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SORPTION OF ORGANIC GASES IN RESIDENTIAL BEDROOMS AND BATHROOMS

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ABSTRACT

Experiments were conducted to characterize organic gas sorption in residential bedrooms (n=4), bathrooms (n=2), and a furnished test chamber. Rooms were studied “as-is” with material surfaces and furnishings unaltered. Surface materials were characterized and areas quantified. Experiments included rapid volatilization of a volatile organic compound (VOC) mixture with the room closed and sealed for a 5-h Adsorb phase, followed by 30-min Flush and 2-h closed-room Desorb phases. The mixture included n-alkanes, aromatics, glycol ethers, 2-ethyl-1-hexanol, dichlorobenzene, and organophosphorus compounds. Measured gas-phase concentrations were fit to three variations of a mathematical model that considers sorption occurring at one surface sink and one potential embedded sink. The 2-parameter sink model tracked measurements for most compounds, but improved fits were obtained for some VOCs with a 3-parameter sink-diffusion or a 4-parameter two-sink model. Sorptive partitioning and initial adsorption rates increased with decreasing vapour pressure within each chemical class.

INDEX TERMS

Adsorption, Field study, Modeling, Residence, Volatile organic compounds

INTRODUCTION

Gaseous air pollutants can reversibly sorb to material surfaces, affecting both the magnitude and timing of indoor concentrations. Sorption of VOCs to relevant indoor materials (e.g., carpet, gypsum wallboard, vinyl flooring) has been studied primarily through experiments in small (<1 m³) chambers (Tichenor et al. 1991; Jorgensen et al. 1999; Won et al. 2001a-b; Zhang et al. 2002). Materials generally were aged by exposure to clean air and studied individually. Sorption models were fit to measured data to infer rate parameters for specific compound-material interactions. These interactions can be combined mathematically to simulate sorption in an entire room or house, but this has been reported in only a few studies (e.g., Tichenor et al. 1991; Won et al. 2001b; Singer et al. 2004). Our group has demonstrated an alternative approach in which sorption is studied in a room-sized 50 m³ environmental chamber that is constructed, finished and furnished with typical materials (Singer et al. 2002; Singer et al. 2004). Furnishings have been aged over years of exposure to particulate and gaseous air pollutants, with intervening exposure to ambient air. Results indicate that sorption to the entire room can be modelled using one or two-sink models having 2 or 4 fitting parameters. Dynamics of low to moderately sorbing compounds such as toluene are captured with the one-sink model, whereas the behavior of highly sorbing compounds (e.g. nicotine and methylnaphthalene) is more closely reproduced with the two-sink model (Singer et al. 2004). Rooms in occupied residences contain many varied materials whose exposed surfaces may present sorption sites that differ from materials used in small chamber experiments. The objectives of this study were (1) to quantify sorption rate parameters for a suite of VOCs in

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actual residential rooms, and (2) to determine if the LBNL chamber is a reasonable surrogate for experiments to characterize sorption in such environments.

RESEARCH METHODS

Experiments were conducted in 4 bedrooms and 2 bathrooms in actual residences (while occupants were absent) and in the LBNL 50-m³ chamber with furnishings. Each experiment started with the rapid volatilization of a liquid VOC mixture into a closed and sealed room with low air change rate (ACR) for better resolution of sorption. The room remained closed for a 5 h Adsorb phase and then was opened. Fresh air was supplied at a high ACR to remove gas-phase VOCs (0.5 h Flush phase). At 5.5 h the room was closed for a 2-h Desorb phase. ACR was determined by the decay of SF₆ tracer gas.

Rooms were characterized by volume and by the area of each material surface exposed to freely moving room air (Hodgson et al. 2004). Materials were grouped into 5 categories: 1) fleecy/padded (upholstery, carpet, fabrics, bedding); 2) painted wallboard/plaster; 3) hard/porous (wood, plastic, laminate); 4) hard/nonporous (glass, metal, tile, etc.); and 5) other.

The VOC mixture included four n-alkanes, three aromatic hydrocarbons, two glycol ethers, 2-ethyl-1-hexanol, and dichlorobenzene to represent common air pollutants and chemical classes. Also included were three organophosphorus (OP) compounds, surrogates for Sarin-like nerve agents, and methyl salicylate, a surrogate for mustard gas (Singer et al. 2005).

Air samples were collected to quantify time-resolved gas-phase VOC concentrations during Adsorb and Desorb phases. Also measured were concentrations in the room before the experiment, at the end of the Flush phase, and in outdoor air. Samples were collected on sorbent tubes that were analyzed by thermal desorption GC/MS. Aside from the durations of Adsorb, Flush, and Desorb phases, experimental details were the same as those described previously (Singer et al. 2004; Singer et al. 2005).

Measured gas-phase concentrations were fitted to a mass balance sorption model (Eqs. 1-3) that tracks mass in room air (C), in the exposed surface sink (M), and potentially in an embedded sink (E) in contact with the surface but not directly with room air. Concentrations C, M, and E are parameterized as the mass in each compartment divided by the room air volume (μg m⁻³). Other parameters are the ACR λ (h⁻¹) and coefficients λ_a, λ_d, k₁, and k₂ (h⁻¹) describing rates of mass transfer among compartments.

$$\frac{dC}{dt} = -(\lambda + \lambda_a)C + \lambda_d M \quad (1)$$

$$\frac{dM}{dt} = \lambda_a C - (\lambda_d + k_1)M + k_2 E \quad (2)$$

$$\frac{dE}{dt} = -k_2 E + k_1 M \quad (3)$$

Eqs. 1-3 are analogs to those used to describe sorption and diffusion of VOCs interacting with single materials in small chambers. Our approach groups all furnishings and room surfaces into a single, conceptual sink. The parameterization of sorption coefficients as rates (h⁻¹) allows direct comparison between sorption and air change time scales. In other formulations, the adsorption coefficient has velocity units (i.e., m h⁻¹) and sorbed mass concentration is normalized to apparent surface area (i.e., μg m⁻²). These formulations differ from our λ_a and M by the apparent surface area to air volume ratio. Relating the mass in each sink to room air volume allows for straightforward evaluation of mass partitioning. Eqs. 1-3 can represent

three conceptual sorption models. The *sink* model ($k_1 = k_2 = 0$) assumes sorption at the surface only. The *sink-diffusion* model adds a simplified diffusion mechanism at rate $k_1 = k_2 = k_{\text{dif}}$ between surface and embedded sinks (Jorgensen et al. 2000). The *two-sink* model allows unequal rates of mass movement between surface and embedded sinks ($k_1 \neq k_2$). Parameter values are obtained by fitting the models to measured gas-phase concentrations. Partitioning coefficients (K_{part}) defined as the ratio of sorbed- to gas-phase mass at equilibrium, were calculated from rate coefficients (Singer et al. 2005).

A goodness-of-fit (GF) metric was calculated as the root mean square of normalized residuals divided by the square root of N measured points (Eq. 4). Normalized residuals were calculated from measured (y_i) and model-predicted (y_i^*) values. Best-fit coefficient values for the models shown in Eqs. 1-3 were determined by minimizing the GFs using all measured data; GFs also were calculated separately for Adsorb and Desorb phases.

$$GF = \sqrt{\frac{\sum \left(\frac{y_i - y_i^*}{y_i} \right)^2}{N}} \quad (4)$$

RESULTS AND DISCUSSION

Example results are shown in Fig. 1a-b. The model fits in Fig. 1a correspond to GFs of 0.21, 0.13, and 0.09 for sink, sink-diffusion and two-sink models, respectively. Fig. 1b shows the varied dynamics observed for VOCs studied. Within each chemical class, sorption increases with decreasing volatility.

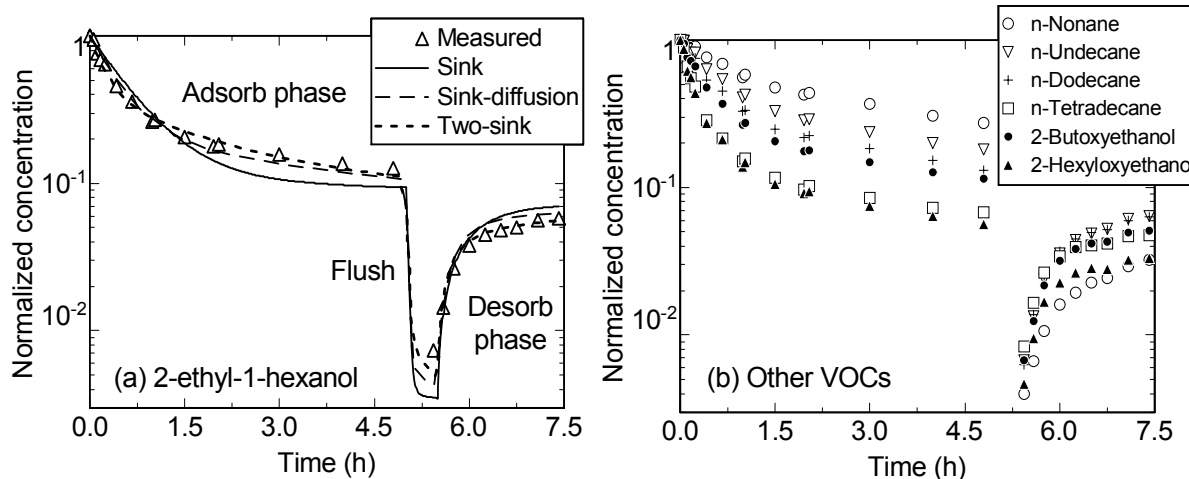


Figure 1. VOC concentrations resulting from sorption-desorption processes in a 12 m³ residential bathroom (Bath2): (a) measurements and model fits for 2-ethyl-1-hexanol; (b) concentration profiles for 4 n-alkanes and 2 glycol ethers.

The room and material characteristics are summarized in Fig. 2. Bathrooms were the smallest rooms studied and contained a high fraction of nonporous materials (fixtures, tile, etc.). In the four bedrooms, the overall surface to volume (S/V) ratio decreased with increasing room volume. The LBNL furnished chamber was larger than the residential rooms with a substantially lower overall S/V ratio; however, S/V ratios of plush materials and wallboard were similar to those measured in bedrooms.

Experimental conditions are shown in Table 1 below. ACRs during all but one of the periods were below 0.3 h⁻¹; the window of Bath1 was not properly resealed after the Flush. The ACR was not measured during the Desorb phase of Bath2 owing to a SF₆ injection error; this period

was modelled assuming the ACR of the Adsorb phase. Temperature and RH varied among experiments, but both were generally consistent during each experimental phase (standard deviations $<0.5\text{ }^{\circ}\text{C}$ and $<2\%$ RH). The one exception was for BR1, in which there were increases of $4.5\text{ }^{\circ}\text{C}$ over the first 1 h, and another $1\text{ }^{\circ}\text{C}$ rise over the remaining 4 h of the Adsorb phase; RH decreased 10% over the first h then remained at a stable level of 55%.

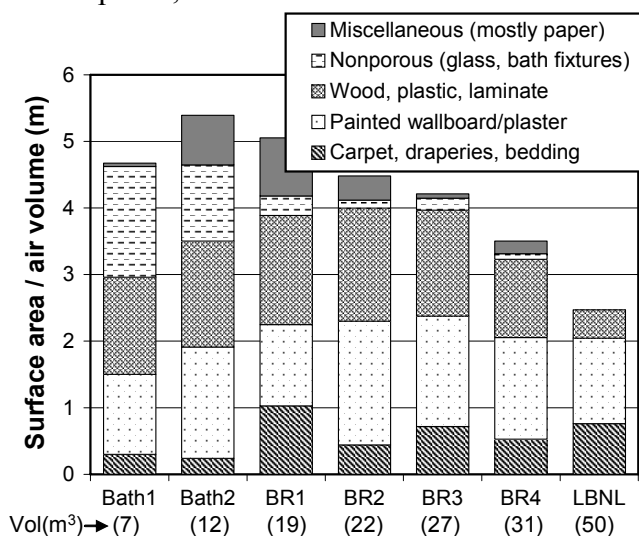


Figure 2. Material characteristics of study rooms

Table 1. Experimental conditions

Expt/ Room	Adsorb/Desorb		
Room	ACR [h^{-1}]	T ¹ (C)	RH ¹ (%)
Bath1	0.24/1.18	(na) ¹	(na) ¹
Bath2	0.21/na ²	23/25	54/51
BR1	0.16/0.20	24/26	56/51
BR2	0.08/0.08	20/20	67/64
BR3	0.11/0.17	21/22	59/56
BR4	0.26/0.26	21/22	64/60
LBNL	0.16/0.17	21/21	61/59

¹ Mean temperature (T) and relative humidity (RH) during Adsorb / Desorb phases.

² Data not available.

Summary sink model results from the 6 residential rooms and the LBNL chamber are provided in Table 2. No obvious systematic trends in parameter values were observed between bedrooms and bathrooms; hence parameter values are presented as the mean \pm standard deviation for all 6 residential rooms. Parameter values for the LBNL chamber generally were similar to those for the 6 rooms. Both λ_a and K_{part} varied substantially while λ_d was relatively consistent across compounds. Adsorption rates spanned a range similar to that observed previously for sink model fits of organic gases in the LBNL furnished chamber (Singer et al. 2004). All study compounds exhibited adsorption rates that are comparable to or greater than residential ACRs, indicating that sorption is a relevant process for many compounds under many or most indoor environmental conditions. The time constant for desorption ($1/\lambda_d$) is on the order of 5-10 h. Calculated K_{part} values attribute 2-40 times as much mass in the sorbed phase relative to the gas-phase at equilibrium.

Improved fits were obtained for many compounds when the sink-diffusion and two-sink models were employed as shown in Fig. 1a and in Table 3 for selected compounds. The values of the added parameters provide information that is consistent with the simpler model. For example, the parameters controlling desorption – λ_d , k_{dif} , and k_2 for sink, sink-diffusion and two-sink models, respectively – are similar (within a factor of 2) across the three models for almost all compounds. The initial adsorption rate coefficient (λ_a) is slightly higher in sink-diffusion vs. sink models, and often much higher in the two-sink model, yet this is offset by an increase in the two-sink model λ_d .

The parameter values determined for specific VOCs in our study may be useful in predicting values for related compounds. For example, Fig. 3 indicates that there is a clear relationship between vapour pressure and adsorption rate for alkanes, with a less precise but still useful relationship for aromatics, alcohols (including methyl salicylate) and dichlorobenzene.

Table 2. Sink model rate parameters for 6 residential rooms and LBNL chamber.

Compound	Residential experiments (4 bedrooms, 2 baths) ¹				LBNL room ²
	λ_a (h ⁻¹)	λ_d (h ⁻¹)	K_{part}	$GF_{(all)}$	$\lambda_a / \lambda_d / K_{part}$
n-Nonane	0.40 ± 0.15	0.24 ± 0.20	2.1 ± 0.8	0.18	0.57 / 0.34 / 1.7
n-Undecane	0.85 ± 0.25	0.18 ± 0.02	4.6 ± 1.3	0.16	0.86 / 0.14 / 6.0
n-Dodecane	1.2 ± 0.4	0.15 ± 0.02	7.9 ± 2.3	0.19	1.1 / 0.11 / 10
n-Tetradecane	2.9 ± 1.0	0.21 ± 0.04	14 ± 3	0.21	2.3 / 0.14 / 16
Ethylbenzene	0.45 ± 0.15	0.13 ± 0.03	3.6 ± 0.9	0.16	0.72 / 0.27 / 2.7
1,3-Diethylbenzene	0.75 ± 0.25	0.14 ± 0.02	5.3 ± 1.4	0.15	1.0 / 0.15 / 6.7
1-Methylnaphthalene	3.3 ± 1.0	0.16 ± 0.03	21 ± 4	0.25	4.0 / 0.14 / 29
1,2-Dichlorobenzene	0.95 ± 0.30	0.14 ± 0.02	7.1 ± 2.1	0.18	1.4 / 0.16 / 8.4
2-Butoxyethanol	1.5 ± 0.5	0.16 ± 0.05	9.4 ± 3.1	0.20	1.2 / 0.06 / 18
2-Ethyl-1-hexanol	1.5 ± 0.4	0.18 ± 0.03	8.3 ± 2.5	0.19	1.7 / 0.12 / 13
2-Hexyloxyethanol	2.7 ± 1.0	0.15 ± 0.04	18 ± 4	0.26	2.6 / 0.11 / 23
Methyl Salicylate	3.0 ± 1.1	0.20 ± 0.05	15 ± 5	0.26	3.3 / 0.15 / 22
DMMP ³	3.2 ± 1.4	0.09 ± 0.03	38 ± 12	0.32	2.5 / 0.08 / 30
DEEP ⁴	3.3 ± 1.3	0.12 ± 0.03	28 ± 8	0.28	3.2 / 0.13 / 26
Triethylphosphate	3.7 ± 1.5	0.13 ± 0.03	28 ± 10	0.29	3.8 / 0.13 / 30

⁽¹⁾ Mean ± standard deviation of fitted parameters from 6 residential experiments; values of λ_a and K_{part} rounded to 0.05 if <1, 0.1 if <10, 1 if > 10. ⁽²⁾ Fitted parameters from single experiment conducted using same protocol in LBNL chamber. ⁽³⁾ Dimethyl methylphosphonate. ⁽⁴⁾ Diethyl ethylphosphonate.

Table 3. Sink-diffusion and Two-sink model rate parameters for selected compounds.

Compound	Model	λ_a (h ⁻¹)	λ_d (h ⁻¹)	$k_{1 \text{ or dif}}$ (h ⁻¹)	k_2 (h ⁻¹)	K_{part}	$GF_{(all)}$
Tetradecane	Sink-dif	3.6 ± 1.1	0.49 ± 0.10	0.27 ± 0.05		15 ± 3	0.12
	2-Sink	4.7 ± 1.1	1.2 ± 0.2	0.79 ± 0.15	0.30 ± 0.07	14 ± 3	0.08
1-Methyl-naphthalene	Sink-dif	3.8 ± 1.1	0.34 ± 0.06	0.22 ± 0.01		22 ± 4	0.16
	2-Sink	5.0 ± 1.3	0.95 ± 0.11	0.63 ± 0.11	0.20 ± 0.04	22 ± 4	0.08
2-Ethyl-1-hexanol	Sink-dif	1.9 ± 0.6	0.42 ± 0.11	0.22 ± 0.03		9 ± 3	0.19
	2-Sink	2.8 ± 0.8	1.3 ± 0.3	0.67 ± 0.19	0.23 ± 0.07	9 ± 3	0.12
2-Hexyloxy-ethanol	Sink-dif	3.2 ± 1.2	0.33 ± 0.09	0.21 ± 0.01		19 ± 4	0.18
	2-Sink	4.6 ± 1.2	1.2 ± 0.3	0.70 ± 0.17	0.19 ± 0.05	19 ± 5	0.09
DMMP	Sink-dif	3.5 ± 1.5	0.17 ± 0.06	0.21 ± 0.01		42 ± 13	0.25
	2-Sink	5.0 ± 1.5	0.86 ± 0.40	0.72 ± 0.16	0.12 ± 0.04	45 ± 17	0.14

CONCLUSION AND IMPLICATIONS

The parameter values developed in this study may be used to model sorption in residential and potentially other (e.g. commercial, office) environments with similar surfaces. Sorption rates and partitioning may be estimated for additional compounds of the same classes using the relationship between the sorptive properties and vapor pressures of the study compounds. Sorption did not vary widely by room type or across rooms of varying size or furnishings. The LBNL furnished chamber appears to be a reasonable surrogate space for studying VOC sorption relevant to residential environments.

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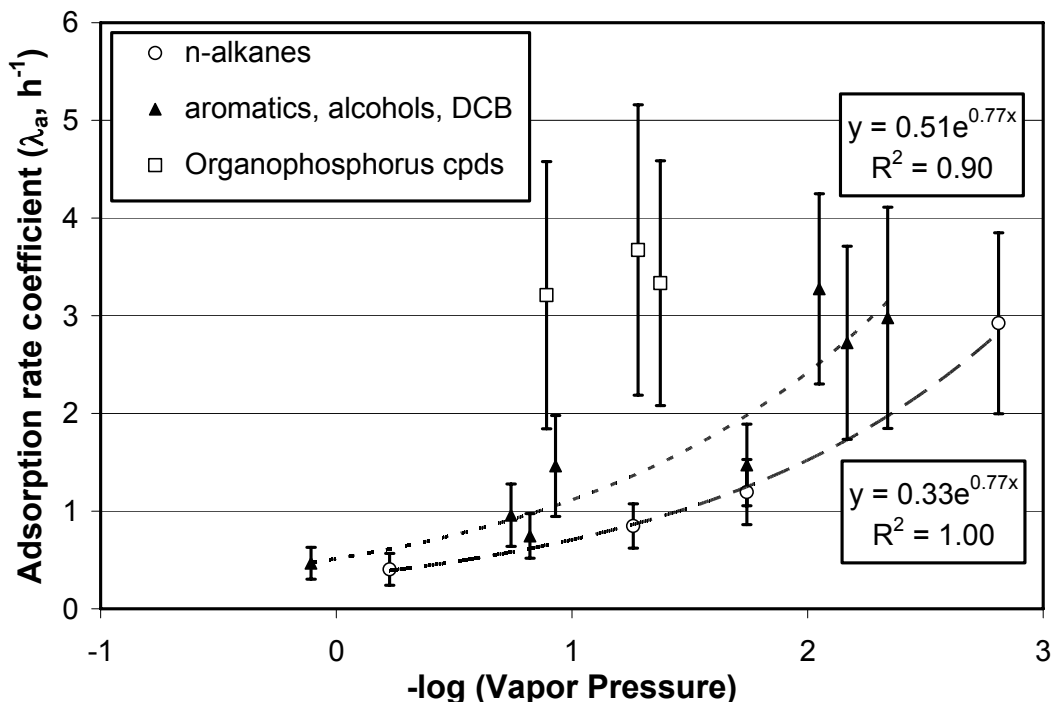


Figure 3. Relationship between vapor pressure (Pa) and adsorption rate for VOCs studied.

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