Analysis of Matrix-Specific Environmental Samples for CWA Degradation Products

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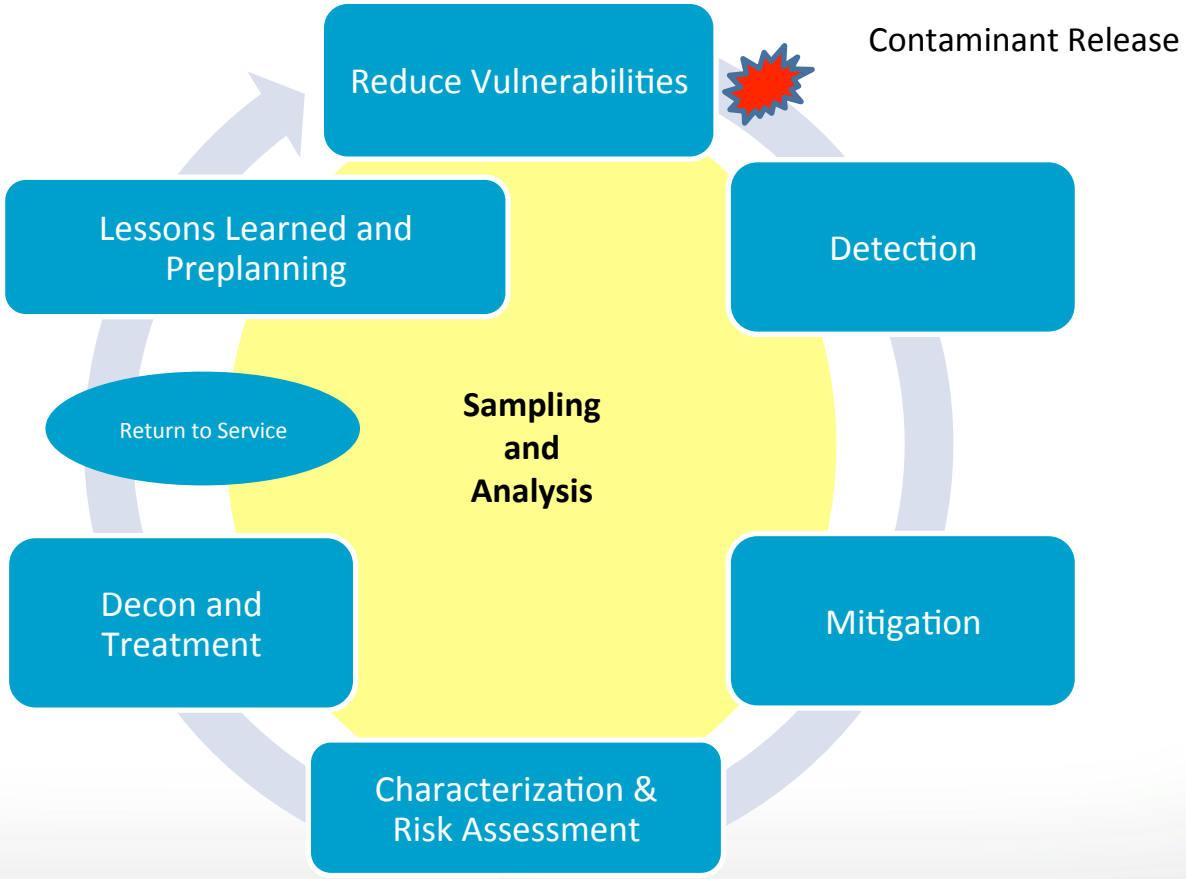
EPA Response to Contamination Events

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 and 2012)
- Syrian civil war CWA chemical attacks (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)

What do these responses have in common?



EPA Homeland Security Drivers and Responsibilities

Drivers

Bioterrorism Act (2002)

Homeland Security Presidential Directives (2003-2008)

National Response Framework (revised 2008)

Elements of:

- Comprehensive Environmental Response, Compensation and Liability Act
- Emergency Planning and Community Right-to-Know Act
- Clean Water Act
- Safe Drinking Water Act
- Oil Pollution Act
- Clean Air Act

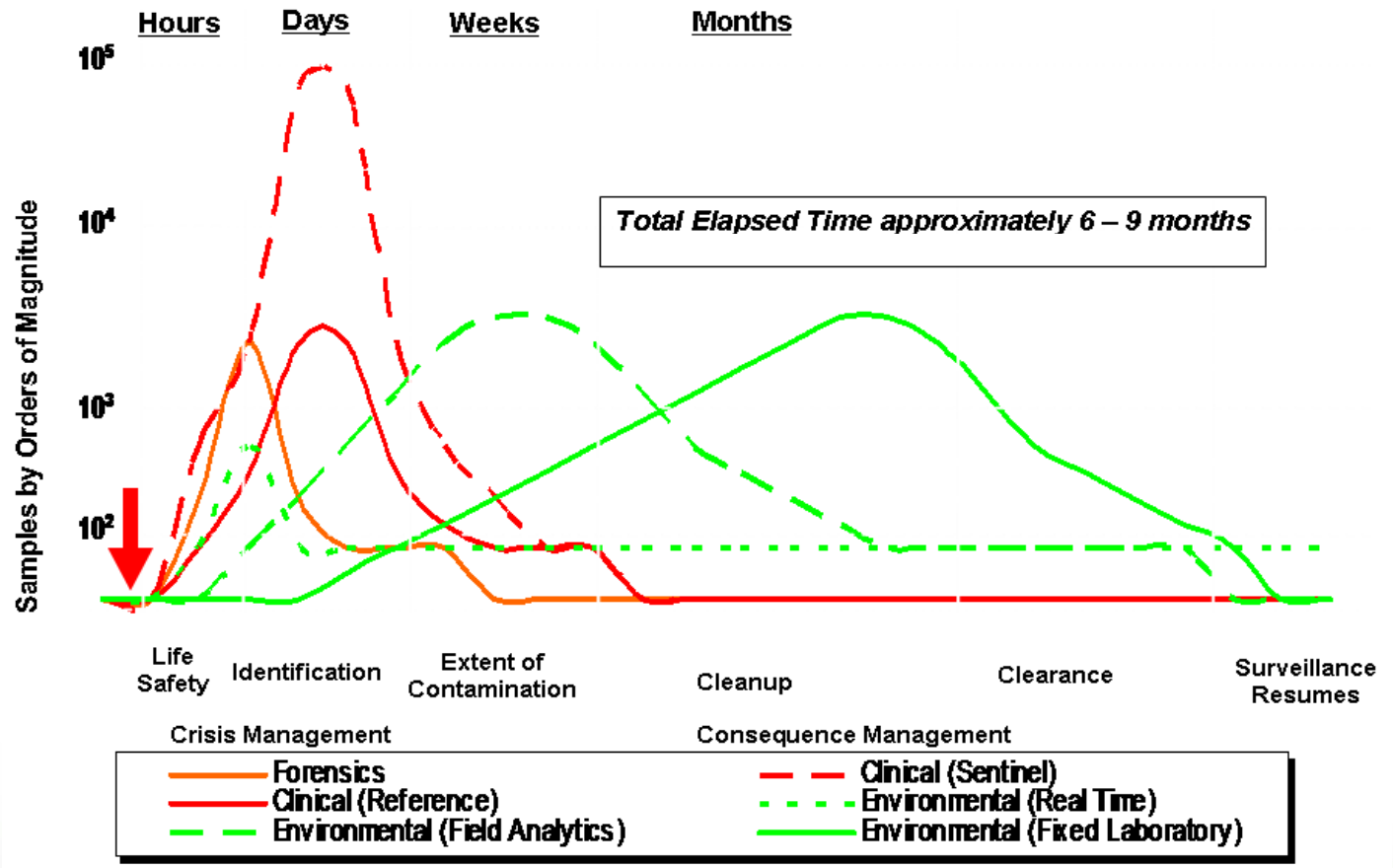
Responsibilities

- **Protect water systems from attacks and for detecting and recovering from successful attacks** affecting water systems by leading efforts to provide States and water utilities guidance, tools and strategies. *EPA is the federal government Sector Specific Agency (SSA) lead for water infrastructure.*
- **Decontaminate buildings and outdoor areas** impacted by a terrorist attack by leading efforts to establish clearance goals and clean up.
- **Develop a nationwide laboratory network** with the capability and capacity to analyze for chemical, biological and radiological agents for routine monitoring and in response to a terrorist attack.

Food Safety Modernization Act of 2010

"provide support for, and technical assistance to, State, local, and tribal governments in preparing for, assessing, decontaminating, and recovering from an agriculture or food emergency"

Sample Collection During an Incident and Potential Effect on Lab Capacity and Capability



Research to Support EPA's Response to Contamination Events and Site-Specific Risk-Based Decisions

Risk assessment is based on the best available data obtained from sampling the site and utilizing secondary resources (literature and models) to estimate potential exposure doses

Sampling

- To detect contaminants
- To determine extent of contamination

Risk assessment

- To assess potential risk of exposure, at harmful doses, and identify exposure pathways

Support Risk Management Decisions

Selected Analytical Methods (SAM)
www.epa.gov/sam

SAM 2012

Published: July 2012, revision scheduled for 2017

Chemical Methods
- 142 analytes
- 5 matrices

Pathogen Methods
- 31 analytes
- 4 matrices

Radiochemical Methods
- 25 analytes
- 6 matrices

Biotoxin Methods
- 18 analytes
- 5 matrices

CWAs and Degradates Listed in SAM

- **Nerve agents:** VX, VR, VE, VG, GA, GB, GD, GF
  - Notable degradation products: EA2192
- **Vesicant agents:** HD, Lewisite, HN-1, HN-2, HN-3
  - Notable degradation products: CVAA

Developed sampling and analysis method for GB, GD, GF, VX, and HD in soil, water, and surfaces; however, degradation products remain a concern

- **Impact of Identifying Degradates:**
  - Identifies potentially toxic degradates, which may persist
  - Degradate analysis allows samplers to identify potentially concentrated areas of concern for parent compound
  - Effectiveness of decontamination operations
  - Another step towards ensuring remediation efforts completed

Identifying Gaps Associated with Sampling and Analysis

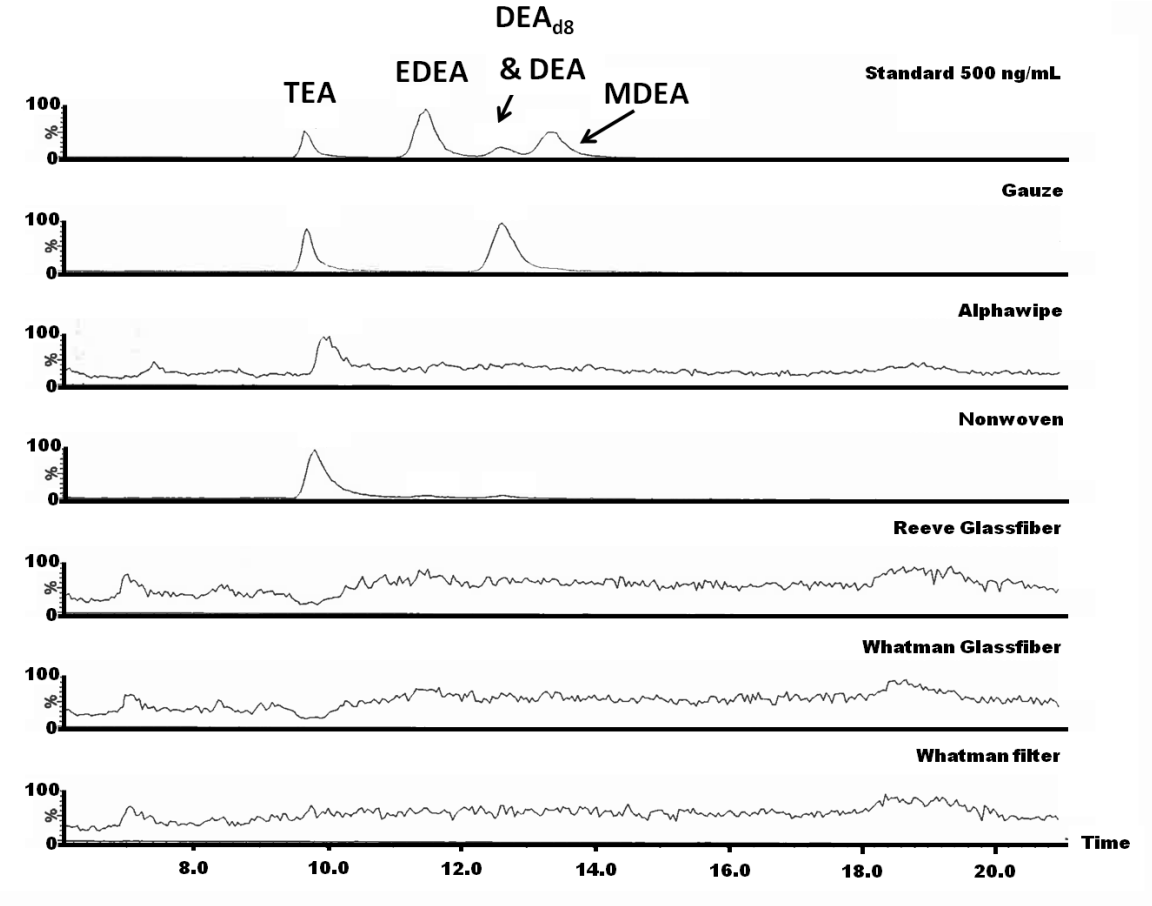
- Selection of appropriate sampling materials and analysis method
- Effect of decontamination operations on methods
- Effect of porous/permeable surfaces on analyte recoveries
- Waste generation from remediation activities

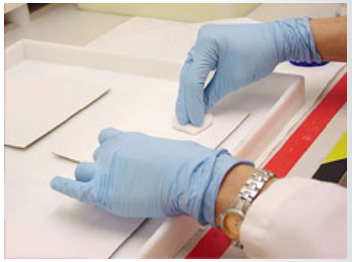
Urban areas can complicate sampling due to the different surfaces types

Drinking water and aqueous liquid samples (surface water, waste water, etc.) are of concern

Example of the Need to Identify Appropriate Sampling Materials

LC/MS/MS Chromatogram of Wipe Blanks from Nitrogen Mustard Degradation Product Analysis*

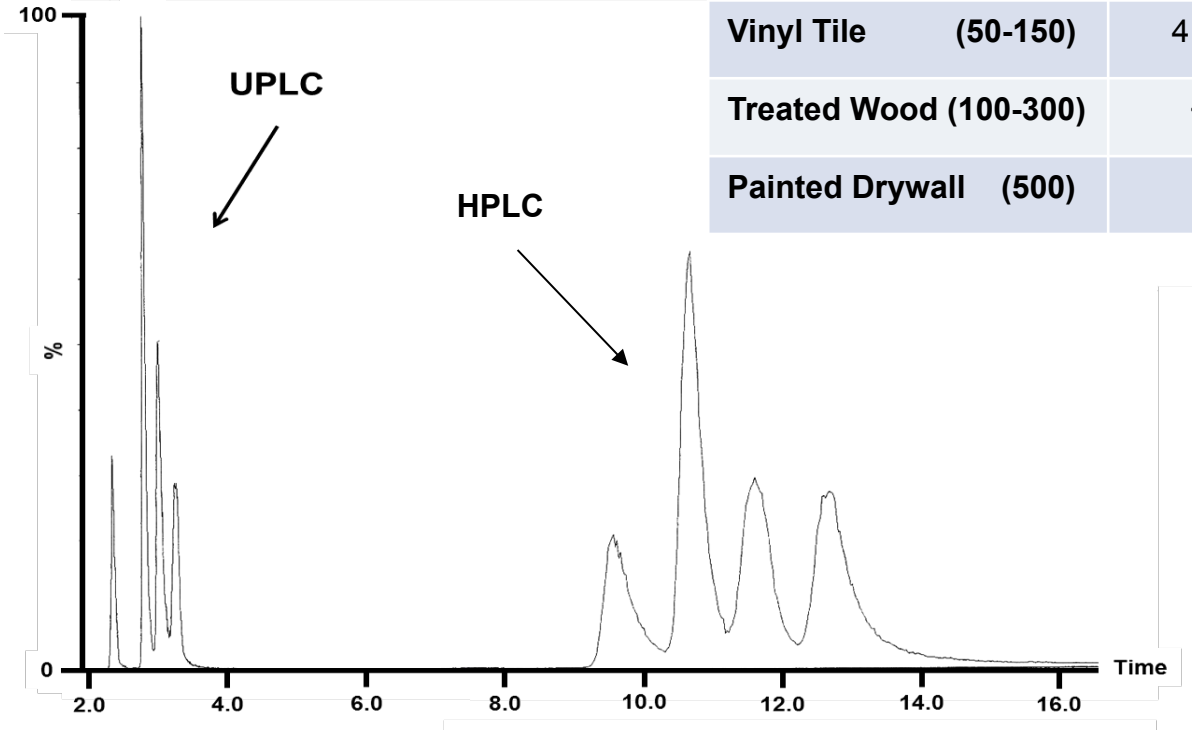




* EPA Reports: EPA 600/R-11/143 and EPA/600/R-12/581

Analysis of Nitrogen Mustard Degradation Products*

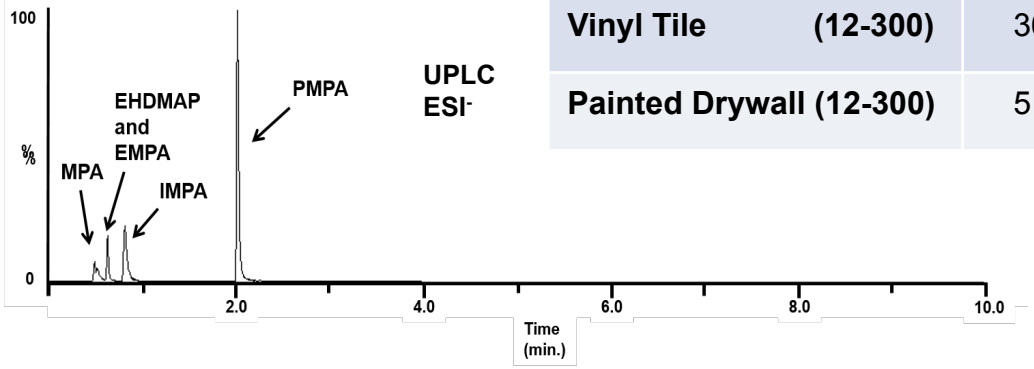
	TEA	EDEA	MDEA	DEA
Average Spike Concentration Range (ng/ml)	**% Recovery (Blank subtracted)**	**% Recovery**	**% Recovery**	**% Recovery (Blank subtracted)**
Laminate (50-150)	81-99	47-71	69-80	71-81
Metal (50-150)	20-46	49-56	54-74	62-79
Glass (50-150)	91-140	31-36	51-61	59-81
Vinyl Tile (50-150)	41-79	7-22	12-32	25-39
Treated Wood (100-300)	~ 2	~ 1	~ 2	~ 1
Painted Drywall (500)	19	8	17	13

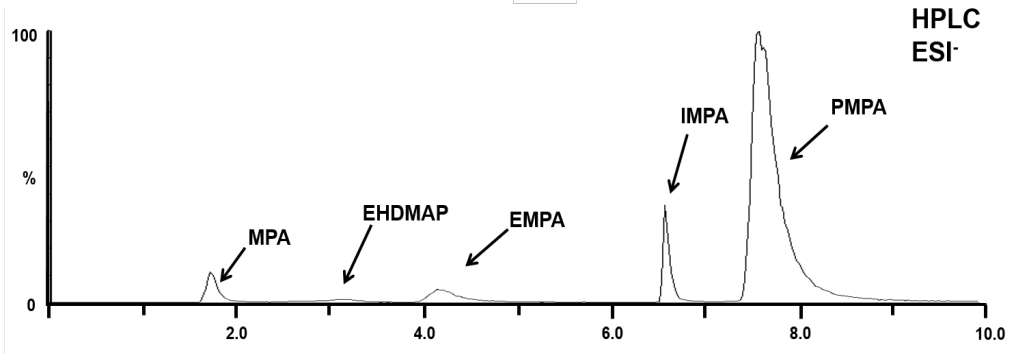


J. Chromatogr. A, 1270 (2012) 72-79

Analysis of Nerve Agent Degradation Products*

	IMPA	MPA	EMPA	EHDMAP	PMPA
Average Spike Concentration Range (ng/ml)	**% Recovery**	**% Recovery**	**% Recovery**	**% Recovery**	**% Recovery**
Laminate (12-300)	80-103	33-59	61-92	41-96	73-85
Metal (12-300)	60-85	3-11	61-66	25-38	60-79
Glass (12-300)	73-89	26-43	70-75	22-51	83-98
Vinyl Tile (12-300)	36-54	4-27	30-51	22-30	33-49
Painted Drywall (12-300)	51-60	7-12	39-139	ND-16	58-70





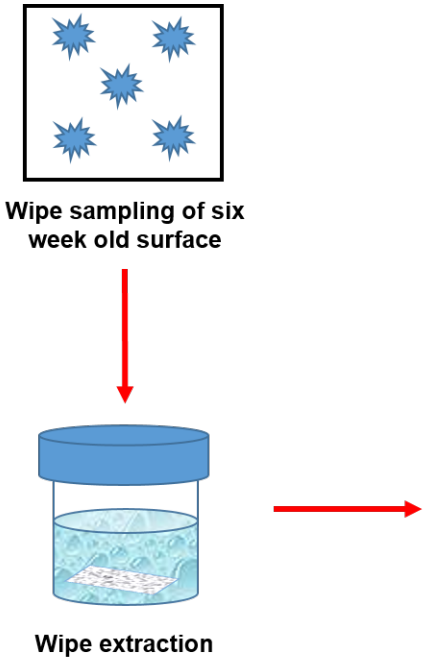
* *Anal. Chem.*, 87 (2015) 1034−1041

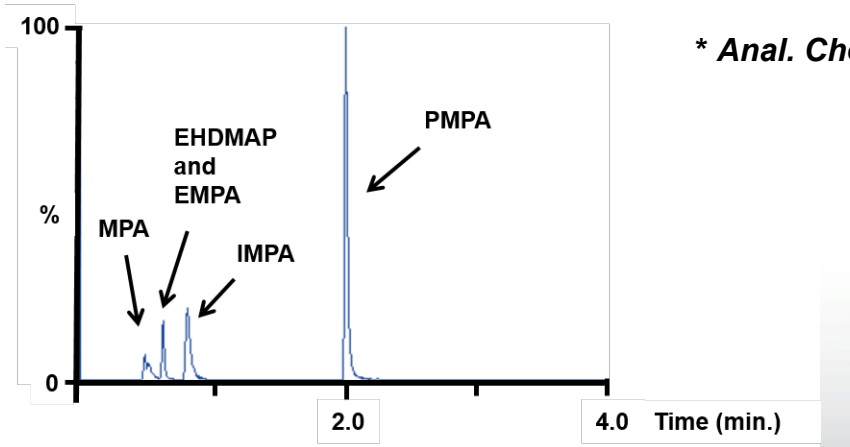
Persistence Investigation on Surfaces

Laminate Surface*					
	IMPA	MPA	EMPA	EHDMAP	PMPA
Time on Surface (days)	% Recovery (± %RSD)	% Recovery (± %RSD)	% Recovery (± %RSD)	% Recovery (± %RSD)	% Recovery (± %RSD)
0	79 ± 11	36 ± 7	83 ± 8	41 ± 13	64 ± 6
1	88 ± 2	27 ± 23	69 ± 11	21 ± 11	97 ± 15
7	58 ± 19	32 ± 9	64 ± 3	ND	59 ± 12
14	65 ± 3	29 ± 8	64 ± 4	ND	68 ± 13
21	55 ± 13	42 ± 8	80 ± 3	ND	59 ± 9
42	62 ± 27	39 ± 21	64 ± 11	ND	56 ± 22

ND = Not detected

* *Anal. Chem.*, 87 (2015) 1034−1041



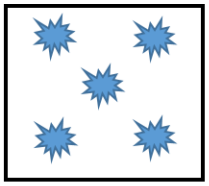


Persistence Investigation on Surfaces

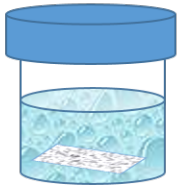
Painted Drywall Surface*					
	IMPA	MPA	EMPA	EHDMAP	PMPA
Time on Surface (days)	% Recovery (± %RSD)	% Recovery (± %RSD)	% Recovery (± %RSD)	% Recovery (± %RSD)	% Recovery (± %RSD)
0	74 ± 9	14 ± 13	56 ± 12	14 ± 17	71 ± 15
1	69 ± 7	7 ± 45	50 ± 26	ND	68 ± 4
7	40 ± 14	7 ± 50	45 ± 8	ND	40 ± 10
14	38 ± 2	9 ± 35	37 ± 5	ND	36 ± 9
21	28 ± 10	16 ± 9	48 ± 6	ND	29 ± 25
42	21 ± 29	14 ± 31	26 ± 15	ND	20 ± 12

ND = Not detected

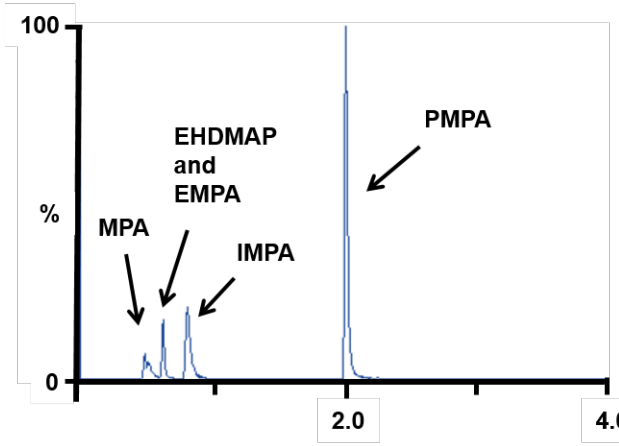
* *Anal. Chem.*, 87 (2015) 1034−1041



Wipe sampling of six week old surface

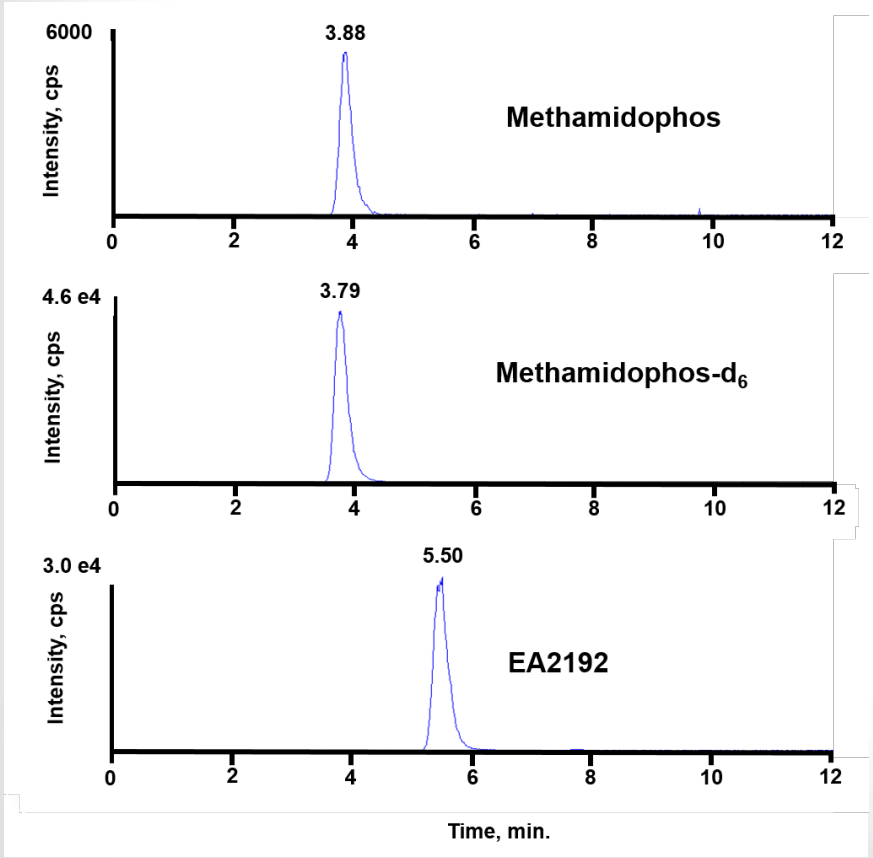


Wipe extraction



LC/MS/MS Analysis of VX Degradation Product in Drinking Water

Adaptation of U.S. EPA Method 538 Conditions and QC Approach for EA2192 Analysis by Liquid Chromatography/Tandem Mass Spectrometry

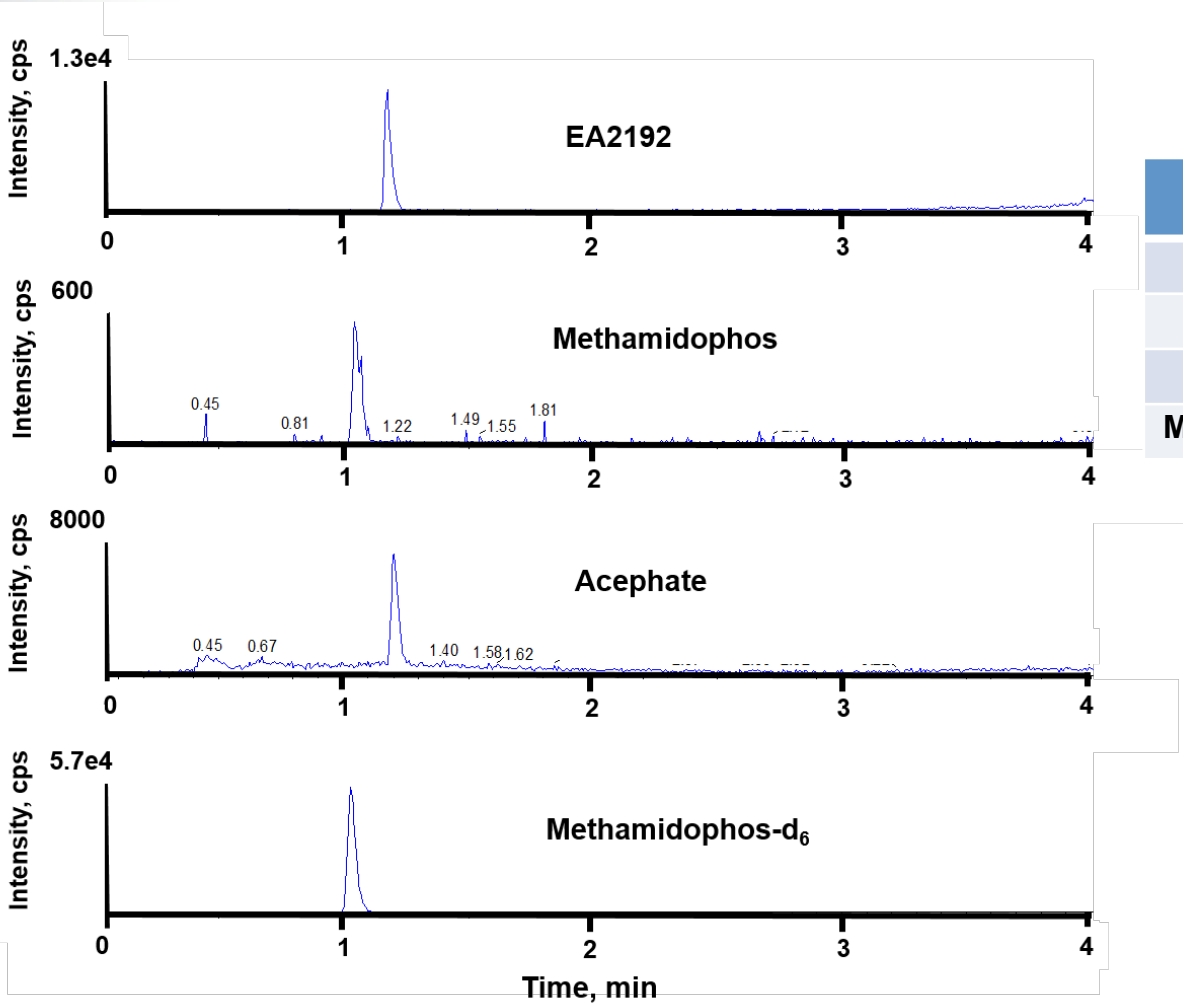


EA2192 Initial Display of Capability	Results
Calibration Curve Accuracy Cal 1 (0.050 µg/L)	96.4 – 105%
Calibration Curve Accuracy Cal 2 -Cal 7 (< 5.00 µg/L)	92.4 – 107%
Laboratory Reagent Blank	ND
Method Detection Limit	0.013 µg/L
Method Reporting Limit	0.125 µg/L
Method Precision at Cal 4 (0.480 µg/L)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

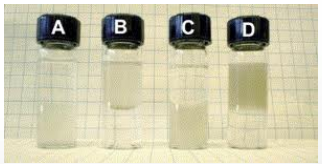
UPLC/MS/MS Analysis of VX Degradation Product in Drinking Water

Preliminary UPLC Analysis of EA2192 to Address Rapid Lab Throughput

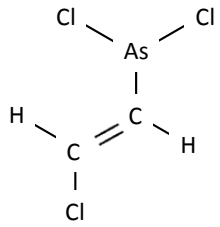


Analyte	HPLC RT (min)	UPLC RT (min)
Methamidophos	3.3	1.1
Acephate	5.2	1.2
EA2192	5.4	1.2
Methamidophos-d_6	3.7	1.1

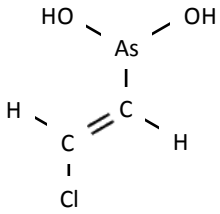
RT = Retention Time
CAL 1 level = 0.05 µg/L



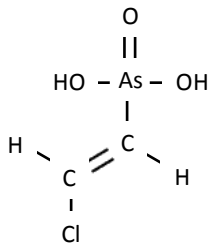
LC/MS/MS Analysis of Lewisite



hydrolysis



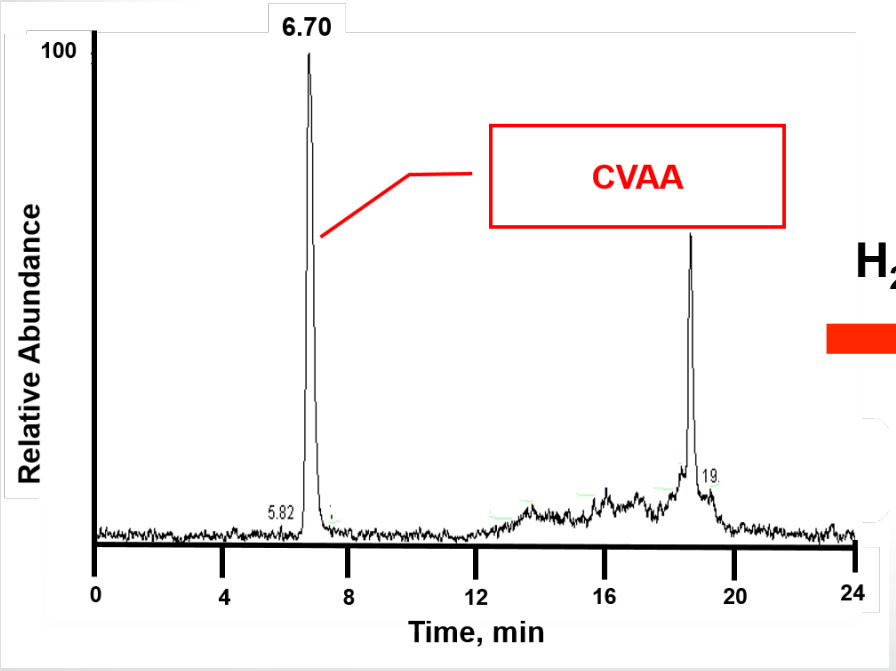
oxidation



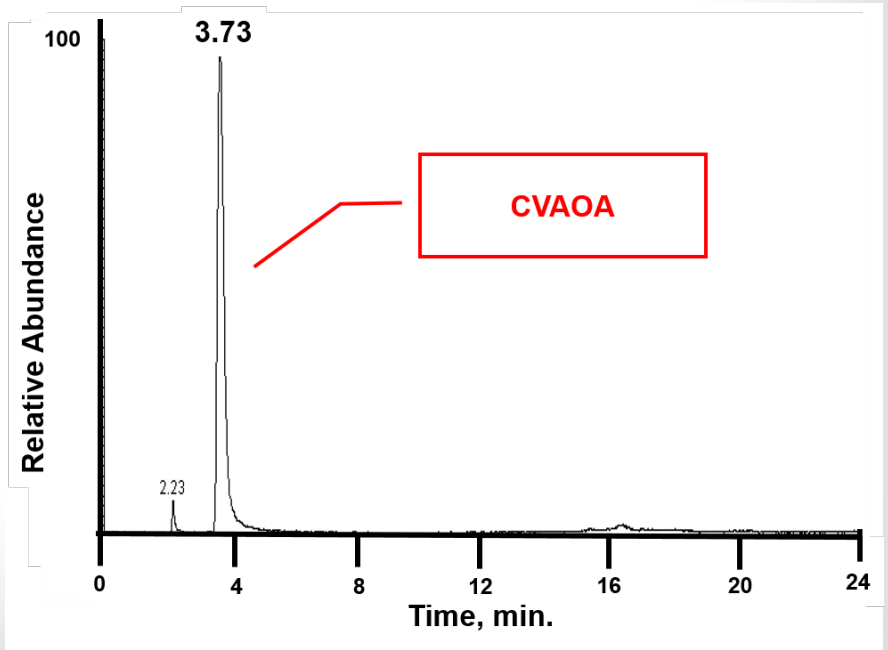
Lewisite I

Chlorovinyl arsonous acid (CVAA)

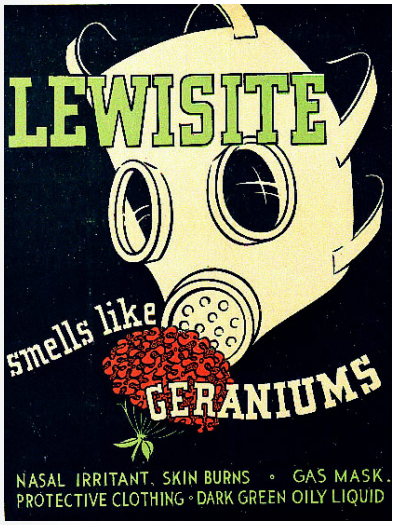
chlorovinyl arsonic acid (CVAOA)



H_2O_2



LC/MS/MS Analysis of Lewisite



Matrix	Spiked CVAOA Concentration	Measured CVAOA Concentration (avg ± std)	Recovery (%)	MDL for CVAOA	ATL[a]
Water	0.20 mg/L	0.22 ± 0.01 mg/L (n=7)	110	0.04 mg/L	0.03 mg/L
Wipe	3.00 µg	3.04 ± 0.12 µg (n=7)	101	0.4 µg	-
Sand	0.20 µg/g	0.17 ± 0.02 µg/g (n=7)	85	0.07 µg/g	0.3 µg/g
NB Soil	0.20 µg/g	0.22 ± 0.01 µg/g (n=7)	112	0.03 µg/g	0.3 µg/g
VA Soil	0.40 µg/g	0.17 ± 0.01 µg/g (n=7)	43	0.03 µg/g	0.3 µg/g
GA Soil	0.40 µg/g	0.32 ± 0.02 µg/g (n=7)	80	0.05 µg/g	0.3 µg/g

[a]Analytical Target Level (ATL) values 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

Identifying Relevant Sampling and Analysis Products and Outputs for Use

- Identifying challenges when developing a method
  - Appropriate sample collection and analysis methods for the target analyte/matrix pair
  - Providing quality data which can be used during risk-based decisions during remediation
  - Addressing data comparability when laboratory capacity and capability issues arise
- Addressing those challenges
  - Develop sampling and analysis methods with a focus on environmental factors/matrices
  - Sample collection guides to address collection procedures
  - Develop a compendium of methods listing available methods and matrix types for data comparability and to address lab capability and throughput – SAM 2012 (update SAM 2017)
- LC/MS/MS used as a key analysis technique for environmental matrices
  - Developing sample collection and rapid analysis methods for degradation products on surfaces
  - Adapting existing EPA method for analysis of key CWA degradation product in drinking water
  - Developing a method for a notoriously complicated analyte (Lewisite) via LC/MS/MS

Contributors/Acknowledgements

Romy Campisano[1], Matthew Magnuson[1], Tonya Nichols[1], Carolyn Koester[2],Terry Smith[3], Terry O'Neill[4], Sandip Chattopdhyay[5]

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