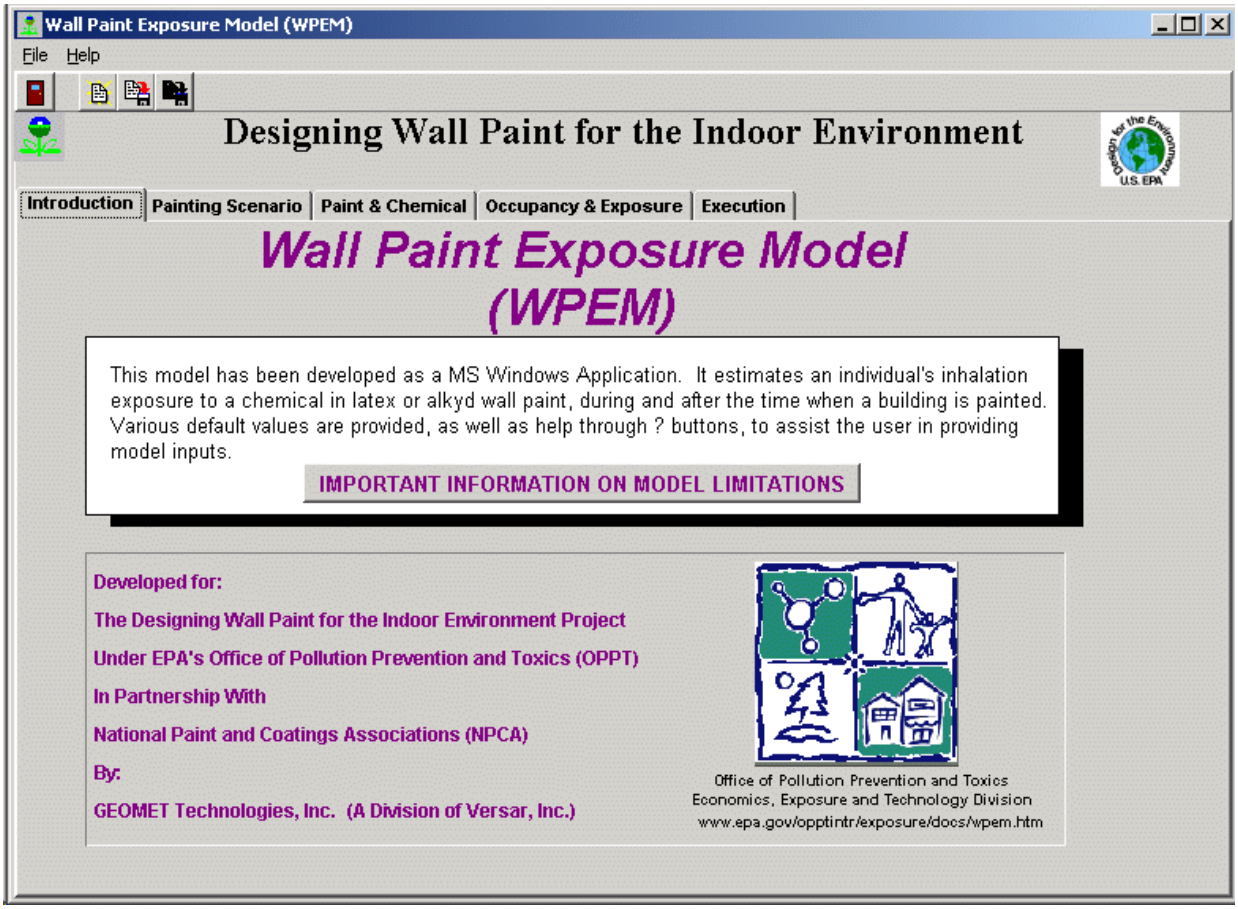
WALL PAINT EXPOSURE MODEL (WPEM):
Version 3.2

USER'S GUIDE



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for
USEPA Office of Pollution Prevention and Toxics
Washington, DC
and
National Paint and Coatings Association
Washington, DC

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DISCLAIMER

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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TABLE OF CONTENTS

1. BACKGROUND AND OVERVIEW

1.1 Project Background

The U.S. Environmental Protection Agency's Office of Pollution Prevention and Toxics (OPPT) has initiated a Design for the Environment (DfE) Project intended to develop a wall paint exposure assessment model for interior latex and alkyd paints. The EPA is working with the National Paints and Coatings Association (NPCA), in addition to paint manufacturers and chemical suppliers, to develop this model. The purpose of the planned model is to allow industry product developers and health and safety officials to more easily and accurately identify chemicals in paint formulations that may pose potential exposure problems. It is envisioned that identification and/or evaluation of potentially problematic chemicals will be done by individual paint manufacturers and chemical suppliers during the design stage of paint development and/or during a product-stewardship effort to fully assess a current line of products.

The EPA has selected latex and alkyd wall paints to evaluate as sources of chemicals emitted into indoor air because of the relatively large number of people exposed and the fact that, as a wet product, paint emissions (and thereby exposures) could be relatively high when compared to dry products. The EPA believes that data generated from small-chamber testing translates well, when an appropriate indoor-air model is used, into exposure estimates. If a suitable exposure model were to be made available, then it would be relatively easy (compared to a field study) to quantitatively assess exposures to one or more chemicals in paint.

Under the DfE project, EPA established a working group to guide additional data collection and development of a wall paint exposure assessment model. The joint government/industry working group identified the data and capabilities needed for the exposure model. Although fairly extensive testing has been done in recent years by the EPA Office of Research and Development's Air Pollution and Prevention Control Division (APPCD) to characterize emissions from latex and alkyd paints through chamber tests, additional data were deemed necessary to (1) cover a broader sample of paints and associated chemicals, and (2) better characterize the behavior of potential indoor sinks such as carpeting and wallboard. In addition, experiments were carried out at EPA's research house in North Carolina to obtain concentration data from "real-world" painting events under carefully controlled and well-documented conditions, for purposes of model evaluation. The data described above were collected by ARCADIS Geraghty & Miller, Inc. Methods for and results of the data collection have been documented in a recent report (ARCADIS 1998).

This document summarizes the model, called the Wall Paint Exposure Model (WPEM), that has been developed under the Wall Paint DfE project. The remainder of this section provides an overview of the model's general features and input requirements, and the model's purpose and limitations. Subsequent sections provide further details on input screens, model outputs, and default scenarios provided with the model, along with a summary of the emission models used in WPEM. The appendices describe procedures and results for chamber emission and sink tests,

development of emission models that are used in WPEM, and procedures for and results of model evaluation.

1.2 Model Overview

WPEM has been developed as a Windows 95/98 application. As noted in the Introduction Screen for the model (Figure 1-1), it estimates an individual's inhalation exposure to airborne concentrations of a chemical released from latex or alkyd primer/paint, during and after the time when a building (residence, office, or standard box) is painted. The model requires certain information from the user in order to provide these estimates. User inputs are gathered in an organized manner through a series of input screens called Painting Scenario, Paint & Chemical, and Occupancy & Exposure (see the tabs in Figure 1-1). Once these inputs have been provided, model calculations can be invoked through the Execution screen.

The following are the major types of information to be provided on each screen:

- **Painting Scenario** screen
  - building volume and airflow rates
  - percent of building painted
  - whether walls, ceilings, or both are painted
  - amount of paint used, painting rate, and resultant painting duration

- **Paint & Chemical** screen
  - type of paint and primer/paint density
  - properties of the chemical to be modeled, weight fraction in the primer/paint
  - chemical emissions model for primer and paint
  - indoor sink model (optional)

- **Occupancy & Exposure** screen
  - type/gender of exposed individual
  - individual's location and breathing rate during the painting event
  - weekday and weekend activity patterns (locations, breathing rates)
  - number of painting events in lifetime
  - length of lifetime and body weight

- **Execution** screen
  - title of run and length of model run
  - results (exposure estimates) after execution
  - option to view/print a report summarizing inputs and outputs

The user is advised to proceed through these screens sequentially. Efforts have been made to provide model defaults wherever possible, and to make certain calculations on behalf of the user. Within each screen, areas where user inputs are required are shown in **white**. For example,

on the Painting Scenario screen the user must choose a residence, office building, or "standard box," and must indicate the number of coats applied for the primer and/or paint. Areas where user inputs are optional are shown in **gray**. For such areas, edit buttons enable the user to override default values that have been provided or calculated by the model. For example, on the Painting Scenario screen there is a default coverage of 400 square feet per gallon (equating to a wet film thickness of 4 mil) for paint, but the user can override this value. Six default scenarios are provided with the WPEM software and can be accessed from the "File" "Open" toolbar in WPEM.

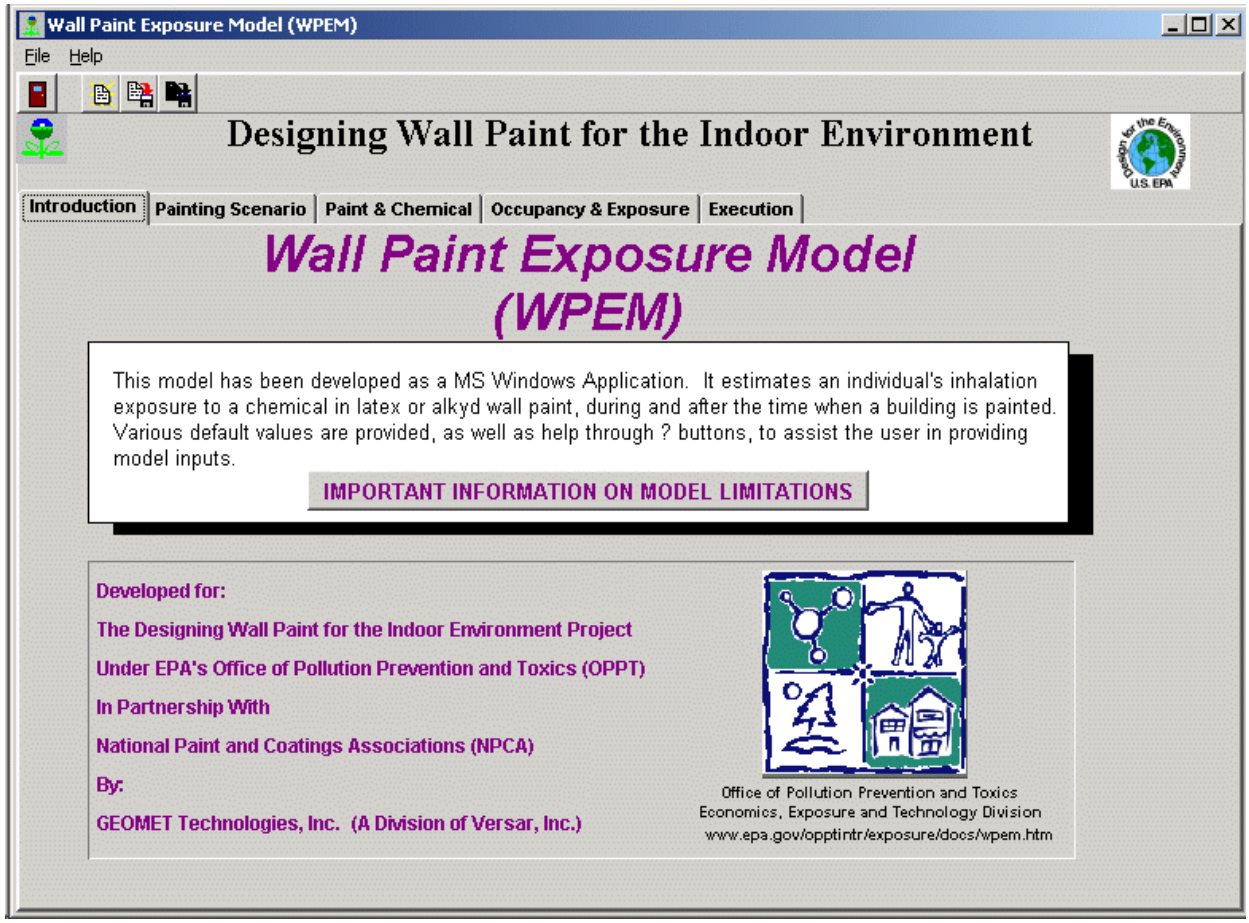

Figure 1-1. WPEM Introduction Screen.

Context-sensitive help for WPEM is provided through ? buttons. Each ? button is located near the input area to which it pertains. These buttons generally provide guidance for editing default selections or values provided with the model. In some cases, they also describe the basis for a default value or the algorithm used by WPEM to calculate the value.

In addition, the following buttons provide background information on specific topic areas:

- IMPORTANT INFORMATION ON MODEL LIMITATIONS, located on the Introduction screen;
- DESCRIPTION OF DEFAULT SCENARIOS, located on the Painting Scenario screen;
- DISPLAY CHEMICALS USED TO DEVELOP EMISSION MODELS, located on the Paint & Chemical screen; and
- MODEL LIMITATIONS, located on the Execution screen.

1.3 Model Purpose and Limitations

As noted in Section 1.1, the primary purpose of the model is to allow industry product developers and health and safety officials to more easily and accurately identify chemicals in paint formulations that may pose potential exposure problems. Once the user has provided model inputs as summarized in Section 1.2 and has executed the model, the resulting outputs can be used to assess inhalation exposure and associated risk for a chemical that is currently formulated, or is being considered for formulation, in primer and/or paint. The model provides both short-term and long-term exposure measures. Short-term measures include the highest instantaneous, 15-minute-average, and 8-hour-average airborne concentration to which an individual is exposed, under the conditions represented by model inputs. Long-term measures include lifetime average daily dose (LADD) and lifetime average daily concentration (LADC).

The IMPORTANT INFORMATION ON MODEL LIMITATIONS button on the Introduction screen (see Figure 1-1) describes some cautions to be considered when using the model. For example, the model is designed to estimate indoor-air concentrations and associated inhalation exposures for interior applications involving alkyd or latex primer/paint. The emission algorithms used in the model, and their relationship to chemical properties, are based on chamber tests specific to interior paints. At present there is no basis for applying these algorithms to other types of products.

The model calculations are intended to represent the time series of indoor concentrations for a chemical, and exposure measures derived from those concentrations, that can be expected when primer or paint is applied in an indoor environment. Although these calculations are based on fundamental principles such as the conservation of chemical mass indoors, there are certain assumptions and/or limitations inherent in the model:

- The emission and sink models used in WPEM are derived from a limited number of small-chamber tests, conducted at a fixed air exchange rate, a fixed loading of wallboard, and a fixed product application rate for one type of application (roller).

- A single-chamber model is used when an entire building is painted; when part of a building is painted, a two-chamber model (painted and unpainted parts) is used.

- Within the modeled compartment(s), uniform mixing is assumed; no distinction is made between airborne chemical concentrations in the applicator's breathing zone versus elsewhere in the compartment where paint is applied.

- Only one chemical can be modeled at a time; within a model run, it is not possible to combine different primer/paint types (e.g., alkyd primer and latex paint), but such a combination can be modeled through separate model runs (see Section 4).

- The indoor-outdoor air exchange rate is treated as a constant (i.e., it cannot vary over time). Model defaults for the air exchange rate assume a closed-building condition, as supporting data for other conditions (e.g., windows open or exhaust fans on) are limited.

- Dose estimates provided by the model are measures of potential inhaled dose (i.e., 100 percent uptake is assumed).

- The model has no capability for Monte Carlo simulation as a means of addressing uncertainty, but another model (MCCEM) developed for OPPT has this capability.

2. INPUT SCREENS

2.1 Painting Scenario Screen

This screen (Figure 2-1) is designed to obtain user inputs on (1) the type of building and the percent of building painted, (2) the building volume and airflow rates, and (3) the painted surface area, amount of paint used, and painting duration.

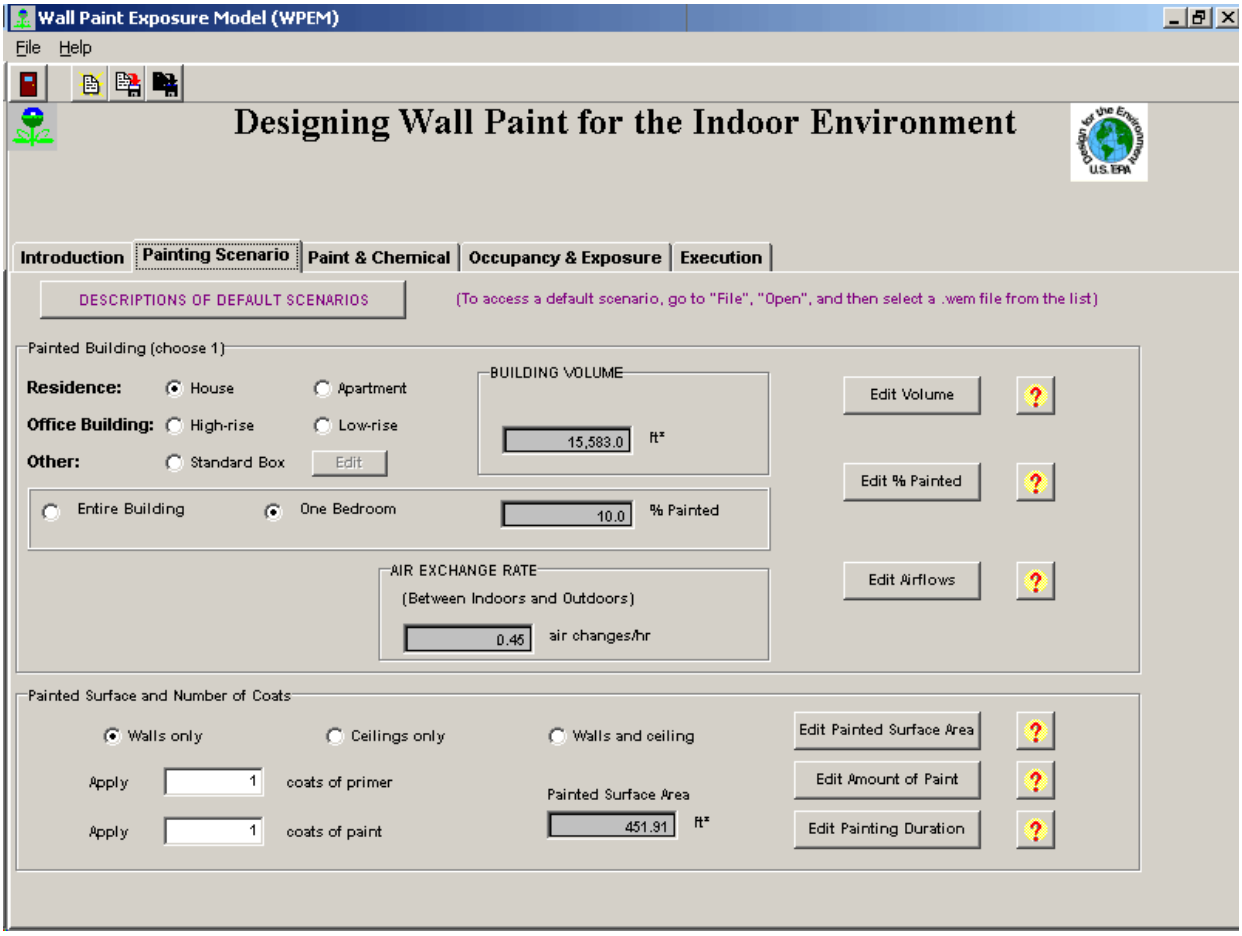

Figure 2-1. Painting Scenario Screen.

Required and optional user inputs for this screen are summarized in Table 2-1. As noted in Section 1, required inputs are indicated in **white** whereas optional inputs are indicated in **gray**. Although defaults are provided for the required inputs, these may not be appropriate for the scenario that the user wishes to model. For the optional inputs, the model always provides or calculates values, but the user is free to override these values through edit buttons that typically are located to the right of corresponding input areas.

Table 2-1. Required and Optional Inputs for Painting Scenario Screen

	Required Inputs	**Optional Inputs**
Building Type/Volume	Choose residence (house or apartment), office building (high-rise or low-rise), or standard box	Edit building volume
Painted Space	Choose entire building/floor or part of building/floor	Edit percent painted
Airflow Rates	--	Edit air exchange rate and interzonal airflow rate
Painted Surface	Choose walls, ceilings, or both	Edit wall/ceiling loading ratio
Amount of Paint	Specify number of coats for primer and paint	Edit primer/paint coverage
Painting Duration	--	Edit number of painters, primer/paint application rate, daily work hours, and start day

2.1.1 Input Sequence and Options

A button near the top of the Painting Scenario screen, labeled DEFAULT SCENARIOS, lists default scenarios that can be accessed by the user. Descriptions of these scenarios and how to access them are provided in Section 4 of this guide.

If a default scenario is not chosen, then the **first step** on this screen is to **select the type of building to be painted**. For a residence, the user can select a house or apartment. For an office building, the user can select a high-rise or low-rise. The first available selection (residence/house) is checked by default when the user enters the model. The model displays the default volume for the selected building to the right. This value cannot be changed where it is displayed in gray color; rather, the user must press the Edit Volume button to change the value. The revised value then will be displayed in the gray area. Within the Edit Volume dialog box, the volume can be edited in cubic feet or in cubic meters (the model automatically converts from one unit to the other), but the volume value displayed on the main screen is in cubic feet.

Another option for the type of painted building is a "standard box." This choice allows the user to customize the scenario by supplying dimensions (length, width, and height) for the building to be painted. When a standard box is selected, the building volume cannot be changed with the Edit Volume button, but rather by editing the building dimensions.

The **second step** is to **choose the building space to be painted**. If residence/house is selected, for example, then the choices are entire building (100 percent) or one bedroom (10 percent). Similar choices are provided for office building, (e.g., entire building or floor) and standard box (entire building or part of building). The choice results in a model default value for percent painted, which is displayed to the right in gray color. This value can be changed using the Edit % Painted button (unless entire building is selected for residence or standard box).

The **third step** (optional) is to **specify an air exchange rate and interzonal airflow rate** for the selected building. The model provides default values keyed to the building types, and the default air exchange rate is displayed in gray color. The user can change this default value, as well as the default value for the interzonal airflow rate, through the Edit Airflows button. There is one cautionary note here – changing the air exchange rate will cause the model to automatically use a preset algorithm for the interzonal airflow rate; thus, if the user wishes to customize both the air exchange rate and the interzonal airflow rate, then the air exchange rate should be changed first.

The **fourth step** is to **choose the painted surface** -- walls, ceilings, or both. The choice leads to a model default value for the loading ratio (i.e., the ratio of surface area to volume). This value is not displayed on the main screen, but can be changed using the Edit Painted Surface Area button. The model uses the loading ratio to calculate the painted surface area, and displays this value in gray color near the bottom-right portion of the main screen. The loading ratio can be edited either in ft^2/ft^3 or in m^2/m^3 (the model automatically converts from one unit to the other).

The **fifth step** is to **choose the number of coats to be applied for primer and/or paint** (one coat for each is shown by default). The user can elect to do painting only, for example, by entering zero coats for primer. Further details relating to the amount of primer/paint used are provided through the Edit Amount of Paint button, where the coverage (ft^2 or m^2 per gallon) and associated wet film thickness (mil, or 1/1000 inch) are displayed. For paint, the model provides a default coverage of 400 ft^2 per gallon (37.2 m^2/gallon or 4.01 mil film thickness); the default coverage for primer is half that of paint. These default values can be edited using any of the units provided; the model calculates and displays the resultant amount of paint used (in gallons) within the dialog box. The amount of paint is not displayed on the main screen.

The **final step** for this screen is to **determine the duration of the painting event**, using the Edit Painting Duration button (see Figure 2-2). Within the associated dialog box, the user can choose a default application rate for a do-it-yourself (DIY) or a professional painter and can edit the number of painters as well as the primer/paint application rates (gallons per hour) and the maximum priming/painting duration per day (hours). The maximum input value for priming or

painting hours per day is 12. Within the dialog box, the model calculates and displays the total duration for priming and painting.

By default, painting starts immediately after priming is finished, but the user can change this default by entering a value in the input area for hours between priming and painting. Optionally, the user can specify that priming starts the next day, or the second day, after painting is finished. The model assumes that each day of painting starts at 9:00 a.m., and the user cannot change that time. The user can select the day of the week when painting starts. The start day can have some effect on the estimated exposure, through interaction with weekday/weekend activity patterns (see Occupancy and Exposure Screen, Section 2.3). The model calculates and displays the total number of days for priming and painting.

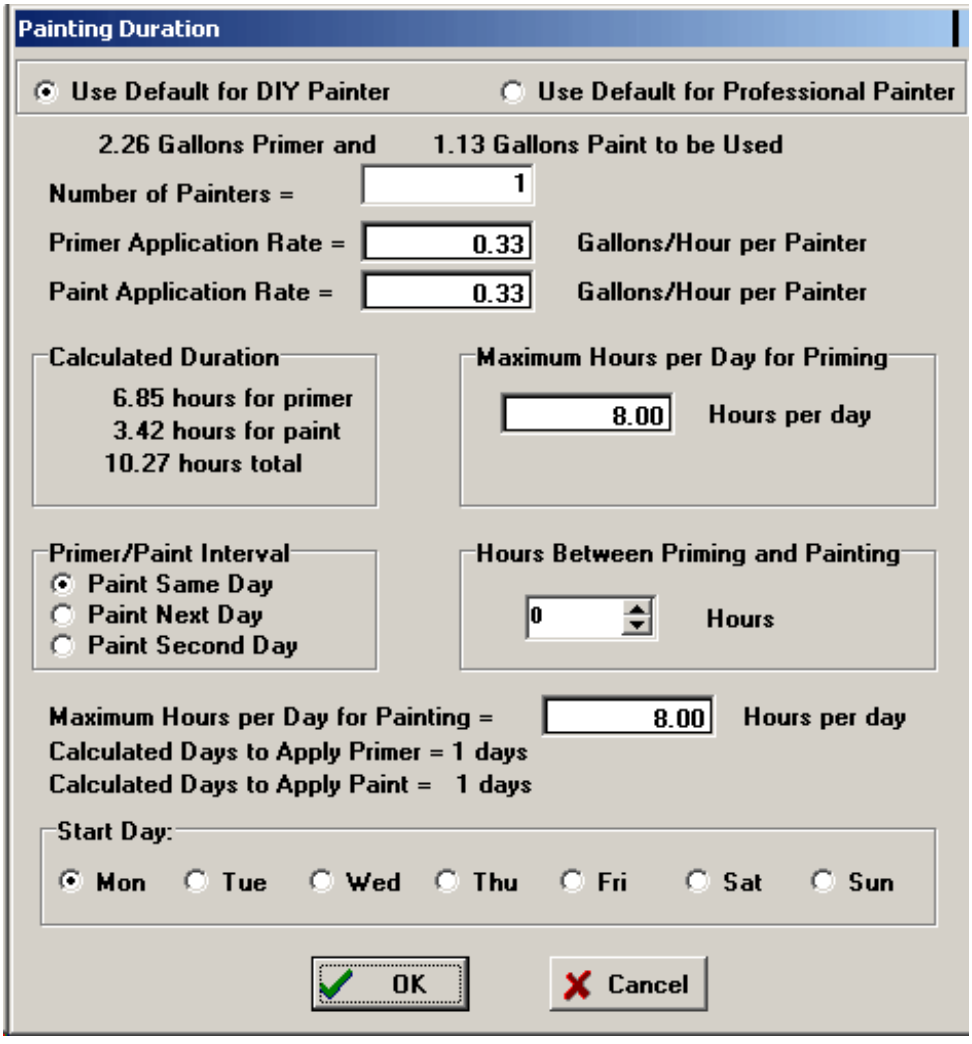

Figure 2-2. Dialog Box for Edit Painting Duration.

2.1.2 Basis for Default Values

The basis for default values assigned on the Painting Scenario screen is summarized in Table 2-2. Some of the values, such as painting hours per day and start day for painting, are arbitrary selections intended to serve simply as "place holders" that the user can change. Several of the values come from the *Exposure Factors Handbook* (USEPA 1997), Volume III, Chapter 17 (Residence Characteristics). These include the default house volume (15,583 ft^3 or 441.3 m^3) and apartment volume (7,350 ft^3 or 208.1m^3), as well as the default residential air exchange rate of 0.45 air changes per hour (ACH).

The default value for the interzonal airflow rate (IAR) for residences, in cubic meters per hour, is calculated by the model from the air exchange rate and house volume according to the following equation:

$$IAR = (0.046 + 0.39*A)*V \quad (2\text{-}1)$$

where A is the air exchange rate (inverse hours), and V is the building volume (cubic meters). The equation is an empirical relationship developed by Koontz and Rector (1995) from an analysis of residential volumes, air exchange rates and interzonal airflow rates. As described in the referenced document, the relationship was developed through regression analysis, using air exchange rates and interzonal airflow rates (between the bedroom and the remainder of the house) that were measured in various field studies for using perfluorocarbon tracers (PFTs).

Table 2-2. Basis for Default Values on Painting Scenario Screen

Variable	**Basis for Default**
Building Volume	*Exposure Factors Handbook* for residences Professional judgment for office buildings
Percent Building Painted	Arbitrary selection
Air Exchange Rate	*Exposure Factors Handbook* for residences Persily (1989) for office buildings
Interzonal Airflow Rate	Koontz and Rector (1995) for residences Professional judgment for office buildings
Wall/Ceiling Loading Ratios	*Exposure Factors Handbook* for residences Professional judgment for office buildings
Paint Coverage	Label on paint containers
Paint Application Rate	*Household Solvent Products: A National Usage Survey* (WESTAT 1987) for DIY painters *Estimating Guide, 19th Edition* (PDCA 1998) for professional painters
Painting Hours Per Day	Arbitrary selection
Start Day for Painting	Arbitrary selection

Because available data are relatively scarce for office buildings, professional judgment was used in developing certain defaults. For example, for the office-building interzonal airflow rate, it was assumed that air communication between the painted and unpainted spaces occurs only through the heating, ventilating, and air-conditioning (HVAC) system for the building. It was further assumed that the internal recirculation of air through the HVAC system is equivalent to one air change per hour; that is, a volume of air equivalent to the total building volume is circulated each hour. Given these assumptions, the interzonal airflow rate (IAR, in m^3/hour) can be calculated as follows:

IAR = building volume * % volume in painted area * % volume in unpainted area (2-2)

For example, if the building volume is 100,000 ft^3 and the painted area is 10 percent of that volume, then the interzonal airflow rate is 100,000 * 0.1 * 0.9, or 9,000 ft^3/hour.

In determining a default loading ratio for ceilings in office buildings, a ceiling height of 10 feet was assumed. Because the volume is the product of the floor area times the ceiling height, the loading ratio for the ceiling (ceiling area/building volume) can be stated as:

ceiling area / (ceiling area * 10 ft) = 0.10 ft^2/ft^3, or 0.33 m^2/m^3 (2-3)

By comparison, the default ceiling loading ratio for residences (from the *Exposure Factors Handbook*) is 0.13 ft^2/ft^3 (0.43 m^2/m^3).

To estimate a default loading ratio for walls in office buildings, a floor plan was laid out for a building with a ceiling height of 10 feet. This floor plan was split equally into two spaces, one with 10 ft by 10 ft offices and associated hallways, and one with several larger areas that would contain cubicles. The resultant loading ratio for walls was estimated to be 0.25 ft^2/ft^3 (0.82 m^2/m^3), as compared to the default value of 0.29 ft^2/ft^3 (0.95 $m^2/m^{3)}$ for residences.

For a standard box, the default air exchange rate, interzonal airflow rate, and loading ratios for walls and ceilings are the same as those for office buildings.

The default value for DIY paint application rate derives from an EPA-sponsored national usage survey of household solvent products. From that survey, the median amount of latex paint used is one gallon and the median duration of use is three hours, corresponding to an application rate of 0.33 gallons/hour. The default application rate for a professional painter derives from an estimating guide developed by the Painting and Decorating Contractors of America (PDCA). According to the guide, the labor production rate for painting is 337.5 ft^2/hour (range of 325 to 350 ft^2/hour) for roller application. Given a paint coverage of 400 ft^2/gallon, the labor production rate equates to an application rate of 0.85 gallons/hour.

2.2 Paint & Chemical Screen

This screen (Figure 2-3) is designed to obtain user inputs on (1) the type of paint used and the primer/paint density, (2) properties of the chemical under assessment, (3) the weight fraction of the chemical in primer and paint, (4) parameters of an emissions model for primer and paint, and (5) parameters for a sink model (or assumption of no indoor sinks).

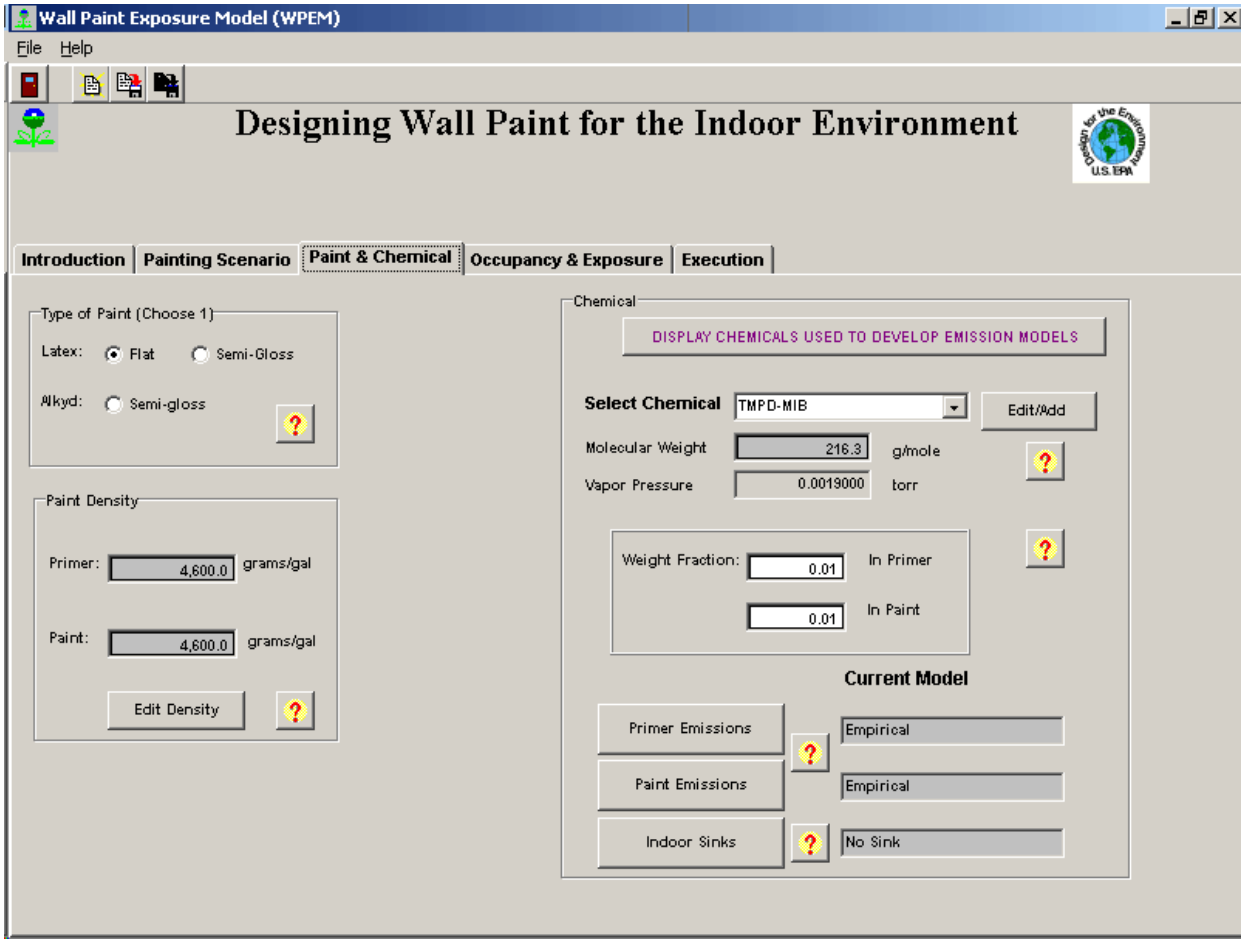

Figure 2-3. Paint & Chemical Screen.

Required and optional user inputs for this screen are summarized in Table 2-3. Unlike the previous (Painting Scenario) screen, for which numerous elements have both required and optional inputs, the inputs for this screen are either required or optional. In the case of weight fraction in primer and paint, default values are provided simply to serve as "place holders" to be edited by the user.

Table 2-3. Required and Optional Inputs for Paint & Chemical Screen

	Required Inputs	**Optional Inputs**
Type of Paint	Choose latex or alkyd	--
Paint Density	--	Edit paint density for primer and/or paint
Chemical Name	Select a chemical from the list, or add to the list	--
Chemical Properties	Use/edit molecular weight and vapor pressure from the list	--
Weight Fraction	Edit weight fraction of chemical in primer/paint	--
Primer/Paint Emissions Model	--	Override default model, edit default parameter estimates
Indoor Sink Model	--	Override default model (no indoor sinks), supply parameter estimates

2.2.1 Input Sequence and Options

The **first step** on this screen is to **select the type of paint** (latex or alkyd) to be applied. There are two choices (flat and semi-gloss) for type of latex paint. Default values for primer and paint density are assigned by the model for each type of paint. These values can be changed by the user using the Edit Density button. Within the Edit Density dialog box, the density can be edited in units of pounds/gallon, grams/gallon, or grams/cm^2; the software automatically makes conversions across the units, and displays the current values on the main screen in grams/gallon.

The **second step** is to **select a chemical**. A button labeled DISPLAY CHEMICALS USED TO DEVELOP EMISSION MODELS lists all chemicals that were measured in small-chamber emission tests under the DfE project, and further highlights the subset of chemicals on which empirical emission models (described below) were based. The range of molecular weights and vapor pressures covered by these chemicals also is described. Figure 2-4 shows the information provided through this button.

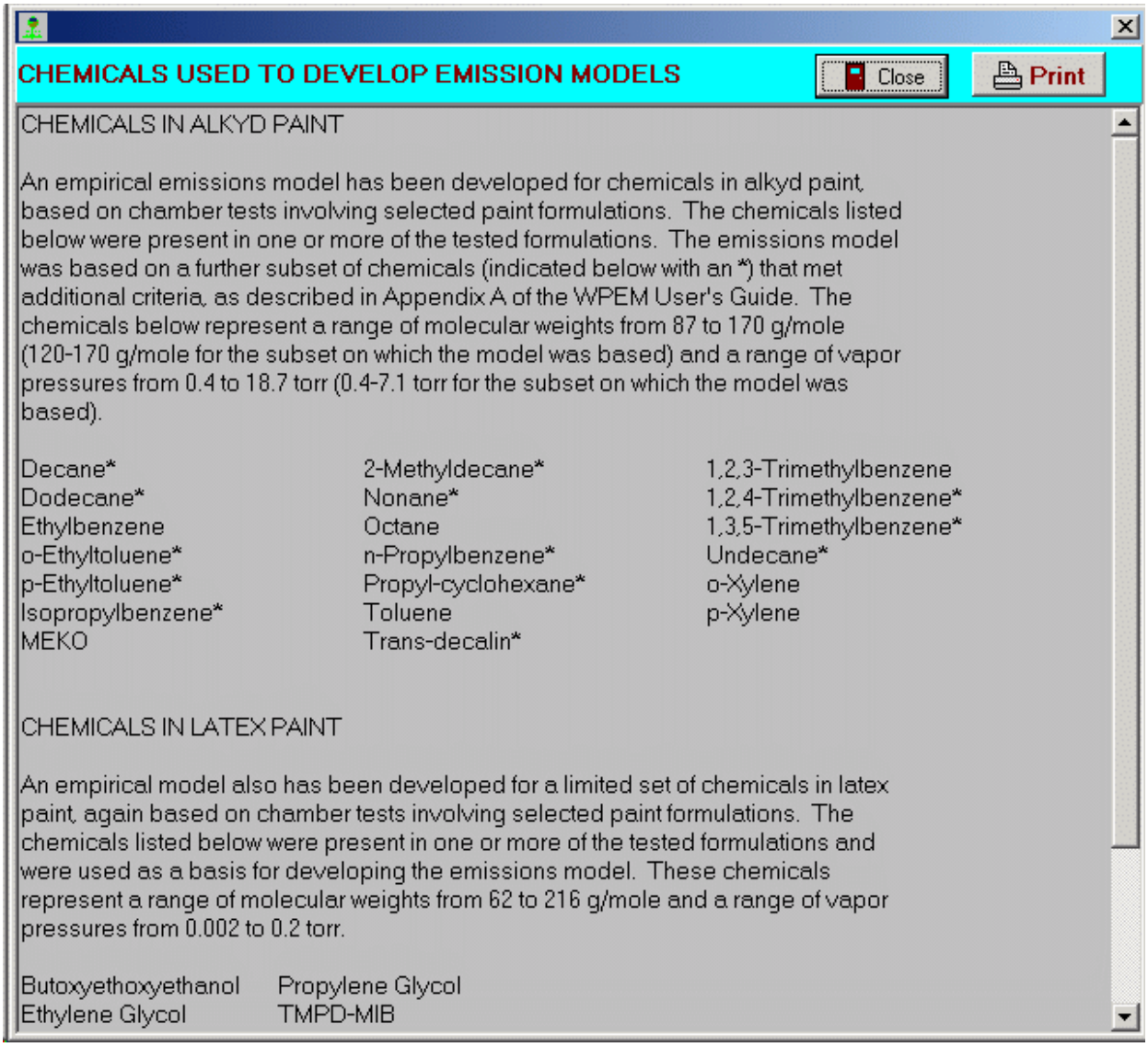

Figure 2-4. Information Shown for Display Chemicals Button.

A chemical can be selected from the drop-down list of the chemicals used in the DfE testing program. Once a chemical has been selected, its name, molecular weight, and vapor pressure are displayed on the main screen. Chemicals on the list can be edited (name and properties), or the user can add chemicals to the list, using the Edit/Add button. Within the dialog box (Figure 2-5), a chemical can be edited by clicking on its name and pressing the Edit button – the name, molecular weight**,** or vapor pressure can then be modified. Edits are not retained, however, until the Save button is pressed.

Similarly, within the dialog box a chemical can be added to the list by pressing add, entering the name and chemical properties, and then pressing Save. Pressing the OK button closes the dialog box. The lowest value allowed for vapor pressure is 0.0000001 torr; if a value below this limit is entered, then the program will issue a warning and reset the value to the minimum. The lowest value allowed for molecular weight is 0.01g/mole. The values for molecular weight and vapor pressure are used by the model in calculating certain default values pertaining to chemical emissions from primer and paint. However, the emission models developed for WPEM are based on a limited set of chemicals and an associated range of molecular weights and vapor pressures (see Figure 2-4). The models may not be valid for chemicals outside these ranges, unless the user has appropriate model inputs from chamber tests.

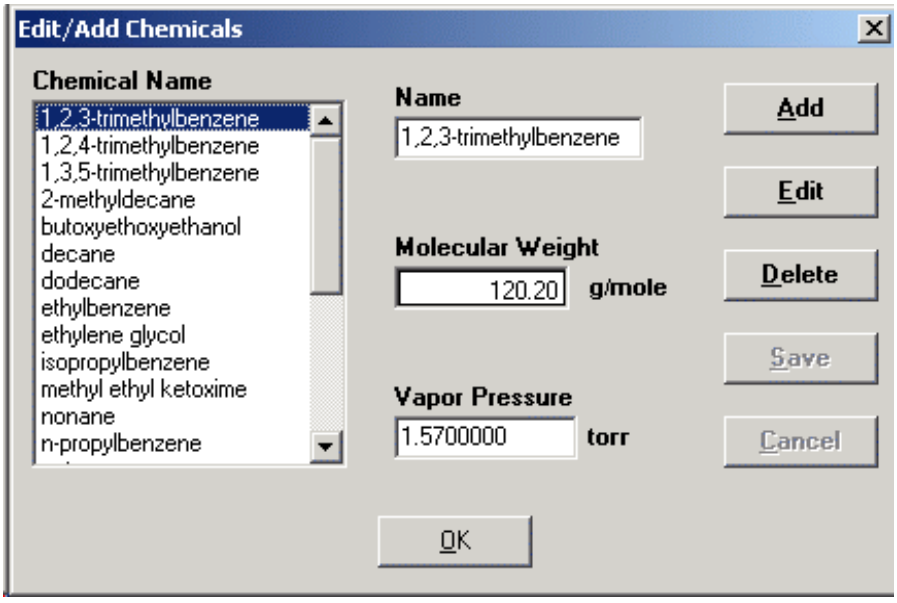

Figure 2-5. Dialog Box for Edit/Add Chemicals.

The **third step** on this screen is to **provide values for the weight fraction** of the chemical in primer and paint. A default weight fraction of 0.01 is provided simply as a "place holder" that the user should override based on knowledge of the primer/paint formulations to be modeled. The lowest value currently allowed is 0.000001; if a value below this limit is entered, then the software will issue a warning and reset the value to the minimum.

The **final entries** on this screen relate to **emission models** for primer and paint, and to **models for indoor sinks**. For alkyd primer or paint, there is a choice of two types of models – empirical model and semi-empirical model – through the Primer Emissions or Paint Emissions button. The algorithms and basis for these models are described in Appendices A and B for alkyd paint and in Appendices C and D for latex paint. In brief, the empirical single-exponential model for chemical emissions from alkyd paint, developed under this project, was derived from a nonlinear regression relating the first-order rate constant for emission decay to wet film thickness and the chemical's molecular weight and vapor pressure. A semi-empirical model developed under a separate project also has an algorithm for the emission decay rate, derived largely from first principles but still requiring use of the chamber testing results from this project to estimate one of its parameters. For chemical emissions from latex paint there is an empirical double-exponential model with one emission rate constant dependent on a chemical's vapor pressure and the other dependent on its molecular weight.

The input array for the empirical model is shown in Figure 2-6. The total mass is determined as the product of the applied primer/paint mass times the chemical weight fraction (for chemicals in latex paint, 25 percent of the applied chemical mass is assumed to be emitted; see Appendix C). For the single-exponential model for alkyd primer/paint, all mass is associated with the first exponential, whereas for the double-exponential model for latex primer/paint 10 percent of the mass is associated with the first exponential (90 percent with the second) by default. Default values for the rate constants are based on algorithms described generally above and in detail in the appendices.

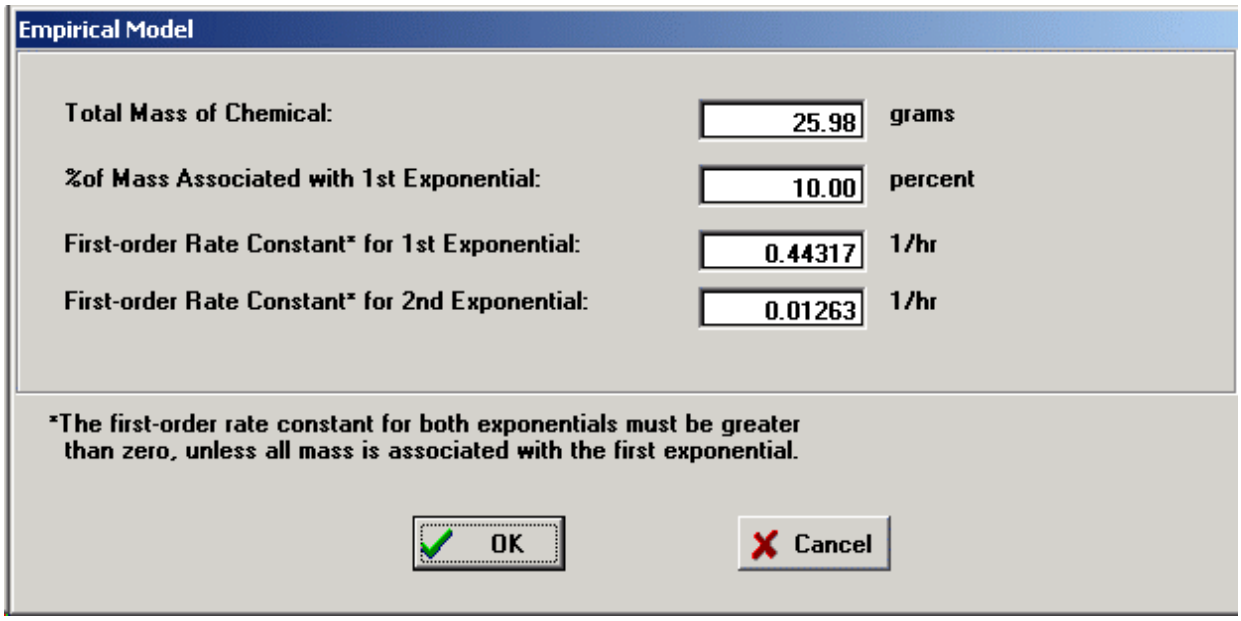

Figure 2-6. Dialog Box for Empirical Emissions Model.

Default values for all parameters needed for the empirical model are supplied by the WPEM software. It is recommended that the user retain these defaults unless there are chemical-specific data (e.g., from small-chamber emission tests) that suggest more appropriate values.

Two types of indoor-sink models -- one-way sink and reversible sink – are available through the Indoor Sinks button (the default is no indoor sinks). With a one-way sink, chemical mass in the indoor air can move into the sink but can never exit it, whereas for a reversible sink chemical mass can enter and leave the sink. The rate of mass entering the sink is governed in WPEM by an adsorption rate constant, and the rate of mass leaving the sink by a desorption rate constant. Thus, for the one-way sink model, inputs are required for the area and adsorption rate for each sink; for the reversible-sink model, inputs are required for a desorption rate as well. The one-way sink model can be viewed as a special case of the reversible-sink model whereby all desorption rates are zero.

The input array for the reversible-sink (Langmuir) model is illustrated in Figure 2-7. The WPEM software calculates areas for selected indoor sinks (carpeting and wallboard) but does not provide any default values for adsorption or desorption rate constants, because the basis for such values is limited at this time. In the absence of appropriate information on the rate constants, it is suggested that the user assume no indoor sinks. This approach will tend to produce conservative (higher) exposure estimates, at least in comparison to estimates from a one-way sink model. A reversible-sink model will tend to lower the peak concentration and to "stretch out" the period of chemical emissions (or re-emissions) indoors. Although the peak concentration will be lower, the time-integrated exposure could be higher in some cases than for the no-sink case. The difference will depend in part on how activity patterns intersect the indoor-air concentration profile over time. In the case of a professional painter who permanently leaves the building once it is painted, the reversible-sink model will lower the overall exposure because its net impact is to effectively delay the chemical emissions.

Table 2-4 list values for adsorption (K_a) and desorption (K_d) rates for selected chemicals and sink materials, based on small-chamber tests conducted under this project (see Appendix A, Section A5) or reported in the published literature. As noted by Tichenor et al. (1991), the ratio K_a/K_d is indicative of the sink strength, or the capability of a sink material to adsorb indoor air pollutants. For the work under this project (ARCADIS 1998), for example, of the four VOCs tested only MEKO had a notable sink strength. The rate constants summarized in the table indicate a considerable range of sink strengths for different chemical-material combinations. It is noteworthy, however, that the investigators used substantially different loading ratios in their respective tests, ranging from 0.4 to 5.0 m^2/m^3. By comparison, loading ratios in residential environments typically are close to 0.95 m^2/m^3 for wall materials such as gypsum board and 0.43 m^2/m^3 for floor/ceiling materials such as carpeting or ceiling tiles. Thus, considerable care must be taken in estimating an input value based on the previous experimental work. Chang et al. (1998) reported strong sink effects for four chemicals in latex paint; the authors indicated that the Langmuir model was adequate for the adsorption phase but failed to predict the relatively slow re-emission process (desorption phase), and suspected that physical/chemical properties of the oxygenated polar compounds that were tested may have significant effects on the sink behavior.

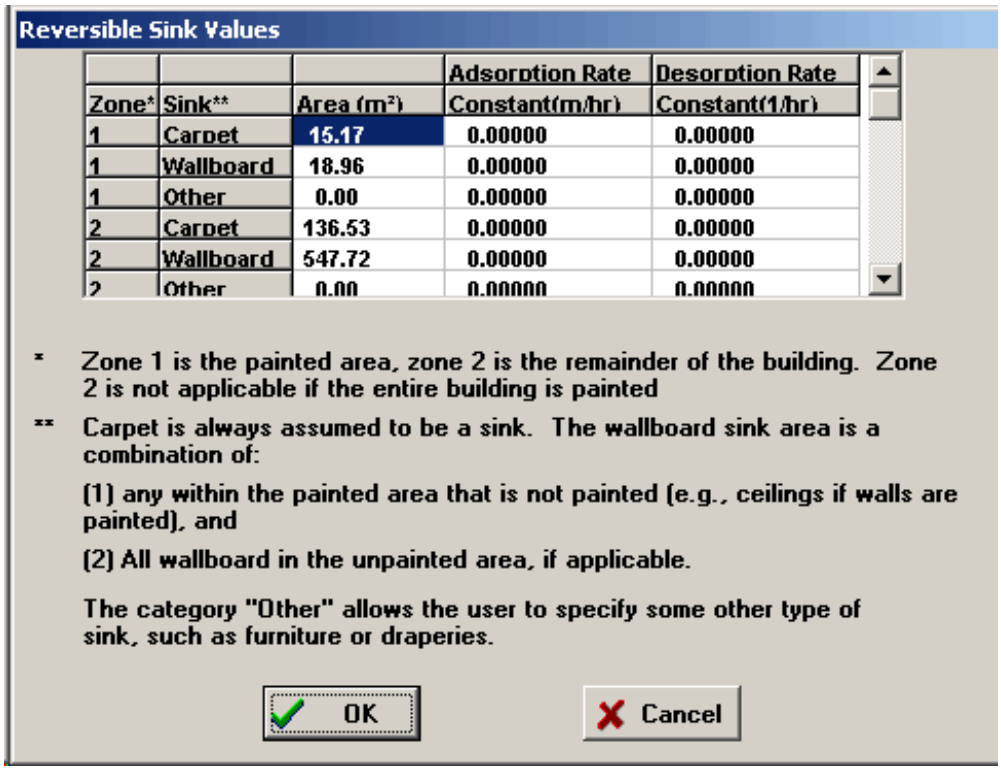

Figure 2-7. Dialog Box for Reversible-Sink Model.

2.2.2 Basis for Default Values

The basis for default values assigned on the Paint & Chemical screen is summarized in Table 2-5. Default values are limited to paint density and certain parameters for emission and sink models. Values for paint density (4,600 grams/gal for latex primer, latex paint and alkyd paint; 5,800 grams/gal for alkyd primer) are based on material safety data sheets accompanying all primer/paint formulations that have been studied (i.e., used in small-chamber tests) under the DfE project.

Default values for primer/paint emissions models are based on an analysis of data from small-chamber emission tests conducted under the DfE project. In brief, nonlinear regression analysis was used to fit a single-exponential emissions model for chemicals in alkyd paint (see Appendix A) and a double-exponential emissions model for latex paint (see Appendix C). The chemical-specific values for rate constants governing the exponential decline in emission rates have been analyzed in relation to molecular weight and vapor pressure, to develop a predictive equation for determination of default values. The fraction of applied chemical mass that one can expect to be emitted also has been analyzed for alkyd and latex paints.

Table 2-4. Parameter Estimates for Langmuir Sink Model from Four Chamber Studies

Chemical	Sink Material	K_a	K_d
Jorgensen et al. (1999) – volume = 0.05 m^3, loading ratio = 4.46 m^2/m^3, air exchange rate = 1.0 ACH, temperature = 23 °C, RH = 50 %			
Toluene	Wool carpet	0.73	1.03
	Nylon Carpet	0.25	0.41
	PVC floor covering	0.07	0.26
	Cotton curtain	0.02	0.31
á-pinene	Wool carpet	0.41	0.21
	Nylon Carpet	0.29	0.17
	PVC floor covering	0.05	0.06
	Cotton curtain	0.03	0.09
ARCADIS (1998) – volume = 0.053 m^3, loading ratio = 1.315 m^2/m^3, air exchange rate = 0.5 ACH, temperature = 23 °C, RH = 50 %			
MEKO	Carpet	0.25	0.04
	Gypsum board	1.10	0.03
1,2,4-trimethylbenzene	Carpet	0.10	6.00
	Gypsum board	0.25	0.25
2-methyldecane	Carpet	0.04	0.03
	Gypsum board	0.90	1.20
Undecane	Carpet	0.06	0.50
	Gypsum board	0.40	0.25
Kirchner et al. (1995) – volume = 1.0 m^3, loading ratio = 0.4 m^2/m^3, air exchange rate = 0.5 ACH, temperature = 23 °C, RH = 45 %			
2-butoxyethanol	Carpet (6 mm thick)	0.49	0.41
	Carpet (10 mm thick)	0.56	0.77
	PVC wall covering	0.50	0.22
	Gypsum board	1.08	0.36
	Acoustic tile	1.32	0.56
Tichenor et al. (1991) – volume = 0.053 m^3, loading ratio=2.64 m^2/m^3 (5.02 m^2/m^3 for pillow), air exchange rate = 1.0 ACH, temperature = 23 °C, RH = 45 %			
Tetrachloroethylene	Carpet	0.13	0.13
	Gypsum board	0.21	1.50
	Ceiling tile	0.10	0.61
	Pillow	0.03	0.10
Ethylbenzene	Carpet	0.08	0.08
	Gypsum board	0.45	1.50
	Ceiling tile	0.24	0.59
	Pillow	0.004	0.016

Table 2-5. Basis for Default Values on Paint & Chemical Screen

Variable	**Basis for Default**
Paint Density	Material safety data sheets for paint formulations studied under the DfE project
Primer/Paint Emissions Model	Fit of empirical (exponential decay of emissions) models to small-chamber concentration data for latex and alkyd paint, relationship of rate constants for emissions decay to vapor pressure and molecular weight (both types of paint) and to wet film thickness of applied product (alkyd paint only) Development of semi-empirical model (alkyd paint only) relating rate constant for exponential emissions decay to paint formulation and wet film thickness of applied product
Indoor Sinks Model	Areas of potential one-way or reversible sinks (carpeting,. wallboard) estimated from floor/wall loading ratios, per *Exposure Factors Handbook* (user must supply values for assumed adsorption/desorption rate constants)

As noted above, currently there are no default values available in the model for adsorption/desorption rate constants for indoor sinks. Default values are provided for the areas of two types of potential sinks – carpeting and wallboard – based on the default wall/ceiling loading ratios provided in WPEM. For carpeting, it is assumed that the floor loading ratio is the same as the ceiling loading ratio, and that 80 percent of the floor area is covered by carpeting. It is assumed that wallboard is present on both walls and ceilings in residences, and on walls only in office buildings or a standard box. In the portion of the building that is not painted, it is assumed that all wallboard will act as a sink. In the portion of the building that is painted, only the unpainted wallboard is assumed to act as a sink. Thus, for example, if walls are painted in a residence, then within the painted portion of the building the sink area is computed as the volume of that space times the ceiling loading ratio.

2.3 Occupancy & Exposure Screen

This screen (Figure 2-8) is designed to obtain user inputs on (1) the type of exposed individual and his/her location during the painting event, (2) weekday/weekend activity patterns (locations and associated breathing rates) for the exposed individual, and (3) parameters needed to develop lifetime exposure measures, such as lifetime average daily dose (LADD).

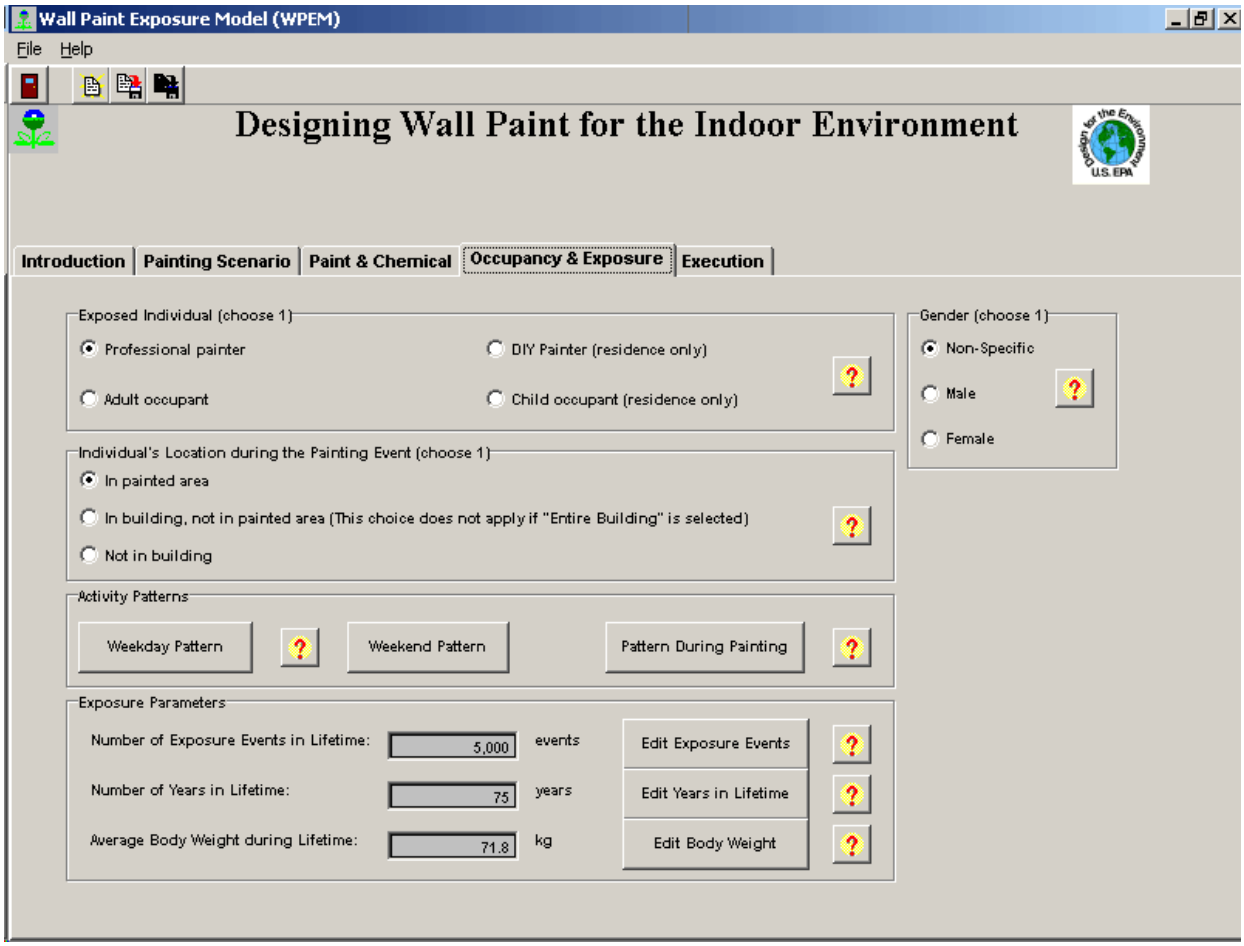

Figure 2-8. Occupancy & Exposure Screen.

Required and optional user inputs for this screen are summarized in Table 2-6. Most of the inputs are optional, as the model provides many default choices or values here. The only choice required of the user is the type of exposed individual (professional painter by default). Once the exposed individual is selected, the model provides a default location during the painting event, which the user can override. Similarly, default values are provided for activity patterns, number of exposure events, years in lifetime, and body weight.

Table 2-6. Required and Optional Inputs for Occupancy & Exposure Screen

	Required Inputs	**Optional Inputs**
Exposed Individual	Choose a type of exposed individual	--
Gender	--	Override default choice (non-specific gender)
Location during the Paint Event	Choose a location (default value is linked to type of exposed individual)	--
Activity Patterns	--	Override default values for time, location, or breathing rate for weekday/weekend patterns (breathing rate only for pattern during painting)
Number of Exposure Events in Lifetime	--	Override default values for events per year and years of exposure
Number of Years in Lifetime	--	Override default value
Body Weight	--	Override default value

2.3.1 Input Sequence and Options

The **first step** on this screen is to **select the type of exposed individual**. Different default activity patterns and lifetime exposure events or years of life are provided in the model for each of four types of exposed individuals – professional painter, do-it-yourself (DIY) painter, adult occupant, and child occupant. Two of these choices – DIY painter and child occupant – are not valid if the user has specified on the Painting Scenario screen that an office building or standard box is being painted.

The **second step** is to **choose the gender** of the exposed individual. The choice of gender (non-specific is the default) affects the default values supplied by WPEM for breathing rate, years in lifetime, and body weight.

The **third step** is to **choose the individual's location during the painting event**, for which the model always provides a default that is tied to the type of exposed individual. For example, by default an adult or child occupant is assumed to be in the building, but not in the painted area, during the painting event. The model will issue a warning if a professional or DIY painter is not placed in the painted area, but will allow the user to make that choice.

The **fourth step** (optional) is to **edit the weekday/weekend activity patterns, or activity patterns during the painting event**, that already are provided by the model. The weekday and weekend patterns (see Figure 2-9 for an example) have been developed to match the typical amounts of daily time spent at home (in bedrooms and in the remainder of the house), at work, and outdoors by the different types of individuals listed above, as reported in the *Exposure Factors Handbook*. The defaults should suffice for most applications.

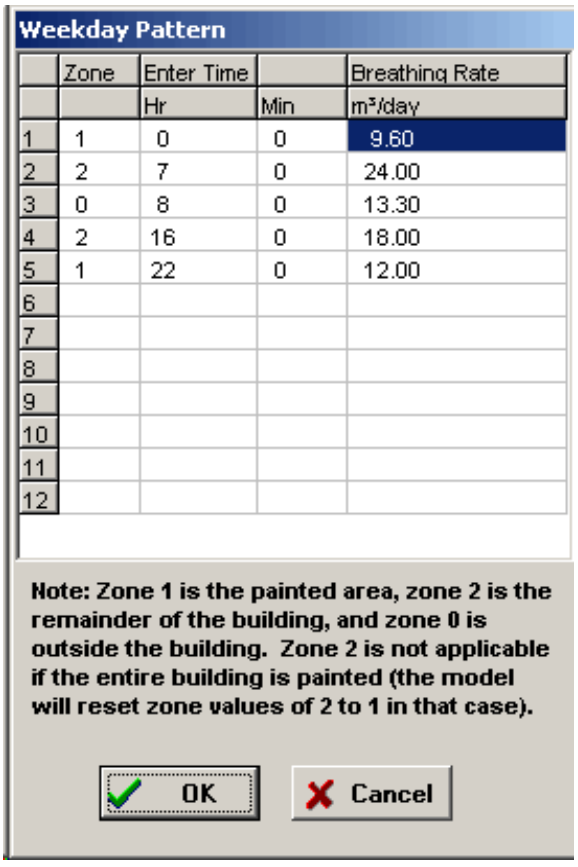

Figure 2-9. Example Default Weekday Activity Pattern.

Items that can be edited for weekday/weekend patterns are the time of day when each environment is entered (enter time), location (zone) at that time, and breathing rate. The enter time is input in separate cells for hour of the day (Hr) and minute with the hour (Min). The entry for hour must be between 0 (midnight, or beginning of the day) and 23 (11 p.m.), and the entry for minute must be between 0 and 59. The first enter time must be 0 Hr, 0 Min, and the user cannot edit that value. Another constraint is that the enter time for any given line must be later than the time for the line that precedes it. Exit times do not need to be entered, as the enter time for the current line equates to the exit time for the previous line. The final entry is in effect until the end of the 24-hour day. For the example in Figure 2-9, the individual enters zone 1 (the painted potion of the building) at midnight, enters zone 2 (the unpainted portion) at 7 a.m., leaves the building (zone 0) at 8 a.m., returns to the building (zone 2) at 4 p.m. (hour 16), and enters zone 1 at 10 p.m. (hour 22).

For the pattern during painting (Figure 2-10), only the breathing rate can be edited; all other inputs are determined by the model based on the user's description of the priming/painting event on the Painting Scenario screen. This restriction prevents the user from entering a pattern that is inconsistent with the previously described painting event. Following the painting event, the individual is placed in the location (zone) indicated by the weekday or weekend activity pattern (whichever applies) at the time when painting is finished.

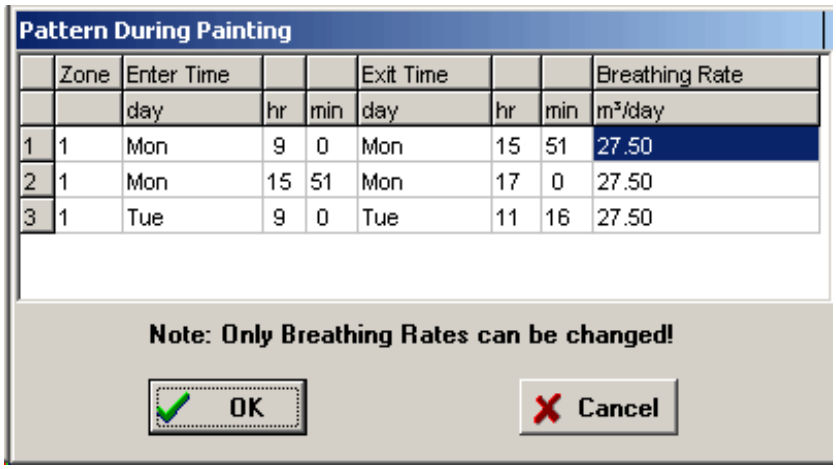

Figure 2-10. Example Activity Pattern During Painting Determined by WPEM.

The **final step** (also optional) is to **edit the exposure parameters** – number of exposure events in lifetime, number of years in lifetime, and body weight – through their associated edit buttons. A change to the default number of lifetime exposure events is accomplished by supplying two values – exposure events per year and years of exposure. The default value for lifetime exposure events is keyed to the type of exposed individual and to the type of building and percent painted, from the Painting Scenario screen. For example, for a DIY painter, if the entire residence is painted then one exposure event every 10 years is assumed by default. By comparison, if only a bedroom is painted then one event per year is assumed. Further details on rules used by WPEM to calculate the default value for lifetime exposure events are provided in Section 2.3.2.

2.3.2 Basis for Default Values

The basis for default values assigned on the Occupancy & Exposure screen is summarized in Table 2-7. Many of the defaults for this screen are based on data contained in the *Exposure Factors Handbook*. In selected cases, such as the location or breathing rate during the painting event, professional judgment has been exercised in developing the defaults.

Table 2-7. Basis for Default Values on Occupancy & Exposure Screen

Variable	**Basis for Default**
Exposed Individual	Arbitrary selection
Location during Painting Event	Professional Judgment
Weekday/Weekend Activity Patterns	National Human Activity Pattern Survey, as reported in the *Exposure Factors Handbook*
Pattern during Painting	Professional judgment *Exposure Factors Handbook*
Number of Exposure Events per Lifetime	Professional judgment *Household Solvent Products: A National Usage Survey* (WESTAT 1987)
Number of Years in Lifetime	Professional judgment for professional painters, children *Exposure Factors Handbook* for DIY painters, adults
Body Weight	*Exposure Factors Handbook*

Default weekday/weekend activity patterns for residence provided with WPEM assume that zone 1 (the painted portion) is a bedroom area and zone 2 is the remainder of the residence (if the entire building is painted, the model collapses zones 1 and 2 to a single zone). The collective times spent by adult/child occupants in zone 1, zone 2, and zone 0 (outside or away from the residence) over a 24-hour period are summarized in Table 2-8 for the default activity patterns.

Table 2-8. Hours Spent in Different Residential Zones, per Default Activity Patterns in WPEM

Zone	Weekday		Weekend	
	Adult	**Child**	**Adult**	**Child**
1 (painted area)	9	11	9.5	11
2 (remainder)	7	7	8	7
0 (outside/away)	8	6	6.5	6

The default breathing rates for these patterns correspond to values for resting, sedentary, or light activities, as given in the *Exposure Factors Handbook* (gender-specific rates for adults were estimated using the method described in the handbook; insufficient data were provided to permit estimation of gender-specific rates for children). Default breathing rates associated with different activity levels are summarized for adults and children in Table 2-9. For the first line of the activity pattern (bedroom, asleep), the rate for resting was assigned. For the second line, a rate corresponding to light activities was assigned. For the third line (away from the residence), a daily-average rate was assigned; this value has no impact on the estimated inhalation exposure, which is zero during times when the individual is outside the residence. For the fourth line, a rate corresponding to the average for sedentary/light activities was assigned. For the fifth line, a rate corresponding to sedentary activities was assigned. For the breathing rate during painting, for a professional or DIY painter the rate was estimated as a combination of light (75 %) and moderate (25 %) activity. For an adult or child occupant (not involved in the painting), the rate during painting was estimated as a combination of sedentary (50 %) and light (50 %) activity.

Table 2-9. Default Breathing Rates for Different Activities, per *Exposure Factors Handbook*

Activity Level	Adult (average)	Adult Male	Adult Female	Child
Resting	9.6	9.6	7.2	7.2
Sedentary	12.0	14.4	12.0	9.6
Light	24.0	26.4	21.6	24.0
Moderate	38.4	43.2	38.4	28.8
Heavy	76.8	86.4	72.0	45.6
Daily average	13.3	15.2	11.3	10.0

The number of lifetime exposure events is calculated by WPEM as the product of number of exposure events per year times the number of years of exposure. The default values for years of exposure, based on professional judgment, are 25 years for a professional painter, 50 years for a DIY painter or an adult occupant, and 10 years for a child occupant. The following rules or algorithms have been developed for exposure events per year, to result in default numbers of lifetime exposure events that are reasonable:

- If a residence is painted and the exposed individual is a DIY painter, then the default number of exposure events per year is equal to 7.5 divided by the percent of building painted (e.g., if percent painted = 10, then events/year = 0.75; if percent painted = 20, then events/year = 0.375). An EPA-sponsored national survey (WESTAT 1987) indicates a median time-since-last-painting of 8 months. Assuming that respondents, on the average, were queried at the halfway point between successive painting events, the median duration between painting events would be 16 months, equating to 0.75 events per year. The median amount of paint per event from that survey would be sufficient to cover about 10 percent of the wall area of a house.

- If a residence is painted and the exposed individual is an adult or child occupant, then the default number of exposure events per year is equal to 10 divided by the percent of building painted (e.g., if percent painted = 10, then events/year =1.0; if percent painted = 20, then events/year = 0.5). This approach is equivalent to the assumption that, when occupants hire professional painters, the entire residence typically is painted in full once every 10 years.

- If an office or a standard box is painted and the exposed individual is an adult occupant, then the number of exposure events per year is equal to 0.2, regardless of the percent painted. This approach is equivalent to the assumption that the office building is painted once every five years.

- Regardless of type of building painted, if the exposed individual is a professional painter then the number of exposure events per year is equal to 1500 divided by the total priming/painting duration (in hours), as determined on the Painting Scenario screen. With this approach, the painter spends 1500 hours per year painting (e.g., 50 weeks per year times 30 hours per week).

Gender-specific defaults taken from the *Exposure Factors Handbook* are provided for years in lifetime. The default values for adults are 79 years for female, 72 years for male, and 75 years for non-specific. For children the default is 10 years, regardless of gender. The default for a child does not correspond to length of lifetime per se, but rather to length of time as a child.

Gender-specific defaults taken from the *Exposure Factors Handbook* also are provided for body weight. The default values for adults are 65.4 kg for female, 78.1 kg for male, and 71.8 kg for non-specific. For children the default is 20.3 kg, regardless of gender. The body weight can be edited in pounds or kg; the model automatically converts from one unit to the other, and displays the edited value in kg on the main screen.

2.4 Execution Screen

This screen (Figure 2-11) is designed primarily for executing the model and reviewing results of that execution. It also provides the user with selected options related to documenting the run and choosing a length of model run and reporting interval.

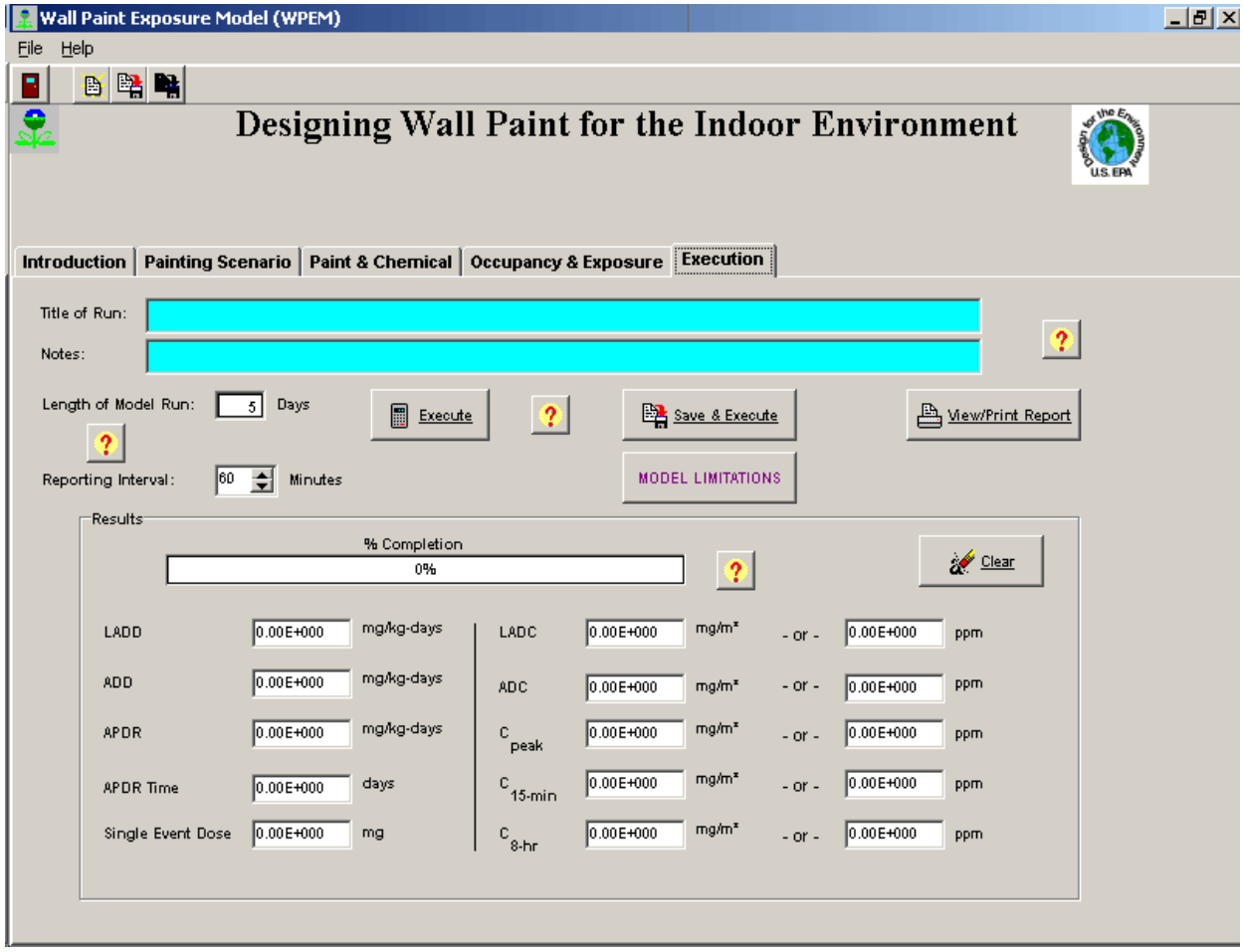

Figure 2-11. Execution Screen (Results before Execution).

2.4.1 Input Sequence and Options

The **first step** on this screen is to provide optional entries for **Title of Run and Notes**. These entries enable the user to provide a general description of the run that is being made, along with some useful reminders such as input choices for one or more key parameters. If it is likely that the full set of inputs for the run may need to be reviewed or perhaps updated at some future point in time, then it is strongly recommended that the user save the inputs (see below).

The **second step** is to provide inputs for **length of model run and reporting interval**. Although the model provides a default value of 5 days for length of model run, this default is intended only as a "place holder," to be edited by the user. The following are some useful tips for determining the length of model run:

- It takes a longer time for emissions from latex paint to decay than for emissions from alkyd paint. The emissions from alkyd paint typically are "gone" within 24 hours after painting is completed, unless a reversible-sink model is being used.

- A reversible-sink model for either latex or alkyd paint will tend to extend the time duration during which chemical emissions (or re-emissions from the sink) are present.

- A professional painter leaves the building once it is painted and does not return. Thus, when a professional painter has been selected as the exposed individual, the length of model run can be set equal to the total number of primer/painting days (or the total number of days plus one), as determined on the Painting Scenario screen.

- A model run that is too short can result in underestimaton of outputs such as single event dose or lifetime average daily dose. To ensure that a model run is sufficiently long, initially select a number of days that is somewhat greater than the total number of priming/painting days, and note the resultant value for single event dose. Next, select a length of model run that is a few days greater than the number previously selected, rerun the model, and compare the value for single-event dose with the previous result. When the dose value is no longer changing, or is changing by a very small amount, the model run is sufficiently long.

The choice of reporting interval has no impact on the results displayed on this screen, as the model uses an internal time step of 30 seconds for calculations in all cases. The reporting

interval does, however, affect the level of detail in a file generated by the model (see Section 3) that contains the time series of concentrations for each zone in the residence and for the concentration to which the individual is exposed. The file can be easily imported into Excel, for example, and plotted using the chart wizard. If the user wishes to examine this file and also wishes to see greater time resolution than for the default reporting interval of 60 minutes, then a shorter interval such as 15 minutes or 5 minutes (as short as one minute) can be selected. A shorter interval will result in greater time-related detail with a corresponding increase in the size of the file.

The **third step** is to **execute the model**. The user has the option of just executing the model (Execute button) or first saving the inputs and then executing (Save & Execute button). The latter option is recommended as a general practice. Once inputs has been developed, documented and saved for a given run, they can readily be edited, for example, to make certain perturbations for examining various "what if" scenarios. Saving can be accomplished without executing through a Save button on the toolbar near the top of the screen. Standard Windows options such as "Save" and "Save As" are available under File at the upper left of the screen. When a file is saved, WPEM always prompt for a name (with the current name displayed) so that existing files are not inadvertently overwritten.

Once the user has pressed Execute or Save & Execute, the Execute button changes to a Stop button that can be used to abort the run. Such an action will save significant time only in the event that the user has selected a relatively long length of model run (e.g., 15-20 days or greater).

Before executing the model, it may be useful to perform a quick review of inputs by pressing the View/Print Report button. As described in Section 3, the report both summarizes model inputs and presents model results. A button below the Save & Execute button, with a title of MODEL LIMITATIONS, lists the limitations that were previously indicated in Section 1.3 of this guide. Following execution, the model results can be reset to zero if desired using the Clear button to the right of the % completion bar in the lower half of the screen.

2.4.2 Modeling Approach and Calculations

Indoor-air concentrations in one or two zones are predicted in WPEM by implementing a deterministic, mass-balance equation. The modeled concentration in each zone is a function of the time-varying emission rate in one or more zone, the zone volumes, the airflow rates among zones and between each zone and outdoors, losses to indoor sinks, and (if a reversible sink model is used) re-emissions from indoor sinks.

Consumer products such as paints that are applied to surfaces are best represented by an incremental source model. This model assumes a constant application rate over time, coupled with an emission rate for each instantaneously applied segment that declines exponentially. The mathematical expression for the total emission rate resulting from the combination of constant application rate and exponential emission rate for each applied segment has been developed by Evans (1994).

The model requires the conservation of pollutant mass as well as the conservation of air mass. WPEM uses a set of differential equations whereby the time-varying concentration in each zone is a function of the rate of pollutant loss and gain for that zone. These relationships can be expressed as follows:

Pollutant Mass Balance

(Change in Pollutant Mass) / (Change in Time) = Production ± Transport - Removal ± Reactions

Neglecting reactions:

$$(d\ Mass) / (dt) = \sum Sources + \sum Mass\ in - \sum Mass\ out \pm \sum Sinks \qquad (2\text{-}4)$$

Or:

$$(Vi\ dCi) / (dt) = \sum Sources + \sum Cj*Qji - \sum Ci*Qij \pm \sum Sinks \qquad (2\text{-}5)$$

where C refers to an air concentration, Q refers to a flow rate, i and j refer to zones (there are up to two indoor zones plus outdoors), and the ± for sinks accounts for the possibility that they may be reversible.

Air Mass Balance

Flows into a zone = Flows out of a zone

Or:

$$\sum Qji = \sum Qij \qquad (2\text{-}6)$$

where Q, i and j are defined as above. The flow rates are input as constants. The pollutant mass balance is used in conjunction with the flow rates to predict the time-varying pollutant concentration in each indoor zone.

The differential equations can be solved by a variety of numerical solution techniques. The fourth-order Runge-Kutta method (also referred to as the Kutta-Simpson formula) is used for temporal integration (Matthews, 1992). Although this method is not as computationally efficient as some others, it is very stable, self-starting, and accurate. The formula takes the following form:

$$C(t + \Delta t) = C(t) + 1/6\,[K1 + 2*K2 + 2*K3 + K4] \qquad (2\text{-}7)$$

where: K1 = dC/dt * (delta t), evaluated at time = t, C = C (t)
K2 = dC/dt * (delta t), evaluated at time = t + (delta t)/2, C = C (t) + K1/2
K3 = dC/dt * (delta t), evaluated at time = t + (delta t)/2, C = C (t) + K2/2
K4 = dC/dt * (delta t), evaluated at time = t + (delta t), C = C (t) + K3.

The Runge-Kutta technique has been evaluated for stability over a wide range of values for time step, zone volumes, and flow rates.

Model calculations relating specifically to outputs (e.g., exposure measures) are described in Section 3.

2.5 Summary of Model Inputs

Table 2-10 provides a summary of model inputs by screen, with a distinction between inputs for which the user should make a deliberate decision (indicated by an asterisk) versus those for which model defaults may suffice. The summary for each screen follows the general flow of inputs for that screen. One choice that is not linked to a particular screen, but should be made at the outset, is whether to open a file containing inputs for a default scenario. The available default scenarios are described in Section 4. Even when a default scenario is chosen, the user should review the inputs with an asterisk in the table below, as certain edits or changes still may be warranted (e.g., selection of a chemical and entry of its weight fraction in primer and paint).

Table 2-10. Summary of Model Inputs

Screen	**Inputs**
General	*Open a file containing inputs for a default scenario
Painting Scenario	*Choose type of building and portion painted Edit building volume Edit % painted Edit air exchange rate and/or interzonal airflow rate *Choose to paint walls, ceilings, or both Edit loading ratio *Choose number of coats for primer/paint Edit type/number of painters, primer/paint application rates, maximum priming/painting hours per day, start day
Paint & Chemical	*Choose type of paint Edit primer/paint density *Choose/add/edit a chemical *Edit chemical weight fraction in primer/paint Choose/edit primer/paint emission models Choose/edit indoor sink model
Occupancy & Exposure	*Choose type of exposed individual *Choose gender for exposed individual Change default location during painting event for exposed individual Edit weekday/weekend patterns, pattern during painting Edit exposure events, years in lifetime, body weight
Execution	Enter title of run and notes *Choose length of model run and reporting interval View/print report before/after execution *Choose to execute or to save inputs and then execute

*Indicates inputs for which user should make a deliberate decision/choice; model defaults may suffice for other inputs.

3. MODEL RESULTS AND OUTPUTS

3.1 Exposure Estimates

An example of the exposure estimates provided by WPEM after executing the model is shown in Figure 3-1. The particular results shown here are obtained when all values in WPEM have been reset to defaults by selecting File at the top left of the screen, then New.

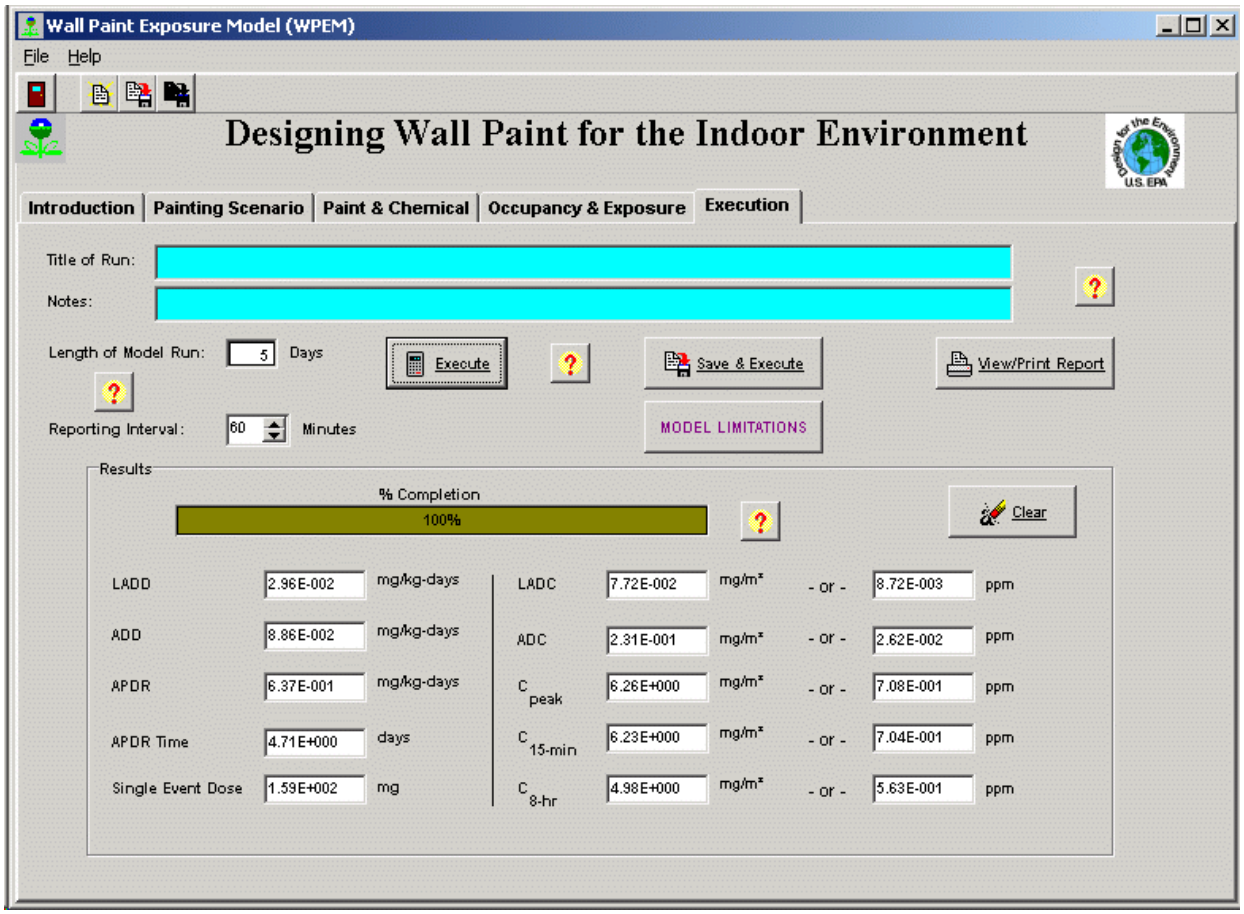

Figure 3-1. Execution Screen (Results after Execution).

Four exposure estimates based on inhalation dose are reported by WPEM: Lifetime Average Daily Dose (LADD); Average Daily Dose (ADD); Acute Potential Dose Rate (APDR); and single event dose. In general, each uses a form of the following equation:

$$\text{Dose} = (C * IR * FQ * D * Y) / (BW * AT * 365 \text{ days/yr}) \quad (3\text{-}1)$$

where: C = average air concentration (mg/m^3)
IR = inhalation rate (m^3/hr)
FQ = frequency (events/year)
D = duration of an event (hours/event)
Y = years of exposure (years)
BW = body weight (kg)
AT = averaging time (years).

The algorithm used in WPEM actually multiplies the air concentration every 30 seconds by the corresponding inhalation rate at that time, rather than using an average concentration as indicated in the simplified expression given above. These products © * IR) for each time interval are summed over the entire length of the model run, to obtain a single event dose that is used in place of C * IR in the equation given above. For the LADD calculation, the averaging time is the lifetime of the exposed individual. For the ADD calculation, the averaging time is the same as the number of years of exposure. For the APDR calculation, an averaging time of one day is used. That is, the APDR is the highest dose over a 24-hour period throughout the model run. The reported APDR time, in days, marks the beginning of the 24-hour period with the highest dose.

Two different long-term measures of inhalation concentration are calculated in WPEM – Lifetime Average Daily Concentration (LADC) and Average Daily Concentration (ADC) – based on the following equation:

$$\text{Concentration} = (TC * FQ * Y) / (AT * 365 \text{ days/yr}) \quad (3\text{-}2)$$

where: TC = time-integrated air concentration per event (mg/m^3-days/event)
FQ = frequency (events/year)
Y = years of exposure (years)
AT = averaging time (years).

The model also provides several short-term concentration measures:

- C_{peak} – the highest instantaneous concentration to which the individual is exposed.
- $C_{15\text{-}min}$ – the highest 15-minute-average concentration to which the individual is exposed.
- $C_{8\text{-}hour}$ – the highest 8-hour-average concentration to which the individual is exposed.

The calculation engine for WPEM currently has no constraint relating to the saturation concentration in air for the chemical that is modeled.

3.2 Report

The report provided by WPEM summarizes the model inputs and presents the model results. If the View/Print button is pressed before the model is executed, then all results show as zeroes but the summary of inputs still is useful for review purposes. The report has two pages (see Figures 3-2 and 3-3) that can be viewed in any sequence. The first page of the report summarizes user inputs for the Painting Scenario screen and the Paint & Chemical screen. The second page summarizes user inputs for the Occupancy & Exposure screen and the Execution screen, and provides the summary model outputs (exposure estimates) as well. Either or both pages of the report can be printed using the Printer command that can be accessed at the top of the report.

3.3 Concentration Time Series

An additional output from the model is a comma-separated (.csv) file that contains details on time-varying concentrations within the modeled building as well as concentrations to which the individual is exposed. This file format can be read directly into spreadsheet software (e.g., Excel) for developing concentration plots or calculating additional summary statistics. The .csv file includes as its first line column headers that are read in along with the model outputs. If the user does not save the inputs, then the file will be named wpem.csv. If the user does save the inputs, then the .csv file will have the same prefix as that associated with the inputs.

Figure 3-4 is an example of the type of plot that can be developed rapidly with the aid of the Excel chart wizard, for example. The time series of modeled concentrations over the length of the model run (5 days) is shown for the painted space (zone 1), the remainder of the building (zone 2), and outdoors. The modeled outdoor concentrations in WPEM are always zero or very small. Figure 3-5 shows a plot of the concentrations to which the individual is exposed, a mixture of those shown by zone in the previous plot and thereby providing an indication of the exposed individual's location by zone over time. In this case the exposed individual is a professional painter who leaves the building permanently when painting is finished on the first day and, thus, has zero exposure thereafter.

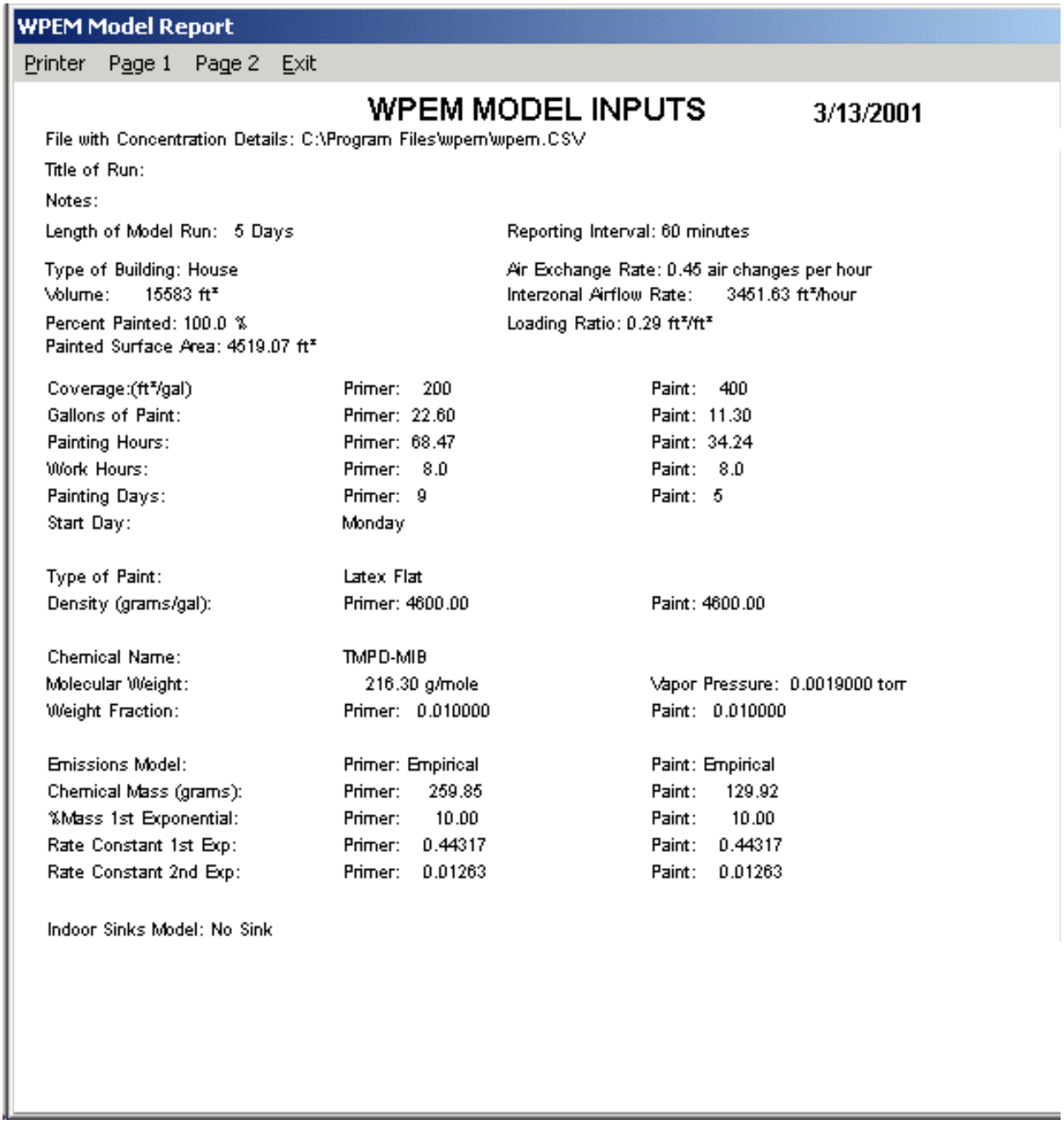

Figure 3-2. Page 1 of WPEM Report.

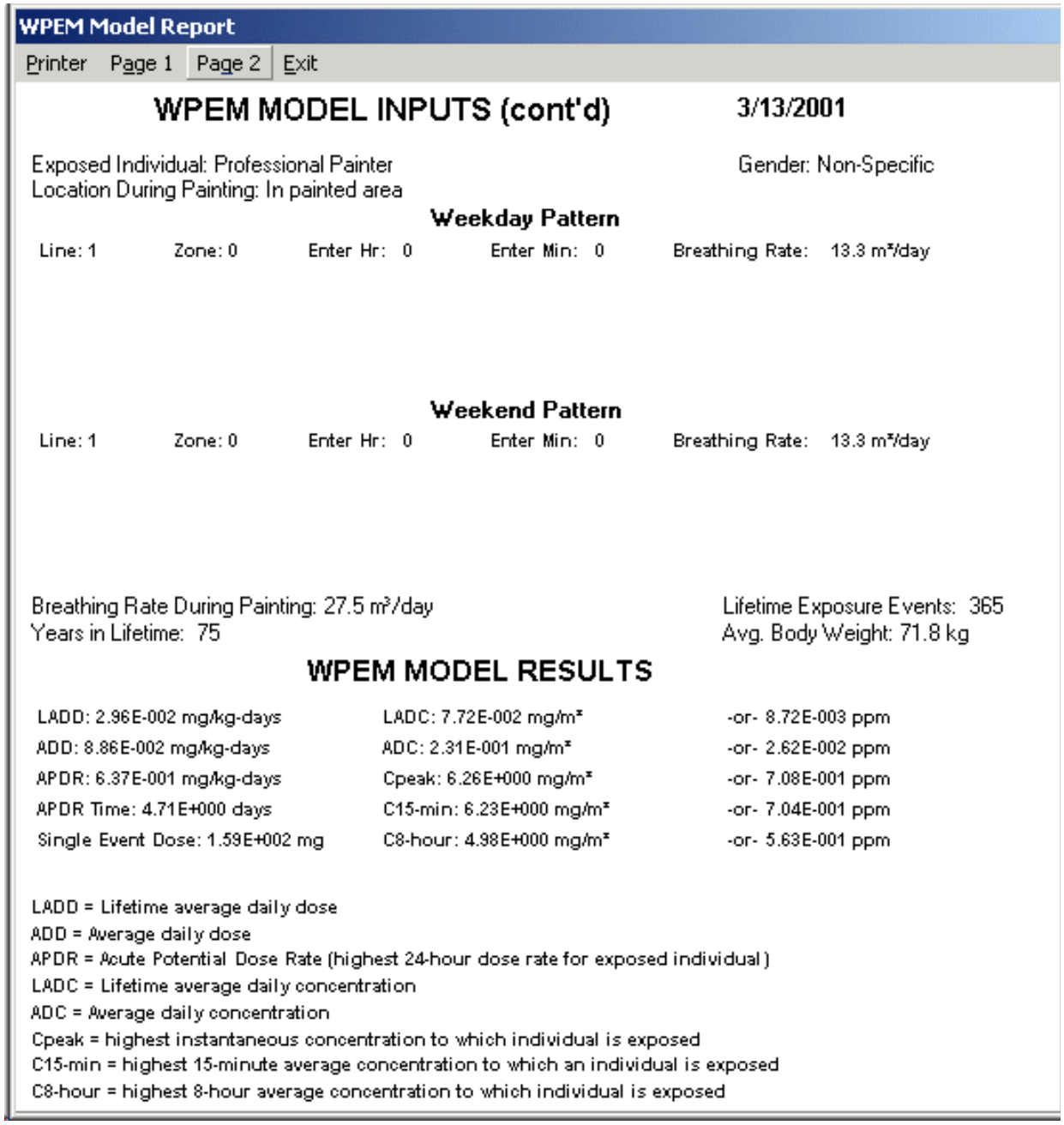

Figure 3-3. Page 2 of WPEM Report.

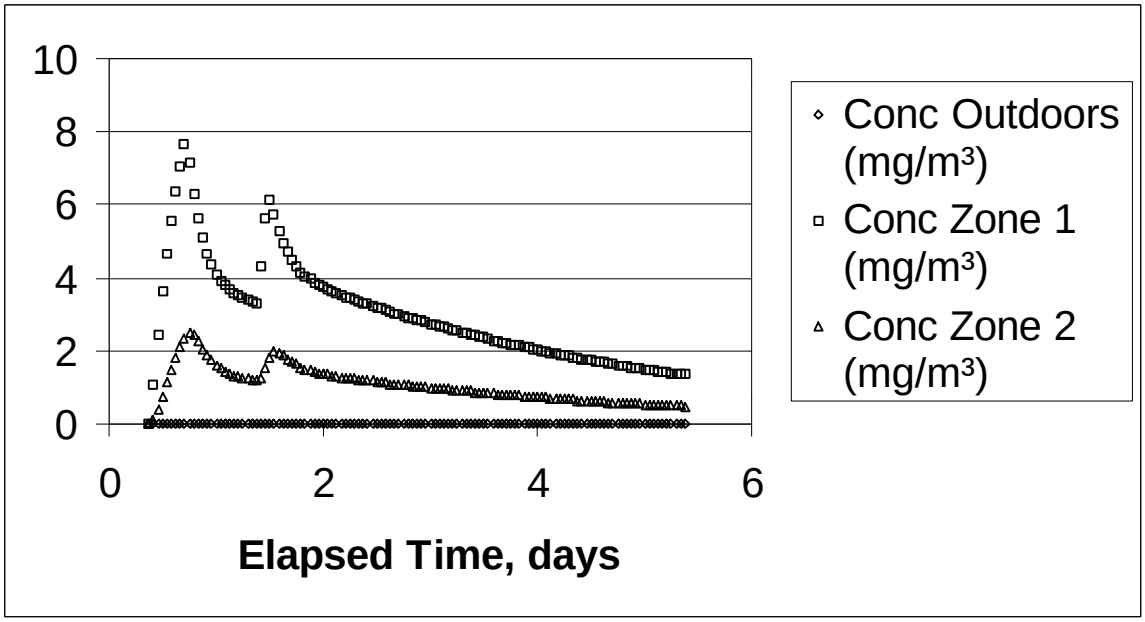

Figure 3-4. Plot of Modeled Concentrations by Zone, from wpem.csv File.

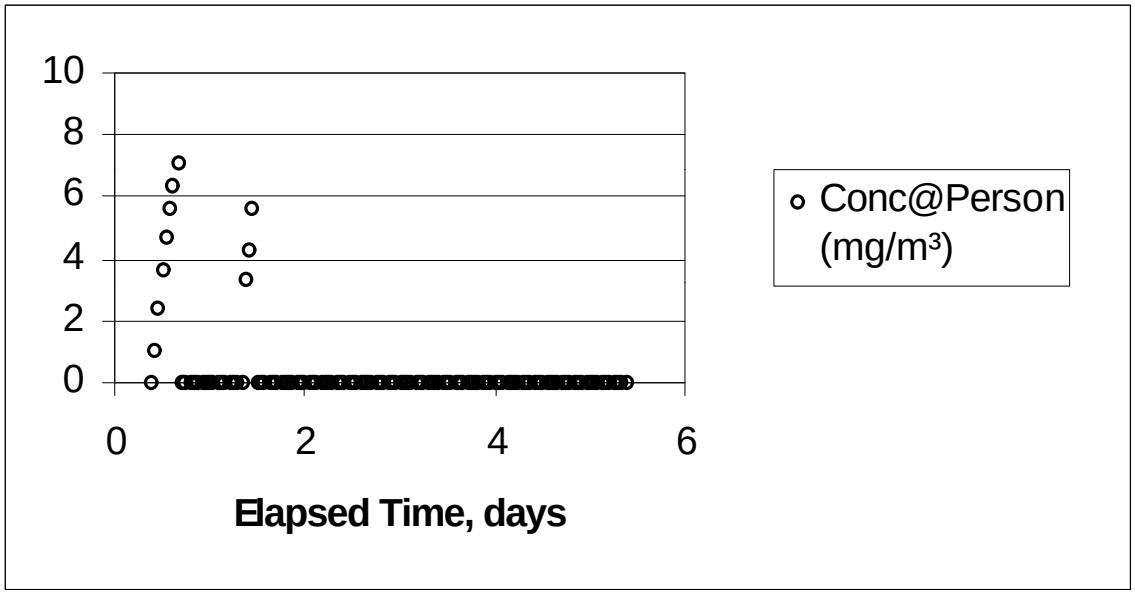

Figure 3-5. Plot of Concentration to Which Individual is Exposed, from wpem.csv File.

4. DEFAULT SCENARIOS AND APPLICATION TIPS

4.1 Default Scenarios

A button near the top of the Painting Scenario screen, labeled DEFAULT SCENARIOS, lists six default scenarios that can be accessed by the user:

- RESDIY – A do-it-yourself (DIY) painter is exposed to a chemical in paint while painting the bedroom of a house.
- RESADULT – An adult located in the non-painted part of the house is exposed to a chemical in paint while a bedroom is painted by a professional painter.
- RESCHILD – A child located in the non-painted part of the house is exposed to a chemical in paint while a bedroom is painted by a professional painter.
- RESPROF – Two professional painters are exposed to a chemical in paint while painting an entire apartment.
- OFFADULT – An office worker is exposed to a chemical in paint after an entire floor of a low-rise office building is painted by ten professionals over a weekend.
- OFFPROF – Ten professional painters are exposed to a chemical in paint while painting an entire floor of a low-rise office building over a weekend.

The name associated with each scenario refers to a file that can be loaded to access that scenario. Such files, provided with the model, are located in the directory from which WPEM is executed and have an extension of .wem. For example, to access the scenario called RESDIY, the user can open the file named resdiy.wem, using the "Open a File" button on the toolbar near the top of the screen. Alternatively, one can click on File at the top left of the screen, then Open, to access the files with default scenarios.

Each file contains defaults for entries such as the type and percent of building painted, the amount of primer and paint applied, the application rate and painting duration, the type of exposed individual and location during the painting event, and the number of lifetime exposure events. There are certain selections that are common across the default scenarios, such as painting of walls only, selection of latex flat paint, selection of TMPD-MIB (texanol) as the chemical, and selection of non-specific gender for the exposed individual. These and other default entries should be reviewed by the user, and changed as needed using appropriate edit buttons, before executing the model.

Table 4-1 summarizes input values used for each of the default scenarios. Exposure descriptors for each scenario follow the table (see Section 4.2). Some application tips are provided in Section 4.3.

Table 4-1. Summary of Inputs for Default Scenarios

Input	Default Scenario					
	RESDIY	**RESADULT**	**RESCHILD**	**RESPROF**	**OFFADULT**	**OFFPROF**
Type of Building	House	House	House	Apartment	Low-rise office	Low-rise office
Percent Painted	One bedroom (10 %)	One bedroom (10 %)	One bedroom (10 %)	Entire building (100 %)	Entire floor (50 %)	Entire floor (50 %)
Painted Surface	Walls only	Walls only	Walls only	Walls only	Walls only	Walls only
Painted Area	452 ft^2	452 ft^2	452 ft^2	2,131.5 ft^2	20,000 ft^2	20,000 ft^2
Number of Coats	0 primer 1 paint	1 primer 1 paint	1 primer 1 paint	1 primer 1 paint	1 primer 1 paint	1 primer 1 paint
Paint Coverage	200/400 ft^2/gal (primer/paint)	200/400 ft^2/gal (primer/paint)	200/400 ft^2/gal (primer/paint)	200/400 ft^2/gal (primer/paint)	200/400 ft^2/gal (primer/paint)	200/400 ft^2/gal (primer/paint)
Number of Painters	1 DIY	1 professional	1 professional	2 professional	10 professional	10 professional
Application Rate per Painter	0.33 gal/hr	0.85 gal/hr	0.85 gal/hr	0.85 gal/hr	0.85 gal/hr	0.85 gal/hr
Priming vs. Painting	N/A	Paint same day	Paint same day	Paint same day	Paint same day	Paint same day
Total Duration	3.42 hours	3.99 hours	3.99 hours	9.4 hours	17.65 hours	17.65 hours
Type of Paint	Latex flat	Latex flat	Latex flat	Latex flat	Latex flat	Latex flat
Chemical	TMPD-MIB	TMPD-MIB	TMPD-MIB	TMPD-MIB	TMPD-MIB	TMPD-MIB
Weight Fractions	0.01 primer 0.01 paint	0.01 primer 0.01 paint	0.01 primer 0.01 paint	0.01 primer 0.01 paint	0.01 primer 0.01 paint	0.01 primer 0.01 paint
Exposed Individual	DIY painter	Adult occupant	Child occupant	Professional painter	Adult occupant	Professional painter
Gender	Non-specific	Non-specific	Non-specific	Non-specific	Non-specific	Non-specific
Location during Painting	In painted area	In building, not in painted area	In building, not in painted area	In painted area	Not in building	In painted area
Total Exposure Events	37.5	50	10	3988	10	2125
Years in Lifetime	75	75	10	75	75	75
Body Weight	71.8 kg	71.8 kg	20.3 kg	71.8 kg	71.8 kg	71.8 kg
Length of Model Run	20 days	20 days	20 days	2 days	20 days	3 days

4.2 Exposure Descriptors

RESDIY (Residential Do-It-Yourself, environment = house, exposed individual = non-professional painter, e.g., homeowner)

The mean house volume (15,583 ft^3 or 441 m^3) and median air exchange rate (0.45 air changes per hour, or ACH) used for this scenario are recommended values from the Exposure Factors Handbook (USEPA 1997). The value for the air exchange rate is indicative of a closed-house condition. A closed-house situation was selected to be conservative. Data on residential air exchange rates under open-window conditions are quite limited. An appropriate value for an open-window situation is probably on the order of 1 to 2 air changes per hour (the 90^{th} percentile for the distribution given in the Exposure Factors Handbook is 1.26 ACH).

Values for the amount of paint, painting duration, and lifetime number of painting events are intended to match closely those from an EPA-sponsored national usage survey of household solvent products (WESTAT 1987). From that survey, for do-it-yourself (DIY) painters the median amount of latex paint used is one gallon and the median duration of use is three hours, for an application rate of 0.33 gallons/hour. The WPEM default house volume is 15,583 ft^3 and the default wall loading ratio is 0.29 ft^2/ft^3 (see Section 2.1.2 of User's Guide), for a total wall area of 4,519 ft^2. Assuming a paint coverage of 400 ft^2/gallon (container label, PDCA 1998) and that only walls are painted, about 9 percent (400 / 4,519) of the wall area would be painted with one gallon. Therefore, for the RESDIY scenario, it is assumed that 10 percent (452 ft^2) of the wall area is painted; this percentage results in 1.13 gallons of paint applied (i.e., 452 ft^2 / 400 ft^2 per gallon) and a painting duration of 3.42 hours (i.e., 1.13 gallons / 0.33 gallons per hour). This duration is close to the median value (3 hours) from the above-cited national survey.

The national survey also indicates a median time-since-last-painting of 8 months. Assuming that respondents, on the average, were queried at the halfway point between successive painting events, the median duration between painting events would be 16 months, equating to 0.75 events per year. The RESDIY scenario has 0.75 events per year over 50 years, or 37.5 painting events per lifetime. It is assumed that for 25 years (i.e., the years of infancy, child, senior), a DIY painter would not paint at all.

The amount of time spent in different locations and the breathing rates for weekday/weekend activity patterns in WPEM are derived from recommended values in the Exposure Factors Handbook. By definition, the DIY painter is in the painted space during the painting event. Breathing rates while painting are a weighted average of recommended values for light and moderate activities, with light receiving a weight of 25 % and moderate a weight of 75 %. The values used for years in lifetime (75) and body weight (71.8 kg for non-specific gender) also are recommended values from the Exposure Factors Handbook.

Default emission rates determined by the WPEM software are based on chamber tests of latex and alkyd paints (ARCADIS 1998) conducted under EPA's Designing Wall Paint for the Environment Project. The default WPEM assumption of no indoor sinks may be conservative, depending on the specific chemical of concern. Chamber sink tests for constituents of alkyd paint, under EPA's Designing Wall Paint for the Environment Project, indicated a significant sink effect for MEKO but little or no effect for 1,2,4-trimethylbenzene, 2-methyldecane, and undecane. Prior EPA sink tests for constituents of latex paint (Chang et al. 1998), again using four target compounds, indicated a substantial sink effect for all four VOCs that were tested.

Figure 4-1. Exposure Descriptor for RESDIY Scenario.

RESADULT (Residential Adult, environment = house, exposed individual = adult occupant)

The mean house volume (15,583 ft^3 or 441 m^3) and median air exchange rate (0.45 air changes per hour, or ACH) used for this scenario are recommended values from the Exposure Factors Handbook (USEPA 1997). The value for the air exchange rate is indicative of a closed-house condition. A closed-house situation was selected to be conservative. Data on residential air exchange rates under open-window conditions are quite limited. An appropriate value for an open-window situation is probably on the order of 1 to 2 air changes per hour (the 90^{th} percentile for the distribution given in the Exposure Factors Handbook is 1.26 ACH).

For this scenario 10 percent of the house is painted each year, based on the assumption that residential occupants who use professional painters have their entire house painted once every 10 years. One coat of primer and one coat of paint are applied to walls by a professional, with WPEM default coverages of 200 ft^2/gallon for primer and 400 ft^2/gallon for paint (per container labels, PDCA 1998). The WPEM default house volume is 15,583 ft^3 and the default wall loading ratio is 0.29 ft^2/ft^3 (see Section 2.1.2 of User's Guide), for a total wall area of 4,519 ft^2. For 10 percent of the wall area (452 ft^2), as used in this scenario, the default coverages result in 2.26 gallons of primer and 1.13 gallons of paint applied. The default primer/paint application rate of 0.85 gallons/hour for a professional painter gives a total painting duration of 3.99 hours. The default application rate is derived from the Estimating Guide developed by the Painting and Decorating Contractors of America (PDCA 1998) – a labor production rate of 337.5 ft^2/hour for painting with a roller (range of 325-350 ft^2/hour given in the guide), with a paint coverage of 400 ft^2/gallon, equates to an application rate of 0.85 gallons/hour (i.e., 337.5 ft^2/hour / 400 ft^2/gallon).

As noted above, for this scenario it is assumed that a house is repainted in its entirety once every 10 years. Since 10 percent of the house is being painted for the specific scenario, the painting event is assumed to occur once a year. Over a period of 50 years of exposure (the WPEM default for an adult), this scenario equates to 50 painting events per lifetime.

The amount of time spent in different locations and the breathing rates for weekday/weekend activity patterns in WPEM are derived from recommended values in the Exposure Factors Handbook. An exposed adult for this scenario is assumed to be in the house, but not in the painted area, during the painting event. The values used for years in lifetime (75) and body weight (71.8 kg for non-specific gender) also are recommended values from the Exposure Factors Handbook.

Default emission rates determined by the WPEM software are based on chamber tests of latex and alkyd paints (ARCADIS 1998) conducted under EPA's Designing Wall Paint for the Environment Project. The default WPEM assumption of no indoor sinks may be conservative, depending on the specific chemical of concern. Chamber sink tests for constituents of alkyd paint, under EPA's Designing Wall Paint for the Environment Project, indicated a significant sink effect for MEKO but little or no effect for 1,2,4-trimethylbenzene, 2-methyldecane, and undecane. Prior EPA sink tests for constituents of latex paint (Chang et al. 1998), again using four target compounds, indicated a substantial sink effect for all four

Figure 4-2. Exposure Descriptor for RESADULT Scenario.

RESCHILD (Residential Child, environment = house, exposed individual = child occupant)

The mean house volume (15,583 ft^3 or 441 m^3) and median air exchange rate (0.45 air changes per hour, or ACH) used for this scenario are recommended values from the Exposure Factors Handbook (USEPA 1997). The value for the air exchange rate is indicative of a closed-house condition. A closed-house situation was selected to be conservative. Data on residential air exchange rates under open-window conditions are quite limited. An appropriate value for an open-window situation is probably on the order of 1 to 2 air changes per hour (the 90^{th} percentile for the distribution given in the Exposure Factors Handbook is 1.26 ACH).

For this scenario 10 percent of the house is painted each year, based on the assumption that residential occupants who use professional painters have their entire house painted once every 10 years. One coat of primer and one coat of paint are applied to walls by a professional, with WPEM default coverages of 200 ft^2/gallon for primer and 400 ft^2/gallon for paint (per container labels, PDCA 1998). The WPEM default house volume is 15,583 ft^3 and the default wall loading ratio is 0.29 ft^2/ft^3 (see Section 2.1.2 of User's Guide), for a total wall area of 4,519 ft^2. For 10 percent of the wall area (452 ft^2), as used in this scenario, the default coverages result in 2.26 gallons of primer and 1.13 gallons of paint applied. The default primer/paint application rate of 0.85 gallons/hour for a professional painter gives a total painting duration of 3.99 hours. The default application rate is derived from the Estimating Guide developed by the Painting and Decorating Contractors of America (PDCA 1998) – a labor production rate of 337.5 ft^2/hour for painting with a roller (range of 325-350 ft^2/hour given in the guide), with a paint coverage of 400 ft^2/gallon, equates to an application rate of 0.85 gallons/hour (i.e., 337.5 ft^2/hour / 400 ft^2/gallon).

As noted above, for this scenario it is assumed that a house is repainted in its entirety once every 10 years. Since 10 percent of the house is being painted for the specific scenario, the painting event is assumed to occur once a year. Over a period of 10 years of exposure (the WPEM default for a child), this scenario equates to 10 painting events per "lifetime."

The amount of time spent in different locations and the breathing rates for weekday/weekend activity patterns in WPEM are derived from recommended values in the Exposure Factors Handbook. An exposed child for this scenario is assumed to be in the house, but not in the painted area, during the painting event. The value used for body weight (20.3 kg for non-specific gender) also is a recommended value from the Exposure Factors Handbook.

Default emission rates determined by the WPEM software are based on chamber tests of latex and alkyd paints (ARCADIS 1998) conducted under EPA's Designing Wall Paint for the Environment Project. The default WPEM assumption of no indoor sinks may be conservative, depending on the specific chemical of concern. Chamber sink tests for constituents of alkyd paint, under EPA's Designing Wall Paint for the Environment Project, indicated a significant sink effect for MEKO but little or no effect for 1,2,4-trimethylbenzene, 2-methyldecane, and undecane. Prior EPA sink tests for constituents of latex paint (Chang et al. 1998), again using four target compounds, indicated a substantial sink effect for all four

Figure 4-3. Exposure Descriptor for RESCHILD Scenario.

RESPROF (Residential Professional, environment = apartment, exposed individual = professional painter)

The mean apartment volume (7,350 ft^3 or 208 m^3) and median air exchange rate (0.45 air changes per hour, or ACH) used for this scenario are recommended values from the Exposure Factors Handbook (USEPA 1997). The handbook does not list air exchange rates for apartments, as all or most measured values have been for attached/detached houses. The chosen value, indicative of a closed-house condition, is intended to be conservative. Data on residential air exchange rates under open-window conditions are quite limited. An appropriate value for an open-window situation is probably on the order of 1 to 2 air changes per hour (the 90^{th} percentile for the distribution given in the Exposure Factors Handbook is 1.26 ACH).

For this scenario it is assumed that two professionals paint an apartment in its entirety. One coat of primer and one coat of paint are applied to walls by the professionals, with WPEM default coverages of 200 ft^2/gallon for primer and 400 ft^2/gallon for paint (per container labels, PDCA 1998). The WPEM default apartment volume is 7,350 ft^3 and the default wall loading ratio is 0.29 ft^2/ft^3 (see Section 2.1.2 of User's Guide), for a total wall area of 2,131.5 ft^2. The default coverages result in 10.66 gallons of primer and 5.33 gallons of paint applied, for a total of 16 gallons. The default application rate by each of the two professionals (0.85 gallons/hour for both primer and paint) results in a total painting duration of 9.4 hours. The default application rate is derived from the Estimating Guide developed by the Painting and Decorating Contractors of America (PDCA 1998) – a labor production rate of 337.5 ft^2/hour for painting with a roller (range of 325-350 ft^2/hour given in the guide), with a paint coverage of 400 ft^2/gallon, equates to an application rate of 0.85 gallons/hour (i.e., 337.5 ft^2/hour / 400 ft^2/gallon).

For this scenario it is assumed that professional painters spend 1,500 hours per year painting (i.e., 30 hours/week times 50 weeks/year). Since the event described above takes 9.4 hours, there would be 159.5 such events in a year of painting. Assuming that a professional painter works for 25 years on average, there would be 3,988 such events over a painting "lifetime."

By definition, the professionals are located in the painted area throughout the entire application, and they are assumed to leave the apartment as soon as painting is finished. Breathing rates while painting are a weighted average of recommended values from the Exposure Factors Handbook for light and moderate activities, with light receiving a weight of 25 % and moderate a weight of 75 %. The values used for years in lifetime (75) and body weight (71.8 kg for non-specific gender) also are recommended values from the Exposure Factors Handbook.

Default emission rates determined by the WPEM software are based on chamber tests of latex and alkyd paints (ARCADIS 1998) conducted under EPA's Designing Wall Paint for the Environment Project. The default WPEM assumption of no indoor sinks may be conservative, depending on the specific chemical of concern. Chamber sink tests for constituents of alkyd paint, under EPA's Designing Wall Paint for the Environment Project, indicated a significant sink effect for MEKO but little or no effect for 1,2,4-trimethylbenzene, 2-methyldecane, and undecane. Prior EPA sink tests for constituents of latex paint (Chang et al. 1998), again using four target compounds, indicated a substantial sink effect for all four VOCs that were

Figure 4-4. Exposure Descriptor for RESPROF Scenario.

OFFADULT (Office Adult, environment = office building, exposed individual = adult office worker)

For this scenario an entire floor (50 percent) of a low-rise office building is painted by a team of ten professional painters. The building volume (160,000 ft^3 or 4,531 m^3) was chosen using professional judgment, and equates to a two-story office building with nominal length of 100 feet, width of 80 feet, and height of 10 feet per story. The air exchange rate (1 air change per hour, or ACH) is close to the average (0.9 ACH) reported by Persily (1989), based on measurements in a number of office buildings.

One coat of primer and one coat of paint are applied to walls by the professionals, with WPEM default coverages of 200 ft^2/gallon for primer and 400 ft^2/gallon for paint (per container labels, PDCA 1998). Based on the WPEM default volume of 80,000 ft^3 for half of the building and the default wall loading ratio of 0.25 ft^2/ft^3 (see Section 2.1.2 of User's Guide), the painted wall area is 20,000 ft^2. The default coverages result in 100 gallons of primer and 50 gallons of paint applied, for a total of 150 gallons. With a team of ten professional painters and an application rate of 0.85 gallons/hour for each painter, the total painting duration is 17.65 hours. The default application rate is derived from the Estimating Guide developed by the Painting and Decorating Contractors of America (PDCA 1998) – a labor production rate of 337.5 ft^2/hour for painting with a roller (range of 325-350 ft^2/hour given in the guide), with a paint coverage of 400 ft^2/gallon, equates to an application rate of 0.85 gallons/hour (i.e., 337.5 ft^2/hour / 400 ft^2/gallon).

For this scenario it is assumed, based on professional judgement, that office buildings are painted in entirety once every 5 years, corresponding to 0.2 exposure events per year. Over a period of 50 years of exposure (the WPEM default for an adult), this scenario equates to 10 painting events per lifetime.

The amount of time spent in different locations and the breathing rates for weekday/weekend activity patterns in WPEM are derived from recommended values in the Exposure Factors Handbook. An exposed adult for this scenario is assumed to be out of the office during the painting event. Following the event, the adult is the office according to the default weekday/weekend activity patterns in WPEM. The values used for years in lifetime (75) and body weight (71.8 kg for non-specific gender) also are recommended values from the Exposure Factors Handbook.

Default emission rates determined by the WPEM software are based on chamber tests of latex and alkyd paints (ARCADIS 1998) conducted under EPA's Designing Wall Paint for the Environment Project. The default WPEM assumption of no indoor sinks may be conservative, depending on the specific chemical of concern. Chamber sink tests for constituents of alkyd paint, under EPA's Designing Wall Paint for the Environment Project, indicated a significant sink effect for MEKO but little or no effect for 1,2,4-trimethylbenzene, 2-methyldecane, and undecane. Prior EPA sink tests for constituents of latex paint (Chang et al. 1998), again using four target compounds, indicated a substantial sink effect for all four VOCs that

Figure 4-5. Exposure Descriptor for OFFADULT Scenario**.**

OFFPROF (Office Professional, environment = office building, exposed individual = professional painter)

For this scenario an entire floor (50 percent) of a low-rise office building is painted by a team of ten professional painters. The building volume (160,000 ft^3 or 4,531 m^3) was chosen using professional judgment, and equates to a two-story office building with nominal length of 100 feet, width of 80 feet, and height of 10 feet per story. The air exchange rate (1 air change per hour, or ACH) is close to the average (0.9 ACH) reported by Persily (1989), based on measurements in a number of office buildings.

One coat of primer and one coat of paint are applied to walls by the professionals, with WPEM default coverages of 200 ft^2/gallon for primer and 400 ft^2/gallon for paint (per container labels, PDCA 1998). Based on the WPEM default volume of 80,000 ft^3 for half of the building and the default wall loading ratio of 0.25 ft^2/ft^3 (see Section 2.1.2 of User's Guide), the painted wall area is 20,000 ft^2. The default coverages result in 100 gallons of primer and 50 gallons of paint applied, for a total of 150 gallons. With a team of ten professional painters and an application rate of 0.85 gallons/hour for each painter, the total painting duration is 17.65 hours. The default application rate is derived from the Estimating Guide developed by the Painting and Decorating Contractors of America (PDCA 1998) – a labor production rate of 337.5 ft^2/hour for painting with a roller (range of 325-350 ft^2/hour given in the guide), with a paint coverage of 400 ft^2/gallon, equates to an application rate of 0.85 gallons/hour (i.e., 337.5 ft^2/hour / 400 ft^2/gallon).

For this scenario it is assumed that professional painters spend 1,500 hours per year painting (i.e., 30 hours/week times 50 weeks/year). Since the event described above takes 17.65 hours, there would be 85 such events in a year of painting. Assuming that a professional painter works for 25 years on average, there would be 2,125 such events over a painting "lifetime."

By definition, the professionals are located in the painted area throughout the entire application, and they are assumed to leave the building as soon as painting is finished. Breathing rates while painting are a weighted average of recommended values from the Exposure Factors Handbook for light and moderate activities, with light receiving a weight of 25 % and moderate a weight of 75 %. The values used for years in lifetime (75) and body weight (71.8 kg for non-specific gender) also are recommended values from the Exposure Factors Handbook.

Default emission rates determined by the WPEM software are based on chamber tests of latex and alkyd paints (ARCADIS 1998) conducted under EPA's Designing Wall Paint for the Environment Project. The default WPEM assumption of no indoor sinks may be conservative, depending on the specific chemical of concern. Chamber sink tests for constituents of alkyd paint, under EPA's Designing Wall Paint for the Environment Project, indicated a significant sink effect for MEKO but little or no effect for 1,2,4-trimethylbenzene, 2-methyldecane, and undecane. Prior EPA sink tests for constituents of latex paint (Chang et al. 1998), again using four target compounds, indicated a substantial sink effect for all four VOCs that

Figure 4-6. Exposure Descriptor for OFFPROF Scenario**.**

4.3 Some Application Tips

Once inputs have been supplied and saved as needed, and the model has been executed, the user may wish to model some other scenario that is different from the one just modeled. To reset all model input parameters to their initial default values, it is not necessary to close WPEM and then reopen the software. The same effect can be achieved by clicking on File at the top left of the screen, then New. Alternatively, a file for a default scenario can be selected to insert the default values for that scenario.

If the user selects a file for one of the default scenarios and then edits the file, it is advisable to save the edits under a new file name, rather than overwriting the file that contains the default scenario. The user is further advised to make copies of the default scenario files (the six sets of files provided with the model that have extensions of .wem and .we1) in a directory that is different from the one from which WPEM is executed (by default, the install package for WPEM places all files in c:\program files\wpem). With this safeguard, a default-scenario file can be restored to its original values in the event that it is inadvertently overwritten, without the need to re-install the software.

The user also may wish to have a customized list of default values for his/her own use. The simplest way of accomplishing this is to first reset all values to their initial defaults (as occurs when first opening WPEM or when clicking on File, then New). Next, the appropriate inputs can be edited to the values that the user would like to keep as a basic set of defaults. Once all edits have been completed, they can be saved to a file with a name of the user's choice by clicking on File, then Save As.

The WPEM software is sufficiently flexible to model a wide variety of situations. For example, even a chamber test can be simulated using the software. The volume of the chamber can be input by selecting residence, for example, and then editing the building volume. The user also should make the choice that the entire building is painted, so that WPEM will use calculations for a single-zone model. Next, the air exchange rate should be edited to match the conditions for the chamber test. The value for the interzonal airflow rate does not matter because a single-zone model will be used. Then one of the painted-surface choices (e.g., walls only) can be selected and the value edited to match the loading in the chamber. The coverage or film thickness also should be edited to match the modeled application. For small-chamber tests, the paint usually is applied nearly instantaneously outside the chamber, after which the painted specimen is inserted. To match this condition closely, the number of painters or the application rate can be edited so that the calculated priming or painting duration (whichever applies) is a small value such as 0.01 hours. The remaining edits would pertain to the type of paint and chemical to be modeled.

5. REFERENCES

ARCADIS, 1998. Testing to Determine Chemical Emissions from Paint in Support of the EPA Designing Wall Paint for the Indoor Environment Project – Description of the Testing Program and Results. Final report prepared by ARCADIS Geraghty & Miller, Inc., for USEPA Office of Pollution Prevention and Toxics under EPA Contract No. 68-W6-0023.

Chang, JCS, Sparks, LE, Guo, Z, and Fortmann, R, 1998. "Evaluation of Sinks Effects on VOCs from a Latex Paint," *J. Air & Waste Manage. Assoc.* 48:953-958.

Evans, WC, 1994. "Development of Continuous-Application Source Terms and Analytical Solutions for One- and Two-Compartment Systems." In *Characterizing Sources of Indoor Air Pollution and Related Sink Effects*, ASTM STP 1287, American Society for Testing and Materials, pp 279-293.

Koontz, MD, and Rector, HR, 1995. Estimation of Distributions for Residential Air Exchange Rates. Final report prepared by GEOMET Technologies, Inc., for USEPA Office of Pollution Prevention and Toxics.

PDCA, 1998. Estimating Guide, Nineteenth Edition. Published by the Painting and Decorating Contractors of America, Fairfax, VA.

Matthews, JH, 1992. Numerical Methods for Mathematics, Science, and Engineering, Second Edition, Prentice Hall, Englewood Cliffs, NJ.

Persily, AK, 1989. "Ventilation Rates in Office Buildings," In *IAQ 1989*, American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE), pp 128-136.

USEPA, 1992. Guidelines for Exposure Assessment. EPA/600/Z-92/001, U.S. Environmental Protection Agency, Office of Research and Development, Office of Health and Environmental Assessment.

USEPA, 1997. Exposure Factors Handbook, Volumes I-III. EPA/600/P-95/002Fa, b, c, U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment.

WESTAT, 1987. Household Solvent Products: A National Usage Survey. Final report prepared for USEPA Office of Pollution Prevention and Toxics under EPA Contract No. 68-02-4243.

APPENDIX A

ALKYD PAINT CHAMBER TESTS

A1. INTRODUCTION

A series of small-chamber tests was conducted by ARCADIS Geraghty and Miller, Inc., to (1) characterize concentrations of various volatile organic compounds (VOCs) emitted from different formulations of alkyd primer and paint, and (2) to explore the interactions of some of these compounds with selected indoor sinks. In addition to the broad objectives of improving the understanding of emission and sink behavior for these chemicals in alkyd primer and paint, a more specific objective was to provide a quantitative basis for development of emission/sink models or for estimating parameters for such models. In addition to the small-chamber tests, ARCADIS Geraghty and Miller, Inc., conducted painting events at EPA's research house in North Carolina for the primary purpose of gathering data to be used for model evaluation.

The sections that follow describe methods and results for bulk analysis of the alkyd primer/paint formulations prior to chamber testing, small-chamber emission tests of these formulations, development of predictive models for VOC emissions from alkyd primer and paint, and sink behavior of selected chemicals in alkyd primer or paint.

A2. BULK ANALYSIS

Prior to conduct of small-chamber emission tests, each formulation of alkyd primer or paint was analyzed to determine its chemical composition by weight. In brief, the procedure for analysis of the bulk product that was followed by ARCADIS Geraghty and Miller, Inc., (ARCADIS 1998) involved (1) extracting alkyd primer and paints with methylene chloride, (2) centrifuging the sample to remove solids, and (3) analyzing the supernatant by GC/MS.

Results of the bulk analysis are shown as chemical weight fractions (mg/g) in Table A-1. The primary constituents of both the primer (formulation AP-F) and one of the paints (formulation ASG-G) were propyl-cyclohexane, decane, and undecane. The second paint (formulation ASG-H) was dominated by 2-methyldecane and various branched undecanes.

Table A-1. Results of Bulk Analysis (mg/g) for Alkyd Primer and Paints

Chemical	AP-F (primer)	ASG-G (paint)	ASG-H (paint)
Toluene	0.40	1.43	0.02
Octane	0.24	0.87	0.004
MEKO	2.63	1.95	2.56
Ethylbenzene	1.27	1.85	0.91
p-Xylene	3.98	5.47	2.93
Nonane	3.88	4.36	0.40
o-Xylene	1.71	2.02	1.28
Propyl-cyclohexane	13.30	16.50	0.59
Isopropylbenzene	0.20	0.17	0.01
n-Propylbenzene	0.90	0.73	0.10
p-Ethyltoluene	3.96	4.07	0.55
1,3,5-Trimethylbenzene	2.07	1.75	0.23
Decane	11.80	21.40	--
n-Decane	--	--	5.71
Branched Decane A	--	--	16.90
Branched Decane B	--	--	6.09
o-Ethyltoluene	1.52	1.20	0.15
1,2,4-Trimethylbenzene	4.78	3.98	0.81
1,2,3-Trimethylbenzene	1.19	1.05	0.16
2-Methyldecane	1.97	3.47	51.50
Trans-decalin	2.41	3.16	1.17
Undecane	8.76	16.50	--
n-Undecane	--	--	5.48
Branched Undecane A	--	--	27.10
Branched Undecane B	--	--	13.40
Branched Undecane C	--	--	49.30
Branched Undecane D	--	--	7.41
Branched Undecane E	--	--	24.90
Branched Undecane F	--	--	21.30
Dodecane	1.85	2.40	0.22

A3. SMALL-CHAMBER EMISSION TESTS

The small-chamber emission tests were conducted by ARCADIS Geraghty and Miller, Inc., in the EPA APPCD Source Characterization Laboratories located in the EPA Environmental Research Center in Research Triangle Park, NC. The tests were conducted using 53-liter, stainless-steel chambers housed in a temperature-controlled incubator. These chambers have been fitted with inlet and outlet manifolds for the air supply, temperature and relative humidity sensors, and a small fan to ensure mixing within the chamber. During each test, clean (VOC- and particle-free) air was supplied to the chamber at a controlled relative humidity. A glass sampling manifold has been connected to the chamber outlet for collection of air samples.

The substrate used in the tests was 0.5-inch gypsum wallboard that was purchased from a local retail outlet in North Carolina. For each test, the substrate was cut to a size of 16 by 16 cm (total area of 256 cm^2 or 0.0256 m^2), resulting in a surface-to-volume loading ratio of about 0.5 m^2/m^3 in the chamber. The edges were sealed and the test specimen was placed on the floor of the chamber during the test. The cut and sealed substrate was conditioned in the chamber for at least 24 hours prior to application of primer/paint.

Primer and paint were applied to the wallboard with a roller purchased at a local retail outlet. The rate of primer/paint application in the tests, and resulting wet film thickness, were based on recommendations from the manufacturers. The mass of paint applied was determined gravimetrically by two methods. Wet film thickness was not measured with a gage during the tests because the gage affects surface film characteristics and the specimen was to be inserted into the chamber as quickly as possible after priming or painting. Based on the measured mass of paint applied and the known specific gravity of the coating, the average calculated wet film thickness was 415 μm (16.4 mil) for the alkyd primer and 105 μm (4.1 mil) for the alkyd paint.

As noted above, the wallboard specimen was conditioned in the chamber at least 24 hours before the test. Background concentrations were measured prior to removing the specimen. Primer then was applied, the specimen was re-inserted in the chamber, and air samples were collected for the next 48 hours. Then the specimen was removed, paint was applied, the wallboard again was inserted in the chamber, and air samples were collected during the next 12 days. Thus, the total monitoring period for each test was 14 days in duration.

Two tests were conducted for alkyd primer and paint. The primer AP-F, for which the

contents (as determined through bulk analysis) were previously described in Table A-1, was used for both tests. Paint formulation ASG-G was used in the first chamber emission test (test A1), and formulation ASG-H was used in the second test (test A2).

It has been observed in previous chamber tests that emission rates for various compounds in paint tend to decline exponentially over time as the reservoir of material that can be emitted is gradually depleted, and as the drying paint forms a barrier that retards emissions. Two types of empirical models for estimating the time-varying emission profile can be used: (1) a single-exponential model governed by an initial emission rate and a rate of decline from the initial rate, and (2) a double-exponential model with two sets of initial emission rates and rates of decline, one to account for an early ("fast") phase of evaporation-dominated emissions and one to account for a later ("slow") phase of diffusion-dominated emissions.

Because chemicals in alkyd paint tend to volatilize quite rapidly, a single-exponential model should be sufficient to describe the emissions behavior. The time-varying emission rate for the single-exponential model is given by the following equation:

$$S(t) = E_0 e^{-kt} \qquad \text{(A-1)}$$

where: $S(t)$ = Source strength as a function of time (mass/time)
E_0 = Initial emission rate (mass/time)
k = First-order rate constant ($time^{-1}$)
t = Time.

The mass-balance equation for an environmental test chamber with a constant airflow rate and a single source is as follows:

$$V \frac{dC}{dt} = S(t) - QC \qquad \text{(A-2)}$$

where: C = Concentration in the chamber (mass/volume)
V = Volume of the chamber
Q = Airflow rate into and out of the chamber (volume/time).

Integrating Equation A-2 with the source term defined by Equation A-1 and assuming an initial concentration of zero gives the following equation:

$$C(t) = \frac{E_0}{V\left(\frac{Q}{V} - k\right)}\left(e^{-kt} - e^{-\frac{Q}{V}t}\right) \qquad \text{(A-3)}$$

For each chamber test, equation A-3 was fit to chamber data for each of the chemicals in alkyd primer and paint using non-linear regression analysis. The measured chamber volume and airflow rate were taken as "knowns," and the initial emission rate and the first-order rate constant for emissions decline were estimated through the regression technique. In each case, the fits were done separately for the priming and painting portions of the test.

Examples fits of the single-exponential emissions model to the chamber concentration data are shown in Figures A-1, A-2, and A-3, for MEKO, decane, and undecane, respectively. All data shown in the figures are from in test A1, involving primer formulation AP-F and paint formulation ASG-G. All three fits are quite good, both for primer and paint, with departure only at the peak value for paint. In some cases the modeled concentrations decrease somewhat more rapidly than indicated by the data, but the overall trend in the data still is followed quite closely by the model.

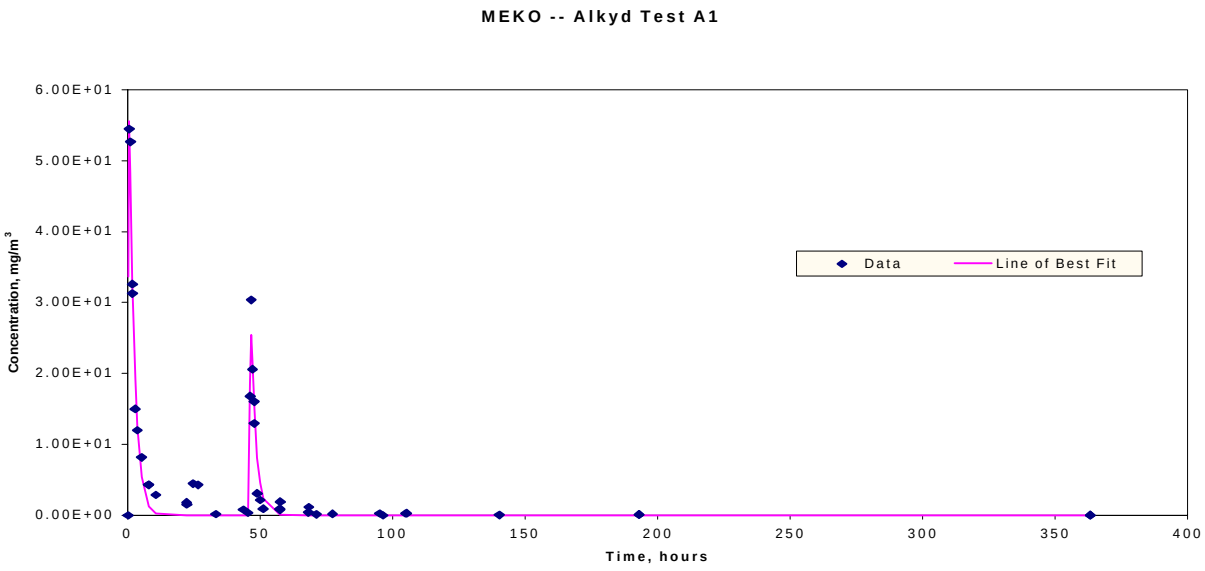

Figure A-1. Fit of Single-Exponential Emissions Model to Alkyd Chamber Data for MEKO.

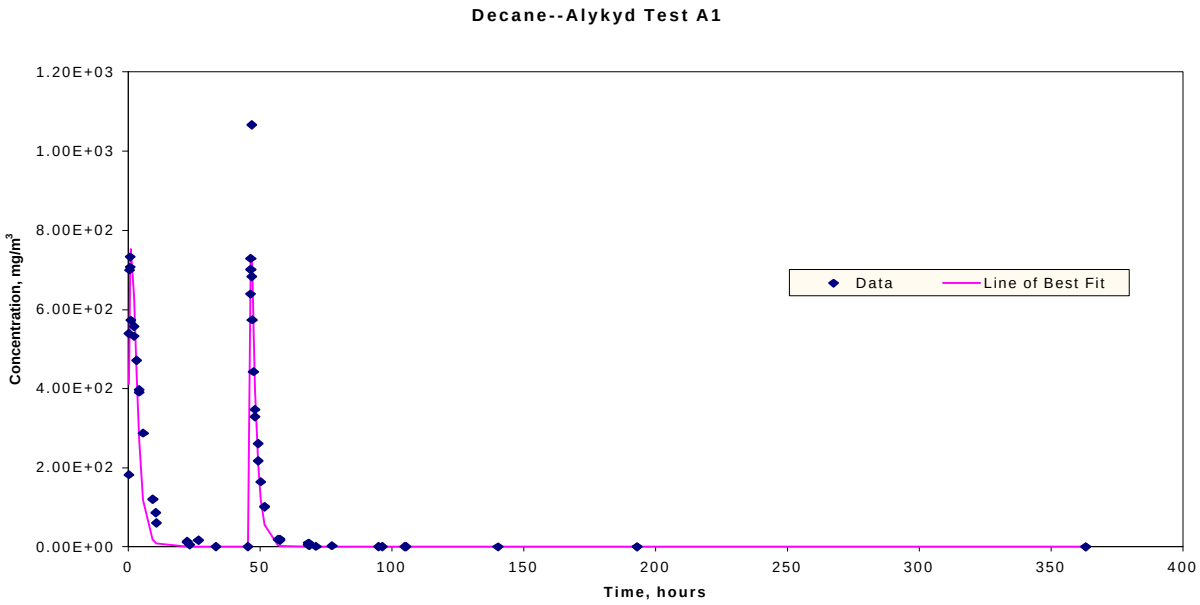

Figure A-2. Fit of Single-exponential Emissions Model to Alkyd Chamber Data for Decane.

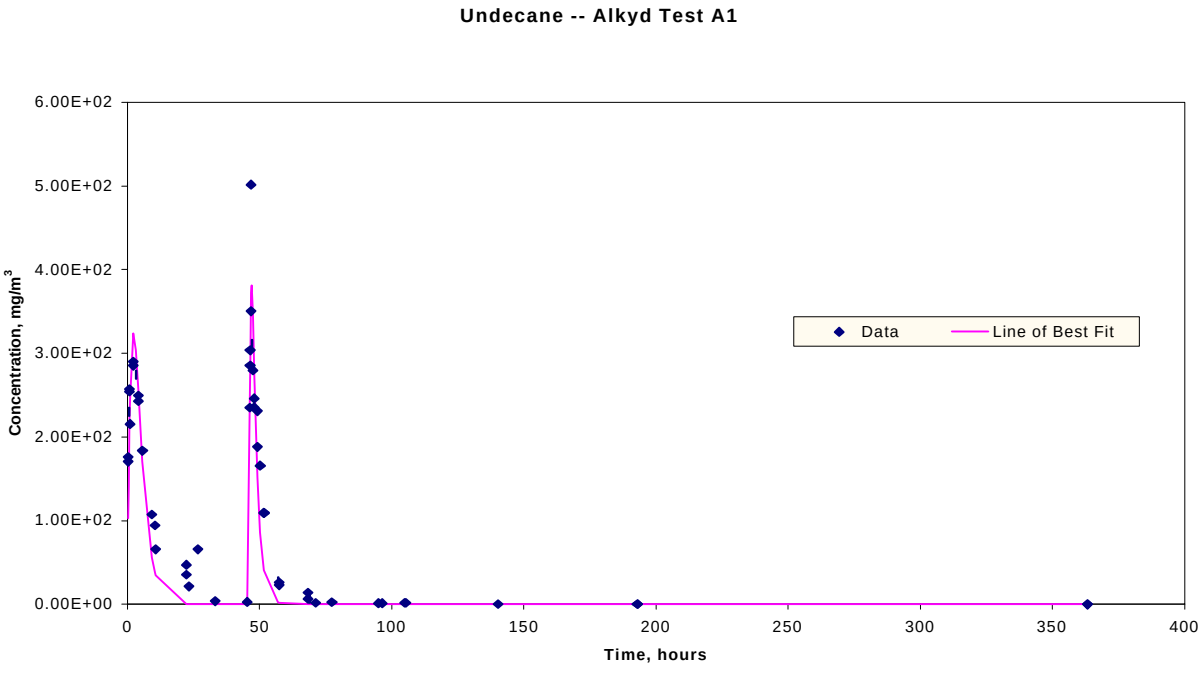

Figure A-3. Fit of Single-exponential Emissions Model to Alkyd Chamber Data for Undecane.

Estimates of the parameters (Eo and k) for the single-exponential emissions model described above are summarized for chemicals in the primer and paint for test A1 in Table A-2 and for test A2 in Table A-3. The R^2 values shown in the table provide a general indication of how well the empirical emissions model fits the data for each chemical, with values of 0.9 or higher indicating particularly good fits. Adequate fits (R^2 value $\geq$ 0.7) were obtained in test A1 for 18 of the 20 chemicals in primer and for all 20 of the chemicals in paint (same chemicals in paint as in primer for this test), and in test A2 for 20 of 28 chemicals in primer and for 20 of 22 chemicals in paint.

One notable difference in the test results is that very good fits were obtained for MEKO, both for primer and paint, in test A1, whereas for test A2 the fits were quite poor. Most of the cases of poorer fits for test A2 were for branched undecanes, for which there may be greater measurement uncertainty due to inability to obtain clear separation in the GC analysis. There also were a few estimates for the decay rate (k) in emissions that appeared to be unduly high, possibly as an artifact of measurement uncertainty, for chemicals in paint for test A2. These potential outlier cases include ethylbenzene, p-xylene, propyl-cyclohexane, and one of the branched undecanes, each with an estimated k value between 45 and 75, or about an order of magnitude higher than most other estimated k values.

Another notable pattern apparent in both Table A-2 and Table A-3 is that, for virtually all chemicals, the estimated decay rate constant is higher (i.e., faster rate of decline) for paint than for primer. This faster rate of decline for chemicals in paint is believed to be related to its lower wet film thickness. That is, a "thinner" film could be expected to result in a more rapid rate of off-gassing or volatilization. This apparent relationship between volatilization rate and wet film thickness is discussed further below under the topic of an empirical emissions model that has been developed for chemicals released from alkyd primer and paint.

The emitted mass for each chemical can be estimated as the integral of equation A-1, or E_0/k (values for E_0 and k are shown for each chemical in Tables A-2 and A-3). The applied mass for each chemical is the total applied paint mass multiplied by the chemical weight fraction from bulk analysis (shown for each chemical in Table A-1). The recovery for each chemical, shown in Table A-4, is defined as ratio of emitted mass to applied mass; ideally, the recovery value would be close to unity, or 100 percent. Considering measurement uncertainty, recovery values in the range of 70 to 130 percent are reasonably close to the ideal value. Cases meeting this criterion, and the criterion of adequate fit for the single-exponential emissions model (i.e., R^2 value of at

least 0.7 in Table A-2 or Table A-3), were used for development of a predictive model for emissions as described below.

Table A-2. Alkyd Parameter Estimates (Single-exponential Emissions Model) for Test A1

Chemical	Primer			Paint		
	Eo (mg/h)	k (h^{-1})	R^2	Eo (mg/h)	k (h^{-1})	R^2
Toluene	5.4	5.8	0.99	3.5	7.9	0.87
Octane	3.6	4.6	0.96	8.9	9.4	0.89
MEKO	16.1	4.0	0.98	9.8	5.6	0.95
Ethylbenzene	18.7	5.0	0.97	15.6	8.0	0.89
p-Xylene	68.5	4.9	0.97	60.4	8.5	0.94
Nonane	84.4	3.5	0.95	82.3	7.8	0.94
o-Xylene	26.5	4.3	0.95	22.1	8.0	0.94
Propyl-cyclohexane	254.8	3.0	0.95	300.6	7.4	0.94
Isopropylbenzene	3.1	3.7	0.91	1.9	5.9	0.90
n-Propylbenzene	14.5	3.1	0.91	10.5	6.9	0.94
p-Ethyltoluene	76.9	3.7	0.85	64.5	8.3	0.94
1,3,5-Trimethylbenzene	21.4	0.8	0.87	65.1	8.6	0.93
Decane	97.1	1.3	0.87	261.2	5.0	0.94
o-Ethyltoluene	12.8	2.2	0.69	14.3	7.4	0.90
1,2,4-Trimethylbenzene	42.8	1.8	0.84	43.5	5.4	0.94
1,2,3-Trimethylbenzene	5.4	1.4	0.78	6.2	4.8	0.93
2-Methyldecane	10.8	1.1	0.87	22.7	3.1	0.90
Trans-decalin	11.0	1.0	0.84	21.7	4.0	0.93
Undecane	21.4	0.4	0.81	67.6	2.1	0.91
Dodecane	0.9	0.1	0.37	1.4	0.3	0.81

Table A-3. Alkyd Parameter Estimates (Single-exponential Emissions Model) for Test A2

Chemical	Primer			Paint		
	Eo (mg/h)	k (h^{-1})	R^2	Eo (mg/h)	k (h^{-1})	R^2
Toluene	6.3	6.4	0.99	--	--	--
Octane	5.5	6.1	0.99	--	--	--
MEKO	6.5	4.1	0.19	0.1	0.0	0.43
Ethylbenzene	19.9	4.6	0.98	43.6	74.5	0.97
p-Xylene	74.0	4.8	0.98	197.7	75.5	0.98
Nonane	82.4	3.1	0.97	9.5	16.9	0.96
o-Xylene	27.8	4.0	0.97	16.9	13.3	0.97
Propyl-cyclohexane	256.1	2.6	0.96	50.9	63.5	0.92
Isopropylbenzene	3.1	3.3	0.93	--	--	--
n-Propylbenzene	15.4	3.1	0.89	--	--	--
p-Ethyltoluene	98.0	4.1	0.89	5.7	7.2	0.91
1,3,5-Trimethylbenzene	42.1	3.7	0.69	2.0	5.2	0.90
Decane	119.3	1.7	0.82	58.5	4.6	0.96
Branched Decane A	42.0	2.4	0.84	209.5	5.5	0.97
Branched Decane B	15.6	2.2	0.78	64.0	4.6	0.97
o-Ethyltoluene	23.4	3.9	0.84	--	--	--
1,2,4-Trimethylbenzene	55.6	2.4	0.78	3.9	4.1	0.91
1,2,3-Trimethylbenzene	5.9	1.5	0.78	--	--	--
2-Methyldecane	6.9	1.0	0.58	265.2	2.2	0.96
Trans-decalin	13.7	1.4	0.69	3.4	1.8	0.87
Undecane	21.6	0.5	0.64	13.2	1.4	0.93
Branched Undecane A	32.0	1.4	0.71	176.1	2.7	0.94
Branched Undecane B	4.1	0.7	0.72	85.2	2.7	0.93
Branched Undecane C	11.6	1.3	0.65	326.9	2.8	0.95
Branched Undecane D	11.2	1.2	0.60	1487.4	45.2	0.68
Branched Undecane E	6.3	0.9	0.33	200.6	3.8	0.81
Branched Undecane F	1.4	0.7	0.85	82.1	1.8	0.90
Dodecane	1.1	0.1	0.71	0.1	0.1	0.93

Table A-4. Recoveries for Chemical in Alkyd Primer and Paints

Chemical	Test A1-Primer			Test A1-Paint			Test A2-Primer			Test A2-Paint		
	Chemical Applied (mg)	Chemical Emitted (Eo/k)	Recovery (%)	Chemical Applied (mg)	Chemical Emitted (Eo/k)	Recovery (%)	Chemical Applied (mg)	Chemical Emitted (Eo/k)	Recovery (%)	Chemical Applied (mg)	Chemical Emitted (Eo/k)	Recovery (%)
Toluene	2.69	0.93	34.58	3.09	0.44	14.38	2.80	0.98	34.97	--	--	--
Octane	1.61	0.77	47.87	1.88	0.95	50.79	1.68	0.89	53.11	--	--	--
MEKO	17.67	4.02	22.73	4.21	1.74	41.41	18.44	1.60	8.67	5.71	3.82	66.99
Ethylbenzene	8.53	3.76	44.01	4.00	1.96	48.93	8.90	4.30	48.32	2.03	0.59	28.88
p-Xylene	26.75	13.98	52.26	11.82	7.12	60.22	27.90	15.43	55.32	6.53	2.62	40.07
Nonane	26.07	23.99	92.00	9.42	10.58	112.29	27.20	26.67	98.04	0.89	0.56	62.76
o-Xylene	11.49	6.15	53.55	4.36	2.77	63.45	11.99	6.99	58.30	2.85	1.27	44.36
Propyl-cyclohexane	89.38	85.76	95.96	35.64	40.57	113.83	93.23	97.07	104.12	1.32	0.80	60.87
Isopropylbenzene	1.34	0.84	62.19	0.37	0.33	89.27	1.40	0.95	68.11	--	--	--
n-Propylbenzene	6.05	4.69	77.51	1.58	1.52	96.39	6.31	5.02	79.55	--	--	--
p-Ethyltoluene	26.61	20.73	77.90	8.79	7.78	88.50	27.76	24.03	86.57	1.23	0.79	64.33
1,3,5-Trimethylbenzene	13.91	25.91	186.29	3.78	7.60	200.95	14.51	11.43	78.74	0.51	0.38	74.85
Decane	79.30	76.81	96.86	46.22	52.72	114.06	82.72	70.70	85.47	12.73	12.78	100.37
Branched Decane A	--	--	--	--	--	--	--	--	--	37.69	37.91	100.60
Branched Decane B	--	--	--	--	--	--	--	--	--	13.58	13.89	102.29
o-Ethyltoluene	10.21	5.86	57.38	2.59	1.93	74.37	10.66	5.99	56.19	--	--	--
1,2,4-Trimethylbenzene	32.12	24.19	75.31	8.60	8.05	93.63	33.51	23.28	69.49	1.81	0.95	52.34
1,2,3-Trimethylbenzene	8.00	3.77	47.13	2.27	1.30	57.15	8.34	4.00	47.92	--	--	--
2-Methyldecane	13.24	9.95	75.14	7.50	7.26	96.86	13.81	7.02	50.81	114.85	118.61	103.27
Trans-decalin	16.20	11.28	69.67	6.83	5.43	79.51	16.89	9.72	57.53	2.61	1.85	71.07
Undecane	58.87	55.07	93.55	35.64	32.20	90.34	61.41	46.03	74.95	12.22	9.55	78.11
Branched Undecane A	--	--	--	--	--	--	--	--	--	60.43	65.58	108.51
Branched Undecane B	--	--	--	--	--	--	--	--	--	29.88	31.53	105.50
Branched Undecane C	--	--	--	--	--	--	--	--	--	109.94	115.22	104.80
Branched Undecane D	--	--	--	--	--	--	--	--	--	16.52	32.89	199.07
Branched Undecane E	--	--	--	--	--	--	--	--	--	55.53	53.16	95.74
Branched Undecane F	--	--	--	--	--	--	--	--	--	47.50	46.88	98.69
Dodecane	12.43	14.63	117.71	5.18	4.30	82.90	12.97	7.06	54.44	0.49	1.09	223.09

As stated earlier, a single-exponential model should be sufficient to describe the emissions behavior of chemicals in alkyd paint, because they tend to volatilize quite rapidly. To verify this assertion, a double-exponential model was fit for selected chemicals in alkyd paint, representing a range of volatilities. The assessment was limited to the painting portion of the test, to have a sufficiently long "tail" to enable a reliable fit to the data (chamber measurements for the priming portion of the test lasted only 48 hours). As described in greater detail for latex paint in Appendix C, the initial emission rate and rate constant for emissions decline were estimated first for the "slow" phase of emissions decline, using concentration data after the first 24 hours following paint application. Next, the entire time series was used to estimate parameters for the "fast" phase, treating the estimates for the slow phase as "knowns."

Results of the assessment are summarized in Table A-5 for the seven chemicals used for this exercise. Although there are parameter estimates for both the fast and the slow phases for the double-exponential model, only the estimates for the fast phase are shown in the table, for direct comparison with those for the single-exponential model. As shown in the table, there is virtually no difference in the two sets of parameter estimates, supporting the assertion that a single-exponential model is adequate for chemicals in alkyd paint. The R^2 values (fraction of variance explained by the model) in the table also are practically identical for the two sets of estimates, indicating that addition of a second exponential makes no significant improvement to the fit. The only chemical for which the R^2 value changed noticeably (from 0.81 to 0.83) was undecane, the least volatile of the chemicals used in this assessment.

Table A-5. Alkyd Parameter Estimates (Single- vs. Double-exponential Emissions Model) for Painting Portion of Test A1

Chemical	Single-exponential Model			Double-exponential Model*		
	Eo (mg/h)	k (h^{-1})	R^2	Eo (mg/h)	k (h^{-1})	R^2
p-Xylene	60.4	8.5	0.94	60.4	8.5	0.94
o-Xylene	22.1	8.0	0.94	22.1	8.0	0.94
n-Propylbenzene	10.5	6.9	0.94	10.5	6.9	0.94
1,2,4-Trimethylbenzene	43.5	5.4	0.94	43.7	5.4	0.94
2-Methyldecane	22.7	3.1	0.90	22.8	3.2	0.90
Undecane	67.6	2.1	0.91	68.1	2.1	0.91
Dodecane	1.4	0.3	0.81	1.4	0.4	0.83

*Estimates shown for Eo and k are for the first ("fast") exponential of the double-exponential model, for direct comparison with the estimates for the single-exponential model; the R^2 value is for both exponentials combined.

A4. DEVELOPMENT OF A PREDICTIVE MODEL

Table A-6 lists the estimated emission decay rates for chemicals in primer and paint from the two chamber tests that were conducted (tests A1 and A2). Chemical properties (molecular weight and vapor pressure) also are listed in the table. Perhaps the most noteworthy relationship apparent from the table is that, for nearly every chemical, the decay rate for the chemical in paint was consistently higher (by about a factor of two) than that for the same chemical in primer. The primary difference between the primer and paint application in these tests was the much greater wet film thickness (by about a factor of four) for primer than paint. Thus, there is an apparent inverse relationship between film thickness and the decay rate – the greater the film thickness (as with primer), the slower the decay rate.

Table A-6. Emission Decay Rates and Chemical Properties for Chemicals in Alkyd Primer and Paints

Chemical	Emission Decay Rates (h^{-1})				Molecular Weight (g/mole)	Vapor Pressure (mm Hg)
	Test A1-Primer	Test A1-Paint	Test A2-Primer	Test A2-Paint		
Toluene	5.82	7.93	6.45	--	92.2	12.10
Octane	4.62	9.38	6.12	--	114.3	18.90
MEKO	4.00	5.64	4.09	0.02	87.1	0.90
Ethylbenzene	4.98	7.98	4.62	74.46	106.2	4.34
p-Xylene	4.90	8.49	4.80	75.53	106.2	4.34
Nonane	3.52	7.79	3.09	16.90	128.3	7.08
o-Xylene	4.30	7.99	3.97	13.32	106.2	4.34
Propyl-cyclohexane	2.97	7.41	2.64	63.50	126.3	4.59
Isopropylbenzene	3.74	5.92	3.28	--	120.2	2.89
n-Propylbenzene	3.09	6.89	3.07	--	120.2	1.56
p-Ethyltoluene	3.71	8.28	4.08	7.21	120.2	1.56
1,3,5-Trimethylbenzene	0.83	8.57	3.69	5.18	120.2	1.57
Decane	1.26	4.96	1.69	4.58	142.3	2.67
Branched Decane A	--	--	2.36	5.53	142.3	2.67
Branched Decane B	--	--	2.15	4.61	142.3	2.67
o-Ethyltoluene	2.19	7.40	3.91	--	120.2	1.56
1,2,4-Trimethylbenzene	1.77	5.41	2.39	4.11	120.2	1.57
1,2,3-Trimethylbenzene	1.43	4.78	1.47	--	120.2	1.57
2-Methyldecane	1.09	3.13	0.99	2.24	156.4	1.82
Trans-decalin	0.97	3.99	1.41	1.84	138.3	1.35
Undecane	0.39	2.10	0.47	1.38	156.4	1.02
Branched Undecane A	--	--	1.45	2.69	156.4	1.82
Branched Undecane B	--	--	0.74	2.70	156.4	1.82
Branched Undecane C	--	--	1.30	2.84	156.4	1.82
Branched Undecane D	--	--	1.18	45.22	156.4	1.82
Branched Undecane E	–	–	0.90	3.77	156.4	1.82

For paint in test A-2, there are six chemicals with estimated emission decay rates greater than ten. Such outcomes are believed to be an artifact, probably due to insufficient values for the rising part of the concentration curve.

Empirical Model

Relationships between the emission decay rate and chemical properties, if any, cannot be deduced readily from Table A-6. The scatter plots in Figures A-4 and A-5 indicate an inverse relationship between the decay rate and molecular weight ($R^2 = 0.45$) and a direct relationship between the decay rate and vapor pressure ($R^2 = 0.12$). That is, higher values of molecular weight are associated with slower emission decay rates, like the relationship between film thickness and decay rate, whereas higher values of vapor pressure are associated with higher emission rates.

The above relationships indicate that the following empirical model may be useful as a tool for predicting the emission decay rate from chemical properties and wet film thickness:

$$k = a * VP^b / (MW^c * FT^d) \quad \text{(A-4)}$$

where k = emission decay rate (inverse hours);
VP = vapor pressure (torr);
MW = molecular weight (g/mole);
FT = film thickness (mil); and
a, b, c, and d are constants to be estimated.

Parameter estimates for the constants were obtained through nonlinear regression analysis. As noted previously, the subset of chemicals from tests A-1 and A-2 that met certain conditions was used in the estimation procedure. The model with parameter estimates can be expressed as follows:

$$E = 2.95 * 10^9 * VP^{0.27} / (MW^{4.02} * FT^{0.58}) \quad \text{(A-5)}$$

This model provides a reasonably good fit to the data, with an R^2 value of 0.86. The relatively strong relationship between emission decay rates estimated from the chamber data and those predicted by the empirical model is illustrated in Figure A-6.

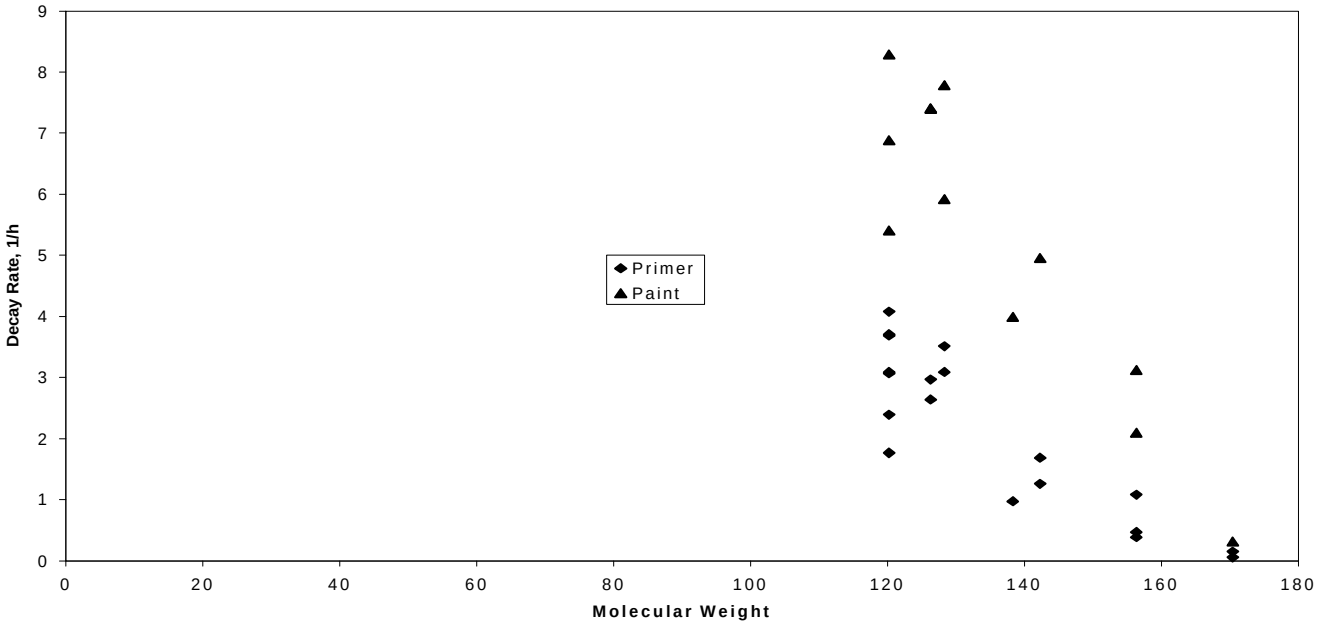

Figure A-4. Relationship between Emission Decay Rate and Molecular Weight.

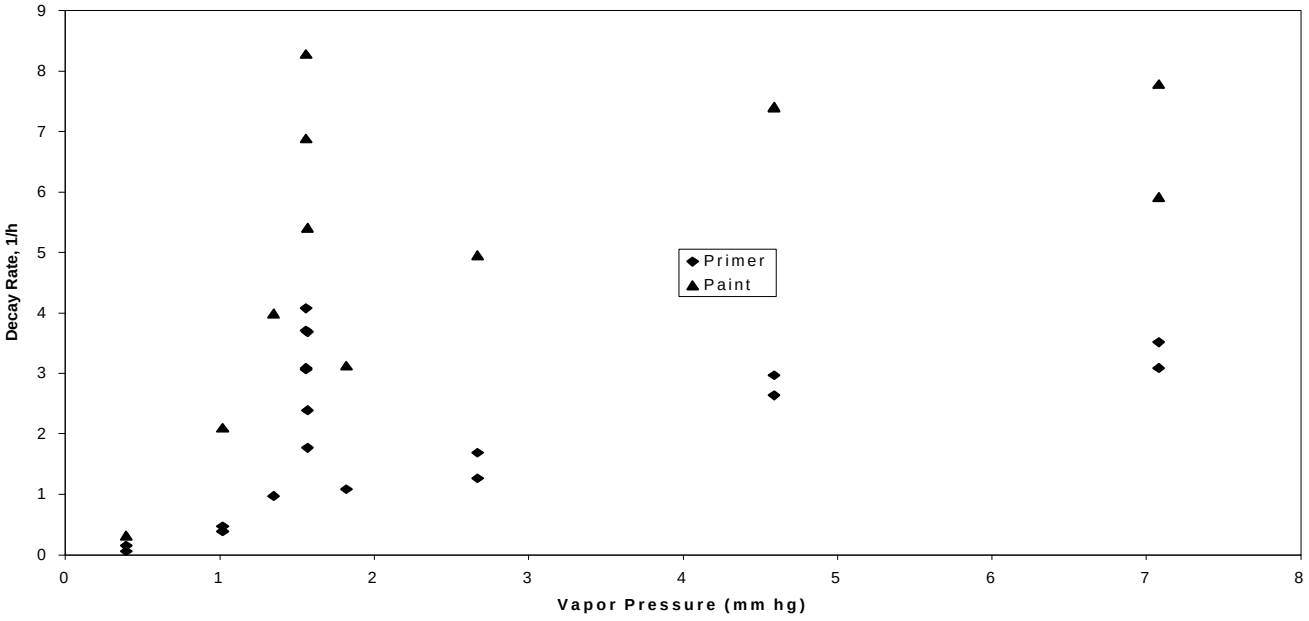

Figure A-5. Relationship between Emission Decay Rate and Vapor Pressure.

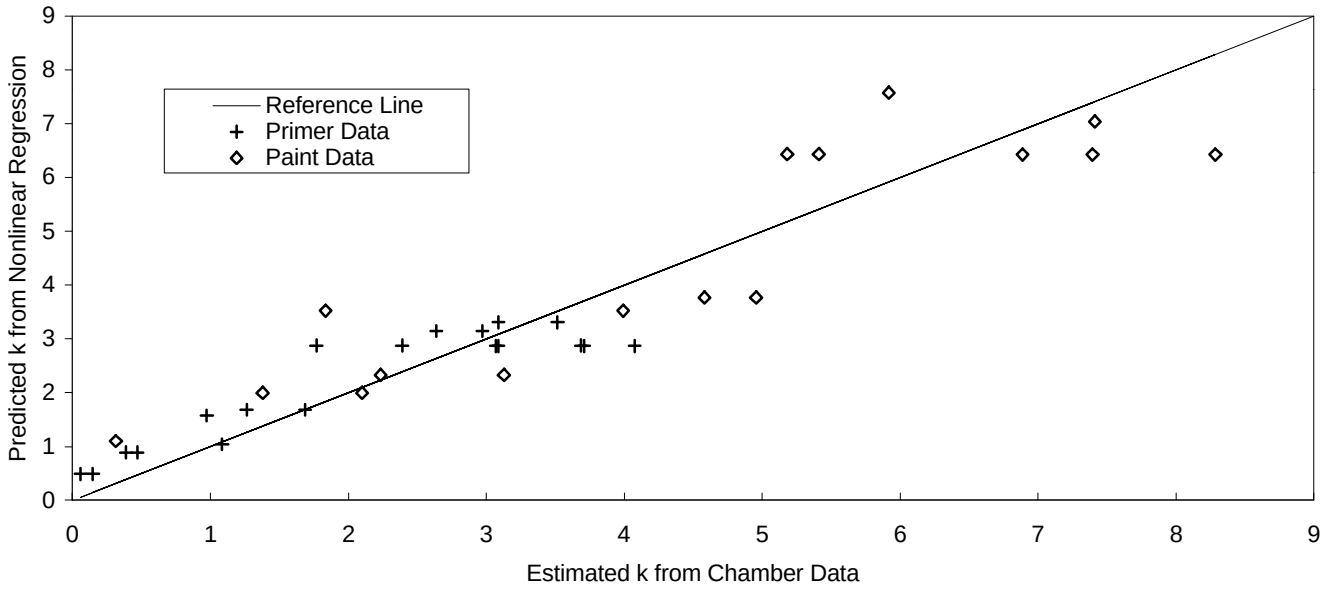

Figure A-6. Comparison of Predicted Emission Decay Rates from Empirical Model with Estimated Decay Rates from Chamber Data.

Table A-7 provides a comparison between predicted emission decay rates, based on the empirical model (see Equation A-5), and decay rates that were estimated from the chamber concentration data. As noted above, not all chemicals were used in developing the empirical model. Most of the chemicals with the largest discrepancy between predicted and estimated rates have larger k values and were not used in development of the predictive model. The majority of the errors have a positive sign, meaning that the predicted decay rate typically is larger then estimated rate. As a result, the empirical model will tend to provide a conservative prediction – that is, a larger k value will result in a higher modeled peak concentration, other things being equal.

The empirical model tends to have a larger prediction error for chemicals with a lower molecular weight (see Figure A-7). Although the relationship is not as pronounced, the model also tends to have a greater prediction error for chemicals with higher vapor pressure (see Figure A-8), with the notable exception of MEKO (which has a relatively low vapor pressure of 0.9 torr but relatively high prediction errors, on the order of 5 and 15 for primer and paint, respectively). As noted above, the greatest prediction errors generally are for chemicals with higher k values; most of these chemicals have a comparatively low molecular weight and high vapor pressure.

Table A-7. Predicted Versus Estimated Emission Decay Rates for Chemicals in Test A1

Chemical	Primer				Paint			
	Predicted k	Estimated k	Error*	Percent Error**	Predicted k	Estimated k	Error	Percent Error
Toluene	14.4	5.8	8.6	147	32.2	7.9	24.3	307
Octane	6.8	4.6	2.2	48	15.3	9.4	5.9	63
MEKO	9.1	4.0	5.1	126	20.3	5.6	14.6	259
Ethylbenzene	6.2	5.0	1.2	25	13.9	8.0	5.9	74
p-Xylene	6.2	4.9	1.3	27	13.9	8.5	5.4	64
Nonane	3.3	3.5	-0.2	6	7.4	7.8	-0.4	5
o-Xylene	6.2	4.3	1.9	44	13.9	8.0	5.9	74
Propyl-cyclohexane	3.1	3.0	0.2	6	7.0	7.4	-0.4	5
Isopropylbenzene	3.4	3.7	-0.4	9	7.6	5.9	1.7	28
n-Propylbenzene	2.9	3.1	-0.2	7	6.4	6.9	-0.5	7
p-Ethyltoluene	2.9	3.7	-0.8	23	6.4	8.3	-1.9	22
1,3,5-Trimethylbenzene	2.9	0.8	2.1	247	6.4	8.6	-2.1	25
Decane	1.7	1.3	0.4	33	3.8	5.0	-1.2	24
o-Ethyltoluene	2.9	2.2	0.7	31	6.4	7.4	-1.0	13
1,2,4-Trimethylbenzene	2.9	1.8	1.1	63	6.4	5.4	1.0	19
1,2,3-Trimethylbenzene	2.9	1.4	1.5	101	6.4	4.8	1.7	35
2-Methyldecane	1.0	1.1	-0.04	4	2.3	3.1	-0.8	26
Trans-decalin	1.6	1.0	0.6	60	3.5	4.0	-0.5	12
Undecane	0.9	0.4	0.5	129	2.0	2.1	-0.1	5
Dodecane	0.5	0.1	0.4	716	1.1	0.3	0.8	247

* Error = (predicted k - estimated k).

**Percent Error = (absolute value of error / estimated k) * 100.

Summary statistics on prediction errors for the empirical model are provided in Table A-8 for three sets of chemicals – (1) chemicals used to develop the model, (2) all chemicals used in test A1, and (3) the subset of chemicals in test A1 that were not used in developing the model. Not unexpectedly, the smallest errors were for the set of chemicals used to develop the model, and the largest errors were for the test-A1 subset not used in developing the model. The medians in the table are more indicative of the central tendency for prediction error, as the mean can be heavily influenced by relatively large prediction errors at the upper tail of the distribution. The median errors are 0.5 (22 percent) for chemicals used to develop the empirical model, 1.1 (30 percent) for all test-A1 chemicals, and 2.1 (63 percent) for the subset of test-A1 chemicals that were not used in developing the model. There generally is a larger prediction error for chemicals in paint than for chemicals in primer.

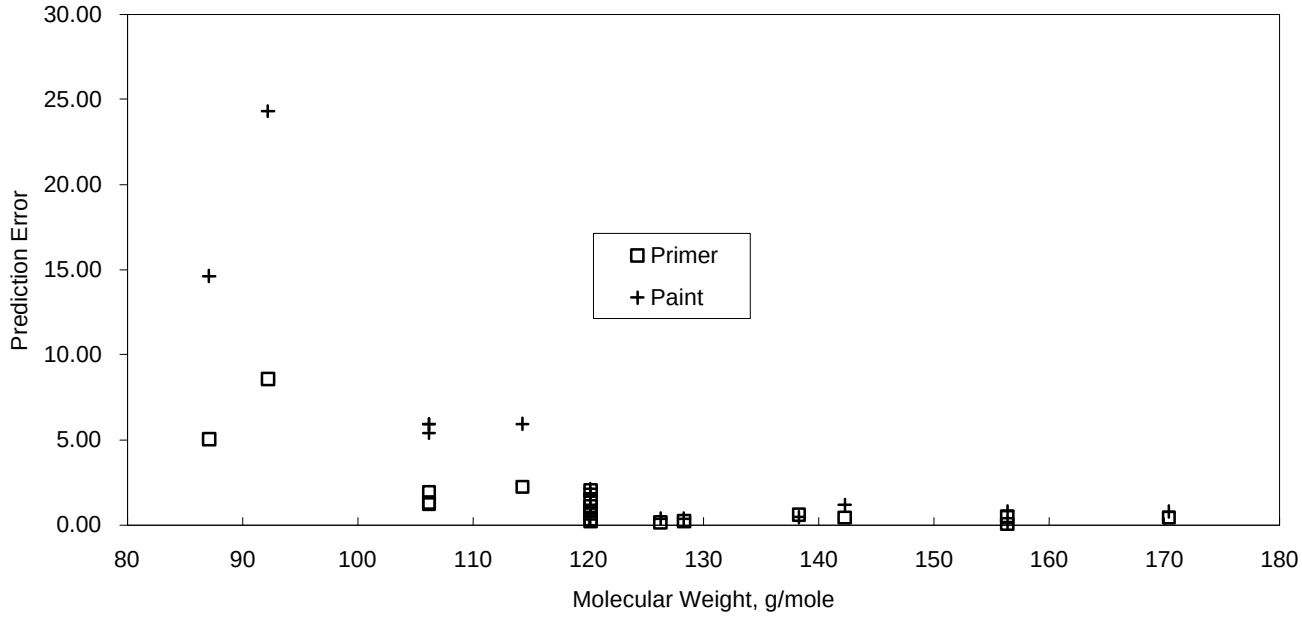

Figure A-7. Relationship between Empirical Model Prediction Error and Molecular Weight.

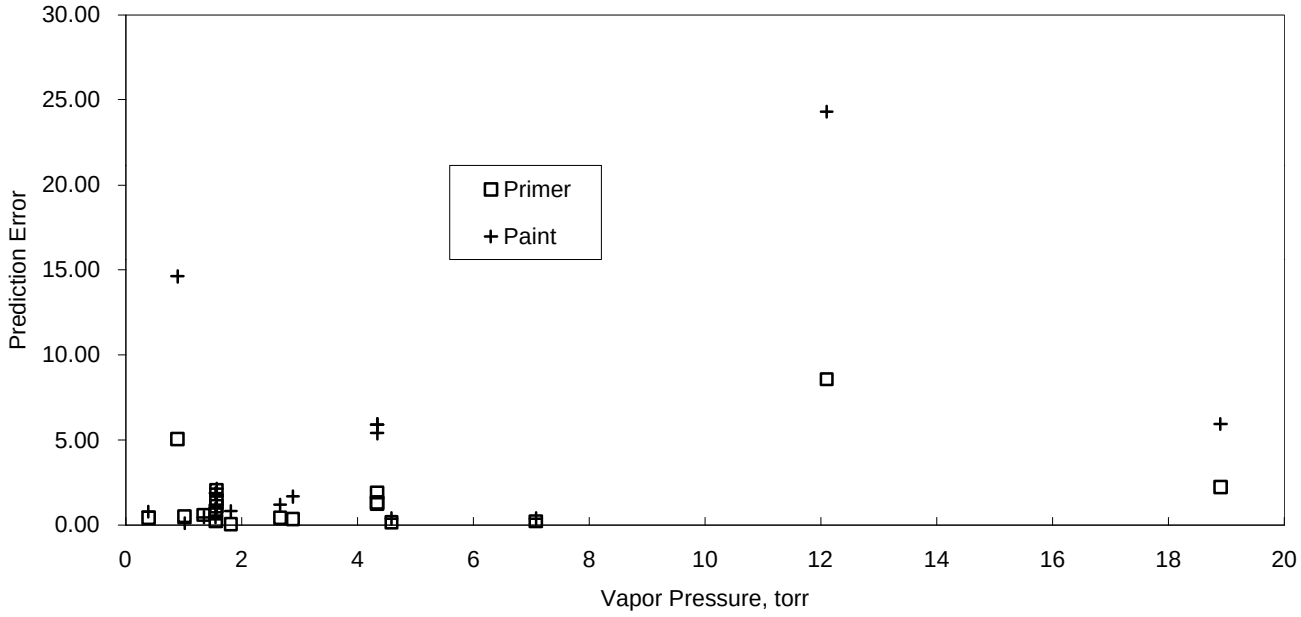

Figure A-8. Relationship between Empirical Model Prediction Error and Vapor Pressure.

Table A-8. Summary Statistics on Errors in Emission Decay Rates Predicted by Empirical Model

Sets of Chemicals (number of chemicals per set)	Error			Percent Error		
	Mean	Median	Range	Mean	Median	Range
All chemicals used for model (35)	0.7	0.5	0.004-1.9	59	22	0.2 - 716
- chemicals in primer (19)	0.5	0.4	0.004-1.2	77	22	0.2 - 716
- chemicals in paint (16)	0.9	0.8	0.1 - 1.9	37	21	4 - 247
All chemicals in test 1 (40)	2.6	1.1	0.05-24.3	79	30	4 - 716
- chemicals in primer (20)	1.5	0.8	0.05 -	93	39	4 - 716
- chemicals in paint (20)	3.8	1.4	8.6	66	25	5 - 37
			0.1 -			
			24.3			
Chemicals in test 1 not used						
for the model (19)	4.8	2.1	0.4 -	90	63	5 - 307
- chemicals in primer (10)	2.5	1.7	24.3	81	46	9 - 246
- chemicals in paint (9)	7.4	5.9	0.4 - 8.6	101	64	5 - 307
			0.4 -			
			24.3			

The prediction errors for the empirical model are not severe, especially when considered in light of the evidence provided below in Table A-9. Once the emission decay rate becomes arbitrarily large (e.g., greater than 5 h^{-1}), doubling the rate has little effect on the peak concentration. Similarly, once the painting duration becomes arbitrarily long (e.g., longer than 3 hours), the decay rate has little effect on the peak concentration except at very low values (e.g., below 1 h^{-1}). As shown in the lower part of the table, the effect of the emission decay rate on single-event dose is even less pronounced, regardless of the painting duration.

For the data shown in Table A-9, a single-zone scenario was modeled whereby the walls of a "standard box" with a volume of 1,000 ft^3 were painted with one coat of paint. The default loading ratio of 0.25 ft^2/ft^3 was used, resulting in a painted surface area of 250 ft^2. The default film thickness for paint was used, and the application rate was varied in sequential model runs to achieve the durations listed in the table. The default density for alkyd paint was used along with an arbitrarily chosen chemical weight fraction of 0.01. For each run of the model, the default emission decay rate was replaced by one of the values listed in the table. The model was run for two days; for purposes of estimating a time-integrated dose over this duration, the exposed individual was placed in the painted box throughout the two-day modeling period.

Table A-9. Effect of Emission Decay Rate and Painting Duration on Modeled Peak Concentration and Single Event Dose

Emission Decay Rate	Painting Duration, hours				
	0.1	1	3	5	10
Peak Concentration, mg/m^3					
0.1	79	79	76	72	61
1	377	361	275	195	102
5	683	576	317	201	102
10	790	613	319	202	102
20	868	630	320	202	102
Single Event Dose, mg					
0.1	562	568	601	645	740
1	568	628	811	929	1040
5	571	721	934	1020	1090
10	574	751	952	1030	1100
20	579	768	962	1040	1100

A final look at the predictive capability of the empirical model was taken by modeling chamber concentrations of selected chemicals for test A1, applying Equation A-3 and using the known conditions of the test (i.e., chamber volume, air exchange rate, and applied mass of primer/paint) along with the chemical weight fraction from the bulk analysis (reported previously in Table A-1). The values for the emission decay rates (k) for primer and paint were taken from the empirical model, and values for the initial emission rates (Eo) were determined from the relationship that applied chemical mass is equal to Eo/k. Modeled chamber concentrations are shown in Figures A-9 to A-11 for nonane, o-xylene, and MEKO, respectively. Nonane is one of the chemicals used in developing the empirical model, and its modeled concentrations match the chamber data very well. The predicted k for o-xylene was 44 percent higher than measured for primer and 74 percent higher for paint; however, this over-estimation appears to have little impact as the modeled data again match measurements very well. For MEKO the predicted k values were substantially higher than estimated, and the modeled chamber concentrations are much higher than measured. However, the discrepancy also is due to the low recovery for MEKO (that is, integrated mass based on chamber concentrations was much lower than applied mass; see Table A-4).

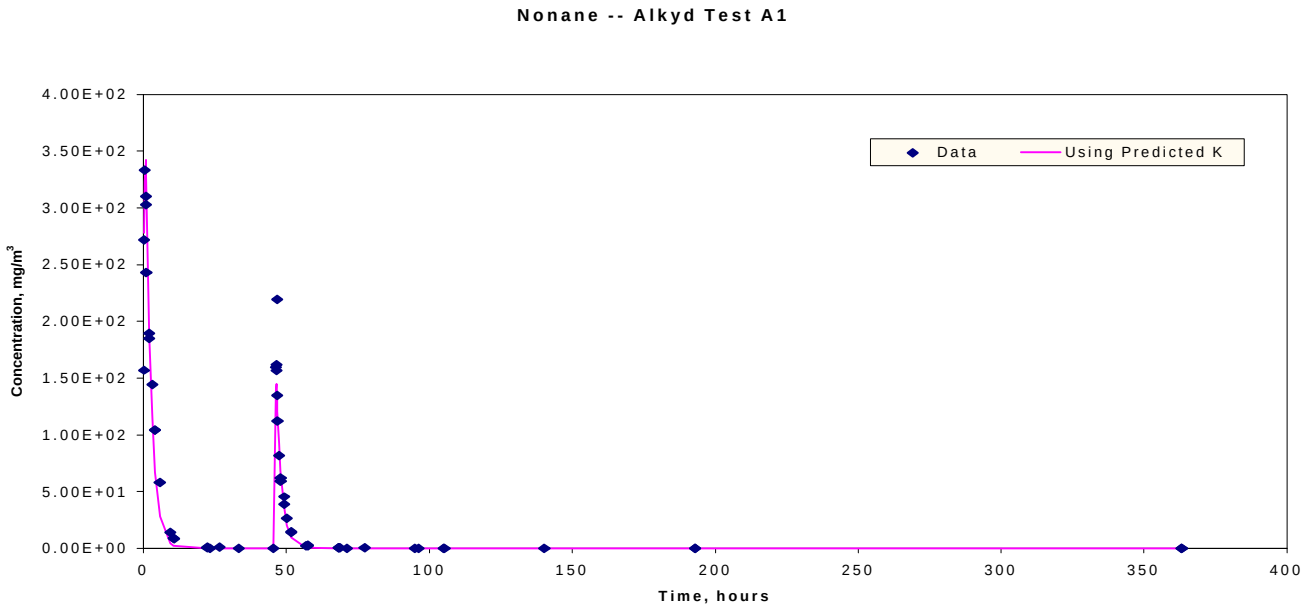

Figure A-9. Modeled Chamber Concentrations for Nonane Using Predicted Emission Decay Rates.

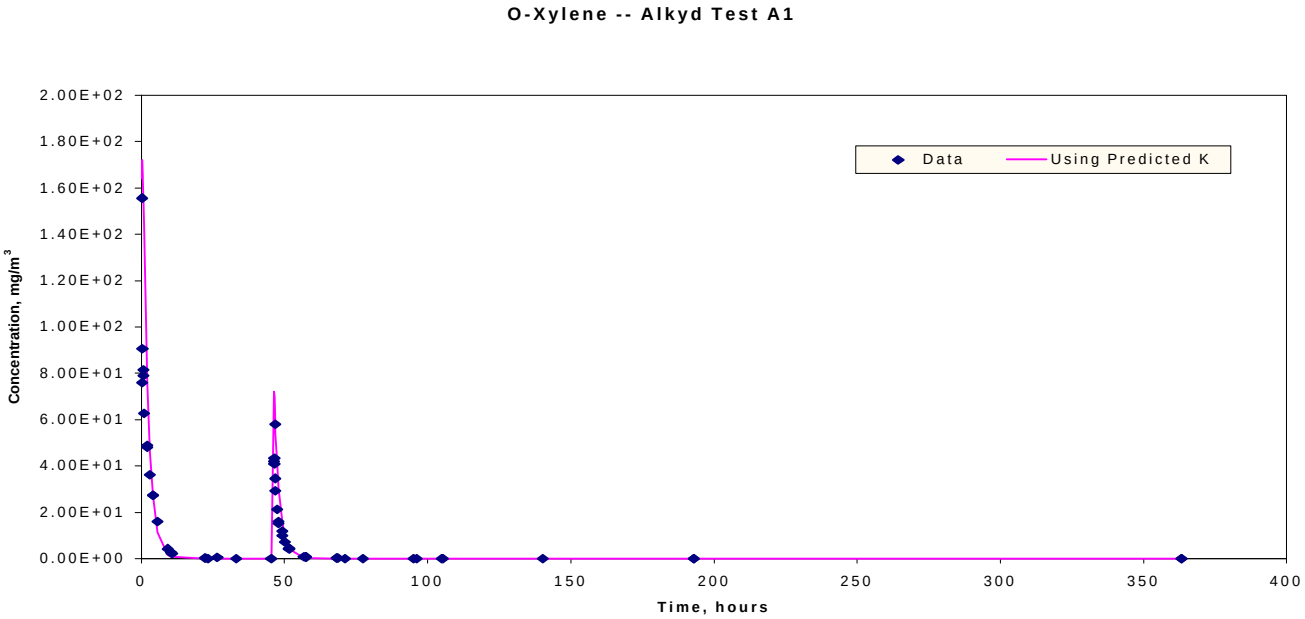

Figure A-10. Modeled Chamber Concentrations for O-xylene Using Predicted Emission Decay Rates.

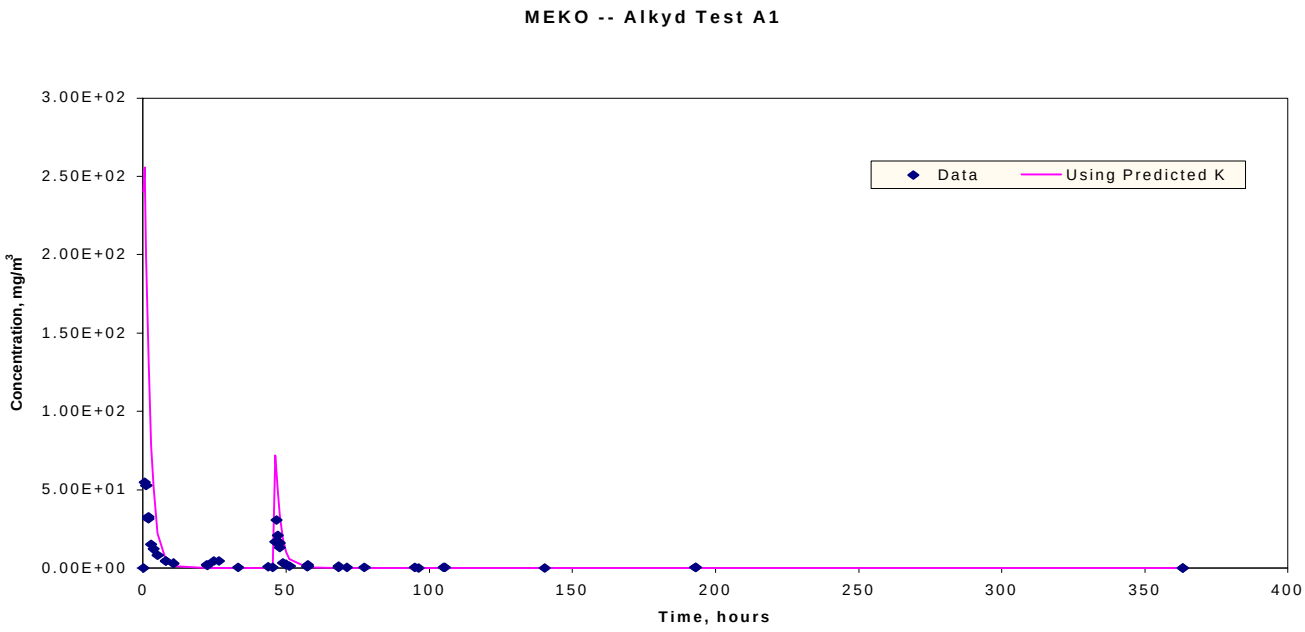

Figure A-11. Modeled Chamber Concentrations for MEKO Using Predicted Emission Decay Rates.

Semi-empirical Model

A potential alternative to the purely empirical model described above is a semi-empirical model suggested by Guo et. al (see Appendix B). The model is termed "semi-empirical" because it is based on chemical/physical principles and has some embedded constants derived from those principles, but it also has one or more parameter to be estimated from the chamber data. As noted earlier, the integral of a single-exponential emissions model is defined as E_o/k, where E_o is the initial emission rate and k is the emission decay rate. Since the integral, by definition, is the total emitted mass (equal to applied mass by assumption), the relationship alternatively can be expressed as:

$$k = E_o / AM \qquad \text{(A-6)}$$

where AM is the applied mass, which is the product of the wet film thickness times the paint density times the chemical weight fraction. Per Appendix B, E_o can be estimated as follows:

$$E_o = 1.32 * MTC * VP * MW/VM * y_i / y_o \qquad \text{(A-7)}$$

where 1.32 is a constant (see Appendix B for details);
MTC = mass transfer coefficient for the chemical;
VP = vapor pressure for the chemical;
MW = average molecular weight of VOCs in the formulation;
VM = volume of 1 mole gas under 1 atm (0.0243 m^3 at 23 °C);
y_i = weight fraction for the chemical; and
y_o = total weight fraction for all VOCs in the formulation.

Because the chemical weight fraction (y_i) appears in the equations for both E_o and AM, equation (A-7) can be simplified slightly as follows:

$$k = (1.32 * MTC * VP * MW/VM) / (FT * PD * y_o) \quad \text{(A-8)}$$

where FT is film thickness and PD is paint density. The mass transfer coefficient, in turn, is dependent on the diffusion coefficient (DC) and several other terms, most of which are constants (see Appendix B for details). The one term that is not a constant is the characteristic length of the emission source (equal to the square root of the source area). However, while this term is of use for applications relating to the chamber where tests were done, it may not apply directly to full-scale settings such as those for which the model is intended to be used. Thus, it can be ignored for this application. Since MTC then depends only on DC and a set of constants, and since MW/VM in the above equation also can be viewed as a constant (for the alkyd primer/paint formulations tested under this project, the average molecular weight was always close to 140 g/mole, the above equation can be reduced further to:

$$k = (A * DC * VP) / (FT * PD * y_o * 0.000623) \quad \text{(A-9)}$$

where A is a constant to be estimated;
DC is the diffusion coefficient for the chemical of interest (m^2/hr);
VP is the vapor pressure for the chemical (mm Hg);
FT is the film thickness (mil);
PD is the paint density (grams per gallon);
y_o is the total VOC weight fraction; and
0.000623 is a factor to convert FT and PD from units in the user interface (mil and g/gal, respectively) to units consistent with the equations in Appendix B.

The diffusion coefficient (DC) for a chemical in the above equation can be estimated from its molecular weight (MW) using the following equation that is provided in EPA's CEB Engineering Manual:

$$DC = (1/29 + 1/MW)^{0.5} * MW^{-0.33} * 0.36 \qquad \text{(A-10)}$$

where 0.36 is a conversion factor from cm^2/sec (the units for equation A-10) to m^2/hr (the units needed for equation A-9).

The above model (equation A-9) for the emission decay rate, although based almost in entirety on chemical/physical principles, still must be termed semi-empirical because of the need to estimate one term (the constant A) using the set of emission decay rates derived from the chamber data. The best-fit value for A, based on linear regression analysis, was determined to be 240. Comparisons of the values for k predicted from the above equation with the values estimated from the chamber data are shown in Figure A-12. Although the fit is relatively modest ($R^2 = 0.49$), the semi-empirical model may have broader applicability (e.g., outside this project) than the empirical model because it is less dependent on the chamber data.

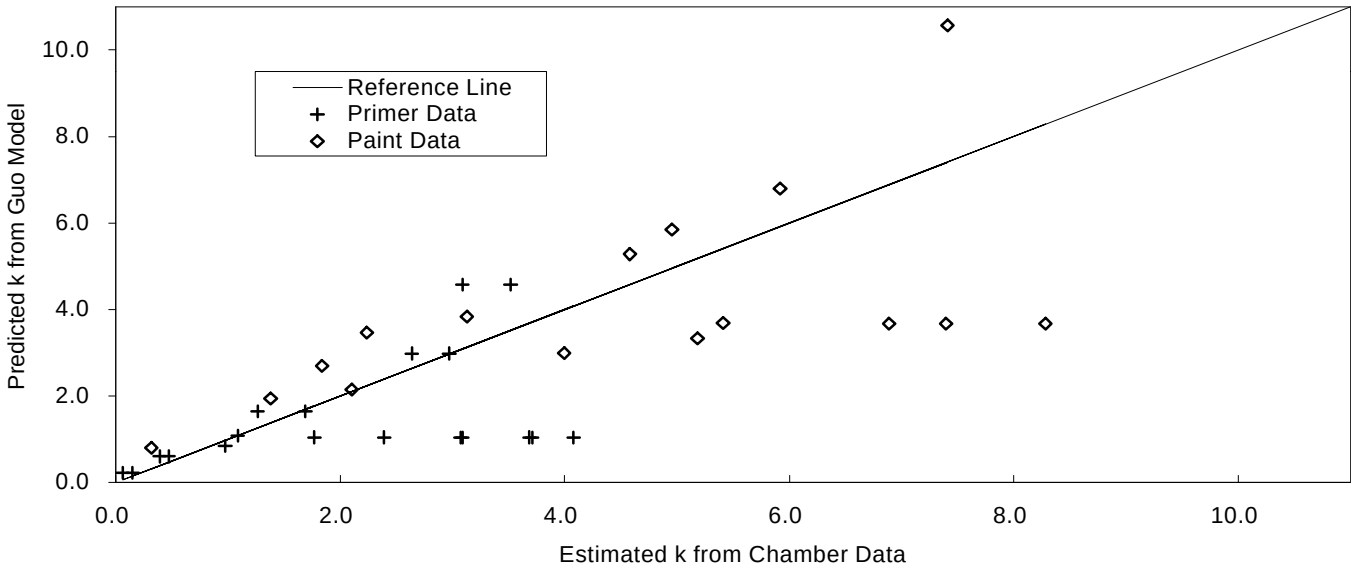

Figure A-12. Comparison of Predicted Emission Decay Rates from Semi-empirical Model with Estimated Decay Rates from Chamber Data.

A5. SMALL-CHAMBER SINK TESTS

Three small-chamber tests were conducted by ARCADIS Geraghty and Miller, Inc., to evaluate sink effects for four VOCs – methyl ethyl ketoxime (MEKO), 1,2,4-trimethylbenzene, 2-methyldecane, and undecane. Two sink tests involved placing either aged carpet or gypsum wallboard in the chamber as a sink material. For the third test, used as a baseline for comparison, there was no sink material in the chamber. The chamber was "dosed" with known input concentrations of the VOCs for 48 hours, after which clean air was supplied to the chamber. The VOCs were generated by passing clean air through diffusion vials that were held at a constant temperature. VOC concentrations in the chamber were measured periodically both in the chamber inlet and outlet streams during the 48-hour dosing period, and then in the chamber outlet stream for 12 days after dosing was terminated.

The chamber used for the sink tests has a volume of 53 liters (0.053 m^3). For both carpet and wallboard the sink area for the tests was 696.8 cm^2 (0.0697), resulting in a loading ratio of 1.315 m^2/m^3. During both tests the air exchange rate averaged 0.51 air changes per hour (ACH). The average temperature was 22.9 °C for the carpet test and 21.9 °C for the wallboard test. The average relative humidity was 51.5 % for the carpet test and 49.9 % for the wallboard test.

Figure A-13 shows the concentrations in the outlet stream for MEKO during the three tests (no sink, carpet, and wallboard). With no sinks, the chamber concentration approached a steady-state value of about 11 mg/m^3, equivalent to the concentration in the input stream. Once dosing was terminated, the concentration rapidly approached zero due to the supply of clean air to the chamber. With carpet as the sink, the peak concentration was reduced to about 9 mg/m^3 and the return toward zero concentration was delayed, indicating a modest sink effect. For wallboard the sink effect was more pronounced – the peak concentration reached only about 4-5 mg/m^3.

Figure A-14 shows the concentrations for undecane during the same three tests. In this case the sink effect was minimal – the rise to the peak chamber concentration with carpet or wallboard was delayed slightly, but the peak still reached 11-12 mg/m^3 (equivalent to that in the input stream) within the 48-hour dosing period. Similarly, after clean air was introduced, the return toward zero concentration was delayed slightly but zero concentration still was reached. By comparison, for MEKO there still were measurable concentrations days after the dosing was terminated. The behaviors for 1,2,4-trimethylbenzene and 2-methyldecane were quite similar to that of undecane.

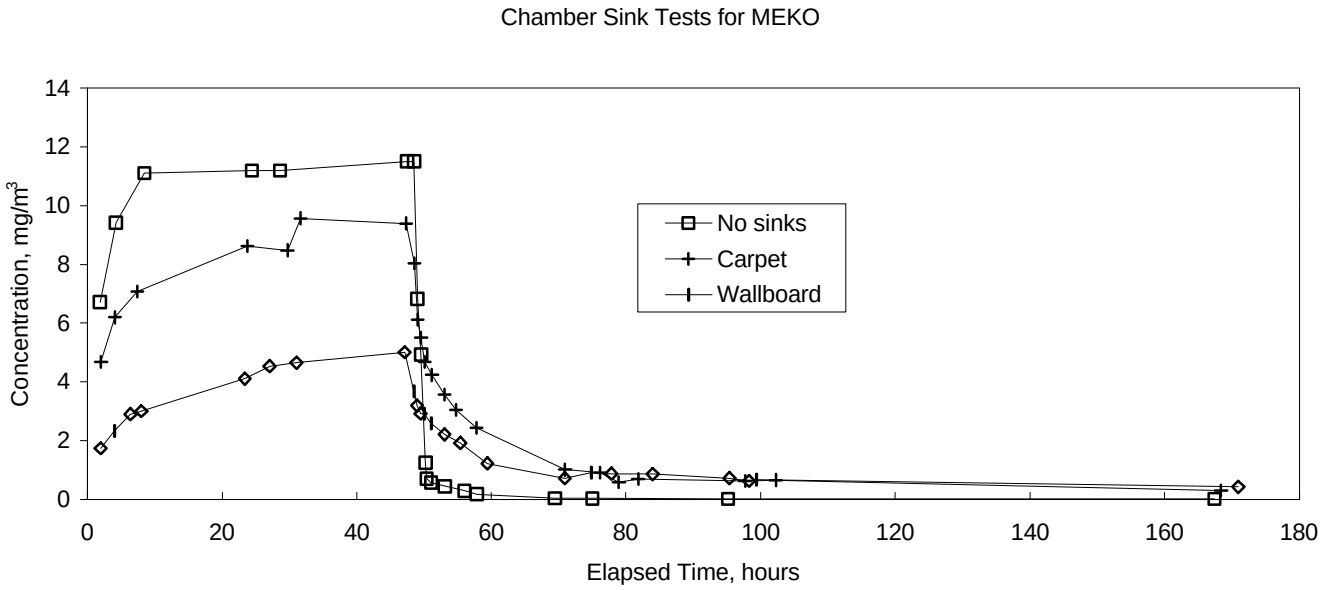

Figure A-13. Chamber Concentrations for MEKO during Sink Tests.

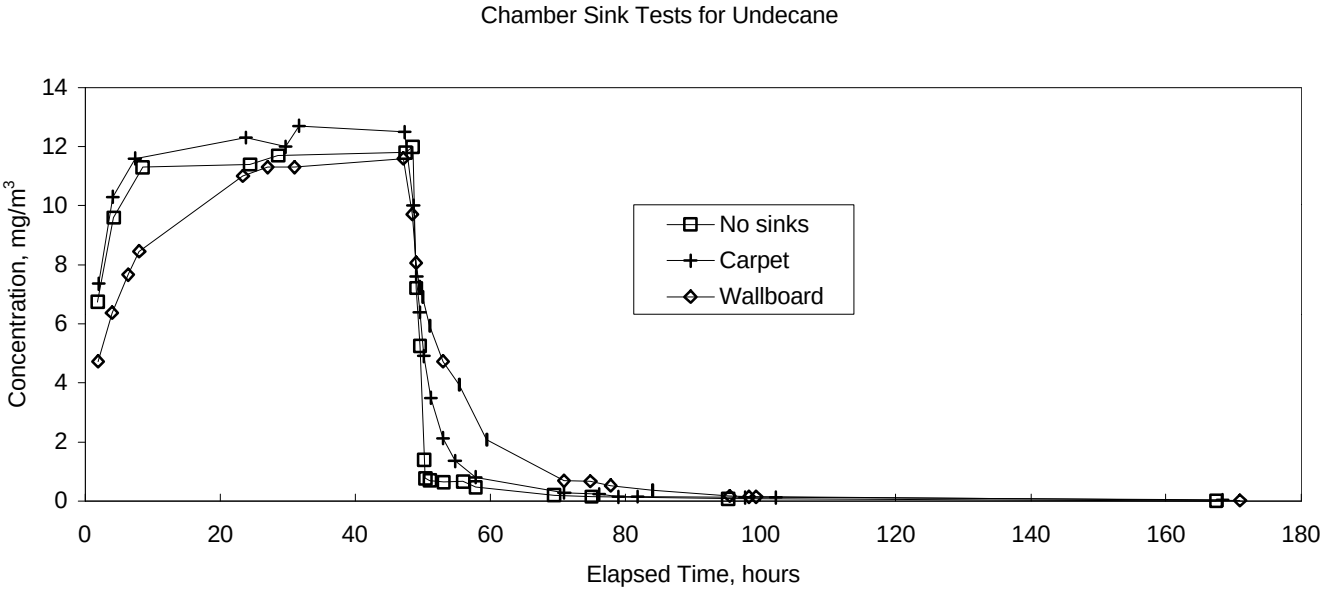

Figure A-14. Chamber Concentrations for Undecane during Sink Tests.

The reversible-sink model used in the calculation engine for WPEM describes adsorptive and desorptive sink behavior based on the Langmuir isotherm, which assumes a monolayer of molecules on a homogeneous surface. The reversible-sink model has both a removal rate and a re-emission rate. The removal rate (rate to the sink) is a product of the sink rate times the indoor-air concentration. The sink rate, in turn, is the product of the deposition velocity (in m/hr) times the sink area (m^2), with resultant units of m^3/hr. Thus, the removal rate has units of mg/hr. The re-emission rate (rate from the sink) is the product of the desorption rate (in inverse hours), the sink area (m^2), and the mass accumulated in the sink (mg/m^2), with resultant units of mg/hr.

The following equations (after Tichenor et al., 1991) describe rates to and from a reversible sink:

$$\textit{Rate to the Sink} = K_a * A * C \qquad \text{(A-11)}$$

$$\textit{Rate from the Sink} = K_d * A * M \qquad \text{(A-12)}$$

where:
- K_a = adsorption rate constant (m/hr)
- A = sink area (m^2)
- C = concentration in air in contact with the sink (mg/m^3)
- K_d = desorption rate constant (inverse hours)
- M = mass accumulated in the sink (mg/m^2).

This sink model assumes that a very small fraction of the potential adsorption sites on the sink are occupied. For this reason, the limitation on saturation of the indoor sink (not to be confused with a pollutant's saturation concentration in air) is neglected in the model.

For each of the four VOCs used in the chamber sink tests, values for K_a and K_d were estimated through an iterative technique, implemented in an Excel spreadsheet, that was designed to find the best fit of the reversible-sink model to the chamber concentration data. The estimated values are listed in Table A-10. For MEKO the estimated value for K_a is considerably larger than that for K_d. For the other VOCs the estimated K_d value generally is close to, or even larger than, the estimated K_a value. In fact, for the VOCs other than MEKO, values of zero for both K_a and K_d fit the data virtually as well as any other combination; this outcome is indicative of a negligible sink effect for those chemicals.

Table A-10. Sink Parameter Estimates for Four Chemicals

Chemical	Chamber Input Concentration, mg/m^3	Peak Concentration in Chamber, mg/m^3	Sink Parameters	
			K_a	K_d
Carpet as a Sink				
MEKO	11.9	9.6	0.25	0.04
1,2,4-trimethylbenzene	10.3	10.0	0.10	6.00
2-methyldecane	10.2	10.5	0.04	0.03
Undecane	12.1	12.7	0.06	0.50
Wallboard as a Sink				
MEKO	10.5	5.0	1.10	0.03
1,2,4-trimethylbenzene	9.9	9.7	0.25	0.25
2-methyldecane	8.0	8.2	0.90	1.20
Undecane	11.1	11.6	0.40	0.25

APPENDIX B

PAPER ON EMISSIONS MODEL FOR ALKYD PAINTS
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Estimation of the Rate of VOC Emissions From Solvent-Based Indoor Coating Materials Based on Product Formulation

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ABSTRACT

Two computational methods are proposed for estimation of the emission rate of volatile organic compounds (VOCs) from solvent-based indoor coating materials based on the knowledge of product formulation. The first method utilizes two previously developed mass transfer models with two key parameters -- the total vapor pressure and the average molecular weight for total volatile organic compounds (TVOCs) -- being estimated based on the VOC contents in the product. The second method is based on a simple, first-order decay model with its parameters being estimated from the properties of both the source and the environment. All the model parameters can be readily obtained. Detailed procedures for computing the key parameters are described by using examples. The predictive errors were evaluated with small chamber data, and the results were satisfactory. Thus, the proposed methods provide a way to predict the VOC emissions in the indoor environment without having to conduct costly chamber testing. The two proposed methods work for both TVOCs and individual VOCs. Pros and cons for each method are discussed.

Key Words

indoor air, emissions, volatile organic compounds, model, coating materials

1. INTRODUCTION

Solvent-based interior coating materials have long been recognized as a major source of volatile organic compounds (VOCs) in the indoor environment (Sterling, 1984). They usually contain more than 25 percent of the solvent that will be released into the air during the drying period. The most commonly used solvent in these products is mineral spirits -- a type of petroleum distillate consisting of aliphatic hydrocarbons with a trace amount of aromatics (Howe-Grant, 1996). Other VOCs are sometimes added to the formulation to enhance its performance, including oxygenated hydrocarbons (such as alcohols), nitrogenated hydrocarbons (such as methyl ethyl ketoxime), and other solvents (such as toluene). Some of the solvent components are identified as hazardous air pollutants (HAPs) in the Clean Air Act Amendments of 1990 (U. S. Public Law 101-549, 1990). The increased exposure to those HAPs and the subsequent health risk are of special concern when solvent-based coatings are used in the indoor environment.

Small environmental chambers have been used to determine the VOC emissions from interior coatings (ASTM, 1995a). The cost of chamber testing could be very high because characterization of emission patterns requires multiple samples over time and this is especially true when the emissions of individual VOCs are to be quantified. A tremendous amount of time and resources can be saved if the emission rates can be predicted based on the properties of the source and those of the environment.

This paper presents two methods that can be used to predict the emissions of TVOCs and individual VOCs from solvent-based indoor coatings. They are both based on gas-phase mass transfer theories but differ in complexity.

The proposed methods should be useful in exposure estimation and risk assessment for they can predict indoor VOC emissions with reasonable accuracy without having to rely on costly chamber testing. These methods should also be useful to manufacturers in developing low-emission products for, once the concentrations of predominant VOCs in a product are known, all the information needed to predict the VOC emission rates is known.

2. LITERATURE REVIEW

Among all available source models for emissions from indoor coating materials, the first-order decay model is the simplest and most widely used (ASTM, 1995a):

$$E = -\frac{dM}{dt} = E_0 e^{-kt} \qquad (1)$$

where E = emission factor, mg m^{-2} h^{-1};

M = amount of VOCs remaining in the source, mg m^{-2};

E_0 = initial emission factor, mg m^{-2} h^{-1};

k = first-order decay rate constant, h^{-1}; and

t = time, h.

This model has several variations, one of which (Clausen, 1993) is:

$$E = -\frac{dM}{dt} = M_0 k e^{-kt} \qquad (2)$$

where $M_0 = E_0/k$ is the amount of VOCs applied, mg m^{-2}.

The major advantage of this family of models is their simplicity. If the air exchange flow rates remain constant, there are analytical solutions to indoor concentrations (Tichenor and Guo, 1991; Evans, 1996). For a single air zone, the solution is:

$$C = \frac{S E_0}{V(N-k)} (e^{-kt} - e^{-Nt}) \qquad \text{(if } N \neq k\text{)} \qquad (3)$$

and

$$C = \frac{S E_0 t}{V} e^{-Nt} \qquad \text{(if } N = k\text{)} \qquad (4)$$

where C = indoor concentration, mg m^{-3};

S = source area, m^2;

V = room volume, m^3; and

N = air exchange rate, h^{-1}.

The first-order decay model has two major drawbacks, however. First, estimation of parameters E_0 and k often relies on costly chamber tests. Second, as an empirical model, it is difficult to scale-up.

Efforts have been made to overcome these problems. Clausen (1993) found that, for a given product, the decay rate constant k is inversely proportional to the wet film thickness:

$$k = \frac{k_{E1}}{è} \qquad (5)$$

where è = wet film thickness, µm; and

k_{E1} = decay rate constant for an evaporative source with wet film thickness of 1 µm, µm h^{-1}. This equation provides a way to adjust k when the wet film thickness changes.

Chang and Guo (1994) reported that, for individual VOCs in a given product, the decay rate constant k can be related to their vapor pressure P:

$$\frac{k_1}{k_2} = \frac{P_1}{P_2} \qquad (6)$$

Such correlation allows estimation of k for one compound relative to another.

Another development allows estimation of k based on the drying time of the solvent (Evans, 1996). Integrating Equation 2 yields:

$$M = M_0 e^{-kt} \qquad (7)$$

If the drying time, t_D, is defined as the time needed for 90 percent of the solvent to evaporate, then Equation 7 becomes:

$$0.1\, M_0 = M_0\, e^{-k\, t_D} \tag{8}$$

or

$$k = -\frac{\ln(0.1)}{t_D} \tag{9}$$

Two mass transfer models were introduced to solve the scale-up problem. One, known as the VB model, is for TVOC (Tichenor, et al., 1993) and the other, known as the VBX model, for individual VOCs (Guo, et al., 1998). These two models are discussed further in the following section.

The gas-phase mass transfer coefficient, which appears in both the VB and VBX models, plays an important role in controlling the rate of VOC emissions from wet sources (Guo, et al., 1996). Two theoretical models have been developed to estimate this parameter in indoor environments (Sparks et al., 1996; Zhang, et al., 1996). Sparks et al. proposed a simple formula based on correlation of the Nusselt and Reynolds. Zhang, et al. reported a slightly more complex formula, which takes into consideration such additional factors as the boundary layer flow condition and the wall shear stress.

To date, no reported methods allow estimation of emission rates for either TVOCs or individual VOCs based on information about the product formulation. The two methods proposed in this paper attempt to fill this gap.

3. DESCRIPTION OF THE METHODS

3.1 Method 1

Method 1 utilizes the VB model (Tichenor, et al., 1993) for TVOCs (Equation 10) and a modified VBX model for individual VOCs (Equation 11):

$$E = k_m \left(C_{v0} \frac{M_T}{M_{T0}} - C\right) \quad (10)$$

where k_m = gas-phase mass transfer coefficient for TVOCs, m h^{-1};

C_{v0} = initial airborne TVOC concentration at air/source interface, mg m^{-3}, based on the total vapor pressure of the TVOCs;

M_T = amount of TVOCs remaining in the source, mg m^{-2};

M_{T0} = amount of TVOCs applied, mg m^{-2}; and

C = TVOC concentration in the bulk air, mg m^{-3}.

$$E_i = k_{mi} \left(C_{vi} \frac{M_i}{M_T} \frac{\overline{m}}{m_i} - C_i\right) \quad (11)$$

where E_i = emission factor for component i, mg m^{-2} h^{-1};

k_{mi} = gas-phase mass transfer coefficient for component i, m h^{-1};

C_{vi} = airborne concentration of component i at air/source interface, mg m^{-3}, based on the vapor pressure of component i;

M_i = amount of component i remaining in the source, mg m^{-2};

$\overline{m}$ = average molecular weight for the organic solvent, g $mole^{-1}$;

m_i = molecular weight for component i, g $mole^{-1}$; and

C_i = concentration of component i in the bulk air, mg m^{-3}.

The term $\frac{M_i}{M_T} \frac{\overline{m}}{m_i}$ is the approximate molar fraction of component i in the solvent mixture. Equation 11 is equivalent to the original VBX model (Guo, et al., 1998) but easier to use because it does not require any unit conversion between (mg m^{-3}) and (mole m^{-3}) for the concentration.

When the emission factor is estimated from the VOC contents in the formulation, it is more convenient to convert C_{v0} and C_{vi} to commonly used pressure units such as (mm Hg):

$$C_{v0} = 10^3 \frac{P_0}{760} \frac{\overline{m}}{v_m} \quad (12)$$

$$C_{vi} = 10^3 \frac{P_i}{760} \frac{m_i}{v_m} \quad (13)$$

where P_0 = total vapor pressure for TVOCs, mm Hg;

P_i = vapor pressure for the pure component i, mm Hg; and

v_m = volume of 1 mole gas under 1 atm, m^3 (v_m = 0.0243 m^3 at 23°C).

Substituting Equation 12 into 10 and Equation 13 into 11:

$$E = k_m (1.32 P_0 \frac{\overline{m}}{v_m} \frac{M_T}{M_{T0}} - C) \quad (14)$$

$$E_i = k_{mi} (1.32 P_i \frac{\overline{m}}{v_m} \frac{M_i}{M_T} - C_i) \quad (15)$$

The room concentration model consists of two differential equations for TVOCs (Equations 16 and 17) and an additional two for each individual VOC (Equations 18 and 19):

$$\frac{dC}{dt} = \frac{SE}{V} - NC \quad (16)$$

$$\frac{dM_T}{dt} = -E \quad (17)$$

$$\frac{dC_i}{dt} = \frac{SE_i}{V} - NC_i \quad (18)$$

$$\frac{dM_i}{dt} = -E_i \quad (19)$$

where E and E_i are from Equations 14 and 15, respectively. The most common initial conditions for Equations 16-19 are: C = 0, C_i = 0, $M_T = M_{T0}$, and $M_i = M_{i0}$ when t = 0. The amount of TVOCs and individual VOCs initially applied, M_{T0} and M_{i0}, can be calculated from:

$$M_{T0} = \grave{e}\, d\, y_0 \tag{20}$$

$$M_{i0} = \grave{e}\, d\, y_i \tag{21}$$

where è = wet film thickness, m;

d = product density, g m^{-3};

y_0 = TVOC content in the product, mg g^{-1}; and

y_i = content of component i in the product, mg g^{-1}.

Equations 20 and 21 are also valid when è is in µm and d in kg L^{-1}.

This method requires knowledge of total vapor pressure (P_0) and average molecular weight ($\overline{m}$) for TVOCs, and mass transfer coefficients (k_m and k_{mi}). Methods to estimate these parameters are described in Sections 4.2-4.4.

3.2 Method 2

In the second proposed method, the first-order decay model (Equation 1) -- the simplest possible source model for decaying sources -- is adopted, with the two model parameters, E_0 and k, being estimated from the two mass transfer models described in the previous section by making certain approximations. At t = 0, Equations 14 and 15 become:

$$E_0 = k_m \left(1.32\, P_0 \frac{\overline{m}}{\nu_m} \frac{M_{T0}}{M_{T0}} - 0\right) = 1.32\, k_m P_0 \frac{\overline{m}}{\nu_m} \tag{22}$$

$$E_{0i} = k_{mi} \left(1.32\, P_i \frac{\overline{m}}{\nu_m} \frac{M_{i0}}{M_{T0}} - 0\right) = 1.32\, k_{mi} P_i \frac{\overline{m}}{\nu_m} \frac{M_{i0}}{M_{T0}} \tag{23}$$

Since $\frac{M_{io}}{M_{T0}} = \frac{y_i}{y_0}$, Equation 23 can be changed to:

$$E_{0i} = 1.32\, k_{mi} P_i \frac{\overline{m}}{\nu_m} \frac{y_i}{y_0} \quad (24)$$

From Equations 1 and 2, the first-order decay rate constant for TVOCs can be calculated from;

$$k = \frac{E_0}{M_{T0}} \quad (25)$$

Substituting Equation 20 into 25:

$$k = \frac{E_0}{\text{è}\, d\, y_0} \quad (26)$$

For an individual VOC, the decay rate constant (k_i) can be derived in a similar manner:

$$k_i = \frac{E_{0i}}{\text{è}\, d\, y_i} \quad (27)$$

Once E_0 and k or E_{0i} and k_i are obtained, Equations 3 and 4 can be used to calculate room concentrations.

4. PARAMETER ESTIMATION

4.1 Overview

The source models used in the two methods are summarized in Table 1. Table 2 is a list of all parameters required to compute indoor VOC concentrations with the two proposed methods: the first three parameters are properties of the environment, and the rest are properties of the source. It is fair to say that all the parameters can be readily obtained except P_0, $\overline{m}$, k_m and k_{mi}. Methods for estimating these parameters are discussed below.

4.2 Estimation of Total Vapor Pressure for TVOC (P_0) from VOC Contents in the Product

To date, parameter P_0 can only be determined by experiment (an example is described below). An alternative method proposed here is to estimate P_0 based on the contents of major VOCs in the solvent. If we assume that the behavior of the solvent is close to an ideal solution, the total vapor pressure can then be estimated from Raoult's law. If the number of VOCs in the mixture is n, then:

$$P_0 = \frac{\sum_{i=1}^{n} (P_i \; y_i \; / \; m_i)}{\sum_{i=1}^{n} (y_i \; / \; m_i)} \qquad (28)$$

Although it is difficult to account for all the constituent VOCs in a petroleum-based solvent, routine chromatographic analysis of the coating material can easily identify one to two dozen major VOC peaks, which provides a good estimate of P_0 by using Equation 28.

To estimate the accuracy of Equation 28, the computed total vapor pressures were compared against those determined by headspace analysis for three test specimens: an alkyd primer, an alkyd paint, and a synthetic wood stain (Tichenor, et al., 1993). About 120 ml of a paint sample was quickly poured into a 250 ml amber bottle, which was then sealed with a Teflon coated septum and placed in an incubator overnight at 23°C. A magnetic stirrer in the bottle helped mix the test specimen. For the synthetic wood stain, a 60 ml bottle was used and the volume of the test specimen

was 20 ml. Samples (200 to 500 µl) were drawn from the headspace the next morning with a syringe which was heated to 60°C and rinsed once with the headspace air. The samples were then injected directly into a gas chromatograph/flame ionization detector (GC/FID) for quantitative analysis. The TVOC mass was computed by using the response factor for toluene and the sum of area counts between toluene and tetradecane, inclusive. In Table 3, the "measured" value was from the headspace analysis and the "computed" value from equation 28. The results showed that the difference between these two methods was no greater than 16 percent. We are uncertain, however, why the computed values are systematically greater than those from the headspace analysis.

Table 4 is an example demonstrating how P_0 can be calculated in an electronic spreadsheet. After entering VOC contents in the product, molecular weights and vapor pressures, the two sums in Equation 28 are obtained. The total vapor pressure can then be calculated:

$$P_0 = \frac{2.348}{0.595} = 3.946 \ (mmHg) \qquad (29)$$

4.3 Estimation of Average Molecular Weight for TVOC ($\overline{m}$) from VOC Contents in the Product

We previously recommended that $\overline{m}$ be represented by the molecular weight for the most predominant constituent in the solvent mixture (Guo, et al., 1998). In the majority of oil-based indoor coating materials we have tested, the most predominant VOC is either decane or undecane. An alternative method is to estimate $\overline{m}$ based on the contents of major VOCs in the product:

$$\overline{m} = \frac{\sum_{i=1}^{n} y_i}{\sum_{i=1}^{n} \frac{y_i}{m_i}} \qquad (30)$$

The calculations can be performed in the same spreadsheet for P_0. No additional information is needed. In the example shown in Table 4, the calculated average molecular weight is:

$$\overline{m} = \frac{78.6}{0.595} = 132 \ g\ mole^{-1} \qquad (31)$$

Parameter $\overline{m}$ estimated from Equation 30 is slightly smaller (less than 10 percent difference) than that represented by the most predominant VOC, which is decane in this example. We believe Equation 30 is more accurate because more than half of the VOC constituents have smaller molecular weights than the most predominant constituent (see data in Table 4 for example).

4.4 Estimation of Gas-Phase Mass Transfer Coefficients (k_m and k_{mi})

Parameters k_m and k_{mi} can be either determined by experiment or estimated based on gas-phase mass transfer theories. For experimental determination, the *p*-dichlorobenzene method (Guo, et al., 1996) is commonly used.

Two theoretical models have been proposed to estimate gas-phase mass transfer coefficients in indoor environments (Sparks, et al., 1996; Zhang, et al., 1996). The model proposed by Sparks, et al. -- the simpler one of the two -- is derived by finding the correlation between the Nusselt number (N_u) and the Reynolds number (R_e) from experimental data:

$$N_u = 0.33\, R_e^{\frac{2}{3}} \qquad (r^2 = 0.98;\ n = 24) \qquad (32)$$

and the equation used to compute the mass transfer coefficient is:

$$k_m = 0.33\, D\, L_c^{-\frac{1}{3}} \left(\frac{\nu \varrho}{\mu}\right)^{\frac{2}{3}} \qquad (33)$$

where D = diffusivity of the VOC in air, $m^2\ h^{-1}$;

L_c = characteristic length of the source (equal to the square root of the source area), m;

v = air velocity over the source, m h^{-1};

ϱ = density of the air, g m^{-3}; and

μ = viscosity of the air, g h^{-1} m^{-1}.

In general, all the parameters in Equation 33 can be obtained readily. The density and viscosity of the air can be found from the literature. Parameters L_c and v vary from case to case. Figure 1 shows the mass transfer coefficient as a function of air velocity and characteristic length for decane (D = 0.0207 m^2 h^{-1}). An air velocity range of 5 to 10 cm s^{-1} is considered typical in indoor environments (Mathews, et, al., 1987).

The following is an example of how the mass transfer coefficient is estimated for decane emissions from a surface with an area of 12 m^2 when the indoor temperature is 23°C and air velocity 10 cm s^{-1}. The values needed to compute k_m are:

$$L_c = \sqrt{12} = 3.464\ m \tag{34}$$

í = 10 cm s^{-1} = 360 m h^{-1} (35)

D = 0.0576 cm^2 s^{-1} = 0.0207 m^2 h^{-1} (36)

ϱ = 1193 g m^{-3} (37)

μ = 184.4 μpoises = 66.52 g h^{-1} m^{-1} (38)

where ϱ and μ were found from the literature (Weast, 1972) and D was calculated by using the FSG method (Layman, et al., 1982). Substituting the above values into Equation 33 yields:

$$k_m = 0.33 \times 0.0207 \times \left(3.464\right)^{-\frac{1}{3}} \times \left(\frac{360 \times 1193}{66.52}\right)^{\frac{2}{3}} = 1.57\ m\,h^{-1} \tag{39}$$

Practically, the mass transfer coefficient for TVOC is represented by that for the most abundant component (Tichenor, et al., 1993).

5. EVALUATION OF MODEL PERFORMANCES

5.1 Chamber Data

Small chamber data for three types of indoor coating materials were used to evaluate the performance of the proposed methods: an alkyd primer, an alkyd paint, and a conversion varnish that cures at room temperature. The solvents used in the first two products were typical petroleum distillate solvents. The conversion varnish contains large amount of aromatic compounds. Table 5 summarizes the properties of the test specimens and the test conditions. Detailed information about these products and test procedures are reported elsewhere (Fortmann, et al., 1998; Howard, et al., 1998). Not all concentration data were used in this evaluation. Data for some VOCs were disqualified for one or more of the following reasons: (1) most data points were below the practical method quantification limit; (2) the chamber recovery was either less than 75 percent or greater than 125 percent; and (3) the vapor pressure for a given VOC was not available at room temperature range. Thus, only 23 sets of concentration data were qualified for the evaluation.

5.2 Results

The performance of the two methods was evaluated by using two indicators: the error in the predicted peak concentration and the normalized mean square error (NMSE) for a given data set. As shown in Table 6, the average percent difference between observed and predicted peak concentrations is 16.6 percent for method 1 and 22.9 percent for method 2. The observed peak concentrations cover a wide range (from 3.79 to 9770 mg/m^3) and, thus, the two methods work for both major and minor components of the solvent mixture. It should be pointed out, however, that the predicted peak concentrations are often (but not always) higher than the observed ones. Possible causes of such overestimation are discussed in the following section.

The NMSE, one of the standard indices for statistical evaluation of indoor air quality models (ASTM, 1995b), is calculated from

$$NMSE = \frac{\sum_{i=1}^{n} (C_{pi} - C_{oi})^2}{n\ \overline{C_o}\ \overline{C_p}} \qquad (40)$$

where C_{pi} = predicted concentrations;

C_{oi} = observed concentrations;

$\overline{C_o} = \sum_{i=1}^{n} C_{oi} / n$;

$\overline{C_p} = \sum_{i=1}^{n} C_{pi} / n$; and

n = total number of data points.

As shown in Table 7, the average NMSE value was 0.159 for method 1 and 0.253 for method 2. According to the ASTM standard guide, an NMSE value of 0.25 or less is generally considered indicative of adequate model performance.

Both indicators suggest that the performances of the two methods are adequate and that, in general, method 1 is more accurate than method 2. Examples of predicted chamber concentrations with good and poor accuracy are shown in Figures 2 and 3, respectively.

6. DISCUSSION

6.1 Comparison of the Two Methods

Each of the two proposed methods has its advantages and disadvantages. The first method provides more accurate predictions and is less sensitive to errors in the input. On the other hand, this method requires solving a system of differential equations numerically and, therefore, is relatively computation intensive.

The second method is less accurate but easier to use. All the calculations can be performed in an electronic spreadsheet. Thus, it is more suitable for product screening purposes. It is also of choice if a large number of calculations are needed (such as in Monte Carlo analysis).

In terms of computational intensity, the difference between these two methods is more significant for individual VOCs than for TVOCs. The reader is reminded that, in a single-zone situation, the VB model has an explicit solution to indoor concentration (Tichenor, el al., 1993). With slightly more computational steps, this mass transfer model offers better accuracy than the first-order decay model.

6.2 Validity of Estimating Total Vapor Pressure for TVOCs from the VOC Contents in the Product

Because of the many constituent VOCs contained in the petroleum-based solvent, the predominant VOCs that can be quantified by routine GC analysis account for only a small portion of the total mass. In the example shown in Table 4, the 15 quantified major VOCs account for about 24 percent of the total weight of the solvent (the TVOC content was 333 mg/g). It is doubtful that 24 percent of predominant VOCs can represent the properties of the solvent if there is no similarity between those components and the remaining 76 percent of the VOCs. As stated in Introduction, above, petroleum-based solvents consist mainly of aliphatic hydrocarbons. Although many less abundant constituents are not the targets in routine GC analysis, their properties are similar to some of the quantified VOCs. For instance, n-decane is the most abundant component in many solvent-based coating products. This compound also has many isomers (e.g., branched decanes), which are not quantified but have molecular weights and diffusivities identical to n-decane and vapor pressures close to n-decane. Thus, n-decane represents a group of VOCs with similar physical properties. The usefulness of Equation 28 is that it makes the headspace analysis unnecessary.

6.3 Overestimation of Peak Concentrations

As shown in Table 6, both methods tend to overestimate the peak concentrations. There are several explanations for the causes. First of all, the test specimen was prepared outside the chamber and it typically took several minutes to apply the coating and to determine the total amount of material applied. Such a delay may cause significant VOC loss before the test specimen is placed in the chamber, especially for more volatile components (Guo, et al., 1996).

The second cause is the substrate effect. When a petroleum-based coating material is applied

to a substrate such as wood or gypsum boards, a small amount of solvent will penetrate the substrate. This fraction of solvent will be emitted in a delayed time. Limited data analysis suggests that this fraction accounts for 5 to 10 percent of the total solvent applied.

The third cause applies only to the second method. It is due to the omission of the back pressure effect. As shown in Equations 10 and 11, the driving force for solvent evaporation is the concentration difference between the surface of the source and the indoor air. As a result, the high chamber concentration in the early hours slows the evaporation process. Method 2 does not take this factor into consideration and, consequently, its predicted peak concentrations are generally higher than those predicted by method 1.

*6.4 Making Use of Information in Material Safety Data Sheets and Product Data Sheet*s

Predicting the emission rate of an individual VOC with the first-order decay model does not require knowledge of the total vapor pressure for TVOCs (Equations 24 and 27). This feature makes it possible to estimate the emission rate based on the information in the Material Safety Data Sheets (MSDSs) and the Product Data Sheets. The United States laws require that the manufacturer provide MSDSs with their products. For indoor coating products, the contents of total volatile matter (TVM) and some hazardous VOCs (if greater than 1 percent by weight) are reported in MSDSs. If the VOC of interest appears in the MSDS, one can use Equations 24 and 27 to roughly estimate its emission rate. The TVOC content can be represented by TVM. The only information lacking about the TVOCs is their average molecular weight. In most indoor coating products we have tested, including wood stain, polyurethane wood finish, floor wax and alkyd paint (Tichenor et al., 1991, 1993; Fortmann, et al., 1998), the most predominant VOC in the solvent is either decane (m_i = 142) or undecane (m_i = 156). The only exception was conversion varnish, in which xylene (m_i = 106) is often the most abundant component in the solvent (Howard, et al., 1998). For screening purposes, we recommend that the average molecular weight of 142 be used when the most abundant component is unknown. The density of the product is always reported in the related Product Data Sheet.

7. CONCLUSIONS

Two methods have been developed to predict the emissions of TVOCs and individual VOCs from solvent-based indoor coating materials based on the product formulation. The first method is based on two mass transfer models with the key parameters being estimated from the contents of major VOCs in the product. The second method utilizes the first-order decay model with its parameters being estimated based on the properties of the source and the environment. Model evaluation using small chamber data indicates that both methods provide reasonable accuracy in predicting emissions to indoor environments, with the average normalized mean square error being 0.159 and 0.253, respectively. Further evaluation with data collected from real rooms, where VOC adsorption and desorption from interior surface are often significant, is desirable.

The first method is more accurate than the second but is more computation intensive. The second method is simple enough to be implemented in an electronic spreadsheet and is more suitable for product screening. These two methods provide a way to obtain exposure information on the indoor use of petroleum-based indoor coating materials without having to perform costly chamber testing.

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REFERENCES

ASTM (1995a), “Standard guide for small scale environmental chamber determination of organic emissions from indoor materials/products,” Philadelphia, PA, American Society for Testing and Materials (ASTM Standard D-5116-90).

ASTM (1995b) “Standard guide for statistical evaluation of indoor air quality models,” Philadelphia, PA, American Society for Testing and Materials (ASTM Standard D-5157-91).

Chang, J. C . S. and Z. Guo (1994), “Modeling of alkane emissions from a wood stain,” *Indoor Air*, Vol. 4, pp 35-39.

Clausen, P. A. (1993), "Emission of volatile and semivolatile organic compounds from water-borne paints -- the effect of the film thickness," *Indoor Air*, Vol. 3, pp 269-275.

Evans, W. C. (1996), “Development of continuous-application source terms and analytical solutions for one- and two-compartment systems,” *Characterizing Sources of Indoor Air Pollution and Related Sink Effects*, ASTM STP 1287, B. A. Tichenor, Ed., American Society for Testing and Materials, pp 279-293.

Fortmann, R., N. Roache, Z. Guo, and J. C. S. Chang (1998), “Characterization of emissions of volatile organic compounds from interior alkyd paint,” accepted for publication by *J. Air Waste Manage. Assoc.*

Guo, Z., B. A. Tichenor, K. A. Krebs, and N. F. Roache (1996), “Considerations on revision of emissions testing protocols,” *Characterizing Sources of Indoor Air Pollution and Related Sink Effects*, ASTM STP 1287, B.A. Tichenor, Ed., American Society for Testing and Materials, pp 225-236.

Guo, Z., L. E. Sparks, B. A. Tichenor, and J. C. S. Chang (1998), “Predicting the emissions of individual VOCs from petroleum-based indoor coatings,” *Atmospheric Environment*, Vol. 32, No. 2, pp 231-237.

Howard, E. M., R. C. McCrillis, K. A. Krebs, R. C. Fortmann, H. Chen-Lao, and Z. Guo (1998), “Indoor emissions from conversion varnishes,” accepted for publication by *J. Air Waste Manage. Assoc.*

Howe-Grant, M., Ed. (1996), *Encyclopedia of Chemical Technology*, Vol. 17, p 1052, John Wiley & Sons, New York.

Layman, W. J., W. F. Reehl, and D. H. Rosenblatt (1982), *Handbook of Chemical Property Estimation Methods*, McGraw-Hill, New York.

Mathews, T. J., C.V. Thompson, D. L. Wilson, A. R. Hawthorne, and D.T. Mage. “Air velocities inside domestic environments: an important parameter for passive monitoring,” *Indoor Air ’87,*

Proceedings of the 4th International Conference on Indoor Air Quality and Climate, Institute for Water, Soil and Air Hygiene, West Berlin, Vol. 1, August 1987. pp. 154-158.

Public Law 101-549, *The Clean Air Act Amendments*, Title III - Hazardous Air Pollutants, United States 101st Congress, November 15, 1990.

Sparks, L. E., B. A. Tichenor, J. Chang, and Z. Guo (1996), "Gas-phase mass transfer model for predicting volatile organic compound (VOC) emission rates from indoor pollutant sources, *Indoor Air*, Vol. 6, pp 31-40.

Sterling, D. A. (1984), "Volatile organic compounds in indoor air: an overview of sources, concentrations, and health effects," Indoor Air and Human Health: Proceedings of the Seventh Life Sciences Symposium, Knoxville, TN, October 29-31, 1984, pp 387-402.

Tichenor, B. A. and Z. Guo (1991), "The effect of ventilation on emission rates of wood finishing materials," *Environment International*, Vol. 17, pp 317-323.

Tichenor, B. A., Z. Guo, and L. E. Sparks (1993), "Fundamental mass transfer model for indoor air emissions from surface coatings," *Indoor Air*, Vol. 3, pp 263-268.

Weast, R. C., Ed., *CRC Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, OH, 1972.

Zhang, Y., F. Haghighat, and P. Fazio, (1996) "Modeling of material emission process," Proceedings of the Seventh International Conference on Indoor Air Quality and Climate, Vol. 1, pp 937-942.

Table 1. Summary of Source Models Used in the Proposed Methods

Method	Category	Representation of Solvent Volatility	
		Vapor Pressure (mm Hg)	Concentration at Air-Source Interface (mg m^{-3})
1	TVOCs	$E = k_m (1.32 P_0 \frac{\overline{m}}{\nu_m} \frac{M_T}{M_{T0}} - C)$	$E = k_m (C_v \frac{M_T}{M_{T0}} - C)$
	VOCs	$E_i = k_{mi} (1.32 P_i \frac{\overline{m}}{\nu_m} \frac{M_i}{M_T} - C)$	$E_i = k_m (C\nu_i \frac{M_i}{M_T} - C_i)$
2	TVOCs	$E_0 = 1.32\ k_m\ P_0 \frac{\overline{m}}{\nu_m}$	$E_0 = k_m C_v$
		$k = \frac{E_0}{q\ d\ y_0}$	
	VOCs	$E_{0i} = 1.32\ k_{mi}\ P_i \frac{\overline{m}}{\nu_m} \frac{y_i}{y_0}$	$E_{0i} = k_{mi}\ C_{vi} \frac{y_i}{y_0}$
		$k_i = \frac{E_{0i}}{q\ d\ y_i}$	

Table 2. List of Parameters Required by the Concentration Models

Parameter	Symbol	Method 1		Method 2	
		TVOC	VOC	TVOC	VOC
room volume	V	X	X	X	X
air exchange rate	N	X	X	X	X
mass transfer coefficient	k_m , k_{mi}	X	X	X	X
source area	S	X	X	X	X
wet film thickness	è	X	X	X	X
product density	d	X	X	X	X
content of TVOC in product	y_0	X	X	X	X
total vapor pressure for TVOC	P_0, C_v	X	X	X	
average molecular weight for TVOC	$\overline{m}$		X		X
content of individual VOC in product	y_i		X		X
vapor pressure for individual VOC	P_i, C_{vi}		X		X
molecular weight for individual VOC	m_i		X		

Table 3. Comparison of Headspace TVOC Concentrations with Theoretically Calculated C_{v0} for Three Wet Sources

Product	Measured C_{v0} [a] ($g\ m^{-3}$)	Computed		Percent Difference
		P_0 (mm Hg)	C_{v0} ($g\ m^{-3}$)	
Alkyd Primer	27.2 ± 1.77	3.49	31.9	15.9
Alkyd Paint A	12.3 ± 1.66	1.44	14.3	15.0
Synthetic Stain	16.6 ± 1.91	2.86	18.4	10.3

[a] mean ± standard deviation; n = 6 for alkyd primer and alkyd paint; and n = 7 for synthetic stain.

Table 4. An Exemplary Worksheet for Estimation of the Total Vapor Pressure P_0 and Average Molecular Weight ($\overline{m}$) for TVOCs

Compound	y_i	m_i	P_i [a]	y_i/m_i	$P_i\, y_i / m_i$
decane	30.7	142	1.575	0.2165	0.3410
nonane	18.4	128	4.144	0.1436	0.5949
octane	15.6	114	7.894	0.1372	1.0831
undecane	6.68	156	0.616	0.0428	0.0264
trans-decalin	2.28	138	3.296	0.0165	0.0543
2-methyldecane	2.19	170	0.616	0.0129	0.0079
p-xylene	1.39	106	7.710	0.0132	0.1014
toluene	0.35	92	24.47	0.0038	0.0921
ethylbenzene	0.29	106	8.850	0.0028	0.0246
o-xylene	0.23	106	5.897	0.0022	0.0129
p-ethyltoluene	0.21	120	2.864	0.0017	0.0050
1,2,4-trimethylbenzene	0.14	120	2.028	0.0012	0.0024
dodecane	0.063	170	0.253	0.0004	0.0001
n-propylbenzene	0.034	120	3.126	0.0003	0.0009
1,3,5-trimethylbenzene	0.023	120	2.526	0.0002	0.0005
sum	78.6			0.595	2.348

[a] at 23 °C.

Table 5. Summary of Test Specimens and Chamber Conditions[a]

Test specimen	Alkyd Primer	Alkyd Paint B	Conversion Varnish
Product density (kg L^{-1})	1.33	1.10	0.97
TVOC content (mg g^{-1})	333	350	516
Most abundant VOC	decane	decane	xylene
No. of VOCs quantified in liquid product	20	20	10
No. of VOCs quantified in air samples	20	20	4
Total vapor pressure (mm Hg)[b]	3.94	2.58	8.39
Average molecular weight[c]	131	133	101
Substrate type	white pine board	white pine board	red oak board
Substrate area (cm^2)	256	256	272
Recommended wet film thickness (µm)	102	102	76~102
Actual wet film thickness (µm)	82.5	74.6	123
Air exchange rate (h^{-1})	0.543	0.543	0.538
Mass transfer coefficient (m h^{-1})[d]	4.36	4.36	4.36

[a] All three tests were conducted in 53-L stainless steel chambers at 23°C and 50% relative humidity.
[b] Estimated from Equation 28.
[c] Estimated from Equation 30.
[d] For decane; estimated from Equation 33.

Table 6. Comparison of Observed and Predicted Peak Concentrations

Concentration Units: mg/m^3

Test Specimen	Compound	Observed	Method 1		Method 2	
			Predicted	% Diff.[a]	Predicted	% Diff.[a]
Alkyd Primer	TVOCs	9.77×10^{3}	8.91×10^{3}	-9.3	1.23×10^{4}	+22
	decane	1.10×10^{3}	8.76×10^{2}	-23	8.92×10^{2}	-21
	nonane	6.63×10^{2}	6.71×10^{2}	+1.2	7.01×10^{2}	+5.6
	trans-decalin	6.76×10^{1}	7.93×10^{1}	+16	8.19×10^{1}	+19
	p-xylene	4.26×10^{1}	5.65×10^{1}	+28	5.94×10^{1}	+33
	ethylbenzene	1.17×10^{1}	1.21×10^{1}	+3.4	1.28×10^{1}	+9.0
	o-xylene	8.31×10^{0}	9.12×10^{0}	+9.3	9.89×10^{0}	+17
	p-ethyltoluene	6.19×10^{0}	7.06×10^{0}	+13	7.29×10^{0}	+16
Alkyd Paint B	TVOCs	6.55×10^{3}	6.36×10^{3}	-2.9	9.32×10^{3}	+35
	decane	4.62×10^{2}	4.87×10^{2}	+5.3	5.45×10^{2}	+16
	undecane	4.01×10^{2}	4.60×10^{2}	+14	5.28×10^{2}	+27
	nonane	1.92×10^{2}	2.05×10^{2}	+6.5	2.23×10^{2}	+15
	trans-decalin	7.37×10^{1}	1.16×10^{2}	+45	1.29×10^{2}	+55
	methylethylketoxime	7.01×10^{1}	5.97×10^{1}	-16	6.69×10^{1}	-4.7
	p-ethyltoluene	3.45×10^{1}	3.82×10^{1}	+10	4.19×10^{1}	+19
	o-xylene	3.01×10^{1}	4.09×10^{1}	+30	5.48×10^{1}	+58
	1,2,4-trimethylbenzene	1.55×10^{1}	2.55×10^{1}	+49	2.54×10^{1}	+48
	n-propylbenzene	7.72×10^{0}	1.07×10^{1}	+32	1.18×10^{1}	+42
	isopropylbenzene	3.79×10^{0}	4.86×10^{0}	+25	5.31×10^{0}	+33
Conversion Varnish	*p*-xylene	9.78×10^{3}	9.11×10^{3}	-7.0	1.00×10^{4}	+2.3
	isobutanol	3.48×10^{3}	3.85×10^{3}	+9.9	3.65×10^{3}	+4.7
	o-xylene	2.79×10^{3}	2.26×10^{3}	-21	2.41×10^{3}	-15
	ethylbenzene	2.31×10^{3}	2.18×10^{3}	-5.9	2.49×10^{3}	+7.3
Average Percent Difference[b]				16.6		22.9

[a] Percent difference.

[b] Average of absolute values.

Table 7. Normalized Mean Square Error (NMSE) as an Indicator of Model Accuracy

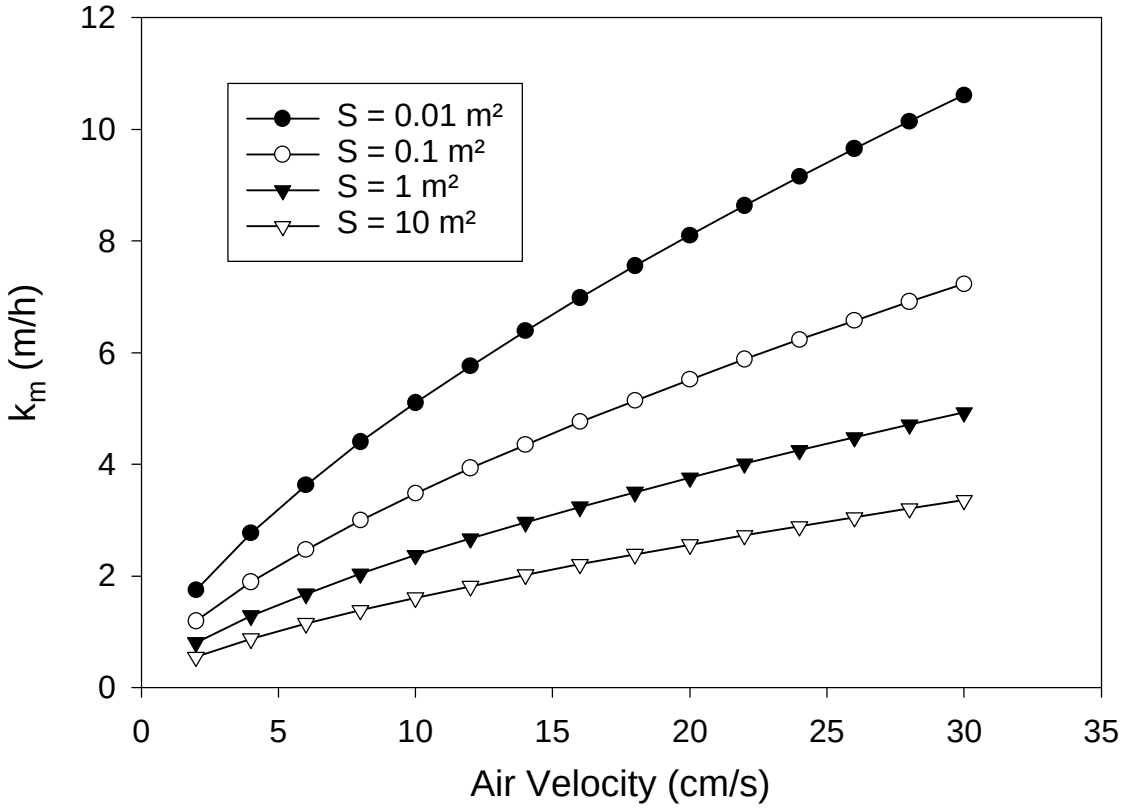
Test Specimen	Compound	Method 1	Method 2
Alkyd Primer	TVOC	0.067	0.044
	decane	0.097	0.106
	nonane	0.024	0.045
	trans-decalin	0.229	0.212
	p-xylene	0.236	0.293
	ethylbenzene	0.032	0.056
	o-xylene	0.036	0.057
	p-ethyltoluene	0.459	0.633
Alkyd Paint B	TVOC	0.116	0.389
	decane	0.111	0.147
	undecane	0.125	0.169
	nonane	0.160	0.218
	trans-decalin	0.542	0.687
	methylethylketoxime	0.204	0.240
	p-ethyltoluene	0.117	0.168
	o-xylene	0.377	0.547
	1,2,4-trimethylbenzene	0.508	0.470
	n-propylbenzene	0.384	0.522
	isopropylbenzene	0.375	0.498
Conversion Varnish	ethylbenzene	0.059	0.064
	o-xylene	0.116	0.111
	isobutanol	0.054	0.068
	p-xylene	0.048	0.070
Average NMSE		0.195	0.253

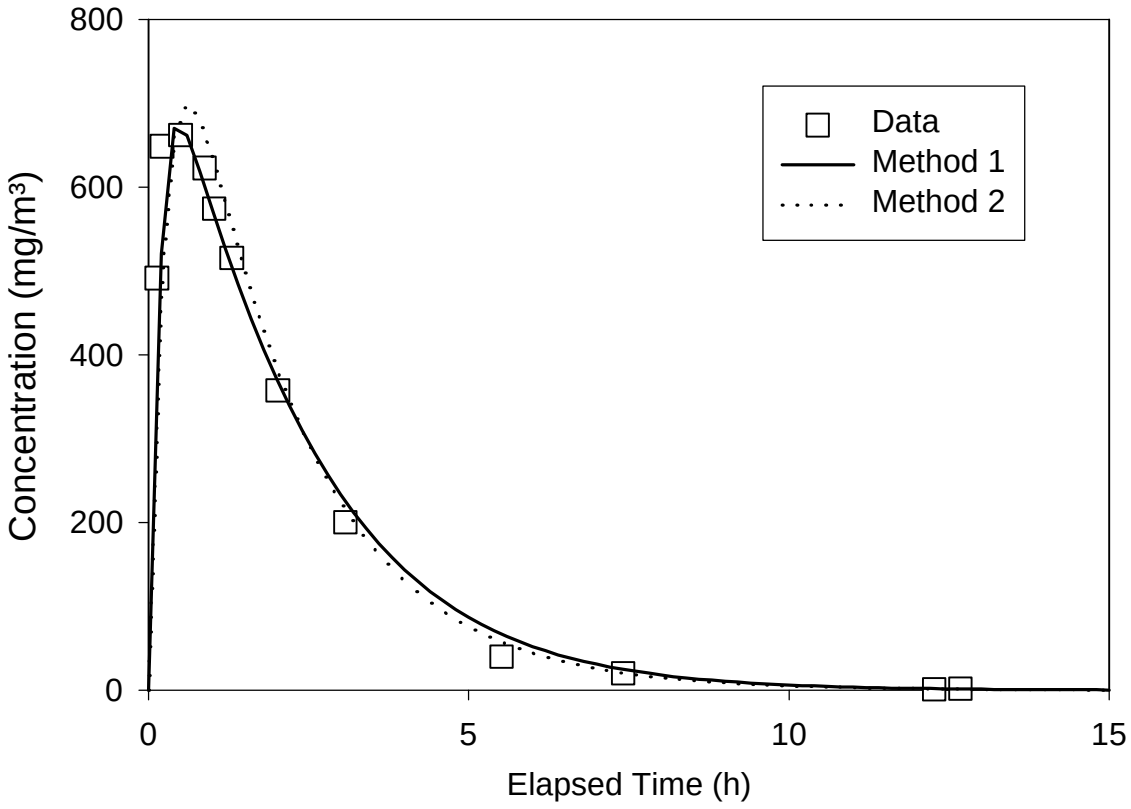
Figure Captions

Figure 1. Gas-phase mass transfer coefficient (k_m) as a function of air velocity and source area (S)

Figure 2. An example of model predictions with good accuracy. NMSE = 0.024 for method 1 and 0.045 for method 2. Data are for nonane in the alkyd primer test.

Figure 3. An example of model predictions with poor accuracy. NMSE = 0.542 for method 1 and 0.687 for method 2. Data are for *trans*-decalin in the alkyd paint test.


S = 0.01 m²
S = 0.1 m²
S = 1 m²
S = 10 m²
k_m (m/h)
Air Velocity (cm/s)
0
2
4
6
8
10
12
0
5
10
15
20
25
30
35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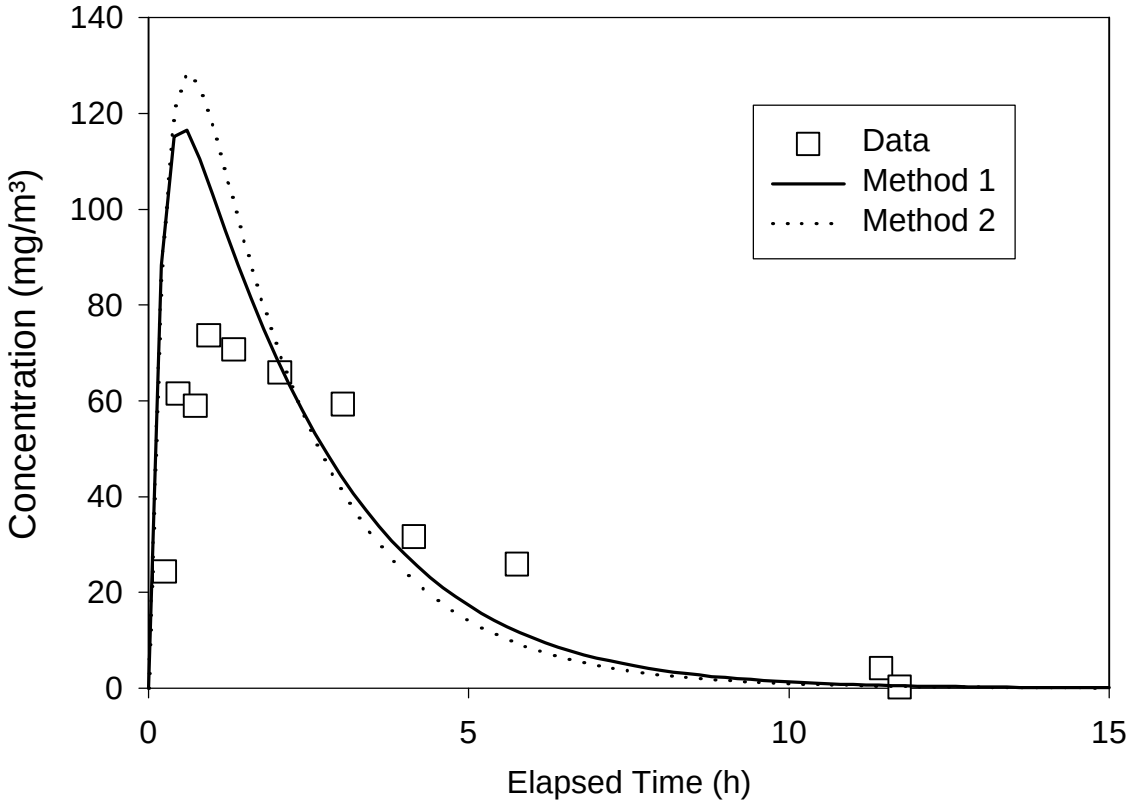
600
400
200
0
Concentration (mg/m³)
0
5
10
15
Elapsed Time (h)
Data
Method 1
Method 2


140
120
100
80
60
40
20
0
Concentration (mg/m³)
0
5
10
15
Elapsed Time (h)
Data
Method 1
Method 2

APPENDIX C

LATEX PAINT CHAMBER TESTS

C1. INTRODUCTION

A series of small-chamber tests was conducted by ARCADIS Geraghty and Miller, Inc., to characterize concentrations of various volatile organic compounds (VOCs) emitted from different formulations of latex primer and paint. In addition to the broad objective of improving the understanding of emission behavior for these chemicals in latex primer and paint, a more specific objective was to provide a quantitative basis for development of emission models or for estimating parameters for such models. In addition to the small-chamber tests, ARCADIS Geraghty and Miller, Inc., conducted painting events at EPA's research house in North Carolina for the primary purpose of gathering data to be used for model evaluation.

The sections that follow describe methods and results for bulk analysis of the latex primer/paint formulations prior to chamber testing, small-chamber emission tests of these formulations, and development of predictive models for VOC emissions from latex primer and paint.

C2. BULK ANALYSIS

Prior to conduct of small-chamber emission tests, each formulation of latex primer or paint was analyzed to determine its chemical composition by weight. In brief, the procedure for analysis of the bulk product that was followed by ARCADIS Geraghty and Miller, Inc., (ARCADIS 1998) involved (1) extracting latex primer and paints with acetone, (2) centrifuging the sample to remove solids, and (3) analyzing the supernatant by GC/MS. Aliquots of the supernatant were diluted as necessary to yield sample concentrations that fell within the calibration range.

Results of the bulk analysis are shown as chemical weight fractions (mg/g) in Table C-1. One primer (designated as formulation LP-A) was used for the chamber tests together with four formulations of paint (LF-B, LF-C, LSG-D, and LSG-E). In the designations for formulation, P indicates primer, F indicates flat paint, and SG indicates semi-gloss paint. Only five VOCs were found in measurable quantities in any of the formulations that were tested. The primer contained ethylene glycol and TMPD-MIB, the flat paints primarily contained propylene glycol and TMPD-MIB, and the semi-gloss paints primarily contained propylene glycol and TMPD-MIB. Thus, TMPD-MIB was the only VOC common to all formulations. One semi-gloss formulation had a measurable, but relatively small, quantity of 2-(2-butoxyethoxy) ethanol (BEE), and one of the flat paints and one of the semi-gloss paints had relatively small quantities of dipropylene glycol.

Table C-1. Results of Bulk Analysis (mg/g) for Latex Primer and Paints

Chemical	LP-A (Primer)	LF-B (Paint)	LF-C (Paint)	LSG-D (Paint)	LSG-E (Paint)
Propylene Glycol	ND*	23.50	0.05	55.20	24.20
Ethylene Glycol	19.60	ND	20.20	0.02	ND
2-(2-Butoxyethoxy) Ethanol	ND	ND	ND	0.16	ND
TMPD-MIB	12.20	16.80	7.05	25.70	7.00
Dipropylene Glycol	ND	0.28	ND	ND	0.12

* Not detected.

C3. SMALL-CHAMBER EMISSION TESTS

The small-chamber emission tests were conducted by ARCADIS Geraghty and Miller, Inc., in the EPA APPCD Source Characterization Laboratories located in the EPA Environmental Research Center in Research Triangle Park, NC. The tests were conducted using 53-liter, stainless-steel chambers housed in a temperature-controlled incubator. These chambers have been fitted with inlet and outlet manifolds for the air supply, temperature and relative humidity sensors, and a small fan to ensure mixing within the chamber. During each test, clean (VOC- and particle-free) air was supplied to the chamber at a controlled relative humidity. A glass sampling manifold has been connected to the chamber outlet for collection of air samples.

The substrate used in the tests was 0.5-inch gypsum wallboard that was purchased from a local retail outlet in North Carolina. For each test, the substrate was cut to a size of 16 by 16 cm (total area of 256 cm^2 or 0.0256 m^2), resulting in a surface-to-volume loading ratio of about 0.5 m^2/m^3 in the chamber. The edges were sealed and the test specimen was placed on the floor of the chamber during the test. The cut and sealed substrate was conditioned in the chamber for at least 24 hours prior to application of primer/paint.

Primer and paint were applied to the wallboard with a roller purchased at a local retail outlet. The rate of primer/paint application in the tests, and resulting wet film thickness, were based on recommendations from the manufacturers. The mass of paint applied was determined gravimetrically by two methods. Wet film thickness was not measured with a gage during the tests because the gage affects surface film characteristics and the specimen was to be inserted into the chamber as quickly as possible after priming or painting. Based on the measured mass of paint applied and the known specific gravity of the coating, the average calculated wet film thickness was 415 μm (16.4 mil) for the alkyd primer and 105 μm (4.1 mil) for the alkyd paint.

As noted above, the wallboard specimen was conditioned in the chamber at least 24 hours before the test. Background concentrations were measured prior to removing the specimen. Primer was then applied, the specimen was re-inserted in the chamber, and air samples were collected for the next 48 hours. Then the specimen was removed, paint was applied, the wallboard was again inserted in the chamber, and air samples were collected during the next 12 days. Thus, the total monitoring period for each test was 14 days in duration.

Four tests were conducted for latex primer and paint. The primer LP-B was used for all tests. Paint formulation LSG-E was used in the first chamber emission test (test L3), paint formulation LSG-D for the second test (test L4), paint formulation LF-B for the third test (test L5), and paint formulation LF-C for the fourth test (test L6).

It has been observed in previous chamber tests that emission rates for various compounds in paint tend to decline exponentially over time as the reservoir of material that can be emitted is gradually depleted, and as the drying paint forms a barrier that retards emissions. Two types of empirical models for estimating the time-varying emission profile can be used: (1) a single-exponential model governed by an initial emission rate and a rate of decline from the initial rate, and (2) a double-exponential model with two sets of initial emission rates and rates of decline, one to account for an early ("fast") phase of evaporation-dominated emissions and one to account for a later ("slow") phase of diffusion-dominated emissions.

Previous work by Wilkes et al. (see Appendix D), for example, has demonstrated that a double-exponential model is needed to properly represent the emission behavior of VOCs released from latex paint. The time-varying emission rate for the double-exponential model is given by the following equation:

$$S(t) = E_{o1}\, e^{-k1t} + E_{o2}\, e^{-k2t} \qquad \text{(C-1)}$$

where:

$S(t)$ = Source strength as a function of time (mass/time);
E_{01} = Initial emission rate (mass/time) for the first exponential;
k_1 = First-order rate constant ($time^{-1}$) for the first exponential;
E_{02} = Initial emission rate (mass/time) for the second exponential;
k_2 = First-order rate constant ($time^{-1}$) for the second exponential; and
t = Time.

For each chamber test, an equation for the chamber concentration reflecting the double-exponential model in equation (C-1) was fit to chamber data for each of the chemicals in latex primer and paint using non-linear regression analysis. The measured chamber volume and airflow rate were taken as "knowns." First, the initial emission rate and the first-order rate constant for the "slow" phase of emissions decline were estimated through the regression technique, using data after the first 24 hours following primer or paint application. Next, these parameter estimates

were taken as "known," along with the chamber volume and airflow, to estimate the initial emission rate and the first-order rate constant for the "fast" phase, using the entire concentration time series after priming or painting. In each case, the fits were done separately for the priming and painting portions of the test, where permitted by the data. (In some cases, examples of which are shown later, the concentrations had not declined sufficiently after priming to enable reliable estimation of these parameters for the priming and/or painting portion of the test.)

Example fits of the double-exponential emissions model to the chamber concentration data are shown in Figures C-1 through C-4. Figure C-1 depicts ethylene glycol concentrations during test L4 (semi-gloss formulation LSG-D). In this case, the concentrations had not declined sufficiently by the time paint was applied to enable reliable estimation of model parameters for emissions from the primer. Although the residual concentrations from priming could influence the parameter estimates for the painting portion of the test, a fit was attempted nonetheless. The double-exponential model appears to fit this portion of the data quite well, both during the rapid and slow phases of concentration decline.

For TMPD-MIB during test L4 (Figure C-2), there were no measurable quantities during the priming portion of the test, even though the bulk analysis indicated presence of TMPD-MIB in the primer. As a result, a reliable fit could be attempted to the concentrations during and after painting. As shown in the figure, the double-exponential model appears to capture the emissions behavior quite well, following the concentration profile closely throughout the test, with the possible exception of slight underestimation near the end of the test.

For test L6, involving flat formulation LF-C, propylene glycol concentrations receded sufficiently before paint application to enable estimation of the emission profile during both the priming and the painting potions of the test (Figure C-3). For both portions of the test, the double-exponential model appears to have represented the emissions behavior quite well, again with the possible exception of underestimation toward the end of the test. For the same test, ethylene glycol concentrations (Figure C-4) similarly had declined sufficiently after priming to permit estimation of model parameters for both portions of the test. In this case, the double-exponential model appears to provide an excellent fit to the concentration data throughout the test.

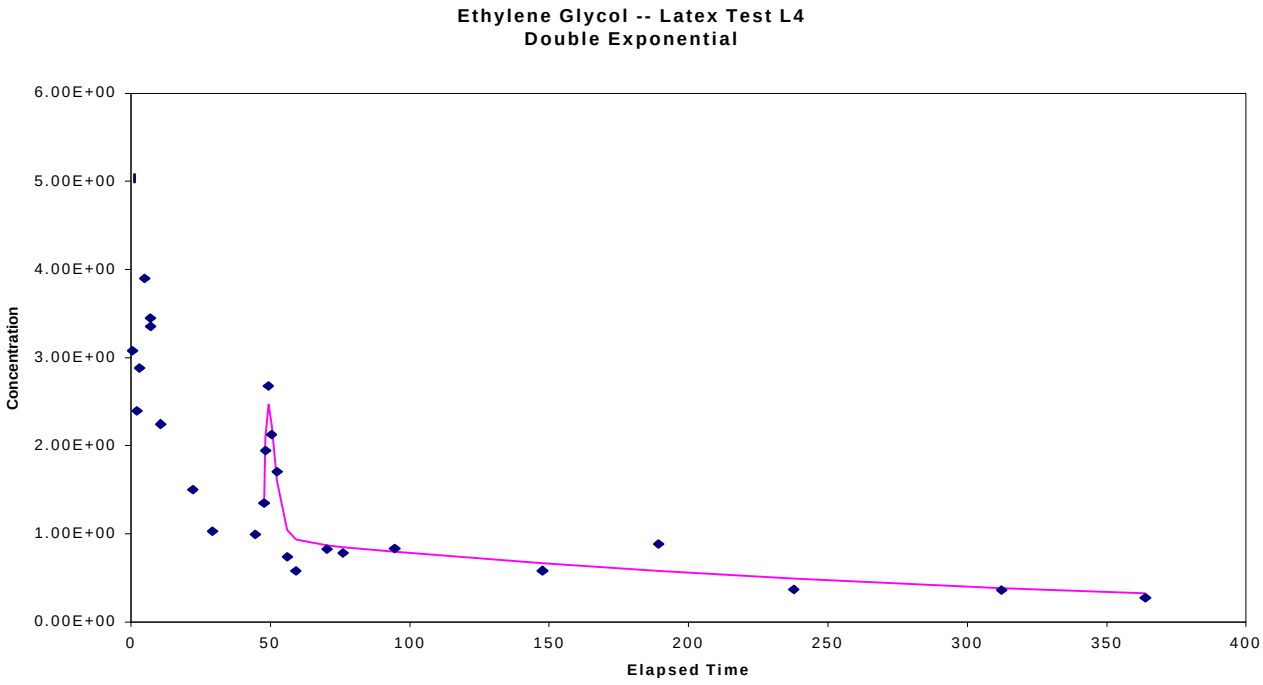


Figure C-1. Ethylene Glycol Concentrations and Model Fit for Test L4 (Latex Paint LSG-D).

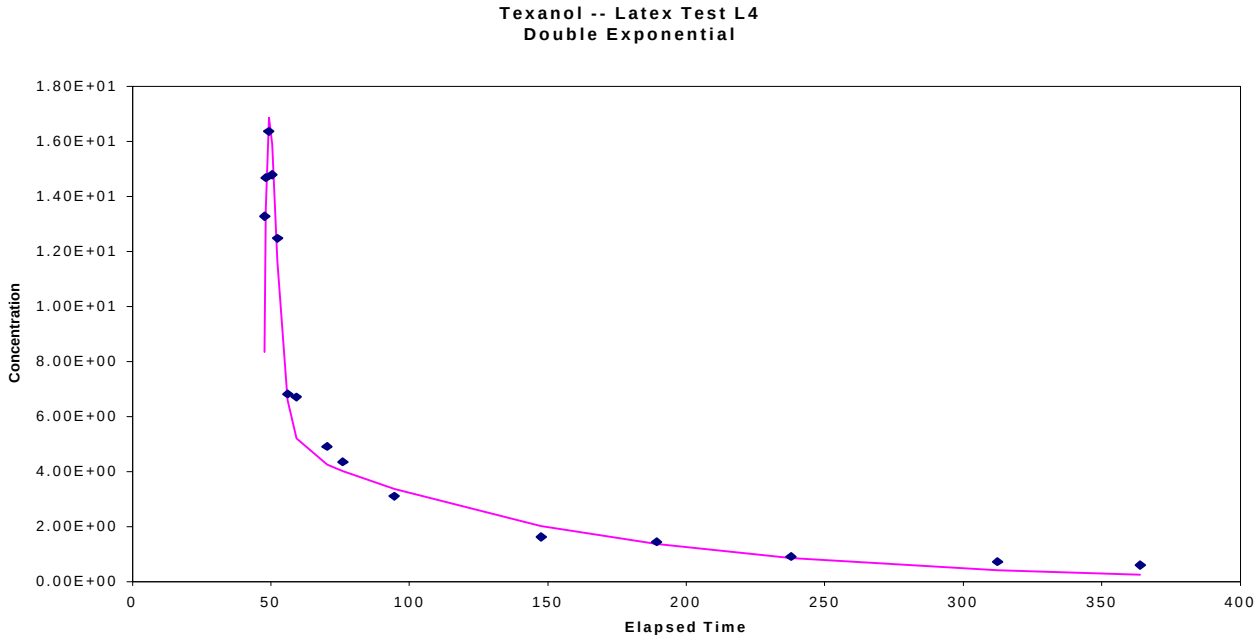


Figure C-2. TMPD-MIB Concentrations and Model Fit for Test L4 (Latex Paint LSG-D).

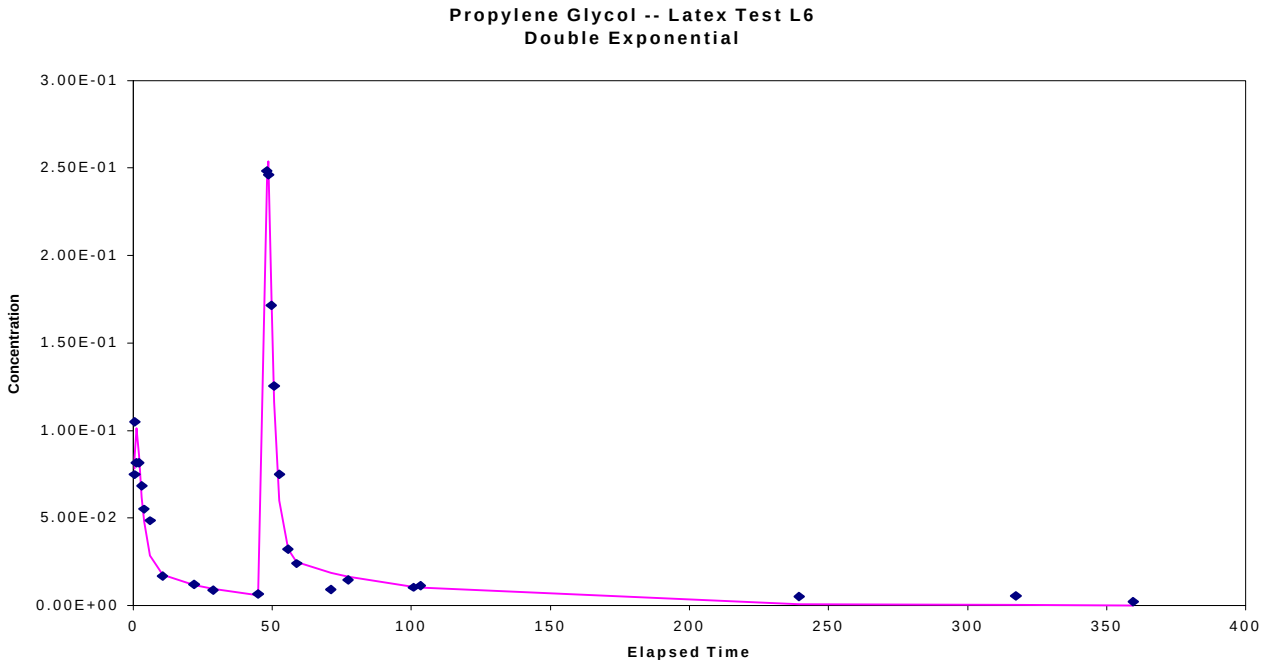


Figure C-3. Propylene Glycol Concentrations and Model Fit for Test L6 (Latex Paint LF-C).

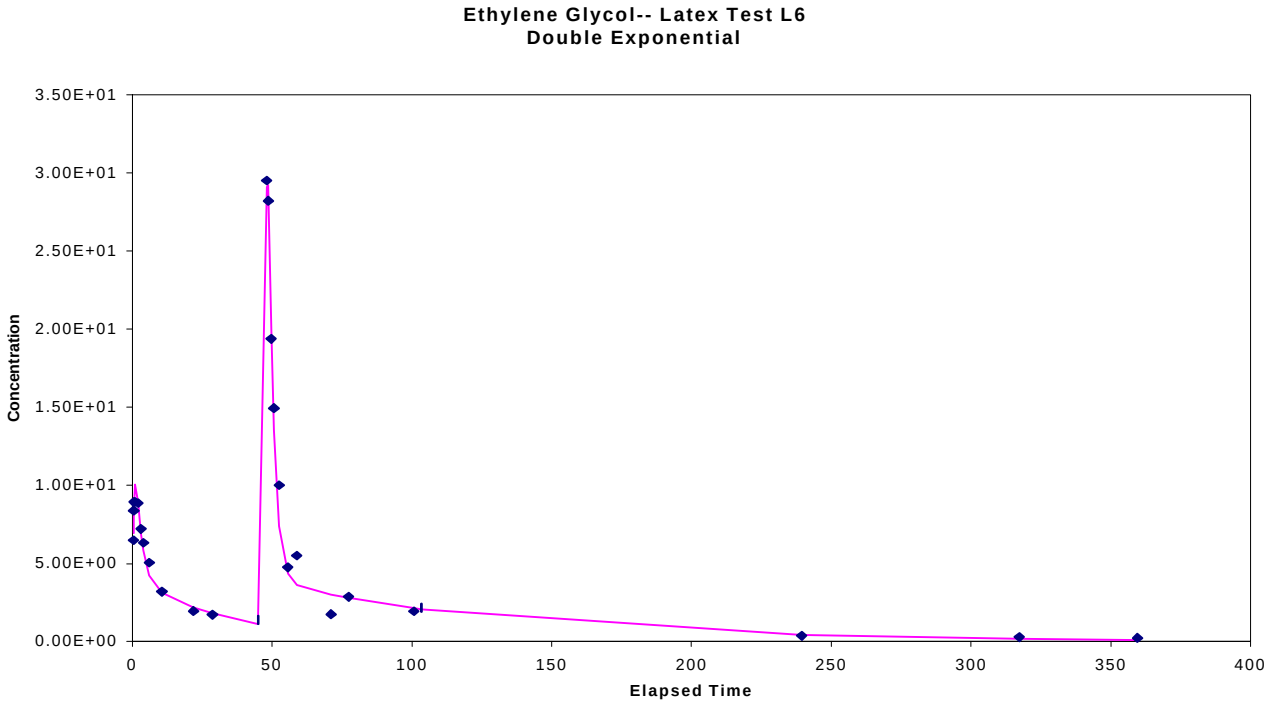


Figure C-4. Ethylene Glycol Concentrations and Model Fit for Test L6 (Latex Paint LF-C).

Estimates of the parameters (E_0 and k) for each of the exponentials in the double-exponential emissions model described above are summarized for chemicals in each paint formulation and the primer in Table C-2. The R^2 value shown for the first exponential is actually the value that results when applying the entire model (first plus second exponentials) to the entire data set for a given chemical during a chamber test. Excellent overall fits to the data were obtained in virtually every case, with the R^2 value at or above 0.85 in all cases and above 0.95 in many cases.

The estimated k values for the emission decay rate for any given chemical were not entirely consistent across paint formulations. The range of the estimates can be summarized as follows:

- K value for first exponential
  - for propylene glycol, varied from 0.9 to 2.7 across five formulations
  - for ethylene glycol, varied from 0.3 to 3.0 across five formulations
  - for TMPD-MIB, varied from 0.5 to 0.9 across three formulations (fourth was 6.5)
  - for dipropylene glycol, varied from 0.2 to 0.8 across two formulations.

- K value for second exponential
  - for propylene glycol, varied from 0.005 to 0.03 across five formulations
  - for ethylene glycol, varied from 0.002 to 0.03 across five formulations
  - for TMPD-MIB, varied from 0.007 to 0.05 across four formulations
  - for dipropylene glycol, varied from 0.007 to 0.03 across two formulations.

The emitted mass for each chemical can be estimated as the integral of equation (C-1), or $E_{01}/k_1 + E_{02}/k_2$. The recovery for each chemical, obtained by expressing this integral as a percentage of the applied mass, is shown in Table C-3. There is one case (ethylene glycol for paint LSG-D) for which the recovery value clearly is an outlier. Otherwise, the recovery values generally range from 10 to 50 percent, averaging about 25-30 percent. This outcome is consistent with results from Wilkes et al.(see Appendix D), who reported a range of recovery values from 20 to 35 percent for chemicals in interior latex paints.

The previous work by Wilkes et al. also indicated that the second exponential accounts for about 90 percent of the emitted mass. Corresponding estimates can be obtained from Table C-3 by expressing the emitted mass associated with the second exponential (E_{02}/k_2) as a percentage of

the total emitted mass ($E_{01}/k_1 + E_{02}/k_2$). Neglecting the outlier case, the estimated percentage ranges from 64 to 96 percent, averaging 80 percent.

Table C-2. Latex Parameter Estimates (Double-exponential Emissions Model)

Chemical	1st Exponential			2nd Exponential		
	E_{01}	K_1	R^2	E_{02}	K_2	R^2
PAINT LSG-E						
Propylene Glycol	3.106	1.429	0.978	0.021	0.005	0.774
Ethylene Glycol	0.152	0.282	0.851	0.013	0.002	0.380
TMPD-MIB	0.549	0.867	0.947	0.025	0.007	0.924
Dipropylene Glycol	0.004	0.177	0.995	0.001	0.007	0.810
PAINT LF-B						
Propylene Glycol	7.156	2.115	0.983	0.043	0.006	0.902
Ethylene Glycol	0.456	1.129	0.958	0.035	0.004	0.936
TMPD-MIB	2.450	1.368	0.930	0.152	0.011	0.978
Dipropylene Glycol	0.006	0.755	0.857	0.002	0.025	0.999
PAINT LSG-D						
Propylene Glycol	6.370	0.908	0.987	0.098	0.006	0.894
Ethylene Glycol	0.166	0.702	0.940	0.025	0.003	0.675
TMPD-MIB	1.005	0.519	0.985	0.140	0.010	0.953
PAINT LF-C						
Propylene Glycol	0.054	2.752	0.995	0.001	0.019	0.854
Ethylene Glycol	6.815	3.044	0.988	0.104	0.012	0.988
TMPD-MIB	11.535	6.481	0.960	0.340	0.049	0.920
PRIMER LF-C						
Propylene Glycol	0.013	1.606	0.892	0.001	0.030	0.976
Ethylene Glycol	1.276	1.699	0.964	0.106	0.029	0.917

Table C-3. Recoveries for Chemicals in Latex Primer and Paints

Chemical	Paint/Chemical Applied		Chemical Emitted		Recovery (%)
	Paint (g)	Chemical (mg)	E_{01}/K_1	E_{02}/K_2	
PAINT LSG-E					
Propylene Glycol	2.29	55.42	2.17	3.78	10.8
Ethylene Glycol	2.29	N/A	0.54	7.53	N/A
TMPD-MIB	2.29	16.03	0.63	3.57	26.2
Dipropylene Glycol	2.29	0.27	0.02	0.12	52.2
PAINT LF-B					
Propylene Glycol	2.56	60.16	3.38	7.63	18.3
Ethylene Glycol	2.56	N/A	0.40	8.95	N/A
TMPD-MIB	2.56	43.01	1.79	13.54	35.6
Dipropylene Glycol	2.56	0.72	0.01	0.08	11.8
PAINT LSG-D					
Propylene Glycol	2.82	157.32	7.02	16.92	15.2
Ethylene Glycol	2.82	0.05	0.24	7.50	14437.4
TMPD-MIB	2.82	72.47	1.94	14.65	22.9
PAINT LF-C					
Propylene Glycol	2.23	0.12	0.02	0.04	50.4
Ethylene Glycol	2.23	45.05	2.24	9.05	25.1
TMPD-MIB	2.23	15.72	1.78	6.93	55.4
PRIMER LF-C					
Propylene Glycol	2.85	N/A	0.01	0.02	N/A
Ethylene Glycol	2.85	55.86	0.75	3.68	7.9

C4. DEVELOPMENT OF A PREDICTIVE MODEL

The number of cases for which emission decay rates could be estimated for the first or the second exponential was insufficient for reliable development of an empirical model to predict such rates. Instead, reliance was placed on an empirical model developed by Wilkes et al. (see Appendix D). In that model, the emission decay rate associated with the first ("fast") exponential is predicted by vapor pressure and the emission decay rate associated with the second ("slow") exponential is predicted by molecular weight, as follows:

- Predicted $k_1 = 233.25 * VP$ (C-2)
- Predicted $k_2 = 0.0000584 * MW$ (C-3)

where VP is vapor pressure (in torr) and MW is molecular weight (in g/mole).

Table C-4 indicates the degree of correspondence between the predicted k_1/k_2 values from the empirical model and those estimated from the chamber emission tests conducted under this project. For k_1 the model substantially over-predicts the measured k_1 values for propylene glycol and ethylene glycol and slightly under-predicts the value for TMPD-MIB, which has the lowest vapor pressure. For k_2 the model is quite close in all cases, toward the lower end of the range of estimated values for propylene glycol and ethylene glycol, and toward the upper end for TMPD-MIB. The fact that the predictions are quite close for k_2 values is encouraging, since the second exponential is believed to account for 80 to 90 percent of the emitted mass.

Table C-4. Comparison of Estimated and Predicted Emission Decay Rates for Chemicals in Latex Paint

Chemical Properties* and K Values	Propylene Glycol	Ethylene Glycol	TMPD-MIB
Molecular Weight (g/mole)	76.1	62.1	216
Vapor Pressure (torr)	0.2	0.05	0.0019
Range of Estimated k_1 Values	0.9 - 2.7	0.3 - 3.0	0.5 - 1.4**
Predicted k_1 Value	46.7	11.7	0.44
Range of Estimated k_2 Values	0.005 - 0.002	0.002 - 0.03	0.007 - 0.011
Predicted k_2 Value	0.004	0.004	0.013

* As reported by Wilkes et al. (see Appendix D).

** Suspected outlier of 6.5 excluded from range of estimated values.

APPENDIX D

PAPER ON EMISSIONS MODEL FOR LATEX PAINT
(presented at Indoor Air '96 Conference)

ESTIMATION OF EMISSION PROFILES FOR INTERIOR LATEX PAINTS

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ABSTRACT

Methods were developed for estimating emission profiles for VOCs released from interior latex paints, for two situations: time-series data are available from small-chamber experiments; and only the weight fractions and physical/chemical properties of the paint constituents are known. A double-exponential model fit the data quite well in most cases. The rate constant for the "fast" (evaporation-dominated) exponential is related to vapor pressure, and the rate constant for the "slow" (diffusion-dominated) exponential is related to molecular weight. Although the fast component dominates the early phase of the emission profile, it generally accounts for 10 percent or less of the released VOC mass. The mass released, in turn, generally was between 20 and 35 percent of the applied VOC mass.

INTRODUCTION

Estimation of human inhalation exposure in residential settings, due to use of consumer products or installation of building materials or furnishings, requires integration of time-varying pollutant concentrations with information on individuals' locations and breathing rates. Often the concentration component is estimated using an indoor air quality (IAQ) model. The accuracy of the exposure estimate is enhanced by providing a faithful depiction of the time-varying airborne concentration which, in turn, relies on reasonable characterization of the emission profile for the chemical(s) of concern.

The main objective of the effort described in this paper was to develop methods for estimating emission profiles for chemicals released from interior latex paints, for two situations: data are available from small-chamber experiments whereby airborne concentrations are measured in the chamber at selected points in time after the paint has been instantaneously applied to a substrate; and only the weight fractions and physical/chemical properties (molecular weight and vapor pressure) of the paint constituents are known. Small-chamber data used for this analysis have been recently collected for latex paint applied to gypsum board (1).

METHODS

The experimental data were collected under sponsorship of the EPA Air and Energy Engineering Research Laboratory (AEERL) in Research Triangle Park, NC. These experiments involved application of two different formulations, called A and B in this paper, of latex paint to a small piece of pre-painted gypsum board. Following the paint application,

the specimen was immediately inserted in a small stainless-steel chamber, and concentrations of four individual VOCs were measured at selected points in time over a period of several hundred hours. Multiple samples were collected during each experiment on Tenax®TA sorbent and analyzed by a gas chromatograph with a flame ionization detector (GC/FID). The sample durations were variable, ranging from an hour or less at the start of the experiment to much longer durations toward the end, when the chamber air concentrations were lower.

Bulk analysis of the paint sample was performed to determine which volatile organic compounds (VOCs) are present in each paint, and to estimate the weight fraction of each VOC. Four individual VOCs were found to comprise the majority of the VOCs present in each paint. The molecular weight (MW) and vapor pressure (VP) of these four compounds were estimated (2) to be:

- Propylene Glycol: MW = 76.1 g/mol VP = 0.2 torr
- Ethylene Glycol: MW = 62.1 g/mol VP = 0.05 torr
- Butoxyethoxyethanol: MW = 162.2 g/mol VP = 0.02 torr
- Texanol: MW = 216 g/mol VP = 0.0019 torr

Various representations of the emission profile were considered, including a mass-transfer representation based on physical and chemical properties, an empirically fit single-exponential model to account for the (assumed) general decline in the emission rate over time, and an empirically fit double-exponential model (the sum of two exponentials) that assumes two components of emissions decline -- a "fast" (evaporation-dominated) component that primarily governs the early stage of emissions and a "slow" (diffusion-dominated) component that governs the later stage. The exponential model is given by the following equation:

$$S(t) = E_0 e^{-kt} \quad (1)$$

where: $S(t)$ = Source strength as a function of time (mass/time)
E_0 = Initial emission rate (mass/time)
k = First-order rate constant (time^{-1})
t = Time.

For estimation of the single- and double-exponential model parameters (an initial emission rate and a first-order rate of decline in the rate), nonlinear regression analysis was applied to the chamber concentration data, taking advantage of the known chamber volume and the experimentally controlled air exchange rate for the chamber.

RESULTS

The mass-transfer model was found by other researchers (1) to provide a good fit to measured air concentrations. However, because of the large number of parameters that are difficult to estimate or must be measured, it was not possible to use this model for this study. Based on the results of the nonlinear estimation process, the single-exponential model did not fit the data well, most likely because it is insufficient to provide an empirical representation of the physical process as the paint dries. The double-exponential model fit the data quite well in most cases.

Chamber data for painted gypsum board currently are limited to two formulations of latex paint. Methods were sought by which to estimate parameters of the double-exponential emission model for brands of latex paint for which only the weight fraction, molecular weight and vapor pressure of a VOC constituent are known, so that the emissions of untested formulations can be estimated. Therefore, the data from experiments with formulation A of latex paint were used to develop relationships between the parameters of the fitted double exponential and the chemical properties of each VOC, and the data from the experiments with formulation B were used to evaluate the predictive ability of these relationships.

It was hypothesized that the "fast" decline would be evaporation-dominated and, hence, the rate term for this decline would be related to a chemical's vapor pressure. Similarly, it was hypothesized that the rate term for the diffusion-dominated "slow" decline would be related to a chemical's molecular weight. These hypotheses were indeed supported by the data. Regression through the origin indicated strong linear relationships between the "fast" decline rate constant (k_1) and vapor pressure ($R^2 = 0.92$), and between the "slow" decline rate (k_2) and molecular weight ($R^2 = 0.96$). Regression not constrained to go through the origin was also examined, but was discarded because of the possibility of predicting a negative rate constant. These relationships are shown in Figure 1.

The parameters of the fitted double exponentials are presented in Table 1. The mass released by each exponential is also given in the table, along with the estimate of the total mass released based on the fitted double exponentials. The fraction of the total applied VOC mass that was released is between 20% and 35%, as estimated by the fitted double exponentials and shown in the table. In addition, the "fast" exponential generally accounts for less than 10% of the released mass**,** leaving the remaining 90% for long-term emissions. Based on these observations, along with the relationships presented in Figure 1, a method for estimating the parameters to a double-exponential representation of the emissions has been developed. The method assumes that 25% of the total available mass (determined based on the bulk analysis of the paint) is ultimately released. Of this 25% total emissions, 10% is assumed to be released as described by the first ("fast") exponential, and the remaining 90% is assumed to be released as described by the second ("slow") exponential. Therefore, the parameters of the two exponentials can be estimated by using the relationships presented in Figure 1 to approximate k_1 and k_2. Then E_{01} and E_{02} can be determined by assigning the appropriate mass to each, recognizing that the released mass associated with each exponential is the ratio of the initial emission rate to the rate constant (E_0/k).

This method was applied to the emissions from the latex paint described as formulation A, as well as a different latex paint (formulation B). The double exponential fits to the chamber data, as well as double exponentials based on the parameter-estimation method described above, are shown for one VOC (butoxyethoxyethanol) in Figure 2 (formulation A) and in Figure 3 (formulation B). In each case, the double exponentials based on the parameter-estimation procedure are not drastically different from those fit directly to the chamber data. The estimated double exponential for formulation B provides some evidence that the estimation method performs reasonably well. This process also was applied with similar success for the other three VOCs. In most cases, the peak chamber concentration predicted by the estimation method was within a factor of two of the measured peak concentration.

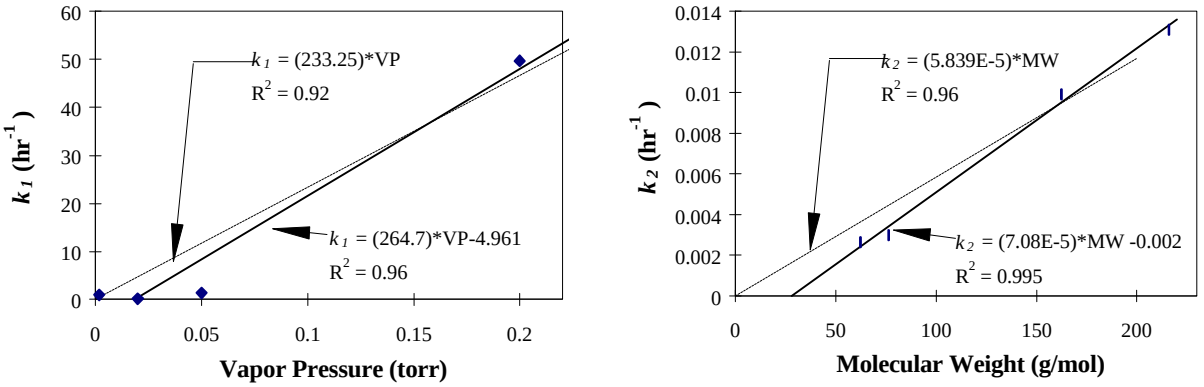

Figure 1 Correlation between chemical properties and parameters of the double exponential.

Table 1 Summary of Parameters of the Double-Exponential Fit for 4 VOCs, Formulation A.

Compound	Exponential	E_0, mg/hr	k, 1/hr	Mass of VOC Released, mg	Total Mass of VOC Applied, mg	Fraction of Applied Mass Released, mg/mg
Propylene Glycol	1st	0.815	49.68	0.02	—	0.002
	2nd	0.0058	0.0030	1.95	—	0.220
	Total	—	—	1.97	8.86	0.222
Ethylene Glycol	1st	2.812	1.344	2.09	—	0.023
	2nd	0.055	0.0026	20.75	—	0.226
	Total	—	—	22.84	91.68	0.249
Butoxyethoxyethanol	1st	0.253	0.158	1.60	—	0.084
	2nd	0.022	0.0099	2.27	—	0.119
	Total	—	—	3.87	19.02	0.203
Texanol	1st	1.46	0.944	1.55	—	0.030
	2nd	0.22	0.013	16.65	—	0.323
	Total	—	—	18.21	51.57	0.353

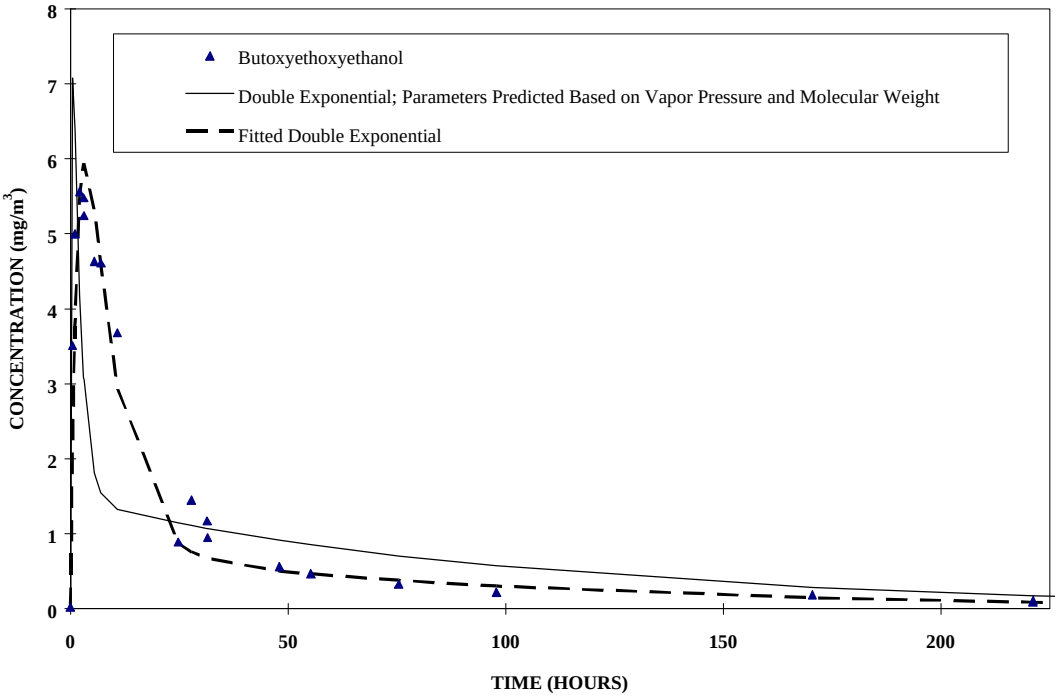

Figure 2 Comparison of Butoxyethoxyethanol Chamber Concentrations to the Fitted Double Exponential and the Predicted Double Exponential for Latex Paint, Formulation A.

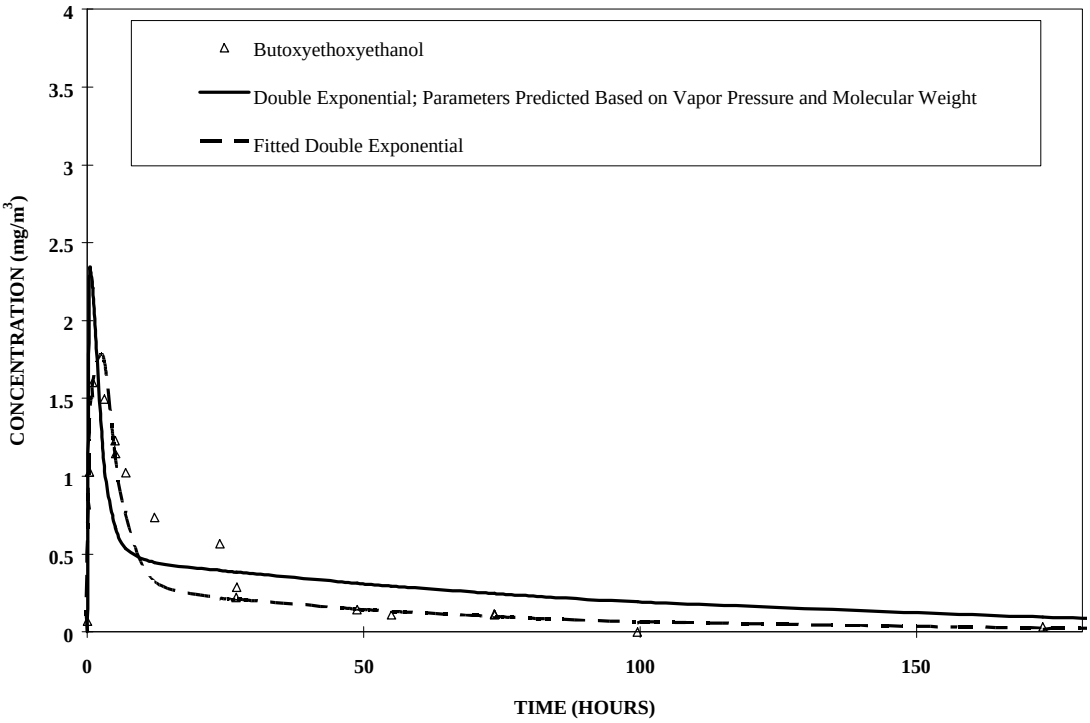

Figure 3 Comparison of Butoxyethoxyethanol Chamber Concentrations to the Fitted Double Exponential and the Predicted Double Exponential for Latex Paint, Formulation B.

CONCLUSIONS

The double-exponential model was found to fit the data quite well in most cases, provided that the second ("slow") exponential was estimated first, by fitting a single-exponential model to the data after the first 48 hours in the chamber. The first ("fast") exponential could then be estimated using all the chamber data, by specifying a double-exponential model with the second exponential's parameters input as "knowns."

Integration of the fitted double-exponential model to infinity provided an estimate of the total emitted mass of each VOC. Comparison of this emitted mass with the applied mass, as estimated from the bulk analysis, indicated that the emitted mass ranged from 20 to 35 percent of the applied mass for those compounds, averaging about 25 percent. Integration of the respective exponentials indicated that the amount of emitted mass attributable to the first ("fast") exponential was generally less than 10 percent. Thus, although this exponential dominates the early emission phase, the later phase of "slow" emissions accounts for most of the total VOC emissions.

A relationship between the parameters of the double exponential and the chemical properties of the VOC was identified. Because the VOCs are leaving the paint primarily through evaporation in the initial phases of the paint-drying process, it is reasonable for the rate constant to be correlated with the VOC's vapor pressure. Similarly, the VOCs are leaving later in the paint-drying process primarily through diffusion, and in this case it is reasonable for the rate constant to the be correlated with the VOC's molecular weight. The number of data points is small, and therefore these relationships cannot be used with great confidence, especially for VOCs with vapor pressures and molecular weights outside the range of those examined in this study. With data from additional chamber tests, the confidence in these relationships could be improved, and a physically/chemically based mass-transfer model could be developed.

Several areas where improved information or theoretical developments would aid any future iterations of estimation procedures for interior latex paints are apparent. More small-chamber experimental data for paint applied to gypsum board are needed so that differences across flat, semi-gloss and gloss paints can be evaluated, and so that a broader array of individual VOCs is available to support development of regression estimates. Ideally, a physically and chemically based model could be developed that accounts for the mass-transfer process yet requires only minimum parameter estimates such as VOC weight faction, vapor pressure and molecular weight, with possible addition of selected parameters specific to the painting event (e.g., paint application rate, indoor volume).

ACKNOWLEDGMENTS

This work was funded by the US Environmental Protection Agency under contract number 68-D3-0013.

REFERENCES

(1) Acurex Environmental Corporation. 1995. “Data Summary for the Latex Paint Assessment Program. II. Dynamic and Static Chamber Testing and Model Development”, Report Prepared for the US Environmental Protection Agency Under Contract Number 68-D4-0005, June 9, 1995.
(2) Environmental Fate Database, Syracuse Research Corporation, Syracuse, NY, USA.

APPENDIX E

MODEL EVALUATION USING DATA FROM EPA RESEARCH HOUSE

E1. INTRODUCTION

A series of two related experiments was conducted by ARCADIS Geraghty and Miller, Inc., at the EPA test house, for the primary purpose of gathering data to be used for model evaluation. One of the experiments involved alkyd primer and paint and the other latex primer and paint. Each of the experiments followed the same general protocol -- one coat of primer was applied to the walls of the front corner bedroom, and approximately 48 hours later one coat of paint was applied to the same walls. For each experiment, new gypsum board was primed and painted. The new wallboard was mounted on furring strips that were temporarily applied to existing walls, so that the source could be removed after each experiment.

The sections that follow describe (1) the EPA test house, (2) certain specifics of the experiment for alkyd primer and paint together with model inputs and modeling results in comparison with measurements, and (3) experiment specifics, model inputs and modeling results for latex primer and paint.

E2. TEST HOUSE DESCRIPTION AND GENERAL TEST CONDITIONS

The EPA test house, located in North Carolina, is a single-family residence of wood frame construction. As shown in Figure E-1, the floor plan consists of three bedrooms, two bathrooms, a combination living/dining room, a small kitchen, and a den. The home is heated with a gas furnace and cooled by a central air conditioning system. All floor areas are carpeted except the kitchen and bathrooms, which have linoleum flooring. All windows have either curtains or shades. The attached garage contains all monitoring and test support instrumentation and is equipped with a heat pump for climate control.

The house has an interior volume of 319 cubic meters, or 11,272 cubic feet. The volume of the front corner bedroom that was painted is 30.25 cubic meters, or 1,069 cubic feet, which accounts for about 9.5 percent of the total house volume. The wall area that was painted in the front corner bedroom totals about 29.5 square meters, or 317.5 square feet. Thus, the loading ratio for the painted space (i.e., ratio of the painted surface area to room volume) was 0.297 ft^2/ft^3 for these experiments, similar to the WPEM default of 0.29 ft^2/ft^3 when only walls are painted.

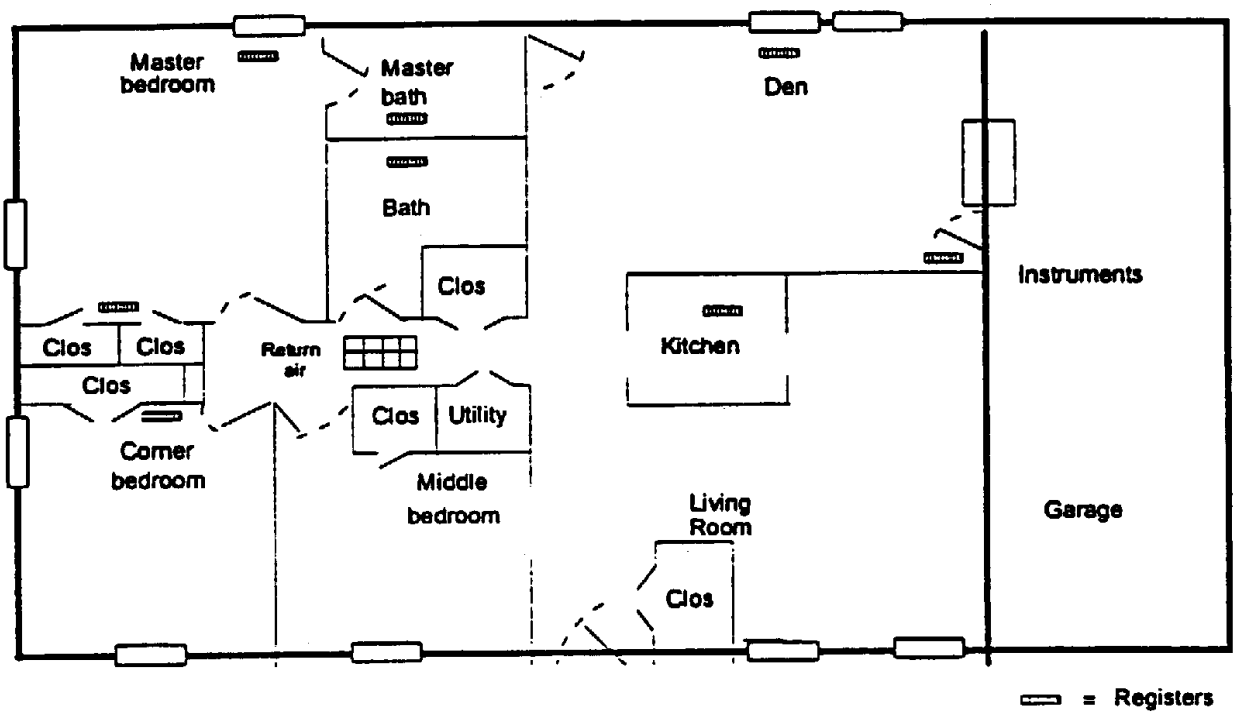

Figure E-1. Floor Plan for the EPA Test House.

Throughout each experiment the air handler fan for the central air conditioner was placed in the constant-operation mode, and ceiling fans were operated and all supply registers were kept open, to ensure good mixing throughout the house. With this configuration, air exchange rates prevailing during the experiments could be measured more accurately (using a tracer-decay method) and air sampling could be restricted to two locations -- the painted bedroom and the den at the opposite end of the house. Exterior doors and windows were closed during each experiment, interior doors were open, and the indoor temperature setting was 72 °F (22.2 °C). The measured air exchange rate averaged 0.48 air changes per hour (ACH) for the alkyd test and 0.47 ACH for the latex test. Based on previous measurements in the supply registers for the painted bedroom, the airflow rate between that room and the remainder of the house was assumed to be 325 m^3 per hour, or 11,484 ft^3 per hour.

Background air samples were collected both outdoors and in the house prior to each of the two experiments. Paint was applied approximately 48 hours after primer application, and air samples were collected over a 14-day period (48 hours after priming and 12 days after painting), at a progressively lower rate as indoor concentrations receded following the priming/painting event. The latex test was conducted first (August 1997). Following the 14-day measurement period, the painted wallboard was removed, the house was aired out, and then new wallboard was installed for the alkyd test (September 1997).

E3. MODEL EVALUATION FOR ALKYD PRIMER AND PAINT

The report of the experiments by ARCADIS Geraghty and Miller, Inc., indicates that, for the alkyd experiment, 6.96 kilograms of primer AP-F were applied to the walls in the front corner bedroom over a period of 43.4 minutes, beginning at 11:13 a.m. on September 9, 1997. Approximately two days later, 4.93 kilograms of paint ASG-G were applied over a period of 33.7 minutes, beginning at 10:41 a.m. on September 11, 1997. The reported wet film thickness was 14.4 mil for primer and 8.05 mil for paint. The measured air exchange rate prevailing during the test averaged 0.48 ACH, as noted previously.

Corresponding WPEM inputs for the painting scenario described above are summarized in Table E-1. The input for house volume matched the actual value listed above. The percent painted was set to 9.5 percent, resulting in a painted volume of 1071 ft^3 (the actual painted volume was 1069 ft^3). The inputs for air exchange and interzonal airflow rates matched the actual values listed above. Based on a loading ratio of 0.30 ft^2/ft^3 for walls, the painted surface area input was 321 ft^2 (the actual area was 317.5 ft^2).

The wet film thickness values reported by ARCADIS Geraghty and Miller, Inc. -- 6 mil for primer and 5.375 mil for paint -- correspond to primer/paint coverages of 267 and 298 ft^2/gallon, respectively. The application rates input for WPEM -- 1.66 gallons/hour for primer and 1.92 gallons/hour for paint -- were chosen to result in priming/painting durations that matched those reported for the experiment at the EPA test house.

Table E-1. WPEM Inputs for Alkyd Painting Scenario at EPA Test House

Input Parameter	**Input Value**
House volume	11,272 ft^3
Percent of house painted	9.5 %
Air exchange rate	0.48 ACH
Interzonal airflow rate	11,484 ft^3/hour
Painted wall surface area	321 ft^2 (using loading ratio of 0.30; actual = 317.5 ft^2)
Wet film thickness	6 mil for primer, 5.375 mil for paint
Calculated amount of paint	1.20 gallons for primer, 1.08 gallons for paint
Application rate	1.66 gallons/hour for primer, 1.92 gallons/hour for paint
Calculated application time	0.72 hours for primer, 0.56 hours for paint
Primer/paint interval	Paint second day after priming

WPEM inputs pertaining specifically to the modeled paint and chemical are listed in Table E-2. The paint density values were chosen such that the product of gallons applied times paint density yielded the applied-mass values reported by ARCADIS Geraghty and Miller, Inc. -- 6.96 kg for primer and 4.93 kg for paint. The first chemical modeled was undecane, one of the primary constituents by weight in both alkyd primer and paint, with physical/chemical properties as listed in the table. The input values for weight fraction were based on the results of bulk analysis for primer and paint (see Appendix A, Section A2). The default emission decay rate calculated by the empirical emissions model in WPEM was used; the basis for the WPEM algorithm to calculate this default value is described in Appendix A, Section A4. Based on results of sink tests conducted by ARCADIS Geraghty and Miller, Inc. (see Appendix A, Section A5), indoor sinks were assumed to be negligible.

A DIY painter was arbitrarily chosen as the exposed individual. WPEM inputs for occupancy and exposure affect exposure/dose calculations, but the interest here was in a comparison of modeled versus measured indoor concentrations (there were no exposure/dose measurements). The model was run for 4 days with a 5-minute reporting interval.

Table E-2. WPEM Inputs for Alkyd Paint and Chemical

Input parameter	**Input Value**
Paint density	5800 grams/gallon for primer, 4565 grams/gallon for paint
Chemical name	Undecane
Molecular weight	156.4 g/mole
Vapor pressure	1.02 torr
Weight fraction	0.00875 for primer, 0.0165 for paint
Chemical mass emitted	60.98 grams for primer, 81.08 grams for paint
Emission decay rate	1.60/hr for primer, 1.70/hr for paint
Sink model	No sinks

Model results (concentrations in the painted bedroom and in the den) are compared with measurement results in Figure E-2. The actual priming and painting were done around 11 a.m., whereas in WPEM priming and painting begin at 9 a.m. Thus, for direct comparison, both model and measurement time scales were normalized to elapsed time after priming was started. Another minor difference is that in WPEM the painting starts exactly 48 hours after priming is started, whereas at the test house the interval was somewhat less (about 47.5 hours). As a result, the measured values for the painting event rise slightly ahead of the modeled values.

There generally is a high degree of correspondence between modeled and measured values, particularly in the painted bedroom. For example, the peak modeled concentrations in the bedroom were about 210 and 300 mg/m^3, respectively, corresponding to peak measured values of about 140 and 210 mg/m^3. The modeled peak values for the den exceeded measured values by a greater amount, on the order of 100 versus 25 mg/m^3 for priming and 150 versus 50 mg/m^3 for painting. Based on paired values at corresponding points in time, the average modeled concentration in the bedroom was 66.5 mg/m^3 (versus 63.9 mg/m^3 measured) and the average modeled value in the den was 38.2 mg/m^3 (versus 20.7 mg/m^3 measured).

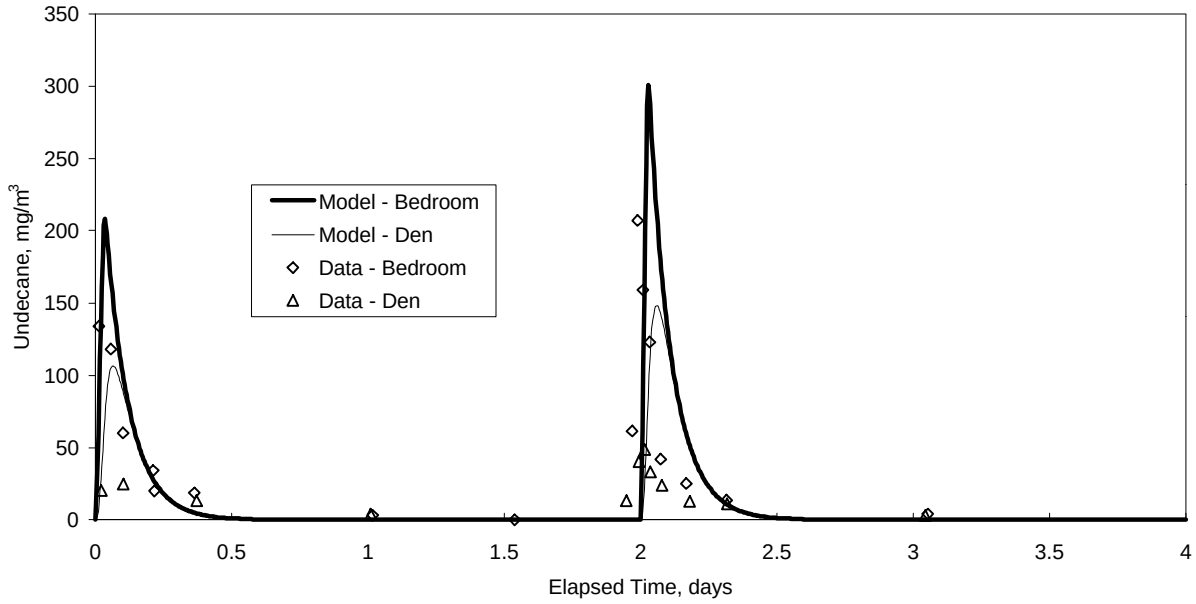

Figure E-2. Modeled and Measured Undecane Concentrations for the EPA Test House.

A second chemical chosen for model evaluation with alkyd primer/paint was p-xylene. Two reasons for this selection were that (1) its molecular weight (106.2) was about 50 percent lower than undecane's and its vapor pressure (4.34 torr) was about a factor of four higher, and (2) unlike undecane, p-xylene was not among the chemicals used in the nonlinear regression to develop an empirical emissions model for VOCs in alkyd primer/paint. Other than molecular weight and vapor pressure, the only differences in inputs for p-xylene were its weight fractions -- 0.00398 for primer and 0.00547 for paint, both lower than for undecane. The emission decay rates for p-xylene calculated by the empirical emissions model in WPEM were considerably higher than for undecane -- 11.1/hour for primer and 11.9/hour for paint.

As with undecane, the concentrations predicted by WPEM for p-xylene were higher than, but generally consistent with, measured values. For example, the peak modeled concentrations in the painted bedroom were 155 and 180 mg/m^3 for priming and painting, respectively, versus measured values of about 80 mg/m^3. The peak modeled concentrations in the den were around 65 mg/m^3 for both priming and painting, compared to measured peaks of about 20 mg/m^3. Based on paired values at corresponding points in time, the average modeled concentration in the bedroom was 30.6 mg/m^3 (versus 20.6 mg/m^3 measured) and the average modeled value in the den was 17.9 mg/m^3 (versus 7.6 mg/m^3 measured).

E3. MODEL EVALUATION FOR LATEX PRIMER AND PAINT

The report of the experiments by ARCADIS Geraghty and Miller, Inc., indicates that, for the latex experiment, 5.26 kilograms of primer LP-A were applied to the walls in the front corner bedroom over a period of 36.4 minutes, beginning at 11:18 a.m. on August 20, 1997. Approximately two days later, 4.65 kilograms of paint LSG-E were applied over a period of 35.4 minutes, beginning at 10:02 a.m. on August 22, 1997. The reported wet film thickness was 7.72 mil for primer and 5.17 mil for paint. The measured air exchange rate prevailing during the test averaged 0.47 ACH.

Corresponding WPEM inputs for the painting scenario described above are summarized in Table E-3. Inputs for house volume, percent painted, interzonal airflow rate and painted surface area were the same as for the alkyd test.

The wet film thickness values reported by ARCADIS Geraghty and Miller, Inc. -- 6.88 mil for primer and 5.17 mil for paint -- correspond to primer/paint coverage rates of 233 and 310 ft^2/gallon, respectively. The input painting rates of 2.27 gallons per hour for primer and 1.76 gallons per hour for paint are higher than typical values that have been reported for do-it-yourself painters (on the order of 0.5 to 1 gallon/hour), but were were chosen to result in priming/painting durations that matched those reported for the experiment at the EPA test house.

Table E-3. WPEM Inputs for Latex Painting Scenario at EPA Test House

Input Parameter	**Input Value**
House volume	11,272 ft^3
Percent of house painted	9.5 %
Air exchange rate	0.47 ACH
Interzonal airflow rate	11,484 ft^3/hour
Painted wall surface area	321 ft^2 (using loading ratio of 0.30; actual = 317.5 ft^2)
Wet film thickness	6.882 mil for primer, 5.171 mil for paint
Calculated amount of paint	1.38 gallons for primer, 1.04 gallons for paint
Application rate	2.27 gallons/hour for primer, 1.76 gallons/hour for paint
Calculated application time	0.61 hours for primer, 0.59 hours for paint
Primer/paint interval	Paint second day after priming

WPEM inputs pertaining specifically to the paint and chemical are listed in Table E-4. The paint density values were chosen such that the product of gallons applied times paint density yielded the applied-mass values reported by ARCADIS Geraghty and Miller, Inc. -- 5.26 kg for primer and 4.65 kg for paint. The first chemical modeled was TMPD-MIB, one of the primary constituents by weight in both latex primer and paint, with physical/chemical properties as listed in the table. The input values for weight fraction were based on the results of bulk analysis for primer and paint (see Appendix C, Section C2). The default emission decay rate calculated by the empirical emissions model in WPEM was used; the basis for the WPEM algorithm to calculate this default value is described in Appendix C (Section C4). Indoor sinks were assumed to be negligible.

Table E-4. WPEM Inputs for Latex Paint and Chemical

Input parameter	**Input Value**
Paint density	3812 grams/gallon for primer, 4471 grams/gallon for paint
Chemical name	TMPD-MIB
Molecular weight	216 g/mole
Vapor pressure	0.0019 torr
Weight fraction	0.0122 for primer, 0.007 for paint
Chemical mass emitted*	16.02 grams for primer, 8.10 grams for paint
Emission decay rate - first exponential - second exponential	 0.44/hr for primer and paint 0.01/hr for primer and paint
Sink model	No sinks

*For the empirical emissions model for latex primer/paint, 25 % of the applied chemical mass is assumed to be emitted.

A DIY painter was arbitrarily chosen as the exposed individual. WPEM inputs for occupancy and exposure affect exposure/dose calculations, but the interest here was in a comparison modeled versus measured indoor concentrations (there were no exposure/dose measurements). The model was run for 7 days with a 5-minute reporting interval.

Model results (concentrations in the painted bedroom and in the den) are compared with measurement results in Figure E-3. The actual priming and painting were done around 10 - 11 a.m., whereas in WPEM priming and painting begin at 9 a.m. Thus, for direct comparison, both model and measurement time scales were normalized to elapsed time after priming was started. Another minor difference is that in WPEM the painting starts exactly 48 hours after priming is started, whereas at the test house the interval was somewhat less (about 47 hours). As a result, the measured values for the painting event rise slightly ahead of the modeled values.

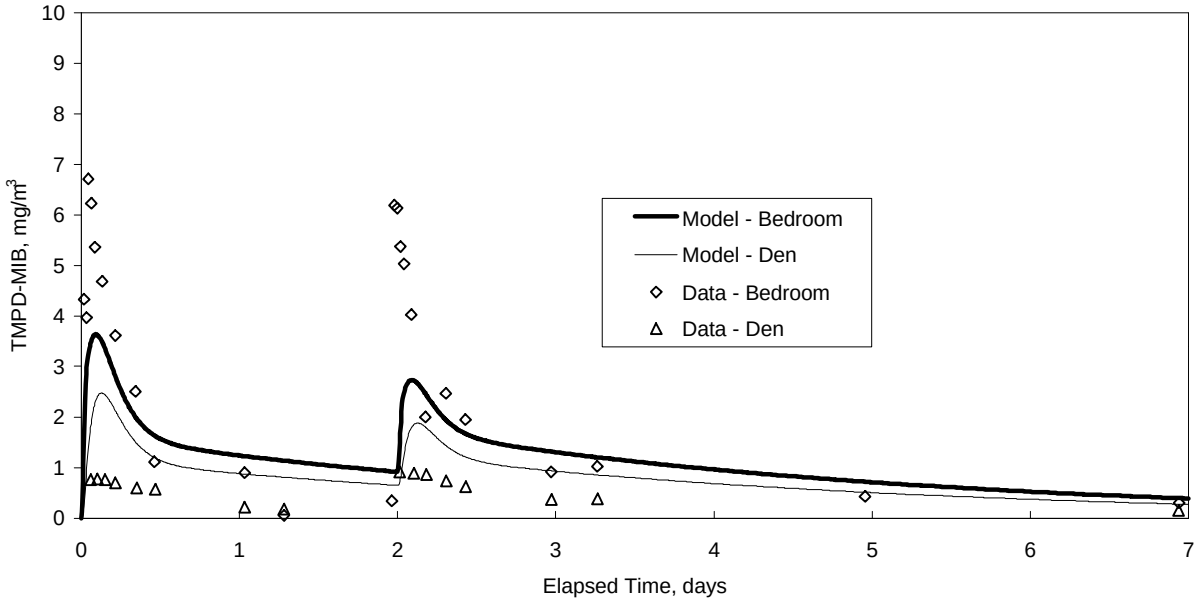

Figure E-3. Modeled and Measured TMPD-MIB Concentrations for the EPA Test House.

The modeled peak concentration for TMPD-MIB in the bedroom was lower than the measured peak by about a factor of two (3-4 mg/m^3 vs. 6-7 mg/m^3), whereas the modeled peak in the den was somewhat higher than measured (2-3 mg/m^3 vs. about 1 mg/m^3). Thus, the modeled values generally bracket the measurements. The higher measured-than-modeled values in the painted bedroom could be related to the model assumption that 25 percent of the applied primer/paint mass is emitted (i.e., the percentage could be somewhat higher for TMPD-MIB), and the lower measured-than-modeled values in the den could be related to sink behavior. Based on paired values at corresponding points in time, the average modeled concentration in the bedroom was 1.96 mg/m^3 (versus 3.15 mg/m^3 measured) and the average modeled value in the den was 1.39 mg/m^3 (versus 0.59 mg/m^3 measured).

The second chemical modeled was propylene glycol. The bulk analysis indicated that this chemical was not detected in primer and had a weight fraction of 0.0242 in the paint. The value entered for the primer weight fraction in WPEM was 0.000001, the lowest value allowed. The modeled peak concentrations in the bedroom and den were about 19 and 7 mg/m^3, as compared with measured values of 8 and 1 mg/m^3. The relatively high modeled peaks are driven primarily by the emission rate decay constant for the first exponential of the empirical (double-exponential) emissions model.

As noted in Appendix C (see Table C-4), the predicted rate value for the decay constant of the first exponential for propylene glycol (46.7/hour) was considerably higher than values estimated from small-chamber emission tests (range from 0.9 to 2.7/hour). With a rate constant of 1.8/hour, the modeled peak concentrations dropped to about 11 mg/m^3 in the bedroom and 5 mg/m^3 in the den. With this rate constant, the average modeled concentration in the bedroom was 1.37 mg/m^3 (versus 1.41 mg/m^3 measured) and the average modeled value in the den was 0.74 mg/m^3 (versus 0.20 mg/m^3 measured).