# Decontamination Options for Sensitive Equipment-Related Materials Contaminated with Persistent Chemical Warfare Agents

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# Disclaimer

- The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed this investigation through Contract No. EP-C-15-002 Task Order 0015 with Battelle. This document has been subjected to the Agency's review and has been approved for presentation. Note that approval does not signify that the contents necessarily reflect the views of the Agency. Mention of trade names or commercial products, or services does not constitute EPA approval, endorsement or recommendation for use

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# Background

- U.S. EPA is responsible for planning for, responding to, and recovering from threats to public health, welfare, or the environment caused by hazardous materials incidents.

- EPA ORD's Homeland Security Research Program conducts research focused on CWA decontamination and remediation strategies.

- Either from accidental or intentional release of CWA or as a result of use during response to a CWA incident, sensitive equipment (SE; e.g. computers, night-vision equipment, PDAs, etc.) can become contaminated by CWA.


# Background (cont.)

- SE is often expensive, and procurement is typically associated with long lead times.
- Decontamination and reuse of SE is preferred over disposal.
- Decontamination must be efficacious, but not degrade SE materials or deter SE functionality.



- Many traditional decontaminants (such as bleach) are known to be corrosive.
- Alternative decontaminants have been developed to be more material-compatible, but CWA decontamination efficacy is not as well-characterized.

# *Project Objectives*

- Quantitatively evaluate the efficacy of candidate technologies to decontaminate CWA contamination from the surface of select SE-related materials.

- Qualitatively evaluate compatibility of the decontamination technologies with the SE-related materials.
  - Visual assessment.
  - Deterioration, degradation, or any damage otherwise.
  - Damage to materials from application of CWAs.

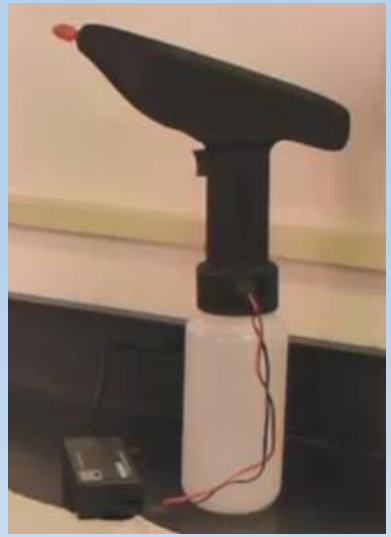
- Limited, semi-quantitative analysis to investigate presence of CWA degradation products following decontamination.

# Decontaminants

- **Dahlgren Decon**
  - First Line Technology
  - Peracetic acid-based
  - Three component system including a surfactant package

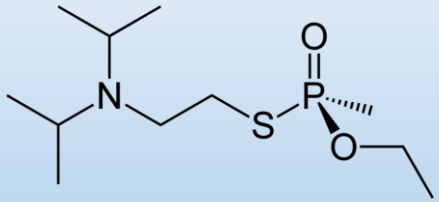

- **EasyDECON DF200**
  - Intelagard
  - Peroxide-based
  - Commercial variant of Sandia National Lab's DF200

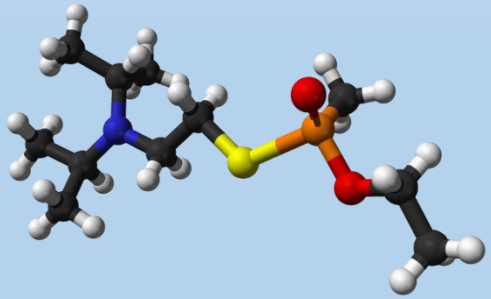

- **Handheld Decontamination Apparatus (HDA)**
  - TDA Research, Inc.
  - Electrochemically-generated aqueous chlorine dioxide ($eClO_2$)



# *Persistent CWAs*

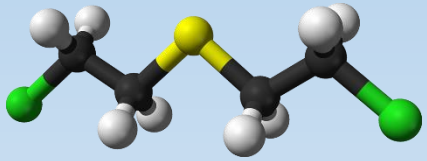
- **VX**
  - *O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate
  - Highly persistent nerve agent
  - Organophosphate acetylcholinesterase inhibitor
  - Estimated lethal dose for skin exposure approx. 3 to 6 mg




**Approximate VX lethal dose volume**

- **HD**
  - Bis(2-chloroethyl) sulfide
  - Powerful vesicant (blister) agent
  - Strongly mutagenic and carcinogenic

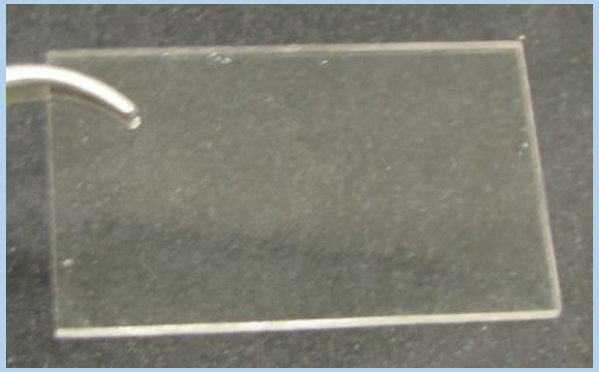



**Blisters caused by exposure to HD**

# Materials

- **ABS molded plastic**
- Electrical enclosures, medical devices, keyboard keycaps
- 4.0 cm length, 2.5 cm width, 6.4 mm thick

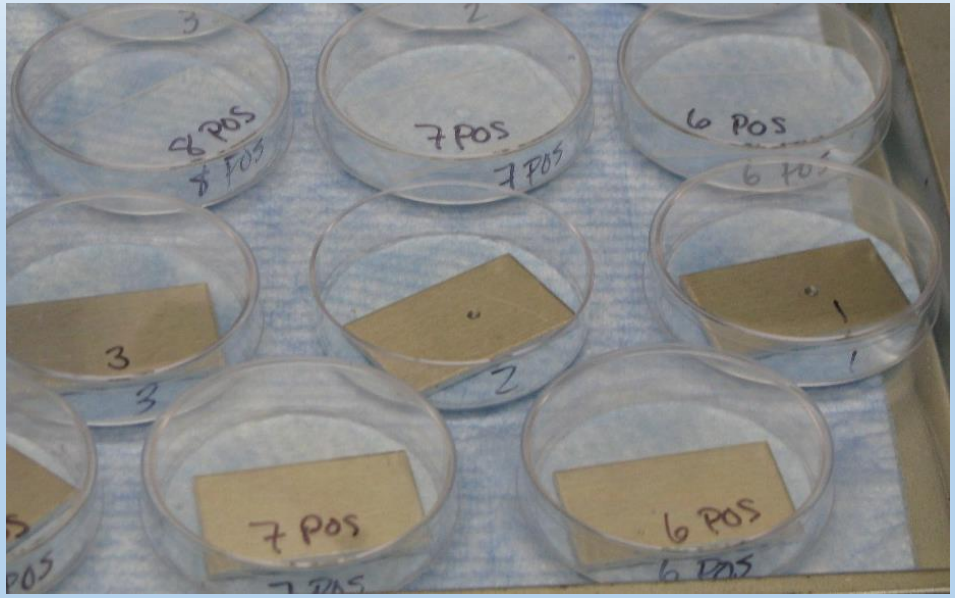
- **Acrylic**
- Semiconductors, dosimeters, LCD displays, optical media such as CDs and DVDs
- 4.0 cm length, 2.5 cm width, 1.6 mm thick

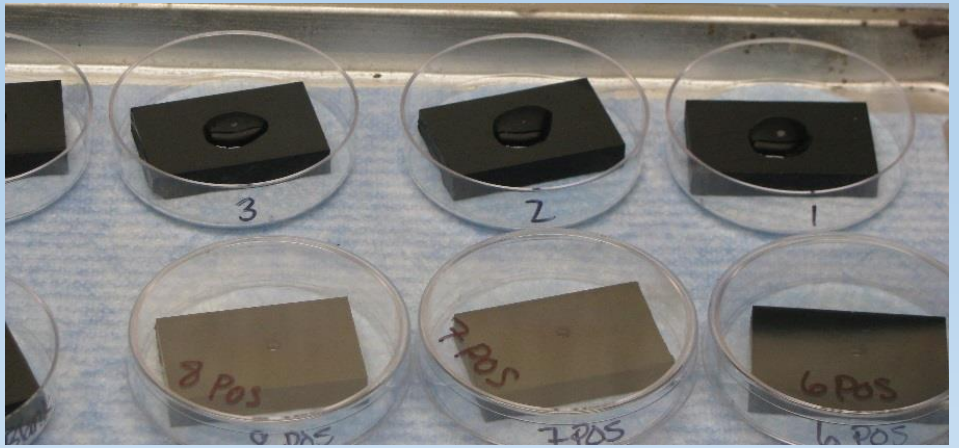



- **Aluminum (6061 alloy)**
- Handheld electronic devices, mobile phones, PC cases
- 4.0 cm length, 2.5 cm width, 2 mm thick

# Experimental Approach

- Bench scale studies to evaluate efficacy of the decontaminants on the surface of material coupons
  1. Coupons were spiked with 2 µL of VX or HD (single 2 µL droplet in center)
     - Nominal 200 µg/cm$^2$ VX
     - Nominal 250 µg/cm$^2$ HD
  2. CWA allowed to weather on coupon surface for 60 minutes (loosely covered)
  3. Following CWA contact period, 100 µL of one of the test decontaminants was applied over the CWA droplet
  4. Decontaminants allowed to react with CWA on the coupon surface for 60 minutes (uncovered)

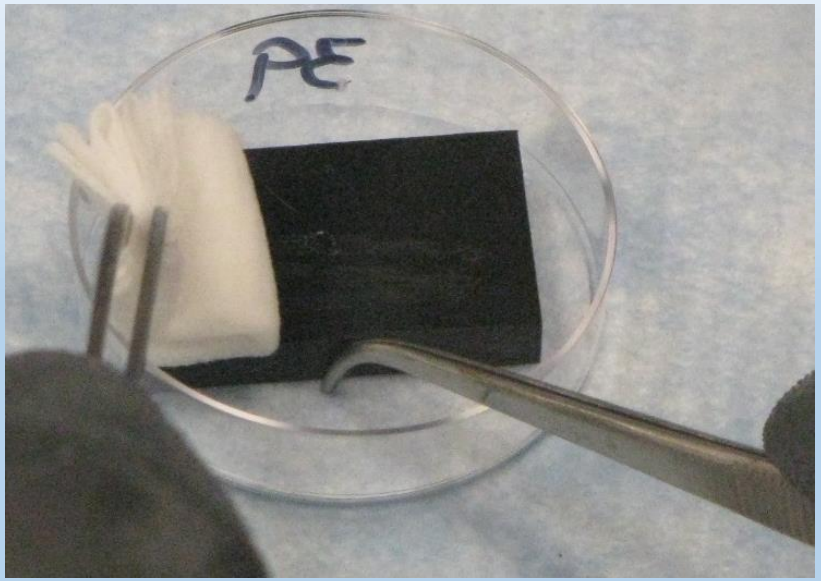


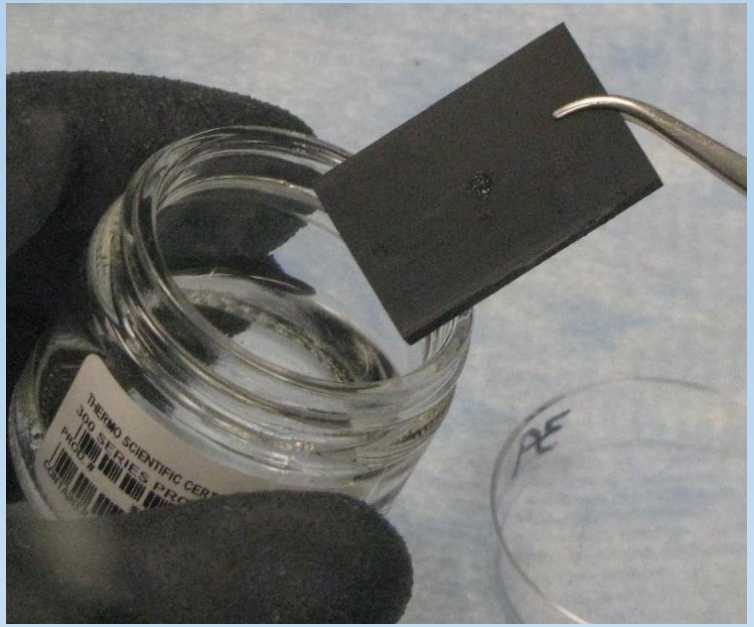



# Experimental Approach

- Following the decontamination period, residual CWA on the coupon surface was sampled via wiping with subsequent coupon extraction (residual decontaminant was quenched)

- Extracts were analyzed via GC/MS to quantify residual VX or HD and qualitatively identify byproducts





# Decontamination Test Matrix

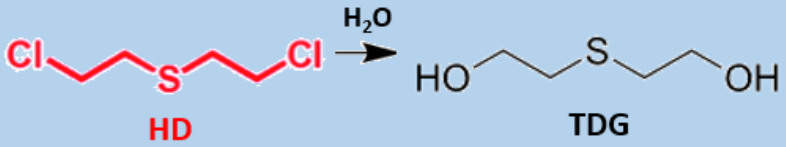
| Test | Sample Type | Material | Decontamination Technology | Replicates |
|---|---|---|---|---|
| 1 | Test Sample | ABS Molded Plastic | EasyDECON DF200 | 5 |
| | Positive Control | ABS Molded Plastic | None | 3 |
| 2 | Test Sample | Acrylic | EasyDECON DF200 | 5 |
| | Positive Control | Acrylic | None | 3 |
| 3 | Test Sample | Aluminum | EasyDECON DF200 | 5 |
| | Positive Control | Aluminum | None | 3 |
| 4 | Test Sample | ABS Molded Plastic | Dahlgren Decon | 5 |
| | Positive Control | ABS Molded Plastic | None | 3 |
| 5 | Test Sample | Acrylic | Dahlgren Decon | 5 |
| | Positive Control | Acrylic | None | 3 |
| 6 | Test Sample | Aluminum | Dahlgren Decon | 5 |
| | Positive Control | Aluminum | None | 3 |
| 7 | Test Sample | ABS Molded Plastic | $eClO_2$ | 5 |
| | Positive Control | ABS Molded Plastic | None | 3 |
| 8 | Test Sample | Acrylic | $eClO_2$ | 5 |
| | Positive Control | Acrylic | None | 3 |
| 9 | Test Sample | Aluminum | $eClO_2$ | 5 |
| | Positive Control | Aluminum | None | 3 |

- Matrix was completed twice
  - VX as the challenge CWA
  - HD as the challenge CWA
- Environmental conditions (laboratory temperature and RH) were monitored and recorded, but not controlled
- QA controls included during every test

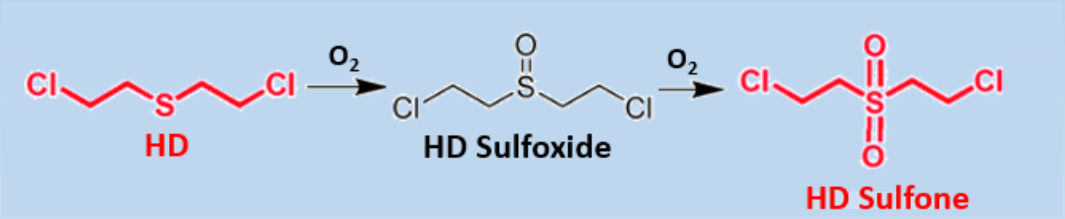
# GC/MS Analysis Methods and Degradation Product Analysis

- **HD degradation product analysis:**
  - Thiodiglycol (TDG)
  - Mustard Sulfone (HD Sulfone)

- HD degradation routes (highly toxic compounds in red)
  - Hydrolysis

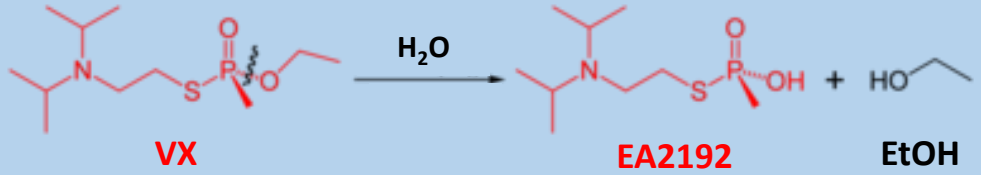



  - Oxidation

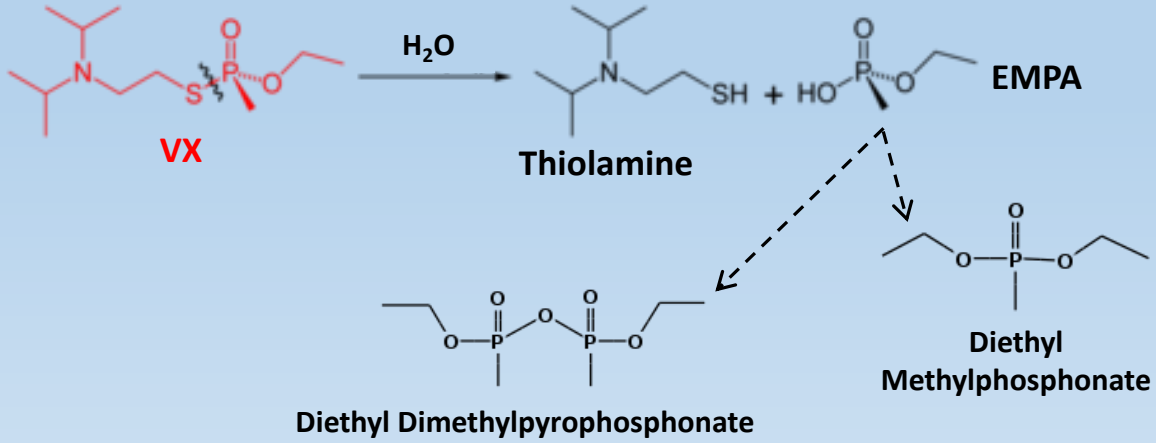



- **VX degradation product analysis:**
  - EA2192 not amenable to analysis by the GC/MS method that was used (requires alternative methods or LC-MS/MS analysis)
  - EMPA byproducts were detectable, and thus used to semi-quantitatively indicate the presence of VX byproducts

- VX hydrolysis routes (highly toxic compounds in red):
  - Cleavage at P-O bond



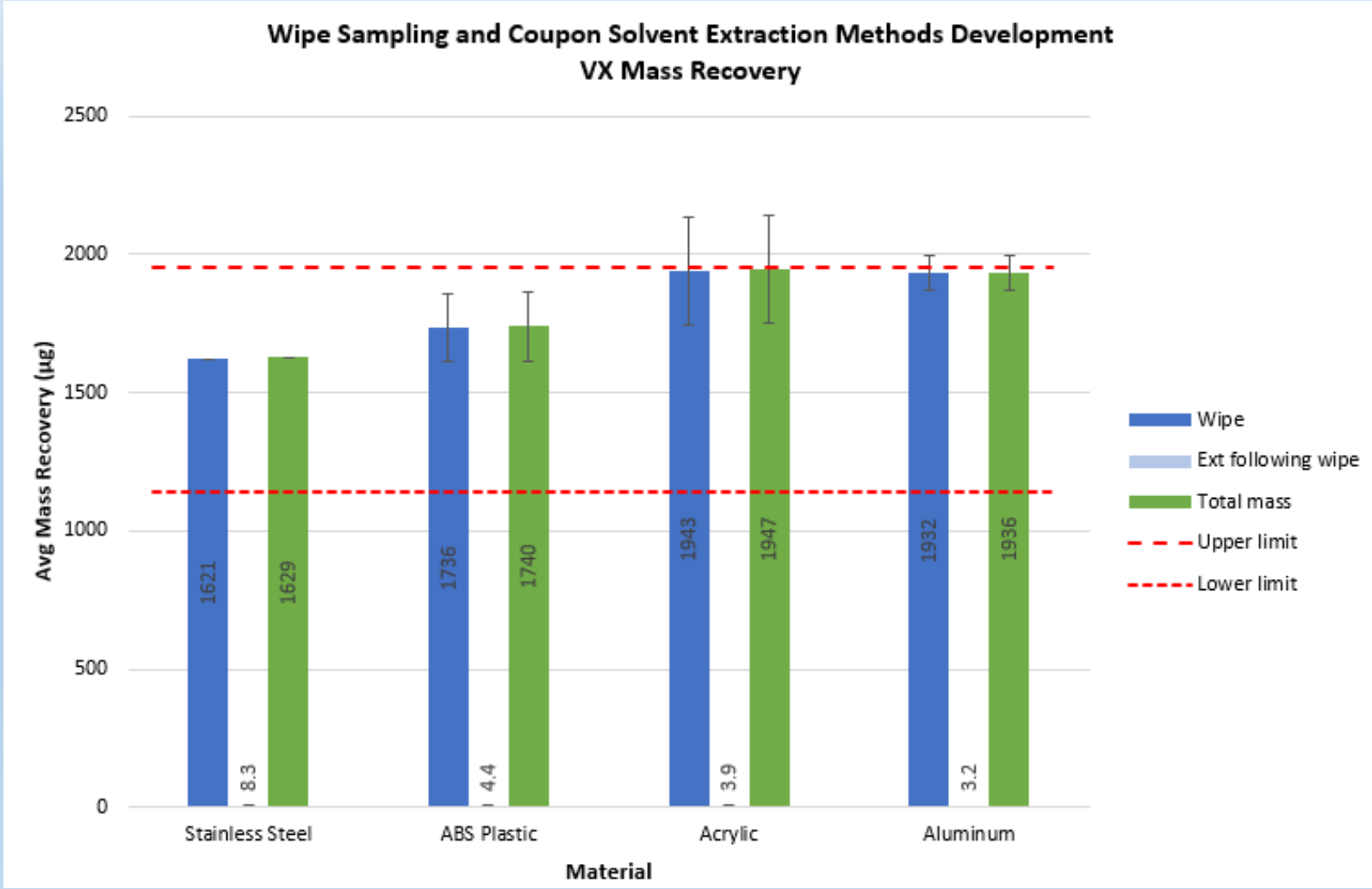

  - Cleavage at P-S bond (dominating)



# Methods Development Results
## VX Wipe Sampling and Coupon Solvent Extraction

- Following VX contact period, coupons were sampled via wiping and then subsequently extracted in solvent
- Stainless steel included as an inert control material
- Hexane was demonstrated as the wipe wetting and wipe and coupon extraction solvent
- Nearly all VX recovered in the wipe samples of all three material types

| Material | Avg Percent Recovery |
|---|---|
| ABS Plastic | 107% |
| Acrylic | 120% |
| Aluminum | 119% |

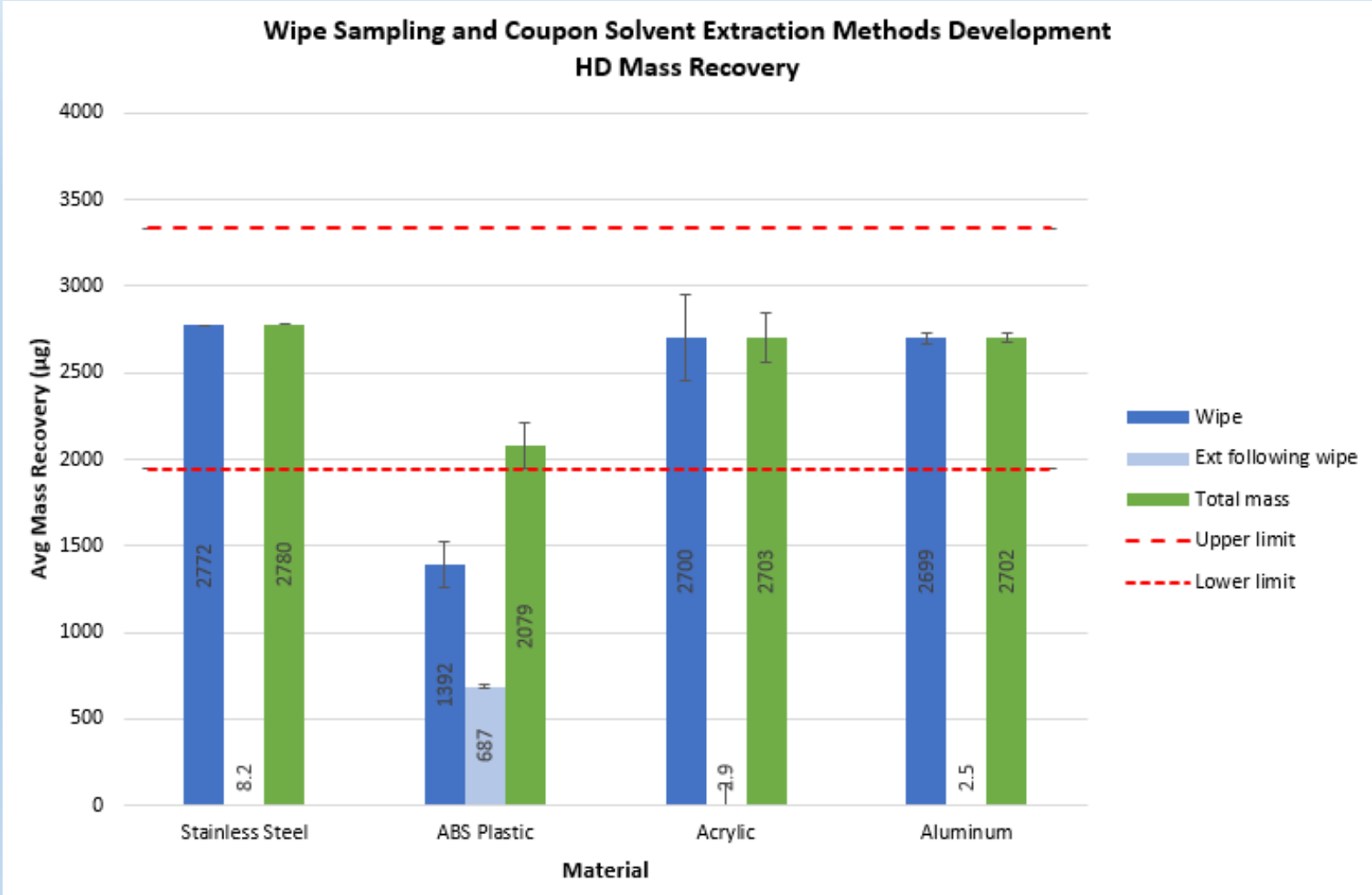



- **Error bars equal ± one standard deviation**
- **Upper limit equals 120% of mean total mass recovery from stainless steel**
- **Lower limit equals 70% of mean total mass recovery from stainless steel**

# Methods Development Results
## HD Wipe Sampling and Coupon Solvent Extraction

- Following HD contact period, coupons were sampled via wiping and then subsequently extracted in solvent
- Stainless steel included as an inert control material
- Hexane was demonstrated as the wipe wetting and wipe and coupon extraction solvent
- Nearly all HD recovered in the wipe samples of ABS and aluminum
- HD demonstrated absorption into ABS plastic

| Material | Avg Percent Recovery |
|---|---|
| ABS Plastic | 75% |
| Acrylic | 97% |
| Aluminum | 97% |




- **Error bars equal ± one standard deviation**
- **Upper limit equals 120% of mean total mass recovery from stainless steel**
- **Lower limit equals 70% of mean total mass recovery from stainless steel**

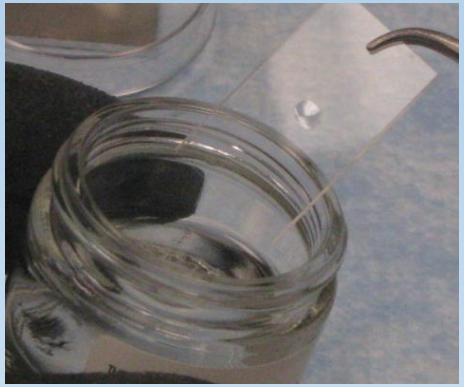
# Methods Development Results
## Decontaminant Quench Methods

**Quench by Solvent Extraction Alone**

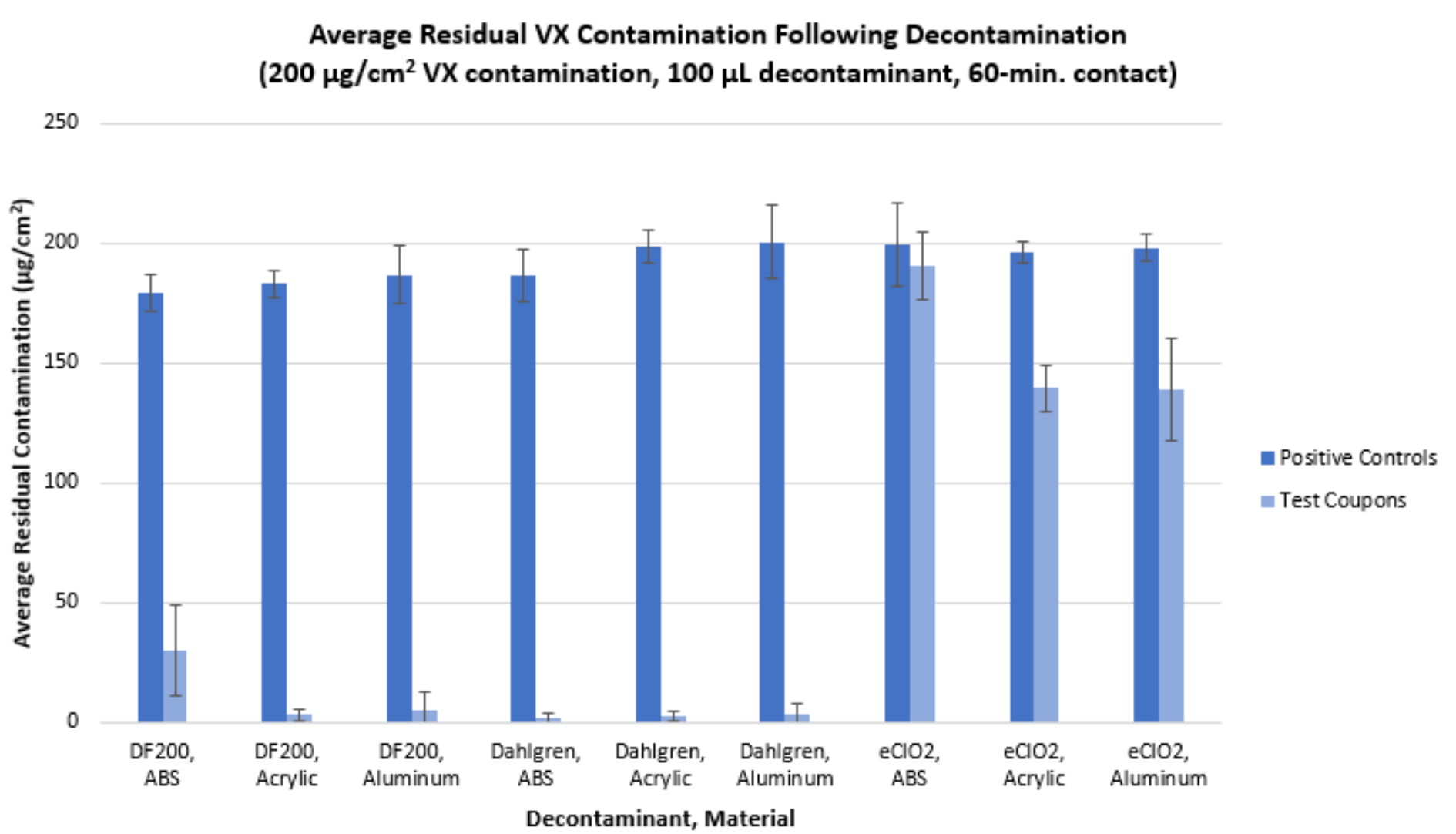
- Decontaminated aluminum wipe and coupon extracts (containing residual decontaminant)
- Post-spiked with dilute solution of VX or HD in hexane (approx. 5 µg/mL)
- Extracts analyzed immediately, and then again after 3 days in storage at -20°C
- **e$ClO_2$ decontamination of HD and VX** and **DF200 decontamination of HD** were quenched by extraction in hexane alone
- Decontamination of post-spiked VX by Dahlgren Decon and DF200 and of post-spiked HD by Dahlgren Decon still occurred

**Quench using 3M Sodium Thiosulfate**

- Second test evaluated use of 3M sodium thiosulfate (STS) as a quench method
- Same procedure as that used during first test, but 3M STS included with solvent used to extract wipes/coupons
- Addition of 3M STS quench appeared to prevent decontamination of post-spiked **VX and HD by Dahlgren Decon** as well as post-spiked **VX by DF200**

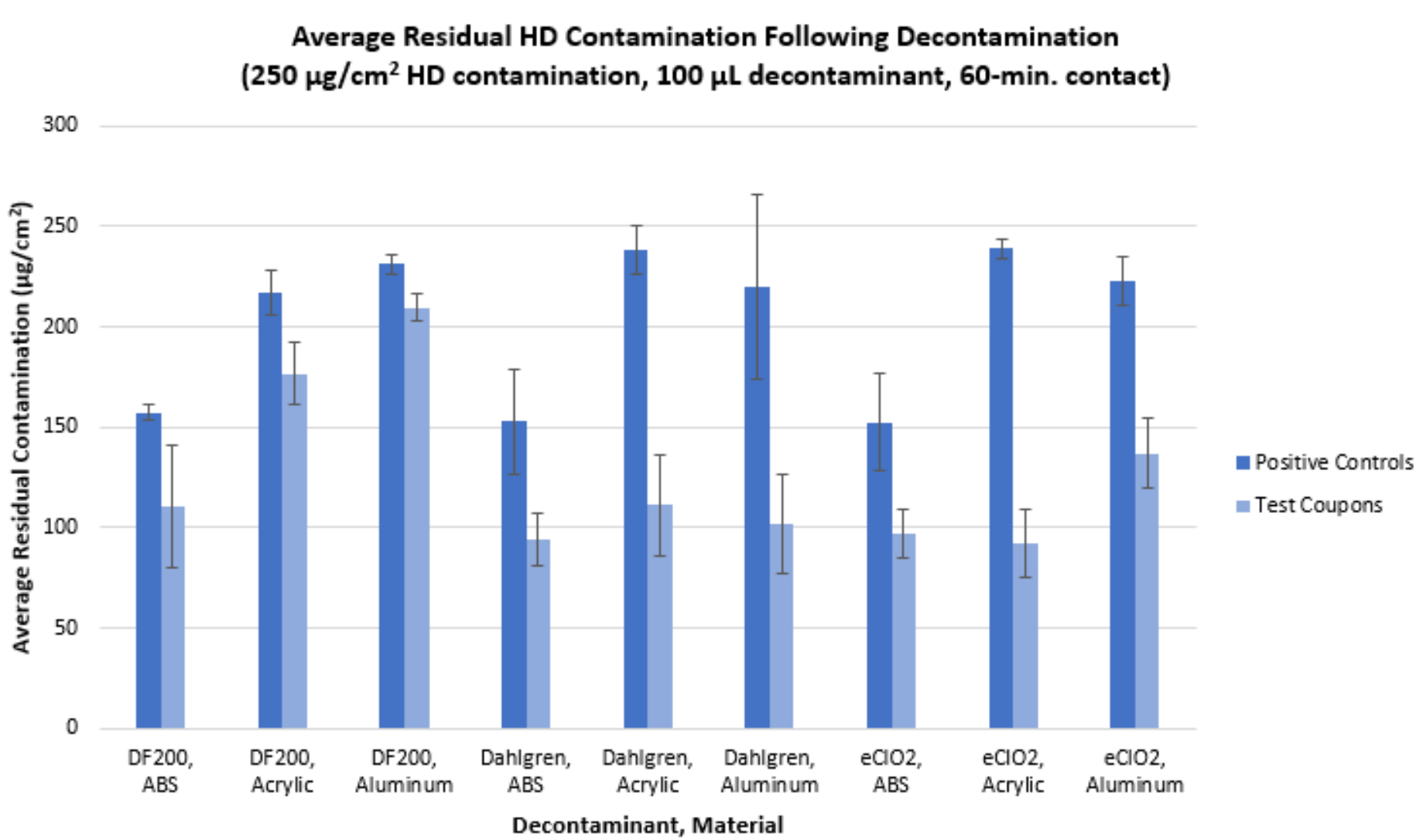


# Decontamination Efficacy Results
## Average Residual VX Contamination




- Error bars equal ± one standard deviation
- n = 3

# Decontamination Efficacy Results
## Average Residual HD Contamination




- Error bars equal ± one standard deviation
- n = 3

# Decontamination Efficacy Results

## Average Percent Decontamination Efficacy

| | Material | EasyDECON DF200 | Dahlgren Decon | TDA $eClO_2$ |
|---|---|---|---|---|
| Average VX Decontamination Efficacy (%) | ABS Plastic | 83% | **99%** | 4.4% |
| | Acrylic | 98% | **99%** | 29% |
| | Aluminum | 97% | **98%** | 30% |
| Average HD Decontamination Efficacy (%) | ABS Plastic | 29% | **38%** | 37% |
| | Acrylic | 19% | 53% | **61%** |
| | Aluminum | 9.4% | **54%** | 39% |

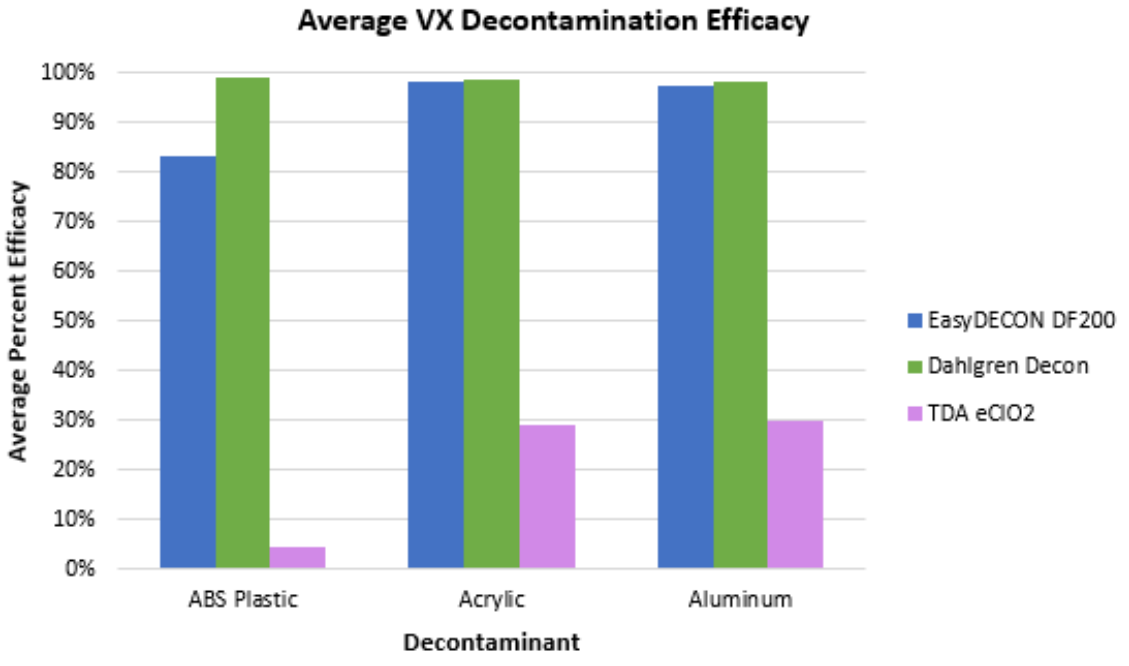
**BOLD:** Highest measured average decontamination percent efficacy for CWA/material combination

- For the decontaminant:CWA ratio (50:1, by volume) and decontaminant contact time (60 minutes) evaluated during this work, the highest average VX decontamination efficacy on all three SE-related material types was obtained using Dahlgren Decon and EasyDECON DF200 (Dahlgren Decon for ABS plastic)
- Highest average HD decontamination efficacy from ABS plastic and aluminum was also obtained using Dahlgren Decon
- Highest average HD decontamination efficacy from acrylic was obtained using TDA's $eClO_2$ decontaminant

# Decontamination Efficacy Results

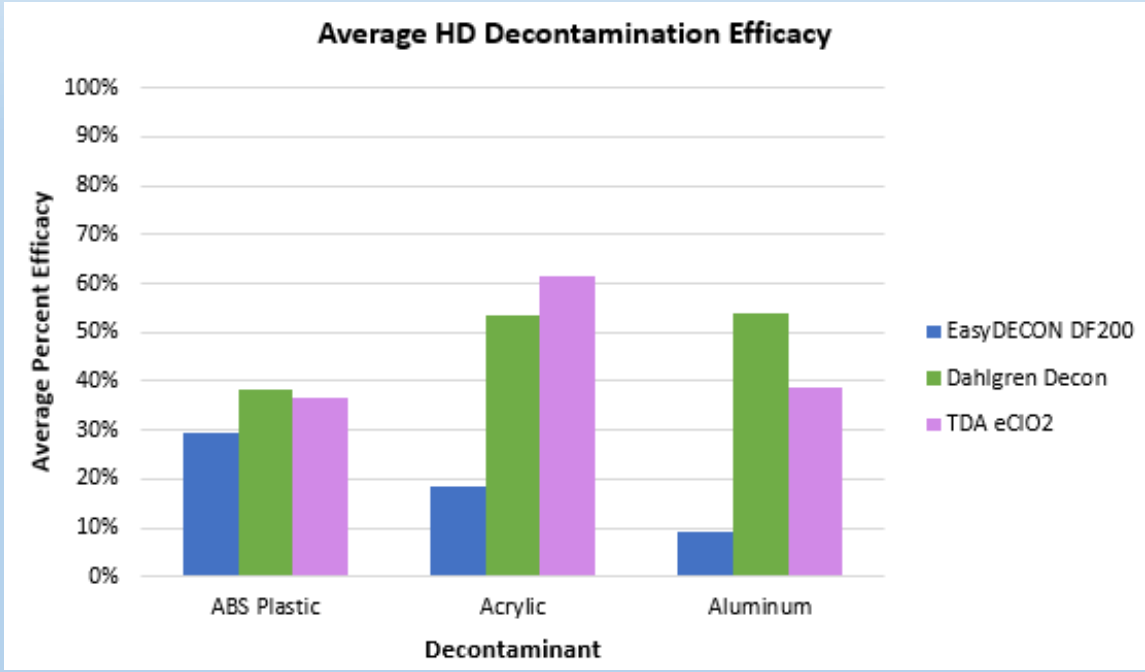
## Average Percent Decontamination Efficacy and Statistical Analyses Results [A]

### Average Percent VX Decontamination Efficacy




- Dahlgren Decon demonstrated statistically significant VX decontamination on ABS plastic compared to DF200 and $eClO_2$
- Dahlgren Decon and DF200 demonstrated statistically significant VX decontamination compared to $eClO_2$ on acrylic
- Dahlgren Decon and DF200 demonstrated statistically significant VX decontamination compared to $eClO_2$ on aluminum

### Average Percent HD Decontamination Efficacy




- No significant statistical differences between decontaminants for HD decontamination efficacy from ABS plastic
- No significant statistical differences between decontaminants for HD decontamination efficacy from acrylic
- Difference between Dahlgren Decon and DF200 for HD decontamination efficacy from aluminum was statistically significant (no significant statistical differences between $eClO_2$ and DF200 or between Dahlgren Decon and $eClO_2$)

[A] **Tukey-adjusted pairwise comparisons of geometric means of ANOVA models**

# Decontamination Efficacy Results
## Degradation Product Analysis Results

VX:

- Neither EMPA-associated VX degradant was detected in any sample

HD:

- No TDG detected in any sample

- Mustard sulfone was detected in 4 of 5 extracts of wipe samples taken from aluminum coupons decontaminated using Dahlgren Decon

- Mustard sulfone detected in extracts of wipe samples taken from all coupons of all three material types decontaminated with $eClO_2$

- Mustard sulfone also detected in extracts of ABS plastic and acrylic coupons decontaminated with $eClO_2$

# Decontaminant/Material Compatibility

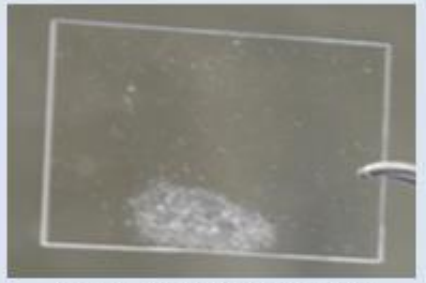
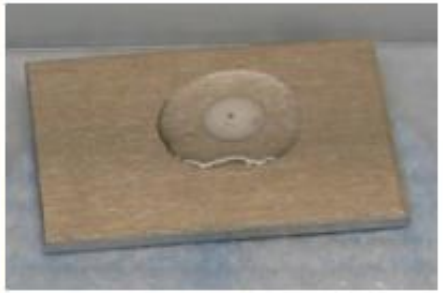
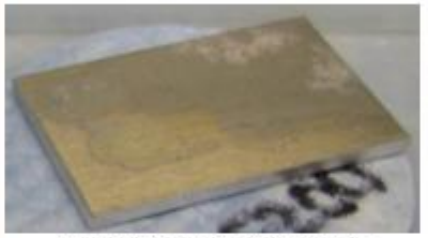
- **Dahlgren Decon**
  - Generally, appeared to demonstrate the highest degree of compatibility with the three SE-related materials
  - Liquid decontaminant still remaining after 1 week; no residue; remaining decontaminant was easily removed
  - Acrylic unaffected
  - Slightly discolored ABS plastic
  - Slightly discolored aluminum
- **DF200**
  - Crystallized residue left after 1 week; easily removed from ABS and acrylic; difficult to remove from aluminum
  - Acrylic unaffected
  - Discolored ABS plastic
  - Discolored aluminum
- **$eClO_2$**
  - White residue left after 1 week; easily removed from ABS and acrylic; difficult to remove from aluminum
  - Acrylic unaffected
  - Slightly discolored ABS plastic
  - Damaged the surface of aluminum coupons (left surface rough/pitted)

- ABS plastic appeared to be most damaged by application of HD rather than by application of any of the three decontaminants (left)
- Plastic debris was removed during wipe sampling where HD contamination was placed (right)

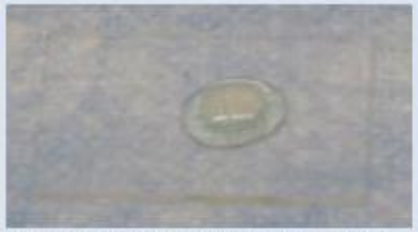
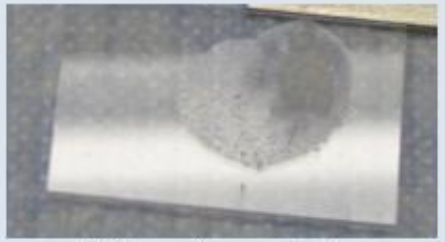
# Decontaminant/Material Compatibility
## Dahlgren Decon

| Material | Following Application | After 1 Day | After 1 Week | Following Wiping/Removal |
|---|---|---|---|---|
| ABS Plastic |  Decontaminant pooled on coupon. |  Decontaminant still appeared wet. |  Decontaminant still wet, but appeared thicker/tacky when wiped. |  Decontaminant easily removed with hexane-soaked wipe. **Very slight discoloration where decon dwelled.** |
| Acrylic |  Decontaminant pooled on coupon. |  Decontaminant still appeared wet |  Decontaminant still wet, but appeared thicker/tacky when wiped. |  Decontaminant easily removed with hexane-soaked wipe. **No deterioration of material observed.** |
| Aluminum |  Decontaminant pooled on coupon. |  Decontaminant still appeared wet. |  Decontaminant still wet, but appeared thicker/tacky when wiped. |  Decontaminant easily removed with hexane wipe. **Very slight discoloration where decon dwelled.** |

# Decontaminant/Material Compatibility
## DF200

| Material | Following Application | After 1 Day | After 1 Week | Following Wiping/Removal |
|---|---|---|---|---|
| ABS Plastic |  Decontaminant pooled on coupon. |  Decontaminant appeared slightly wet/crystallized. |  Crystallized/crusty residue remaining. |  Residue easily removed with hexane-soaked wipe. **Discoloration where decontaminant dwelled.** |
| Acrylic |  Decontaminant pooled on coupon. |  Decontaminant spread and appeared slightly wet/crystallized. |  Crystallized/crusty residue remaining. |  Residue easily removed with hexane-soaked wipe. **No deterioration of material observed.** |
| Aluminum |  Decontaminant pooled on coupon. |  Decontaminant spread and appeared dry/crystallized. |  Crystallized/crusty residue remaining. |  Residue not easily removed with either hexane-soaked or water-soaked wipe. **Discoloration/white residue present where decontaminant dwelled.** |

# Decontaminant/Material Compatibility
## TDA $eClO_2$

| Material | Following Application | After 1 Day | After 1 Week | Following Wiping/Removal |
|---|---|---|---|---|
| ABS Plastic |  Decontaminant pooled on coupon. |  Decontaminant still appeared wet. |  White residue remaining. |  Residue easily removed with hexane-soaked wipe. **Very slight discoloration where decontaminant dwelled.** |
| Acrylic |  Decontaminant pooled on coupon. |  Decontaminant still appeared wet. |  White residue remaining. |  Residue easily removed with hexane-soaked wipe. **No deterioration of material observed.** |
| Aluminum |  Decontaminant pooled on coupon. |  Decontaminant appeared slightly wet/crystallized. |  White residue remaining. |  Residue not easily removed with either hexane-soaked or water-soaked wipe. **Discoloration/possible pitting present where decontaminant dwelled.** |

# Summary

## Decontamination Efficacy

- For five of the six CWA/SE-related material combinations evaluated, Dahlgren Decon demonstrated the highest average percent decontamination efficacy
  - Decontamination of VX on ABS plastic, acrylic, and aluminum
  - Decontamination of HD on ABS plastic and aluminum
- TDA's $eClO_2$ decontaminant demonstrated the highest efficacy for the remaining CWA/material combination (HD/acrylic)

**Highest Average Percent Decontamination Efficacy by CWA/Material [A]**

| | ABS Plastic | Acrylic | Aluminum |
|---|---|---|---|
| VX | Dahlgren Decon (99%) | Dahlgren Decon (99%) | Dahlgren Decon (98%) |
| HD | Dahlgren Decon (38%) | TDA $eClO_2$ (61%) | Dahlgren Decon (54%) |

[A] May not be statistically different from other decontaminants

## Material Compatibility

- Dahlgren Decon
  - Demonstrated greatest degree of compatibility with the three SE-related materials
- DF200
  - Demonstrated compatibility with acrylic, but discolored ABS plastic and aluminum
  - Left residue on the surface of coupons (difficult to remove from aluminum)
- $eClO_2$
  - Compatible with acrylic, but discolored ABS plastic and damaged the surface of aluminum
  - Left residue on the surface of coupons (difficult to remove from aluminum)
- ABS was significantly damaged by HD

# *Further Study…*

- Expand degradation product analysis capabilities; include LC-MS/MS analysis of extracts to investigate presence of EA2192 and EMPA directly
- Decontamination efficacy tests using actual SE (system-level decontamination efficacy tests)
  - Subsequent compatibility tests can include full functionality tests
  - ASTM tests for material compatibility (originally intended for this work but limited by funding)
- CWA vapor contamination
- Evaluation of alternative decontaminants
  - Hot air decontamination
  - Fumigants/volumetric decontaminants
  - Plasma
- Extended contact hazard tests (prolonged contact) or repeated contact hazard tests (multiple repeated wipe samples of the same area – cumulative transferred hazard) following decontamination
- Vapor offgas testing following decontamination

# *Questions?*