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

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Outline

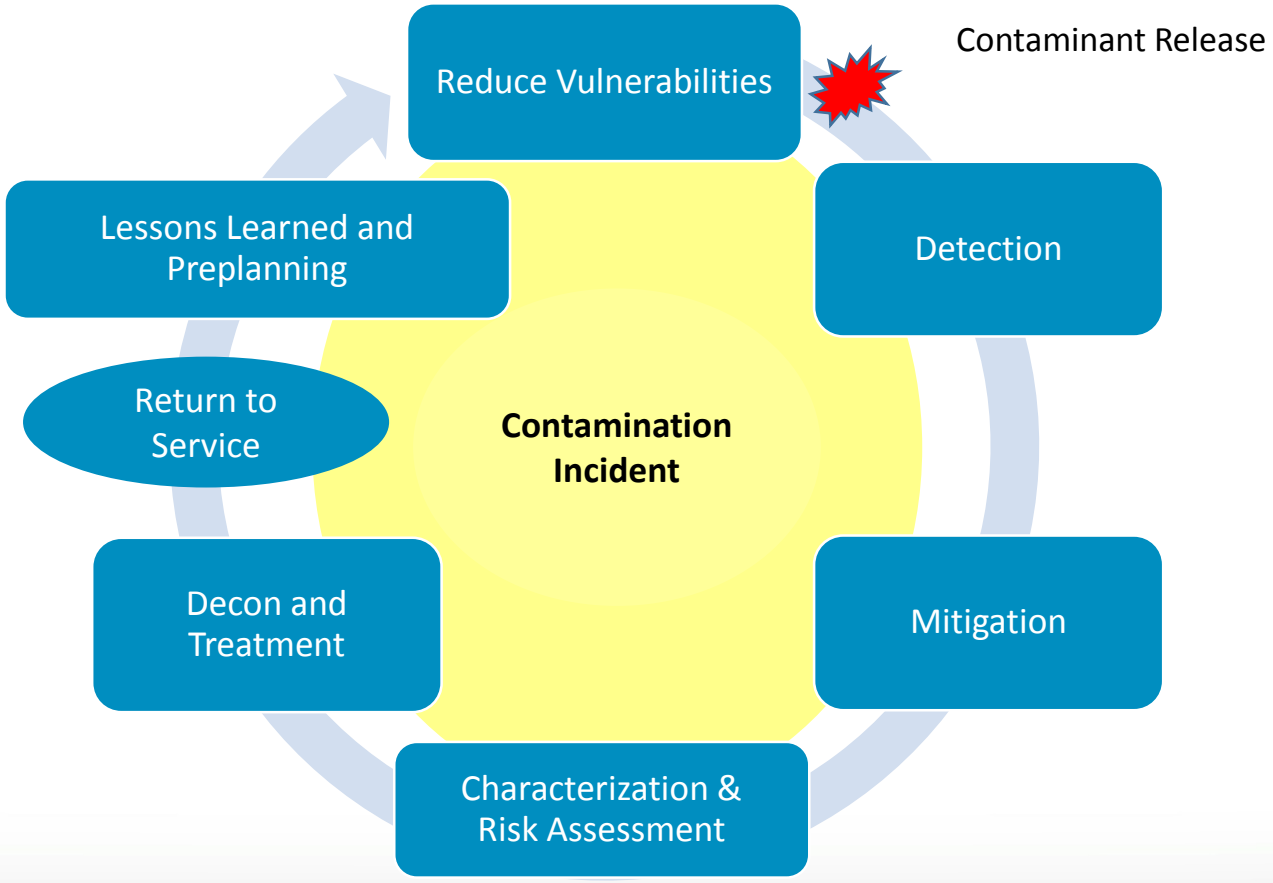
- **Homeland Security Relevance to Chemical (Warfare Agent) Incidents and Incident Response Cycle**
- **Identification of Gaps/Needs: PARTNER Process and Stakeholder Priorities**
- **Current High Stakeholder Priorities**
- **Research Efforts to meet these Needs/Gaps**
  - ❑ Selected Analytical Methods (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**

Response to Contamination Events

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



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?

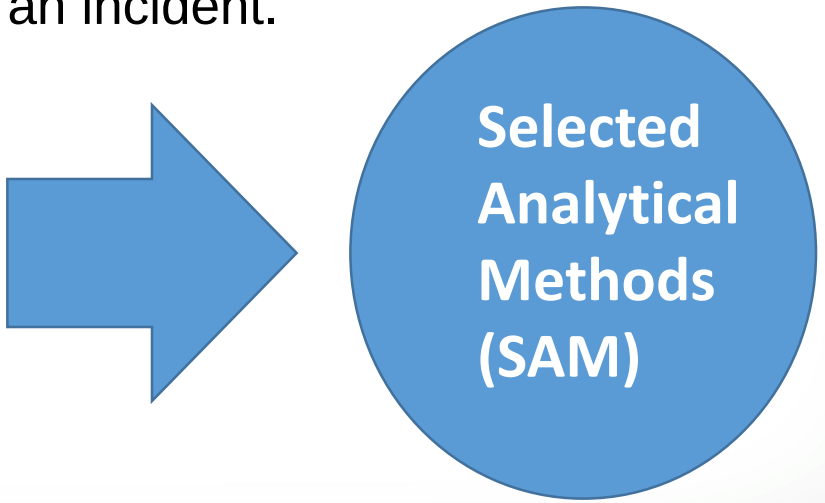
GAP/Need: Validated and standardized methods for CWAs and degradates for all environmental matrices of concern

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.*



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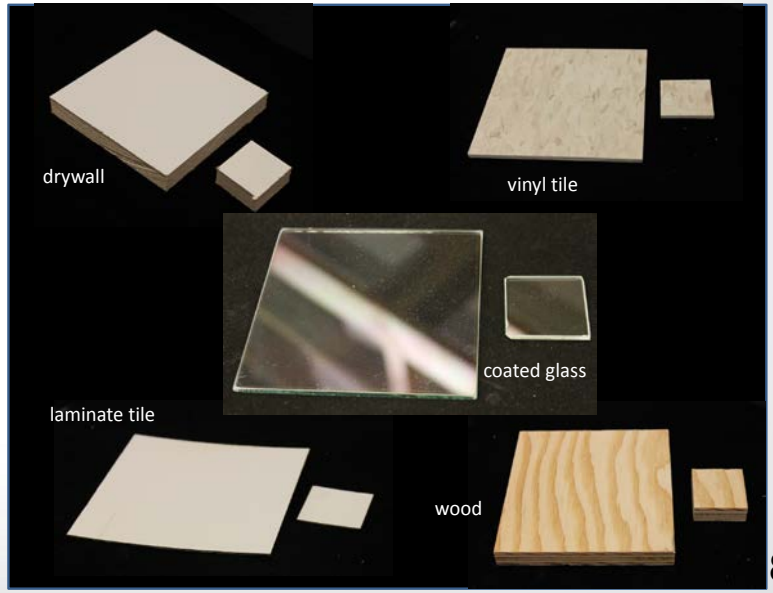
*ORD, OAR, OW, OLEM, OEI, OPP, Regions (1,2,4,6).

CWA Method Development and Wipe Efficiency Studies on Surfaces

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?

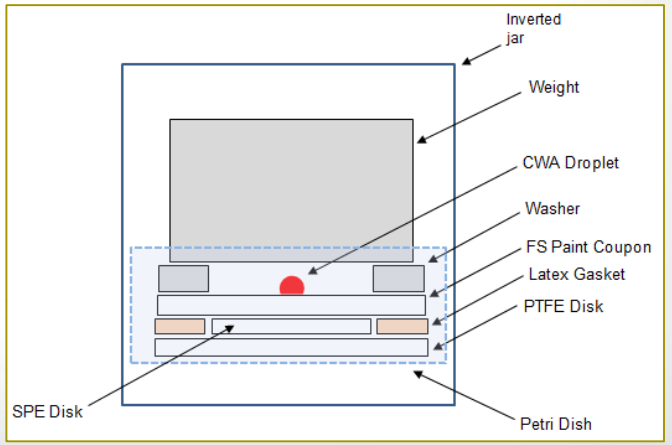
Gap/Need: Lack of information/data on the fate of CWAs in an urban setting

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)

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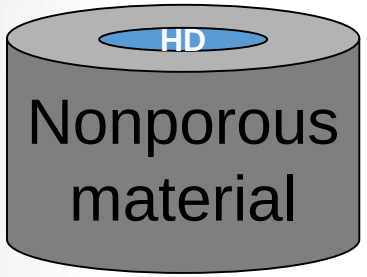
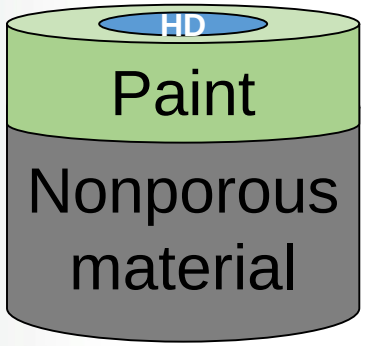


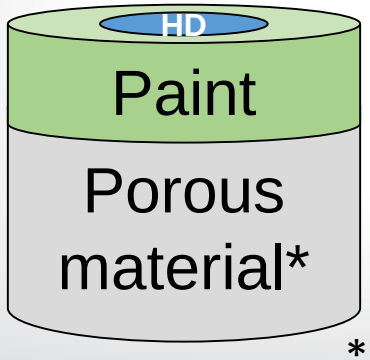
Wipe: HD on surface
Extract: Remaining HD
Measure of Persistence

II



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

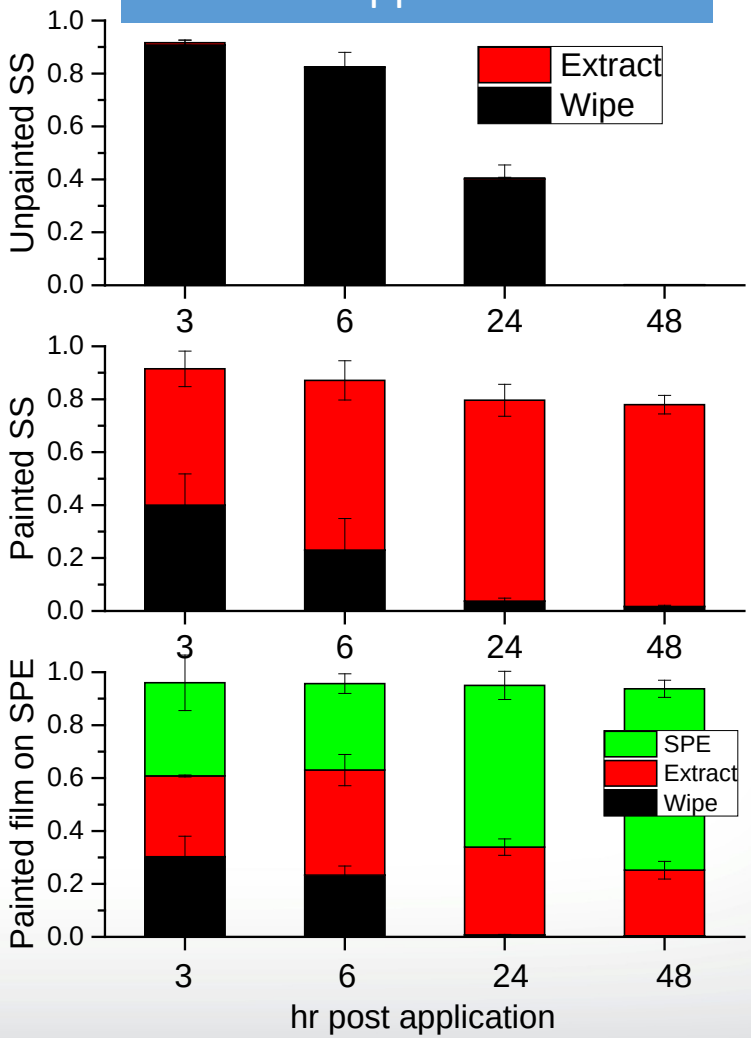
III



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

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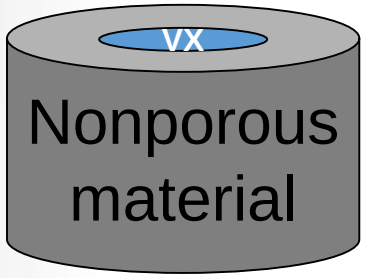
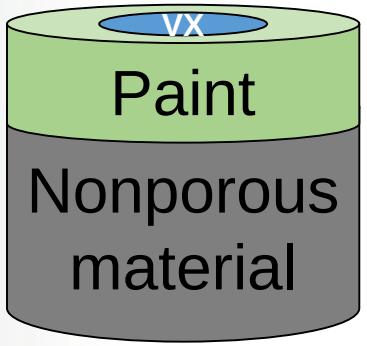


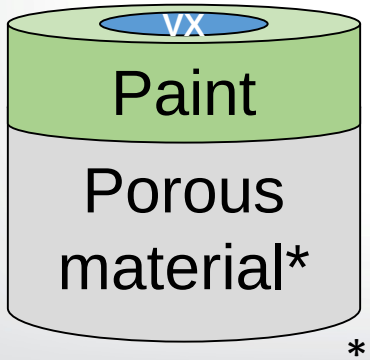
Wipe: VX on surface
Extract: Remaining VX
Measure of Persistence

II



Wipe: VX on surface
Measure of Persistence
Extract: VX in paint (Latex Flat)
Measure of VX in paint

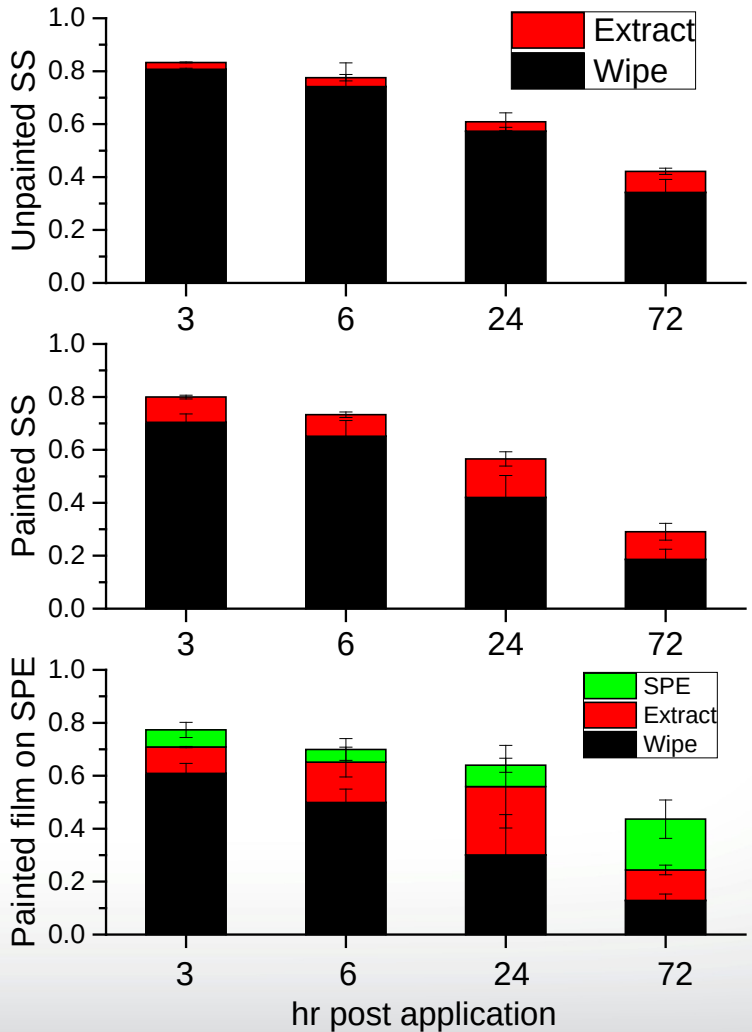
III



Wipe: VX on surface
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



F&T Observations & Impact:

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

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:

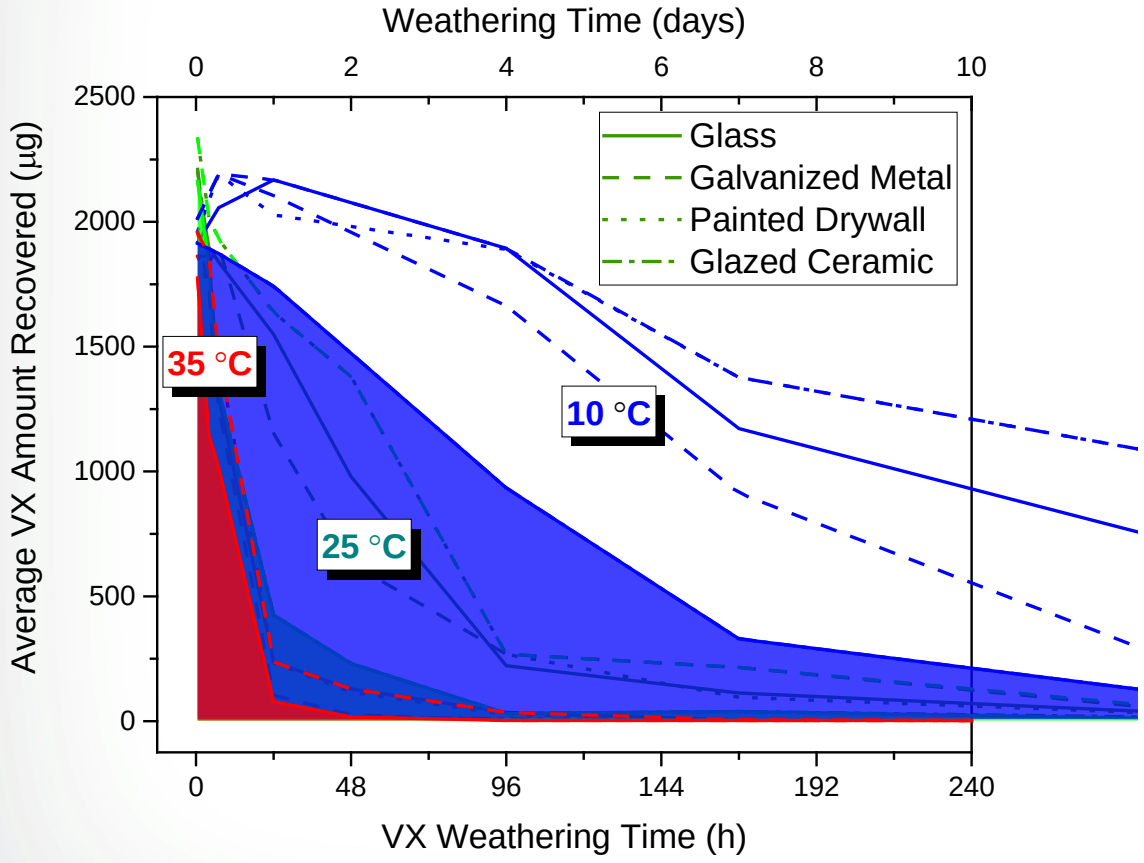
Identification of decontamination methods to clean up (critical) infrastructure materials.

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:



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

Outcomes: Persistence is
- Temperature dependent
- Material dependent

Ongoing research:
- Inclusion of porous materials

Preliminary Remediation Goal for VX *is approx.* ***1 nanogram*** *for a 10 cm² surface area*

➢ 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

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.

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.)

RESEARCH EFFORT:

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

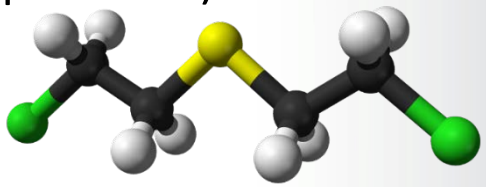
Surface Decontamination Studies of HD, L, and HL

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

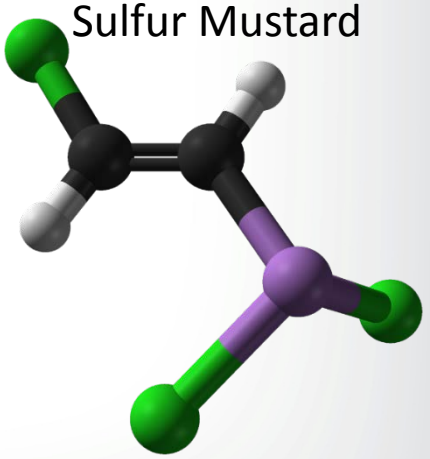
BACKGROUND:

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)



Sulfur Mustard



Lewisite

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

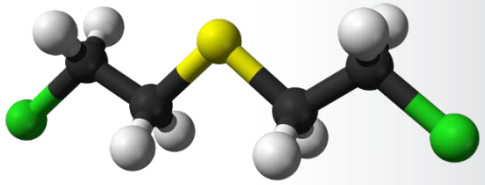
Surface Decontamination Studies of HD, L, and HL

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

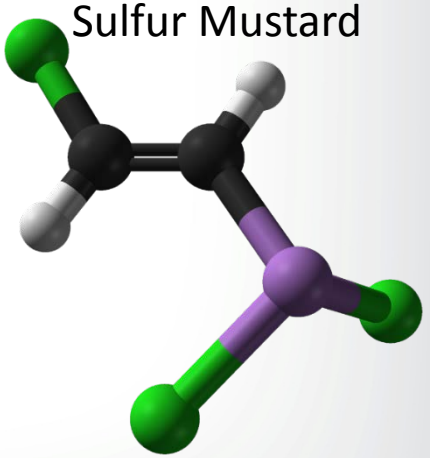
EXPERIMENTAL APPROACH:

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 + decon time (30 or 60 min): Recover residual agent
- t=30 + (30 or 60 min): Recover residual agent from material *without decon*



Sulfur Mustard



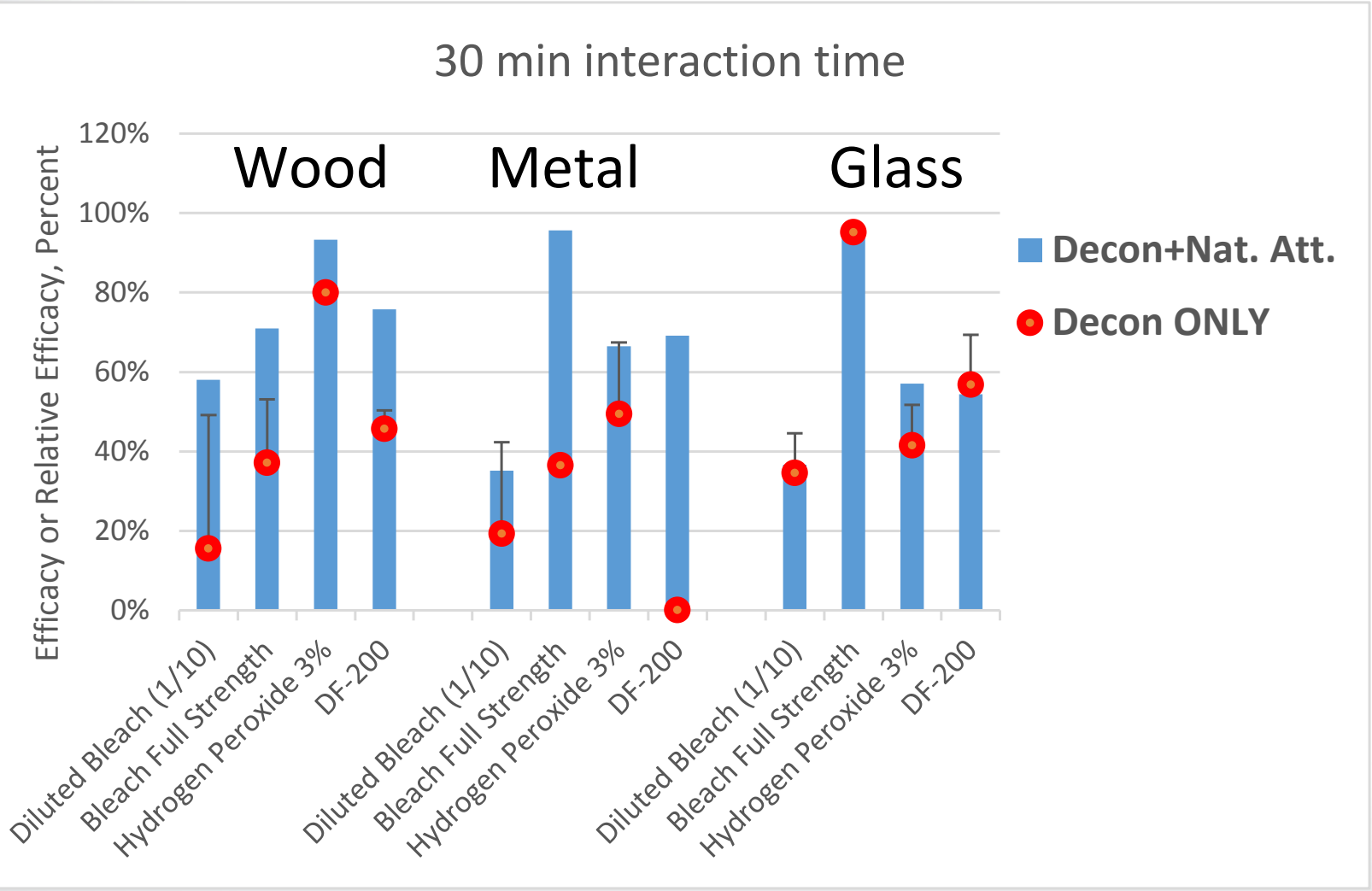
Lewisite

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

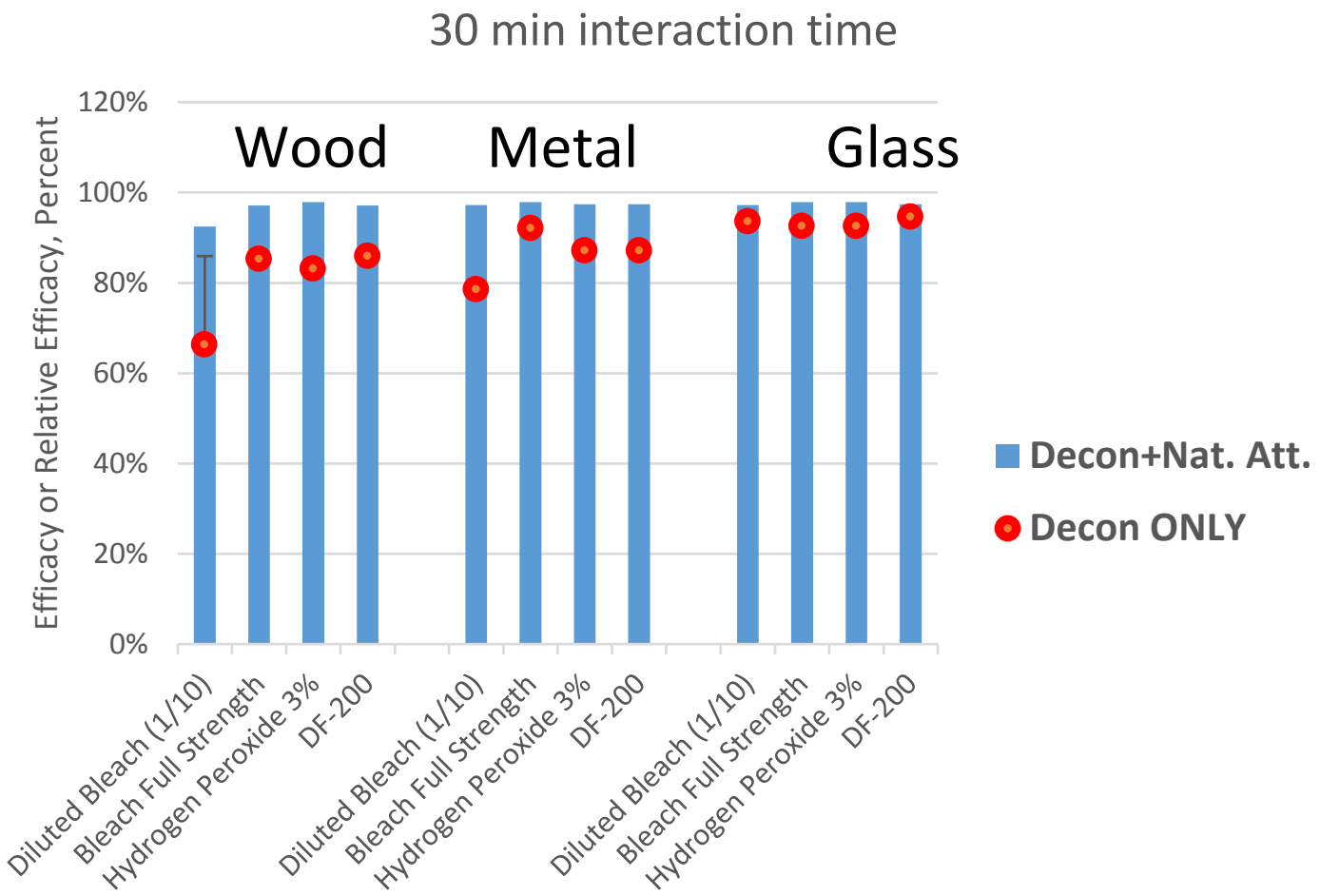
Gap/Need: Effective decontamination methods for porous/permeable materials



- 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

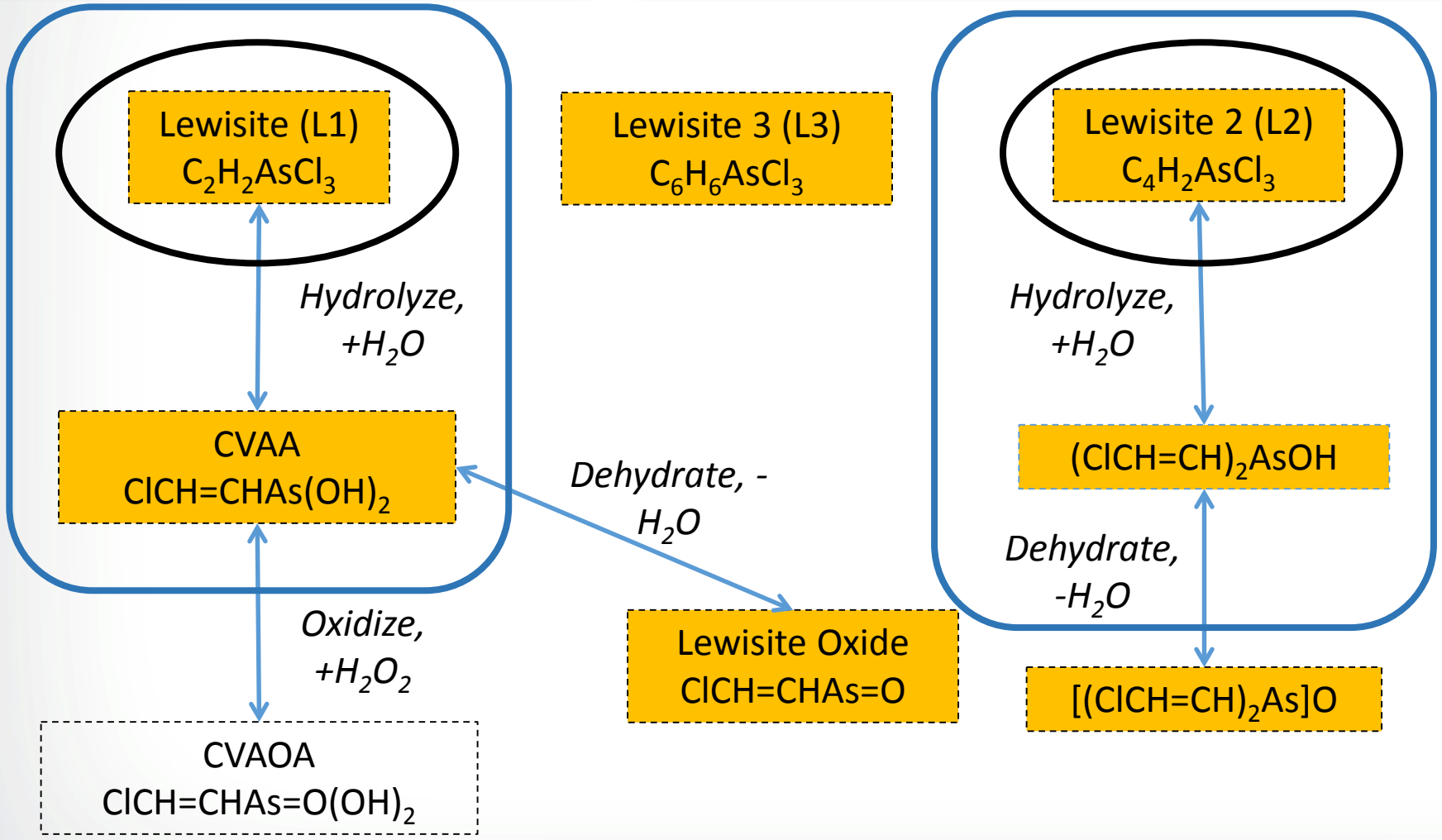
Gap/Need: Effective decontamination methods for porous/permeable materials



- 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



Methods

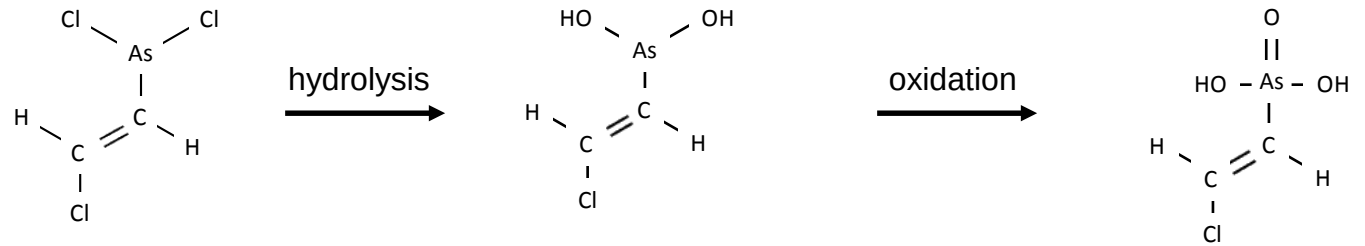
GC/MS (cool on column)

GC/MS (derivatization)

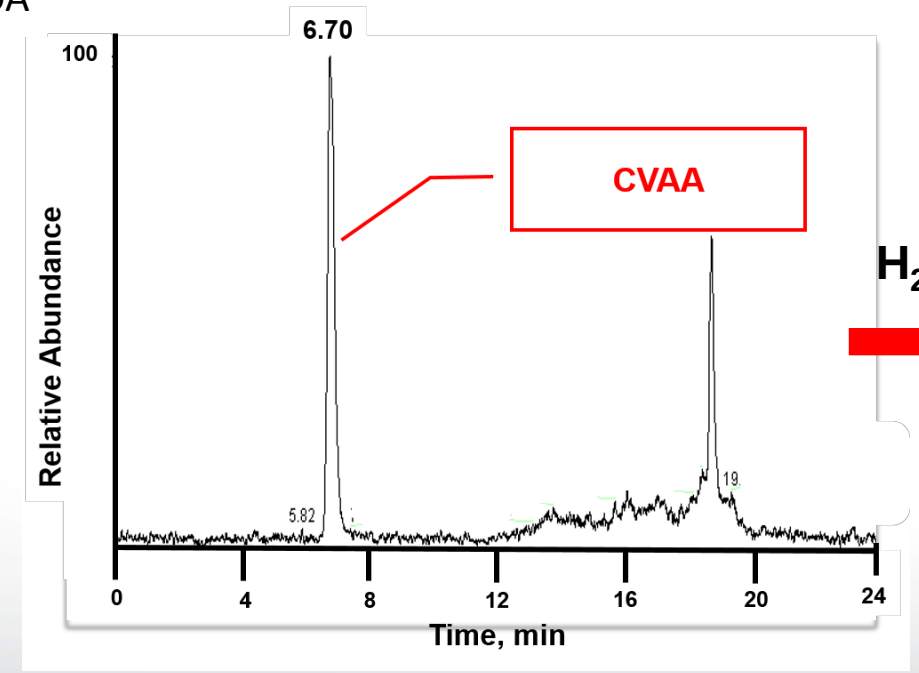
LC-MS/MS Analysis of Lewisite

Lewisite:

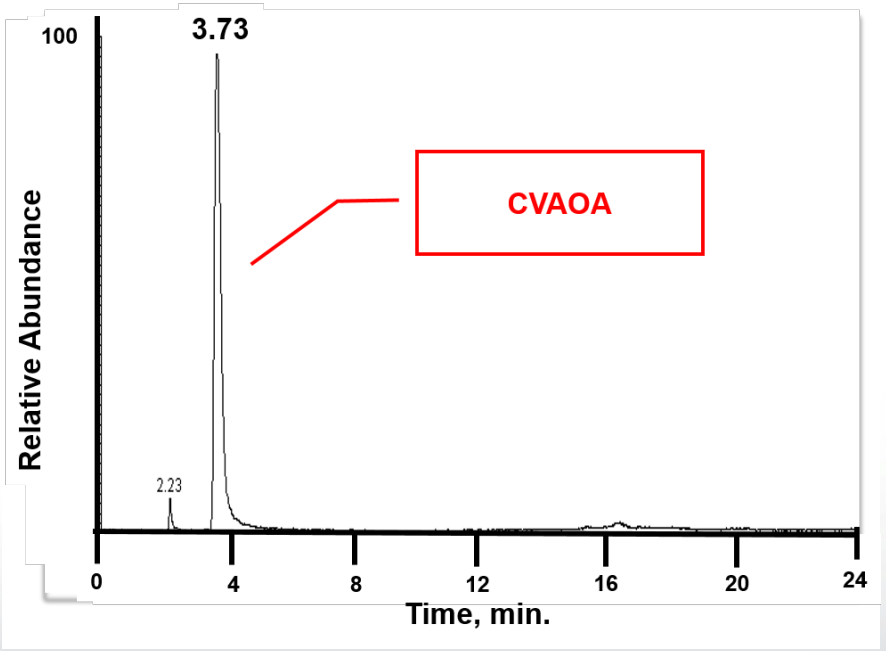
- Organoarsenic compound that is a blister agent and lung irritant
- Doesn't occur naturally in the environment
- CVAA & CVAOA persist



Lewisite I | **Chlorovinyl arsonous acid (CVAA)** | **Chlorovinyl arsonic acid (CVAOA)**

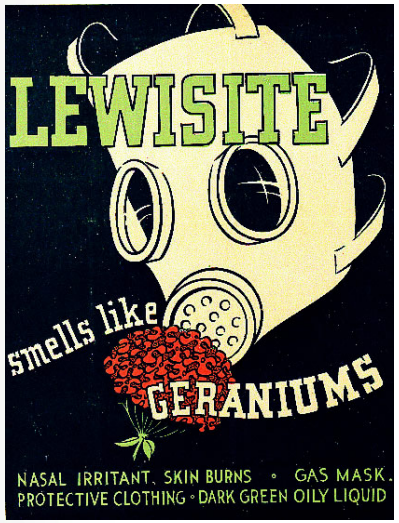


H_2O_2



LC-MS/MS Analysis of Lewisite

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



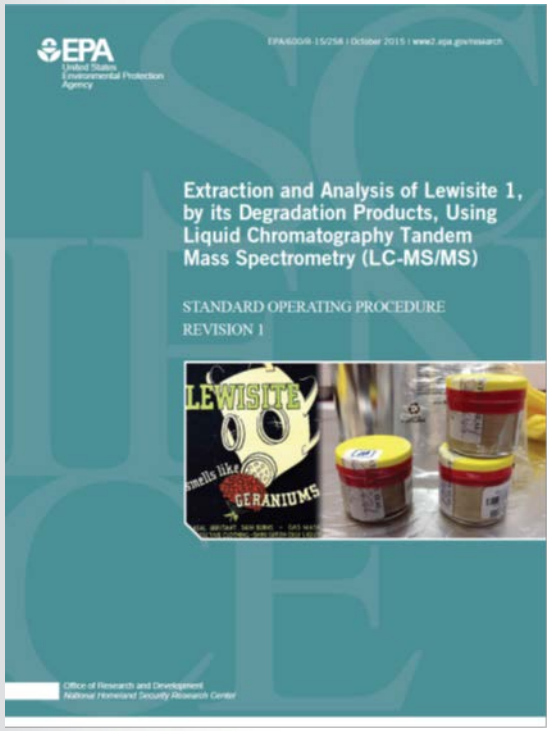
Matrix	Spiked CVAA Concentration	CVAOA Recovery (%)	MDL for CVAOA	ATL[a]
Water	0.20 mg/L	110	0.04 mg/L	0.03 mg/L
Wipe	3.00 µg	101	0.4 µg	-
Sand	0.20 µg/g	85	0.07 µg/g	0.3 µg/g
NB Soil	0.20 µg/g	112	0.03 µg/g	0.3 µg/g
VA Soil	0.40 µg/g	43	0.03 µg/g	0.3 µg/g
GA Soil	0.40 µg/g	80	0.05 µg/g	0.3 µg/g

[a]Analytical Target Level (ATL) values for Lewisite I based on *U.S. Army Public Health Command Chemical Agent Health-Based Standards and Guidelines Summary Table 2: Criteria for Water, Soil, Waste*, 7/2011.

	Water	Wipes	Soil
Extraction	none	Shaker table for 30 min with 10 mM HCl	Shaker table for 30 min with 10.0 mL 50/50 (v/v) 10 mM HCl /methanol
Oxidation	1:1 dilution with 30% H_2O_2	1:1 dilution with 30% H_2O_2	1:1 dilution with 30% H_2O_2

Impact of Method Development

Example: **2014 WLA/ERLN Priority:** Sampling and analysis method for Lewisite and its by-products



EPA/600/R-15/258 | October 2015 | www2.epa.gov/research

- 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

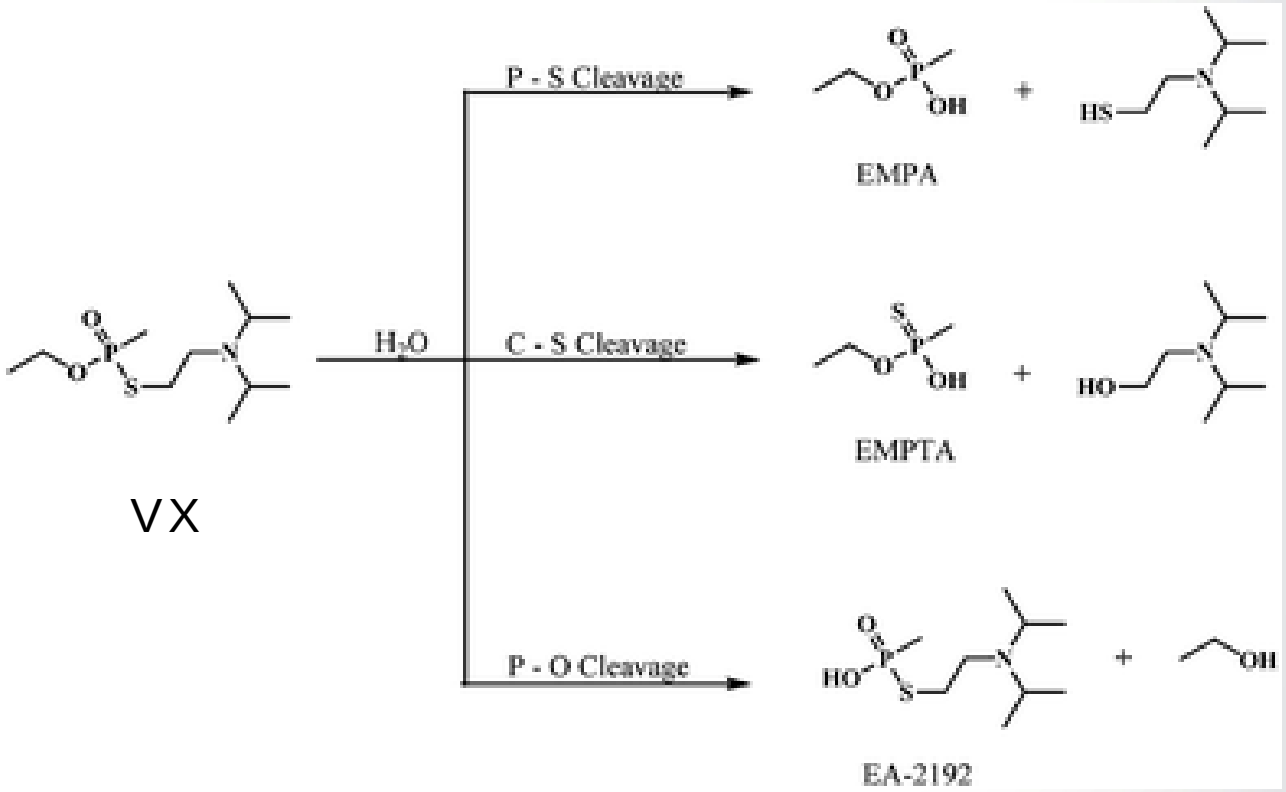
Gap/Need: Identifying priority contaminants for method development and/or evaluation

WLA/ERLN Priority:

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

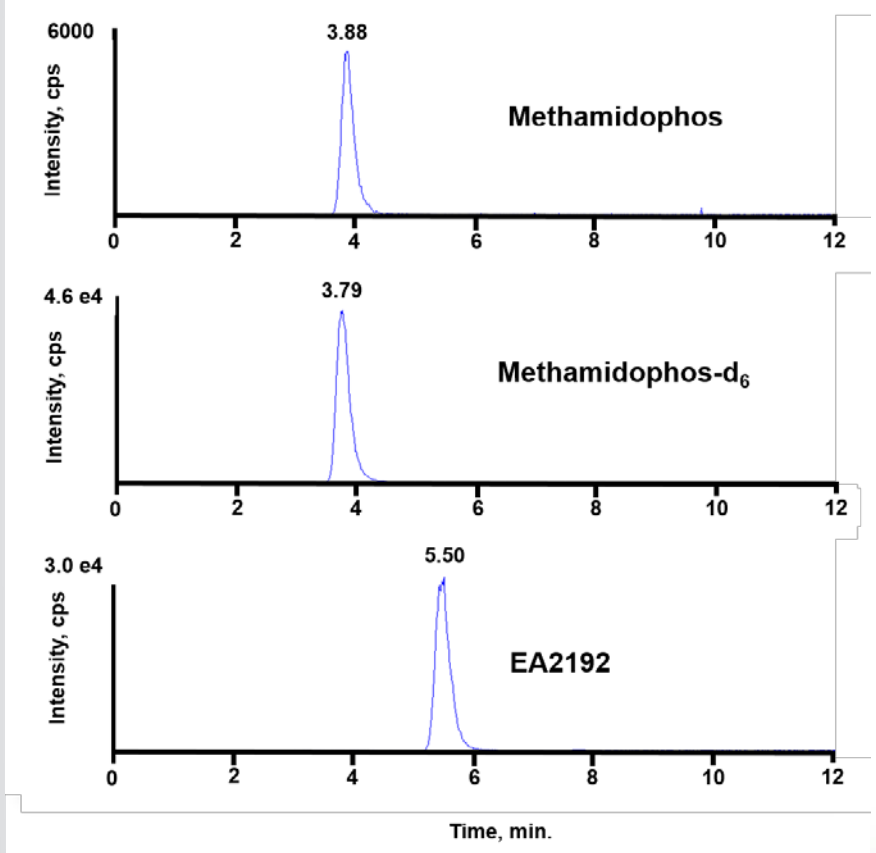
EA-2192:

- **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

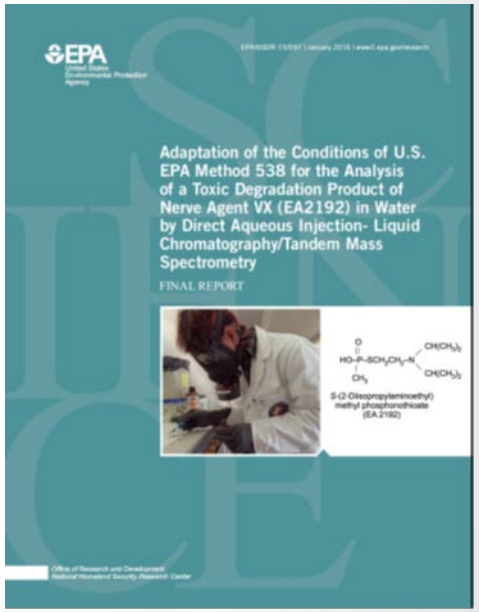


EA2192 Initial Display of Capability	Results
Calibration Curve Accuracy Cal 1 (0.050 µg/L)	96.4 – 105%
Calibration Curve Accuracy Cal 2 -Cal 7 (< 5.00 µg/L)	92.4 – 107%
Laboratory Reagent Blank	ND
Method Detection Limit	0.013 µg/L
Method Reporting Limit	0.125 µg/L
Method Precision at Cal 4 (0.480 µg/L)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

Source #	Water Type	Day 28 % of Day 0
1	In-house Deionized Water	86.7%
2	Low TOC, chlorinated surface water	91.3%
3	High TOC, chloraminated surface water	93.4%
4	Low TOC, chloraminated surface water	99.7%
5	High hardness, chlorinated ground water	112%
6	DI Water +1 mg/L free Cl, no preservatives	ND at day 0

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

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

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**

Summary

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

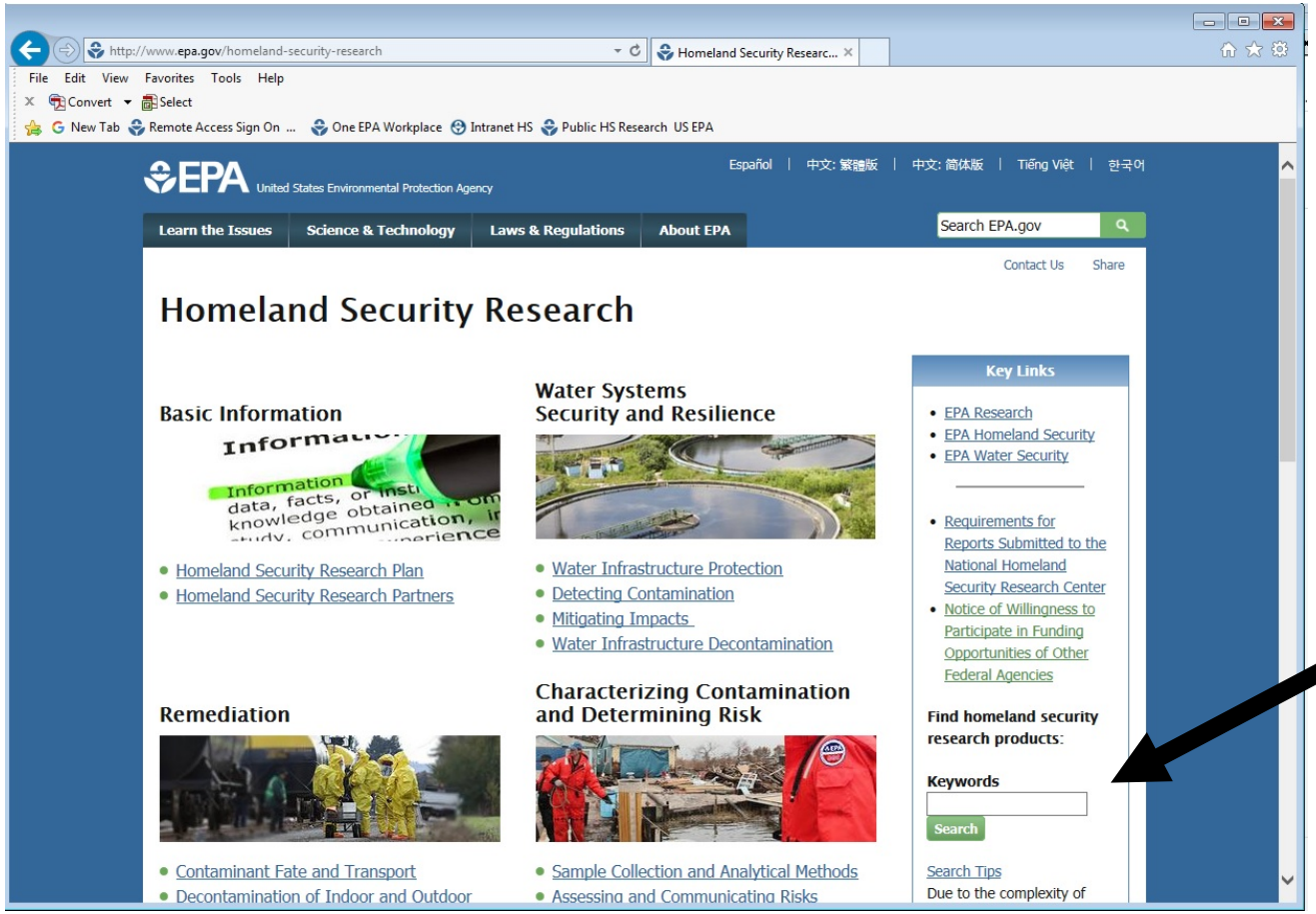
- Lack of information/data on the fate of CWAs in an urban setting and alternative decontamination technologies (e.g., natural attenuation)
  - Research Efforts:
    - Fate and Transport of VX and HD in/through paints/sealants
    - Natural Attenuation of VX on nonporous materials
    - Natural Attenuation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

Summary

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?



Keyword Search: e.g., CWA

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

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

Questions

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ORD's Homeland Security Research Program

ADVANCING OUR NATION'S SECURITY THROUGH SCIENCE

Mission: to conduct research and develop scientific products that improve the capability of the Agency to carry out its homeland security responsibilities