Estimating Exposure via Mathematical Modeling for On-Site Worker Health Risk Assessment

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Our Goal

Estimate the concentration of a toxic chemical in an individual's breathing zone during future chemical use scenarios.

There are two approaches.

The Field Measurement Approach

Directly measure the breathing zone concentrations during many different use scenarios so we have measurements for all future scenarios.

Need to make repeat measurements per scenario.

But … there are many unique scenarios and it is costly to make measurements, so this approach is not feasible, in general.

The Modeling Approach [1-3]

Use a mathematical model that predicts exposure intensity based on knowing:

- the total mass of the chemical used
- the time course of chemical use
- the time course of emission during and after use
- for indoor use, the room volume and ventilation rate (ACH)
- the air speed near the application sites

Testing in a Controlled Environment

Consider a scenario, say, spraying onto a surface. Spray in a test room and use the measurements to develop a reasonably predictive model.

Factors Controlled and Recorded

- the total mass of the chemical applied

- the total application time

- the room volume V, m^3

- the room air supply rate Q, m^3/min

- the room temperature

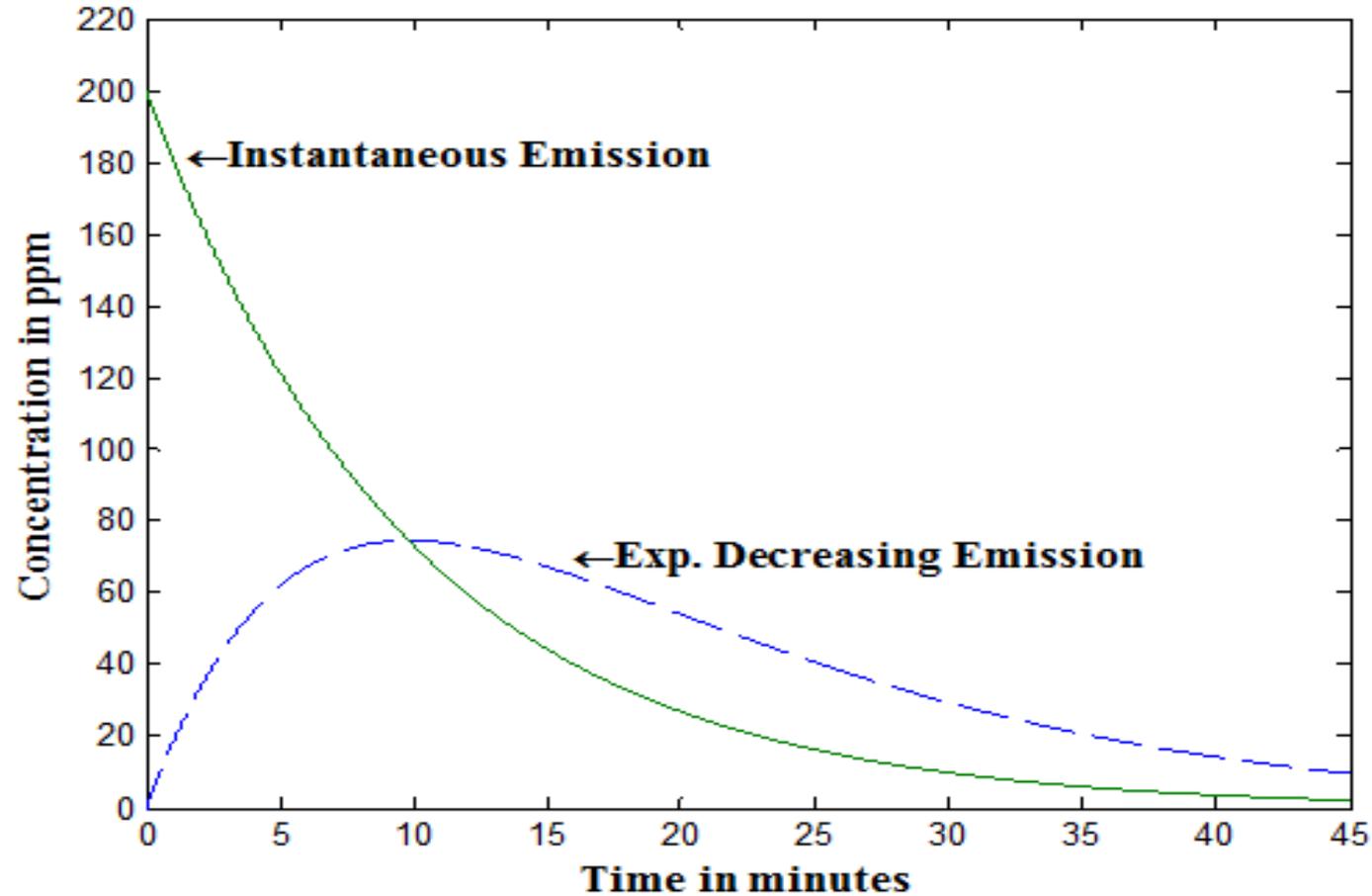# The Emission Rate Time Series E(t)

For the same total mass emitted, the shape of the concentration time series depends on the pattern of emission. Consider that mass M_0 is quickly applied to a surface in a well-mixed room. Two possible emission time series:

- instantaneous emission of M_0
- exponentially decreasing emission:

$$E(t) = \alpha \times M_0 \times \exp(-\alpha \times t)$$

α is a first-order constant, fraction/minute

Concentration Time Series with Bolus Application

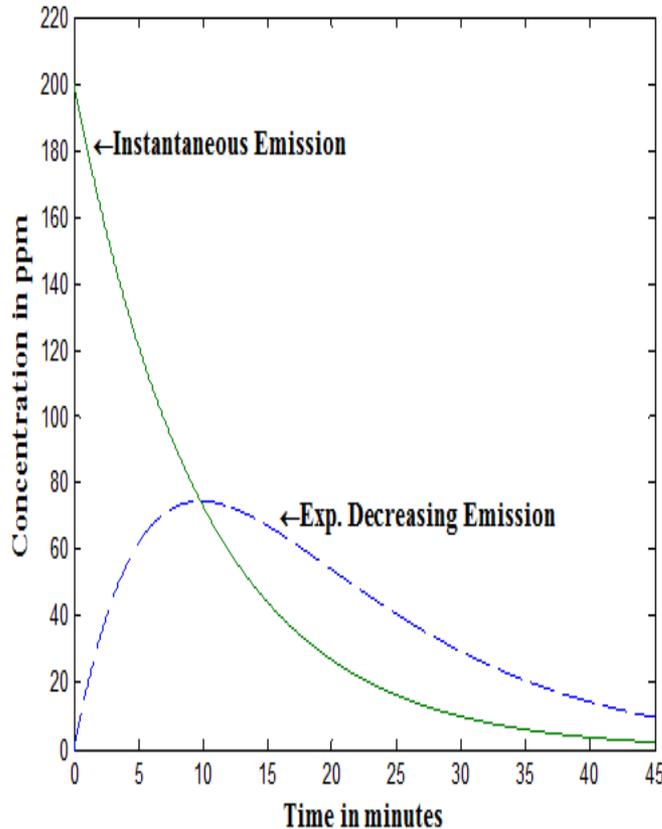# The Concentration Time Series C(t) Depends on the Emission Time Series

Instantaneous Emission:

$$C(t) = \frac{M_0}{V} \times \exp\left(-\frac{Q}{V} \times t\right)$$

Exponentially Decreasing Emission:

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

Some Items to Note

- For exponentially decreasing emission here, 99% of mass M_0 is emitted by 45 minutes

- Time-averaged levels over 45 minutes are about the same value, 43 ppm

- Peak levels differ by five-fold – 43 ppm vs. 200 ppm

- Peak concentrations may be toxicologically important.

- In general, rapid emission leads to higher peak exposure.

Continuous and Uniform Application

• Consider a scenario in which the chemical is not applied as a bolus, but is applied at a constant rate to a surface (e.g., sprayed), denoted I (mg/min).

• For the chemical mass applied in any short time interval, consider that emission is instantaneous versus exponentially decreasing.

Emission Rate (mg/min) during Application

instantaneous emission: $E(t) = I$

exp. decreasing emission: $E(t) = I \times [1 - \exp(-\alpha \times t)]$

Concentration Time Series with Continuous Uniform Application
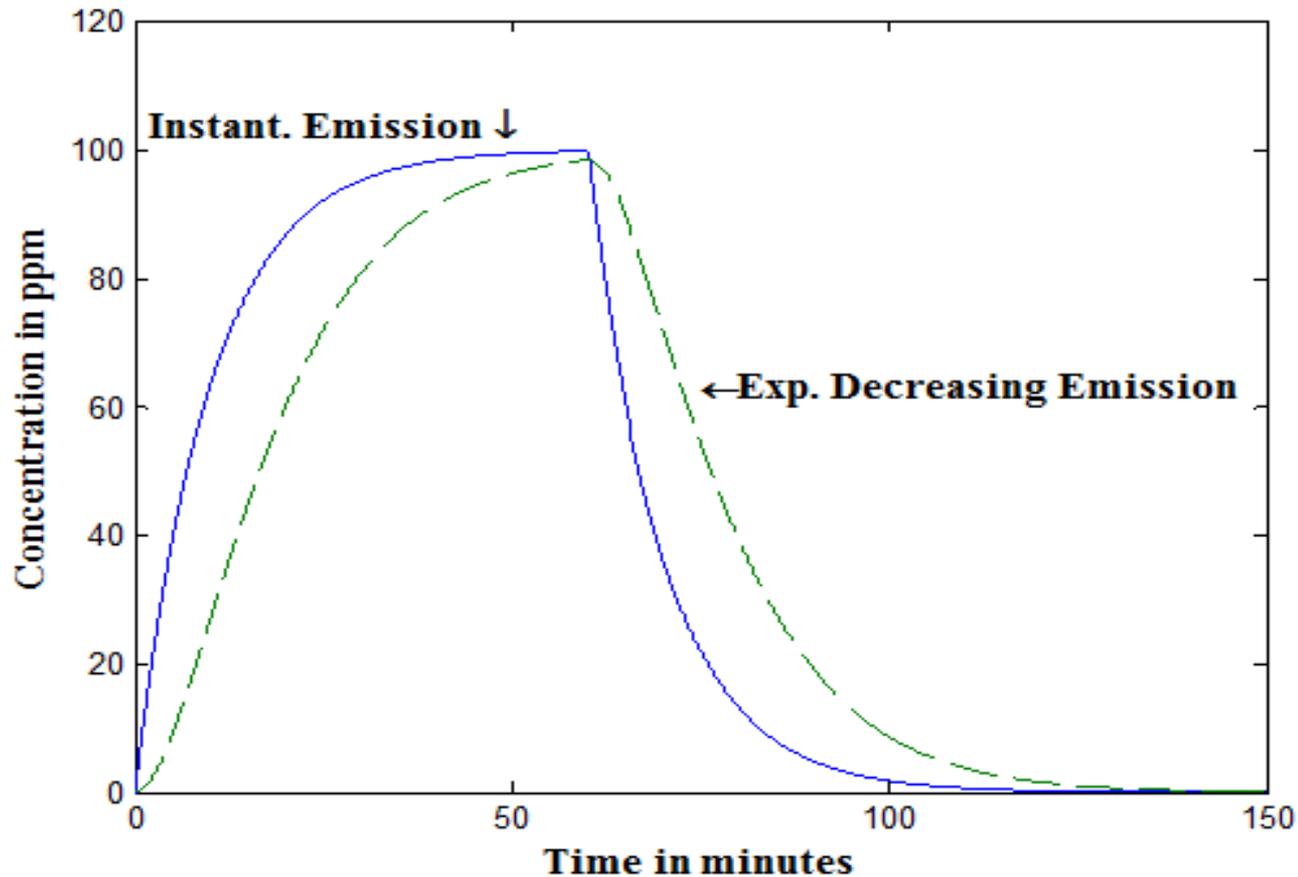
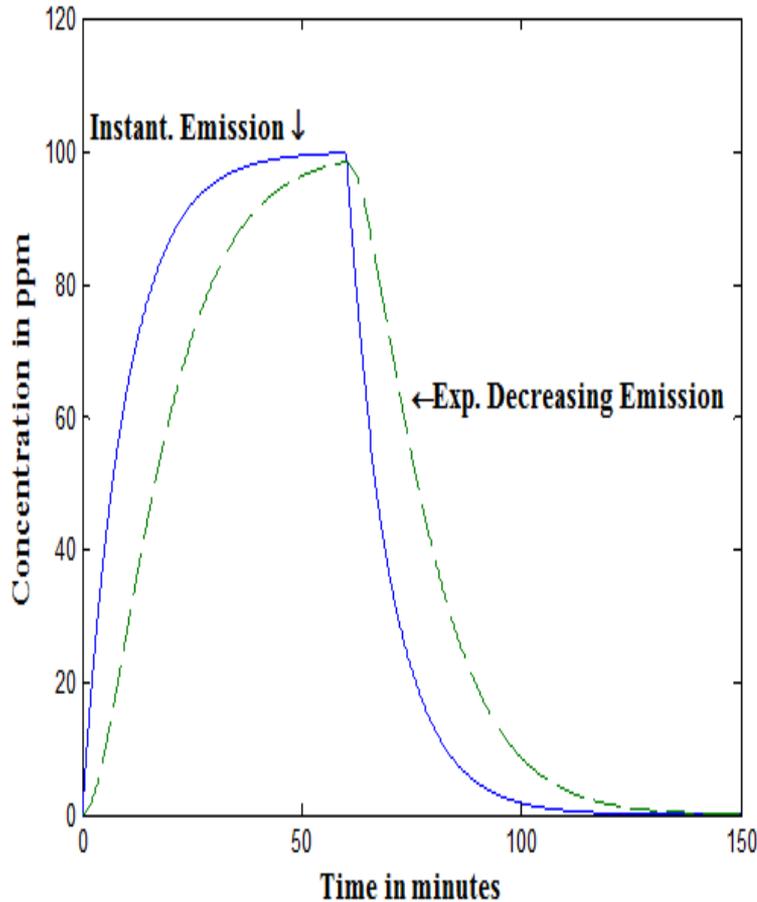# The Concentration Time Series C(t) Depends on the Emission Time Series

Instantaneous Emission:

$$C(t) = \frac{I}{Q} \times \left[1 - \exp\left(-\frac{Q}{V} \times t \right) \right]$$

Exponentially Decreasing Emission:

$$C(t) = \frac{I}{Q} \times \left[1 - \exp\left(-\frac{Q}{V} \times t \right) \right] + \frac{I}{Q - \alpha V} \times \left[\exp\left(-\frac{Q}{V} \times t \right) - \exp(-\alpha \times t) \right]$$

Some Items to Note

- Time-averaged levels over the first 60 minutes are 83 ppm vs. 67 ppm for, respectively, instantaneous vs. exponentially decreasing emission.

- Time-averaged levels over the next 60 minutes are 17 ppm vs. 32 ppm for, respectively, instantaneous vs. exponentially decreasing emission.

- Exposure immediately after application must be considered.

Test Protocol to Estimate the Emission Rate during Continuous Application

- Use a room with known volume, known air supply rate, known temperature, and one exhaust air outlet.

- Apply a known chemical mass at a constant rate over T minutes.

- Mix the room air with fans.

- Continuously measure the chemical concentration at the exhaust outlet and other locations for T minutes.

- When application stops, keep measuring at the exhaust outlet and other room locations.

- Pick the simplest emission rate function that matches the observed concentration time series.

Like in Real Estate, Location is Key

- In addition to the chemical emission rate, consider the location of the individual relative to the source of emission.

- In general, the closer one is to the source of emission, the higher one's exposure intensity.

- Location affects how we choose to describe chemical dispersion in air.

Three Approaches to Model Dispersion

• The room is well-mixed, i.e., the chemical instantaneously and uniformly disperses through-out room air.

• A near field zone surrounds the source and the rest of the room is the far field zone. Air in each zone is well-mixed, but air exchange between the zones is limited.

• Room air motion is complex. There is turbu-lent motion (a random walk) with advective air currents (straight-line flows) .

Modeling Dispersion in Room Air

• The well-mixed room is the most frequently used but least realistic model. It can substantially underestimate exposure intensity near the emission source.

• However, the well-mixed room approach works reasonably well for persons not located near the emission source, and for all room occupants several minutes after emission ceases.

Modeling Dispersion in Room Air

• The most realistic approach is turbulent diffusion with advection. It is also the most difficult to model mathematically, and the actual patterns of turbulence and advection will be unknown.

• Computational fluid dynamics, a high-level computer intensive technique, can be used to predict patterns of turbulence and advection, but human movement is seldom considered.

Modeling Dispersion in Room Air

- The near field/far field (NF/FF) dispersion approach can be used when the individual is close to the emission source.

- It is a compromise between the over-simplicity of the well-mixed room model and the complexity of modeling turbulent diffusion with advection.

The NF/FF Model

• One poses a geometry for the NF zone that contains the individual's breathing zone. For example, if chemical is being used on a small work table, the NF zone might be a box of air with its base on the table and its height from the base to the individual's face.

• The NF zone has volume (V_{NF}) and a free surface area (FSA) through which air moves. No air leaves the NF zone directly to outside the room.

The NF/FF Model

- Assume there is a random air speed S (it could also be measured) at the interface of the NF and FF zones. Default values are S = 10 fpm when there are no strong sources of air currents near the NF zone, and S = 50 fpm when there are.

- Airflow rate into and out of the NF zone:
$$\beta \ (m^3/min) = \tfrac{1}{2} \times S \times FSA$$

- The room has volume V and air supply rate Q.

The NF/FF Model
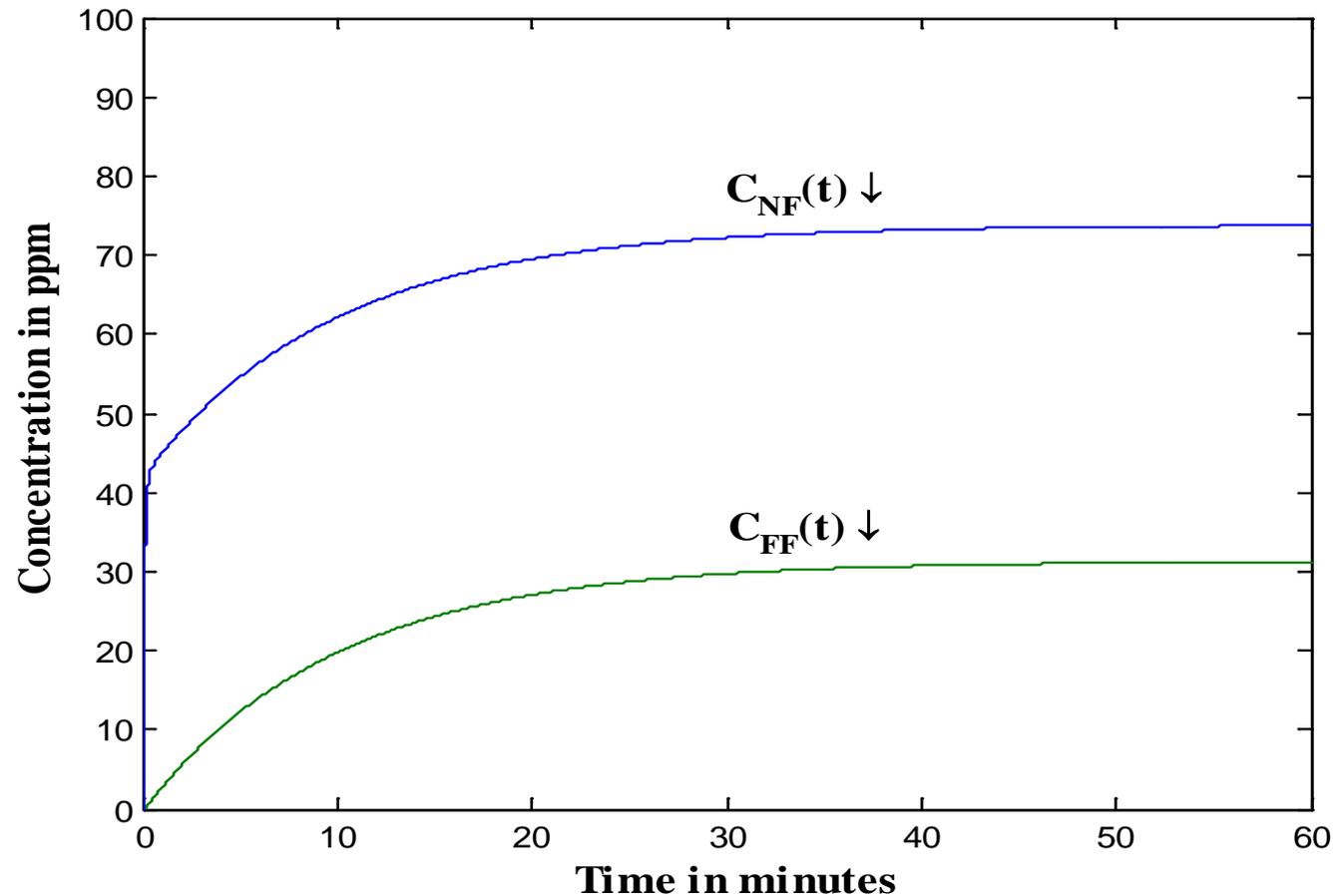
If chemical emission is constant at rate I (mg/min), there are exact, gnarly equations for the concentrations in the NF and FF zones. Here are approximations.

Far Field:
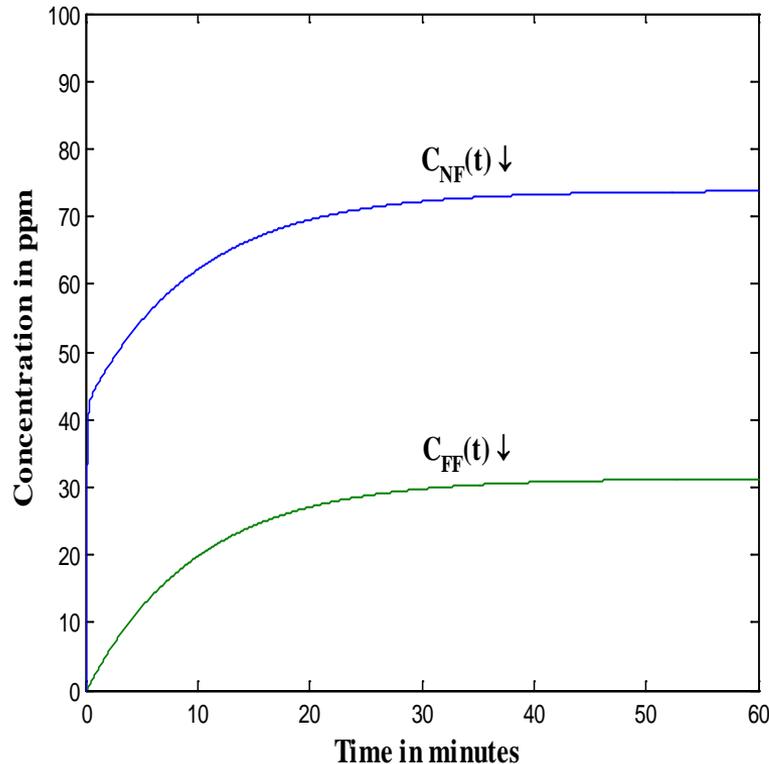$$C_{FF}(t) \cong \frac{I}{Q} \times \left[1 - \exp\left(-\frac{Q}{V} \times t \right) \right]$$

Near Field:

$$C_{NF}(t) \cong \frac{I}{Q} \times \left[1 - \exp\left(-\frac{Q}{V} \times t \right) \right] + \frac{I}{\beta} \times \left[1 - \exp\left(-\frac{\beta}{V_{NF}} \times t \right) \right]$$

The NF/FF Model - Constant Application and Instantaneous Emission

Some Items to Note

- Time-averaged levels over the first 60 minutes are 68 ppm vs. 26 ppm for, respectively, the NF zone vs. the FF zone.

- At steady state, $C_{FF} = I/Q$ and $C_{NF} = I/Q + I/\beta$.

- In general, the larger the room, the higher the Q value with little effect on the β value. In turn, the relative difference between the NF and FF concentrations increases.

Test Protocol for the NF/FF Model

- Use a room with known volume V, known air supply rate Q, known temperature, and one exhaust air outlet.

- Apply a known chemical mass at a constant rate over T minutes.

- Do <u>not</u> mix the room air with fans. Measure the air speed S near the application point.

- Continuously measure the chemical concentration in the BZ, at the exhaust outlet and at other locations.

- Assess if the chosen emission rate and the NF/FF dispersion pattern lead to predictions that reasonably match the observed BZ concentrations.

Some Past Test Data for the NF/FF Model

Process	Measured	Predicted
methanol to	NF: 57 ppm	65 ppm
clean wafers	FF: 16 ppm	25 ppm
(Ref. 4)	NF: 115 ppm	135 ppm
	FF: 51 ppm	100 ppm
cyclohexane	NF: 68 ppm	71 ppm
on metal parts	FF: 44 ppm	35 ppm
(Ref. 5)	NF: 51 ppm	37 ppm
	FF: 52 ppm	35 ppm

Outdoor Air Scenarios

• Pose a geometry for the NF zone such that it contains the emission source and the individual's breathing zone.

• Wind speeds can be quite variable across time. I suggest that if the chemical application is at ground level, assume S = 2 mph, and if it's higher up, assume 5 or 10 mph.

• Treat the NF zone as a "well-mixed room" with volume V_{NF} and ventilation rate β. Because chemical leaving the NF zone is greatly diluted, ignore the FF zone effect.

Outdoor Air Scenarios

For a constant chemical emission rate I (mg/min):

$$C_{NF}(t) \cong \frac{I}{\beta} \times \left[1 - \exp\left(-\frac{\beta}{V_{NF}} \times t \right) \right]$$

Utility of Mathematical Modeling

- In general, one can combine any chemical emission rate function with any dispersion pattern in air.

- Once the model is formulated, the inputs can be made specific for the scenario of concern to predict the breathing zone concentrations.

- There is always uncertainty in a model estimate, but there is also substantial variability in exposure measurements when performing nominally the same task.

- If one wants to confirm model predictions for a specific scenario, direct exposure measurements can be made in the field when that specific chemical use task is performed.

References

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2. Nicas M: "Mathematical Modeling of Indoor Air Contaminant Concentrations," Chapter 17 (pages 661-693), *Volume 2*, *Evaluation and Control*, *Pattys Industrial Hygiene Sixth Edition*, Eds. B Cohrssen and V Rose, John Wiley & Sons, Inc., New York, NY, 2010

3. Nicas M: "Quantitative Surveying – Application of Mathematical Modeling to Estimate Air Contaminant Exposure," in *Modern Industrial Hygiene, Volume I, Recognition and Evaluation of Chemical Agents, Second Edition*, by Jimmy L. Perkins, ACGIH, Cincinnati, OH, 2008

4. Gaffney S, et al.: Worker exposure to methanol vapors during cleaning of semiconductor wafers in a manufacturing setting, J. Occup. Environ. Hygiene 5:313-324, 2008

5. Spencer J and M Plisko: A comparison study using a mathematical model and actual exposure monitoring for estimating solvent exposure during disassembly of parts, J. Occup. Environ. Hygiene 4:253-259, 2007

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6. Nicas M: Using mathematical models to estimate exposure to workplace air contaminants, Chem. Health Safety 10:14-21, 2003
7. Jayjock M., et al.: The Daubert standard as applied to exposure assessment modeling using the two-zone (NF/F) model estimation of indoor air breathing zone as an example, J. Occup. Environ. Hygiene 8:D114-122, 2011.