

# 1 Characterizing Airborne Phthalate Concentrations and Dynamics in a 2 Normally Occupied Residence

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## 17 **ABSTRACT**

18 Phthalate esters, commonly used as plasticizers, can be found indoors in the gas phase, in  
19 airborne particulate matter, in dust, and on surfaces. The dynamic behavior of phthalates indoors  
20 is not fully understood. In this study, time-resolved measurements of airborne phthalate  
21 concentrations and associated gas-particle partitioning data were acquired in a normally occupied  
22 residence. The vapor pressure and associated gas-particle partitioning of measured phthalates  
23 influenced their airborne dynamic behavior. Concentrations of higher vapor pressure phthalates  
24 correlated well with indoor temperature, with little discernable influence from direct occupant  
25 activity. Conversely, occupant-related behaviors substantially influenced the concentrations and  
26 dynamic behavior of a lower vapor pressure compound, diethyl hexyl phthalate (DEHP), mainly  
27 through production of particulate matter during cooking events. The proportion of airborne  
28 DEHP in the particle phase was experimentally observed to increase under high particle mass  
29 concentrations and lower indoor temperatures in correspondence with theory. Experimental

30 observations indicate that indoor surfaces of the residence are large reservoirs of phthalates. The  
31 results also indicate that two key factors influenced by human behavior – temperature and  
32 particle mass concentration – cause short-term changes in airborne phthalate concentrations.

33

## 34 **1 INTRODUCTION**

35 Past indoor measurements of semivolatile organic compounds (SVOCs) have generally utilized  
36 sample collection methods that yield time-averaged results over sampling periods on the order of  
37 a day to a week.<sup>1-3</sup> Higher time-resolution measurements of indoor SVOCs are needed to  
38 investigate indoor dynamic processes relevant to understanding emissions, concentrations, and  
39 exposures. A few studies have explored the dynamic behavior of phthalates directly in real  
40 residential settings or in test houses.<sup>4-6</sup> In this study, we report an extensive sequence of phthalate  
41 diester measurements with hourly resolution in a normally occupied residence. Phthalate diesters  
42 are SVOCs of anthropogenic origin whose metabolites have been found in more than 95% of the  
43 US population.<sup>7,8</sup>

44 Several known and suspected adverse health effects are associated with phthalate exposures,  
45 including impaired reproductive development,<sup>9,10</sup> infertility,<sup>11,12</sup> asthma,<sup>13,14</sup> and obesity.<sup>15,16</sup>  
46 Phthalates are industrially produced and utilized on large scales. Phthalates are found broadly  
47 throughout the environment: in soil,<sup>17,18</sup> in sediment,<sup>17,19</sup> in wastewater,<sup>17,20</sup> in indoor and  
48 outdoor air,<sup>21,22</sup> in the Arctic,<sup>23</sup> and in biota.<sup>24,25</sup> Certain phthalates are commonly found at  
49 elevated concentrations indoors and have been reported on surfaces, in settled dust, in airborne  
50 particles, and in the gas phase.<sup>1,22,26</sup>

51 The abundance of airborne indoor phthalates indicates potentially important contributions to  
52 human exposure.<sup>27</sup> Ingestion, dermal uptake from direct contact, air-to-skin dermal absorption,

53 and inhalation represent major modes of phthalate exposure, with relative strengths that are  
54 related to compound volatility. Exposure to lower volatility species, such as diethyl hexyl  
55 phthalate (DEHP), occurs primarily by ingestion. Higher volatility species, such as dibutyl  
56 phthalate (DBP), are subject to additional non-dietary modes of exposure, and exposure to the  
57 highest volatility phthalates, such as diethyl phthalate (DEP) and dimethyl phthalate (DMP), is  
58 expected to be dominated by nondietary routes such as inhalation and dermal absorption.<sup>28-33</sup>  
59 Because, on average, people spend 90% of their time indoors and 60% of their time in their own  
60 residence,<sup>34-36</sup> it is important to understand and characterize the processes driving indoor airborne  
61 phthalate dynamic behavior, especially in residences.

62 Chemical properties of phthalates are related to their industrial uses and affect their physical  
63 behaviors. Phthalates with higher vapor pressures, such as DMP, DEP, and DBP, can be found in  
64 high abundance in certain cosmetics, personal care products, and medications.<sup>31, 37-40</sup> Phthalates  
65 with lower vapor pressures, such as DEHP, butyl benzyl phthalate (BBzP), and diisononyl  
66 phthalate (DINP), are widely used as plasticizers, constituting large mass fractions of certain  
67 building materials.<sup>41,42</sup>

68 Increased temperature should favor partitioning of phthalates into the gas phase. However, prior  
69 field studies comparing phthalate concentrations across similar indoor environments have  
70 yielded mixed results regarding the role of temperature. Some survey-based studies did not find  
71 correlations between temperature and gas-phase phthalate concentrations.<sup>26,43,44</sup> Gaspar et al.  
72 noted that concentrations of three higher vapor pressure phthalates, DEP, diisobutyl phthalate  
73 (DIBP), and DBP, correlated with temperature while two lower vapor pressure phthalates, BBzP  
74 and DEHP, did not.<sup>32</sup> Conversely, an in-depth study in a test-house demonstrated that a 9 °C  
75 temperature difference could change concentrations of two lower vapor pressure phthalates,

76 BBzP and DEHP, by 300%.<sup>6</sup> Qualitatively, these results corroborate findings from laboratory  
77 studies.<sup>45, 46</sup>

78 Particle concentration is known to affect the airborne abundances of lower volatility SVOCs,  
79 including lower vapor pressure phthalates such as DEHP and BBzP. Liu et al. developed a model  
80 characterizing how airborne particulate matter affects SVOC fluxes between indoor surfaces and  
81 indoor air, predicting that elevated particle concentrations could markedly increase SVOC  
82 emission fluxes from surfaces.<sup>47</sup> Total airborne SVOC abundances are expected to increase with  
83 elevated particle concentrations as SVOC material partitions from reservoirs such as dust or  
84 surfaces onto airborne particulate matter. However, full equilibrium partitioning of SVOCs to  
85 particles may not be reached for lower volatility species when the ventilation timescale  
86 (reciprocal of the air-exchange rate) is less than the timescale to approach equilibrium.<sup>48-50</sup>

87 Chamber studies have been undertaken to explore the role of particle concentration and  
88 composition on SVOC behavior. Benning et al. showed that the emission rate of DEHP is  
89 enhanced in the presence of ammonium sulfate particles.<sup>51</sup> Similarly, Lazarov et al. demonstrated  
90 that increased particle concentrations enhanced the emission rate of organophosphate flame  
91 retardants from materials.<sup>52</sup> Recent experiments by Wu et al. found DEHP particle/gas partition  
92 coefficients are higher in the presence of organic particles (squalane and oleic acid) than in the  
93 presence of inorganic particles (ammonium sulfate).<sup>53</sup>

94 Weschler and Nazaroff described an equilibrium model of indoor SVOC partitioning between  
95 the gas phase and settled dust using the octanol-air partitioning coefficient ( $K_{oa}$ ); that model can  
96 also be applied to airborne particles.<sup>49</sup> In Equation 1, the particle-gas partition coefficient,  $K_p$ , is

97 determined where  $f_{om\_part}$  refers to the volume fraction of organic matter in airborne particles, and  
98  $\rho_{part}$  refers to the density of particles.

$$99 \quad K_p = \frac{f_{om\_part} \times K_{oa}}{\rho_{part}} \quad (1)$$

100 Now, let  $C_p$  refer to the particle-phase SVOC concentration, let  $C_g$  refer to the gas-phase SVOC  
101 concentration, and let  $TSP$  refer to the mass concentration of airborne particles. Then, the particle  
102 fraction of airborne SVOCs can be estimated using Equation 2.

$$103 \quad F_p = \frac{C_p}{C_p + C_g} = \frac{TSP \cdot K_p}{1 + TSP \cdot K_p} \quad (2)$$

104 Weschler and Nazaroff describe how gas-phase SVOC abundances are expected to decrease with  
105 increased particle concentration, while total airborne (gas-plus-particle) SVOC concentrations  
106 are expected to increase. The magnitude of these effects increases with increasing particle  
107 concentration.<sup>48</sup>

108 This study presents a more detailed investigation of a subset of SVOCs reported by Kristensen et  
109 al.<sup>54</sup> Here, we report hourly measurements of four phthalates — DEP, DIBP, DBP, and DEHP —  
110 in a normally occupied northern California residence over a two-week monitoring period. We  
111 examine their dynamic behavior and explore the factors controlling their concentrations,  
112 emissions, and gas-particle partitioning. We investigate how the physicochemical properties of  
113 phthalates — specifically their vapor pressure and octanol-air partition coefficient — affect  
114 dynamic behavior. This work has relevance for modeling efforts assessing indoor SVOC  
115 exposure as there are limited experimental data available for model evaluation.<sup>55-58</sup> The results

116 also have potentially important implications for better understanding human phthalate exposure  
117 and opportunities for exposure mitigation.

## 118 **2 MATERIALS AND METHODS**

119 **Field Site:** Measurements were conducted at a normally occupied single-family residence in  
120 Contra Costa County, California, from 7 December 2017 to 4 February 2018. The single-story  
121 California ranch style wood-framed house was built in 1951, with 180 m<sup>2</sup> (1970 ft<sup>2</sup>) of living  
122 space. The house temperature was controlled by a forced air gas-furnace with the thermostat  
123 programmed to operate only during morning (6:45 – 7:15 AM) and evening (5:45 – 10:00 PM)  
124 hours. Occasional variations in the baseline heating cycle were applied by manual occupant  
125 override, or by operating a vented gas-fireplace situated in the family room. A MERV 13 filter in  
126 the central-heating system efficiently removed particulate matter from recirculated indoor air  
127 when the furnace fan was on. The house contained a kitchen, living/dining room, family room,  
128 three bedrooms, and two bathrooms. Regular household activities included cooking, social  
129 gatherings, and professional house cleanings, as reported by Kristensen et al.<sup>54</sup> Data analyses  
130 presented here focus on the period 16 – 27 December 2017, the longest interval of SVOC  
131 monitoring with consistently high data quality and well characterized experimental parameters.  
132 Phthalate behavior trends were characterized during two distinct periods in this interval  
133 differentiated by house occupancy status. The house was regularly occupied (the “occupied  
134 period”) from 16 to 21 December. The house was unoccupied (the “vacant period”) from 22 to  
135 27 December.

136 **Instrumentation and Measurement Methods:** The semivolatile thermal desorption aerosol gas  
137 chromatograph with in-situ derivatization (SV-TAG) is a two channel GC mass spectrometer  
138 instrument that quantifies gas-plus-particle or particle only concentrations of organic species and

139 their associated gas-particle partitioning with hourly time resolution. Organic compounds with  
140 vapor pressures ranging from C14 to C30+ alkanes are routinely measured, with limits of  
141 detection varying from high parts-per-quadrillion to low parts-per-trillion depending on the  
142 compound of interest.<sup>59-63</sup> SV-TAG was housed in a temperature-controlled shed adjacent to the  
143 house and sampled air from the dining room and from the outdoors. Indoor concentrations were  
144 acquired hourly. Outdoor concentrations, outdoor-gas particle partitioning, and indoor gas-  
145 particle partitioning were acquired every four hours on a rotating sampling basis. Three phthalate  
146 species (DEP, DBP, and DEHP) were identified and quantified using authentic external  
147 standards and a fourth (DIBP) was identified referencing mass spectra available in the  
148 NIST/EPA/NIH Mass Spectral Library. Detailed descriptions of SV-TAG operation, including  
149 instrumental positioning, instrumental sampling schedules, potential biases, and method quality  
150 assurance, are contained within the SI.

151 **Supporting Measurements:** Metadata collected in the house were used during source  
152 apportionment. A series of SmartThings motion sensors (temperature/motion;  $n = 8$ ),  
153 SmartThings position sensors (door and window position/temperature;  $n = 34$ ), SmartThings  
154 appliance sensors ( $n = 5$ ), Netatmo weather stations (temperature/relative  
155 humidity/pressure/noise/CO<sub>2</sub>;  $n = 10$ ), and HOBO™ sensors (temperature/humidity;  $n = 10$ )  
156 were used to characterize household state, indoor environmental parameters, and occupant  
157 activities. In this report, “indoor air temperature” refers to the temperature measured in the  
158 family room. Temperature sensors throughout the house strongly covary with the house heating  
159 cycle with small differences observed between main living spaces and the hallway. Occupants  
160 also kept detailed activity logs recording the timing of their presence/absence within the house  
161 and general activities, including cooking, cleaning, and sleeping. A Grimm 11-A aerosol

162 spectrometer sampled continuously to quantify particle number concentrations in 31 diameter  
163 bins between 0.25 and 32  $\mu\text{m}$ . Mass concentrations were calculated using an assumed particle  
164 density of 1.67  $\text{g}/\text{cm}^3$  based on densities commonly used in the literature for characterizing  
165 ambient  $\text{PM}_{2.5}$ .<sup>64, 65</sup>

### 166 **3 RESULTS AND DISCUSSION**

167 Airborne concentrations of four phthalates (DEP, DIBP, DBP, and DEHP) were quantified with  
168 hourly time resolution throughout the normally occupied (Dec 16-21) and vacant (Dec 22-27)  
169 periods. Key characteristics of these phthalates and overall measurement results are summarized  
170 in Table 1. Other phthalates commonly reported in indoor air studies — including DMP, BBzP,  
171 DINP, and diisodecyl phthalate (DIDP) — were not identifiable above the background  
172 chromatographic signal, suggesting that their concentrations were much lower than those of the  
173 four reported phthalates. The three higher-vapor pressure phthalates, DEP, DIBP, and DBP, were  
174 present at median concentrations of 196  $\text{ng}/\text{m}^3$ , 133  $\text{ng}/\text{m}^3$ , and 93  $\text{ng}/\text{m}^3$ , respectively, for the  
175 occupied period. These concentrations are generally consistent with past surveys of indoor  
176 environments; for example, median concentrations of DEP (330, 590, 180;  $\text{ng}/\text{m}^3$ ), DIBP (130,  
177 N/A, N/A;  $\text{ng}/\text{m}^3$ ), and DBP (140, 220, 310;  $\text{ng}/\text{m}^3$ ) were reported in surveys of (1) northern  
178 California residences, (2) Cape Cod MA residences, and (3) Boston MA indoor environments,  
179 respectively.<sup>1,22,66</sup>

180 Throughout the occupied period, concentrations of higher vapor pressure phthalates displayed  
181 remarkably small temporal variance. Maximum and minimum concentrations of DIBP and DBP  
182 differed by  $\leq 32\%$  from the mean ( $\text{RSD} \leq 11\%$ ), and concentrations of DEP fluctuated by no  
183 more than 47% ( $\text{RSD} = 15\%$ ). In contrast, indoor concentrations of DEHP were highly variable,  
184 ranging from 1.6 to 112  $\text{ng}/\text{m}^3$  during the occupied period ( $\text{RSD} = 183\%$ ) and from 2.3 to 8.8



185 ng/m<sup>3</sup> during the vacant period (RSD = 34%). The median DEHP concentration during the  
186 occupied period (4 ng/m<sup>3</sup>) was considerably lower than median residential concentrations  
187 reported in the surveys mentioned previously (77 ng/m<sup>3</sup>, 68 ng/m<sup>3</sup>, N/A).

188 In a recent study of the dynamic behavior of volatile organic compounds in an occupied  
189 residence, Liu et al. used measured mean-to-median ratios (MMR) to classify indoor species  
190 emissions as being primarily from static contents (MMR < 1.06) or primarily related to episodic  
191 occupant activities (MMR > 1.5).<sup>67</sup> In Table 1, we show that MMR < 1.06 for all three higher  
192 volatility phthalates, during both the occupied and unoccupied periods. These low values are  
193 strongly suggestive of the importance of ongoing emissions from static sources in the residence.  
194 In contrast, for DEHP during the occupied period, MMR = 2.1, indicating the importance of  
195 episodic events controlling the release of DEHP into indoor air.

196 Concentrations of DEP, DIBP, and DBP were significantly higher indoors than outdoors at all  
197 times. On average, phthalate concentrations were 3 times higher indoors than outdoors for DEP  
198 and 3.5 times higher for DBP and DIBP. Average concentrations of DEHP during the occupied  
199 period were 2.5 times higher indoors than outdoors, and were roughly equivalent between the  
200 indoors and outdoors during the vacant period. Outdoor time series for the analysis periods are  
201 displayed in Figures S3 and S4.

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207 **Table 1:** Characteristics of observed phthalate species along with major measurement results.<sup>a</sup>

	<b>DEP</b> diethyl phthalate	<b>DIBP</b> diisobutyl phthalate	<b>DBP</b> dibutyl phthalate	<b>DEHP</b> di-2-ethylhexyl phthalate
<b>Log Saturation Vapor Pressure<sup>b</sup></b>	-6.83	-8.30	-8.47	-11.85
<b>Log <math>K_{oa}</math><sup>b</sup></b>	8.21	9.62	9.83	12.89
<i>Properties</i> <b>CAS Number</b>	84-66-2	84-69-5	84-74-2	117-81-7
<b>Chemical Formula</b>	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>
<b>Molecular Weight (g/mol)</b>	222.24	278.35	278.35	390.56
<b>Occupied Concentration</b>	201 ± 30	133 ± 15	91 ± 8	9 ± 16
<b>Mean-to-median Ratio</b>	1.03	1.00	0.99	2.13
<i>Indoor</i> <b>Vacant Concentration</b>	200 ± 16	135 ± 17	93 ± 10	4.1 ± 1.4
<b>Mean-to-median Ratio</b>	1.01	1.01	1.00	1.15
<b>Occupied <math>F_p</math></b>	0.05 ± 0.03	0.12 ± 0.01	0.16 ± 0.04	0.74 ± 0.22
<b>Vacant <math>F_p</math></b>	0.04 ± 0.01	0.11 ± 0.01	0.14 ± 0.02	0.68 ± 0.17
<b>Occupied Concentration</b>	36 ± 21	44 ± 10	31 ± 5	3.4 ± 0.4
<i>Outdoor</i> <b>Vacant Concentration</b>	54 ± 17	45 ± 6	32 ± 4	3.9 ± 0.8
<b>Occupied <math>F_p</math></b>	0.16 ± 0.08	0.19 ± 0.03	0.21 ± 0.04	0.79 ± 0.18
<b>Vacant <math>F_p</math></b>	0.11 ± 0.02	0.16 ± 0.02	0.19 ± 0.02	0.59 ± 0.20

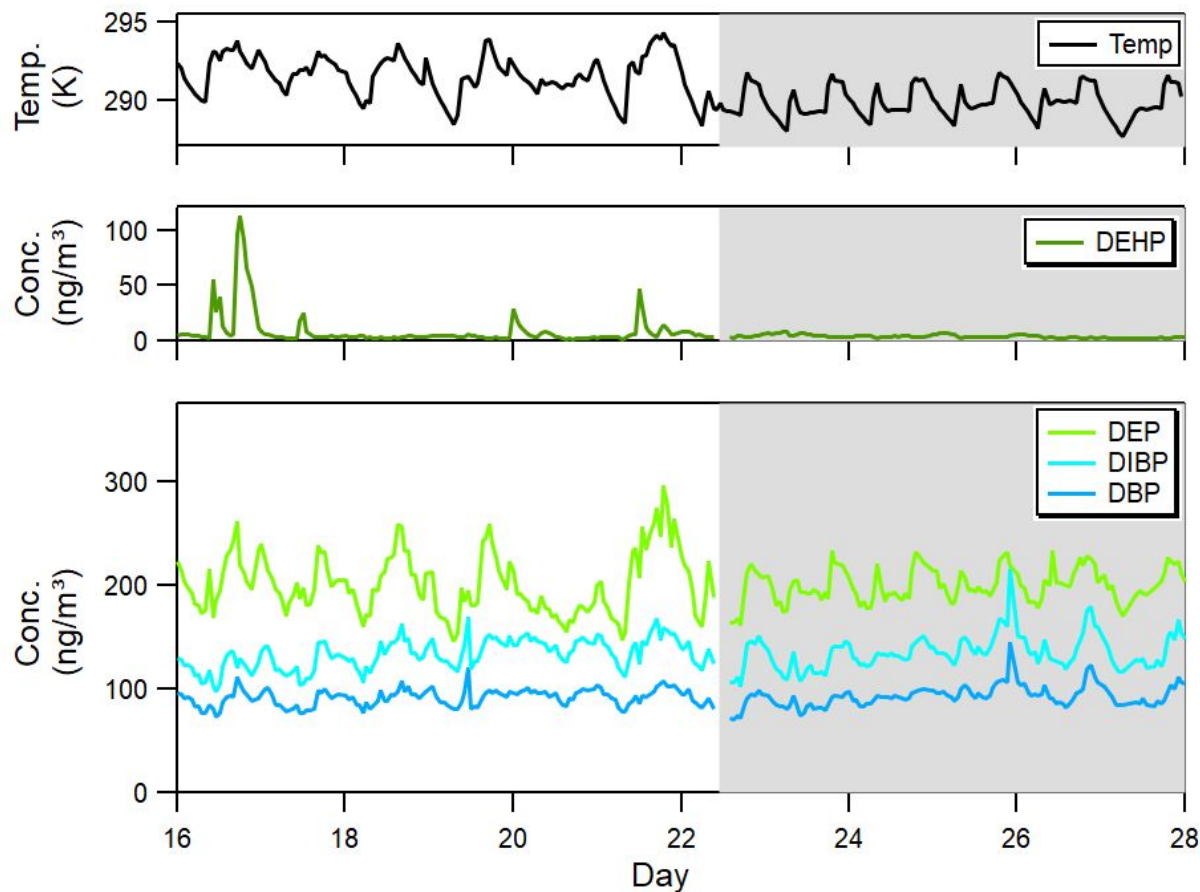
208 <sup>a</sup> All values are reported as mean ± standard deviation. Total (gas-plus-particle) concentrations are reported in  
 209 ng/m<sup>3</sup>. Fraction in particle phase ( $F_p$ ) is defined as the measured SVOC concentration associated with  
 210 particles divided by the total (gas-plus-particle) concentration. Mean  $F_p$  is reported as the average of  
 211 calculated values in the analysis window. Variability of  $F_p$  is reported as the standard deviation of the  
 212 population.

213 <sup>b</sup> Phthalate saturation vapor pressures vary by orders of magnitude among published measurements, but  
 214 generally decrease with increasing molecular weight. Values of the saturation vapor pressure in atm and  
 215 the octanol-air partition coefficient ( $K_{oa}$ ) as determined by theory are reported by Salthammer et al. at T =  
 216 298 K.<sup>68</sup>

217 **Time-Varying Phthalate Concentrations:** Figure 1 presents time series of phthalate  
218 concentrations and indoor air temperature. Diel plots of concentrations and temperature are  
219 shown in Figures S5 and S6. Concentrations of the primarily gaseous species (DEP, DIBP, and  
220 DBP) are characterized by a stable background with small perturbations associated with the  
221 indoor air temperature. Temperature profiles were regulated by wintertime home heating applied  
222 in mornings (6:45-7:15 AM) and evenings (5:45-10 PM) and, accordingly, DEP, DIBP, and DBP  
223 concentrations were higher on average during the warmer waking hours and lower during cooler  
224 sleeping hours. By contrast, concentrations of DEHP were much lower at baseline levels but  
225 exhibited substantial episodic enhancements during the occupied period. Multiple factors are  
226 expected to influence indoor phthalate concentrations. Among these are ongoing background  
227 emissions from static building materials and furnishings, episodic primary emissions from  
228 product usage, and dynamic phase-partitioning flows between indoor air and reservoirs including  
229 surface films and dust. Reversible sorptive interactions would be sensitive to dynamic changes in  
230 physical conditions, such as temperature and airborne particle concentrations, which would alter  
231 equilibrium partitioning between condensed and gaseous phases. Static emissions may contribute  
232 to a stable background, whereas episodic emissions of sufficient strength would be readily  
233 apparent from the time series of concentrations. Cosmetics, personal care products and  
234 medication are commonly reported sources of DEP, DIBP, and DBP.<sup>31, 37-40</sup> Strikingly, although  
235 multiple residents applied multiple personal care products throughout the campaign, no episodic  
236 concentration enhancements were observed for the three higher volatility phthalates.

237 SVOCs may interact with the envelope of household occupants at meaningful rates, such as  
238 during uptake on clothing or dermal absorption.<sup>48</sup> However, no associations were observed  
239 between occupancy and DEP concentrations. Weak associations between (increased) occupancy

240 and (decreased) concentrations of two phthalates, DIBP and DBP, were observed during the  
241 occupied period. (Figure S2).



242  
243 **Figure 1:** Total (gas-plus-particle) concentration time series of four phthalates over the occupied  
244 (left) and vacant (right, in gray) periods. Indoor air temperature is displayed in the upper panel.  
245 The horizontal axis is labeled with day of the month, December 2017.

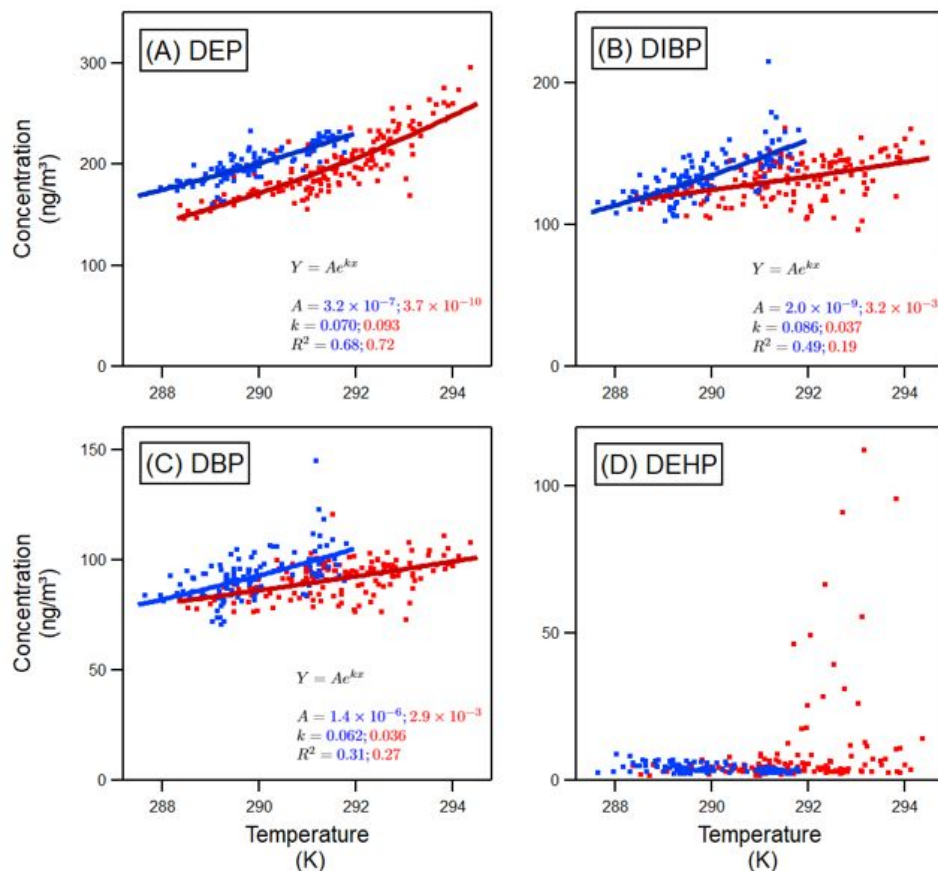
246  
247 **Temperature and Surface-Air Partitioning:** The hourly-averaged concentrations of the four  
248 measured phthalates are compared with indoor air temperature in Figure 2. The extent to which  
249 concentrations correlate with temperature diminishes with increasing molecular weight and

250 decreasing vapor pressure. Specifically, DEP concentrations exhibited strong temperature  
251 dependence during both the vacant and occupied periods, whereas DBP and DIBP concentrations  
252 exhibited only moderate temperature dependence. Average DEP concentrations were essentially  
253 equivalent between the occupied (201 ng/m<sup>3</sup>) and vacant (200 ng/m<sup>3</sup>) periods and strongly  
254 correlated with the house heating cycle. Overall, however, indoor air temperatures were slightly  
255 colder (~2 K) during the vacant period than the occupied period. It is possible that the measured  
256 air temperature was not fully representative of reservoir surface temperatures throughout the  
257 residence and that the air-surface temperature relationship was different between occupied and  
258 vacant periods.

259 Conversely, DEHP was characterized by a low baseline concentration punctuated by episodic  
260 spikes unrelated to temperature. It is well known that the emissions of DEHP, which can be a  
261 major constituent of certain types of materials such as vinyl flooring, increase strongly as  
262 temperature increases.<sup>46</sup> Remarkably, airborne DEHP concentrations displayed no observable  
263 correlations with temperature in the occupied period in this study. Furthermore, concentrations  
264 were weakly anticorrelated with temperature during the vacant period. Evidence suggests that  
265 airborne DEHP, which is primarily a particle-phase compound, was effectively removed by  
266 filtration during the morning and evening house-heating intervals (Figure S6).

267 Observed concentrations of DEP, DIBP, and DBP, were several orders of magnitude below their  
268 respective gas-phase saturation concentrations. DEHP was roughly one order of magnitude  
269 below its gas-phase saturation concentration. (Vapor pressure values are as reported in  
270 Salthammer et al.; substantial variation in vapor pressures exists throughout the literature.<sup>68</sup>)  
271 Interactions between organic surface films and the bulk air may influence airborne SVOC  
272 concentrations and these interactions have been modeled using octanol-air partition

273 coefficients.<sup>69</sup> Observed median concentrations of each phthalate species strongly correlate with  
274 the octanol-air partition coefficient (log-log plot,  $R^2 = 0.94$ , Figure S7), a parameter describing  
275 the strength of interactions between air and a model organic film. Furthermore, the dynamics  
276 associated with the observed heating cycle may be tied to thermodynamic changes in the octanol-  
277 air partition coefficient. Temperature dependence of the saturation vapor pressure, which is  
278 anticorrelated with the octanol-air partition coefficient, has been experimentally determined for  
279 DIBP and DBP.<sup>70</sup> In Figure S8, the concentrations of DIBP and DBP are plotted against their  
280 saturation vapor pressures as a function of indoor air temperature, revealing a strong positive  
281 correlation ( $R^2 = 0.71$ ). Together, these factors suggest that substantial condensed-phase  
282 reservoirs exist throughout the residence and that  $K_{oa}$  could be a key controlling variable related  
283 to both dynamics and observed airborne concentrations with additional contributions possible  
284 from static sources. Additionally, these factors suggest that the decreasing abundance of larger  
285 phthalate homologues ( $C_{DEP} > C_{DIBP} > C_{DBP} > C_{DEHP}$ ) may be coupled to their physical  
286 parameters such as their respective vapor pressures and octanol-air partition coefficients.



287

288 **Figure 2:** Total (gas-plus-particle) indoor-air concentrations of DEP, DIBP, DBP, and DEHP  
 289 versus temperature. Data are differentiated by color between the occupied (red) and vacant (blue)  
 290 periods, and regression lines correspond to an exponential fit. Units of measure on the fit  
 291 parameters are inverse temperature for  $k$  (1/K) and concentration for  $A$  (ng/m<sup>3</sup>).

292

293 **Particle Mass Concentration Influences DEHP Airborne Abundance:** Indoor particle mass  
 294 concentrations strongly correlated with total (gas-plus-particle) DEHP concentrations during the  
 295 vacant and occupied periods. Occupant activities like cooking can markedly influence indoor  
 296 particle concentration, composition and size distribution. Particle resuspension also can occur  
 297 during occupant activities, but this process is more important for coarse particles and less

298 important for particles smaller than 2.5  $\mu\text{m}$  that are sampled by SV-TAG.<sup>71</sup> The effects of  
299 occupant-associated particle sources are explored in Figure 3, which displays DEHP  
300 concentrations against PM<sub>2.5</sub> concentration and activity type during the occupied period.  
301 Notwithstanding diversity among particle sources, a linear relationship between particle mass  
302 concentration and total airborne phthalate concentrations is observed with DEHP accounting for  
303 about 0.3% of indoor PM<sub>2.5</sub> by mass. DEHP concentrations are strongly associated with particle  
304 emission events from cooking. The absence of cooking events over the vacant period affected  
305 average DEHP concentrations. While concentrations of DEP, DIBP, and DBP were similar  
306 between the occupied and vacant periods, the average concentration of DEHP over the occupied  
307 period was nearly two times greater than during the vacant period.

308 It has been demonstrated in both modeling and chamber studies that the presence of airborne  
309 particles can enhance DEHP emissions from surfaces.<sup>51,72</sup> Particles enhance surface mass transfer  
310 by increasing the gas-phase concentration gradient in the near-surface boundary layer. Particles  
311 act as an airborne sink, sorbing SVOCs from the gas-phase, thereby depleting gas-phase SVOCs  
312 in the bulk air and effectively increasing SVOC flux from surfaces. Similarly, total airborne  
313 concentrations of species with high  $K_p$  values are expected to increase with particle mass  
314 concentration, with minimal effect on low  $K_p$  species that are predominantly in the gas-phase.

315 It is worthwhile to consider whether direct cooking emissions of DEHP might account for  
316 episodic concentration enhancements. Food-borne DEHP has been reported at low ppb to low  
317 ppm concentrations. When oily food has been stored in jars with PVC gaskets, DEHP can  
318 approach upper ppm concentrations.<sup>73</sup> We considered a hypothetical emission event where food-  
319 borne DEHP was fully transferred into residential air and assumed a food-borne phthalate  
320 concentration of 10 mg/kg, a typical upper bound. Assuming one kg of food cooked, a cooking



321 event could release an upper bound of 10 mg of DEHP from food, which, when diluted  
322 throughout the house volume of 380 m<sup>3</sup>, would yield a transient peak DEHP concentration of up  
323 to 25 ng/m<sup>3</sup>. However, this value is below the measured concentrations associated with many  
324 cooking events, suggesting that direct DEHP emission from food was not a dominant contributor  
325 to airborne DEHP enhancements during major source events. Instead, we infer that the increased  
326 airborne particle concentrations enhanced the net rate of transfer of DEHP from static sources  
327 and/or from indoor surface films to indoor air.

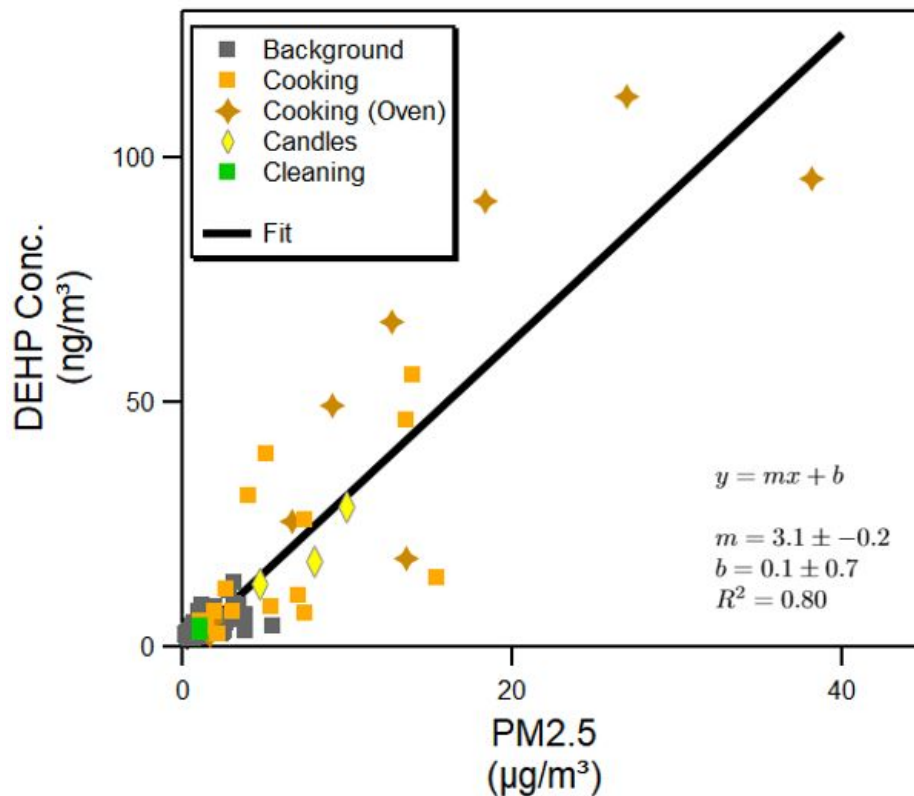
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334 **Figure 3:** Total (gas-plus-particle) DEHP concentrations during the occupied period are  
335 compared against PM2.5 concentration. Concurrent indoor activities with the potential to  
336 influence airborne SVOC concentrations are highlighted: cooking, candle combustion, and  
337 cleaning. Units of measure on the fit parameters are  $\text{ng}/\mu\text{g}$  (parts per thousand) for the slope,  $m$ ,  
338 and  $\text{ng}/\text{m}^3$  for the intercept,  $b$ .

339

340 PM2.5 concentrations strongly correlated with airborne DEHP concentrations under vacant  
341 conditions (Figure 4). Total (gas-plus-particle) concentrations of DEHP were comparable  
342 between the indoors and outdoors over the vacant period (Figure S4). However, outdoor DEHP-  
343 bearing particles are not expected to penetrate the building envelope with full efficiency. For the  
344 duration of the vacant period, indoor PM2.5 was always less than or (approximately) equal to

345 outdoor PM<sub>2.5</sub> concentrations with an average indoor:outdoor particle mass ratio of 1:4 for the  
346 duration of the vacant period. Because no occupants were present and because indoor particles  
347 were intermittently removed in association with the filter in the house's forced air heating  
348 system, nearly all indoor particles are believed to have originated from outdoor intrusion through  
349 the building envelope. Over the vacant period, outdoor DEHP constituted 0.10% of outdoor  
350 PM<sub>2.5</sub> by mass on average. Together, these observations suggest that particulate matter entering  
351 the house rapidly acquires DEHP from indoor dust, surfaces, and the gas-phase such that DEHP  
352 comprises 0.24% of indoor PM<sub>2.5</sub> by mass with contributions from both indoor and outdoor  
353 sources. Similar relations between airborne DEHP concentrations and PM<sub>2.5</sub> are observed  
354 during the occupied period (event-driven spikes excluded), albeit with greater variability.

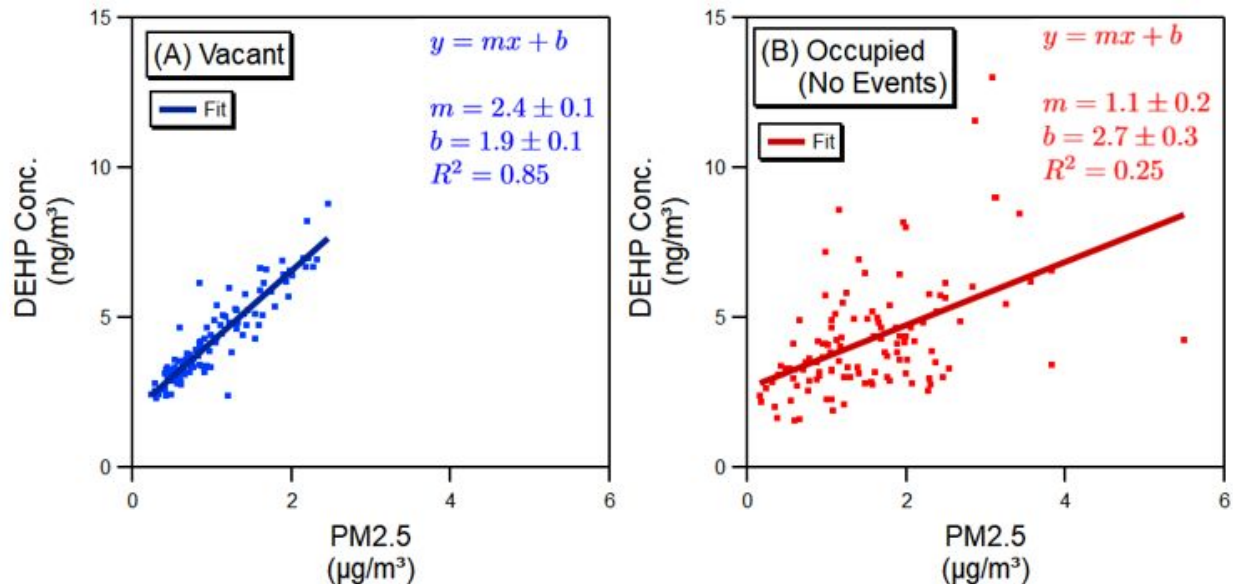
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361 **Figure 4:** The gas-plus-particle concentration of DEHP is compared against PM2.5  
362 concentration during the vacant period (A) and the occupied period when no cleaning, cooking,  
363 or combustion events were occurring (B). Units of measure on the fit parameters are ng/µg (parts  
364 per thousand) for the slope,  $m$ , and ng/m<sup>3</sup> for the intercept,  $b$ .

365

366 **Gas-Particle Partitioning:** The higher vapor-pressure phthalates (DEP, DBP, DIBP) were  
367 present primarily in the gas-phase (Table 1). Their particle fractions, while small, consistently  
368 increased as their molecular size and associated octanol-air partition coefficients increased ( $F_p$   
369 values follow this order: DEP < DBP < DIBP). The particle-phase fraction of these species was  
370 largely independent of particle mass concentration and temperature in the ranges encountered in  
371 the studied residence. Observed particle fractions for DEP, DIBP, and DBP (5%, 12%, 16%,)  
372 were qualitatively similar yet quantitatively higher than those estimated by Weschler and  
373 Nazaroff who reported expected particle fractions to be 0%, 3%, and 5%, respectively.<sup>49</sup>

374 Increasing particle mass concentration can drive gas-particle partitioning towards the particle  
375 phase. Airborne gas-particle partitioning of DEHP is associated with both PM<sub>2.5</sub> concentration  
376 and indoor air temperature as revealed in Figure 5. At PM<sub>2.5</sub> concentrations above 3  $\mu\text{g}/\text{m}^3$ ,  
377 airborne DEHP concentrations were predominantly in the particle phase. Similar effects are  
378 observable with cooler temperatures promoting partitioning into particles and an increased  $F_p$ .

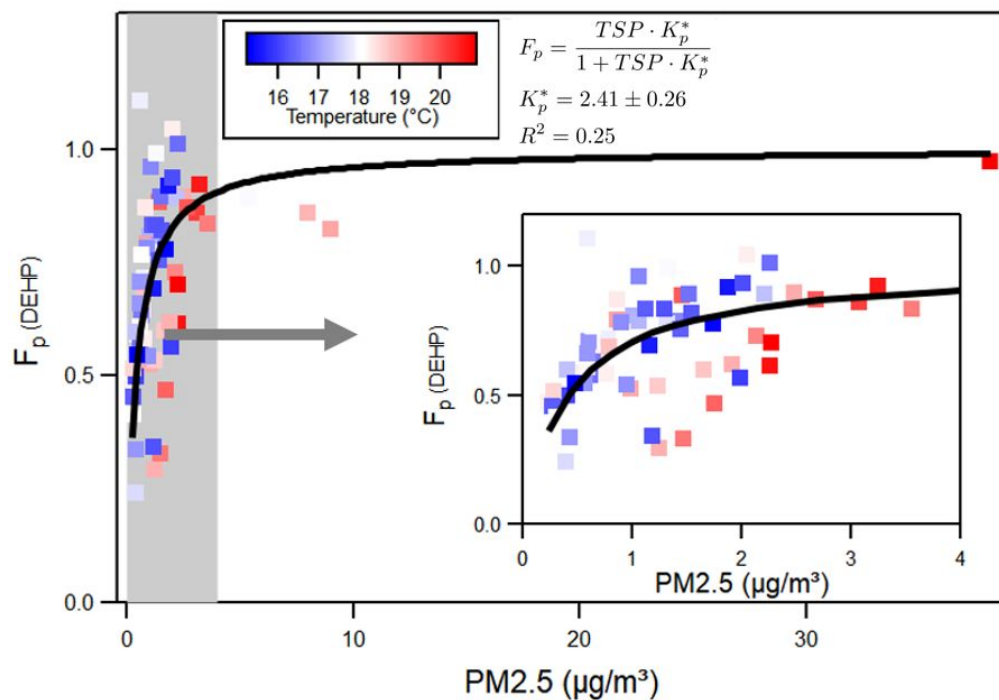
379 Using the model described in Equation 2 an apparent partition coefficient  $K_p^*$  was evaluated to be  
380  $2.4 \pm 0.3 \text{ m}^3/\mu\text{g}$  under observed conditions. This empirically-derived partition coefficient is  
381 affected by assumptions about equilibrium conditions, the temperature, and by the experimental  
382 approach. Time-scales to approach gas-particle phase equilibrium vary depending on  $K_{oa}$  values  
383 and particle size.<sup>48,50</sup> For DEHP, gas-particle equilibration time scales may approach hundreds of  
384 hours for particle diameters in the vicinity of 2.5  $\mu\text{m}$  and would be minutes to hours for particle  
385 sizes near 100 nm. Considering the residence's average air-exchange period of 2.2 h, the DEHP  
386 phase-partitioning system may be far from equilibrium for larger particles but is expected to be  
387 at or near equilibrium for smaller particles.<sup>48, 50, 54</sup> Experimentally, the  $F_p$  values were determined  
388 only for particles smaller than 2.5  $\mu\text{m}$ , the SV-TAG particle-size cutoff. In addition, the stated  
389 PM<sub>2.5</sub> concentrations do not include particles with diameters smaller than 250 nm that were not  
390 quantified by the Grimm 11-A OPC.

391 Using the van't Hoff equation, and assuming equilibrium conditions,  $K_p^*$  is expected to change  
392 by roughly 3 $\times$  over the observed indoor temperature range (288 – 294 K).<sup>74</sup> After normalizing  
393 each particle fraction measurement from the measured indoor air temperature to the standard  
394 state temperature, the best-estimate  $K_p^{*298}$  value at  $T = 298 \text{ K}$  is  $0.80 \pm 0.09 \text{ m}^3/\mu\text{g}$  (Figure S9).  
395 This value can be compared to the partition coefficient calculated using the model developed by  
396 Weschler and Nazaroff ( $3.2 \text{ m}^3/\mu\text{g}$ ), which assumed equilibrium conditions, a  $\log K_{oa}$  value of

397 12.9, a particle density of  $1 \times 10^6 \text{ g m}^{-3}$ , and a volume fraction of organic matter associated with  
398 airborne particles ( $f_{om\_part}$ ) of 0.4.<sup>49</sup> The particle partitioning coefficient determined from this  
399 field-monitoring campaign is larger than has been reported in laboratory studies where  $K_p =$   
400  $0.032 \text{ m}^3/\mu\text{g}$  for ammonium sulfate particles,  $0.23 \text{ m}^3/\mu\text{g}$  for oleic acid particles, and  $0.11 \text{ m}^3/\mu\text{g}$   
401 for squalene particles.<sup>51,70</sup> A recent theoretical prediction yielded  $K_p = 0.19 \text{ m}^3/\mu\text{g}$ .<sup>74</sup> Given the  
402 order of magnitude variability in  $K_p$  depending on literature source, particle composition, and  
403 ambient temperature, determinations of the apparent partition coefficient in real indoor  
404 environments are valuable. As the relative gas-particle abundance can influence consequent  
405 exposures and potential health risks, such observations and inferences are relevant for improving  
406 our understanding of the nature and significance of human phthalate encounters in indoor  
407 environments.

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410

411 **Figure 5:** The particle fraction of DEHP is compared against  $\text{PM}_{2.5}$  concentration, with points  
 412 colored by indoor air temperature. The lower right panel highlights the low  $\text{PM}_{2.5}$  concentration  
 413 region between 0 and 4  $\mu\text{g}/\text{m}^3$ .

414

415 **Implications:** Among the four quantified phthalates, concentrations of three higher-volatility  
 416 species (DEP, DIBP and DBP) were found to be influenced mainly by indoor air temperature,  
 417 whereas the lower volatility species (DEHP) varied with systematic and episodic indoor airborne  
 418 particle mass concentrations. Ultimately, factors observed to affect airborne phthalate  
 419 concentrations were indirectly related to human behavior. Spikes in DEHP concentrations were  
 420 associated with particles generated by episodic emission events related to occupant activities  
 421 such as stovetop cooking, oven usage, and candle combustion. Dynamic changes in gas-phase  
 422 phthalate concentrations largely followed the occupant-influenced indoor temperature cycle.  
 423 Overall gas-phase abundances may be related to factors external to the indoor temperature cycle

424 such as the octanol-air partition coefficient and the presence of static sources in the residence.  
425 Perturbations affecting DEHP concentrations were also observed in association with particle  
426 removal by filtration during the operation of the central forced-air heating system.

427 Increased understanding of the factors that control airborne phthalate concentrations is important  
428 to gain insight into human phthalate exposure. The complex partitioning behavior exhibited in  
429 the case of DEHP suggests that human exposure assessments relying on static measures of  
430 concentrations and gas-particle partitioning are incomplete. In this residence, increasing PM<sub>2.5</sub>  
431 concentrations from 0.5  $\mu\text{g}/\text{m}^3$  to 3  $\mu\text{g}/\text{m}^3$  could drive DEHP completely into the particle phase,  
432 thereby altering the inhalation mode of occupant exposure. This level of PM<sub>2.5</sub> perturbation was  
433 regularly encountered during cooking events. These results illustrate that variable particle mass  
434 concentrations may influence occupant uptake by altering both DEHP concentrations and gas-  
435 particle partitioning. This finding points to the potential utility of particle reduction techniques as  
436 a means of reducing indoor airborne exposure to low-volatility phthalates and related SVOCs.

437

438 **Supporting Information:** SV-TAG operation; QA/QC; association between occupancy and  
439 airborne phthalate concentrations; outdoor phthalate concentrations; diel concentration plots;  
440 comparison of phthalate abundance and  $K_{\text{oa}}$ ; comparison of phthalate abundance and vapor  
441 pressure; comparison of temperature-corrected DEHP  $F_p$  and particle mass loading

442

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