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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.[1-3] 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.[4-6] 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.[7,8]

44   Several known and suspected adverse health effects are associated with phthalate exposures,

45   including impaired reproductive development,[9,10] infertility,[11,12] asthma,[13,14] and obesity.[15,16]

46   Phthalates are industrially produced and utilized on large scales. Phthalates are found broadly

47   throughout the environment: in soil,[17,18] in sediment,[17,19] in wastewater,[17,20] in indoor and

48   outdoor air,[21,22] in the Arctic,[23] and in biota.[24,25] 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. [1,22,26]

51   The abundance of airborne indoor phthalates indicates potentially important contributions to

52   human exposure.[27] 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.[28-33]

59   Because, on average, people spend 90% of their time indoors and 60% of their time in their own

60   residence,[34-36] 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. [31, 37-40] 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.[41,42]

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.[26,43,44] 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.[32] 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%.[6] Qualitatively, these results corroborate findings from laboratory

77 studies.[45, 46]

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.[47] 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.[48-50]

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.[51] Similarly, Lazarov et al. demonstrated

90 that increased particle concentrations enhanced the emission rate of organophosphate flame

91 retardants from materials.[52] 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).[53]

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.[49] 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   ρ_{part} refers to the density of particles.

$$K_p = \frac{f_{om\_part} \times K_{oa}}{\rho_{part}}$$

99   **(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.

$$F_p = \frac{C_p}{C_p + C_g} = \frac{TSP \cdot K_P}{1 + TSP \cdot K_p}$$

103   **(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.[48]

108   This study presents a more detailed investigation of a subset of SVOCs reported by Kristensen et

109   al.[54] 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.[55-58] 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^2 (1970 ft^2) 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.[54] 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.[59-63] 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_2; $n = 10$), 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 μm. Mass concentrations were calculated using an assumed particle

164   density of 1.67 g/cm^3 based on densities commonly used in the literature for characterizing

165   ambient PM2.5.[64, 65]

3 RESULTS AND DISCUSSION

166

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 ng/m^3, 133 ng/m^3, and 93 ng/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; ng/m^3), DIBP (130,

177   N/A, N/A; ng/m^3), and DBP (140, 220, 310; ng/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. [1,22,66]

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 ≤ 32% from the mean (RSD ≤ 11%), and concentrations of DEP fluctuated by no

183   more than 47% (RSD = 15%). In contrast, indoor concentrations of DEHP were highly variable,

184   ranging from 1.6 to 112 ng/m^3 during the occupied period (RSD = 183%) and from 2.3 to 8.8

185   ng/m^3 during the vacant period (RSD = 34%). The median DEHP concentration during the

186   occupied period (4 ng/m^3) was considerably lower than median residential concentrations

187   reported in the surveys mentioned previously (77 ng/m^3, 68 ng/m^3, 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).[67] 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.[a]

|		**DEP** diethyl phthalate	**DIBP** diisobutyl phthalate	**DBP** dibutyl phthalate	**DEHP** di-2-ethylhexyl phthalate
Properties	**Log Saturation Vapor Pressure[b]**	-6.83	-8.30	-8.47	-11.85
	Log K_{oa}[b]	8.21	9.62	9.83	12.89
	CAS Number	84-66-2	84-69-5	84-74-2	117-81-7
	Chemical Formula	$C_{12}H_{14}O_4$	$C_{16}H_{22}O_4$	$C_{16}H_{22}O_4$	$C_{24}H_{38}O_4$
	Molecular Weight (g/mol)	222.24	278.35	278.35	390.56
Indoor	**Occupied Concentration**	201 ± 30	133 ± 15	91 ± 8	9 ± 16
	Mean-to-median Ratio	1.03	1.00	0.99	2.13
	Vacant Concentration	200 ± 16	135 ± 17	93 ± 10	4.1 ± 1.4
	Mean-to-median Ratio	1.01	1.01	1.00	1.15
	Occupied F_p	0.05 ± 0.03	0.12 ± 0.01	0.16 ± 0.04	0.74 ± 0.22
	Vacant F_p	0.04 ± 0.01	0.11 ± 0.01	0.14 ± 0.02	0.68 ± 0.17
Outdoor	**Occupied Concentration**	36 ± 21	44 ± 10	31 ± 5	3.4 ± 0.4
	Vacant Concentration	54 ± 17	45 ± 6	32 ± 4	3.9 ± 0.8
	Occupied F_p	0.16 ± 0.08	0.19 ± 0.03	0.21 ± 0.04	0.79 ± 0.18
	Vacant F_p	0.11 ± 0.02	0.16 ± 0.02	0.19 ± 0.02	0.59 ± 0.20

208   [a] All values are reported as mean ± standard deviation. Total (gas-plus-particle) concentrations are reported in

209   ng/m³. 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   [b] 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.[68]

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.[31, 37-40] 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.[48] 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).
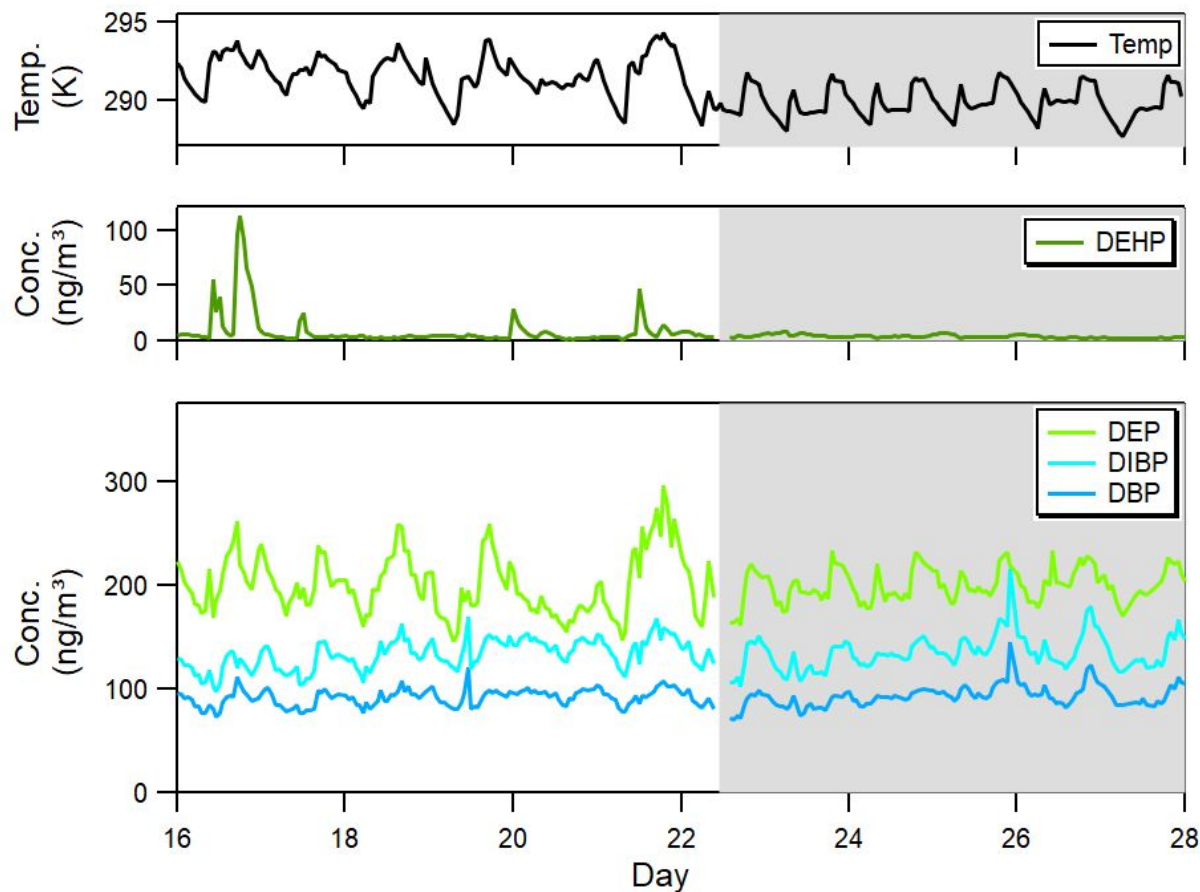
242

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^3) and vacant (200 ng/m^3) 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.[46] 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.[68])

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.[69] 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.[70] 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
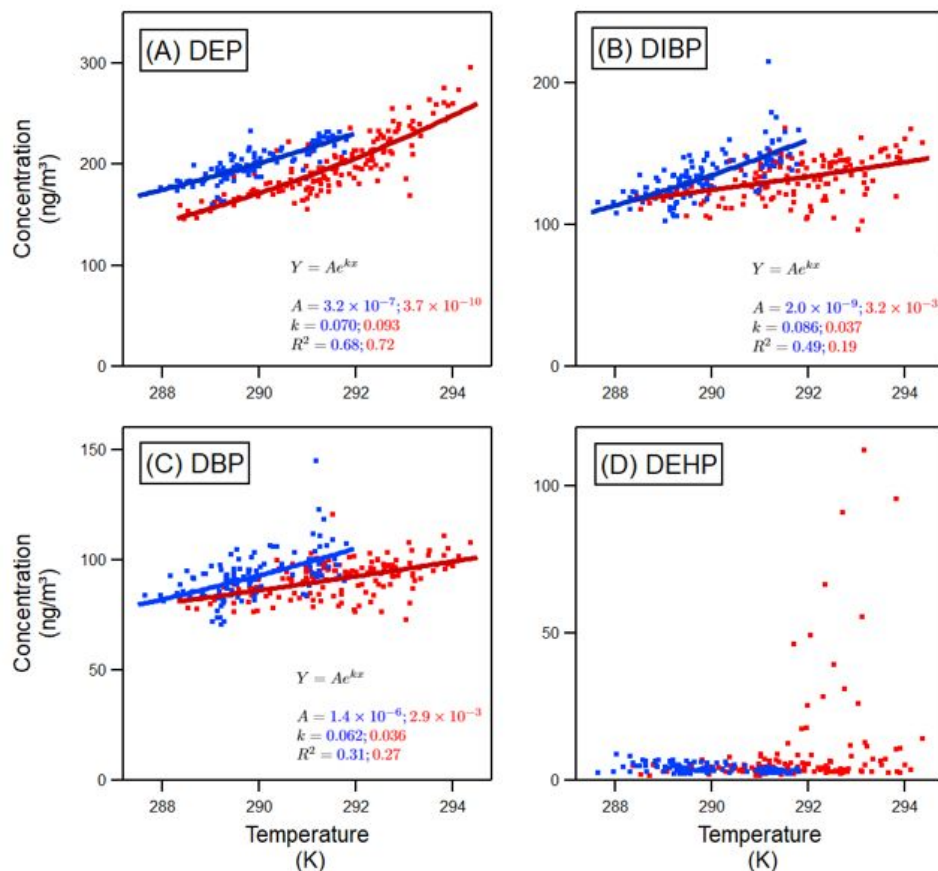
Figure 2: Total (gas-plus-particle) indoor-air concentrations of DEP, DIBP, DBP, and DEHP

versus temperature. Data are differentiated by color between the occupied (red) and vacant (blue)

periods, and regression lines correspond to an exponential fit. Units of measure on the fit

parameters are inverse temperature for k (1/K) and concentration for A (ng/m^3).

Particle Mass Concentration Influences DEHP Airborne Abundance: Indoor particle mass

concentrations strongly correlated with total (gas-plus-particle) DEHP concentrations during the

vacant and occupied periods. Occupant activities like cooking can markedly influence indoor

particle concentration, composition and size distribution. Particle resuspension also can occur

during occupant activities, but this process is more important for coarse particles and less

298   important for particles smaller than 2.5 μm that are sampled by SV-TAG.[71] The effects of

299   occupant-associated particle sources are explored in Figure 3, which displays DEHP

300   concentrations against PM2.5 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 PM2.5 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.[51,72] 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.[73] 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^3, would yield a transient peak DEHP concentration of up

323　　to 25 ng/m^3. 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
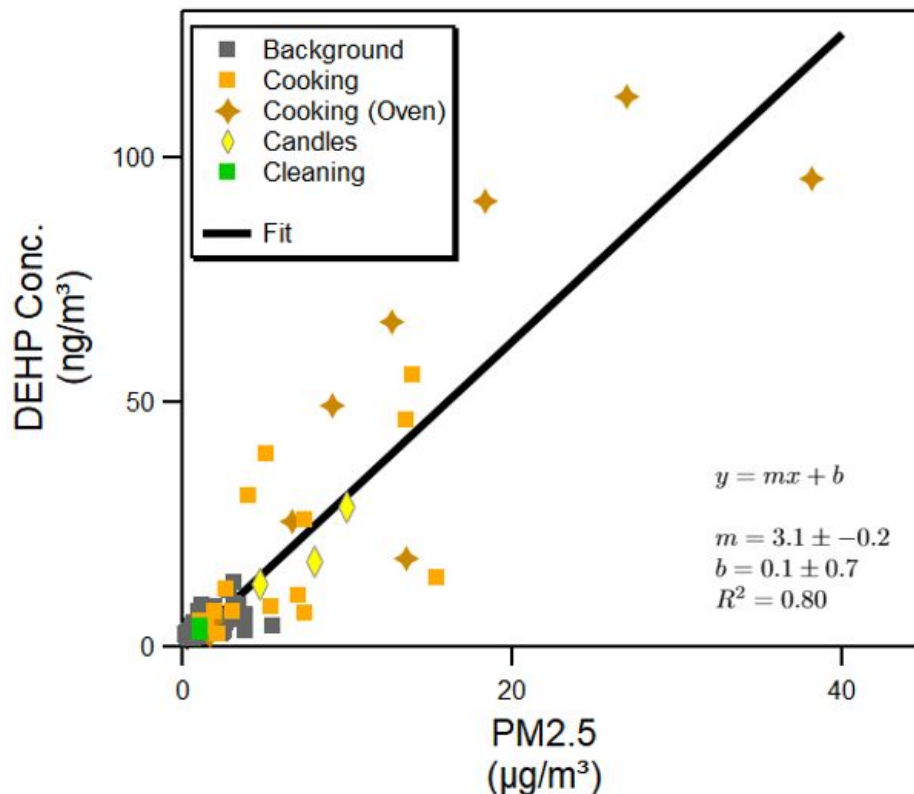
327　　and/or from indoor surface films to indoor air.

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Figure 3: Total (gas-plus-particle) DEHP concentrations during the occupied period are

compared against PM2.5 concentration. Concurrent indoor activities with the potential to

influence airborne SVOC concentrations are highlighted: cooking, candle combustion, and

cleaning. Units of measure on the fit parameters are ng/μg (parts per thousand) for the slope, *m*,

and ng/m³ for the intercept, *b*.

339

PM2.5 concentrations strongly correlated with airborne DEHP concentrations under vacant

conditions (Figure 4). Total (gas-plus-particle) concentrations of DEHP were comparable

between the indoors and outdoors over the vacant period (Figure S4). However, outdoor DEHP-

bearing particles are not expected to penetrate the building envelope with full efficiency. For the

duration of the vacant period, indoor PM2.5 was always less than or (approximately) equal to

345   outdoor PM2.5 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   PM2.5 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 PM2.5 by mass with contributions from both indoor and outdoor

353   sources. Similar relations between airborne DEHP concentrations and PM2.5 are observed

354   during the occupied period (event-driven spikes excluded), albeit with greater variability.
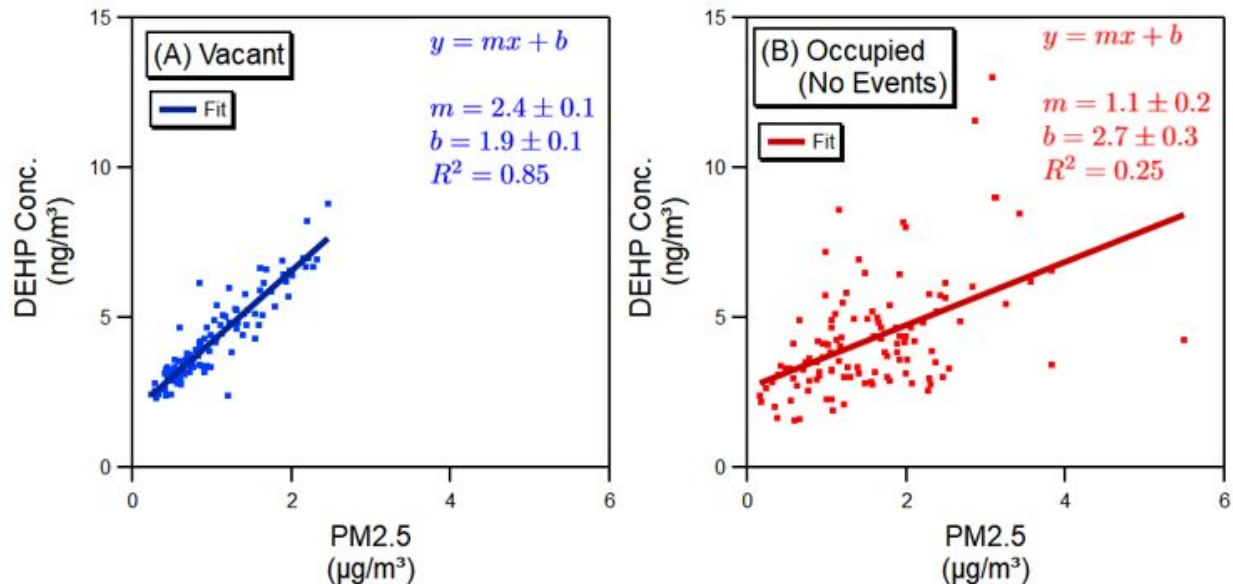
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361   **Figure 4:** The gas-plus-particle concentration of DEHP is compared against PM2.5

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/m³ 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.[49]

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 PM2.5 concentration

376   and indoor air temperature as revealed in Figure 5. At PM2.5 concentrations above 3 μg/m³,

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 ± 0.3 m³/μg 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. [48,50] For DEHP, gas-particle equilibration time scales may approach hundreds of

384   hours for particle diameters in the vicinity of 2.5 μm 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.[48, 50, 54] Experimentally, the F_p values were determined

388   only for particles smaller than 2.5 μm, the SV-TAG particle-size cutoff. In addition, the stated

389   PM2.5 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× over the observed indoor temperature range (288 – 294 K).[74] 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 $T = 298$ K is 0.80 ± 0.09 m³/μg (Figure S9).

395   This value can be compared to the partition coefficient calculated using the model developed by

396   Weschler and Nazaroff (3.2 m³/μg), which assumed equilibrium conditions, a log K_{oa} value of

397   12.9, a particle density of 1×10^6 g m^{-3}, and a volume fraction of organic matter associated with

398   airborne particles (f_{om_part}) of 0.4.[49] 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 m^3/µg for ammonium sulfate particles, 0.23 m^3/µg for oleic acid particles, and 0.11 m^3/µg

401   for squalene particles. [51,70] A recent theoretical prediction yielded $K_p = 0.19$ m^3/µg.[74] 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.

408

409

$$F_p = \frac{TSP \cdot K_p^*}{1 + TSP \cdot K_p^*}$$

$$K_p^* = 2.41 \pm 0.26$$

$$R^2 = 0.25$$

410
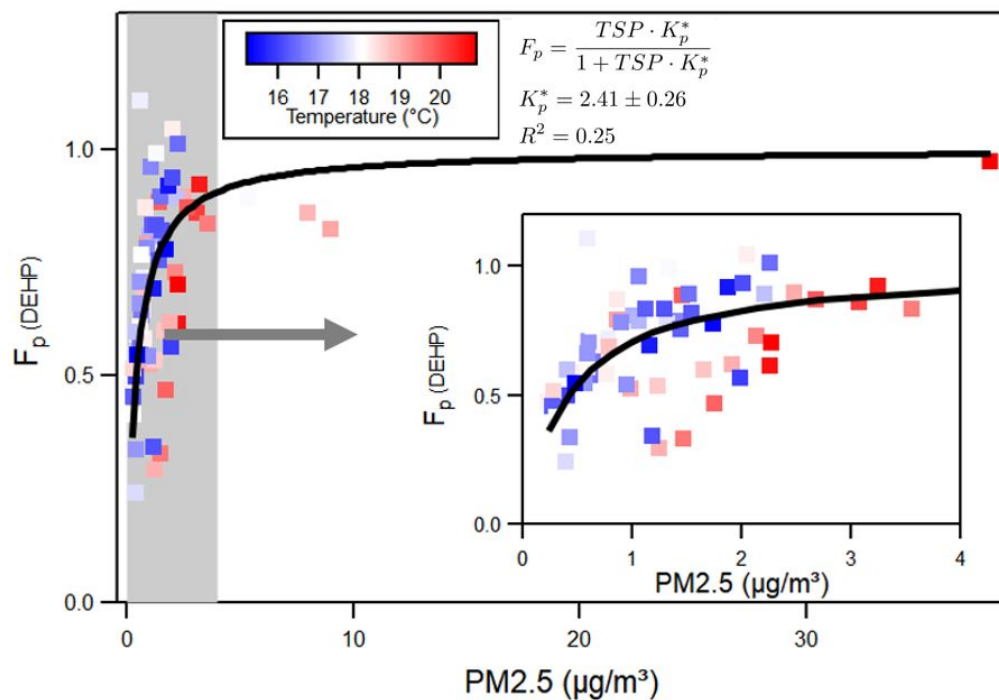
Figure 5: The particle fraction of DEHP is compared against PM2.5 concentration, with points

colored by indoor air temperature. The lower right panel highlights the low PM2.5 concentration

region between 0 and 4 μg/m³.

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Implications: Among the four quantified phthalates, concentrations of three higher-volatility

species (DEP, DIBP and DBP) were found to be influenced mainly by indoor air temperature,

whereas the lower volatility species (DEHP) varied with systematic and episodic indoor airborne

particle mass concentrations. Ultimately, factors observed to affect airborne phthalate

concentrations were indirectly related to human behavior. Spikes in DEHP concentrations were

associated with particles generated by episodic emission events related to occupant activities

such as stovetop cooking, oven usage, and candle combustion. Dynamic changes in gas-phase

phthalate concentrations largely followed the occupant-influenced indoor temperature cycle.

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 PM2.5

431 concentrations from 0.5 $\mu g/m^3$ to 3 $\mu g/m^3$ could drive DEHP completely into the particle phase,

432 thereby altering the inhalation mode of occupant exposure. This level of PM2.5 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_{oa}; comparison of phthalate abundance and vapor

441 pressure; comparison of temperature-corrected DEHP F_p and particle mass loading

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