determined from passive samplers by one of three methods: use of deuration compounds,^{2–4,7,9,13} active sampling calibrations,^{4,13–15} and modeling approaches.^{16,17} Spiking samples with deuration compounds (DC) prior to deployment is preferred and considered the most accurate way to incorporate site-specific information.⁶ Unfortunately, the DC method is expensive, labor intensive, and does not provide essential information about sampler performance over the entire deployment time. For example, the DC method does not indicate if the accumulated compounds have become equilibrated and does not describe the effective sampling volumes for every compound that can be collected on the sampler. Determining effective sampling volumes using active samplers to calibrate the passive samplers is often considered the gold standard: Active sampling methods are promoted as official methods of the U.S. Environmental

Protection Agency.^{18–22} Passive sampling methods are not yet so recognized. Nevertheless, active sampler calibration are inaccurate when passive samplers are deployed in a different environment than the original calibration. Modeling methods are the most promising but have not yet become widely accepted and adopted.

We provide a mathematical model to cheaply and effectively determine the effective sampling volume of any gas-phase pollutant collected by the most commonly used passive sampler method: the PUF-PAS sampler designed by Harner and colleagues.^{3,9,12,14,23–25} Our model requires no deuration compounds and no calibration with active samplers. It accounts for equilibration of compounds caused by high temperatures and long deployments. It works as well for compounds sampled during linear uptake as well as accumulation in the curvilinear or equilibrium modes. The specific objectives of this study were to (1) improve the uptake model originally published by Petrich et al.¹⁷ through hourly temperature correction of the K_{PUF} partition coefficient and include the effective sampling volume calculation; (2) assess the reliability of PUF-PAS

Special Issue: Jerry Schnoor's Lasting Influence on Global and Regional Environmental Research

Received: January 20, 2016

Revised: March 4, 2016

Accepted: March 10, 2016

Published: March 10, 2016

concentrations determined by our model by comparing with active data; (3) evaluate the performance of the new method in Matlab code (available in the SI), under varying meteorological scenarios. This model is based on an approach we have previously reported for a small set of samples collected in Chicago.¹⁷ Here we show its effectiveness using independent reports from samples collected in Toronto, Canada and Lancaster, UK.^{13,26}

Our model can be used anywhere in the world to determine effective sampling volumes for PUF–PAS deployments. Local hourly meteorological data and the deployment start and stop times are the only required metadata. We examine the method effectiveness with a subset 180 samples collected in Chicago. The samples were analyzed for all 209 PCB congeners and integrated air concentrations are calculated. The impact of our model is most striking for lower molecular weight congeners and long deployments. We show that for these certain compounds and situations, previous methods underestimate ambient concentrations, and therefore underestimate the magnitude of current sources and exposures.

■ DETERMINING EFFECTIVE SAMPLING VOLUMES

In passive air sampling, air passes through a passive air sampler (PAS) chamber where the chemical contaminants are deposited on a sampling media, such as polyurethane foam (PUF). The uptake of PCBs on a PUF–PAS sampler can be modeled as a function of the air-side mass transfer coefficient (k_v) and the concentration gradient between the surrounding air and PUF sampler (eq 1).

$$\frac{dM_{\text{PUF}}}{dt} = k_v A_s \left(C_{\text{air}} - \frac{C_{\text{PUF}}}{K_{\text{PUF}}} \right) \quad (1)$$

where M_{PUF} is the mass (ng) of the PCB congener on the sample (PUF), k_v is the air-side mass transfer coefficient (m d^{-1}), A_s is the surface area of the PUF (m^2), C_{air} is the PCB concentration in the air (ng m^{-3}), C_{PUF} is the PCB concentration on the PUF (ng g^{-1}), and K_{PUF} is the PUF-air equilibrium partitioning coefficient ($\text{m}^3 \text{g}^{-1}$).^{1,3,7,9,13,17} K_{PUF} is the congener specific PUF-air partition coefficient.

This study is based on our previously reported method for estimating deployment and congener specific hourly sampling rate (R_s) from hourly meteorological data using first-principle chemistry, physics, and fluid dynamics, calibrated from depuration compounds.¹⁷ The method used in this study requires a uniform and widely available meteorological data and physical-chemical parameters including hourly weather data parameters for temperature (K), pressure (Pa), wind speed (m s^{-1}), wind direction (degrees), water vapor mixing ratio (Q_w , kg/kg), molecular weight (MW), octanol-air partitioning coefficient (K_{oa}) at 25 °C, and internal energies of octanol–air transfer (dU_{oa}). For hourly weather data, the model uses the Integrated Surface Database (ISD) data set obtained through NOAA's National Centers for Environmental Information (NCEI) Web site.²⁷ We utilize the ISD Lite data set, which is a derived product from the full ISD data set, providing data for air temperature, dew point temperature, sea level pressure, wind direction, wind speed, cloud cover, and precipitation. ISD data sets are processed in Matlab to convert them to the necessary input format for the effective sampling volume model and calculate the water vapor mixing ratio (this script is provided in the SI).

With these inputs our Matlab script calculates hourly measurements of internal PAS chamber air flow, molecular diffusivity, dynamic and kinematic viscosities for both air and water, air-side mass transfer coefficient (k_v), sampling rate (R_s), and finally the effective sampling volume (V_{eff}). The only empirical parameter from the Petrich model is the advective mass transfer coefficient (γ), which was determined by calibration with results from depuration experiments. The range of ambient temperature used in the depuration calibration was -6.4 to 23.3 °C, and range of wind speed was 3.3 to 4.8 m s^{-1} .

If the compound accumulated on the PUF–PAS in the linear uptake phase, the effective sampling volume is equivalent to the amount of airflow through the sampler (i.e., sampling rate times time, $R_s t$). If the sample has passed the linear uptake phase, the effective sampling volume is corrected for equilibrium. The time to equilibrium (i.e., maximum effective sampling volume) is directly proportional to K_{PUF} .³ The congener specific effective sampling volume was determined at each time step (1 h) by rearranging eq 1 in terms of air volume as follows,

$$\frac{dV_{\text{eff}}}{dt} = \frac{k_v \cdot A_s}{V_{\text{PUF}}} \left(V_{\text{PUF}} - \frac{V_{\text{eff}}}{K_{\text{PUF}} \cdot d_{\text{PUF}}} \right) \quad (2)$$

where V_{eff} is the effective sampling volume (m^3), V_{PUF} is the volume of the PUF (m^3), and d_{PUF} is the density of the PUF (g m^{-3}). The final congener specific airborne concentrations were determined by applying the final cumulative effective sampling volume to the lab-determined analyte mass on the PUF using eq 3.

$$C_{\text{air}} = \frac{M_{\text{PCB}}}{V_{\text{eff}}} \quad (3)$$

The model was also modified to adjust the PUF-air partitioning for hourly temperature, instead of assuming it to be constant for the deployment time. The congener specific K_{PUF} value was calculated from an empirical relationship with K_{oa} developed by Shoeib and Harner.⁹ The K_{PUF} was adjusted for temperature at each time step (1 h) by adjusting the K_{oa} used to calculate it using the following equation from Li et al. (2003),²⁸

$$\log K_{\text{oa}(T)} = \log K_{\text{oa}(25^\circ\text{C})} - \frac{\Delta U_{\text{oa}}}{2.303 \times R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad (4)$$

where T is temperature (K), ΔU_{oa} is the internal energy of octanol–air transfer (J mol^{-1}), R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$). The reference $\log K_{\text{oa}}$ values at 25 °C, were calculated for all congeners based on their relative retention time using the methods described by Harner and Bidleman.²⁹

■ MODEL IMPLEMENTATION

The model and the script for processing the raw ISD Lite data sets (meteorological data) were developed and run in Matlab version R2015a. Both these files are provided as Matlab files in the SI. An accompanying file with the necessary physical-chemical properties of all 209 PCB is provided as a CSV (comma separated values) file in the SI. This file is critical to running the model. A step-by-step README file to assist with identifying an appropriate weather station, downloading the correct weather data, processing the data with the provided script, and setting up a run to obtain congener and deployment specific effective sampling volumes, is also provided as a PDF in

the SI. The outputs of the model are a deployment specific effective sampling volume (m^3) and sampling rate (m^3/d) for each PCB congener. The user is also alerted of high wind speed measurements ($\sim >5 m s^{-1}$), given as a percent of the total number of measurements, for each sample.

MATERIALS AND METHODS

This study examines a subset of 180 PUF–PAS samples collected in the metropolitan Chicago area to evaluate the model with active sampling comparison and characterize the model's function under varying meteorological scenarios. The “flying saucer” PAS sampler design (with a 24 cm top bowl and 19.5 cm bottom bowl) is based on the “Harner” PUF–PAS Design.^{3,9,12,14,23–25} The PUF disk were purchased from Tisch Environmental (Clevs, OH). Dimensions, 14 cm diameter \times 1.3 cm thick; surface area of 365 cm^2 ; and density of 0.0236 $g cm^{-3}$. Samples were collected in approximately 6-week intervals (average of 45 days) from January 2012 to January 2014. All samples were collected in pairs with one sample remaining at the University of Iowa for analysis, and the other sample being sent to Indiana University for analysis for a different suite of environmental contaminants.⁸ A subset of 10 samples were analyzed for PCBs at both laboratories.

Prior to deployment of the samplers, the sampling media (PUF disk) was cleaned with multiple 24 h Soxhlet extractions, dried by low-flow nitrogen blow-down, wrapped in aluminum foil, and stored in a freezer until shipment and deployment.^{30,31} After collection, samples were wrapped in combusted aluminum foil and shipped back to the University of Iowa, where they were kept refrigerated at $-20^\circ C$ until extraction. The PUF samples were spiked with 50 ng of surrogate standards (PCB14 (3,5-dichlorobiphenyl), PCB65-d5 (2,3,5,6-tetrachlorobiphenyl-d5, deuterated), and PCB166 (2,3,4,4',5,6-hexachlorobiphenyl)), extracted with a 1:1 hexane:acetone mixture in an accelerated solvent extractor, cleaned with an acidified silica column, and concentrated with a Caliper TurboVap II.^{7,30,32} The samples were then spiked with 50 ng of internal standard (PCB30-d5 (2,4,6-trichlorobiphenyl-2',3',4',5',6'-d5, deuterated) and PCB204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl)) just prior to analysis by gas chromatography with tandem mass spectrometry (GC-MS/MS, Agilent 6890N Quattro Micro GC, Waters Micromass MS Technologies) using a modified EPA method 1668a.³³ All 209 PCB congeners were quantified as a collection of 156 individual or coeluting chromatographic peaks.

Quality Assurance/Quality Control. Quality assurance and control (QA/QC) was evaluated with the use of surrogate PCB standards, method and field blanks, and a comparison study with the Indiana University lab. The average surrogate percent recoveries for PCB14, PCB 65-d5, and PCB166, were $75\% \pm 14\%$, $77\% \pm 16\%$, and $88\% \pm 15\%$ respectively. Method blanks and field blanks were analyzed in tandem with samples. Both method and field blanks experience the same Soxhlet cleanup as samples, but while the field blanks get shipped to deployment site along with samples, method blanks remain in the laboratory freezer. Total PCB masses (Geometric Mean (Geometric Standard Error)) found in method blanks ($n = 24$) and field blanks ($n = 17$) were 4.5 (1.0) and 4.9 (1.1) ng per PUF, respectively. A congener specific limit of quantification (LOQ) was applied to every sample and was calculated as the upper limit of the 95% confidence interval of method blanks. If congener masses in samples were below than the LOQ, values were substituted with zero. On average the congener specific

LOQ was 0.051 $ng sample^{-1}$, and all LOQs were below 0.5 $ng sample^{-1}$, with the exception of a coelution of three congeners (PCBs 85 + 116 + 117) which had an LOQ of 0.53 $ng sample^{-1}$.

The extracts of 10 samples from Indiana University were analyzed at the University of Iowa with the parameters described previously. These 10 samples were selected for varying times of the year. The \sum PCB mass found from the two different data sets had no statistically significant difference ($p = 0.28$, two-tailed paired t test).

RESULTS AND DISCUSSION

Evaluation of V_{eff} to Published Reports. Our model was evaluated by comparing PUF–PAS results obtained using the model determined effective sampling volumes and Hi-Vol sampling at the same sampling site. These comparisons were done for Chicago, IL, Lancaster, UK, and Toronto, Canada.^{13,19,26}

The first evaluation was conducted using five PUF–PAS samples and thirty-one Hi-Vol samples collected at the IADN site at the Illinois Institute of Technology (IIT).^{19,34} The samples were all collected between January first, 2012, and February ninth, 2013 and analyzed for 42 PCB congeners or coeluting congeners with varying physical-chemical properties. The second evaluation used data reported from a field study in Lancaster, UK, where PUF–PAS and Hi-Vol samplers were deployed simultaneously for the purposes of calibrating V_{eff} for the PUF–PAS samples.²⁶ Specifically, one component of the Lancaster study was to derive field based uptake rates. The investigators deployed 23 PUF–PAS samples and collected them at 1, 2, 3, 4, 6, and 8 weeks. They calibrated them using a weekly active sample collected simultaneously. The third evaluation used data from a study conducted by Melymuk et al. (2011), where PUF–PAS and low volume air samplers were deployed simultaneously in Toronto, also for calibration purposes.

The dimension of the PUF disk and sampler housing for all three experiments are given in Table S2 of the SI. The PUF disk parameters are specified in the first few lines of the script and can be modified to accommodate a specific study. The sampler housing dimensions are assumed to be the same as the “flying-saucer” design described in Tuduri et al.,²⁵ to calculate the internal air velocity. However, this relationship can be modified to accommodate another sampler if the relationship between internal air velocity and external air velocity is known.

In all three cases, we calculated the concentrations measuring using the PUF–PAS with the chemical mass that accumulated on the PUF media reported from each study, eq 3, and the V_{eff} from our Matlab code. The PUF parameters were changed to accommodate the specific PUF disk parameters specified by the authors (such as length, thickness, density, and surface area). The chemical masses were measured in our laboratory for the Chicago study, and the concentrations for the Chicago IADN Hi-Vol samples were provided by Dr. Ronald A. Hites.¹⁹ The chemical masses on the PUF and concentrations on the Hi-Vols were published by Chaemfa et al. for the Lancaster study,²⁶ and were provided by Dr. Lisa Melymuk for the Toronto study.¹³ In the case of Chicago, the weather data was downloaded for the Chicago O'Hare Airport (ORD). For the Lancaster study, we used weather data from Barrow/Walney Island Airport (BWF). For the Toronto study, we used weather data from Toronto Pearson International Airport (YYZ). We

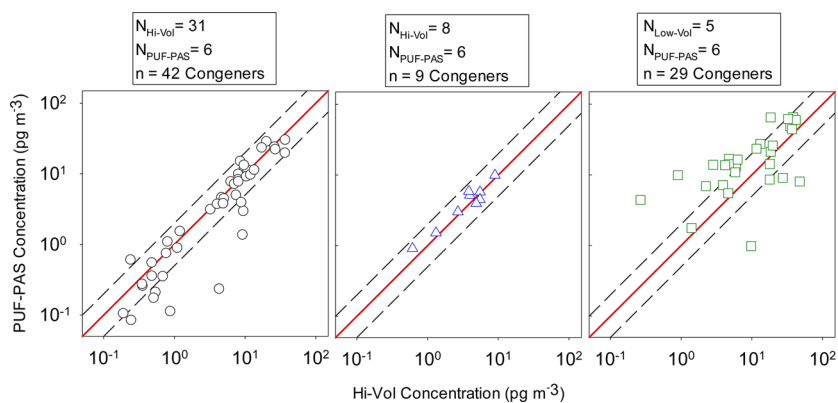


Figure 1. PUF–PAS vs Hi-Vol comparison for select PCB congeners for Chicago, IL (left), Lancaster, UK (middle), and Toronto, Ontario (right). Both Hi-Vol and PUF–PAS values were taken as geometric means. The red line represents the 1:1 line and the dashed lines represent the 2:1 lines (i.e., factor of 2).

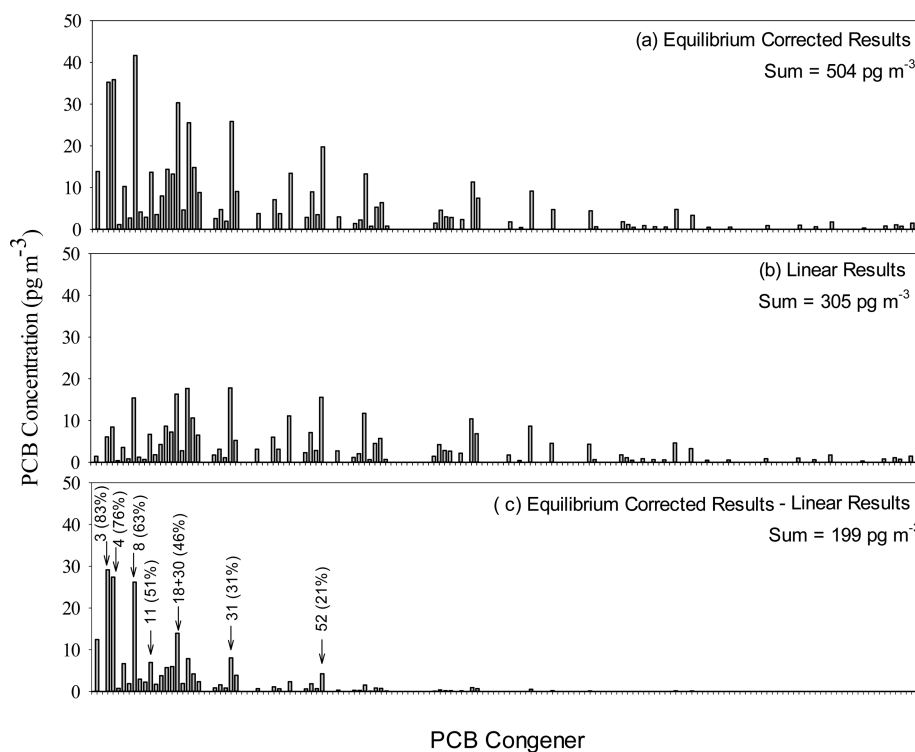


Figure 2. Congener concentrations determined from a PUF–PAS sample (a) using the V_{eff} calculated by this study, (b) using an assumption of linear uptake, (c) and the difference between the two results. The percentages in parentheses are the percent difference between equilibrium corrected and linear results.

then compared our calculated concentrations from the PUF–PAS to that of the active samplers in each case (Figure 1).

A good agreement was found between our approach for estimating concentrations from PUF and Hi-Vol determined concentrations for the three comparison conducted, yielding an average congener specific method ratio (Active/Passive) of 1.1 ± 1.2 . The Chicago comparison displayed bias toward PUF–PAS sampling with an average method ratio was 1.59 ± 1.45 . While the Lancaster and Toronto comparisons showed bias toward Hi-Vol sampling, with average method ratios of 0.91 ± 0.20 and 0.62 ± 0.58 , respectively.

Some variability for these comparison could be due to PAS concentrations representing 4–8 weeks, while Hi-Vol measured concentrations were calculated as the average value of 8–24 h measurements. This difference in collection methods might

lead to variability in the detection ability of the respective sampling media at low concentration. For congener concentrations above 1 pg m^{-3} , the average method ratio was 0.99 ± 0.92 , while congener concentrations below 1 pg m^{-3} , the average method ratio was 1.98 ± 1.86 . Other sources of variability could be attributed to meteorological variability during the deployment period and differences in sampler design/installation. Previous studies have shown that sampler installation (fixed or freely swinging) can affect the internal air velocity,^{35,36} and that slight changes in bowl dimensions can affect uptake performance.³⁷ The model was designed for a fixed sampler installation with the dimension given (Table S2), therefore differences from the assumed installation can lead to uncertainty in the model performance.

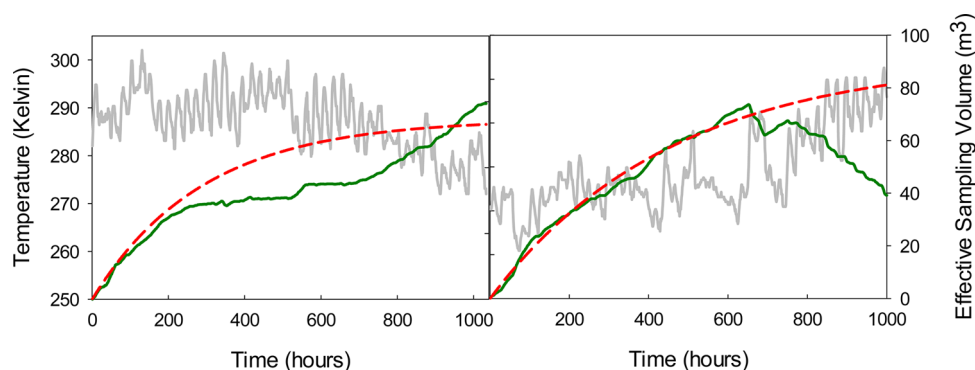


Figure 3. Example effective sampling volume curves for deployments with decreasing temperature (left) and increasing temperature (right) at a K_{oa} of 10^6 (\sim PCB 1). The solid gray line represents hourly air temperature. The solid green line represents the effective sampling volume calculated using the method of this study, including hourly adjustments on k_v and K_{PUF} . The dashed red line, represent effective sampling volume calculated using average values for k_v and K_{PUF} .

Equilibrium Corrections. PUF–PAS samplers are commonly run in accumulation mode and uptake is linear as a function of time and the sampling rate (R_s). As accumulation approaches equilibrium, this assumption is no longer valid and the use of R_s will underestimate the airborne concentrations, particularly for lower molecular weight compounds.¹ The effective sampling volume approach implemented in our model corrects for equilibrium using hourly adjustments for K_{PUF} . We evaluate the severity of this problem and illustrate the impact for a sample collected in Chicago. For this sample (Lemont site, deployed: 7/18/12–9/13/12) the impact was especially severe because it was a warm period (average deployment temperature: 23.5 °C) and the deployment time (57 days) was longer than average (Figure 2). Using our model, the total concentration of PCBs yielded 504 pg m^{-3} , while assuming linear uptake the airborne concentration would be 305 pg m^{-3} . This is a 40% difference in concentrations when assuming linear uptake. This reduction is even more severe for lower molecular weight congeners. For example, monochlorinated PCB congeners show approximately an 85% difference and dichlorinated PCB congeners show approximately a 65% difference. Therefore, samples with a profile skewed to lower molecular weight congeners (Aroclor 1016/1242), the total airborne PCB concentration could be significantly under predicted using a linear approach.

Effects of Temperature Changes. Large changes in temperature during deployment, and temperature increases in particular, can lead to errors in interpreting concentrations. Temperature changes affect gas-particle partitioning of PCBs, sampling medium, and airborne concentration,^{6,15} which can lead to difficulty in interpreting results. We accounted for the effects of temperature changes on the sampling medium with hourly temperature adjustments on K_{PUF} (a function of K_{oa}). We examined the impact of changing K_{PUF} hourly compared to a method of averaging the adjusted K_{PUF} over the entire deployment time.¹⁴

When the air temperature increases over the deployment period, the capacity of the PUF disk to uptake PCBs decreases. This results in a shorter time to equilibrium and could cause degassing of accumulated chemical. This is a difficult problem that our method addresses. Similarly, temperature changes at the end of a deployment can dramatically impact the interpretation of the integrated air concentrations. Using average values will not adequately account for a consistent trend of temperature change,¹⁴ and would display a bias for

temperatures at the beginning of the deployment. Figure 3 shows effective sampling volume curves for a compound with K_{oa} of 10^6 with trends of decreasing and increasing temperature. Increasing temperatures can result in compounds reaching equilibrium during deployment. PCB1 is a clear example: the temperature trends at the end of the deployment has a significant effect on the final effective sampling volume computed with our approach because of the impact on the mass transfer driven by K_{PUF} . However, PCB congeners with K_{oa} greater than or equal to 10^8 are still in the curvilinear or linear phase at the end of the deployment, and the mass uptake is driven by k_v and a temperature jump toward the end of the deployment has little to no effect (Figure S2).

Long Deployment Periods. Although the PUF–PAS is designed to be deployed for 4–8 weeks, longer deployments are convenient when sampling in remote places. Our model for determining V_{eff} is effective for such events. We examine the utility of our method through a set of samples collected at the Jardine Water Plant in Chicago. Although most samples at this site were deployed for 6 weeks, one sample was deployed for 344 days from October 3th, 2011 to November 11th, 2012 (Figure 4). By the end of the deployment, we predict that 80 PCB congeners were no longer in the linear uptake and instead

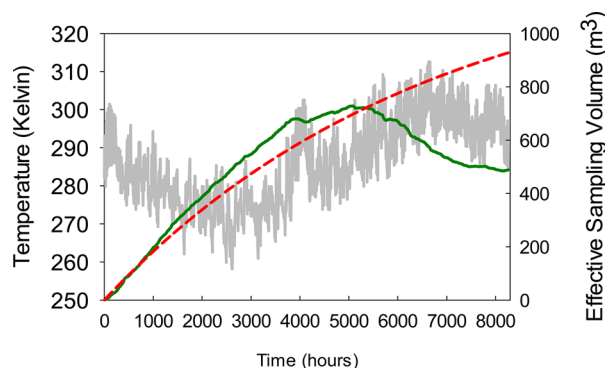


Figure 4. Trend in V_{eff} is plotted for a compound with a K_{oa} of 10^8 that accumulated in a PUF–PAS sampler deployed in Chicago over an unusually long deployment period (344 days). The solid gray line represents the hourly air temperature. The solid green line represents the effective sampling volume calculated using the method of this study, including hourly adjustments on k_v and K_{PUF} . The dashed red line represents the effective sampling volume calculated without hourly adjustment of k_v and K_{PUF} .

were at equilibrium, degassing, or in the curvilinear portion of the uptake curve. Using our model to predict the final V_{eff} for every compound in the sample, we find the \sum PCB concentration for the long deployment sample was 780 pg m^{-3} . This was not significantly different than the mean of all samples collected at the same site ($800 \pm 110 \text{ pg m}^{-3}$). This was true for most of the 159 congener sets as well: only six congeners or coeluting congeners (PCB3, PCB4, PCB16, PCB35, PCBs40 + 41 + 71, PCB159) during the long deployment exhibited concentrations outside the range of what was observed in all other samples ($n = 11$) (Figure S4).

Effects of High Wind Speeds. Wind speeds at higher velocities can create sharply increased sampling rates, therefore decreasing the time for the effective sampling volume to reach equilibrium levels. Increased wind speeds decrease the thickness of the air-side boundary layer and therefore increase the sampling rate.¹ Tuduri et al. demonstrated in laboratory experiments that once the internal air velocity becomes greater than 1 m s^{-1} ($\sim 5 \text{ m s}^{-1}$ external air velocity), the sampling rates increase drastically.²⁵ These results have also been observed in the field using depuration compound determined sampling rates at windy, coastal, and mountain sites.^{6,12,24,38}

Our model does not provide drastically increased sampling rates at values greater than $\sim 5 \text{ m s}^{-1}$ because it is calibrated using depuration compound results with average wind speeds over the deployment period ranged from 3.3 to 4.8 m s^{-1} . This at least partly explains why we predict higher concentrations using the PUF–PAS in Toronto than measured with a Hi-Vol. The average wind speed in Toronto during the study period was $5.1 \pm 3.0 \text{ m s}^{-1}$ and the average during the first 25 days of the study was $6.0 \pm 3.4 \text{ m s}^{-1}$. At wind speeds greater than the calibration range, the effective sampling volume will be under-predicted using our model.

Implications. The results of this study elucidate and solve a major challenge in using PUF–PAS samplers for determining concentrations of semivolatile organic compounds (SVOCs) in air. This study provides an accessible method for determining the effective sampling volume for any PUF–PAS sample deployed in an environment similar to our calibration environment in Chicago. The model only requires basic Matlab knowledge, sampling metadata (spatial location, deployment data, collection date), the appropriate ISD meteorological data (processing with the provided script), and laboratory determined analyte mass.

The model results for the Chicago comparison was also compared with results obtained using the commonly used GAPS template.²³ When using the GAPS template it was assumed that the sampling rate was 4 (the default) and particle phase sampling rate as a fraction of gas-phase rate was 1 (i.e., equivalent). From only a subset of congeners compatible between the data sets, the method ratio using the GAPS template calculation was 0.75, while the method rate using the model was 1.09. A graph of this comparison can be found in the SI (Figure S5). For the lower molecular weight congeners (mono- to tetrachlorinated PCBs), the method ratio using the GAPS template calculation was 0.70, while the method rate using the model was 1.02. While the GAPS template provided a very similar result the model is able to calculate a compound specific sampling rate (R_s) instead of assuming the default from the GAPS template.

We also explored the possibility of using a linear free energy relationship (LFER) to predict K_{PUF} for PCBs partitioning to polyurethane foam disks.^{39–41} The comparison of the K_{PUF}

values for all 209 PCB congeners between the LFER method and the K_{oa} method was an average of 0.8 log units different at $0 \text{ }^\circ\text{C}$, and an average of 0.1 log units different at $35 \text{ }^\circ\text{C}$. A graph of this comparison can be found in the SI (Figure S6). The model results for the Chicago comparison were recalculated using the temperature dependent LFER for polyurethane foam given by Sprunger et al.⁴¹ modified from Kamprad and Goss.⁴⁰ It was found the average method ratio for the Chicago comparison using the LFER determined K_{PUF} was 1.63, compared to 1.59 for the comparison using the temperature corrected K_{PUF} determined by the empirical relationship proposed by Shoeib and Harner.⁹ A graph of this comparison can be found in the SI (Figure S7). For PCBs with lower K_{oa} values ($<10^9$), the LFER was 1.45 compared to 1.47 with the Shoeib and Harner relationship. For PCBs with higher K_{oa} values ($>10^9$), the LFER was 1.84 compared to 1.70 with the Shoeib and Harner relationship. From these results we decided to utilize the empirical relationship proposed by Shoeib and Harner for our study on PCBs.⁹ However, the option to use the LFER to determine K_{PUF} remains an option in the model, if the user chooses.

There are several uncertainties in passive sampling methods that could improve the effectiveness of the model in certain scenarios. For example, the effect of particle-phase sampling on the PUF–PAS is still a debated issue.^{1–4,6,15,23,37} At this time the model does not consider the effects of particle-phase sampling rates on the effective sampling volume equation. PCBs are largely in the gas-phase and so this consideration is not important for this study. We have also assumed that the internal PAS housing temperature is equivalent to the ambient air temperature, but increased internal sampler temperature could affect the capacity of the PUF disk. Some studies have also shown that SVOCs accumulate at greater levels in the outer layers of the passive sampling media, indicating a kinetic resistance to chemical transfer exists in the sampling media.^{42,43} This has also been observed in field calibration studies of passive air samplers.^{26,35,42} Due to a lack of complete understanding of this process, the model does not currently account for sampler side resistance. Adjustments in the field operations or the model could potentially improve the accuracy of the V_{eff} prediction due to these issues.

Despite these uncertainties, we assert that the model described here can be utilized in any environment with weather parameters similar to the temperature calibration range (-6 to $23 \text{ }^\circ\text{C}$) and wind speed calibration range (3 – 5 m s^{-1}). Higher wind speeds will increase the uncertainty of predicting the effective sampling volume, and therefore the prediction of airborne SVOC concentrations. This approach can be used with other SVOCs.⁸ However, the effects of particle-phase sampling rates should be considered for SVOCs with large K_{oa} values ($\sim 10^{11}$). Given that the model was calibrated with a limited number of samples, increasing the number of samples, as well as increasing spatial and temporal variability, this calibration could better describe a wider range of meteorological conditions than what is observed in the city of Chicago.

Contrary to methods using depuration compounds and Hi-Vol calibrations, our approach provides a platform for accounting for deployments with significant temperature changes. The equilibrium status of PCB congeners, particularly the low molecular weight congeners (mono-, di-, and tri- PCB homologue groups) can be significantly affected by temperature changes toward the end of the deployment period causing a shift in the equilibrium level. This model can also allow for

interpretation of long deployment samples. Changes in temperature and wind speed can vary greatly over the course of a long deployment, thus using average weather parameters to calculate effective sampling volume can lead to an under prediction of airborne SVOC concentrations.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.6b00319](https://doi.org/10.1021/acs.est.6b00319).

The Matlab Script, ISD weather data processing script, and the necessary support files for determining V_{eff} as well as information about the quality control and analytical methods (PDF) (ZIP)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the U.S. Environmental Protection Agency's Great Lakes National Program Office (Grant No. GL-00E00515-0) and the Superfund Research Program of the National Institute of Environmental Health Sciences (Grant No. NIH P42ES013661) for funding; the Integrated Atmospheric Deposition Network (Ronald A. Hites, principal investigator) for the Hi-Vol data from Chicago; Lisa Melymuk for active and passive sampling data for Toronto comparison; Ronald A. Hites and Angela A. Peverly for sample extracts used in QA/QC comparison; Austen Smith for Matlab assistance, cleaning up the model, and developing weather processing scripts; Scott Spak for assistance with model discussions; Sean Nichols for assistance in laboratory work and data analysis; Jon Durst and Eric Jetter for managing the analytical lab. Anissa Lambertini collected the samples deployed in Chicago. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health or the U.S. EPA.

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