Mathematical Models for Exposure Assessment
What Is A Mathematical Model?

- A mathematical model is an equation, or set of equations, that predicts the behavior of a system given specified values for model parameters.

- In our context, a mathematical model predicts the airborne concentration of a contaminant at different times and/or at different positions in a room.
Reasons for Mathematical Modeling

- To estimate exposure prospectively for a process being planned or for an accident scenario:
  - engineering control design, respirator selection,
  - consumer product liability concerns

- To prioritize exposure monitoring efforts:

- To estimate exposure retrospectively for a process that no longer exists:
  - legal case, epidemiology study
Steps to build an Exposure Scenario

- Identify, explore and structure the use(s) of the substance
- Compile one or more tentative Exposure Scenarios covering the typical, actual conditions of use of the substance. Identify core determinants of exposure.
- Assess exposure and risk.
- Determine the effect of assumptions.
Three Elements of an Exposure Model

- The contaminant mass emission rate function
- The contaminant dispersion pattern in room air
- The exposed individual’s time-activity pattern
The Mass Emission Rate Function

- Common emission rate functions for a contaminant source in the room:
  - constant mass emission rate
  - exponentially decreasing vapor/gas mass emission rate
- Any time-varying function can be modeled
The Contaminant Dispersion Pattern in Room Air

- **Well-mixed room** - the concentration is uniform throughout the room
- **Near field/far field** - the concentration is highest in the near field of the source, and lower in the far field (the remainder of the room); within each respective field or zone, the concentration is uniform
- **Turbulent diffusion** - the concentration continuously decreases with distance from the source symmetrically or asymmetrically
- **Computational fluid dynamics modeling.**
The Individual’s Time-Activity Pattern

- A worker may be in a room with one or more emission sources for only part of the shift, or the source(s) may emit for only part of the shift.

- A worker may spend time at different locations relative to the same emission source. Need to account for spatial variation in the airborne contaminant level.

- The time-activity pattern must be determined to estimate the 8-hr TWA exposure level.
Key Parameters in Mathematical Models

- The room or space volume $V$ (e.g., m$^3$)
- Supply/exhaust air rate $Q$ (e.g., m$^3$/min)
- Emission rate function $G(t)$ (e.g., mg/min)
- Dispersion factors:
  - Random air speed in room $s$ (m/sec or feet/min)
  - Advective air flow speed $U$ (m/sec or feet/min)
  - Turbulent eddy diffusion coefficient $D_T$ (m$^2$/sec)
Deterministic Versus Probabilistic Models

- **Deterministic**
  A value is specified for each model parameter. If each respective value is always the same, the model output is always the same.

- **Probabilistic**
  A distribution of possible values is specified for some or all model parameters. A distribution of possible outcome values is obtained.
A Quote Attributed to Albert Einstein

“Things should be kept as simple as possible, but not simpler.”

In our context, we should use the simplest model that provides the detail required for the exposure assessment scenario.
A Tiered Approach to Mathematical Modeling (from Simple to Complex)

- Saturation Vapor Pressure Model
- Well Mixed Room Model with Constant Emission
- Well Mixed Room Model with Variable Emission
- Near Field/Far Field Model with Constant Emission
- Near Field/Far Field Model with Variable Emission
- Turbulent Eddy Diffusion Model with Constant Emission
- Computational fluid dynamics models
Tier 1 - Simplest Model
Saturation Vapor Pressure Model

- Consider a sealed container half-filled with the liquid of a pure chemical, and half-filled with pure air in the headspace above the liquid.

- Liquid-phase chemical molecules with sufficient kinetic energy escape the liquid and enter the headspace air.

- As chemical molecules collect in the headspace, some strike the surface of the liquid and condense back into the liquid phase.
**Saturation Vapor Pressure Model**

- When the rate of evaporation equals the rate of condensation the system is at equilibrium, and the headspace air is saturated with chemical vapor.

- The partial pressure exerted by the gas phase chemical molecules in the headspace at equilibrium is alternatively termed the chemical’s vapor pressure, equilibrium vapor pressure, or saturation vapor pressure - \( P_v \).
According to the ideal gas law, the mole fraction of a constituent, denoted $Y_i$ for the $i^{th}$ constituent, is equal to its partial pressure divided by $P_{TOTAL}$:

$$Y_i = \frac{P_i}{P_{TOTAL}}$$

The airborne concentration of the $i^{th}$ constituent in ppm is equal to its mole fraction multiplied by one million:

$$C \text{ in ppm } = Y_i \times 10^6$$
- The “worst case” assumption is that the chemical’s partial pressure in air will equal its vapor pressure value. This is equal to saying that the chemical’s airborne concentration is the same as its saturation concentration in air.

- This worst case assumption requires that:

  1. the chemical is continually exposed to room air
  2. there is no room ventilation, or $Q = 0 \, m^3/min$
  3. room and liquid temperature is constant
  4. there is sufficient time to reach equilibrium
  5. there is a sufficient mass of chemical in the room such that liquid (or solid) chemical remains at equilibrium
  6. the ideal gas law holds
- A perchloroethylene \((C_2Cl_4)\) container is left open in a nonventilated chemical storage cabinet. An employee opens the door and gets exposed to the cabinet air. To what ppm concentration of perchloroethylene is the employee exposed in the first couple of breaths?

- The following values are known:

\[
T = 20 \, ^\circ\text{C}, \quad P_V = 14 \, \text{mm Hg (at } 20^\circ\text{C)}
\]

Initial pressure = 760 mm Hg in the cabinet
We assume that the employee was exposed to a saturated concentration of perchloroethylene at 20 °C. We are implicitly assuming that equilibrium vapor pressure was attained in the cabinet, and that the contaminated air was not significantly diluted by room air prior to inhalation.

\[ C_{\text{sat \ in \ ppm}} = \frac{14}{760} \times 10^6 = 18,420 \ ppm \]
## Exposure Potential Vapors: Rule-of-10

<table>
<thead>
<tr>
<th>Level of Control</th>
<th>Fraction of Saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Confined Space – Virtually no circulation</td>
<td>1/10(^\text{th}) of Saturation</td>
</tr>
<tr>
<td>Poor – Limited Circulation</td>
<td>1/ 100(^\text{th}) of Saturation</td>
</tr>
<tr>
<td>Good – General ~ 6 air turnovers/hr</td>
<td>1/1,000(^\text{th}) of Saturation</td>
</tr>
<tr>
<td>Capture</td>
<td>1/10,000(^\text{th}) of Saturation</td>
</tr>
<tr>
<td>Containment</td>
<td>1/100,000 of Saturation</td>
</tr>
</tbody>
</table>
Container filling operation

- Consider the air displaced from the headspace of a container being filled with a pure liquid chemical. If we assume the headspace air is saturated with the chemical’s vapor, the volumetric rate at which the container is filled provides a worst-case vapor mass emission rate into the airspace outside the container.

\[
V_{\text{CONT}} = \text{container volume (m}^3\text{)}
\]
\[
F = \text{volumetric filling rate (m}^3/\text{min})
\]
\[
C_{\text{sat}} = \text{saturated vapor concentration (mg/m}^3\text{)}
\]

- The vapor mass emission rate (mg/min) during filling is \(G_{\text{FILL}}\):

\[
G_{\text{FILL}}, \text{mg/min} = C_{\text{sat}} (\text{mg/m}^3) \times F (\text{m}^3/\text{min})
\]
Henry’s Law

- Consider chemical A in an aqueous solution.

- Let $C_{A(aq)}$ denote the concentration of chemical A in the aqueous solution (mol/L, mg/m$^3$).

- Let $C_{A(air)}$ denote the concentration of chemical A in air (mol/L, mg/m$^3$).

- In a closed system of air and water at equilibrium, the partitioning of chemical A between air and water is given by the “dimensionless” Henry’s Law constant, denoted $H_A$:

$$H_A = \frac{C_{A(air)}}{C_{A(aq)}}$$

- $H_A$ is specific for chemical A in water and air, and depends on the temperature of the system.
Example Applying Henry’s Law

- Benzene is in an aqueous solution containing 10 mg benzene/L water (0.001% wt/wt).

- A tank containing 1 m$^3$ (264 gallons) of the solution is in a closed room at 25 °C with $V = 100$ m$^3$ and $Q = 0$ m$^3$/min.

- Assuming that equilibrium is attained between the benzene in water and air, what is the benzene concentration in air?

- Given: $H_{\text{Benzene}} = 0.22$ at 25 °C.
Mass Balance:

Initial Benzene Mass in Water =

Final Benzene Mass in Water + Final Benzene Mass in Air

- The initial benzene mass is 10,000 mg. At equilibrium, the benzene mass in air and water must equal 10,000 mg:

\[ C_{\text{Benzene (air)}} \times 99 \text{ m}^3 + C_{\text{Benzene (aq)}} \times 1 \text{ m}^3 = 10,000 \text{ mg} \]

where the benzene concentrations are in mg/m³

- We substitute: \( C_{\text{Benzene (air)}} = 0.22 \ C_{\text{Benzene (aq)}} \) into the mass balance equation:

\[ 0.22 \ C_{\text{Benzene (aq)}} \times 99 \text{ m}^3 + C_{\text{Benzene (aq)}} \times 1 \text{ m}^3 = 10,000 \text{ mg} \]
• The mass balance equation is now in one unknown, $C_{\text{Benzene(aq)}}$. We solve and obtain:

$$C_{\text{Benzene(aq)}} = 439 \text{ mg/m}^3$$

$$C_{\text{Benzene(air)}} = 0.22 \ C_{\text{Benzene(aq)}}$$

$$= 0.22 \ (439 \text{ mg/m}^3)$$

$$= 96.6 \text{ mg/m}^3$$

• For $P_{\text{TOTAL}} = 760 \text{ mm Hg}$ and $25 \degree \text{C}$, this represents a benzene concentration in air of 30 ppm, which is 30-times the OSHA 8-hr TWA PEL, and 300-times the NIOSH recommended exposure limit.
Tier 2 Models
Well-Mixed Room Model

Diagram:
- $Q \text{ m}^3/\text{min}$ entering the room
- $C_{\text{IN}}$
- $G \text{ mg/min}$ internal generation
- $C_{\text{ROOM}}$
- $k_L$
- $Q \text{ m}^3/\text{min}$ exiting the room
Well-Mixed Room with Constant Emission Rate

- Constant emission means that $G(t) = G \, \text{mg/min}$ throughout the time period of interest.

- There are likely few sources satisfying this description.

- Using a constant emission rate in a model fails to capture the intensity of peak or short-term exposures that may occur due to a highly variable emission rate.

- If these peak exposures are important in terms of toxicology and/or regulation, a constant emission rate should not be assumed.
The Constant Emission Rate Assumption

- However, if toxicological/regulatory interest focuses on the 8-hr TWA exposure level, assuming a constant emission rate is reasonable.

- Why? Consider an 8-hr shift as the period of interest. If the same total contaminant mass is released into room air either as one pulse, a series of smaller pulses, or uniformly over the shift, the shift-average concentration in room air will be nearly the same.
The Well Mixed Room Assumption

- The room is considered a perfectly mixed box. Perfect mixing means that contaminant is dispersed instantaneously throughout the room to create a uniform concentration. The concentration is the same at 1 cm versus 10 m from the source.

- Perfect mixing is physically unrealistic. Assuming perfect mixing can lead to seriously underestimating exposure intensity for an individual located close to a point source of contaminant emission, because exposure intensity is greater close to the emission source, in general.
The Well Mixed Room Assumption

- Although perfect mixing is physically unrealistic, the well mixed room construct provides a reasonable exposure estimate in three situations:

  (1) for individuals working in the room at some distance from a point source, say, > 2 meters.

  (2) for all individuals working in the room about two minutes after emission from a point source ceases.

  (3) for all individuals working in the room if the emissions are from a large surface area, e.g., painted walls.
Contaminant Gain Terms

- We will consider two possible sources of contaminant:

(1) The in-room source for which: \( G(t) = G \), in \( \text{mg/min} \).

(2) Contaminant in supply air at concentration \( C_{IN} \) (mg/m\(^3\)). The rate at which this mass moves into the room is the product:

\[ C_{IN} \text{ (mg/m}^3\text{)} \times Q \text{ (m}^3\text{/min)}, \text{ in mg/min} \]
Contaminant Loss Terms

- Consider four possible contaminant removal pathways:

  1. The exhaust air flow at rate $Q$ (m$^3$/min). The rate at which contaminant mass is exhausted from the room is the product:

     $$C_{ROOM} \text{ (mg/m}^3\text{)} \times Q \text{ (m}^3\text{/min)}, \text{ in mg/min}$$

  2. Adsorption onto room surfaces

  3. For molecules, chemical reaction (decomposition or transformation)

  4. For particles, gravitational settling
Contaminant Loss Terms

- The removal rates via sorption (pathway 2), molecular reaction (pathway 3), and particle settling (pathway 4) are denoted as $k_2$, $k_3$ and $k_4$, respectively, and have the units of fraction of contaminant mass removed per unit time, in this case, min$^{-1}$.

- These rates are usually difficult to estimate. For simplicity, we gather all the non-ventilation removal rates into a single removal rate term $k_L$. The rate at which contaminant mass is removed from room air by pathways (2) – (4) is:

$$k_L \text{ (min}^{-1}) \times C_{\text{ROOM}} \text{ (mg/m}^3\text{)} \times V \text{ (m}^3\text{)}, \text{ in mg/min}$$
Summary of Gain and Loss Terms

Gain Terms

• In-room source: $G$, in mg/min

• Supply Air: $C_{IN} \text{ (mg/m}^3\text{)} \times Q \text{ (m}^3\text{/min)}, \text{ in mg/min}$

Loss Terms

• Exhaust Air: $C_{ROOM} \text{ (mg/m}^3\text{)} \times Q \text{ (m}^3\text{/min)}, \text{ in mg/min}$

• Other Pathways:

$$k_L \text{ (min}^{-1}\text{)} \times C_{ROOM} \text{ (mg/m}^3\text{)} \times V \text{ (m}^3\text{)}, \text{ in mg/min}$$
• In the infinitesimal interval $t$ to $t + dt$, we account for all the contaminant mass entering room air and removed from room air. The change in contaminant mass in this interval is the mass gain minus the mass loss. By equating change in mass as the gain minus the loss, we say that mass is conserved.

**Change in Mass in “$dt$”**

$$= \text{Mass Gain in “$dt$”} - \text{Mass Loss in “$dt$”}$$

• The change in mass in the interval $t$ to $t + dt$ must equal the product of the room volume $V$ (m$^3$) and the infinitesimal change in the contaminant concentration in room air, denoted $dC$ (mg/m$^3$), during this interval:

**Change in Mass in “$dt$”**

$$= V \text{ (m}^3\text{)} \times dC \text{ (mg/m}^3\text{)} = \text{mass in mg}$$
• This notation leads to a mass balance equation:

Change in Mass in “dt” = Mass Gain in “dt” − Mass Loss in “dt”

\[ V \cdot dC = G(t) \cdot dt + C_{IN} \cdot Q \cdot dt - C(t) \cdot Q \cdot dt - k_L \cdot C(t) \cdot V \cdot dt \]

• In turn, this mass balance equation leads to a “differential” equation involving the unknown function \( C(t) \) and its first derivative. Solving the differential equation means specifying the function \( C(t) \), the time-varying function for the contaminant concentration in room air.
\[ V \cdot dC = G(t) \cdot dt + C_{IN} \cdot Q \cdot dt - C(t) \cdot Q \cdot dt - k_L \cdot C(t) \cdot V \cdot dt \]

\[ \downarrow \text{divide through by } V \text{ and } dt \]

\[ \frac{dC}{dt} = \frac{G(t)}{V} + \frac{C_{IN} \cdot Q}{V} - \frac{C(t) \cdot Q}{V} - C(t) \cdot k_L \]

\[ \downarrow \text{collect } C(t) \text{ terms and rearrange} \]

\[ \frac{dC}{dt} + \left( \frac{Q + k_L \cdot V}{V} \right) \cdot C(t) = \frac{G(t) + C_{IN} \cdot Q}{V} \]
If \( C_{IN} > 0 \) (contaminant in the supply air), and \( k_L > 0 \) (loss mechanisms other than exhaust air)

\[
C(t), \text{mg/m}^3 = \frac{G + C_{IN} \cdot Q}{Q + k_L \cdot V} \left[ 1 - \exp \left( -\frac{Q+k_L\cdot V}{V} \cdot t \right) \right] \\
+ \ C_0 \cdot \exp \left( -\frac{Q+k_L\cdot V}{V} \cdot t \right)
\]

\( C(t) = \) contaminant concentration at time \( t \) (min)

\( G = \) contaminant mass emission rate (mg/min)

\( Q = \) room supply/exhaust air rate (m\(^3\)/min)

\( V = \) room volume (m\(^3\))

\( C_0 = \) contaminant concentration at \( t = 0 \)
If \( C_{IN} = 0 \) (no contaminant in the supply air), and \( k_L = 0 \) (no loss mechanisms other than exhaust air)

\[
C(t), \text{ mg/m}^3 = \frac{G}{Q} \left[1 - \exp\left(-\frac{Q}{V} \cdot t\right)\right] + C_0 \cdot \exp\left(-\frac{Q}{V} \cdot t\right)
\]

\( C(t) \) = contaminant concentration at time \( t \) (min)

\( G \) = contaminant mass emission rate (mg/min)

\( Q \) = room supply/exhaust air rate (m\(^3\)/min)

\( V \) = room volume (m\(^3\))

\( C_0 \) = contaminant concentration at \( t = 0 \)
• There is a room with $V = 200 \text{ m}^3$ and $Q = 20 \text{ m}^3/\text{min}$ (6 ACH for this room).

• Starting at time zero, $G = 1000 \text{ mg/min}$ of solvent vapor is emitted into room air.

• Supply air contains no vapor, $C_{IN} = 0$, and there are no vapor removal mechanisms other than exhaust air, $k_L = 0$. The vapor level in room air at time zero is $C_0 = 0$. We want to find the equation for $C(t)$. 
\[ C(t) = 50 \cdot [1 - \exp(-0.1 \cdot t)] \]
The Steady State Room Concentration

- If the in-room emission rate is a constant value $G$, and emission continues for a long time, the contaminant concentration will reach a steady-state value, $C_{SS}$.

\[ C_{SS}, \text{mg/m}^3 = \frac{G + C_{IN} \cdot Q}{Q + k_L \cdot V} \]

- In the previous figure, it appears that the concentration is reaching a steady-state value of 50 mg/m$^3$. This is expected because:

\[ C_{SS} = \frac{1000 + 0.20}{20 + 0.200} = 50 \text{ mg/m}^3 \]
The Well Mixed Room Purging Equation

- Consider an initial room concentration $C_0$. Assume no further contaminant emission into room air, $G = 0$, and no contaminant in the supply air, $C_{IN} = 0$.

- The well mixed room model equation simplifies to an exponential “purging” equation:

$$C(t), \text{mg/m}^3 = C_0 \cdot \exp\left(-\frac{Q + k_L \cdot V}{V} \cdot t\right)$$

- Because it is usually assumed that $k_L = 0$, this equation traditionally appears in reference texts as:

$$C(t), \text{mg/m}^3 = C_0 \cdot \exp\left(-\frac{Q}{V} \cdot t\right)$$
• Consider the same room in Example #1 with \( V = 200 \text{ m}^3 \) and \( Q = 20 \text{ m}^3/\text{min} \) (6 ACH for this room).

• The initial vapor concentration is \( C_0 = 50 \text{ mg/m}^3 \).

• No further vapor enters room air: \( G = 0 \) and \( C_{IN} = 0 \). There is no vapor removal pathway other than exhaust air, so \( k_L = 0 \). We want to find the equation for \( C(t) \).
\[ C(t) = 50 \cdot \exp(-0.1 \cdot t) \]
Variation on the WMR model
The Exponentially Decreasing Contaminant Emission Rate Function

Let: $G_0 =$ mass emission rate at $t = 0$, or $G(0)$

**Constant Emission:** $G(t) = G_0$

**Backpressure:** $G(t) = G_0 \cdot \left(1 - \frac{C(t)}{C_{\text{sat}}} \right)$

**Exponentially Decreasing:** $G(t) = G_0 \cdot \exp(-\alpha \cdot t)$

$\alpha =$ emission (evaporation) rate constant, min$^{-1}$
The Exponentially Decreasing Contaminant Emission Rate Function

This emission rate function applies to several common processes:

- vapor emission from a small spill of solvent

- emission of a minor constituent a liquid mixture in a tank from a small spill of solvent

- offgassing of residual fumigants such as ethylene oxide and methyl bromide
Contaminant Mass Remaining in the Source

\[ M(t), \text{mg} = M_0 \cdot \exp(- \alpha \cdot t) \]

\( M(t) \) = contaminant mass (mg) remaining in the source at time \( t \) (min)

\( M_0 \) = initial contaminant mass in the source (mg), \( M(0) \)

\( \alpha \) = emission rate constant (min\(^{-1}\))

Mass Emission Rate from the Source

\[ G(t), \text{mg/min} = \alpha \cdot M_0 \cdot \exp(- \alpha \cdot t) \]

Note: \( G_0 = \alpha \cdot M_0 \)
The Well Mixed Room Model with an Exponentially Decreasing Emission Rate

If $C_{IN} = 0$ (no contaminant in the supply air),

$$k_L = 0$$ (no loss mechanisms other than exhaust air)

$C_0 = 0$ (zero initial concentration)

$$C(t), \text{mg/m}^3 = \frac{\alpha \cdot M_0}{\alpha \cdot V - Q \left[ \exp \left( -\frac{Q}{V} \cdot t \right) - \exp(-\alpha \cdot t) \right]}$$

$C(t) = \text{contaminant concentration at time } t \text{ in min}$

$M_0 = \text{initial contaminant mass in the source (mg)}$

$\alpha = \text{emission rate constant (min}^{-1})$

$Q = \text{room supply/exhaust air rate (m}^3/\text{min})$

$V = \text{room volume (m}^3)$
Example time trend for a small spill
Scenario 1

Sally has a 10 oz can of adhesive that contains hexane (TLV-TWA = 50 ppm) & toluene (TLV-TWA = 100 ppm; STEL = 150 ppm) at 5% and 20% respectively.

She is using the spray adhesive to make 4 poster boards of pictures. She will use 100% of the can in 3 minutes spraying the backs of pictures and attaching them to the poster boards.

She is in a 25 ft X 25 ft X 10 ft size room that has a ventilation rate somewhere between 1-5 air changes per hour.
## Worst Case Exposure

**TLV-TWA of hexane** = 50 ppm

**Hexane**

\[
C(ppm) = \frac{130}{760} \times 10^6 = 171,052 \text{ ppm}
\]

**TLV-TWA of toluene** = 100 ppm  
**STEL for toluene** = 150 ppm

**Toluene**

\[
C(ppm) = \frac{22}{760} \times 10^6 = 2,631 \text{ ppm}
\]
WMR Model Parameters

- **Volume of room**
  - $25 \text{ ft} \times 25 \text{ ft} \times 8 \text{ ft} \times (0.3048 \text{ m/ft})^3 = 137 \text{ m}^3$

- **Mass Generation Rates**
  - $(10 \text{ oz} \times 28.3 \text{ gm/oz} \times 1000 \text{ mg/gm} \times 0.05)/3 \text{ minutes} = 4717 \text{ mg/min} (\text{HEXANE})$
  - $(10 \text{ oz} \times 28.3 \text{ gm/oz} \times 1000 \text{ mg/gm} \times 0.20)/3 \text{ minutes} = 18,867 \text{ mg/min} (\text{TOLUENE})$

- **Ventilation Rate**
  - **3 air change/ hour** $\times 137 \text{ m}^3/60 \text{ min} = 6.85 \text{ m}^3/\text{min}
Well Mixed Room Model - Hexane

TLV-TWA = 176 mg/m³ (50 ppm)

TWA (60 min) = 101 mg/m³

Concentration in mg/m³

Time in minutes
Well Mixed Room Model - Toluene

- TLV-TWA = 375 mg/m³ (100 ppm)
- STEL = 560 mg/m³ (150 ppm)
- TWA (60 min) = 24.5 mg/m³
- TWA (15 min) = 53 mg/m³
Toluene Uncertainty Analysis

<table>
<thead>
<tr>
<th>Q</th>
<th>TWA-60 min</th>
<th>TWA-15 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ach</td>
<td>47</td>
<td>63</td>
</tr>
<tr>
<td>3 ach</td>
<td>25</td>
<td>54</td>
</tr>
<tr>
<td>5 ach</td>
<td>16</td>
<td>44</td>
</tr>
</tbody>
</table>

Concentration in mg/m³

Time in minutes
Near Field-Far Field Model

<table>
<thead>
<tr>
<th>Zone</th>
<th>TWA-60 min</th>
<th>TWA-15 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF</td>
<td>298</td>
<td>624</td>
</tr>
<tr>
<td>FF</td>
<td>23</td>
<td>47</td>
</tr>
</tbody>
</table>

Graph showing the concentration in mg/m³ over time in minutes.
Scenario 2

For a 100 cm² piece of super reflective tape, Perry uses an FTIR instrument to derive an offgasing rate for toluene. However, he is not super-confident of this number.

You sell small rolls of the tape (12 in. wide and 16 in. diameter) to a customer who stores them as inventory in a work room (30 ft x 30 ft x 20 ft) with low ventilation (~ 1 ach).

If the customer receives a full shipment (30 rolls) on a Friday, what would be the maximum concentration that may occur over the weekend?
WMR with Exponential Decay

- **Volume of room**
  - $30\text{ ft} \times 30\text{ ft} \times 20\text{ ft} \times (0.3048\text{m/ft})^3 = 509\text{ m}^3$

- **Initial Mass**
  - $(1\text{ mg/100 cm}^2) \times 30\text{ rolls} \times \text{SA of one roll} \times (2\pi \times 8 \times (12+8) \times (2.54)^2 \text{ cm}^2 = 1945\text{ mg}$

- **Evaporation rate** $= 0.2/\text{min}$

- **Ventilation Rate**
  - $0.1\text{ m}^3 /\text{min}$
Well Mixed Room Model - Toluene

Cmax (3.8 mg/m³) occurs after 60 minutes and slowly decreases thereafter.
Accounting for the mass in the inside layers of the rolls

- Each layer has a thickness of 1 mm, and can be thought of as a cylinder of length 12 in. and with a radius varying from 1 mm to 8 \times 2.54 \text{ cm}.
- Total area of 1 roll = 396543 \text{ cm}^2
- Total initial mass of toluene in 30 rolls
  \[ = 30 \times 396543 \text{ cm}^2 \times \left(\frac{1 \text{ mg}}{100 \text{ cm}^2}\right) \]
  \[ = 118963 \text{ mg} \]
Need to Modify Evaporation Rate

- Since most of the layers are not open to the environment, we can imagine the toluene in the inner layers slowly migrating to the surface of the roll and then evaporating.

- Assume effective evaporation rate = 0.0002/min
C increases throughout the weekend. Person opening the workroom will get a significant whiff of toluene.
The diagram illustrates the effect of uncertainty in evaporation rates on concentration over time.

- The graph shows four different evaporation rates: $\alpha = 0.2/\text{min}$, $\alpha = 0.02/\text{min}$, $\alpha = 0.002/\text{min}$, and $\alpha = 0.0002/\text{min}$.

- The concentration is measured in mg/m$^3$.

- The time is plotted on the x-axis in minutes, ranging from 0 to 4000 minutes.

- The concentration increases rapidly at first for $\alpha = 0.2/\text{min}$ and decreases gradually for slower rates, demonstrating the impact of different evaporation rates on the final concentration.

- The graph highlights the significance of evaporation rates on the final concentration, with slower rates resulting in higher concentrations over time.
Uncertainty Analysis
Nature of Probability

Classical or Frequentist View:

The probability of an event’s occurring in a particular trial is the frequency with which it occurs in a long sequence of similar trials.

For example, repeat weighings of a filter.

Or, repeat measurements of the air concentration of a pollutant in a steady state environment using an instrument.
Personalist of Bayesian View:
In many cases, it is not clear what the relevant population of trials should be.

For example, estimating the air flow rate (air changes per hour) through a room in the absence of any measurements.

An ‘expert’ can estimate it to be between 5 and 9 air changes/hr, with each value being equally likely.

But, there is NO population of air flow measurements.

This is a subjective description of the state of information or knowledge of the expert.
Sources of Uncertainty

1. Random error and statistical variation

   Most studied and best understood kind of uncertainty arises from random errors in direct measurement of some quantity. E.g., repeat measurements of a blank filter can determine the error associated with gravimetry.

2. Variability

   Quantities vary over time and space, and can be represented by a probability distribution. E.g., the exposure of a worker category can vary from day to day or from worker to worker. It can change seasonally.

3. Incomplete scientific or technical knowledge

   “We don’t know what we don’t know”

   (1a.) and (1b.) type of uncertainties can be represented by sampling statistics.

   (2.) type of uncertainty can be large, and dominate the overall uncertainty.
Common and Useful Probability Distributions

Uniform Distribution

Its use is appropriate when we are able and willing to identify a range of possible values for some variable, but unable to decide which values within this range are more likely to occur than others.
Normal Distribution

Arises in many applications. Quantities formed by adding many uncertain quantities tend to be normally distributed. The PDF takes on values over the entire range of real numbers. Evaluation of the CDF can be done using statistical tables. The parameters of the distribution are related to the first and second moments.
Triangular Distribution

This describes a situation where you know the minimum, maximum, and values most likely to occur.

For example, we might describe the gallons of a particular chemical used per week in a workplace. Past records might indicate that a minimum of 3,000 gallons to a maximum of 7,000 gallons are used per week, with most weeks showing usage of 5,000 gallons.
Propagating Uncertainty

- Suppose we have constructed a model to predict some quantity such as the concentration or a worker’s exposure.
- Suppose we have identified various uncertainties in the inputs.
- How can we propagate these uncertainties through the model to discover the uncertainty in the model output?
  - Can provide insights about the relative importance to our conclusions of our various assumptions and uncertainties in the model inputs.
  - Can help us decide whether it is worthwhile gathering more information to reduce uncertainty.
Consider a model represented by a function $f$, with two uncertain inputs $x_1$ and $x_2$, and one output $y$.

$$y = f(x_1, x_2)$$

Let us consider three values for each input - **low**, **medium**, and **high**.

To investigate the possible interactions between the effects of all the inputs at various levels, we will have to look at all possible combinations of input values.
\[ \begin{align*}
\text{x}_1 &= 0.3 \\
& \quad \text{p} = 0.33 \\
& \quad \text{x}_2 = 0.5 \\
& \quad \text{y} = 0.8 \\
& \quad \text{P} = 0.066 \\
& \quad \text{p} = 0.34 \\
& \quad \text{x}_2 = 1.0 \\
& \quad \text{y} = 1.3 \\
& \quad \text{P} = 0.068 \\
& \quad \text{p} = 0.33 \\
& \quad \text{x}_2 = 1.5 \\
& \quad \text{y} = 1.8 \\
& \quad \text{P} = 0.066 \\
\text{x}_1 &= 1.0 \\
& \quad \text{p} = 0.33 \\
& \quad \text{x}_2 = 0.5 \\
& \quad \text{y} = 1.5 \\
& \quad \text{P} = 0.198 \\
& \quad \text{p} = 0.33 \\
& \quad \text{x}_2 = 1.0 \\
& \quad \text{y} = 2.0 \\
& \quad \text{P} = 0.204 \\
& \quad \text{p} = 0.34 \\
& \quad \text{x}_2 = 1.5 \\
& \quad \text{y} = 2.5 \\
& \quad \text{P} = 0.198 \\
\text{x}_1 &= 1.7 \\
& \quad \text{p} = 0.33 \\
& \quad \text{x}_2 = 0.5 \\
& \quad \text{y} = 2.2 \\
& \quad \text{P} = 0.066 \\
& \quad \text{p} = 0.33 \\
& \quad \text{x}_2 = 1.0 \\
& \quad \text{y} = 2.7 \\
& \quad \text{P} = 0.068 \\
& \quad \text{p} = 0.34 \\
& \quad \text{x}_2 = 1.5 \\
& \quad \text{y} = 3.2 \\
& \quad \text{P} = 0.066
\end{align*} \]
Limitations of this approach:

Two variables with 3 levels each = $3^2 = 9$

Ten variables with 3 levels each = $3^{10} = 59,049$

Very often the uncertain quantities are continuous and not discrete. Then we may more naturally use probability density functions to represent the input parameters.

Usually difficult to obtain analytical expressions for the output in such cases.

One way out of this quandary is to select a moderate-sized, random sample of scenarios for evaluation. This is called Monte Carlo sampling.

Each scenario is generated by selecting each branch at a node according to its assigned probability. The branch values are generated from the underlying continuous probability distribution.
Example from Jayjock (1997)

Simple indoor air concentration model

\[ C = \frac{G}{Q} \]

\( C \) = equilibrium air concentration \((\text{mg/m}^3)\)

\( G \) = steady generation rate \((\text{mg/hour})\)

\( Q \) = steady ventilation rate \((\text{m}^3/\text{hour})\)

\textbf{G:} Assume that data is available on the source. The data is \textbf{normally distributed} with mean of 50 mg/hour and a standard deviation of 5 mg/hour

Thus, worst case might be \( 50 + 3 \times 5 = 65 \text{ mg/hr} \)
Best case might be \( 50 - 3 \times 5 = 35 \text{ mg/hr} \)

\textbf{Q:} No measurements available. But we can estimate from existing literature that the ventilation rate will not be below 0.2 air changes per hour (ACH) and will not be greater than 30 ACH.
Worst case = 0.2 ACH
Best case = 30 ACH
Monte Carlo Analysis

Generation Rate (mg/hour)

Ventilation Rate $m^3/hr$
10,000 independent samples (sets of values of G and Q) are obtained randomly from their respective probability distributions.

For each set of (G, Q), a value of C is predicted using the model equation.

Thus, we obtain 10,000 values of C. These can be plotted as a probability distribution for C.
Mean = 0.46 mg/m³
Median = 0.19 mg/m³
5th percentile = 0.09 mg/m³
95th percentile = 1.54 mg/m³
Sensitivity Analysis

Shows how much the uncertainty in each variable contributes to the overall variability.

This can help decide where to allocate resources to reduce uncertainty.
Scenario 1
Scenario 1

- A spray adhesive ("Brand A+ Adhesive") is filled into aerosol cans on an automatic fill machine line.
- Every 4 hours a worker takes a 55 gallon drum and hooks it up to the fill line by putting a long 2" tube into the drum.
- It takes them about 5 minutes to open the drum, slide the tube into the drum and then make sure that the line is primed. No local exhaust is used.
- The solvent of interest is hexane (other isomers) - OEL = 500 ppm at about 25% of the total volume. There is a limited amount of n-hexane (OEL = 50 ppm) - <5% of the total hexane.
Scenario 1

- The room is 20 feet X 40 feet X 12 feet and has general ventilation at 6 ACH (air changes per hour).

The vapor pressure for N-hexane is 130 mm Hg at 20 °C.
Leak Scenario-1

- Assume that there is a leak in the fill line, and as the adhesive mixture flows through it, there is a 0.01% loss to the room air over the 4 hour period.

0.01% loss = \(55 \text{ gal} \times 3.78 \text{ l/gal} \times 1000 \text{ cc/l} \times 0.0001 = 20.8 \text{ cc / 4 hr}\)

- 0.1% loss = \(208 \text{ cc / 4 hr}\)
WMR Model Parameters

- **Volume of room**
  \[20 \text{ ft} \times 40 \text{ ft} \times 12 \text{ ft} \times (0.3048 \text{ m/ft})^3 = 272 \text{ m}^3\]

- **Ventilation Rate**
  \[6 \text{ air change/hour} \times 272 \text{ m}^3/60 \text{ min} = 27.2 \text{ m}^3/\text{min}\]

- **Mass Rate of hexane**
  \[
  \left(55 \text{ gal} \times 3.78 \text{ l/gal} \times 1000 \text{ cc/l} \times 0.66 \text{ gm/cc} \times 1000 \text{ mg/gm} \times 0.25 \times 0.0001\right)/240 \text{ minutes} = 14.3 \text{ mg/min}
  \]
  \[
  \left(55 \text{ gal} \times 3.78 \text{ l/gal} \times 1000 \text{ cc/l} \times 0.66 \text{ gm/cc} \times 1000 \text{ mg/gm} \times 0.25 \times 0.001\right)/240 \text{ minutes} = 143 \text{ mg/min}
  \]
Well Mixed Room Model Prediction

TLV hexane = 1760 mg/m³ = 500 ppm

Time in minutes

<table>
<thead>
<tr>
<th>Concentration in mg/m³</th>
<th>Time in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.5 mg/m³</td>
<td>250</td>
</tr>
<tr>
<td>5.03 mg/m³</td>
<td>250</td>
</tr>
</tbody>
</table>

0.1% leak

0.01% leak
WMR Model Parameters

- Volume of room
  - $20 \text{ ft} \times 40 \text{ ft} \times 12 \text{ ft} \times (0.3048 \text{ m/ft})^3 = 272 \text{ m}^3$

- Ventilation Rate
  - $6 \text{ air change/hour} \times 272 \text{ m}^3/60 \text{ min} = 27.2 \text{ m}^3/\text{min}$

- Mass Rate of n-hexane
  - $(55 \text{ gal} \times 3.78 \text{ l/gal} \times 1000 \text{ cc/l} \times 0.66 \text{ gm/cc} \times 1000 \text{ mg/gm} \times 0.05 \times 0.0001)/240 \text{ minutes} = 2.85 \text{ mg/min}$
  - $(55 \text{ gal} \times 3.78 \text{ l/gal} \times 1000 \text{ cc/l} \times 0.66 \text{ gm/cc} \times 1000 \text{ mg/gm} \times 0.05 \times 0.001)/240 \text{ minutes} = 28.5 \text{ mg/min}$
Well Mixed Room Model Prediction

TLV n-hexane = 176 mg/m³ = 50 ppm

![Graph showing concentration over time for different leak rates and TWA values. The graph indicates the concentration in mg/m³ on the y-axis and time in minutes on the x-axis. Two lines are shown: one for TWA = 1 mg/m³ and 0.1% leak, and another for TWA = 0.1 mg/m³ and 0.01% leak.](image)
NF-FF Model Parameters

- Volume of room = 272 m$^3$
- $Q = 6$ air change/hour = 27.2 m$^3$/min
- Mass Rate of $n$-hexane
  - $(55 \text{ gal} \times 3.78 \text{ l/gal} \times 1000 \text{ cc/l} \times 0.66 \text{ gm/cc} \times 1000 \text{ mg/gm} \times 0.05 \times 0.001)/240 \text{ minutes} = 28.5 \text{ mg/min}$
- Volume of NF = $\frac{2}{3} \pi r^3 = \frac{2}{3} \pi (0.8)^3 = 1.1 \text{ m}^3$
- $\beta = 0.5 \times \text{surface area of hemisphere} \times \text{random air velocity} = 0.5 \times (2 \pi r^2) \times 3 \text{ m/min} = 6 \text{ m}^3/\text{min}$
Near Field-Far Field Model

TLV n-hexane = 176 mg/m³ = 50 ppm

TWA = 5.7 mg/m³

TWA = 1.0 mg/m³

0.1% leak

Time in minutes

Concentration in mg/m³
Exploding Aerosol Can Scenario-1

- 20 oz can of spray adhesive explodes
- It takes 15 minutes to clean up.
- **Small spill model** is appropriate
- Mass of spill = 20 oz × 29.6 cc/oz × 0.66 gm/cc × 1000 mg/gm = 390,720 mg
- Evaporation rate = 0.1 - 0.2/min
Small Spill Model Prediction – Hexane (No STEL; TLV-TWA = 1760 mg/m³)

15 min TWA = 141 mg/m³; alpha = 0.2/min
15 min TWA = 104 mg/m³; alpha = 0.1/min
Small Spill Model Prediction – n-Hexane (No STEL; TLV-TWA = 176 mg/m³)

15 min TWA = 28.3 mg/m³; α = 0.2/min

15 min TWA = 20.2 mg/m³; α = 0.1/min
Scenario 2
Scenario 2

Another task occurs about once per week which involves cleaning the filling equipment surfaces to remove the adhesive.

The workers use a rag dipped in solvent containing xylene (OEL = 100 ppm) and wipes adhesive. They also use a scraper tool along with the rag and solvent.

This cleaning task occurs once per week for about 4 hours. One gallon of solvent (50% xylene) is used.

The room is 20 feet X 40 feet X 12 feet and has general ventilation at 6 ACH (air changes per hour). No local exhaust is used in this room.
Volume of room
- 20 ft x 40 ft x 12 ft x (0.3048 m/ft)^3 = 272 m^3

Ventilation Rate
- 6 air change/hour x 272 m^3/60 min = 27.2 m^3/min

Mass Rate of xylene
- (1 gal x 3.78 l/gal x 1000 cc/l x 0.88 gm/cc x 1000 mg/gm x 0.25)/240 minutes = 6930 mg/min
Well Mixed Room Model Prediction

TLV xylene = 435 mg/m³ = 100 ppm

TWA = 61 mg/m³
NF-FF Model Parameters

- Volume of room = 272 m³
- \( Q = 6 \) air change/hour = 27.2 m³ /min
- Mass Rate of xylene = 1732 mg/min (0.5 gal of 25% xylene)

\[
\frac{2}{3} \pi r^3 = \frac{2}{3} \pi (0.8)^3 = 1.1 \text{ m}^3
\]

- \( \beta = 0.5 \times \text{surface area of hemisphere} \times \text{random air velocity} = 0.5 \times (2 \pi r^2) \times 3 \text{ m/min} = 6 \text{ m}^3/\text{min} \)
Near Field Far Field Model

TLV xylene = 435 mg/m³ = 100 ppm

![Graph showing time series data]

- **TWA = 348 mg/m³**
- **TWA = 61 mg/m³**
Effect of uncertainty in xylene used on Near Field concentration

- NF for 0.5 gal/hour
- NF for 0.1 gal/hour
Xylene NF Uncertainty Analysis

Uncertain Inputs

- Amount of xylene used for cleaning
  - Typically 200 ml used over 4 hours but very variable
  - Assume **Lognormal**: GM = 200 ml; GSD = 3

- Percent xylene in solvent
  - Assume **Uniform**: Min = 10%, Max = 50%

- Ventilation rate (ACH)
  - Assume **Triangular**: Min = 5, Mode = 6, Max = 7
Amount of xylene used for cleaning

Typically 200 ml used over 4 hours but very variable
Assume Lognormal: GM = 200 ml; GSD = 3
Percent xylene in solvent

Assume **Uniform**: Min = 10%, Max = 50%
Ventilation rate (ACH)

Assume **Triangular**: Min = 5, Mode = 6, Max = 7
4 hour TWA Distribution

GM = 38; GSD = 3.5
Scenario 3
Scenario 2: Professional Worker

- An employee uses this adhesive to spray fabric used to cover airplane seats. ("Brand A+ Adhesive")
- The solvent of interest is hexane (other isomers) - OEL = 500 ppm at about 25% of the total volume.
- The worker will cover 3 seats per hour and use one can (15 ounces) for all 3 seats.
- The worker performs this job for about 6 hours per day (6 cans).
- The job is performed in a section of a warehouse 100 feet X 200 feet X 20 feet with a general ventilation rate of 3 ACH.
WMR Model Parameters

- Volume of room = _____________ m³

- Ventilation Rate
  3 ACH = _________________ m³ /min

- Mass Rate of hexane (1 oz = 29.6 cc; Density of hexane = 0.66 gm/cc)
  = __________________________ mg/min
WMR Model

- Steady State Concentration = ______ mg/m³
- Time weighted average = ______ mg/m³
Volume of room = ____ m³

Q = 3 air change/hour = _____ m³ /min

Mass Rate of hexane = _____ mg/min

Volume of NF =______ m³

β = 0.5 x surface area of hemisphere x random air velocity = ___________ = ___________ m³/min
NF-FF Model

- Steady State Concentration in NF = ______ mg/m³

- Time weighted average for NF = ______ mg/m³
To Keep in Mind

- Use a tiered approach to using models.
- Be aware of assumptions of model
- Assess the effects of uncertainties in model parameters
- Focus on decision-making