Modeled Comparisons of Health Risks Posed by Fluorinated Solvents in a Workplace Spill Scenario

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The purpose of this study was to illustrate how available physical–chemical exposure models can be used to compare potential risks and define risk management measures for non-routine exposure events, such as spills, leaks, or process upset conditions. A two-zone physical–chemical model was used to quantify and compare the potential exposure risks from five fluorinated solvents used in the manufacturing of electronic materials during an anticipated spill scenario. A 1-l spill scenario in a room measuring 2.74 m (9 ft) high by 3.66 m (12 ft) wide by 9.14 m (30 ft) long was constructed for modeling exposures using 'The Two-zone Model with An Exponentially Decreasing Contaminant' in available freeware 'IH MOD' (a PC based program available from the American Industrial Hygiene Association). This treatment was followed by using the results from an experimental chamber study in which the evaporation rates and vapor concentrations of the five fluorinated solvents were measured under realistic conditions and then compared to exposure model outputs. The breathing zone concentration/time profiles predicted for the five solvents were compared to their exposure limits to estimate the relative risk. This information was used to help define operationally sufficient risk management options for the safe handling of spills in laboratories, warehouses, or manufacturing facilities. The model indicated that each solvent presented very different risk profiles for the same 1-l liquid spill scenario. Potential exposure concentrations relative to short-term exposure limit (15 min) and Ceiling (C) exposure limit available for some of the solvents are predicted to be exceeded within a few minutes in the area near the spill and in the far field. In addition, the model showed that near-field concentrations for one solvent exceeded the published LC-50 (the concentration predicted to cause 50% mortality in the test animals), which indicates a very high degree of risk for this material in similar scenarios. Given the speed of evaporation during these spills for the materials tested in this study, donning personal protective equipment in the area may not be a viable option and short-term evacuation of the area immediately surrounding the spill would appear to be a practical risk management response.

Keywords: exposure assessment; exposure scenario; model; REACH; solvent; spill

INTRODUCTION

Risk management recommendations for a product's use require knowledge of the risk posed during normal use and undesired events, such as spills or leaks. Typically, this involves matching the available information on the toxic effects of the substance [occupational exposure limits (OEL)] with the actual human exposure that is expected to be incurred during its various use scenarios. Occupational hygienists most often refer to a product's material safety data sheet

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(MSDS) to identify applicable OELs, physical properties for each material, and risk management measures, such as protective clothing, respiratory protection, exhaust ventilation, and usage recommendations (Popendorf, 1984). Then, exposure assessments are made using available information and data for all the possible use scenarios to determine which may need exposure risk management measures. If chemicals pose acute effects, short-term exposure limits can be used to evaluate exposure controls for the brief term in situations where these exposures are most significant. Typically, open material handling tasks, leaks, spills, and other poorly controlled events occurring during production or maintenance are the most common types of activities, which produce the greatest short-term exposure risks. Unfortunately, sampling data are rarely available for these types of scenarios. Therefore, physical–chemical models can be valuable tools for predicting potential exposures in order to define proper respiratory protection or evacuation thresholds (Keil and Nicas, 2003).

Recently, computing power has enabled broader use and application of complex physical–chemical models to predict and manage potential exposures. Because there are an almost infinite number of possible operating conditions for many materials, MSDSs cannot clearly specify detailed recommendations for when a leak or spill of a given material will require specific respiratory protection or the need for emergency procedures. The analysis and results of this study are presented from the perspective of a working occupational hygienist approaching the question of exposure and risk associated with spilling these solvents.

A primary purpose of this study was to illustrate how reasonably available or obtainable information can be used to determine potential exposures by determining the critical emission rate, ventilation rate, and air movement data required to implement a two-zone inhalation exposure model for five different products released within a realistic spill scenario. Since estimation of the emission rate for modeling is not readily available or is considered difficult to obtain, this work endeavors to provide the means for the typical occupational hygienist to acquire it. Our approach was to first determine the details of a workplace scenario of interest and measure the evaporation rates for a number of selected solvents under these conditions. Using equipment readily available to most industrial hygienists, a simple method for determining evaporation rates for single-component liquids was employed. Then, a series of relatively sophisticated laboratory experiments were

conducted to measure the airborne concentration of these solvents during evaporation. The concentration profiles of each solvent were compared to the modeled results to determine the applicability of the models for these solvents and exposure scenarios.

This work is ultimately designed to demonstrate the usefulness of physical–chemical modeling to evaluate the exposure risk of spills within a facility by applying it to five products currently being used as cleaning solvents in electronics manufacture. The outputs of the physical–chemical models were compared with real-time data collected for spills generated in a specially designed chamber to illustrate their ability to accurately predict vapor concentrations for each compound. The resulting information can be useful for hygienists to better specify risk management measures for a broad range of potential exposure events.

METHODS

The often noted first task of occupational hygiene is listed as the 'anticipation' of a potential risk to worker health as a result of an expected exposure. Thus, in considering the possibility of worker exposure from a solvent spill within a room, the hygienist might first devise a reasonable scenario in which the spill or release might occur. This is often done by identifying the various locations and possible sizes of spills by interviewing individuals familiar with operations. The hygienist may consider a spill of some finite amount of solvent that could be expected during routine or special-case operations for a given room in a facility. They could then determine whether the exposure potential is high enough to either warrant further action, based on monitoring data, exposure models, or even actual events that may have already occurred. In this work, the modeling estimation process is formalized and the determinants or drivers of exposure will be explicitly set forth by the hygienist in the defined scenarios as listed below.

Information gathering

Quantitative evaluation of exposure and risk requires that the model system adequately represent an actual exposure scenario. Indeed, the values for room dimensions, floor surface type, ambient temperature, ambient air speed, and general ventilation were all taken from an actual facility. These values are presented in Table 1. The determinants shown in this table are relatively straightforward for the hygienist to obtain or calculate using readily available

tools and provide the basis for quantitative model estimates of the potential exposure.

The next task would be to evaluate the solvents used or being considered for use within the scenario along with their physical–chemical properties. The solvents considered in this study are listed in Table 2, which shows information taken directly from the available MSDSs for the various solvents.

The third task an occupational hygienist might perform in assessing the risk of spilling these solvents would be to obtain the OEL and toxicological information from the respective MSDSs. Table 3

presents a summary of the OELs and acute toxicity values.

Regulations do not require MSDSs to list the specific health effects that determine the assignment of a given exposure limit. Indeed, the OELs, if listed, often represent the limit of information that an occupational hygienist has to work with when estimating the potential risk of exposures to a given substance. Review of the Solvent 1 MSDS noted possible anesthetic effects, which may prevent self-rescue and was listed as a basis for an 'emergency exposure limit' or EEL. The Solvent 1 MSDS recommends that evacuation procedures should be implemented for scenarios that could produce exposures above the EEL of 500 p.p.m.V. A similar health effect that could hinder self-rescue was also mentioned for Solvent 5, i.e. central nervous system depression with dizziness, confusion, drowsiness, or unconsciousness. All these effects are considered serious and, therefore, warrant the development of emergency procedures and spill thresholds for proper

Table 1. Spill scenario parameters

Volume of liquid spill	1 l
Ambient temperature	25°C
Ambient air speed over the spill	1.5 cm s^{-1}
Room dimensions	9.14 m (30.0 ft) × 3.66 m (12.0 ft) × 2.74 m (9.00 ft) high
Room volume	91.7 m^3
Room ventilation	551 m^3 h^{-1} or 9.17 m^3 min^{-1} (six air changes per h)

Table 2. Physical/chemical properties of solvents used in this study

Solvent	Formula	CAS number	Molecular weight	Liquid density (g ml^{-1} @ 25°C)	Vapor pressure (mm Hg @ 25°C)
1	$CHF_2CF_2OCH_2CF_3$	406-78-0	200	1.47	233
2	$CF_3CF_2CF_2CF_2OCH_3$	163702-07-6[a]	250	1.52	202
	$(CF_3)_2CFCF_2OCH_3$	163702-08-7[a]			
3	$CF_3CF_2CF_2CF_2OC_2H_5$	163702-05-4[a]	264	1.43	109
	$(CF_3)_2CFCF_2OC_2H_5$	163702-06-5[a]			
4	$(CF_3)_2CFCF(OCH_3)C_2F_5$	132182-92-4	350	1.66	45
5	$CF_3CFHCFHC_2F_5$	138495-42-8	252	1.58	226

[a]Solvents 2 and 3 are mixtures of two inseparable isomers and act as and were analyzed as single-component solvents.

Table 3. Occupational exposure limits[a] and LC-50 data of solvents used in this study

Solvent	Ceiling value (C)	15-min STEL	8-h TWA	Concentration estimated to cause death in 50% of animals tested >4 h (LC-50)
1	1000 p.p.m.V[b] (8200 mg m^{-3})	500 p.p.m.V (4100 mg m^{-3})	50 p.p.m.V (410 mg m^{-3})	>3010 p.p.m.V (>25 000 mg m^{-3}) estimated[c]
2	None listed[d]	None listed[d]	750 p.p.m.V (7700 mg m^{-3})	>110 000 p.p.m.V (>1 130 000 mg m^{-3})
3	None listed[d]	None listed[d]	200 p.p.m.V (2200 mg m^{-3})	>92 000 p.p.m.V (>994 000 mg m^{-3})
4	None listed[d]	None listed[d]	100 p.p.m.V (1400 mg m^{-3})	>30 000 p.p.m.V (>429 000 mg m^{-3})
5	400 p.p.m.V (3700 mg m^{-3})	None listed[d]	200 p.p.m.V (1900 mg m^{-3})	11 400 p.p.m.V (117 000 mg m^{-3})

[a]Exposure limits from MSDSs as set by respective manufacturers.
[b]The MSDS was unclear as to why Solvent 1 has a ceiling limit only three times lower than the LC-50 when minimum safety factors for extrapolation from different species is usually a minimum of 10.
[c]The LC-50 in the MSDS was indicated as 'estimated'.
[d]A review was conducted of each MSDS relative to the exposure limits and toxicological information shown in Table 3. For solvents without ceiling or STELs, this review of available toxicological information did not indicate short-term effects, such as 'irritation, chronic or irreversible tissue damage, dose–rate-dependent toxic effect, or narcosis of sufficient degree to increase the likelihood of accidental injury, impaired self-rescue, or materially reduced work efficiency' as suggested by the American Conference of Governmental Industrial Hygienists in ACGIH (2008).

respiratory protection. The specific documentation of the health effects driving each OEL could possibly be pursued further by the hygienist with the manufacturers. However, for the purpose of this analysis, we are going to use the above LC-50s (the concentration predicted to cause 50% mortality in the test animals) and OELs in our estimation of risk, using a classic hazard index (HI) approach. The risk or HI is the ratio of the estimated exposure to the selected limit, and values of HI greater than unity (1.0) are considered to present an unacceptable risk. Prudent risk management means lowering the potential exposure to the worker in order to lower risk to an acceptable level.

Exposure modeling methods and tools

As mentioned above, a critical task for the successful modeling of inhalation exposure resides in the reasonable determination of the emission rate of contaminant to the air. The two common evaporation scenarios of interest to the occupational hygienist are an evaporating source that is relatively constant and one that is decreasing with time. The constant source would be representative of a scenario with constant surface area as would occur in an open vessel or a larger (possibly dammed) spill. A decreasing evaporation rate would be expected as a result of a shrinking spill surface area during evaporation, representing a small spill. The constant evaporation rate is often designated (G) with the units of mass/time. The decreasing evaporation rate is typically assumed to be represented by first-order decay kinetics with the following equation:

$$\frac{M}{M_0} = e^{-\alpha(t)}, \qquad (1)$$

where M = remaining spill mass at time t (milligrams), M_0 = initial spill mass (milligrams), α = evaporation rate constant (per min).

Our approach in this work is to first simply investigate the weight loss of relatively large/deep spills to estimate G and small/shallow spills to estimate α. This was done in a well-mixed chamber designed to provide a realistic simulation of air movement over a real spill and general ventilation rate. In addition to simple weight loss, the airborne concentration as function of time was measured using Fourier transform infrared spectroscopy operated in real-time to determine the well-mixed gas phase concentrations of each product during evaporation. This allowed us to determine the validity of both the gravimetric analysis and the well-mixed box (WMB) models. The complete details of this work

are provided as a supplementary appendix at *Annals of Occupational Hygiene* online.

Given the above information regarding emission rates and other model inputs, the hygienist can choose to run physical–chemical models to estimate the exposure potential of the various solvents within the above defined scenario. Modeling of exposure potential within the realm of occupational exposure is comprehensively presented in a recent book by Keil *et al.* (2009). A freeware spreadsheet software implementation tool, IH MOD (a PC based program available from the American Industrial Hygiene Association) by Drolet *et al.* (2010), is available online and included as a companion tool for this reference.

Essentially, all models designed to predict gas phase concentrations of toxic agents within a workroom volume require an estimate of the emission rate of the agent into the volume. As such, regardless of which model hygienists choose, they will need to estimate the rate of emission, in this case, evaporation rate of the spill. It is intuitively obvious that typically unrestricted spills in the real world will initially spread out and become relatively thin. During evaporation, the initial evaporation rate will decrease as the spill shrinks and cools. As such, the best model to describe this condition would be one that includes an evaporation rate that decreases with time (Keil *et al.*, 2009). One standard approach is to assume that the source decreases as a first-order decay rate alpha (α). The value of α for each solvent must be determined experimentally, either by gravimetric means or by curve fitting of concentration values within a well-mixed chamber. This experimental work to obtain a first-order decay rate alpha (α) was done using gravimetric methods for these five solvents. The details of this and all work done to estimate the evaporation rates of these solvents are presented in the previously mentioned supplementary appendix at *Annals of Occupational Hygiene* online.

Given a valid evaporation rate (α), the first principle model of airborne concentration as a function of time in a well-mixed volume [presented by Reinke *et al.*, (2009)] is:

$$C = \frac{\alpha \cdot M_0}{\alpha \cdot V - Q}\left[e^{\frac{Q}{V}t} - e^{-\alpha \cdot t}\right], \qquad (2)$$

where α = evaporation rate (per min), M_0 = initial spill mass (milligrams), V = space or room volume (cubic meter), Q = ventilation rate of fresh air into and contaminated air out of the space (cubic meter per min), t = time (min).

Measured or determined data for these variables (α, M_0, V, and Q) from experimental chamber studies where used to predict concentration (C) as a function of time. The details of this work are presented in the supplementary appendix at *Annals of Occupational Hygiene* online. The modeled values compared to measured concentrations under the same conditions are shown in Fig. 1.

Thus, this model works very well for well-mixed volumes; however, it is obvious to most hygienists that typical workrooms are not well mixed and that the concentration of airborne contaminants will be significantly higher (at least initially) near a rela-

tively small source than it will be at some distance from the source in the same room volume.

This limitation led to the development of a variation of the WMB model by Nicas (1996) in which there are two mathematically described zones within the box. The inner, or near-field zone, is immediately proximate to the sources, while all the volume outside the near-field zone is considered the far field. Both zones are also considered to be well mixed. The concentration within the near-field volume is driven by both the general ventilation rate and the rate of exchange of air between it and the far-field volume. Figure 2 illustrates this model.
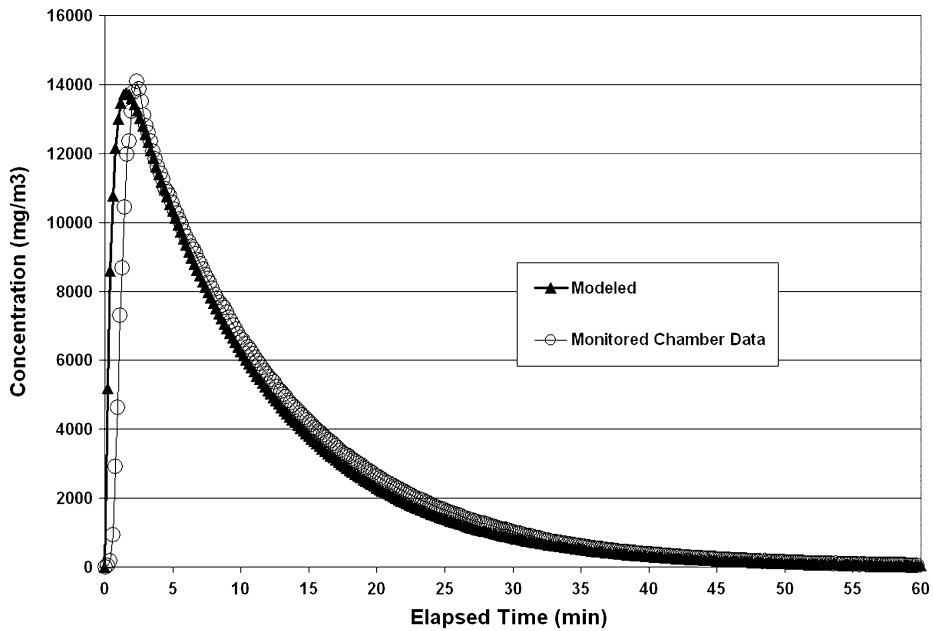

Fig. 1. Comparison of measured and modeled (WMB with decreasing source) concentrations for Solvent 1 using gravimetrically determined evaporation rate (α).
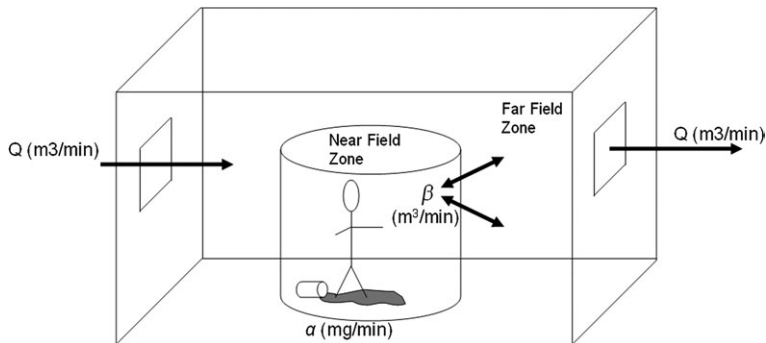

Fig. 2. Two-zone model.

This model (two zones with an exponentially decreasing source rate) is relatively simple conceptually but quite complicated mathematically (Nicas, 1996, 2009; Keil and Nicas, 2003). In addition to α described above, the input variables in this model include:

V_n = the near-field volume (cubic meter),
V_f = the far-field volume (cubic meter) = $V–V_n$,
 β = airflow rate (cubic meters per min) between the near and far fields.

The outputs are the time-dependent variables:

CN_t = the near-field concentration (milligrams per cubic meter),
CF_t = the far-field concentration (milligrams per cubic meter).

The real advantage of the two-zone model over the single WMB model described above is that it provides an estimate of average near-field exposure as well as the average exposure within the far field. Thus, it can be used to estimate the exposure to workers near the spill as well as those in the room but not in the immediate vicinity of the spill itself.

Using the above scenario, the following assumption concerning the near-field volume was utilized in the two-zone model. We chose to describe the near-field volume over the spill as a 2 m high and 2 m radius cylinder whose bottom is on the floor. This cylindrical volume (25.1 m^3) would include the breathing zone of any 2 m tall (or shorter) person standing within 2 m of the spill's center. The determination of β is simply ½ the free surface area of the near-field volume multiplied by the local air velocity as described by Nicas (1996). The free surface area of a 2-m tall cylinder (one top surface and side

walls) with 2 m radius is 37.7 m^2. As previously shown, the local air velocity measured in a real laboratory and chosen for the scenario is 1.5 cm s^{-1} or 0.9 m min^{-1}.

Thus,

$$\beta = \frac{1}{2}\,(37.7 \text{ m}^2)\,(0.9 \text{ m min}^1) \;=\; 17 \text{ m}^3 \text{ min}^1.$$
(3)

As mentioned above, the two-box model is relatively complicated mathematically; however, the freeware tool IH MOD can perform these calculations with a user-friendly interface. The point-in-time and time-weighted average (TWA) concentration versus time profiles for near-field (CN_t) and far-field (CF_t) exposures were calculated using IH MOD for all the solvents using the scenario inputs as listed above.

Estimation of peak (ceiling) and 15-min TWA exposures

Specific IH MOD model input for Solvent 1 is shown in Fig. 3. The output near-field concentration curves (CN_t) and far-field concentration curves (CF_t) for each solvent are presented in Figs. 4–8 for the time period of 0–15 min. The IH MOD software allows users to select any time point to view the corresponding near-field and far-field concentrations. The tool also provides a good illustration of the short-term exposure within 15 min after the spill for comparison to the short-term exposure limits (STELs) denoted as TWA NF and TWA FF in Figs. 4–8. The peak concentration for each solvent spill scenario was compared to existing LC-50 and ceiling exposure limits, while the 15-min TWA concentration was compared to the STEL exposure limit when available.
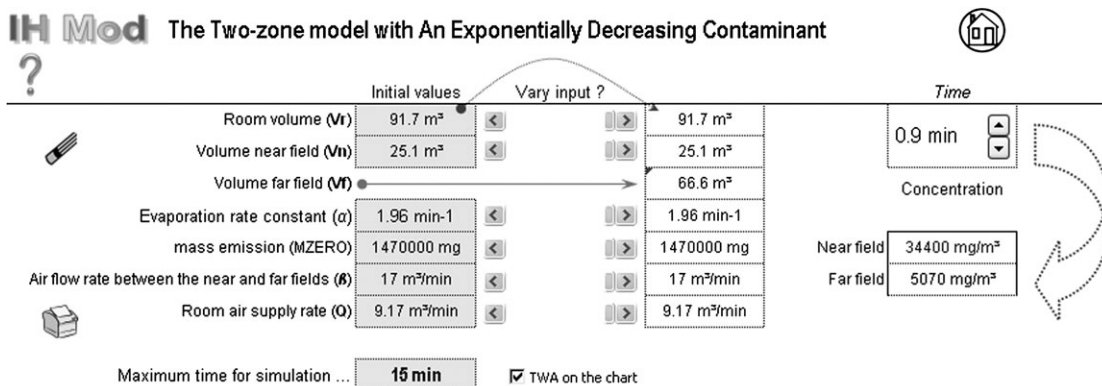

Fig. 3. Model input section for Solvent 1 in IH Mod 'The Two-zone model with an Exponentially Decreasing Contaminant'.
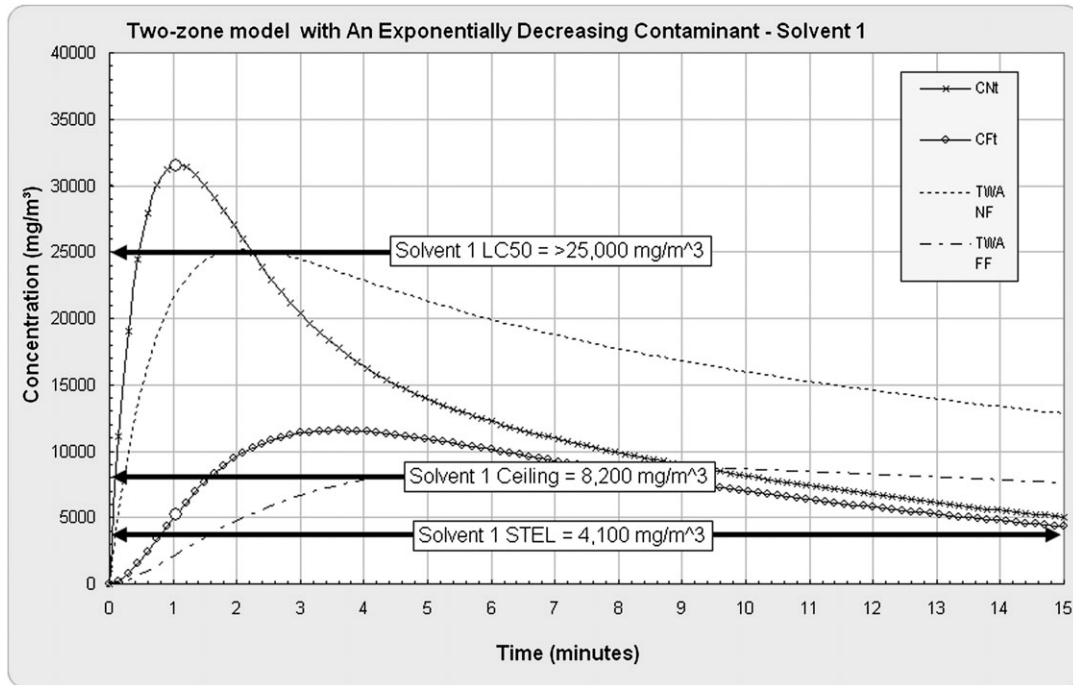
Fig. 4. IH Mod chart of 0- to 15-min model concentrations for near field (CNt), far field (CFt), TWA concentration near field (TWA NF), and far field (TWA FF) in the 1-l Solvent 1 laboratory spill scenario.
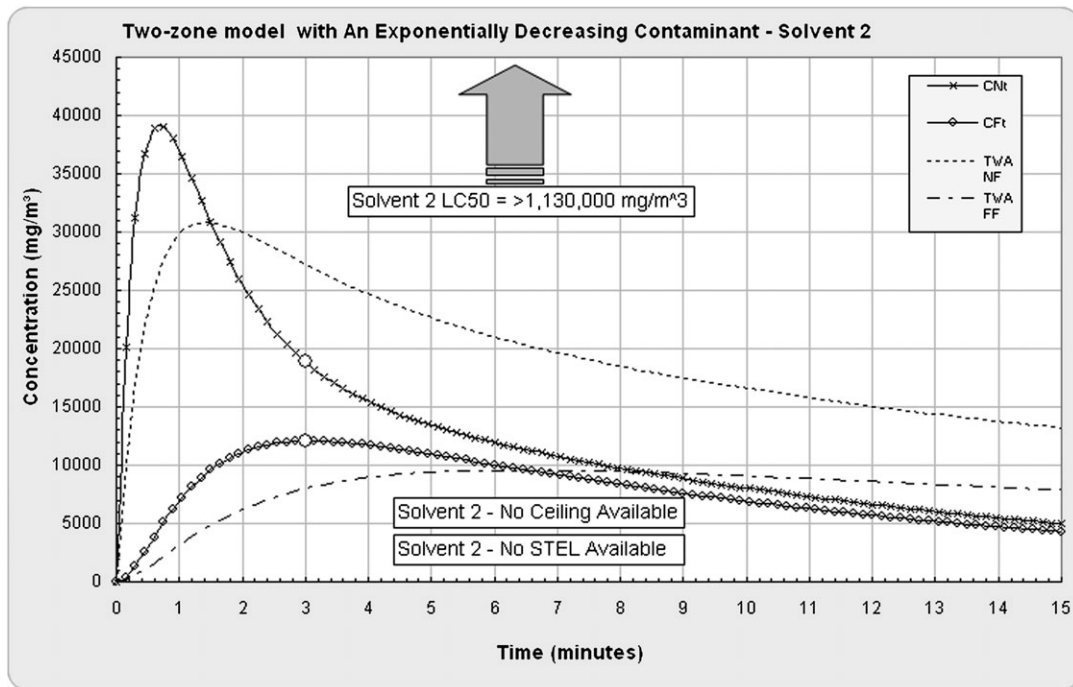
Fig. 5. IH Mod chart of 0- to 15-min model concentrations for near field (CNt), far field (CFt), TWA concentration near field (TWA NF), and far field (TWA FF) in the 1-l Solvent 2 laboratory spill scenario.

Fig. 6. IH Mod chart of 0- to 15-min model concentrations for near field (CNt), far field (CFt), TWA concentration near field (TWA NF), and far field (TWA FF) in the 1-l Solvent 3 laboratory spill scenario.
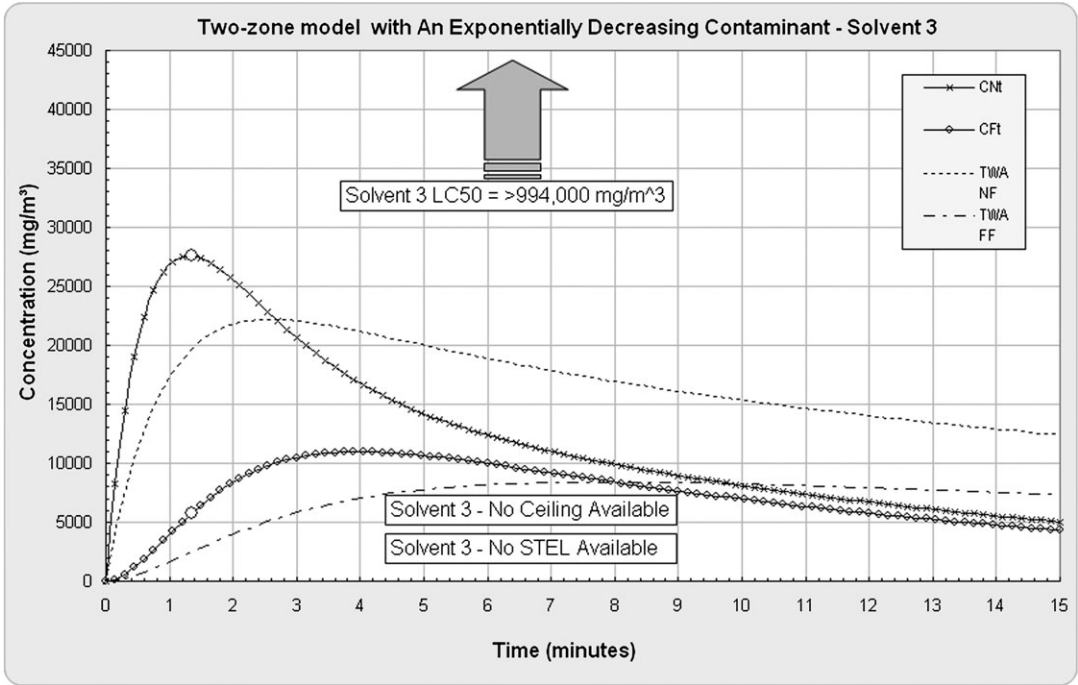

Fig. 7. IH Mod chart of 0- to 15-min model concentrations for near field (CNt), far field (CFt), TWA concentration near field (TWA NF), and far field (TWA FF) in the 1-l Solvent 4 laboratory spill scenario.

Fig. 8. IH Mod chart of 0- to 15-min model concentrations for near field (CNt), far field (CFt), TWA concentration near field (TWA NF), and far field (TWA FF) in the 1-l Solvent 5 laboratory spill scenario.
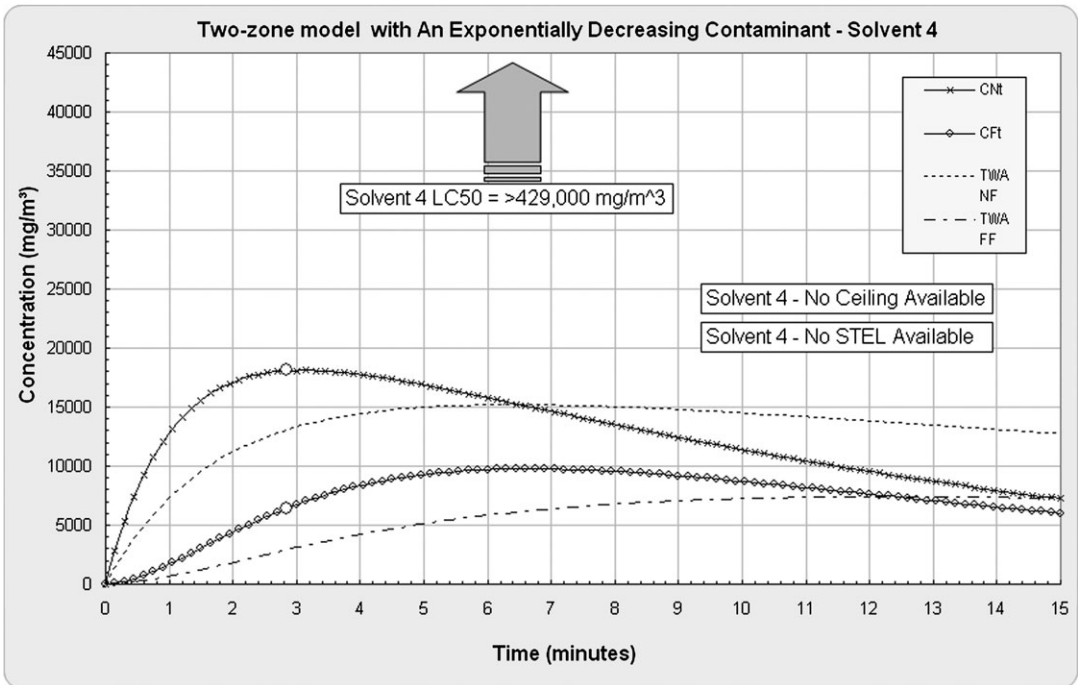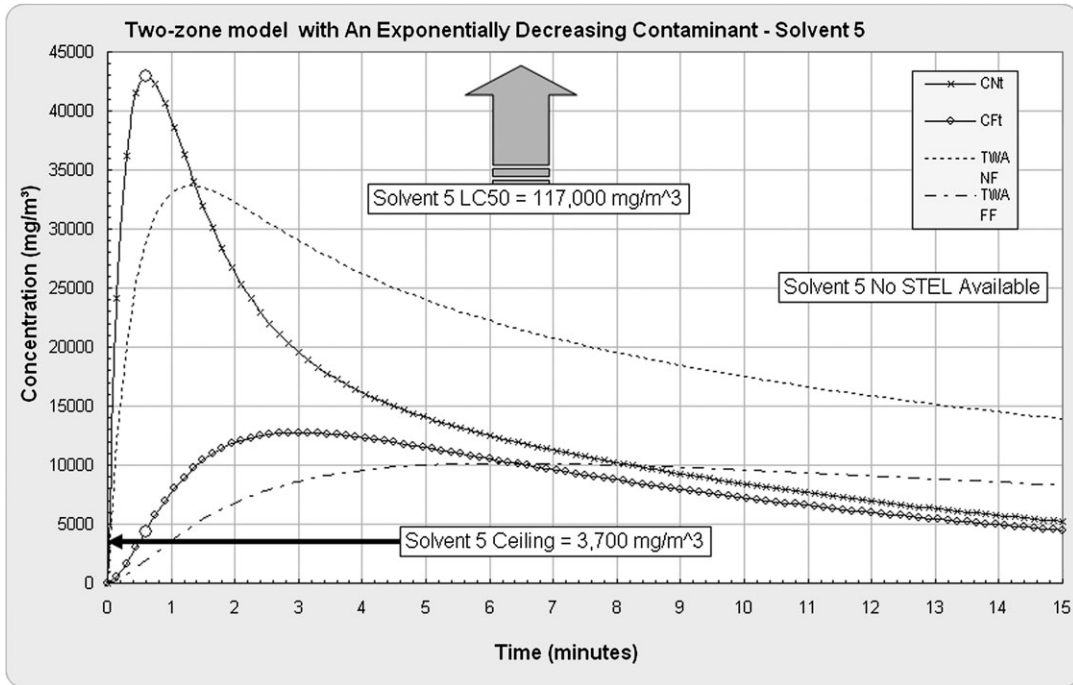
Estimation of 8-h TWA exposures

Because IH MOD uses a technique of equal spacing of a predetermined number of intervals for performing its calculations, it will sometimes underestimate the 8-h TWA concentration when one is modeling scenarios with very rapidly rising concentration. To reduce this potential error, the time intervals used in IH MOD should be reasonably short to capture these changes.

Because of this potential error in the IH MOD, the 8-h TWA exposure for this work was estimated by a different method. Given a high evaporation rate and the relatively high rate of ventilation within the room (six volume changes per h), there is a high degree of certainty that all the released solvent will be gone from the room well before 8 h. Thus, the 8-h TWA exposure can be calculated exactly and directly from the total quantity of solvent evaporated and the ventilation rate within that zone. The rate of ventilation for the overall room and the far field is given by Q,

$$\text{Ventilation\_Rate}_{FF} = Q. \qquad (4)$$

The rate of ventilation in the near field is given by the following expression derived elsewhere (Keil *et al.*, 2009):

$$\text{Ventilation\_Rate}_{NF} = \left(\frac{\beta}{\beta + Q}\right) \cdot Q. \qquad (5)$$

Thus, the ventilation rate in the near field is always less than that of the far field and this will affect the TWA concentration over any time interval including 8 h. In our scenario, the ventilation rate in the far field is 9.17 m^3 min^{-1}. Using equation (5), the ventilation rate in the near field is ∼65% of this rate or 6 m^3 min^{-1}. The 8-h (480 min) TWA concentration in the near field and far field will be calculated using the following relationship:

$$\text{Concentration}_{8hTWA} = \frac{\frac{M_0}{480min}}{\text{Ventilation\_Rate}}. \qquad (6)$$

Thus, the TWA for any solvent that is totally evaporated into and subsequently purged from a volume during that time is directly proportional to the mass spilled (M_0) and inversely proportional to the constant ventilation rate within that volume. Since all the solvents were considered to be released at the same liquid volume and under the same conditions,

their 8-h TWA concentrations within the near-field or far-field volume only vary by the densities of the spilled liquids.

RESULTS

The modeling outputs of all five solvents are presented in Figs. 4–8. All use the following inputs:

$\beta = 17$ m^3 min^{-1}
Vn $= 25.1$ m^3
Vr $= 91.7$ m^3
Vf $= 91.7$ m$^3 - 25.1 = 66.6$ m^3
$Q = 9.17$ m^3 min^{-1}

The only solvent-specific variables will be α and the amount spilled (M_0) (based on the product 1000 cm^3 × density of the solvent × 1000 mg g^{-1}). The evaporation rate for the five solvents is presented in Table 4.

Tables 5–7 presents the model predicted exposure potential for workers in the near field or far field along with the corresponding HI from the applicable manufacturer's assigned exposure limit(s).

DISCUSSION

Using straightforward techniques to obtain reasonably accurate evaporation rates (see supplementary appendix at *Annals of Occupational Hygiene* online), a hygienist can estimate exposure potentials for scenarios that represent spills or leaks inside rooms. These estimates can help determine risk management measures specific to the materials handled in a given scenario. The solvents in this study have similar physical characteristics, but their different toxicological properties present very different risk potentials. These differences reflect the relative gravity or seriousness required in the implementation of risk management actions. The models used in this study are particularly valuable for evaluating exposure potentials in various scenarios to define emergency plans, engineering controls, work practices, and personal protective equipment.

The applicable HIs should be evaluated based on the possible exposure times from the given scenarios. When utilizing exposure models to evaluate acute exposure potentials, the most significant

Table 4. Alpha (α) (min^{-1}) from controlled chamber data and scenario M_0 for five fluorinated solvents

Solvent	1	2	3	4	5
Alpha (α) (min^{-1})	1.96	2.92	1.10	0.32	3.45
M_0 (mg)	1.47×10^6	1.50×10^6	1.43×10^6	1.60×10^6	1.58×10^6

Table 5. Model estimated near-field and far-field exposure peak concentrations and LC-50 HI for each solvent in the 1-l spill scenario

	Solvent 1	Solvent 2	Solvent 3	Solvent 4	Solvent 5
Near field (mg m^{-3})	34 400	39 000	27 600	18 100	42 900
Far field (mg m^{-3})	11 700	12 100	11 000	9770	12 700
LC50 (mg m^{-3})	>25 000	>1 130 000	>994 000	>429 000	117 000
HI near field	1.38	0.03	0.03	0.04	0.37
HI far field	0.47	0.01	0.01	0.02	0.11

Table 6. Model estimated near-field and far-field exposure peak concentrations and ceiling HI for each solvent in the 1-l spill scenario

	Solvent 1[a]	Solvent 2	Solvent 3	Solvent 4	Solvent 5
Near field (mg m^{-3})	34 400	39 000	27 600	18 100	42 900
Far field (mg m^{-3})	11 700	12 100	11 000	9770	12 700
Ceiling limit	8 200	Not listed	Not listed	Not listed	3700
HI near field	4.20				11.59
HI far field	1.43				3.43

[a]It was noted that the MSDS for Solvent 1 listed a 15-min emergency exposure limit $= 4100$ mg m^{-3}. Figure 4 shows the near-field and far-field 15-min exposures to be 12 830 mg m^{-3} and 7620 mg m^{-3}, which correspond to a HI of 3.13 and 1.86, respectively.

Table 7. Model estimated 8-h TWA near-field and far-field exposure concentrations and 8-h HI for each solvent in the 1-l spill scenario.

	Solvent 1	Solvent 2	Solvent 3	Solvent 4	Solvent 5
Near field (mg m^{-3})	510	521	497	556	549
Far field (mg m^{-3})	334	341	325	364	359
8-h TWA (mg m^{-3})	410	7700	2200	1400	1900
HI near field	1.24	0.07	0.23	0.40	0.29
HI far field	0.81	0.04	0.15	0.26	0.19

exposure metric is an LC-50 HI. This HI represents a potentially lethal threshold where effects have been confirmed in animal studies without incorporating various safety factors included in exposure limits and therefore will warrant the most stringent and urgent risk management measures. The most significant finding in this study was the LC-50 HI (1.38) for Solvent 1, indicating that exposure risks mandate immediate evacuation in similar scenarios (Table 5, Fig. 4). In addition, Solvent 1 appears to have a HI >1 for every exposure metric listed on the MSDS for the given scenario in this study (Tables 5–7). The Solvent 5 ceiling HI was >1 and appeared to be higher than Solvent 1; however, Solvent 5 also has a relatively higher LC-50 (Tables 5 and 6). This discrepancy could be a source of confusion for hygienists evaluating similar scenarios who may need to consult a toxicologist familiar with these materials for additional information and guidance.

Depending on the type of production environment, spills could occur periodically as a part of material handling in production areas contributing to a worker's full-shift exposure. The 8-h TWA exposures estimated based on the spill scenario assumes that the spill was the only exposure source, which underestimates full-shift exposure risk if other significant sources were present in addition to the spill. If spills with characteristics similar to this scenario were routine in a work area, the full-shift exposure to Solvent 1 would also be considered unacceptable given the 8-h HI of 1.24 (Table 7). In addition, the near-field excursion HI for each solvent would be >1 for all solvents in this scenario and therefore an occupational hygienist would likely recommend risk management measures to control short-term exposures <5 times the 8-h TWA concentration (ACGIH, 2009). The materials in this study have relatively high evaporation rates; therefore, donning personal protective equipment in the area of a similar size spill would not be recommended. Rather short-term evacuation of the area immediately surrounding the spill would appear to be a more practical risk management response.

The two-zone model with exponentially decreasing emission rates used in this study can also be used to estimate the volume of a spill that would not result in overexposure by keeping all the scenario variables the same and just reducing the amount of evaporated solvent until the HI falls well below a reasonable level for a given scenario. For example, assuming a spill of Solvent 5 is 80 cm^3 and inputting this information into IH MOD results in a predicted peak concentration in the near field of 3590 mg m^{-3} and reduces the ceiling HI to 3590/3700 = 0.97. The threshold spill size of concern predicted by this model is ~80 ml. One can also run 'what if' analyses by varying the ventilation rate (Q) and air speed around the spill, which will impact β and subsequently the predicted exposure concentration profile.

It is interesting to note that the predicted ceiling or peak concentrations, which varied from roughly 20 000–40 000 mg m^{-3} in the near field and 10 000–13 000 mg m^{-3} in the far field, appear to be proportional to and driven by α. Similarly, the 8-h TWA concentration only varied with the density of the solvents and was predicted to range from 500 to 560 mg m^{-3} in the near field and 325–364 mg m^{-3} in the far field. As such, except for the peak or ceiling exposure values, the predicted exposure concentrations of the five solvents are remarkably similar. This supports the concept of utilizing vapor hazard ratios to compare exposure risks from different substances in a given scenario (Popendorf, 1984).

Given the similarity, especially of ≥15-min time-weighted exposures, the differential in worker health risk posed by these solvents during spills is driven primarily by the difference between acute exposure effects levels for each solvent. In particular, the comparison between LC-50, ceiling (C), and 15-min STEL limits become critical. Solvents 1 and 5 have assigned ceiling exposure limits and Solvent 1 also has an assigned STEL. These limits are predicted to be significantly exceeded in this scenario. Therefore, risk management options to reduce potential

exposures to levels below these limits would be warranted. The urgency for risk management should be dependent on the anticipated adverse health effect(s) for which the exposure limit was set and specific conditions in possible scenarios. As mentioned above, the occupational hygienist often does not have direct access to this specific information and should either pursue the manufacturer for more detail or default to worst-case assumptions regarding the seriousness of the potential overexposure.

CONCLUSIONS

It is recognized that the chamber methods used in this work may not be available to all occupational hygienists. However, the critical factor for the determination of both constant and decreasing evaporation rates for single-component liquids resides in the simple gravimetric measurement of evaporative solvent weight loss with time. The practicing hygienist should consider conducting gravimetric measurement of evaporation rates for both models (constant rate for constant sources and decreasing rates for spills) using tools that should be readily available to most investigators. This would involve placing a small container on a scale accurate to within 0.1 g in a laboratory hood. The liquid of interest would be placed in the container and mass loss recorded versus time. The type of scenario to be modeled would determine the specific experimental setup. Constant emission sources, such as an open vessel with evaporating solvent could be simulated with a petri dish or bottle cap with a small surface area to volume ratio in an attempt to produce a constant rate of evaporation for a constrained surface area. Simulation of a spill (an exponentially decreasing source) might use a petri dish, paint can lid, or floor tile in which the solvent thickness represents a realistic value by using a spill volume, which barely reaches the perimeter of the selected surface area. For the constant evaporation rate experiments, given a known surface area and representative air movement over the liquid (measured with an anemometer), one could readily calculate the evaporation rate per unit area. For the exponentially decreasing sources, alpha (α) could also be calculated. The details of both calculation techniques are described in the supplementary material at *Annals of Occupational Hygiene* online.

Hygienists are routinely confronted with questions on the relative risk between groups of materials for many different scenarios. This study illustrates how a hygienist or risk manager can reasonably assess potential exposures in the absence of sampling data for similar scenarios by using available physical–chemical exposure models. In cases where evacuation or emergency response is necessary, these models can help define reentry procedures, respiratory protection, and ventilation requirements. Additional studies should be done to evaluate their application in different types of exposure scenarios.

SUPPLEMENTARY DATA

Supplementary data can be found at http://annhyg .oxfordjournals.org/

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