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Characterizing Airborne Phthalate Concentrations and Dynamics in a Normally Occupied Residence

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ABSTRACT

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

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

1 INTRODUCTION

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

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

The abundance of airborne indoor phthalates indicates potentially important contributions to human exposure.[27] Ingestion, dermal uptake from direct contact, air-to-skin dermal absorption,

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

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

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

BBzP and DEHP, by 300%.[6] Qualitatively, these results corroborate findings from laboratory studies.[45, 46]

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

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

Weschler and Nazaroff described an equilibrium model of indoor SVOC partitioning between the gas phase and settled dust using the octanol-air partitioning coefficient (K_{oa}); that model can 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.

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

99

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.

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

103

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

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

2 MATERIALS AND METHODS

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

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

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

Supporting Measurements: Metadata collected in the house were used during source apportionment. A series of SmartThings motion sensors (temperature/motion; $n = 8$), SmartThings position sensors (door and window position/temperature; $n = 34$), SmartThings appliance sensors ($n = 5$), Netatmo weather stations (temperature/relative humidity/pressure/noise/CO_2; $n = 10$), and HOBO™ sensors (temperature/humidity; $n = 10$) were used to characterize household state, indoor environmental parameters, and occupant activities. In this report, "indoor air temperature" refers to the temperature measured in the family room. Temperature sensors throughout the house strongly covary with the house heating cycle with small differences observed between main living spaces and the hallway. Occupants also kept detailed activity logs recording the timing of their presence/absence within the house and general activities, including cooking, cleaning, and sleeping. A Grimm 11-A aerosol

spectrometer sampled continuously to quantify particle number concentrations in 31 diameter bins between 0.25 and 32 μm. Mass concentrations were calculated using an assumed particle density of 1.67 g/cm^3 based on densities commonly used in the literature for characterizing ambient PM2.5.[64, 65]

3 RESULTS AND DISCUSSION

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

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

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

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

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

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

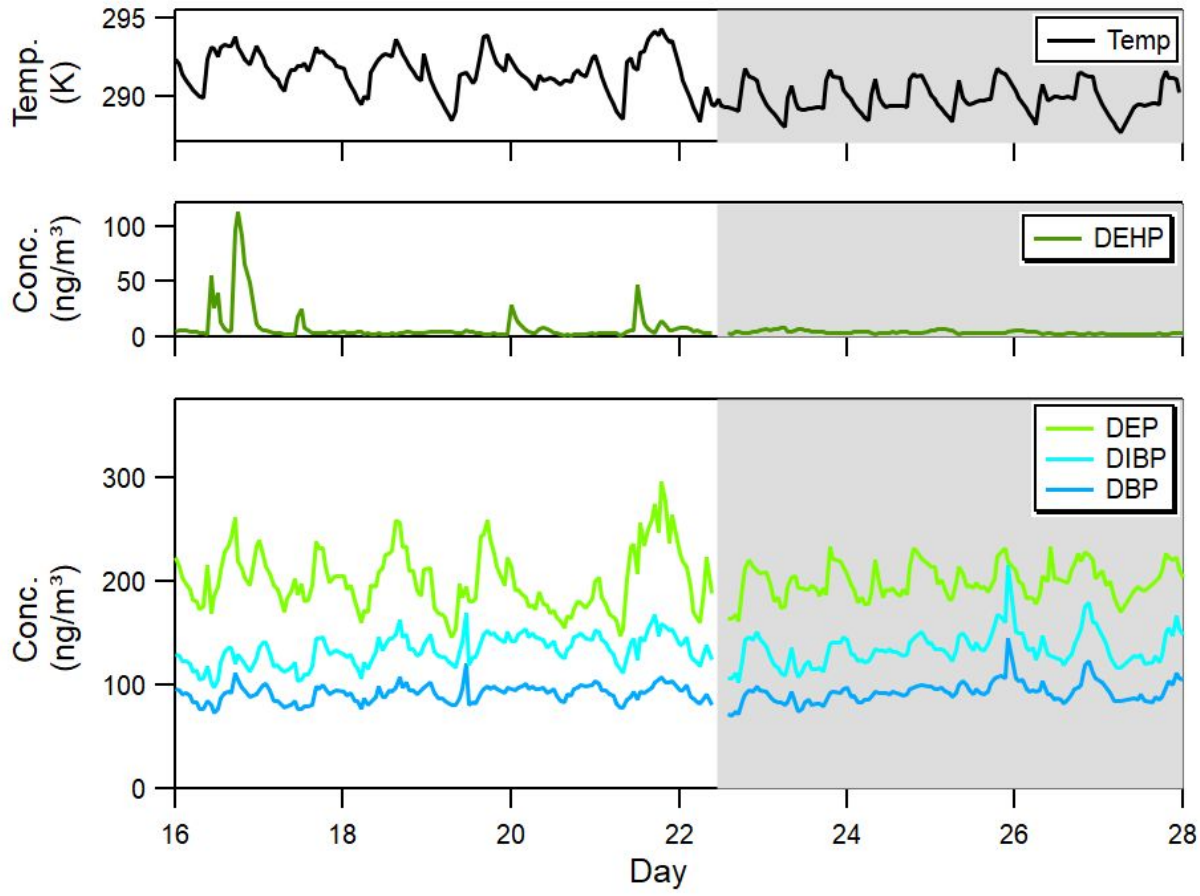
[a] All values are reported as mean ± standard deviation. Total (gas-plus-particle) concentrations are reported in ng/m^3. Fraction in particle phase (F_p) is defined as the measured SVOC concentration associated with particles divided by the total (gas-plus-particle) concentration. Mean F_p is reported as the average of calculated values in the analysis window. Variability of F_p is reported as the standard deviation of the population.

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

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

SVOCs may interact with the envelope of household occupants at meaningful rates, such as during uptake on clothing or dermal absorption.[48] However, no associations were observed 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

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

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

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

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

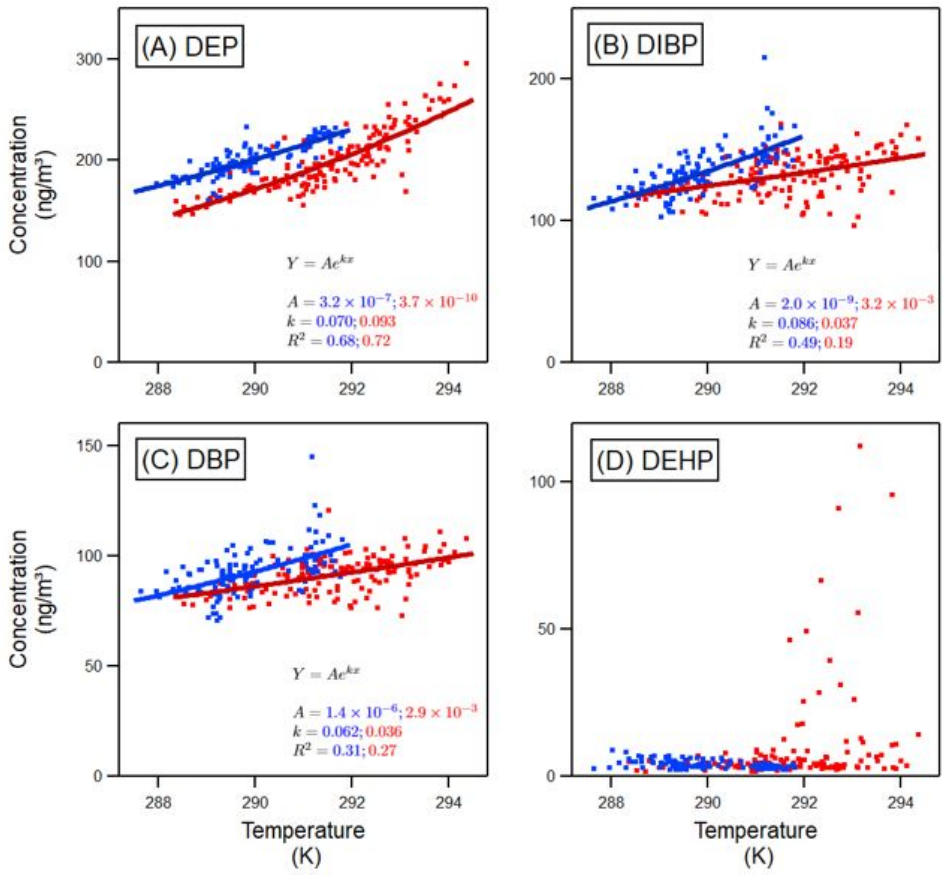


Figure 2: Total (gas-plus-particle) indoor-air concentrations of DEP, DIBP, DBP, and DEHP versus temperature. Data are differentiated by color between the occupied (red) and vacant (blue) periods, and regression lines correspond to an exponential fit. Units of measure on the fit parameters are inverse 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

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

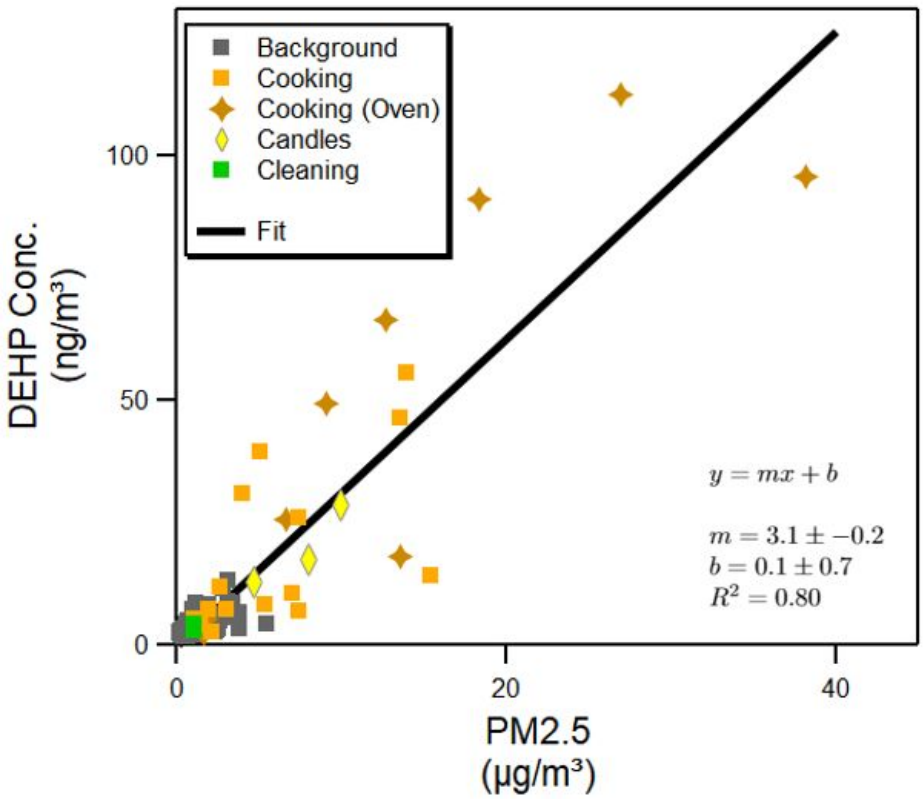


Figure 3: Total (gas-plus-particle) DEHP concentrations during the occupied period are compared against PM2.5 concentration. Concurrent indoor activities with the potential to influence airborne SVOC concentrations are highlighted: cooking, candle combustion, and cleaning. Units of measure on the fit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

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

outdoor PM2.5 concentrations with an average indoor:outdoor particle mass ratio of 1:4 for the duration of the vacant period. Because no occupants were present and because indoor particles were intermittently removed in association with the filter in the house's forced air heating system, nearly all indoor particles are believed to have originated from outdoor intrusion through the building envelope. Over the vacant period, outdoor DEHP constituted 0.10% of outdoor PM2.5 by mass on average. Together, these observations suggest that particulate matter entering the house rapidly acquires DEHP from indoor dust, surfaces, and the gas-phase such that DEHP comprises 0.24% of indoor PM2.5 by mass with contributions from both indoor and outdoor sources. Similar relations between airborne DEHP concentrations and PM2.5 are observed during the occupied period (event-driven spikes excluded), albeit with greater variability.

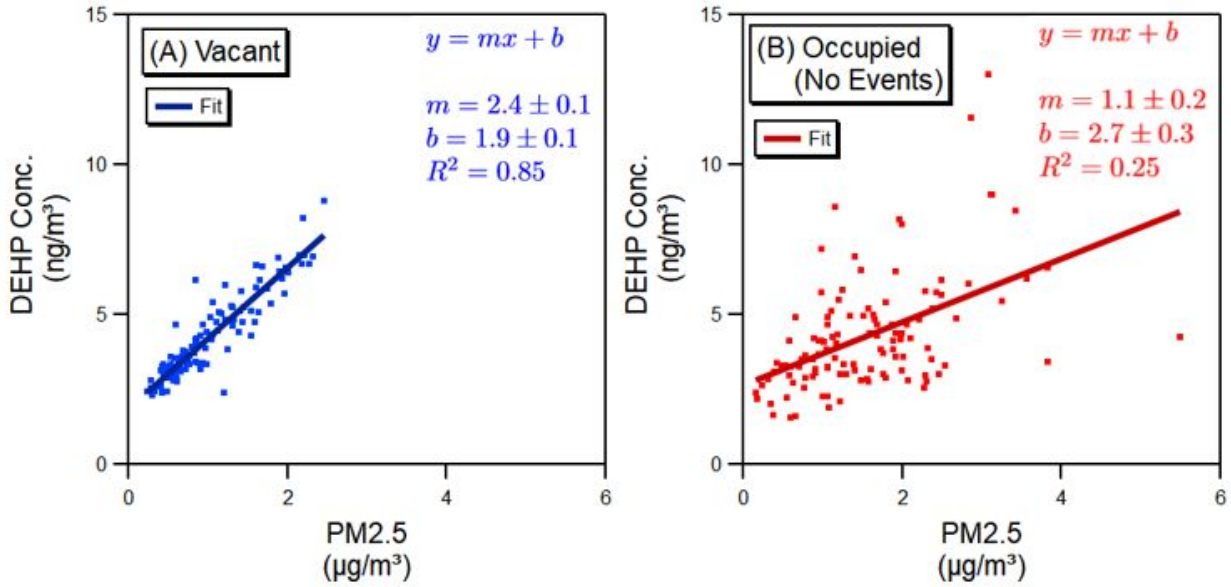


Figure 4: The gas-plus-particle concentration of DEHP is compared against PM2.5 concentration during the vacant period (A) and the occupied period when no cleaning, cooking, or combustion events were occurring (B). Units of measure on the fit parameters are ng/µg (parts per thousand) for the slope, *m*,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

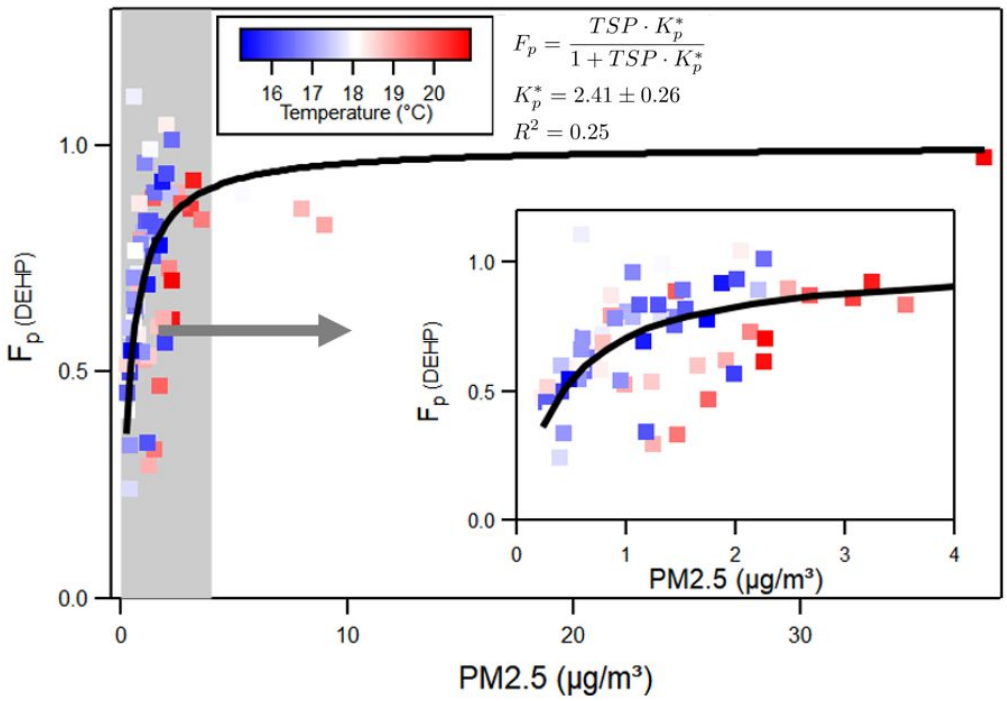
Gas-Particle Partitioning: The higher vapor-pressure phthalates (DEP, DBP, DIBP) were present primarily in the gas-phase (Table 1). Their particle fractions, while small, consistently increased as their molecular size and associated octanol-air partition coefficients increased (F_p values follow this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

Increasing particle mass concentration can drive gas-particle partitioning towards the particle phase. Airborne gas-particle partitioning of DEHP is associated with both PM2.5 concentration and indoor air temperature as revealed in Figure 5. At PM2.5 concentrations above 3 μg/m^3, airborne DEHP concentrations were predominantly in the particle phase. Similar effects are observable with cooler temperatures promoting partitioning into particles and an increased F_p.

Using the model described in Equation 2 an apparent partition coefficient K_p^* was evaluated to be 2.4 ± 0.3 m^3/μg under observed conditions. This empirically-derived partition coefficient is affected by assumptions about equilibrium conditions, the temperature, and by the experimental approach. Time-scales to approach gas-particle phase equilibrium vary depending on K_{oa} values and particle size. [48,50] For DEHP, gas-particle equilibration time scales may approach hundreds of hours for particle diameters in the vicinity of 2.5 μm and would be minutes to hours for particle sizes near 100 nm. Considering the residence's average air-exchange period of 2.2 h, the DEHP phase-partitioning system may be far from equilibrium for larger particles but is expected to be at or near equilibrium for smaller particles.[48, 50, 54] Experimentally, the F_p values were determined only for particles smaller than 2.5 μm, the SV-TAG particle-size cutoff. In addition, the stated PM2.5 concentrations do not include particles with diameters smaller than 250 nm that were not quantified by the Grimm 11-A OPC.

Using the van't Hoff equation, and assuming equilibrium conditions, K_p^* is expected to change by roughly 3× over the observed indoor temperature range (288 – 294 K).[74] After normalizing each particle fraction measurement from the measured indoor air temperature to the standard state temperature, the best-estimate K_p^{*298} value at T = 298 K is 0.80 ± 0.09 m^3/μg (Figure S9). This value can be compared to the partition coefficient calculated using the model developed by Weschler and Nazaroff (3.2 m^3/μg), which assumed equilibrium conditions, a log K_{oa} value of

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



410

411 **Figure 5:** The particle fraction of DEHP is compared against PM2.5 concentration, with points
412 colored by indoor air temperature. The lower right panel highlights the low PM2.5 concentration
413 region between 0 and 4 µg/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 PM2.5
431 concentrations from 0.5 μg/m^3 to 3 μg/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

442

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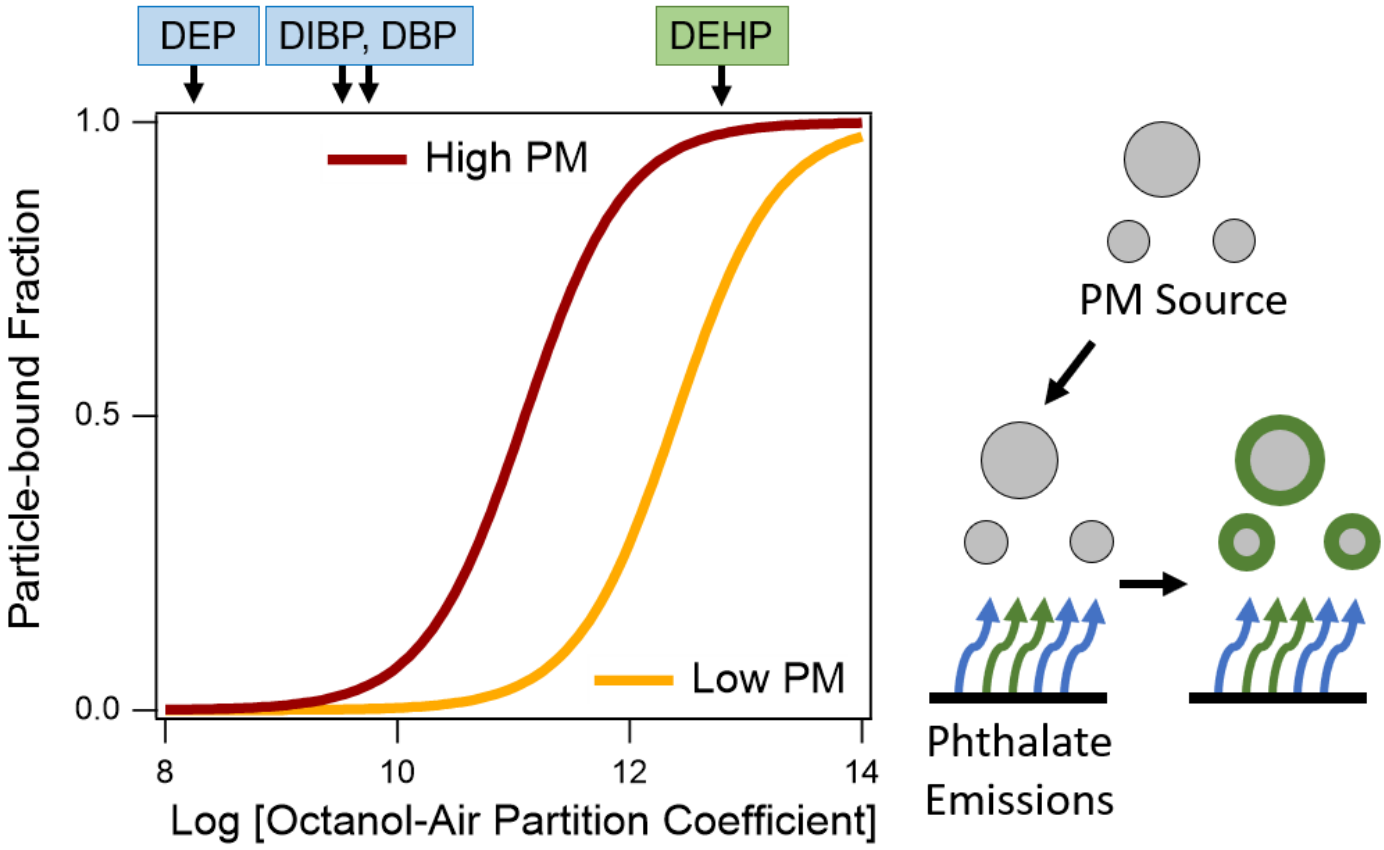
DEP
DIBP, DBP
DEHP
1.0
0.5
0.0
High PM
Low PM
Particle-bound Fraction
8
10
12
14
Log [Octanol-Air Partition Coefficient]
PM Source
Phthalate
Emissions