Responding to a Chemical Warfare Agent Incident: from sampling and analysis to decontamination and waste management

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• Homeland Security Relevance to Chemical (Warfare Agent) Incidents and Incident Response Cycle

• Identification of Gaps/Needs: PARTNER Process and Stakeholder Priorities

• Current High Stakeholder Priorities

• Research Efforts to meet these Needs/Gaps
  - Selected Analytical Methods (SAM) Document
    - CWA Method Development and Wipe Efficiency Studies on Surfaces
  - Fate and Transport of CWAs
    - Natural Attenuation of VX
  - Decontamination of Vesicant/Blister CWAs HD, L, HL
  - Analytical Method Development: Lewisite; EA 2192
  - Best Practices Document for Waste Media from Remediation Activities

• Summary
Since 9/11, multiple chemical/biotoxin contamination events have occurred in the United States and worldwide:

- Several ricin incidents (2002-2014)
- Deepwater Horizon oil spill (April 2010)
- Kalamazoo River oil spill (July 2010)
- CWA sulfur mustard clam shells (2010)
- CWA chemical attacks (Syria, Middle East) (March-August 2013 and April 2014-current)
- Elk River chemical spill in West Virginia (January 2014)
- Toxic algae blooms in Toledo, OH (August 2014)
- Arsenic-contaminated soil in Kentucky potentially containing CWA Lewisite (March 2015)
- (Organophosphate-) Pesticide over- or misuse across USA in relation to bed bug epidemic (current)
Response Cycle

Contaminant Release

- Contamination Incident
- Reduce Vulnerabilities
- Detection
- Mitigation
- Lessons Learned and Preplanning
- Decon and Treatment
- Characterization & Risk Assessment
- Return to Service
Stakeholder Input / Partner Engagement

Indoor / Outdoor Decon
EPA Program Offices (OLEM, OW, OAR, OCSPP, OHS) & Regions

PARTNER

Water Resilience and Security
EPA Program Offices (OW, OHS) & Regions, Critical Infrastructure Partnership Advisory Council (CIPAC) for Water

All partners engaged in:
- Needs prioritization
- Research implementation
- Product formulation/delivery
Addressing Gaps Associated with CWAs during Remediation

Examples of (High) Stakeholder Priorities:

• Validated and standardized methods for CWAs and degradates for all environmental matrices of concern

• Identifying priority contaminants for method development and/or evaluation

• Lack of information/data on the fate of CWAs in an urban setting and alternative decontamination technologies (e.g., natural attenuation)

• Effective decontamination methods for porous/permeable materials

• Treatment and disposal options for large volumes of chemical-agent contaminated water and wastewater
Why the Need for Homeland Security Analytical Methods?

OBJECTIVE: Improve the nation’s laboratory capacity and capability to quickly respond to large-scale incidents requiring environmental sample analysis.

BACKGROUND: EPA’s Homeland Security Laboratory Capacity Workgroup* identified the critical need for a list of pre-selected, pre-evaluated, standardized analytical methods to be used by all laboratories when analyzing samples from an incident.

Having pre-selected and evaluated methods would:
• reduce confusion
• permit sharing of sample load between laboratories
• improve data comparability
• simplify the task of outsourcing analytical support to the commercial laboratory sector
• improve the follow-up activities of tasks of validating and analyzing data and making decisions.

GAP/Need: Validated and standardized methods for CWAs and degradates for all environmental matrices of concern

*ORD, OAR, OW, OLEM, OEI, OPP, Regions (1,2,4,6).
OBJECTIVE: Improve the nation’s laboratory capacity and capability to analyze CWAs in environmental matrices and identify recovery efficiencies from porous/permeable surfaces.

BACKGROUND: CWA protocol developed to analyze low-level concentrations for GB, GD, GF HD, and VX. Protocol was multi-lab tested and is available for use by OEM-established CWA labs.

- Follow-on research investigated wipe efficiencies/recoveries from porous/permeable surfaces (vinyl tile, wood, coated glass, painted drywall, laminate)
  - Direct extraction results suggest that wipe sampling may underestimate CWA concentrations on/in these matrices
  - Wipe sampling most likely will only account for analyte on the surface and not necessarily from within a porous/permeable material
  - Isotopically-labelled VX (VX-d_{14}) was used as an extracted internal standard to improve the accuracy of VX recovery from the tested surfaces
Why the Need for Fate and Transport Data?

Gap/Need: Lack of information/data on the fate of CWAs in an urban setting

**OBJECTIVE:** *Improve the understanding of the fate and transport processes of CWAs in the urban environment*

- As to improve on existing (less efficacious) decontamination options for chemicals on/in/under porous/permeable materials

**BACKGROUND:** *Decontamination studies on porous/permeable materials indicate poorer efficacy of decontaminants that are otherwise effective for decontamination of nonporous materials*

- Attributed to inability of the decontaminant to reach agent that permeates into a material
- Unknown is the degree of permeation:
  - Chemical agent specific?
  - Paint, sealant, material dependence?
  - Time dependence?
  - How about painted/sealed porous materials?
Research: F&T Sulfur Mustard (HD)

I. Nonporous material
   - Wipe: HD on surface
   - Extract: Remaining HD
     Measure of Persistence

II. Paint
   - Wipe: HD on surface
     Measure of Persistence
   - Extract: HD in paint (Latex-Flat)
     Measure of HD in paint

III. Paint
    - Wipe: HD on surface
      Measure of Persistence
    - Extract #1: HD in paint (Latex-Flat)
      Measure of HD in paint
    - Extract #2: HD in porous media

*: solid phase extraction (SPE) disk

HD amount recovered as ratio of applied amount
Research: F&T of VX

I. Nonporous material
   - Wipe: VX on surface
   - Extract: Remaining VX
     Measure of Persistence

II. Paint
    - Wipe: VX on surface
      Measure of Persistence
    - Extract: VX in paint (Latex Flat)
      Measure of VX in paint

III. Paint
     - Measure of Persistence
     - Extract #1: VX in paint (Latex Flat)
       Measure of VX in paint
     - Extract #2: VX in porous media

*: solid phase extraction (SPE) disk

VX amount recovered as ratio of applied amount

Unpainted SS

Painted SS

Painted film on SPE

hr post application
INVESTIGATED: Three paints and two sealants:
- Latex Flat; Latex Semi Gloss; and Oil Gloss
- Epoxy-based and Polyurethane-based Sealant

OBSERVATIONS:
- Permeation of HD and VX into the paint/sealant occurs and is dependent on paint/sealant type and agent
- Further transport occurs into porous material below paint/sealant; rate/amount depends on paint/sealant type and chemical agent

IMPACT of STUDY:
- Decontamination with e.g. bleach would probably not neutralize agent within the paint layer or in the porous material below the paint/sealant
- Traditional wipe method may result in false negatives
Why the Need for Decontamination?

Gap/Need: Effective decontamination methods for porous/permeable materials

OBJECTIVE:

Identification of decontamination methods to clean up (critical) infrastructure materials.

BACKGROUND:

Natural attenuation (i.e., leave the event site alone and “wait and see”) is not advantageous considering the low volatility of some of the agents and/or when re-occupancy or re-use is time critical (e.g., transportation hub, buildings of high significance, etc.)
Example: Natural Attenuation of VX

**Impact of Nonporous Material and Temperature:**

Outcomes:
- Temperature dependent
- Material dependent

Ongoing research:
- Inclusion of porous materials

Data extends beyond 10 days; detects for VX on all materials after 35 days at 10 °C on 4 of 5 materials after 14 days at 25 °C

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- Modified glovebox
- Tight T and RH control
- 4.0 cm x 2.5 cm coupons
- 2 μL droplet of VX / coupon

**Preliminary Remediation Goal for VX is approx. 1 nanogram for a 10 cm² surface area**
Decontamination of CWA contaminated materials

Gap/Need: Effective decontamination methods for porous/permeable materials

OBJECTIVE:

Identification of decontamination methods to clean up (critical) infrastructure materials.

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Natural attenuation (i.e., leave the event site alone and “wait and see”) is not advantageous considering the low volatility of some of the agents and/or when re-occupancy or re-use is time critical (e.g., transportation hub, buildings of high significance, etc.)

RESEARCH EFFORT:

Surface decontamination efficacy studies for blister agents sulfur mustard (HD), Lewisite (L), and Agent Yellow (HL)
BACKGROUND:

Decontamination/neutralization data, including data on removal of residual arsenic, are lacking.
- Decontamination data for L limited to military studies (different –harsh- decon approaches)
- Decontamination data for HD more readily available
- No decontamination information exists for HL (mixture of HD and L)

OBJECTIVES:

Determine efficacy of several decontaminants applied to nonporous building materials.
- Apply to surfaces contaminated with HD, L and HL
- Semi-quantitative analysis to determine whether toxic byproducts are formed
Gap/Need: Effective decontamination methods for porous/permeable materials

**EXPERIMENTAL APPROACH:**

Bench-scale study of the decontamination of building materials using four decontaminants

- \( t=0 \) min: Contaminate surface with CWA
- \( t=30 \) min: Apply decontamination solution
- \( t=30 + \text{decon time} \) (30 or 60 min): Recover residual agent
- \( t=30 + (30 \text{ or } 60 \text{ min}) \): Recover residual agent from material without decon

**EFFICACY MEASUREMENTS:** *Decon product Efficacy versus Overall Efficacy*

- HD and L are less persistent CWAs (than VX).
- Outcome of a decontamination effort is a combination of decontaminant efficacy and natural attenuation that occurs
Decontamination Results for HL: HD

- Bleach (full strength) is more efficacious than diluted bleach.
- Relative efficacy improves appreciably for 60 min interaction with hydrogen peroxide.
- Hydrogen peroxide (3%) is efficacious when applied to decon wood; less for metal and glass.
- Vesicant HD decon byproduct (mustard sulfone) observed following decon with hydrogen peroxide (3%).
Decontamination Results for HL: L

- High efficacy for all four decontaminants; bleach is more efficacious than diluted bleach.
- Water by itself would degrade Lewisite (hydrolysis) but would result in vesicant byproducts.
- Vesicant properties may have been removed; arsenic containing decontamination (end-) products are still present on coupons.

Outcomes were incorporated in National Response Team (NRT) Quick Reference Guides (QRGs) for CWAs
Detection of Lewisite and Degradation Products

Lewisite (L1)
C₂H₂AsCl₃

- Hydrolyze, +H₂O

CVAA
CICH=CHAs(OH)₂

- Oxidize, +H₂O₂

CVAOA
CICH=CHAs=O(OH)₂

Lewisite 3 (L3)
C₆H₆AsCl₃

- Hydrolyze, +H₂O

Dehydrate, -H₂O

Lewisite Oxide
CICH=CHAs=O

Lewisite 2 (L2)
C₄H₂AsCl₃

- Hydrolyze, +H₂O

Dehydrate, -H₂O

[(CICH=CH₂)₂As]O

GC/MS
(cool on column)

GC/MS
(derivatization)

Methods
LC-MS/MS Analysis of Lewisite

Lewisite:
- Organoarsenic compound that is a blister agent and lung irritant
- Doesn’t occur naturally in the environment
- CVAA & CVAOA persist

Lewisite I → Chlorovinyl arsonous acid (CVAA) → Chlorovinyl arsionic acid (CVAOA)

H₂O₂ → CVAA → CVAOA
**Gap/Need:** Identifying priority contaminants for method development and/or evaluation

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**LC-MS/MS Analysis of Lewisite**

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Spiked CVAA Concentration</th>
<th>CVAOA Recovery (%)</th>
<th>MDL for CVAOA</th>
<th>ATL*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.20 mg/L</td>
<td>110</td>
<td>0.04 mg/L</td>
<td>0.03 mg/L</td>
</tr>
<tr>
<td>Wipe</td>
<td>3.00 µg</td>
<td>101</td>
<td>0.4 µg</td>
<td>-</td>
</tr>
<tr>
<td>Sand</td>
<td>0.20 µg/g</td>
<td>85</td>
<td>0.07 µg/g</td>
<td>0.3 µg/g</td>
</tr>
<tr>
<td>NB Soil</td>
<td>0.20 µg/g</td>
<td>112</td>
<td>0.03 µg/g</td>
<td>0.3 µg/g</td>
</tr>
<tr>
<td>VA Soil</td>
<td>0.40 µg/g</td>
<td>43</td>
<td>0.03 µg/g</td>
<td>0.3 µg/g</td>
</tr>
<tr>
<td>GA Soil</td>
<td>0.40 µg/g</td>
<td>80</td>
<td>0.05 µg/g</td>
<td>0.3 µg/g</td>
</tr>
</tbody>
</table>


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<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Wipes</th>
<th>Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction</td>
<td>none</td>
<td>Shaker table for 30 min with 10 mM HCl</td>
<td>Shaker table for 30 min with 10.0 mL 50/50 (v/v) 10 mM HCl /methanol</td>
</tr>
<tr>
<td>Oxidation</td>
<td>1:1 dilution with 30% H₂O₂</td>
<td>1:1 dilution with 30% H₂O₂</td>
<td>1:1 dilution with 30% H₂O₂</td>
</tr>
</tbody>
</table>
Example: **2014 WLA/ERLN Priority:** Sampling and analysis method for Lewisite and its by-products

- LC/MS method analyzes for Lewisite by-products (CVAA and CVAOA) which are only identified in the presence of Lewisite (indirect method for Lewisite detection).
- NHSRC worked with LLNL to analyze the samples for the ERLN using the LC/MS method and further confirmed by GC/MS.
- The analysis confirmed that the arsenic was not from Lewisite contamination.
- Analyzed for approximately thirteen arsenic by-products (e.g., Lewisite Oxide) and concluded arsenic acid was contamination source (identified by LC-MS/MS)
LC/MS/MS Analysis of VX Degradation Product in Drinking Water

Gap/Need: Identifying priority contaminants for method development and/or evaluation

WLA/ERLN Priority:

- Develop a method for characterizing EA-2192 contamination in water samples

EA-2192:

- Environmentally persistent
- Similar toxicity to VX (parent agent)
LC-MS/MS Analysis of VX Degradation Product in Drinking Water

Adaptation of U.S. EPA Method 538 Conditions and QC Approach for EA-2192 Analysis by Liquid Chromatography/Tandem Mass Spectrometry

<table>
<thead>
<tr>
<th>EA2192 Initial Display of Capability</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration Curve Accuracy Cal 1 (0.050 μg/L)</td>
<td>96.4 – 105%</td>
</tr>
<tr>
<td>Calibration Curve Accuracy Cal 2 -Cal 7 (&lt; 5.00 μg/L)</td>
<td>92.4 – 107%</td>
</tr>
<tr>
<td>Laboratory Reagent Blank</td>
<td>ND</td>
</tr>
<tr>
<td>Method Detection Limit</td>
<td>0.013 μg/L</td>
</tr>
<tr>
<td>Method Reporting Limit</td>
<td>0.125 μg/L</td>
</tr>
<tr>
<td>Method Precision at Cal 4 (0.480 μg/L)</td>
<td>9.61%</td>
</tr>
<tr>
<td>Method Accuracy at Cal 4 (0.480 μg/L)</td>
<td>21.8%</td>
</tr>
</tbody>
</table>

Risk-Based Criteria for VX in drinking water is **0.021 μg/L**

*Risk-Based Criteria to Support Validation of Detection Methods for Drinking Water and Air, EPA/600/R-08/021, 2008*

Preliminary UPLC Analysis of EA-2192 to Address Rapid Lab Throughput: RT: 1.2 min (UPLC) vs. 5.5 min (HPLC)
Waste Management

Develop Standard Operational Guidelines (SOGs) or “Best Practices” Document for waste media from remediation activities for residual agents:

- **Objective:** Gather available information about adapting sampling and analysis protocols for chemical agents from environmental sampling activities and adapt them for use to sample and analyze solid waste materials or other applicable forms of waste (e.g., large volumes of wastewater). This information will allow for composite sampling so that laboratory resource requirements are reduced and a possible uniform approach may be applied to future processes.

- Intended to be used as a “Best Practices” document. Not intended to be used for policy, but provide recommendations for strategies for environmental sampling and as a repository of “options and relevant information” for decision-makers

- **Planned SOG development:**
  1) Characterizing and determining the extent of contamination and from post-decontamination activities (e.g. verifying decontamination efficacy)
  2) Composite sampling from large quantities of waste and waste disposal

- Experimental work will investigate findings from SOG

Gap/Need: Treatment and disposal options for large volumes of chemical-agent contaminated water and wastewater
Needs/Gaps:

- Validated and standardized methods for CWAs and degradates for all environmental matrices of concern
  - Research Efforts:
    - CWA Protocol developed and multi-lab tested for OEM-established CWA labs
    - LC-MS/MS method for Lewisite & Lewisite degradation products
    - LC-MS/MS method for EA-2192, a VX degradation product

- Lack of information/data on the fate of CWAs in an urban setting and alternative decontamination technologies (e.g., natural attenuation)
  - Research Efforts:
    - Fate and Transport of VX and HD in/through paints/sealants
    - Natural Attenuation of VX on nonporous materials
    - Natural Attenuation of VX on porous materials [in progress]
Needs/Gaps:

- Effective decontamination methods for porous/permeable materials
  - Research Efforts:
    - Ongoing / near completion

- Treatment and disposal options for large volumes of chemical-agent contaminated water and wastewater
  - Research Efforts:
    - SOG development - Ongoing
Where can you find HSRP products/outputs?

http://www.epa.gov/homeland-security-research

Keyword Search: e.g., CWA
Stakeholder Input / Partner Engagement

Indoor / Outdoor Decon
EPA Program Offices (OLEM, OW, OAR, OCSPP, OHS) & Regions

Water Resilience and Security
EPA Program Offices (OW, OHS) & Regions, Critical Infrastructure Partnership Advisory Council (CIPAC) for Water

All partners engaged in:
- Needs prioritization
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Questions

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ORD’s Homeland Security Research Program

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