Supporting Information

A MODEL USING LOCAL WEATHER DATA TO DETERMINE THE EFFECTIVE SAMPLING VOLUME FOR PCB CONGENERS COLLECTED ON PASSIVE AIR SAMPLERS

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Integrated Surface Database (ISD) Lite Dataset Processing Script
For hourly weather parameter, the Model uses the Integrated Surface Database (ISD) Lite database accessed through NOAA’s National Centers for Environmental Information (NCEI) website. A Matlab script, developed and run in Matlab version R2015a, for processing the Raw ISD Lite datasets is attached as a Matlab file (process_isd_met_data.m).

PUF-PAS Effective Volume Model
The Matlab script, developed and run in Matlab version R2015a, for calculating PUF-PAS Effective Volume is attached as a Matlab file (PUF_PAS_Effective_Volume_Model.m).

PCB Physical Chemical Properties (CSV File)
The model requires the physical-chemical properties for all PCB congeners, such as molecular weight (MW), octanol-air partitioning coefficient (Koa) at 25 °C, and internal energies of octanol–air transfer (dUoa). These values are given in an accompanying CSV (comma separated values) file that is critical to use of the PUF-PAS Effective Volume Model (PCB_PROPERTIES_MW_DU_KOA.csv). Ensure this file is in the same workspace as the PUF-PAS Effective Volume Model script.

PCB LFER Descriptors (CSV File)
If the user decides to use the linear free energy relationship (LFER) to predict K_{PUF} for PCBs partitioning to polyurethane foam disks, the model will require the accompanying CSV file containing the descriptors for PCBs (PCB_LFER_descriptors.csv). Ensure this file is in the same workspace as the PUF-PAS Effective Volume Model script.
### Chicago Sampling Locations

Table S1: Summary of site locations, longitude, latitude, and number of samples collected at that site.

| Site ID | Sampling Site Name                          | Longitude   | Latitude    | N  | Mean Concentration (pg m⁻³) | Standard Error |
|---------|--------------------------------------------|-------------|-------------|----|----------------------------|----------------|
| AU      | Aurora                                     | -88.329374  | 41.784717   | 9  | 74                         | 1.25           |
| CN      | Channahon Park                             | -88.187542  | 41.468465   | 9  | 102                        | 1.29           |
| CP      | Chase Park                                 | -87.669303  | 41.967150   | 3  | 241                        | 1.35           |
| GE      | Graves Elementary School                   | -87.805740  | 41.782596   | 6  | 289                        | 1.34           |
| HC      | Harrison Crib                              | -87.572256  | 41.916117   | 1  | 998                        | N/A            |
| *IT     | Illinois Institute of Technology (IIT)     | -87.624700  | 41.834400   | 6  | 571                        | 1.05           |
| JP      | Jefferson Park                             | -87.762946  | 41.968148   | 14 | 198                        | 1.22           |
| JT      | Joliet Township                            | -88.124903  | 41.529934   | 12 | 2507                       | 1.18           |
| JN      | Jardine Water Plant - Over Intake          | -87.606188  | 41.895905   | 12 | 1907                       | 1.19           |
| *JS     | Jardine Water Plant - Southeast Corner     | -87.602717  | 41.89355    | 12 | 716                         | 1.17           |
| KC      | Kane County Health Department              | -88.329528  | 41.784623   | 2  | 230                        | 1.18           |
| *LM     | Lemont                                     | -87.990570  | 41.668120   | 11 | 277                         | 1.12           |
| NC      | Naperville City Hall                       | -88.153036  | 41.770978   | 11 | 98                          | 1.28           |
| NP      | Norwood Park                               | -87.794134  | 41.986593   | 7  | 154                         | 1.23           |
| PP      | Portage Park                               | -87.762161  | 41.955091   | 12 | 313                         | 1.19           |
| SP      | Sauganash Park                             | -87.737399  | 41.988401   | 12 | 286                         | 1.19           |
| SL      | Schiller Park                              | -87.865005  | 41.954700   | 10 | 215                         | 1.17           |
| VM      | Village of McCook                          | -87.832527  | 41.800371   | 11 | 131                         | 1.20           |
| WH      | Waukegan Harbor                            | -87.822736  | 42.363092   | 6  | 391                         | 1.24           |
| WP      | Winnemac Park                              | -87.684438  | 41.974165   | 14 | 165                         | 1.11           |

*Denotes sites with samples in the subset of 180 total samples specifically examined in this study.
Figure S1: The 20 sampling sites used for the study in the Metropolitan Chicago area are denoted above on the map with their corresponding site IDs as noted in Table S1.
## Sampler Design for Comparison Studies

Table S2: Description of PUF disk and sampler housing differences between the comparison studies.

|                  | This Study | Melymuk et al (2011)² | Chaemfa et al (2008)³ -Lancaster Design |
|------------------|------------|------------------------|----------------------------------------|
| **PUF Disk**     |            |                        |                                        |
| Manufacturer     | Tisch      | PacWill                | Klaus Ziemer GmbH                      |
|                  | Environmental | Environmental          |                                        |
| Length (cm)      | 14         | 14                     | 14                                     |
| Thickness (cm)   | 1.35       | 1.35                   | 1.2                                    |
| Density (g cm⁻³) | 0.0213     | 0.0213                 | 0.035                                  |
| Surface Area (cm²)| 365        | 365                    | 365                                    |
| **Housing Design** |            |                        |                                        |
| Top              |            |                        |                                        |
| Diameter (cm)    | 24.0       | 23.0                   | 26.0                                   |
| Depth (cm)       | 8.0        | 8.0                    | 10.5                                   |
| Bottom           |            |                        |                                        |
| Diameter (cm)    | 20.0       | 19.0                   | 19.5                                   |
| Depth (cm)       | 7.0        | 7.0                    | 7.0                                    |
| Gap depth (cm)   | 1.5        | 0.75                   | 1.5                                    |
| Gap width (cm)   | 2.0        | 2.0                    | 2.5                                    |
Effects of Temperature Changes

Figure S2: Example effective sampling volume curves for deployments with decreasing temperature (left) and increasing temperature (right). The solid grey 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 $K_{PUF}$. 
Long Deployment Periods

Figure S3: One sample involved in our study was deployed for 344 days from October 3rd, 2011 to November 11th, 2012. The solid grey 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 kv and KPUF. The dashed red line, represent effective sampling volume calculated using average values for kv and KPUF.
Figure S4: Profile comparison of long deployment sample (denoted with red x) at Jardine Water Plant - Southeast Corner (JS) site and all other samples (grey circles) for JS site. The six PCB congeners (3, 4, 16, 35, 40+41+71, and 159) that fell out of the range of what was observed at the JS site in all other samples collected at the JS site, are denoted on the x-axis.
Figure S5: The model results for the Chicago comparison was also compared with results obtained using the commonly used GAPS template. 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 datasets, the method ratio using the GAPS template calculation was 0.75, while the method rate using the model was 1.09.
Figure S6: Comparison of the $K_{PUF}$ values for all 209 PCB congeners using the temperature dependent LFER method for polyurethane foam given by Sprunger et al.\textsuperscript{5} modified from Kamprad and Goss.\textsuperscript{6} and empirical relationship with $K_{oa}$ proposed by Shoeib and Harner.\textsuperscript{7}
Figure S7: The model results for the Chicago comparison were recalculated using the temperature dependent LFER for polyurethane foam given by Sprunger et al.\textsuperscript{5} modified from Kamprad and Goss.\textsuperscript{6} 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.\textsuperscript{7}
Steps to Run Effective Volume Model:

1. Identify the Site ID of the NOAA Integrated Surface Dataset that corresponds to the spatial location of your study using the Map Tool provided on the NOAA website
   a. Go to → https://gis.ncdc.noaa.gov/mapviewer/
   b. Click on Hourly/Sub-Hourly under the Time-Related Maps tab on the map GUI
   c. Use the Map to zoom into the spatial location of your sampling location
d. Click on the information cursor option in the upper left hand corner of the screen

![Hourly/Sub-Hourly Observational Data](image)

Select a weather station that is spatially close to your sampling location and ensure the weather data spans the appropriate time to encapsulate your study. (From our experience the best data quality typically comes from Airport data and we recommend selecting airport data where possible.)

![Results](image)

f. If the weather station spans the appropriate time span, record the AWS and WBAN number, for future reference (from above example 725300-94846)
2. Obtain the Raw NOAA ISD Lite file for the given year/years of your study and download them into your MATLAB workspace
   
a. Go to ftp://ftp.ncdc.noaa.gov/pub/data/noaa/isd-lite

b. Select the appropriate year for your study

![Index of /pub/data/noaa/isd-lite](image)

c. Location the weather station ID previously recorded via the map tool (We recommend using the search function control-f)

![Extract files](image)

d. Download the appropriate file and extract the zip file.

e. Move the extracted file to the folder containing the `process_isd_met_data.m` script

f. Repeat Steps B through E for each required year of meteorological data (if your study spans more than one year)

![Directory listing](image)
3. Check the data quality and convert the meteorological data to the required format of each individual year using the `process_isd_met_data.m` script.
   
a. The input should be in the form of

   ```matlab
   process_isd_met_data('XXXXXX-XXXXX',iYear, NumberYears);
   ```

   where,

   i. ‘XXXXXX-XXXXX’ = the site ID to be combine formatted as a string (i.e. enclosed in apostrophes ‘ ’).
   
   ii. iYear = the first year of the data to be combined
   
   iii. NumberYears = the number of years to be combined
b. A final formatted csv file with the site ID will be created with a summary of the data quality for each year that will be both printed to the screen after the run and saved as a readme file to be accessed later. The readme file will overwrite any previous version of the file. The script will provide a summary of missing values for all 5 weather parameters and detect any gaps greater than 12 hours.

c. Below is an example of a weather data station being run for 3 consecutive years and the resulting data quality summary.
d. The script will also detect if there are any gaps in data greater than 12 hours. This threshold can be changed in line 68 of the process_isd_met_data.m script if desired. In the example shown below there are 4 gaps greater than 12 hours for temperature, wind speed, and wind direction, while pressure and dew point are missing all measurements for the year. This data quality would be insufficient for the flowrate model since it does not contain any pressure or dew point measurements, and a different weather station would need to be selected (steps 1-2)
4. After the met data has been converted use the **PUF_PAS_Effective_Volume_Model.m** script to obtain congener and deployment specific effective sampling volumes and sampling rates [Note: ensure the accompanying PCB physical-chemical properties CSV file (**PCB_PROPERTIES_MW_DU_KOA.csv**) and the PCB LFER descriptors CSV file (**PCB_LFER_descriptors.csv**) are in the same location as the **PUF_PAS_Effective_Volume_Model.m** script].

   a. Prior to running the script a few modifications at the beginning of the script may need to be made at the beginning of the script.

      1. **Line 12**: Output file name (Use a name descriptive to the specific run)

      2. **Line 17**: Select the method for determining the air/PUF partition coefficient

         a. Method 1 is the empirical relationship (with temperature adjusted Koa) from Shoeib and Harner (2002) ^7

         b. Method 2 is the temperature dependent linear free energy relationship for polyurethane foam from Sprunger et al. (2007)^5

   3. **Lines 21-24**: PUF Disk Parameters specific to the study.

     Note: A screen shot of the beginning of the script where the above parameters can be adjusted is shown below.
b. The input should be in the form

\[ \text{PUF\_PAS\_Effective\_Volume\_Model(Deployment,Collection,PUF\_ID,}\text{MET\_ID)}; \]

where,

i. Deployment = PUF Deployment Date formatted as YYYYMMDDHH

ii. Collection = PUF Collection Date formatted as YYYYMMDDHH

iii. PUF\_ID = Numerical PUF ID for identification in output data

iv. MET\_ID = string of AWS site ID formatted as 'XXXXXX-XXXXX' for the weather data to be used for the PUF deployment
c. The final output file will produce a comma delimited file that can be opened in Microsoft Excel.

| A | B          | C          | D       | E           | F       | G       | H       | I       | J       |
|---|------------|------------|---------|-------------|---------|---------|---------|---------|---------|
| 1 | 5          | 2012012812 | 2012031412 | 1105       | 46.78733 | 1       | 63.37986 | 103.706 | 108.0177 | 127.0171 |
| 2 | 5          | 2012012812 | 2012031412 | 1105       | 46.78733 | 2       | 4.517572 | 4.792622 | 4.821794 | 4.710386 |

Numerically Coded Output Variables:
1 = Effective Sampling Volume (m³)
2 = Sampling Rate (m³/d)

% of wind speed measurements that exceed calibration range (> 5 m/s)

Deployment (YYYYMMDDHH)
Collection (YYYYMMDDHH)
Deployment Length (hours)
Numeric PUF ID

PCB 1
PCB 2
PCB 209
5. (OPTIONAL) If you want to run many samples in a row, a new script can be set up to run PUF consecutively.

   a. First open a new blank script by clicking “New Script” in the open left-hand corner of the MATLAB window.

   

   b. Then repeat the format from step 4B for as many PUF as needed and hit run (highlighted in red box)
c. These run commands can also be created in excel using the concatenate function and pasted into the new script to speed up this process.

```
=CONCATENATE("PUF_PAS_Effective_Volume_Model(\"B16,\",\"C16,\",\"A16,\",\"D16\")\")
```

d. If this is done the output file will have the same format as previously described preceding down the columns in the order the PUF were run

```
| A   | B                      | C         | D         | E         | F       | G     | H      | I      | J         | K    | L     |
|-----|------------------------|-----------|-----------|-----------|---------|-------|--------|--------|-----------|------|-------|
| 1   | 5                      | 2012012812| 2012031412| 1105      | 46.75733| 1     | 63.37986| 103.706| 108.0177  | 127.0171| 169.9775 | 163.9116 |
| 2   | 5                      | 2012012812| 2012031412| 1105      | 46.75733| 1     | 63.37986| 103.706| 108.0177  | 127.0171| 169.9775 | 163.9116 |
| 3   | 9                      | 2012012812| 2012031412| 1105      | 46.75733| 1     | 63.37986| 103.706| 108.0177  | 127.0171| 169.9775 | 163.9116 |
| 4   | 9                      | 2012012812| 2012031412| 1105      | 46.75733| 1     | 63.37986| 103.706| 108.0177  | 127.0171| 169.9775 | 163.9116 |
| 5   | 10                     | 2012011112| 2012031612| 1561      | 44.52274| 1     | 58.13245| 107.882| 113.4394  | 142.424| 207.1933 | 197.7077 |
| 6   | 10                     | 2012011112| 2012031612| 1561      | 44.52274| 1     | 58.13245| 107.882| 113.4394  | 142.424| 207.1933 | 197.7077 |
| 7   | 11                     | 2012020712| 2012032612| 1153      | 44.57936| 1     | 37.76773| 69.94987| 74.10364  | 97.1599| 148.5119| 140.5724 |
| 8   | 11                     | 2012020712| 2012032612| 1153      | 44.57936| 1     | 37.76773| 69.94987| 74.10364  | 97.1599| 148.5119| 140.5724 |
| 9   | 14                     | 2012020812| 2012040912| 1465      | 45.80205| 1     | 50.57058| 85.92163| 90.42468  | 115.4995| 178.3171| 168.3355 |
| 10  | 14                     | 2012020812| 2012040912| 1465      | 45.80205| 1     | 50.57058| 85.92163| 90.42468  | 115.4995| 178.3171| 168.3355 |
| 11  | 15                     | 2012031012| 2012041712| 913       | 44.24973| 1     | 46.80622| 77.45519| 81.04287  | 98.83027| 139.6872| 133.5291 |
| 12  | 15                     | 2012031012| 2012041712| 913       | 44.24973| 1     | 46.80622| 77.45519| 81.04287  | 98.83027| 139.6872| 133.5291 |
| 13  | 16                     | 2012031012| 2012041712| 913       | 44.24973| 1     | 46.80622| 77.45519| 81.04287  | 98.83027| 139.6872| 133.5291 |
| 14  | 16                     | 2012031012| 2012041712| 913       | 44.24973| 1     | 46.80622| 77.45519| 81.04287  | 98.83027| 139.6872| 133.5291 |
| 15  | 19                     | 2012030612| 2012042112| 1105      | 47.69231| 1     | 49.67255| 82.53264| 86.51863  | 107.1889| 156.6825| 149.045 |
| 16  | 19                     | 2012030612| 2012042112| 1105      | 47.69231| 1     | 49.67255| 82.53264| 86.51863  | 107.1889| 156.6825| 149.045 |
6. **(OPTIONAL)** The outputs (as well as meteorological data) can be saved directly in MATLAB to create figures and view trends.

a. Assign Variable for the PUF array and meteorological data

b. After running the `PUF_PAS_Flowrate_Model.m` script, the Meteorological Data Array and PUF Variable Array are available in the workspace.
c. The PUF Variables are defined on lines 103-113 of the PUF_PAS_Effective_Volume_Model.m script and additional variables can be defined here by increasing the size of the PAS_Array to examine other trends if desired.

```
102 %Fill in PAS_Array for variables. This is a 3D array that gets populated during the run
103    PAS_Array(t,C,1) = Rs;
104    PAS_Array(t,C,2) = kw;
105    PAS_Array(t,C,3) = KPUF;
106    PAS_Array(t,C,4) = Veff;
107
108    %Index 5 is time integrated effective volume
109    if t == 1
110        PAS_Array(t,C,5) = Veff;
111    else
112        PAS_Array(t,C,5) = Veff + PAS_Array(t-1,C,5);
113    end
114    end
```

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