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## Calibration and Evaluation of PUF-PAS Sampling Rates across the Global Atmospheric Passive Sampling (GAPS) Network

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### Abstract

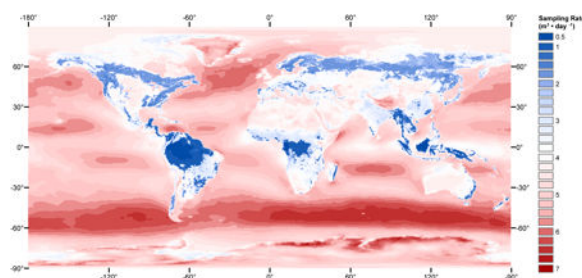
Passive air samplers equipped with polyurethane foam (PUF-PAS) are frequently used to measure persistent organic pollutants (POPs) in ambient air. Here we present and evaluate a method to determine sampling rates ( $R_S$ ), and the effective sampling volume ( $V_{\text{eff}}$ ), for gas-phase chemical compounds captured by a PUF-PAS sampler deployed anywhere in the world. The method uses a mathematical model that requires only publicly available hourly meteorological data, physical-chemical properties of the target compound, and the deployment dates. The predicted  $R_S$  is calibrated from sampling rates determined from 5 deuration compounds (<sup>13</sup>C PCB-9, <sup>13</sup>C PCB-15, <sup>13</sup>CPCB-32, PCB-30, and d<sub>6</sub>-γ-HCH) injected in 82 samples from 24 sites deployed by the Global Atmospheric Passive Sampling (GAPS) network around the world. The dimensionless fitting parameter, gamma, was found to be constant at 0.267 when implementing the Integrated Surface Database (ISD) weather observations and 0.315 using the Modern Era Retrospective-Analysis for Research and Applications (MERRA) weather dataset. The model provided acceptable agreement between modelled and deuration determined sampling rates, with <sup>13</sup>C PCB-9, <sup>13</sup>C PCB-32, and d<sub>6</sub>-γ-HCH having mean percent bias near zero (±6%) for both weather datasets (ISD and MERRA). The model provides inexpensive and reliable PUF-PAS gas-phase  $R_S$  and  $V_{\text{eff}}$  when deuration compounds produce unusual or suspect results and for sites where the use of deuration compounds is impractical, such as sites experiencing low average wind speeds, very cold temperatures, or remote locations.

### Graphical abstract

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Supporting Information: The Supporting information includes the Matlab model script, ISD weather data processing script, and the necessary support files for determining  $V_{\text{eff}}$  as well as information about the quality control and analytical methods.

**Conflicts of Interest:** There are no conflicts to declare.



## Introduction

Passive air samplers equipped with polyurethane foam (PUF-PAS) are commonly used to measure and assess atmospheric concentrations of persistent organic pollutants (POPs). PUF-PAS samplers have been used to measure regional spatial and temporal trends in urban areas,<sup>1-12</sup> estimate the human exposure potential<sup>1, 9</sup>, and assess the global fate and transport of POPs.<sup>6, 13-16</sup> Despite their widespread use by researchers, PUF-PAS samplers can be subject to significant human error and uncertainty in interpretation. These challenges are often associated with the determination of sampling rates and effective sampling volumes.

The most widely accepted method for determining effective sampling rates for PUF-PAS samplers relies on the loss of deuration compounds.<sup>9, 13, 14, 17-25</sup> Harner and colleagues have used this method to determine the sampling rates for thousands of samples deployed by the Global Atmospheric Passive Sampling network (GAPS) and published a widely used spreadsheet for calculating sample effective volume from deuration recoveries.<sup>8, 9, 13-15, 22, 26-28</sup> This approach has been shown to be effective as long as the deuration compounds are injected and recovered in a consistent and reproducible way. Unfortunately, consistent and reliable use of these compounds requires skilled personnel and reproducible laboratory methods not always available for sample deployment worldwide. They are also expensive to use, prone to human error, unsuitable for sampling in low temperatures, and are only applicable to a narrow range of chemicals.

In the absence of reliable deuration compounds, a constant value ( $4 \text{ m}^3 \text{ d}^{-1}$  for polychlorinated biphenyls (PCBs), for example) may be assumed for the sampling rate.<sup>10, 13, 24, 29</sup> For PCBs, this value was approximated from deuration data and also from other reports that used uptake experiments and calibration with other sampling methods, including low volume and high volume active samplers.<sup>7, 11-13, 18, 21, 23, 24, 30, 31</sup> This approach fails to resolve variability in local meteorological conditions and is inappropriate for estimating sampling rates for other compounds.<sup>21, 32-34</sup> In extreme environments, like high mountaintops and remote regions of the world, the inability to consider the effect of local meteorological conditions may negate the benefit of using passive samplers.<sup>15, 24, 28</sup>

We have previously shown that sampling rates of gas-phase PCB congeners for a PUF-PAS sample can be modelled as an air-side diffusive mass transfer process, calibrated using flow rates determined from deuration compounds and meteorological measurements (temperature, pressure, wind speed, humidity) as well as chemical characteristics (octanol-air partitioning coefficient ( $K_{oa}$ ), molecular weight (MW), and internal energy of transfer).

<sup>4, 35</sup> A model was calibrated from and tested on airborne PCBs collected in Chicago and other locations with local meteorology similar to our calibration sample set.<sup>4</sup> However, when we applied the model to a more geographically diverse dataset, our model failed in regions that experienced more extreme weather conditions. At very high and very low wind speeds, the Chicago sampling rate model produced unreasonable results (Figure S1).

The central goal of this study was to develop a useful and practical tool to predict sampling rates for specific PUF-PAS deployments without the use of deuration compound recoveries while still resolving the effect of local meteorological conditions. We hypothesized that a recalibrated model using a larger and more diverse dataset of sampling rates would be able to predict sampling rates for deployment of the PUF-PAS samplers anywhere in the world with accuracy comparable to or better than known analytical uncertainties when using deuration compounds. The specific objectives of this study were to 1) Calibrate a model from flow rates determined from deuration compounds that were deployed in a wide variety of conditions around the world; and 2) Examine the performance and the global spatial distribution of the modelled sampling rates.

## Theory

The uptake of semi-volatile organic compounds (SVOCs) on a PUF disk has been represented as a function of a diffusive sampling rate ( $R_S$ ,  $\text{m}^3 \text{d}^{-1}$ ) and the concentration gradient between the air and PUF sample (eqn. 1).<sup>4, 18, 20, 26, 31, 33, 35</sup>

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

where  $M_{\text{PUF}}$  is the mass of the target compound measured on the PUF sample. The sampling rate can be determined as a function of an air-side resistance dominated mass transfer coefficient ( $k_v$ ,  $\text{m s}^{-1}$ ) and the surface area of the sampling PUF ( $A_S$ ).

$$R_S = k_v A_S \quad (2)$$

Here we describe the mass transfer coefficient using the equation for laminar flow along a flat plate.<sup>36</sup> Although we do not expect the flow to be laminar within the sampler, this equation was selected as reasonably representative of the effect of wind speed and air temperature on the diffusion-limited mass transfer coefficient. The equation is as follows

$$\frac{k_v l}{D} = \gamma \left( \frac{V_i l}{v} \right)^{1/2} \left( \frac{v}{D} \right)^{1/3} \quad (3)$$

where  $\gamma$  is a dimensionless empirically calibrated constant,  $D$  is the molecular diffusivity for each compound ( $\text{m}^2 \text{s}^{-1}$ ),  $V_i$  is the wind speed inside the PAS chamber ( $\text{m s}^{-1}$ ),  $\nu$  is the kinematic viscosity of the air ( $\text{m}^2 \text{s}^{-1}$ ), and  $l$  is the length of mass transfer (m). If the system was ideal,  $\gamma$  would equal 0.646 for laminar flow along a flat plate, but due to non-ideal behavior we expect this value to be different. We previously reported a more complex version of the above equation as a method for predicting mass transfer that had  $\gamma$  as a function of wind speed and temperature for the calibration of sampling rates predicted in our Chicago study.<sup>4, 35</sup>

While the focus of this study was the estimation of  $R_S$ , the final output of the model is an effective sampling volume ( $V_{\text{eff}}$ ,  $\text{m}^3$ ) specific for the compound as well as the deployment site and dates. The effective sampling volume accounts for non-linear uptake and the model calculates a compound-specific effective sampling volume integrated at 1 hour time intervals over the deployment period with the following equation,

$$\frac{dV_{\text{eff}}}{dt} = \frac{R_S}{V_{\text{PUF}}} \left( V_{\text{PUF}} - \frac{V_{\text{eff}}}{K_{\text{PUF}} \cdot d_{\text{PUF}}} \right) \quad (4)$$

where  $V_{\text{PUF}}$  is the volume of the PUF disk ( $\text{m}^3$ ),  $K_{\text{PUF}}$  is the temperature corrected PUF-air equilibrium partitioning coefficient ( $\text{m}^3 \text{g}^{-1}$ ), and  $d_{\text{PUF}}$  is the density of the PUF disk ( $\text{g m}^{-3}$ ).<sup>4</sup> The  $V_{\text{eff}}$  used to calculate air concentrations ( $C_{\text{air}}$ ) from the chemical mass on the PUF disk sample is the summation of the hourly effective sampling volume ( $dV_{\text{eff}}$ ) over the deployment period, as given by equation 5.

$$C_{\text{air}} = \frac{M_{\text{PUF}}}{V_{\text{eff}}} \quad (5)$$

## Methods

### Data Sources

The Global Atmospheric Passive Sampling (GAPS) Network was selected as the global recalibration dataset. The GAPS network was formed in December of 2004 and has included more than 50 sites around the world.<sup>19</sup> The GAPS program is operated by a volunteer network that is coordinated through a central laboratory operated by Environment and Climate Change Canada (ECCC), where samples are analyzed.<sup>37</sup> Our study considered 290 samples deployed in 2006 and 2007 and spiked with seven deuration compounds [<sup>13</sup>C labelled PCB congeners 9, 15, 32, 107, and 198, PCB-30, and gamma-Hexachlorocyclohexane ( $d_6$ - $\gamma$ -HCH)]. The GAPS network is operated with extensive quality assurance and quality control (QA/QC), generally having method recoveries greater than 85% and has instrumental detection limits (IDL) below 1 pg. Both field and lab blanks are analyzed regularly and typically show levels at or below the IDL.<sup>14, 15</sup>

We examined two potential sources of meteorological data: local measurements collected at a nearby airport or meteorological station; and meteorological data estimated from a global weather reanalysis. Measurements of local hourly and synoptic meteorological conditions at 14,000 active sites are reported through the Integrated Surface Database (ISD) released by the National Oceanic and Atmospheric Administration's (NOAA) National Environmental Information (NCEI).<sup>38, 39</sup> We acquired ISD weather data from the nearest observations for 38 GAPS sites, at a median distance of 13 km from their respective sampler. Before implementation of the ISD dataset, we ran quality tests to detect any missing or erroneous data and removed them from consideration. Only sites for which the weather data meet the following quality constraints were used: (1) a minimum resolution of 3-hour measurements for each variable, (2) no continuous missing data for any single parameter longer than 72 hours, and (3) site is reasonably close/representative (median distance 13 km) of sampler deployment location conditions. For instances where a weather parameter was not present for a given hour, a persistence policy was used by assigning it the last observed value for that interval.

The second weather dataset was the Modern Era Retrospective-Analysis for Research and Applications (MERRA) maintained by the National Aeronautics and Space Administration (NASA) agency. The MERRA dataset is a global weather reanalysis that provides hourly two-dimensional data, including surface, fluxes, and vertical integrals, generated using version 5 of the Goddard Earth Observing System Data Assimilation System (GEOS-5 DAS) at one-half by two-thirds degree resolution.<sup>40</sup> The MERRA dataset offers meteorological data for temperature, specific humidity, and wind speed at 2 m or 10 m above ground level (AGL), while also offering wind speed at 50 m. The MERRA wind speed used for this study was at 2 m AGL, consistent with the GAPS observational protocol.

Initially, supplying local measurements for weather data (with the ISD dataset) for each sample was preferred for all components of the model. However, upon expanding the scope of applicability and wanting to ensure the model could be used anywhere on the globe, it was necessary to use modeled weather data that was accurate and available anywhere on the globe (with the MERRA dataset).

## Model Calibration

The value of  $\gamma$  was empirically determined using a calibration subset of depuration derived sampling rates reported for 290 samples deployed in 2006 and 2007 by the GAPS program. Sampling rates for all seven depuration compounds (<sup>13</sup>C labelled PCB congeners 9, 15, 32, 107, and 198, PCB-30, and d<sub>6</sub>- $\gamma$ -HCH) were considered for the calibration subset. Depuration compounds are most effective for sampling rate determination if a portion, but not the total, injected mass volatilizes during sample deployment. Therefore, we selected the calibration subset of sampling rates from only samples with acceptable depuration compound recoveries and complete meteorological data. We chose only those sampling rates calculated from depuration compounds with recoveries below 65% to ensure significant loss, consistent with guidelines in Pozo et al.<sup>14</sup> This excluded all samples below 0°C from use in the calibration. The effectively nonvolatile compounds, <sup>13</sup>C PCB-107 and <sup>13</sup>C PCB-198, were used as a normalizing factor for calculating the recovery of the others. Each of the

samples selected had acceptable results for at least one of the five remaining deperation compounds. We further restricted the calibration subset to deployments with nearby meteorological stations and complete meteorological data as described above. This approach produced a calibration subset of sampling rates for 82 samples deployed at 24 locations (Table S2) from the initial 290 samples. For this calibration subset,  $\gamma$  was calculated for each deperation compound in the 82 samples.

Many different forms of multiple linear regressions (MLRs) and regression trees were explored as potential methods for the recalibration of  $\gamma$ . These regression methods were evaluated using the Matlab R2016a software. The MLRs were primarily done with the Curve Fitting Toolbox add-in. MLRs are global models and rely on a single simple relationship explaining the dataset, while a regression tree is a form of decision tree where binary nodes are used to group data in to small, related subgroups that can be simply expressed with real numbers.<sup>41</sup> The regression tree approach is often much better for handling large datasets with many inputs (predictors) that interact in very complicated, non-linear ways.<sup>42</sup> To avoid over-fitting the data, a leave-one-out cross-validation method was used when creating regression trees.

## Results and Discussion

A detailed discussion about the recalibration process is available in the supporting information. Briefly, the most reliable  $\gamma$  value was a constant  $\gamma$  for all deployments and compounds. Unsurprisingly, the two different weather datasets produced different calibration factors because they are fundamentally different. The constant  $\gamma$  was determined to be 0.267 for the ISD weather dataset and 0.315 for the MERRA weather dataset. Recall, for laminar flow along a flat plate  $\gamma$  would equal 0.646, therefore our results seem reasonable. The results of the model calibration are evaluated for PUF-PAS deployments in a wide range of conditions, including those with very low wind speeds, gusty environments, polar and other remote locations, and near urban areas and large sources.

The 2006-2007 GAPS sample set has the potential to provide 1796 unique deperation determined sampling rates. Of those 1796, 346 were stable deperation compounds used to normalize the other compounds, reducing the usable number to 1450. After removing samples with greater than 65% deperation compound recovery, samples with average temperatures below zero °C, and other outliers, that number is reduced to 857. Thus, only 48% of the initially available unique deperation values were considered useful for determination of a sampling rate. Of the initial 290 GAPS samples, 41 did not yield any reliable deperation results. The model now allows these samples to be accurately interpreted by providing a deployment specific sampling rate estimate.

### Global Distribution of Sampling Rates

This model provides compound-specific sampling rates for any location across the globe over any current or historical deployment. To illustrate, we calculated an annual sampling rate (for 2006) at a 2 m height above the ground, across the entire global MERRA weather grid (Figure 1) for a tri-chlorinated PCB congener (MW = 257 g mol<sup>-1</sup>). The global average sampling rate can be determined for any compound appropriate for PUF-PAS sampling. For

example, the average global sampling rate for a tri-chlorinated PCB congener in 2006 was  $4.58 \pm 1.17 \text{ m}^3 \text{ d}^{-1}$ . The sampling rates calculated for all deployments were not strongly correlated to latitude ( $R^2 = 0.157$ ) or temperature ( $R^2=0.001$ ), and were primarily a function of wind speed ( $R^2=0.910$ ). At the global scale, there is little seasonal variability for a tri-chlorinated PCB congener, and global average for  $R_S$  varies less than 1% between each quarter of 2006. However, individual locations displayed differences in seasonal averages. For example, in Chicago (Latitude: 41.881832; Longitude; -87.623177) the sampling rate varied from  $4.2 \text{ m}^3 \text{ d}^{-1}$  in quarter 1 to  $3.9$ ,  $3.5$ ,  $4.1 \text{ m}^3 \text{ d}^{-1}$ , for quarters 2, 3, and 4, respectively. These quarterly averages for sampling rates are strongly correlated with quarterly average wind speed ( $R^2 = 0.987$ ). As expected, the average global sampling rate for tri-chlorinated PCBs is near  $4 \text{ m}^3 \text{ d}^{-1}$ . For a tri-chlorinated PCB congener, approximately 50% of the earth's surface would fall in a range of  $4 \pm 1 \text{ m}^3 \text{ d}^{-1}$ , while 88% of the earth's surface would fall in a range of  $4 \pm 2 \text{ m}^3 \text{ d}^{-1}$ . Similarly, for the samples collected by the GAPS Network in 2006 and 2007, approximately 31% of deuration results for tri-chlorinated biphenyls fall in a range of  $4 \pm 1 \text{ m}^3 \text{ d}^{-1}$ , while 62% of deuration results fall in a range of  $4 \pm 2 \text{ m}^3 \text{ d}^{-1}$ .

### Model Performance in Low Wind Speeds

The modeled  $R_S$  method is a particularly good alternative to deuration compounds for deployments with very low average wind speeds; conditions common at sites with heavy forest cover, such as the boreal forest or Amazon Rainforest. In these conditions, a small percentage (<20%) of the injected deuration compounds are volatilized during deployment, leading to highly uncertain sampling rate determination. Approximately 8.7% of the earth's surface had an annual sampling rate below  $3 \text{ m}^3 \text{ d}^{-1}$ , while 5.4% was less than  $2 \text{ m}^3 \text{ d}^{-1}$  and 1.3% was less than  $1 \text{ m}^3 \text{ d}^{-1}$  for trichlorobiphenyls (Table 1). Low  $R_S$  values are expected because the model uses 2 m heights for the meteorological data, consistent with the deployment heights used by GAPS. At this height of 2 m forest cover significantly effects the meteorological conditions. If the sample were deployed in a forest clearing or above the forest canopy, corrections would be required. Fortunately, MERRA provides the capability to directly simulate  $R_S$  at 10 m or 50 m AGL. It is expected that the calibration described here would be valid for any height, although this was not specifically tested, and may be biased at wind speeds substantially higher than those represented in the calibration dataset.

Two GAPS sampling sites from 2006 or 2007 with deuration results (excluded from the recalibration) helped to validate model performance at low sampling rates. One of these sites was Tapanti National Park in Costa Rica and the other was Lasqueti Island, British Columbia, Canada. The comparison between deuration and modelled sampling rates for  $^{13}\text{C}$  PCB-9 for these sites is shown in Figure 3. The deuration results from Tapanti National Park for 2006 and 2007 averaged  $0.6 \text{ m}^3 \text{ d}^{-1}$ , while the model results averaged  $1.1 \text{ m}^3 \text{ d}^{-1}$ . At the Lasqueti Island sampling site, the deuration results averaged  $2.0 \text{ m}^3 \text{ d}^{-1}$ , while the model results averaged  $1.4 \text{ m}^3 \text{ d}^{-1}$ . Both the predicted  $R_S$  and the deuration  $R_S$  values were significantly lower than the global average, with similar values that support the validity of the method. The deuration method is subject to analytical uncertainty, and we expect that uncertainty is the explanation for the differences between the  $R_S$  values from the two methods illustrated in Figure 3. Only 23 of 60 deuration compounds measurements in the

12 samples listed in Figure 3 were considered “reliable,” and 10 of those “reliable” results were for  $^{13}\text{C}$  PCB 9, the most volatile of the depuration compounds used. No depuration results were reliable for the Tapanti National Park sample deployed from July 7, 2007 to December 2, 2007. The model presented here is a good substitute should depuration compounds be found questionable in a sample. If a sampling rate of  $4 \text{ m}^3 \text{ d}^{-1}$  were assumed for this sample instead of using the modelled value of  $1.02 \text{ m}^3 \text{ d}^{-1}$ , the estimated airborne concentration would be underestimated by a factor of 4.

### Model Performance in Polar Regions

The modeled  $R_S$  method is a good alternative to depuration compounds for PUF-PAS deployments in the Polar Regions. Samples collected in extremely cold temperatures typically do not exhibit enough loss of depuration compound to accurately determine a sampling rate. Therefore, there are few measurements in this domain to compare with modelled results. Between 2006 and 2007 there were 22 GAPS samples deployed in the Arctic (above  $66.563^\circ$  latitude). Of the 5 depuration compounds in each sample, only 40% were deemed reliable and only 32% were deemed reliable when the mean temperature was less than  $0^\circ\text{C}$ . The depuration results showed a high variability ranging from  $0.9$  to  $24 \text{ m}^3 \text{ d}^{-1}$  for all compounds, and individual samples often showed disagreement between depuration compounds, averaging a 300% difference between the maximum and minimum. The difficulty of assessing depuration compound results from Polar Regions is alleviated with the model. The average modelled sampling rate for a tri-chlorinated PCB congener in the Arctic was  $4.15 \pm 0.61 \text{ m}^3 \text{ d}^{-1}$ .

### Model Performance in High Wind Speeds

The model is less effective for sites with very high average wind speeds. Sampling rates in gusty environments can be difficult to interpret because of the high variability over the deployment period. This effect has been observed in depuration compound results at windy sites.<sup>14, 15, 28</sup> The model calculates a sampling rate from hourly meteorology instead of using average weather parameters, thereby capturing some of the variability but not intense and short term variations. At high wind speeds ( $>5 \text{ m s}^{-1}$ ) the PUF-PAS sampler may also behave differently, and experience non-linear aerodynamics.<sup>24, 43</sup> At high wind speeds, the air side controlled mass transfer assumption is less reliable. It is helpful to note, however, that higher wind speeds often result in a rapid approach to chemical equilibrium. The model corrected for this non-linear uptake and approach to equilibrium through the calculation of effective sampling volume. This feature of the model has been discussed in detail previously.<sup>4</sup>

### Independent Datasets

We evaluated the performance of the  $R_S$  model against independent measurements in three ways. First, as described above, we evaluated the performance for GAPS samples with high quality depuration data that also were not used for calibration (Figure 3). Second, we evaluated samples deployed near a major PCB source with depuration compounds measured in our laboratory. Third, we calculated and compared  $R_S$  for deployments reported in the literature.



Our laboratory collaborated with Boston University to deploy and measure airborne PCBs near a major source, New Bedford Harbor (NBH), a Superfund site in Massachusetts contaminated with PCBs. Details of the study are provided elsewhere.<sup>47</sup> During the summer and fall of 2015, PUF-PAS samples were deployed at 17 or 18 different locations for 3 periods lasting ~6 weeks, shorter than the typical deployment of 3 months used by GAPS. Prior to deployment, each of the 53 samples were spiked with 3 deuration compounds - one of which was used as a positive control - providing 106 potential values for  $R_S$ . Only 7 showed deuration compound recovery less the criteria of 65%, rendering the deuration results unreliable – a situation that we now understand is common. These seven values rates compare very well to modeled  $R_S$  values for the same samples (Figure 4).

The average bias for these 7 samples was 11%, and drops to just 5% if removing one outlier sample deployed at the NBH-15 site from 07/09/2015 – 08/20/2015. This sample was collected at a site immediately adjacent to the bay and may have experienced different meteorological conditions from the other sites. This highlights the sensitivity of the weather data and the notion that some samplers may experience microclimates within a sampling region that are not all perfectly represented by the weather data, while also highlighting that most samples in a region can be described by a central measurement. However, the modeled and deuration results are still in reasonable agreement and we conclude that the modeled  $R_S$  method is a particularly good alternative to deuration compounds for PUF-PAS deployments near major sources. Samples collected near major sources require shorter deployment periods to reach analytical detection limits. However, shorter deployment periods reduce the precision and accuracy of the deuration results by not allowing for adequate loss (< 65% recovery.) In addition, high levels of target compounds on the PUF samples may interfere with the detection of deuration compounds, especially when the ambient concentrations are unexpectedly high or unlabeled deuration compounds are implemented.

We also compared our modelled sampling rates to deployments reported in the literature. We identified a set of studies reporting sampling rates for PCB compounds from either deuration compounds or chemical uptake studies. These studies report a range of chemical compounds in a range of environmental conditions with varying analytical protocol. In some instances for the comparison the locations/deployments times had to be approximated. Model modifications were made to appropriately account for the nuances of varying sampler designs and PUF substrate where appropriate and possible. However, not everything could be accounted for such as sampler height or wind speed adjustments (based on building/tree interference), because they were not reported. Of the 19 studies examined for this comparison, 5 studies fell within  $\pm 10\%$  bias between modelled and measured sampling rate, 9 studies fell within  $\pm 20\%$  bias, and 13 studies fell within  $\pm 30\%$  bias. It is difficult to determine the reasons for the nuanced differences between modelled and measured sampling rates for these studies due to the wide scope of protocols, samplers, geography, etc. However, in general it appears that studies that cover a larger spatial scales displayed higher mean biases between measured and modelled value, likely due to the influence of more outlier sites/measurements. It also appears that in general sampling rates determined from active sampler calibrations exhibit greater bias when compared to PUF-PAS concentrations that use our sampling rate predictions. They may be due to the other differences in the two

approaches – including the collection of air over different time scales. The difference may also be due to particle phase sampling with PUS-PAS.

## Conclusion

This model (provided in the Supporting Information) maybe used to predict a gas-phase sampling rate for a PUF-PAS sample in any environment on the globe for a “flying saucer” PUF-PAS sampler (24 cm top bowl, 20 cm bottom bowl, 12 cm height, 2 cm gap, 1.5 cm overlay).<sup>15, 22, 26-28, 31, 43</sup> The model provides a sampling rate in any environment while removing much of the uncertainty involved in the use of depuration compounds. It only requires hourly weather inputs and the molecular weight of the compound of interest to determine a compound specific, deployment specific, and location specific sampling rate based on hourly calculations. With a few addition chemical properties a compound specific, deployment specific, and location specific effective sampling volume can also be determined. The ISD and similar surface observational data can be simply used directly as a weather data source, and the MERRA weather dataset can be used in the absence of local observations. This allows the model to serve as a platform for examining large global datasets with less uncertainty attributed to the sampling rate determination. Although assuming a sampling rate from prior reported field studies has been shown to be reasonable for most locations, it does not account for the effect of local meteorology as the model does. The model also provides a tool to generate information in the pre-deployment stage of the sampling campaign. It can be used to provide insights on length of deployment to stay in linear uptake phase, potential behavior of new chemical contaminants, and location siting.

In addition to the  $R_S$  value predicted by this model for any location on the globe, the model also predicts the effective sampling volume ( $V_{\text{eff}}$ ), as a function of the deployment site, deployment period, and target compound. The model calculates the cumulative effective sampling volume for every hour of deployment. The benefit of calculating the effective sampling volume hourly, instead of using weather parameters averaged over the sample deployment period, has been discussed elsewhere.<sup>4</sup>

The validity of this model is dependent on the accuracy of the depuration compound method for determining sampling rates: the model assumes that the dynamics of labeled depuration compounds are representative of any compound that can be sampled with PUF-PAS. Similarly, this model is meant for gas-phase compounds only, as it does not consider the uptake processes of particle-phase compounds. To account for particle phase sampling there would need to be consistent globally applicable datasets for total suspended particles, a measure of the gas/particle partitioning, and an estimate of the flow of particles into the sampler housing and onto the PUF. Given the uncertainty in these processes and the ongoing research on the topic,<sup>13, 21, 29, 55</sup> sampling of particle-associated POPs are not supported in this version of the model. Some studies have also shown that SVOCs experience a kinetic resistance to chemical transfer from chemicals accumulating in the outer layers of the cylindrical PUF plug sampling media.<sup>44, 45</sup> This has also been observed in field studies.<sup>30, 44, 46</sup> However, calibration studies of the PUF disk sampler have not revealed a bias of lower sampling rates for high Koa chemicals in PUF disks suggesting that this resistance is less important for the thin-disk geometry of the PUF disk, where air flow and chemical

exchange occurs from the top and bottom of the disk, which would enhance chemical movement/dispersion within the disk.<sup>13</sup> Due to a lack of complete understanding of this process, the model does not currently account for sampler side resistance, however, potential effects of sampler side-resistance, if significant, would be accounted for in the empirical data used to calibrate the model.

Although the model was calibrated and implemented using PCB depuration compounds and lindane ( $\log(K_{oa}) \sim 7-9$ ), it is applicable to other POPs if the physical-chemical properties are known. However, caution should be exercised towards particle dominated POPs ( $\log(K_{oa}) \gg 10$ ), and highly volatile ( $\log(K_{oa}) \ll 6$ ) POPs as they start to drastically deviate from the calibration dataset. Despite these remaining uncertainties, this study provides an accurate unified method of determining sampling rates for large-scale PUF-PAS studies.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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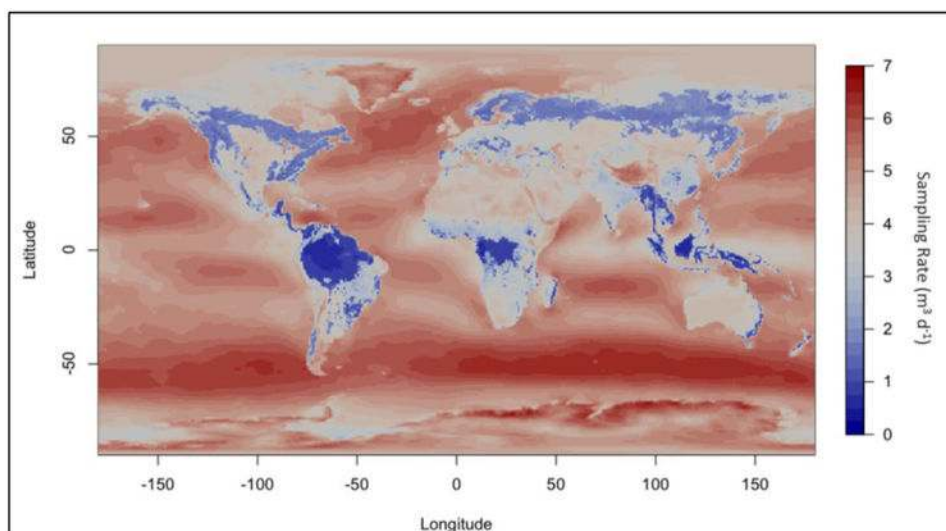
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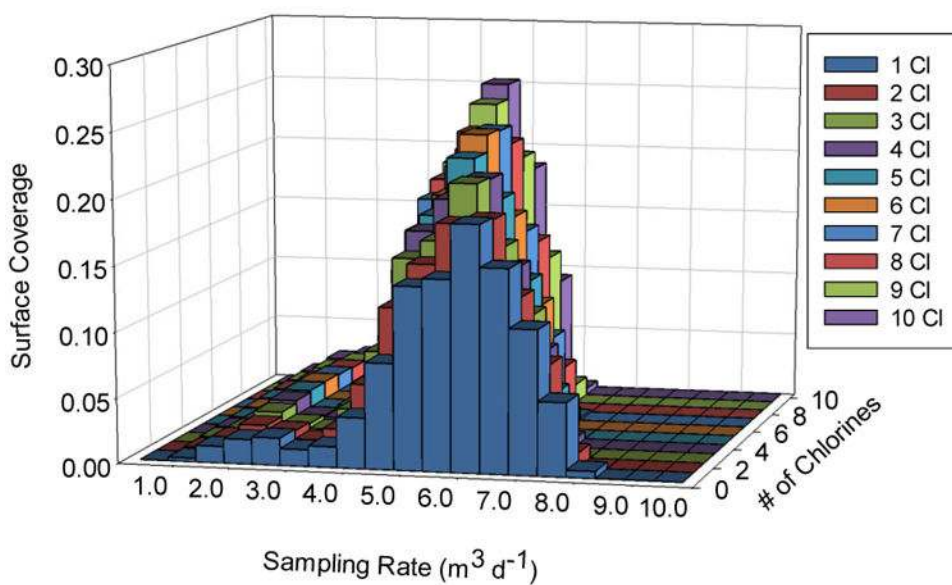
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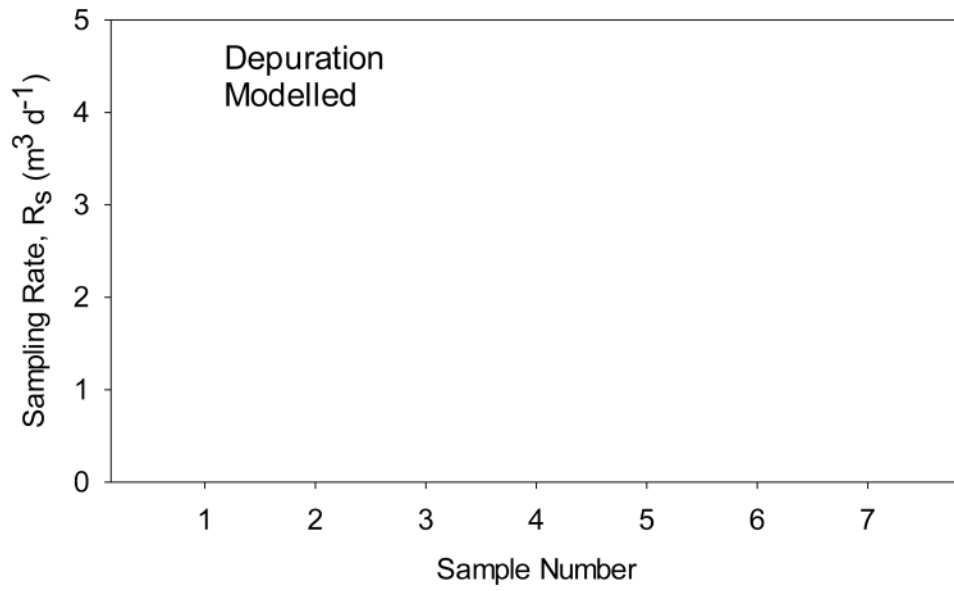
**Figure 1.** Annual mean PUF-PAS sampling rate (m<sup>3</sup> d<sup>-1</sup>) of a tri-chlorinated PCB congener in 2006.



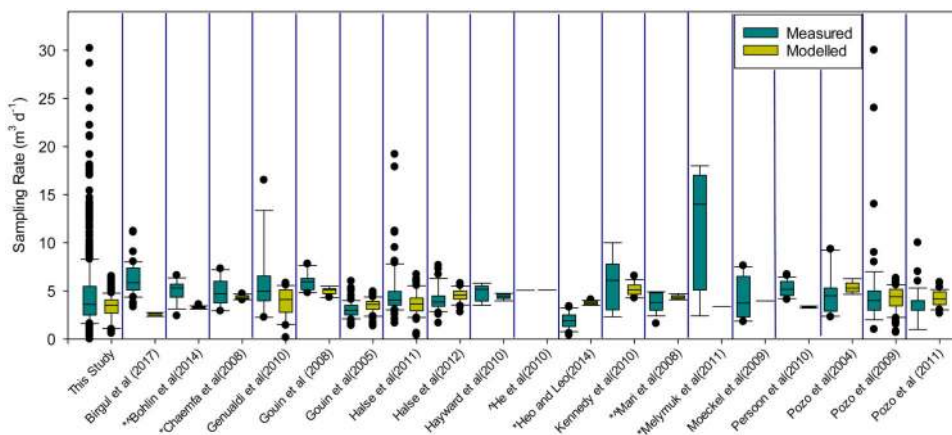
**Figure 2.** Histogram of the yearly averaged (2006) modelled sampling rates for PCB congeners with percent of global surface coverage as the bin value.







**Figure 4.** Comparison of depuration-determined and modelled sampling rates in an independent dataset deployed in the summer and fall of 2015 in the New Bedford Harbor (NBH) area. All values presented here are for  $^{13}\text{C}$  PCB-28 and had a depuration recovery ( $C/C_0$ ) less than 65%.



**Figure 5.** Approximated modelled results for numerous independent studies reporting PUF-PAS sampling rates for a range a different chemicals in a range of different environmental conditions. 2, 6, 9, 14, 15, 17, 21-23, 28, 30, 33, 34, 48-54 The \* denotes studies that conducted active sampler comparison (no \* indicates DCs were used). The ^ denotes studies with a different sampler design than the default design (24 cm top bowl, 20 cm bottom bowl).

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**Table 1**

Summary of mean sampling rates ( $\text{m}^3 \text{d}^{-1}$ ) and percent surface coverage for the different PCB homolog groups.

<i>Homolog</i>	<b>Rs (<math>\text{m}^3 \text{d}^{-1}</math>)</b>	<b>St. Dev</b>	<b>% Surface Coverage &lt; 2 <math>\text{m}^3 \text{d}^{-1}</math></b>
<i>Mono-</i>	5.08	1.30	4.6%
<i>Di-</i>	4.80	1.23	5.0%
<i>Tri-</i>	4.58	1.17	5.4%
<i>Tetra-</i>	4.39	1.12	5.6%
<i>Penta-</i>	4.23	1.08	5.9%
<i>Hexa-</i>	4.09	1.05	6.1%
<i>Hepta-</i>	3.97	1.02	6.3%
<i>Octa-</i>	3.86	0.99	6.5%
<i>Nona-</i>	3.76	0.96	6.6%
<i>Deca-</i>	3.67	0.94	6.8%