Produced Water Characterization and Treatment: Task 3.0: Organics, Inorganics and Critical Minerals Characterization

Solutions for Today | Options for Tomorrow

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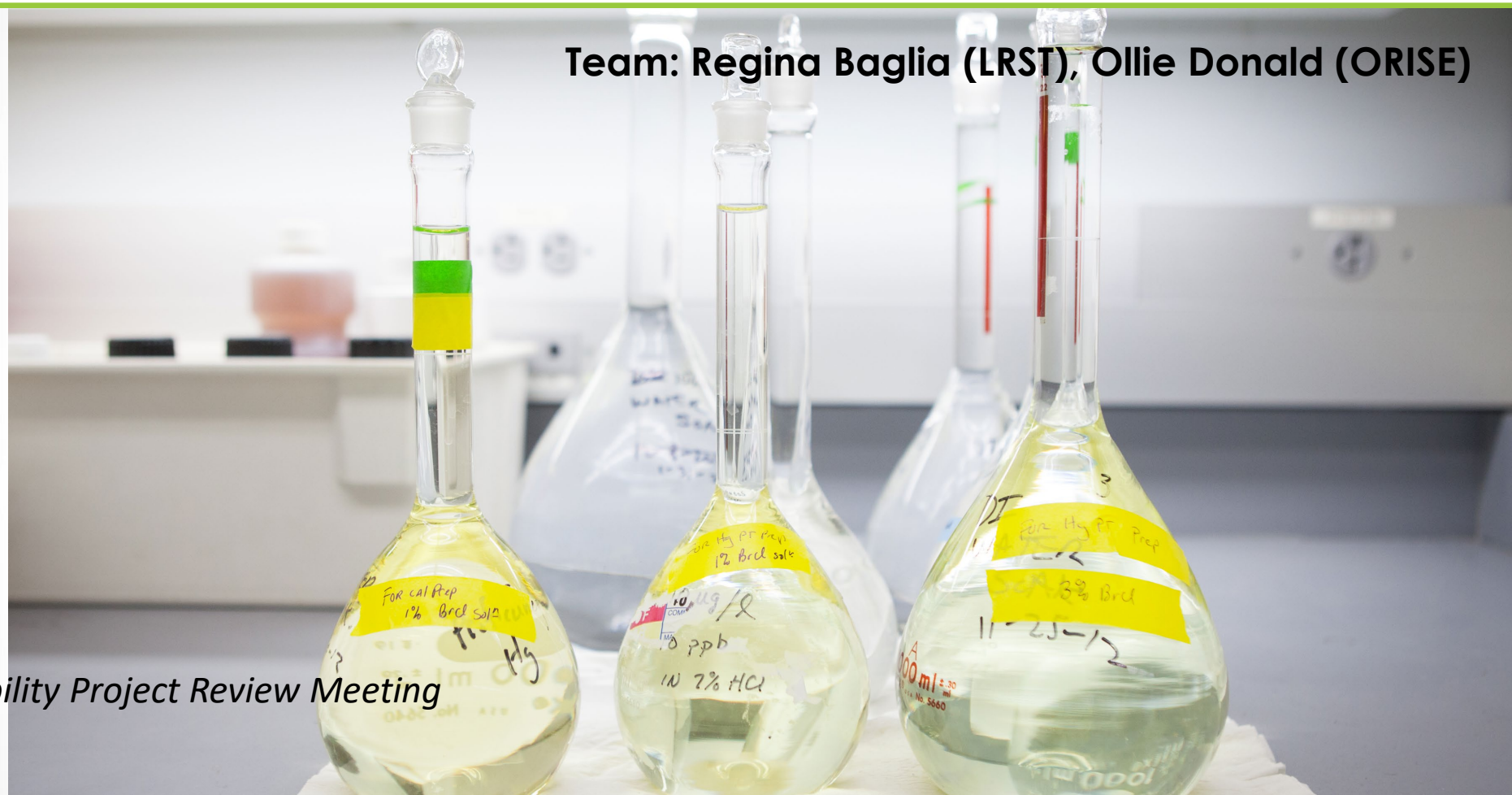
Geochemistry Team



Presentation to Resource Sustainability Project Review Meeting
April 3, 2024

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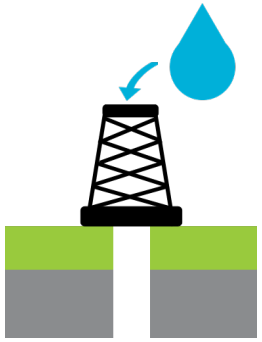
Project Overview

Produced Water Characterization and Treatment, Task 3.0

Problem

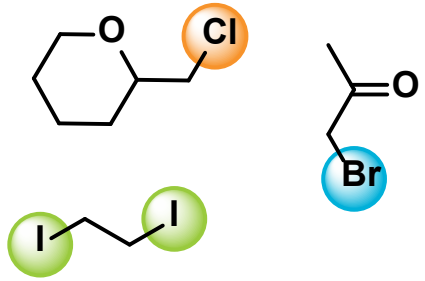
Shale well production generates large volumes of wastewater. Beneficial reuse avenues are needed. However, ***unpredicted types and concentrations of pollutants*** make treatment expensive and difficult



Research Question

Are pollutants observed ***across multiple basins***?

Do pollutants persist ***throughout water treatment stages***?



End Products

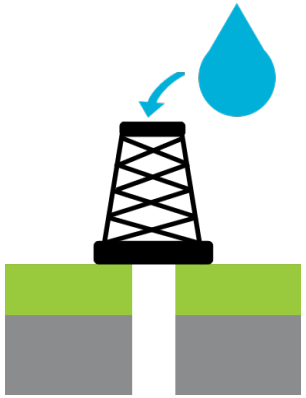
Summary of known organics in produced waters from major U.S. O&G basins.

Summary of relationships identifying when organics of interest in produced water may need focused treatment

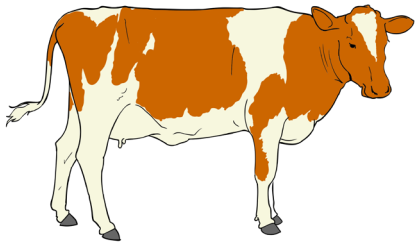
Enabling Beneficial Reuse of Produced Water

Better Solutions are Needed for Managing Produced Water

Current Management:
Disposal Wells

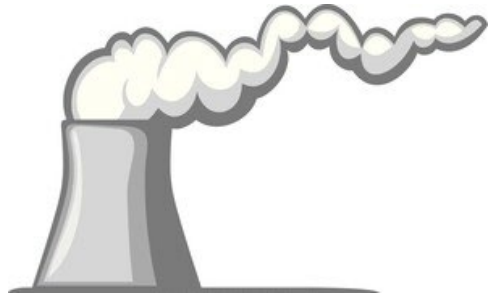


Avenues of Reuse



Livestock Watering

Municipal Use



Industrial Cooling

What's in the water?

Agriculture

Stream Augmentation

- Volume up to 14,000,000 L/well
- Ratio of Water/Oil: 3 to 20
- Hazards vary by location and production time

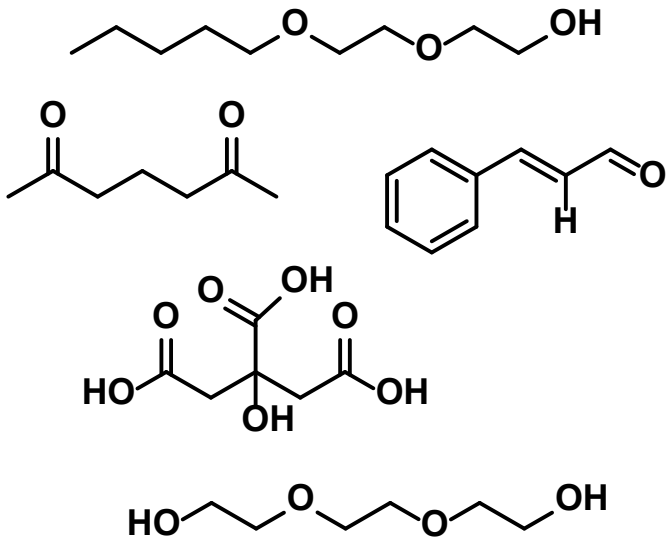
Danforth, C.; McPartland, J.; Blotevogel, J.; Coleman, N.; Devlin, D.; Olsgard, M.; Parkerton, T.; Saunders, N., Alternative Management of Oil and Gas Produced Water Requires More Research on Its Hazards and Risks. *Integrated Environmental Assessment and Management* **2019**, *15*, 677-682.

Organic Chemicals in Produced Water

Unpredicted Types and Concentrations of Organic Contaminants Make Treatment Expensive and Difficult

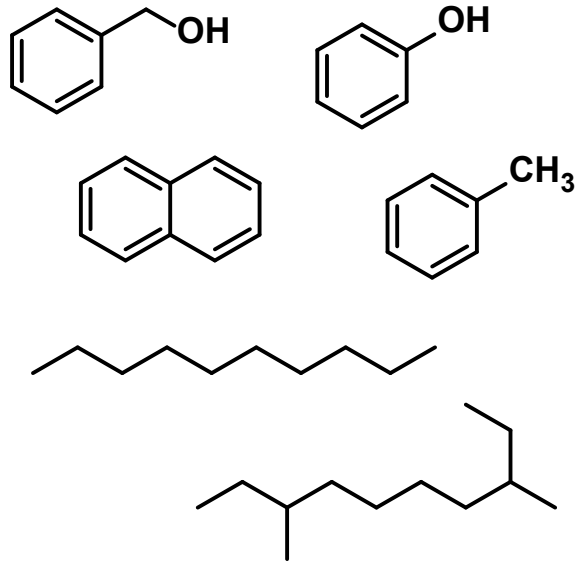
Injected Chemicals

- Surfactants, biocides, etc.
- Listed in FracFocus



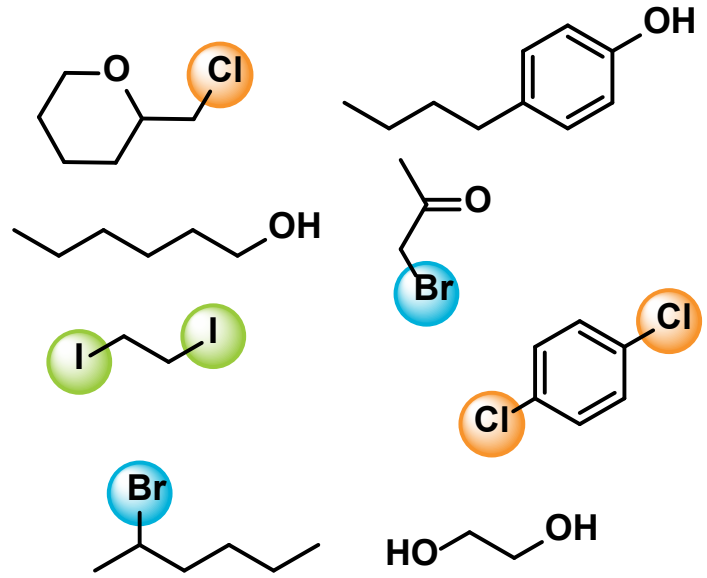
Subsurface Chemicals

- Phenols, aromatics, hydrocarbons
- Unknown concentrations



Transformation Products

- Halogenated, alcohols, PEGs
- Unknown concentrations
- High potential toxicity



Hoelzer, K.; Sumner, A. J..; Karatum, O.; Nelson, R. K.; Drollette, B. D.; O'Connor, M. P.; D'Ambrio, E. L.; Getzinger, G. J.; Ferguson, P. L.; Reddy, C. M.; Elsner, M.; Plata, D. L.; Indications of Transformation Products from Hydraulic Fracturing Additives in Shale-Gas Wastewater. *Environ. Sci. Technol.*, **2016**, 50, 8036-8048.

Our Approach

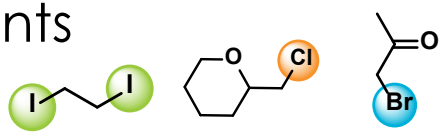
NATIONAL ENERGY TECHNOLOGY LABORATORY

Obtain produced water samples from across multiple basins and treatment stages

Test inorganics and CM concentrations at PAL

Optimize ***sample preparation*** techniques

Identify organic compounds using LC-MS and GC-MS with a focus on halogenated pollutants



Quantify concentrations of halogenated pollutants using chemical standards

Evaluate toxicity through collaboration with U.S. EPA

Obtain Produced Water Samples

4 Basins, between 2- 7 treatment stages

Basin	Facility	Treatment Stages
Marcellus	Privately owned produced water treatment facility	Raw, treated
Denver Julesburg	Produced Water Partnership	Raw, UF Feed, PreGAC, RO Feed, RO Perm 1st Pass, RO Perm 2nd pass, RO Conc.
Eagle Ford	Produced Water Partnership	Raw, Pre-treat, distillate, concentrate
Permian	Produced Water Partnership	Raw, pre Treat, distillate, concentrate

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Brine Extraction Storage Site (BEST)

Photo from https://netl.doe.gov/carbon-management/carbon-storage/BEST

Identify organic compounds by LC-MS and GC-MS

NATIONAL ENERGY TECHNOLOGY LABORATORY

Separate and identify compounds using chromatography and mass spectrometry

Hydrophilic Compounds

Agilent 1290 LC
Agilent 6520B QTOF

LC-QTOF-MS at NETL-PGH

Hydrophobic Compounds

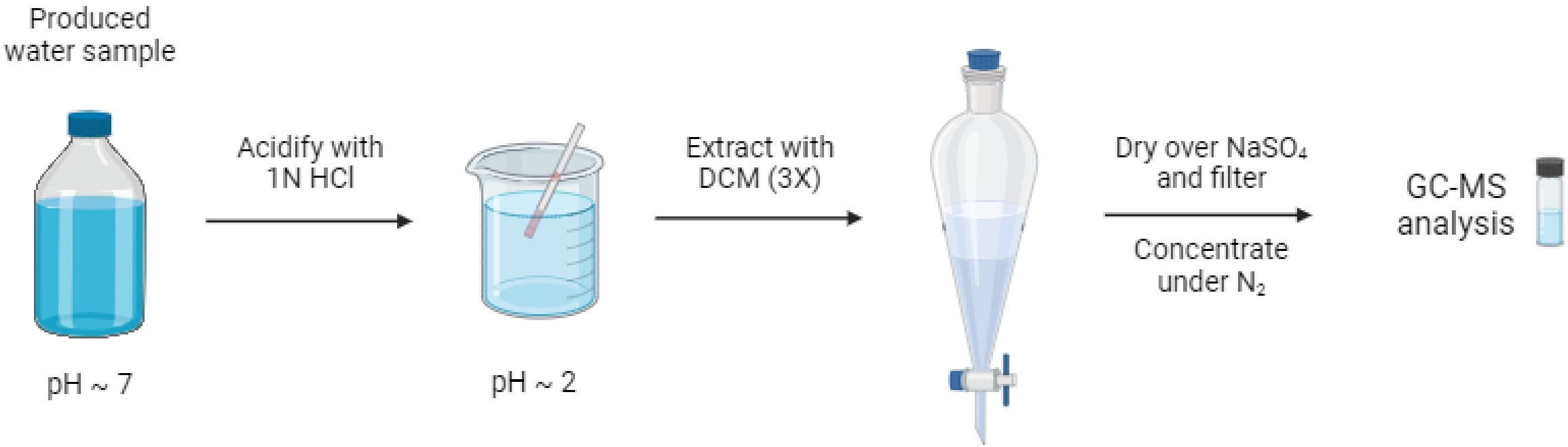
Agilent 7890A GC
Agilent 5975C MSD

gas chromatography-mass spectrometry

Optimize Sample Preparation Techniques

Produced water sample preparation for GC-MS: liquid-liquid extraction (LLE)

- Objective: Isolate organics, remove salts and concentrate for improved detection
- Challenges: Compound retention

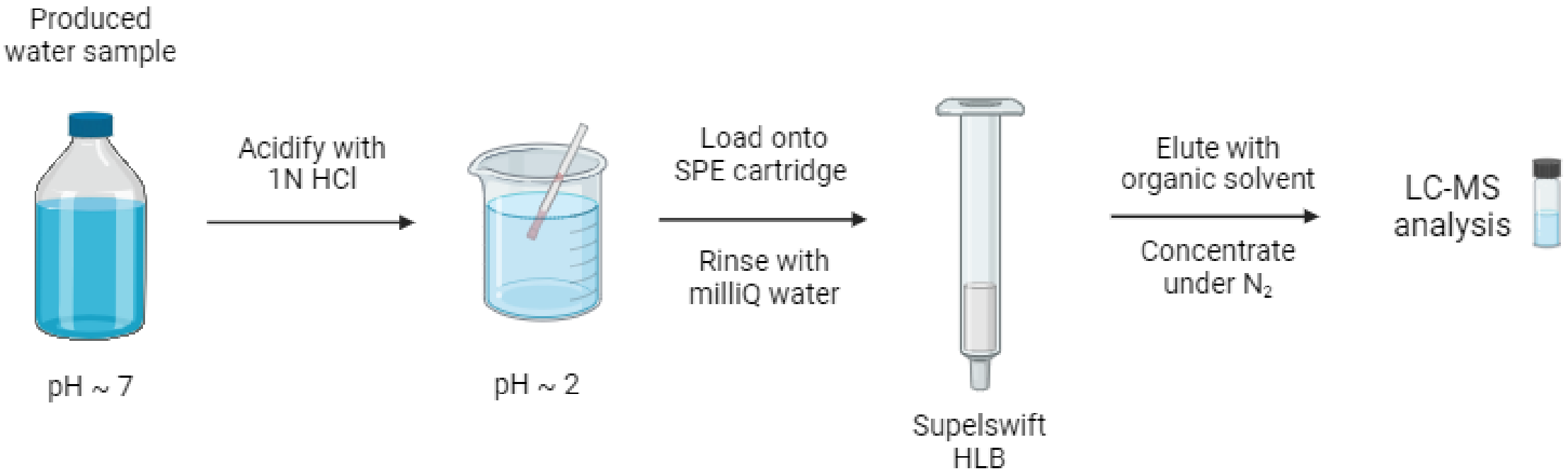


Experimental schemes created with BioRender.com

Optimize Sample Preparation Techniques

Produced water sample preparation for LC-MS: Solid Phase Extraction (SPE)

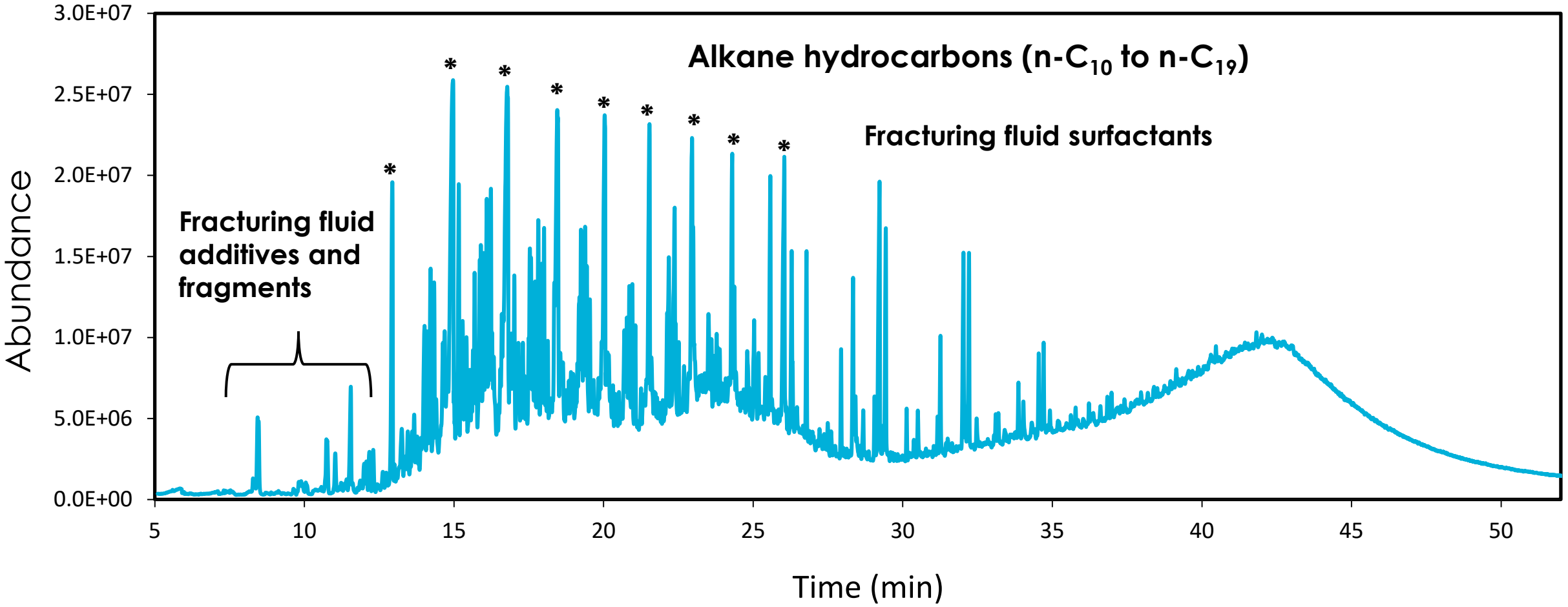
- Objective: Isolate organics, remove salts and concentrate for improved detection
- Challenges: Compound retention



Experimental schemes created with BioRender.com

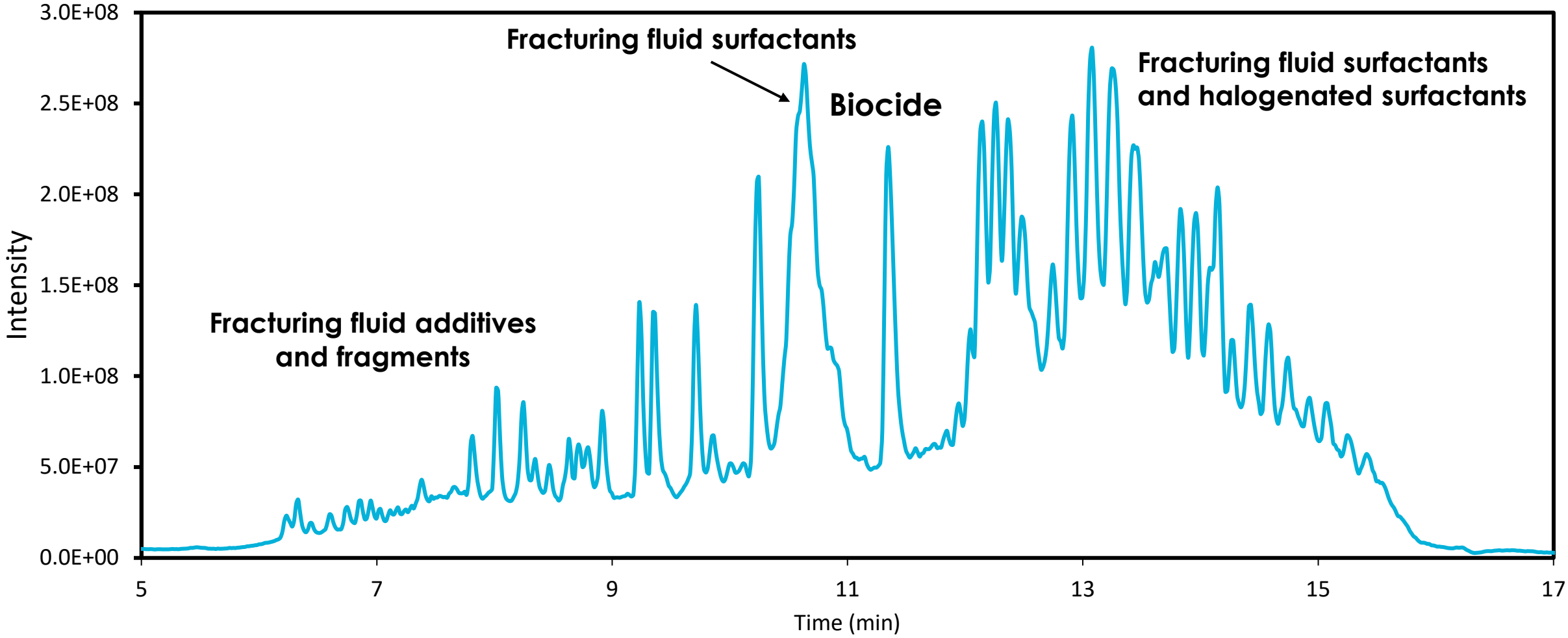
Identify Organic Compounds: GC-MS Results

Raw Marcellus produced water



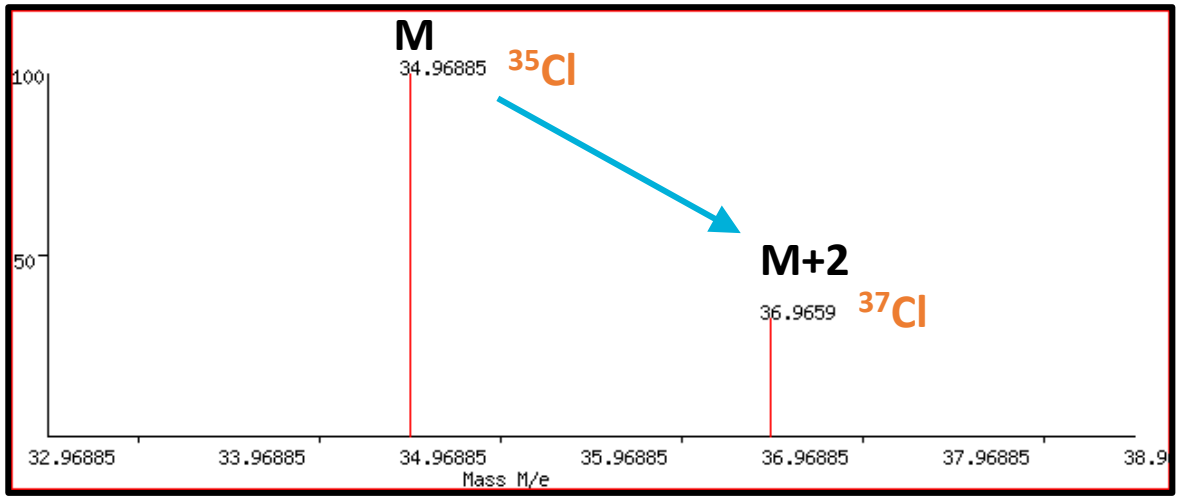
Identify Organic Compounds: LC-MS Results

Raw Marcellus produced water



HaloSeeker: A Nontargeted Screening Software for Identifying Suspected Halogenated Organics

- Utilizes high-resolution mass spectrometry datasets
- Identifies important features: m/z, retention time, intensity
- Pairs Cl- and Br- containing isotopologues based on exact mass differences and isotopic abundance ratios
- Results in interactive plot in their GUI
- Allows for formula generation and annotation

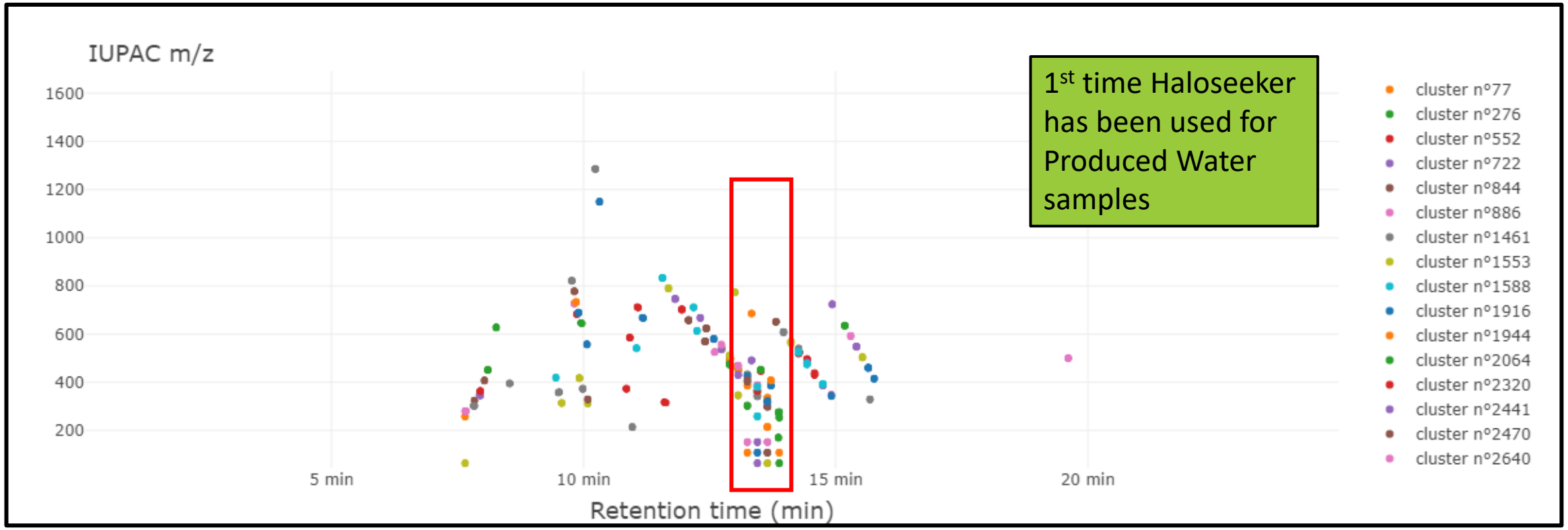


Isotopes of interest (% abundances):

- Chlorine: ^{35}Cl (75%), ^{37}Cl (25%)
- Bromine: ^{79}Br (50%), ^{81}Br (50%)

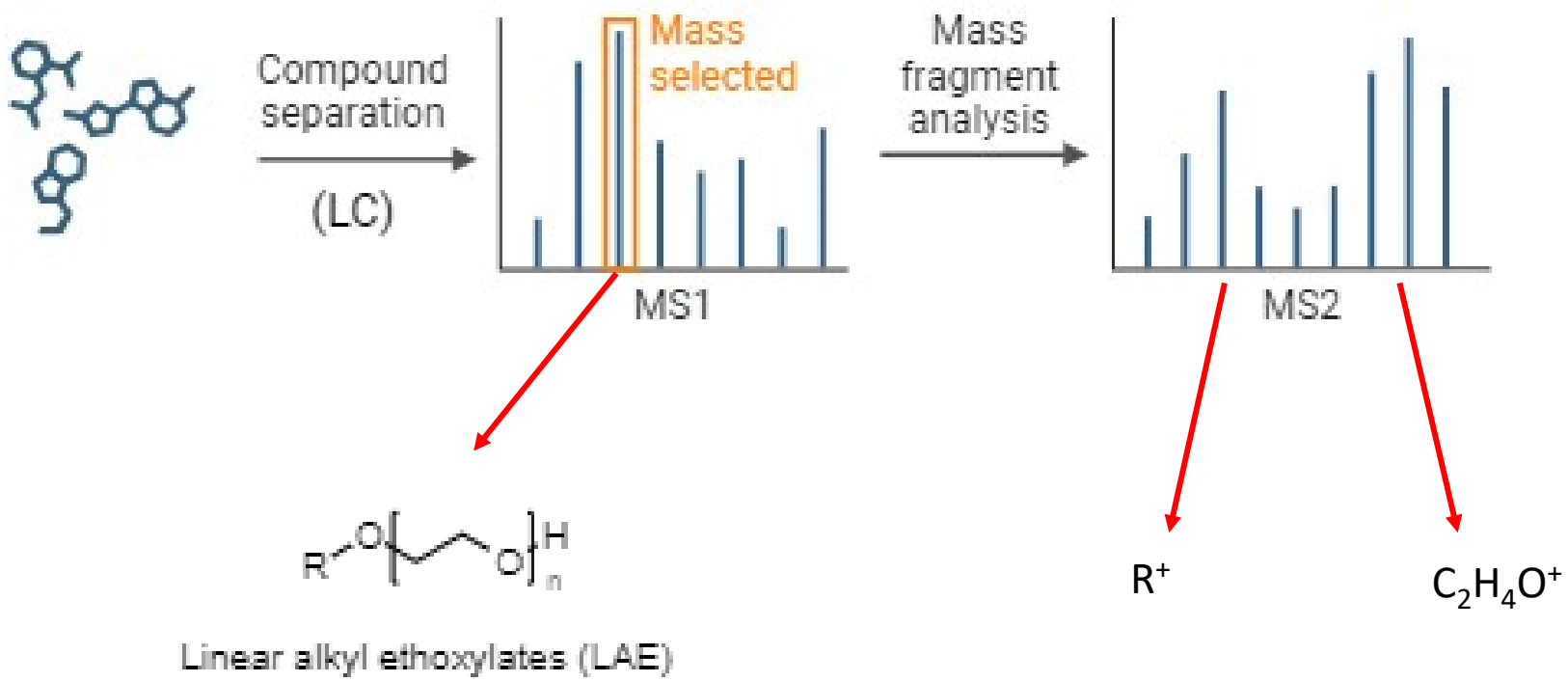
HaloSeeker 1.0: A User-Friendly Software to Highlight Halogenated Chemicals in Nontargeted High-Resolution Mass Spectrometry Data Sets Alexis Léon, Ronan Cariou, Sébastien Hutinet, Julie Hurel, Yann Guitton, Céline Tixier, Catherine Munschy, Jean-Philippe Antignac, Gaud Dervilly-Pinel, and Bruno Le Bizec, *Analytical Chemistry* **2019** *91* (5), 3500-3507

HaloSeeker: A Nontargeted Screening Software for Identifying Suspected Halogenated Organics



SUSPECTED halogenated compounds filtered out by intensity. The higher the intensity, the higher the confidence that they are likely halogenated. The highlighted box is where we focus because they are still assigned after an intensity filter is applied.

Structural studies of suspected halogenated compounds by tandem mass spectrometry

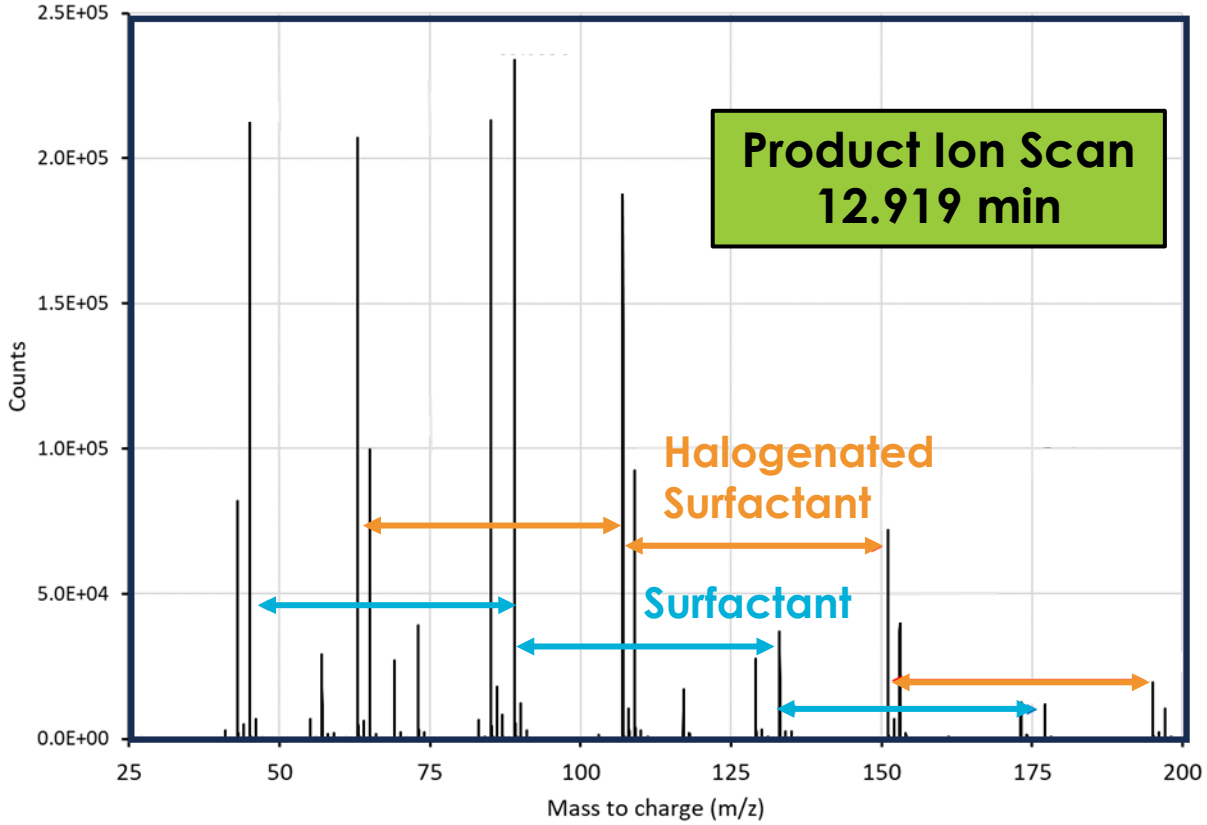


Mass fragmentation allows for understanding structure of unknown compounds.

Identify Organic Compounds: LC-MS Results

Marcellus Shale Raw Water

Once suspected halogenated organics are identified, tandem mass-spectrometry to interrogate and confirm structure (multiple iterations necessary)



Next Steps

Obtain produced water samples from across multiple basins and treatment stages

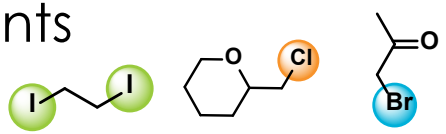
Complete, additional Marcellus sampling trips planned

Test inorganics and CM concentrations at PAL

Optimize ***sample preparation*** techniques

Complete

Identify organic compounds using LC-MS and GC-MS with a focus on halogenated pollutants



In Progress, Haloseeker and Tandem MS-MS

Quantify concentrations of halogenated pollutants using chemical standards

Next Steps: Synthesize halogenated compounds

Evaluate toxicity through collaboration with U.S. EPA

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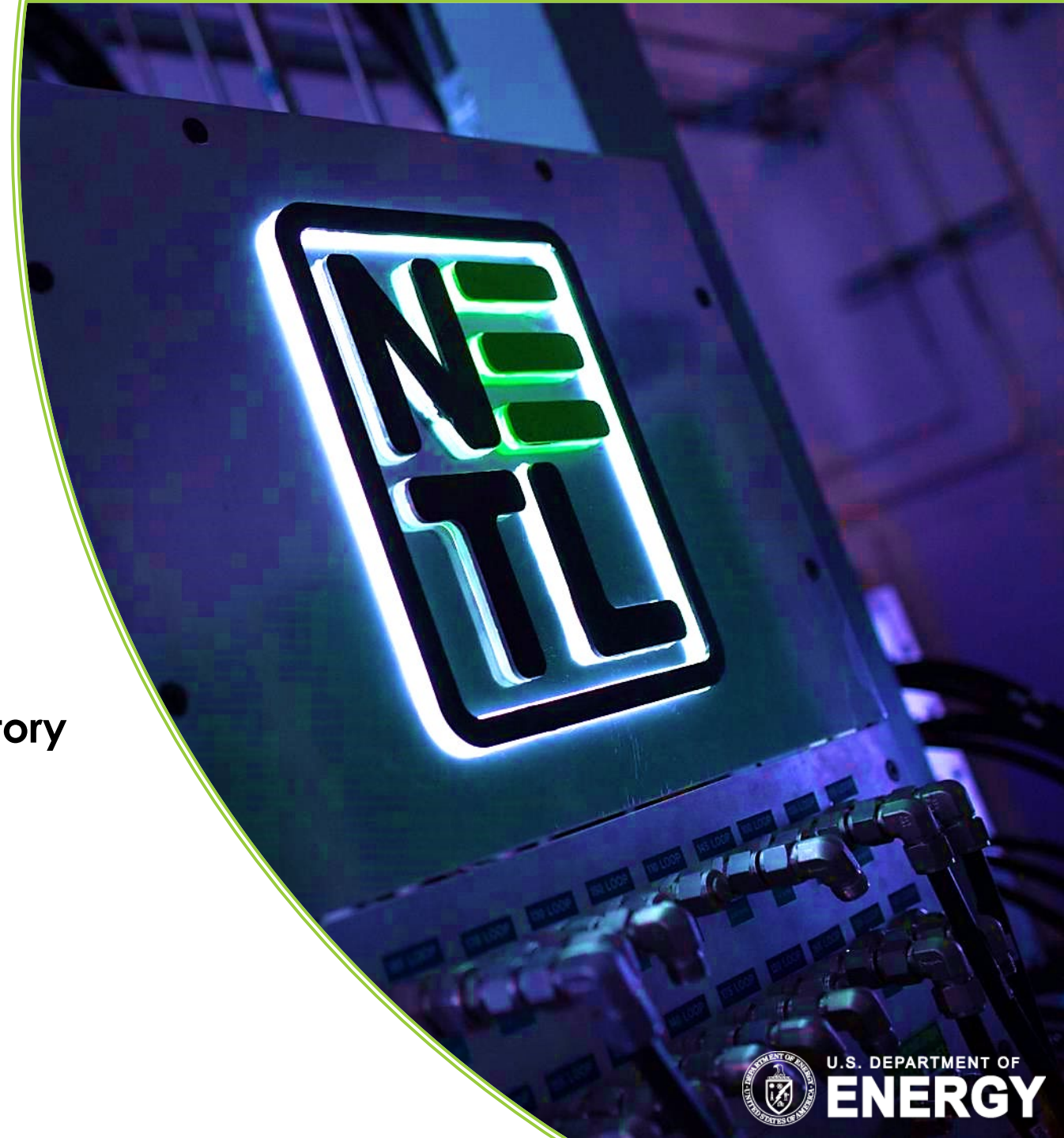
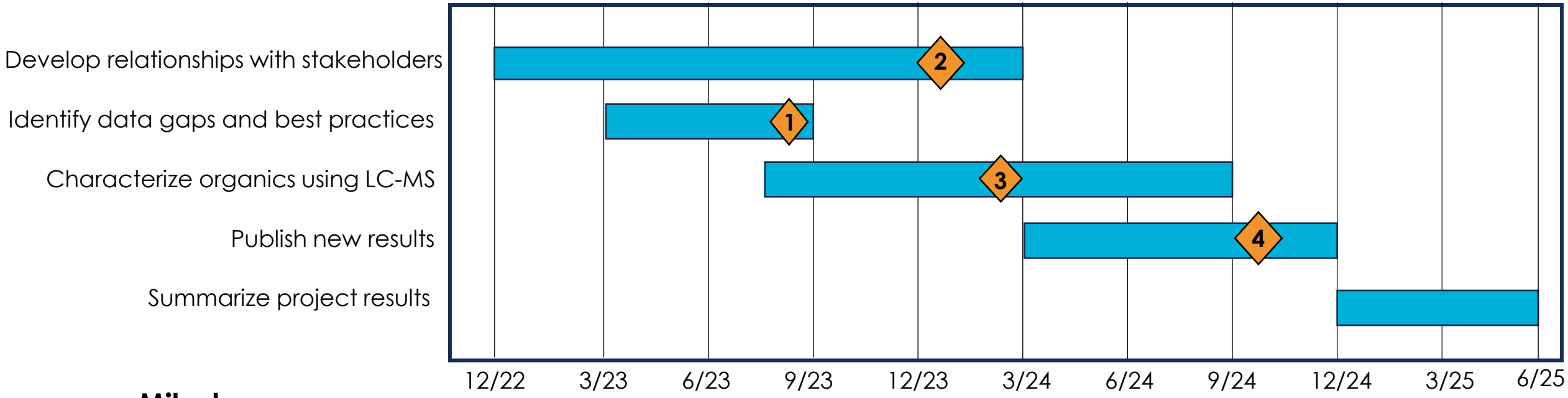


U.S. DEPARTMENT OF ENERGY

Gantt Chart



Milestones

1. Completed Literature review of organics characterization in produced water
2. Presented work to American Society of Mass Spectrometry (ASMS), Regina Baglia LRST
3. Identified halogenated surfactants in Marcellus produced water
4. Submit publication to journal

Task Milestones Table

Identifier	Type[1]	Expected Completion Date	Description (What, How, Who, Where)
EY22.3.A	Project	10/2022	**Completed.** Develop relationships with water treatment facilities and other stakeholders to accurately identify the organic classes the team should address.
EY23.3.B	Major	07/2023	**Completed** Identify data gaps and best practices for organics sampling in produced water.
EY24.3.C	Major	08/2024	**In Progress, On Track.** Characterize organics using LC-MS based techniques in samples from selected locations.
EY24.3.D	Project	12/2024	**In Progress, On Track.** Publish new results associated with the project for use by water management companies and government agencies.
EY25.3.E	Project	06/2025	Summarize project results and identify whether additional PWC is required to enable beneficial use.