Environmental Fate Of Chemical Warfare Agents: Agent Fate Modeling

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**Objectives:**
- Measure and understand the physico-chemical processes of CW agents on surfaces in order to predict their persistence and fate in operational scenarios via agent fate models.

**Payoffs:**
- Support research and acquisition decisions of all capability areas: detection, protection, decontamination
- Support and improve Operational Risk Management decisions based on inhalation and contact hazard.
- JFOC - Battle Management: Battlespace Analysis and Planning
- Augments operational and mission area analysis tools such as Joint Effects Model (JEM) and Joint Operational Effects Federation (JOEF)
Agent Fate Modeling

Improve prediction of CWA secondary evaporation and liquid contact & pickup

CWA Hazard Prediction Model

- Initial Vapor
- Liquid Drops
- Evaporation
- Secondary Vapor
- Vapor from Falling Drops
- Liquid Deposition

Larger Droplets  Smaller Droplets

Hazard
- Challenge
  - threat
  - dissemination
  - evaporation
  - T&D
- Toxicity
- Exposure
- Protection
- Risk

Release

Wind
## Model Development Approach

Concurrently Pursuing Wide Range of Modeling Approaches
Semi-Empirical Model Is Contractual Requirement

### How Data Is Used

<table>
<thead>
<tr>
<th>Model Type</th>
<th>Data used to define response</th>
<th>Data used to understand response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical (fit to data)</td>
<td>Semi-empirical (theory with empiricism)</td>
<td>Theoretical (first principles)</td>
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</table>

### Model Type Examples

<table>
<thead>
<tr>
<th>Regression</th>
<th>Chinn</th>
<th>PR2515</th>
<th>Roberts</th>
<th>STP 386</th>
<th>VLSTRACK</th>
<th>FOA</th>
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Agent Fate Data Needs

- Major factors
  - Agent, substrate, temperature, wind speed, humidity, droplet size
- 3 classical agents
- Substrates: asphalt, concrete, grass, sand, soil
- 3 factor levels for environmental conditions
  - Curvilinear effects
  - Based on operational data
- Full factorial matrix > 10,000 experiments
  - Experimental design trims to about 1300 experiments
  - Additional investigations to further reduce test matrix

Need comprehensive high quality data
Current State of Agent Fate Data

Less than 400 usable live agent fate experiments exist Circa 1999

- Deficiencies of Existing Data Points:
  - Sparse
  - No coordination between tests
  - Limited test duration
  - No repeatability
  - Missing data
  - Illegible source material
  - Antiquated test equipment
  - Significance versus quantification testing

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Agent Fate Program will start to fill the holes in this matrix
(Comprehensive, systematic, and integrated program)
State Of Data At End Of Program

Program Provides Comprehensive Data Set For 3 Classical Agents

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Data added via Agent Fate Program
Agent Fate Testing

Multiple levels of agent fate test data needed for model development

Wind Tunnel Tests
- Controlled environment
- Factor effects on evaporation
- Primary source of model development data
- Limited scrutiny on agent/substrate interaction effects

Outdoor Trials
- “Ground truth”
- Correct wind tunnel model
- Validate field model

Lab Experiments
- Agent/substrate interaction
- ID substrate parameters affecting evaporation
- Expands WT model to surfaces beyond those tested
Semi-Empirical Evaporation Model

F1 = mass transfer - primary evaporation
F2 = mass transfer - absorption
F3 = mass transfer - desorption
F4 = mass transfer - decomposition

Approach:
• Droplet-based evaporation
• Segregate mass transfer into constituent components
• Add key physico-chemical processes
• Calibrate unknown model parameters to empirical data
• Limited model inputs with extensibility

Droplet-based physics model with empirical fit to data
Non-Porous Surface Evaporation Model

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
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<tr>
<td>Drop-Surface</td>
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<tr>
<td>contact angle</td>
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<td>9.5 degree</td>
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<td>Drop-Air</td>
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<tr>
<td>temperature</td>
<td>21.2</td>
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<td>diffusion layer</td>
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<td>0.143 mm</td>
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<tr>
<td>Air</td>
<td>0.97</td>
<td>- atm</td>
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</table>

- Volume constant Angle
- Volume constant Base
- Volume cap absorbed: ‘base only’
- Volume cap absorbed: ‘base + cap’
- Volume torus absorbed: ‘base only’
- Volume torus absorbed: ‘base + torus’

100 drop model - Constant Base
Non-Porous Surface Evaporation Model Example

HD On Glass

- 120 drop experiment 18 May 2000 - sample 1 - fit 95%
- 100 drop model - constant base - fit 95%

Volume [%]

Time [h:mm]

CAP, Constant Base

Non-Porous Surface Evaporation Model Example
Porous Surface Evaporation Model

HD On Sand

- 42 drop experiment 10 november 2000, sample 2
- Single drop model - 1/2 Torus filled - both surfaces - fit 80%
- Single drop model - Spherical Cap - both surfaces - fit 80%

- Base + torus evaporation, HALF FILLED TORUS
- Base + cap evaporating equally, constant contact angle

- Drop:
  - Weight initial drop: 6.57 mg
  - Agent: HD
- Drop-Surface:
  - Contact angle: 8.0 degree
- Drop-Air:
  - Temperature: 29.60 °C
  - Diffusion layer: 0.50 mm
- Substrate:
  - 1-Porosity: 0.60 volume fraction solid
  - Fill fraction: 0.90 volume fraction gas phase
  - Air pressure: 0.97 atm
Field trials contain effects not accounted for in wind tunnel model so when you plug field trial observation data into wind tunnel model there are differences.

Difference is noted by $\frac{\text{Time}_{\text{exp}} (\text{RMF})}{\text{Time}_{\text{model}} (\text{RMF})}$
- Ratio = 1 exp and model agree, < 1 model overpredicts, > 1 model underpredicts

Can adjust prediction to match experiment (if error is systematic)

**Field model is correction of wind tunnel model to achieve agreement with experimental observation**
Agent Fate Technology Transition

Agent Fate Program Products

- Technical Reports
- Liquid Contact & Pickup Model
- Evaporation Model
- Agent Fate Data

CHEMRAT

JPEO-CBD (JPMIS)

- JOEF
- JEM

WARFIGHTER

- TTPs
- CCW-CONOPs
- Decision-Aid Tools
- Persistence Tools
- ORM

OTHER AREAS OF CBDP

- JSTO
- JRO
- JTE
Summary

• DTO objective is to develop better persistence models
  – Improve secondary evaporation and liquid contact/pickup models
• Pursuing empirical, semi-empirical, and theoretical model development efforts
  – Semi-empirical model is contractual requirement
• Wide range of indoor/outdoor persistence testing and analytical chemistry needed to develop models
• Non-porous semi-empirical evaporation model completed
• Limited development of non-porous surface model
• Wind tunnel models must be converted to field models
• Models and data transition to CBDP and warfighter
  – Evaporation model program of record is Joint Effects Model