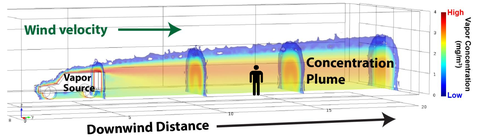
Agent to Simulant Correlations for Materials Decontamination

T. P. Pearl [2], M. J. Varady [2], J. P. Myers [1], B. A. Mantooth [1]
(1) U.S. Army Edgewood Chemical Biological Center, (2) OptiMetrics, Inc.

Introduction

- Polymer systems can absorb and subsequently reemit various toxic chemicals as a vapor
- Chemical warfare agent simulants are often used for environmental testing in place of the highly toxic agents or as part of decontaminant development

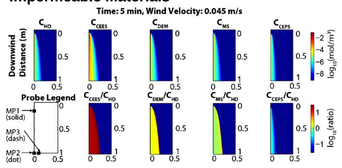


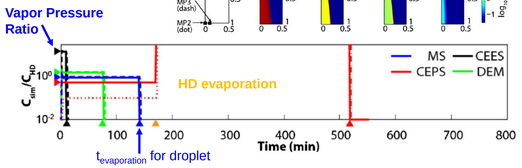
- Work sets the foundation for modeling liquid-phase decontamination of absorbing polymeric materials with the focus on determining relationships between agents and simulants
- Diffusion modeling of the subsurface transport of simulants and live chemical warfare agents was conducted for various polymer systems
- Results demonstrate that the contaminant-material interactions can dominate vapor flux
- Work establishes an understanding of the surface and subsurface chemistry relationships of simulant to live chemical warfare agents that indicate how simulant data could be analyzed to estimate the decontaminant performance of more toxic chemical warfare agents

Vapor Phase Transport

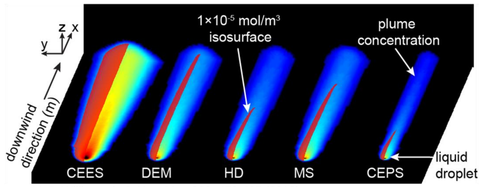
Impermeable Materials

- Vapor pressure ratio correlated to vapor concentration ratio
- Correlation is valid until one droplet evaporates





Concentration Plumes

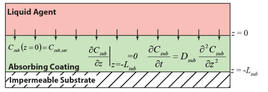


M. P. Willis et al., J. Haz. Mat. **263**, 479-485 (2013)

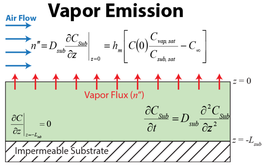
Vapor and Material Phase Transport:

Permeable Materials

Contamination



Vapor Emission



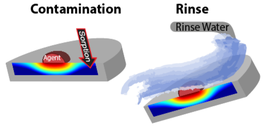
$h_m = f(\text{air velocity, flow geometry})$

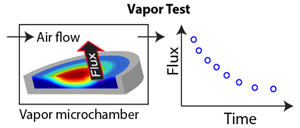
- Chemical transport is modeled using Fick's second law
- 1D models are used for coatings (50 µm thickness), 2D models for silicone materials
- Vapor flux is regulated by transport of contaminant from the bulk to the surface and emission as a vapor from the surface
- Agent to simulant correlations involve properties of:
  - $C_{sat,\,vap}$ – vapor pressure (mol/m³)
  - $C_{sat,\,mat}$ – material saturation (mol/m³)
  - D_{sub} – material diffusivity (m²/s)
  - h_m – convection coefficient

Vapor emission can be limited by transport in the material or transport in the vapor phase

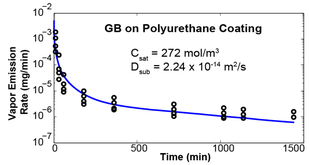
Approach

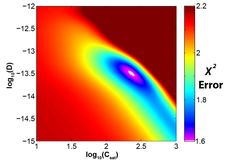
- Measure time-resolved vapor flux from a contaminated substrate
- Contamination process generates agent concentration distribution
- Agent emission from the material leads to surface concentration depletion, which affects vapor emission
- Use inverse methods to obtain parameters:
  1. Model the experimental response
  2. Minimize chi-square error to determine parameters **β = [C_{sat}, D]**
  3. Global min. indicates unique parameters





$$\chi^2 = \sum_i \frac{\left(y_{exp}(t_i) - y_{mod}(t_i, \boldsymbol{\beta})\right)^2}{\sigma_i^2}$$





Contaminants

Wide range of vapor pressure

Mustard and simulants

	MW (g/mol)	Vapor Pressure (torr)
Distilled Mustard (HD)	159.1	0.11
2-Chloroethyl ethyl sulfide (CEES)	124.6	3.4
2-Chloroethyl phenyl sulfide (CEPS)	172.7	0.0186
Methyl Salicylate (MS)	152.2	0.04

Organophosphate nerve agents

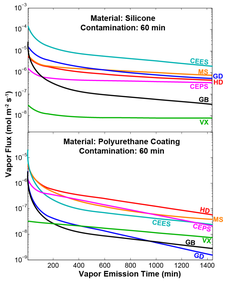
	MW (g/mol)	Vapor Pressure (torr)
Sarin (GB)	140.1	2.1
Soman (GD)	182.2	0.4
VX	267.4	0.0007

S. L. Bartelt-Hunt et al., Critical Reviews in Env. Sci. and Tech. **38**, 112-136 (2008)

Materials

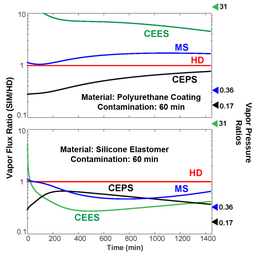
- Polyurethane coating (paint) system – glassy engineered coating (< Tg)
- Silicone elastomer – rubbery polymer (>Tg)

Results: Experiment and Computation



	Silicone		Polyurethane	
Contam	C_{sat} (mol/m³)	D (m²/s)	C_{sat} (mol/m³)	D (m²/s)
HD	2962	5.38×10^{-12}	2153	5.17×10^{-14}
MS	171	2.54×10^{-10}	277	1.07×10^{-13}
CEES	1143	1.36×10^{-10}	2309	2.10×10^{-14}
CEPS	117	2.10×10^{-10}	685	1.20×10^{-13}
GB	50.3	8.21×10^{-11}	273	2.26×10^{-14}
GD	1075	1.60×10^{-11}	237	4.51×10^{-14}
VX	126*	1.15×10^{-10}	39.7	7.70×10^{-13}

** Liquid extraction technique*



- Silicone rubbery elastomer has higher diffusivities than glassy polyurethane
- Higher vapor pressure ≠ higher flux
- Data enables calculation of concentration field evolutions and determination of rate limiting process beyond the tested ranges (i.e., confident extrapolation)

Compare HD to common simulants

- For polyurethane coating
  - MS, CEES and CEPS provide flux within time varying factor of 3 × lower than HD
- For silicone elastomer
  - MS 2 × higher flux than HD
  - CEES 8-10 × higher flux than HD
- Relationships of simulants vary with material properties
- Physics-based modeling best captures material effects

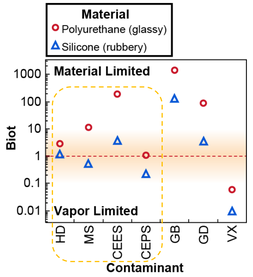
Evaluate Vapor and Material Phase Limitations

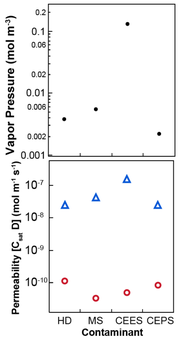
Nondimensional Mass Transfer Biot Number

$$Bi = \frac{R_{interface}}{R_{material}} = \frac{h_m L_{sub} C_{sat,vapor}}{C_{sat,sub} D_{sub}}$$

Bi >> 1	Material resistance limited
Bi ≈ 1	Both processes influential
Bi << 1	Vapor resistance limited

Simulants for vapor flux correlation should have similar rate limiting processes





Polyurethane Coating:

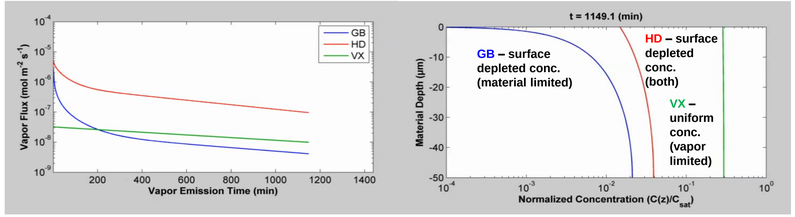
$Bi_{GB} = 1.4 \times 10^3$ (material limited)
- Large concentration gradient near surface
- Emission occurs faster than material can replenish

$Bi_{HD} = 2.9 \times 10^0$ (transition regime)
- Moderate concentration gradient near surface
- Emission occurs on time scale similar to material transport

$Bi_{VX} = 5.6 \times 10^{-2}$ (vapor limited)
- Minimal depletion at surface
- Transport in material is faster than removal via vapor emission

- Rate limiting process describes concentration evolution of contaminant in the material
- Ideal simulants for vapor flux should have similar transport characteristics
- Wide dispersion in HD and common simulants

Comparison across agents-Material: Polyurethane Coating



Conclusions

- Inverse analysis approach coupled with physics-based models enables determination of transport parameters of chemicals in materials
- Material specific interactions with each simulant affect the rate limiting process and vapor flux that would affect exposure to personnel near decontaminated materials
- Relative reaction rates and solubility of contaminant in decontaminant affect vapor flux complicating correlations

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