# Produced Water Analytical Sampling List Working Group Accomplishments Panel and 2022 Goals and Discussion

| | |
|---|---|
| **Moderator** | **Jason Herman, NMED** |
| **Panelists** | **Dan Mueller, EDF** |
| | **Pei Xu, NMSU** |
| | **Ryan Hall, NGL** |
| | **Robert Young, NMSU** |

**NM Produced Water Research Consortium – Year-end Meeting**
**December 1-2, 2021**

NM STATE NEW MEXICO PRODUCED WATER RESEARCH CONSORTIUM

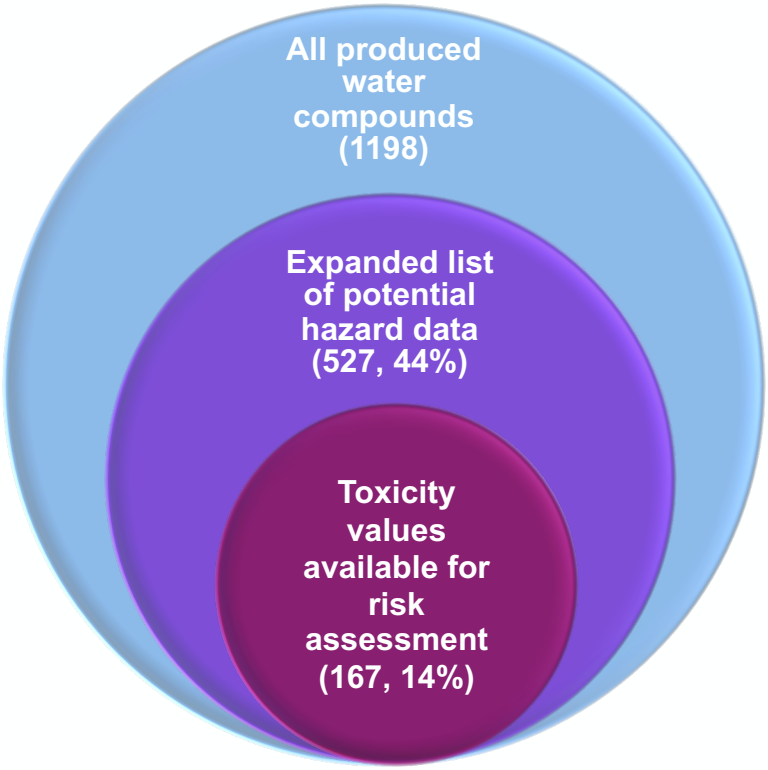
be the Future.

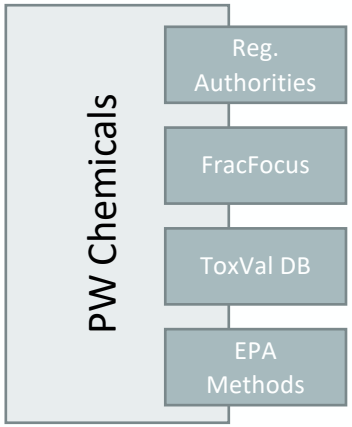
# The Challenge in Determining What is in Produced Water

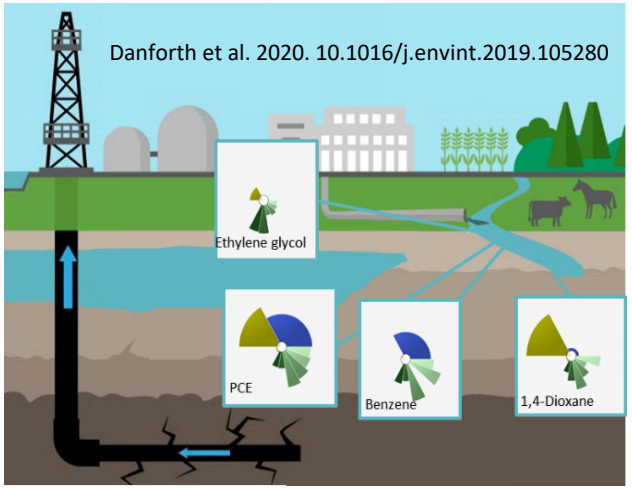
- Highly variable
  - Varies by region
  - Varies within an oil or gas play
  - Varies with time

- It is about more than just the total dissolved solids
  - Typical elevated TDS levels do present challenges for analytical methods and treatment processes
- But a number of organics, inorganics and radionuclides are also present
  - Formation water
  - Injected chemicals (well completion and on-going well maintenance)
  - Transformation/degradation products

# Building Awareness on Produced Water Chemicals



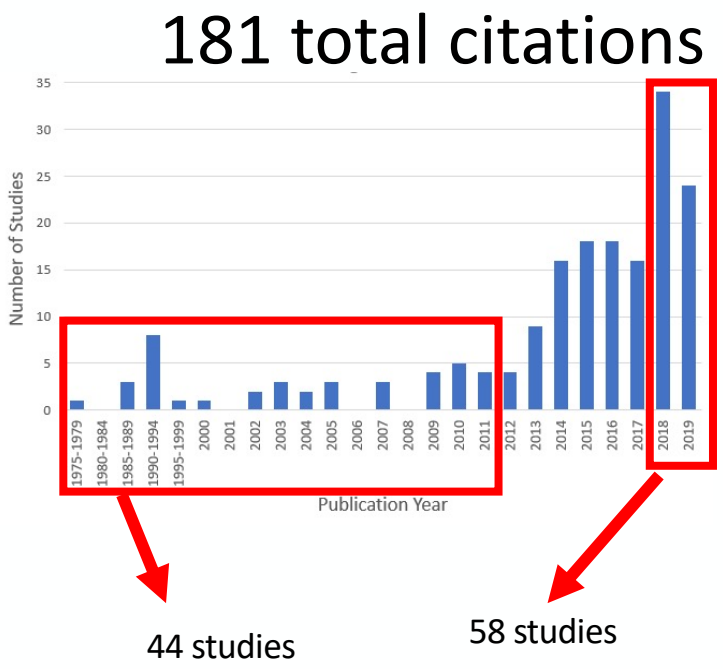

**Cloelle Danforth & Elena Craft**, Environmental Defense Fund

**Ivan Rusyn & Weihsueh Chiu** TAMU Veterinary Medicine and Biomedical Sciences

Endocrine Disruption Exchange (TEDx): **Carol Kwiatkowski, Kim Schultz, Ashley Bolden**

# Updated Database

- Updated lit review
  - Updated through 11/12/2019
  - Re-ran search terms:
    - 2544 citations → 181 citations
  - 1358 PW chemicals

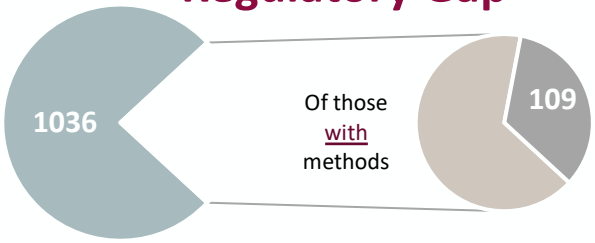


# Knowledge Gaps

## EDF Database (updated): 1358 produced water chemicals (national)

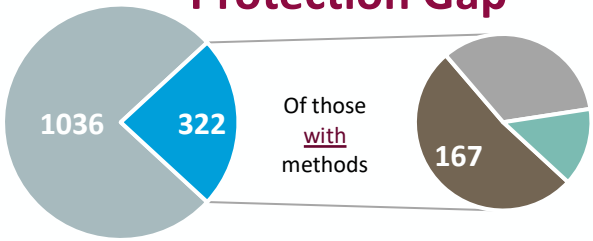
We lack EPA-approved analytical methods for ~76% *(over 1,000 chemicals)*

### Regulatory Gap




*109 (8% of total PW chemicals)* are covered by existing federal CWA criteria, guidelines, Priority Pollutant lists

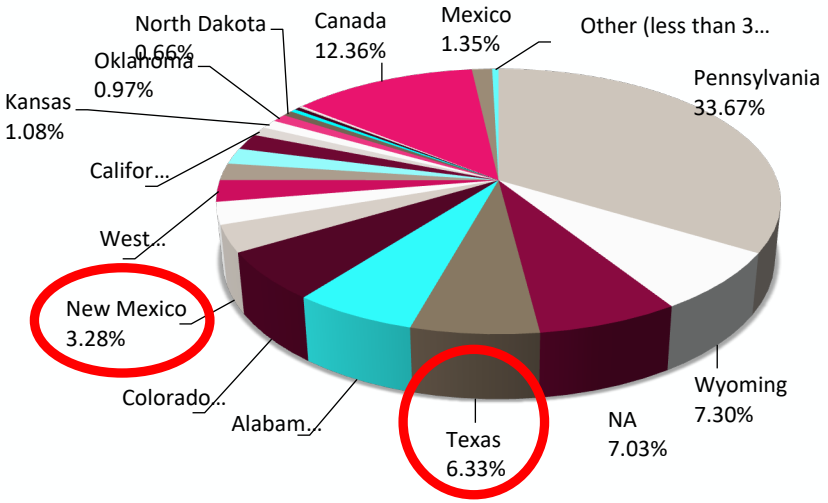
### Protection Gap




~12% of produced water chemicals have a method & have toxicity data but lack a federal water quality standard or criteria

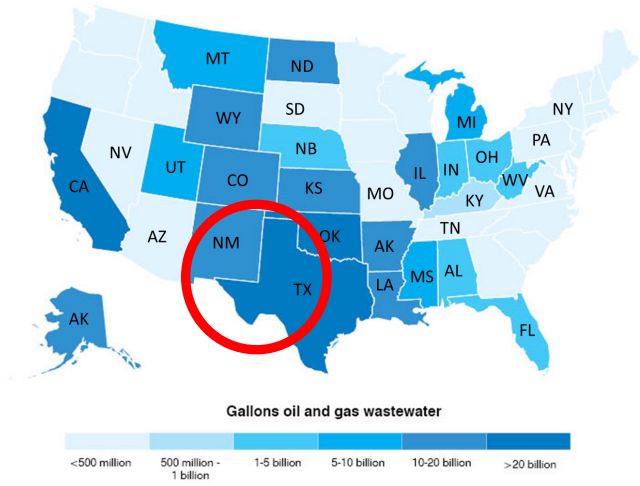
# Importance of Regional Data

**Distribution of Produced Water Studies by State**




Note: States producing high volumes & most heavily investigating reuse are underrepresented in published produced water studies (<10%).

**Produced water intensity map developed using data from Veil 2020**



# Analytical Sampling List
# Critical Element in Pilot Testing Program

- Sufficient effluent monitoring to evaluate treatment efficacy and reliability

- Sufficient time period to determine capabilities and limitations of treatment technology
  - Produced water is highly variable

- Sufficient evaluations to more accurately evaluate total treatment costs
  - Power cost
  - Operation and maintenance cost
  - Solids management costs

# Objectives of the Water Quality Working Group

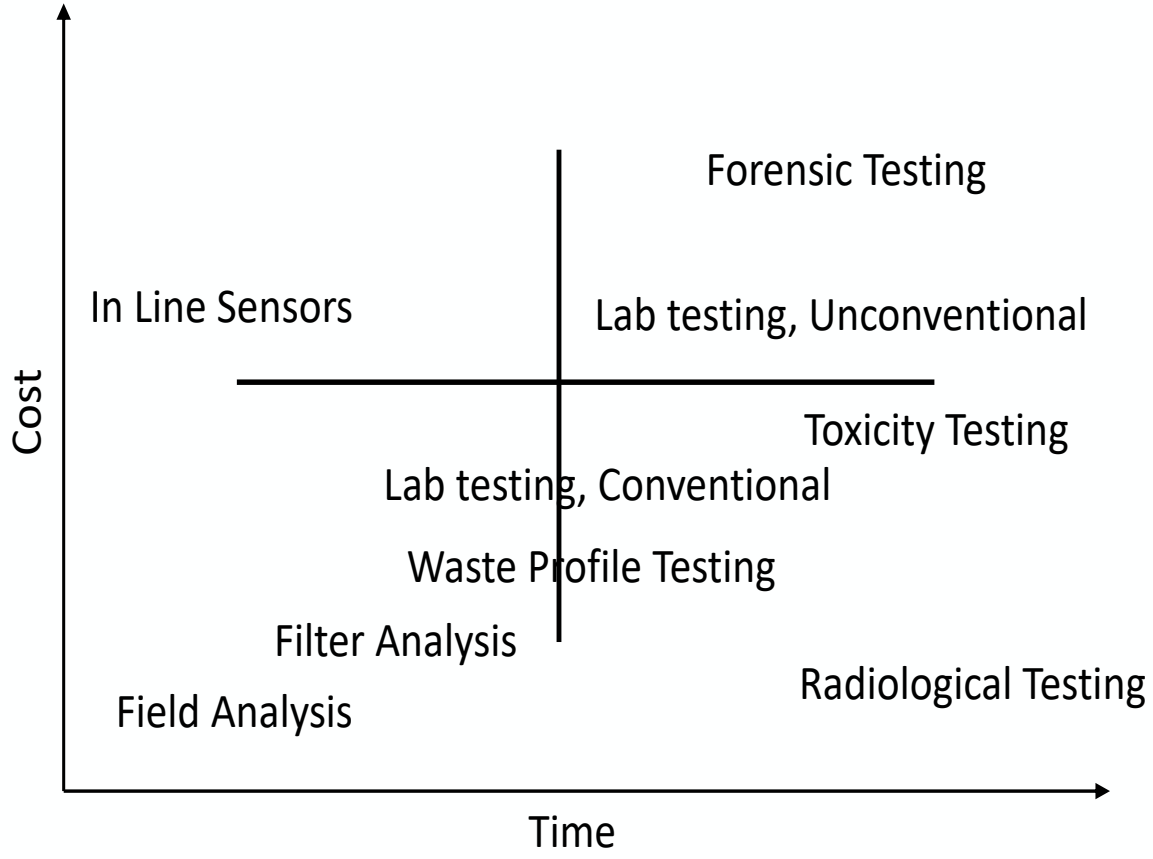
- Identify PW analytical sampling list to provide interim treatment guidance for bench- and pilot testing projects
  - Comprehensive characterization of produced water and treated water quality
  - Protection of environment and public health
  - Provide timely monitoring and cost-effective analysis of water quality
- Fill scientific and technical knowledge gaps on understanding water quality that are necessary to assist in establishing regulations and policies for the treatment and reuse of produced water

# Methodology

- Conduct literature review, document water quality requirements for discharge and beneficial use of treated produced water
  - Case studies of water regulations (surface water and groundwater) and PW discharge criteria in nine states: NM, CA, OK, CO, TX, PA, OH, WV, and WY
  - Beneficial use standards for drinking water, irrigation, wildlife and livestock, road spreading, aquaculture, land application, industrial uses (e.g., reuse in O&G field, power plants)
- Conduct literature review on analytical methods for target and non-target analysis, and collect and analyze PW quality
- Request for information on analytical capabilities of commercial labs and universities
- Biweekly meetings in 2020 and 2021 with ~ 20 working group members to review and discuss water quality analysis and criteria

# Treatment Testing and Evaluation Program Plan

- **Multi-tiered approach for produced water characterization**




The cost and turnaround time of produced water analysis

# Treatment Testing and Evaluation Program Plan

- **Multi-tiered approach for produced water characterization**

| Level | Use | Parameters | Frequency | Costs/Sample |
|---|---|---|---|---|
| **Tier 1** | Continuous monitoring, bulk testing, rapid analysis, process control | Flow<br>TSS/Turbidity<br>TDS/EC<br>TOC/DOC/COD<br>pH<br>ORP<br>Iron (total, dissolved, $Fe^{2+}$)<br>$H_2S$<br>$NH_3$<br>Alkalinity<br>Hardness (total, dissolved)<br>Specific gravity<br>Percent Moisture<br>Optional: UV-Vis, Fluorescence excitation-emission matrix (F-EEM) | Baseline, real-time, continuous, and routine | Feed/produced water<br><br>Product water |

# Treatment Testing and Evaluation Program Plan

- **Multi-tiered approach for produced water characterization**

| Level | Use | Parameters | Frequency | Costs/sample |
|---|---|---|---|---|
| **Tier 2** | Detailed characterization, routine monitoring, and Tier 1 data verification | **Inorganics**<br>• Metal elements (33), SW-864 6020A, dissolved, total Hg, SW-846 7470<br>• Anions (7), EPA 300<br>  • Optional: iodide and bromate<br>• Radionuclides<br>  • Radium 226, 228<br>  • Gross Alpha/Beta<br>  • U 235, 236, 238<br>  • Strontium 90<br>  • Optional/1-2 screening testing<br>  • Gamm Scan<br>  • Thorium Th228, 230, 232<br>  • Lead 210 | Baseline (at least once)<br>Demonstrating treatment efficacy and reliability, beneficial reuse investigation | Feed/produced water<br>Product water |

# Treatment Testing and Evaluation Program Plan

- **Multi-tiered approach for produced water characterization**

| Level | Use | Parameters | Frequency | Costs/sample |
|---|---|---|---|---|
| **Tier 2** | Detailed characterization, routine monitoring, and Tier 1 data verification | **Organics**<br>• Oil and Grease<br>• GRO [C6-C10] by 8015D<br>• DRO [C10-C28] by 8015D<br>• MRO (C28-40) by 8015D<br>• VOCs SW-846 8260 (91)<br>• SVOC - General by 8270E (139)<br>• SVOC - TPH by 8015 (8)<br>• 1-2 samples for screening:<br>  • VOC - TPH by 8015<br>  • SVOC - Explosives by 8330B<br>  • SVOC - Agent Breakdown Products<br>  • SVOC - Pesticides/Herbicides by 8081B<br>  • SVOC - Polychlorinated biphenyls (PCBs) (8280A)<br>  • SVOC - PAHs<br>  • SVOC - Organic Acids by 8015D<br>  • SVOC – Dioxins<br>  • TOX by SW 846 9020<br>  • PFOA, PFOS & PFHxS by EPA 537.1 Modified | Baseline (at least once), Demonstrating treatment efficacy and reliability, beneficial reuse investigation | Feed/ produced water<br><br>Product water |

# Treatment Testing and Evaluation Program Plan

- **Multi-tiered approach for produced water characterization**

| Level | Use | Parameters | Frequency | Costs |
|---|---|---|---|---|
| **Tier 2** | Detailed characterization, routine monitoring, and Tier 1 data verification | **Others/Optional**<br>• Cyanide, Total<br>• As3 and As5<br>• Se4 and Se6<br>• Cr3 and Cr6<br>• SM5540C - Methylene blue active substances - anionic surfactants<br>• Asbestos by EPA 100.1 or 100.2<br>• Rare earth elements | Baseline, Demonstrating treatment efficacy and reliability, beneficial reuse investigation | |

# Treatment Testing and Evaluation Program Plan

- **Multi-tiered approach for produced water characterization**

| Level | Use | Parameters | Frequency | Costs/sample |
|---|---|---|---|---|
| **Tier 3** | Risks and toxicology assessment<br><br>Fate/transport modeling. | WET Testing Acute and chronic toxicity | Phase 1 - Product water (at least once) | WET test $1500 |
| | | HiRes LC-MS non-target screening | | |
| | | Analysis of treated effluent on soil, plant, tissue samples | | |
| | | Microbial profile | Produced water and product water (at least once) | $200 |
| **Tier 4** | Waste and residual characterization | Mass balance | As needed | |

# Chemical Analysis of Produced Water

## Suspect and Nontargeted Screening with Liquid Chromatography - High Resolution Mass Spectrometry

**Robert B. Young, Ph.D.**

Director, Chemical Analysis & Instrumentation Laboratory

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NM STATE **BE BOLD.** Shape the Future.

# Outline

- Liquid chromatography - high resolution mass spectrometry (LC-HRMS) overview
- Targeted vs. non-targeted analysis
- Challenges in complex samples
- Produced water analysis

**NMSU CAIL Facility**

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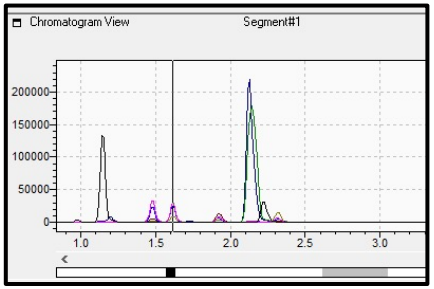
# Liquid Chromatography-Mass Spectrometry

Separates chemical mixtures

LC system

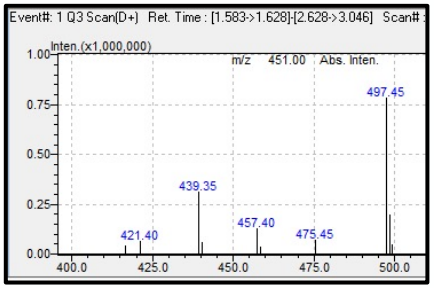
Mass spectrometer

Detects charged molecules & fragments (ions)




Retention times

- Ion abundance vs. time




Mass spectra

- Ions detected at any specific time

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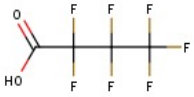
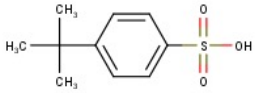
# High Resolution Mass Spectrometry

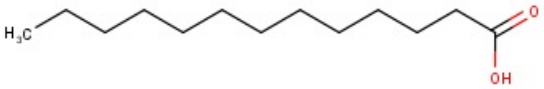
- Measures “accurate mass” from specific elemental composition to several digits
- Can produce chemical separation by mass alone



$C_4HF_7O_2$ = 213.98648 u



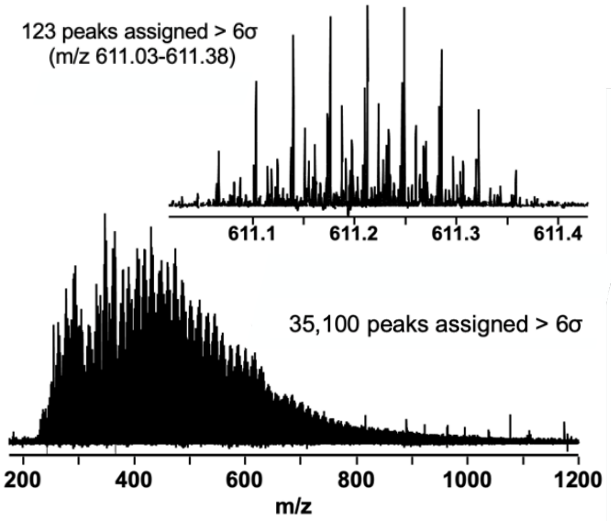
$C_{10}H_{14}O_3S$ = 214.06637 u



$C_{13}H_{26}O_2$ = 214.19328 u

All ~214 Da

**Natural Organic Matter (NOM)**




Roth et al. 2021 (in preparation)

# Targeted Analysis

Chemical standard

Analysis in Advance

- Retention time
- Characteristic fragmentation pattern
- Best ionization method
- Optimized instrument parameters

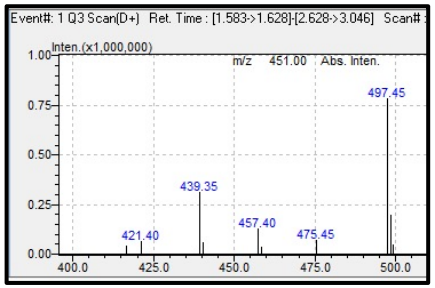
Use during Sample Analysis

- Calibration curve (determine quantities)
- Determine recovery efficiency
- Characterize matrix effects (effect of other complex sample components)

# Non-Targeted Analysis

- Benefits of chemical standards are lost
- **BUT** no need to determine targets in advance

Generic Sample Analysis




Compare accurate masses to lists of known contaminants

Suspect Screening

Compare fragmentation spectra to spectral databases

Database Matching

Contaminant lists and spectral databases are limited

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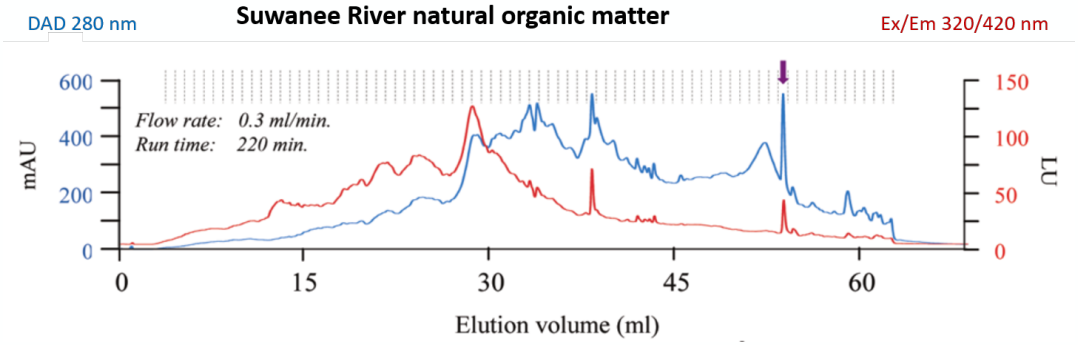
# Natural Water Samples are Complex




Woods et al., 2011, doi: 10.1021/es103425s.

No meaningful separation after > 3.5 h!

### Chemical separation

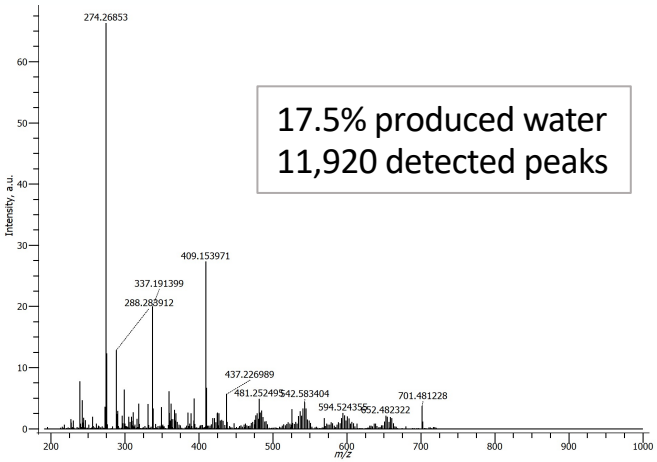
- Difficult
- Requires masses and retention times

### Characteristic mass spectra

- Convoluted without chemical separation
- Difficult to match with spectral databases

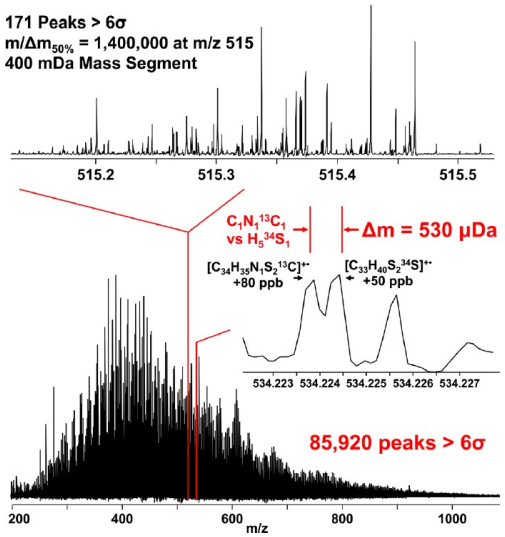
# Produced Water Samples are also Complex

- Flowback water includes injected fluids
- Produced water includes gas and oil from formation water




17.5% produced water
11,920 detected peaks

**Petroleum from Natural Seep**




McKenna et al., 2014, doi: 10.1021/ef5002452

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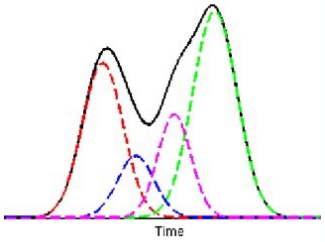
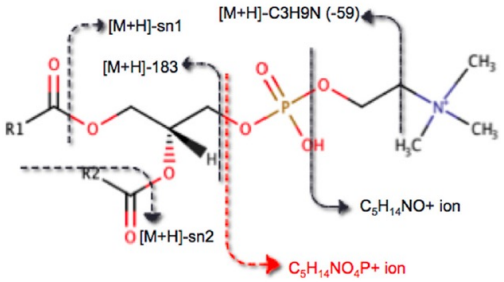
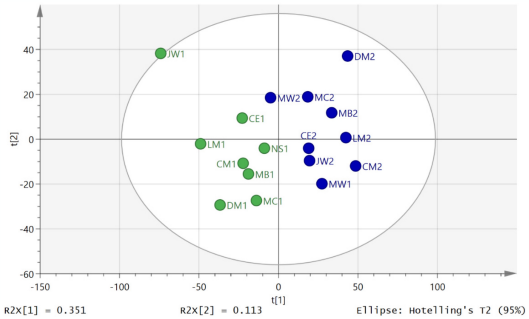
# Tools to Facilitate Analysis



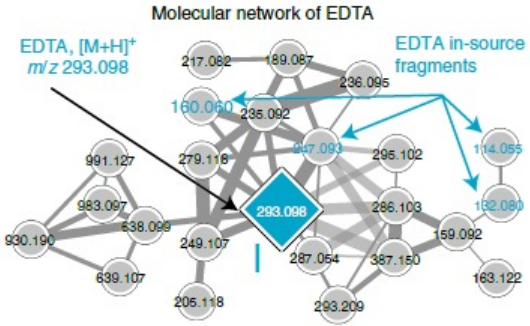

Peak Deconvolution & Alignment Software




In Silico Fragment Prediction Software




Multivariate Analyses




Feature-Based Molecular Networks

# Produced Water: Path Forward

- Improve lists of known contaminants and spectral databases
- Design studies to leverage sample differences
  - Flowback vs. produced water
  - Pre- and post-treatment
- Develop sample preparation methods to selectively analyze specific compound classes
- Other?

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# Achievements of Working Groups

- Completed the Produced Water Analytical Sampling List, and the List is under review by NMED.
- The List will be integrated with the Guidance on Produced Water Treatment Pilot Demonstration Planning, Testing, and Evaluation
- Guidance on Produced Water Sampling Procedures
- Critical review of produced water analytical methods to improve characterization and evaluation. Water, 2021. https://www.mdpi.com/2073-4441/13/2/183
- Characterization of produced water and surrounding surface water in Permian Basin for over 300 constituents, report under review
- Seven case study reports on regulatory framework and beneficial use of produced water in different states. Review completed.

# Future Research in 2022

- Work with bench and pilot PW treatment projects to implement the Analytical List
- Characterize the quality of produced water and treated water, including “unknown” constituents, and investigate if these constituents present concerns for adverse impacts to human health and environment
- Develop analytical methods to address constituents of concern potentially present in PW and treated water, and to evaluate their impacts to human health and environment
- Fill scientific and technical knowledge gaps on PW constituents that are necessary to establish regulations and policies for the treatment and reuse of produced water

# Thank you!

Dan Mueller: dmueller@edf.org

Ryan Hall: Ryan.Hall@nglep.com

Robert Young: rbyoung@nmsu.edu

Pei Xu: pxu@nmsu.edu