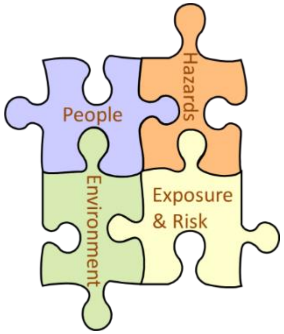
INTRODUCTION TO MATHEMATICAL MODELS AND IH MOD 2.0
IN FOUR PARTS

Tom Armstrong, CIH, PhD
TWA8HR Occupational Hygiene Consulting, LLC
twa8hr@gmail.hcom

Daniel Drolet
Retired
Daniel.drolet@sympatico.ca

With contributions by many members of the
Exposure Assessment Strategies Committee, especially Mike Jayjock

UNDERSTANDING EXPOSURES AND HEALTH RISKS,
PAST, PRESENT AND FUTURE



WE WILL COVER THE FOLLOWING ASPECTS

Part 1. Brief review of physical and chemical theory supporting modeling to estimate exposures

Part 2. Estimation of Contaminant Generation Rates

Part 3. Estimation of and sources of information on work space ventilation, random air velocities and turbulent diffusion coefficients

Part 4. Contents, navigation, layout and examples of use of IH Mod 2.0

- **Interpreting the results from IH Mod 2.0**
- **Case studies using IH Mod 2.0 for selected occupational and consumer exposure scenarios**

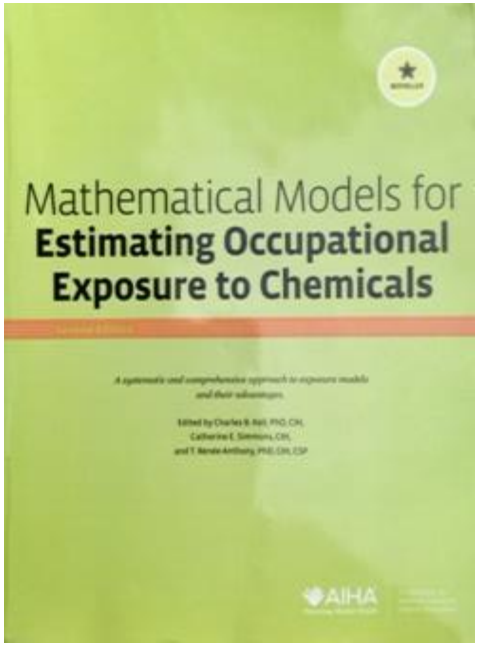
IH Mod 2.0 REQUIRES a version of MS Excel. It will not run in other spreadsheet software

Any fairly recent computer with MS Excel will suffice, including Apple computers with Excel for MAC. I ran IH Mod 2.0 OK but a bit slowly on a 10 + year old netbook with an Atom processor and 2 GB Ram. You will need to enable MACROS in Excel. In some corporate of government operations, you may need to see Computer Support for administrative rights help/

WHAT IS A MODEL AND WHY ARE THEY IMPORTANT IN EXPOSURE ASSESSMENTS?

- **In our context, models are mathematical equations that can estimate the concentration of a contaminant in a work space based on physical and chemical input parameters**
- **Modeling is a way to estimate exposures when we cannot measure, for example in the past, or to anticipate future exposures**
- **Understanding the mathematical models also helps us to better understand the influence of main exposure determinants, such the substance vapor pressure, quantity released to air, workspace volume, workspace ventilation, worker proximity to the source, and more.**
- **IH Mod was developed for task based exposure estimation, and is relevant for many consumer and occupational scenarios**

This book is an important companion to IH Mod 2.0


Mathematical Models for
Estimating Occupational
Exposure to Chemicals

A concise guide to the models

Keil CB., Simmons CE., Anthony TR. ***Mathematical Models for Estimating Occupational Exposure to Chemicals.*** 2nd ed. AIHA Press, Fairfax, VA, 2009.

REVIEW OF A FEW PHYSICAL AND CHEMICAL PRINCIPLES RELATED TO EXPOSURE MODELING

IF YOU NEED MORE DETAILS THAN GIVEN HERE, THERE'S A LOT OF TUTORIALS AVAILABLE ON YOUTUBE

FROM HIGH SCHOOL AND COLLEGE GENERAL CHEMISTRY

Combined Gas Law to adjust to different pressures and temperatures **Remember, consistent units**

$$\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2}$$

Chemical Vapor Pressure (VP)

Equilibrium Vapor Pressure <= Saturation Vapor Pressure

The partial pressure (Pv) of gas-phase chemical molecules in the headspace of a sealed inert vessel at equilibrium is the chemical's vapor pressure, equilibrium vapor pressure, or saturation vapor pressure.

A convenient on-line source of P_V values (at 20 C= 68 F) is the NIOSH "Pocket Guide for Chemical Hazards": http://www.cdc.gov/niosh/npg/npgd0000.html

A discussion of sources of P_V values is presented in Appendix II, "Mathematical Models for Estimating Occupational Exposure to Chemicals," AIHA Exposure Assessment Strategies Committee

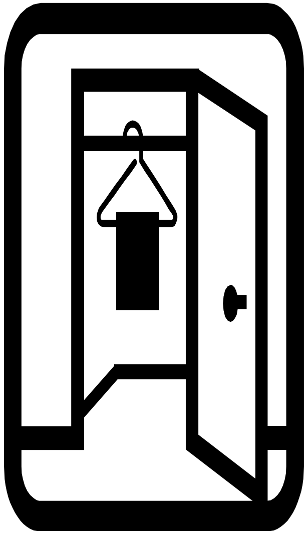
FROM HIGH SCHOOL AND COLLEGE GENERAL CHEMISTRY (CONTINUED)

- The concentration of saturated vapor Csat is an important to know "upper bound" (usually) on exposure concentration

- A chemical's P_V value increases as the temperature of the system increases.
  For benzene: P_V = 75 mm Hg at 20 C and P_V = 96 mm Hg at 25 C so 95/75 = 1.3 X higher at 25 C
- Look up the Clausius–Clapeyron or Antoine equation or Wagner equation if you need P_V at other temperatures. See Appendix II of "Mathematical Models …"
- Different chemicals will have different Antoine coefficients and thus different Pv vs T curves
- See a discussion with benzene as the example at: https://www.youtube.com/watch?v=YxplklxQDml

AN EXAMPLE OF APPLYING THE SATURATION VAPOR PRESSURE MODEL

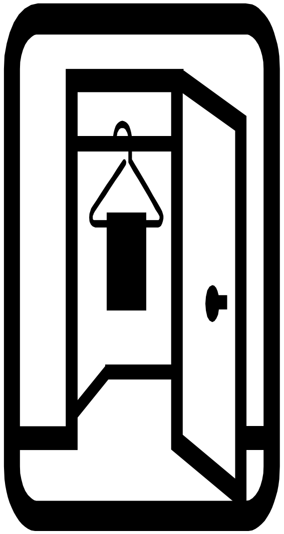
- **An opened 500 gram package of 1,4-dichlorobenzene moth balls is spilled and left in a tight closet.**
- **The closet has a tight sealing door and a volume of 3 cubic meters with no ventilation.**
- **A homeowner opens the door and gets exposed to the closet air.**
- **If at saturation what is the ppm concentration of 1,4-dichlorobenzene the person was exposed to in the first few breaths?**



AN EXAMPLE OF APPLYING THE SATURATION VAPOR PRESSURE MODEL

We can assume:

- **The person was exposed to a saturated concentration of 1,4-dichlorobenzene at 25 C.**
- **This implicitly assumes**
  - **Equilibrium vapor pressure was attained in the closet, <u>and</u>**
  - **The contaminated air was *not* significantly diluted by room air prior to inhalation**
- **The chemical formula is $C_6H_4Cl_2$ and the molecular weight is 147 g/mol.**
- **The vapor pressure is 1.36 mm Hg at 25 °C**
- **Csat (ppm) = [1.36*10^6]/760 = 1790 ppm (10,800 mg/m^3)**



By mass balance is this possible? Yes. 500 grams = 500,000 mg in 3 m^3

SATURATION VAPOR PRESSURE OF A COMPONENT IN A MIXTURE

Raoult's "Rule" Commonly called Raoult's LAW

Chemical A is a component in a liquid mixture.

- Chemical A has a molecular structure similar to the other mixture components.
  - X_A denotes the mole fraction of A in the liquid.
    - # Moles$_A$ = (grams$_A$ / molecular weight$_A$)
    - Mole fraction$_A$ = (#Moles$_A$ / Sum of all Moles of all constituents)
  - $P_{V,A}$ denotes the saturation vapor pressure of pure chemical A
- In a closed system of air and excess liquid chemical, the *partial pressure* of chemical A's vapor in the airspace, denoted P_A, is given by:

$$P_A = X_A \cdot P_{V,A}$$

AN EXAMPLE

A solvent of mixed xylenes with 15% methylene chloride (MeCl) by weight --- (not a really similar compound mixture, but let us look at it)

What is C_{sat} for MeCl?

determine the mole fractions

- **MW: MeCl = 84.9 g/mol, Xylene = 106 g/mol**
- **In 100 g,**
  - **15 g ÷ 84.9 g/mol = 0.18 moles MeCl**
  - **85 g ÷ 106 g/mol = 0.80 moles xylene**
  - **Total 0.98 moles**
- **Mole Fraction MeCl = 0.18/0.98 = 0.18**
- **Mole Fraction xylenes = 0.80/0.98 = 0.82**

AN EXAMPLE… STEPS 2 AND 3

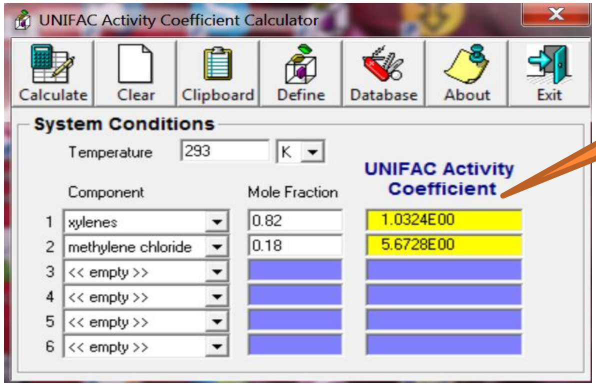
STEP 2: Saturation vapor pressures of

- **MeCl is 350 torr at 20 °C**
- **Xylenes 7 torr at 20 °C**

STEP 3: Activity Coefficient?

- **Not a very pure mixture, neither X_{MeCl} and $X_{xylenes}$ approach 0.99….**
- **Use UNIFAC Calculator (a general method)… or alternate methods**
- **Measured activity coefficients are best but UNIFAC estimates are OK, but there are limits to UNIFAC … do not use for mixtures containing polymers or for electrolyte mixtures. Do not use at more than a few atmospheres of pressure or above 150 °C**

ACTIVITY COEFFICIENT EXAMPLE 15% BY WEIGHT METHYLENE CHLORIDE IN MIXED XYLENES

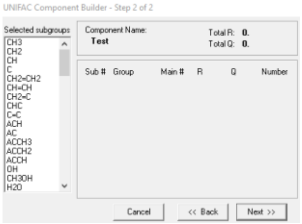


System Conditions

Temperature 293 K

	Component	Mole Fraction	UNIFAC Activity Coefficient
1	xylenes	0.82	1.0324E00
2	methylene chloride	0.18	5.6728E00
3	<< empty >>		
4	<< empty >>		
5	<< empty >>		
6	<< empty >>		

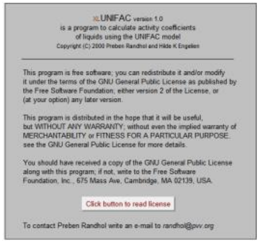
Note the exponents!



Component Name: **Test**

Total R: 0.
Total Q: 0.

This older but reliable calculator has become hard to find. Write to me twa8hr@gmail.com for a copy, or download from this Dropbox link.
Link to Dropbox for UNIFACAL.exe copy



XLUNIFAC version 1.0
is a program to calculate activity coefficients
of liquids using the UNIFAC model
Copyright (C) 2000 Preben Randhol and Hilde K Engelien

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To contact Preben Randhol write an e-mail to randhol@pvv.org

Or an Excel tool from The Netherlands
Link to Spreadsheet, XLUnifac

Also see Mike Jayjock's coverage in his BLOG:
Activity Coefficients an UNIFAC Calculator or From The Netherlands, XLunifac

In this example, both components deviate high, to different extents. In other mixtures, some deviations may be downward.

AN EXAMPLE

Apply Raoult's Rule to estimate MeCl vapor pressure in a mixture with xylenes

- ***Without Activity Coefficient***

$$P_A = X_A \times P_{V,A} = 0.18 \times 350 = 63 \text{ torr}$$

$$C_{sat} = 63 \text{ torr} \times 10^6 \div 760 \text{ torr} = 83{,}000 \text{ ppm}$$

- ***With* Activity Coefficient**

$$P_A = X_A \times P_{V,A} \times A_{coef} = 0.18 \times 350 \times 5.7 = 360 \text{ torr}$$

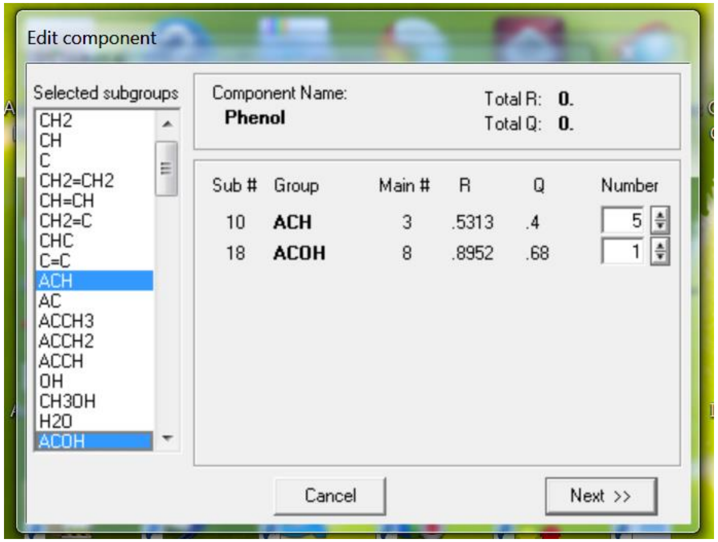
$$C_{sat} = 360 \text{ torr} \times 10^6 \div 760 \text{ torr} = 470{,}000 \text{ ppm}$$

Hmm! Might the difference of 5.7 x be IMPORTANT?!

BUILDING MOLECULES IN THE UNIFAC CALCULATOR

- See http://www.aim.env.uea.ac.uk/aim/info/UNIFACgroups.html for more information on molecular fragment contributions
- Example Phenol. 5 x ACH & 1 x ACOH It is then added to the local database
- This freeware calculator does not include all possible molecular groups.
- Unfortunately, we do not have time to talk much about the compound database or how to add new compounds.

Call or write to me after the course. The XLUnifac Spreadsheet takes a bit of study to use



Component Name: Phenol

Total R: 0.

Total Q: 0.

Sub #	Group	Main #	R	Q	Number
10	ACH	3	.5313	.4	5
18	ACOH	8	.8952	.68	1

SUMMARY: WHAT DID WE JUST LEARN?

If we have pure liquid in equilibrium:

- **Find the vapor pressure (at your temperature)**
- **Compute Saturation Concentration:**
  - C_{sat} **in PPM =** $P_v / 760\text{mm Hg} \times 10^6$
  - **If in *sealed* room or space, adjust denominator for the increase in pressure by the substance… (very very rarely necessary)**
    - $C_{sat} = (P_v * 10^6)/(760\text{mm Hg} + P_v)$

If we have a mixture

- **Use Raoult's law if the target chemical makes up >99% … or use if >90% *and* is similar to other components:**

  $$P_A = X_A \cdot P_{V,A}$$

- **Or use Raoult's Rule with Known or Estimated Activity Coefficients if <90 to 99% or dissimilar (differing polarity or differing homologous series) materials**

- **Use Henry's law if chemical exists in small proportion (<0.1%) and is in aqueous solution:**

$$H_A = \frac{C_A(\text{air})}{C_A(\text{aq})}$$

Henry's Law can be used for non-aqueous systems, but few non-aqueous system coefficients are available. Watch units when you look up H_A values.

PART 2.

MASS BALANCE, EVAPORATION RATES, GENERATION RATES, AND THEIR CALCULATION

WITHIN ALL TYPES OF EMISSION:

There is always some consideration of the time course of contaminant generation.

- **Instantaneous (or approximately so)**
- **Constant (infinitely replenished) – (evap/inject)**
  - **Spill within containment**
  - **Vapor leak – constant pressure or limiting orifice**
  - **Slowly filling a partially full gasoline container**
- **Decreasing**
  - **Evaporation – decreasing in size or concentration**
    - **Spill after source is off- resulting in a shrinking pool**
    - **More volatile component of mixture in a pool.**
  - **Vapor leak – decreasing pressure**

IH MOD 2.0 HANDLES THE FOLLOWING:

- **The Rate of Emission is Constant.**
  - **Sometimes called "zero order"**
- **The Emission Rate is Decreasing with Time**
  - **Some models in IH MOD can handle "first order" decreases in the source and require a value for k in G = G_0 (-exp kt)**
  - **Example: a spill with shrinking diameter**
- **The Emission is a Bolus or considered an instantaneous finite release in SOME of the Eddy Diffusion Models.**

This will handle the BULK of what you want to do; however, if you want or need to get more sophisticated you will probably need a more advanced modeling platform like MathCAD or MATLAB or more specific advanced models.

Often, for a time-varying generation rate, an average or a maximum can be sufficient

ESTIMATING G BY A MATERIAL MASS BALANCE

Simple Material Mass Balance can be a useful estimate for a generation rate:

$$G = \frac{\text{Mass (mg) emitted into air in interval T}}{\text{T (min)}}$$

- **Example of the Material Mass Balance**
  - 20 ml of adhesive containing 15% toluene vol/vol is used per 15 minute task. **All** the toluene is assumed to evaporate.
  - Toluene's liquid density is 0.866 g/mL
  - What is G or the average rate of release over T?
- **Answer**
  - 20 ml x 0.15 = 3 mL toluene
  - 3 mL x (866 mg/mL) = 2600 mg toluene
  - G = (2600 mg/15 min) = 173 mg/min

- Example 2. 1 kg of a degreasing solvent is lost over an 8 hour day (by how much is added to keep the degreaser at full.

1000 grams/480 minutes = 2.1 grams/minute = 2100 mg/min

Tom Armstrong WWW.TWA8HR.com

ESTIMATING G BY RATE OF INJECTION INTO AIR

Again,

$$G = \frac{\text{Mass (mg) emitted into air in interval T}}{\text{T (min)}}$$

- **Examples of Injection:**
  - **Hair Spray: 5 grams of isopropanol per 2 seconds in a 1 m^3 sphere around the mouth and nose of the User.**
  - **Container Filling: Volume of the container is displaced into the air with vapors from the filling liquid. Example: pouring gasoline into a lawn tractor tank.**
  - **Sanding, sawing, sweeping or other ways of throwing particulate into the air.**

HYPOTHETICAL EXAMPLE: a metal finishing operation involves fine polishing. By before and after weighing of parts, 0.1% of the mass is lost. If 100 kg polished, 0.1 kg is released. If respirable, 100 grams/480 minutes =

0.21 grams/minute = 208 mg/min

ESTIMATING G BY EVAPORATION FROM A SMALL SPILL ALGORITHM FOR PREDICTING THE VAPOR MASS EMISSION RATE FROM A PURE LIQUID SURFACE

Hummel: $$G = \frac{165.6\ MW^{0.833}\, P_V \left(0.0345 + \frac{1}{MW}\right)^{0.25} A}{T^{.05}} \sqrt{\frac{U}{L\, P_{atm}}}$$

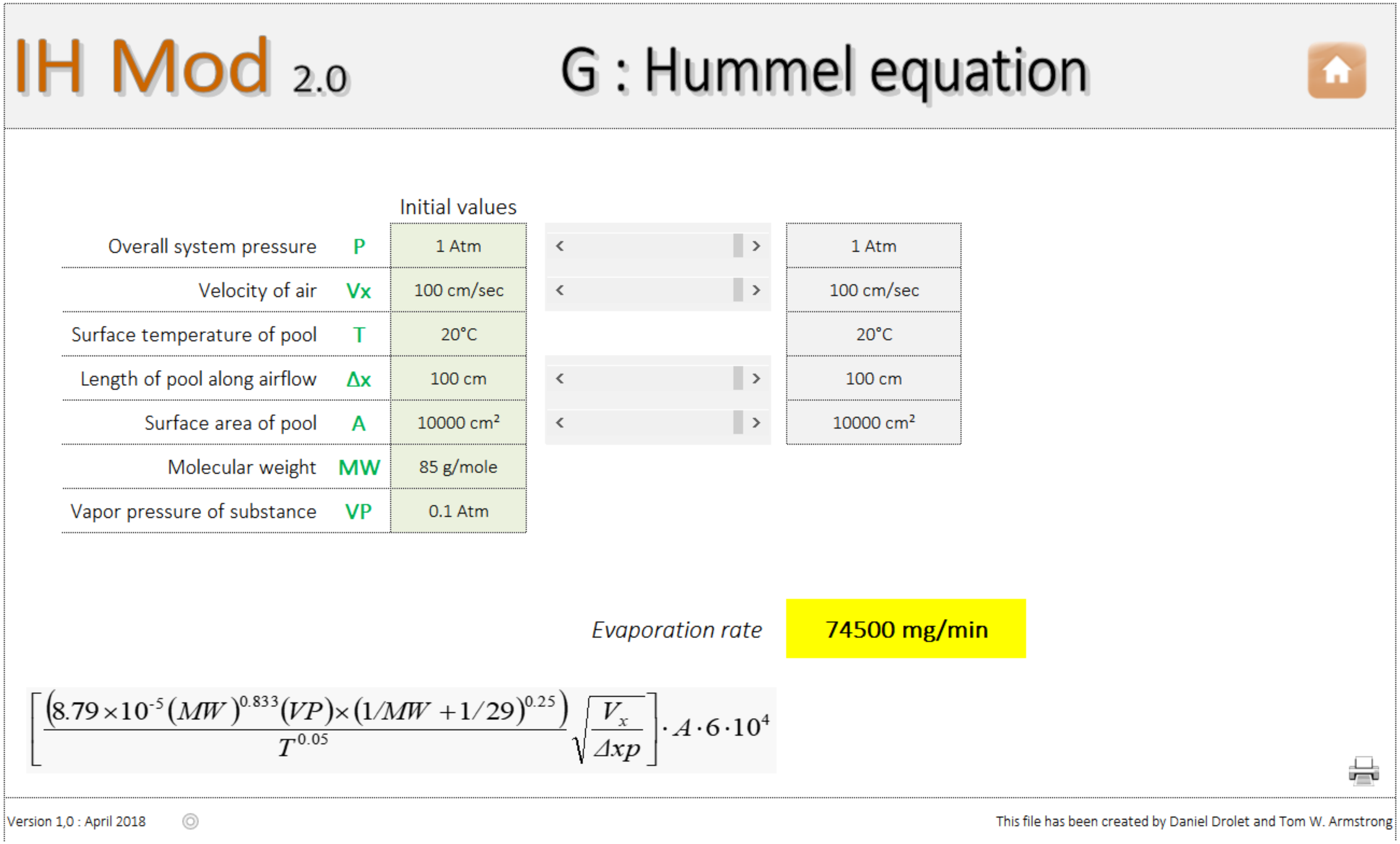
G = vapor emission rate (mg/min)
D_M = molecular diffusion coefficient in air (m^2/sec)
ν = kinematic viscosity of air (m^2/sec)… 1.52×10^{-5} @ 20 C; 1.56×10^{-5} @ 25 C (m^2/s)
U = air speed over the liquid pool (m/sec)
P_v = vapor pressure of evaporating chemical (Pascal, Pa)
P_{atm} = atmospheric pressure (Pa) [note: 1 atm = 101,325 Pa]
R = ideal gas constant, 8.314 $Pa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}$
MW = molecular weight of the chemical (g/mol)
A = surface area of liquid pool (m^2)
L = surface length of liquid pool (m) *along airflow direction*
T = temperature of the liquid (K)

Hummel, Braun & Fehrenbacher
American Industrial Hygiene Association Journal
Volume 57, 1996 - Issue 6 pp 519-525

HUMMEL VAPOR EMISSION RATE ALGORITHM ASSUMPTIONS

- If we assume that the liquid temperature and pool size are **constant** as evaporation proceeds, this algorithm predicts a **constant vapor mass emission rate**.
- For simplicity, a **constant temperature** and constant **liquid pool size** are frequently assumed in generation rate algorithms and experiments.
  - These factors may ***not*** be constant.
  - Why?
- If the liquid's temperature and/or surface area **decrease** as evaporation proceeds, the vapor mass emission rate will also decrease. Sometimes all you really need though is an INITIAL Generation rate
- VP is limited to 0.05 atm or 38 mm Hg

HUMMEL IN IH MOD SUPPORT FILE TYPICAL WORKPLACE CONDITIONS SMALL SPILL
NOTE UNITS USED! UNIT CONVERTER IN SUPPORT FILE



G : Hummel equation

		Initial values		
Overall system pressure	P	1 Atm	< >	1 Atm
Velocity of air	Vx	100 cm/sec	< >	100 cm/sec
Surface temperature of pool	T	20°C		20°C
Length of pool along airflow	Δx	100 cm	< >	100 cm
Surface area of pool	A	10000 cm²	< >	10000 cm²
Molecular weight	MW	85 g/mole		
Vapor pressure of substance	VP	0.1 Atm		

Evaporation rate **74500 mg/min**

$$\left[\frac{\left(8.79\times10^{-5}(MW)^{0.833}(VP)\times(1/MW+1/29)^{0.25}\right)}{T^{0.05}}\sqrt{\frac{V_x}{\Delta xp}}\right]\cdot A\cdot 6\cdot 10^{4}$$

Version 1,0 : April 2018

This file has been created by Daniel Drolet and Tom W. Armstrong

Tom Armstrong WWW.TWA8HR.com

HOW GOOD IS THIS? VALIDATION FROM HUMMEL
THEORY = EQ 18 HUMMEL MANUSCRIPT

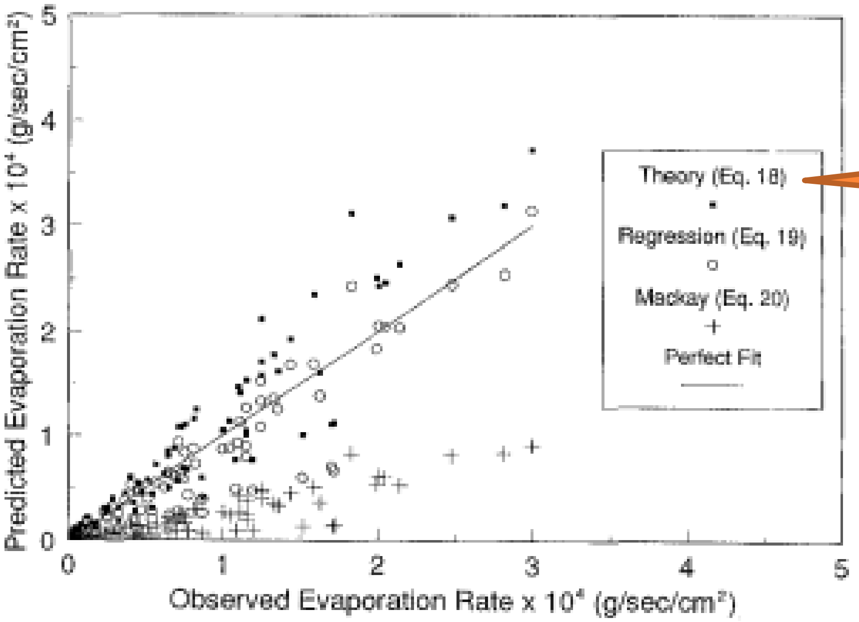


FIGURE 5. Comparison of the predicted versus observed experimental evaporation rates for the theoretical equation, a regression fit, and the Mackay equations

The black dots are the Hummel equation predictions

I have wondered how well this would do for an initial evaporation rate for a substance in a mixture if the mole fraction and activity coefficient were applied to get the partial pressure of the substance in the mixture. I may have missed it but I am not aware of reports on this.

HOW DO I GET G IF?

- You are dealing with a particulate (e.g., dust from a power saw)?
  - Determine by experimental measurements
  - Back calculate from a survey report
  - Apply a “dustiness index”*
- You can not live with the limitation of Hummel? That is, must be a pure substance, must have VP less than .05 atm, or need better than “Ball Park” accuracy as described by the authors of the Hummel model.
  - Maybe estimate based on relative evaporation rate from an OK compound.
  - Determine experimentally or back calculate from a survey

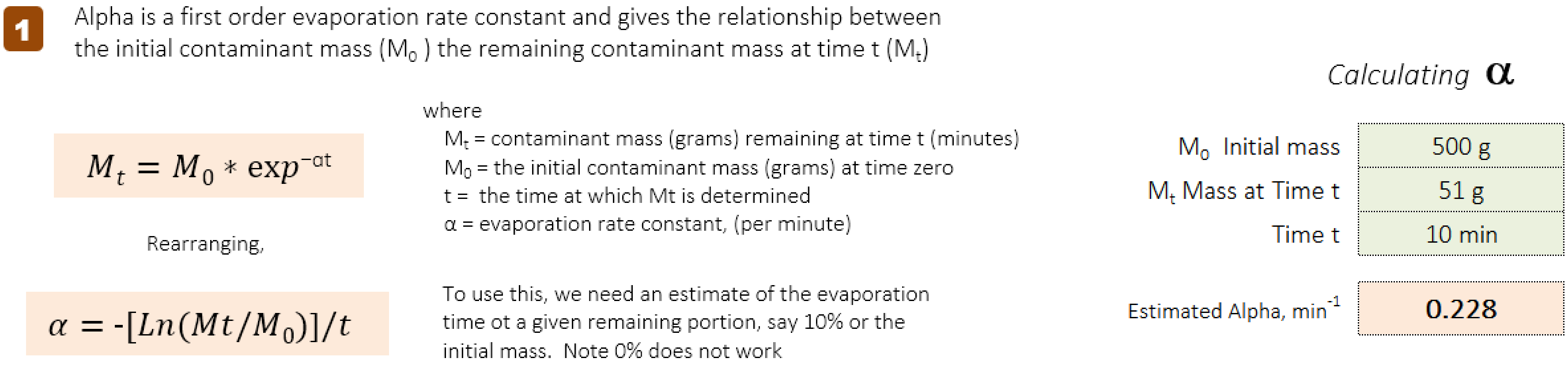
***Schneider and Jensen, 2009 Relevance of aerosol dynamics and dustiness for personal exposure to manufactured nanoparticles. J. Nanopart. Res. 11, 1637–1650.**

*** Levin et al., 2014 Release and exposure assessment of four pharmaceutical powders based on dustiness and evaluation of damaged HEPA filters. J. Occup. Environ. Hyg. 11, 165–177.**

RELATIVE EVAPORATION RATE

- If you have a generation rate for a chemical with a published relative evaporation rate, you can use this to estimate the generation rate for another chemical with a published evaporation rate.
- This is shown in the IH Mod 2.0 Support File for estimating Alpha (See next slide) but can be used for a “relative” generation rate too
- This could be very useful when the chemical of interest is very toxic or otherwise hazardous
- The Hummel generation rate appears to give the right “order of magnitude” or better and is generally conservative but has an increasing error above its stated VP limits.

FIRST ORDER EVAPORATION RATE CONSTANT (AKA ALPHA IN IH MOD 2.0), AS GIVEN IN THE IH MOD 2.0 SUPPORT FILE



1 Alpha is a first order evaporation rate constant and gives the relationship between the initial contaminant mass (M_0) the remaining contaminant mass at time t (M_t)

$$M_t = M_0 * \exp^{-\alpha t}$$

where
M_t = contaminant mass (grams) remaining at time t (minutes)
M_0 = the initial contaminant mass (grams) at time zero
t = the time at which Mt is determined
α = evaporation rate constant, (per minute)

Rearranging,

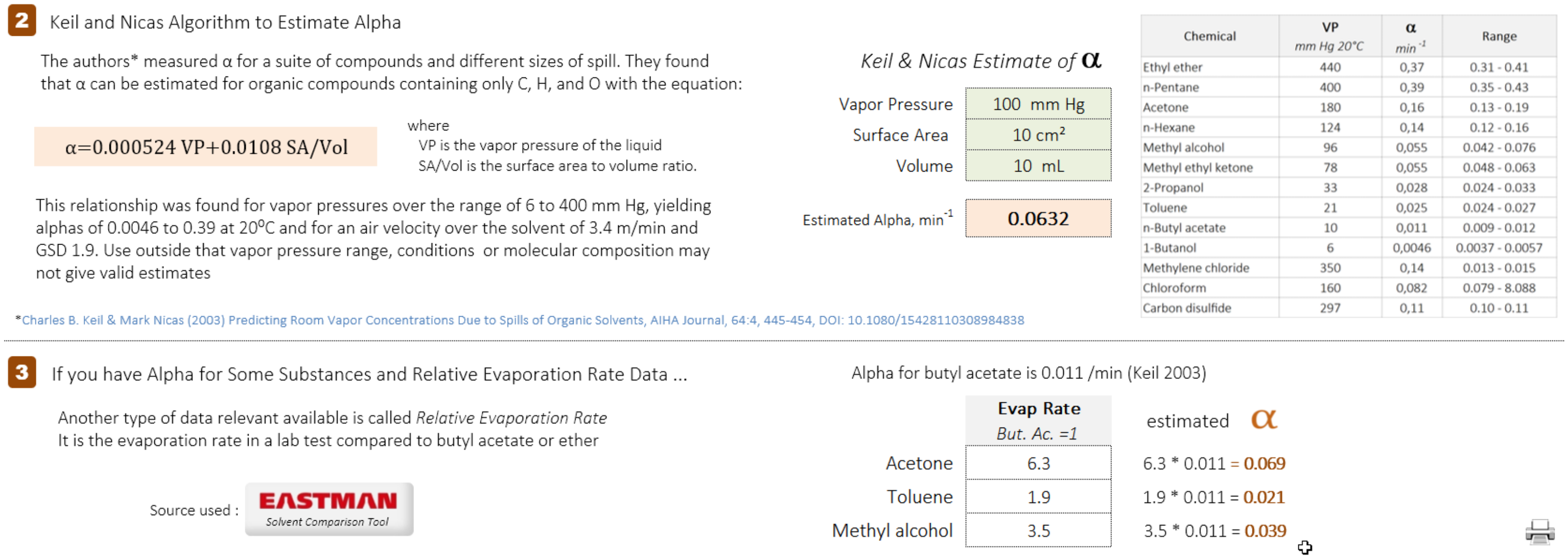
$$\alpha = -[Ln(Mt/M_0)]/t$$

To use this, we need an estimate of the evaporation time ot a given remaining portion, say 10% or the initial mass. Note 0% does not work

Calculating α

M_0 Initial mass	500 g
M_t Mass at Time t	51 g
Time t	10 min
Estimated Alpha, min^{-1}	0.228

ALPHA CONTINUED (FROM IH MOD 2.0 SUPPORT FILE)



2 Keil and Nicas Algorithm to Estimate Alpha

The authors* measured α for a suite of compounds and different sizes of spill. They found that α can be estimated for organic compounds containing only C, H, and O with the equation:

$$\alpha = 0.000524\ VP + 0.0108\ SA/Vol$$

where
VP is the vapor pressure of the liquid
SA/Vol is the surface area to volume ratio.

This relationship was found for vapor pressures over the range of 6 to 400 mm Hg, yielding alphas of 0.0046 to 0.39 at 20°C and for an air velocity over the solvent of 3.4 m/min and GSD 1.9. Use outside that vapor pressure range, conditions or molecular composition may not give valid estimates

Keil & Nicas Estimate of α

Vapor Pressure	100 mm Hg
Surface Area	10 cm^2
Volume	10 mL
Estimated Alpha, min^{-1}	0.0632

Chemical	VP mm Hg 20°C	α min^{-1}	Range
Ethyl ether	440	0,37	0.31 - 0.41
n-Pentane	400	0,39	0.35 - 0.43
Acetone	180	0,16	0.13 - 0.19
n-Hexane	124	0,14	0.12 - 0.16
Methyl alcohol	96	0,055	0.042 - 0.076
Methyl ethyl ketone	78	0,055	0.048 - 0.063
2-Propanol	33	0,028	0.024 - 0.033
Toluene	21	0,025	0.024 - 0.027
n-Butyl acetate	10	0,011	0.009 - 0.012
1-Butanol	6	0,0046	0.0037 - 0.0057
Methylene chloride	350	0,14	0.013 - 0.015
Chloroform	160	0,082	0.079 - 8.088
Carbon disulfide	297	0,11	0.10 - 0.11

*Charles B. Keil & Mark Nicas (2003) Predicting Room Vapor Concentrations Due to Spills of Organic Solvents, AIHA Journal, 64:4, 445-454, DOI: 10.1080/15428110308984838

3 If you have Alpha for Some Substances and Relative Evaporation Rate Data ...

Another type of data relevant available is called *Relative Evaporation Rate*
It is the evaporation rate in a lab test compared to butyl acetate or ether

Source used : EASTMAN *Solvent Comparison Tool*

Alpha for butyl acetate is 0.011 /min (Keil 2003)

	Evap Rate *But. Ac. =1*	estimated α
Acetone	6.3	6.3 * 0.011 = 0.069
Toluene	1.9	1.9 * 0.011 = 0.021
Methyl alcohol	3.5	3.5 * 0.011 = 0.039

WHAT IF EXPOSURE CONTROLS ARE PRESENT?

- **How effective are the controls? For example, see Fransman, W., Schinkel, J., Meijster, T., Van Hemmen, J., Tielemans, E., Goede, H., 2008. Development and Evaluation of an Exposure Control Efficacy Library (ECEL). Ann. Occup. Hyg. 52, 567–575.**
- **Proportionally reduce the generation rate estimated without controls**

REFERENCES ON GENERATION RATES

- US EPA “Ap42” but mostly industrial emissions
- Chapter 3, Modeling Pollutant Generation Rates in “Mathematical Models for Estimating Occupational Exposure to Chemicals”, C. Keil et al, AIHA Press, 2009. Tasks approaches relevant to consumers
- In EU, approaches are evolving to standardize consumer exposure scenarios, but not much is available on specifics relevant to generation rates
- US EPA Exposure Factors Handbook
- Specific literature reports
- No known comprehensive compilations

PART 3.

VENTILATION RATES, RANDOM AIR VELOCITY, TURBULENT DIFFUSION COEFFICIENT ESTIMATES

VENTILATION RATES

Air change rates, typically air changes per hour (ACH), can easily be converted to m^3/min given a known room volume.

- **See https://www.engineeringtoolbox.com/air-change-rate-room-d_867.html for generally recommended ACH by building/room type**
- **ASHRAE Standard Ventilation for Acceptable Indoor Air Quality**
- **Performance Criteria of Buildings for Health and Comfort. CIB Publication no. 292 PDF available at: www.isiaq.org/docs/TG42-report.pdf**
- **US EPA Exposure Factors Handbook, Chapter 19 Building characteristics,**

PDF available at: https://www.epa.gov/sites/production/files/2015-09/documents/techoverview_efh-complete.pdf

- **Ventilation for non-residential buildings — Performance requirements for ventilation and room-conditioning system CEN/TC 156 Date: 2006-07**

PDF available at:

http://www.cres.gr/greenbuilding/PDF/prend/set4/WI_25_Pre-FV_version_prEN_13779_Ventilation_for_non-resitential_buildings.pdf

VENTILATION RATES (CONTINUED)

- **Much can be found via specific literature searches, including the following examples**
  - **Jayjock and Havics give data on residential interzonal ventilation rates,** **J Occup Environ Hyg. 2018 May;15(5):376-388. doi: 10.1080/15459624.2018.1438615.**
  - **Yamamoto et al summarize residential air exchange rates in three major US metropolitan areas. Indoor Air. 2010 Feb;20(1):85-90. doi: 10.1111/j.1600-0668.2009.00622.x. Epub 2009 Jul 31.**
- **Measurements can be done, from simple to complex tracer gas studies**

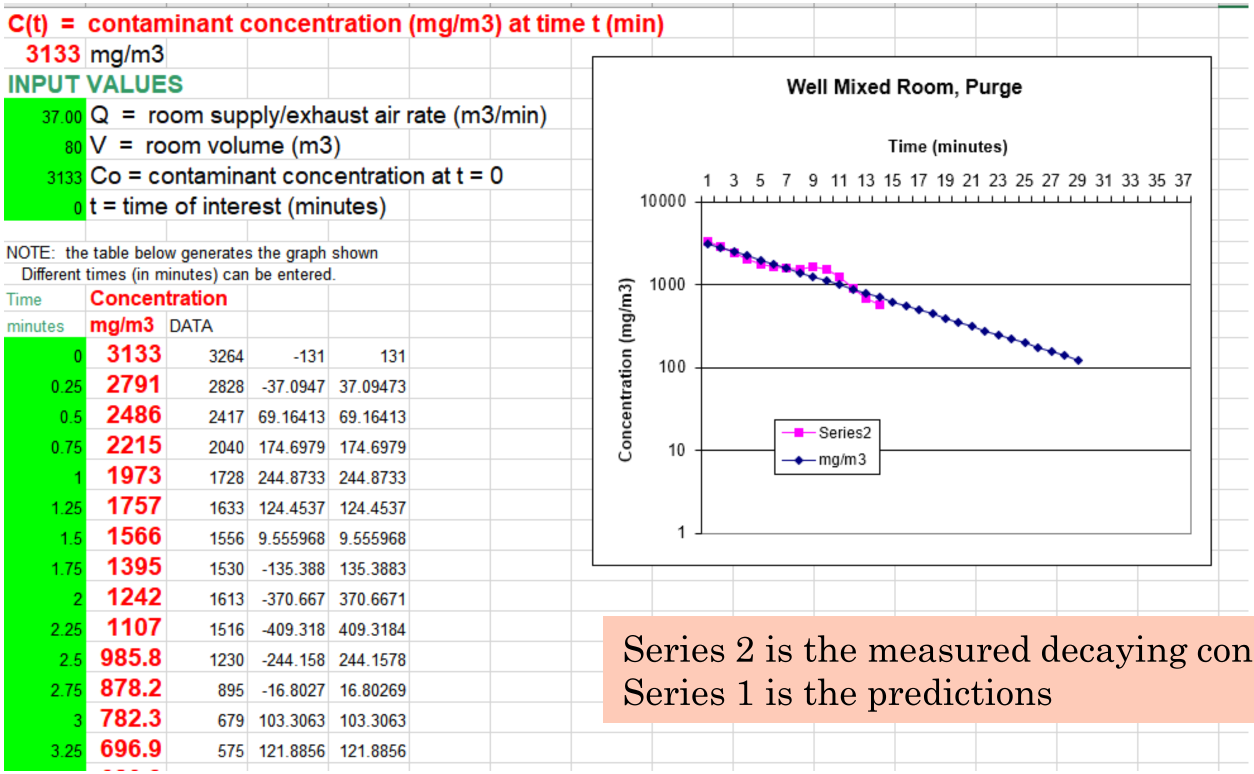
Jeff Burton recommends some simple techniques

https://www.aiha.org/membercenter/SynergistArchives/2018SynergistArchives/Pages/Six-Ways-to-Approximate-Airflow.aspx

I think there is more about natural and mechanical ventilation rates in older factories in the older industrial engineering and industrial hygiene literature, but I do not know of a bibliography of all that pre-1970s literature. For example, A Physiological Study of the Ventilation and Heating in Certain Factories. VERNON, H. M. ; BEDFORD, T. in Medical Research Council. Indust. Fatigue Res. Board. Rep. 1926 No.35 pp.iv+84 ref.19

Older does not mean useless!

EXPERIMENT. WELL MIXED ROOM PURGE AND ESTIMATED VENTILATION RATE (THIS WAS NOT DONE IN MOD 2.0)



C(t) = contaminant concentration (mg/m3) at time t (min)

3133 mg/m3

INPUT VALUES

37.00 Q = room supply/exhaust air rate (m3/min)

80 V = room volume (m3)

3133 Co = contaminant concentration at t = 0

0 t = time of interest (minutes)

NOTE: the table below generates the graph shown
Different times (in minutes) can be entered.

Time minutes	Concentration mg/m3	DATA		
0	3133	3264	-131	131
0.25	2791	2828	-37.0947	37.09473
0.5	2486	2417	69.16413	69.16413
0.75	2215	2040	174.6979	174.6979
1	1973	1728	244.8733	244.8733
1.25	1757	1633	124.4537	124.4537
1.5	1566	1556	9.555968	9.555968
1.75	1395	1530	-135.388	135.3883
2	1242	1613	-370.667	370.6671
2.25	1107	1516	-409.318	409.3184
2.5	985.8	1230	-244.158	244.1578
2.75	878.2	895	-16.8027	16.80269
3	782.3	679	103.3063	103.3063
3.25	696.9	575	121.8856	121.8856

We crushed a calculated mass of dry ice to stay below STEL, spread it on the floor, used box fans to rapidly mix the CO_2, measured CO_2 until it no longer rose, shut off the fans and measured the decay vs time with CO_2 direct reading instruments.

We then use the well mixed room purge model varying Q to back calculate the effective ventilation rate giving the closest match to the measured decay values.

Series 2 is the measured decaying concentration
Series 1 is the predictions

RANDOM AIR VELOCITIES (NEEDED FOR TWO-ZONE MODELING)

For too many years, published data on this has been sparse.

- **A classic is Baldwin and Maynard [Ann Occup Hyg.] 1998 Jul;42(5):303-13. This is the source for the often used 3.6 m/min, GSD 1.96. The source gives details on specific workplace types. They report PERSONAL measurements were typically 3 m/min higher than static measurements.**
- **More recent data out of the University of Minnesota chamber studies evaluated and verified for five workplaces gave median air velocities of 3 to 30 m/min and another study yielded a mean air speed of 4 m/min with a standard deviation of 3.0 for measurements in 12 rooms with volumes from 79 to 1137 m^3 and air change rates of 3.3 to 8.6 per hour.**

Arnold SF, Shao Y, Ramachandran G. Evaluation of the well mixed room and near-field far-field models in occupational settings. J Occup Environ Hyg. 2017;14(9):694–702.

Keil C, Zhao Y. Interzonal airflow rates for use in near-field far-field workplace concentration modeling. J Occup Environ Hyg. 2017;14(10):793–800.

Also, see Koivisto et al. 2019, Table 3. https://doi.org/10.1016/j.scitotenv.2019.02.398

RANDOM AIR VELOCITY DATA ARNOLD, 2017*

Summary of Table 2*							
		Vent Q m^3/min		**Room Vol m^3**	**ACH**		**Random air V m/min**
Scenario	**Description**	**max**	**max**		**min**	**max**	
1	Iron foundry	80	100	1200	4	5	19
2	Iron foundry	80	100	1200	4	5	19
3	Dry wall finishing	1.4	4.3	860	0.098	0.3	5.6
4	Dry wall finishing	1.4	4.3	860	0.098	0.3	5.6
5	Weighitng, trensferring	2.7	4	126	1.289	1.90	3.9
6	Mixing powder	2.7	4	126	1.29	1.90	3.9
7	Collecting samples	94	140	379	14.9	22.2	3
8	Sand molding in foundry	8.3	10.4	125	3.98	4.99	30
9	Salon manuicure	6.2	7.7	31	12	14.9	15
10	Cleaning mixer	10.1	15.1	126	4.81	7.19	7.7

* Arnold SF et al. Evaluation of the well mixed room and near-field far-field models in occupational settings. J Occup Environ Hyg. 2017;14(9):694–702.

Also, See Koivisto et al. 2019, Table 3. https://doi.org/10.1016/j.scitotenv.2019.02.398

TURBULENT EDDY DIFFUSION COEFFICIENT D_T

Even less is available on turbulent eddy diffusion values tna on random air velocity.

- **Turbulent eddy diffusion involves the random motion of eddies of air that carry chemical molecules (or particles) away from the source. Turbulent eddy diffusion is akin to a three-dimensional random walk.**
- **However, envision D_T in meters squared per minute as the planar area in meters squared (a plane dissecting the diffusion pattern) that a molecule in a "random walk" could cover in that time due to random air velocity.**
- **Dt values are on the order of 0.1 to 10 m2/min**
- **Visualizing the "dust motes" in a sunbeam, or dispersion of a puff of smoke from a smoke tube can help visualize this. In a relatively unventilated room, the D_T could be in the 0.1 or lower range. With a bit of mixing energy, 0.5 to 1.0. With strong mixing such as with fans, 10 or more.**
- **Shade* suggested a linear correlation of D_T as a function of air speed:**

$$D_T\ (m^2/min) = 0.162 \bullet \text{air speed (m/min)}.$$

* Shade, W.D. and Jayjock M.A.: Monte Carlo Uncertainty Analysis of a Diffusion Model for the Assessment of Halogen Gas Exposure during Dosing of Brominators. American Industrial Hygiene Association Journal 58: 418-424 (1997).

TURBULENT EDDY DIFFUSION SUMMARY OF SHAO 2017

J Occup Environ Hyg. 2017 Mar;14(3):195-206. doi: 10.1080/15459624.2016.1238476.

"For the first time, a mathematical expression for the relationship between D_T and ACH has been derived that also corrects for non-ideal conditions, and the calculated value of the slope between these two parameters is very close to the experimentally determined value." [Please read the published materials for details on the predictive equation and its limitations]

m²/min				
min	max	typical	Study Environment	
0.114	0.4128		158 m³ residential room	Cheng 2011
0.0642	0.774		59 m³ residential room	Cheng 2011
<0.06			31 m³ closed room	Drivas 1996
0.084	11.4		Indoor industrial space	Nicas 2001
0.048	11.4	0.162	Indoor industrial space	Jayjock 2007
0.066	0.5568		12 m³chamber study	Shao 2017

The Shao et al equation fits data better than the earlier Cheng equation

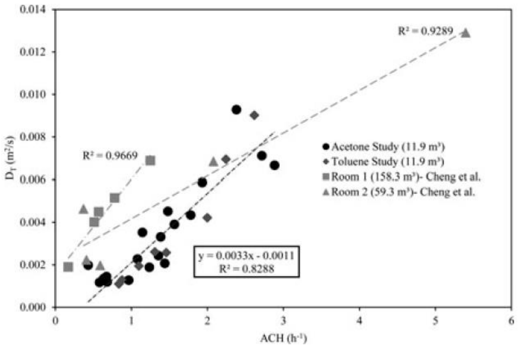
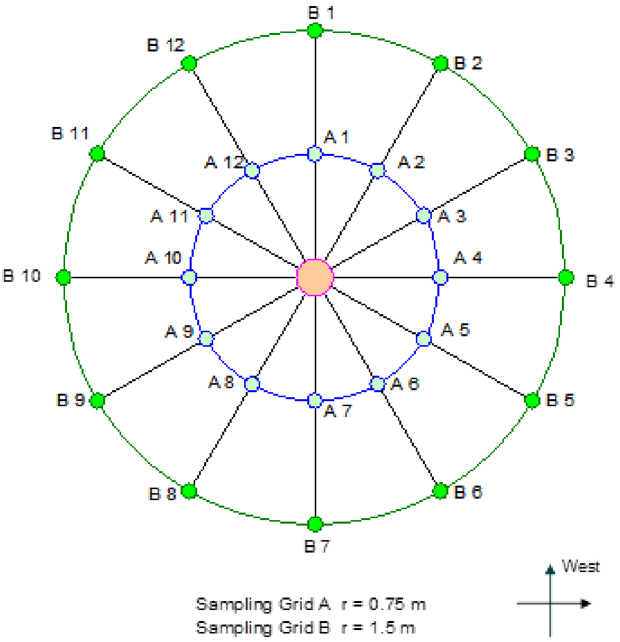


Figure 4. The relationship between D_T and ACH in this study and from Cheng et al.[4]

Tom Armstrong WWW.TWA8HR.com

EXPERIMENTAL DETERMINATION OF D_T

- **In a room where we measured the ventilation rate and had a known generation rate of contaminant, we measured an air contaminant at multiple points in two spherical arrays of two different radii.**
- **Using the Turbulent Diffusion Continuous release model we will soon see, one can find the D_T value that gives the best fit to the data**
- **This could be done with CO_2 and continuous monitors**



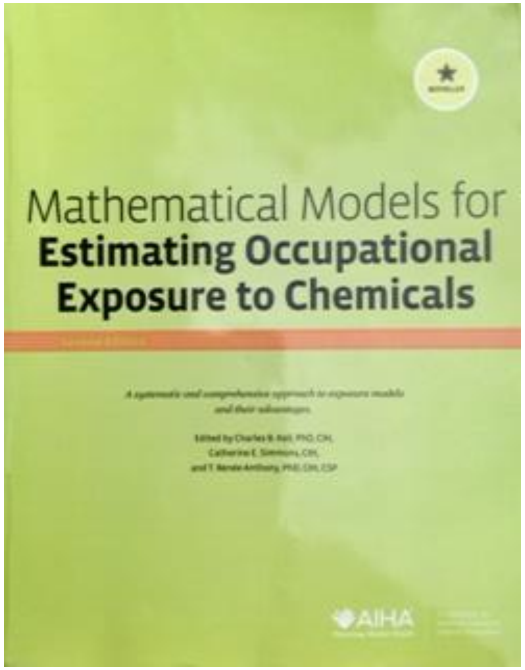
Tom Armstrong WWW.TWA8HR.com

PART 4.

IH MOD2.0 OVERVIEW AND DISCUSSION OF SPECIFIC MODELS AND THEIR USES

IHMOD 2.0 INTRODUCTION

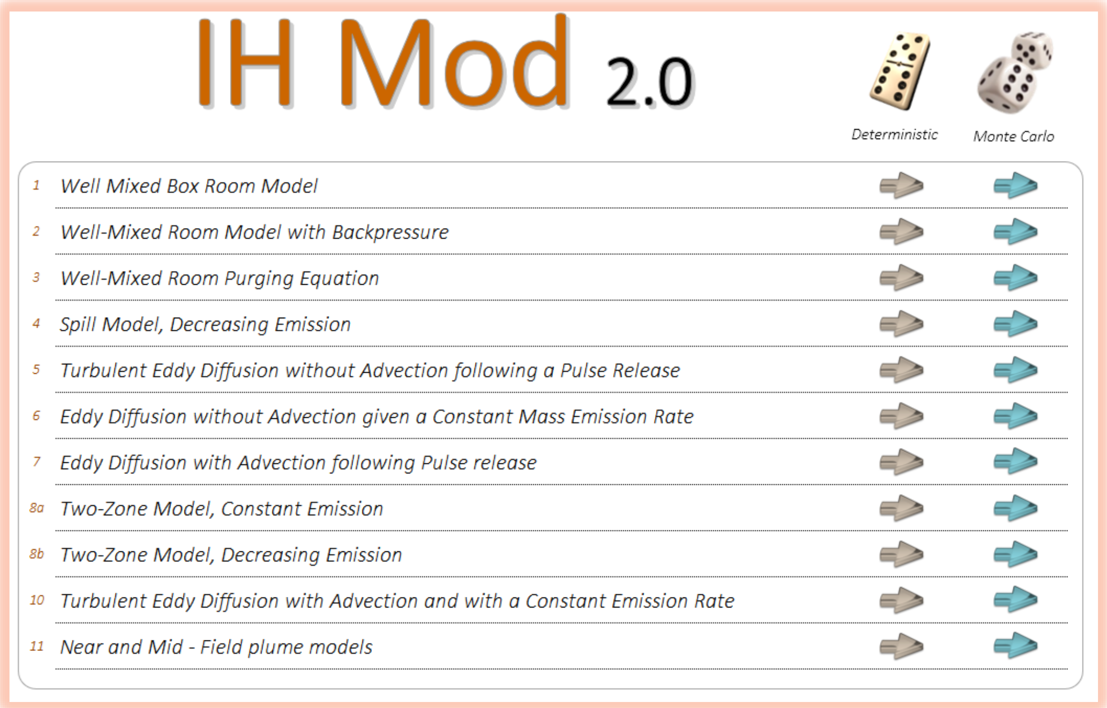
- Disclaimer
- Structure
- Help System
- Data Entry / Data Sliders
- Graphics
- Printing Options
- Parameter definition
- Unit conversions
- NOTE the book is ESSENTIAL to REALLY use IH Mod 2.0 with understanding!


Mathematical Models for
Estimating Occupational
Exposure to Chemicals

A concise guide to the models

IH MOD2.0 CONTAINS ELEVEN OF THE MODELS COVERED IN THE TEXT “MATHEMATICAL MODELS FOR ESTIMATING OCCUPATIONAL EXPOSURE TO CHEMICALS“

- We will not cover all of them today
- The text does a great job describing the models and their uses
- IH Mod2.0 SUPPORT FILE includes short, specific HELP on each model included

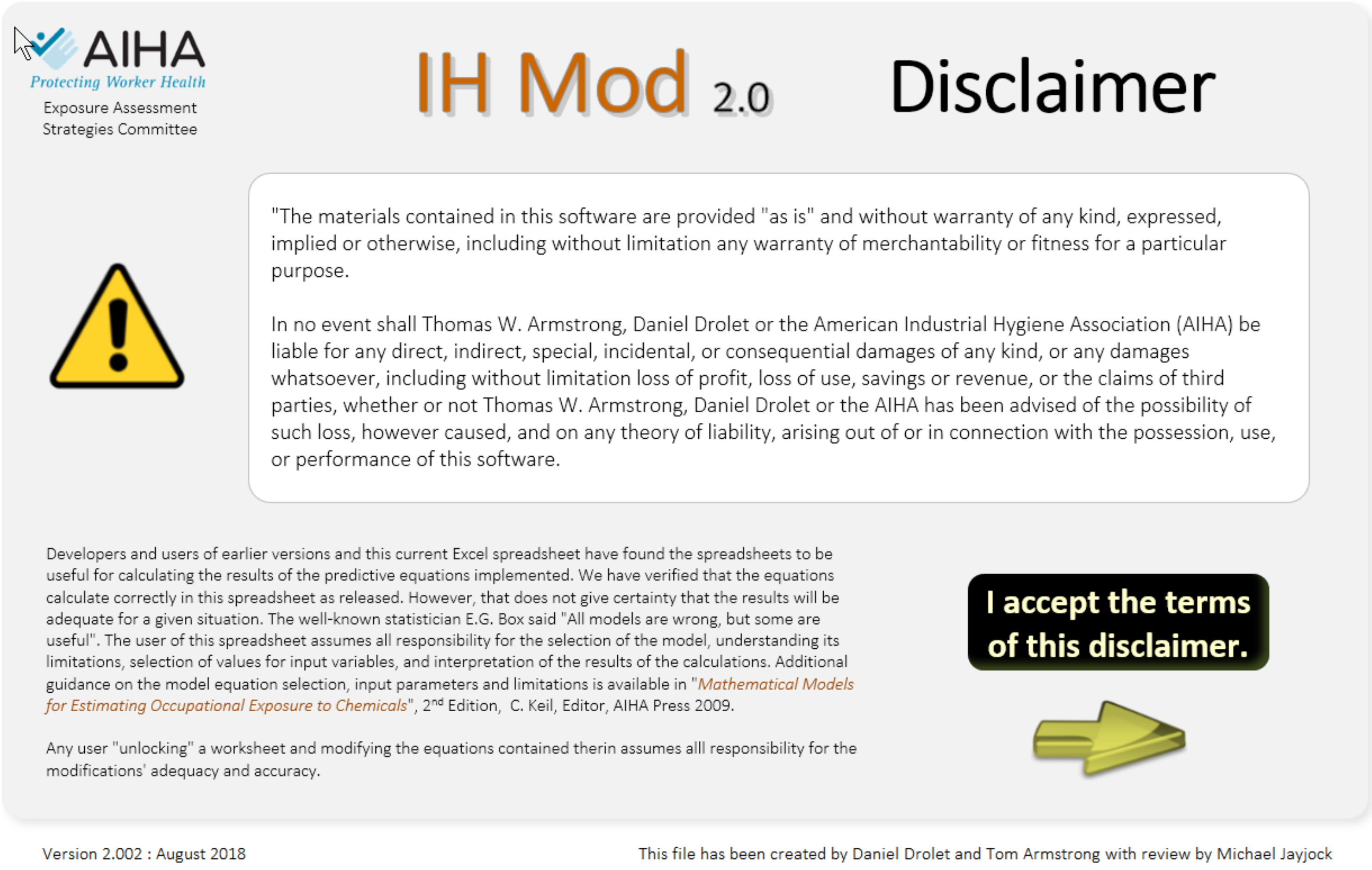


IH Mod 2.0

		Deterministic	Monte Carlo
1	Well Mixed Box Room Model	➡	➡
2	Well-Mixed Room Model with Backpressure	➡	➡
3	Well-Mixed Room Purging Equation	➡	➡
4	Spill Model, Decreasing Emission	➡	➡
5	Turbulent Eddy Diffusion without Advection following a Pulse Release	➡	➡
6	Eddy Diffusion without Advection given a Constant Mass Emission Rate	➡	➡
7	Eddy Diffusion with Advection following Pulse release	➡	➡
8a	Two-Zone Model, Constant Emission	➡	➡
8b	Two-Zone Model, Decreasing Emission	➡	➡
10	Turbulent Eddy Diffusion with Advection and with a Constant Emission Rate	➡	➡
11	Near and Mid - Field plume models	➡	➡

THERE ARE MULTIPLE MODEL PARAMETERS – THESE ARE THE MOST PREVALENT BESIDES G – BUT THE LIST VARIES BY MODEL!

- V = “room” volume
- Q = room air supply /exhaust ventilation rate
- Alpha = an evaporation rate constant
- Csat = saturation vapor concentration for the contaminant
- Mo = initial contaminant mass
- Dt = turbulent diffusion coefficient
- U = advective air speed
- Beta = air exchange rate between zone one and zone two (two zone model)



IH Mod 2.0 Disclaimer

"The materials contained in this software are provided "as is" and without warranty of any kind, expressed, implied or otherwise, including without limitation any warranty of merchantability or fitness for a particular purpose.

In no event shall Thomas W. Armstrong, Daniel Drolet or the American Industrial Hygiene Association (AIHA) be liable for any direct, indirect, special, incidental, or consequential damages of any kind, or any damages whatsoever, including without limitation loss of profit, loss of use, savings or revenue, or the claims of third parties, whether or not Thomas W. Armstrong, Daniel Drolet or the AIHA has been advised of the possibility of such loss, however caused, and on any theory of liability, arising out of or in connection with the possession, use, or performance of this software.

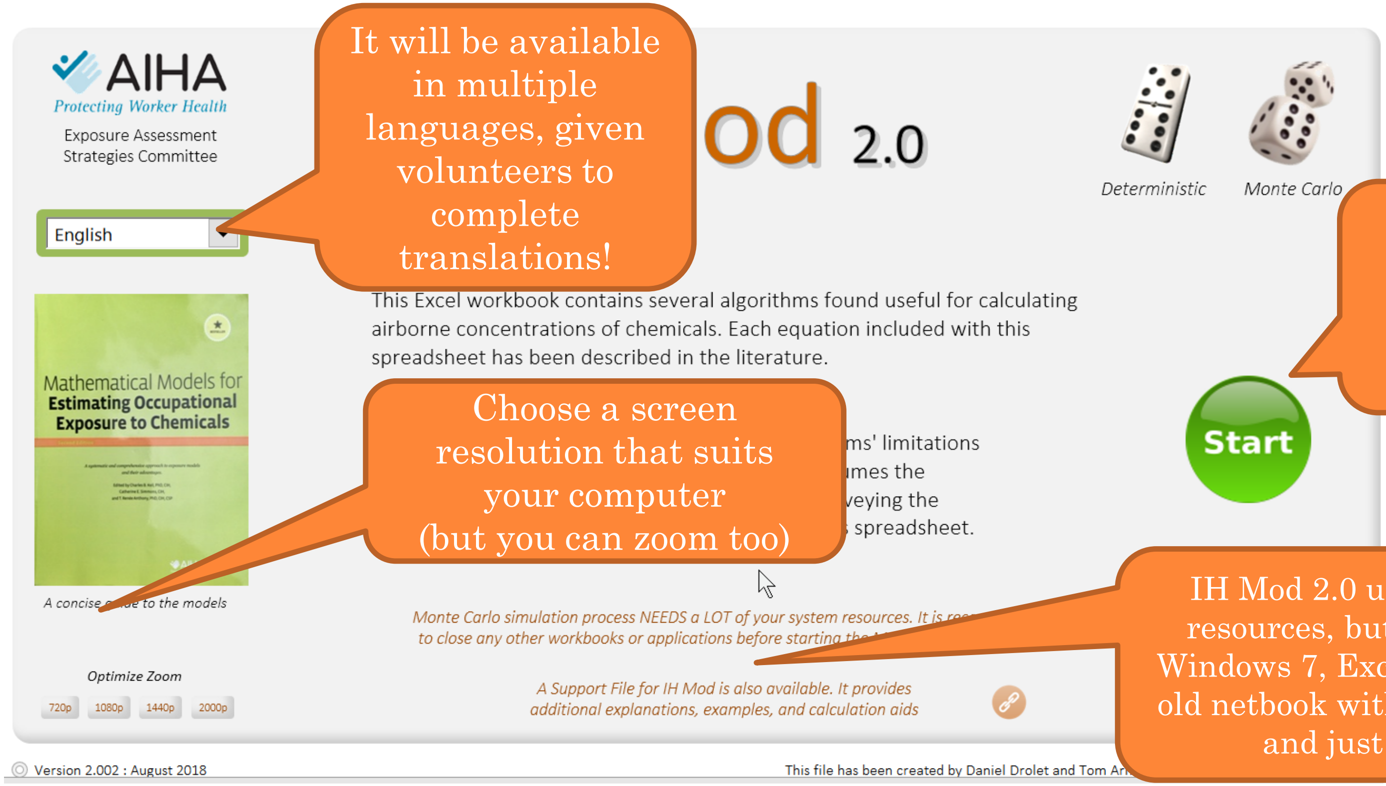
Developers and users of earlier versions and this current Excel spreadsheet have found the spreadsheets to be useful for calculating the results of the predictive equations implemented. We have verified that the equations calculate correctly in this spreadsheet as released. However, that does not give certainty that the results will be adequate for a given situation. The well-known statistician E.G. Box said "All models are wrong, but some are useful". The user of this spreadsheet assumes all responsibility for the selection of the model, understanding its limitations, selection of values for input variables, and interpretation of the results of the calculations. Additional guidance on the model equation selection, input parameters and limitations is available in "*Mathematical Models for Estimating Occupational Exposure to Chemicals*", 2nd Edition, C. Keil, Editor, AIHA Press 2009.

Any user "unlocking" a worksheet and modifying the equations contained therin assumes alll responsibility for the modifications' adequacy and accuracy.

Version 2.002 : August 2018

This file has been created by Daniel Drolet and Tom Armstrong with review by Michael Jayjock

THIS IS "THE FIRST SCREEN" IN IH MOD … AFTER MACROS WERE ENABLED AND AFTER THE DISCLAIMER!



A concise … to the models

This Excel workbook contains several algorithms found useful for calculating airborne concentrations of chemicals. Each equation included with this spreadsheet has been described in the literature.

…ms' limitations
…mes the
…veying the
… spreadsheet.

Monte Carlo simulation process NEEDS a LOT of your system resources. It is rec…
to close any other workbooks or applications before starting th…

A Support File for IH Mod is also available. It provides additional explanations, examples, and calculation aids

Version 2.002 : August 2018

This file has been created by Daniel Drolet and Tom Ar

It will be available in multiple languages, given volunteers to complete translations!

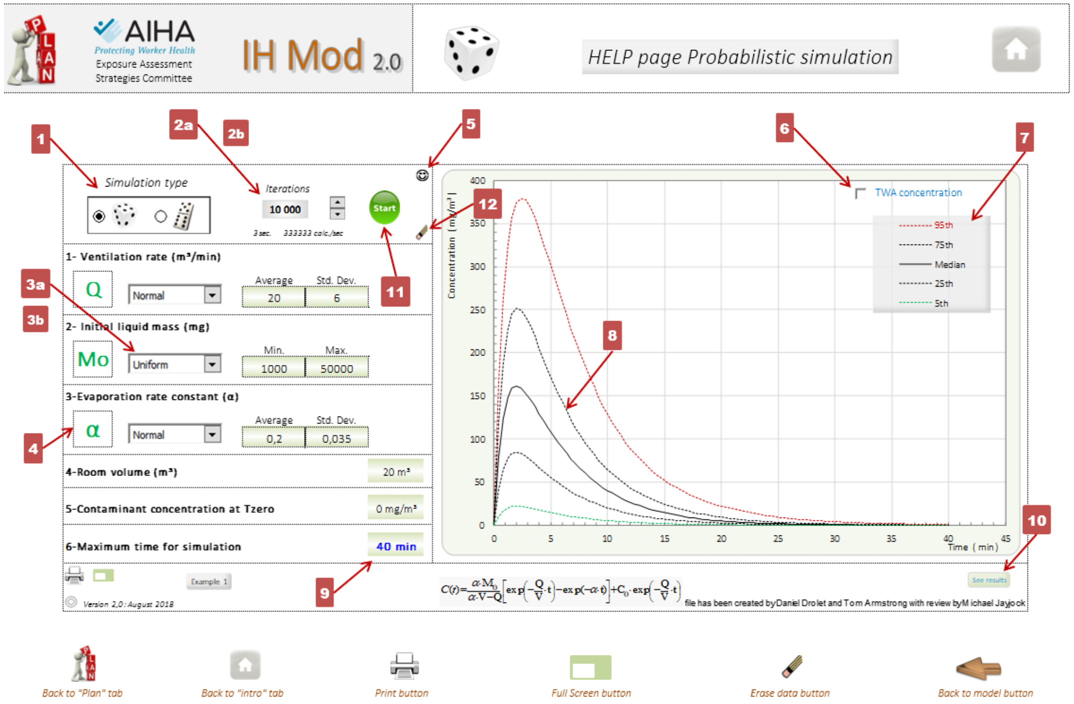
Click Here to Start

Choose a screen resolution that suits your computer (but you can zoom too)

IH Mod 2.0 uses a lot of system resources, but we have run it in Windows 7, Excel 2010 on a 10 year old netbook with an Atom processor and just 2 GB of ram.

Tom Armstrong WWW.TWA8HR.com

THIS IS THE MCS HELP SCREEN –



Simulation type ● ○

Iterations 10 000

3 sec. 333333 calc./sec

1- Ventilation rate (m³/min): Q — Normal — Average 20 — Std. Dev. 6

2- Initial liquid mass (mg): Mo — Uniform — Min. 1000 — Max. 50000

3-Evaporation rate constant (α): α — Normal — Average 0,2 — Std. Dev. 0,035

4-Room volume (m³): 20 m³

5-Contaminant concentration at Tzero: 0 mg/m³

6-Maximum time for simulation: 40 min

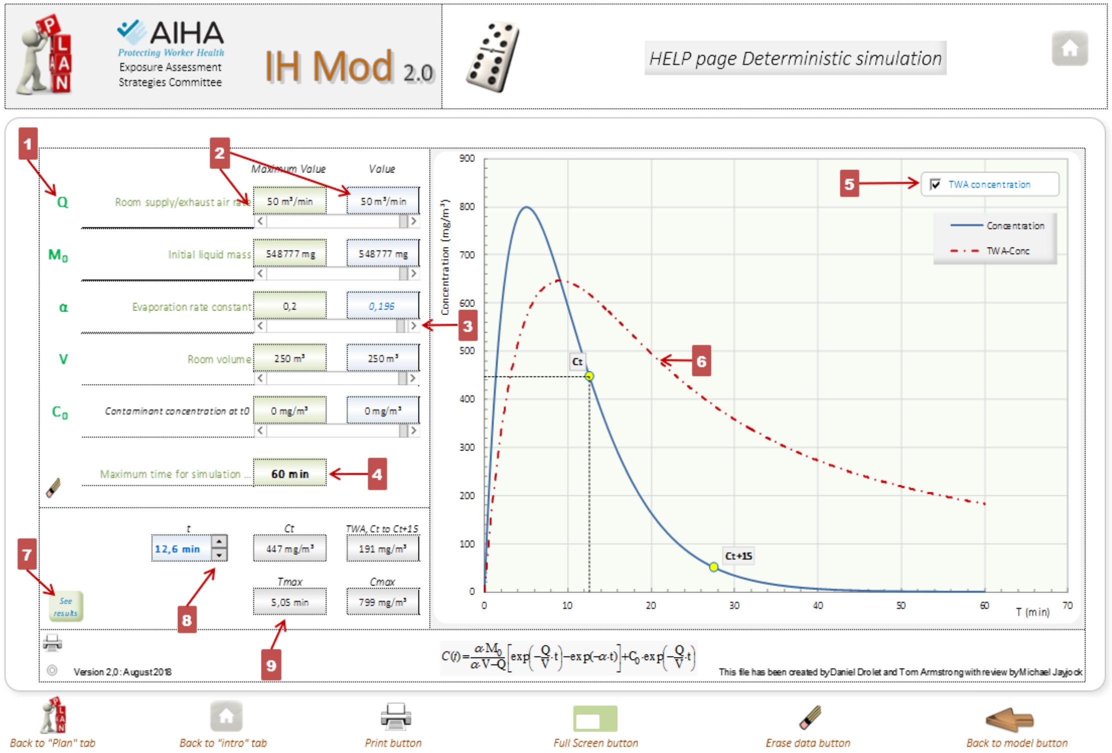
Version 2,0 : August 2018

$$C(t)=\frac{\alpha\cdot M_0}{\alpha\cdot V-Q}\left[\exp\left(-\frac{Q}{V}\cdot t\right)-\exp(-\alpha\cdot t)\right]+C_0\cdot\exp\left(-\frac{Q}{V}\cdot t\right)$$

file has been created by Daniel Drolet and Tom Armstrong with review by Michael Jayjock

1	Chose to run the model either in Probabilistic or Deterministic mode. The deterministic mode will use one value from the middle of each distribution.
2a	Set the number of iterations with the scrolling arrows. Choices are 1, 200, 1000, 5000, 10000, 20000, 50000 or 100000. In Probabilistic mode, 1 iteration will take a random value from each distribution.
2b	How many iterations do you need? It depends on parameter variability! Start low, run twice and compare the results. If quite divergent, increase the iterations until you have satisfactory "stability" from run to run.
3a	Choose the distribution type with the scrolling arrow and then set the parameters for the type of distribution in the green cells to the right.
3b	Distribution choices are Fixed Value, Normal, Uniform, Lognormal or Triangular. The Normal distribution is truncated to prevent negative values.
4	Parameters in Green are required to run the model. Those in Black are optional.
5	A Smile means everything is specified and the model is OK to run. A Frown means something is missing or not correctly specified.
6	Check the box to see the TWA to time T graph. Unchecked shows only the Concentration vs time graphs.
7	The program is set to show the 5th, 25th, 50th (median), 75th and 95th percentiles of the results over time.
8	Hold the mouse pointer over a specific point on a graphed line to see the value at that time, shown in parentheses as (time, concentration).
9	Set the maximum time over which to simulate the exposure scenario, up to 24 hours (1440 minutes). Several models include an option to set the time to end generation and begin the room purge calculation.
10	Click the box to see the results.
11	The Start button calls up a "pop up" box to verify "start the simulation."
12	"Erase Data" button

THIS IS THE DETERMINISTIC HELP SCREEN



	Maximum Value	Value
Room supply/exhaust air rate	50 m³/min	50 m³/min
Initial liquid mass	548777 mg	548777 mg
Evaporation rate constant	0,2	0,196
Room volume	250 m³	250 m³
Contaminant concentration at t0	0 mg/m³	0 mg/m³
Maximum time for simulation ...	60 min	

t	Ct	TWA, Ct to Ct+15
12,6 min	447 mg/m³	191 mg/m³

Tmax	Cmax
5,05 min	799 mg/m³

$$C(t)=\frac{\alpha \cdot M_0}{\alpha \cdot V - Q}\left[\exp\left(-\frac{Q}{V}\cdot t\right)-\exp(-\alpha \cdot t)\right]+C_0 \cdot \exp\left(-\frac{Q}{V}\cdot t\right)$$

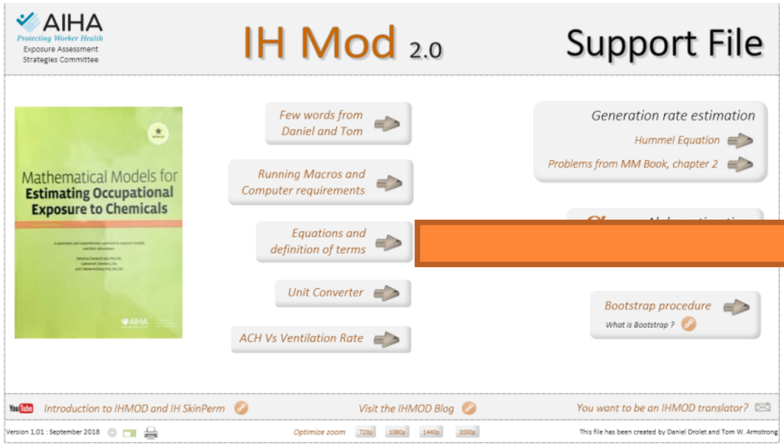
Version 2,0 : August 2018

This file has been created by Daniel Drolet and Tom Armstrong with review by Michael Jayjock

1	Green parameters are required to run the model. Those in Black are optional.
2	Enter the parameter value in the green shaded maximum value cells. The actual value used in the calculations in value cell to the right
3	Use the data slider function to see the effect of reducing the parameter value from its maximum. Note it changes to blue color text if less than 100% of the Maximum Value.
4	Set the maximum time over which to simulate the exposure scenario, up to 24 hours (1440 min). Several models include an option to set the time to end generation and begin the purge calculation.
5	Check the box to see the TWA to time T graph. Unchecked shows only the Concentration vs time graphs.
6	Hold the mouse pointer over a specific point on a graphed line to see the value at that time, shown in parentheses as (time, concentration).
7	Click the box to see the results in a table.
8	Set a chosen time to see the predicted concentration at that time. The program also calculates the TWA from that time over the following 15 minutes. These are also shown on the graph.
9	The program calculates the time at which the predicted maximum concentration occurs.

ADDITIONAL HELP IS IN THE IH MOD 2.0 SUPPORT FILE

WE EXPECT TO EXPAND THE INFORMATION IN THIS FILE PERIODICALLY



AIHA
Protecting Worker Health
Exposure Assessment
Strategies Committee

IH Mod 2.0 Support File

Mathematical Models for Estimating Occupational Exposure to Chemicals

- Few words from Daniel and Tom
- Running Macros and Computer requirements
- Equations and definition of terms
- Unit Converter
- ACH Vs Ventilation Rate

Generation rate estimation
- Hummel Equation
- Problems from MM Book, chapter 2

Bootstrap procedure
- What is Bootstrap ?

Introduction to IHMOD and IH SkinPerm

Visit the IHMOD Blog

You want to be an IHMOD translator?

Version 1.01 : September 2018

Optimize zoom: 720p, 1080p, 1440p, 2000p

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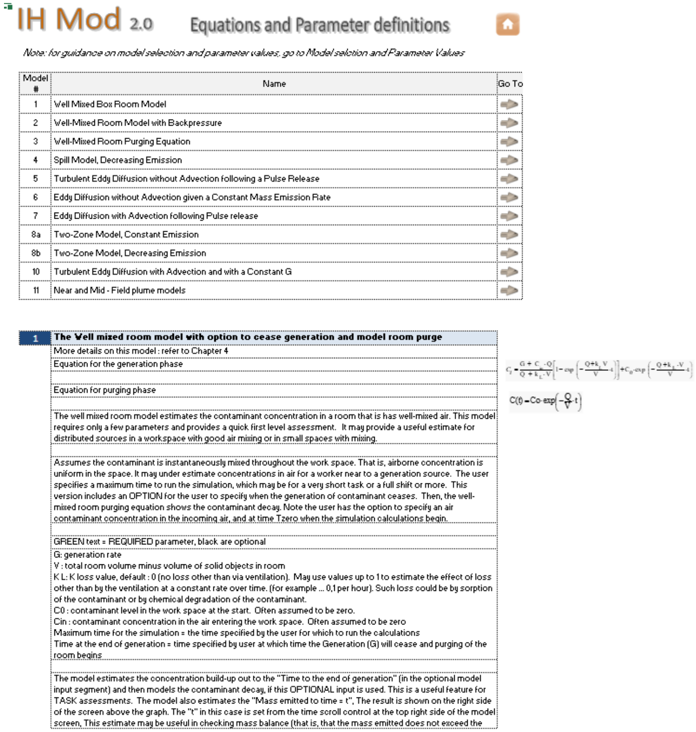


IH Mod 2.0 Equations and Parameter definitions

Note: for guidance on model selection and parameter values, go to Model selction and Parameter Values

Model #	Name	Go To
1	Well Mixed Box Room Model	➡
2	Well-Mixed Room Model with Backpressure	➡
3	Well-Mixed Room Purging Equation	➡
4	Spill Model, Decreasing Emission	➡
5	Turbulent Eddy Diffusion without Advection following a Pulse Release	➡
6	Eddy Diffusion without Advection given a Constant Mass Emission Rate	➡
7	Eddy Diffusion with Advection following Pulse release	➡
8a	Two-Zone Model, Constant Emission	➡
8b	Two-Zone Model, Decreasing Emission	➡
10	Turbulent Eddy Diffusion with Advection and with a Constant G	➡
11	Near and Mid - Field plume models	➡

1 The Well mixed room model with option to cease generation and model room purge

More details on this model : refer to Chapter 4

Equation for the generation phase

$$C_t = \frac{G + C_{in}\cdot Q}{Q + k_L\cdot V}\left[1 - \exp\left(-\frac{Q+k_L V}{V}\cdot t\right)\right] + C_0\cdot\exp\left(-\frac{Q+k_L\cdot V}{V}\cdot t\right)$$

Equation for purging phase

$$C(t) = Co\cdot\exp\left(-\frac{Q}{V}\cdot t\right)$$

The well mixed room model estimates the contaminant concentration in a room that is has well-mixed air. This model requires only a few parameters and provides a quick first level assessment. It may provide a useful estimate for distributed sources in a workspace with good air mixing or in small spaces with mixing.

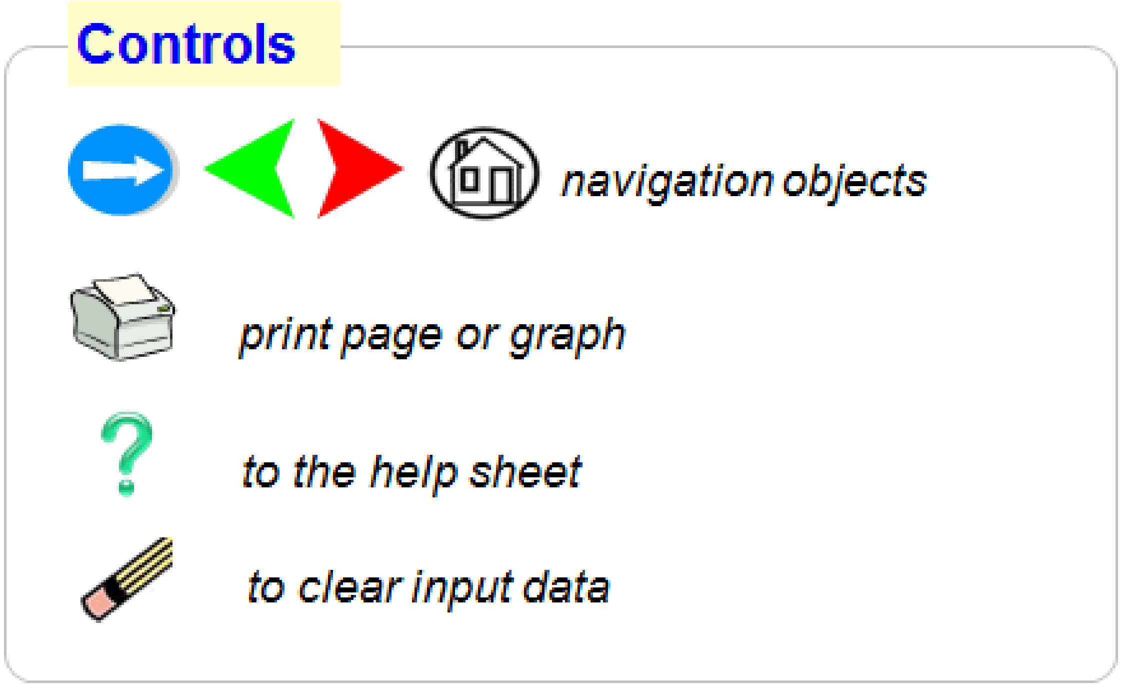
Assumes the contaminant is instantaneously mixed throughout the work space. That is, airborne concentration is uniform in the space. It may under estimate concentrations in air for a worker near to a generation source. The user specifies a maximum time to run the simulation, which may be for a very short task or a full shift or more. This version includes an OPTION for the user to specify when the generation of contaminant ceases. Then, the well-mixed room purging equation shows the contaminant decay. Note the user has the option to specify an air contaminant concentration in the incoming air, and at time Tzero when the simulation calculations begin.

GREEN text = REQUIRED parameter, black are optional

G: generation rate
V : total room volume minus volume of solid objects in room
K L: K loss value, default : 0 (no loss other than via ventilation). May use values up to 1 to estimate the effect of loss other than by the ventilation at a constant rate over time. (for example ... 0,1 per hour). Such loss could be by sorption of the contaminant or by chemical degradation of the contaminant.
C0 : contaminant level in the work space at the start. Often assumed to be zero.
Cin : contaminant concentration in the air entering the work space. Often assumed to be zero
Maximum time for the simulation = the time specified by the user for which to run the calculations
Time at the end of generation = time specified by user at which time the Generation (G) will cease and purging of the room begins

The model estimates the concentration build-up out to the "Time to the end of generation" (in the optional model input segment) and then models the contaminant decay, if this OPTIONAL input is used. This is a useful feature for TASK assessments. The model also estimates the "Mass emitted to time = t", The result is shown on the right side of the screen above the graph. The "t" in this case is set from the time scroll control at the top right side of the model screen, This estimate may be useful in checking mass balance (that is, that the mass emitted does not exceed the

IH MOD'S NAVIGATION CONTROLS EXPLAINED NOW IN THE MCS OR DETERMINISTIC HELP SCREENS


Controls

navigation objects

print page or graph

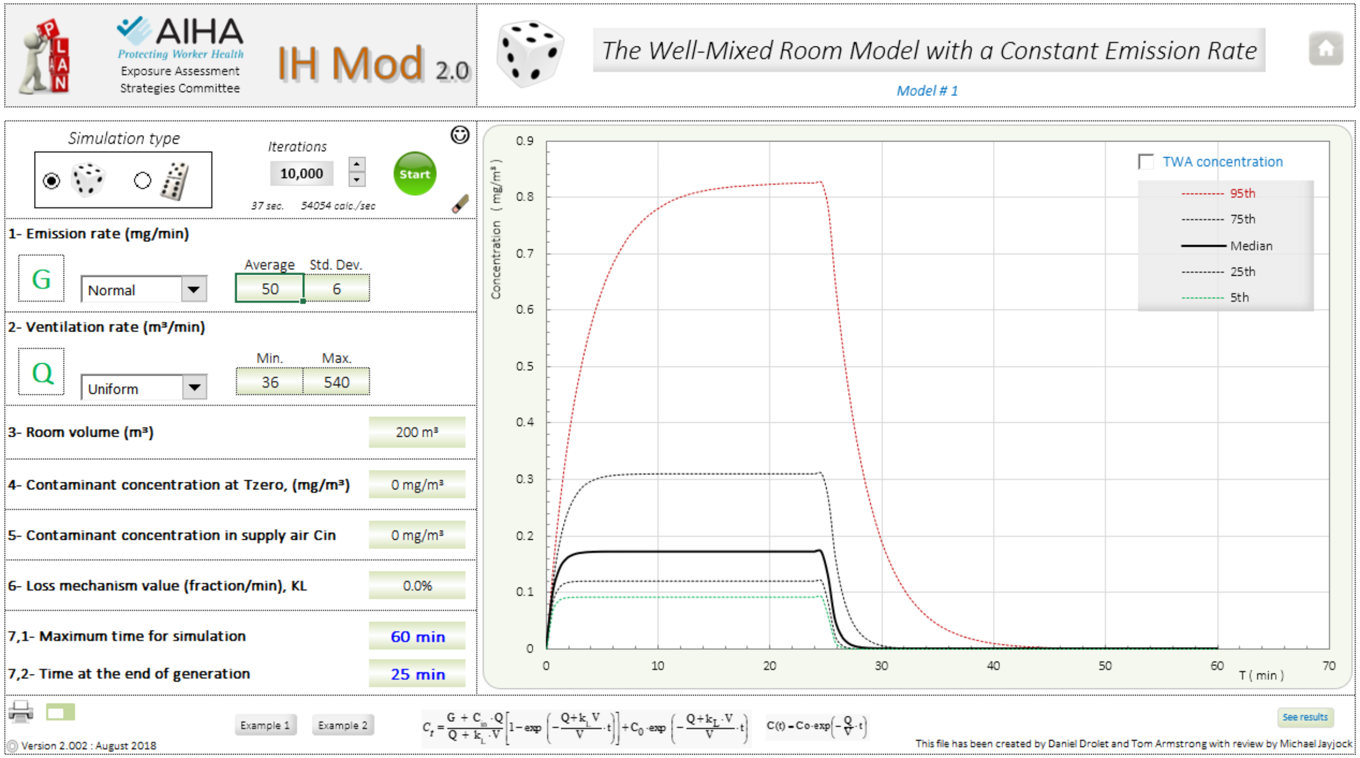
to the help sheet

to clear input data


Deterministic

Monte Carlo

HERE IS AN EXAMPLE OF THE MCS WELL MIXED ROOM MODEL



The Well-Mixed Room Model with a Constant Emission Rate

Model # 1

Simulation type ● ○

Iterations 10,000

37 sec. *54054 calc./sec*

1- Emission rate (mg/min)

G Normal — Average: 50 — Std. Dev.: 6

2- Ventilation rate (m³/min)

Q Uniform — Min.: 36 — Max.: 540

3- Room volume (m³) 200 m³

4- Contaminant concentration at Tzero, (mg/m³) 0 mg/m³

5- Contaminant concentration in supply air Cin 0 mg/m³

6- Loss mechanism value (fraction/min), KL 0.0%

7,1- Maximum time for simulation 60 min

7,2- Time at the end of generation 25 min

☐ TWA concentration

$$C_t = \frac{G + C_{in}\cdot Q}{Q + k_L\cdot V}\left[1-\exp\left(-\frac{Q+k_L V}{V}\cdot t\right)\right] + C_0\cdot\exp\left(-\frac{Q+k_L\cdot V}{V}\cdot t\right)$$

$$C(t) = Co\cdot\exp\left(-\frac{Q}{V}\cdot t\right)$$

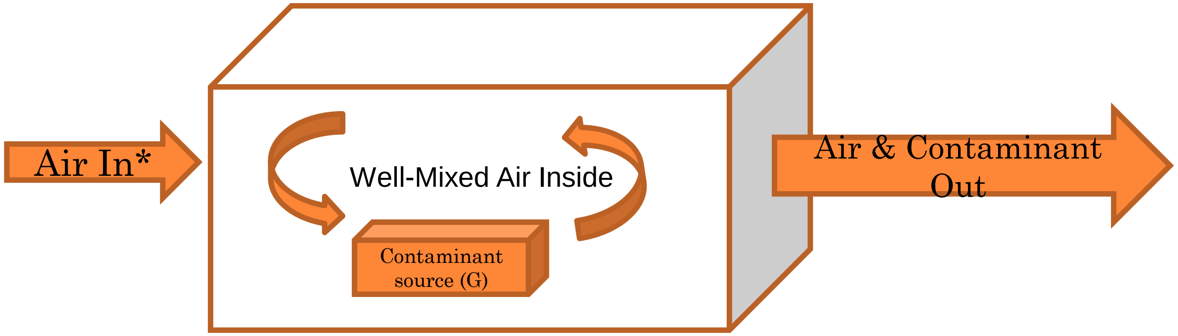
Ⓒ Version 2.002 : August 2018

This file has been created by Daniel Drolet and Tom Armstrong with review by Michael Jayjock

WHAT ARE THE MATHEMATICAL ASPECTS OF THE ONE COMPARTMENT BOX MODEL?

Mass balance is a major part of it!

- **Mass accumulated + Mass out = Mass generated + Mass in**
- **See the book Mathematical Models for Estimating Occupational Exposure to Chemicals for the differential equations and solutions**



Contaminants released inside the box are ***completely and instantaneous well-mixed.***

* The air in could bring some contaminant with it

DID YOU *REALLY* MEAN…COMPLETELY AND *INSTANTANEOUSLY* WELL-MIXED?!

- **In this model, YES!**
- **Any model we use makes simplifying assumptions (necessary for mathematical tractability and we hope appropriate!)**
- **More complex models may make fewer assumptions but then they require more input parameters**
- **The art of modeling hinges on choosing a model that is simple enough to be tractable yet adequate to represent the conditions of the scenario**
- ***Instantaneous can be a relative consideration***

This can work well for estimating exposures from multiple sources in a room with a lot of mixing ventilation. Example: solvent exposures from solvent in shoe assembly by 12 workers in a basement of a home in a developing country with just floor fans for cooling.

SCENARIO – CONTAINER FILLING, 2 BUTOXY ETHANOL

You are asked to review a new use of a chemical (2BE) as an additive to consumer automobile windshield wash solvent. It is semi-volatile with a pure substance vapor pressure of 1 mm Hg and a molecular weight of 118. It will be sold in 4 liter containers, with a composition (by weight) stated by the manufacturer:

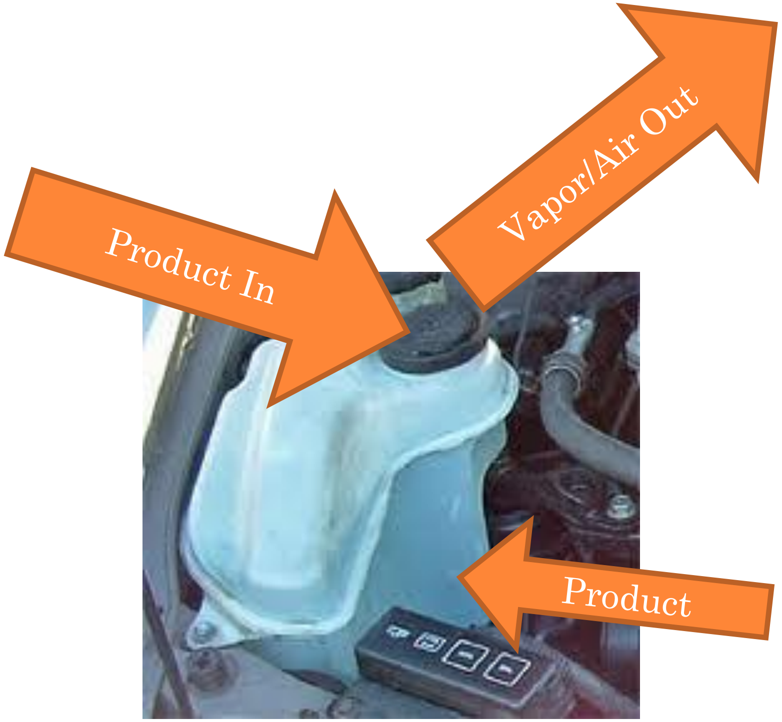
Water >70%

2BE <30%

What is the generation rate and exposure from filling an automotive windshield wash reservoir with this material? First fill? Subsequent fills?

Assume the whole 4 liters is used. The filling takes about 0.5 minute, for a RATE of 8 L/min = 0.008 M^3/min

WHAT GOES ON IN CONTAINER FILLING?



What is the vapor displacement rate and concentration?

Top “splash” loading generates higher concentration vapor more quickly than submerged filling.

Could there be a difference in vapor concentration out for a new fill versus a refill with a “heal” of product in the reservoir?

WHAT IS G FOR THIS SCENARIO?!

- **The mole fraction of 2BE is 0.06:**

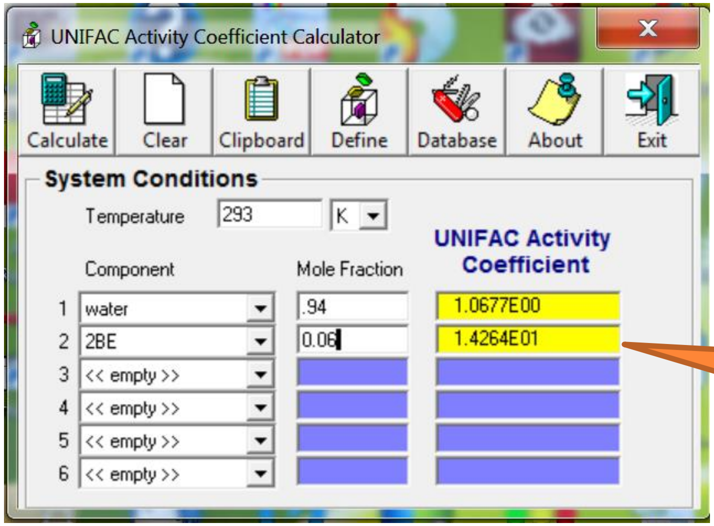
	Weight %	MW	Moles	Mole Fraction
water	70	18	3.9	0.94
2BE	30	118	0.25	0.06
			4.14	

- **Using RAOULT's Law**

$$P_A = X_A \times P_{V,A} = 0.06 \times 1 \text{ Torr} = 0.06 \text{ Torr}$$

$$C_{sat} = (0.06*10^6)/760 = 79 \text{ ppm} = 380 \text{ mg/m}^3$$

COULD ACTIVITY BE IMPORTANT? LETS' CHECK THE ACTIVITY COEFFICIENT



System Conditions

Temperature: 293 K

	Component	Mole Fraction	UNIFAC Activity Coefficient
1	water	.94	1.0677E00
2	2BE	0.06	1.4264E01
3	<< empty >>		
4	<< empty >>		
5	<< empty >>		
6	<< empty >>		

A **positive** deviation from ideality. 14 x Watch the exponents!

$$P_A = \gamma \text{ x } X_A \times P_{V,A} = 14 \text{ x } 0.06 \times 1 \text{ Torr} = 0.84 \text{ Torr}$$

$$Csat = (0.84*10\hat{\ }6)/760 = 1100 \; ppm = 7420 \; mg/M^3$$

WHAT DO WE HAVE FOR OUR ESTIMATE OF G?

The estimate of the generation rate is 7420*mg/m*^{3} *x 0.008 m*^{3}*/min = 60* mg/min

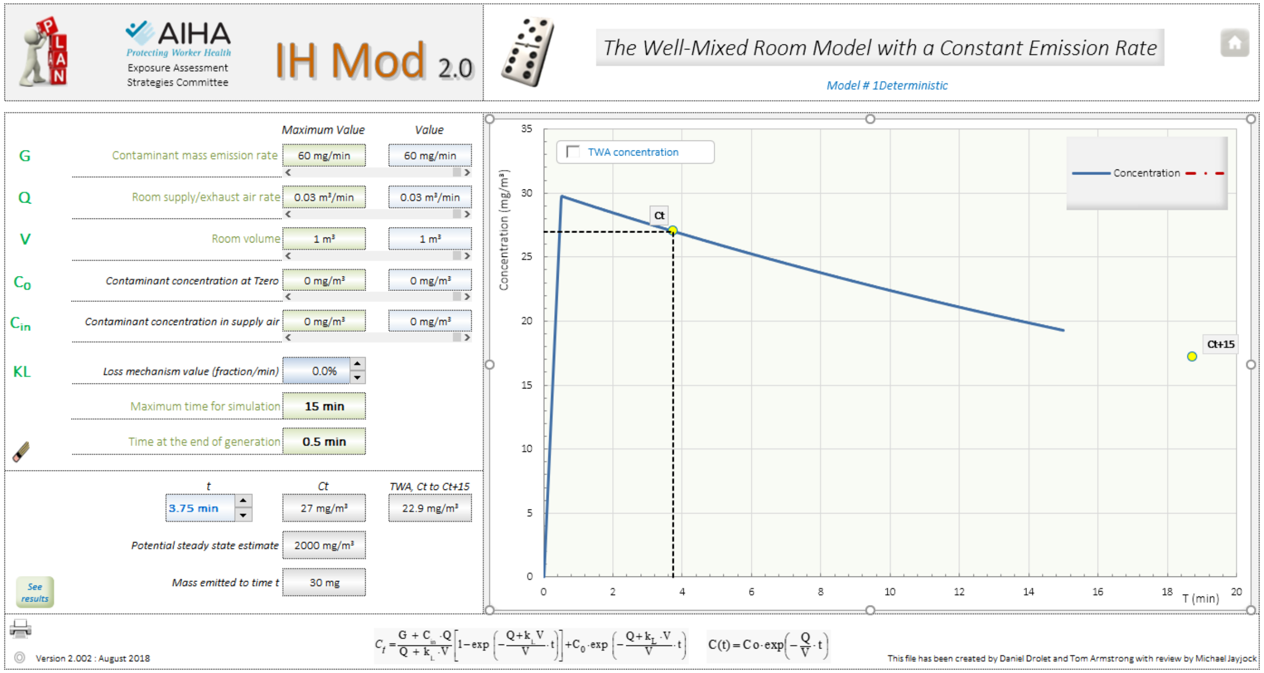
- **Submerged filling of NEW material, can reduce by up to 0.5.**
- **Top splash can generate aerosol and vapor, so up to 1.45**
- **Using a “factor” of 1, G = 60 mg/min**

OTHER ASSUMPTIONS

- User zone of 1 m^3 (around breathing zone)
- Garage ventilation is at 2 ACH = 0.03 ACM so Q in the user zone PROPORTIONALLY is
  - 0.03 m^3/min for the 1 M^3 zone
  - 1.2 m^3/min for the whole garage

Total garage volume is about 40 m^3

LOOKING TO IH MOD 2.0 WELL MIXED ROOM



The Well-Mixed Room Model with a Constant Emission Rate

Model # 1Deterministic

		Maximum Value	Value
G	Contaminant mass emission rate	60 mg/min	60 mg/min
Q	Room supply/exhaust air rate	0.03 m³/min	0.03 m³/min
V	Room volume	1 m³	1 m³
C_0	*Contaminant concentration at Tzero*	0 mg/m³	0 mg/m³
C_{in}	*Contaminant concentration in supply air*	0 mg/m³	0 mg/m³
KL	*Loss mechanism value (fraction/min)*	0.0%	
	Maximum time for simulation	**15 min**	
	Time at the end of generation	**0.5 min**	

t	*Ct*	*TWA, Ct to Ct+15*
3.75 min	27 mg/m³	22.9 mg/m³

Potential steady state estimate 2000 mg/m³

Mass emitted to time t 30 mg

☐ TWA concentration

$$C_t = \frac{G + C_{in} \cdot Q}{Q + k_L \cdot V}\left[1 - \exp\left(-\frac{Q + k_L V}{V} \cdot t\right)\right] + C_0 \cdot \exp\left(-\frac{Q + k_L \cdot V}{V} \cdot t\right) \qquad C(t) = Co \cdot \exp\left(-\frac{Q}{V} \cdot t\right)$$

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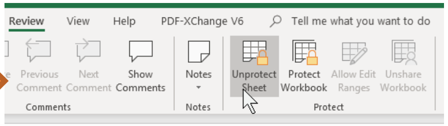
Generating the GRAPH to this scale required deleting a data RANGE. “Review, unprotect sheet”
The VB programming currently has Excel scale to the “potential steady state”. Delete that range to rescale when << steady state.



NEAR FIELD, FAR FIELD MODEL

- Conceptual zone of contamination around a person
- Arbitrarily defined
  - Movement zone
  - 0.8 to 1 m radius sphere or hemisphere default often "works"

The person's movements during the task may change the appropriate volume

NF & FF EQUATIONS HAVE SIMILAR COMPLEXITY)

THE INITIAL SETUP OF THIS IN EXCEL WAS CHALLENGING.
MAKING IT WIDELY ACCESSIBLE WAS A GOAL OF IH MOD

$$C_{\mathrm{NF}}(t)(\mathrm{mg}/\mathrm{m}^3) = \frac{G}{Q} + \frac{G}{\beta} + G\left(\frac{\beta Q + \lambda_2 V_{\mathrm{NF}}(\beta + Q)}{\beta Q V_{\mathrm{NF}}(\lambda_1 - \lambda_2)}\right)$$

$$\times \exp(\lambda_1 \times t)\left(\frac{\beta Q + \lambda_1 V_{\mathrm{NF}}(\beta + Q)}{\beta Q V_{\mathrm{NF}}(\lambda_1 - \lambda_2)}\right) \times \exp(\lambda_2 \times t)$$

where

$$\lambda_1\left(\mathrm{min}^{-1}\right) = 0.5\left[-\left(\frac{\beta V_{\mathrm{FF}} + V_{\mathrm{NF}}(\beta + Q)}{V_{\mathrm{NF}} V_{\mathrm{FF}}}\right) + \sqrt{\left(\frac{\beta V_{\mathrm{FF}} + V_{\mathrm{NF}}(\beta + Q)}{V_{\mathrm{NF}} V_{\mathrm{FF}}}\right)^2 - 4\left(\frac{\beta Q}{V_{\mathrm{NF}} V_{\mathrm{FF}}}\right)}\right]$$

$$\lambda_2\left(\mathrm{min}^{-1}\right) = 0.5\left[-\left(\frac{\beta V_{\mathrm{FF}} + V_{\mathrm{NF}}(\beta + Q)}{V_{\mathrm{NF}} V_{\mathrm{FF}}}\right) - \sqrt{\left(\frac{\beta V_{\mathrm{FF}} + V_{\mathrm{NF}}(\beta + Q)}{V_{\mathrm{NF}} V_{\mathrm{FF}}}\right)^2 - 4\left(\frac{\beta Q}{V_{\mathrm{NF}} V_{\mathrm{FF}}}\right)}\right]$$

FOR THE TWO ZONE MODEL WE NEED A FEW MORE PARAMETERS

- **Near Field Volume = a "virtual" volume of air around the worker, smaller than the total room volume**
- **G remains as for the well mixed room**
- **Beta is an important new parameter**

Beta = ½ FSA*S

FSA = free surface area of the near field geometry and volume a

S= the random air exchange between the near field and the far field

For a sphere Beta = $2\pi(r^2)*s$

More on this is available in the 2nd edition math modeling book, but IH Mod 2.0 calculates Beta for the user

HERE'S AN EXAMPLE OF HOW TO ESTIMATE BETA

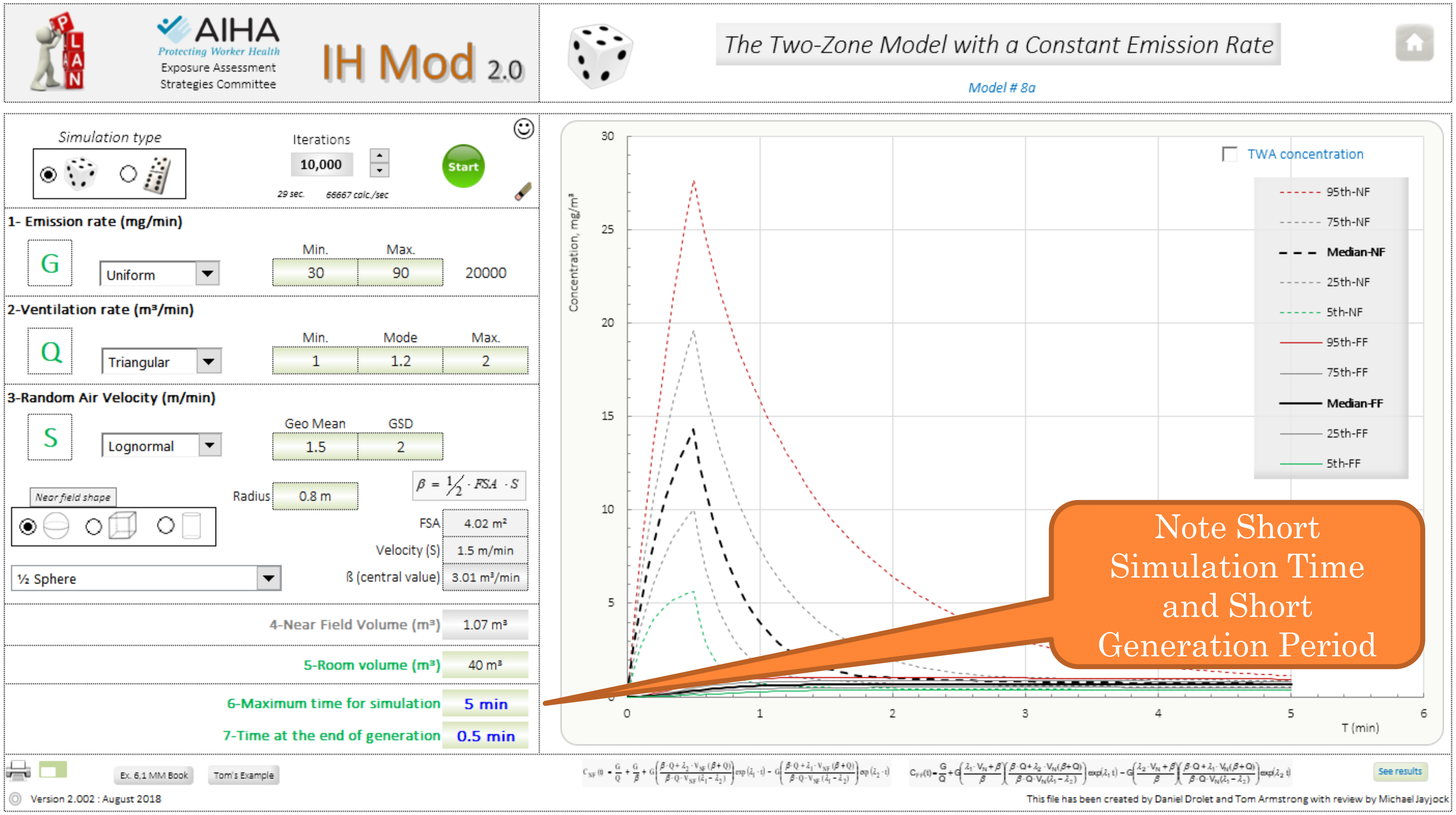
- **We will assume "arm length" of the person from the source, and that is about 0.8 Meter, as radius of the sphere.**
- **Vnear field = 2.1 cubic meter (WHY? V sphere = 4/3 pi r^3)**
- **Free Surface Area = the surface area of a sphere of volume chosen, Surface Area = 4 *pi* r^2 = 8 m^2**
- **For S, default values based on studies of average air speeds in Workplaces and Homes are:**
  - **Absent strong sources of air motion near the source:**
    s = 3 to 4.5 m/min. We will assume 3 m/min
  - **Given strong sources of air motion near the source:**
    s = 7.6 m/min

Then Beta = 1/2FSA*S = 12

There is a real, positive but minimum value for S, it will Not be zero due to breathing, personal movement, and the body thermal plume. 3 m/min may be a reasonable "default" value. It may be lower for a seated worker with minimal arm movement.

As we will soon see, Beta is calculated automatically in IH Mod 2.0 Two Zone models, for several typical geometries

NF-FF (AKA 2 ZONE) MONTE CARLO SIMULATION MODE



The Two-Zone Model with a Constant Emission Rate

Model # 8a

Simulation type ● ○

Iterations 10,000

29 sec. *66667 calc./sec*

1- Emission rate (mg/min)

G Uniform

Min.	Max.	
30	90	20000

2-Ventilation rate (m³/min)

Q Triangular

Min.	Mode	Max.
1	1.2	2

3-Random Air Velocity (m/min)

S Lognormal

Geo Mean	GSD
1.5	2

Near field shape ● ○ ○

Radius 0.8 m

$\beta = \frac{1}{2} \cdot FSA \cdot S$

FSA 4.02 m²

Velocity (S) 1.5 m/min

ß (central value) 3.01 m³/min

½ Sphere

4-Near Field Volume (m³) 1.07 m³

5-Room volume (m³) 40 m³

6-Maximum time for simulation 5 min

7-Time at the end of generation 0.5 min

$C_{NF}(t) = \frac{G}{Q} + \frac{G}{\beta} + G\left(\frac{\beta \cdot Q + \lambda_2 \cdot V_{NF}(\beta+Q)}{\beta \cdot Q \cdot V_{NF}(\lambda_1 - \lambda_2)}\right)\exp(\lambda_1 \cdot t) - G\left(\frac{\beta \cdot Q + \lambda_1 \cdot V_{NF}(\beta+Q)}{\beta \cdot Q \cdot V_{NF}(\lambda_1 - \lambda_2)}\right)\exp(\lambda_2 \cdot t)$

$C_{FF}(t) = \frac{G}{Q} + G\left(\frac{\lambda_1 \cdot V_N + \beta}{\beta}\right)\left(\frac{\beta \cdot Q + \lambda_2 \cdot V_N(\beta+Q)}{\beta \cdot Q \cdot V_N(\lambda_1 - \lambda_2)}\right)\exp(\lambda_1 t) - G\left(\frac{\lambda_2 \cdot V_N + \beta}{\beta}\right)\left(\frac{\beta \cdot Q + \lambda_1 \cdot V_N(\beta+Q)}{\beta \cdot Q \cdot V_N(\lambda_1 - \lambda_2)}\right)\exp(\lambda_2 t)$

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Note Short Simulation Time and Short Generation Period

Tom Armstrong WWW.TWA8HR.com

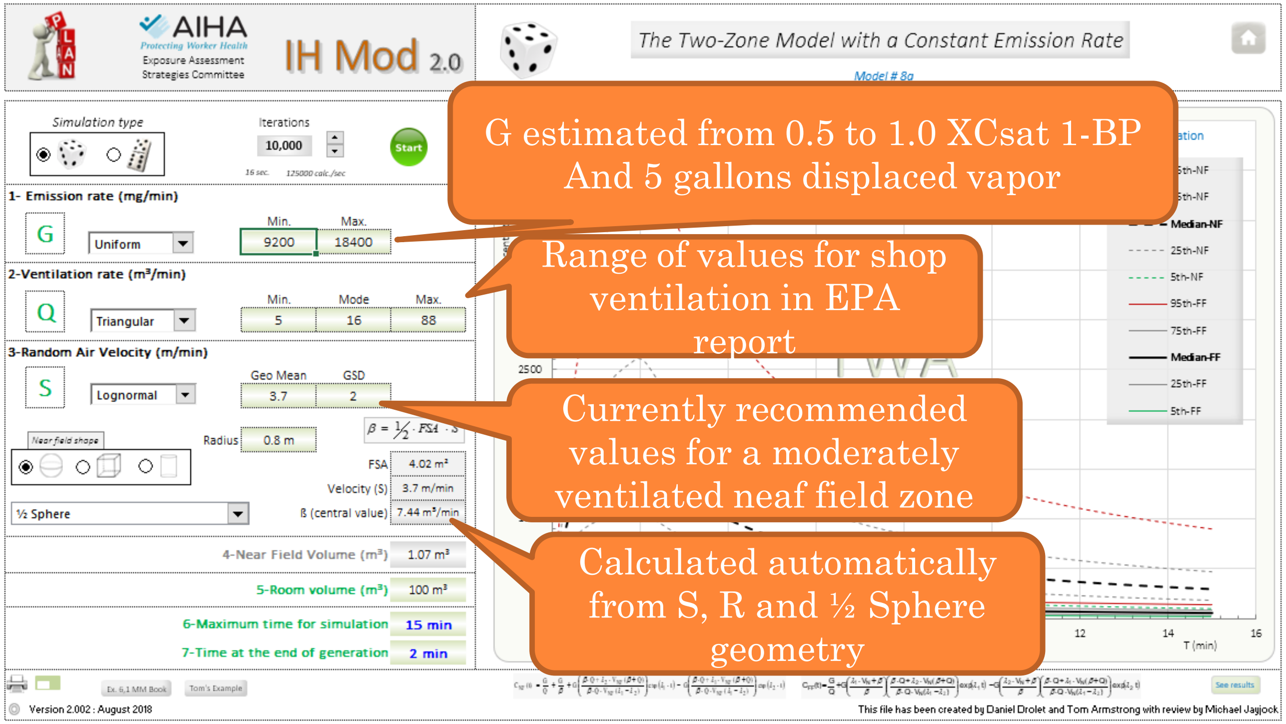
LET'S WORK ANOTHER EXAMPLE WITH THE 2 ZONE MODEL. USE OF A HIGH VOLATILITY SOLVENT IN DRY CLEANING OPERATIONS (1-BROMOPROPANE)

- **Specific tasks**
  - **Addition of 5 gallons of the solvent through the front door of a 3rd generation (dry to dry cycle) dry cleaning machine**
  - **Removal of clothes at end of dry cleaning cycle and exposure to residual solvent vapor from the washer**
- **Blando 2010, Journal of the Air & Waste Management Association, 60:9, 1049-1056,**
  - **Shop A volume 280 m³**
  - **Number of solvent additions and load/unload cycles**
- **Ventilation rate not specified in available reports**
  - **Assume Air Changes per Hour from US EPA EPA Document# 740-R1-5001 February 2016**
  - **Other determinants derived from the same EPA document**
- **Evaluate near field operator exposures, for tasks and full shift average**

ESTIMATING THE PARAMETERS GENERATION RATE & BETA

- G for solvent addition based on Csat and 5 gallons of such vapor displaced while filling. Pure 1-BP, Csat = 96,800 mg/m^3
- The mass in 5 gallons of saturated vapor = 18,000 mg
- Combining, at 1 minute to 2 minutes task time to add the solvent, the estimate for G is 9,200 to 18,400 mg/min
- For the near field we will use an "arm's length" radius of 0.8 meters and hemispherical geometry.
- From Blando 2010 the Shop A volume is 240 m3
- From the US EPA report, the distribution of ACH in dry cleaning shops is 1 to 19, with a typical value of 3.5 leading to an estimated triangular distribution of minimum 5, mode 16 and maximum 88
- For S we will use the typical moderately mixed space value of 3.7 GSD 2

MODELING SOLVENT ADDITION TO A "3RD GENERATION" DRY CLEANING MACHINE, *SHOWING TWA TO 15 MINUTES*



The Two-Zone Model with a Constant Emission Rate

Model # 8a

Simulation type: ● ○

Iterations: 10,000

16 sec. 125000 calc./sec

1- Emission rate (mg/min)

G — Uniform — Min. 9200 — Max. 18400

2-Ventilation rate (m³/min)

Q — Triangular — Min. 5 — Mode 16 — Max. 88

3-Random Air Velocity (m/min)

S — Lognormal — Geo Mean 3.7 — GSD 2

$\beta = \frac{1}{2} \cdot FSA \cdot S$

Near field shape: ● ○ ○

Radius: 0.8 m

FSA: 4.02 m²

Velocity (S): 3.7 m/min

ß (central value): 7.44 m³/min

½ Sphere

4-Near Field Volume (m³): 1.07 m³

5-Room volume (m³): 100 m³

6-Maximum time for simulation: 15 min

7-Time at the end of generation: 2 min

Version 2.002 : August 2018

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G estimated from 0.5 to 1.0 XCsat 1-BP
And 5 gallons displaced vapor

Range of values for shop ventilation in EPA report

Currently recommended values for a moderately ventilated neaf field zone

Calculated automatically from S, R and ½ Sphere geometry

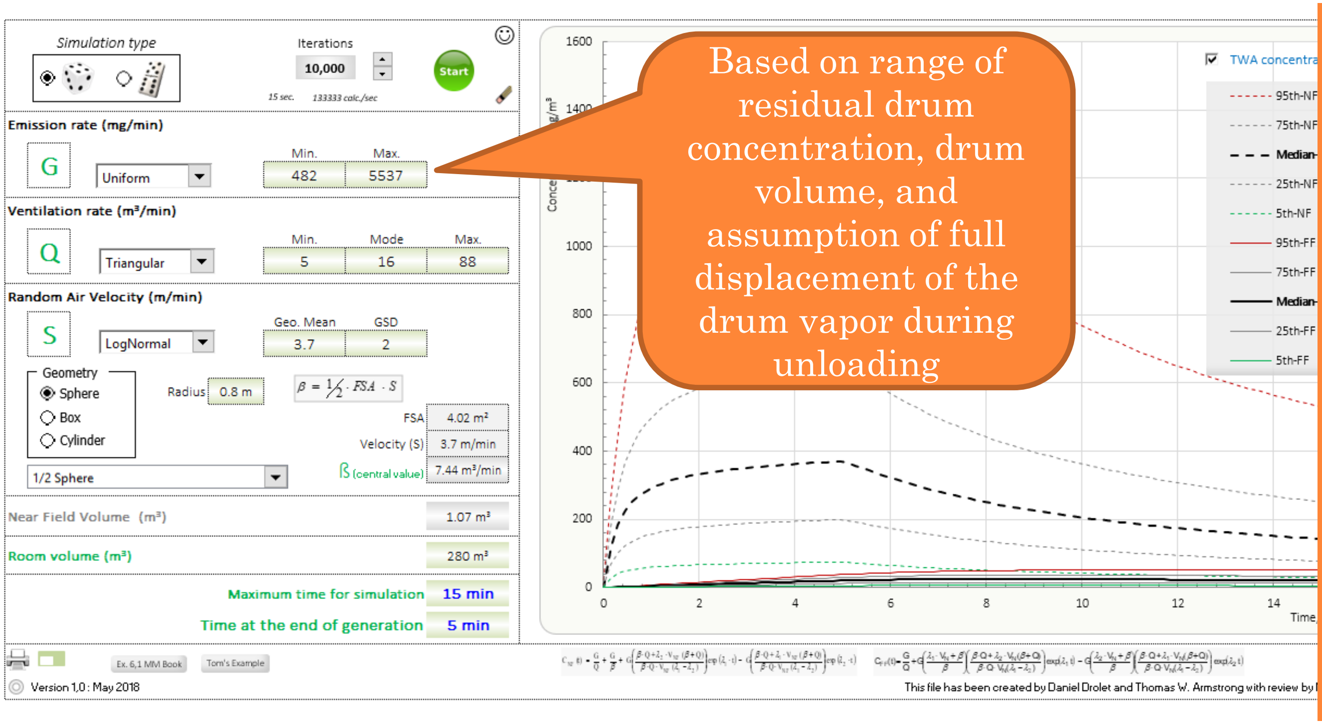
NEAR FIELD
15 Min TWA mg/m³

5th	102
Median	293
95th	902

Tom Armstrong WWW.TWA8HR.com

DRY CLEANING MACHINE UNLOADING TASK EXPOSURE

SOME PARAMETER VALUES BASED ON APP K, EPA DOCUMENT# 740-R1-5001 FEBRUARY 2016



Simulation type

● ○

Iterations: 10,000

15 sec. *133333 calc./sec*

Emission rate (mg/min)

G: Uniform

Min.	Max.
482	5537

Ventilation rate (m³/min)

Q: Triangular

Min.	Mode	Max.
5	16	88

Random Air Velocity (m/min)

S: LogNormal

Geo. Mean	GSD
3.7	2

Geometry
- ● Sphere
- ○ Box
- ○ Cylinder

1/2 Sphere

Radius: 0.8 m

$\beta = \frac{1}{2} \cdot FSA \cdot S$

FSA: 4.02 m²

Velocity (S): 3.7 m/min

ß (central value): 7.44 m³/min

Near Field Volume (m³): 1.07 m³

Room volume (m³): 280 m³

Maximum time for simulation: 15 min

Time at the end of generation: 5 min

Version 1,0 : May 2018

This file has been created by Daniel Drolet and Thomas W. Armstrong with review by I

Based on range of residual drum concentration, drum volume, and assumption of full displacement of the drum vapor during unloading

Near Field
mg/m³
15 min TWA
5th
31
Median 150
95th
565

Far Field
mg/m³ **Median**

26
95th
87

Tom Armstrong WWW.TWA8HR.com

What is the eight hour TWA?
Via off to the Side calculations

Estimated 8 hour TWA from one solvent addition + fourteen unloads + remaining time (240 minutes) at room background (far field results)

Median = (293 * 15min + 151*14min +2.2 *240 min)/480min = 76 mg/m^3 = 15 ppm

75th = (466*15 min + 262*14*15min + 12*240min)/480 min = 130 mg/m^3 = 26 ppm

95th = (902*15 min + 565*14 +240*41)/480min = 296 mg/m^3 = 59 ppm

Available* measured 8 hr TWA AM 32 ppm

95th 82 ppm

Blando 2010

THE 2 ZONE MODEL IS REASONABLY VALIDATED

Of course, garbage parameters give garbage results.

From "The Daubert Standard as Applied to Exposure Assessment Modeling Using the Two-Zone (NF/FF) Model Estimation of Indoor Air Breathing Zone Concentration as an Example", Jayjock, Armstrong, Taylor, JOEH 8, D114-122, 2011

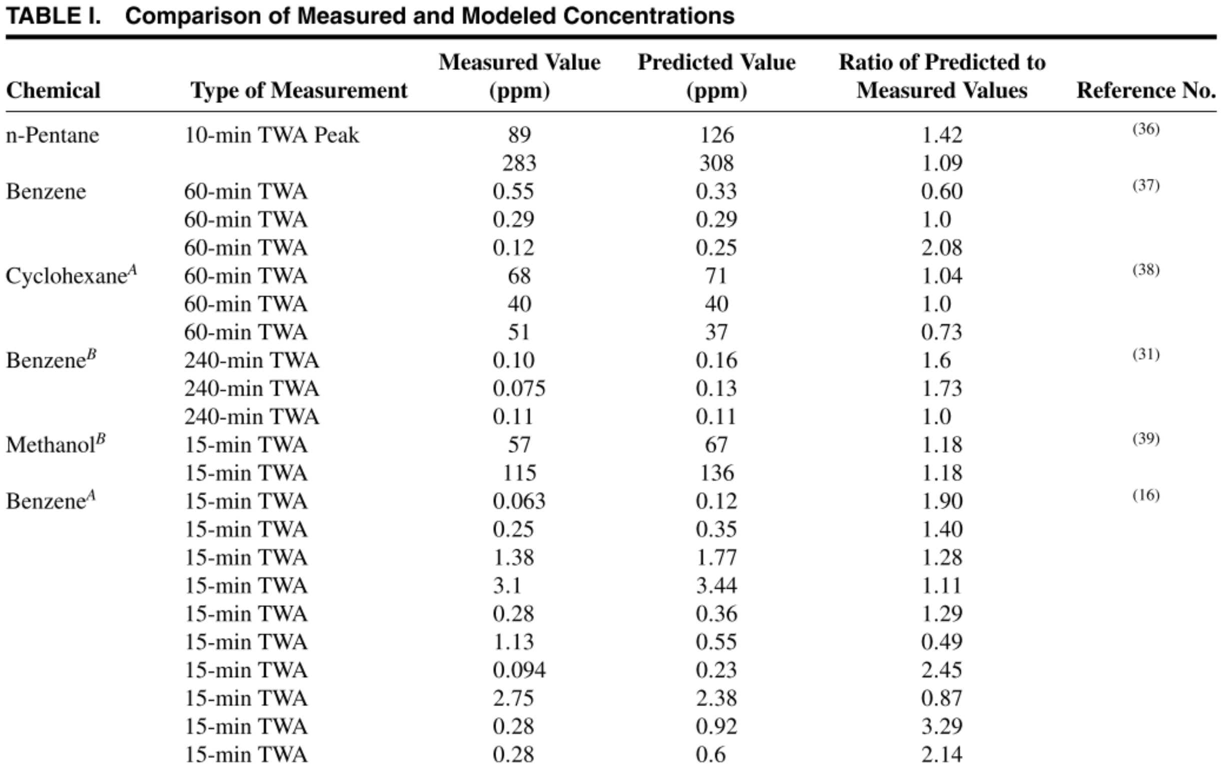


TABLE I. Comparison of Measured and Modeled Concentrations

Chemical	Type of Measurement	Measured Value (ppm)	Predicted Value (ppm)	Ratio of Predicted to Measured Values	Reference No.
n-Pentane	10-min TWA Peak	89	126	1.42	(36)
		283	308	1.09	
Benzene	60-min TWA	0.55	0.33	0.60	(37)
	60-min TWA	0.29	0.29	1.0	
	60-min TWA	0.12	0.25	2.08	
Cyclohexane[A]	60-min TWA	68	71	1.04	(38)
	60-min TWA	40	40	1.0	
	60-min TWA	51	37	0.73	
Benzene[B]	240-min TWA	0.10	0.16	1.6	(31)
	240-min TWA	0.075	0.13	1.73	
	240-min TWA	0.11	0.11	1.0	
Methanol[B]	15-min TWA	57	67	1.18	(39)
	15-min TWA	115	136	1.18	
Benzene[A]	15-min TWA	0.063	0.12	1.90	(16)
	15-min TWA	0.25	0.35	1.40	
	15-min TWA	1.38	1.77	1.28	
	15-min TWA	3.1	3.44	1.11	
	15-min TWA	0.28	0.36	1.29	
	15-min TWA	1.13	0.55	0.49	
	15-min TWA	0.094	0.23	2.45	
	15-min TWA	2.75	2.38	0.87	
	15-min TWA	0.28	0.92	3.29	
	15-min TWA	0.28	0.6	2.14	

Also, see Koivisto et al. 2019, https://doi.org/10.1016/j.scitotenv.2019.02.398

LETS TAKE QUICK LOOKS AT SOME OF THE OTHER IH MOD MODELS

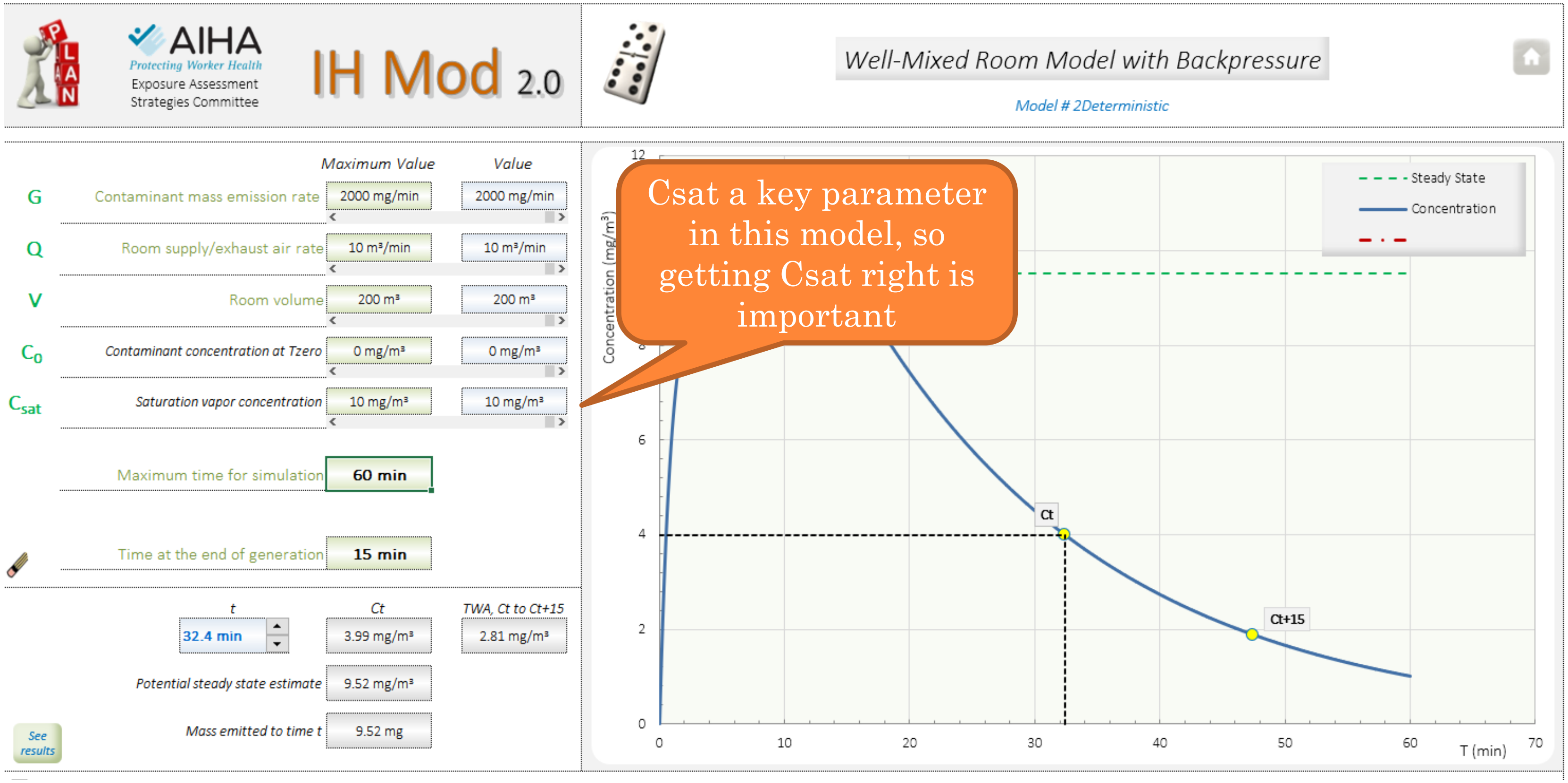
WMR WITH BACKPRESSURE

- Because the net rate of evaporation into room air decreases as the chemical's partial pressure in air increases, the airborne chemical is said to exert a ***backpressure*** on the liquid or solid chemical. That is, the material can partition back into the source liquid or solid.
- To be clear, backpressure does not mean that the rate of evaporation into air decreases.
- The rate of evaporation into air remains the same, but the net rate of evaporation decreases.

THE BACKPRESSURE EFFECT

- The backpressure effect can be important, regardless of their vapor pressure. It comes to play in scenarios where the airborne concentration can become a significant portion of Csat. It can be a high or low VP material.
- An inherently high VP material in a mixture at low concentration could have a relatively low Csat due to its limited partial pressure and if given enough surface area, back pressure could have a large impact.
- Backpressure can be important for a low VP material, say < 1 mm Hg, but present in large amounts such that evaporation causes their partial pressure to approach their saturation vapor pressure value P_V (corresponding to their saturation concentration in air, C_{sat}).
- For example, toluene has P_V = 21 mm Hg at 20 °C. For room pressure at 760 mm Hg, $C_{sat} \approx$ 28,000 ppm.
- Fortunately, it would be unusual for the toluene concentration in an indoor workplace to approach even 5% of this value (1400 ppm).

NOW, IN IH MOD, DETERMINISTIC VERSION



AIHA Protecting Worker Health Exposure Assessment Strategies Committee

IH Mod 2.0

Well-Mixed Room Model with Backpressure

Model # 2Deterministic

		Maximum Value	Value
G	Contaminant mass emission rate	2000 mg/min	2000 mg/min
Q	Room supply/exhaust air rate	10 m³/min	10 m³/min
V	Room volume	200 m³	200 m³
C_0	Contaminant concentration at Tzero	0 mg/m³	0 mg/m³
C_{sat}	Saturation vapor concentration	10 mg/m³	10 mg/m³

Maximum time for simulation: 60 min

Time at the end of generation: 15 min

t	Ct	TWA, Ct to Ct+15
32.4 min	3.99 mg/m³	2.81 mg/m³

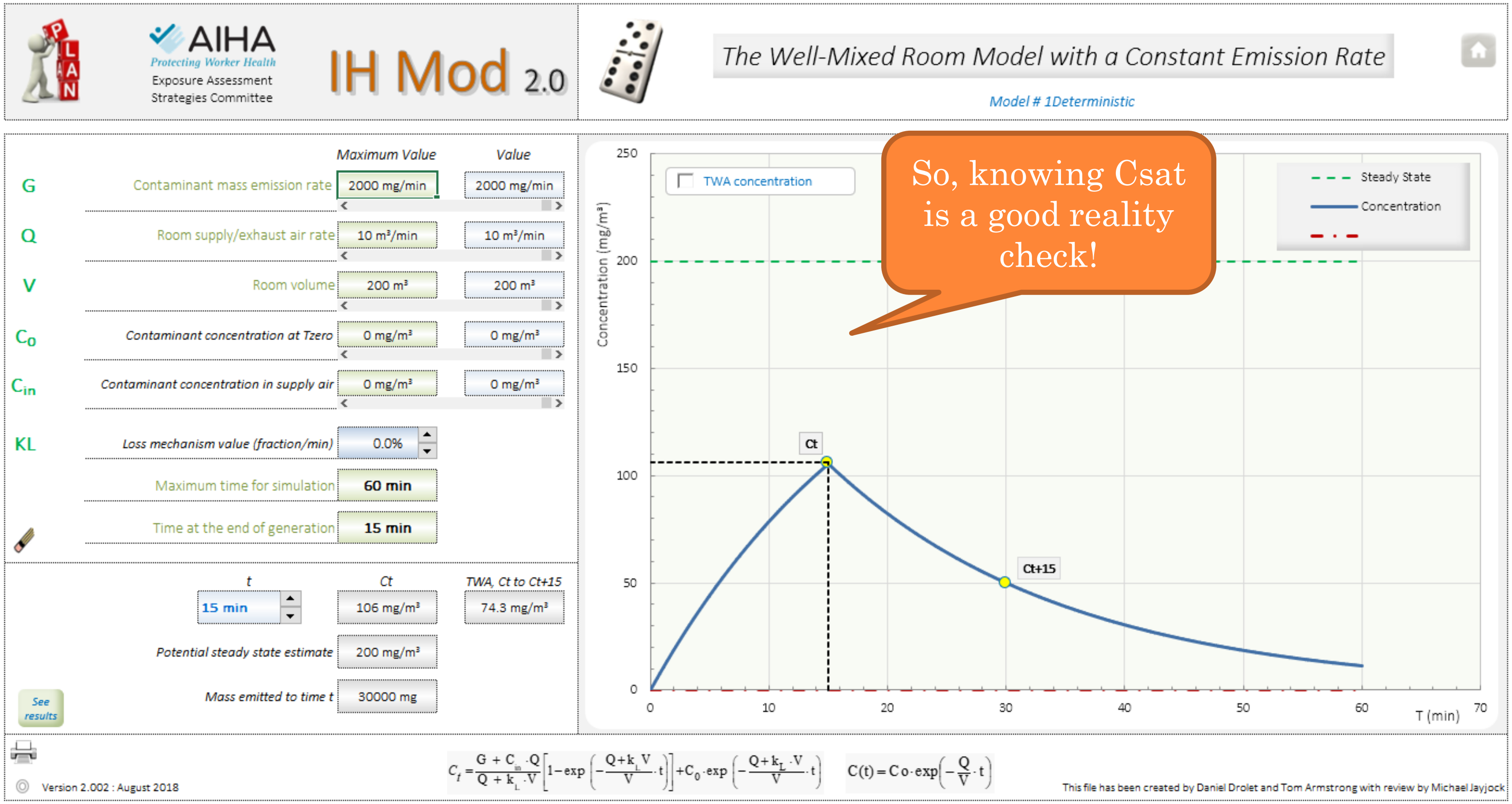
Potential steady state estimate: 9.52 mg/m³

Mass emitted to time t: 9.52 mg

Csat a key parameter in this model, so getting Csat right is important

If we neglect backpressure – Well Mixed Room Model CAN predict concentrations above saturation Csat 10 mg/m^3

Example conditions are a bit extreme and are set just to show the point.



		Maximum Value	Value
G	Contaminant mass emission rate	2000 mg/min	2000 mg/min
Q	Room supply/exhaust air rate	10 m³/min	10 m³/min
V	Room volume	200 m³	200 m³
C_0	Contaminant concentration at Tzero	0 mg/m³	0 mg/m³
C_{in}	Contaminant concentration in supply air	0 mg/m³	0 mg/m³
KL	Loss mechanism value (fraction/min)	0.0%	
	Maximum time for simulation	60 min	
	Time at the end of generation	15 min	

t	Ct	TWA, Ct to Ct+15
15 min	106 mg/m³	74.3 mg/m³

Potential steady state estimate: 200 mg/m³

Mass emitted to time t: 30000 mg

$$C_t = \frac{G + C_{in} \cdot Q}{Q + k_L \cdot V}\left[1 - \exp\left(-\frac{Q + k_L V}{V} \cdot t\right)\right] + C_0 \cdot \exp\left(-\frac{Q + k_L \cdot V}{V} \cdot t\right)$$

$$C(t) = Co \cdot \exp\left(-\frac{Q}{V} \cdot t\right)$$

This file has been created by Daniel Drolet and Tom Armstrong with review by Michael Jayjock

So, knowing Csat is a good reality check!

ANOTHER MODEL – WELL MIXED ROOM WITH EXPONENTIALLY DECREASING EMISSION RATE (SMALL SPILL MODEL)

This emission rate function applies to several common processes:

- vapor emission from a small spill of solvent
- emission of a minor constituent of a liquid mixture in a tank
- offgassing of residual fumigants such as ethylene oxide and methyl bromide

SMALL SPILL OF AN ORGANIC SOLVENT

G(t) decreases over time for two reasons *not* involving a backpressure effect.

1. **As the chemical evaporates, the liquid cools. In turn, the tendency of the chemical to evaporate decreases.**
2. **As the chemical evaporates, the pool size shrinks. In turn, the surface area from which the chemical can evaporate decreases.**

WHEN IS A SPILL "SMALL" SUCH THAT THE BACKPRESSURE EFFECT CAN BE IGNORED AND THE EXPONENTIALLY DECREASING EMISSION RATE APPLIED?

Example for Perchloroethylene

- **P_V = 14 mm Hg (20 °C), Liquid Density = 1.65 g/mL**
- **C_{sat} = 125,000 mg/m^3 = 125 g/m^3**
- **Consider a room with V = 100 m^3 (≈ 18 ft x 20 ft x 10 ft)**
- **Saturated air contains (125 g/m^3)(100 m^3) = 12,500 g perc**
- **10% saturated air contains: = 758 mL perc**
- **In this room, a "small" perchloroethylene spill is ≤ 758 mL.**

THE RELATIONSHIP BETWEEN THE REMAINING CONTAMINANT MASS AND THE EXPONENTIALLY DECREASING MASS EMISSION RATE

Contaminant Mass Remaining in the Source

- **$M(t)$, mg = $M_0 \cdot \exp(-\alpha \cdot t)$**
- **$M(t)$ = contaminant mass (mg) remaining in the source at time t (min)**
- **M_0 = initial contaminant mass in the source (mg), $M(0)$**
- **α = emission rate constant (min^{-1})**

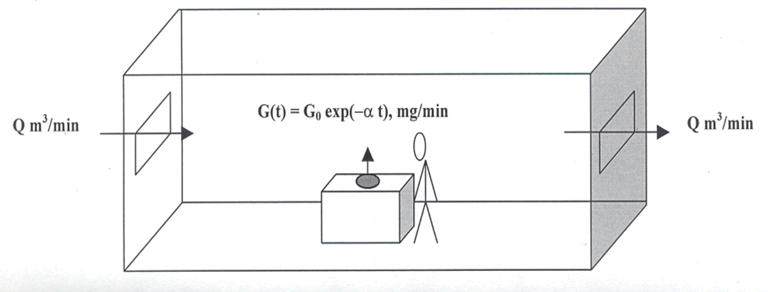
Mass Emission Rate from the Source

- **$G(t)$, mg/min = $\alpha \cdot M_0 \cdot \exp(-\alpha \cdot t)$**

Note: $G_0 = \alpha \cdot M_0$

SMALL SPILL EXAMPLE

A 15 mL spill of n-pentane occurs in a room at 20°C and 760 mm Hg. Assume that the vapor mass emission rate is exponentially decreasing, and that the room is well-mixed. We want to find C(t).



Given:

$M_0 = 9450$ mg

$\alpha = 0.28\ \text{min}^{-1}$

$V = 22.7\ \text{m}^3$

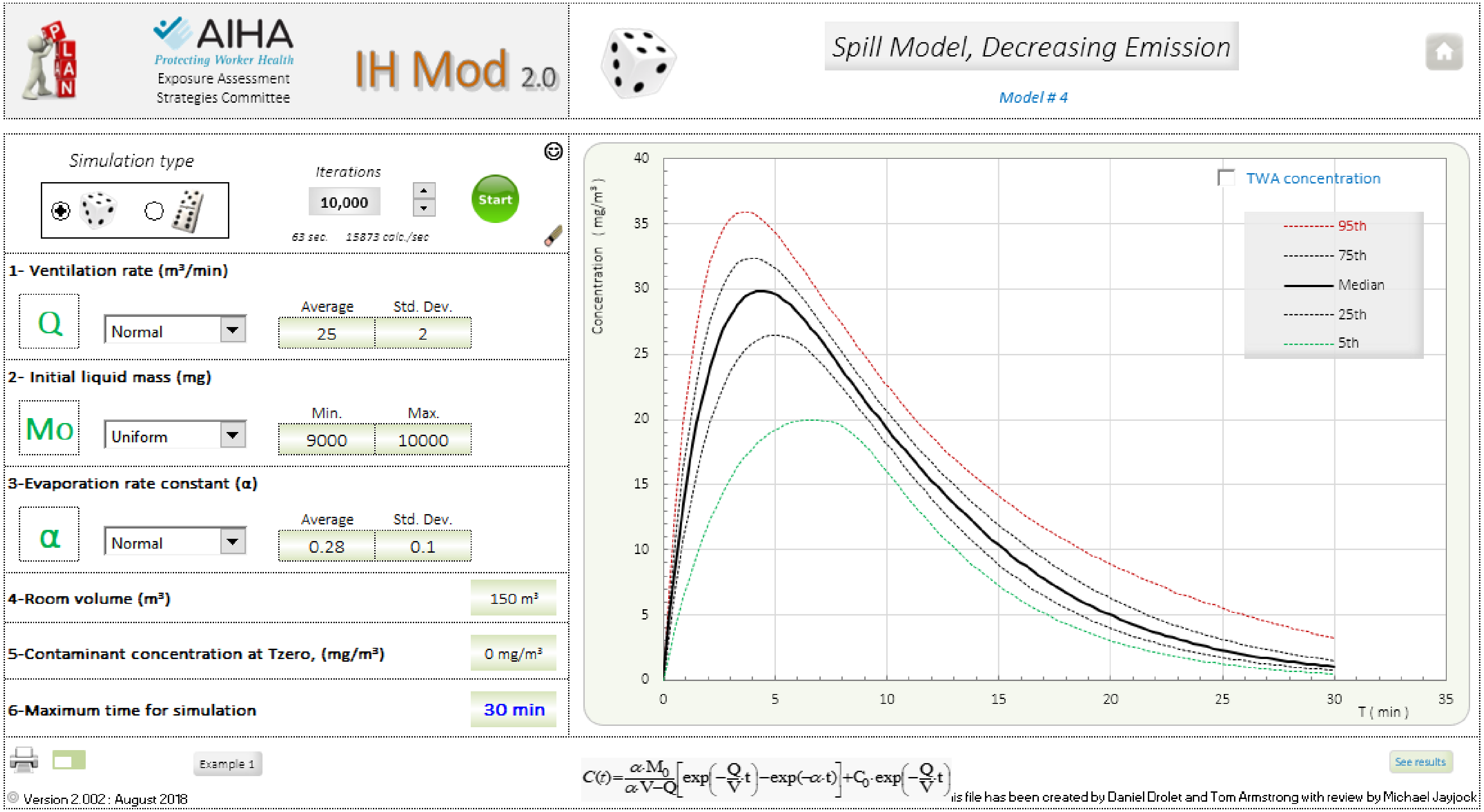
$Q = 18.6\ \text{m}^3/\text{min}$ (49 ACH)

Question

Is 15 mL n-pentane a small spill in this room?

Tom Armstrong WWW.TWA8HR.com

Now in IH Mod



Simulation type: ● (Monte Carlo) ○

Iterations: 10,000

63 sec. 15873 calc./sec

1- Ventilation rate (m³/min): Q — Normal — Average 25, Std. Dev. 2

2- Initial liquid mass (mg): Mo — Uniform — Min. 9000, Max. 10000

3-Evaporation rate constant (α): α — Normal — Average 0.28, Std. Dev. 0.1

4-Room volume (m³): 150 m³

5-Contaminant concentration at Tzero, (mg/m³): 0 mg/m³

6-Maximum time for simulation: 30 min

$$C(t)=\frac{\alpha\cdot M_0}{\alpha\cdot V-Q}\left[\exp\left(-\frac{Q}{V}\cdot t\right)-\exp(-\alpha\cdot t)\right]+C_0\cdot\exp\left(-\frac{Q}{V}\cdot t\right)$$

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Tom Armstrong WWW.TWA8HR.com

HOW DOES ONE OBTAIN α FOR A SMALL SPILL?

- **Experimentally determine it by timing the mass loss from liquid placed in a watchglass on an electronic balance. [note there may be SCALING and other parameter effects!]**
- **In the alternative, for hydrocarbon compounds containing carbon, hydrogen and oxygen**

$$\alpha = .000524\,P_V + .0108\,SA/VO$$

P_V = **saturation vapor pressure in mm Hg at 20 °C**

SA/VOL = initial surface-area-to-volume ratio of the spill, cm^{-1}

Source: C. Keil and M. Nicas: "Predicting room vapor concentrations due to spills of organic solvents.", Am. Ind. Hyg. Assoc. J., July 2003

EXPERIMENTAL DETERMINATIONS

α is correlated with the saturation vapor pressure

Chemical	P_V (mm Hg at 20 °C)	α (min^{-1}) mean
ethyl ether	440	0.37
n-pentane	420	0.39
acetone	180	0.16
n-hexane	124	0.14
methanol	96	0.055
methyl ethyl ketone	78	0.055
2-propanol	33	0.028
toluene	21	0.025
n-butyl acetate	10	0.011
1-butanol	6	0.004
methylene chloride	350	0.14
carbon disulfide	297	0.11
chloroform	160	0.082

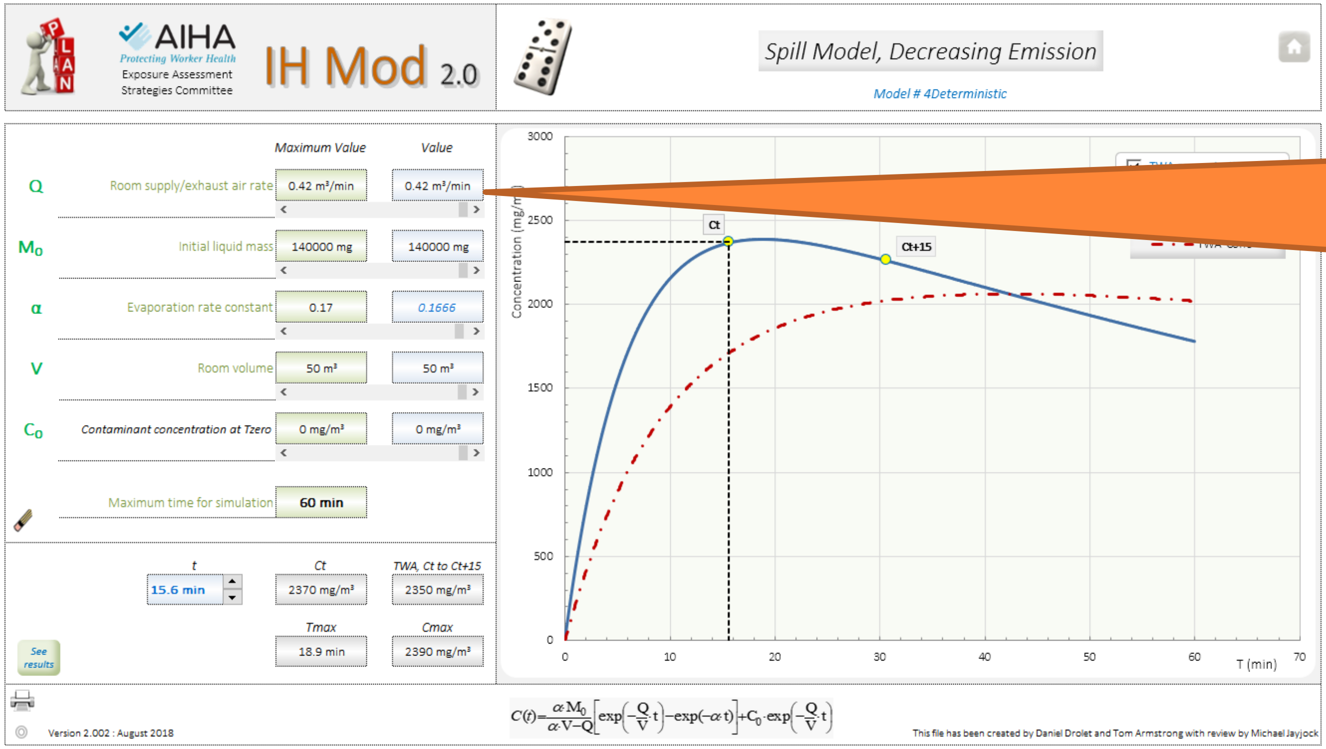
Source: C. Keil and M. Nicas: "Predicting room vapor concentrations due to spills of organic solvents.", Am. Ind. Hyg. Assoc. J., July 2003

PROBLEM

- **Dichloromethane (MeCl$_2$) is used in paint strippers for consumer use.**
  - **Molecular weight 84.93**
  - **Vapor pressure 352 Torr at 25 C**
  - **An experimental study (MRI*) gives data to estimate a first order exponential decay rate of approximately 10/hour = 0.17 per minute**
  - **TLV 50 ppm = 174 mg/m^3**
- **A typical paint stripper contains 20% by weight MeCl$_2$ in the paint stripper, and is applied to 10 square feet at 208 grams/ft2. A study on Me Cl$_2$ in paint removers (MRI*) suggests about 66% of the MeCl$_2$ remains in the removed paint, with about 33% emitted rapidly to air.**
  - **416 grams MeCl$_2$ applied**
  - **33% to air = 140 grams = 140,000 mg**
- **The work is done in a home workshop, volume 50 m^3, with 0.5 ACH, for a ventilation rate of 25 m^3/hr = 0.42 m^3/min**
- **The application takes about 5 minutes followed by 30 minutes of wait time before scraping. However, to simplify, assume the whole mass emitted to air is applied at T$_0$.**

* Midwest Research Institute. Consumer Exposure to Paint Stripper Solvents, Final Report. Report to the USEPA, EPA Contract No. 68-DO-0137, Work Assignment No. 4-06 (EPA, 1994a);

WELL MIXED ROOM WITH EXPONENTIALLY DECREASING EMISSION



Spill Model, Decreasing Emission

Model # 4Deterministic

		Maximum Value	Value
Q	Room supply/exhaust air rate	0.42 m³/min	0.42 m³/min
M_0	Initial liquid mass	140000 mg	140000 mg
α	Evaporation rate constant	0.17	0.1666
V	Room volume	50 m³	50 m³
C_0	Contaminant concentration at Tzero	0 mg/m³	0 mg/m³
	Maximum time for simulation	60 min	

t	Ct	TWA, Ct to Ct+15
15.6 min	2370 mg/m³	2350 mg/m³

Tmax	Cmax
18.9 min	2390 mg/m³

$$C(t)=\frac{\alpha \cdot M_0}{\alpha \cdot V-Q}\left[\exp\left(-\frac{Q}{V}\cdot t\right)-\exp(-\alpha \cdot t)\right]+C_0 \cdot \exp\left(-\frac{Q}{V}\cdot t\right)$$

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What would ventilation need to be to reduce this by 10X?
> 1 ACM (> 50 M³/min)

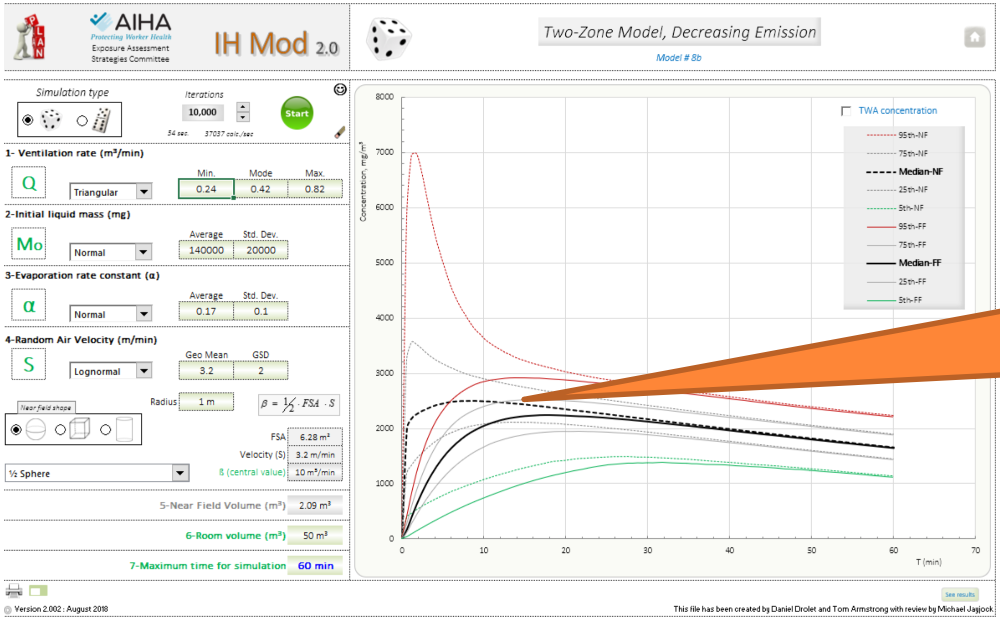
Tom Armstrong WWW.TWA8HR.com

WHAT IF WE USE THE 2 ZONE WITH EDR MODEL?

For this model, we also need beta, the interzonal mixing ventilation

Assume a near field volume as a hemisphere of radius 1 meter for a NF

ximately 6 M². With an s of



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IH Mod 2.0

Two-Zone Model, Decreasing Emission

Model # 8b

Simulation type: ● ○

Iterations: 10,000

54 sec. 37037 calc./sec

1- Ventilation rate (m³/min)

Q: Triangular

Min.	Mode	Max.
0.24	0.42	0.82

2-Initial liquid mass (mg)

Mo: Normal

Average	Std. Dev.
140000	20000

3-Evaporation rate constant (α)

α: Normal

Average	Std. Dev.
0.17	0.1

4-Random Air Velocity (m/min)

S: Lognormal

Geo Mean	GSD
3.2	2

Radius: 1 m

$\beta = \frac{1}{2} \cdot FSA \cdot S$

Near field shape: ● ○ ○

½ Sphere

FSA: 6.28 m²

Velocity (S): 3.2 m/min

ß (central value): 10 m³/min

5-Near Field Volume (m³): 2.09 m³

6-Room volume (m³): 50 m³

7-Maximum time for simulation: 60 min

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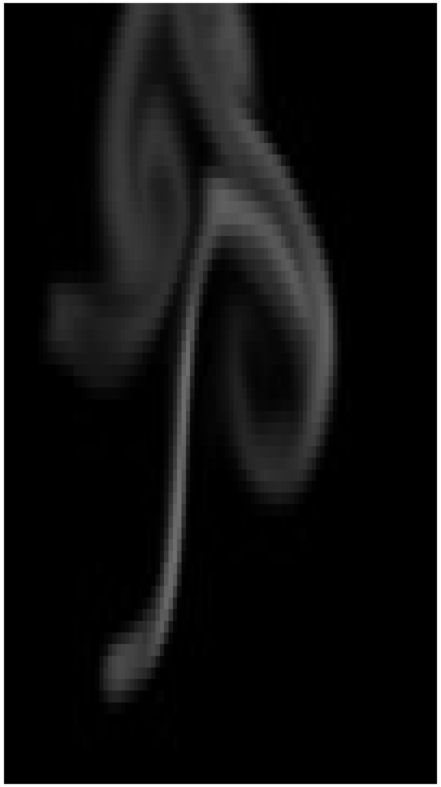
The Near Field Median is in the same range as from the Well Mised Room simulation we just looked at.

TURBULENT DIFFUSION MODELS

TURBULENT (AKA EDDY) DIFFUSION MODELS

- Intuition and experience show that:
  - Rooms are ***not*** perfectly mixed (the well mixed room model), and
  - Rooms do not consist of contiguous, perfectly mixed zones with limited air exchange between the zones (the near field/far field model).
- Rather, there is a **gradient** in concentration as one moves away from an emission source.
- In theory, three dimensional contour "surfaces" of equal concentration could be mapped around an emission source:
  - All points on a surface would ***not*** be equidistant from the source, and the surface would not be "symmetrical" in shape
  - The shape and contours could shift over time



For the Turbulent Diffusion Models, the Parameter D_T Is Essential

ACH is NOT equal to internal space turbulence

Some reported eddy diffusion coefficients

Room Dimensions	Air changes per hour	D (m^2/min)	Other
150 ft x 120 ft x 16 ft 288,000 ft^3	0.3	11.5	
110 ft x 40 ft x 20 ft 88,000 ft^3	11	0.1 – 1.3	
180 ft x 120 ft x 20 ft 432,000 ft^3	5	0.1 – 0.8	
770,000 ft^3	5.7	0.085 – 0.885	mean 0.354, SD .29 median 0.279
289,000 ft^3	8.2	0.085 – 9.988	mean 1.26, SD 2.9 median 0.304
64.5 ft × 60.5 ft × 12 ft 47,000 ft^3	10.5	0.11 – 0.23	mean 0.16, SD .04 median 0.16

See “Mathematical Models for Estimating Occupational Exposure to Chemicals” for details and citations

Also, refer back to Slide 39

THE TURBULENT EDDY DIFFUSION COEFFICIENT

- **There has unfortunately been little research on the values of D_T in workplaces and even less in residential settings. Some data are presented in Chapter 7 of the text: *"Mathematical Models for Estimating Occupational Exposure to Chemicals", AIHA Exposure Assessment Strategies Committee, Editor: C. Keil, 2nd Edition, AIHA Press, 2009.***
- **The following algorithm* for predicting D_T in an isothermal room (no temperature gradients) has been suggested, although its overall validity is unknown:**

$$D_T\ ,\ m^2/\min = 60(ACS \cdot U_{IN}^2 \cdot H^4 \cdot 0.08)^{1/3}$$

ACS = number of room air changes <u>per second</u>

U_{IN} = discharge velocity (m/sec) of supply air into the room through air inlets

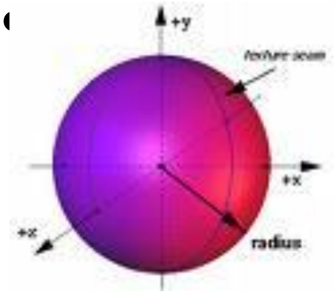
H = height of room (m)

ALWAYS check the UNITS in any equation!

* Based on isothermal solution to equation given by Drivas (1996) "Modeling Indoor Exposure for Short Term Point Source Releases", Indoor Air 6:271-277.

SPHERICAL DIFFUSION WITHOUT ADVECTION FOLLOWING A PULSE RELEASE

- C(x,y,z,t) = contaminant concentration at
  Position (x, y, z) relative to the pulse release positi



- Pulse release (M_0) position is at x = 0, y = 0, z = 0
  Time t (min) after the pulse release.
  All distances are in m

$$C(x,y,z,t), mg/m^3 = \frac{M_0}{8\cdot(\pi\cdot D_T\cdot t)^{1.5}}\cdot \exp\left(-\frac{x^2+y^2+z^2}{4\cdot D_T\cdot t}\right)$$

- M_0 = mass (mg) released as a pulse at time zero
- D_T = turbulent eddy diffusion coefficient (m^2/min)
- No directional air flow (Advection)
- Contaminant diffuses outward equally in all directions

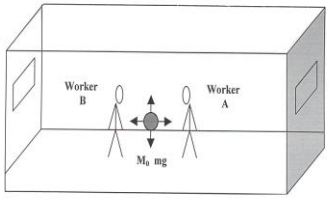
LET'S LOOK AT THIS MODEL WITH IH MOD 2.0

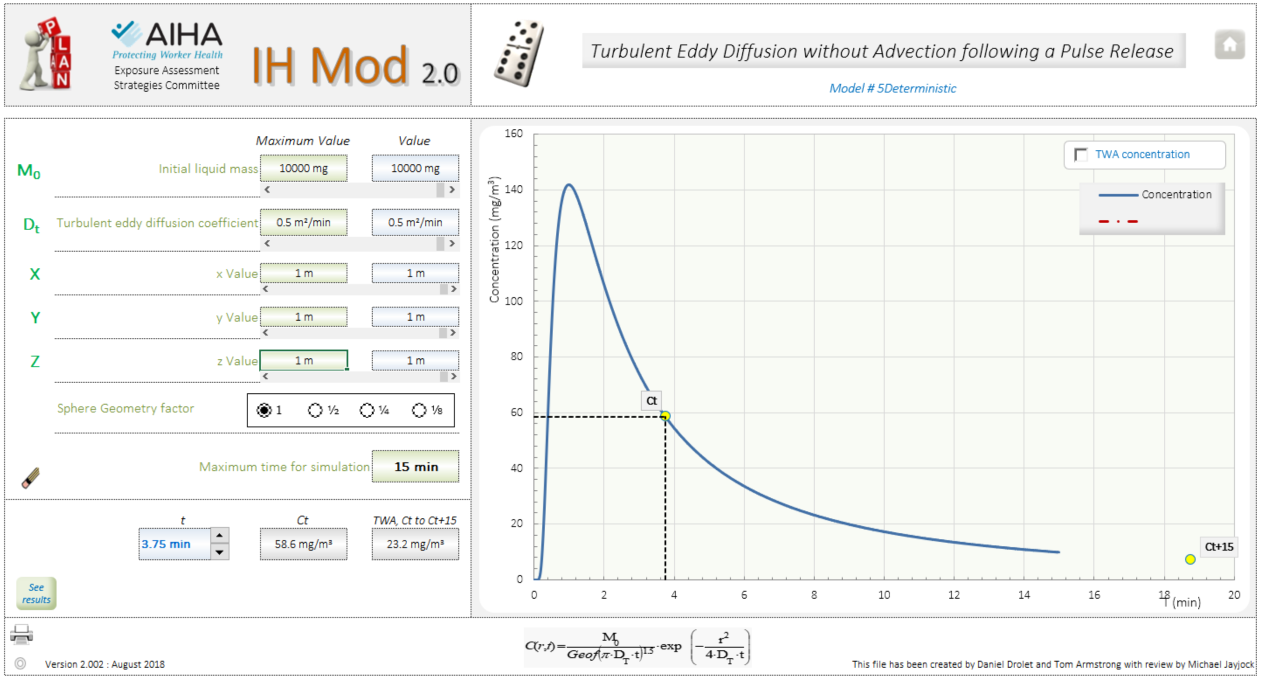
- **A contaminant is emitted in the middle of a large room such that the source can reasonably be treated as a point source. The release position is the origin (x = 0, y = 0, z = 0) in three-dimensional space.**
- **At time zero, M_0 = 10,000 mg is emitted.**
- **Assume that spherical turbulent diffusion occurs with D_T = 0.50 m^2/min, and with no advective air flow in the vicinity of the release (= 0).**
- **Worker A's breathing zone is at (x = 1, y = 1 z = 1).**

  Worker B's breathing zone is at

  (x = –1, y = 0, z = 1).
- **We want to know their exposure concentrations.**

Results in IH Mod 2.0 Deterministic





Turbulent Eddy Diffusion without Advection following a Pulse Release

Model # 5Deterministic

		Maximum Value	Value
M_0	Initial liquid mass	10000 mg	10000 mg
D_t	Turbulent eddy diffusion coefficient	0.5 m²/min	0.5 m²/min
X	x Value	1 m	1 m
Y	y Value	1 m	1 m
Z	z Value	1 m	1 m

Sphere Geometry factor ● 1 ○ ½ ○ ¼ ○ ⅛

Maximum time for simulation **15 min**

t	Ct	TWA, Ct to Ct+15
3.75 min	58.6 mg/m³	23.2 mg/m³

$$C(r,t)=\frac{M_0}{Geof(\pi\cdot D_T\cdot t)^{1.5}}\cdot\exp\left(-\frac{r^2}{4\cdot D_T\cdot t}\right)$$

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EXAMPLE INTERPRETATION

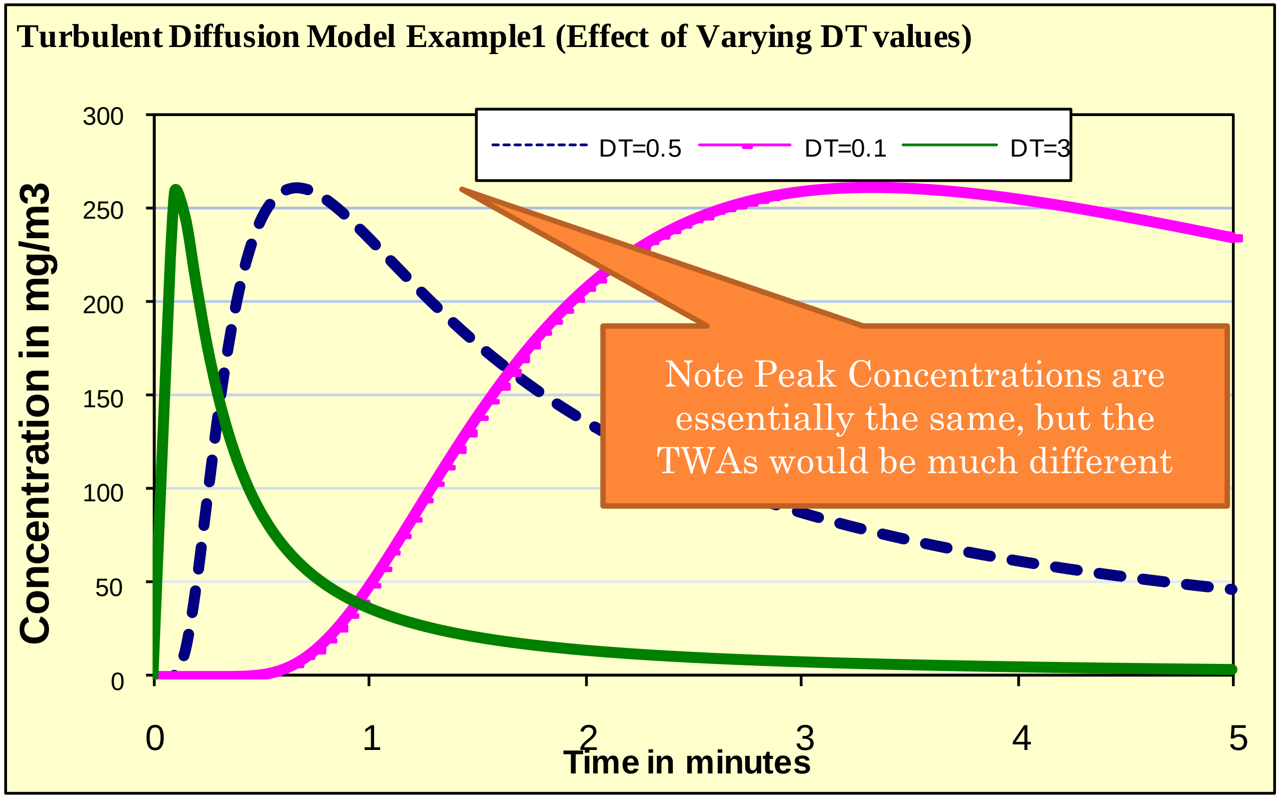
- **A “wave front” of contaminant moves past each worker’s position**
- **The concentration increases to a peak value of 260 mg/m^3 at about 0.7 min after the pulse release, and decreases thereafter**
- **If the radial distance were smaller than 1 m, the concentration values would be *higher* overall, and the peak concentration would occur prior to 0.7 min**
- **If the radial distance were larger than 1.0 m, the concentration values would be *lower* overall, and the peak concentration would occur later than 0.7 min**

EXAMPLE INTERPRETATION

- ***Decreasing*** **the D_T value:**
  - **Results in slower dispersion process**
  - **The contaminant wave would pass each position more slowly**
  - **Yet, the peak concentration would be similar**
  - **15 minute TWA would be higher**
- ***Increasing*** **the D_T value:**
  - **Results in faster dispersion process**
  - **The contaminant wave would pass each position more quickly**
  - **Yet, the peak concentration would again be similar**
  - **15 minute TWA would be lower**

Let's go to IH Mod and TRY changing D_T (to < and > 0.5) and watch

- **This effect is evident in the next graph (Not generated in IH Mod)**
  - **The predicted concentration time series for the same scenario with alternative D_T values of 0.1, 0.5 and 3.0 m^2/min.**
- **Note, the TIME WEIGHTED AVERAGE concentration and dose could be different!**



Turbulent Diffusion Model Example1 (Effect of Varying DT values)

Note Peak Concentrations are essentially the same, but the TWAs would be much different

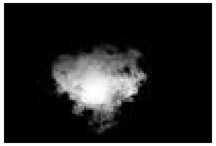
Graph not done in IH Mod

SPHERICAL DIFFUSION *WITH* ADVECTION FOLLOWING A PULSE RELEASE

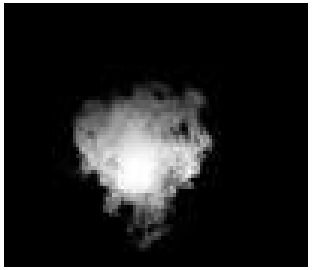
- **Contaminant mass M_0 (mg) is released as a pulse at time zero.**
- **The release position is the origin in a three-dimensional coordinate system,**

  (x = 0, y = 0, z = 0).
- **Mass <u>STILL</u> disperses away from the origin in a spherically symmetrical pattern via turbulent diffusion with coefficient D_T (m^2/min).**
- **Assume there *is* an advective air flow near the source, or U > 0. Denote the magnitude of the flow vector by U (m/min).**
- **The advective air flow is parallel to the x-axis, with the flow going from left to right (from negative x values towards positive x values).**
- **A D_T = 1 m^2/min means random diffusion over a cross sectional area of 1 m^2 in one minute**

T1 X1



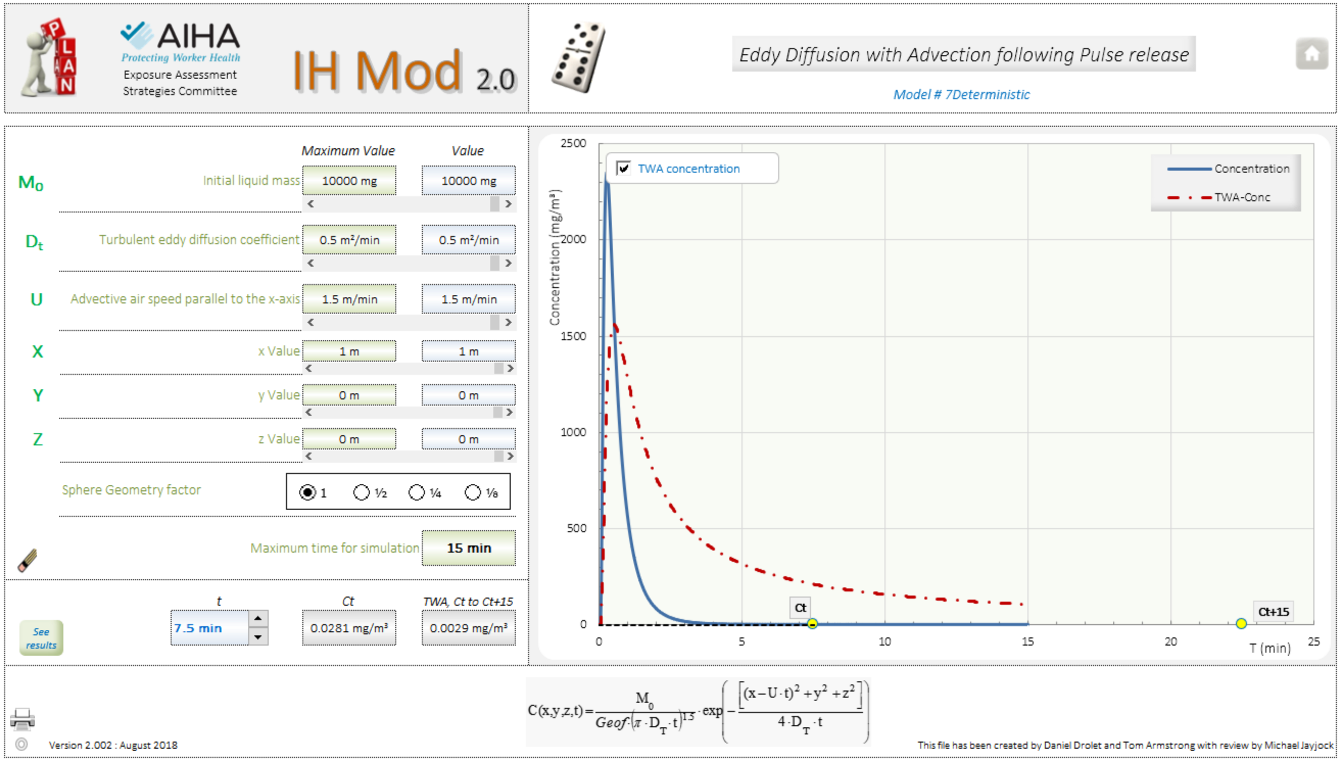
T2 X2



T3 X3

Tom Armstrong WWW.TWA8HR.com

IN IH MOD DETERMINISTIC



		Maximum Value	Value
M_0	Initial liquid mass	10000 mg	10000 mg
D_t	Turbulent eddy diffusion coefficient	0.5 m²/min	0.5 m²/min
U	Advective air speed parallel to the x-axis	1.5 m/min	1.5 m/min
X	x Value	1 m	1 m
Y	y Value	0 m	0 m
Z	z Value	0 m	0 m

Sphere Geometry factor ● 1 ○ ½ ○ ¼ ○ ⅛

Maximum time for simulation **15 min**

t	Ct	TWA, Ct to Ct+15
7.5 min	0.0281 mg/m³	0.0029 mg/m³

$$C(x,y,z,t)=\frac{M_0}{Geof\cdot(\pi\cdot D_T\cdot t)^{1.5}}\cdot\exp\left(-\frac{\left[(x-U\cdot t)^2+y^2+z^2\right]}{4\cdot D_T\cdot t}\right)$$

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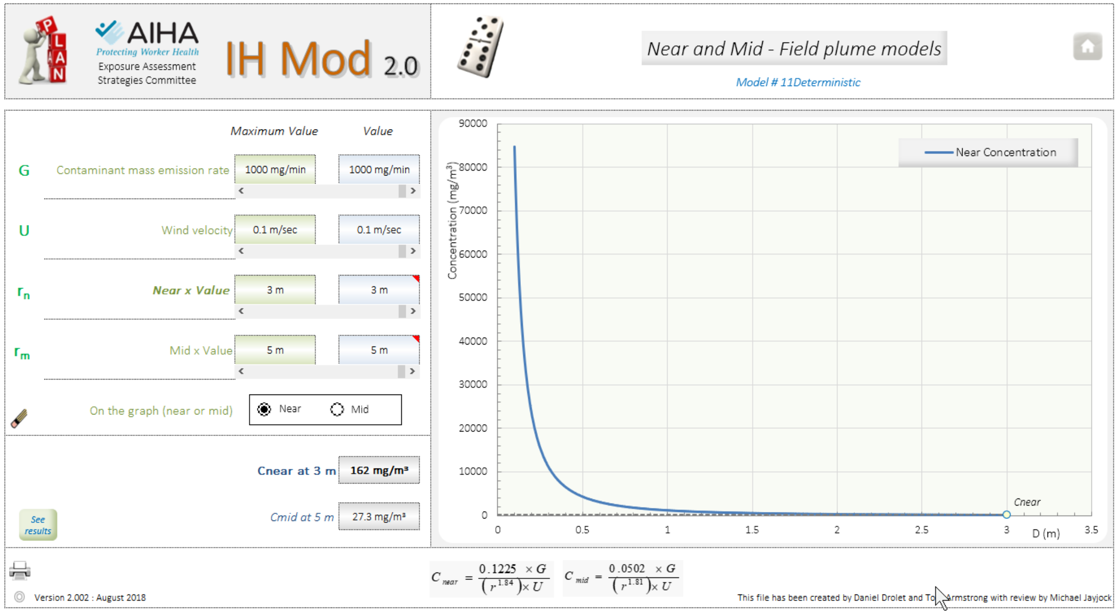
SOME LIMITATIONS OF TURBULENT DIFFUSION MODELS IN IH MOD

- **The diffusion models presented in this course are not based on the mass balance of contaminant in the room containing the emission source.**
  - **They are based on the mass balance of contaminant in a zone around the emission source**
  - **IH Mod DOES give capability to "reality check" the mass balance**
- **The diffusion models presented in this course *do not account for the removal* of contaminant from a room via exhaust air flow or other mechanisms.**
  - **The terms V, Q and k_L do not appear in the model equations.**
- **In general, these diffusion models are intended for *estimating exposure intensity* close to an emission source, say, within 2 m.**
  - **In this region, removal by exhaust air flow does not apply (in the absence of local exhaust ventilation), and the principle of conservation of mass is not violated**
- **D_T values may be difficult to chose with certainty. 0.5 as a default? MORE RESEARCH NEEDED! Remember, moderate changes in Tt do not greatly impact the peak concentration, but do influence the TWA.**

AND HERE ARE TWO OTHER MODELS YOU MAY FIND A USE FOR!



Near and Mid - Field plume models

Model # 11Deterministic

		Maximum Value	*Value*
G	Contaminant mass emission rate	1000 mg/min	1000 mg/min
U	Wind velocity	0.1 m/sec	0.1 m/sec
r_n	***Near x Value***	3 m	3 m
r_m	Mid x Value	5 m	5 m

On the graph (near or mid) ● Near ○ Mid

Cnear at 3 m **162 mg/m³**

Cmid at 5 m 27.3 mg/m³

$$C_{near} = \frac{0.1225 \times G}{(r^{1.84}) \times U} \quad C_{mid} = \frac{0.0502 \times G}{(r^{1.81}) \times U}$$

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What does the HELP file say? Check "THE BOOK" and the IH Mod 2.0 Support File for more information on these plume models

GIVEN ALL THESE CHOICES…
WHAT MODEL(S) DO YOU USE?

- See Chapter 12 of the book for some guidance … especially from pages 100 and 101
- Keep it simple to start
- Add complexity if needed
- Which model has simplifying assumptions and parameters reasonable for your scenario?

Some additional thoughts …

HOW DO YOU ESTIMATE THE 95TH PERCENTILE FROM MODEL RESULTS?

- **First, why might we care about the 95th percentile?**
- **This is a GOOD question, one just recently asked.**
- **Research on this needs to be done.**
- **For now:**
  - **If you have estimates of the parameter distributions, it is easy to get the 95th percentile from Monte Carlo simulation (MCS) results as in IH Mod 2.0 MCS models**
  - **Lacking that, use the "rule of thumb" 2 to 4**

times the mean and assume the model results are a mean ... ***unless you purposely use upper end G and lower end Q, etc.***

HERE ARE A FEW IMPORTANT REMINDERS!

- **Watch the units!**
  - **IH Mod 2.0 gives mg/m^3 not PPM … CAN YOU CONVERT?**
  - **Ventilation input is Q not ACH … CAN YOU CONVERT? CAUTIONS?**
- **Check the Input Value "slider" positions in the Deterministic versions**
- **Remember to clear prior results**
- **Remember the difference between C_t and TWA_t**
- **DOCUMENT your thinking! You can save the file with a new name**
  - **What are your assumptions?**
  - **Where or how did you get your input parameter values**
- **Remember the model's stated limitations. Can you "live" with them?**

SOME MORE REFERENCES

- **Matthews, T.G. “Air Velocities Inside Domestic Environments: An Important Parameter in the Study of Indoor Air Quality and Climate”, Envir. Int. V 15, pp 545-550 1989.**
- **Baldwin, P.E.J and A.D. Maynard, “A Survey of Wind Speeds in Indoor Workplaces”, Ann Occup. Hyg. V 42 N 5, 393-313, 1998 (includes residential)**

MORE RESOURCES
AIHA PDCS OFFERED IN THE PAST

- **Exposure Assessment Strategies and Statistics (2-Day)**
- **Bayesian Statistics: Overview and Applications in IH Data Interpretation and Exposure Risk Assessment (1 Day)**
- **Professional Judgment in Exposure Assessment (2 Day)**
- **Dermal Exposure Assessment & Modeling (1 Day)**
- **Using Mathematical Models to Estimate Exposure (IHMOD) (2 Day)**
- **Advanced Excel for Industrial Hygiene Calculations (1 Day)**
- **Monte Carlo Techniques in Exposure and Risk Assessment (1 day)**

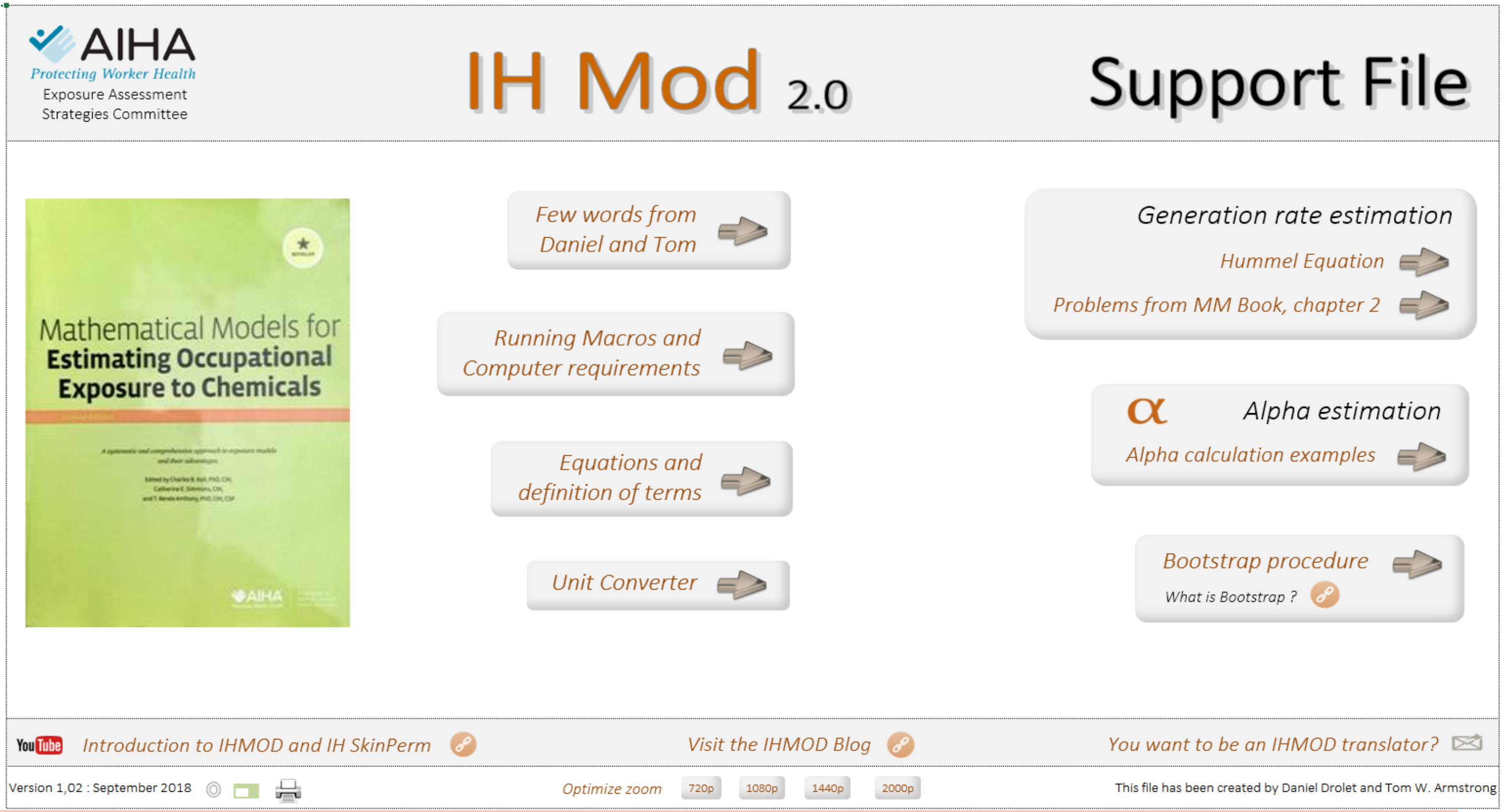
What's the future of IH Mod?

- Further guidance in the support file for reasonable scenario and specific model default parameters
- Further guidance on generation rate estimation
- Further guidance on estimation of ventilation rates, near field random air velocity, turbulent diffusion values
- Additional model equations? Always provide a comparison to Saturated Vapor Concentration?
- Slight revamp of the MCS summary. AM? GSD? Other?
- Maintenance
- EVERYTHING in IH Mod 2.0 was done on a volunteer basis, and its long term future will depend on additional volunteer contributions

For periodic news about IH Mod 2.0, visit the IH Mod BLOG site www.IHMod.org

WE GIVE ADDITIONAL GUIDANCE IN A SUPPORT FILE

HTTP://BIT.LY/EASCAIHA



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Exposure Assessment
Strategies Committee

IH Mod 2.0

Support File

Mathematical Models for Estimating Occupational Exposure to Chemicals

Version 1,02 : September 2018

This file has been created by Daniel Drolet and Tom W. Armstrong

We have been encouraging others to contribute to this file.

We expect expanded contents on parameter choices, sources, and more examples

Note the link to a blog on IH Mod www.IHMod.org

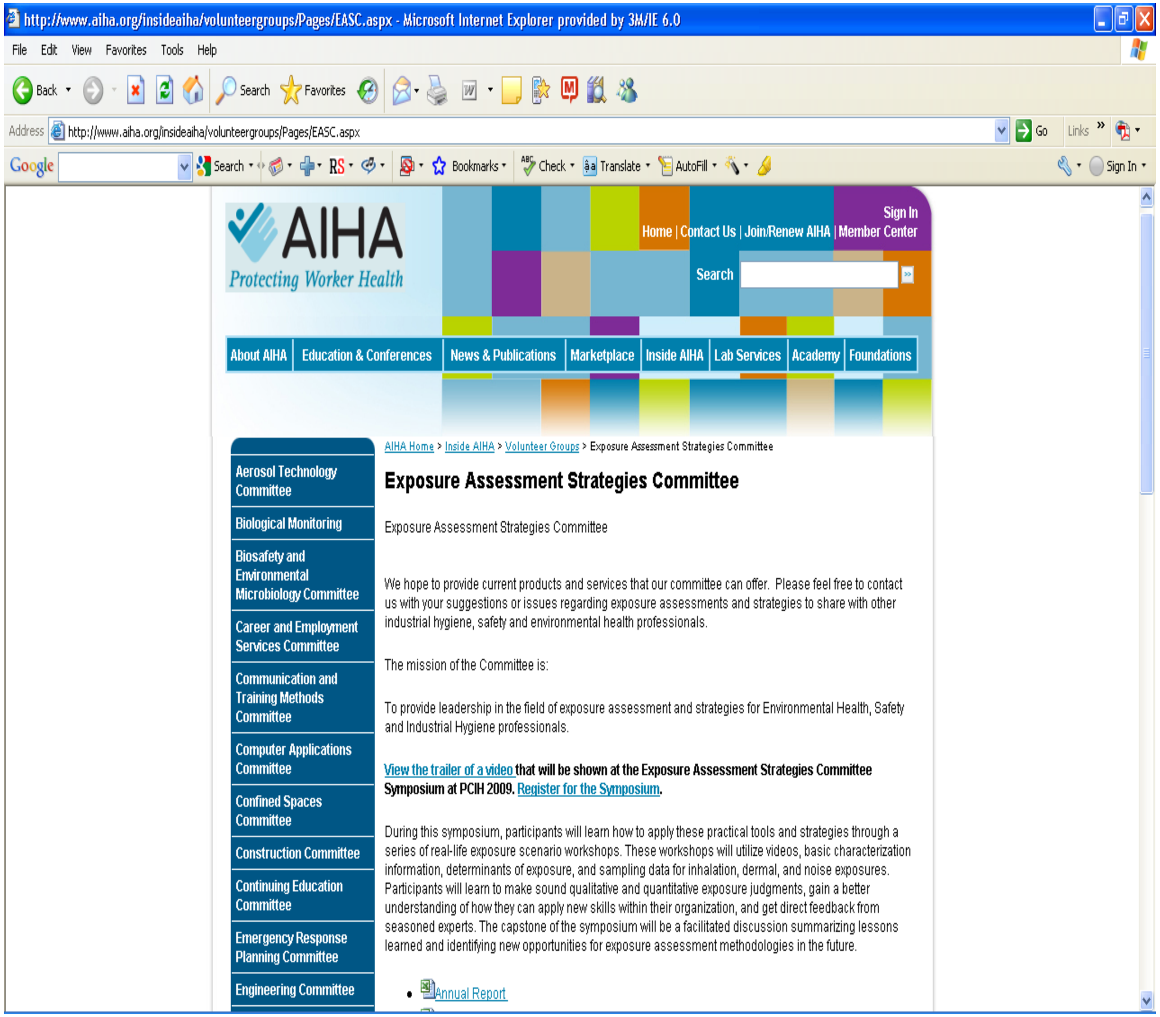
MORE RESOURCES

Check the AIHA EASC Website for updated tools!

http://www.aiha.org/INSIDEAIHA/VOLUNTEERGROUPS/EASC/Pages/EASCTopics.aspx

- **IH STAT**
- **IH MOD**
- **IH SkinPerm**

Resources



Exposure Assessment Strategies Committee

Exposure Assessment Strategies Committee

We hope to provide current products and services that our committee can offer. Please feel free to contact us with your suggestions or issues regarding exposure assessments and strategies to share with other industrial hygiene, safety and environmental health professionals.

The mission of the Committee is:

To provide leadership in the field of exposure assessment and strategies for Environmental Health, Safety and Industrial Hygiene professionals.

View the trailer of a video that will be shown at the Exposure Assessment Strategies Committee Symposium at PCIH 2009. Register for the Symposium.

During this symposium, participants will learn how to apply these practical tools and strategies through a series of real-life exposure scenario workshops. These workshops will utilize videos, basic characterization information, determinants of exposure, and sampling data for inhalation, dermal, and noise exposures. Participants will learn to make sound qualitative and quantitative exposure judgments, gain a better understanding of how they can apply new skills within their organization, and get direct feedback from seasoned experts. The capstone of the symposium will be a facilitated discussion summarizing lessons learned and identifying new opportunities for exposure assessment methodologies in the future.

- Annual Report

THANK YOU!!!
QUESTIONS?
DISCUSSION?