

Supporting Information for

**Characterizing Airborne Phthalate Concentrations and Dynamics in a  
Normally Occupied Residence**

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**SI Contains:**

14 pages

9 figures

## SV-TAG Operation:

In this study, the SV-TAG resided in an external temperature-controlled shed built specifically to contain instrumentation throughout the campaign. The SV-TAG unit was situated approximately 0.5 m from the residence. The SV-TAG instrument is equipped with two sampling cells that are operated in parallel. One sampling cell was dedicated to measuring indoor gas-plus-particle concentrations. It sampled through a 1.6-m stainless steel inlet extending from the house's dining room. The inlet was positioned approximately 30 cm from the exterior room wall and 1.5 m above the floor. A second cell alternately collected indoor air from the same indoor inlet or from a separate outdoor air sampling port through a 2.0-m stainless steel tube extending outside the shed. The second cell was switched hourly among four states: indoor gas-plus-particle, indoor particle only, outdoor gas-plus-particle, and outdoor particle only, with a complete cycle occurring every four hours. Gas-phase removal for the particle-only measurements was accomplished by passing sample air through a carbon monolith denuder (500 channels, 30 mm OD  $\times$  40.6 cm; MAST Carbon) thereby removing all gas-phase organic compounds from the air stream before collection. Particle-only measurements (and corresponding gas-particle partitioning measurements) determined by the denuder method have, if any, a negative bias due to repartitioning and loss within the denuder.<sup>1</sup> Gas-particle partitioning of phthalates may be influenced by sorption of gas-phase species to sampling lines; however, past investigations indicate that such biases are minimal for the experimental conditions of this study.<sup>2,3</sup> Concurrent gas-plus-particle measurements in the two cells were used to normalize any cell differences when quantifying gas-particle partitioning. This cell-correction factor was adjusted downwards in the case of DEHP such that gas-particle partitioning maximized at 100% in the particle phase.

Both cells sampled air at 10 L/min through a PM2.5 cyclone (BGI, Inc.; SCC 2.654) for the first 15 minutes of each hour for the duration of the campaign. During sampling, the cell temperatures were controlled at 30 °C. After sample collection, the captured organic mass was thermally desorbed by raising the collection cell temperature to 320 °C. The organic mass was carried by helium gas saturated with a derivatization agent, MSTFA (N-methyl-N-(trimethylsilyl)trifluoroacetamide, > 98.5%, Sigma Aldrich), towards a concentrating trap before valveless injection into an Agilent 7890A gas chromatograph. Separation was achieved by linearly ramping the temperature (50 °C to 330 °C, over 14 minutes) with helium flow (0.5 standard cm<sup>3</sup>/min to 1.0 standard cm<sup>3</sup>/min through minute 12, then 1.0 standard cm<sup>3</sup>/min to 3.0 standard cm<sup>3</sup>/min to the end) through the column (Restek, Rtx-5Sil MS, 20 m  $\times$  0.18 mm  $\times$  0.18  $\mu$ m). Species exited from the column into an Agilent 5975C quadrupole mass spectrometer (MS) for subsequent electron impact (EI) analysis. Mass spectral interpretation and quantification used a single-ion peak fitting approach via the TERN software.<sup>4</sup>

Time-resolved measurements of DEP, DIBP, DBP, and DEHP were acquired hourly. Peak areas were normalized by deuterated internal standards to account for cell-loading matrix effects and a general ion source decline over the duration of the field campaign. DBP, DIBP, and DEHP were normalized to dibutyl phthalate-3,4,5,6-d4 (Sigma Aldrich), a deuterated analogue of DBP. DEP was normalized to a deuterated isotopologue of

pentadecanol, considering similarities in retention time. Absolute concentrations were determined by multipoint linear calibration curves with a zero-point intercept that were generated every four days during the campaign. Calibration standards from the EPA 525 update phthalate esters mix were added to a 50/50 methanol/chloroform solution with other relevant chemical standards. Limits of detection (LODs), set at 3× the background chromatographic signal, are analyte dependent and variable depending on acquisition parameters, instrument status, chromatographic coelutions, and matrix interferents. These same factors affect uncertainties, which are typically less than 20% on a relative scale.<sup>5</sup> Typical LODs for DEP, DIBP, and DBP were on the order of 10 ng/m<sup>3</sup>. Typical LODs for DEHP were on the order of 1 ng/m<sup>3</sup>.

Throughout the campaign, three phthalate species (DEP, DBP, and DEHP) were identified by authentic external standards and a fourth (DIBP) was identified referencing mass spectra available in the NIST/EPA/NIH Mass Spectral Library.<sup>6,7</sup> Major phthalate species, excluding dimethyl phthalate, have a prominent characteristic ion at  $m/z = 149$ . This characteristic ion was used to search for other phthalate species during periods with high temperature and high particle mass concentrations, when phthalate concentrations are expected to be highest. No additional species above background chromatographic signal were identified as phthalates; see Figure S1 of the Supporting Information.

#### SV-TAG Quality Assurance and Quality Control:

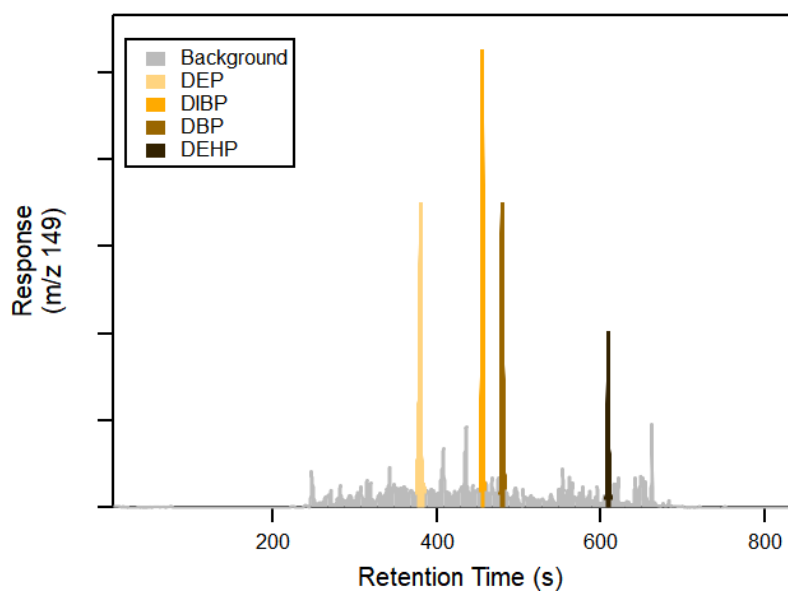
**Method Blanks:** Method blanks were conducted at the beginning, middle, and end of the sampling campaign by injecting pure solvent containing only deuterated internal standards onto the thermal desorption collection cells via an automated liquid injection system. Possible contamination of blanks by phthalates could occur from incomplete desorption of the collection cells, or from release of plastic components within the SV-TAG system. Such artifacts were minimally observed. Measured phthalate signals during method blank measurements relative to the prior gas-plus-particle measurement were: DEP: < 0.5%; DIBP: <3%; DBP: <4%; DEHP: <5%.

**Internal Standards:** The primary purpose of the internal standard was to account for any changes in the efficiency of the analytical system as a function of time during the experiment. A solvent solution containing 45 deuterated internal standards was injected onto the thermal desorption collection cell on top of each ambient air sample by an automated injection system. These internal standards encompassed a broad range of chemical functionalities and volatilities. All internal standards qualitatively showed similar trends, with decreased responses being observed as the campaign progressed owing to degraded performance of the mass spectrometer's ion-source as it became dirtier. Internal standard responses were restored after an ion-source cleaning. Some variability in response was also observed, presumably because of sample matrix effects; these were corrected based on the internal standard response.

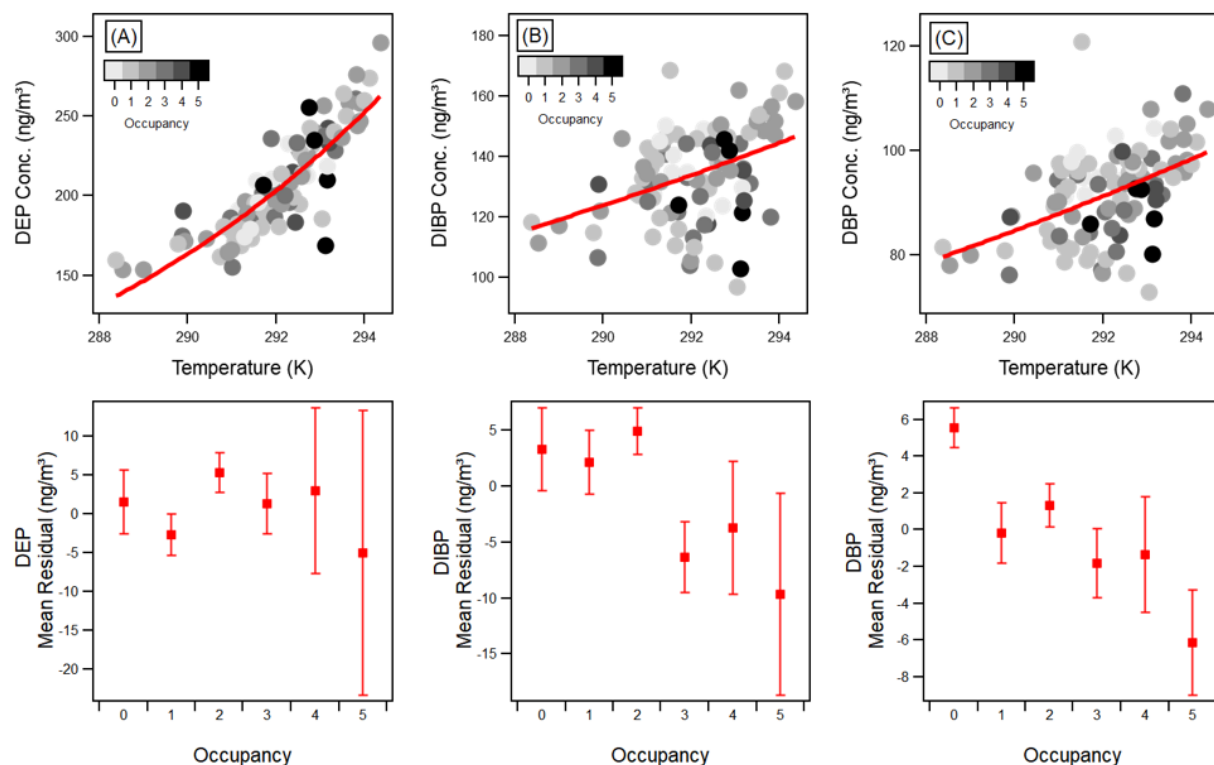
**External Standards:** External standards were run every 25 hours such that a three-point calibration curve was generated every three to four days. After internal standard normalization to account for changes in the mass spectrometer's ion-source and sample matrix effects, calibration curves did not significantly differ over the course of the measurement period.

**Sensitivity Testing:** Although particle densities are known to vary, such as during different types of source events, we assume a constant particle density of  $1.67 \text{ g/cm}^3$  in congruence with past studies.<sup>8,9</sup> Sensitivity testing was conducted by renormalizing particle mass concentrations using densities of 1 and  $2 \text{ g/cm}^3$ , approximately spanning the range of expected values. Using these extrema, the slope of Figure 3 could vary between 1.9 and  $3.8 \text{ ng/}\mu\text{g}$  (parts per thousand), the slope of Figure 4A could vary between 1.4 and  $2.8 \text{ ng/}\mu\text{g}$  (parts per thousand), and the resulting estimate of  $K_p^*$  in Figure 5 could vary between 2.0 and  $4.0 \text{ m}^3/\mu\text{g}$ .

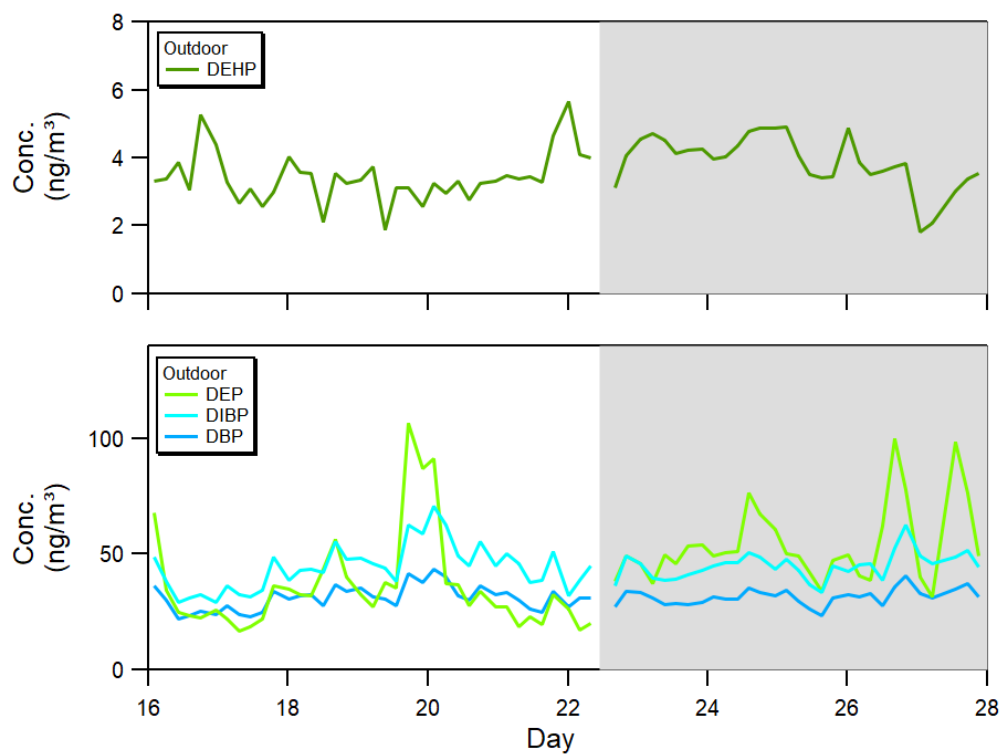
**Data Selection:** Non-representative house venting occurred between the occupied and vacant periods; four associated measurements were excluded from analysis. One single-point particle concentration determined from the Grimm 11-A particle counter on 21 Dec 2017 was similarly excluded. The point corresponded to the beginning of an emission event and may not have been fully representative of the house because of incomplete mixing.



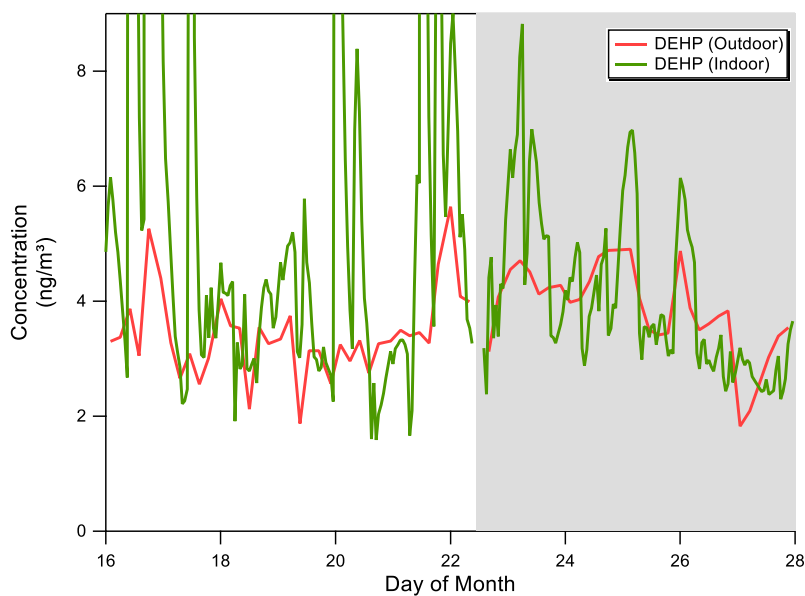
142  
 143 **Figure S1:** The response of ion  $m/z = 149$  is plotted against the chromatograph retention time on  
 144 16 Dec 2017, a period of high particle loading when phthalate levels are expected to be elevated.  
 145 Phthalate diesters (other than dimethyl phthalate) have a prominent characteristic ion at  $m/z =$   
 146 149. In the above spectrum, DEP, DIBP, DBP, and DEHP were clearly identified in comparison  
 147 to a mass spectral database and the known retention times of authentic external standards (EPA  
 148 525 phthalate esters update mix: DMP, DEP, DBP, DEHP, butyl benzyl phthalate). No other  
 149 species above chromatographic background levels were identifiable as phthalates in reference to  
 150 the NIST/EPA/NIH Mass Spectral Library over the selected analysis periods.



**Figure S2:** Upper: Total (gas-plus-particle) indoor phthalate concentrations are plotted against temperature during waking hours of the occupied period. Lower: The residuals of respective exponential fits are compared against residential occupancy, where uncertainties correspond to the standard error of the mean. Parameters of the exponential fits ( $y = Ae^{kx}$ ) are:  $A = 3.5 \times 10^{-12}$ ,  $k = 0.109$ ,  $R^2 = 0.73$  (panel A),  $A = 1.8 \times 10^{-3}$ ,  $k = 0.038$ ,  $R^2 = 0.15$  (panel B),  $A = 1.6 \times 10^{-3}$ ,  $k = 0.038$ ,  $R^2 = 0.23$  (panel C). Units of measure on the fit parameters are inverse temperature for  $k$  (1/K) and concentration for  $A$  (ng/m<sup>3</sup>).

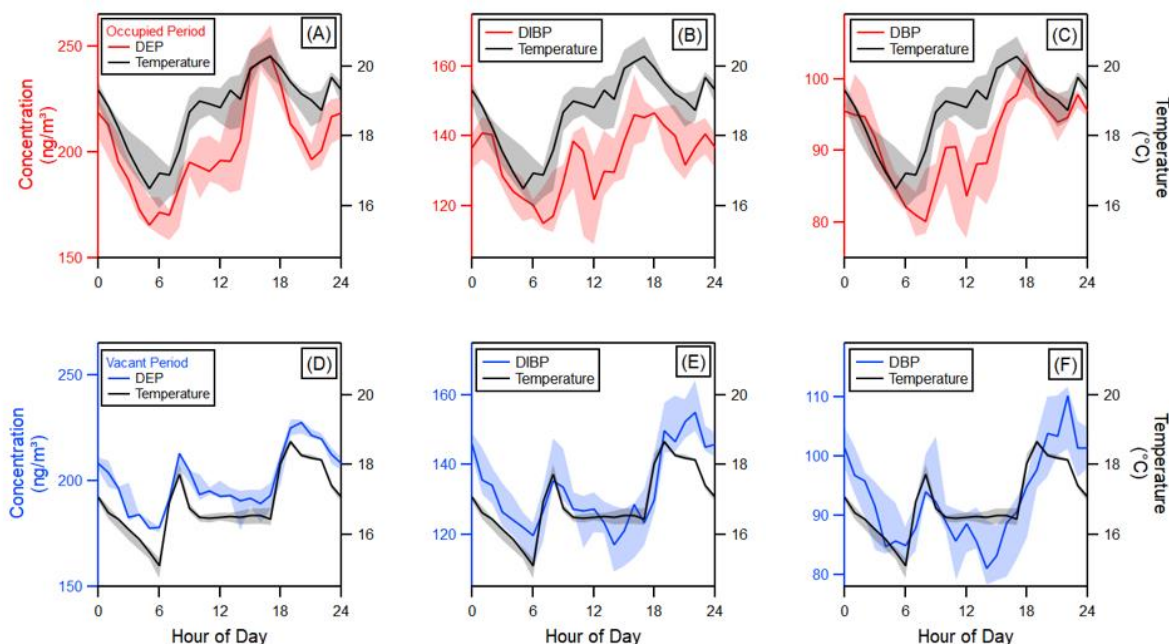


**Figure S3:** The gas-plus-particle outdoor concentrations of DEP, DIBP, DBP, and DEHP are displayed, where the shaded region corresponds to the vacant period.

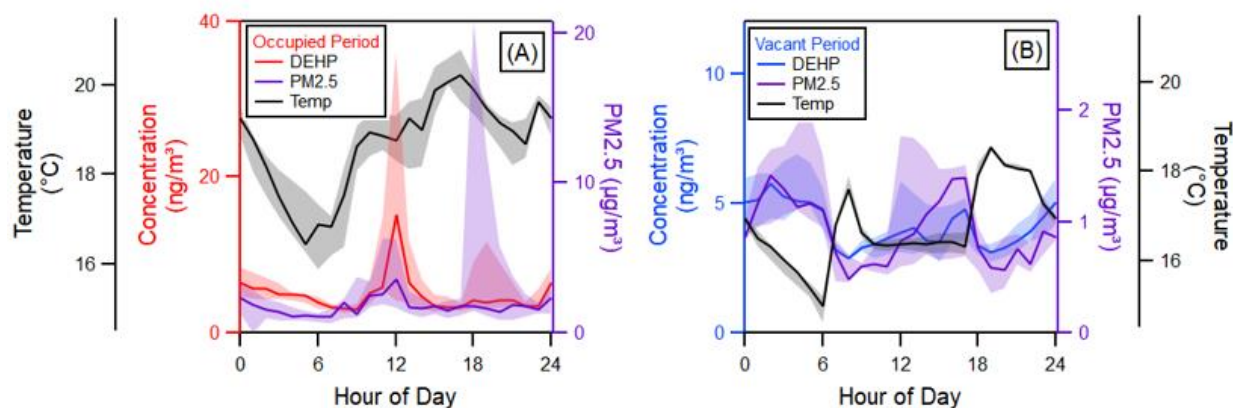


**Figure S4:** The total (gas-plus-particle) indoor and outdoor concentrations of DEHP are displayed, where the scaling emphasizes baseline concentrations and excludes episodic concentrations above 9 ng/m<sup>3</sup>. The shaded region corresponds to the vacant period.

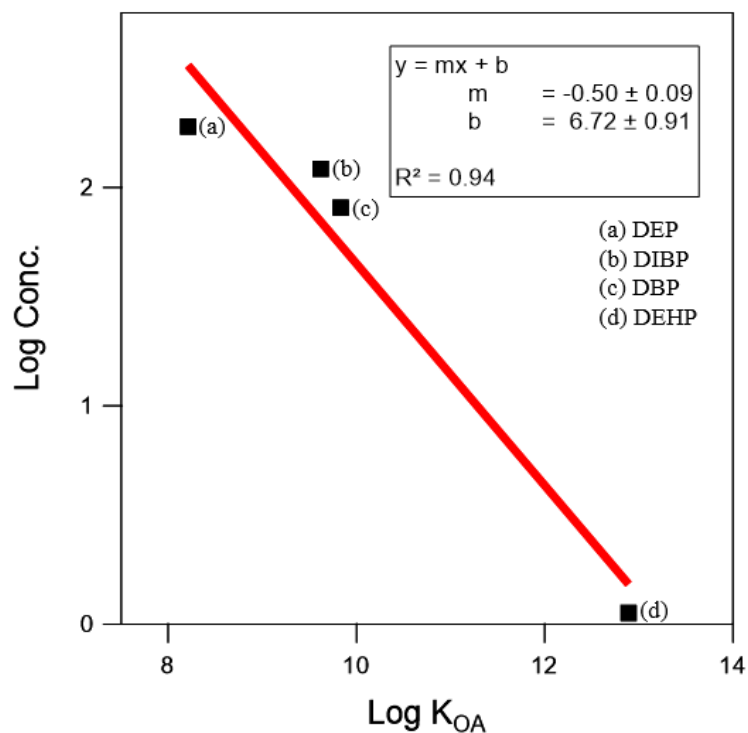




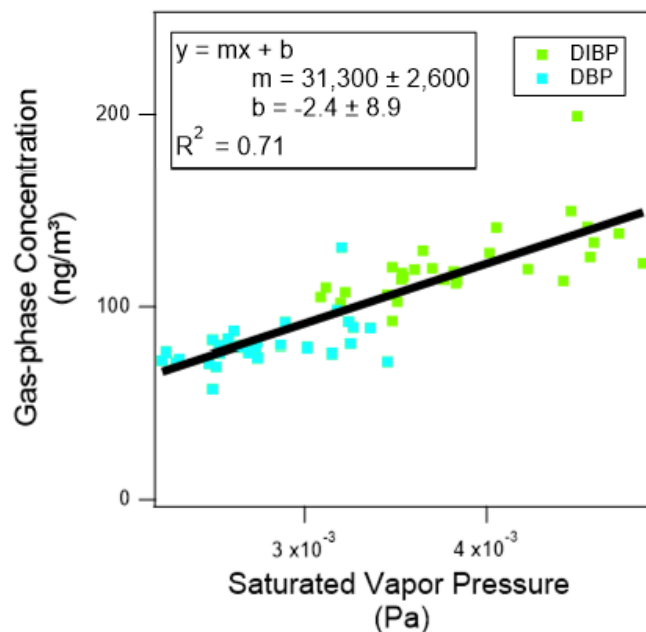
**Figure S5:** Diel plots (median, interquartile range by hour of day) are shown for gas-plus-particle DEP, DIBP, and DBP concentrations and indoor air temperature over the occupied (upper frames) and vacant (lower frames) periods.



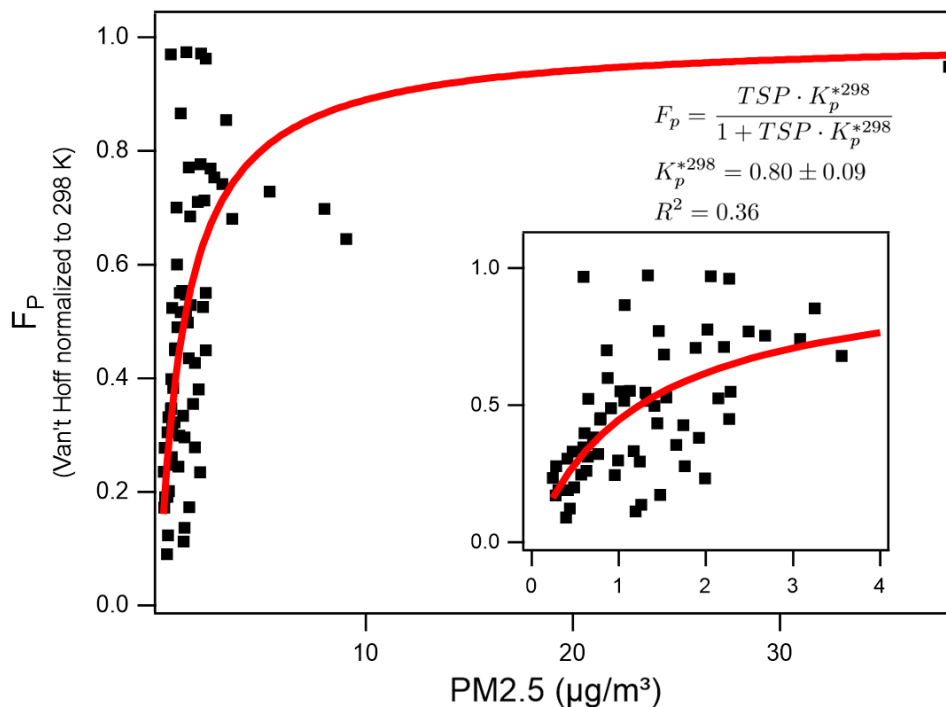
**Figure S6:** Diel plots (median, interquartile range by hour of day) are shown for gas-plus-particle DEHP concentrations and PM2.5 particle loading over the occupied (left frame) and vacant (right frame) periods.



**Figure S7:** The median gas-phase concentration in  $\text{ng}/\text{m}^3$  of each phthalate species over the vacant period is compared against the octanol-air partition coefficient at  $T = 298 \text{ K}$  (as reported by Salthammer et al.<sup>10</sup>) on a log-log scale. A linear least-squares fit of the transformed data is presented.



**Figure S8:** The measured gas-phase concentrations of DIBP and DBP are displayed against the calculated saturation vapor pressure at the measured indoor air temperature. Vapor pressures for DIBP and DBP as a function of temperature were calculated according to Wu et al.<sup>11</sup> Units of measure for the fit parameters are ng/{m<sup>3</sup> Pa} for the slope,  $m$ , and ng/m<sup>3</sup> for the intercept,  $b$ .



**Figure S9:** Each particle fraction value of DEHP is normalized from ambient air temperature to 298 K using the van't Hoff equation and assuming -116,700 J/mol as the phase-change enthalpy.<sup>12</sup> Normalized particle fractions are compared against PM2.5 mass concentrations as measured throughout the campaign. The inset panel highlights the dynamic region with PM2.5 concentrations between 0 and 4 µg/m<sup>3</sup>. Three datapoints with experimentally determined  $F_p$  greater than one were defined to have maximum particle:gas fractions of 100:1 (i.e.,  $F_p = 0.99$ ) to facilitate the normalization process.

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