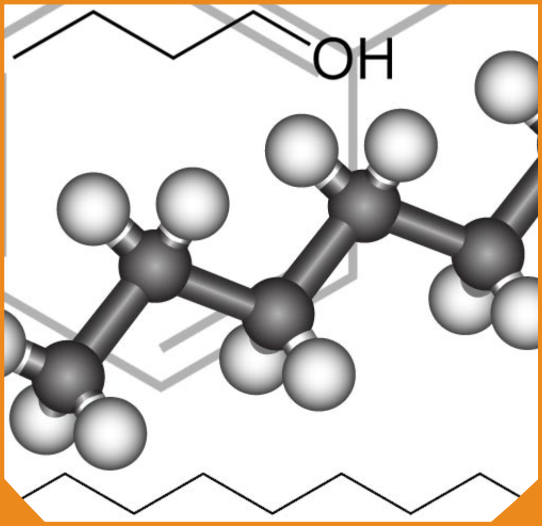
United States
Environmental Protection
Agency

Determination of Sorption Parameters for 36 VOC/Material Combinations

FINAL REPORT



Office of Research and Development
National Homeland Security Research Center

October 2007 EPA 600/R-07/035-R1

Determination of Sorption Parameters for 36 VOC/Material Combinations Final Report

Submitted to:

Dr. Zhishi Guo
U.S. Environmental Protection Agency
Office of Research & Development
National Risk Management Research Laboratory
Air Pollution Prevention & Control Division
Indoor Environment Management Branch

Submitted by:

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Office of Research and Development
National Homeland Security Research Center, Decontamination and Consequence Management Division

NOTE: This report was revised in October 2007. The following letter explains the reason for the revision. The previous version of this report has been removed from the NHSRC web site. This version should be used.

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MEMORANDUM

To: Dr. Zhishi Guo
U.S. Environmental Protection Agency
Office of Research & Development
National Risk Management Research Laboratory
Air Pollution Prevention & Control Division
Indoor Environment Management Branch

From: Dr. John Little

Professor
Environmental and Water Resources Engineering Program
Department of Civil and Environmental Engineering
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Date: 1 October, 2007

Subject: Balance Malfunction Affecting Partition Coefficient Measurement

Measuring the material/air partition coefficient (K) for a VOC in a building material requires exposing a material sample to a gas stream containing a known concentration of target VOC. The mass of the sample is recorded as the VOC partitions to the surface and then diffuses into the material until the sample reaches gravimetric equilibrium. The equilibrium concentration of VOC in the material is calculated by dividing the sample mass gain by the sample volume. K is the ratio of material-phase VOC concentration to gas-phase VOC concentration.

The VOC laden gas stream is produced using a VICI Dynacalibrator. The Dynacalibrator contains a vial containing the target VOC. A clean gas stream is passed through the diffusion cell at a known flowrate. VOC is emitted from the diffusion vial at a constant rate into the gas stream. The gas-phase VOC concentration is calculated by dividing the VOC mass emission rate by the gas flowrate. The gas stream flowrate is controlled using a mass-flow controller. The diffusion vial emission rate is determined by measuring the mass of the vial before and after the experiment using a mechanical balance.

The problem with the initial K measurements was the result of a malfunction in a mechanical balance. One of the balance rings in the mechanical balance became dislodged from a support hook. This condition allowed the user to accurately zero the balance, but produced an erroneous reading when the diffusion vial was placed on the balance. The erroneous diffusion vial mass obtained from the mechanical balance produced errors in gas-phase VOC concentration calculations.

The mechanical balance was repaired and the K measurements were satisfactorily repeated. A revised report was produced. To eliminate the possibility of similar malfunctions occurring in the future the mechanical balance operation procedures have been modified. The revised procedures require that after zeroing the balance a calibration weight be used to confirm accurate balance operation before each use.

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1.
Introduction

1.1 Problem Statement

Sorptive interactions between gaseous pollutants and materials can be beneficial in terms of lowering pollutant concentrations and, thus, human exposure to those pollutants in buildings. However, the sorption process also leads to contamination of indoor materials and prolonged desorption of pollutants from materials. Scenarios for which sorptive interactions affect indoor air quality range from routine activities in buildings, e.g., use of cleaners or fragrances in homes to cigarette smoking in bars, to infrequent and extreme events, e.g., chemical spills in laboratories or terrorist releases of chemical warfare agents. A critical need in modeling indoor air quality during either routine or extreme events is the ability to model sorptive interactions between gaseous pollutants and indoor materials. However, the existing database is sparse with respect to model parameters for a wide range of chemicals and indoor materials. We address that need in this study through the use of seven chemicals with a wide range of physico-chemical properties and six different test materials that are commonly found in buildings.

1.2 Purpose of Study

The purpose of this study is to provide data to the United States Environmental Protection Agency (USEPA) for the evaluation of mathematical models that are best suited for analysis of the fate of chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) that could be employed during acts of terror on buildings.

1.3 Scope of Study and Division of Responsibilities

This study involved 36 combinations of test chemicals and materials. Material/air partition coefficients (K) and effective diffusion coefficients (D_e) were determined for 30 of those combinations; values of K and D_e could not be determined for mortar. These parameters were determined for use in models that predict chemical migration into and out of materials based on an equilibrium partitioning between air and the exterior surfaces of the material, and effective diffusion within the material. Examples of such models include those developed by Little et al., 1994; Cox et al., 2002; Zhao et al., 2002; Xu and Zhang, 2003; Kumar and Little, 2003; Deng and Kim, 2004; and Lee et al., 2005). Procedures to determine the key model parameters for these mechanistic models (including K and D_e) have been described by Haghighat and Zhang, 1999; Bodalal et al., 1999; Cox et al., 2001a; Cox et al., 2001b; Blondeau et al., 2003; Zhang and Niu, 2003; Zhao et al., 2004; and Li and Niu, 2005.

Two bench-top laboratory systems were employed to conduct the study. Twenty-four chemical/material combinations were tested at the University of Texas at Austin (UT) using a dual-volume diffusion chamber. Twelve chemical/material combinations were tested at Virginia Tech (VT) using a dynamic microbalance system. The experimental methods and data analysis procedures are described separately for each of these approaches in Chapters 2 and 3, respectively. Results are combined in Chapter 4 and summarized in Chapter 5. A discussion of quality assurance metrics is included in Appendix A.

Project team responsibilities were divided between staff at UT (dual-volume diffusion chamber experiments) and staff at VT (dynamic microbalance experiments). Staff at UT included Dr. Richard L. Corsi, Dr. Neil Crain, and John Fardal. Staff at VT included Dr. John Little and Ying Xu. It is noted that the VT Ph.D. student who was originally intended to work on the project (Huali Yuan) graduated earlier than expected. As a result, a new VT Ph.D. student (Ying Xu) was trained in the microbalance procedure and was the primary person responsible for collecting the experimental sorption/desorption data.

2.
Experimental Methodologies

2.1 Test Materials

This project involved experiments to quantify the sorptive interactions between six materials and seven test chemicals. The test materials were unpainted gypsum board, painted gypsum board, PVC-backed carpet, mortar, vinyl flooring, and polyurethane foam. A summary of test materials is presented in Table 2-1. All test specimens were provided to either UT or VT by the USEPA with two exceptions. Mortar specimens were generated at UT. Polyurethane foam samples were secured by VT. Unpainted gypsum board was marketed as 1/2" (1.27 cm) thickness wallboard, which was confirmed by direct measurement. Painted gypsum board was slightly (less than 0.005 cm) thicker than unpainted gypsum board. Carpet specimens were characterized by closed-loop nylon fibers attached to a PVC backing. The mean thickness of the carpet (backing and fibers) as measured using a Vernier caliper was 3.40 mm ($\sigma = 0.01$ mm; n= 5). The mean thickness of the carpet backing (fibers shaved off) was 1.23 mm ($\sigma = 0.12$ mm; n = 5). A common lot of each test material was used throughout the experimental program to ensure consistency.

Table 2-1. Summary of test materials.

Material	Sample Size	Description
Unpainted Gypsum Board	Unpainted gypsum board was cut into 26 cm diameter circles using a Roto-Zip spiral saw. The measured thickness of the unpainted gypsum board was 1.27 cm.	The nominal ½-inch gypsum board was manufactured by National Gypsum Company, Charlotte, NC 28211. The material was purchased on 8/9/04 from Home Depot in the Raleigh, NC area.
Painted Gypsum Board	Painted gypsum board was cut into 26 cm diameter circles using a Roto-Zip spiral saw. The measured thickness of the painted gypsum board was 1.27 cm.	Same as above but painted by US EPA with Classic 99 Flat Interior Latex Paint manufactured by Sherwin Williams. Type: Base color: 6405-10178 Color: Dover White Color Code: A27W51 SW6385 The paint was purchased in the Raleigh, NC area on 4/7/04.
Vinyl Carpet	Vinyl Carpet was cut into 26 cm diameter circles using a template and a utility knife. The mean thickness of the carpet (backing and fibers) was determined to be 3.40 mm. The mean thickness of the carpet backing (fibers shaved off) was 1.23 mm.	The vinyl carpet was manufactured by Surfaces. The product description was given as Type: ST103 Stratos/830 Gray item #97937, outdoor marine carpet. The carpet was purchased 11/04 from Lowe's in the Raleigh, NC area.
Mortar	Mortar specimens were cast in plywood molds to a diameter of 26 cm and a nominal thickness of 1.27 cm.	The mortar was prepared using screened oven-dried ¾-in. siliceous river gravel, oven-dried ASTM C 33 siliceous sand, Type I/II cement, and tap water. Prior to testing, the mortar specimens were cured for 28 days in a room at 70 °F and 100% relative humidity (RH).
Vinyl Flooring	The vinyl flooring sample tested had dimensions of 3.78 cm (length) × 2.66 cm (width) × 0.0175 cm (thickness).	
Polyurethane Foam	The polyurethane foam sample tested had dimensions of 1.39 cm (radius) × 4.70 cm (length).	A flexible polyether-type, open cell polyurethane foam was purchased from Airtex (Cokato, MN). The bulk density was measured to be 0.022 g/cm^3 at 21 °C and an RH of 21%, and bulk porosity of 97.6%. This commercial product is widely used in pillows, beds, sofa pads, and cushions in both homes and offices.

2.2 Test Chemicals

Seven different organic test chemicals were used in this study: ethylbenzene, n-butanol, hexanal, decane, undecane, dodecane, and tetradecane. The first six were employed by UT, using a dual-volume diffusion chamber. The latter six were employed by VT, using a dynamic microbalance. Thus, five test chemicals comprised a "base case" that was used for testing with each method. Sulfur hexafluoride (SF_6) was also used for four of the six test materials. Sulfur hexafluoride is an effective inert tracer, i.e., it does not adsorb to test materials and can be used to determine actual diffusion coefficients through materials in the absence of sorption processes. Materials, corresponding chemicals, and test methods are listed in Table 2-2. Several relevant properties of test chemicals are listed in Table 2-3.

Table 2-2. Test materials, chemicals, and methods.

Test Materials	Chemicals	Test Method
Unpainted gypsum board	Base case + ethylbenzene + SF_6	Dual-volume chamber
Painted gypsum board	Base case + ethylbenzene + SF_6	Dual-volume chamber
PVC-backed carpet	Base case + ethylbenzene + SF_6	Dual-volume chamber
Mortar	Base case + ethylbenzene + SF_6	Dual-volume chamber
Vinyl flooring	Base case + tetradecane	Microbalance
Polyurethane foam	Base case + tetradecane	Microbalance

Note: Base-case: n-butanol, hexanal, decane, undecane, dodecane

Table 2-3. Some relevant properties of test chemicals.

Chemical	CAS #	Molecular Weight (g/mol)	Boiling Point (°C)	Vapor pressure (mm Hg) at 20 °C
n-Butanol*	71-36-3	74.1	118	4.4
Hexanal*	66-25-1	100.2	128–131	10
Ethylbenzene	100-41-4	106.2	136	7
Decane*	124-18-5	142.3	173–174	2.7
Undecane*	1120-21-4	156.3	196	1 (33 °C)
Dodecane*	112-40-3	170.3	216	0.3
Tetradecane	629-59-4	198.4	252	1 (76 °C)

Note: Boiling point and vapor pressure values based on Verschueren (1996).
* = base-case chemical

2.3 Dual-Volume Diffusion Chamber Experiments

2.3.1 Experimental System

Two separate dual-volume experimental chamber assemblies were used for this study and were operated in parallel. A diagram of the dual-volume chamber assemblies is provided as Figure 2-1. Digital images of the system are provided in Figure 2-2. Each chamber assembly was constructed of electro-polished stainless steel to minimize nonspecific sorption. The assemblies were comprised of two sections, corresponding to the top and bottom chambers. Each section had a nominal volume of 8.5 liters, with a slight reduction in the top chamber when a test material was placed in the system.

The test material was seated atop a neoprene gasket on a lip around the perimeter of the bottom section of the chamber. Another neoprene gasket was placed on the top lip of the test material. The top section of the chamber slid over the bottom section across an o-ring with 4/1000 of an inch tolerance and compressed the material specimen around its perimeter. The o-ring was seated in a groove around the perimeter of the bottom section of the chamber. An external flange was bolted around the system perimeter to secure the seal around the material specimen. The diameter of the exposed surface of the material was 26 cm.

Both chambers of the experimental system contained a small fan used to promote mixing. The top section contained three injection/sample ports, which contained ¼" Swagelok™ fittings with silicon-lined septa for syringe injection/sampling. The bottom section contained two ports of similar design. Both chamber assemblies were previously leak tested using sulfur hexafluoride.

Figure 2-1. Schematic of experimental dual-volume diffusion chamber.

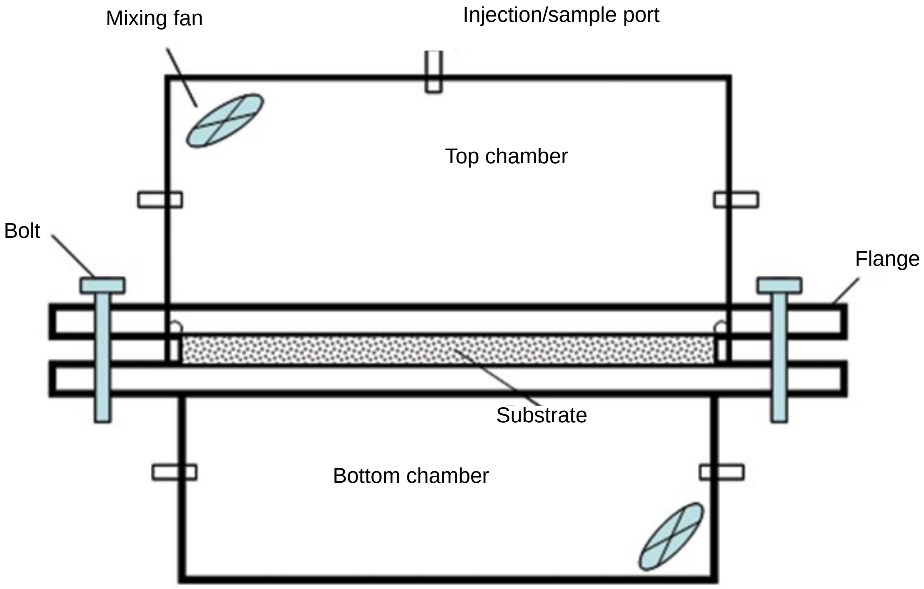
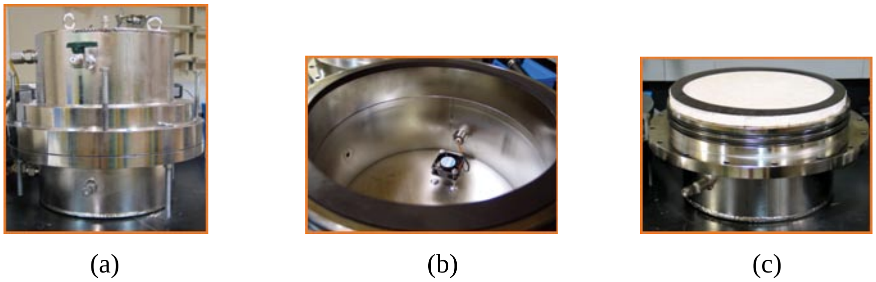


Figure 2-2. Digital images of experimental dual-volume chamber system: (a) fully-assembled, (b) view into bottom chamber with mixing fan visible, (c) bottom half with gypsum board seated (o-rings visible around circumference).


(a) (b) (c)

2.3.2 Experimental Procedure for SF_6

The experimental chamber was cleaned prior to starting any experiment. The cleaning procedure involved several steps. First, the chamber was disassembled and cleaned with methanol. Following the methanol cleaning, the chamber was reassembled and placed in an electric oven for 12 to 18 hours. An electric controller was used to maintain the oven temperature at 115 °C. Following heat treatment in the oven, the chamber was removed and allowed to cool before being disassembled. Finally, the chamber was again cleaned with methanol.

Once the chamber had been cleaned, the test material was sealed in the chamber and allowed to “rest” for at least four hours before background samples were collected from both the top and bottom chambers. A10-µL volume of pre-diluted SF_6 was drawn from a Tedlar™ bag, using a gas-tight syringe, and injected into the top chamber through a septum on the injection port. An initial sample was collected approximately one minute after injecting the SF_6. Samples were collected from the top and bottom chambers using gas-tight syringes inserted through Teflon™-lined septa into side sampling ports. Sample volumes of 25 mL were collected and immediately direct injected into a GC/ECD calibrated for analysis of SF_6 (Lagus Applied Technology, Inc. - Autotrac).

For tests involving gypsum board, subsequent samples were collected over two to three hours until the SF_6 concentrations in the top and bottom chambers were approximately equal. The tests conducted using mortar, however, lasted for more than two months and were terminated before equilibrium conditions were achieved. The effective diffusion coefficient for SF_6 could not be determined for carpet specimens due to the rapid migration of SF_6 through the specimens. All dual-volume chamber experiments were completed at a temperature of 24 ± 2 °C and relative humidity between 30 and 50 percent.

2.3.3 Experimental Procedure for Organic Test Chemicals

Experiments with organic test chemicals involved the same pre-cleaning procedure described above for the SF_6 experiments. Background samples were also collected from each chamber before the test chemical was introduced into the top chamber.

To initiate experiments, the selected organic compound was added to a 2-L glass bottle fitted with a septum. The compound was allowed to reach an equilibrium condition, i.e., creating a saturated headspace. A volume of between 50 and 600 mL of headspace gas was drawn from the bottle, using a gas-tight syringe, and injected into the top chamber of an experimental system; greater volumes were injected for compounds with lower vapor pressure. A purge valve was left open during injections into the top chamber so as to avoid over-pressurization of the system, and was closed immediately after injection.

Following the injection of the test compound, samples were sequentially withdrawn from both the top and bottom chambers at time intervals approximately 2 to 24 hours apart. Samples were collected from the top and bottom chambers until the system reached an equilibrium condition, i.e., the concentrations of the test chemical in the top and bottom chambers were approximately equal and constant. The first sample was collected approximately 30 seconds after the test compound was introduced to the top chamber. The time required to achieve system steady state for the tests with gypsum board and carpet ranged from several hours to several days. However, experiments with mortar did not achieve a steady-state condition over a period of more than two months.

All samples were collected by withdrawing 25 to 100 mL of chamber air through a sorbent tube connected to a gas-tight syringe. Sorbent tubes were actually large-volume gas chromatograph glass injection inserts packed with 100 mg of Tenax™-TA (80/100 mesh), allowing for zero-path thermal desorption of samples (see section 2.3.4).

Experiments involving mortar were conducted using a mixture of all six organic compounds. This change was made in an attempt to allow the test compounds to come to system steady state over an extended experimental period. The sample collection and analytical procedures used to test the mortar sample were the same as those used to test the gypsum board and carpet samples, although a steady-state condition was not achieved for experiments involving mortar, even after two months of sampling.

2.3.4 Analytical Methods

Samples were thermally desorbed using a programmable injector and large-volume injection port (ATAS Optic 2), with subsequent analysis using GC/FID (Hewlett-Packard 6890 GC; RTX 502.2 50 m mega-bore column with 0.53 mm i.d.) with a 1:1 split ratio. All analyses were completed using a ramped oven temperature from 60 to 280 °C. The oven temperature ramp rate was fixed at 30 °C/min. The initial injector temperature for all experiments was fixed at 60 °C. The injector temperature ramped to 280 °C in the first minute. A detector temperature of 300 °C was used for all samples. Calibration standards were generated by spiking sorbent tubes with known volumes of the organic test chemical dissolved in methanol, followed by purging of the tube with helium for 20 minutes at 25 mL/min. Seven-point external calibration curves were generated, with a minimum correlation coefficient (R^2) of over 0.99 for all experiments.

Figure 2-3. Schematic of the microbalance test system.

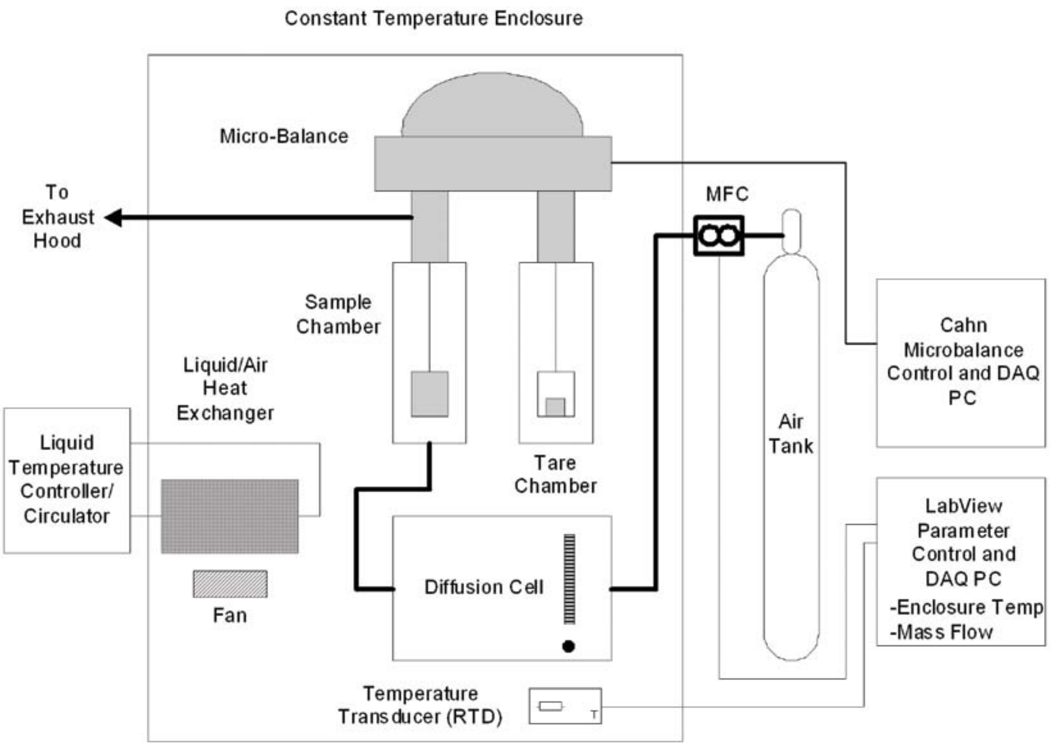


Figure 2-4. Digital images of microbalance test system: (a) whole test system, (b) microbalance system, (c) diffusion cell.

(a) (b) (c)

2.4 Dynamic Microbalance Experiments

Dynamic microbalance experiments were completed in the Air Quality Laboratory of the Department of Civil and Environmental Engineering at Virginia Tech. Measurements were conducted using a high-resolution (0.1 to 0.5 μg) dynamic micro-balance (Model D200-02, Cahn) equipped with a PC-based data-acquisition system (DAQ) as shown in Figure 2-3. This procedure was described in detail by Cox et al. (2001b) but is briefly reviewed here. Digital images of the system are provided in Figure 2-4.

The microbalance was placed on a marble balance stand that damped out vibrations. An enclosure was erected around the microbalance and covered with foil-faced polyethylene insulation to minimize potential signal fluctuations due to thermal variation or electromagnetic radiation. The temperature in the microbalance enclosure was controlled to within 25.6 ± 0.3 °C, using a constant temperature circulator (Isotemp, 1028D, Fisher Scientific) connected to a heat exchanger within the enclosure. The sample chamber was constructed of borosilicate glass. A glass frit was installed at the inlet end of the sample chamber to improve gas flow distribution.

For sorption tests, a gas concentration of a specific VOC was generated, using a constant temperature diffusion cell (Dynacalibrator Model 190, VICI Metronics, Inc.) modified as needed by substituting a stainless steel/glass flow path. For desorption tests, clean, dry air was supplied from gas cylinders (Medical Air USP, UN1002, Air Products). The flow path was constructed of 3.2-mm I.D. 304 stainless steel and Teflon tubing with stainless steel fittings. Mass flow controllers (MFC, Model FC-280S, Tylan-General) were used to control the air flow rates.

The material sample was suspended on the microbalance in the sample chamber. Samples were pre-conditioned in a separate chamber that was flushed with clean, dry air. This substantially reduced the time it took for the sample to reach equilibrium once it was placed on the microbalance prior to the start of the sorption/desorption experiment. After it was put in the microbalance, the sample mass was allowed to stabilize by passing clean, dry air through the sample chamber until equilibrium was obtained. An air stream containing a constant and known VOC concentration was then passed through the sample chamber. The air flow rate for the entire series of experiments was 0.334 actual L/min. VOC sample mass gain over time was monitored until equilibrium was reached. Influent air was then switched to clean air and the desorption process was monitored until equilibrium was reestablished. The airflow rate was relatively slow, and did not significantly influence the sample weighing procedure. For example, toward the end of the preconditioning period, turning off the air flow rate did not result in a noticeable change in microbalance response. A wider tube than supplied by the manufacturer was used to reduce the air velocity and a glass frit was introduced at the chamber entrance to ensure a uniform air velocity profile across the diameter of the sample chamber.

The diffusion vial with liquid VOC was weighed four times before sorption, after sorption, and after desorption. The emission rates were determined from the difference in the average mass of the diffusion vial divided by the time between the two measurements. The final emission rate was taken as the mean of the two emission rate values. The measured emission rates are shown in Table 2-4.

Table 2-4. Diffusion vial emission rates.

Chemicals	Emission Rate (μg/min)	
	VF	PUF
n-Butanol	217.5	194.1
Hexanal	186.0	–
Decane	42.9	43.0
Undecane	15.9	21.6
Dodecane	6.9	10.2
Tetradecane	5.1	8.3

3.

Data Analysis

3.1 Dual-Volume Diffusion Chamber Experiments

3.1.1 Determination of Equilibrium Partition Coefficients for Test Chemicals

The equilibrium partition coefficient (K) is a measure of the sorption capacity of a material for a specific chemical. Throughout this study we have assumed a linear sorption relationship between test chemical concentrations in air and on a material at equilibrium. As such, the equilibrium partition coefficient was calculated as the ratio of the sorbed-phase concentration (solid- or material-phase concentration) to that in the air adjacent to the material at a condition of equilibrium and was assumed constant for all values of C_{air}:

$$K = \frac{C_s}{C_{air}} \tag{3-1}$$

where,

K = equilibrium partition coefficient $[(mg/m^3_{material})/(mg/m^3_{air})]$ or $(m^3_{air}/m^3_{material})$,

C_s = sorbed concentration of test chemical $(mg\ /m^3_{material})$, and

C_{air} = concentration in air at equilibrium (mg/m^3_{air}).

The concentration in air should be the same in the top and bottom chamber sections at equilibrium. In fact, small (emphasized) differences existed in the top and bottom chamber air concentrations at equilibrium. As such, C_{air} reflects the average of test chemical concentrations in top and bottom chamber air.

The mass of chemical sorbed to the test material at equilibrium was determined as the difference between mass added (minus mass removed in test samples) and the mass contained in the air of each chamber. Adsorption of test chemicals to stainless-steel chamber walls was assumed to be negligible. The chemical concentration associated with the material (sorbed-phase concentration) was determined in accordance with Equation 3-2:

$$C_s = \frac{m_T - C_{air,t,e}V_t - C_{air,b,e}V_b - \sum m_{samp,i}}{V_{solid}} \tag{3-2}$$

where,

m_T = total mass of test chemical injected into the system (mg),

$m_{samp,i}$ = mass of test chemical removed from system during i^th sample (mg),

V_t, V_b = volumes of top and bottom chambers, respectively (m^3),

V_{solid} = volume of material (m^3),

$C_{air,t,e}$ = concentration of test chemical in top chamber air at equilibrium condition (mg/m^3), and

$C_{air,b,e}$ = concentration of test chemical in bottom chamber air at equilibrium condition (mg/m^3).

3.1.2 Determination of Effective Diffusion Coefficients for Test Chemicals

Carpet. For experiments involving carpet, the test chemical concentrations in the top and bottom chambers rapidly reached equal values and then gradually decreased in both chambers for a prolonged period of time. The following equations from Crank (1975) were employed to determine effective diffusion coefficients:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n{}^2} \exp\left(\frac{-D_e q_n t}{l^2}\right) \tag{3-3}$$

$$\frac{M_t}{M_\infty} = (1+\alpha)\left\{1 - \frac{\alpha}{\pi^{\frac{1}{2}}T^{\frac{1}{2}}} + \frac{\alpha^3}{2\pi^{\frac{1}{2}}T^{\frac{3}{2}}} - \frac{3\alpha^5}{4\pi^{\frac{1}{2}}T^{\frac{5}{2}}} + \ldots\ldots\right\} \tag{3-4}$$

where,

M_t = mass sorbed to the material at time t (mg),

M_∞ = mass sorbed to the material at equilibrium as determined experimentally (mg),

α = ratio of volume of the air chamber to the material (-),

q_n = non-zero positive roots of the mathematical expression: tan $q_n = -\alpha\, q_n$.

l = thickness of the material (m)

t = time (hr),

D_e = effective diffusion coefficient through material (m^2/hr), and

$T = \frac{D_e t}{l^2}$ (-).

An alternate solution to Equation 3-3 for small values of T is given by Equation 3-5:

$$\frac{M_t}{M_\infty} = (1+\alpha)\left\{1-\exp\left(\frac{T}{\alpha^2}\right)\mathrm{erfc}\left(\frac{T}{\alpha^2}\right)^{1/2}\right\} \qquad (3\text{-}5)$$

Equation 3-4 is obtained from Equation 3-5 by substituting the asymptotic expansion for

$\exp\left(\frac{T}{\alpha^2}\right)\mathrm{erfc}\left(\frac{T}{\alpha^2}\right)^{1/2}$ when $\frac{T}{\alpha^2}$ is large.

For carpet, a total normalized, squared residual between predicted and observed mass sorbed fractions was defined as:

$$R = \sum_{i=1}^{n}\left(\frac{\left\{{M_{t,i}}/{M_\infty}\right\}_{experimental} - \left\{{M_{t,i}}/{M_\infty}\right\}_{predicted}}{\left\{{M_{t,i}}/{M_\infty}\right\}_{experimental}}\right)^2 \qquad (3\text{-}6)$$

where,

R = total normalized squared residual (-), and

i = counter for each of n values of M_t (-).

The effective diffusion coefficient was selected as the value that minimized the total residual R.

Gypsum board. In the case of gypsum board (unpainted and painted), the initial concentrations in the top and bottom chambers were not equal and changed with time. An analytical solution could not be derived or found for these conditions. A finite difference approximation was therefore used to predict chemical diffusion through the gypsum board, from the top chamber to the bottom chamber. Mass balances were completed on the top and bottom chambers, with mass loss from the top chamber due to diffusive flux (Fick's first law) into the gypsum board and mass gain to the bottom chamber by diffusive flux (Fick's first law) passing out the bottom of the gypsum board. Fick's second law was applied to predict chemical diffusion through the gypsum board (a minimum of 10 layers/nodes was used for discretization of the gypsum board). Equilibrium conditions were assumed between chamber air and the exposed outer surfaces of the gypsum board. Although gypsum board is porous, it was treated as a solid slab for consistency with the models used for other materials in this study. Resulting finite difference expressions solved for concentration are presented in Appendix B.

A residual analysis similar to that described above for carpet was completed, with the exception of the normalized residual involving measured and predicted concentrations in top and bottom chamber air. The effective diffusion coefficient was chosen to minimize the total residual as defined by:

$$R = \sum_{i=1}^{n}\left(\frac{C_{air,\,experimental} - C_{air,\,predicted}}{C_{air,\,experimental}}\right)^2 \qquad (3\text{-}8)$$

All variables are as described previously (the concentrations in Equation 3-7 include those in both the top and bottom chambers). Due to the large number of calculations required to find a minimum residual, a program was written using the Java programming language to facilitate timely results. The source code for that program is included in Appendix B, along with the key equations used in the numerical solution.

In addition to determining effective diffusion coefficients for test chemicals and materials, i.e., that do not separate the effects of sorption and diffusion, effective diffusion coefficients (separated from the effects of sorption) were also estimated for unpainted and painted gypsum board and each test chemical. Effective diffusion coefficients were estimated through the use of sulfur hexafluoride (SF_6), an inert chemical not affected by sorption processes in gypsum board, and theoretical relationships between SF_6 and each organic test chemical. Specifically, the ratio of diffusion coefficients in air for a test chemical and SF_6 should be equal to the ratio of effective diffusion coefficients through a porous test material, e.g., gypsum board, and can be described by Equation 3-8:

$$\psi = \frac{D_{voc}}{D_{SF6}} = \frac{D_{e,voc}}{D_{e,SF6}} \approx \sqrt{\frac{M_{r,voc}}{M_{r,SF6}}}\left\{\frac{\Omega_{SF6}}{\Omega_{voc}}\right\}\left\{\frac{\sigma^2_{SF6}}{\sigma^2_{voc}}\right\} \qquad (3\text{-}8)$$

where,

Ψ = ratio of diffusion coefficients in air for a test chemical and SF_6 (-),

D_{voc} = molecular diffusion coefficient of VOC (test chemical) in air (m^2/hr),

D_{SF6} = molecular diffusion coefficient of SF_6 in air (m^2/hr),

$D_{e'voc}$ = effective diffusion coefficient of VOC in material pores (m^2/hr),

$D_{e'SF6}$ = effective diffusion coefficient of SF6 in material pores (m^2/hr),

Ω_{voc} = collision integral for VOC (-),

Ω_{SF6} = collision integral for SF_6 (-),

Ω_{voc} = characteristic length of VOC molecule interacting with air molecules (m), and

σ_{SF6} = characteristic length of SF_6 molecule interacting with air molecules (m).

Methods for estimating the collision integral and characteristic lengths of interaction can be determined based on Tucker and Nelken (1990). Resulting values are listed in Table 3-1.

Table 3-1. Collision integrals and characteristic lengths for select test chemicals.

Chemical	Collision Integral (-)	Characteristic Length (Å)
n-Butanol	1.174	4.627
Hexanal	1.180	4.923
Ethylbenzene	1.185	4.922
Decane	1.207	5.467
Undecane	1.219	5.580
Dodecane	1.230	5.687
Sulfur hexafluoride	1.048	4.374

The parameter M_r includes the molecular weight of air and chemical i (VOC or SF_6) in accordance with Equation 3-9:

$$M_{r,i} = \frac{M_{air} + M_i}{M_{air} M_i} \qquad (3\text{-}9)$$

where,

M_{air} = molecular weight of air = 29 g/mol, and

M_i = molecular weight of i (VOC or SF_6) (g/mol).

This approach allows a comparison between effective diffusion coefficients that were determined from experiments and that do not separate the effects of sorption with those that should occur in the absence of sorption. For example, if the former is similar to the latter, then sorption plays only a small role in retarding chemical migration through a material such as gypsum board. In contrast, a large difference indicates a substantial effect of sorption in terms of retarding migration through a material. The diffusion coefficient of SF_6 in air can also be normalized by its effective diffusion coefficient through a material to determine a tortuosity factor that reflects the average increased diffusion path length through a material.

Example concentration-time profiles are shown in Figures 3-1 and 3-2 for sulfur hexafluoride and undecane diffusion through unpainted gypsum board. In each case, the convergence of concentrations in top and bottom chambers is obvious, as is the fact that equilibrium is reached much faster for SF_6 than for undecane.

3.2 Dynamic Microbalance Experiments

3.2.1 Determination of Equilibrium Partition Coefficients for Test Chemicals

Using the sorption and desorption data recorded by the microbalance, the equilibrium and kinetic parameters, K and D_e, were determined (Cox *et al.*, 2001b). For a particular VOC, the sorption equilibrium was described using a partition coefficient:

$$K = \frac{C_s}{C_{air}} \qquad (3\text{-}10)$$

where,

K = equilibrium partition coefficient ($[mg/m^3_{material}]/[mg/m^3_{air}]$) or ($m^3_{air}/m^3_{material}$),

C_s = sorbed concentration of test chemical ($mg/m^3_{material}$), and

C_{air} = concentration in air at equilibrium (mg/m^3_{air}).

For a linear relationship, a higher K value represents a higher sorption capacity for a specific VOC. The equilibrium concentration in the material phase was obtained from the difference between the initial and equilibrium weight of the sample specimen, whereas C_{air} was calculated from:

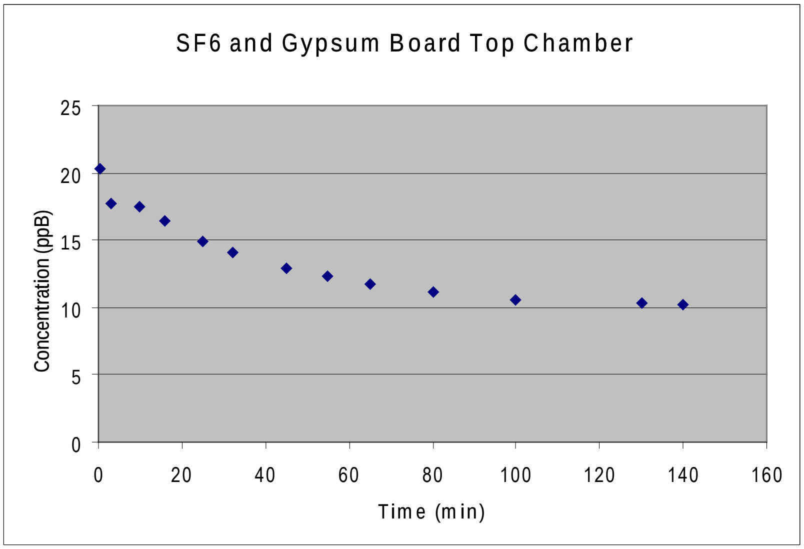
$$C_{air} = \frac{E}{Q} \qquad (3\text{-}11)$$

where,

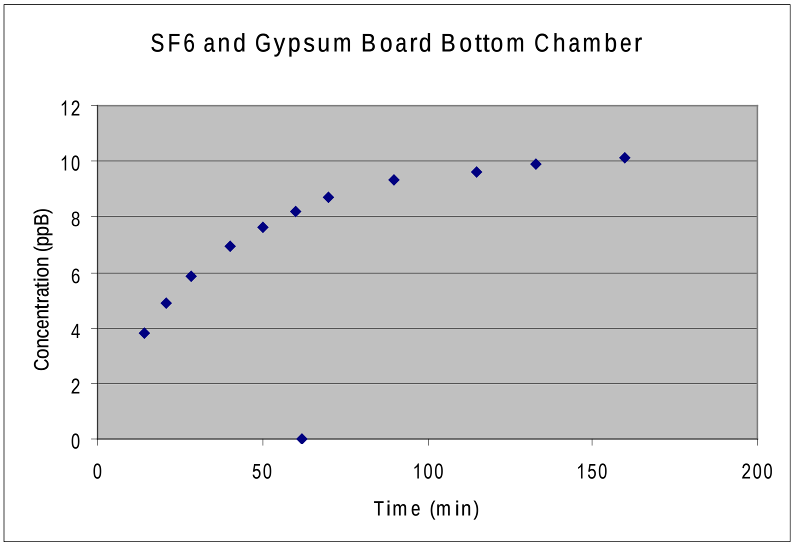
E = constant emission rate of VOC generated by the diffusion cell (mg/s), and

Q = air flow rate through the system (m^3/s).

Figure 3-1. Sulfur hexafluoride concentration profiles for unpainted gypsum board in the top chamber (a) and bottom chamber (b) of the dual-volume diffusion chamber.

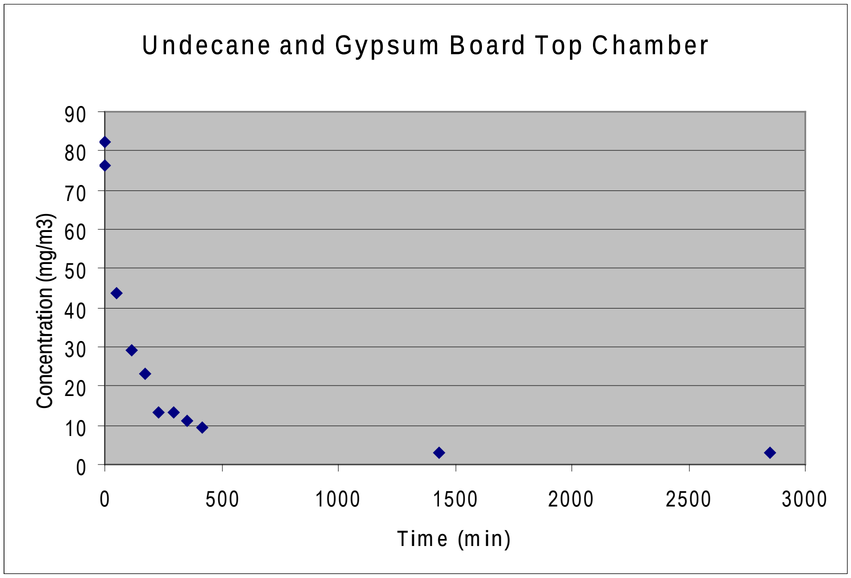


(a)

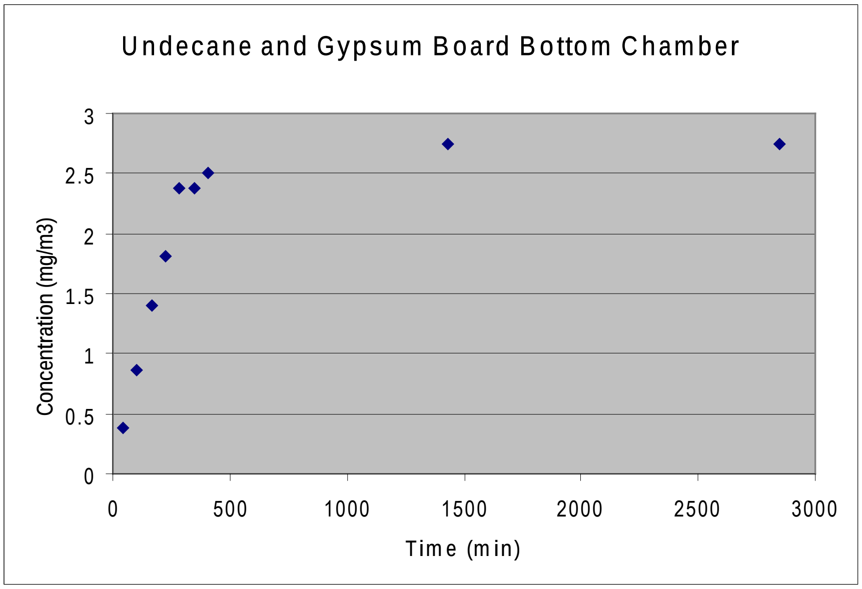


(b)

Figure 3-2. Undecane concentration profiles for unpainted gypsum board in the top chamber (a) and bottom chamber (b) of the dual-volume diffusion chamber.



(a)



(b)

3.2.2 Determination of Effective Diffusion Coefficients for Test Chemicals

The effective diffusion coefficient, D_e, was determined by fitting a diffusion model to the experimental sorption and desorption data. For the vinyl flooring samples, which conform to the geometry of a thin slab, under the experimental conditions, the rate of change in mass due to Fickian diffusion is given by Crank (1976):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left\{ \frac{-D_e (2n+1)^2 \pi^2 t}{4L^2} \right\} \quad (3\text{-}12)$$

where,

M_t = total mass of a VOC that has entered or left the slab in time t (g),

M_∞ = corresponding quantity after equilibrium has been reached (g),

2L = thickness of the material sample (m), and

D_e = effective diffusion coefficient (m^2/s).

The counter n is varied from zero to a large number until the sum of terms converges.

For the polyurethane foam samples, which conform to the geometry of a cylinder, the rate of change in mass due to Fickian diffusion is given by Crank (1976):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{4}{a^2 \alpha_n^{\,2}} \times \exp\left(- D_e \alpha_n^{\,2} t\right) \qquad (3\text{-}13)$$

where,

the α_n values are the positive roots of $J_0(a\alpha_n) = 0$,

a = radius of the cylinder, and

J_0 = Bessel function of the first kind of zero order.

Figures 3-3 and 3-4 show example microbalance sorption/desorption data for vinyl flooring (VF) and polyurethane foam (PUF), respectively. In both cases, the compound being absorbed and desorbed is dodecane. All the other data sets for both VF and PUF are provided in Appendix B. The appropriate models (Equations 3-12 or 3-13) were fitted to the data using MS EXCEL.

Figure 3-3. Dodecane sorption/desorption profiles for vinyl flooring with fitted diffusion model.

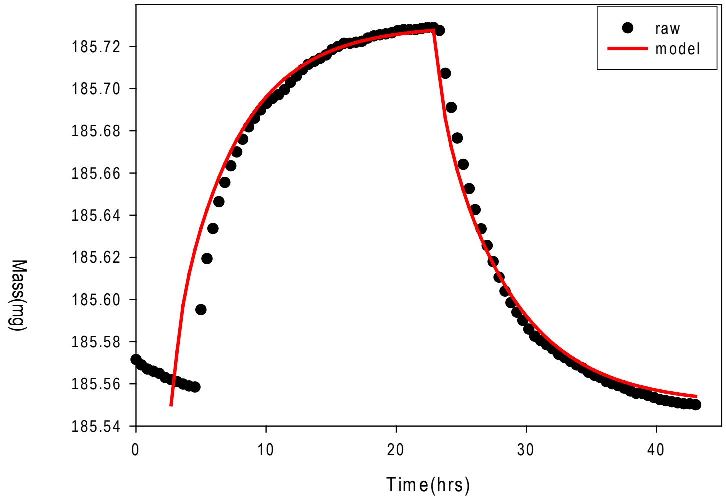
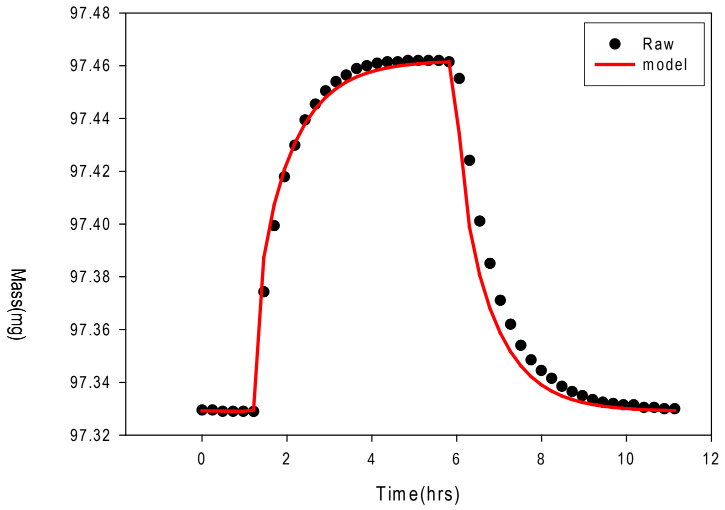


Figure 3-4. Dodecane sorption/desorption profiles for polyurethane foam with fitted diffusion model.



4.
Results

Equilibrium partition coefficients (*K*) and effective diffusion coefficients (D_e) are presented in Tables 4-1 through 4-5. These parameters were not determined for mortar due to the length of time required for chemicals to diffuse through mortar specimens. However, several observations related to mortar experiments are included in Section 5.

Table 4-1. Equilibrium partition and diffusion coefficients (Gypsum Board - Unpainted).*

Test Chemical	K $(mg/m^3)_{solid}/(mg/m^3)_{air}$	D_e (m^2/hr)
n-Butanol	920	2.2×10^{-5}
Hexanal	590	1.9×10^{-5}
Ethylbenzene	100	3.4×10^{-5}
Decane	230	1.7×10^{-5}
Undecane	1,640	3.8×10^{-5}
Dodecane	4,160	4.6×10^{-7}
Sulfur hexafluoride	—	7.8×10^{-4}

* Analysis by dual-volume chamber.

Table 4-2. Equilibrium partition and diffusion coefficients (Gypsum Board - Painted).*

Test Chemical	K $(mg/m^3)_{solid}/(mg/m^3)_{air}$	D_e (m^2/hr)
n-Butanol	720	7.8×10^{-6}
Hexanal	350	1.4×10^{-5}
Ethylbenzene	38	3.4×10^{-5}
Decane	130	1.3×10^{-5}
Undecane	270	9×10^{-6}
Dodecane	1,130	3.1×10^{-6}
Sulfur hexafluoride	—	1.6×10^{-3}

* Analysis by dual-volume chamber.

Table 4-3. Equilibrium partition and diffusion coefficients (Carpet, PVC-backed).*

Test Chemical	K $(mg/m^3)_{solid}/(mg/m^3)_{air}$	D_e (m^2/hr)
n-Butanol	710 / 180	2.4×10^{-11} / 3.3×10^{-10}
Hexanal	1090 / 280	1.9×10^{-11} / 4.4×10^{-10}
Ethylbenzene	2,600 / 660	2.3×10^{-12} / 3.6×10^{-11}
Decane	5,730 / 2,070	1.9×10^{-10} / 1.4×10^{-9}
Undecane	8,600 / 2,200	1.3×10^{-10} / 1.7×10^{-9}
Dodecane	72,300 / 18,400	2.7×10^{-12} / 4.4×10^{-11}
Sulfur hexafluoride	—	—

* Analysis by dual-volume chamber.

Values for D_e based on thickness of carpet backing (left of /) and on thickness of backing + fibers (right of /).

Table 4-4. Equilibrium partition and diffusion coefficients (Vinyl Flooring).*

Test Chemical	K $(mg/m^3)_{solid}/(mg/m^3)_{air}$	D_e (m^2/hr)
n-Butanol	1,100	2.7×10^{-09}
Hexanal	46,000	2.0×10^{-09}
Decane	6,000	1.8×10^{-09}
Undecane	17,000	2.0×10^{-09}
Dodecane	47,000	6.9×10^{-10}
Tetradecane	110,000	4.2×10^{-10}

* Analysis by microbalance.

Table 4-5. Equilibrium partition and diffusion coefficients (Polyurethane Foam).*

Test Chemical	K $(mg/m^3)_{solid}/(mg/m^3)_{air}$	D_e (m^2/hr)
n-Butanol	110	3.0×10^{-05}
Hexanal	—	
Decane	72	2.2×10^{-06}
Undecane	490	1.1×10^{-05}
Dodecane	1,400	7.7×10^{-06}
Tetradecane	5,400	5.4×10^{-07}

* Analysis by microbalance.

Equation 3-8 was used in conjunction with D_e for sulfur hexafluoride to predict effective diffusion coefficients for organic test chemicals in the absence of sorption. Results are presented in Table 4-6. The multiplier Ψ was determined as described in Section 3 (Equation 3-8). Effective diffusion coefficients in the absence of sorption are shown for both unpainted and painted gypsum board. The ratio of measured effective diffusion coefficients (with sorption) to those predicted for the case of no sorption are listed for each chemical and both types of gypsum board.

Table 4-6. Predicted D_e for gypsum board in the absence of sorption.

Test Chemical	Ψ Eq. 3-7	Unpainted D_e (m^2/hr)	Unpainted [sorption/ no sorption]	Painted GB D_e (m^2/hr)	Painted [sorption/ no sorption]
SF_6*	1	7.8×10^{-4}	—	1.6×10^{-3}	—
n-Butanol	0.856	6.7×10^{-4}	0.033	1.4×10^{-3}	0.0056
Hexanal	0.725	5.7×10^{-4}	0.033	1.2×10^{-3}	0.012
Ethylbenzene	0.718	5.6×10^{-4}	0.061	1.1×10^{-3}	0.031
Decane	0.557	4.3×10^{-4}	0.040	8.9×10^{-4}	0.015
Undecane	0.525	4.1×10^{-4}	0.093	8.4×10^{-4}	0.011
Dodecane	0.498	3.9×10^{-4}	0.0012	8.0×10^{-4}	0.0039

* measured value.

5.
Discussion and Summary

5.1 Gypsum Board (Unpainted and Painted)

For gypsum board (both unpainted and painted) the equilibrium partition coefficients for n-butanol and hexanal were both greater than for ethylbenzene, presumably due to polar-polar interactions between the oxygenated compounds and calcium sulfate in gypsum board. The equilibrium partition coefficients for the three n-alkane compounds increased in a predictable order, from highest to lowest vapor pressure (decane to dodecane).

The effective diffusion coefficients through gypsum board were of comparable magnitude for all organic test compounds other than dodecane, which had a significantly lower effective diffusion coefficient than other test chemicals. For painted gypsum board, the effective diffusion coefficients for the n-alkane series decreased with increasing carbon number (decreasing vapor pressure), and was inversely proportional to the equilibrium partition coefficient. For unpainted gypsum board, the effective diffusion coefficients for decane and undecane were reversed from what was expected based on carbon number and K value; the difference in D_e may be due simply to experimental error and uncertainties in the parameter estimation method (Section 3 and Appendix B).

The large effective diffusion coefficients for sulfur hexafluoride, an inert tracer compound, relative to organic test chemicals underscores the significant effects of sorption processes on chemical migration through gypsum board. When D_e for SF_6 are translated to organic test chemicals (Table 4-6), the ratio of chemical-specific D_e for the case of sorption to the case of no sorption was between approximately 0.09 and 0.0011, i.e., a 91 percent to 98.9 percent reduction in D_e caused by sorption. The effective diffusion coefficients for SF_6 can also be used to estimate tortuosity factors for gypsum board. Using an SF_6 diffusion coefficient in free air of 0.073 cm^2/s (= 0.026 m^2/hr) at near room temperature (Ward and Williams, 1997) and dividing this value by the effective diffusion coefficients determined in this study (Table 4-6) yields tortuosity factors of 16 and 33, i.e., diffusion path lengths through material of 16 and 33 times the actual thickness of painted and unpainted gypsum board, respectively.

The results for unpainted and painted gypsum board are largely counter-intuitive when compared against one another. It seems logical that the paint film would increase the equilibrium partition coefficient, since diffusion through the gypsum board is required to achieve equilibrium and the paint provides a second sorptive medium for test chemicals. However, the equilibrium partition coefficients for each chemical were greater for unpainted than for painted gypsum board. It would also seem logical that a paint film would reduce the migration rate through gypsum board by providing an additional layer of resistance to diffusion. This was true for four of the six chemicals; D_e was identical in each case for ethylbenzene and greater for painted gypsum board than unpainted gypsum board for dodecane. However, the effective diffusion coefficient for sulfur hexafluoride was observed to be a factor of two greater for painted than unpainted gypsum board.

The reasons for some counter-intuitive effects for D_e and gypsum board may have been due to differences in the extent of chemical sorption inside the gypsum board caused by components of the paint wicking into the gypsum board or diffusing into the gypsum board and consuming sorption sites. This could have lead to the higher partition coefficients of unpainted versus painted gypsum board, i.e., there were greater sorption capacities for test chemicals inside the gypsum board that had not already been challenged by paint components such as ethylene glycol and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate. This would also account for lower D_e for unpainted gypsum board, since the additional sorption would slow the diffusive migration of test chemicals through the gypsum board.

5.2 Carpet

For both K and D_e, two values are presented (/) in Table 4-3. The first (left of /) corresponds to parameter estimation based on an assumption that all partition and diffusion occurs in/through the backing material; only the volume and thickness of the PVC backing was used in calculations. The second (right of /) corresponds to parameter estimation based on use of the entire carpet (backing and fibers); the volume and thickness of the entire carpet was used in calculations.

The equilibrium partition coefficients for carpet increased with increasing molecular weight; the trend for the n-alkane series was increasing partition coefficient with increasing carbon number or decreasing vapor pressure. The effective diffusion coefficients decreased with increasing carbon number (increasing K and decreasing vapor pressure) for the n-alkane series. A similar trend was observed for the other three chemicals if treated in isolation from the n-alkanes; effective diffusion coefficients decreased with increasing K and molecular weight. Effective diffusion coefficients for sulfur hexafluoride could not be determined for carpet because of the rapid transport through the carpet specimen and rapid approach to equal SF_6 concentrations in each of the dual-volume chambers. Initial mixing of organic test chemicals was also rapid through the carpet (quickly reaching equal concentrations in top and bottom chamber) but was followed by a period of very slow decline in concentration of test chemicals as they diffused into the carpet system.

With the exception of n-butanol, the K values for carpet, particularly in the case of carpet backing only, were greater than those for gypsum board. This indicates that carpet has a greater sorption capacity than gypsum board, although there is typically a greater area of gypsum board than carpet in most buildings. However, the effective diffusion coefficients for PVC-backed carpet are orders of magnitude lower than for gypsum board. As such, while the sorption capacity for carpet is high, diffusion into the carpet may preclude an approach to equilibrium, especially during transient source events, i.e., capacity is high but the actual extent of sorption may be much lower than capacity.

5.3 Vinyl Flooring

The K values for vinyl flooring (VF) range from 1,100 to 110,000 $(\mathrm{mg/m^3})_{solid}/(\mathrm{mg/m^3})_{air}$. This indicates that VF has a similar sorption capacity to carpet. The effective diffusion coefficients for VF range between 2.7×10^{-9} and 4.2×10^{-10} $\mathrm{m^2/hr}$ and are also similar to those for carpet. While the sorption capacity for VF is high, diffusion into the VF is slow and may preclude equilibrium being established during rapid transient source events.

5.4 Polyurethane Foam

The K values for polyurethane foam (PUF) range from 72 to 5,400 $(\mathrm{mg/m^3})_{solid}/(\mathrm{mg/m^3})_{air}$. This indicates that PUF has a similar sorption capacity to gypsum board. The effective diffusion coefficients for PUF range between 3.0×10^{-5} and 5.4×10^{-7} $\mathrm{m^2/hr}$ and are also similar to those for gypsum board. While the sorption capacity for PUF is low, diffusion into the PUF is rapid and may mean that equilibrium is established during rapid transient source events. Two experiments were conducted for hexanal in PUF, but both yielded unusual results (as shown in Appendix D). It appeared that the hexanal reacted with the PUF in some way. This one set of results (hexanal/PUF) was therefore abandoned.

5.5 Mortar

Experiments involving mortar did not approach equilibrium conditions over a two-month period. Only small amounts of sulfur hexafluoride were observed in the bottom chamber over this period. Of the organic test chemicals, only a small amount of ethylbenzene was observed in the bottom chamber after two months. Hexanal was rapidly removed from the top chamber, to undetectable levels, but never appeared in the bottom chamber. None of the other four test chemicals were observed in the bottom chamber after two months. As such, it was impossible to determine either K or D_e for mortar and any of the test chemicals.

An interesting observation is that for all test chemicals, there was a relatively rapid reduction in chemical concentrations within the first 30 or 50 hours of an experiment, followed by a very slow decay in concentration within the top chamber. These two stages of decay are evident in the plots provided in Appendix C. It is conceivable that the first stage corresponds to a relatively rapid adsorption of test chemicals to the exterior surface of the mortar and the second stage corresponds to a much slower diffusion process into the pores of the mortar. The fact that test chemicals never appeared in the bottom chamber suggests that substantial sorption occurs in the pores of the mortar during the slow diffusion stage.

5.6 Summary

Two different methods were used in this study, dual-volume diffusion chamber and dynamic microbalance, to determine equilibrium partition coefficients (K) and effective diffusion coefficients (D_e) through common building materials. The goal was to provide these parameters for use in models to predict the sorptive interactions between contaminants such as chemical warfare agents (CWA) and indoor materials. Attempts were made to determine these parameters for 36 chemical/material combinations. These attempts were successful for 30 of the combinations; parameters could not be determined for mortar due to the extended period required for chemical diffusion through the mortar specimens.

Results indicate that diffusion within gypsum board (unpainted and painted) and polyurethane foam is much more rapid than through mortar, PVC-backed carpet, or vinyl flooring. This is important in so much as it suggests that even though the latter materials may have high sorption capacities, equilibrium conditions may not be approached for transient source events for which diffusion into these materials is limited. This result underscores the need for models that can predict both the diffusive and adsorptive behavior of materials, i.e., as opposed to simply assuming an instantaneous equilibrium condition.

Generally, the results demonstrate that the dual-volume chamber method is better suited to measure the sorption properties of the more volatile VOCs, whereas the microbalance method is better suited to measure the sorption properties of the less volatile VOCs. The effective mass resolution of the microbalance is ~1 μg. To accurately determine both K and D_e using the microbalance method, the K value has to be sufficiently large to allow an overall mass increase that is ~20 μg or more. This mass increase is related to the imposed gas-phase VOC concentration and the magnitude of K. Thus, for a given gas-phase concentration, the higher the K value, the larger the overall mass increase, the more reliably the parameters can be determined.

As described in Section 5.1, the results for unpainted and painted gypsum board are somewhat counter-intuitive. We believe that the internal properties of painted gypsum board may be significantly modified relative to unpainted gypsum board by paint component (glycol, glycol ethers, and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) consumption of available sorption sites.

The authors hope that this study provides meaningful parameters that will facilitate the USEPA's needs with respect to modeling sorptive interactions between CWA and other contaminants with materials in buildings.

6.
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Appendix A
Quality Assurance Metrics

This appendix includes relevant excerpts from the initial quality assurance project plan (QAPP). The text of some sections was removed for brevity and the reader is referred to the original QAPP for text. The original QAPP section numbers are used for cross-referencing. Below each section we have provided a brief response related to quality assurance metrics. UT refers to use of the dual-volume diffusion chamber at the University of Texas. VT refers to the dynamic microbalance used by Virginia Tech.

2.0. SAMPLING

2.1 Sampling Points

UT: Sampling points were as described in the QAPP.

VT: Sampling points were as described in the QAPP.

2.2 Sampling Frequency

UT: A minimum of five (5) samples will be collected from both chambers (top and bottom) for each experiment, for a minimum of 10 samples to be analyzed. The time interval between samples will depend on the material/chemical combination, which will affect the time to reach an equilibrium condition in the experimental system. This time interval may be as low as 20 minutes or less for a highly porous material, to tens of hours for a relatively nonporous material.

Response – We exceeded the QAPP requirements for all tests — more than five samples were collected from both top and bottom chambers.

VT: The sample mass gain or loss over time will be monitored every five minutes during the sorption/desorption process.

Response – Although we exceeded the QAPP requirements for all tests — more than one measurement every five minutes, fewer data were plotted for purposes of clarity.

2.3 Expected Measurements

UT: The goal of the experimental program is to determine the equilibrium partition coefficient and effective diffusion coefficient for each combination of test chemical and material. This will require several types of measurements. Air samples will be used to determine test chemical concentrations in the top and bottom volumes of the chamber apparatus depicted in Figure 2-1. Optimal methods for determining the effective diffusion coefficient for each test material may differ by material. As such, for some or all of the materials tested, material density and porosity will be measured. Alternately, for some or all of the test materials, sulfur hexafluoride (SF_6) diffusion through test materials will be determined, and gaseous SF_6 samples will be collected in top and bottom volumes of the experimental chamber system.

Response – Air samples were collected and used to determine test chemical concentrations in top and bottom chambers. Porosity and bulk density were not determined. Porosity was not required for the specific model to be employed based on this study. The original intent for determining bulk density was to determine the solid-phase concentration. However, this was not needed in Equation 3-2. Sulfur hexafluoride injections and analyses in top and bottom chambers were completed for all test materials, not just some.

VT: Several types of measurements will be required in the experiment. The dimensions of the material sample will be carefully measured. In addition, the emission rate of VOC generated by the diffusion cell will be gravimetrically obtained by weighing the diffusion cell before and after the run.

Response – No changes to original QAPP.

2.4 Site-Specific Factors That May Affect Sampling Procedures

UT: We do not anticipate any major factors that will affect sampling procedures at UT. It is always possible that instrumentation requires repair or troubleshooting, but such events can not be anticipated.

As described above, the actual method for determining effective diffusion coefficients for each chemical/material combination will need to be determined. Two methods are available to the research team as described in Section 5.1. One method requires determination of material porosity. Our experience is that this is difficult with some materials due to interstitial voids that can not be effectively wetted, leading to underestimates for gas-phase porosity. For other materials, submergence in water to determine porosity can lead to material breakdown. As such, we will employ a method based on diffusion of SF_6, a non-adsorbing tracer, with theoretical adjustment to test chemicals. This method does not require analysis of material porosity to determine D_e.

Response – See item 2.3 above. Sulfur hexafluoride measurements were made and were employed to estimate theoretical effective diffusion coefficients for test chemicals in the absence of sorption. However, this analysis was done only for the unpainted and painted gypsum board specimens, since transport of sulfur hexafluoride was too rapid across carpet specimens and the mortar experiments far exceeded the time constraints of this study.

VT: Aside from regular maintenance, we do not anticipate any special site-specific factors that will affect sampling procedures at VT. We have already used the microbalance quite extensively in conducting these types of measurements (for example, see Cox et al., 2001 and Zhao et al., 2004).

Response – No changes to original QAPP.

2.5 Site Preparation Needs

UT: There are no site preparation requirements at UT.

VT: There are no site preparation requirements at VT.

2.6 Sampling Procedures and Maintenance Requirements

UT: Air samples for determination of test chemical concentrations will be collected using adsorbent tubes outfitted with personal sampling pumps. Sample collection rates will range from 25 to 50 mL per minute. Ultimate sample sizes will depend on the vapor pressure of the test chemical and its mass concentration in chamber air. All personal sampling pumps used for this work will be calibrated every 10 samples.

The personal sampling pumps used for these experiments are SKC Pocket Pump 210-1000 series. These units have a manufacturer provided “accuracy variance between LCD reading and actual flow rate (after calibration) of +/- 5%.” The personal sample pumps are calibrated daily using a Gillian Bubble Flow Meter.

If used, sulfur hexafluoride samples will be collected in gas-tight syringes. SGE gas-tight syringes will be used for this work. The manufacturer states these syringes have an “accuracy and reproducibility of +/-1% of volume.”

Response – We did not use the personal sampling pumps described above as they were found to be prone to flow faults and had to be shipped frequently back to the manufacturer for maintenance. Instead, we attached gas-tight syringes to the back end of adsorbent tubes and collected samples by drawing known volumes of air through the sorbent tubes using syringes. We believe that this method is more accurate than the use of sample pumps, particularly for relatively low-volume (e.g., 50 mL) sampling. Gas-tight syringes were used for both test chemical sample collection (through sorbent tubes) and direct sampling of sulfur hexafluoride

VT: The mass gain/loss of the material sample will be recorded by the PC-based data-acquisition system. The ultimate number of data points will depend on the time required for the test chemicals to reach equilibrium during either sorption or desorption.

Response – For vinyl flooring, there was a constant emission of some substance (we believe it to be a vinyl plasticizer) that did not abate after several weeks in the microbalance. To remove this, we subjected the vinyl flooring to a short “bake-out” period. For polyurethane foam, there were no changes to the original QAPP.

2.7 Compositing/Splitting of Samples

UT: Compositing/splitting of air samples for test chemicals or SF6 is not required for this project. The actual material specimens used for experiments will be cut into smaller pieces for analysis of material density and porosity, where required. Material properties will be evaluated based on one specimen from a specific batch of a material that will be used for all analyses with that material and after use of the specimen in the test chamber. One exception might be mortar, since each specimen would be formed separately.

Response – See Section 2.3 above. Thickness measurements were made of gypsum board, carpet, and carpet backing using Vernier calipers. Thickness measurements were not made for mortar, since the lack of diffusion through the mortar precluded any attempts at parameter estimation.

VT: Sample compositing/splitting is not required for this project.

Response - No QAPP modifications.

2.8 Sample Quantity Requirements

UT: The air sample volume for test chemicals (volume pulled through adsorbent tubes) will depend on the vapor pressure of the test chemical being tested and its anticipated concentration in chamber air. Based on previous experience, we expect sample volumes to be on the order of 100 mL or less.

When employed, SF6 samples will be collected in gas-tight syringes with volumes less than or equal to 1 mL.

When material properties are determined, a minimum of three replicate analyses will be completed to determine mean bulk density and porosity, and spread around the mean.

Response – To sample for organic test chemicals, the sample volumes varied between 25 mL and 100 mL, depending on the concentration in the chamber, e.g., lower volumes were required initially in the top chamber, since concentrations were at a maximum. For accurate measurements of SF6 a volume of 25 mL was required, i.e., greater than the 1 mL specified in the QAPP. This was due to using a lower concentration SF6 source that was available to us for this project, i.e., relative to what we had originally planned. For material properties (thickness), five instead of three samples were collected to determine a mean and standard deviation (see Section 2.1 of main report).

VT: The mass gain for test chemicals will depend on the vapor pressure of the chemical being tested, its concentration in the microbalance chamber air and the volume of the test material. Based on previous experience, we expect mass gain to be at least 200 µg for the most volatile compound tested. For vinyl flooring, the sample specimens are chosen to be roughly 1 cm wide by 4 cm long by 0.03 cm thick.

Response – A Vernier caliper was used to measure the length and width of vinyl flooring, and the length and radius of the polyurethane foam. A screw micrometer was used to measure the thickness of the vinyl flooring. Each measurement was repeated four times and the average was used as the final value. The vinyl flooring had a dimension of 3.78 cm (length) × 2.66 cm (width) × 0.0175 cm (thickness). The polyurethane foam’s dimension was 1.39 cm (radius) × 4.70 cm (length).

2.9 Containers Used for Sample Collection, Transport, and Storage

UT: All air samples for target chemicals will be collected onto Tenax TA 80/100 mesh packed into glass tubes. The glass tubes are actually large volume injection liners that allow for zero-path thermal desorption directly onto a GC column (to minimize analyte losses in the transfer lines of conventional thermal desorption systems). Samples will be analyzed as collected (within 15 minutes of collection in the case of two samples drawn simultaneously). Samples will not be transported or stored.

When employed, SF_6 samples will be collected in gas-tight syringes. They will be analyzed immediately. As such, there will be no transport or storage issues associated with samples that contain SF_6.

Test materials will be maintained in plastic bags in a secure office environment prior to testing.

Response – Air samples (organic test chemicals and SF_6) were collected and analyzed as described above. Test materials were not maintained in plastic bags, but rather were wrapped in aluminum foil and maintained in the office of Dr. Neil Crain prior to usage.

The GC method used for this study required 21 minutes to complete. Simultaneously collected samples were analyzed within 30 minutes of collection.

To provide the data required to the model the diffusion of organic chemicals through the vinyl carpet required eight to ten samples be collected in the first 30 minutes of the experiment. These additional sample tubes were stored in color-coded stainless steel tubes until they could be analyzed. These samples were analyzed within four hours of collection.

VT: The VT method employs a micro-balance for gravimetric analysis. Measurements are made directly by mass changes. Air sample collection, transport, and storage are not required. Test materials will be stored in aluminum foil in a refrigerator prior to testing.

Response – No changes to original QAPP.

2.10 Sample Preservation Methods

UT: Air samples (adsorbent tubes for test chemicals and gas-tight syringes for SF6) will be analyzed as collected. As such, preservation methods are not required. Test materials will be maintained in plastic bags in a secure office environment prior to testing.

Response – Air samples were analyzed as described above. Test materials were not maintained in plastic bags, but rather were wrapped in aluminum foil and maintained in the office of Dr. Neil Crain prior to usage.

VT: There are no samples to be preserved using the micro-balance method. Test materials will be stored in aluminum foil in a refrigerator prior to testing.

Response – No changes to original QAPP.

2.11 Requirements for Shipping of Samples

UT: Air samples (adsorbent tubes for test chemicals and gas-tight syringes for SF6) will be analyzed as collected. No air samples will be shipped. The USEPA may provide some of the test materials to UT. These material samples will be mailed directly to the point of contact noted in Section 1 of this document.

Response – The USEPA shipped three of the four test materials (carpet, unpainted, painted gypsum board) to the University of Texas for testing. Mortar specimens were developed by the Materials Engineering group within the Department of Civil, Architectural, and Environmental Engineering at the University of Texas.

VT: No air samples will be shipped. The USEPA will provide some of the test materials to VT. These material samples will be tightly packed within aluminum foil and mailed directly to the point of contact noted in Section 1 of this document.

Response – No changes to original QAPP.

2.12 Holding Time Requirements

UT: Air samples (adsorbent tubes for test chemicals and gas-tight syringes for SF6) will be analyzed as collected. As such, there are no holding time requirements for air samples. Test materials will be maintained in a secure office environment as described above. There should be no specific holding requirements for test materials.

Response – No changes to original QAPP.

VT: There are no holding time requirements for the VT analysis method. Test materials will be stored in a refrigerator as described above.

Response – No changes to original QAPP.

2.13 Sample Tracking and Chain of Custody

UT: Air samples (adsorbent tubes for test chemicals and gas-tight syringes for SF6) will be analyzed as collected by laboratory personnel. The same individual who collects an air sample will prepare the sample for direct analysis. Test materials will be maintained in plastic bags in a secure office environment prior to testing. The contents of the bags will be marked on the exterior of each bag with a notice not to move or open without the permission of Dr. Crain or Dr. Corsi.

Response – Material specimens were wrapped in aluminum foil as described above. Dr. Neil Crain was the only staff member to handle material specimens throughout this entire study.

VT: Test materials will be stored in a refrigerator prior to testing. The contents of the bags will be marked on the exterior of each bag with a notice not to move or open without the permission of Dr. Little.

Response – No changes to original QAPP.

2.14 Information Recording and Maintenance by Field Personnel

UT: A dedicated laboratory notebook will be maintained for this experimental effort. Sample records will be noted on a sample record sheet, and sheets for each experiment will be maintained in a three-ringed binder stored after each experiment in Dr. Crain's office. The sample record sheet will be transcribed to an EXCEL spreadsheet each day that a set of samples is analyzed. The EXCEL file will be backed up to electronic media on a weekly basis and also sent to Dr. Corsi for separate storage every two weeks or sooner.

Response – Results of all GC/FID analyses were printed as hard copies and maintained in a three-ringed binder. All sample records were transcribed to an EXCEL spreadsheet and sent from Dr. Crain to Dr. Corsi on an approximate bi-weekly basis. Electronic copies are maintained by both Dr. Crain and Dr. Corsi.

VT: A dedicated laboratory notebook will be maintained for the entire experimental effort. The data record sheet for each experimental run will be transcribed to an EXCEL spreadsheet. The EXCEL file will be backed up to electronic media and also sent to Dr. Little for separate storage after each sorption/desorption cycle.

Response – No changes to protocol.

3.0 TESTING AND MEASUREMENT PROTOCOLS

3.1 Specific Analytical Methods

UT: Air sample measurements for test chemicals will be completed using a modified version of USEPA TO-17, "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes." Tenax-TA will be the primary adsorbent used in this study. However, a different adsorbent may be substituted as needed, depending on the specific test chemicals that are employed. A GC/FID with zero-path length thermal desorption will be employed for sample analysis. The mass of the test chemical will be measured by comparison with an external calibration curve for that chemical. The gaseous concentration of the test chemical will be calculated as mass collected divided by volume of air sample.

If employed, SF_6 samples will be analyzed by direct injection from a gas-tight syringe to a GC/ECD tuned specifically for analysis of SF_6.

For material specimens in which material properties are evaluated, gravimetric and volume displacement methods will be used to determine these properties. Specifically, material specimens will be weighed to determine mass of the bulk specimen. The volume of the specimen will be determined by use of precision calipers or initial displacement of water upon submergence (for relatively impermeable materials). Bulk density will be determined as the ratio of specimen mass to volume. Porosity will be determined by submergence of a material for a period sufficient to achieve complete saturation. The difference between bulk volume (measured as described above) and volume displacement at complete saturation will be normalized by bulk volume to determine material porosity.

Response – Air samples were analyzed as described above for both organic test chemicals and sulfur hexafluoride. As described above, other than material thickness the material properties were not measured or needed for this study.

VT: Specifically, the diffusion vial with VOC will be weighed. The emission rate generated by the diffusion cell will be determined from the difference in mass of diffusion cell divided by the time between the two measurements.

Response – The diffusion vial with liquid VOC was weighed four times before sorption, after sorption, and after desorption. The emission rates were determined from the difference in the average mass of the diffusion vial divided by the time between the two measurements. The final emission rate was taken as the mean of the two emission rate values. The measured emission rates are shown in Table A-1.

Table A-1. Emission rates from diffusion vials.

Chemicals	Emission Rate (µg/min)	
	VF	PUF
n-Butanol	217.5	194.1
Hexanal	186.0	-
Decane	42.9	43.0
Undecane	15.9	21.6
Dodecane	6.9	10.2
Tetradecane	5.1	8.3

3.2 Modifications to EPA-Approved or Other Validated Analytical Methods

UT: Some of the test chemicals (e.g., decane and dodecane) are not specifically listed for analysis using USEPA Method TO-17. However, they will be analyzed using the procedures outlined in EPA TO-17.

Response – No changes to protocol.

VT: No modifications required.

Response – No modifications required.

4.0 QA/QC CHECKS AND PROTOCOLS

4.1 Analytical System Calibration and Checks

UT: Prior to experiments involving a specific test chemical, a five-point calibration curve will be developed and will span the anticipated range of experimental concentrations. The R^2 value for each calibration curve will be greater than or equal to 0.97. If the criterion R^2 is not achieved, individual calibration points will be repeated until the criterion R^2 is achieved. The calibration of the GC/FID system will be confirmed using a mid-point standard injection every 12 samples or 24 hours, whichever comes first. The criterion for mid-point check will be ± 15 percent of the calibration curve. If this criterion is not satisfied, the mid-point check will be repeated. If the criterion is not met the second time, a new calibration curve will be generated for the target chemical.

Response – We exceeded the calibration curve requirement, completing seven-point instead of five-point external calibrations. The R^2 values always exceeded 0.994 (greater than the QAPP requirement of 0.97). Mid-point checks were completed as described above on a daily basis during experiments. The mid-point check of ± 15 percent was violated only once (for ethylbenzene) and was corrected as described above.

VT: A minimum of three replicates will be completed for determination of emission rate generated by the diffusion cell. This gravimetrically determined emission rate is used to calculate the gas-phase concentration passing through the microbalance chamber.

Response – The diffusion vial with VOC was weighed four times before sorption, after sorption, and after desorption.

4.2 Determination of Method Detection Limits

UT: Method detection limits for air samples containing test chemicals will be determined as per Section 14.2 of EPA Method TO-17 (United States Environmental Protection Agency, 1999), i.e., by making seven replicate measurements of a concentration of the compound of interest for the lowest calibration concentration, computing the standard deviation and multiplying by 3.14 (the Student's t value for 99 percent confidence for seven values).

The method detection limit for SF_6 using existing instrumentation at UT is approximately 50 parts per trillion by volume. If SF_6 is employed, we will maintain minimum concentrations at least three times greater than the method detection limit.

Response – Minimum detection limits on GC/FID area counts were determined as described above and were extremely low (area counts of 8.6 for undecane to 73 for hexanal). Importantly, these minimum detection limits were generally two or more orders of magnitude lower than minimum area counts in samples. Sulfur hexafluoride concentrations in experimental samples were generally at least 10 x greater than the 50 ppt MDL (always exceeding the QAPP requirement of 3 x MDL).

VT: The experimental limit for the microbalance measurements is about 100 µg. If the overall mass gain is lower than this, the signal to noise ratio becomes too large to obtain very good results.

Response – Some of the experimental runs for PUF had an overall mass gain of only about 40 µg. However, as shown in the raw data provided in Appendix D, the microbalance was working well and the signal to noise ratio was well below this level.

4.3 Background Sampling / Experimental Blanks

UT: All experimental samples will be collected from existing dual chamber systems located at the University of Texas at Austin. Background air samples will be collected from the laboratory prior to sealing the experimental chambers. Experimental blanks will be collected from the sealed experimental chambers prior to the introduction of the experimental VOCs. If the background concentration for the VOC of interest is more than 5 percent of the expected experimental concentration, the chamber will be re-cleaned. If the background chemical concentration arises from the material sealed in the chamber (e.g. plywood) the background chemical concentration will be subtracted from the measured experimental concentration.

Response – Background (laboratory) and experimental blank air samples were collected prior to each experiment and test chemicals never exceeded 5 percent of experimental concentrations (in most cases were not identifiable at all).

VT: Before use, the sample materials will be pre-conditioned for several weeks in a special chamber and then again within the microbalance for at least 24 hours prior to commencing the sorption/desorption run.

Response – No changes to original QAPP.

4.4 Laboratory Sample Blanks

UT: Laboratory sample blanks will be injected every 10 samples or 24 hours, whichever comes first. The laboratory blank will be accepted if the measured concentration is less than 5 percent of the measured experimental concentration. If the laboratory sample is more than 5 percent of the experimental concentration, measurements will be stopped until the background level can be brought below 5 percent of the measured experimental concentration.

Response – Laboratory sample blanks were injected every 24 hours during the experiments. Sample blanks never exceeded 5 percent of experimental concentrations.

VT: Before starting the experiment, the sample materials will be conditioned in clean air in the microbalance for at least 24 hours to get a stable data baseline.

Response – No changes to original QAPP.

4.5 Sample Breakthrough Analysis

UT: Triplicate analyses of breakthrough will be conducted for each test chemical at the maximum expected concentration in the chamber system. For each analysis, two adsorbent tubes will be connected in series and a standard sample volume pumped though the adsorbent tube. If any of the triplicate samples contain a test chemical mass in the breakthrough tube that exceeds 10 percent of the primary (first) tube, or if the triplicate average mass in the breakthrough tube is greater than or equal to 5 percent of the primary tube, two tubes in series will be employed and analyzed for each sample. Results of the breakthrough analysis will be reported in the final quality assurance summary for this project.

Response – Triplicate analysis of breakthrough was completed at the maximum possible concentration of each test chemical (saturated headspace samples) at collection volumes consistent with those used during experiments. No mass (of any test chemical) was ever observed on the breakthrough tube, i.e., even under extreme conditions the first tube captured all test chemical mass.

VT: Thermal breakthrough analysis is not relevant to the VT microbalance method.

Response - Thermal breakthrough analysis is not relevant to the VT microbalance method.

4.6 Sequential Thermal Desorption Analysis

UT: For each test chemical, each primary tube (the first of two tubes in series) used for breakthrough analyses (see Section 4.5 above) will be thermally-desorbed twice in sequence. Thus, three thermal desorption analyses will be completed for each test chemical. This will allow analysis for any residual test chemical mass on Tenax-TA following the standard thermal desorption process, and possible adjustments to the thermal desorption temperature program. If the mass of test chemical observed during the second desorption analysis exceeds 10 percent for any one sample or if the mean exceeds 5 percent for all three samples, the thermal desorption program will be adjusted and this process will be repeated until the mean mass associated with the second desorption is less than or equal to 5 percent of the first desorption. Residual mass will be reported in the final quality assurance summary for this project.

Response – We observed complete thermal desorption from the first tube used in breakthrough analyses for each test chemical, i.e., there was no observable test chemical mass upon the second thermal desorption of the tube. No adjustments were necessary.

VT: Thermal desorption is not relevant to the VT microbalance method.

Response – Thermal desorption is not relevant to the VT microbalance method.

4.7 Sample Duplicates

UT: One air sample (for test chemical) duplicate measurement will be made for each material/chemical combination. Sample duplicate analyses will be reported in the final quality assurance summary for this project.

As described above, when material properties are determined, a minimum of three replicate analyses will be completed.

Response – Four duplicate samples were collected for each test chemical over the course of all experiments. The relative difference in duplicate samples was determined as follows:

$$\% \, difference = X = 2 \times \frac{C_{air,1} - C_{air,2}}{C_{air,1} + C_{air,2}} \times 100 \qquad \text{(A-1)}$$

where,

$C_{air,1}$ and $C_{air,2}$ = Gaseous concentrations of duplicate air sample collected in series at equilibrium (mg/m^3).

The mean and standard deviation of differences in duplicate sample concentrations (X) are presented in Table A-2. The mean differences in duplicate samples were all less than 8 percent. The only duplicate samples that varied by greater than 10 percent were butanol for painted gypsum board (13.8%), hexanal for carpet (12.3 percent), and undecane for mortar (10.2 percent). Over one-half (13 of 24) of the duplicate measurements (X values) varied by less than 5 percent.

Table A-2. Results of duplicate sample analyses for test chemicals (n = 4 samples).

Chemical	Mean % difference (X)	Standard Deviation (%)
n-Butanol	7.8	4.2
Hexanal	6.0	4.7
Ethylbenzene	3.0	2.1
Decane	5.5	2.1
Undecane	7.3	3.0
Dodecane	4.9	1.9
SF_6	0.98	0.15

VT: Sample duplicates are not relevant to the VT microbalance method.

Response – Sample duplicates are not relevant to the VT microbalance method.

4.8 Experimental Replicates

UT: At least one chemical/material combination experiment will be completed in triplicate to characterize general repeatability of experiments. Time permitting, additional experiments will also be completed in duplicate or triplicate.

Response – Prolonged experiments involving mortar put the project team behind schedule. As such project time constraints precluded doing a replicate experiment.

VT: At least one chemical/material combination experiment will be completed in triplicate to characterize general repeatability of experiments. Time permitting, additional experiments will also be completed in duplicate or triplicate.

Response – One chemical/material combination experiment was completed in duplicate for both types of material (VF and PUF) using dodecane as the common test compound. The difference between the two measurements for VF was within 5 percent for K and 7 percent for D_e. For PUF the difference was within 8 percent for K and 3 percent for D_e. These results demonstrate quite reasonable reproducibility for the entire experimental measurement procedure.

4.9 Cleaning of Experimental System

UT: The experimental system will be disassembled, and heat treated (cleaned by desorption) in a drying oven for a minimum of 24 hours at a temperature greater than 115 °C following each experiment. If experimental blanks fail to meet the QA criterion (see Section 4.3), the heat treatment procedure will be repeated, possibly using a longer conditioning time or oven temperature. The process will be repeated until the blank criterion is achieved.

Response – A heating time of 12 hours (less than QAPP plan of 24 hours) at 125 °C (greater than QAPP 115 °C) was employed to expedite system cleaning. This protocol was found to effectively clean the experimental system (see Section 4.3 of this appendix).

VT: Clean air will be passed through the microbalance chamber for at least 24hr for cleaning.

Response – No changes to original QAPP.

4.10 Reporting of QA/QC results

UT: A summary of QA/QC results will be reported in an appendix of the final report.

Response – The summary is provided in this appendix.

VT: A summary of QA/QC results will be reported in an appendix of the final report.

Response – The summary is provided in this appendix.

Appendix B

Finite Difference Equations and Program to Calculate D_e for Gypsum Board

Top Chamber

The change in concentration in the top chamber was determined based on a mass balance on the top chamber and diffusive flux into the gypsum board for each time step “n”:

$$C_{air,t}^{\;n+1} = \frac{C_{air,t}^{\;n} + C_{1,s}^{\;n}\left[\dfrac{2D_e A\Delta t}{V_{top}\Delta x}\right]}{1+\dfrac{2KD_e A\Delta t}{V_{top}\Delta x}} \qquad \text{(B-1)}$$

where,

$C_{air',t}$ = chemical concentration in the air of the top chamber at time step n (mg/m^3_{air}),

$C_{1',s}$ = sorbed-phase concentration at the midpoint of the top (first) layer of gypsum board (mg/$m^3_{material}$),

D_e = effective diffusion coefficient (m^2/hr),

A = exposed surface area of material adjacent to air in each chamber (m^2),

Δt = time interval of the time steps used in the numerical solution (hr),

Δx = thickness of each slice of material as used in the numerical calculation (m),

V_{top} = volume of the top chamber (m^3), and

K_{eq} = equilibrium partition coefficient ($m^3_{air}/m^3_{material}$).

The concentration at the mid-point of the first layer ($C_{1',s}$ above) was predicted as:

$$C_{1,s}^{\;n+1} = \frac{C_{1,s}^{\;n} + \dfrac{D_e\Delta t}{\Delta x^2}\left[2C_{surface,top}^{\;n+1} + C_{2,s}^{\;n}\right]}{1+\dfrac{3D_e\Delta t}{\Delta x^2}} \qquad \text{(B-2)}$$

where,

$C_{surface,top}^{\;n+1}$ = concentration on the top surface of the material (mg/$m^3_{material}$): $C_{surface,top}^{\;n+1} = KC_{air,t}^{\;n+1}$.

All other variables are as defined previously.

Interior Gypsum Board

Fick’s second law was used to develop a finite difference solution for diffusion through the gypsum board. The sorbed-phase concentration of a test chemical in all “i” layers of gypsum board, other than the top and bottom layers, was predicted as:

$$C_{i,s}^{\;n+1} = \frac{C_{i,s}^{\;n} + \dfrac{D_e\Delta t}{\Delta x^2}\left[C_{i-1,s}^{\;n+1} + C_{i+1,s}^{\;n}\right]}{1+\dfrac{2D_e\Delta t}{\Delta x^2}} \qquad \text{(B-3)}$$

where,

Δx = thickness of gypsum board layer i (m).

All other variables are as described previously.

The sorbed-phase concentration in the bottom, or final, layer of material was predicted as:

$$C_{final,s}^{\;n+1} = \frac{C_{final,s}^{\;n} + \dfrac{D_e\Delta t}{\Delta x^2}\left[2C_{final-1,s}^{\;n+1} + C_{surface,bot}^{\;n}\right]}{1+\dfrac{3D_e\Delta t}{\Delta x^2}} \qquad \text{(B-4)}$$

$C_{surface,bot}^{\;n}$ = concentration on the bottom surface of the material (mg/$m^3_{material}$):

$$C_{surface,bot}^{\;n} = KC_{air,b}^{\;n} \,,$$

$C_{air',b}^{\;n}$ = chemical concentration in air of bottom chamber at time n (mg/m^3_{air}).

Bottom Chamber

The change in concentration in the bottom chamber was determined based on a mass balance and Fick’s first law for estimating flux into the chamber from the lower side of the gypsum board. A finite difference approximation led to:

$$C_{air,b}^{\;n+1} = \frac{C_{air,b}^{\;n} + C_{final,s}^{\;n+1}\left[\dfrac{2D_e A\Delta t}{V_{bot}\Delta x}\right]}{1+\dfrac{2KD_e A\Delta t}{V_{top}\Delta x}} \qquad \text{(B-5)}$$

where,

V_{bot} = volume of the bottom chamber (m^3).

All other variables are as defined previously.

Java Program

Source code for program used to calculate De
for painted and unpainted gypsum board:

```
import java.awt.*;
import java.awt.event.*;
import javax.swing.*;


public class DiffusionSolver extends JFrame implements ActionListener {
       private JButton done;


       private String sThickness;
       private String sArea;
       private String sVolTop;
       private String sVolBot;
       private String sWeight;
       private String sCTopEq;
       private String sCBotEq;
       private String sDeltaT;
       private String sLayers;


       private double [][] aTopTimeAndConc, aBotTimeAndConc, aMaterialTimeAndConc;
       private double [] aPredictedTopConc, aPredictedBottomConc;


       private JTextField tThickness, tArea, tVolTop, tVolBot, tWeight, tCTopEq, tCBotEq,
tDeltaT, tLayers;
       private JTextField tTTime1,tTTime2,tTTime3,tTTime4,tTTime5,tTTime6,tTTime7,tTTime8,tTTim
e9,tTTime10;
       private JTextField tBTime11,tBTime12,tBTime13,tBTime14, tBTime15;
       private JTextField tBTime1,tBTime2,tBTime3,tBTime4,tBTime5,tBTime6,tBTime7,tBTime8,tBTim
e9,tBTime10;
       private JTextField tTTime11,tTTime12,tTTime13,tTTime14, tTTime15;
       private JTextField tTConc1,tTConc2,tTConc3,tTConc4,tTConc5,tTConc6,tTConc7,tTConc8,tTCon
c9,tTConc10;
       private JTextField tTConc11,tTConc12,tTConc13,tTConc14, tTConc15;
       private JTextField tBConc1,tBConc2,tBConc3,tBConc4,tBConc5,tBConc6,tBConc7,tBConc8,tBCon
c9,tBConc10;
       private JTextField tBConc11,tBConc12,tBConc13,tBConc14, tBConc15,tD,tKeq,tSampledMass;


       private int iTopSize,iBotSize;
       private double dThickness, dArea, dVolTop, dVolBot, dWeight, dCTopEq, dCBotEq, dDeltaT,
dLayers, dD, dKeq, dResidual,dSampledMass,dBestResidual;


       private Container c;
       private GridBagLayout gbGrid;
       private GridBagConstraints gbConstraints;
```

```
public DiffusionSolver() {
       super( “Diffusion Solver” );

       c = getContentPane();
       gbGrid = new GridBagLayout();
       c.setLayout(gbGrid);

       gbConstraints = new GridBagConstraints();

       done=new JButton(“Find D”);

       sThickness = new String(“Thickness”);
       sArea = new String(“Area”);
       sVolTop = new String(“VolTop”);
       sVolBot = new String(“VolBot”);
       sWeight = new String(“Weight”);
       sCTopEq = new String(“CTopEq”);
       sCBotEq = new String(“CBotEq”);
       sDeltaT = new String(“Delta T”);
       sLayers = new String(“Layers”);

       tThickness = new JTextField(“.0125”);
       tArea = new JTextField(“.06742”);
       tVolTop = new JTextField(“.008665”);
       tVolBot = new JTextField(“.008665”);
       tWeight = new JTextField(“548”);
       tCTopEq = new JTextField();
       tCBotEq = new JTextField();
       tDeltaT = new JTextField(“.1”);
       tLayers = new JTextField(“10”);
       tSampledMass = new JTextField();

       aTopTimeAndConc = new double [2][15];
       aBotTimeAndConc = new double [2][15];

       tTTime1 = new JTextField();
       tTTime2 = new JTextField();
       tTTime3 = new JTextField();
       tTTime4 = new JTextField();
       tTTime5 = new JTextField();
       tTTime6 = new JTextField();
       tTTime7 = new JTextField();
       tTTime8 = new JTextField();
       tTTime9 = new JTextField();
```

```
tTTime10 = new JTextField();
tTTime11 = new JTextField();
tTTime12 = new JTextField();
tTTime13 = new JTextField();
tTTime14 = new JTextField();
tTTime15 = new JTextField();

tTConc1 = new JTextField();
tTConc2 = new JTextField();
tTConc3 = new JTextField();
tTConc4 = new JTextField();
tTConc5 = new JTextField();
tTConc6 = new JTextField();
tTConc7 = new JTextField();
tTConc8 = new JTextField();
tTConc9 = new JTextField();
tTConc10 = new JTextField();
tTConc11 = new JTextField();
tTConc12 = new JTextField();
tTConc13 = new JTextField();
tTConc14 = new JTextField();
tTConc15 = new JTextField();

tBTime1 = new JTextField();
tBTime2 = new JTextField();
tBTime3 = new JTextField();
tBTime4 = new JTextField();
tBTime5 = new JTextField();
tBTime6 = new JTextField();
tBTime7 = new JTextField();
tBTime8 = new JTextField();
tBTime9 = new JTextField();
tBTime10 = new JTextField();
tBTime11 = new JTextField();
tBTime12 = new JTextField();
tBTime13 = new JTextField();
tBTime14 = new JTextField();
tBTime15 = new JTextField();

tBConc1 = new JTextField();
tBConc2 = new JTextField();
tBConc3 = new JTextField();
tBConc4 = new JTextField();
tBConc5 = new JTextField();
tBConc6 = new JTextField();
```

```
tBConc7 = new JTextField();
tBConc8 = new JTextField();
tBConc9 = new JTextField();
tBConc10 = new JTextField();
tBConc11 = new JTextField();
tBConc12 = new JTextField();
tBConc13 = new JTextField();
tBConc14 = new JTextField();
tBConc15 = new JTextField();

tD=new JTextField();
tKeq=new JTextField();

addComponent(done,21,0,1,1);

addComponent(new JLabel(sThickness,SwingConstants.RIGHT),0,0,1,1);
addComponent(new JLabel(sArea,SwingConstants.RIGHT),1,0,1,1);
addComponent(new JLabel(sVolTop,SwingConstants.RIGHT),2,0,1,1);
addComponent(new JLabel(sVolBot,SwingConstants.RIGHT),3,0,1,1);
addComponent(new JLabel(sWeight,SwingConstants.RIGHT),4,0,1,1);
addComponent(new JLabel(sCTopEq,SwingConstants.RIGHT),0,2,1,1);
addComponent(new JLabel(sCBotEq,SwingConstants.RIGHT),1,2,1,1);
addComponent(new JLabel(sDeltaT,SwingConstants.RIGHT),2,2,1,1);
addComponent(new JLabel(sLayers,SwingConstants.RIGHT),3,2,1,1);
addComponent(new JLabel("Sampled Mass",SwingConstants.RIGHT),4,2,1,1);
addComponent(new JLabel("Top Chamber Time",SwingConstants.RIGHT),5,0,1,1);
addComponent(new JLabel("Top Chamber Conc",SwingConstants.RIGHT),5,1,1,1);
addComponent(new JLabel("Bottom Chamber Time",SwingConstants.RIGHT),5,2,1,1);
addComponent(new JLabel("Bottom Chamber Conc",SwingConstants.RIGHT),5,3,1,1);
addComponent(new JLabel("D (*10^-6 m^2/hr)",SwingConstants.RIGHT),21,2,1,1);
addComponent(new JLabel("Keq",SwingConstants.RIGHT),21,3,1,1);

gbConstraints.fill = GridBagConstraints.HORIZONTAL;
gbConstraints.weightx=1;
addComponent(tThickness,0,1,1,1);
addComponent(tArea,1,1,1,1);
addComponent(tVolTop,2,1,1,1);
addComponent(tVolBot,3,1,1,1);
addComponent(tWeight,4,1,1,1);
addComponent(tCTopEq,0,3,1,1);
addComponent(tCBotEq,1,3,1,1);
addComponent(tDeltaT,2,3,1,1);
addComponent(tLayers,3,3,1,1);
addComponent(tSampledMass,4,3,1,1);
addComponent(tTTime1,6,0,1,1);
```

```
addComponent(tTTime2,7,0,1,1);
addComponent(tTTime3,8,0,1,1);
addComponent(tTTime4,9,0,1,1);
addComponent(tTTime5,10,0,1,1);
addComponent(tTTime6,11,0,1,1);
addComponent(tTTime7,12,0,1,1);
addComponent(tTTime8,13,0,1,1);
addComponent(tTTime9,14,0,1,1);
addComponent(tTTime10,15,0,1,1);
addComponent(tTTime11,16,0,1,1);
addComponent(tTTime12,17,0,1,1);
addComponent(tTTime13,18,0,1,1);
addComponent(tTTime14,19,0,1,1);
addComponent(tTTime15,20,0,1,1);
addComponent(tTConc1,6,1,1,1);
addComponent(tTConc2,7,1,1,1);
addComponent(tTConc3,8,1,1,1);
addComponent(tTConc4,9,1,1,1);
addComponent(tTConc5,10,1,1,1);
addComponent(tTConc6,11,1,1,1);
addComponent(tTConc7,12,1,1,1);
addComponent(tTConc8,13,1,1,1);
addComponent(tTConc9,14,1,1,1);
addComponent(tTConc10,15,1,1,1);
addComponent(tTConc11,16,1,1,1);
addComponent(tTConc12,17,1,1,1);
addComponent(tTConc13,18,1,1,1);
addComponent(tTConc14,19,1,1,1);
addComponent(tTConc15,20,1,1,1);
addComponent(tBTime1,6,2,1,1);
addComponent(tBTime2,7,2,1,1);
addComponent(tBTime3,8,2,1,1);
addComponent(tBTime4,9,2,1,1);
addComponent(tBTime5,10,2,1,1);
addComponent(tBTime6,11,2,1,1);
addComponent(tBTime7,12,2,1,1);
addComponent(tBTime8,13,2,1,1);
addComponent(tBTime9,14,2,1,1);
addComponent(tBTime10,15,2,1,1);
addComponent(tBTime11,16,2,1,1);
addComponent(tBTime12,17,2,1,1);
addComponent(tBTime13,18,2,1,1);
addComponent(tBTime14,19,2,1,1);
addComponent(tBTime15,20,2,1,1);
addComponent(tBConc1,6,3,1,1);
```

```
        addComponent(tBConc2,7,3,1,1);
        addComponent(tBConc3,8,3,1,1);
        addComponent(tBConc4,9,3,1,1);
        addComponent(tBConc5,10,3,1,1);
        addComponent(tBConc6,11,3,1,1);
        addComponent(tBConc7,12,3,1,1);
        addComponent(tBConc8,13,3,1,1);
        addComponent(tBConc9,14,3,1,1);
        addComponent(tBConc10,15,3,1,1);
        addComponent(tBConc11,16,3,1,1);
        addComponent(tBConc12,17,3,1,1);
        addComponent(tBConc13,18,3,1,1);
        addComponent(tBConc14,19,3,1,1);
        addComponent(tBConc15,20,3,1,1);
        addComponent(tD,22,2,1,1);
        addComponent(tKeq,22,3,1,1);

        done.addActionListener(this);

        setSize(680,680);
        show();
        }

    private void addComponent(Component component, int row, int column, int width, int
height) {
        gbConstraints.gridx=column;
        gbConstraints.gridy=row;
        gbConstraints.gridwidth=width;
        gbConstraints.gridheight=height;
        gbGrid.setConstraints(component,gbConstraints);
        c.add(component);
        }

    public void actionPerformed (ActionEvent e) {
            getData();
            initializeValues();
            calculateKeq();
            startIterations();
            printResults();
        }

    public void getData() {
        if(tThickness.getDocument().getLength()>0)
            dThickness = Double.parseDouble(tThickness.getText());
        if(tArea.getDocument().getLength()>0)
            dArea = Double.parseDouble(tArea.getText());
```

```
if(tVolTop.getDocument().getLength()>0)
       dVolTop = Double.parseDouble(tVolTop.getText());
if(tVolBot.getDocument().getLength()>0)
       dVolBot = Double.parseDouble(tVolBot.getText());
if(tWeight.getDocument().getLength()>0)
       dWeight = Double.parseDouble(tWeight.getText());
if(tCTopEq.getDocument().getLength()>0)
       dCTopEq = Double.parseDouble(tCTopEq.getText());
if(tCBotEq.getDocument().getLength()>0)
       dCBotEq = Double.parseDouble(tCBotEq.getText());
if(tDeltaT.getDocument().getLength()>0)
       dDeltaT = Double.parseDouble(tDeltaT.getText());
if(tLayers.getDocument().getLength()>0)
       dLayers = Double.parseDouble(tLayers.getText());
if(tSampledMass.getDocument().getLength()>0)
       dSampledMass = Double.parseDouble(tSampledMass.getText());

if(tTTime1.getDocument().getLength()>0)
       aTopTimeAndConc[0][0] = Double.parseDouble(tTTime1.getText());
if(tTTime2.getDocument().getLength()>0)
       aTopTimeAndConc[0][1] = Double.parseDouble(tTTime2.getText());
if(tTTime3.getDocument().getLength()>0)
       aTopTimeAndConc[0][2] = Double.parseDouble(tTTime3.getText());
if(tTTime4.getDocument().getLength()>0)
       aTopTimeAndConc[0][3] = Double.parseDouble(tTTime4.getText());
if(tTTime5.getDocument().getLength()>0)
       aTopTimeAndConc[0][4] = Double.parseDouble(tTTime5.getText());
if(tTTime6.getDocument().getLength()>0)
       aTopTimeAndConc[0][5] = Double.parseDouble(tTTime6.getText());
if(tTTime7.getDocument().getLength()>0)
       aTopTimeAndConc[0][6] = Double.parseDouble(tTTime7.getText());
if(tTTime8.getDocument().getLength()>0)
       aTopTimeAndConc[0][7] = Double.parseDouble(tTTime8.getText());
if(tTTime9.getDocument().getLength()>0)
       aTopTimeAndConc[0][8] = Double.parseDouble(tTTime9.getText());
if(tTTime10.getDocument().getLength()>0)
       aTopTimeAndConc[0][9] = Double.parseDouble(tTTime10.getText());
if(tTTime11.getDocument().getLength()>0)
       aTopTimeAndConc[0][10] = Double.parseDouble(tTTime11.getText());
if(tTTime12.getDocument().getLength()>0)
       aTopTimeAndConc[0][11] = Double.parseDouble(tTTime12.getText());
if(tTTime13.getDocument().getLength()>0)
       aTopTimeAndConc[0][12] = Double.parseDouble(tTTime13.getText());
if(tTTime14.getDocument().getLength()>0)
       aTopTimeAndConc[0][13] = Double.parseDouble(tTTime14.getText());
```

```
if(tTTime15.getDocument().getLength()>0)
        aTopTimeAndConc[0][14] = Double.parseDouble(tTTime15.getText());

if(tTConc1.getDocument().getLength()>0)
        aTopTimeAndConc[1][0] = Double.parseDouble(tTConc1.getText());
if(tTConc2.getDocument().getLength()>0)
        aTopTimeAndConc[1][1] = Double.parseDouble(tTConc2.getText());
if(tTConc3.getDocument().getLength()>0)
        aTopTimeAndConc[1][2] = Double.parseDouble(tTConc3.getText());
if(tTConc4.getDocument().getLength()>0)
        aTopTimeAndConc[1][3] = Double.parseDouble(tTConc4.getText());
if(tTConc5.getDocument().getLength()>0)
        aTopTimeAndConc[1][4] = Double.parseDouble(tTConc5.getText());
if(tTConc6.getDocument().getLength()>0)
        aTopTimeAndConc[1][5] = Double.parseDouble(tTConc6.getText());
if(tTConc7.getDocument().getLength()>0)
        aTopTimeAndConc[1][6] = Double.parseDouble(tTConc7.getText());
if(tTConc8.getDocument().getLength()>0)
        aTopTimeAndConc[1][7] = Double.parseDouble(tTConc8.getText());
if(tTConc9.getDocument().getLength()>0)
        aTopTimeAndConc[1][8] = Double.parseDouble(tTConc9.getText());
if(tTConc10.getDocument().getLength()>0)
        aTopTimeAndConc[1][9] = Double.parseDouble(tTConc10.getText());
if(tTConc11.getDocument().getLength()>0)
        aTopTimeAndConc[1][10] = Double.parseDouble(tTConc11.getText());
if(tTConc12.getDocument().getLength()>0)
        aTopTimeAndConc[1][11] = Double.parseDouble(tTConc12.getText());
if(tTConc13.getDocument().getLength()>0)
        aTopTimeAndConc[1][12] = Double.parseDouble(tTConc13.getText());
if(tTConc14.getDocument().getLength()>0)
        aTopTimeAndConc[1][13] = Double.parseDouble(tTConc14.getText());
if(tTConc15.getDocument().getLength()>0)
        aTopTimeAndConc[1][14] = Double.parseDouble(tTConc15.getText());

if(tBTime1.getDocument().getLength()>0)
        aBotTimeAndConc[0][0] = Double.parseDouble(tBTime1.getText());
if(tBTime2.getDocument().getLength()>0)
        aBotTimeAndConc[0][1] = Double.parseDouble(tBTime2.getText());
if(tBTime3.getDocument().getLength()>0)
        aBotTimeAndConc[0][2] = Double.parseDouble(tBTime3.getText());
if(tBTime4.getDocument().getLength()>0)
        aBotTimeAndConc[0][3] = Double.parseDouble(tBTime4.getText());
if(tBTime5.getDocument().getLength()>0)
        aBotTimeAndConc[0][4] = Double.parseDouble(tBTime5.getText());
if(tBTime6.getDocument().getLength()>0)
```

```
        aBotTimeAndConc[0][5]  = Double.parseDouble(tBTime6.getText());
if(tBTime7.getDocument().getLength()>0)
        aBotTimeAndConc[0][6]  = Double.parseDouble(tBTime7.getText());
if(tBTime8.getDocument().getLength()>0)
        aBotTimeAndConc[0][7]  = Double.parseDouble(tBTime8.getText());
if(tBTime9.getDocument().getLength()>0)
        aBotTimeAndConc[0][8]  = Double.parseDouble(tBTime9.getText());
if(tBTime10.getDocument().getLength()>0)
        aBotTimeAndConc[0][9]  = Double.parseDouble(tBTime10.getText());
if(tBTime11.getDocument().getLength()>0)
        aBotTimeAndConc[0][10]  = Double.parseDouble(tBTime11.getText());
if(tBTime12.getDocument().getLength()>0)
        aBotTimeAndConc[0][11]  = Double.parseDouble(tBTime12.getText());
if(tBTime13.getDocument().getLength()>0)
        aBotTimeAndConc[0][12]  = Double.parseDouble(tBTime13.getText());
if(tBTime14.getDocument().getLength()>0)
        aBotTimeAndConc[0][13]  = Double.parseDouble(tBTime14.getText());
if(tBTime15.getDocument().getLength()>0)
        aBotTimeAndConc[0][14]  = Double.parseDouble(tBTime15.getText());

if(tBConc1.getDocument().getLength()>0)
        aBotTimeAndConc[1][0]  = Double.parseDouble(tBConc1.getText());
if(tBConc2.getDocument().getLength()>0)
        aBotTimeAndConc[1][1]  = Double.parseDouble(tBConc2.getText());
if(tBConc3.getDocument().getLength()>0)
        aBotTimeAndConc[1][2]  = Double.parseDouble(tBConc3.getText());
if(tBConc4.getDocument().getLength()>0)
        aBotTimeAndConc[1][3]  = Double.parseDouble(tBConc4.getText());
if(tBConc5.getDocument().getLength()>0)
        aBotTimeAndConc[1][4]  = Double.parseDouble(tBConc5.getText());
if(tBConc6.getDocument().getLength()>0)
        aBotTimeAndConc[1][5]  = Double.parseDouble(tBConc6.getText());
if(tBConc7.getDocument().getLength()>0)
        aBotTimeAndConc[1][6]  = Double.parseDouble(tBConc7.getText());
if(tBConc8.getDocument().getLength()>0)
        aBotTimeAndConc[1][7]  = Double.parseDouble(tBConc8.getText());
if(tBConc9.getDocument().getLength()>0)
        aBotTimeAndConc[1][8]  = Double.parseDouble(tBConc9.getText());
if(tBConc10.getDocument().getLength()>0)
        aBotTimeAndConc[1][9]  = Double.parseDouble(tBConc10.getText());
if(tBConc11.getDocument().getLength()>0)
        aBotTimeAndConc[1][10]  = Double.parseDouble(tBConc11.getText());
if(tBConc12.getDocument().getLength()>0)
        aBotTimeAndConc[1][11]  = Double.parseDouble(tBConc12.getText());
if(tBConc13.getDocument().getLength()>0)
```

```
                        aBotTimeAndConc[1][12] = Double.parseDouble(tBConc13.getText());
                if(tBConc14.getDocument().getLength()>0)
                        aBotTimeAndConc[1][13] = Double.parseDouble(tBConc14.getText());
                if(tBConc15.getDocument().getLength()>0)
                        aBotTimeAndConc[1][14] = Double.parseDouble(tBConc15.getText());
                }

        public void calculateKeq() {
                dKeq=(aPredictedTopConc[0]*dVolTop-dCTopEq*dVolTop-dCBotEq*dVolBot-dSampledMass)/
(dArea*dThickness)/((dCTopEq+dCBotEq)/2.0);
                tKeq.setText(Double.toString(dKeq));
                }

        public void startIterations() {
                int i,j;
                double dCurrentD, dBestD, dIncrement;
                double [] aDValues = new double[10];

                dCurrentD=.000000001;
                dIncrement=.0000000001;
                dBestD=1;
                dBestResidual=10000;
                while(dCurrentD<.00000001) {
                        dD=dCurrentD;
                        calculateChamberConcentrations();
                        calculateResidual();
//System.out.println("dCurrentD: "+dCurrentD);
                        if(dResidual<dBestResidual) {
                                dBestD=dCurrentD;
                                dBestResidual=dResidual;
                                }
                        dCurrentD+=dIncrement;
                        }

                dCurrentD=.00000001;
                dIncrement=.000000001;
                while(dCurrentD<.0000001) {
                        dD=dCurrentD;
                        calculateChamberConcentrations();
                        calculateResidual();
//System.out.println("dCurrentD: "+dCurrentD);
                        if(dResidual<dBestResidual) {
                                dBestD=dCurrentD;
                                dBestResidual=dResidual;
                                }
```

```
                    dCurrentD+=dIncrement;
                    }

             dCurrentD=.0000001;
             dIncrement=.00000001;
             while(dCurrentD<.000001) {
                    dD=dCurrentD;
                    calculateChamberConcentrations();
                    calculateResidual();
//System.out.println(“dCurrentD: “+dCurrentD);
                    if(dResidual<dBestResidual) {
                           dBestD=dCurrentD;
                           dBestResidual=dResidual;
                           }
                    dCurrentD+=dIncrement;
                    }

             dCurrentD=.000001;
             dIncrement=.0000001;
             while(dCurrentD<.00001) {
                    dD=dCurrentD;
                    calculateChamberConcentrations();
                    calculateResidual();
//System.out.println(“dCurrentD: “+dCurrentD);
                    if(dResidual<dBestResidual) {
                           dBestD=dCurrentD;
                           dBestResidual=dResidual;
                           }
                    dCurrentD+=dIncrement;
                    }

             dCurrentD=.00001;
             dIncrement=.000001;
             while(dCurrentD<.0001) {
                    dD=dCurrentD;
                    calculateChamberConcentrations();
                    calculateResidual();
//System.out.println(“dCurrentD: “+dCurrentD);
                    if(dResidual<dBestResidual) {
                           dBestD=dCurrentD;
                           dBestResidual=dResidual;
                           }
                    dCurrentD+=dIncrement;
                    }
```

```
        dCurrentD=.0001;
        dIncrement=.00001;
        while(dCurrentD<.001) {
            dD=dCurrentD;
            calculateChamberConcentrations();
            calculateResidual();
//System.out.println(“dCurrentD: “+dCurrentD);
            if(dResidual<dBestResidual) {
                dBestD=dCurrentD;
                dBestResidual=dResidual;
                }
            dCurrentD+=dIncrement;
            }

        dD=dBestD*60/.000001;
        tD.setText(Double.toString(dD));
        }

    public void calculateResidual() {
        int i,iTimeStep;
        double dExpTime, dExpConc, dPredictedConc;

        dResidual=0.0;
        for(i=1;i<iTopSize;i++) {
            dExpTime=aTopTimeAndConc[0][i];
            dExpConc=aTopTimeAndConc[1][i];
            dPredictedConc=aPredictedTopConc[(int)(dExpTime/dDeltaT)];
            dResidual+= Math.pow((dExpConc-dPredictedConc)/dExpConc,2.0);
//System.out.println(“residual for top predicted: “+dPredictedConc+”, and experimental:
“+dExpConc+”, Residual: “+dResidual);
            }
        for(i=0;i<iBotSize;i++) {
            dExpTime=aBotTimeAndConc[0][i];
            dExpConc=aBotTimeAndConc[1][i];
            dPredictedConc=aPredictedBottomConc[(int)(dExpTime/dDeltaT)];
            dResidual+= Math.pow((dExpConc-dPredictedConc)/dExpConc,2.0);


//System.out.println(“residual for bottom predicted: “+dPredictedConc+”, and experimental:
“+dExpConc+”, Residual: “+dResidual);


            }
        }



    public void initializeValues() {
        int i=0;
```

```
        while(aTopTimeAndConc[0][i]!=0.0) i++;

        double dLongestTime;
        dLongestTime=aTopTimeAndConc[0][i-1];

        iTopSize=i-1;
        i=0;
        while(aBotTimeAndConc[0][i]!=0.0) i++;

        iBotSize=i-1;

        if(dLongestTime < aBotTimeAndConc[0][i-1])
            dLongestTime=aBotTimeAndConc[0][i-1];

        aMaterialTimeAndConc = new double [(int)(dLongestTime/dDeltaT)+1][(int)dLayers];
//System.out.println(“Time Steps: “+aMaterialTimeAndConc.length+”   Layers:
“+aMaterialTimeAndConc[0].length);
        aPredictedTopConc = new double [(int)(dLongestTime/dDeltaT)+1];
        aPredictedBottomConc = new double [(int)(dLongestTime/dDeltaT)+1];

        for(i=0;i<aMaterialTimeAndConc[0].length;i++)
            aMaterialTimeAndConc[0][i]=0.0;
        aPredictedTopConc[0]=aTopTimeAndConc[1][0];
        aPredictedBottomConc[0]=0.0;


//System.out.println(“Starting top chamber conc: “+aPredictedTopConc[0]);
        }

    public void calculateChamberConcentrations() {
        int j=0;
        int i=0;
        for(i=1;i<aMaterialTimeAndConc.length;i++) {
            aPredictedTopConc[i]=(aPredictedTopConc[i-1]+aMaterialTimeAndConc
[i-1][0]*2*dD*dArea*dDeltaT/(dVolTop*dThickness/dLayers))/(1+dKeq*2*dD*dArea*dDeltaT/
(dVolTop*dThickness/dLayers));
            aMaterialTimeAndConc[i][0]=(aMaterialTimeAndConc[i-1][0]+dD*dDeltaT/
Math.pow(dThickness/dLayers,2.0)*(2*aPredictedTopConc[i]*dKeq+aMaterialTimeAndConc[i-
1][1]))/(1+3*dD*dDeltaT/Math.pow(dThickness/dLayers,2.0));
            for(j=1;j<(int)aMaterialTimeAndConc[0].length-1;j++)
                aMaterialTimeAndConc[i][j]=(aMaterialTimeAndConc[i-1][j]+dD*dDeltaT/
Math.pow(dThickness/dLayers,2.0)*(aMaterialTimeAndConc[i][j-1]+aMaterialTimeAndConc[i-
1][j+1]))/(1+2*dD*dDeltaT/Math.pow(dThickness/dLayers,2.0));
            aMaterialTimeAndConc[i][j]=(aMaterialTimeAndConc[i-1][j]+dD*dDeltaT/Math.
pow(dThickness/dLayers,2.0)*(aMaterialTimeAndConc[i][j-1]+2*aPredictedBottomConc[i-1]*dKeq))/
(1+3*dD*dDeltaT/Math.pow(dThickness/dLayers,2.0));
            aPredictedBottomConc[i]=(aPredictedBottomConc[i-
1]+aMaterialTimeAndConc[i][j]*2*dD*dArea*dDeltaT/(dVolBot*dThickness/dLayers))/
(1+dKeq*2*dD*dArea*dDeltaT/(dVolBot*dThickness/dLayers));
            }
```

```
                }

        public void printResults() {
                dD=dD*.000001/60;
                calculateChamberConcentrations();
                dD=dD*60/.000001;
System.out.println(“Top Chamber Predicted Final Conc: “+aPredictedTopConc[aPredictedTopConc.
length-1]);
System.out.println(“Top Chamber Experimental Final Conc: “+aTopTimeAndConc[1][iTopSize]);
System.out.println(“Bottom Chamber Predicted Final Conc: “+aPredictedBottomConc[aPredictedBotto
mConc.length-1]);
System.out.println(“Bottom Chamber Experimental Final Conc: “+aBotTimeAndConc[1][iBotSize]);
System.out.println(“Original Mass: “+aTopTimeAndConc[1][0]*dVolTop);
                double dFinalSorbedMass = 0.0;
                int j;
                for(j=0;j<(int)dLayers;j++) {
                        dFinalSorbedMass+=aMaterialTimeAndConc[aMaterialTimeAndConc.length-
1][j]*dThickness/dLayers*dArea;
System.out.println(“C”+j+”: “+aMaterialTimeAndConc[aMaterialTimeAndConc.length-1][j]);
                        }
                double dFinalPredictedMass=aPredictedTopConc[aPredictedTopConc.length-1]*dVolTop+
dFinalSorbedMass+aPredictedBottomConc[aPredictedBottomConc.length-1]*dVolBot;
System.out.println(“Predicted Final Mass: “+dFinalPredictedMass);
System.out.println(“Best residual: “+dBestResidual);
System.out.println(“D: “+dD);
                int i,iTimeStep;
                double dExpTime, dExpConc, dPredictedConc;

                for(i=1;i<iTopSize;i++) {
                        dExpTime=aTopTimeAndConc[0][i];
                        dExpConc=aTopTimeAndConc[1][i];
                        dPredictedConc=aPredictedTopConc[(int)(dExpTime/dDeltaT)];
System.out.println(“Predicted top conc: “+dPredictedConc+”, and experimental conc: “+dExpConc+”
at time: “+dExpTime);
                        }
                for(i=0;i<iBotSize;i++) {
                        dExpTime=aBotTimeAndConc[0][i];
                        dExpConc=aBotTimeAndConc[1][i];
                        dPredictedConc=aPredictedBottomConc[(int)(dExpTime/dDeltaT)];
System.out.println(“Bottom predicted conc: “+dPredictedConc+”, and experimental conc:
“+dExpConc);
                        }
                }

        public static void main(String args[]) {
                DiffusionSolver diff = new DiffusionSolver();
```

```
        diff.addWindowListener(new WindowAdapter() {
                public void windowClosing(WindowEvent e) {
                        System.exit(0);
                        }
                });
        }
}
```

Appendix C
Results for Mortar Experiments

The following plots show the relative concentration parameter, -ln(C/Co)A/V, in the top chamber of the dual-volume system versus time for five of six organic test chemicals and mortar. Here, Co is the initial concentration (time = 0) in the gas phase of the top chamber, C is the chemical concentration in the gas phase of the top chamber at a specific time, A is the area of the exposed surface of mortar in the top chamber, and V is the air volume of the top chamber.

Figure C-1. Relative concentration parameter versus time for mortar exposed to n-butanol.

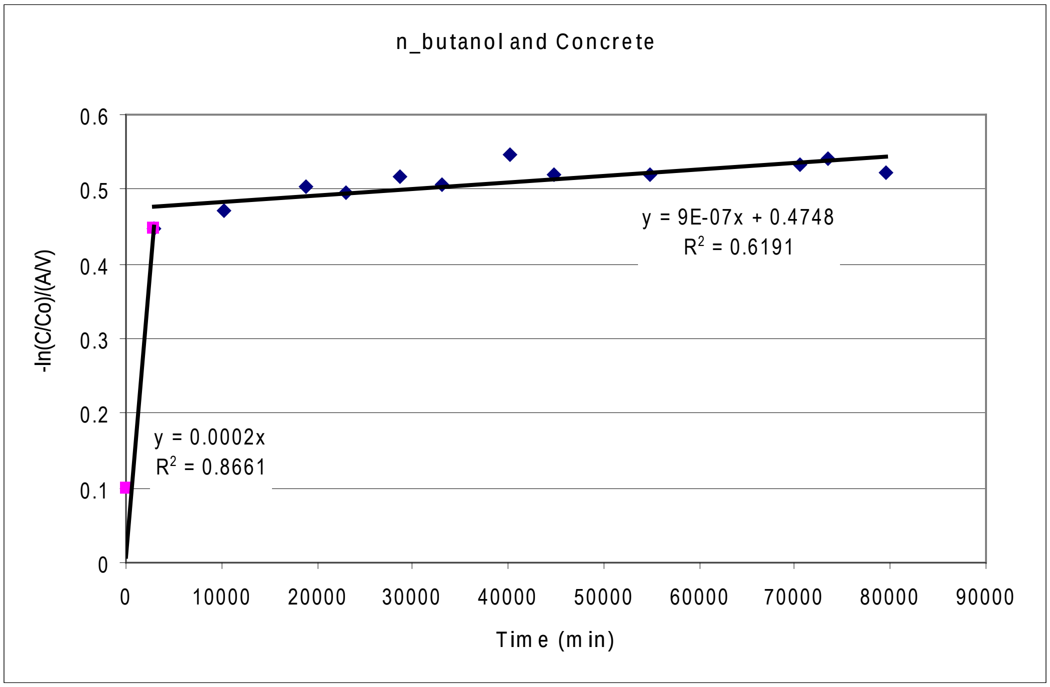


Figure C-2. Relative concentration parameter versus time for mortar exposed to ethylbenzene.

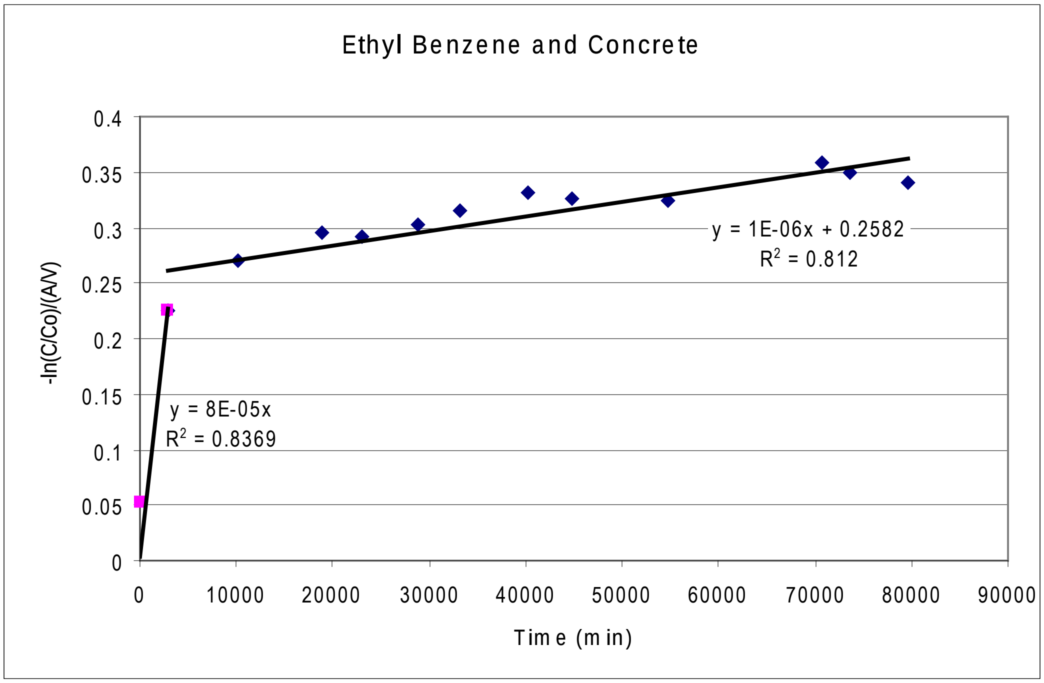


Figure C-3. Relative concentration parameter versus time for concrete exposed to decane.

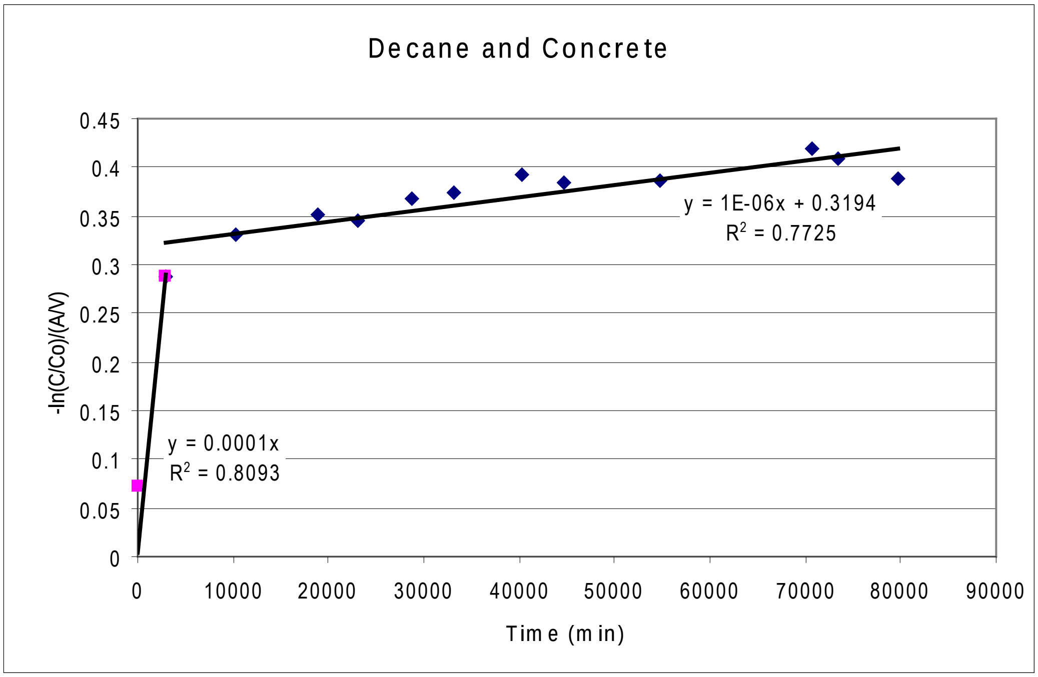


Figure C-4. Relative concentration parameter versus time for mortar exposed to undecane.

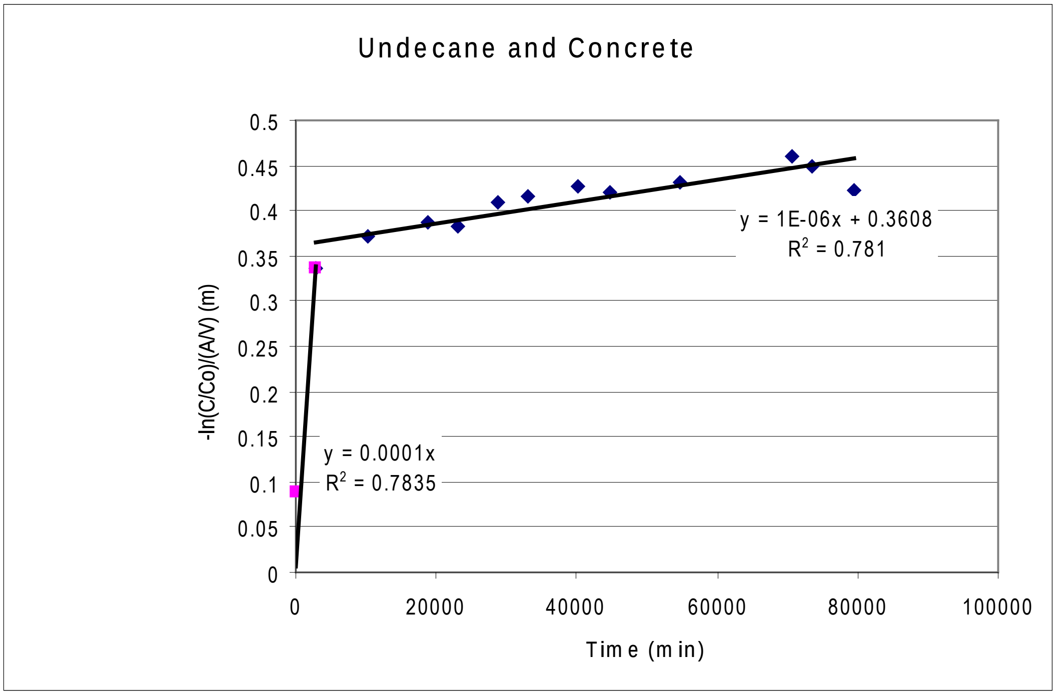
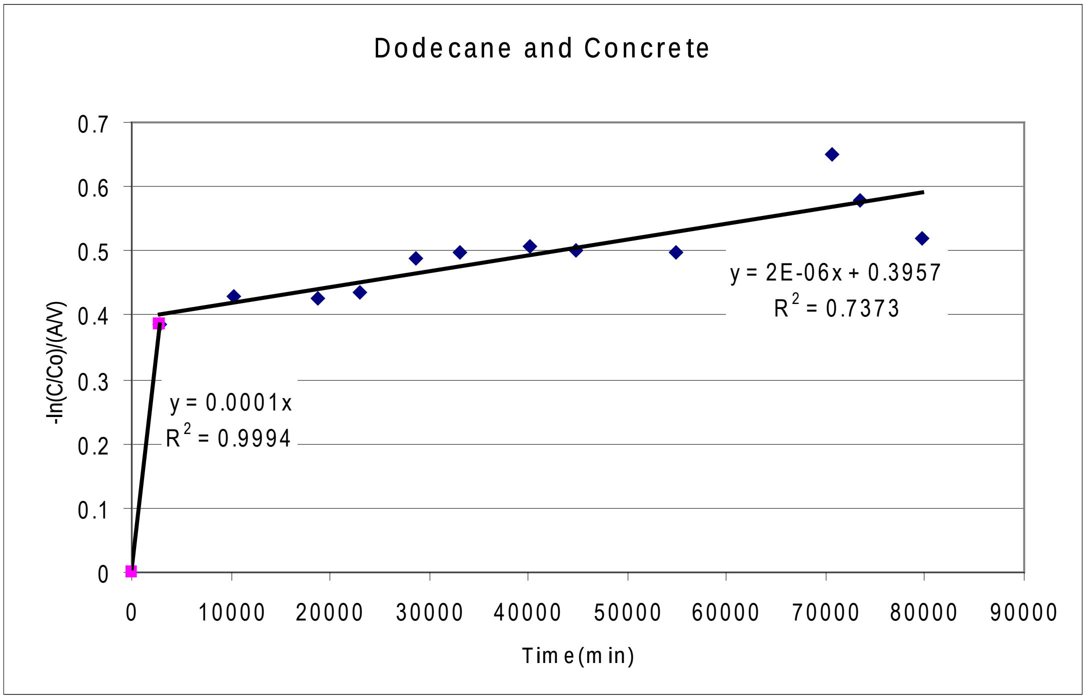


Figure C-5. Relative concentration parameter versus time for motar exposed to dodecane.



Appendix D
Results for VF and PUF

Figure D-1. Raw data and fitted diffusion model for sorption and desorption of hexanal in vinyl flooring.

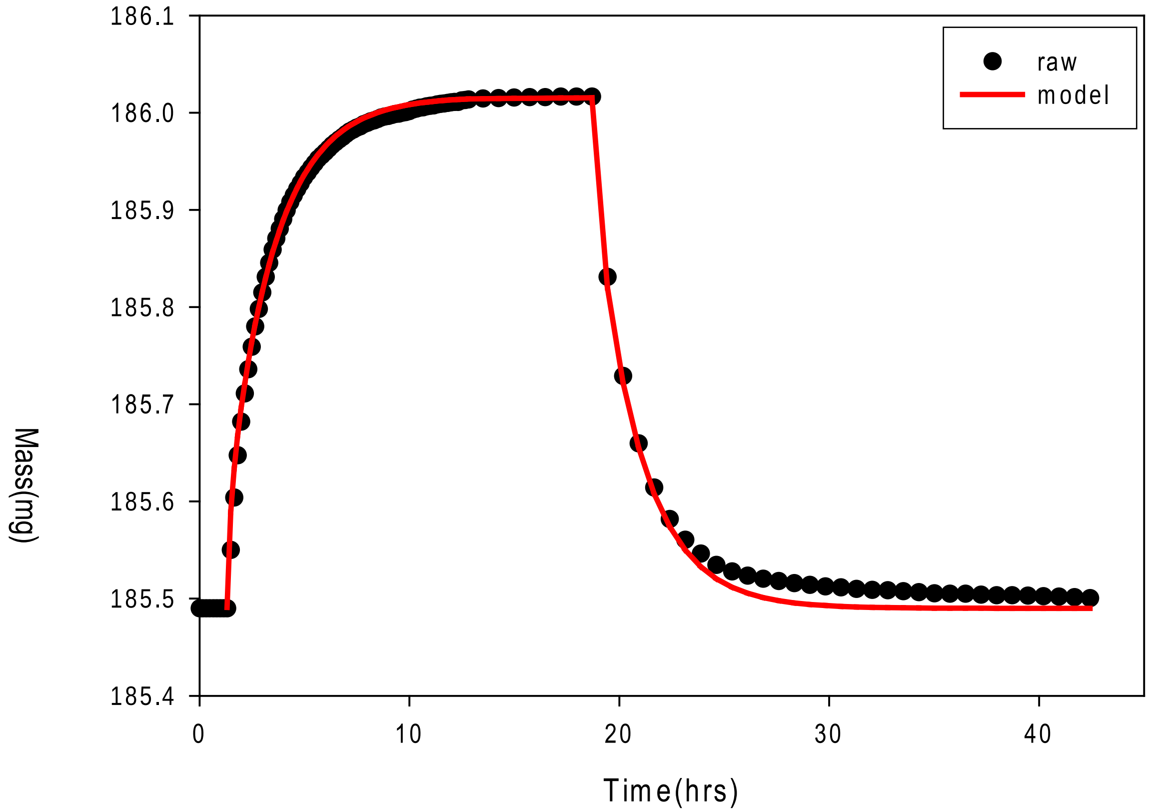


Figure D-2. Raw data and fitted diffusion model for sorption and desorption of decane in vinyl flooring.

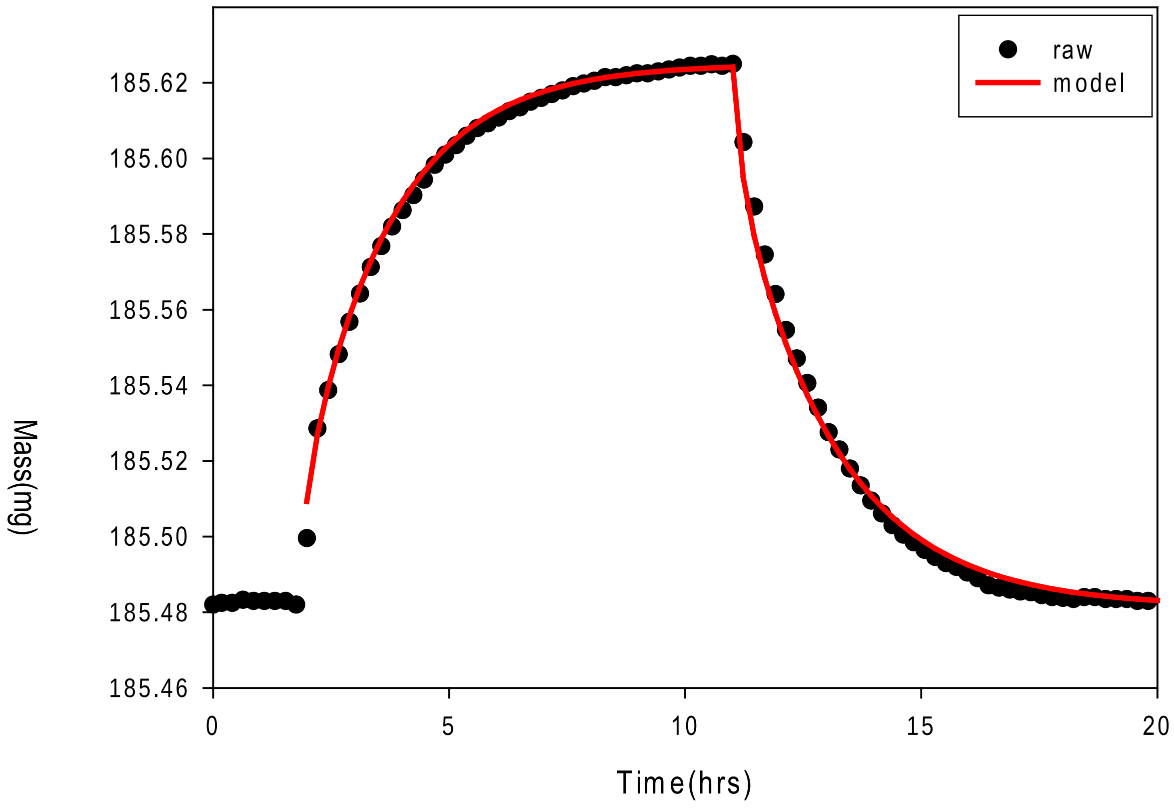


Figure D-3. Raw data and fitted diffusion model for sorption and desorption of dodecane (first replicate) in vinyl flooring.

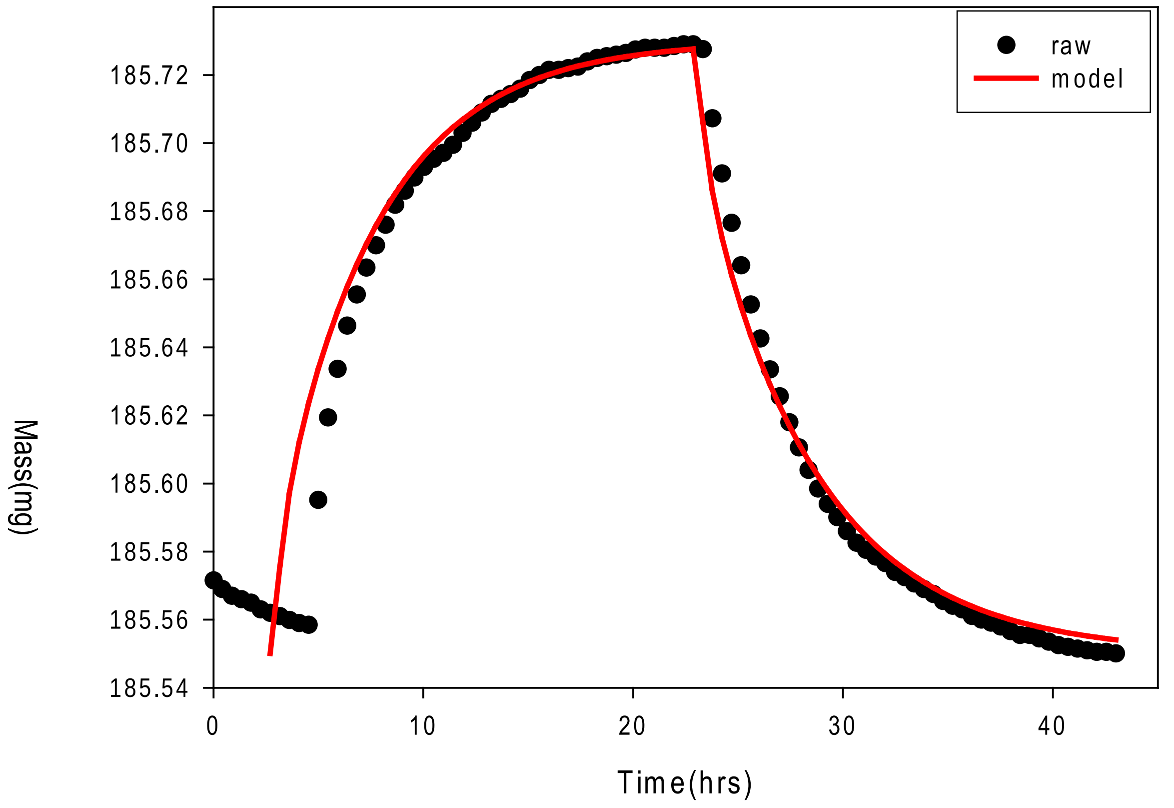


Figure D-4. Raw data and fitted diffusion model for sorption and desorption of dodecane (second replicate) in vinyl flooring.

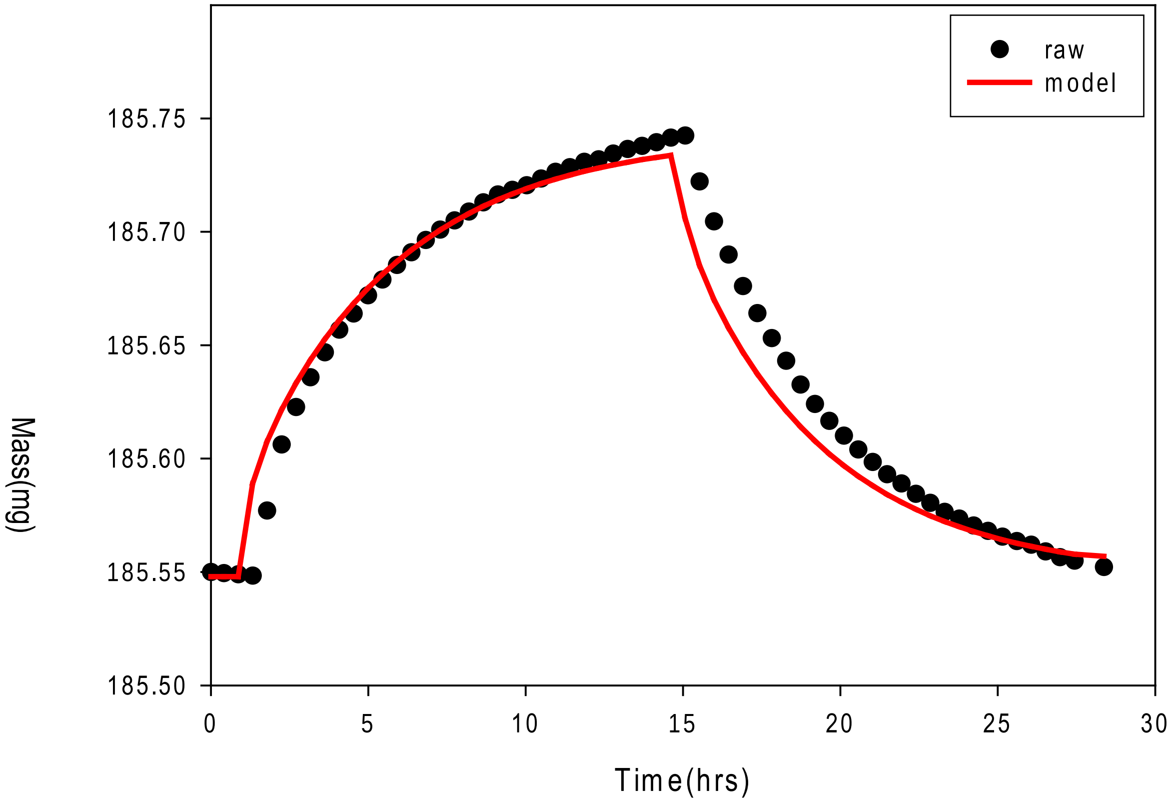


Figure D-5. Raw data and fitted diffusion model for sorption and desorption of undecane in vinyl flooring.

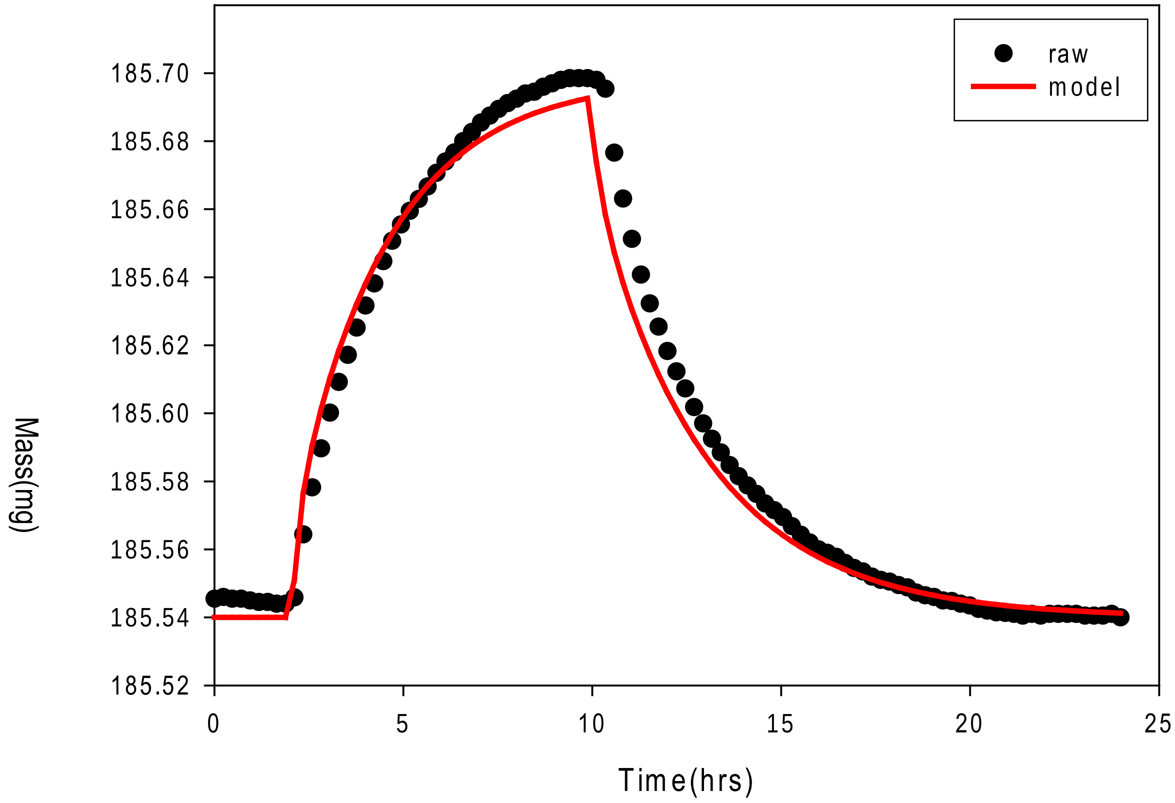


Figure D-6. Raw data and fitted diffusion model for sorption and desorption of butanol in vinyl flooring.

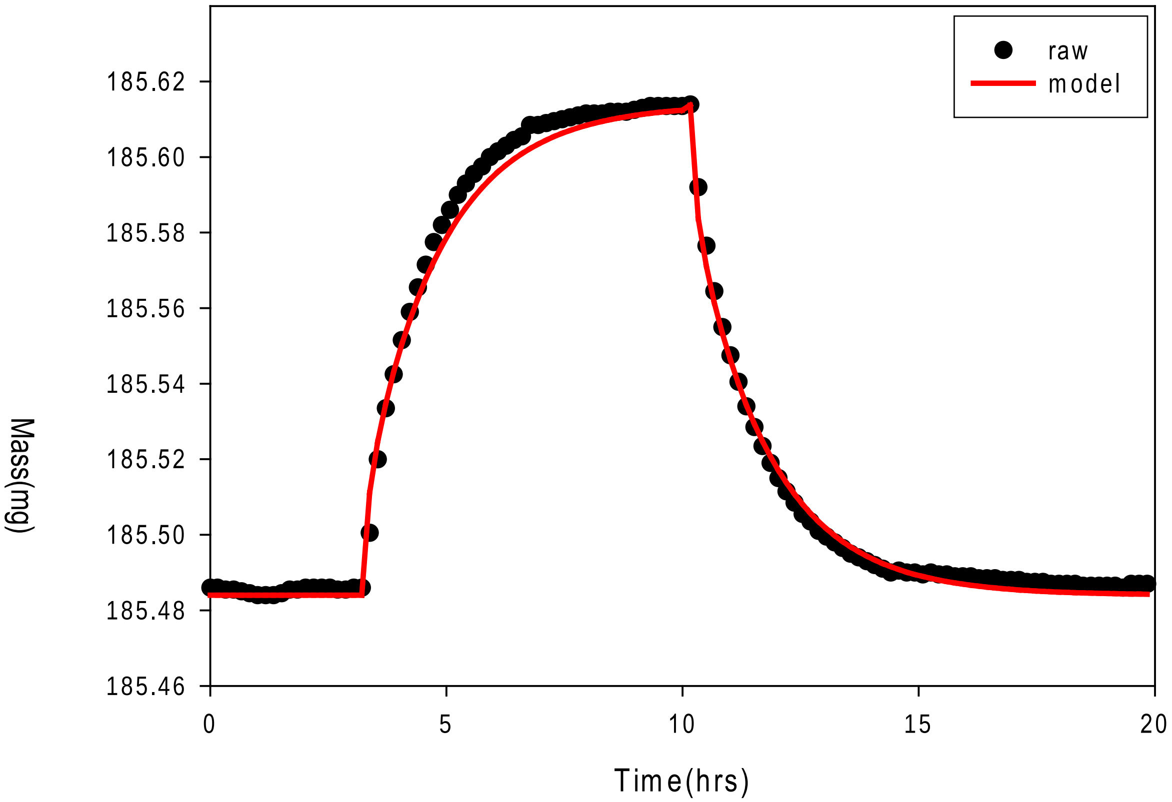


Figure D-7. Raw data and fitted diffusion model for sorption and desorption of tetradecane in vinyl flooring.

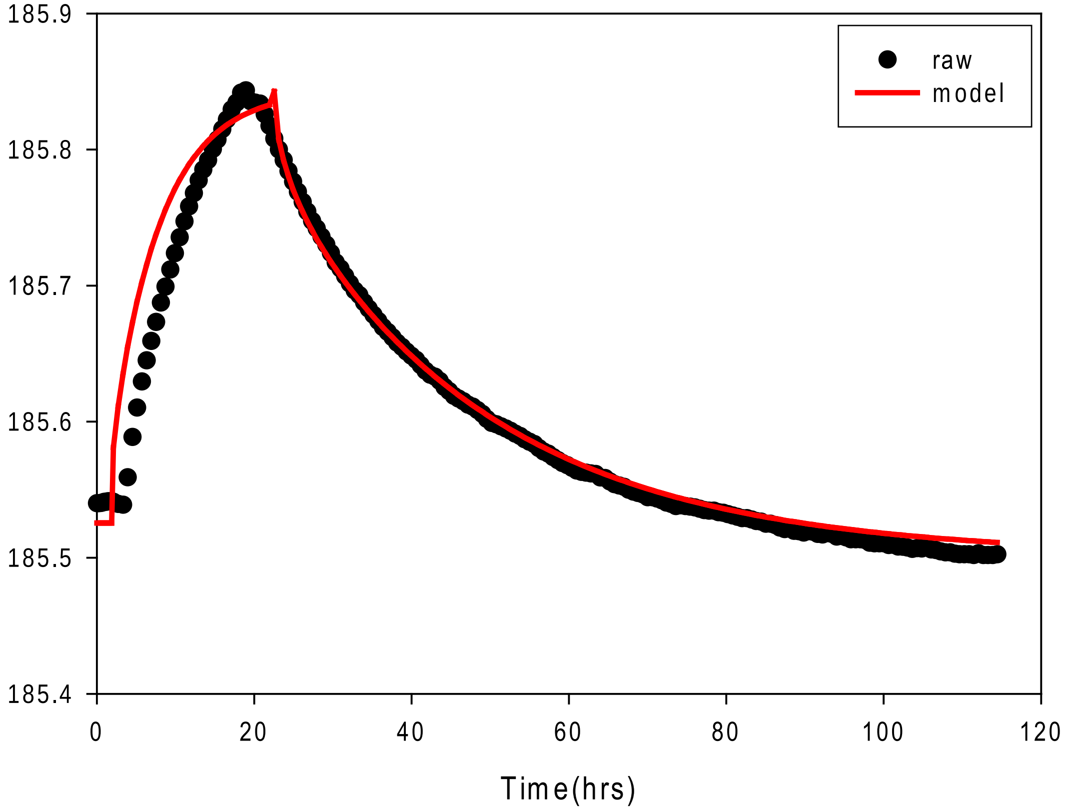


Figure D-8. Raw data and fitted diffusion model for sorption and desorption of undecane in polyurethane foam.

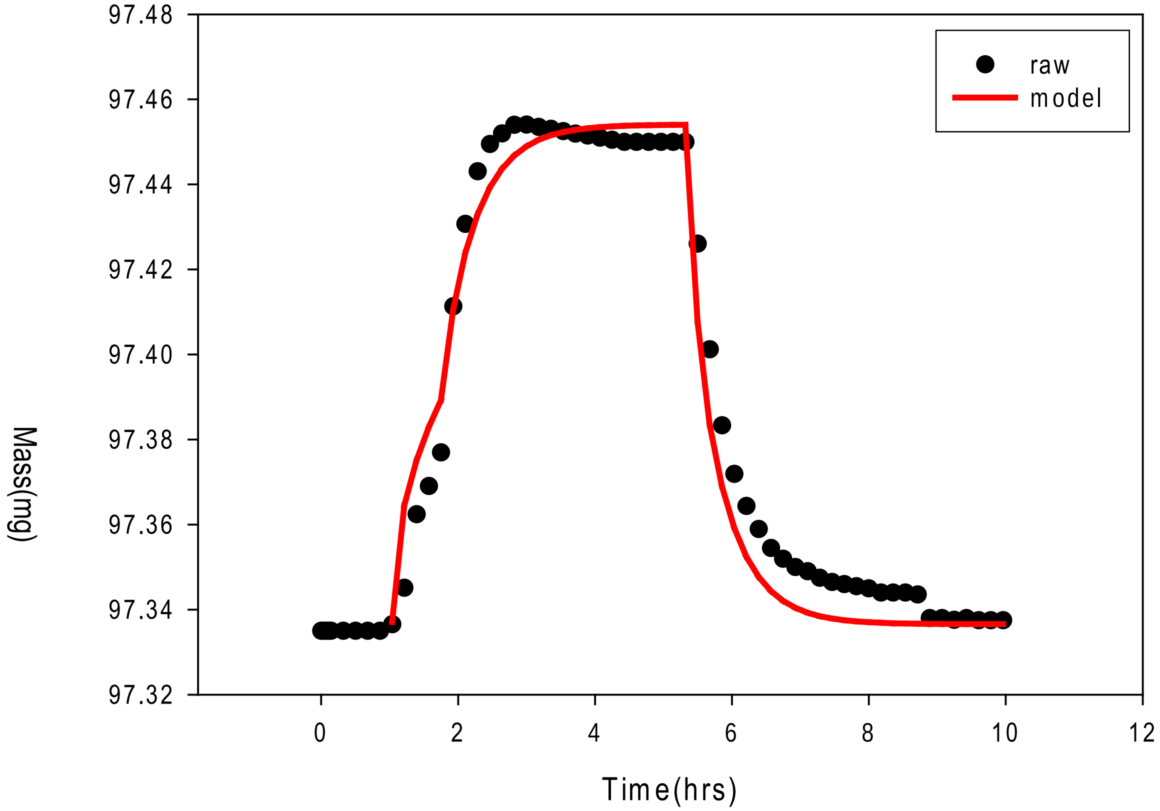


Figure D-9. Raw data and fitted diffusion model for sorption and desorption of butanol in polyurethane foam.

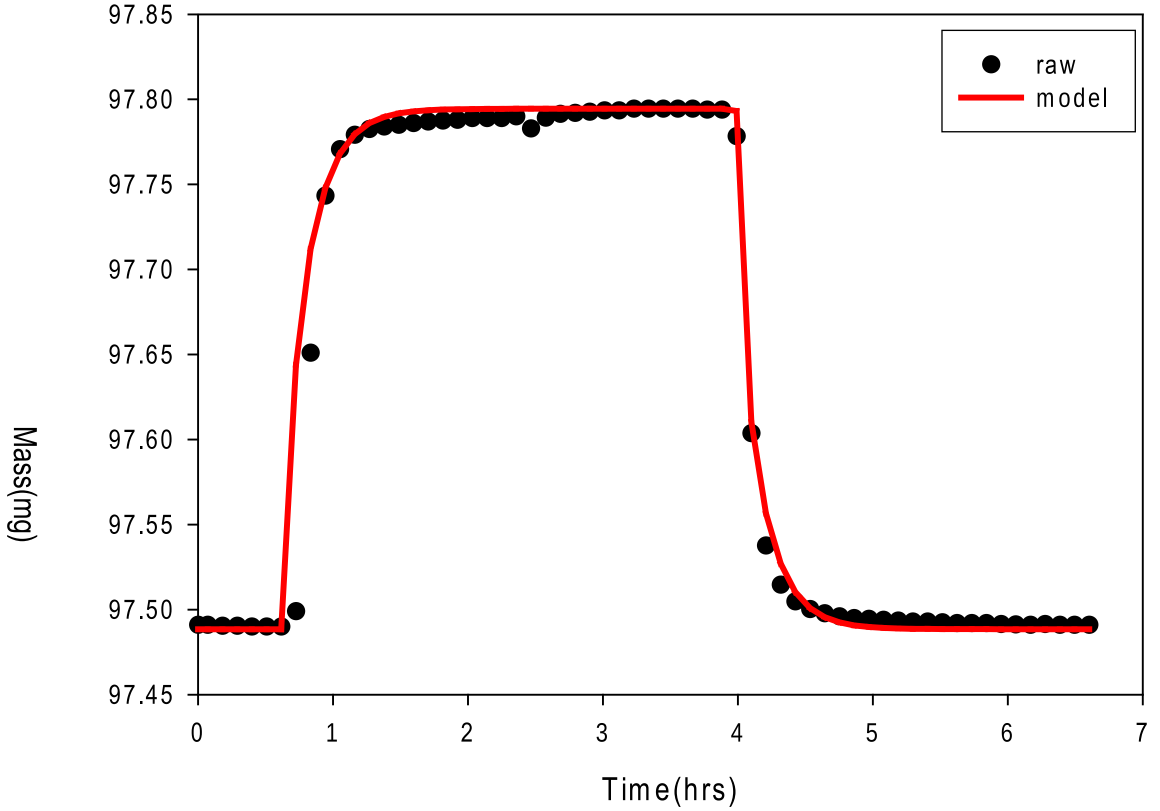


Figure D-10. Raw data and fitted diffusion model for sorption and desorption of decane in polyurethane foam.

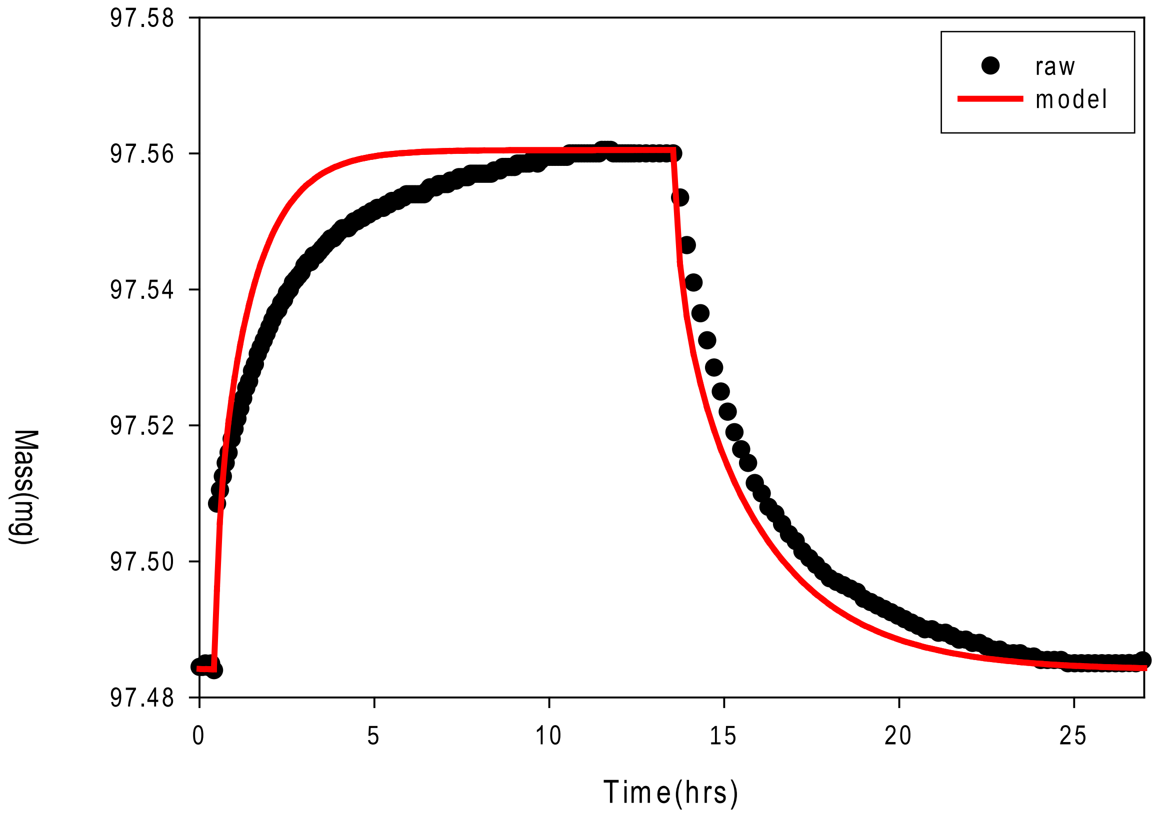


Figure D-11. Raw data and fitted diffusion model for sorption and desorption of dodecane (first replicate) in polyurethane foam.

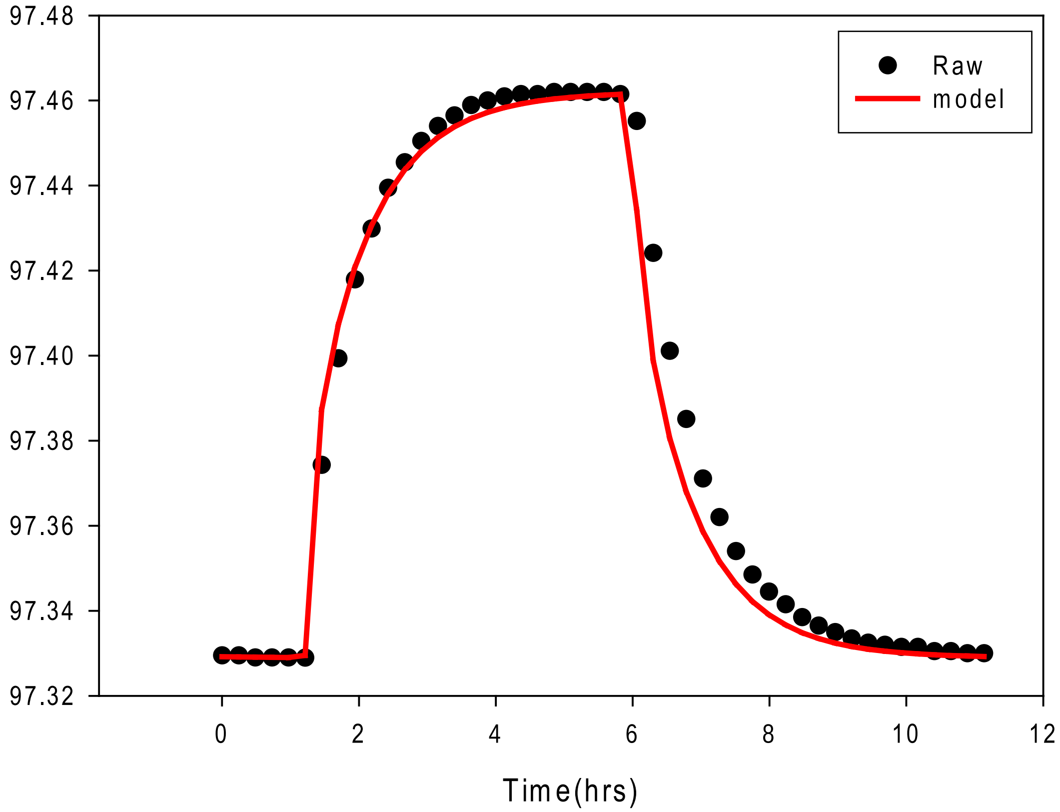


Figure D-12. Raw data and fitted diffusion model for sorption and desorption of dodecane (second replicate) in polyurethane foam.

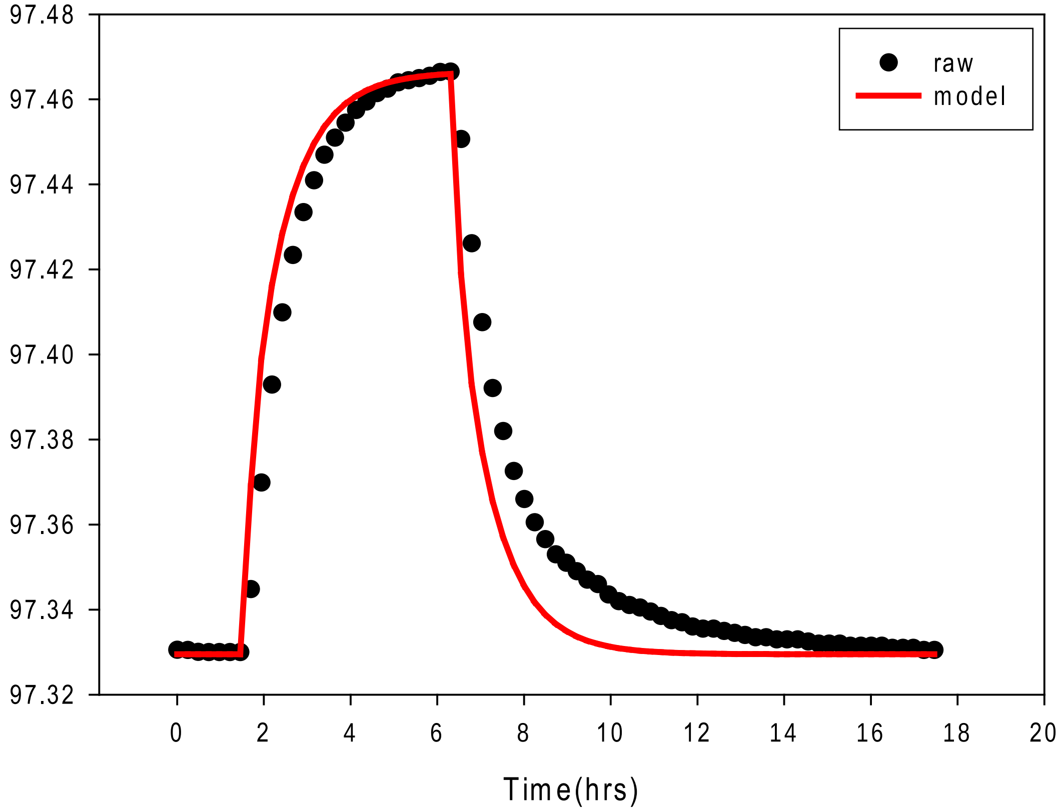


Figure D-13. Raw data and fitted diffusion model for sorption and desorption of tetradecane in polyurethane foam.

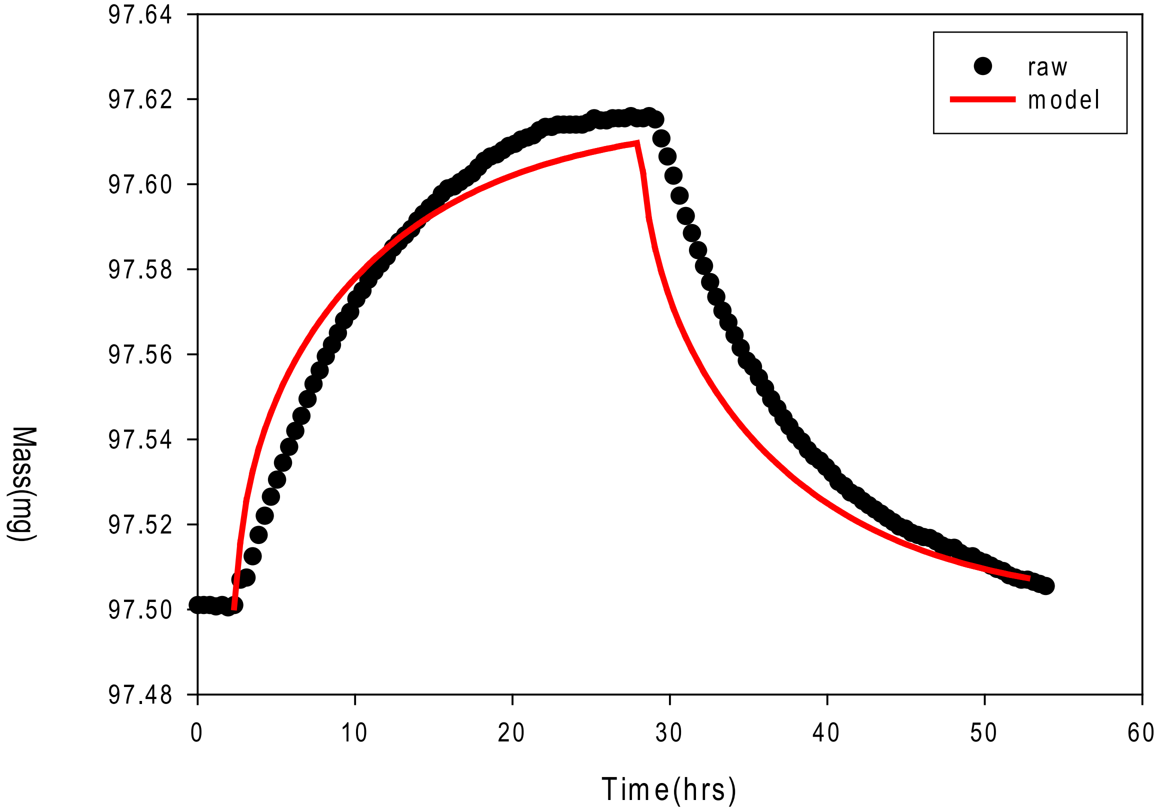


Figure D-14. Raw data for sorption and desorption of hexanal (first replicate) in polyurethane foam.

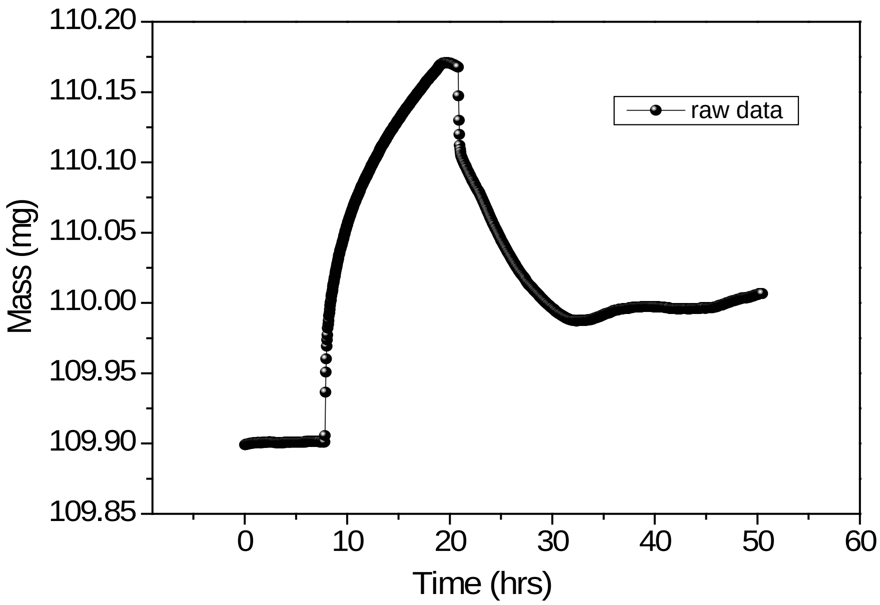
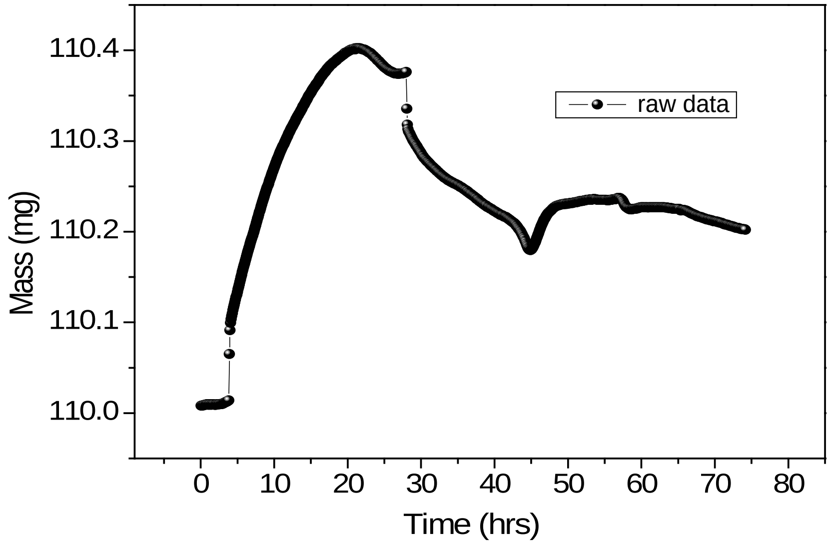


Figure D-15. Raw data for sorption and desorption of hexanal (second replicate) in polyurethane foam.



EPA 600/R-07/035-R1 | August 2007 | www.epa.gov/ord

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