



# **Global Net on “CONSUMER EXPOSURE MODELLING”**

Report of the Workshop no. 2

on

**Source Characterization, Transport and Fate**

**20-21 June 2005, Intra (Italy)**



Editors: *Stylianos Kephelopoulos, Athanasios Arvanitis, Mike Jayjock*

The mission of the Institute for Health and Consumer Protection is to provide scientific support to the development and implementation of EU policies related to health and consumer protection. The IHCP carries out research to improve the understanding of potential health risks posed by chemicals, biocides, genetically modified organisms, contaminants released from food contact materials and consumer products.

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**Workshop Coordinator: *Stylianos Kephelopoulos***

**Workshop Rapporteur: *Athanasios Arvanitis***

**Workshop Moderator: *Michael A Jayjock***

*It is the recommendation of the Workshop participants that the work products presented herein to be used in the systematic development of human exposure models for their use in a tiered approach to exposure/risk assessment.*

*Given that the 5 bins presented herein represent a consensus taxonomy or universe of sources, the workshop participants advise that a reasonably representative subset of this comprehensive listing be selected for specific laboratory analysis and model development. It was further suggested that exposure models designed to describe these sources of exposure and the transport and fate of substances should be constructed using a step-wise approach as outlined in this report.*

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## **PREFACE**

The Exposure Modeling Sector of the Physical and Chemical Exposure Unit, Institute for Health and Consumer Protection of the European Commission's Joint Research Centre, organized a series of five specialized Workshops on “***Consumer Exposure Models Inter-comparison (Phase II) – Framework/Policy and Research/Science major issues***”. These workshops, were held in June 20-24, 2005, in Intra (Italy), and constituted the top event of the activities of the Global Net on “Consumer Exposure Modeling” for 2005, a growing consortium of expert model developers and users from Europe, America, Canada and Asia, aiming at harmonizing and validating existing consumer exposure models on the basis of common procedures and protocols. This activity is contributing to the consumer exposure assessment efforts of the PCE Unit, supporting the EU General Product Safety Directive (2001/95/EC) and providing technical support to aspects of REACH (*Registration, Evaluation and Authorisation of CHemicals*).

During the first Global CEM Net Workshop on “*Consumer Exposure Models Inter-comparison (Phase I) – The state of the science and research needs*” held in Ispra, on 26-27 of October 2004, the need on focusing on five major topics was identified concerning model harmonization and validation. A series of five Workshops has been then organized in June 2005, based on the draft agendas prepared in the first Global CEM Net Workshop, dealing with the following five major topics:

### Research/Science

#### **Workshop no. 1 – “Dermal transfer and penetration algorithms”**

*Monday 20<sup>th</sup> to Tuesday 21<sup>st</sup> of June, 2005*

Moderator: J. J. van Hemmen

Rapporteur: K.E. van der Jagt

#### **Workshop no. 2 – “Source characterization, transport and fate”**

*Monday 20<sup>th</sup> to Tuesday 21<sup>st</sup> of June, 2005*

Moderator: M. Jayjock

Rapporteur: A. Arvanitis

### Framework/Policy

#### **Workshop no. 3 – “Exposure modelling framework/model management issues”**

*Wednesday 22<sup>nd</sup> of June, 2005*

Moderator: M. Jantunen

Rapporteur: A. Arvanitis

### “In-between”

#### **Workshop no. 4 – “Exposure-related data”**

*Thursday 23<sup>rd</sup> of June, 2005*

Moderator: J. van Engelen, C. Money and P. Price

Rapporteur: A. Arvanitis

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**Workshop no. 5 – Scenario development**

Friday 24<sup>th</sup> of June, 2005

Moderator: J. van Engelen

Rapporteur: A. Arvanitis

The **Workshop no. 2** on “**Source characterization, transport and fate**” held on Monday 20<sup>th</sup> and Tuesday 21<sup>st</sup> of June 2005.

The general rationale of this workshop was:

*Identification, facilitation and communication of generic research on exposure models that will characterize people’s exposure to chemicals and raise the confidence and lower the uncertainty for quantitative estimates of exposure associated with potential human health effects to chemicals.*

This specific workshop addressed two general areas separately; viz., **source characterization** and **contaminant transport in indoor air**.

The purpose of this workshop was:

- 1. To survey and discuss the general state-of -the-science of physicochemical micro-environmental model development specifically in the areas of source characterization relative to strength, time-course, and transport and fate of emissions from predominantly indoors sources.*
- 2. Provide specific recommendations – consensus or clear majority opinion on the path forward for this research.*

The focus of the workshop has not been on specific substances but on the identification and development of general modeling constructs capable of describing the above factors for the multitude of substances impacting on human exposure from near field contact indoors.

The expected duties of and opportunities for the participants have been to:

1. Review nascent plans at the Joint Research Centre (JRC) to set up a Source Characterization Laboratory Facility. This was presented by Dr. John Little and member(s) of the JRC IHCP/PCE Laboratory.
2. Formally or informally present relevant research that they have done or have specific knowledge of, relative to these two general areas of study.
3. Participate in a decision-making process on forward plans for the JRC Laboratory and possible collaboration.

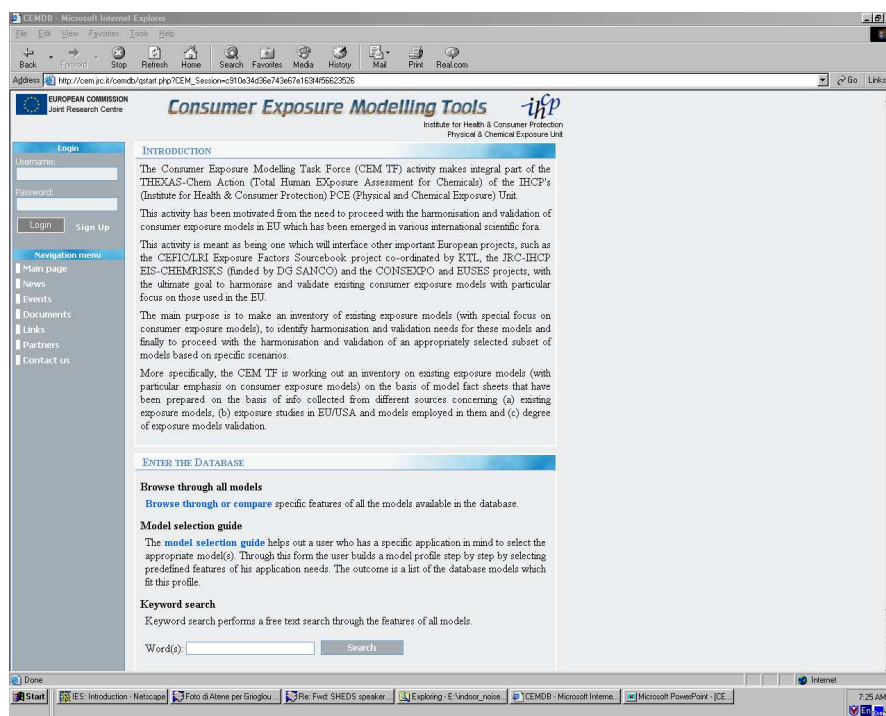
In previous workshops, formal presentations in the plenary session by the participants have significantly helped to set the tone for subsequent discussions. As such, participants were encouraged to present their (and others) work. They were also kindly asked to

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advise the Moderator concerning the topic of the presentations and time required. The JRC coordinator and the Moderator have in turn planned the workshop potentially balancing the advantages of these presentations with the time available.

The report of this Workshop as well as other related documentation could be downloaded from the following Global CEM Net Website:

<http://cem.jrc.it/cemdb/gstart.php>



**Dr. Stelios Kephalopoulos** (*Global CEM Net Co-ordinator*)

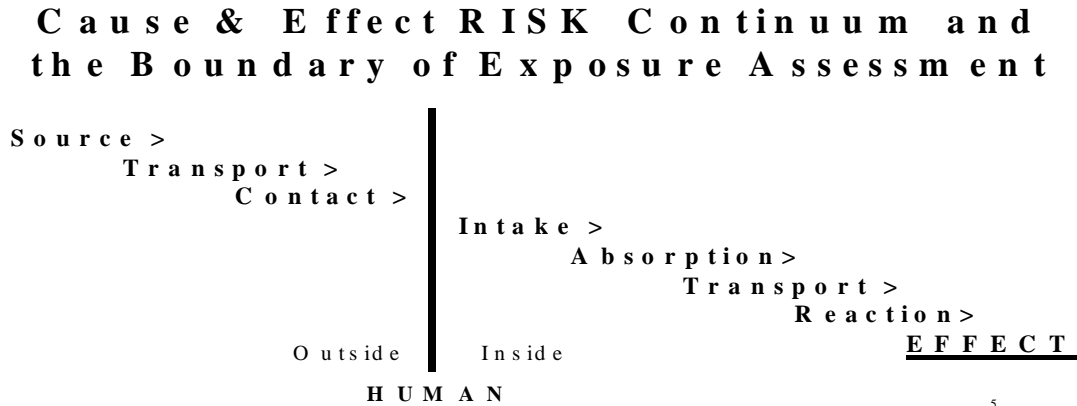
**Dr. Thanos Arvanitis** (*Global CEM Workshop no. 2 Rapporteur*)

**Dr. Mike Jayjock** (*Global CEM Net Workshop no. 2 Moderator*)



## BACKGROUND

By definition, human exposure potential in the context of health risk from exposure starts with the sources of that exposure. The illustration below shows the natural cause and effect continuum that begins with and is literally driven by sources of exposure.



Since the outputs from sources become the inputs to subsequent processes, errors or lack of knowledge within the realm of sources or other early events on the continuum can only propagate and grow throughout the entire process. Any error in the estimation or characterization of the source or transport will translate throughout this continuum and results in subsequent errors in the estimations of risk.

Assuming that we wish to estimate exposure via modeling, accurate source characterization is thus critical.

### Organization of this Report

The main body of this document represents the final results of the deliberations that occurred during the workshop and a consensus of the participants. In the months leading up to the workshop a pre-workshop report was drafted by the moderator and copied to all of the anticipated and potential participants. This text ultimately included contributions from some of those who would attend the workshop and others who could not attend but wanted to provide input. The document underwent 4 drafts and its final version is presented in Appendix B.

The reader will note some redundancy between this main document and Appendix B; however, this was included for completeness to show the results and evolution of the deliberations before and during the June workshop.

## WORKSHOP DESCRIPTION

In this Global CEM Net June 2005 workshop no. 2, the Institute for Health and Consumer Protection, Physical and Chemical Exposure Unit, within the Joint Research Centre of the European Commission (JRC) brought together human exposure modeling experts and model users from Europe, America and Asia in an effort to identify and characterize the state-of-the-science and point to the most expeditious and cost-effective path for future advancements. Every effort was made to network within our team to recognize and invite additional experts or users to this workshop. Indeed, we encourage the distribution of this report and other work products from this workshop to further engage the worldwide scientific community in this effort.

Except for preplanned presentations on June 20 2005, specific agenda topics for June 21 2005 remained flexible and were significantly changed during the proceedings by the workshop participants with agreement from Dr. Kephelopoulos; as a result, the participants of this meeting rendered the following:

1. Development of a complete taxonomy of indoor pollution sources and sinks that would have a major impact on indoor air, surface concentrations, exposure and subsequent risk to human health.
2. A decision **not** to outline, characterize or explicitly build upon the currently available source sub-models beyond the draft workshop report done before the meeting (Appendix B). Instead the workshop participants endeavored to build a framework for this body of scientific work from “the ground up”. Existing models, where available, were mentioned or otherwise used to fill in this framework.
3. Identification of specific operational model elements in the above taxonomy in a progressive tiered approach for each comprising **zero tier**, **first tier** and **n-tier** mechanistic source models.
4. The same type of framework was outlined for transport and fate models.
5. It was anticipated that given this comprehensive framework, practitioners will be able to potentially match-up the elements of each with existing model tools; however, in many cases, the specific sub-models do not exist and will require focused research and development.

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## **WORKSHOP PRESENTATIONS – June 20, 2005**

## **MODEL UNCERTAINTY ANALYSIS CASE STUDY: VOCs FROM CONTAMINATED WATER DURING SHOWERING AND BATHING**

*(Thomas E. McKone)*

### **Overview and Background**

For many years regulatory agencies considered only the consumption of water and ingestion of fish as pathways for human exposure in the development of drinking-water standards. For contaminated tap water, a contact rate of two liters of tap water per day consumed by a representative 70-kg adult was used to set standards. Because two liters corresponds to total daily fluid intake by a reference adult and because, on average over a lifetime, most adults only consume a small fraction of their daily fluid intake directly from the tap, this two-liter contact rate was assumed to be a health conservative value (*i.e.* plausible but higher than the average value). However, recent efforts to improve the scientific basis for assessing human exposure to contaminated tap water demonstrate clearly that significant exposures to organic compounds occur from exposure during showering and bathing.

In this section we present an example of a complete exposure assessment with explicit treatment of uncertainty to illustrate how uncertainty is handled at different levels. The case study is based on ingestion, indoor-inhalation, and dermal exposures to volatile organic chemicals in tap water. The case is used to illustrate different types of uncertainty, distinguish a deterministic from a probabilistic exposure assessment, and demonstrate the value of model evaluation.

The case study includes the conceptual model, the modeling approach, data available, construction of input distributions, and variance propagation methods. When evaluating uncertainty it is important to consider how each of these elements contributes to overall uncertainty.

### **Conceptual Model**

The goal of the conceptual exposure model in the case study is to establish exposure links via multiple exposure pathways to different exposure routes and the relative magnitude of uptake or intake by these different exposure routes.

The general intake model use for the case studies is adapted from an Environmental Protection Agency (EPA) model. We use this model in the form adopted for generalized multi-pathway exposure modeling as described in the WHO-IPCS Environmental Health Criteria report 214 “Human Exposure Assessment” (Chapter 6, IPCS, 2000). In this form the model expresses the potential average daily intake or potential daily dose,  $ADD_{pot}$  over an averaging time AT as



$$ADD = \frac{C_i}{C_k} \times \left[ \frac{IU_i}{BW} \right] \times \frac{EF \times ED}{AT} \times C_k$$

where  $[C_i / C_k]$  is the intermedia transfer function that relates concentration in medium  $k$  to concentration in medium  $i$  (for example tap water to indoor air);  $C_i$  is the contaminant concentration in the exposure medium  $i$ ;  $C_k$  is the concentration in environmental media  $k$ ;  $IU_i$  is the intake/uptake factor (per body size  $[BW]$ ) for exposure media  $i$ ;  $EF$  is the exposure frequency (day/year) for this population,  $ED$  is the exposure duration (years), and  $AT$  is the averaging time for population exposure (days).

### Modeling Approach

In applying the case study to any particular volatile chemical, we use the  $ADD_{pot}$  equation with the following information to make exposure estimates for the exposed population:

- (1) The magnitude of the source medium concentration: that is, the level of contaminant that is measured or estimated at a release point.
- (2) The contaminant concentration ratio: which defines how much a source-medium concentration changes as a result of dilution, transport, and inter-media transfers before human contact occurs.
- (3) The level of human contact: which describes (often on a body-weight basis) the frequency (days per year) and magnitude (kg/day) of human contact with a potentially contaminated exposure medium.
- (4) The duration of potential contact: relates to the fraction of lifetime, for the population of interest, during which an individual is potentially exposed.
- (5) The averaging time: the appropriate averaging time is based on the type of health effects under consideration. The averaging time can be the lifetime (as is typical for cancer as an endpoint), the exposure duration (as is typical for long-term chronic but non-cancer endpoints) or some relatively short time-period (as is the case for acute effects).

### Constructing Input Distributions

The value of information derived from a parameter uncertainty analysis depends very much on how well the input parameter distributions reflect variability and uncertainty. One begins the process of constructing a distribution function for a given parameter by assembling values from the literature or from personal knowledge. These values should be consistent with the model and its particular application. The values will vary as a result of measurement error, spatial and temporal variability, extrapolation of data from one situation to another, lack of knowledge, etc. The processes of constructing a distribution from limited and imprecise data can be highly subjective. Because the

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uncertainty analyst must often apply judgment to this process, there is a need for expertise and wisdom. This process becomes more objective as the amount of data for a given parameter increases. However, a large set of data does not necessarily imply the existence of a suitable distribution function.

### **Exposures to Volatile Chemicals In Water Supplies**

This case study is based on ingestion, indoor-inhalation, and dermal exposures to volatile organic multimedia, multi-pathway pollutants where exposure is principally from a water supply. Both adults and children are exposed, but for our case study, we will consider them as separate groups for the exposure assessment and focus on the adults for illustrating comparisons. Our goal is to calculate and characterize uncertainty in the lifetime average daily potential dose,  $ADD_{pot}$ , for a specified population cohort drinking contaminated water and using the contaminated water for showering or bathing.

### **Sources of uncertainty**

The process of assessing the potential health impacts for tap water contamination has a number of sources of uncertainty.

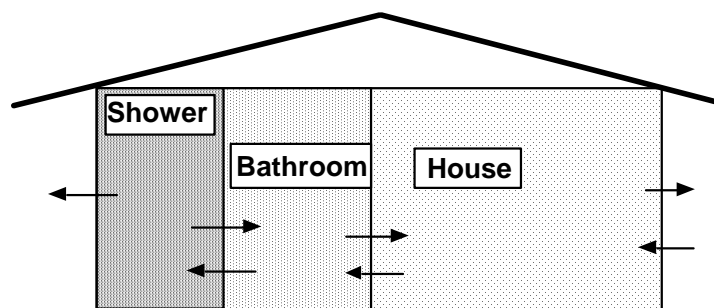
#### Conceptual model uncertainty

How do we establish and confirm the validity of the conceptual model?

#### Model selection uncertainty

Are there alternatives for model algorithms, such as intermedia transfers, that contribute to uncertainty in model results?

A key issue for the indoor inhalation model is how we structure the near-field (shower-stall and bathroom) exposure relative to the far-field (full house volume) exposure.



#### Parameter values

What data are used to establish the magnitude, range, and distribution of parameter values used in the model?

With regard to the exposure uncertainty, we must confront the following issues.

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What are the principal pathways of exposure, *i.e.*, the transfer of the contaminant from ground water to tap water and indoor air such that the exposed population can have inhalation and ingestion contact?

What is the relative contribution of water supply to cumulative intake based on consideration of other sources of exposure such as consumer products?

How much data is available to characterize the magnitude and variability of exposure?

Are there exposure models available? Are they precise? accurate?

Are the biomarker data available with which to test hypothesis about the magnitude and source of exposure?

### **Building Confidence through Model Evaluation**

Chloroform, which is an unavoidable by-product of the chlorination of water containing organic materials, is found in many water supplies throughout the U.S. Experimental support for the significance of inhalation and dermal exposures to VOCs in tap water can be found in the work of Jo *et al.* (1990), who measured chloroform levels after 10-min showers in the breath of subjects who first showered normally and then repeated their shower routine on a later date wearing protective rubber suits to eliminate the dermal route. Based on comparison to ingestion intake of chloroform from the same water supply, breath levels from these showering events indicated significant levels of chloroform intake. The breath levels dropped by about half when the subjects wore rubber suits, leading Jo *et al.* (1990) to conclude that the chloroform dose from inhalation and dermal uptake were about equal during a shower. Their results imply that the dermal uptake and inhalation in the showers are equivalent to 0.6 liter each of ingestion or an additional uptake of 1.2 liter per day.

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## **RECOMMENDATION TO USE FUGACITY APPROACH AND TIME-DEPENDENT TRANSFER EFFICIENCY FOR INDOOR SOURCE**

*(Yoshihide Matoba)*

Fugacity approach is found useful to describe indoor behaviour of chemicals easily. By introducing the concept of a time-dependent transfer efficiency to hands and body surfaces, more realistic exposure level for room occupants can be estimated through the fugacity approach.

### **1. Fugacity approach**

A basic concept of the fugacity approach is as follows: In the first step, the environment for consideration is conveniently divided into appropriate compartments. In each compartment, the concentration of a chemical  $N/V$ , where  $N$  is a chemical mass and  $V$  is a compartment volume, can be expressed as the product of fugacity  $f$  and fugacity capacity  $Z$ . The fugacity means an escaping or fleeing tendency of a chemical and a compartment with high fugacity capacity is able to absorb a greater quantity of a chemical, yet retains a low fugacity. Differential equations of the formula  $N/V = f Z$  for each compartment can describe the chemical movement such as emission, transference and degradation as well as temporal volume and/or fugacity capacity of the compartment. Solving the equations determines time-dependent fugacities to estimate concentrations of the chemical in each compartment by multiplying the fugacity by the fugacity capacity.

The fugacity approach is applicable to the indoor environment as follows, giving an example of the InPest developed by us. When a space aerosol containing an insecticide is sprayed into the air in a room, large aerosol droplets settle down to the floor quickly while small droplets float in the air for a certain time. The aerosols become smaller with time because of evaporation of a dominant solvent of the droplets. These phenomena can be incorporated into the fugacity approach and the InPest calculations correlate well with the measurements. The good correlation is observed even in the residual spraying, which is conventionally done with an aerosol including pesticides at the corners of the room where pests such as cockroaches are seen frequently.

A broadcast spraying is conducted to control the harmful household pests living on the carpet. The broadcast liquid including a pesticide emulsion is sprayed to the carpet, and the part of the liquid floats in the air as mixtures of large and small airborne droplets. The liquid decreases in volume by evaporation and finally disappears. The pesticide resides in an organic solvent layer of the emulsion. Once the organic solvent begins to evaporate, the fugacity capacity gradually decreases to the fugacity capacity of water. The InPest can describe the phenomena, and the calculations correspond to the measurements.

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For an electric vaporizer to control household mosquitoes, all of the chemical is initially evaporated as complete vapor from the vaporizer but some chemical condenses to yield droplets since the evaporating rate exceeds an upper limit of chemical existing as complete vapor. A pre-calculation using a super computer and a fluid dynamics program gives time-dependent concentrations. Taking the above into account, the InPest calculations are in agreement with the measurements.

The fugacity approach has been widely used for calculating the behaviour of variety of chemicals in the environment. Especially, this approach has a great convenience in environmental partitioning calculations of chemicals. A fugacity model InPest can describe the complex indoor behaviour by a relatively simple form and the calculations of indoor behaviour correlate well with actual measurements. The InPest only needs molecular weight, vapor pressure, water solubility and octanol water partition coefficient of a chemical for a basic calculation. The minimum requirement of the physicochemical properties is very convenient for any chemicals.

## **2. Time-dependent transfer efficiency**

Transfer efficiency means available fraction of a chemical for transfer to the hands and body after an application of the chemical. Thus, residential dermal exposure is estimated by using floor residue of a chemical, contact area and exposure period as well as the transfer efficiency. The floor residue can be simulated or measured. For the other factors, the US EPA recommends constant values based on several experiments or observations. Here, the constancy raises two questions: 1) Is the transfer efficiency independent of the time after application? 2) How do we estimate the dermal exposure during multiple applications?

To investigate time-dependent profile of the transfer efficiency, we conducted a wipe test at specified intervals after an application of a pyrethroid on three different floor materials. In any cases the transfer efficiency decreased with time. An equation to express the time-dependent curve for transfer efficiency can be developed, taking into consideration the mechanistic behaviour of chemicals on floor materials. Floor residue permeates the floor material with time after deposition, and the depth of permeation of a chemical is given by  $2 (D_m t)^{0.5}$ , where  $D_m$  is diffusion constant of the chemical. In contrast, the amount of residue transferred to the wipe-pad was determined by a constant weight applied as the pad contacted the floor and hence, the pressure-related depth  $h$  is constant for each material. Therefore, when the wipe-pad contacts the floor under pressure, the diffusion depth of the chemical with regard to transference phenomena is  $h / 2 (D_m t)^{0.5}$ . This indicates that the decrease of transfer efficiency can be expressed by the function of time  $t^{-0.5}$ . Higher  $r$  values were derived when the transfer efficiency  $TE(t)$  was obtained from  $TE(t) = i (1 + j t)^{-0.5}$ .

The product of the floor residue and transfer efficiency is the transferable residue, which means available residue to the hands and body when human touches the contaminated floor. When the transfer efficiency is assumed to be a constant, the transferable residue

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during multiple applications can be calculated by multiplying sum of the floor residue by the constant transfer efficiency (i.e.,  $[\Sigma \text{ floor residue}] \times \text{TE}$ ). However, when the transferable residue is time-dependent, the transferable residue does not follow this equation because the floor permeation depth is different for the first and second applications. The transferable residue during the multiple applications should be the sum of the transferable residues for each application (i.e.,  $\Sigma [\text{floor residue} \times \text{TE}]$ ). As a result, the approach of time-dependent transferable efficiency enables us to estimate residential exposure levels more precisely.

## **HOW EXISTING MODELS HANDLE SOURCES AND TRANSPORT**

*(Muhilan Pandian)*

The use of consumer products in the living space of human receptors results in exposures to chemicals released by the products. The process of estimating exposures involves source characterization, description of use environment, and receptor characterization (activity patterns and human factors). Source characterization deals with describing chemical release rate, release medium (gas, droplets, dust, etc.), and release duration. And transport deals with estimating breathing zone air concentrations and contact surface concentrations after applying source parameters to a use environment.

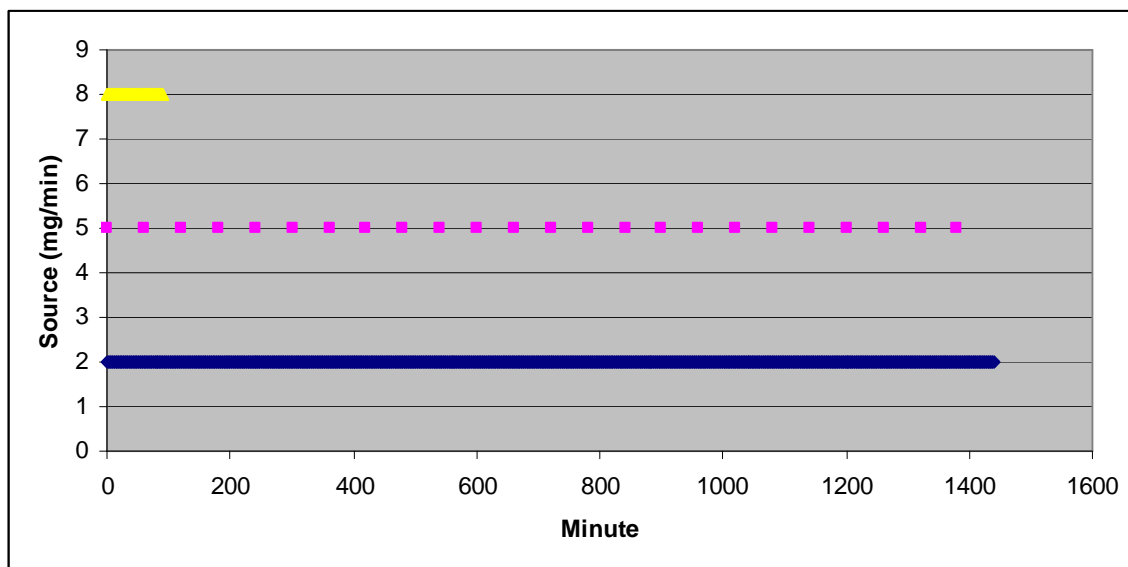
Source models currently in use (based on the models CONSEXPO, EFAST, IAQX, Notitia, SCIES, and WPEM) address one or more of the following concepts:

- constant source, instantaneous or for an extended period
- intermittent variable source
- single exponential decay,
- multiple exponential decay,
- spill source (evaporation based),
- wall paint source, and
- spray (droplets) source.

The above models can be applied to most products to describe the release parameters of chemical(s) of concern, usually in units of mg/min.

Constant source models represent a source with a constant release rate instantaneously, intermittently or continuously. In the figure below, the yellow line represents a constant source continuous for about 100 minutes, the magenta points represent intermittent constant point sources once every 60 minutes, and the blue line represents a constant source for 1440 minutes.

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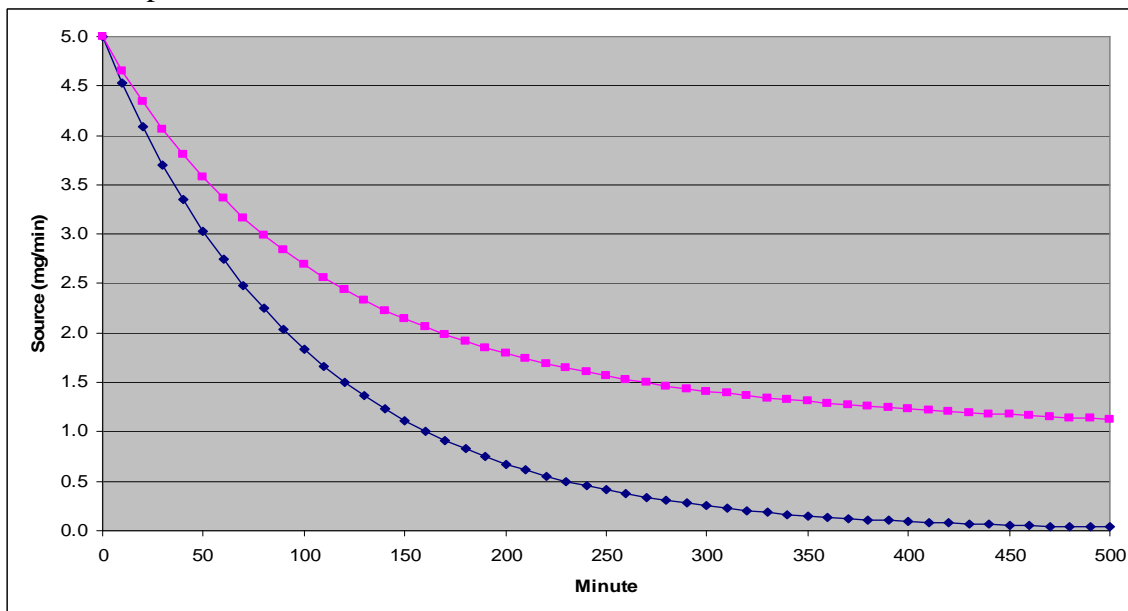
Intermittent variable source models are an extension of constant sources; during intermittent releases, the rates could be different.

Single and multiple exponential decay source models represent those sources with decaying release rates with time.

Single exponential:  $\text{Source} = S_1 \exp(-k_1 t)$

Double exponential:  $\text{Source} = S_1 \exp(-k_1 t) + S_2 \exp(-k_2 t)$

The constants for the decay characteristics are usually determined experimentally. In the figure below, the blue line represents a single exponential and the magenta line represents a double exponential.





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Spill source models can be applied to scenarios where a chemical of concern is released from a liquid spill or from an evaporating surface. An algorithm in EFAST uses the following calculations to estimate the evaporation time and the evaporated mass of a pure liquid that spills on a floor.

$$\begin{aligned}\text{Volatility (mg/m}^3\text{)} &= (\text{Molecular Weight, g/gmol}) \times (\text{Vapor Pressure, torr}) \times \\ &\quad (16036) / (\text{Temperature, } ^\circ\text{K}) \\ \log_{10}(\text{Evaporation Time, sec}) &= 7.3698 - 0.9546 \times \log_{10}(\text{Volatility, mg/m}^3\text{)} \\ \text{Mass Evaporated (mg/min)} &= (\text{Mass Spilled, mg}) \times 0.9 \times 60 / (\text{Evaporation Time, sec})\end{aligned}$$

Wall paint source models account for differential release rates based on differing paint application durations. An algorithm in IAQX uses the following calculations to estimate the chemical mass released during the painting process.

$$\begin{aligned}\text{Mass Released (mg/min)} &= [ R_0 \times A ] / [ 1 + ( k \times R_0 \times t ) ] \\ \text{Where } R_0 &= \text{emission rate at } t = 0, \text{ mg/m}^2/\text{min} \\ A &= \text{area painted, m}^2 \\ K &= \text{empirical constant (m}^2/\text{mg; default = 0.003).}\end{aligned}$$

If the use environment is assumed to be indoors like a house, focusing specifically on the inhalation post-application exposure route, transport models currently in use include

- 1-Zone model,
- 2-Zone model, and
- N-Zone model.

All indoor models are based on the equations ( $i = 1, \dots, N$ ) shown below:

$$V_i \frac{dC_i}{dt} = S_i - L_i + \sum_{j=1}^{N, j \neq i} Q_{j \rightarrow i} C_j - \sum_{j=0}^{N, j \neq i} Q_{i \rightarrow j} C_i$$

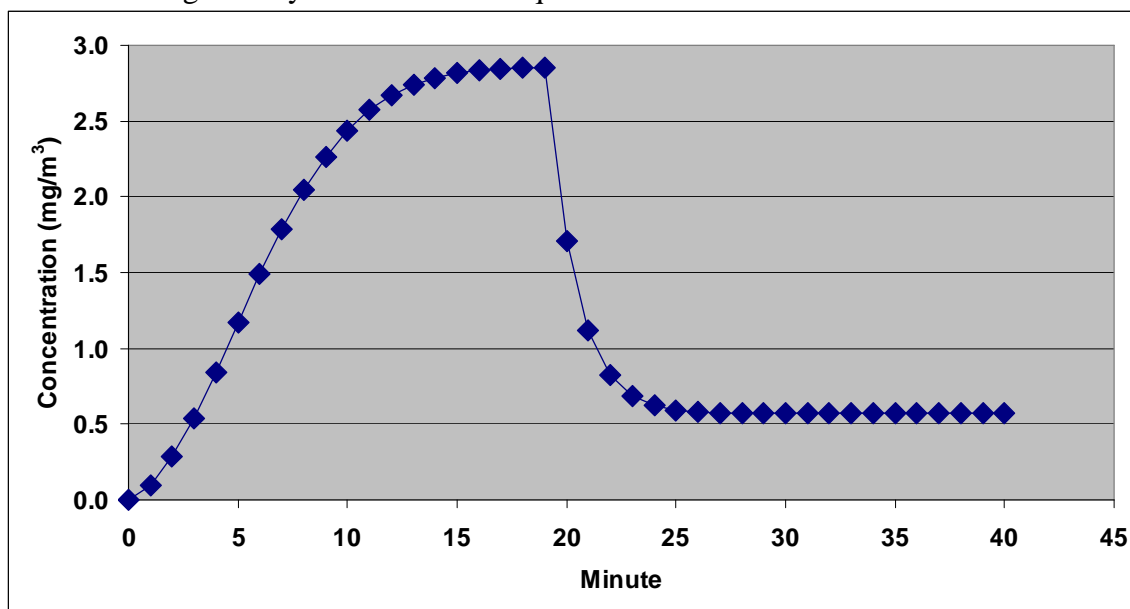
where

C	= concentration	mg/m <sup>3</sup>
L	= loss rate	mg/min
N	= number of zones	
Q	= air flow rate	m <sup>3</sup> /min
S	= source release rate	mg/min
t	= time	min
V	= volume	m <sup>3</sup>
0	= zone 0 = outdoor	
i	= zone of interest	$i = 1, \dots, N$

Simple applications use the 1-Zone model ( $N = 1$ ) and higher tiered ones consider population based, probabilistic modeling approaches. These models are usually solved

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numerically to determine concentrations as a function of time. The figure below is a plot of concentration vs. time. It is based on the use of a source in a single zone, where source is set to a higher release setting until 20 minutes, resulting in the gradual rise in concentration. Once the source is set to a lower setting after 20 minutes, the concentration gradually decreases to an equilibrium level.



For the dermal exposure pathway, chemical concentrations on relevant surfaces that humans contact have to be estimated. Models specific to this pathway usually address the transfer process of chemical from surfaces to skin.

## **INTAKE FRACTION: QUANTIFYING EMISSIONS-TO-INTAKE RELATIONSHIPS**

(William W Nazaroff)

### **Introduction**

This workshop emerges from concerns about the health risks that may be posed by human exposure to pollutants resulting from processes that occur or from products that are present in indoor environments. An ultimate objective is to protect human health from excessive risk. One of the major technological and policy approaches for achieving such protection is to limit emissions from sources. To pursue this approach, we are led these questions. Which contaminants should be controlled? From which sources? And to what extent? To answer these questions rationally, tools are needed that link processes and products to effects. Among the needs are information and methods that can connect emissions to exposure or, as is proposed here, to connect emissions to intake. Such information and methods would support what is here termed “source-oriented exposure assessment.”

This note addresses two objectives. First, it broadly (but briefly) argues that a tiered approach is needed to support the broad goals of source-oriented exposure assessment. Second, a specific metric for such assessments — the intake fraction — is described. The concept is introduced, examples are presented for how it can be evaluated, and its utility is briefly explored. For a more thorough introduction to intake fraction as an exposure metric, see DH Bennett *et al.* (*Environmental Science & Technology* **36**, A206-A211).

An important caveat must be stated. This summary only considers inhalation as a route of human exposure. It is well recognized that other pathways are important for many species. Many (if not all) of the ideas presented here can be generalized to incorporate other pathways.

### **Tiered approach**

Environmental systems are enormously complex. Typically, many indicators are needed to properly characterize the state of the system. These indicators may be difficult to measure. Many factors can influence the values taken on by the indicators. The dependence of the indicators on governing factors may be poorly understood. Incomplete understanding impedes model development. Conventional experimental methods such as laboratory investigations of isolated elements may not accurately represent systems with scale-dependent behaviors or complex feedbacks. Experimental manipulation of natural environments to observe responses may be impractical. Furthermore, quantitative indicators and governing factors can vary over staggeringly large scales. In trying to understand the terrestrial environment, we encounter important phenomena that occur on linear scales ranging from molecular to global and on temporal scales ranging from microseconds (or shorter) to millennia (or longer).

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Narrowing our focus to the particular issue of human exposure to environmental pollutants associated with indoor emissions simplifies matters to only a limited extent. Many indicators are needed; their dependences on controlling factors are complex and imperfectly understood. Models are hampered by our limited understanding and appropriate experiments are challenging to devise and conduct. Linear dimensions associated with processes of interest span ranges from molecular to the size of buildings, and relevant time scales can vary from seconds to decades.

Given the complexity of the system, one should not expect that a single approach, a single method, or a single perspective would suffice as a basis for understanding or action. Like the artist, the carpenter, or the surgeon, we need a richly constituted tool kit to effectively comprehend the system of the human health risk associated with products and processes in indoor environments. Included in this tool kit should be screening methods that can quickly and cost-effectively sort situations where health risks are negligible from those where health risks are potentially substantial. The cases in the former group could then be cost-effectively removed from further attention, while more detailed (and more expensive) assessment methods can be focused on cases in the latter group.

### **Intake fraction**

It is helpful at this stage to consider an air pollution health effects paradigm. (I first saw this paradigm well articulated by KR Smith, *Annual Review of Energy and the Environment* **18**, 529, 1993). The paradigm begins with sources that emit pollutants into air. Those pollutants are transported, dispersed, and transformed to yield time-varying concentration fields. As people move about, they encounter this concentration field, and are thereby exposed. Intake represents the inhalation of contaminants owing to their presence in the air inhaled, and uptake refers to the transfer of such contaminants into the body. Subsequent biochemical and biophysical processes transform uptake into dose (e.g. to organs or tissues). If doses are excessive, then an adverse health effect results. Ultimately, we would like to understand this paradigm not only schematically, but also quantitatively and mechanistically. Understanding components of the system can help realize the ultimate goal.

The intake fraction focuses attention on the emissions-exposure relationship. For the inhalation pathway, the intake fraction is defined as the attributable mass of a pollutant inhaled per unit mass released. By “attributable,” we mean the pollution that is ascribable to a particular source or source class. With respect to the population exposed, the intake fraction can be partitioned into its components. Thus, the total population intake fraction is the individual intake fraction summed over each of the persons exposed.

If intake fraction along with some other information is known, then the source-oriented health risk may be estimated from a simple expression, as follows. For each pollutant of concern, the partial health risk would be estimated as the product of four terms: usage factor, emission factor, intake fraction, and toxicity. The total source-oriented health risk would be the partial health risks summed over all pollutants of concern. This is but one example of how intake fraction information can be used. It is important to keep in mind

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that the intake fraction is a metric, not a method. We can think of it as a lens or a window through which to view certain aspects of exposure.

### **Evaluating intake fraction**

The intake fraction may be evaluated through a variety of modeling and measurement approaches. Modeling methods can range from “back-of-the-envelope” estimation techniques to sophisticated fate-and-transport models. Measurement methods typically rely on tracers, either deliberately released or associated naturally with sources. One important finding from early work on intake fractions is that values associated with indoor releases are commonly in the range 1,000 to 10,000 per million, whereas values associated with outdoor releases are commonly in the range 1-20 per million. This remarkable difference has been named the “rule of 1000.” As articulated by KR Smith (Environment 30(8), 10, 1988), “A typical pollutant release indoors is ~ 1000 times as effective in causing human exposure as the same release to outdoor air.”

The main factors that affect the intake fraction for indoor releases can be clustered into three groups: (a) building attributes, such as ventilation rate; (b) pollutant attributes, such as the tendency to sorb or otherwise interact with indoor surfaces; and (c) human attributes, such as breathing rates and occupancy patterns.

In the simplest case, a nonreactive (and nonsorbing) pollutant is emitted from some indoor source into a well-mixed space. In the event of steady occupancy by  $N$  persons, each of whom is inhaling air at an average volume rate of  $Q_B$ , the intake fraction is  $N \times Q_B / Q$ , where  $Q$  is the volumetric ventilation rate of the space. Remarkably, this simple result holds regardless of the temporal pattern of emissions.

The simplifying assumptions can be relaxed. So, for example, if the released pollutant experiences first-order loss with a rate constant  $k$  (dimension: inverse time) in a space of volume  $V$ , then the intake fraction from the previous example is modified to  $N \times Q_B / (Q + kV)$ . Analogously, one can account for time-varying occupancy and imperfect mixing in relatively direct manner.

To date, the most detailed assessment of intake fraction for indoor releases has been carried out by Neil Klepeis in his PhD dissertation (“Using computer simulation to explore multi-compartment effects and mitigation strategies for residential exposure to secondhand tobacco smoke,” UC Berkeley, 2004). He incorporated human activity pattern data survey into a sophisticated fate-and-transport model to investigate exposure to environmental tobacco smoke constituents in a multizone single-family residence. For carbon monoxide (effectively an inert tracer) and for a high-exposure cohort of individuals who spent at least 2/3 of their time at home, the individual intake fractions were determined to be reasonably well described by a lognormal distribution with GM = 1400 per million and GSD = 1.8.

### **Summary**

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The intake fraction metric focuses attention on source-receptor relationships, a matter that is at the heart of source-oriented exposure assessments. The metric has many virtues, including facilitating communication and being readily apportioned (both by source and by receptor). As an organizing principle for information, or as a lens through which to glimpse some important aspects of human exposure, it has much potential, most of which has not yet been exploited. Efforts to further develop information about intake fractions associated with indoor sources will help make exposure assessments simpler to conduct and convey.

## **MODEL SELECTION AND MODEL PERFORMANCE EVALUATION**

*(Thomas E. McKone)*

### **Perspectives on the Use of Models**

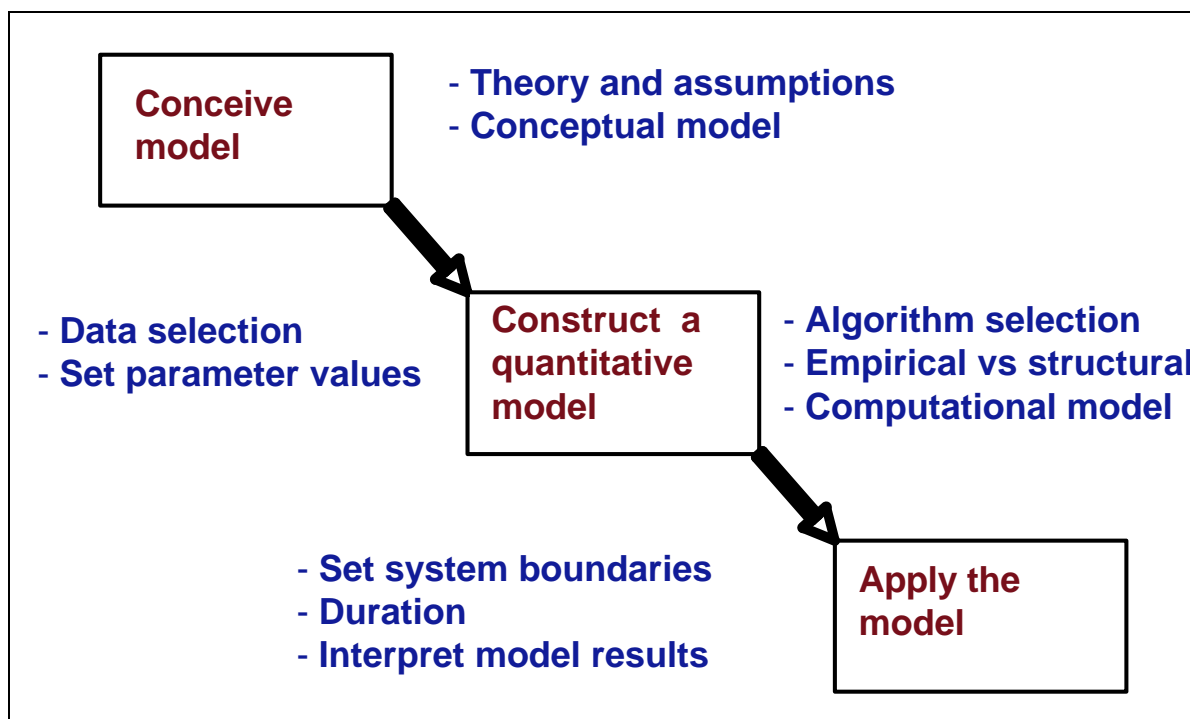
Whether used to assess indoor exposures to consumer products or to assess releases to the ambient environment, source and transport characterization models are used to support decisions to tolerate, regulate or monitor existing and new chemicals uses. In this role, source/fate models provide prospective analyses of impacts from new chemicals and retrospective analyses of the links between health outcomes and various chemical uses. In using models to support regulation and monitoring policies, decision makers struggle with the question of how likely are they to make unwarranted choices and what the associated health, economic, and political consequences of those choices are. To confront these questions, decision makers rely on modelers to quantify the representativeness (fidelity) and reliability of their model predictions.

In this section we explore the issues of model selection and model performance evaluation. We consider three issues—perspectives on the use of models, the process of model performance evaluation, and choices about how simple or complex to make a model in order to address the question at hand.

### **Perspectives on the Use of Models**

In order to carry out model selection and model evaluation we need to define and characterize the life stages of a model. The life-cycle of a source-fate model has at least three states—problem formulation to establish the conceptual model, model building, and model application (see Figure 1). Historically the management of model quality at many regulatory and policy agencies has been incomplete and inconsistent. This is due in part to failures to recognize the impact of errors and omissions in the early stages of the life-cycle of the model. At many organizations, the model evaluation process only begins in the model building and model application stages. Yet formulating the wrong model questions or even confronting the right questions with the wrong conceptual model will lead to serious quality problems in the use of a model. But these quality issues are difficult to discover and even more difficult to resolve (if discovered) when model evaluation is only used at the late stages of the model life cycle.

As is the case for all models, source and fate models have inherent capabilities and limitations. The limitations arise because models are simplifications of the real system that they describe and all assessments using the models are based on imperfect knowledge of input parameters. This gives rise to inherent uncertainty. This realization provides insight into how the models should be applied and for deciding whether and/or how to make the models more detailed.



**Figure 1.** The stages of the life-cycle of a model and the potential types of model evaluation that can be applied at each of these stages

### **The Model Evaluation Process—Building Confidence**

Confronting the capabilities and limitations of models requires a model performance evaluation. This evaluation should estimate the degree of uncertainty in the assessment and illustrates the relative value of increasing model complexity, providing a more explicit representation of uncertainties, or assembling more data through field studies and experimental analysis. Here we summarize current methods used to evaluate the performance of source/fate models with a particular emphasis on methods for model sensitivity and uncertainty analysis.

### **Sensitivity and Uncertainty Analyses**

Sensitivity and uncertainty analyses are powerful tools for assessing the performance and reliability of models. As applied to mathematical models, sensitivity analysis is quantification of changes in model outputs as a result of changes in individual model parameters. Uncertainty analysis is the determination of the variation or imprecision in the output function based on the collective variation of the model inputs. A full discussion of sensitivity and uncertainty analysis is provided in the text by Morgan and Henrion (1990) and the volume edited by Saltelli et al (2000). The goal of a sensitivity analysis is to rank input parameters, model algorithms or model assumptions on the basis of their contribution to variance in the model output. Sensitivity analyses can be either local or global. A local sensitivity analysis is used to examine the effects of small



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changes in parameter values at some defined point in the range of outcome values. A global sensitivity analysis quantifies the effects of variation in parameters over their entire space of outcome values.

### **Sources of uncertainty**

Uncertainty in model predictions arise from a number of sources, including specification of the problem; formulation of the conceptual model, estimation of input values and calculation, interpretation, and documentation of the results. Of these, only uncertainties due to estimation of input values can be quantified in a straightforward manner based on variance propagation techniques. Uncertainties that arise from miss-specification of the problem and model formulation errors can be assessed using tools such as decision trees or based on elicitation of expert opinions (Ragas et al., 1999).

### **Uncertainty importance and ranking**

A framework for the analysis of uncertainty in environmental models is described by Morgan and Henrion (1990) and Finkel (1990) and has been applied by Hertwich et al. (2000) to fate and source models. This framework distinguishes among parameter uncertainty, model uncertainty, decision rule uncertainty, and natural variability in any of the parameters and calls for a separate treatment of the different types of uncertainty. For example, in evaluating parameter uncertainty and variability Hertwich et al. (2000) considered both uncertainty in chemical-specific input parameters as well as the variability in exposure factors and environmental system parameters.

### **Model Evaluation and Confidence Building**

Many model users assume that reliable models are ones that have been truly “validated”. However, there continues to be wide disagreement and confusion in the scientific and regulatory communities about what it means to validate a model and if true validation is even possible. Recent papers have made convincing arguments that comparison of model output to observations is not a sufficient measure of acceptability on its own to “validate” a model (Oreskes et al., 1994; Beck et al., 1997; Oreskes, 1998).

Oreskes et al. (1994), point out that models that are not truly validateable are common in the environmental sciences and require a more thoughtful and systematic process for building confidence among model users. It is possible to build confidence in these models through a series of evaluation exercises. The models can be used to put bounds on the likely range of outcomes. The greater the number and the diversity of confirming observations that can be made, the more probable it is that the conceptualization embodied in the model is not flawed. Confirming observations do not demonstrate the veracity of the model, but they do support the probability that the model is useful and that the hypotheses that it supports are not false. Although validity may not accrue with these evaluation exercises, user confidence will increase. Confidence is further enhanced if the user can easily inspect or verify the operation of the algorithms and data transformations

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and determine whether the model is internally consistent and contains no logical flaws or technical errors, such as incorrect code implementation. Easy access to the raw data used as inputs, the steps of data transformations used in the calculation, and the computer coded algorithms underlying these data transformations enhances user confidence in the model. For source/fate models in particular, credibility is further enhanced by clearly quantifying the effects of variability and uncertainty in input parameters on model predictions.

**Simple versus complex--How to decide?**

The complexity of a model is its spatial and temporal resolution and the nature and extent of feedback processes captured by the model. When selecting the spatial and temporal scales to use for modeling sources and fate, there are two key considerations. First, what are the overall scales needed to describe a particular chemical--how far a chemical is likely to spread and how long it is likely to persist in the environment? Second, what is the resolution of the time and spatial steps needed to achieve the desired level of detail in the output as well as to account for temporal and spatial variation in the inputs?

The modeler and model user must determine how scale and detail will impact the model evaluation process. For example, will increasing spatial and temporal resolution change the trend in concentrations, or merely add fluctuation around a mean value? Or how does the external boundary of a system influence concentrations within a system?

There is an ongoing need to establish and improve upon the confidence placed in source-fate models by decision makers. There is also the opportunity to build more complex and spatially explicit models. Are these two trends compatible? The increasing capability of personal computers makes possible more complex models, and some equate complexity with credibility. But sometimes the opposite is the case--complexity makes the models much more difficult to verify and evaluate and makes it particularly difficult to assess data limitations. Fidelity tends to be enhanced by added complexity while reliability and user confidence are enhanced by simplicity. Thus, future source, fate, and exposure models will have to find an acceptable balance between the model's fidelity to the system/problem of concern and the need for reliability and user confidence.

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## **REACTIVE CHEMISTRY: SIGNIFICANCE FOR SOURCE CHARACTERIZATION**

*(William W Nazaroff)*

### **Introduction**

Chemical transformations can and do occur in indoor air. Such transformations influence the kind and amounts of pollutants to which people are exposed, and therefore alter source-oriented health risks. As we are concerned about the health risks associated with products and processes in indoor environments, we should recognize the potential for chemical transformations and seek to understand their significance.

In this matter, a strong analogy exists with motor vehicle emissions into urban air. Pollutants directly emitted from motor vehicles are termed primary emissions. These include unburned and partially oxidized organics from fuel, nitrogen oxides from high-temperature combustion, carbon monoxide from fuel-rich combustion conditions, and particulate matter both from the tail pipe and from abrasive wear of brakes, tires, and road surfaces. Adverse health consequences can result from exposure to these primary pollutants.

In the atmosphere, the primary pollutants can undergo chemical transformations. Nitrogen oxides and volatile organic compounds combine in the presence of sunlight to form a suite of secondary pollutants, among which are ozone, hydrogen peroxide, peroxyacetyl nitrate, aldehydes, organic and inorganic acids, and secondary particulate matter. Exposure to these species also can pose serious risks of adverse health consequences. Thus, if one seeks to understand the health risks associated with motor vehicle use, one should not only consider the primary emissions, but also the formation of secondary pollutants in the atmosphere.

Evidence is emerging that the same principle applies for indoor environments. Source-oriented health risks are not solely a consequence of primary emissions, but may also have important contributions from secondary pollutants.

### **Contrasting indoor and outdoor environments**

Three important parameters that influence chemical reactivity in air are residence time, light-energy flux, and surface-to-volume ratio. By comparing these parameters in indoor and outdoor environments, we can gain some insight about the types of transformations that may be important indoors.

The residence time of air in an urban atmosphere is about an order of magnitude larger than that in a typical indoor environment, ~ 10 h as compared with ~ 1 h. Much of the reactive chemistry in urban atmospheres is initiated by certain species absorbing a photon of ultraviolet light from the sun. The light energy flux in outdoor air is typically very much larger than in indoor air, ~ 1000 W m<sup>-2</sup> as compared to ~ 1 W m<sup>-2</sup>. On the other hand, when we consider the amount of surface area exposed per unit air volume, an urban

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atmosphere may have 2-3 orders of magnitude less surface than indoors,  $\sim 0.01 \text{ m}^2 \text{ m}^{-3}$  as compared with  $\sim 3 \text{ m}^2 \text{ m}^{-3}$ . A key lesson in these comparisons is that, while photolytic reactions play a central role in urban atmospheric chemistry, they are much less important indoors. On the other hand, surface-mediated reactions are likely to be much more important indoors than in outdoor air.

**Chemical processes of interest in indoor air**

Several broad classes of chemical reactions may occur in indoor air. These include oxidation-reduction reactions, acid-base reactions, hydrolysis reactions, decomposition reactions, phase-change processes, and sorption. A specific example is the hydrolysis of di(2-ethylhexyl) phthalate (DEHP), a widely used plasticizer. When vinyl flooring is installed on poorly cured concrete, DEHP in the vinyl comes into contact with the moist, high pH surface. A hydrolysis reaction leads to the formation of 2-ethylhexanol, which has a relatively low odor threshold, and monoethylhexylphthalate.

**Ozone-initiated chemistry: An important class**

Because of the low levels of light indoors, the chemical energy to trigger reactive chemistry generally must come from a source other than indoor photolysis. Ozone is an important carrier of oxidative chemical potential. Ozone from ambient air enters buildings along with ventilation. Some products used indoors also may generate ozone, including certain air cleaners and photocopiers. Indoor ozone levels exceeding 20 ppb on a transient basis are not uncommon. Pollutants that react at a meaningful rate with ozone include nitrogen oxides, unsaturated volatile organics, terpenoids, and unsaturated fatty acids and oils. The reaction rates can vary markedly. Given the  $\sim 1$  h residence time, gas-phase reactions must be relatively fast to have a significant impact on indoor air quality; this constraint is relaxed for surface reactions. The products of ozone-initiated indoor chemistry are diverse, including free radicals (e.g., OH), peroxides (e.g.,  $\text{H}_2\text{O}_2$ ), short-lived organics (e.g., ozonides), and stable organics (e.g., carbonyls).

Evidence is emerging for adverse effects associated with exposure to the products of ozone-initiated chemistry in indoor environments. For example, hydroperoxides derived from ozone-alkene interactions have been identified as potent contact allergens. As a second example, exposure of human eyes to a mixture of indoor-relevant levels of limonene and ozone produced a significant change in blink rate, suggesting eye irritation, whereas no change was observed with exposure to either chemical alone.

The next two sections provide brief case studies of ozone-induced chemistry relevant to characterizing emissions from indoor sources.

*Case 1: Ozone interaction with carpet*

Experiments were conducted to study the rate of ozone uptake on carpet surfaces and the volatile secondary products that were formed as a result of ozone-initiated chemistry. In four separate experiments, a small sample of carpet was placed in an environmental test chamber to which was supplied ozone at a fixed relative humidity (50%). A feedback loop was employed to maintain the ozone level in the chamber at a constant level of 100 ppb. In the absence of ozone exposure, the four carpet samples emitted very low levels

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of aldehydes, on the order of  $10 \mu\text{g m}^{-2} \text{h}^{-1}$  or less. However, when exposed to ozone, aldehyde emissions jumped to  $\sim 200 - 800 \mu\text{g m}^{-2} \text{h}^{-1}$ . When only the primary gaseous emissions were exposed to ozone, aldehyde levels were relatively low, indicating that most of the reactive chemistry involved surfaces. The dominant aldehydes formed were nonanal and 2-nonenal (highly odorous). These may be oxidative byproducts of ozone-induced decomposition of organic fatty acids that were on the carpet fibers owing to their processing. Modeling results suggest that these compounds could persist at concentrations above their odor thresholds for a few years in a typical residential environment.

*Case 2: Ozone interactions with terpenes*

Terpenes are a class of volatile organic compounds derived from certain plants. They are widely used in consumer products owing to their effective solvent properties and their pleasant smell. They are also favored as “green” alternatives to petroleum-based solvents. Many terpenes react rapidly with ozone. Among the reaction byproducts are aldehydes, the hydroxyl radical, and secondary particulate matter.

A series of laboratory experiments is being conducted to investigate the interactions of ozone with cleaning products and air fresheners that contain terpenes or terpene-like compounds. In one set of experiments, the volatile components of cleaning products are continuously supplied to a 200-L chamber. A separate line supplies ozone. Steady-state concentrations of primary constituents and secondary products are measured. With realistic reactant levels and ventilation rates for indoor conditions, we observed marked decomposition of ozone, significant degradation of certain terpenoids, and substantial production of oxygenated organics, such as aldehydes, organic acids, and ketones.

We also observed the formation of new particles, presumably created from low-volatility secondary organics. After steady conditions are established in the chamber with only cleaning product emissions supplied, ozone is introduced. Immediately, we observe the burst formation of ultrafine particles. These particles serve as condensation sites for continued production of low-volatility products, which causes the particles to grow. These observations share many features with nucleation events recently reported in urban and remote atmospheres. Among the causes for interest and concern in such events is evidence of adverse health consequences from inhalation exposure to ultrafine particles.

**Summary**

The health risks associated with emissions from indoor products and processes may be influenced by reactive chemistry. Because of this, health-protective public policies that are aimed at source characterization and control must incorporate appropriate information about the formation of secondary pollutants and their relationship to source emissions. Research tools and techniques for studying the formation of secondary pollutants are available. To date, these have been applied, but only on a limited basis, to understand the nature, scale, and significance of secondary pollutant formation owing to reactive chemistry in indoor air. Devising practical methods of incorporating this emerging information into indoor source characterization remains a challenge.

## **DEVELOPING AND VALIDATING FUNDAMENTAL SOURCE MODELS FOR CONSUMER PRODUCTS**

*(John Little)*

### **Background and Objectives**

Modern consumers are exposed to a vast array of consumer products, many of which release contaminating chemicals into the near-field environment. Volatile organic compounds (VOCs) constitute an important class of such contaminants. Amongst the primary sources are adhesives, caulks, sealants, paints, solvents, wood stain, floor wax, carpets, textiles, wallboard, treated wood, urethane coatings, pressed-wood products, vinyl flooring, and office equipment such as computers, copiers and printers. Also, attention has recently turned to semi-volatile organic compounds (SVOCs) such as plasticizers, flame retardants, and biocides. In contrast to VOCs, where the emission rate may be high, but relatively short-lived, the emission rates of SVOCs are much lower, but are usually more toxic and may continue for a very long duration. Volatile emissions are a probable cause of acute health effects and discomfort among building occupants (Andersson *et al.*, 1997) and are known to diminish worker productivity (Fanger, 2002). Although volatile emissions from these consumer products have historically been empirically characterized in small test chambers, more fundamental mechanistic approaches have been developed for several of the common source types, including solvent-based “wet” sources (Guo *et al.*, 1999) as well as “dry” sources (Cox *et al.*, 2002). As a specific example, emissions from vinyl flooring have recently been shown (Cox *et al.*, 2002) to depend primarily on three fundamental parameters ( $C_0$ , the initial material-phase concentration,  $K$ , the material/air partition coefficient, and  $D$ , the material-phase diffusion coefficient). The development of the overall method included new ways to measure  $C_0$  (Cox *et al.*, 2001a) as well as  $K$  and  $D$  (Cox *et al.*, 2001b). This conceptual break-through suggests that it should be possible to directly measure the key parameters and then use exposure models to predict the impact on human health and the environment.

There are literally thousands of consumer products, many of which contain a vast array of different VOCs and SVOCs. Empirically characterizing emission of individual contaminants from each one of these different consumer products in small chambers is quite simply an impossible task. Fortunately, the fundamental mechanisms governing emissions appear to be very similar for several broad classes of consumer products. For example, “dry” materials such as vinyl flooring (VF) (Cox *et al.*, 2002), polyurethane foam (PUF) (Zhao *et al.*, 2004), polystyrene foam (PSF) (Yuan *et al.*, 2005), and even oriented strand-board (OSB) (Yuan *et al.*, 2005), all appear to behave in a similar fashion. This means that once the approach has been validated for a specific product or class of products, it should become routine to rapidly measure the key model parameters and then simply predict (*a priori*) the emission rate. This fundamental source characterization approach would be greatly facilitated if the values of  $K$  and  $D$  could be predicted, as opposed to being measured, each time a new contaminant is identified. Fortunately, it

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has been shown (Cox *et al.*, 2001b) that D and K tend to correlate with molecular weight and vapor pressure, respectively. If such correlation equations can be deduced for the typical consumer products, perhaps based on different classes of organic compounds, all that would be required is the identification and measurement of the initial concentration of individual VOCs in the material phase. Once the individual VOCs have been identified and quantified (i.e.,  $C_0$  is determined), values for D and K can be obtained from the correlation equations and used to predict emission rates without further effort (Cox *et al.*, 2002).

This approach could significantly reduce the costs of characterizing emission from consumer products. As already mentioned, recent evidence suggests that the same mechanisms govern the release of contaminants from several other consumer products (for example, the same governing phenomena appear to control emission of VOCs from vinyl flooring, polystyrene foam, oriented strand board, and polyurethane foam). In addition, as the controlling mechanisms are clearly elucidated, methods to reduce the emission rate by changing the manufacturing process become apparent, increasing the already considerable return on the research investment. Even more exciting, recent preliminary results (Xu and Little, 2005) suggest that it may be possible to use an analogous approach to predict the emission rate of SVOCs (for example, plasticizers (such as di-(2-ethylhexyl) phthalate) and flame retardants (such as polybrominated diphenyl ethers)) from polymer-based consumer products (such as vinyl products and children's toys).

In this research, we will apply these very promising theoretical advances to consumer products that are of interest in the European context. The research will be conducted in a close collaboration between IHCP and VT, and will require some development of the laboratory infrastructure at IHCP. The overall goal will be to develop and/or validate source models to predict emissions of VOCs from “wet” sources such as solvent-based coating materials (Guo *et al.*, 1999), as well as emissions of both VOCs and SVOCs from “dry” sources such as vinyl flooring (Cox *et al.*, 2002; Xu and Little, 2005). Because the basic models for predicting emissions of VOCs from both wet and dry sources are already available, these two approaches will only need to be developed, tested, and validated at IHCP. The preliminary model to predict emission of SVOCs from “dry” sources needs to be further developed and validated, and this research will be carried out initially at VT, but will subsequently be transferred to IHCP, as the laboratory capacity at IHCP develops. Specific research objectives include:

1. For each of the source classes (wet/VOC, dry/VOC, and dry/SVOC), develop and/or validate fundamental emissions model using small chambers;
2. Evaluate and further develop reliable methods to directly measure the key source model parameters;
3. As data on model parameters accumulates, develop methods to correlate the parameters with readily available physical-chemical properties of the volatile contaminants;
4. Using large chambers and/or the test house at IHCP, prove the overall validity of the approach by demonstrating that the source model validated in the small



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chamber studies can be scaled-up to predict consumer product emissions and exposure in full-scale, real-world scenarios.

5. As the research evolves, build a taxonomy of generic source classes that spans the entire range of consumer products. For each of these source classes, elucidate the fundamental mechanisms that govern emissions, formulate a mechanistic source model, and repeat steps 1 through 4.

### Research Approach

The research will involve close collaboration between IHCP and Virginia Tech. The validation of the wet/VOC model will be carried out entirely at IHCP. The validation of the dry/VOC model will also be carried out at IHCP, but some of the procedures will be replicated at VT to ensure overall scientific integrity. Because of the difficulties involved in working with SVOCs, the development and validation of the dry/SVOC model will begin at VT, but will be transferred to IHCP as the laboratory capacity is developed. Replication of tests at both IHCP and VT will again increase the overall scientific confidence in the results. Both Dr. Little and the VT graduate student will visit IHCP for several weeks each year to work in collaboration with Dr. Arvanitis and Dr. Kephelopoulos. In this way, over the three-year duration of the project, the scientific infrastructure and capacity at IHCP will be developed. Following this three-year period, the development and validation of fundamental source models for all classes of consumer products can continue unimpeded. IHCP and Virginia Tech together will together choose the specific consumer product examples we will work on for each of the three product classes (wet/VOC, dry/VOC, and dry/SVOC). The validated models will be completed as follows:

Year 1 – Validated model for wet/VOC (octane (and other VOCs) in alkyd paint?)

Year 2 – Validated model for dry/VOC (styrene (and other VOCs) in carpet?)

Year 3 – Validated model for dry/SVOC (phthalates in vinyl flooring?)

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## **OVERVIEW OF CANADIAN NATIONAL RESEARCH PROGRAM ON INDOOR SOURCES - RESULTS AND LESSONS**

*(Doyun Won)*

In 1996, the Institute for Research in Construction, National Research Council Canada (IRC/NRC) launched the Material Emissions and Indoor Air Quality Modeling project (MEIAQ). The research is to develop the knowledge and tools needed to estimate concentrations of volatile organic compounds (VOCs) generated by the emissions from building materials and furnishings in order to gain a better understanding of the effects of those products on indoor air quality (IAQ). The second phase of the project was completed in 2004. A brief summary of the tasks involved in Phase II is given below.

### ***Target VOC List***

This task is to provide criteria for analyzing emission data. First, 3 to 5 most abundant VOCs were quantitatively analyzed in any emission test. Secondly, the emission data were analyzed for a target VOC list, which was assembled to contain 90 VOCs, including those known to be emitted from various materials, and, especially, those known to have health or irritation effects. These 90 VOCs were selected based on the review of 11 published lists and the experience gained by IRC from its material emissions testing. All selected VOCs are included in at least one of the 12 published lists (11 referenced lists plus the California target compound list) with 7 exceptions, which are from IRC emission data. Of the 90 VOCs, half of these chemicals have human health implications and the other half are associated with large emission rates.

### **Factors Affecting Material Emissions**

#### ***Specimen Variability: A Case Study***

This task aimed to determine quantitatively the uncertainty of VOC emission rates from a single material likely due to the non-homogeneous nature of raw material ingredients, manufacturing processes, and handling/storing processes. A series of samples of oriented strand board (OSB) were collected and subjected to chamber tests for VOC emissions under standardized conditions (23°C, 50% RH, 1 air change per hour, 0.4 m<sup>2</sup>/m<sup>3</sup> loading). Specimens were collected directly from the mill sites of three different manufacturers. Repeat samples were also collected from the same retail outlet on three separate occasions (same manufacturer, 3 different production dates), from separate panels produced on the same production date, and from multiple locations within the same panel. Variability in the VOC emissions from these samples was found to exceed the analytical uncertainty by an order of magnitude in some cases.

#### **Effects of Environmental Factors on VOC Emissions from a Wet Building Material**

In addition to inherent specimen variability, environmental conditions can also affect VOC emissions from building materials. A series of experiments were conducted for VOC emissions from a solvent-based paint with varied environmental conditions and

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initial concentrations. It was found that the emissions from a paint sample were affected by air velocity ( $v$ ), air temperature ( $T$ ), and initial concentration within the coating ( $C_o$ ), while there were no effects of relative humidity ( $RH$ ). The effects were quantified by correlating the model coefficients, i.e., diffusion ( $D$ ) and evaporation ( $\alpha$ ) coefficients, with the environmental variables. It was shown that  $D$  is linearly proportional to  $T$  and  $C_o$ , while  $\alpha$  is related to  $v$  through a hyperbolic mathematical relationship. Additionally, it was found that  $D$  and  $\alpha$  can be expressed as a function of chemical properties, i.e., molecular weight ( $MW$ ) and vapor pressure ( $VP$ ), respectively. As a result, a correlation equation for  $D$  as a function of  $MW$ ,  $T$ , and  $C_o$  and another for  $\alpha$  as a function of  $VP$  and  $v$  were derived in a mathematical form.

### **Database and Simulation of Indoor Concentrations**

#### ***Material Emission Testing and MEDB-IAQ Software***

A total of 69 building materials were tested in a 50-L stainless-steel chamber in accordance with ASTM Standards. The test information and the emission characteristics of 90 target VOCs and 3-5 abundant VOCs are packaged in to software called **Material Emissions DataBase** and **Indoor Air Quality Modeling (MEDB-IAQ)**. In addition to the database, the software has an IAQ simulation tool with which indoor air concentrations can be predicted for chemicals coming from building materials based on choices of materials, chemicals and ventilation schemes.

The software was validated with IAQ measurements in a research house for more than 8 months after the completion of the house. The software tends to under-predict long-term emissions. This is likely due to the fact that only 12 sources were modeled among hundreds of building materials used in the house and the fact that some building materials may have acted as sinks of VOCs.

### **Development and Validation of a Theoretical Model for Wet Building Materials**

#### ***Model Development for VOC Emissions from Wet Building Materials***

While the MEDB-IAQ used empirical source models mainly for simplicity, mass-transfer based theoretical models were also developed for more advanced modeling. The coefficients of theoretical models have physical meaning and, therefore, can be extrapolated to other settings beyond tested environmental conditions.

To apply this model to VOC emissions from wet building materials, it is necessary to know the evaporation (mass-transfer) and diffusion coefficients of VOCs emitted from the coating materials. A companion experimental method was developed to determine both the evaporation and diffusion coefficients for six aliphatic hydrocarbons and six aromatic hydrocarbons from solvent-based paint. The results indicate that diffusion coefficients are inversely proportional to molecular weight, while evaporation coefficients are proportional to vapor pressure of VOCs.

***Validation of a Mass-transfer Model for VOC Emissions from Wet Building Materials***

This task attempts to validate the mass-transfer model that was developed for VOC emissions from wet building materials mentioned above. The validation was done for 10 compounds emitted from a solvent-based paint applied on a primer-coated gypsum wallboard. While the mass-transfer model tends to under-predict the results at lower concentrations (longer times), the performance of the model is very encouraging in general.

The model performance for 5 compounds successfully passed five out of six statistical measures for assessing the general agreement and bias between the measured and predicted data. The model predictions for the other 5 compounds did not pass most of the statistical measures. The measurements of initial chemical concentrations in the paint sample were identified as an error source for 4 compounds, which are more volatile than the 5 chemicals that passed the statistical analysis. With modified initial concentration data, the model performance for the four most volatile compounds was improved to similar levels of agreement for the first 5 compounds. The poor performance of the model for the one remaining compound is likely due to multiple error sources including errors in measurements of model parameters and/or errors in the assumption of no mass flux at the interface between the paint layer and the latex-based primer-coated substrate.

## SUMMARY OF TRANSPORT AND FATE MODELS

(Michael Jayjock - with material contributions from Chris Keil, Mark Nicas and Susan Arnold)

Historically, the well-mixed box representation has dominated as the indoor transport model of choice. In this construct transport is conveniently handled by assuming that any molecule released into a microenvironment (e.g., a residential room) will be instantaneously mixed within the volume of the room. In this model the average concentration is considered to be homogeneous throughout the volume of the room. That is, there are no gradients of concentration between the source and any point within the microenvironment.

Given a steady source, the well-mixed box model renders the following simple relationship for the average airborne concentration of a nonreactive/nonsorbing species with a source rate in mass/time and ventilation rate in volume/time:

$$Concentration = \frac{Source\_Rate}{Ventilation\_Rate}$$

These assumptions are reasonably valid for scenarios with large diffuse or multiple sources emitting to relatively small microenvironments with rapidly moving and well-mixed air. This approach may also work reasonably well for predicting time-averaged exposure concentrations over extended time intervals. However, the assumptions are not valid for predicting transient exposures to emissions from point sources proximate to the exposed individual.

Clearly, point sources in real rooms have strong gradients of concentration from the source to distal points within the room. A technical construct was used to successfully describe this situation by Dr. John Franke in his 1985 PhD Thesis<sup>1</sup>. Dr. Franke used a diffusion model originally developed for heat flow<sup>2</sup> and applied to indoor air modeling<sup>3,4</sup>. The equation for a continuous point source is presented in the references to predict concentration at any distance  $r$  and time  $t$ .

$$C = \frac{G}{4\pi(D)(r)} \left[ 1 - \operatorname{erf} \left( \frac{r}{\sqrt{4(t)(D)}} \right) \right]$$

where:

- C = concentration, mass/volume, mg/m<sup>3</sup>
- erf = the error function (dimensionless)
- G = steady-state emission rate, mass/time, mg/hr

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$r$  = the distance from the source to the person's breathing zone, m  
 $D$  = the eddy diffusivity, area/time,  $m^2/hr$   
 $t$  = elapsed time, hr

In this model, contaminants emitting from a point source are dispersed not by their molecular diffusion but rather by the natural air currents existent in every interior space. Indeed, molecular diffusion is miniscule compared to the diffusion caused by turbulent eddy air currents. These natural indoor air movements or eddies determine the size of  $D$  (the eddy diffusion coefficient) which is entirely dependent on the amount of turbulent kinetic energy of the air and independent of any properties of the transported chemical species. Thus, this model presents a detailed portrayal of these exposure gradients in typical rooms that do not have strong level of directionality to the natural movement of air within the room.

Other attempts <sup>5,6,7</sup> have been made to describe this reality of high concentration near a source and lower concentrations at points away from the source. The two-zone or “near-field/far field” model conceptualizes a room as containing two contiguous zone- a “near field” zone surrounding the emission source, and a “far field” zone comprising the rest of the room. The air within each zone is treated as being perfectly mixed, but with limited air exchange between the two zones. This model scenario means that the contaminant concentration is uniform throughout the near field zone, and is uniform throughout the far field zone, and in general the near field concentration is higher than the far field concentration.

The general mass balance equations for the Near Field/Far Field Model and a constant emission rate are as follows:

	Change in Mass	= Mass Gain	-	Mass Loss
Near Field:	$V_N dC_{NF} =$	$[G dt + \beta C_{FF} dt]$	-	$\beta C_{NF} dt$
Far Field:	$V_F dC_{FF} =$	$\beta C_{NF} dt$	-	$\beta C_{FF} dt + Q C_{FF} dt]$

where:  
 $C_{NF}$  = the near field concentration ( $mg/m^3$ )  
 $C_{FF}$  = the far field concentration ( $mg/m^3$ )  
 $V_{NF}$  = the near field volume ( $m^3$ )  
 $V_{FF}$  = the far field volume ( $m^3$ )  
 $G$  = constant mass emission rate ( $mg/min$ )  
 $\beta$  = air flow rate ( $m^3/min$ ) between the near and far fields  
 $Q$  = room supply/exhaust air rate ( $m^3/min$ )  
 $dt$  = an infinitesimal time interval

## **INHALATION EXPOSURE TO AEROSOLS FROM SPRAY CANS EN TRIGGER SPRAYS: EXPERIMENTS EN MODEL**

*(Christiaan Delmaar)*

### **ConsExpo**

ConsExpo is a computer program that comprises a set of relatively simple exposure models that can be used to estimate the exposure of consumer to chemicals from consumer products. In 2004 RIVM in collaboration with TNO Rijswijk has conducted research to the potential inhalation exposure of consumers to non-volatile chemicals released as aerosols from spray cans (sprayed product driven out by the expansion of a propellant gas) and trigger sprays (aerosols driven out by mechanical pressure (pumping)). The experimental measurements of concentration levels arising during use of various sprays were used to develop a simple, descriptive exposure model that has been implemented in the ConsExpo program.

### **Exposure Experiments**

Aerosols that are inhaled will deposit at various sites in the respiratory tract, depending on their size and shape (see, for instance, Freijer J.I. , Cassee F.R. and van Bree L. (1997) Modelling of particulate matter deposition in the human airways, RIVM report 624029001).

Only droplets that are small enough (diameter  $< \sim 20 \mu\text{m}$ ) will penetrate into the lower regions of the lung and lead to inhalation exposure. The conducted study focussed on these inhalable droplets.

In selecting the spray products to be used for the experiments an attempt was made to make the selection as broad and representative for products available on the market as possible. Products chosen included cosmetics, cleaning products, paints, but a special interest was in pest control products in view of their importance as potentially hazardous products.

Selected products included both spray cans and trigger sprays but since spray cans on average produce smaller aerosols and are therefore more important as a source of inhalation exposure these were more represented in the product selection. In addition, in making the product selection attention was paid to the way the product should be used as this is anticipated to be a large determinant of exposure. The following use categories were distinguished:

- 1) product used as an air space application,
- 2) product used to target a surface or spot (i.e. crack and crevice, on a plant),
- 3) the product sprayed directly toward a person.

The initial selection consisted of 23 sprays (18 spray cans, 5 trigger sprays).



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**Droplet size distributions**

For the initial set the mass emitted in 10 seconds of spraying (spray cans) or in 10 squeezes (trigger spray) and the initial aerosol size distribution of the spray were determined. Aerosol size distributions were determined for both the case that spray cans were full and nearly empty. The measurements of the droplet size distributions were performed using a Mastersizer/S (Malvern Instruments, UK). As a rule trigger sprays produce larger droplets (median droplet diameters  $> 200 \mu\text{m}$ ). Droplet sizes of the spray cans showed a larger variation. Median diameters range from  $20 \mu\text{m}$  up to above  $100 \mu\text{m}$ .

**Measurement of aerosol air concentrations of the sprayed products**

For a second series of experiments the selection of 23 spray products was reduced to a number of 8, which included 2 trigger sprays and 6 spray cans. For these sprays droplet size distributions and total air concentrations in a climatically controllable room were measured as a function of time under conditions simulating the anticipated use of the product.

The measurements of air concentrations were performed with an Aerodynamic Particle Sizer (APS) in a room of volume  $19.5\text{m}^3$  ( $3.90\text{m} \times 2.10\text{m} \times 2.38\text{m}$ ).

Measurements of the air concentration were performed at heights of 25 cm and 150 cm (approximately the human breathing zone) above the ground at various positions in the experimental room. Both the time profile of the total droplet mass concentration and the droplet size distribution as a function of time were determined.

The measured concentration profiles initially showed a marked inhomogeneity since the droplets are released in a cloud. Due to advective transport (turbulent air movement) droplets are dispersed through the room. In spite of the fact that sources of turbulent air movement (ventilation, thermal sources, personal movement), were kept at a minimum in the experiments, dispersion of the droplet cloud proved to be fast ( $\sim 1\text{-}2$  minutes). After dispersion, concentration profiles settled at constant ratios across the room that were within one order of magnitude, in other words air mixing was quick but seemed not to be complete.

It should be noted, however, that in a practical exposure situation this mixing will be better due to the presence of turbulent air sources.

**Descriptive model**

The experimental measurements were used to formulate and verify a simple descriptive model that is to be used for estimation of the exposure of consumers to chemicals released as droplets from spray products. Aerosol air concentrations in the room are determined by dispersion of the droplets, removal due to ventilation and removal due to gravitational settling. Dispersion of the droplets was seen to be a relatively fast process, ventilation was not included in the experiments at this stage. Gravitational settling depends on the droplet size and shape (see, for instance Hinds, *Aerosol Technology*, Wiley, 1982). The size of the aerosols is determined by the initial size (at the instant the droplets leave the spray nozzle) and by the subsequent evaporation of solvents. This

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evaporation of solvent is a fast process for small droplets (<20 µm): the lifetime of a droplet of water with an initial diameter of 20 µm is about 1 second (at an air humidity of 50%), (Hinds).

Thus, since dispersion of the initial cloud by advective transport and evaporation of solvents from the droplets seem to be fast processes on the timescale of these experiments and are assumed not to play an important role. Hence, the concentration is supposed to be mainly determined by the gravitational settling of droplets (the room was not ventilated). Using the Stokes settling velocity  $v_s(d)$  and assuming well-mixed air conditions at all times as a very simple model the room air concentrations can be described by:

$$C(t) = \frac{1}{V} \sum_d \frac{\pi d^3}{6} \rho N(d, 0) e^{-v_{s(d)} t / h}$$

Which follows from the initial droplet size distribution  $N(d, 0)$  as measured in the first part of the experiment. (In this equation  $\rho$  is the density of the product,  $d$  the droplet diameter,  $t$  the time and  $h$  the release height of the spray).

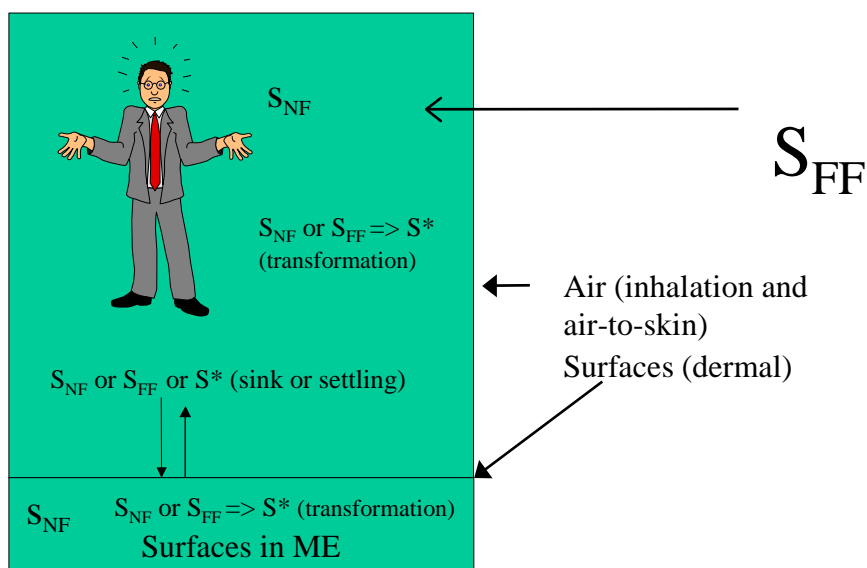
Comparing results of this simple model with the experimental data for spray cans yields satisfactory results for exposure estimation purposes. For the case of trigger sprays, the model provided a less satisfactory description. This may be explained by the fact that the dispersion of the initial cloud may be slower for larger droplets. Also for droplets >~100 µm containing relatively slow evaporizing solvent such as water (almost exclusively used as the solvent in trigger sprays), the evaporation of the solvent may play an important part and can not be discarded.

## **DISCUSSION ON JUNE 21, 2005**

The presentations of the previous day were followed by a discussion on Tuesday, June 21, 2005 of the topic of an engineering or “Systems Approach” to modeling and model development as suggested by Dr. Elaine Cohen Hubal. The elements of such an approach were outlined as:

- *Consider the system of interest (indoor microenvironment)*
- *Develop an illustrated and detailed conceptual framework for the modeling (i.e., a figure showing all potential chemical sources and losses to the system, consideration of temporal and spatial characteristics, representing the most general and most complex model – though not necessarily something that would ever be developed) (See Figure below)*
- *Identify and Classify Sources*
- *Develop a potential suite of initially simplified conceptual models that could be used for each type of source (assuming steady state, assuming uniform distribution of contaminant, etc.). These are then followed with more sophisticated models that describe more realistic (less simplified) scenarios and thus provide more accurate estimates.*
- *Conduct theoretical “experiments” to identify/verify model requirements based on the characteristics of sources/emissions, properties of compounds, characteristics of the microenvironment (what are the important temporal scales, spatial scales, rate determining processes, when can an intermittent source be treated as a continuous source, etc.).*
- *Identify data required to apply models for predictive exposure assessment and then design experiments.*
- *Provide criteria for, and guidance on, model selection based on exposure scenario (e.g., properties of sources/emissions, characteristics of the microenvironment, dimensionless parameters that incorporate consideration of the critical elements that could be driving the exposure, etc.)*

## SYSTEM OF SOURCES INDOOR MICROENVIRONMENT (ME)



$S_{NF}$  = near field source (source occurring within the microenvironment – *e.g.*, benzene from spray paint)

$S_{FF}$  = far-field source (source occurring outside the microenvironment but penetrating into it) – *e.g.*, benzene from general use within a geographical area)

$S^*$  = chemically reacted and thus generated species as a source.

This was then followed by a discussion and construction of a taxonomy of sources for human exposure indoors. Given that our purpose is to model exposure, the categories or BINS below were chosen by the participants with the idea that sources within any bin could be potentially described by a single model or by reasonably straightforward (but increasing sophisticated) variations of that source sub-model.

This exercise was designed to identify and classify the universe of exposure sources indoors. The workshop participants decided to divide this universe into 5 bins:

1. Vapor emitted from **DRY SOURCES**,
2. Vapor from **WET SOURCES**,
3. **PARTICULATE MATTER SOURCES** (solid and liquid aerosol),
4. **COMBUSTION SOURCES** (particulate and vapor), and
5. **CHEMICAL REACTION SOURCES** (particulate and vapor).

A more detail description of these BINS is presented below:

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**VAPOR from DRY SOURCES:**

Chemicals contained within, diffusing and emitting from solids. Specific examples are listed below:

- Dried coatings (e.g., dry paint) and underlying substrate
- Dry or dried pesticide (e.g., moth crystals)
- Treated wood
- Plastic films, surfaces or cabinets
- Engineered Wood Products (Oriented strand board, composition board, plywood)
- Composite products (e.g., furniture)
- Polyurethane foam
- Polystyrene foam
- Carpet and carpet backing
- Fabric
- Wall coverings
- Building materials
  - Sheetrock (gypsum board)
  - Other flooring materials (linoleum, vinyl composite tile, etc.)
  - Caulking, sealants, and adhesives
  - Insulation
- Paper products (e.g., formaldehyde from printed paper, off gassing from cardboard and its adhesives)
- Electronic products/components (circuitry within appliances, computers, monitors, etc.)

**VAPOR from WET SOURCES :**

Chemicals emitting from wet sources. Specific examples are presented below:

- Coatings (paint, varnish)
- Building material (caulks and adhesives)
- Cleaning products (wiped, brushed or mopped on; sprayed on)
- Wet Pesticides
- Personal Care or Cosmetic Products
- Laundry products
- Solvent Uses
- Air fresheners
- Fugitive emissions from stored liquid products (e.g., home heating fuel and gasoline in attached garages).
- Contaminated Potable Water (showering/bathing/laundrying)
- Basement wet or damp with contaminated water
- Spills

### **PARTICULATE MATTER SOURCES:**

Substances emitted as particulate matter during use. Specific examples are presented below:

- Sprayed pesticides (Aerosol and VOC)
- Cleaning products (Aerosol and VOC)
- Sprayed personal care products (Aerosol and VOC)
- Welding (fumes)
- Handling “dusty” materials (aerosol)
- Particles brought into the residence and re-entrained (*e.g.*, pesticides tracked into house from lawn and garden) (aerosol)
- House dust containing SVOCs (aerosol)
- Particulate emissions from spray humidifiers
- Particles re-suspended (*e.g.* from vacuuming or other processes)

### **COMBUSTION SOURCES (PARTICULATE and VAPOR):**

Particulate and vapor emitted from the combustion of organic substances. Specific examples are presented below:

- Cooking (combustion of the fuel (when present), the heating of the food, the heating of oils, and the heating of the utensils)
- Candles, incense and other combusted aromatherapy products
- Self-cleaning oven emissions
- Vented home heating
- Unvented space Heaters
- Wood burning
- Environmental tobacco smoke (ETS)

### **CHEMICAL REACTION SOURCES**

Sources that originate from chemical reactions. Examples are presented below:

- Reactions in the air (*e.g.*, oxygenated VOC species from ozone reaction)
- Reactions in water (*e.g.*, dishwashers and laundry)
- Reactions within the material
- Reactions on surfaces

Sources of Reactive Gases

- Ozone generators and “ionizers”
- Penetration of polluted outdoor air
- Combustion

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Photocatalytic oxidation devices (POD)  
Air filters (as reservoirs and reaction surfaces for nasty stuff)  
Microbiological decomposition as a source of chemicals

Given that the above 5 bins represent a taxonomy or universe of all sources, the workshop participants advised that a reasonably representative subset of this comprehensive listing should be selected for specific laboratory analysis. It was further advised by this group that exposure models used to describe these sources of exposure should be forwarded in a **tiered approach** in which simple models would be devised initially (**zero tier**) to provide an initial crude estimate of exposure potential. In some instances these lowest tier relationships might be sufficient to answer the question at hand. Where they are not, more refined versions of the model would be developed in **second-tier** and then **n-tier** efforts of increasing sophistication, accuracy and cost in order to provide appropriately accurate answers.

The participants then considered criteria for setting research priorities among these emissions classes. Specifically, it was determined that once the possibility for exposure to potentially toxic substances was established, the models needed to be available and adequate to reasonably estimate the human exposure potential to these substances.

At this point, the participants decided to use the remaining available time of the workshop to outline specific examples as to how a tiered approach to model development would proceed starting with vapor emitted from **WET SOURCES** as the first example.

## **WET SOURCE MODELING**

A generic tiered approach to building mechanistic sources models for wet sources would first include a relatively simple **zero tier** in which, for example, one would take all of the mass available and put it into the air instantaneously. Such simplistic assumptions are not realistic for all compounds but provide bounding analysis for compounds that volatilize rapidly.

The next step would be a **first-tier** approach in which one would invoke a simple dynamic mass-balance model such as put forth by Dr. Zhishi Guo in 1999. Other features of this level of modeling could include having a non-variant mixture of active substances in wet material and an assumed film thickness (~1mm) at a constant concentration.

The input needed for such a **first-tier** model would typically be vapor pressure ( $K_{aw}$ ) and the external mass transfer coefficient

A **second-tier** approach might include a time varying mixture of independent active substances in wet material with dynamic time-variant dimensions such as film thickness.

The **n<sup>th</sup> tier** represents a dramatic increase in the level of model sophistication and frankly asked the question; how far can or should we go in developing the complexity of

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the model to answer the questions about exposure? Some elements that might be built into such a model include:

- Heterogeneous mixtures where one component alters the behavior of others
- Ability to handle substrate effects
- Dynamic behavior of SVOCs affecting emissions.
- Transition dynamics within the system as it goes from wet to dry
- Time and location dependent diffusivity of the chemical substances
- Exogenous reactive chemistry
- Endogenous (incidental/intentional) reactive chemistry

As mentioned above, this modeling would be applicable to:

- Coatings (paint, varnish)
- Building material (caulks and adhesives)
- Cleaning products (wiped, brushed or mopped on; sprayed on)
- Wet Pesticides
- Personal Care or Cosmetic Products
- Laundry products
- Solvent Uses
- Air fresheners
- Fugitive emissions from stored liquid products (e.g., home heating fuel and gasoline in attached garages).
- Contaminated Potable Water (showering/bathing/laundrying)
- Basement wet or damp with contaminated water
- Spills

The workshop participants then worked to provide a similar approach to building mechanistic source models for generic **DRY SOURCE** modeling presented below:

### **DRY SOURCE MODELING**

**Zero tier**— Initial concentration ( $C_o$ ) model. This would involve the release of  $C_o$  contained within the dried material to the air over some relevant time period which would typically be based on the characteristic time of diffusion.

**First tier**— This is available in the work reported by Little *et al* in 1994. It is a three-parameter model ( $C_o$ ,  $K$  and  $D$ ) that would require laboratory work to parameterize this source model for the universe of material of interest. A slight enhancement of this approach would be the Little (1994) model with adjustment provided by Xu and Zhang (2003). It is a four parameter model  $C_o$ ,  $K$ ,  $D$ , and  $h_m$  again requiring laboratory work to parameterize.



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**Second tier**— These would be multi-layer models exemplified by the two-layer model of Kumar and Little, 2003. This involves four parameters ( $C_o$ ,  $K$ ,  $D$ , and  $h_m$ ) with the addition of multiple layers provide by Zhang, 2003 ( $C_o$ ,  $K$ ,  $D$  in each layer and  $h_m$ ).

**N<sup>th</sup> tier**—all of the above plus the following level of sophistication:

- Anisotropic matrix
- Concentration dependent parameters
- Heterogeneous mixtures where one component alters the behavior of others
- Able to handle substrate effects
- Dynamic behavior of SVOCs affecting emissions.
- Time and location dependent diffusivity
- Exogenous reactive chemistry
- Endogenous (incidental/intentional) reactive chemistry
- Non-linear partition isotherms
- Use of macro-scale effective diffusion coefficients (Lee *et al*, 2005)
- Accounting for the role of porosity
- Accounting for humidity and temperature
- Accounting for compositional variability

As indicated above, such modeling would be applicable to:

- Dried paint
- Dry or dried pesticide (e.g., moth crystals)
- Treated wood
- Plastic films, surfaces or cabinets
- Oriented strand board
- Composition board
- Plywood
- Insulation
- Carpet and carpet backing
- Electronic products/components (circuitry within appliances, computers, monitors, etc.)

The workshop participants then pressed on to provide illustrative details for this approach in building mechanistic source models for generic **PARTICULATE MATTER SOURCE** modeling.

## **PARTICULATE MATTER SOURCE MODELING**

**Zero tier** — This might assume instantaneous or constant release of a defined portion of the material to air as well as ideal gas behavior.

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**First tier** — This would be exemplified by the approach used in the RIVM ConsExpo model; that is, introduce a known quantity with a known size distribution into a volume of air. Such an approach produces a more realistic assessment of time history of release and allows for some level of fate and transport in particle source assessment. It would also account for the initial (over some reasonable time scale) chemical phase distributions, deposition/re-suspension and transformation in a simple way (*e.g.*, it could possibly use fugacity models) for key loss/transport mechanisms.

**N<sup>th</sup> tier** — All of the above plus the following level of model sophistication:

- Dynamics of secondary contaminant formation
- SVOCs and VOCs interacting with particles
- Size-resolved chemical composition for aerosols
- Internally vs externally mixed systems
- Particle morphology and aerodynamics
- Distinguish wet and dry particle sources (dynamic transition from wet to dry)
- Linear vs nonlinear sorption on particles
- Exogenous reactive chemistry
- Endogenous (incidental/intentional) reactive chemistry
- Electrostatic charge
- Particle Friability
- Resuspendability/adhesive characteristics
- Humidity and surface moisture
- Mechanisms of re-suspension

As mentioned previously, such modeling would be applicable to:

- Sprayed pesticides (Aerosol and VOC)
- Cleaning products (Aerosol and VOC)
- Sprayed personal care products (Aerosol and VOC)
- Welding (fumes)
- Handling “dusty” materials (aerosol)
- Particles brought into the residence and re-entrained (*e.g.*, pesticides tracked into house from lawn and garden) (aerosol)
- House dust containing SVOCs (aerosol)
- Particulate emissions from spray humidifiers
- Particles re-suspended (*e.g.* from vacuuming or other processes)

## **TRANSPORT AND FATE MODELING**

Given some remaining time on the last day of the workshop, the participants set about to devise the same modeling framework elements for modeling the **TRANSPORT AND FATE** of emissions indoors.

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**Zero tier**— Simple well-mixed one-box model

- Mass/Volume estimated for pulse release followed by first-order exponential decay
- Concentration =  $G/Q$  for continuous and constant release rates
- No reactions
- No settling
- No sorbing
- No back pressure retarding evaporation
- Constant ventilation

**First tier**— Steady well-mixed one to n (small) chamber model

- Steady-state mass balance
- First-order degradation or generation reactions (homogeneous or surface)
- Particle deposition accounted for in transport
- Simple Gas phase partitioning (reversible)
- Constant emissions
- Constant ventilation
- Air cleaning (modeled as steady-state)

**Second tier**— Well-mixed dynamic one to n model

- Dynamic mass balance
- First-order reactions (homogeneous or surface)
- Sized resolved particle deposition
- Gas phase partitioning (reversible)
- Time dependent emissions
- Variable ventilation
- Air cleaning
- Multiple sources
- Simple approach to capture proximity effect (Nicas indoor near/far field model)

**N<sup>th</sup> tier**— Many “compartments” or nodes within the indoor volume

- Dynamic mass balance
- High fidelity reaction chemistry models (n level coupled reactions)
- Sized resolved particle deposition
- Coagulation, re-suspension, phase change
- More spatial resolution of concentration (gradient or more detailed approach to capture proximity effect (near/far field))
- Gas phase partitioning (reversible and irreversible)
- Time dependent emissions
- Variable ventilation
- Air cleaning
- Multiple sources (in space and time with interactions)
- Short time scales
- Distinguish among surfaces (walls, ceilings, floors, furniture)
- Spatially and temporally resolved environmental conditions

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Effect of coupled uninhabited spaces (attic, crawl spaces)  
Complex residential floor plans

## **FINAL ANSWERS TO QUESTIONS POSED TO WORKSHOP ATTENDEES**

**GAP ANALYSIS FOR EXISTING MODELS (How inaccurate are the existing models or how important is it to close any particular gap? This includes identification of “best” currently available models and a research path forward to close the gaps)**

As mentioned above, during the second day of the workshop a significant change in direction was advised by the participants and agreed to by Dr. Kephelopoulos. Specifically, it was agreed that we would **not** outline, characterize or explicitly build upon the currently available source sub-models beyond the draft workshop report done before the meeting. Instead the workshop participants endeavored to build a framework for this body of scientific work from “the ground up”. Existing models, where available, were mentioned or would be otherwise used to fill in this framework. Thus, it was decided and agreed upon during the workshop that the participants would not explicitly address this question.

The primary reason for this decision was a consensus that a critical mass of reasonably formed models of human exposure to fill a matrix simply does not exist. That is, the current state of exposure modeling is relatively underdeveloped such that very few models have been reasonably fashioned or have undergone any sort of parameterization and evaluation under real world conditions.

Given this decided lack of model development and data, a relatively large task is envisioned for a research path forward. It is advised that the JRC research plan should be purposely sized to fill a funded research effort relative to this perceived need and the resources allocated to it. That is the resource allocation should be substantial with the number and types of experiments will initially be determined within this resource allocation and schedule. This schedule will also be subject to change depending on what is learned during the testing.

More specific details on gaps and research to fill them are available in Appendix B.

### **WHAT IS THE TOP PRIORITY FOR SOURCE OR TRANSPORT MODELING RESEARCH ISSUES?**

Exposure to any substance has no contextual meaning relative to human health risk without understanding the health effect related to that exposure. Thus unless one has a reasonable data base of the sources, substances and their toxicity, assigning priority to the exposure piece relative to the potential risk is problematic. Indeed, as mentioned in the pre-Workshop report, the answer to this question is essentially unknowable *a priori* since

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it is somewhat like knowing the answer first so that one asks the correct question. See Appendix B for further thoughts and perspective on this from the participants.

Given the relative lack of well-developed models, the priority should be driven by the need to answer the questions at hand. In the case of sources it should include those scenarios considered or judged to provide the highest level of personal exposure ((concentration)(time)) potential to substances with the highest level of toxicity.

From a regulatory perspective it would be those sources receiving the most attention presumably because they present the highest risk. This could well be substances that are intended to be released to the environment during use. Prime examples would be wet sources and aerosols. Indeed, aerosol are clearly intended to be released and it can be reasonably argued that wet sources carry this same intention because they are explicitly meant to dry out.

### **STRATEGY FOR USING EXISTING SOURCE/TRANSPORT EXPOSURE MODELS AND EXISTING SCENARIOS**

As mentioned above, it was decided in the workshop that we would not identify the best existing source/transport models and make specific recommendations for how they might be used absent (or before) the benefit derived from a research program to improve them.

Existing models in their current state are useable, however, in many cases, not extremely useful. In any given scenario the current strategy is or should be obvious: use the best current (but generally underdeveloped and unevaluated) models, bias the model inputs to overestimate exposure (to guard against the uncertainty of underestimation), document your actions and hope for the best.

## **RESEARCH PLAN RECOMMENDATION SUMMARY**

The point in all of this is that the above source and transport and fate models need to be developed and matched to the needs of the risk assessment. Where simple screening, prioritization or ranking is the requirement, lower tier development of a basic model could be sufficient. These will undoubtedly overestimate the exposure potential but an overestimate may still be useful and adequate for making decisions. If it is subsequently determined these overestimates are not sufficient, then a more accurate prediction of the true exposure levels is required and higher level model enhancements (higher tiers) will need to be developed. To the extent that this iterative process will result in tools that effectively facilitate the estimation of exposure for a reasonably broad base of scenarios and substances, the research and development cost would be cost-effective.

Thus, matching the source model to the needs of the risk assessment is an iterative process that proceeds from simple to more complex relationships to predict exposures at an appropriate level of accuracy. Once it is determined which type of source and transport and fate model(s) (from whatever tier or level of sophistication) is required to answer the scenario-based risk assessment questions at hand, specific models (hypotheses) as determined by a consensus of scientific and stakeholder participants would be proposed.

If it is determined that a model has not previously been specifically developed and evaluated then this would mean that experimental work would be required to build it. This would involve gathering of experimental emission data for a representative listing of sources under question. These laboratory simulations studies would provide data for two purposes; first, to parameterize the model and second to evaluate the predicting algorithm under a range of realistic conditions to “ground truth” the measured exposure potential against the model prediction. This would, in turn, lead to either an acceptance of the model as developed or a modification/enhancement with subsequent retesting.

## **WORKSHOP OUTCOMES AND RECOMMENDATIONS**

The two-day workshop resulted in the following primary work products:

- Identification of existing source sub-models: presented in the pre-workshop report and references
- Defined a Taxonomy of Sources
- Identification and definition of the attributes and characteristics of First Principle Mechanistic Source and Transport/Fate Models to be developed in a tiered approach.

The details of these outcomes are described in the above text and Appendix B containing the pre-workshop report and references.

The specific selection of which area(s) to work on initially should be guided by the stakeholders and the regulatory mandate(s) under consideration. For example, if the initial implementation of the REACH program will be limited to priority assessment of chemical substances that are designed to be released into the environment, then the initial research and development should perhaps focus on emissions from WET SOURCES or PARTICULATE MATTER SOURCES in the context of scenarios where release is intended as part of the material's use.

Models developed as a result of such research will be of general use, scientific interest and lasting value on a worldwide basis for any and all attempting to estimate human exposure from chemicals.



## **APPENDICES:**

### **Appendix A - Original Workshop Agenda (issued June 15, 2005)**

JUNE 20, 2005

#### BACKGROUND AND INTRODUCTION

8:30	Welcome and Background on JRC Program	<i>Kephalopoulos</i>
8:45	Opening Remarks and Self Introductions	<i>ALL</i>
9:15	Review Workshop Outline, Objectives and Agenda	<i>Jayjock</i>

#### PARTICIPANT PRESENTATIONS

9:30	Model Uncertainty Analysis Case Study: VOCs from Contaminated Water During Showering and Bathing	<i>McKone</i>
10:00	Fugacity Modeling of the Microenvironment Indoors - InPest (comparison of estimations and measurements)	<i>Matoba</i>
10:30	BREAK	
10:45	How Existing Models Handle Sources and Transport	<i>Pandian</i>
11:15	Intake Fraction: Quantifying emission-to-intake relationship	<i>Nazaroff</i>
11:45	Discussion of Morning's Presentations	<i>ALL</i>
12:00	LUNCH	
13:00	Evaluation of Models for Regulatory Decisions	<i>McKone</i>
13:30	Reactive chemistry and its significant to indoor source characterization	<i>Nazaroff</i>
14:00	Modeling VOC Emissions from Solids and Liquid Sources – Theoretical Modeling Construct and Outline	<i>Little</i>
14:30	BREAK	

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14:45	Overview of Canadian National Research Program on Indoor Sources - Results and Lessons Learned	<i>Won</i>
15:30	Indoor Transport Models	<i>Jayjock/Nicas</i>
16:00	Further discussion of what we heard today and its meaning	<i>ALL</i>
16:20	Review of Next Day’s Agenda and Workshop Objectives with adjustments as necessary	<i>ALL</i>
17:00	Adjourn	

JUNE 21, 2005

THE REAL WORK OF DECIDING AND RECOMMENDING

8:00	Welcome Back and Review of Agenda	<i>Jayjock</i>
8:15	Discussion - SYSTEMS APPROACH TO MODELING RESEARCH	<i>Hubal/Jayjock</i>
	<ul style="list-style-type: none"> <li>• Conceptual Framework for Indoor Microenvironments</li> <li>• Review and Modify Illustration of all potential sources and losses to the system</li> </ul>	
9:00	Classification of Source Types and Assignment of Specific Sources within Each	<i>ALL</i>
10:00	BREAK	
10:15	Review “Straw-Man” Source Type Taxonomy Additions and Changes Ranking of Source Types and Sources	<i>ALL</i>
11:15	Identification of Available Models for the Above Source Types	<i>ALL</i>
12:00	LUNCH	
13:00	Within the various Source Types – Are the Available Models Adequate to Estimate Exposure for Regulatory Decisions? If not, specifically what is needed to refine or evaluate these tools to the point that they are adequate? Outline specific research needs and cost estimates for each.	

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16:00 Review the activities of the workshop and make and rank specific recommendations with cost estimates for research

17:00 Adjourn

## **Appendix B: Pre-WORKSHOP REPORT**

European Commission – DG Joint Research Centre  
Institute for Health and Consumer Protection, Physical and Chemical Exposure Unit,  
Exposure Modeling Sector

### **Global Net on “Consumer Exposure Modeling”**

**Workshop no. 2**  
**on**  
**“Sources, Transport & Fate”**

**20-21 June 2005, Intra (Italy)**

#### **Background**

This was one of 5 workshops that were conducted by the Institute for Health and Consumer Protection, European Commission Joint Research Centre (JRC) in Intra (Italy) during the week of 20-24 June 2005. The workshops addressed general and specific topics related to modeling human exposure to chemicals. It had been decided by the workshop sponsors that each moderator would be responsible for writing a complete and detailed report, on the issues addressed in the Workshop and on the anticipated and hoped-for and, ultimately, the final results of the gathering.

The choice was made to initiate a pre-workshop report on existing models and issues as a vehicle for getting everyone involved before the meeting so as to assure that participants came to the meeting on roughly the same “page” and the actual meeting time was well spent.

This preliminary or pre-workshop report went through four working drafts and the final version is provided herewith as an appendix (B) to the proceeding report.

Specific contributors to this pre-workshop report are listed as authors in roughly order of the extent of their contribution. It is anticipated that the entire workshop report including this pre-workshop report appendix will be published as a JRC document as part of the publication of the workshop proceedings; however, it has been agreed by the JRC that all authors/contributors of technical material for this workshop will retain the right to publish their work independently.

*Pre-Workshop Report*

**Indoor Sources of Chemical Exposure  
Rates, Transport and Fate  
Research Needs and Program Plan**

*Michael Jayjock, William Nazaroff, Richard Corsi, John Little, Doyun Won, Elaine Cohen Hubal, Mark Mason, David McCready, William Shade, Stylianos Kephelopoulos and Athanasios Arvanitis*

**Abstract**

Any program that mandates a quantitative human health risk-based approach to chemical regulation and management will need two basic elements. The first is dose-response data on the toxicity of the chemicals of interest. The second equally important component is specific and confident knowledge relating the toxic potency of these chemicals with their actual level of exposure to people.

A comprehensive plan to evaluate the quantitative levels of human exposure to a large universe of chemicals is a daunting task. Indeed, it is clear to anyone embarking on such a mission that we will not be able to directly measure every exposure, to everyone in every scenario. It becomes equally apparent that general scientific constructs portraying and predicting the reality of exposure (*i.e.*, models) need to be developed or refined to attain a reasonable and cost-efficient means of understanding and estimating exposure.

This reports presents the background and pre-workshop activity before a workshop held on this subject on June 20-21 in Intra/Verbania (I) under the auspices of the EC Joint Research Centre (JRC) Institute for Health and Consumer Protection (IHCP). It outlines the preliminary work product of the participants in anticipation of that gathering; that is, a current state-of-the-science summary and a draft research plan to move forward in the specific areas of the characterization of emissions and the transport and fate of chemical sources indoors.

**Introduction**

In 1995, one of us (M. Jayjock) had an opportunity to present testimony to a U.S. Presidential Commission on Risk Assessment and Risk Management. The following excerpt from this ten-year-old testimony remains reasonably current today, as we pass the midway point of the first decade of this new century:

*As someone identifiable as a “risk assessor”, I am very concerned that risk assessment is being touted as an entity that promises things it cannot deliver at this point. It is a remarkably useful and potent paradigm. Indeed, I believe that it is entirely capable of ultimately providing a strong rational evaluation of the*

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*potential for adverse outcome for any and all scenarios of concern. As such, it could be an invaluable aid to the regulatory decision making process. It is, however, at this juncture a relatively embryonic science that is in need of a significant amount of scientific research and development.*

*My fear is that risk assessment is currently being over-sold to Congress and the public as a ready “answer” to most or all questions regarding the regulation and management of risk from chemicals. Indeed, it is now and will remain an important tool for risk managers and others who deal with overall policy considerations. My apprehension with the current situation, however, is that it will play out into a political backlash in which this yet underdeveloped science is blamed for a failure to provide quick, reasonable and decisive answers and is thus abandoned or at least ignored.*

*This brings me to my central message:*

- *SCIENTIFIC UNCERTAINTY is the BANE of RISK ASSESSMENT potentially limiting the usefulness, objectivity and ultimately the credibility of the process.*
- *This Uncertainty needs to be DESCRIBED and COMMUNICATED but more important it needs to be REDUCED through the concerted development of the scientific knowledge base.*
- *To the extent that the REDUCTION OF UNCERTAINTY can be attacked as a generic problem (e.g., exposure assessment methods) it should be done as a PUBLIC WORKS project.*

Human exposure to chemicals has been defined as the time integral of concentration occurring at the human interface<sup>8</sup>. This has been mathematically described as:

$$E = \int_{t_1}^{t_2} C(t)dt$$

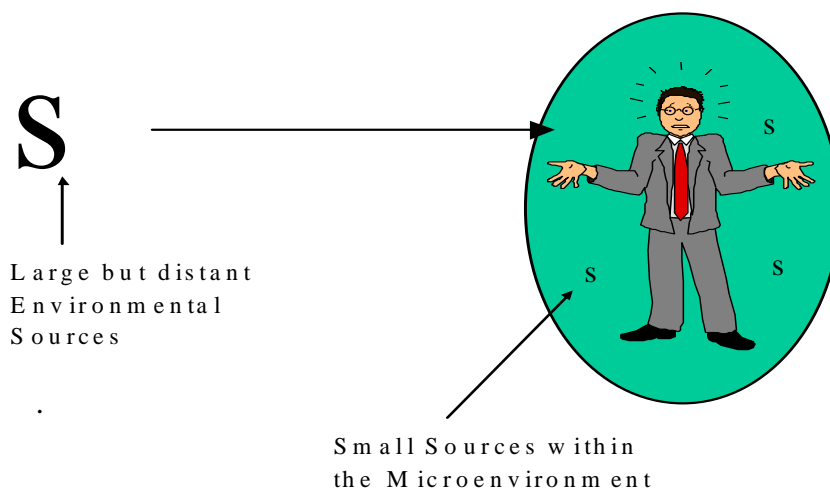
where C(t) is the functional relationship of concentration with time for the interval t<sub>1</sub> through t<sub>2</sub>. E has the units of (concentration)×(time).

Human exposure occurs in a conceptual volume known as the *microenvironment*. The microenvironment entails an immediately surrounding compartment or space in which the person resides and is exposed. Another way of thinking about this compartment is to imagine a volume immediately surrounding a person where the sources and the subsequent contaminant concentrations and exposures per unit time are either relatively constant or at least potentially well characterized. It is also important and useful to think of and classify the sources as either occurring within the microenvironment (the near-field) or originating outside and coming into the microenvironment from an external or

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far-field source. Indeed, this construct could be extended somewhat to include the near-field in the immediate surroundings of the individual and a second, larger, zone microenvironment in which the person spends a significant amount of time. This could be a passenger compartment of a transportation vehicle, a room in a building or the entire building. The third zone would be the far field, which, in this construct, would represent the outdoor environment.

The cartoon below attempts to illustrate the concept of the microenvironment in which a person's exposure is impacted by relatively large distant (far-field) sources and smaller sources that originate in the individual's near-field.



The distant and near sources are ultimately moderated by controlling factors such as dispersion/dilution and physical/chemical loss that impact the exposure to the person in the microenvironment. It is also interesting to note that large but distant sources represent “environmental” exposure that can affect humans and nonhuman targets while near-field sources primarily affect the human(s) in that particular microenvironment. Indeed, given two levels of microenvironment as discussed above, the emissions in the nearest field will have an amplified impact on the person(s) in that environment. The user of a consumer product may get an enhanced exposure owing to the personal cloud, relative to the exposure of another occupant of the indoor space. For an indoor emission not associated with human activity, all occupants are exposed, at levels that *a priori* don't favor one person over another.

We spend most of our time indoors and airborne concentrations of (and human exposure to) common chemical toxicants are typically much higher than those occurring outdoors. This fact and a number of studies<sup>9</sup> argue for the predominance of near-field sources in

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human inhalation exposure. Also, because of our major residence is indoors we also experience the majority of our dermal exposure from sources in this environment.

Human health risk assessment is currently impaired by a lack of knowledge (*i.e.*, uncertainty born of ignorance) around indoor near-field inhalation and dermal source identification and characterization in both the occupational and non-occupational settings. Indeed, for Semi-volatile Organic Compounds (SVOCs) that partition strongly into dust, *e.g.* phthalates, the dominant pathway for human intake is not clearly either inhalation or dermal and may be ingestion. The risk assessor who uses models is often forced to render a dramatic over-estimation of exposure because absent having better information he or she is driven to use worst-case defaults. The result is often un-trusted risk management options triggered by these unrealistically (but necessarily) high estimates of exposure and risk.

In 1993, the Chemical Manufacturers Association - Exposure Assessment Task Group commissioned a study of the state-of-the-science for indoor air modeling which was completed by Dr. Harry Rector of GEOMET Corp.<sup>10</sup>. This work shows rather convincingly that indoor source characterization presents the single greatest opportunity for uncertainty reduction in the model-estimation of human exposure.

About the time of the GEOMET report there was also an announcement by the US Environmental Protection Agency (EPA), which listed "Source Characterization (Chemical)" as the number one priority for resource allocation.<sup>11</sup> This work was done in response to a recommendation from the Science Advisory Board of the US Environmental Protection Agency. The EPA's Indoor Air Engineering Research Program participants consulted with a panel of key researchers and planners within government, industry, and academia to help identify priority program areas for indoor air engineering research. Eight areas were identified and prioritized (including "other"). "Indoor Source Characterization" was ranked at the top.

In another sector of the EPA, source emissions were judged as being the most important exposure factor data gap and research need identified in a July 1995 Workshop to help finalize the Exposure Factors Handbook.<sup>12</sup>

The above priority for indoor source research was reaffirmed in the MICROENVIRONMENTAL MODELING SESSION, Chemical Manufacturers Association (CMA) Exposure Workshop, CIIT, Research Triangle Park, NC, May 18 and 19, 1999 and a subsequent American Chemical Council (ACC *nee* CMA)-sponsored study and "White Paper on Microenvironmental Modeling" research done by Mr. Michael Koontz of GEOMET, Inc for the CMA.<sup>13</sup>

Given the above, one might question why a significant level of research and progress in this specific area has not been forthcoming in the last decade. A primary reason for this current state is that until recently a risk-based approach to evaluate common existing chemicals present in our general environment has not been (and because of a lack of basic hazard information for many chemicals could not be<sup>14</sup>) mandated or applied within



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any public or private scheme. Absent such a scheme there was no sufficiently compelling reason to do the research.

Change now appears to be at hand as the European Union has initiated REACH (Registration, Evaluation, and Authorization of Chemicals) as a basic regulatory program that promises to require both hazard and exposure data in an integrated risk-based evaluation as a fundamental part of European Union’s chemical regulatory system. A workshop specifically dedicated to research needs for exposure sources happened on June 20-21, 2005 in Intra (Italy) under the auspices of the EC Joint Research Centre (JRC) Institute for Health and Consumer Protection (IHCP). Participants are listed in the main body of the proceedings report.

The research proposed during this workshop is to be specifically designed to address the emerging regulatory needs by providing critical modeling tools as a basic prerequisite for the widespread and accurate evaluation of human exposure to existing chemicals.

This research should focus to the extent possible on model algorithms that have the broadest general utility; that is, those that use tolerably simple, easily measured or reasonably available (or readily developed) predictor variable data as input. This research should provide, evaluate and validate specific model algorithms to render a reasonable and appropriately accurate model-predicted time-course of emission and dynamic behavior profiles along with their transport and fate for relevant chemical compound classes.

Thus, this workshop will set the plan for research designed to develop (propose, evaluate and refine with experimental data) a library of quantitative models of indoor sources, dynamic behaviors, and resulting concentrations of airborne chemicals. Once developed, these models are anticipated to become the most useful and active tools of scientific exposure/risk assessment of chemicals in general commerce. They will be used as parts of other models that will estimate the breathing zone concentrations and exposure to chemicals via inhalation of ambient indoor air and possibly dermal exposure from contact with surfaces indoors.

Another critical area of exposure research briefly addressed in this workshop will be in the area of chemical transport and fate. That is, once the source is characterized the next step in the process is to describe the general time course of movement, location and concentration within the indoor environment.

The scope of the source categories to be addressed in this workshop has been left purposely broad and applicable to those sources coming from potentially regulated (under REACH) existing and new chemicals being used in commerce to which humans may be exposed. This could include both residential and occupational exposure.

A significant amount of regulation and risk assessment science already exists for many far-field substances; as such, the work considered herein will concentrate on the near-

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field modeling of any source causing human exposure to any of these substances and their progeny.

### **Workshop Framework**

The focus of the workshop is on the modeling of sources of airborne and dislodge-able surface concentrations of chemicals that could subsequently impact human exposure. It is further suggested that a greater emphasis be placed on the development of more mechanistic and less empirical models, which tend to dominate the field today. Mechanistic models provide a better basic understanding of the effects of material composition and environmental factors on emissions, and are also more transportable to conditions other than those for which model parameters were derived. As such, we believe that the science will be better served and advanced by concentrating on understanding basic causes.

The anticipated primary elements of the workshop are presented below beginning with consensus taxonomy of indoor source types, followed by brief description of the current state-of-the-science for the description of sources, transport and fate. Finally, a gap analysis is provided which could afford the impetus for the subsequent outline of a multi-year research plan.

As a center point for organization, a systems approach will be considered to develop a library of indoor source and indoor fate and transport models to be used in predictive exposure assessment. The operational method of doing this would be to:

- Consider the system of interest (indoor microenvironment)
- Develop an illustrated (and detailed) conceptual framework for the modeling (a figure showing all potential chemical sources and losses to the system, consideration of temporal and spatial characteristics, representing the most general and most complex model – though not necessarily something we would ever develop) (See Attachment A)
- Classify sources (See Below)
- Develop potential suite of simplified conceptual models that could be used for each type of source (assuming steady state, assuming uniform distribution of contaminant, etc.)
- Conduct theoretical “experiments” to identify/verify model requirements based on characteristics of sources/emissions, properties of compounds, characteristics of the microenvironment (what are the important temporal scales, spatial scales, rate determining processes, when can an intermittent source be treated as a continuous source, etc.)
- Identify data required to apply models for predictive exposure assessment, design experiments

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- Provide criteria for, and guidance on, model selection based on exposure scenario (e.g., properties of sources/emissions, characteristics of the microenvironment, dimensionless parameters that incorporate consideration of these, etc.)

It is anticipated that a great deal of this information is intuitive to many of the modelers that have been working in this area; however, by systematically running through this more formalized approach, the results can be better communicated. Indeed, because the scheme includes multiple sources and intermittent emissions, the number of factors goes well beyond what can be easily accommodated by intuition. Thus, by doing these theoretical experiments we should be able to optimize the laboratory work.

Identifying the universe of sources of human exposure is important; however, we should also be aware of the need to maintain a perspective on the broad issue regarding the task at hand. Indeed, every component, every product, and every process in the indoor environment is a potential source of chemical exposure whose importance can vary continuously from trivial to severe. Clearly, developing models for the unimportant sources should not be a priority; thus, we need tools for sorting sources according to their importance. This suggests that the overall modeling process should be viewed hierarchically. Simple, crude assessment tools (models) should be available to quickly sort sources according to importance, while more detailed tools should be available to apply to the sources (and pollutants) that deserve greater attention.

A primary topics to be considered in the context of a systems framework is:

**A CONSENSUS CLASSIFICATION OF CRITICAL INDOOR SOURCE-TYPES AND SPECIFIC SOURCES WITHIN EACH OF THOSE TYPES.**

It is suggested that the first classification of sources should be along the lines of primary versus secondary origin. Secondary sources refer to emissions that occur following the formation, usually by chemical reaction and often by oxidation or hydrolysis reactions, of new products that were not in the initial source. Secondary sources are very relevant for most building materials such as paint, wood products, carpet, linoleum, and electronic products. Good examples of this are the formation of carbonyls from ozone-initiated chemistry on and in carpet, wood and paper products. Another example comes from the hot zones of many electronic devices that can lead to secondary emissions through accelerated oxidation processes in devices such as computers. Wet sources can also be secondary; for example, laundry and dishwasher detergents that contain sodium hypochlorite can lead to the formation of large amounts of chloroform via reactions with organic soiling of clothing and foodstuffs on plates and utensils<sup>15,16</sup>.

After division into primary and secondary sources, a number of schemes could be used to classify sources. For example, two primary dichotomous features describing sources are: WET vs DRY and SHORT-TERM (minutes to hours) vs LONG-TERM (days to months) duration. As a general observation these facets are somewhat collinear; that is, WET sources are generally short term while DRY sources typically represent long-term

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emissions. The sources below are first sorted by WET and DRY with additional bins added to include other generally recognized classes of sources. For example, this scheme uses the general source characteristic as to whether the material exists (and is emitted) as a VAPOR or as a PARTICULATE (either as a neat material or in association with other ambient particulate such as dust).

Given that our purpose is to model exposure, the categories or BINS below were chosen with the idea that sources within any bin could be potentially described by a single model or reasonably simple variations on that model.

VAPOR from DRY SOURCES:

Chemicals contained within, diffusing and emitting from solids:

- Dried paint and underlying substrate
- Dry or dried pesticide (*e.g.*, moth crystals)
- Treated wood
- Plastic films, surfaces or cabinets
- Engineered Wood Products (Oriented strand board, composition board, plywood)
- Insulation
- Polyurethane foam
- Polystyrene foam
- Carpet and carpet backing
- Sheetrock
- Other flooring materials (linoleum, vinyl composite tile, etc.)
- Paper products (*e.g.*, formaldehyde from printed paper, off gassing from cardboard and its adhesives)
- Electronic products/components (circuitry within appliances, computers, monitors, etc.)
- [other furnishing materials: fabrics, wall coverings]

VAPOR from WET SOURCES :

Chemicals emitting from wet sources:

[Note: Many of these have both storage-phase and use-phase emissions; these phases would likely be modeled differently.]

- Architectural Coatings (paint, varnish)
- Building material (caulks and adhesives)
- Cleaning products (wiped, brushed or mopped on; sprayed on)
- Wet Pesticides
- Personal Care or Cosmetic Products

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Laundry products  
Solvent Uses  
Air fresheners  
Fugitive emissions from liquid home heating fuel and gasoline in attached garages.  
Contaminated Potable Water (showering/bathing/laundrying)  
Basement wet or damp with contaminated water

Subset:  
Material Transfer (*i.e.*, tank filling)

NEAT VAPOR SOURCES:

Vapor intrusion from soil (far-field)  
Vapor intrusion from ambient air (far-field)  
Fugitive emissions from gas home heating fuel (near-field)

SOURCES of PARTICULATE Matter:

Sprayed pesticides (Aerosol and VOC)  
Cleaning products (Aerosol and VOC)  
Sprayed personal care products (Aerosol and VOC)  
Welding (fumes)  
Handling “dusty” powder (aerosol)  
Personal care (sprayed) aerosol  
Particles brought into the residence and re-entrained (e.g., pesticides tracked into house from lawn and garden) (aerosol)  
House dust containing SVOCs (aerosol)  
Particulate intrusion from ambient air (aerosol) (far-field)  
Particulate emissions from spray humidifiers  
Particles re-suspended (e.g. from vacuuming or other processes)

COMBUSTION SOURCES (PARTICULATE and VAPOR):

Cooking [Note: cooking is an exposure source both because of the combustion of the fuel (when present) and also because of the heating of the food.]  
Space Heaters  
Candles, incense and other combusted aromatherapy products  
Self-cleaning oven emissions  
Fugitive emissions from home heating  
Fugitive emissions from fireplaces  
Incense  
Cigarettes and environmental tobacco smoke ETS? (note: May be more important than anything else on this list but may not be regulated by REACH)

INDOOR CHEMISTRY

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Reactions taking place in the air  
Reactions taking place in water (e.g. dishwashers and laundry)  
Reactions taking place within the material  
Reactions taking place at the material/air interface

Sources of Reactive Gases

- Ozone generators and “ionizers”
- Penetration of polluted outdoor air
- Combustion

## REVIEW AND DESCRIPTION OF THE CURRENT STATE-OF-THE SCIENCE FOR MODELS OF SOURCE TYPES

Note: Zhishi Guo compiled and reviewed 52 indoor source emission models and 48 parameter estimation methods. The manuscript, in two parts is titled “Review of indoor emission source models. Part 1. “Overview” and “Review of indoor emission source emission models” Part 2. “Parameter estimation”, *Environmental Pollution* 120 (2002) 533-549, 551-564.<sup>17</sup>

Dr. Guo’s conclusion in this work is consistent with the anticipated consensus of workshop participants; *viz.*, for models to be useful, there must be methods to determine (and verify) parameters of these relationships.

Also note that Morrison *et al*<sup>18</sup> describe a method to measure the mass transfer coefficient. This method might be used to verify model-calculated values of the mass transfer coefficient. The method uses the deposition velocity sensor (DEVS) which continuously evaluates the evaporation rate of octadecane from the surface of a microbalance. This is a “real-time” measurement of the transport-limited deposition velocity (also the mass transfer coefficient) for octadecane. Octadecane evaporates from the microbalance at a rate dependent on the transport conditions of the room (e.g. higher indoor air velocities or more intense mixing/turbulence results in higher evaporation rates). The mass transfer coefficient  $K_t$  (cm/s) = the flux from the surface ( $\text{g}/\text{cm}^2 \text{ s}$ ) divided by the vapor concentration ( $\text{g}/\text{cm}^3$ ) near the surface. The vapor concentration is derived from the vapor pressure.

### ALGORITHMS: VAPOR from DRY SOURCES:

Basic models and algorithms for the emission of VOCs from dry materials indoors have been developed<sup>19,20,21,22</sup>. This includes a single-layer model that has been applied to carpets and vinyl flooring, and also a double-layer model. As will be discussed later,

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these models include the ability of the material to act as both a source and a sink. The single-layer model was initially developed for a situation where the external gas-phase mass transfer was relatively unimportant, but more recently, researchers have extended the basic model to include the external gas-phase resistance<sup>23, 24</sup>. These workers examined the conditions for which the external gas-phase resistance becomes important. More recently, the overall approach has been shown to be applicable to porous materials as well, provided the additional material-phase model parameters are known<sup>25</sup>.

For the models to be more useful, it is necessary to develop methods to estimate the model parameters of diffusion and/or mass-transfer coefficients. These include the initial material-phase concentration, material/air partition coefficients, material-phase diffusion coefficients, as well as the external gas-phase convective mass-transfer coefficients. The techniques to estimate diffusion coefficients can be grouped into three broad categories: a non-steady analysis method, a steady-state analysis method, and a porosity-based method. The two-chamber system with no flow by Bodalal *et al*<sup>26</sup> and the flow-through microbalance system by Cox *et al*<sup>27</sup> as well as Zhao *et al*<sup>28</sup> belong to the first category. The second category includes the cup method adopted by Kirchner *et al*.<sup>29</sup> and the twin chamber methods used by Meininghaus *et al*<sup>30,31</sup>. The cup method is not desirable if used with pure solvent because under these high-concentration conditions, the diffusion coefficient is expected to become dependent on concentration. For most of the VOCs, the material-phase concentrations are relatively low and the diffusion and partition coefficients have been found to be independent on concentration<sup>32</sup>. Essentially all the models developed thus far assume that these constants are independent of concentration. Generally, the two-chamber methods entail more experimental effort, but are more suitable for the highly volatile compounds. The microbalance method is simpler, but works better for the somewhat lower volatility compounds because the absorbed mass is greater and more easily measured.

Blondeau *et al*<sup>33</sup> used mercury intrusion porosimetry tests to obtain diffusion coefficients. It should be noted that the estimated coefficients varied in a wide range as reported by Haghighat *et al*<sup>34</sup>. A method to measure the initial material-phase concentration in vinyl flooring has also been developed by Cox *et al*<sup>35</sup>. Because this is the most important parameter in these VOC emission models, further work to develop improved techniques to measure the initial concentration of volatiles in various materials would be of real value. It is most convenient if the initial concentration is uniform, but it is also possible to predict emissions for a non-uniform initial concentration<sup>36</sup>, provided it is known. Interestingly, Xu and Zhang<sup>37</sup> showed that the longer-term emission rate is not all that strongly dependent on the shape of the non-uniform initial concentration if the material-phase diffusion rate is fairly high.

There has been very little effort to develop methods for determining mass-transfer coefficients that are used to describe mass-transfer resistances at the material-air interface and in the boundary layer above it. This is partly because there has been a large amount of research focused on heat transfer research in a boundary layer. Through the analogy between heat and mass transfer, the theories developed for thermal boundary layer

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behavior are commonly used for the concentration boundary layer. The mass-transfer coefficient used in Huang and Haghghat<sup>38</sup> and Deng and Kim<sup>39</sup> was based on the relationship between dimensionless numbers of Sherwood number, Reynolds number, and Schmidt number, which were developed originally from heat-transfer research. These methods appear to be fairly well accepted for predicting mass-transfer coefficients, although there is probably a need to validate them for a wider range of indoor environmental conditions.

Work exists on external mass-transfer coefficients, which derives from studies of the complementary problem of predicting the rates of surface reaction/uptake from indoor air. The mass-transport-limited mass-transfer coefficient from those studies would apply both for the source and the sink associated mass transport problem. Nazaroff and Cass<sup>40</sup> framed the broad issue. Morrison and Nazaroff<sup>41</sup> present an analysis for turbulent mass-transport through a boundary layer adjacent to an indoor surface, utilizing studies of boundary-layer eddy diffusivity from direct numerical simulation of turbulent transport.

#### ALGORITHMS : VAPOR from WET SOURCES:

Some useful models have been developed for specific wet/vapor sources such as paint. The Wall Paint Exposure Model (WPEM)<sup>42</sup> developed by the US Environmental Protection Agency uses simple input (vapor pressure, weight percent and MW of chemical of interest in the paint) to predict the time course of emission and residential room concentration for that chemical species.

Another general emission model accounting for internal diffusion and surface evaporation was developed for architectural coatings. A companion experimental method was developed to determine both the diffusion and evaporation (mass-transfer) coefficient. The results indicate that the diffusion coefficient is inversely proportional to molecular weight, while the evaporation coefficient is proportional to vapor pressure of VOCs as reported by Won and Shaw<sup>43</sup>. This supports that a general emission model can be utilized based on simple inputs of chemical properties.

More general models have been forwarded by the US EPA and others for the evaporation rate of pure substances<sup>44,45</sup> and mixtures<sup>46,47</sup> over vaporizing pools, from contaminated water<sup>48,49,50,51,52</sup> or from solvent-based indoor coating material.<sup>53</sup>

General models are also available for emissions of VOCs from contaminated water during general use within the residence (e.g., showering, bathing, laundering.<sup>54,55,56,57,58,59,60,61,62,63</sup>

#### ALGORITHMS: NEAT VAPOR SOURCES (occurring within the near field or penetrating into the microenvironment):

Work has been done on the prediction of indoor contaminant levels from vapor intrusion originating with VOC contaminated soil or groundwater. A model developed by Johnson



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and Ettinger<sup>64,65</sup> has emerged as a standard tool for screening-level assessments. Only limited experimental evidence is available for validating such models.<sup>66,67</sup> The problem of radon migration from soil into buildings is closely related, and significant work on the development of models for predicting soil-gas intrusion has been conducted to better characterize soil as a source of indoor radon.<sup>68,69,70,71</sup>

Workers have quantified the level of vapor penetration indoors from ambient concentrations outdoors for standard VOCs (further text, references: ??)

#### SOURCES of PARTICULATE MATTER:

Ongoing work and models are being developed for personal exposure to aerosol spray (references: RIVM)

Outdoor particles can penetrate into indoor air along with air that enters a building for ventilation. Building ventilation is conventionally divided into three modes. Natural ventilation refers to indoor-outdoor air exchange induced by flow through open windows or other designed openings in the building envelope. Infiltration refers to uncontrolled flow of air through leaks. Mechanical ventilation refers to airflow induced by fans. Particle penetration from outdoors to indoors varies significantly among these ventilation modes. For natural ventilation, particles are expected to penetrate without loss. For infiltration, particles may be lost on the surfaces of building cracks owing to deposition mechanisms such as gravitational settling and Brownian diffusion. A modeling approach has been developed to predict the degree of penetration as a function of leakage path characteristics, airflow characteristics, and particle size<sup>72</sup>. In the case of mechanical ventilation, particles in the supply air may be attenuated either by removal on a particle filter<sup>73</sup>, by deposition on heat-exchanger coils<sup>74</sup>, and by deposition on the surfaces of ventilation ducts<sup>75</sup>. An integrated approach to predicting indoor particles of outdoor origin has been presented by Riley *et al.*<sup>76</sup>.

#### COMBUSTION SOURCES (PARTICULATE and VAPOR)

Dr. Guo and colleagues have researched and reported on emissions from candles and incense<sup>77,78,79,80,81</sup>.

Work has also been done on the types and rates of emissions from space heaters indoors.<sup>82,83,84</sup>

Emissions from cigarettes and other tobacco products have also been extensively studied, including both particulate matter (Klepeis *et al.*, 2003)<sup>85</sup> and vapors (Singer *et al.*)<sup>86,87</sup>.

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## ALGORITHMS: SINKS

Once emitted to the air the fate of a chemical vapor is limited to the following possibilities:

1. Advection and removal from the microenvironment around the person by the normal dilution ventilation provided by mixing air changes.
2. Sorption onto a fixed surface within the microenvironment.
3. Chemical transformation either while airborne or after deposition within the microenvironment.
4. Removal by means of an active air-cleaning device.
5. Uptake by an airborne particle.

The non-ventilatory loss from sorptive uptake on fixed surfaces is the so-called sink. If the material ultimately re-volatilizes from the surface after a period of time then the effect of the sink is to lower the peak concentration but to prolong the total time of emission and potential exposure. If the material degrades or chemically transforms on the surface or remains indefinitely bound to the surface then the total inhalation exposure to the chemical species is reduced. The higher the molecular weight and the lower the vapor pressure of a chemical the more prone to sorption to sinks it will be. Other chemical properties of compounds can influence the degree to which they are affected by sinks, including polarity and acid-base attributes.

EPA has developed a theoretical framework for indoor sinks based upon the Langmuir adsorption isotherm equation. This equation assumes that a surface can sorb a maximum of one monolayer of molecules. The surface is assumed to be homogeneous with all sites mutually independent and identical<sup>88</sup>. Small chamber methods were devised to determine sorption and desorption rate constants for ethylbenzene and tetrachloroethylene and several indoor surfaces<sup>89</sup>. Chamber study results suggested that the Langmuir model was appropriate for relatively flat and smooth surfaces such as wallboard and ceiling tile, but not appropriate for more complex surfaces such as carpet and pillows<sup>90</sup>. The modeling approach was evaluated by comparing observed concentrations and “Langmuir sink” model predictions for wood stain applied to a floor in a research test house<sup>91</sup>. The model failed to accurately predict emissions for time periods beyond 48 hours.

The US EPA (Dr. Guo) is currently evaluating sink models and expects to report findings either late in 2005 or early 2006.

The sink effects were also investigated in small-scale chamber tests for the interactions between various VOCs and building materials. The most common modeling approach was to use a linear sorption and desorption model. Correlation equations of the sorption and desorption coefficient with chemical properties such as vapor pressure were also derived as reported by An *et al.*<sup>92</sup>, Won *et al.*<sup>93,94</sup> and Singer *et al.*<sup>95</sup>

A validation study of the linear sink model was attempted with two types of scale-up experiments. From the large-scale laboratory experiment, relatively good agreement was

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observed between measurements and predictions by the sink model. In contrast, the level of sorption in the field test was observed to be at least 9 times greater than was predicted by the model as reported by Won *et al*<sup>96</sup>

The sink effect with chemical degradation within the sink has been incorporated into a model developed to predict indoor air concentrations from the use of treated wood indoors.<sup>97</sup>

The work of Little *et al* naturally incorporates the “sink effect” for dry surfaces as part of the above modeling for emissions from these dry materials, as described by Zhao *et al*<sup>98</sup> and Kumar and Little<sup>99</sup>.

## TRANSPORT AND FATE MODELS

Historically, the well-mixed box representation has dominated as the indoor transport model of choice. In this construct transport is conveniently handled by assuming that any molecule released into a microenvironment (*e.g.*, a residential room) will be instantaneously mixed within the volume of the room. In this model the average concentration is considered to be homogeneous throughout the volume of the room. That is, there are no gradients of concentration between the source and any point within the microenvironment.

Given a steady source, the well-mixed box model renders the following simple relationship for the average airborne concentration of a non reactive/non sorbing species with a source rate in mass/time and ventilation rate in volume/time:

$$Concentration = \frac{Source\_Rate}{Ventilation\_Rate}$$

These assumptions are reasonably valid for scenarios with large diffuse or multiple sources emitting to relatively small microenvironments with rapidly moving and well-mixed air. This approach may also work reasonably well for predicting time-averaged exposure concentrations over extended time intervals. However, the assumptions are not valid for predicting transient exposures to emissions from point sources proximate to the exposed individual.

Clearly, point sources in real rooms have strong gradients of concentration from the source to distal points within the room. A technical construct was used to successfully describe this situation by Dr. John Franke in his 1985 PhD Thesis.<sup>100</sup> Dr. Franke used a diffusion model originally developed for heat flow<sup>101</sup> and applied to indoor air modeling<sup>102,103</sup>. The equation for a continuous point source is presented in the references to predict concentration at any distance *r* and time *t*.

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$$C = \frac{G}{4\pi(D)(r)} \left[ 1 - \operatorname{erf} \left( \frac{r}{\sqrt{4(t)(D)}} \right) \right]$$

where:

- C = concentration, mass/volume, mg/m<sup>3</sup>
- erf = the error function (dimensionless)
- G = steady-state emission rate, mass/time, mg/hr
- r = the distance from the source to the person's breathing zone, m
- D = the eddy diffusivity, area/time, m<sup>2</sup>/hr
- t = elapsed time, hr

In this model, contaminants emitting from a point source are dispersed not by their molecular diffusion but rather by the natural air currents existent in every interior space. Indeed, molecular diffusion is miniscule compared to the diffusion caused by turbulent eddy air currents. These natural indoor air movements or eddies determine the size of D (the eddy diffusion coefficient) which is entirely dependent on the amount of turbulent kinetic energy of the air and independent of any properties of the transported chemical species.

Other attempts<sup>104, 105, 106</sup> have been made to describe the reality of high concentration near a source and lower concentrations at points away from the source. The two-zone or “near-field/far field” model conceptualizes a room as containing two contiguous zone-a “near field” zone surrounding the emission source, and a “far field” zone comprising the rest of the room. The air within each zone is treated as being perfectly mixed, but with limited air exchange between the two zones. This model scenario means that the contaminant concentration is uniform throughout the near field zone, and is uniform throughout the far field zone, and in general the near field concentration is higher than the far field concentration.

The general mass balance equations for the Near Field/Far Field Model and a constant emission rate are as follows:

	Change in Mass	= Mass Gain	-	Mass Loss
Near Field:	$V_N dC_{NF} =$	$[G dt + \beta C_{FF} dt]$	-	$\beta C_{NF} dt$
Far Field:	$V_F dC_{FF} =$	$\beta C_{NF} dt$	-	$\beta C_{FF} dt + Q C_{FF} dt]$

- where:
- $C_{NF}$  = the near field concentration (mg/m<sup>3</sup>)
  - $C_{FF}$  = the far field concentration (mg/m<sup>3</sup>)
  - $V_{NF}$  = the near field volume (m<sup>3</sup>)
  - $V_{FF}$  = the far field volume (m<sup>3</sup>)
  - G = constant mass emission rate (mg/min)
  - $\beta$  = air flow rate (m<sup>3</sup>/min) between the near and far fields

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Q = room supply/exhaust air rate (m<sup>3</sup>/min)  
dt = an infinitesimal time interval

The preliminary (and subsequent) opinions of the workshop participants were that fate and transport models are very important but that there is probably no one model that will work for all cases. What is needed is a good tool kit, rather than one good tool.

Fate and transport models for predicting exposures in indoor environments need to account for pollutant-related characteristics, building-related characteristics, airflow characteristics, and (probably) human subject characteristics. The models also need to account for the important dynamic processes that can affect pollutant levels in the indoor environment. These include emissions, transport, transformation, and removal.

The workshop participants acknowledged the substantive richness of this aspect of indoor air exposure modeling but given the limitations of time chose to remain focused on sources. One of the workshop participants (Nazaroff) has recently published work<sup>107</sup> that substantially summarizes the transport-and-fate issues for indoor particulate matter which provides help in framing the subject.

#### **GAP ANALYSIS FOR THE ABOVE**

(How inaccurate are the existing models or how important is it to close any particular gap? This includes identification of “best” currently available models and a research path forward to close the gaps).

Estimating or discussing how accurate the existing models are in predicting real world exposures is somewhat problematic because very few have undergone any sort of evaluation under real world conditions. Those that have were typically specific-purpose models such as the Wall Paint Exposure Model and were not evaluated in the context of a general model of emissions. McCready and Fontaine<sup>108</sup> did a literature review on experimental studies and modeling the evaporation of surface coatings. Some details of their work and its references are included in Attachment B below. Indeed, this type of work provides us with excellent insight into the models and their possibilities but the specific conditions tested in these studies invariably represent a very small portion of scenarios of interest.

Given this decided lack of model development and data, a relatively large task is presented for a research path forward. It is suggested that a reasonably comprehensive subset of the above taxonomy be selected for specific laboratory analysis. For example specific laboratory test devised for selected analytes from:

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VAPOR from DRY SOURCES:

Chemicals contained within, diffusing and emitting from solids:

- Dried paint
- Dry or dried pesticide (e.g., moth crystals)
- Treated wood
- Plastic films, surfaces or cabinets
- Oriented strand board
- Composition board
- Plywood
- Insulation
- Carpet and carpet backing
- Electronic products/components (circuitry within appliances, computers, monitors, etc.)

VAPOR from WET SOURCES :

Chemicals emitting from wet sources:

- Coatings (paint, varnish)
- Cleaning products (wiped, brushed or mopped on)
- Wet Pesticides
- Personal Care or Cosmetic Products
- Wet Laundry products
- Solvent Uses
- Airfreshners

In all cases a specific model (hypotheses) as determined by a consensus of workshop participants would be proposed. The critical predictor variables would be identified and characterized. In all likelihood this may mean an experimental run to parameterize the model. Next, experimental emission data for a representative listing of substrates would be conducted under various realistic conditions and the results matched against the model prediction.

Enough representative sampling of each type of substrate (and analyte type within each substrate) will be carried out so that a level of variation within each type of substrate can be quantified. This will be further evaluated as a function of substrate age or other potentially critical factors.

NOTE: Many factors can affect the variability in experimental and modeling outcomes of indoor source emissions. In addition to inherent variability in specimens (specimen variability), external factors such as air velocity and

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temperature (environmental variability) can play a role in inducing variability in emission data.

An excellent study of the extent of specimen variability can be found in a case study with a series of samples of oriented strand board, which were collected from the same retail outlet on three separate occasions (same manufacturer, 3 different production dates), from separate panels produced on the same production date, and from multiple locations within the same panel. Variability in the VOC emissions from these samples was found to exceed the analytical uncertainty by an order of magnitude in some cases as reported by Magee *et al*<sup>109</sup>. Environmental factors such as air velocity and air temperature can also affect emissions from wet sources (Won *et al*<sup>110</sup>, 2004; Won and Shaw<sup>111</sup>, while emissions from dry materials can be affected by air temperature (Cain *et al*<sup>112</sup> and material temperature (Won *et al*<sup>113</sup>.

This portion of the research plan should be purposely sized to fill a full-time research effort relative to the research allocated to it. That is, the number and types of substrates will initially be determined within this resource allocation and schedule. This schedule will be subject to change depending on what is learned during the testing.

It is anticipated that the above program will proceed smoothly for the JRC Laboratory characterization of emission rates of volatile organic compounds VOCs from the various substrates. It is also projected that the theoretical basis for modeling emissions of SVOCs will require significantly more theoretical and conceptual work in the university laboratory of Dr. Little. Once these SVOC models are developed they will be advised for integration into the JRC Laboratory Model Development effort as described above.

A final active and immediate research program for consideration by the JRC Laboratory includes parameterization of some of the transport and fate models discussed in the workshop. This would include the possibility of some work developing the Eddy Diffusivity or the Nicas two-box model. Indeed, the actual measurement of D (diffusivity coefficient) is somewhat involved technically and, as a result, only a handful of values for typical indoor environments currently exist. To make matters worse these measurements represent a fairly broad range of values, which means having a large variation in any concentrations predicted by this model.

It is intuitively obvious that eddy diffusivity, two-box and other indoor transport models will be driven by or correlated to other relatively easily measured variables associated with indoor room air. Such variables as:

- Average air velocity
- Air exchange rate
- Windows open or closed
- Outside versus Inside Temperature
- Outside wind speed
- Number of persons per square meter of room area

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Number of electrical devices (e.g. computers) per square meter

A comprehensive research testing program could be formulated by technical experts to be executed first in the INDOORTRON laboratory testing facility at the EC Joint Research Centre and later in real rooms could provide a library or algorithm(s) to predict D and other critical parameters in the various models under various room conditions which would be invaluable to anyone developing and using these currently under-used models.

Plans for follow-up including a publication of this workshop’s proceedings and plans for the next workshop on this critical topic or identified subtopics (e.g., predicating particle source terms from cutting, sanding or handling).

It is anticipated that this active JRC laboratory effort designed to develop VOC and SVOC emission models for the critical substrates as listed above will begin yielding useful results within 6 months. It is suggested that a brief report be written by the Principle Investigator every 3 months outlining the progress and emerging issues from these efforts to be reviewed in a conference call by interested workshop attendees.

It is further suggested that additional source/fate modeling workshops be held at the JRC every 6-8 months on topics as discussed and identified at this workshop. Some current suggestions include:

Particulate Source Rate Modeling from Handling “Dusty” Material  
SVOC Modeling from Dry Substrates

As mentioned above, the plan is to complete this report and publish it as the workshop proceedings.

**WHAT ARE THE TOP PRIORITY SOURCE OR TRANSPORT MODELING RESEARCH ISSUES?**

This answer to this question is essentially unknowable *a priori* since it is somewhat like knowing the answer first so that one can then ask the correct question.

Some thoughts for discussion within the workshop include the fact that the most useful models are generally not overly complex. Indeed, it is anticipated that critical variables within larger models may be identified and experimentally characterized independently of other parameters within the larger model. Thus, simple models can be integrated into higher order models, i.e., source models provide input to IAQ models, which in turn will provide confident input to exposure models. Thus the desire is to focus on critical source components.



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In the US the focus has typically been on sources associated with pesticides, known carcinogens (e.g., PAH) and chlorinated hydrocarbons; that is, substances with a high level of biological activity and toxic potential.

Top or high priority might be ascribed by the participants during and as a result of the workshop discussion; however, as mentioned above its determination may be problematic given a lack of information on which to base such decisions. In the case of sources such decisions should naturally include those considered or judged to provide the highest level of personal exposure ((concentration)(time)) potential to substances with the highest level of toxicity.

### **STRATEGY FOR USING EXISTING SOURCE/TRANSPORT EXPOSURE MODELS AND EXISTING SCENARIOS**

In many scenarios the current strategy is or should be obvious: use the best current (but generally unevaluated) models, bias the model inputs to overestimate exposure (to guard against the uncertainty of underestimation), document your actions and consider this to be the best that can be done with the limited information at hand.

The workshop participants will be asked to identify the best existing source/transport models and make specific recommendations for how they might be used absent (or before) the benefit derived from a research program to improve them. In some instances where we truly lack information, for example, in considering emission from handling a dusty solid the current default may have to be an estimated breathing zone concentration based on experience or empirical data rather than a model.

## **Attachment A**

### **Pre-Workshop Source Categories System of Sources in the MICROENVIRONMENT**

The premise for this workshop is that exposure to humans within microenvironments (ME) as described above is determined to a large extent by the sources of substances that occur within or enter into that specific volume. Of course, human exposure is ultimately moderated by individual factors associated with the substance, the activity, contact and biological delivery; however, our focus here is on the characterization of the sources within this system.

It is suggested that the general categories below could be helpful in the classification of sources of human exposure:

## CATEGORIES OF INDOOR SOURCES OF EXPOSURE

### 1. SOURCES INTO AIR (mass/time)

#### a. PRIMARY

- i. DIRECT INJECTION
  - Entrained (e.g., Sprayed liquid or particles)
  - Positive Displacement (e.g., Drum filling headspace injection)
- ii. WET
  - Evaporation (e.g., Spilled liquid)
- iii. DRY
  - Vaporization (e.g., Diffusion from solids)

#### b. SECONDARY (reaction products)

- i. WET
  - Reaction products vaporizing to air (e.g., O<sub>3</sub> oxidation of pinene)
- ii. DRY
  - Reaction products vaporizing to air (e.g., O<sub>3</sub> oxidation of VOCs in dried paint)
- iii. FORMING IN AIR

### 2. SOURCES of Dislodge able Material **ONTO SURFACES** (mass/((area)(time)))

#### c. PRIMARY

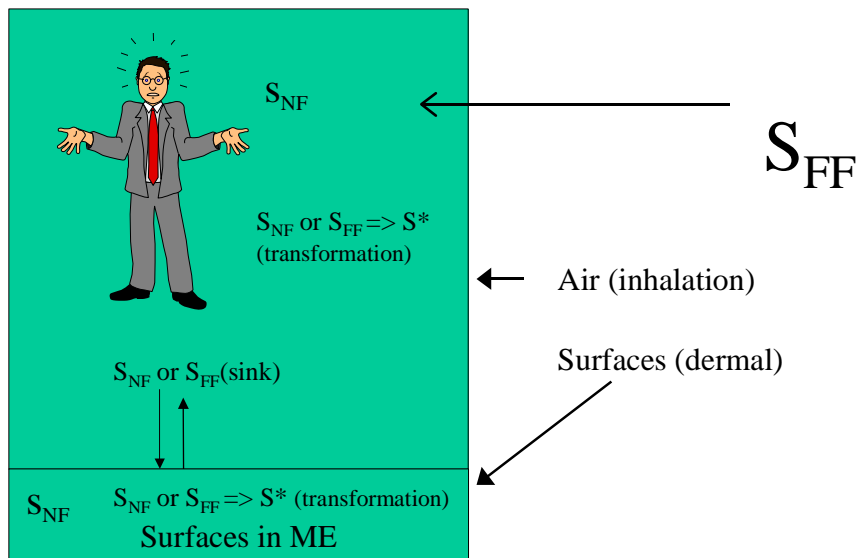
- i. WET
  - Direction application (e.g., cleaning material on surfaces)
- ii. DRY
  - Vaporization (e.g., diffusion from solids to surface for dislodge able residue)
  - Particle deposition (e.g. settle onto surfaces of neat particles)
- iii. VAPOR (air to surface deposition)
  - Air to surface deposition (e.g., sorbed species directly to surfaces)
  - VOC or SVOC-to-dust-to-surface

#### d. SECONDARY (reaction products)

- i. WET
  - Reaction products occurring in wet surfaces (e.g., O<sub>3</sub> oxidation of pinene)
- ii. DRY
  - Reaction products occurring on dry surfaces as dislodge able residue
- iii. VAPOR (air to surface deposition)
  - Airborne reaction products depositing on surfaces as dislodge able residue

The illustration below is a conceptual depiction of a microenvironment system of substance sources and is intended to show all potential sources of airborne intrusion (mass/time) into the air volume or dislodge able residue development (mass/((time)(area)) onto surfaces within the microenvironment.

## SYSTEM OF SOURCES INDOOR MICROENVIRONMENT (ME)



**S:** Any chemical source extant in the microenvironment either originating in it or penetrating from outside that results in inhalation or dermal exposure potential. This particular universe of sources under consideration does not include persistent and bioaccumulating substances that concentrate in food.

**S<sub>FF</sub>:** Sources that occurs outside of the microenvironment and then penetrate into it. Sometimes they are referred to as FARFIELD sources. Examples include general air pollution, contaminated ground water used for drinking and washing and soil gases that permeate into the home.

**S<sub>NF</sub>:** Sources that originate inside of the microenvironment. Sometimes they are referred to as NEARFIELD sources. Examples include:

- Sprayed products
- Fugitive cooking and heating gases and vapors
- Wet and dry paint emissions
- Solvent use
- Emission from building products

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- Emission from articles within the microenvironment
- Emission from appliances

$S \Rightarrow S^*$       Source that is chemically transforming within the microenvironment whether it originated within or penetrated into it. These sources could provide the chemical of interest (+) by converting a precursor to the chemical or take it away by reacting it (-).

S (sink):      Loss (-S) or gain (+S) of the chemical of interest to or from a sorptive surface.

For inhalation exposure assessment the following relationship describes the summation of all sources going into the **air** of the microenvironment.

$$Gdt = \sum_0^n S_{FF} dt + \sum_0^m S_{NF} dt + \sum_0^o S^* dt + \sum_0^p S(SINK) dt$$

The potential sources  $S_{FF}$  are from air penetrating into the microenvironment air.

The potential sources of  $S_{NF}$  into the microenvironment air come from:

- a primary vaporizing surface
- an emitting sink surface
- direct injection into the air.

The potential sources  $S^*$  are from chemical transformation in air or in sinks forming (+) the chemical species of interest or transforming (-) the chemical of interest to another species.

The potential sources  $S(SINKS)$  are from air-to-surface sorption (-) or surface-to-air (+) desorption of the chemical of interest in the ME system.

Note: Units of  $G$ ,  $S_{FF}$ ,  $S_{NF}$ ,  $S^*$  and  $S(SINK)$  all in **weight/time**. All sources considered to be going into the air are (+).

Please note that the same basic algorithm is applicable for dermal exposure (or hand to mouth oral exposure) from surfaces within the microenvironment except that the actual source terms are somewhat different. The terms in this case describe the summation of all sources going onto surfaces and available as dislodge able content.

The potential sources  $S_{FF}$  and  $S_{NF}$  come from the same places ( i.e., far and near field) however, instead of representing sources **to** the air they represent sources transferred to and from the **microenvironment surface from the air.**

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The potential sources  $S^*$  are from chemical transformation in the surface sinks forming (+) the chemical species of interest or transforming (-) the chemical of interest to another species.

The potential sources  $S(\text{SINKS})$  are from air-to-surface sorption (+) or surface-to-air (-) desorption of the chemical of interest in the ME system.

It is important to note that the units are different. The variables of  $G$ ,  $S_{\text{FF}}$ ,  $S_{\text{NF}}$ ,  $S^*$  and  $S(\text{SINK})$  for dermal (or hand to mouth oral) exposure potential from surfaces are all in  $\text{mass}/((\text{surface area})(\text{time}))$ . All sources considered to be going onto the surface are deemed to be (+).

The above conceptual system as described does not consider direct application to the skin via application of liquid or deposition from the air. This can be simply accommodated by adding an additional source terms to the above equation.

This conceptual model may or may not ever be translated into an actual holistic operational model for indoor sources. Its purpose is merely to provide a chart of the overall system and assist in pointing the way to the most relevant research tasks that will most accurately and effectively describe the exposure potential.

## **Attachment B**

### **McCready and Fontaine Survey of Wet Source Modeling**

McCready and Fontaine (2003) provided a literature review on experimental studies and modeling the evaporation of surface coatings. Table 1 summarizes a number of these indicating the study type, surface coating, chemical of concern, author, and date. Several types of surface coatings have been evaluated for a number of products; latex paint, alkyd paint, wood stain, polyurethane floor finish, and synthetic solvents using small chamber and room scale experiments. In some of these studies there were general models based on fundamental engineering principles; these models can be applied to a range of conditions. In contrast, curve fit models may perform better in some instances but are often limited to specific experimental data set and conditions.

**Table 1.** *A summary of some surface coating studies*

<b>Study Type</b>	<b>Surface Coating</b>	<b>Chemicals of Concern</b>	<b>Author</b>	<b>Date</b>
CE, L	Floor wax and caulking	Alkanes and Trimethylbenzene (TMB)	Tichenor <sup>114</sup>	1987
L	Survey on use	Miscellaneous solvents	Seedorff <i>et al</i> <sup>115</sup>	1990
CE, M	Wood stain, floor wax, polyurethane	Alkanes and Trimethylbenzene	Tichenor <sup>116</sup>	1991

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CE, M	Wood stain	Alkanes and TMB	Chang and Guo <sup>117</sup>	1992
CE, L, M	Waterborne paint	Taxanol, propanediol, and bitoxyethoxyethanol	Clausen <sup>118</sup>	1993
CE, L	Water-based paint	Miscellaneous VOC's	Gehrig <i>et al</i> <sup>119</sup>	1993
CE, M, RE, L	Wood stain, floor wax, polyurethane	Total VOC	Tichenor <i>et al</i> <sup>120</sup>	1993
L, M, RE	Wood stain	Alkanes	Chang and Guo <sup>121</sup>	1994
CE, M, RE, L	Synthetic solvent, moth cakes	Total VOC	Sparks <i>et al</i> <sup>122</sup>	1996
L, M	Interior paints and coatings	Miscellaneous	Brown <sup>123</sup>	1997
CE, L, M	Latex paint	Miscellaneous VOC	Chang <i>et al</i> <sup>124</sup>	1998
CE, L	Alkyd paint	Miscellaneous VOC's	Fortmann <i>et al</i> <sup>125</sup>	1998
CE, L	Conversion varnish	Formaldehyde, xylene, and total VOC	Howard <i>et al</i> <sup>126</sup>	1998
CE, RE, M	Synthetic solvent	VOC – alkanes	Guo <i>et al</i> <sup>127</sup>	1998
RE, M, L	Alkyd paint	Miscellaneous alkanes	Van Veen <i>et al</i> <sup>128</sup>	1999
CE, RE, M, L	Latex and alkyd paint	Miscellaneous VOC's	EPA <sup>129</sup>	2001
CE, RE, M, L	Latex and alkyd paint	Miscellaneous VOC's	EPA <sup>130</sup>	2001

CE = Small chamber scale experiment  
RE = Room scale experiment  
M = Modeling study  
L = Literature review

## STUDY CONCLUSIONS

Models typically focus on the initial drying stage when the evaporation rate and room concentrations are highest. During this stage, worker exposure is likely to be the greatest. Models appear to perform satisfactorily for estimating potential worker exposure. The models usually over-predict peak concentrations. The model prediction of the timing of the peak concentration did not match well with the experimental data set; this is possibly due to non-ideal behavior of the solvents. Two model input variables, mass transfer factor and room mixing factor, significantly affect the predicted vapor concentrations. These variables must be estimated. The experimental data are useful to validate the models and to identify the non-idealities, such as timing of the peak concentration.

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**Abstract:**

The purpose of the Global Net on “Consumer Exposure Modelling” Workshop no. 2 on “*Source characterisation, transport and fate*” took place on 20-21 June 2005 in Intra (Italy) was:

1. To survey and discuss the general state-of -the-science of physicochemical micro-environmental model development specifically in the areas of source characterization relative to strength, time-course, and transport and fate of emissions from predominantly indoors sources.
2. Provide specific recommendations – consensus or clear majority opinion on the path forward concerning this research.

The outcome of the Workshop is summarized below:

1. A complete taxonomy of indoor pollution sources and sinks that would have a major impact on indoor air, surface concentrations, exposure and subsequent risk to human health was developed.
2. A decision not to outline, characterize or explicitly build upon the currently available source sub-models beyond the draft workshop report done before the meeting. Instead the workshop participants endeavored to build a framework for this body of scientific work from “the ground up”. Existing models, where available, were mentioned or otherwise used to fill in this framework.
3. Identification of specific operational model elements in the above taxonomy in a progressive tiered approach for each comprising *zero tier*, *first tier* and *n-tier* mechanistic source models.
4. The same type of framework was outlined for transport and fate models.
5. It was anticipated that given this comprehensive framework, practitioners will be able to potentially match-up the elements of each with existing model tools; however, in many cases, the specific sub-models do not exist and will require focused research and development.



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