# Methods for Estimating Evaporation of Liquids and Their Use in EPHA Development

Kelly Parker
AlphaTRAC, Inc.

# Why Do We Care?

- Liquid spills are a common accident in a variety of environments
  - Research laboratories
  - Transportation
- Necessary to characterize plume accurately
  - Takes into account volatility of liquid
  - Considers surrounding environment
  - Allows for release over a period of time

# In This Presentation

- Discuss two methods for evaporating liquids
  - Differences, pluses, negatives
- Use for planning purposes
- Coupling evaporation and dispersion

# General Principles

- Described by mass transfer coefficient
- Depends on wind profile above the puddle

$$E = \rho_{sat} k_m$$

| | | |
|---|---|---|
| $E$ | ≡ | Evaporation rate per unit area ($kg \cdot s^{-1} \cdot m^{-2}$) |
| $\rho_{sat}$ | ≡ | Saturated vapor concentration ($kg \cdot m^{-3}$) |
| $k_m$ | ≡ | Mass transfer coefficient ($m \cdot s^{-1}$) |

- $K_m$ can be simple or complex

# Simple Model

- *The Evaporation of Volatile Liquids* (Kawamura and Mackay 1987)
- Assumes simple mass transfer coefficient

$$k_m = 0.0048 u^{7/9} Sc^{-2/3} d^{-1/9}$$

| | | |
|---|---|---|
| u | ≡ | Reference wind speed ($m \cdot s^{-1}$) |
| Sc | ≡ | Laminar Schmidt number (unitless) |
| d | ≡ | Diameter of puddle (m) |

- No temperature variation

# Simple Model

- Assumes ideal gas behavior

$$\rho_{sat} = \frac{M_c P_v}{R T_p}$$

$M_c$ ≡ Molecular weight ($kg \cdot kmol^{-1}$)

$P_v$ ≡ Vapor pressure at temperature, T (Pa)

$R$ ≡ Universal gas constant = 8,314 ($J \cdot kmol^{-1} \cdot K^{-1}$)

$T_p$ ≡ Temperature of the puddle (K)

# Simple Model

**Pros**

- Requires few chemical properties available from MSDS sheets
  - Vapor pressure and density at reference temperature
  - Molecular weight
- Not computationally intensive

**Cons**

- Ignores changes in puddle temperature
- Overly conservative??
- Cannot take into account all ambient conditions

# Complex Model

- *Evaporation from a plane liquid surface into a turbulent boundary layer* (Brighton 1985)
- Complex mass transfer coefficient

$$k_m = f(d, \kappa_{ac}, u_*, z_0, \nu)$$

| | | |
|---|---|---|
| $\kappa_{ac}$ | ≡ | Diffusivity of material in air-vapor mixture ($m^2 \cdot s^{-1}$) |
| $u_*$ | ≡ | Friction velocity ($m \cdot s^{-1}$) |
| $z_0$ | ≡ | Effective surface roughness (m) |
| $\nu$ | ≡ | Kinematic viscosity of air ($m^2 \cdot s^{-1}$) |

# Complex Model

- Solution of E requires energy budget analysis

$$\frac{dT_p(t)}{dt} = \frac{1}{c_{pl}\rho_p\delta_p}(F_S + F_\uparrow + F_\downarrow + F_G + F_E + F_H)$$

| | | | |
|---|---|---|---|
| $t$ | ≡ Time (s) | $F_\uparrow$ | ≡ Longwave flux to atmosphere ($W \cdot m^{-2}$) |
| $c_{pl}$ | ≡ Specific heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$) | $F_\downarrow$ | ≡ Longwave flux from atmosphere ($W \cdot m^{-2}$) |
| $\rho_p$ | ≡ Density of the puddle ($kg \cdot m^{-3}$) | $F_G$ | ≡ Heat exchanged with ground ($W \cdot m^{-2}$) |
| $\delta_p$ | ≡ Depth of the puddle (m) | $F_E$ | ≡ Heat flux due to evaporation ($W \cdot m^{-2}$) |
| $F_S$ | ≡ Shortwave flux ($W \cdot m^{-2}$) | $F_H$ | ≡ Sensible heat flux ($W \cdot m^{-2}$) |

# Complex Model

- Non-ideal gas behavior (requires complex equation of state)
- Assumes temperature variation due to internal and external energy exchanges
- Requires chemical properties to become time dependent

# Complex Model

**Pros**

- More accurate results
- Realistic plume development
- Accounts for actual environment

**Cons**

- Time-dependence requires physical properties not readily available
- Equations for time-dependence introduce additional errors
- Computationally intensive

# Comparison with Three Examples

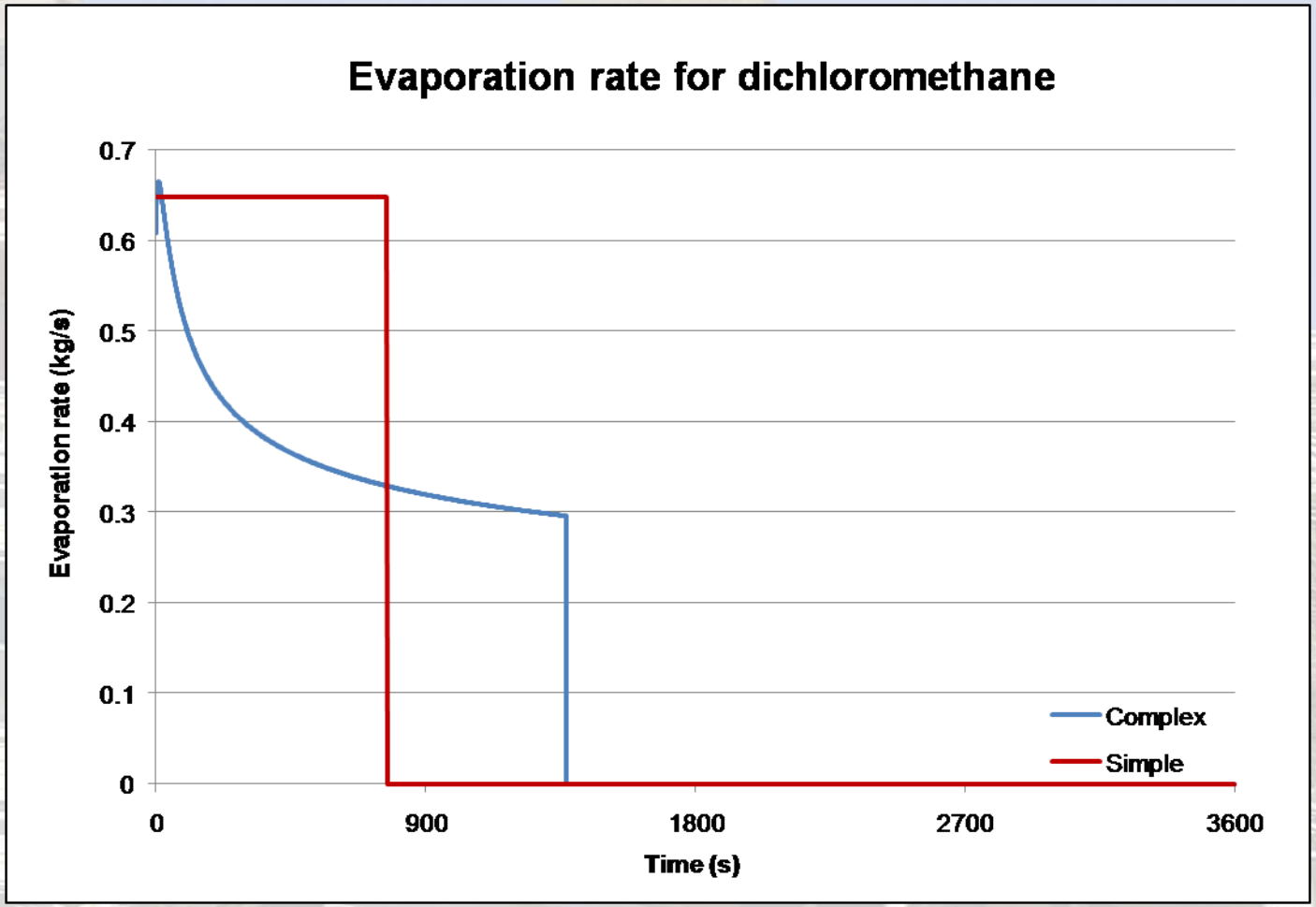
- Volatile liquid – dichloromethane
  - Vapor pressure ~ 350 mmHg at STP
- Liquid similar to water – pyridine
  - Vapor pressure ~ 18 mmHg at STP
- Non-volatile liquid – hydrogen peroxide
  - Vapor pressure ~ 1 mmHg at STP

# Assumptions

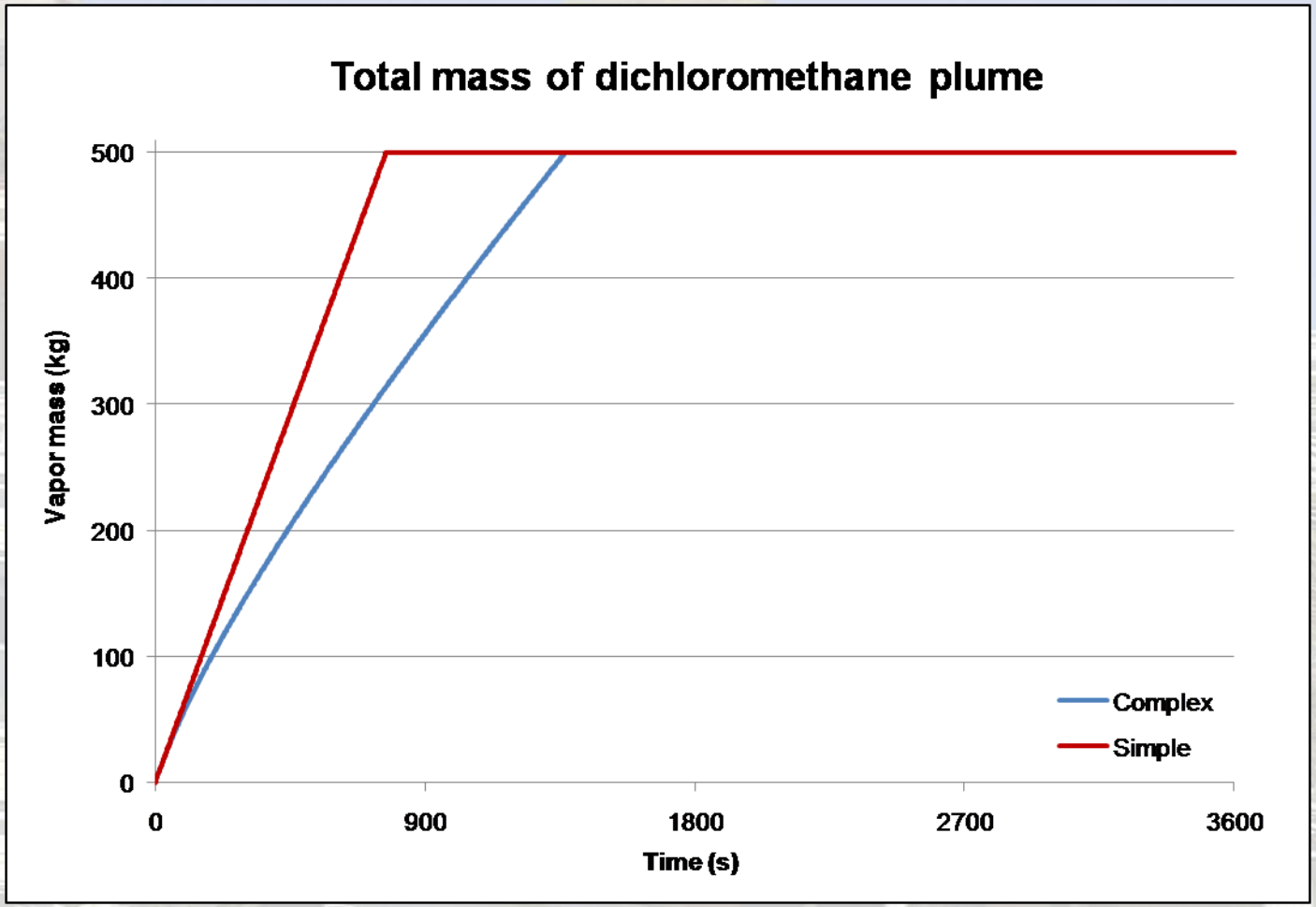
- May 2, 2011, Charleston Marriott
- Around noon
- Warm, partly cloudy
- Light winds
- 50% relative humidity
- Spill of 500 kg liquid

emi sig
EMERGENCY MANAGEMENT ISSUES SPECIAL INTEREST GROUP

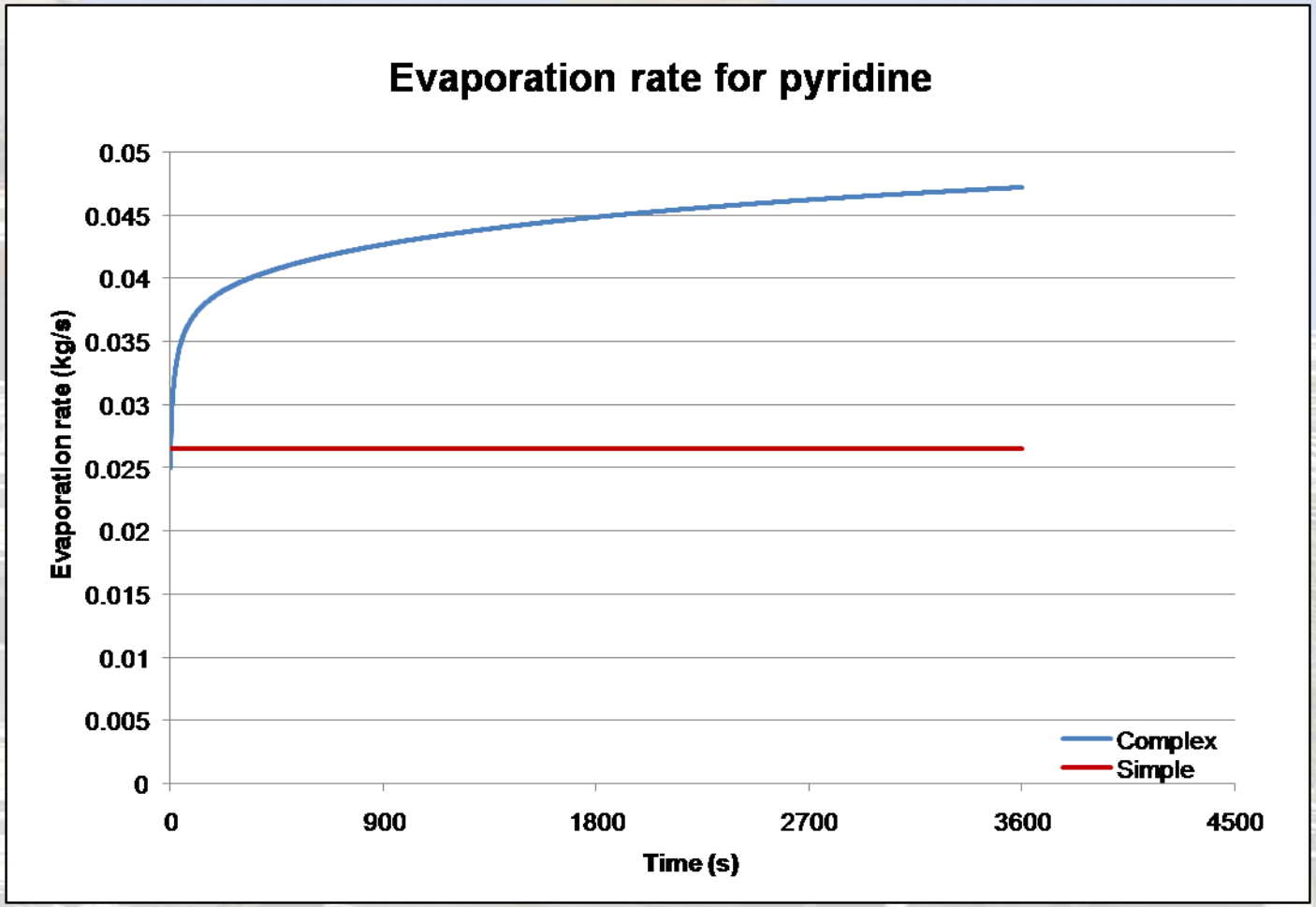
# Volatile Liquid Evaporation



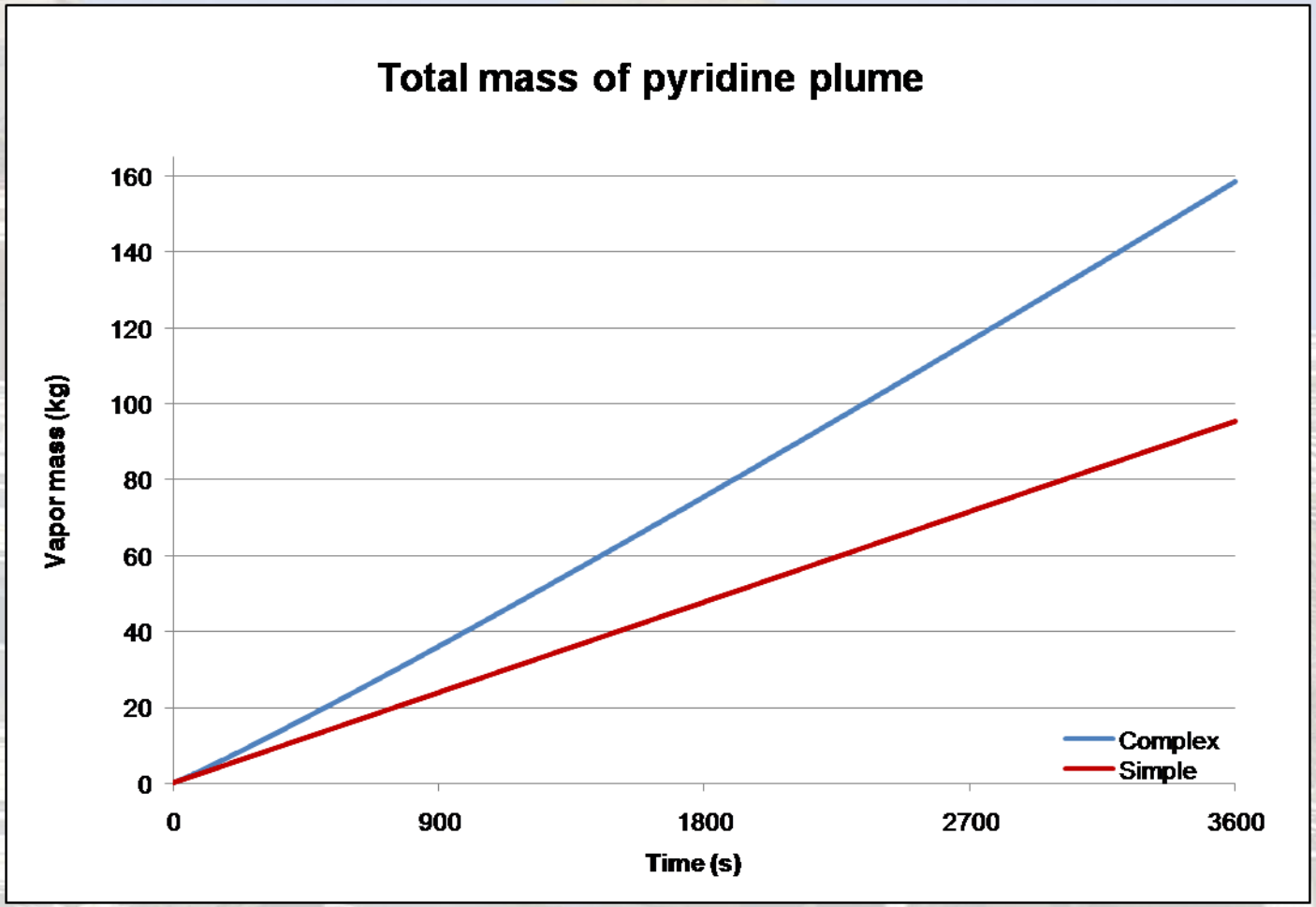
# Volatile Liquid Evaporation



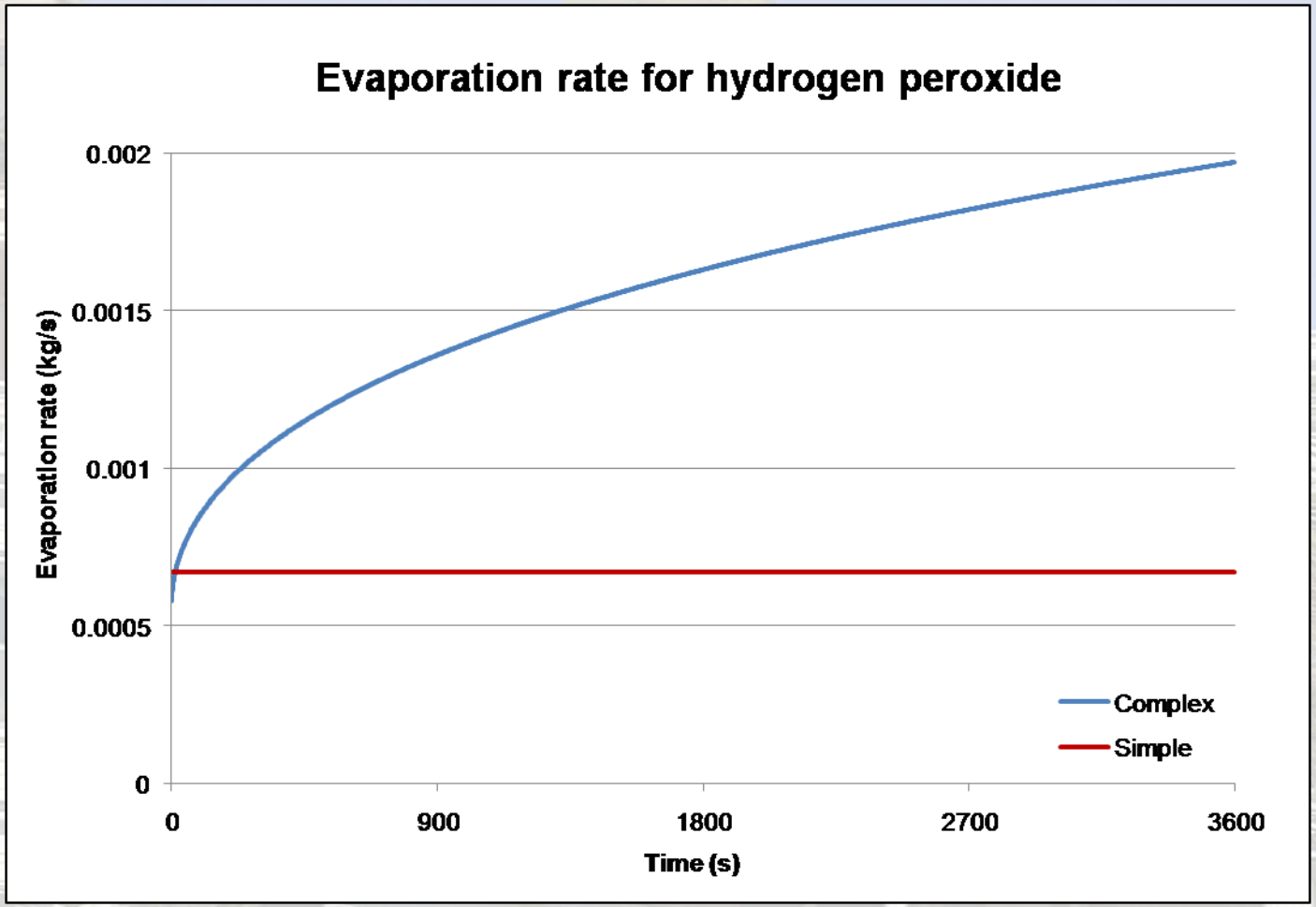
# Water-like Liquid Evaporation



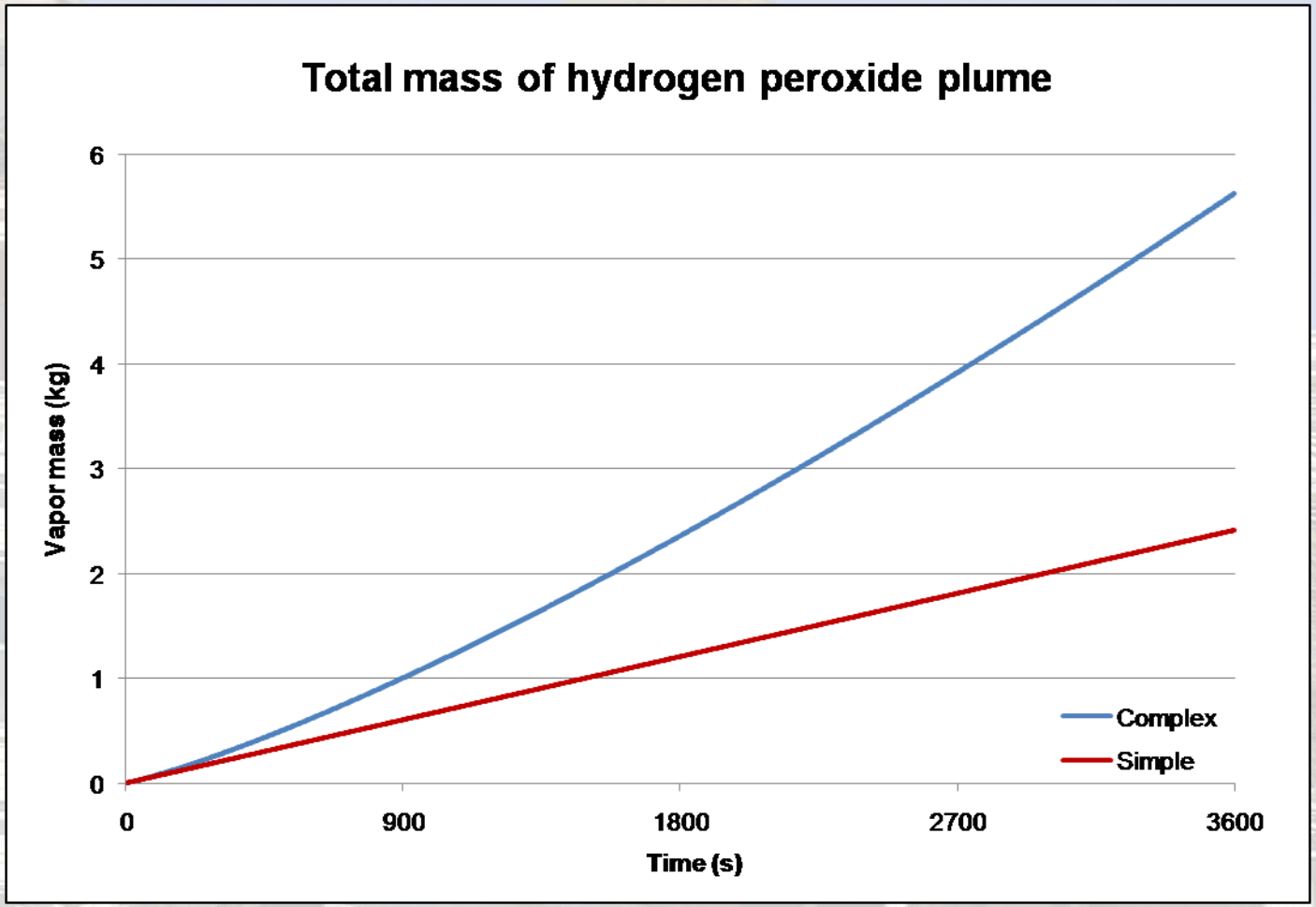
# Water-like Liquid Evaporation



# Non-volatile Evaporation



# Non-volatile Evaporation



# What It Means

- The complex model is sometimes more conservative:
- During conditions with significant solar insolation
  - Increased heat input results in increased evaporation rate
- For non-volatile liquids
  - Cooling due to evaporation is not significant

# How to Plan

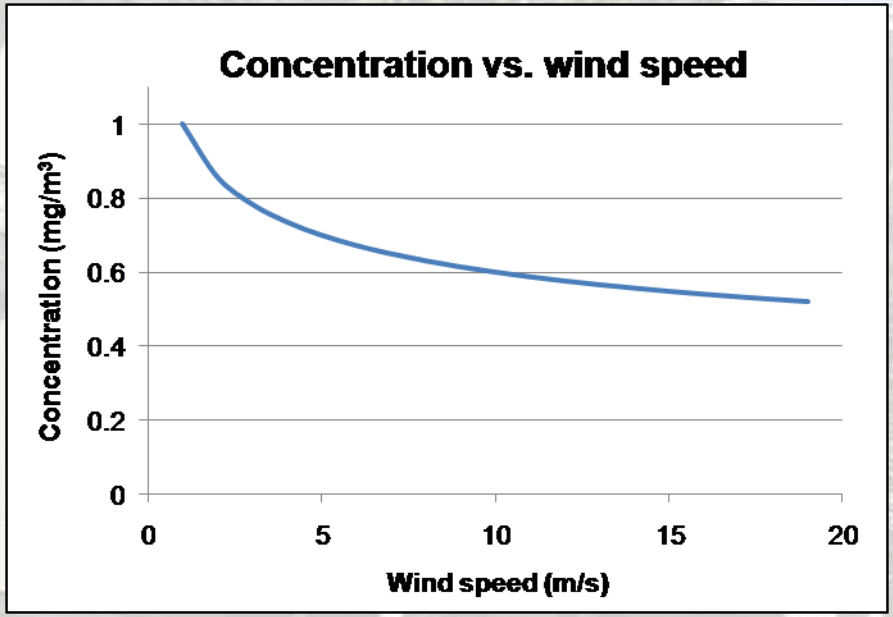
- In general, we are concerned with volatile liquids
- The simple model will conservatively estimate the evaporation of volatile liquids
- Must keep evaporation and dispersion coupled when developing worst case scenarios for EPHAs

# Evaporation + Dispersion

- Evaporation rate has $u^{7/9}$ dependence (simple model)
- Straight-line Gaussian has $u^{-1}$ dependence

$$C \propto \frac{u^{7/9}}{u} = u^{-2/9}$$

C ≡ Downwind concentration ($mg \cdot m^{-3}$)



emi sig
EMERGENCY MANAGEMENT ISSUES SPECIAL INTEREST GROUP

# Summary

- The simple model will conservatively model volatile chemicals
- Lower wind speeds produce lower evaporation rate but overall higher downwind concentration
- Use of the complex model should be considered if the chemical properties are available
  - during emergency response
  - for developing very specific EPHA scenarios

emi sig
EMERGENCY MANAGEMENT ISSUES
SPECIAL INTEREST GROUP

# Questions?