

Modeling small-scale spills of aqueous solutions in the indoor environment

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Abstract

A mass transfer model is proposed to estimate the rates of chemical emissions from aqueous solutions spilled on hard surfaces inside buildings. The model is presented in two forms: a set of four ordinary differential equations and a simplified exact solution. The latter can be implemented in a spreadsheet. User input includes ten parameters, which represent either the properties of the source or those of the building. All of them can be readily obtained. The proposed model is tested against and in good agreement with the measurements of simulated spill events in a room-sized environmental chamber. This model can be used by emergency response planners to estimate the time history of contaminant concentrations in indoor air.

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1. Introduction

Accidental spillage or intentional release of toxic liquids inside a building may pose a serious health threat to the occupants and emergency response personnel. It is important for emergency response planners to have some idea in advance about what to expect following a liquid spill, and it is desirable to make predictions based on the properties of the liquid, the size of the spill, and the features of the building. Many studies have been conducted and many models have been developed for estimating the emissions of chemicals from liquid spills, but most are for outdoor environments. There are significant differences between indoor and outdoor spills. For instance, the scale of indoor spills is much smaller; the indoor air speed is often much lower than the wind speeds outside; many indoor flooring materials are not seen outside; and the indoor concentration is strongly affected by building features. So far, published indoor spill models are all for pure liquids [1,2]. In this paper, we propose a mass transfer model for predicting the indoor concentrations following spills of aqueous solutions, and report the preliminary results

of model evaluation with experimental data collected in a large environmental chamber by using surrogate chemicals.

2. Model description

The proposed model calculates the pollutant concentrations in indoor air (C) and spilled liquid (C_L) based on estimations of the change of spill area over time (A), the rate of water evaporation (R_w), and the emission rate of the solute (R_s).

2.1. The change of spill area over time

When a spilled aqueous solution evaporates, both the area and thickness of the liquid film may change over time. Modeling both variables has proven difficult. To simplify the case, it is usually assumed that, as water vaporizes, only the area of the wet film changes while the film thickness remains the same [1,3]. Thus, the spill area is proportional to the volume of the aqueous solution remaining on the floor:

$$A = A_0 \frac{V_L}{V_{L0}} = A_0 \frac{\rho_0 W}{\rho W_0} \quad (1)$$

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Nomenclature

Symbols

A	spill area at any time (m^2)
A_0	initial spill area (m^2)
C	solute concentration in room air (g/m^3)
C_L	solute concentration in spilled liquid (g/m^3)
C_{L0}	initial solute concentration in spilled liquid (g/m^3)
C_∞	solute concentration in room air in equilibrium with the liquid, $C_\infty = HC_L$ (g/m^3)
D_a	diffusivity of solute in air (m^2/h)
D_L	diffusivity of solute in water (m^2/h)
H	dimensionless Henry's constant (i.e., $H = C_\infty/C_L$)
k_{gs}	gas-phase mass transfer coefficient for solute (m/h)
k_{gw}	gas-phase mass transfer coefficient for water vapor (m/h)
k_{Ls}	liquid-phase mass transfer coefficient for solute (m/h)
K_{OL}	overall liquid-phase mass transfer coefficient for solute (m/h)
L	characteristic length of the source and $L = A^{0.5}$ (m)
m	water vapor concentration in indoor air (g/m^3)
m_{out}	water vapor concentration in ambient air or building supply air (g/m^3)
m_{sat}	saturated water vapor concentration in indoor air (g/m^3)
N	air change rate of building and $N = Q/V$ (h^{-1})
p	lumped first-order decay constant for water evaporation (h^{-1})
P_{w0}	water vapor pressure (mmHg)
q	lumped first-order decay constant for solute emission from liquid film (h^{-1})
Q	air change flow rate of building (m^3/h)
r_h	relative humidity in indoor air (fraction)
Re	Reynolds number
R_s	rate of solute emission from spilled liquid (g/h)
R_w	rate of water evaporation from spilled liquid (g/h)
Sc	Schmidt number
Sh	Sherwood number
t	time (h)
T	liquid temperature (K)
V	volume of the room (m^3)
V_L	volume of aqueous solution remaining on the floor and $V_L = A\theta$ (m^3)
V_{L0}	initial volume of aqueous solution spilled and $V_L = A_0\theta$ (m^3)
W	mass of aqueous solution remaining on the floor (g)
W_0	mass of aqueous solution spilled (g)
x_L	molar fraction of solute in aqueous solution (fraction)
x_w	molar fraction of water in aqueous solution (fraction)

Greek letters

γ	activity coefficient of a solute in water
θ	liquid film thickness (m)
ρ	density of aqueous solution (g/cm^3)
ρ_0	initial density of aqueous solution (g/cm^3)

If the density of the liquid does not change significantly over time (i.e., $\rho \approx \rho_0$), Eq. (1) can be simplified:

$$A = A_0 \frac{W}{W_0} \quad (2)$$

2.2. The rate of water evaporation

The rate of water vaporization from an aqueous solution is proportional to the area of the liquid surface, the gas-phase mass transfer coefficient for water vapor, and the concentration difference of water vapor between the water–air interface and the bulk air [13]. Thus,

$$R_w = A k_{gw}(x_w m_{sat} - m) \quad (3)$$

where m – the water vapor concentration in indoor air – is a variable affected by water evaporation from the liquid film and indoor/outdoor air exchange. For a dilute solution, x_w can be ignored (i.e., $x_w \approx 1$).

2.3. The rate of solute emission

Many models have been developed for estimating the rate of solute emission from an aqueous solution. They fall into two categories: those based on Henry's constant and overall mass transfer coefficient [4,5] and those based on Functional Group Activity Coefficients [6,7]. The latter is also known as the UNIFAC method. One drawback of the UNIFAC method is that some of the data are proprietary. In this work, the method based on Henry's constant and overall mass transfer coefficient is used. The advantage of this approach is that all data necessary are readily available in handbooks or can be easily calculated.

According to the two-layer theory [4], the rate of the solute emission from the liquid film is determined by the liquid area, overall mass transfer coefficient, and the concentration difference at the air–water interface adjusted by the fugacity capacity ($1/H$):

$$R_s = A K_{OL} \left(C_L - \frac{C}{H} \right) \quad (4)$$

When Eq. (4) is applied to spill events, it is implicitly assumed that, at room temperatures, the solute is either a gas – such as hydrogen cyanide (HCN), hydrogen chloride (HCl), hydrogen fluoride (HF), nitrogen pentoxide (N_2O_5) and ammonia (NH_3) – or a volatile liquid, such as acetone and methanol. Thus, the solute does not stay on the floor after the wet film dries up. If the solute is less volatile than water, the emission from the “dry” film has to be considered.

2.4. The differential equation model and initial conditions

The proposed model consists of four differential equations (Eqs. (5)–(8)), which determine, respectively, the mass of solution remaining on the floor, water vapor concentration in indoor air, solute concentration in spilled solution, and solute concentration in indoor air. Briefly, the loss rate of the solution mass remaining on the floor is the sum of the emission rate of solute and that of water (Eq. (5)). The change of water vapor concentration in room air is determined by the emission from the spill and indoor–outdoor air exchange (Eq. (6)). The loss rate of the solute mass remaining in the spilled liquid is proportional to the emission rate of the solute (Eq. (7)). The change of the solute concentration in room air is determined by the emission rate of the solute and the indoor–outdoor air exchange assuming that the solute concentration in the outdoor air is negligible (Eq. (8)).

$$\frac{dW}{dt} = -R_w - R_s \quad (5)$$

$$V \frac{dm}{dt} = R_w + Q(m_{\text{out}} - m) \quad (6)$$

$$V_L \frac{dC_L}{dt} = -R_s \quad (7)$$

$$V \frac{dC}{dt} = R_s - QC \quad (8)$$

where R_w and R_s are determined by Eqs. (3) and (4), respectively.

Typical initial conditions are: $W = W_0$, $m = m_{\text{out}}$, $C_L = C_{L0}$, and $C = 0$ when $t = 0$.

2.5. The simplified model

With additional assumptions and approximations, this differential equation model can be simplified to yield an exact solution for solute concentration in indoor air (Eqs. (9) and (10)). Step-by-step derivation is provided in Appendix A.

$$C = \frac{A_0 K_{OL} C_{L0}}{V(q - N)} [e^{-Nt} - e^{-qt}] \quad (9)$$

where

$$q = \frac{A_0 k_{gw} m_{\text{sat}} (1 - r_h)}{W_0} + \frac{K_{OL}}{\theta} \quad (10)$$

3. Experimental

3.1. Chemical agents and materials

Acetone and ammonia solutions were used in the spill experiments. The former was selected as a surrogate of highly volatile toxic liquids and the latter as one of toxic gases. The test solutions were prepared by diluting acetone (Sigma/Aldrich, 99.9% pure) and ammonia (ACROS, 0.1 and 0.5N solutions) with HPLC-grade water. Ammonia concentrations in stock solutions were verified by an independent laboratory.

Three types of materials were used as the receiving surfaces of the spill: stainless steel sheet (used as a reference surface),

household vinyl flooring, and carpet (medium pile with a fiber backing).

3.2. Test facility

Spill experiments were conducted in a 30 m³ (approximately 4 m L × 2.8 m W × 2.6 m H) stainless steel chamber equipped with clean air generation, air conditioning, and air distribution systems. Experimental conditions of temperature, air pressure, relative humidity, and ventilation airflow rate can be set, maintained, and recorded through a control and data acquisition system. The design and operation of this chamber conforms to ASTM Standard Guide D-6670-01 [8]. During the spill experiments, the chamber was operated in a single pass mode, where supply air was exhausted from the chamber without recirculation. A small fan was used to maintain good air mixing in the chamber. To measure the temperature of the spilled liquid, a temperature sensor was placed near the center of receiving surface. The tracer gas dilution method [9] was used as the primary method for determining the air change rate and the concentration of the hexafluorine sulfide tracer gas was measured by a chromatograph (HP 5890 Series II) with an electron capture detector. The chamber air change flow was measured with a calibrated pressure transducer and the results were used as the backup method for the tracer gas measurements. The targeted air change rates were 0.5 and 1.0 h⁻¹. The air speed of chamber air over the receiving surface was measured at nine points with a Brüel & Kjær 1213 Indoor Air Climate Monitor. The mean air speed for the spill tests ranged from 18.5 to 21 cm/s.

To simulate spill events in a repeatable manner, a remotely operated spill apparatus was designed and constructed (Fig. 1). The apparatus consists of three major components: a DC 12 V gear motor (McMaster Carr, 0.01 horse power, 4 rotations per

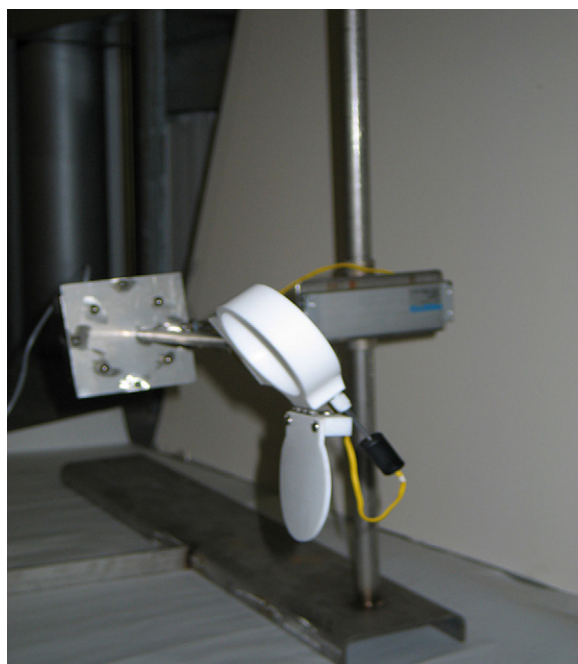


Fig. 1. The remotely controlled spill apparatus. The cup is in the “spill” position.

minute), a non-rotary air cylinder (10.2 cm stroke), and a hemispheric polytetrafluoroethylene cup (100 or 150 mL) with a hinged lid. The rotation of the cup can be controlled from outside of the chamber. The height of the spill cup can be adjusted from 24 to 107 cm. The device was placed on a rotating turntable to allow it to be moved from the center of the chamber to near the chamber wall after the spill.

3.3. Air sampling and analyses

The acetone concentration in chamber air was measured by an INNOVA 1314 Photoacoustic Infrared Multi-gas Analyzer with a calibrated No. 970 filter. The ammonia concentration was monitored using a Model 5200 Ammonia Monitor (CEA Instruments). The monitor was calibrated at the factory with a linear range from 0 to 500 ppm. The air sampling port was located 114 cm above the chamber floor, 137 cm from the front wall, and 53 cm from the right-side wall.

3.4. Measurement of the spill area

The spill area was determined by the digital imaging method. The images of the liquid spills were captured by a digital camera located at the ceiling of the chamber, and then analyzed by the AutoCAD LT 2005 software (Autodesk, Inc.). It was observed that the spill area consisted of pools, puddles, and splatters. The area of pools and puddles was determined by chart integration with AutoCAD. This method was validated by comparing the measured area of the standard grid in AutoCAD to the physical measurements of the grid. However, estimating the areas of individual splatters was proven unpractical. Thus, the liquid area of splatters was determined in two steps: first, determining the splattered floor area, which is defined as the floor area that contains at least 10 liquid droplets in a 5 cm × 5 cm grid; second, multiplying the splattered floor area by 15%. This multiplying factor was determined based on the analyses of multiple images. Thus, the total spill area is the area of pools and puddles plus 15% of the splattered floor area.

4. Results

4.1. Summary of chamber experiments

Fifteen chamber experiments were conducted. Results of four tests were discarded because of incomplete data collection. Thus, only 11 tests were used to evaluate the proposed model. Test conditions are summarized in Table 1.

In addition to routine quality assurance and quality control measures implemented during the chamber experiments, the solute recovery from the chamber experiments was used as an indicator of the overall data quality. The recovery is defined as the ratio of the amount of solute detected in the chamber to the amount of solute spilled. The former is calculated by integrating the time-concentration data [8]. A recovery between 75% and 125% was considered acceptable. The recoveries for the acetone experiments, ranging from 85% to 110%, were all acceptable. The two experiments with ammonia (Tests 10 and 11) gave good precision but unacceptable recoveries. For the purpose of model evaluation, the ammonia concentration data were adjusted to 100% recovery and, thus, should be considered semi-quantitative.

4.2. Estimation of model parameters

4.2.1. User input

The simplified model requires user input for 10 parameters. Six are used directly by the model: room volume, ventilation rate, initial concentration of aqueous solution, amount of solution spilled, initial spill area, and relative humidity of indoor air. The remaining four parameters are needed to calculate the two mass transfer coefficients and saturation concentration of water vapor, and they are: dimensionless Henry's constant for the solute, temperature of indoor air, temperature of spilled liquid, and the average air speed over the liquid.

4.2.2. Henry's constants

Henry's constants for acetone and ammonia were obtained by averaging the literature values compiled by the National

Table 1
Summary of experimental conditions^a

Test ID	Substrate type ^b	Solute name	Concentration (% w/w)	Solution spilled (g)	Initial spill area (m ²)	Temperature of air (°C)	Relative humidity (%)	Temperature of liquid (°C)	Air change rate (h ⁻¹)
1	SS	Acetone	10.6	102	0.169	24.8 ± 0.02	52.7 ± 1.5	20.9 ± 0.3	1.00
2	SS	Acetone	10.6	101	0.158	25.5 ± 0.10	51.6 ± 0.8	22.2 ± 0.4	1.01
3	SS	Acetone	5.0	99.8	0.198	23.0 ± 0.02	50.1 ± 0.1	19.0 ± 0.5	1.00
4	SS	Acetone	5.0	100	0.170	23.5 ± 0.03	69.3 ± 0.5	20.5 ± 0.1	0.51
5	Vinyl	Acetone	5.0	99.0	0.136	23.3 ± 0.10	48.8 ± 1.4	21.6 ± 0.8	1.00
6	Vinyl	Acetone	5.0	97.9	0.093	24.6 ± 0.04	51.0 ± 0.5	20.9 ± 0.1	0.47
7	Vinyl	Acetone	5.0	99.4	0.090	24.6 ± 0.02	50.6 ± 0.7	21.2 ± 1.1	0.47
8	Vinyl	Acetone	5.3	149	0.107	23.7 ± 0.02	51.1 ± 0.9	21.8 ± 1.1	1.01
9	Carpet	Acetone	5.0	99.2	0.021	23.8 ± 0.03	50.0 ± 1.1	20.3 ± 3.3	1.00
10	SS	Ammonia	1.3	99.2	0.207	23.4 ± 0.02	69.6 ± 1.3	20.4 ± 1.1	0.51
11	SS	Ammonia	1.3	99.1	0.202	23.4 ± 0.03	69.7 ± 0.8	20.3 ± 0.1	0.51

^a Air temperature, relative humidity, and liquid temperature are given as mean ± standard deviation for the first 5 h data.

^b SS, stainless steel sheet; vinyl, vinyl flooring.

Institute of Standards and Technology [10] with outliers discarded. The results are $1.49 \times 10^{-3} \pm 1.91 \times 10^{-4}$ ($n = 14$) for acetone and $6.69 \times 10^{-4} \pm 6.82 \times 10^{-5}$ ($n = 14$) for ammonia. Note that Henry's constants are reported in many different units. The values shown here are the dimensionless air/water partition coefficients (i.e., the concentration in air divided by the concentration in solution at equilibrium).

4.2.3. Calculated parameters

The gas-phase mass transfer coefficient for water vapor (k_{gw}) was calculated from the dimensionless Sherwood number (Sh) [11,12]:

$$Sh = \frac{k_{gw}L}{D_a} \quad (11)$$

where Sh is estimated from its correlations with Schmidt and Reynolds numbers. For instance, Eq. (12) is used for laminar flows [11]:

$$Sh = 0.664Sc^{1/3}Re^{1/2} \quad (12)$$

The overall liquid-phase mass transfer coefficient for the solute (K_{OL}) was calculated in two steps: first, calculating the liquid-phase mass transfer coefficient (k_{Ls}) by a method (Eq. (13)) proposed by Guo and Roache [13], and then calculating the overall liquid-phase mass transfer coefficient by its definition (Eq. (14)):

$$k_{Ls} = 2.99 D_L^{0.5} \quad (13)$$

where D_L is calculated by the Hayduk and Laudie method [14].

$$\frac{1}{K_{OL}} = \frac{1}{k_{Ls}} + \frac{1}{k_{gs}H} \quad (14)$$

The saturation concentration for water vapor (m_{sat}) at a given temperature was converted from water vapor pressure (P_{w0}) given by Eq. (15) [15]:

$$\log_{10} P_{w0} = a + \frac{b}{T} + c \log_{10} T + dT + eT^2 \quad (15)$$

Table 3
Predictive errors for peak, 1 h average, and 5 h average concentrations (mg/m^3)^a

Test ID	Peak			1 h average			5 h average		
	Observed	Modeled	Error (%)	Observed	Modeled	Error (%)	Observed	Modeled	Error (%)
1	295	223	-24	216	172	-20	70.6	61.7	13
2	275	217	-21	204	168	-17	66.3	60.7	-8.5
3	116	112	-3.6	91.0	85.4	-6.1	31.4	30.3	-3.5
4	128	124	-2.8	111	102	-7.3	57.1	55.3	-3.2
5	99.1	102	3.1	82.6	80.2	-2.9	31.7	29.8	-6
6	123	132	7.4	105	109	3.7	56.9	57.2	0.5
7	125	112	-9.8	107	90.5	-16	57.7	57.4	-0.5
8	163	136	-17	123	109	-12	47.3	47.3	0
9	71.6	53.2	-26	56.5	37.2	-34	31.1	28.2	-9.3
10 ^b	28.7	33.9	18	23.4	27.9	19	15.1	14.7	-2.9
11 ^b	29.8	34.0	14	26.3	28.1	6.7	15.9	14.8	-7.2

^a Predictive error = (modeled - observed)/observed \times 100%.

^b Observed concentrations are semi-quantitative in this test.

Table 2

Comparison of predicted concentrations by the differential equation model and the simplified model for Test 1 (concentration unit: mg/m^3)

Elapsed time (h)	Differential equation model	Simplified model	R.S.D.
Peak time	222	223	0.3%
1.0	141	136	2.6%
2.0	52.7	50.4	3.3%
5.0	2.65	2.51	3.8%

where P_{w0} is in (mmHg), T the temperature in (K), $a = 29.8605$, $b = -3.1522 \times 10^3$, $c = -7.3037$, $d = 2.4247 \times 10^{-9}$, and $e = 1.8090 \times 10^{-6}$.

These calculations are not difficult but rather tedious. In this work, computer program PARAMS was used [16]. This program can be downloaded from the U.S. EPA website <http://www.epa.gov/appcdwww/iemb/model.htm>. For the 11 tests listed in Table 1, k_{gw} ranged from 9.07 to 16.3 m/h, K_{OL} from 3.29×10^{-3} to 4.13×10^{-3} m/h, and m_{sat} from 16.5 to 20.1 g/m^3 .

4.3. Evaluation of the simplified model

When the differential equation model and the simplified model were applied to the chamber data, their difference was negligible (Table 2). Therefore, only the results of the simplified model are presented. Peak, 1 h average, and 5 h average concentrations calculated by the simplified model are compared to the chamber concentration data in Table 3. On average, the predicted error is 13.3% for the peak concentration, 13.2% for 1 h average and 4.9% for 5 h average. Figs. 2 and 3 show the two acetone experiments with the smallest and largest predictive errors; Fig. 4 shows the modeling result for one ammonia experiment.

Three statistical methods recommended by ASTM 5157-97 [17] were used to evaluate the model performance and the results are presented in Table 4. Normalized mean square error (NMSE) is an indicator of the overall performance of the model and normalized or fractional bias (FB) is for assessing the bias of the

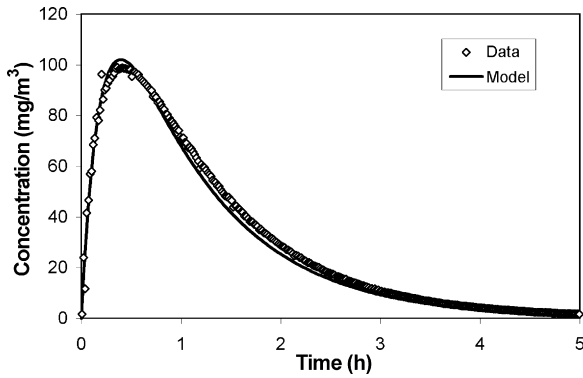


Fig. 2. Modeling result with the smallest predictive errors among the 11 tests (Test 5—acetone solution spilled on vinyl flooring).

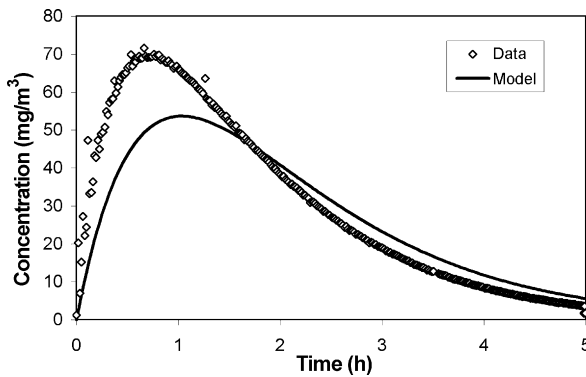


Fig. 3. Modeling result with the largest predictive errors among the 11 tests (Test 9—acetone solution spilled on carpet).

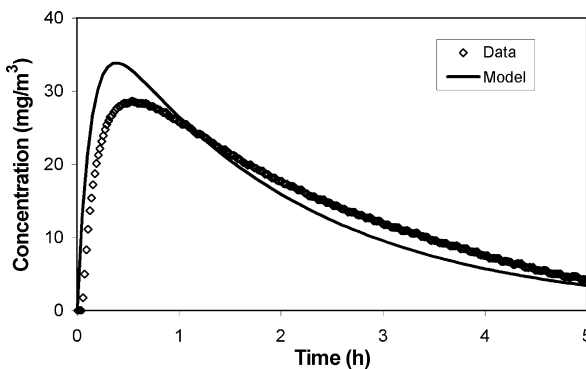


Fig. 4. Modeling result for Test 10 (ammonia solution spilled on carpet).

Table 4
Statistical evaluation of the proposed model

Test ID	NMSE	FB	FB ₁₀
1	0.150	-0.133	-0.223
2	0.104	-0.097	-0.180
3	0.004	-0.029	-0.039
4	0.006	-0.024	-0.043
5	0.009	-0.056	-0.016
6	0.021	-0.005	-0.116
7	0.026	0.003	-0.128
8	0.040	0.007	-0.114
9	0.101	-0.080	-0.308
10	0.047	-0.007	0.134
11	0.034	-0.059	0.088

model. To evaluate the bias in the high concentration range, bias in the mean of highest 10% of concentrations (FB₁₀) is also calculated. According to ASTM 5157-97, the following values are considered to be generally indicative of adequate model performance: NMSE ≤ 0.25, FB and FB₁₀ ≤ 0.25 (absolute value). As shown in Table 4, all the results are within the range of adequate performance except the FB₁₀ in Test 9 (acetone solution spilled on carpet). More discussion on applying the proposed model to fleecy surfaces such as carpet is provided in Section 5.4.

5. Discussion

5.1. The differential equation model versus the simplified model

The simplified model (Eqs. (9) and (10)) is a single-zone indoor air quality model. It is derived by assuming that the air in the room is well mixed. Therefore, the model gives the average concentration in the room. The simplified model is easier to use than the differential equation model and, thus, can be used as a range-finding tool.

The differential equation model (Eqs. (5)–(8)) requires the assistance of computational software, but is more flexible. For instance, it can be incorporated into indoor air quality models that contain air cleaning devices, surface adsorption, and indoor chemistry mechanisms; it can also be used in multi-zone indoor air quality models and computational fluid dynamic models. In addition, several parameters in the differential equation model can be treated as variables. For instance, the density of the liquid can change over time, and the two mass transfer coefficients (k_{gw} and K_{OL}) can be recalculated at each integration step to reflect the change in spill area. Thus, the differential equation model is more suitable for use in complex indoor air quality models such as multi-zone models.

5.2. Temperature drop of spilled liquid

On average, the temperature of the spilled liquid was 2–4 °C lower than the air temperature. An example of the temperature profiles are shown in Fig. 5.

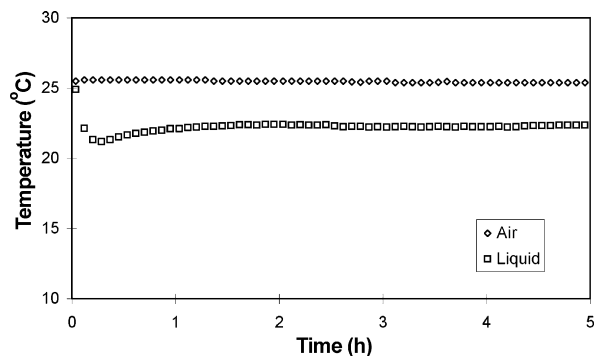


Fig. 5. Temperature drop of spilled liquid in Test 2 (10% acetone on stainless steel sheet).

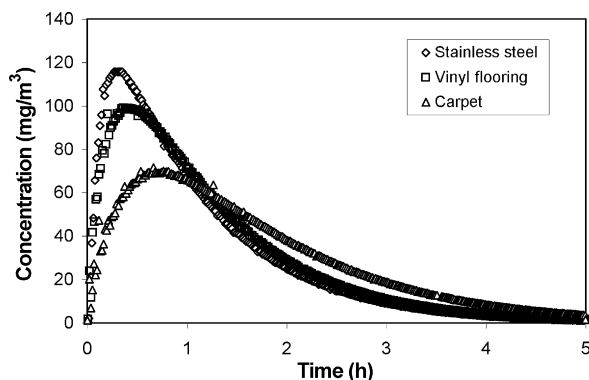


Fig. 6. The effect of substrate on indoor concentrations: stainless steel sheet (Test 3), vinyl flooring (Test 5), and carpet (Test 9).

5.3. Effect of flooring materials on spill area

The initial spill area is determined by many factors, including the properties of the surface (e.g., evenness, porosity, and wettability), the properties of the solution (e.g., viscosity and surface tension), and the release height, which affects the impact speed. It is observed that the area of spill on carpet is much smaller than on hard surfaces. Consequently, the peak concentration for carpet is much lower and appears later than stainless steel and vinyl flooring (Fig. 6).

5.4. Applying the proposed model to fleecy or porous surfaces

As shown in Tables 3 and 4, the proposed model gives greater predictive errors for the spill test on carpet (Test 9). This can be explained by the fact that, for fleecy surfaces, the actual liquid area is greater than that estimated by the digital imaging method. Adjusting the initial spill area can reduce the predictive errors significantly. For instance, increasing the initial spill area in Test 9 by a factor of 1.8 reduces the predicted error for the peak concentration from -26% to -2.4% (Fig. 7). It is therefore recommended that the concept of “effective liquid film thickness” be used for fleecy or porous surfaces. For instance, in test 9, the effective initial spill area is equivalent to 0.038 m^2 (0.021×1.8) hard surface. Since the liquid volume is 99.2 mL or

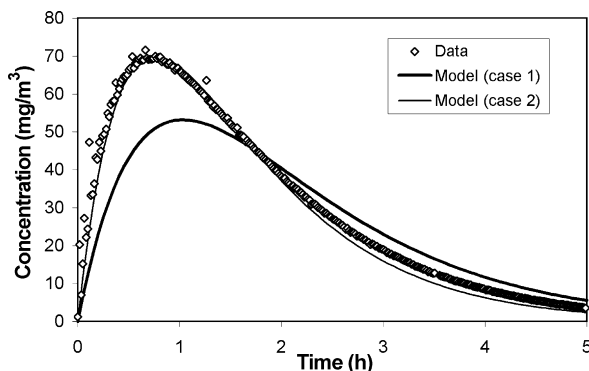


Fig. 7. Modeling results for spill of acetone solution on carpet (Test 9). Case 1: measured spill area; case 2: measured spill area multiplied by 1.8.

$9.92 \times 10^{-5} \text{ m}^3$, the effective liquid film thickness for the carpet tested is $9.92 \times 10^{-5} \text{ m}^3 / 0.038 \text{ m}^2 = 0.0026 \text{ m}$.

It is also observed that the spill area on carpet does not change significantly over time. Therefore, for fleecy or porous flooring materials, the spill area can be treated as a constant (i.e., $A = A_0$). Consequently, Eq. (10) can be simplified to:

$$q = \frac{K_{OL}}{\theta} \quad (16)$$

5.5. The liquid spreading process

It was observed that, when an aqueous solution is spilled onto the floor, it took approximately 1 min to reach the maximum area. The proposed model omits this spreading process by assuming that the maximum area occurs immediately after the spill. This omission causes the peak concentration in the room to appear slightly earlier. It is possible to add simulation of the spreading process to the differential equation model (Eqs. (5)–(8)). The simplified model cannot accommodate the liquid spreading process.

5.6. Data limitations

The results of model evaluation presented in this paper should be considered preliminary because (1) the spill volume was limited to 100 mL, (2) only two solutes were tested, and (3) the concentration range was also limited (1–10%).

5.7. Model limitations

The proposed model requires knowledge of Henry’s constant of the solute. Most Henry’s constants in the literature are determined with dilute solutions. In this work, solute concentrations ranged to 1–10%. The applicability of the Henry’s constants to even higher concentrations is yet to be evaluated. Furthermore, the proposed model may not be applicable at all to highly concentrated aqueous solutions such as fuming nitric acid.

5.8. Spill model based on activity coefficient

As described in Section 2.3, there are two approaches to modeling the rate of solute emissions from aqueous solutions, and the proposed model is based on the Henry’s constant and overall mass transfer coefficient. However, the model can be easily adapted to the activity coefficient approach. This can be done by replacing Eq. (4) with Eq. (17).

$$R_s = Ak_{gs}(\gamma x_L C_{\text{sat}} - C) \quad (17)$$

The spill model based on Eq. (17) may be more useful for complex aqueous solutions if the activity coefficient for the solute of interest (γ) is known.

5.9. Future research needs

To further evaluate the proposed model, the following experiments are recommended: (1) experiments with greater spill

volumes (e.g., in the range of 1 to 2 L), (2) experiments with a broad range of flooring materials, (3) experiments with chemicals covering a broader range of Henry's constants, and (4) experiments with high solute concentrations.

6. Conclusion

A mass transfer model is proposed to predict the concentrations of hazardous chemicals inside buildings following spills of aqueous solutions. The model is presented in two forms: a system of differential equations and a simplified exact solution. The former is more flexible while the latter easier to use. All parameters required from the user can be readily obtained. Preliminary evaluation with data from large chamber experiments shows satisfactory performance for hard surfaces. The model underestimated the peak concentrations by 26% for the spill on carpet because the actual emitting area is greater than the wet area captured by the digital camera. Such underestimation can be corrected by introducing the concept of "effective liquid film thickness". To make the proposed model more useful in emergency response planning, the effective liquid film thicknesses for different flooring materials should be determined.

Appendix A. Derivation of the simplified model

A.1. The differential equation model

The differential equation model described in Section 2 in the main body is given as Eqs. (A1)–(A5) below.

$$\begin{aligned} \frac{dW}{dt} &= -R_w - R_s \\ &= -A k_{gw}(x_w m_{sat} - m) - A K_{OL} \left(C_L - \frac{C}{H} \right) \end{aligned} \quad (A1)$$

$$V \frac{dm}{dt} = A k_{gw}(x_w m_{sat} - m) + Q(m_{out} - m) \quad (A2)$$

$$V_L \frac{dC_L}{dt} = -R_s = -A K_{OL} \left(C_L - \frac{C}{H} \right) \quad (A3)$$

$$V \frac{dC}{dt} = R_s - Q C = A K_{OL} \left(C_L - \frac{C}{H} \right) - Q C \quad (A4)$$

where

$$A = A_0 \frac{W}{W_0} \quad (A5)$$

A.2. Exact solution for the area of liquid film (A)

If the rate of water evaporation is much greater than that of the solute (i.e., $R_w \gg R_s$), Eq. (A1) can be simplified to:

$$\frac{dW}{dt} = -R_w = -A k_{gw}(x_w m_{sat} - m) \quad (A6)$$

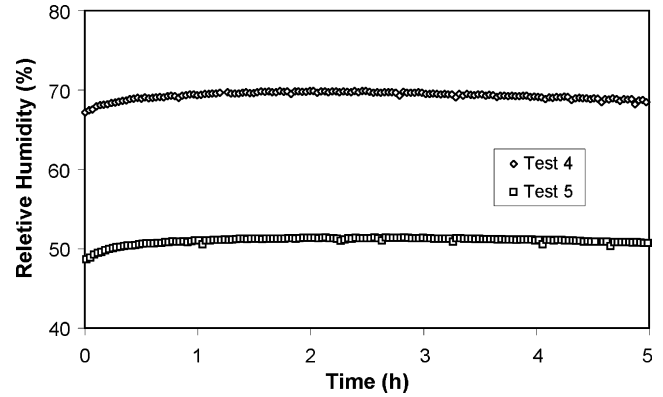


Fig. A1. Relative humidity in chamber tests 4 and 5.

For dilute solutions (e.g., $x_w > 0.9$), Eq. (A6) can be further simplified to:

$$\frac{dW}{dt} = -A k_{gw}(m_{sat} - m) \quad (A7)$$

Furthermore, if the moisture content in the building (i.e., m in Eq. (A7)) is approximately constant and is not significantly affected by the evaporation water from spilled solution (see experimental results in Fig. A1), Eq. (A2) is no longer needed, and Eq. (A7) can be rewritten:

$$\frac{dW}{dt} = -A k_{gw} m_{sat} (1 - r_h) \quad (A8)$$

where r_h is a constant. Substituting Eq. (A5) into (A8):

$$\frac{dW}{dt} = -A_0 \frac{W}{W_0} k_{gw} m_{sat} (1 - r_h) \quad (A9)$$

Given the initial conditions $t=0$ and $W=W_0$, Eq. (A9) can be solved:

$$W = W_0 e^{-pt} \quad (A10)$$

where

$$p = \frac{A_0 k_{gw} m_{sat} (1 - r_h)}{W_0} \quad (A11)$$

Substituting Eq. (A10) into Eq. (A5) gives:

$$A = A_0 e^{-pt} \quad (A12)$$

A.3. Exact solution for solute concentration in the liquid-phase

If the concentration of the solute in indoor air is far below its equilibrium concentration (i.e., $C_L \gg C/H$ in Eq. (A3)), the term C/H can be ignored (see Appendix B for justification). Eq. (A3) then becomes:

$$V_L \frac{dC_L}{dt} = -A K_{OL} C_L \quad (A13)$$

Rearranging Eq. (A13) yields:

$$\frac{dC_L}{dt} = -\frac{K_{OL} C_L}{\theta} \quad (A14)$$

where $\theta = V_L/A$.

Note that the liquid film thickness (θ) is a constant as explained in Section 2.1. Given the initial concentrations $t=0$ and $C_L = C_{L0}$, Eq. (A14) can be solved:

$$C_L = C_{L0} e^{K_{OL}t/\theta} \quad (\text{A15})$$

A.4. Exact solution for pollutant concentration in indoor air

Similar simplification can be made to Eq. (A4) by ignoring the term C/H :

$$V \frac{dC}{dt} = AK_{OL}C_L - QC \quad (\text{A16})$$

Substituting Eqs. (A12) and (A15) into (A16):

$$V \frac{dC}{dt} = A_0 e^{-pt} K_{OL} C_{L0} e^{-(K_{OL}/\theta)t} - QC \quad (\text{A17})$$

or

$$V \frac{dC}{dt} = A_0 K_{OL} C_{L0} e^{-(p+K_{OL}/\theta)t} - QC \quad (\text{A18})$$

Given the initial conditions $t=0$ and $C=0$, Eq. (A18) gives:

$$C = \frac{A_0 K_{OL} C_{L0}}{V(q-N)} (e^{-Nt} - e^{-qt}) \quad (\text{A19})$$

where $N=Q/V$ is the air change rate and q is given by:

$$q = p + \frac{K_{OL}}{\theta} = \frac{A_0 k_{gw} m_{sat} (1 - r_h)}{W_0} + \frac{K_{OL}}{\theta} \quad (\text{A20})$$

Appendix B. Comparison of solute concentration in indoor air with its equilibrium concentration

In deriving the exact solution for the solute concentration in indoor air, it is assumed that the solute concentration in indoor air is far below its concentration equilibrated with the liquid-phase (Section A.3 of Appendix A). Justification for such assumption is given below.

B.1. Air concentration in equilibrium with the liquid-phase

According the definition of Henry's constant, the air concentration can be calculated by Eq. (B1) at equilibrium conditions:

$$C_\infty = HC_L \quad (\text{B1})$$

B.2. Air concentration under the steady-state condition

The solute concentration in indoor air is given by Eq. (B2) (i.e., Eq. (5) in the main body).

$$V \frac{dC}{dt} = A_0 K_{OL} \left(C_L - \frac{C}{H} \right) - QC \quad (\text{B2})$$

At steady state, the left-hand side becomes zero:

$$C = \frac{A_0 K_{OL} H}{A_0 K_{OL} + QH} C_L \quad (\text{B3})$$

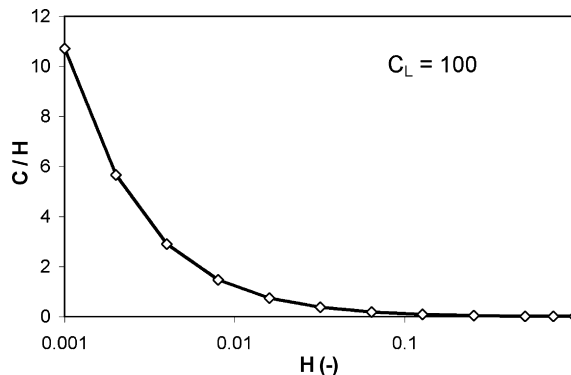


Fig. B1. The steady-state C/H values as function of H ($C_L = 100 \text{ g/m}^3$).

B.3. Comparing C/H with C_L

The following “typical” values are used as an example to compute the values of C/H by using Eq. (B3): $A_0 = 2 \text{ m}^2$, $K_{OL} = 0.003 \text{ m/h}$, and $Q = 100 \text{ m}^3$ (1 air change per hour for a 100 m^3 room). As shown in Fig. B1, with Henry's constant ranging from 0.001 to 1, the C/H ratio is less than 11% of the solute concentration in liquid-phase. Thus, the term C/H in Eq. (B2) can be ignored.

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