

1 Sorption of organic gases in a furnished room

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6 Abstract

7 We present experimental data and semi-empirical models describing the sorption of organic
8 gases in a simulated indoor residential environment. Two replicate experiments were conducted
9 with 20 volatile organic compounds (VOCs) in a 50-m³ room finished with painted wallboard,
10 carpet and cushion, draperies and furnishings. The VOCs span a wide volatility range and
11 include ten Hazardous Air Pollutants. VOCs were introduced to the static chamber as a pulse and
12 their gas-phase concentrations were measured during a net adsorption period and a subsequent
13 net desorption period. Three sorption models were fit to the measured concentrations for each
14 compound to determine the simplest formulation needed to adequately describe the observed
15 behavior. Sorption parameter values were determined by fitting the models to adsorption period
16 data then checked by comparing measured and predicted behavior during desorption. The
17 adequacy of each model was evaluated using a goodness of fit parameter calculated for each
18 period.

19 Results indicate that sorption usually does not greatly affect indoor concentrations of
20 methyl-*tert*-butyl ether, 2-butanone, isoprene and benzene. In contrast, sorption appears to be a
21 relevant indoor process for many of the VOCs studied, including C₈-C₁₀ aromatic hydrocarbons
22 (HC), terpenes, and pyridine. These compounds sorbed at rates close to typical residential air
23 change rates and exhibited substantial sorptive partitioning at equilibrium. Polycyclic aromatic
24 HCs, aromatic alcohols, ethenylpyridine and nicotine initially adsorbed to surfaces at rates of 1.5
25 to >6 h⁻¹ and partitioned 95 to >99% in the sorbed phase at equilibrium.

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1 **Key Words**

2 Volatile organic compounds, adsorption, desorption, residential, indoor air quality, hazardous air
3 pollutants, tobacco smoke tracers

4 **1. Introduction**

5 Volatile organic compounds (VOCs) of outdoor origin, including a number of compounds
6 regulated as Hazardous Air Pollutants (HAPs) under the 1990 Amendments to the U.S. Clean Air
7 Act (U.S. EPA, 2003), penetrate buildings through ventilation and infiltration. In addition, there
8 are a large number of indoor sources of VOCs active on various time scales. People in the U.S.
9 spend about 90% of our time indoors and about 70% of our time at home (Klepeis et al., 2001).
10 Much human exposure to VOCs of both indoor and outdoor origin thus occurs indoors. A variety
11 of indoor processes modify the concentrations and temporal patterns of air pollutants within
12 buildings. These processes include indoor-outdoor air exchange; heterogeneous and gas-phase
13 chemical reactions, which also may produce secondary pollutants of concern; changes in gas-
14 particle partitioning; and sorptive interactions between gases and interior material surfaces.
15 Understanding these dynamic processes is essential for predicting concentrations and potential
16 indoor exposures to VOC air pollutants. Air exchange is often the primary removal mechanism
17 for indoor gas-phase pollutants. Other processes can be important if they remove pollutants from
18 the air at rates that are of similar magnitude or greater than the rate at which pollutants are
19 removed by air exchange. The goal of this study was to develop models to describe the effects of
20 sorption on concentrations of a broad range of VOCs, including a number of HAPs, in residential
21 indoor environments. Special attention is paid to the identification of compounds for which
22 sorption occurs at a fast enough rate to be competitive with air exchange as a removal process.

23 Sorption onto indoor surfaces has been investigated primarily through experiments in small
24 chambers containing individual materials. Measured gas-phase concentrations were fit to
25 equations developed from theory to obtain key parameter values, yielding semi-empirical
26 sorption models (e.g., An et al., 1999; Bodalal et al., 2001; Bouhamra and Elkilani, 1999;
27 Colombo et al., 1993; Jorgensen and Bjorseth, 1999; Jorgensen et al., 2000; Meininghaus et al.,

1 1999; Piade et al., 1999; Tichenor et al., 1991; Van Der Wal et al., 1998; Van Loy et al., 2001;
2 Won et al., 2000, 2001a, 2001b). In the most extensive of these studies, Won et al. (2001a)
3 reported adsorption and desorption rate coefficients for eight VOCs interacting with gypsum
4 wallboard, carpet and cushion, acoustic ceiling tile, wood flooring, vinyl flooring, and fiberglass.
5 Sorption also has been studied in the context of predicting emissions from materials, such as
6 carpet and vinyl flooring (Cox et al., 2002; Little et al., 1994).

7 One objective for quantifying interactions between VOCs and individual materials in
8 small-scale experiments is to computationally simulate the potential effects in a realistic room
9 containing multiple materials. Attempts to validate this approach have not yielded consistently
10 favorable results (Bouhamra and Elkilani, 1999; Tichenor et al., 1991; Won et al., 2001b).

11 Singer et al. (2002) demonstrated an alternate approach for characterizing sorption effects
12 for environmental tobacco smoke (ETS) constituents in a realistic room. Sorption was examined
13 by measuring gas-phase ETS concentrations in a room-sized (50-m³) chamber constructed,
14 finished, and furnished with materials commonly found in indoor environments. Experiments
15 were conducted to determine exposure relevant emission factors (EREFs) for 26 gas-phase
16 organic components of ETS at varied ventilation, furnishing, and smoking levels. These EREFs
17 accounted for short-term adsorption onto, and desorption from all surfaces in the room to
18 quantify the amount of mass available for inhalation exposure over a designated time period. The
19 current study adapted experimental methods from the ETS exposure research to quantify and
20 model the sorption of gas-phase organic compounds in the same room.

21 **2. Experimental methods**

22 *2.1. Chamber and furnishings*

23 Two replicate experiments were conducted in a 50-m³ chamber whose walls and ceiling were
24 finished with 64.2 m² of gypsum wallboard finished with a single coat of low VOC flat latex
25 paint. The surface layer of wallboard was 0.95-cm thick on the walls and 1.59-cm thick on the
26 ceiling. An additional layer of 1.59-cm thick wallboard was present beneath all walls and the
27 ceiling. Two walls and the ceiling were constructed with plywood under the wallboard. The

1 20.4-m² plywood floor was covered first with aluminum sheeting then rebounded urethane
2 cushion (~1-cm thick) and carpet. The carpet consisted of an approximately 1-cm long Nylon
3 face fibers bonded to a coarse polypropylene mesh backing. Additional material surfaces
4 included several pieces of wood-veneer furniture (18.7 m²), four chairs with polyurethane foam
5 cushioning and polyester fabric (13.9 m²), and pleated cotton drapery covering 5 m² of wall area.
6 All materials were aged over several years of use.

7 The chamber was housed within a small building. Ventilation air for the chamber was
8 drawn from outdoors through virgin coconut shell activated carbon (Applied Air Filters, Fremont,
9 CA) to remove organic gases. Chamber air was circulated with four (10-cm) axial fans placed
10 ~1.5 m from the corners, alternately at about 0.8 and 1.6 m from the floor. Temperature was
11 controlled with the building thermal conditioning system. Temperature and relative humidity
12 (RH) were measured with HOBO H8 Pro sensors (Onset Computer Corp) placed at three heights
13 in the room center and on several walls. Temperature and RH (Table 1) were stable during the
14 experiments. Air velocities of $0.07 \pm 0.05 \text{ cm sec}^{-1}$ ($\mu \pm \sigma$) were measured at 39 locations at a
15 distance of 5 cm above the floor and wall surfaces; 5 cm was approximately at the edge of the
16 laminar boundary layer. These free air velocities are typical of those reported for residential
17 settings (e.g. Kovanen et al., 1987; Matthews et al., 1989; Thatcher et al., 2002).

18 2.2. *Experimental procedure*

19 The experiments were designed to isolate periods of net adsorption following a spike
20 introduction, and net desorption following rapid flushing of chamber air. The chamber was
21 sealed during the adsorption and desorption periods so sorption would be the dominant source of
22 pollutant removal or addition to chamber air.

23 Prior to initiating each experiment, the chamber was ventilated at $\geq 2 \text{ h}^{-1}$ for two days to
24 facilitate removal of previously sorbed mass, then sealed for one or more days. Background
25 levels of test compounds measured just before each experiment were $<0.5\%$ of $C(0)$ in Expt 1
26 and $<1.5\%$ of $C(0)$ in Expt 2. The net adsorption period started when two VOC mixtures were
27 flash vaporized inside the sealed chamber. The chamber remained sealed for one day, after which

1 chamber air was flushed at 5-7 h⁻¹ over a 1-h period to remove compounds in the gas-phase. The
2 chamber was resealed for the one-day net desorption period, then ventilated at 2.4 h⁻¹ for >1 day
3 to complete an experiment. Air change rates (ACH) during static and ventilated conditions were
4 measured by tracer gas (SF₆) decay. The infiltration rate for the sealed chamber was 0.02-0.03 h⁻¹.
5 The periods are indicated in Figure 1. Period durations and ventilation rates are summarized in
6 Table 1.

7 *2.3. Test compounds, sampling and analysis*

8 Twenty VOCs were selected to span wide ranges of volatility and chemical functionality (Table
9 2). They included a series of single-ring aromatic hydrocarbons of increasing molecular mass
10 from benzene (C₆) through 1,3-diethylbenzene (C₁₀), and three polycyclic aromatic hydrocarbons
11 (PAH), naphthalene, 1-methylnaphthalene, and 2,3-dimethylnaphthalene. Oxygenated
12 compounds included highly volatile methyl-*tert*-butyl ether (MTBE), acrolein, methyl ethyl
13 ketone (2-butanone, MEK), and less volatile aromatic alcohols, phenol and *o*-cresol. Also
14 included were isoprene; two terpene hydrocarbons, α -pinene and d-limonene; and three
15 compounds with relevance for ETS research, pyridine, 4-ethenylpyridine (4-EP, a surrogate for
16 3-ethenylpyridine), and nicotine. Ten of the selected VOCs are regulated as HAPs (Table 2).

17 Two mixtures of pure compounds were prepared prior to each experiment. The first
18 contained MTBE, acrolein, MEK, isoprene, benzene, and ethylbenzene; the second contained all
19 other test compounds. At time $t=0$, the second mixture was injected into a glass dish pre-heated
20 on a laboratory hot plate. We estimate the glass temperature was between 180 and 240 °C based
21 on measurements with a surface temperature sensor (Raytek model RAYRPM30L3U) conducted
22 later under similar operating conditions. The first mixture was injected into an unheated glass
23 dish. Both mixtures appeared to vaporize within 30 s. A 25-cm household fan set on “low”
24 forced air across the two glass dishes for 10 min after injection.

25 Air samples were collected on Tenax-TA™ sorbent tubes (P/N CP-16251; Varian, Inc.)
26 modified by substituting a 15-mm section of Carbosieve S-III 60/80 mesh (P/N 10184, Supelco
27 Inc., Bellefonte, PA, USA) for Tenax-TA™ at the outlet end. Sorbent tubes were attached to

1 stainless steel tubing and inserted through ports in the chamber wall so that air was drawn
 2 directly into the tubes from the room, 0.4 m away from the wall. Air samples were collected at
 3 $\sim 100 \text{ cm}^3 \text{ min}^{-1}$. Sample flow rates measured before each experiment were used to calculate
 4 organic gas concentrations. Samples were quantitatively analyzed by thermal desorption-gas
 5 chromatography/mass spectrometry (TD-GC/MS) generally following U.S. EPA Method TO-1
 6 (U.S. EPA, 1984). Samples were thermally desorbed and concentrated on a cryogenic inletting
 7 system (Model CP-4020 TCT, Varian, Inc.) fitted with a Tenax-packed trap (P/N CP-16425,
 8 Varian, Inc.). Sample desorption temperature was 235 °C for 6.5 min. The trap was held at -100
 9 °C, then heated to 235 °C for injection. Multi-point calibrations were referenced to an internal
 10 standard of 1-bromo-4-fluorobenzene. Uncertainty in the quantitation of each compound was
 11 calculated from 13 pairs of duplicate samples. The difference between samples in each pair was
 12 normalized to the average of the two. The normalized deviations for the 13 pairs were then
 13 averaged. Uncertainty was 5% or less for all compounds except MTBE (8%), acrolein (17%),
 14 isoprene (16%), and 2,3-dimethylnaphthalene (8%).

15 **3. Mathematical modeling methods**

16 The model most frequently applied by past researchers considers sorption only at the exposed
 17 surface, with overall adsorption and desorption rates linearly dependent on the gas- and sorbed-
 18 phase concentrations. This model is summarized in Equations 1-2 for gas-phase concentrations C
 19 ($\mu\text{g m}^{-3}$) and sorbed-phase concentrations M ($\mu\text{g m}^{-2}$) normalized to projected surface area. Other
 20 parameters are the room air volume V (m^3), air change rate λ (h^{-1}), adsorption rate coefficient k_a
 21 (m h^{-1}), desorption coefficient k_d (h^{-1}), and projected surface area to volume ratio S/V ($\text{m}^2 \text{ m}^{-3}$).

$$22 \quad \frac{dC}{dt} = -\lambda C - k_a C \frac{S}{V} + k_d M \frac{S}{V} \quad (1)$$

$$23 \quad \frac{dM}{dt} = k_a C - k_d M \quad (2)$$

24 Tichenor et al. (1991) showed that the parameterization of a linear sorption isotherm is consistent
 25 with a theoretical Langmuir model at low surface loading.

26 Jorgensen et al. (2000) developed a model that includes diffusion to an embedded sink (E)
 27 that represents the bulk of the material. This model is summarized by Equations 1, 3 and 4. As

1 the model includes only two nodes, k_{diff} is not a true diffusion coefficient but rather a coefficient
 2 indicating the rate of mass movement between the surface and embedded sinks. Jorgensen et al.
 3 used this model to predict sorption and diffusion of toluene and α -pinene onto and into carpet.

$$4 \quad \frac{dM}{dt} = k_a C - k_d M - k_{diff} (M - E) \quad (3)$$

$$5 \quad \frac{dE}{dt} = k_{diff} (M - E) \quad (4)$$

6 The central element of our approach in this study was to consolidate all room surfaces into
 7 a single, conceptual material. Specifically, we attempted to describe experimental data using
 8 three model formulations summarized in Equations 5-7.

$$9 \quad \frac{dC}{dt} = -(\lambda + \lambda_a)C + \lambda_d M \quad (5)$$

$$10 \quad \frac{dM}{dt} = \lambda_a C - (\lambda_d + k_1)M + k_2 E \quad (6)$$

$$11 \quad \frac{dE}{dt} = -k_2 E + k_1 M \quad (7)$$

12 This generalized formulation allows for mass to accumulate in three sinks: the room air, the
 13 surface of the material in contact with the bulk air, and an embedded third sink in contact with
 14 the surface-sink, but not directly with room air. Concentrations in these sinks are respectively
 15 represented as C, M, and E. Concentrations in all sinks were expressed as the total mass in the
 16 sink normalized to the room air volume ($\mu\text{g m}^{-3}$). Other parameters are the air change rate λ (h^{-1}),
 17 and rate coefficients λ_a , λ_d , k_1 , and k_2 (h^{-1}) describing the rates of mass transfer among the sinks.

18 Equations 5-7 are similar to Equations 1, 3, and 4 with several differences. While the
 19 earlier equations were applied for sorptive interactions with a single material, Equations 5-7 were
 20 applied to the room and its contents as a system. Thus, the surface and embedded sinks represent
 21 composites of all materials. Another difference is reflected in the units of the rate coefficients.
 22 We chose to represent all rate coefficients as analogs to the air change rate (ACH, h^{-1}); λ_a is thus
 23 equivalent to $k_a(S/V)$. This alternative is acceptable since neither the adsorption coefficient nor
 24 the sorbed mass concentration in the conventional formulation is fundamental, i.e., they include
 25 an unspecified factor relating the apparent area to the actual area of exposed material surface
 26 participating in sorptive interactions. Our approach allowed for straightforward evaluation of

1 mass partitioning among the sinks in the room and direct comparisons of the time scale of each
2 process. The conventional approach, on the other hand, mathematically allows for scaling of
3 small chamber results to other scenarios with varying material-specific surface-to-volume ratios.
4 Three conceptual model formulations were tested for their ability to describe the measured
5 concentration profiles. The *surface-sink* model is described by Eqs. 5-7 with $k_1 = k_2 = 0$; it
6 considers only reversible sorption at the material surface. The *sink-diffusion* model is an analog
7 to that used by Jorgensen et al. (2000), with $k_1 = k_2 = k_{\text{diff}}$. Since diffusion is envisioned to occur
8 only in a reversible fashion between two sinks, this model may represent sorption and diffusion
9 in materials like carpet or a solid matrix, in which diffusion is followed by sorption within the
10 bulk material. The addition of a parameter (k_{diff}) should yield a better fit if the fundamental
11 physical-chemical mechanism has a first order dependence on the surface-sorbed mass. The *two-*
12 *sink* model allows for unequal rate coefficients k_1 and k_2 governing mass movement between the
13 surface and embedded sinks. Mathematical flexibility increases with the addition of another
14 fitting parameter. Physically, the second sink could represent any change in state that results in
15 tighter binding than that occurring with initial surface sorption.

16 Parameter values were determined by fitting the models to the net adsorption period data.
17 Expected initial concentrations were calculated using compound masses in the flash-evaporated
18 mixtures. Modeled initial concentrations were allowed to vary within 10% of these values for
19 mid-volatility compounds, within 20% for the most volatile (acrolein, isoprene, MTBE), and
20 least volatile compounds (PAH, phenol, cresol, and nicotine). The increased freedom for the
21 most volatile compounds is justified by higher uncertainty in their introduction and analysis.
22 Lower volatility compounds may not have volatilized completely or may have sorbed prior to
23 completely being mixed in room air. A goodness of fit (GF) metric was calculated as the root
24 mean square of the normalized residuals, divided by the square root of the number of measured
25 points (Equation 8). Residuals were calculated as the differences between the measured values y_i
26 and model-predicted values y_i^* , normalized to the measured values. GF was calculated
27 separately for the net adsorption and net desorption periods.

$$GF = \frac{\sqrt{\sum \left(\frac{(y_i - y_i^*)}{y_i} \right)^2}}{\sqrt{N}} \quad (8)$$

4. Results

4.1 Measured concentration patterns

The primary results are the measured gas-phase concentration patterns. The temporal pattern observed for many compounds is illustrated by limonene in Figure 1. Concentrations are shown beginning at $t = 0$, corresponding to volatilization into chamber air. Initial concentrations based on model fits to the measured values are shown for all compounds in Table 3. During period 1 (adsorption), concentrations initially decreased with the net movement of mass from the gas to the sorbed phase, then stabilized as equilibrium partitioning was established. During period 2 (flushing), gas-phase levels declined rapidly. Modeling of the experiments indicated that sorbed mass concentrations were reduced by <10% for most compounds during the flush period. The exceptions include isoprene (-21%), α -pinene (-15%), benzene (-22%) and the C₇-C₈ aromatics (-13 to -16%). When the chamber was resealed initiating period 3, concentrations increased reflecting net desorption. Concentrations achieved at the end of period 3 reflect equilibrium partitioning. Starting at $t = 50$ h (period 4), the room was ventilated at 2.4 h⁻¹ and gas-phase concentrations rapidly declined.

MEK, α -pinene, all single-ring aromatic hydrocarbons, and pyridine exhibited temporal patterns similar to limonene. The gas-phase concentrations of these mid-volatility compounds decreased sharply over about the first 3 hours as adsorption dominated. The rates of decline slowed over a period of 3-9 hours consistent with increasing desorption resulting from higher sorbed mass concentrations. Adsorption and desorption approached equilibrium by about 12 h for most of these compounds. Progression towards equilibrium during the net adsorption period was somewhat slower for MEK and benzene. There were substantial differences in equilibrium gas-phase concentrations at the ends of the adsorption and desorption periods. The adsorption

1 equilibrium concentrations shown for limonene in Figure 1 indicate dominant partitioning to the
2 sorbed phase.

3 Isoprene and MTBE, the most volatile compounds, appeared to sorb very slowly (Figure
4 2). Concentrations of these compounds in the adsorption period decreased only slightly more
5 rapidly than the profile predicted for a non-sorbing tracer gas. However, the rise in MTBE
6 concentrations during the desorption period indicated some sorption likely occurred.

7 The general pattern for the least volatile compounds is represented by the concentrations of
8 1-methylnaphthalene (Figure 3). Similar behavior was observed for phenol, cresol, the
9 naphthalenes, 4-EP and nicotine. These compounds sorbed rapidly and extensively. Their
10 concentrations declined sharply over a time scale of tens of minutes then continued to decrease
11 for several hours. Equilibrium partitioning for these compounds was almost entirely in the sorbed
12 phase. Gas-phase concentrations declined during the flush period, but rapidly returned to the
13 adsorption period equilibrium level when the chamber was resealed. Since little of the total
14 compound mass was removed during flushing, the observed partitioning appears to represent a
15 quasi-equilibrium state, at least on the time scale of hours.

16 *4.2 Parameter values and model fits*

17 The three models were fit to the measured adsorption period concentrations from each
18 experiment. Best-fit parameter values shown in Table 3 reflect an average of those obtained for
19 the two experiments. We started with the surface-sink model for all compounds, and progressed
20 to more complex models only if the GF value was >5% for the adsorption period. Model
21 predicted concentrations are shown for limonene in Figure 1 and methylnaphthalene in Figure 3.

22 The surface sink model achieved excellent fits (GF <5%) to the adsorption period data for
23 benzene, toluene, o-xylene, α -pinene and MEK. Adsorption period GF values of 5-10% were
24 obtained when the surface sink model was applied to data for limonene, ethylbenzene, and the
25 high volatility compounds MTBE, acrolein, and isoprene. Reasonable fits corresponding to
26 adsorption period GFs of 10-15% were obtained when the surface sink model was applied for
27 trimethylbenzene, diethylbenzene, and pyridine. However, the surface sink model poorly

1 reproduced the observed dynamic pattern near the inflection point as shown for limonene (Figure
2 1) and methylnaphthalene (Figure 3). The discrepancy increased with decreasing vapor pressure
3 and was most pronounced for the lowest volatility, highest sorbing compounds. As a result,
4 substantially larger adsorption period GFs were obtained when the surface sink model was
5 applied for naphthalenes, aromatic alcohols, 4-EP and nicotine.

6 The sink-diffusion and two-sink models provided better fits for trimethylbenzene,
7 diethylbenzene, and pyridine, resulting in adsorption period GFs of 6-8% for the sink-diffusion
8 model and 1.6-2.8% for the two-sink model. The improved fits, especially at the inflection point
9 of the adsorption period can be seen for limonene in Figure 1. This improvement indicates the
10 importance of another physical process with an associated time scale differing from those
11 indicated by the linear model. The more complex models capture the shape of the increase in
12 gas-phase concentrations during the net desorption period and in many cases predict lower, more
13 accurate equilibrium concentrations following desorption.

14 The two-sink model yielded substantially better fits than the surface-sink or the sink-
15 diffusion models for the higher-sorbing compounds. Using the two-sink model, adsorption
16 period GFs of <10% were observed for naphthalene, phenol, and 4-EP; and GFs of <15% were
17 achieved for cresol and dimethylnaphthalene. As shown for methylnaphthalene in Figure 3, all of
18 the models over-predicted equilibrium concentrations for the higher sorbing compounds at the
19 ends of the adsorption and desorption periods.

20 Figures 1 and 3 and the last column of Table 3 show that the best-fit model and parameter
21 values derived from adsorption period data provide good predictions of behavior during the
22 desorption period for many compounds. However, since the parameter estimates were obtained
23 from the adsorption period data, desorption period GFs were almost always higher than those
24 from corresponding adsorption periods. Desorption GFs were in the range of 13-23% for the
25 surface sink applied to MEK and most of the aromatic and terpene hydrocarbons. Desorption
26 GFs were <5% for many of these compounds when the sink-diffusion model was applied (some
27 not shown in Table 3). Desorption GFs of 10-20% were calculated using the two-sink model for
28 naphthalenes, aromatic alcohols, 4-EP, and nicotine.

1 *4.3 Correlation of parameter values with physical and chemical properties*

2 To extrapolate the results to other organic compounds, it is desirable to establish relationships
3 between sorption characteristics and key physical and chemical properties. Correlations between
4 sorption properties and vapor pressure P_0 have been demonstrated by An et al. (1999) and Won
5 et al. (2001a) for linear sorption (sink model) onto individual materials. The potential predictive
6 value of the octanol-air partitioning coefficient K_{oa} has been discussed by Pankow (1998) in
7 relation to gas-particle partitioning and investigated by Won et al. (2001a) in relation to material
8 sorption.

9 Our results indicated that both P_0 and K_{oa} are useful in predicting sorption characteristics.
10 As an example, Figure 4 shows that the sink model equilibrium partitioning coefficient ($K_{eq} =$
11 λ_a/λ_d) was strongly correlated with the inverse of P_0 (see An et al., 1999 for discussion of this
12 relationship). Linear regressions are presented separately for polar compounds (including the
13 carbonyls, phenols, N-aromatics) and the relatively non-polar hydrocarbons. Figure 5 shows that
14 $\log K_{oa}$ is a good predictor of the surface adsorption rate coefficient for the best-fit model for
15 each compound. Additional relationships may be derived from the parameter values in Table 3
16 and compound properties in Table 2.

17 *4.4 Predicting sorption from published parameter values for individual materials*

18 The current experiments differed from previous work in both the size of the chamber and the
19 combination of materials. We attempted to relate our results to the prior literature by simulating
20 our experiments with published sorption parameter values for individual materials. Linear model
21 parameters from Won et al. (2001a) for MTBE, toluene, ethylbenzene and dichlorobenzene
22 (DCB) were selected. We compared the model predictions for DCB, the second lowest volatility
23 compound in the earlier study, ($P_0 = 200$ Pa, $\log K_{oa} = 4.27$) to our measurements of
24 trimethylbenzene ($P_0 = 280$ Pa, $\log K_{oa} = 4.34$). The surfaces in our chamber were approximated
25 using the closest analogs among the materials tested by Won et al., which included painted
26 gypsum wallboard and nylon carpet with cushion. Our wood and veneer furniture was modeled
27 with their wood floor parameter values, and our draperies were modeled with their cotton

1 upholstery results. One-half of the area of our upholstered chairs was modeled as carpet with
2 cushion to account for the polyurethane foam cushioning in the chairs.

3 Figure 6 compares the measured results from Experiment 1 with the simulation
4 predictions. Use of the sorption parameter values from the small chambers resulted in substantial
5 over-prediction of the initial sorption of MTBE. However, the adsorption period partitioning of
6 toluene and ethylbenzene were reasonably approximated by application of small chamber
7 parameter values; predicted gas-phase equilibrium concentrations were higher than measured
8 values by about 15% for toluene and 30% for ethylbenzene. Simulation predictions for these two
9 compounds were close to measurements for the desorption period as well. The simulation based
10 on previously published dichlorobenzene sorption parameters reasonably predicted the observed
11 adsorption and desorption of trimethylbenzene. These results support the use of parameter values
12 from small chamber testing for modeling of moderately sorbing compounds in real settings.

13 **5. Discussion**

14 *5.1 Relevance of sorption in residences*

15 We have categorized the study compounds into three general groups based on their measured and
16 modeled sorption behavior: (A) those for which sorption would not be a substantially relevant
17 process under typical indoor residential conditions; (B) those for which sorption would
18 materially affect concentrations in a manner dependent upon the air change rate; and (C) those
19 for which sorption would have a major impact on gas-phase concentrations in most residential
20 situations.

21 The major factors guiding our categorization of the study compounds were the time
22 required to approach equilibrium partitioning, as measured by adsorption rates, and the extent of
23 sorption, as indicated by equilibrium partitioning. The initial adsorption rate (λ_a) is particularly
24 important; if the adsorption rate is much slower than the air change rate, VOCs will be removed
25 by ventilation before they have a chance to sorb. Adsorption rates should therefore be considered
26 in reference to air change rates.

1 A nationwide database of residential air change rates has been compiled (Murray and
2 Burmaster, 1995). The overall distribution was lognormal with a geometric mean of 0.53 h^{-1} and
3 geometric standard deviation of 2.3. All-season 10th and 90th percentile values were 0.21 and
4 1.48 h^{-1} . Compounds with adsorption rates near or below the lower range of this distribution
5 would be affected by sorption only minimally in most residences. Compounds in this category
6 based on their adsorption rates (Table 3) are MTBE, acrolein, MEK, isoprene, and benzene.
7 Compounds with initial adsorption rates of about $0.2\text{-}1.5 \text{ h}^{-1}$ combined with substantial capacity
8 for partitioning to surfaces, would partition measurably to surfaces in most residential situations.
9 The terpene hydrocarbons, C_7 and higher single-ring aromatic hydrocarbons and pyridine with
10 adsorption rate coefficients of $0.2\text{-}1 \text{ h}^{-1}$ fit this category. Compounds adsorbing at rates $>1.5 \text{ h}^{-1}$
11 and having high sorption capacities would partition substantially to surfaces even in residences
12 with moderate to high air change rates. The naphthalenes, aromatic alcohols, 4-EP, and nicotine
13 fit this category.

14 The importance of sorption in residences depends also on equilibrium partitioning. This
15 was evaluated using the best-fit models and parameter values (Table 3). Modeling allowed for
16 the simultaneous tracking of both gas- and sorbed-phase concentrations so that partitioning could
17 be calculated. Figure 7 presents the fraction of each compound remaining in the gas-phase at 2 h
18 and 12 h. Results at 12 h are indicative of equilibrium partitioning for most compounds studied,
19 while the 2 h results capture the importance of both equilibrium and dynamic effects. For
20 reference, the nationwide 25th and 75th percentile air change rates of 0.35 and 0.85 h^{-1} would
21 respectively yield 50 and 82% reductions in the gas-phase concentrations of a non-sorbing tracer
22 gas over 2 h.

23 The sorption potentials indicated in Figure 7 support the same grouping of the study
24 compounds. At 2 h, $> 90\%$ of the MTBE, acrolein, isoprene and $>80\%$ of the MEK and benzene
25 remained in the gas-phase, indicating little sorption even in the near absence of ventilation for
26 group A compounds. Partitioning to the sorbed phase increased monotonically with molecular
27 mass for the single-ring aromatic hydrocarbons. These aromatics, terpene hydrocarbons, and
28 pyridine remained about 40-80% in the gas-phase at 2 h indicating significant sorption in the

1 absence of ventilation for group B compounds. At 2 h, the sorbed phase accounted for ~85% of
2 the naphthalene and 4-EP, 90% of the methyl- and dimethylnaphthalenes, 96% of the aromatic
3 alcohols, and 99% of the nicotine. At 12 h, even more mass (95 to >99%) of these group C
4 compounds was sorbed to surfaces.

5 *5.2 Insight into process time scales*

6 Analysis of the sorption parameter values in Table 3 provides further insight into the time scales
7 and physical processes that apparently control sorption in a furnished residential environment.
8 The more complex models generally yielded parameter values that were consistent with those
9 obtained using the surface sink model. Initial adsorption rates appeared to increase with the
10 complexity of the model. For example, more than a factor of two increase was observed for
11 trimethylbenzene and diethylbenzene when going from the surface sink to the two-sink model.
12 But when this occurred, the rate controlling mass transfer to the second conceptual sink (k_1) was
13 similar to the adsorption rate λ_a for the surface sink model. For the higher sorbing group C
14 compounds, the rate of initial adsorption to the surface λ_a , increased incrementally with model
15 complexity, but the overall increase did not appreciably change the predicted time scale of initial
16 adsorption. Another notable result is that using a more complex model did not change the time-
17 scale controlling desorption for many compounds, even as the parameter controlling that time
18 scale did change. For example, the sink model desorption coefficient λ_d for trimethylbenzene
19 was 0.10 h^{-1} . When trimethylbenzene was fit to the sink-diffusion and two-sink models, the
20 desorption time scale was dictated by k_d and k_2 , respectively, both of which were estimated to be
21 0.10 h^{-1} . Similar desorption time constants across the three models (i.e., less than a factor of two
22 variation) were observed for diethylbenzene, naphthalenes, aromatic alcohols, pyridine, and 4-
23 EP.

24 *5.3 Fundamental processes*

25 Two physical processes are required for sorption to occur: transport to the surface and bonding to
26 the material. Transport is a function of near-surface airflow; rates increase as the concentration
27 boundary layer is compressed. Sorptive bonding occurs for only a fraction of the collisions

1 between gas molecules and the solid surface; this fraction is the sticking probability. The system
 2 of ozone reactions on indoor surfaces provides insight into these processes. Morrison and
 3 Nazaroff (2002) have shown that for given room airflow conditions, a critical reaction
 4 probability can be calculated. Below the critical value, the log of the deposition velocity is
 5 linearly dependent on the log of the reaction probability (reaction-limited regime). When
 6 reaction probability exceeds the critical value, deposition scales with the transport rate
 7 (transport-limited regime). Morrison and Nazaroff calculated transport-limited ozone deposition
 8 velocities of 0.02-0.2 cm s⁻¹, based on typical indoor friction velocities (u*) of 0.03-0.3 cm s⁻¹.
 9 Using the same equations and assuming sticking probabilities above the critical value for all
 10 surfaces in our chamber (total S/V = 2.3 m⁻¹) yields transport-limited adsorption coefficients of
 11 2.4-24 h⁻¹ (for nicotine molecular mass of 162). The highest estimated adsorption coefficient (λ_a)
 12 of 8 h⁻¹ (nicotine, two-sink model; Table 3) corresponds to the transport-limited rate for u* = 0.1
 13 cm s⁻¹. This result suggests nicotine may sorb at or close to the transport-limited rate. Sorption
 14 for the other compounds studied should be correlated with sticking probability on a log-log plot.
 15 This is consistent with the relationship shown in Figure 5 and supports the use of K_{oa} as a
 16 predictor of sorption.

17 Another process of potential relevance is diffusion through the pore spaces in wallboard.
 18 Meininghaus and Uhde (2002) reported diffusion coefficients (D) of 0.001-0.003 m² h⁻¹ for low
 19 polarity organic compounds in gypsum wallboard. We estimated the potential pore diffusion loss
 20 rate (L_d, h⁻¹) in our chamber using Equation 9 with Δx_i as the thickness for i = 5 surfaces (4 walls
 21 + ceiling).

$$22 \quad L_d = \sum_{i=1,5} \frac{D}{\Delta x_i} \left(\frac{S_i}{V} \right) \quad (9)$$

23 Assuming no diffusion through the walls with plywood yields L_d = 0.017-0.05 h⁻¹. Assuming the
 24 wallboard diffusion rates also apply to plywood yields L_d = 0.04-0.12 h⁻¹. The lower end of these
 25 estimates corresponds to the observed adsorption period decay rate for the lowest/non-sorbing
 26 compounds. Losses of mass via pore diffusion could not have been larger than the observed

1 decay rates. The sealed chamber infiltration rates in Table 1, as measured by SF₆ decay, may
2 reflect pore diffusion loss, rather than air change.

3 **Conclusions**

4 Sorption processes affecting the indoor gas-phase concentrations of VOCs will influence
5 inhalation exposures of occupants to these compounds. Adsorption rates of several important
6 mid and low volatility organics gases to typical residential surfaces treated as a single assembly
7 were shown to be sufficient to reduce gas-phase concentrations on time scales competitive with
8 typical residential ventilation rates. Equilibrium partitioning to the surface assembly also was
9 shown to favor reductions in gas-phase concentrations of the same compounds over extended
10 periods. A logical step to advance this technique for estimating indoor exposures to outdoor
11 generated HAPs is to link these models and model parameters to temporal models of ambient
12 HAP concentrations and human activity patterns.

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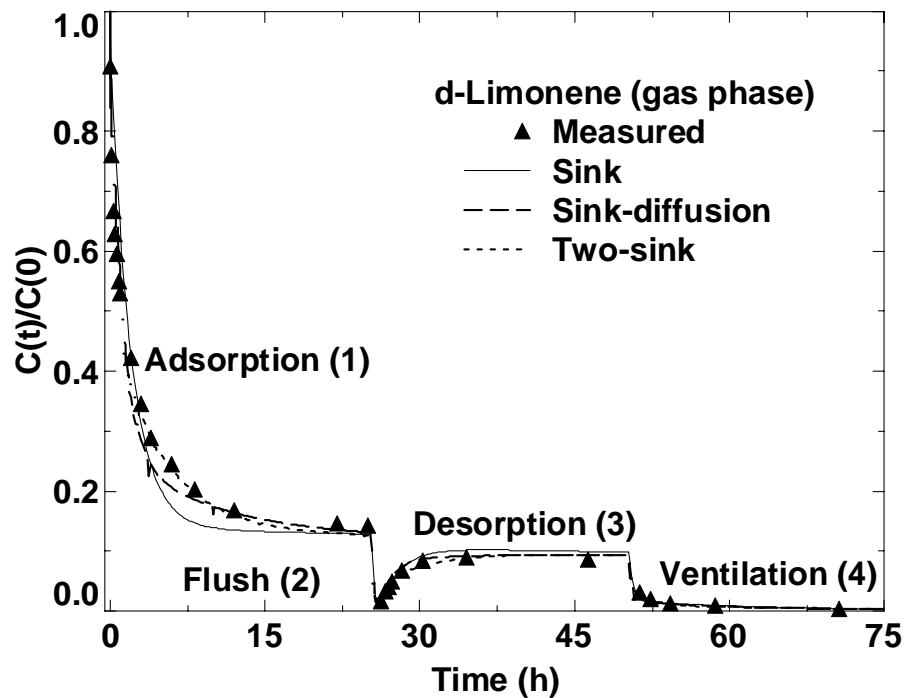
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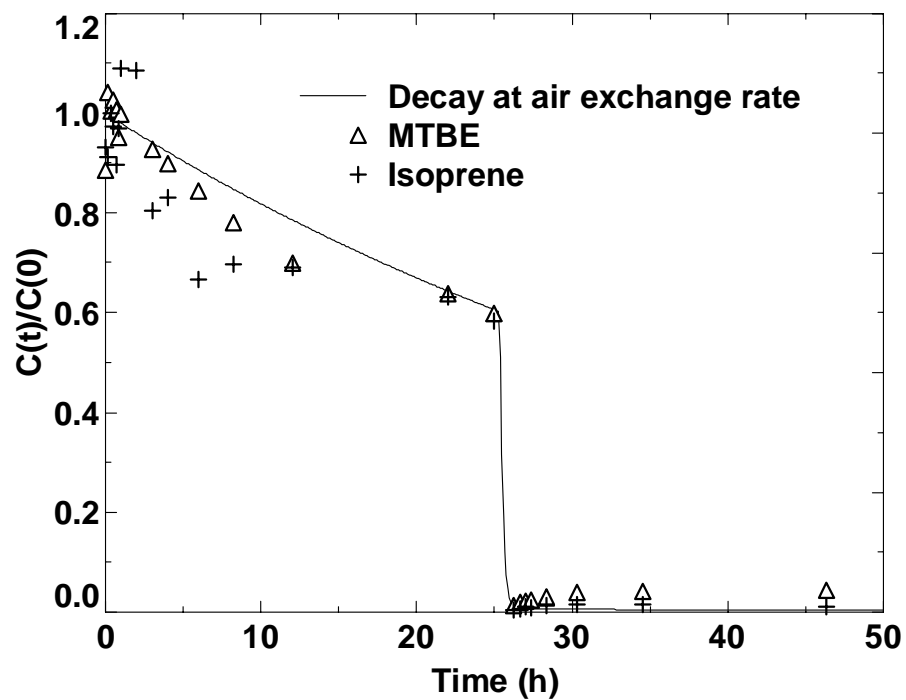
15 **Figure Captions**

- 16 **Figure 1.** Measured and model predicted normalized concentrations for d-limonene in
17 Experiment 1. Labels define experimental periods 1-4.
- 18 **Figure 2.** Measured normalized concentrations of MTBE and isoprene for Experiment 1 with
19 concentration profile predicted by solely decay due to air change rate.
- 20 **Figure 3.** Measured and model predicted normalized concentrations for 1-methylnaphthalene in
21 Experiment 1. Inset plots same data over smaller concentration range.
- 22 **Figure 4.** Correlation of sink model equilibrium coefficient ($K_{eq} = \lambda_a/\lambda_d$) with inverse of
23 compound vapor pressure (P_0).
- 24 **Figure 5.** Correlation of adsorption rate coefficient of best-fit model with octanol-air partition
25 coefficient for each compound.
- 26 **Figure 6.** Measured and simulated normalized concentrations for MTBE, toluene, ethylbenzene
27 and trimethylbenzene in Experiment 1. Simulations for the assembled materials were based
28 on published sorption rates for individual compound-material combinations (Won et al.,
29 2001). Published dichlorobenzene sorption parameters were used for trimethylbenzene.
- 30 **Figure 7.** Fraction of each study VOC remaining in the gas phase after 2 and 12 h based upon
31 the most appropriate model for the compound (mean of results for Experiments 1 and 2).
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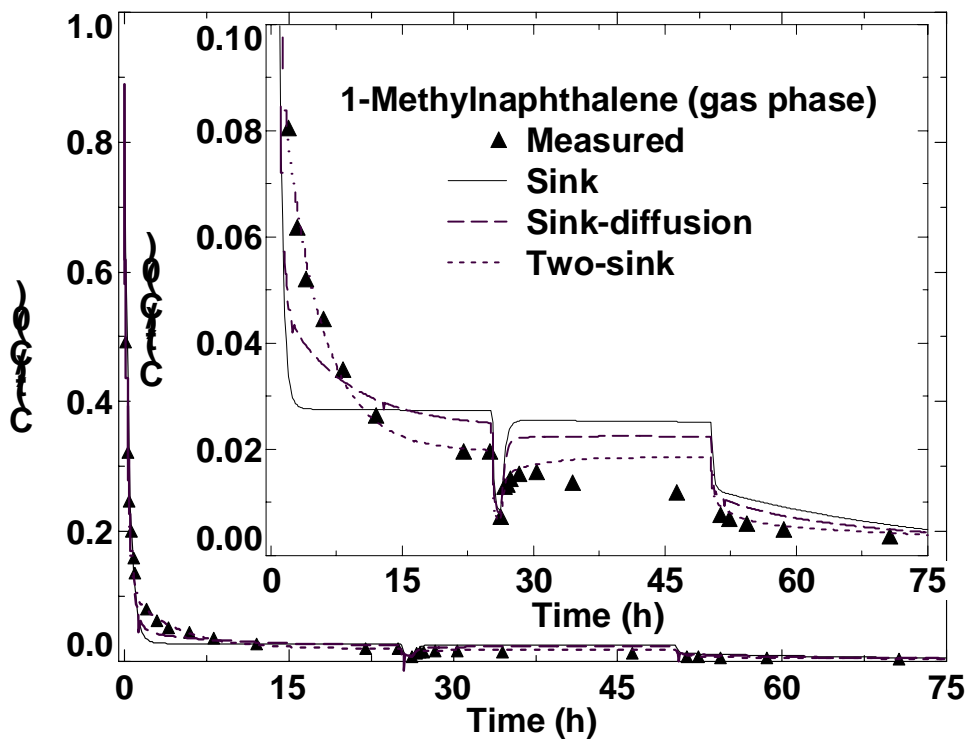
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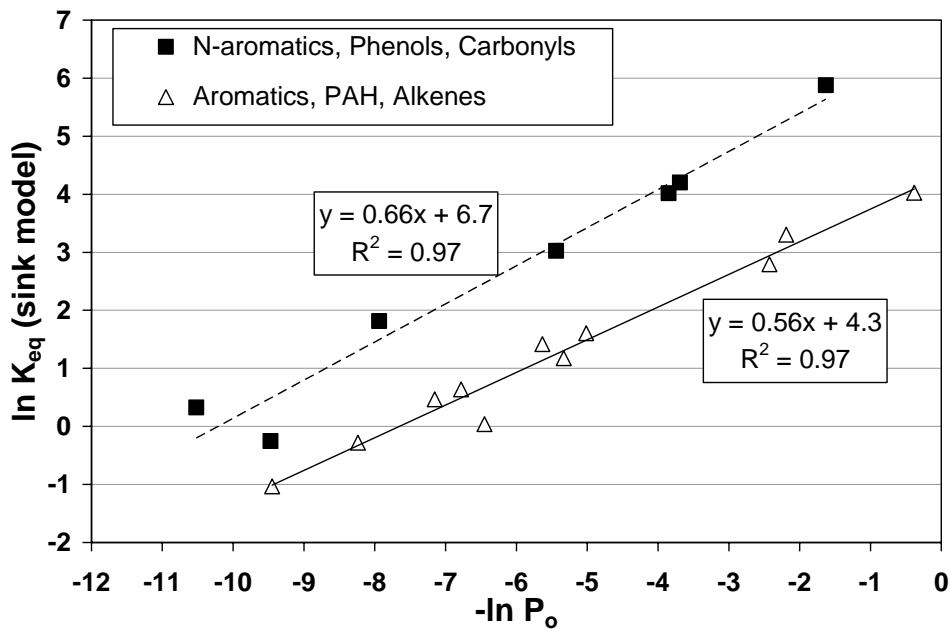
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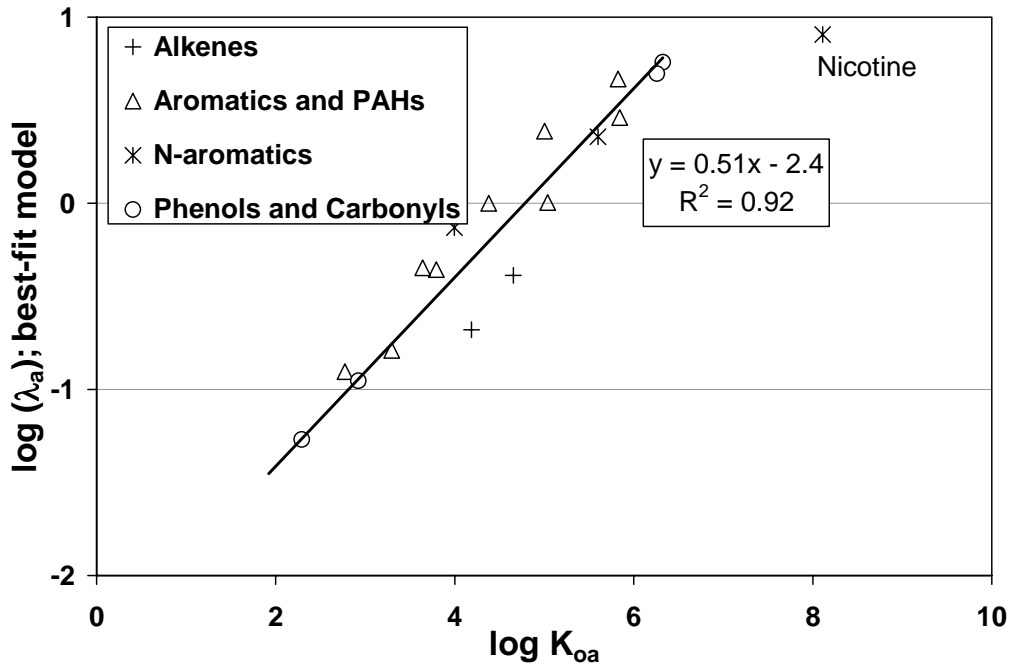


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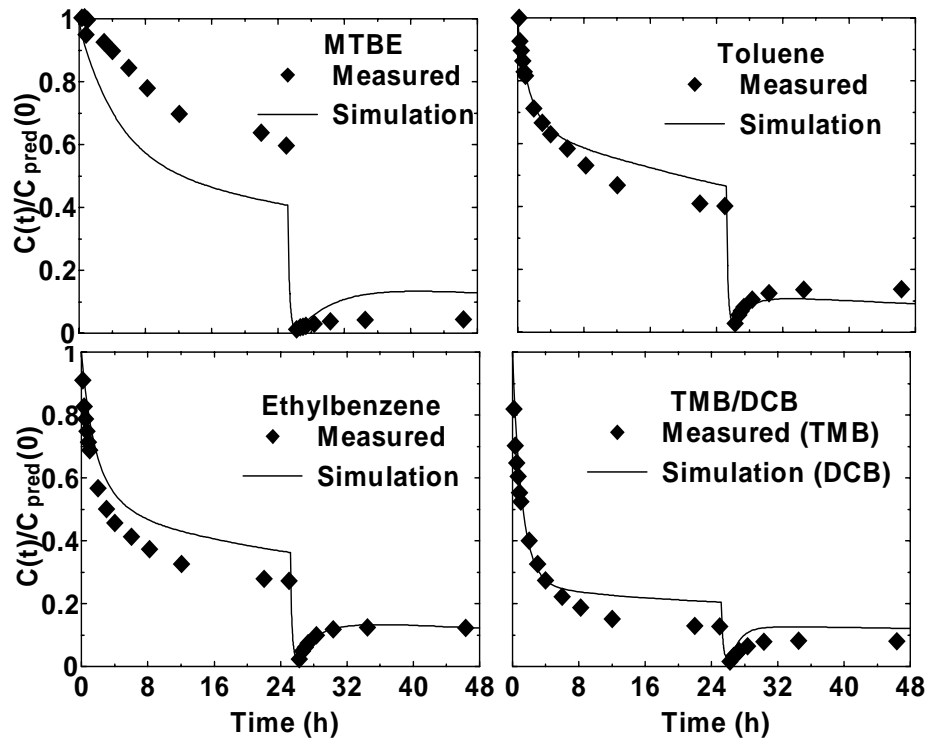


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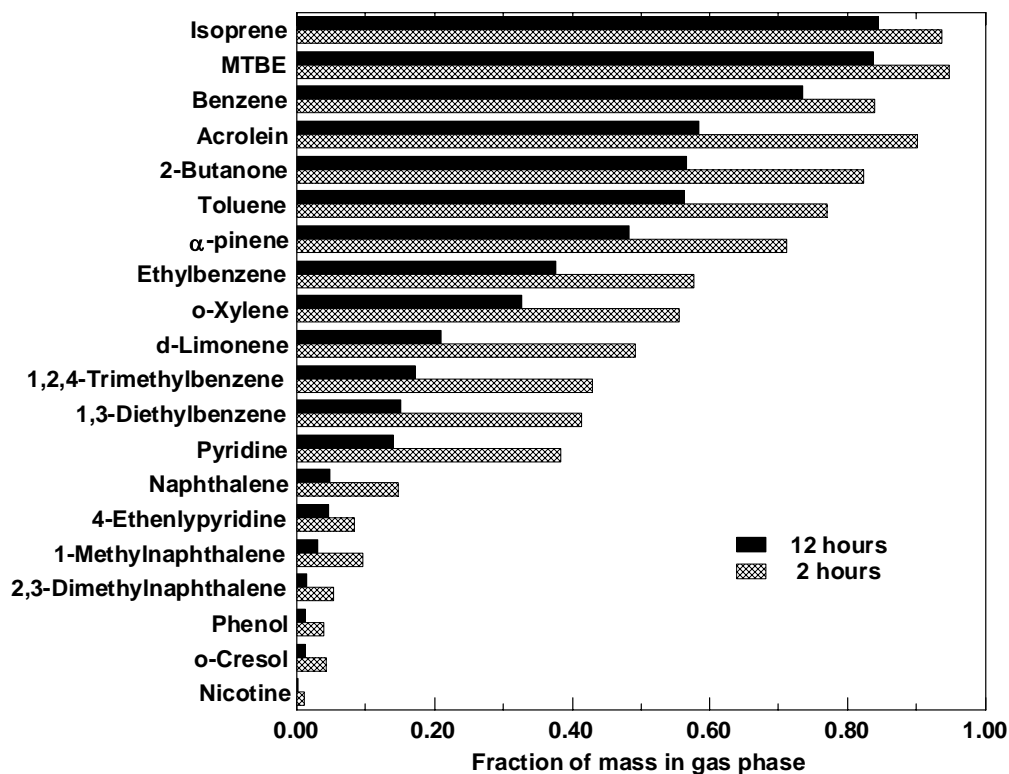
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Table 1. Experimental conditions

Experiment/ Period	Duration (h)	ACH (h ⁻¹)	Temp. ^a (°C)	Rel. Humid. ^a (%)	Measure- ments (#) ^b
Experiment 1					
Net adsorption	25.5	0.02	21.6 (0.6)	35 (<1)	14
Flush	1	4.8	21.6 (0.1)	35 (<1)	1
Net desorption	24	0.03	21.8 (0.5)	36 (1)	7
Vent. desorption	>24	2.4	21.7 (0.2)	42 (4)	5
Experiment 2					
Net adsorption	22	0.02	21.4 (0.4)	40 (<1)	12
Flush	1	7.3	20.9 (0.0)	40 (<1)	1
Net desorption	24	0.02	21.1 (0.2)	39 (1)	5
Vent. desorption	>24	2.4	20.9 (0.1)	40 (1)	3

7 ^a Mean (standard deviation) of 10-minute average values for each experimental period.
8 Each 10-min value calculated as the average of 8 sensors placed around the room.
9 ^b Number of times gas-phase concentrations were measured

1

2 **Table 2.** Test compounds and properties.^a Hazardous air pollutants indicated by asterisk.

Compound ^b	Grouping	Formula	B.P. ^c (°C)	P ₀ ^c (Pa)	Log K _{ow} ^c	K _H ^c [M/atm]	Log K _{oa} ^d
MTBE*	Ether	C ₅ H ₁₂ O	55	3.3E+04	0.94	1.6E+00	2.53
Acrolein*	Carbonyl/ Alkene	C ₃ H ₄ O	53	3.7E+04	-0.01	7.4E+00	2.25
MEK*	Carbonyl	C ₄ H ₈ O	80	1.2E+04	0.29	2.0E+01	2.98
Isoprene	Alkene	C ₅ H ₈	34	7.3E+04	2.42	2.8E-02	2.26
α-Pinene	Alkene	C ₁₀ H ₁₆	156	6.3E+02	4.83	4.9E-02	4.91
d-Limonene	Alkene	C ₁₀ H ₁₆	176	2.0E+02	4.23	3.9E-02	4.21
Benzene*	Aromatic	C ₆ H ₆	80	1.3E+04	2.13	1.8E-01	2.77
Toluene*	Aromatic	C ₇ H ₈	111	3.8E+03	2.73	1.5E-01	3.29
Ethylbenzene*	Aromatic	C ₈ H ₁₀	136	1.3E+03	3.15	1.2E-01	3.62
o-Xylene*	Aromatic	C ₈ H ₁₀	144	8.8E+02	3.12	1.9E-01	3.79
1,2,4-TMBenzene	Aromatic	C ₉ H ₁₂	169	2.8E+02	3.78	1.5E-01	4.34
1,3-DEBenzene	Aromatic	C ₁₀ H ₁₄	182	1.6E+02	4.44	1.2E-01	4.91
Naphthalene*	PAH ^e	C ₁₀ H ₈	218	1.2E+01	3.3	2.1E+00	5.01
1-Me-Naphth	PAH ^e	C ₁₁ H ₁₀	245	7.2E+00	3.87	3.9E+00	5.85
2,3-DiMe-Naphth	PAH ^e	C ₁₂ H ₁₂	264	1.9E+00	4.61	1.7E+00	6.23
Phenol*	Phenolic	C ₆ H ₆ O	182	4.7E+01	1.46	2.9E+03	6.31
o-Cresol*	Phenolic	C ₇ H ₈ O	191	4.0E+01	1.95	8.3E+02	6.26
Pyridine	N-aromatic	C ₅ H ₅ N	115	2.8E+03	0.65	1.1E+02	4.08
4-EP	N-aromatic	C ₇ H ₇ N	65	2.3E+02	1.54	3.2E+02	5.43
Nicotine	N-aromatic	C ₁₀ H ₁₄ N ₂	247	5.1E+00	1.17	3.6E+05	8.11

3

4 a) Source: Meylan and Howard (1997).

5 b) MTBE = methyl tert butyl ether; MEK = Methyl ethyl ketone (2-Butanone); TMBenzene = 1,2,4-
6 trimethylbenzene; DEBenzene = 1,3-diethylbenzene; Me-Naphth = 1-methylnaphthalene; DiMe-
7 Naphth = 2,3-dimethylnaphthalene; 4-EP = 4-ethenylpyridine.8 c) B.P. = boiling point; P₀ = Pure compound vapor pressure at 25 C; K_{ow} = Octanol-water partitioning
9 coefficient; K_H = Henry's constant for water-air partitioning10 d) Octanol-air partitioning coefficient. Estimated as $K_{oa} = 10^3 RT K_{ow} K_H^{-1}$, in accordance with
11 Boethling and Mackay (2000), p.117.

12 e) Polycyclic aromatic hydrocarbons.

13

14

15

1 **Table 3.** Best-fit parameter values by compound. ^a

Compound (sorption category) ^b	Model	C(0) Exp 1 [$\mu\text{g m}^{-3}$]	C(0) Exp 2 [$\mu\text{g m}^{-3}$]	λ_a [h^{-1}]	λ_d [h^{-1}]	$k_{\text{dif}/1}$ [h^{-1}]	k_2 [h^{-1}]	GF ^d (adsorb)	GF ^d (desorb)
MTBE (A)	Sink	417	381	0.03	0.16			0.06	1.05
Acrolein (A)	Sink	391	322	0.05	0.04			0.08	0.45
MEK (A)	Sink	385	395	0.11	0.14			0.03	0.23
Isoprene (A)	Sink	723	352	0.04	0.22			0.09	2.59
α -Pinene (B)	Sink	383	408	0.21	0.20			0.03	0.12
d-Limonene (B)	Sink	366	366	0.32	0.10			0.07	0.15
	Sink-diff	366	370	0.41	0.23	0.12		0.04	0.08
Benzene (A)	Sink	425	411	0.12	0.35			0.03	0.17
Toluene (B)	Sink	392	418	0.16	0.21			0.03	0.17
Ethylbenzene (B)	Sink	391	391	0.32	0.20			0.07	0.18
	Sink-diff	396	391	0.45	0.49	0.12		0.04	0.06
o-Xylene (B)	Sink	383	383	0.28	0.15			0.05	0.13
	Sink-diff	400	406	0.44	0.39	0.14		0.02	0.07
1,2,4-Trimethyl- benzene (B)	Sink	392	392	0.41	0.10			0.10	0.20
	Sink-diff	392	392	0.51	0.22	0.10		0.06	0.09
	Two-sink	421	432	1.00	1.05	0.44	0.10	0.02	0.08
1,3-Diethyl- benzene (B)	Sink	376	376	0.40	0.08			0.12	0.24
	Sink-diff	376	376	0.50	0.18	0.09		0.06	0.23
	Two-sink	405	412	1.01	0.95	0.38	0.07	0.02	0.09
Naphthalene (C)	Sink	880	813	1.64	0.10			0.27	1.11
	Sink-diff	880	813	1.78	0.19	0.07		0.18	0.83
	Two-sink	886	927	2.44	0.56	0.24	0.05	0.06	0.46
1-Methyl- naphthalene (C)	Sink	761	761	2.20	0.08			0.29	0.71
	Sink-diff	761	761	2.35	0.15	0.08		0.20	0.49
	Two-sink	761	788	2.89	0.42	0.25	0.06	0.08	0.24
2,3-Dimethyl- naphthalene (C)	Sink	880	797	3.30	0.06			0.34	0.74
	Sink-diff	880	797	3.48	0.11	0.08		0.25	0.55
	Two-sink	880	853	4.66	0.46	0.37	0.06	0.12	0.33
Phenol (C)	Sink	880	722	4.13	0.07			0.32	0.59
	Sink-diff	880	722	4.43	0.14	0.09		0.22	0.41
	Two-sink	935	802	5.73	0.39	0.33	0.08	0.10	0.23
o-Cresol (C)	Sink	822	822	3.77	0.06			0.34	0.69
	Sink-diff	822	822	3.97	0.11	0.08		0.25	0.50
	Two-sink	822	842	4.97	0.37	0.34	0.06	0.12	0.29
Pyridine (B)	Sink	437	437	0.42	0.07			0.13	0.50
	Sink-diff	437	437	0.51	0.14	0.07		0.07	0.32
	Two-sink	456	462	0.74	0.38	0.20	0.06	0.03	0.25
4-Ethenyl- pyridine (C)	Sink	838	419	1.53	0.07			0.32	1.05
	Sink-diff	838	419	1.65	0.14	0.07		0.24	0.82
	Two-sink	838	419	2.28	0.60	0.26	0.04	0.07	0.35
Nicotine (C)	Sink	792	792	6.56	0.01			0.47	0.74
	Sink-diff	792	792	6.87	0.04	0.08		0.39	0.62
	Two-sink	792	792	8.07	0.16	0.41	0.05	0.21	0.39

2 a) Mean of parameters estimated from two replicate experiments.

3 b) Importance of sorption in real settings, roughly A=not, B=sometimes, C=always. See text for details.

4 c) Calculated as the root mean square of the normalized residuals divided by the square root of the
5 number of data points (Equation 8); from net adsorption or desorption period as indicated.