

Nontargeted Screening of Produced Water

Preliminary Studies of Pretreated & Treated Produced Water Samples

Himali M. K. Delanka-Pedige, Robert B. Young, Maha Abutokaikah, Lin Chen,
Mauricio Tarazona, Yanyan Zhang, Huiyao Wang, Pei Xu



BE BOLD. Shape the Future.



Outline



- Overview of nontargeted screening
- Take-away messages
- Our analytical method
- Case studies
 - Study 1: Permian Basin produced water treated via membrane distillation (MD) processes
 - Study 2: San Juan Basin produced water treated via seawater reverse osmosis (SWRO) process
 - Study 3: Permian Basin produced water treated by thermal distillation and post-treatment via granular activated carbon (GAC)/Zeolite

Big Picture Question

- How is non-targeted analysis used to characterize produced water and its reuse risks?

Analogy to a Criminal Investigation:

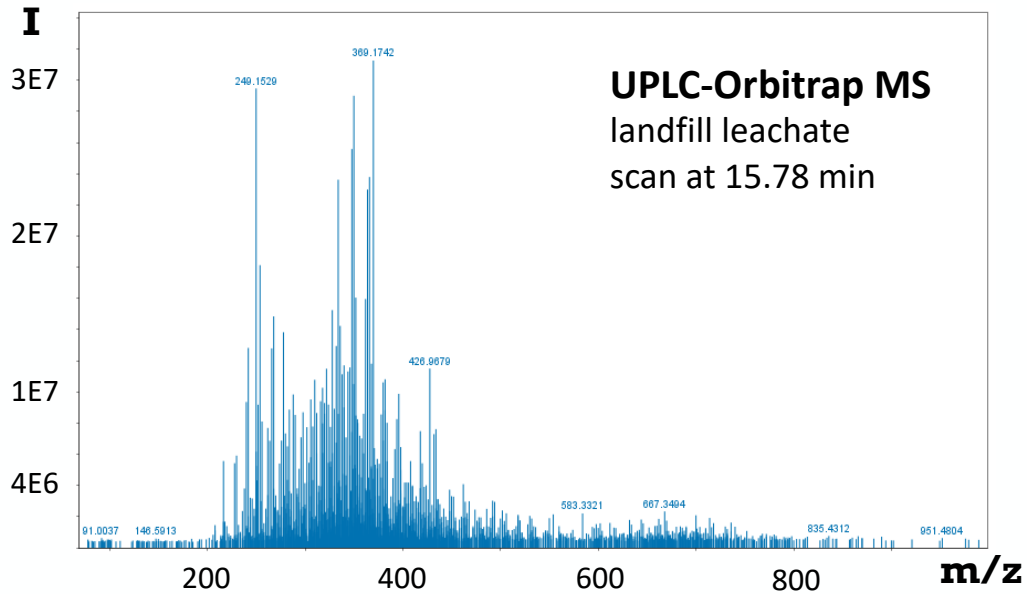
- Murder suspect (toxic chemical)
- Fingerprints } (mass spectral data)
- Blood drops }



It's like we're part of NCIS!



Population of Suspects



- Should we carefully analyze every member of the population?

This is only one moment in a 30-minute analysis!

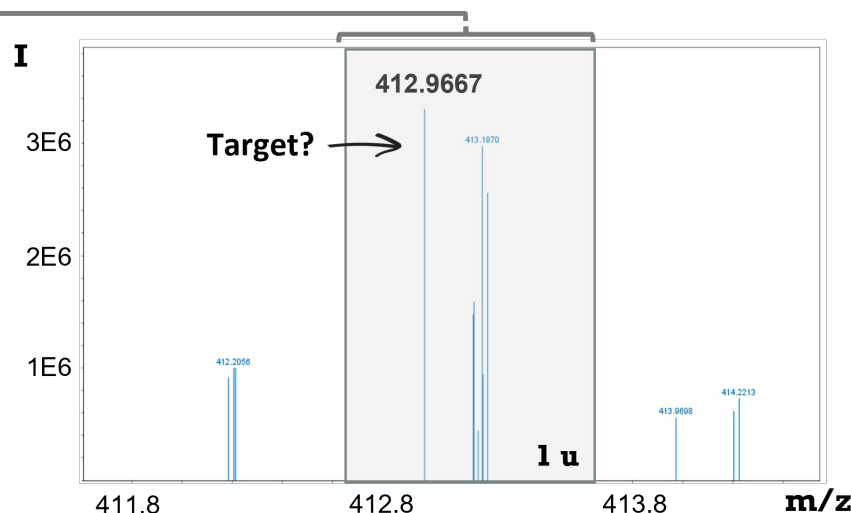
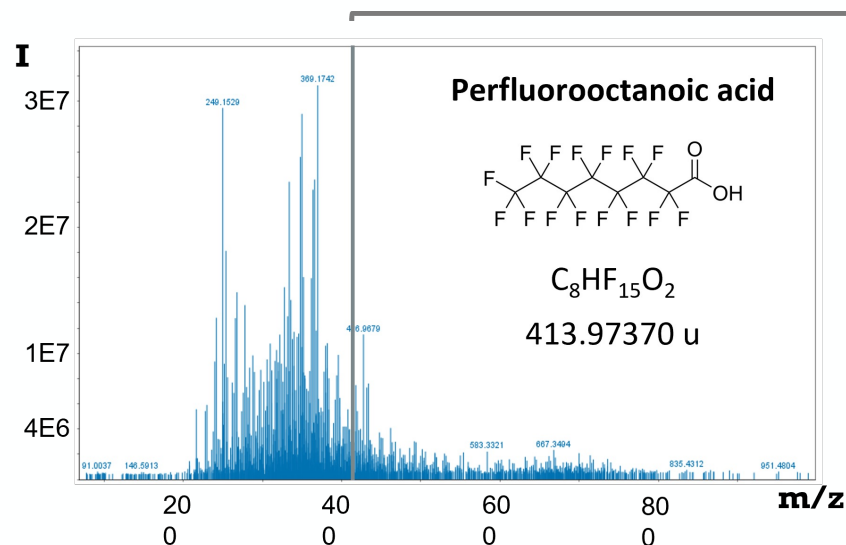


- What if we already have evidence for one or more suspects (e.g., criminal histories)?

(toxic chemicals: Chloelle Danforth's list)

Particular Suspect – Targeted Analysis

Is this a high confidence identification?



Negative ESI⁻
(deprotonated)

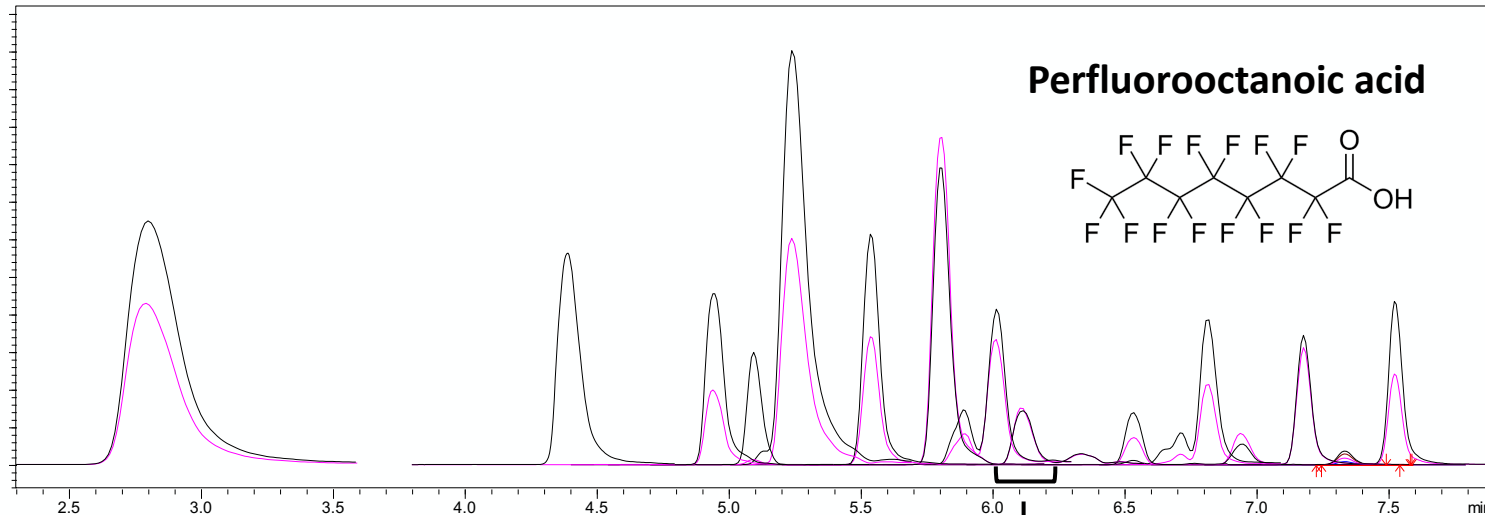
413.97370
– 1.00728
412.96642 u

No*

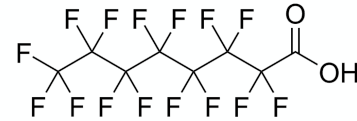
But we can add
corroborating
evidence?

- **Method:** Look at information specific to the suspect and ignore the remaining population

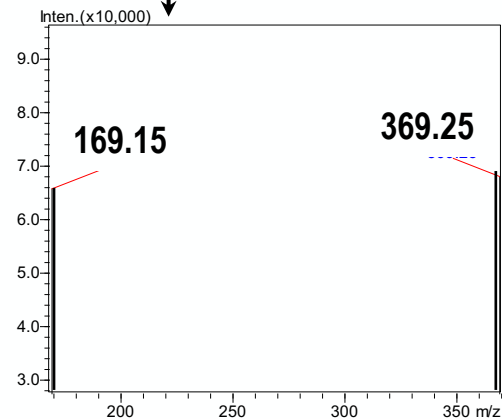
Highest Confidence – Level 1



Perfluorooctanoic acid



Ch	Precursor m/z	Product m/z	Dwell Time (msec)	Q1 Pre Bias(V)	CE
Ch1	412.9000	169.1500	29.0	15.0	16.0
Ch2	412.9000	369.2500	29.0	21.0	11.0



Advantages:

Sensitive & selective

- Limited precursors
- Limited products

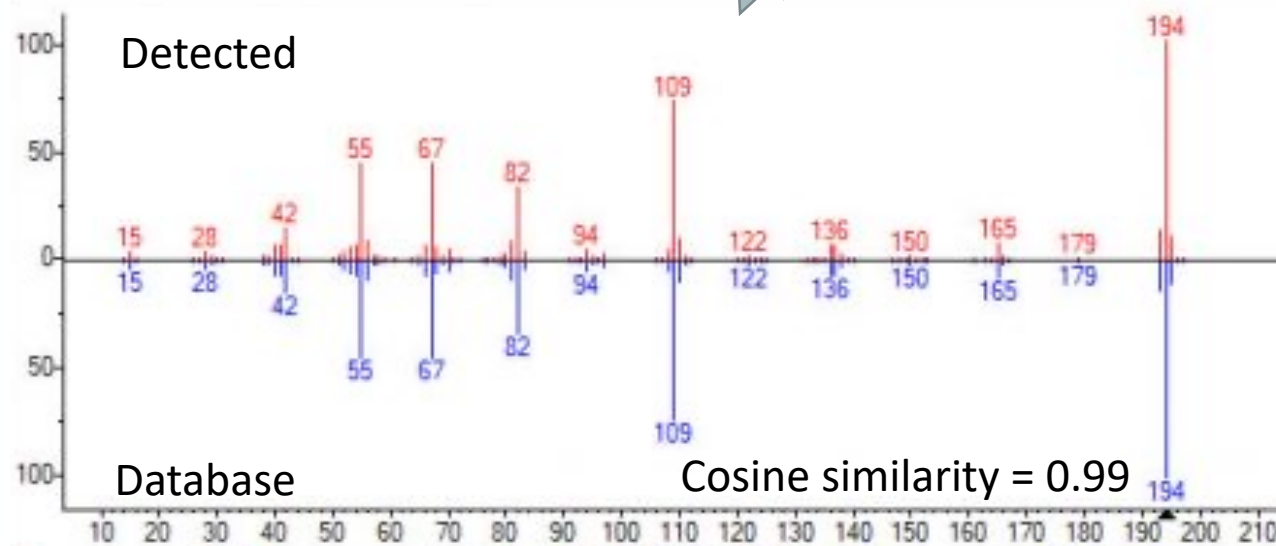
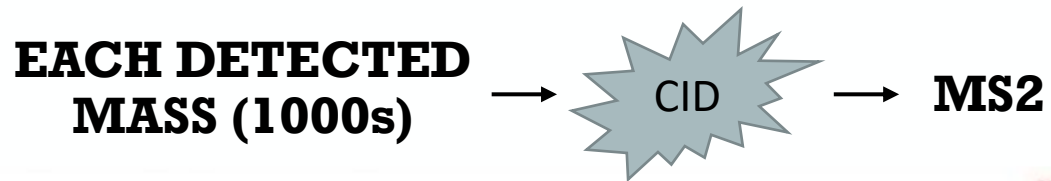
Disadvantages:

Known before analysis

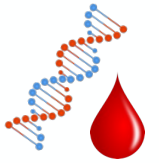
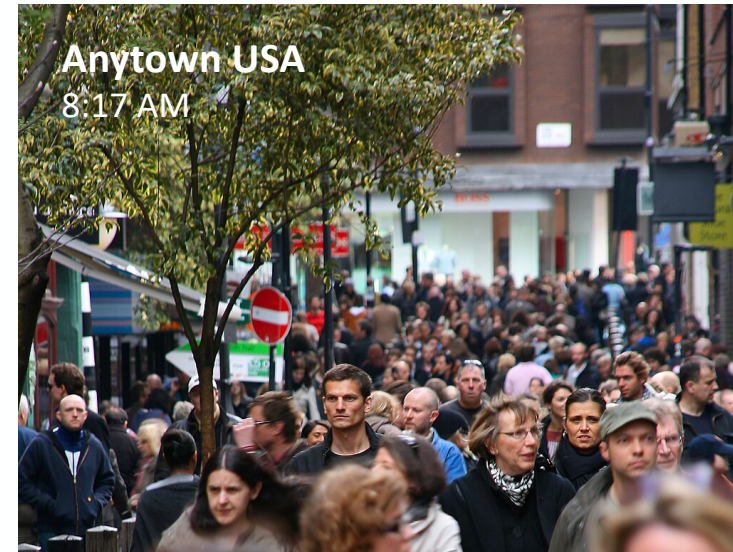
Compared to chemical standard:

- Same product ions ✓
- Same ratio ✓
- Same retention time ✓

No Particular Suspects – Nontargeted Analysis

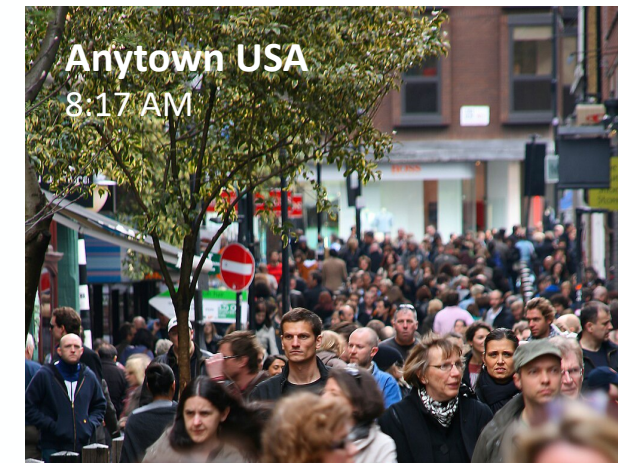
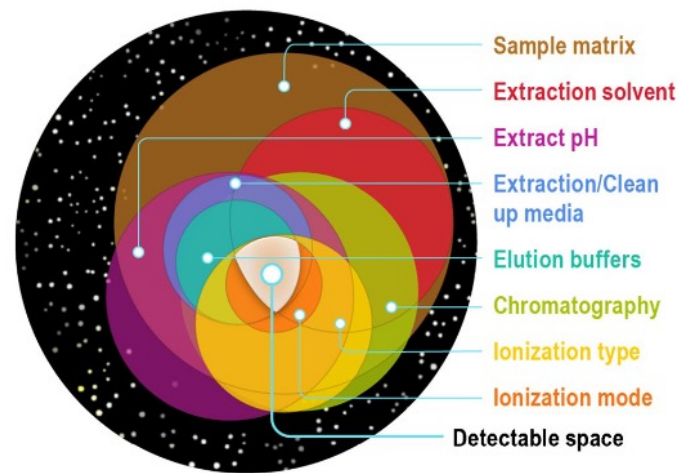
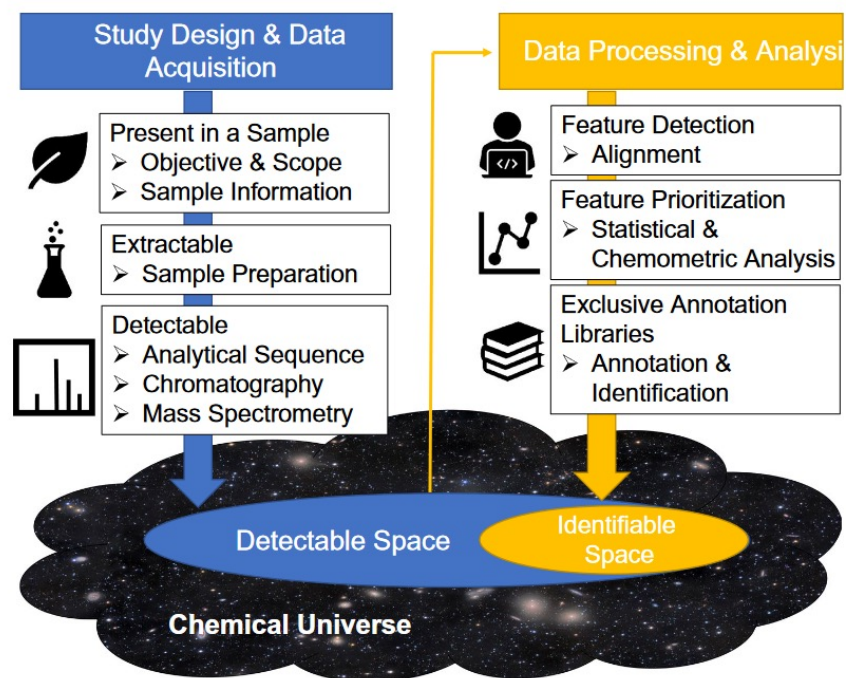


- **Method:** Database searching and more
- Spectral databases do not include all chemicals
- Cosine similarity = 0.7 sufficient?



- Fingerprint databases do not include all people
- 8-12 points of similarity are sufficient
- Similar DNA? Genetic genealogy (GNPS, Sirius)

Chemical Space



- Sample preparation, instrumentation, and databases affect what we detect & identify
- One method cannot detect all chemicals present

- Murder suspect may not even be in the population we are analyzing



Study Planning & Reporting Tools



<https://nontargetedanalysis.org>

analytical
chemistry

(e.g., what do the researchers even mean by “nontargeted analysis”)

pubs.acs.org/ac

Article

Nontargeted Analysis Study Reporting Tool: A Framework to Improve Research Transparency and Reproducibility

Katherine T. Peter,^{*} Allison L. Phillips,^{*} Ann M. Knolhoff, Piero R. Gardinali, Carlos A. Manzano, Kelsey E. Miller, Manuel Pristner, Lyne Sabourin, Mark W. Sumarah, Benedikt Warth, and Jon R. Sobus

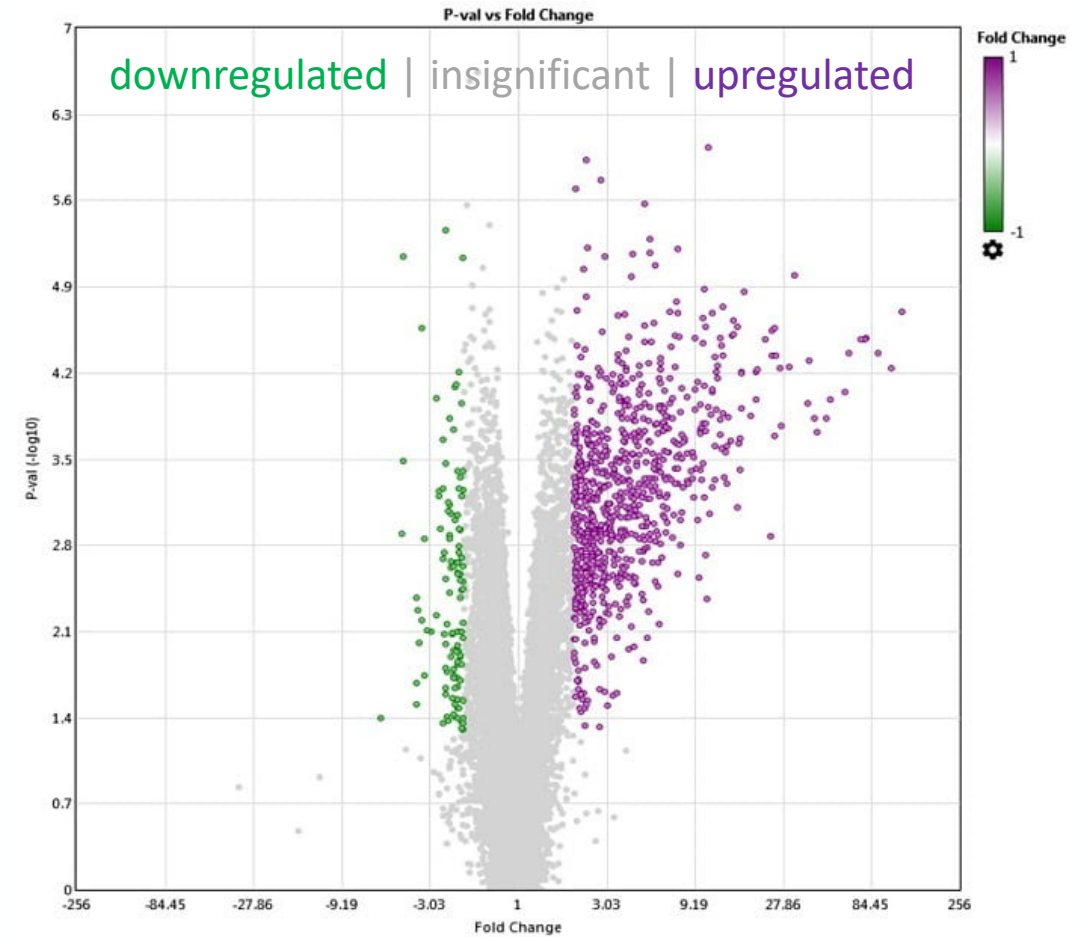
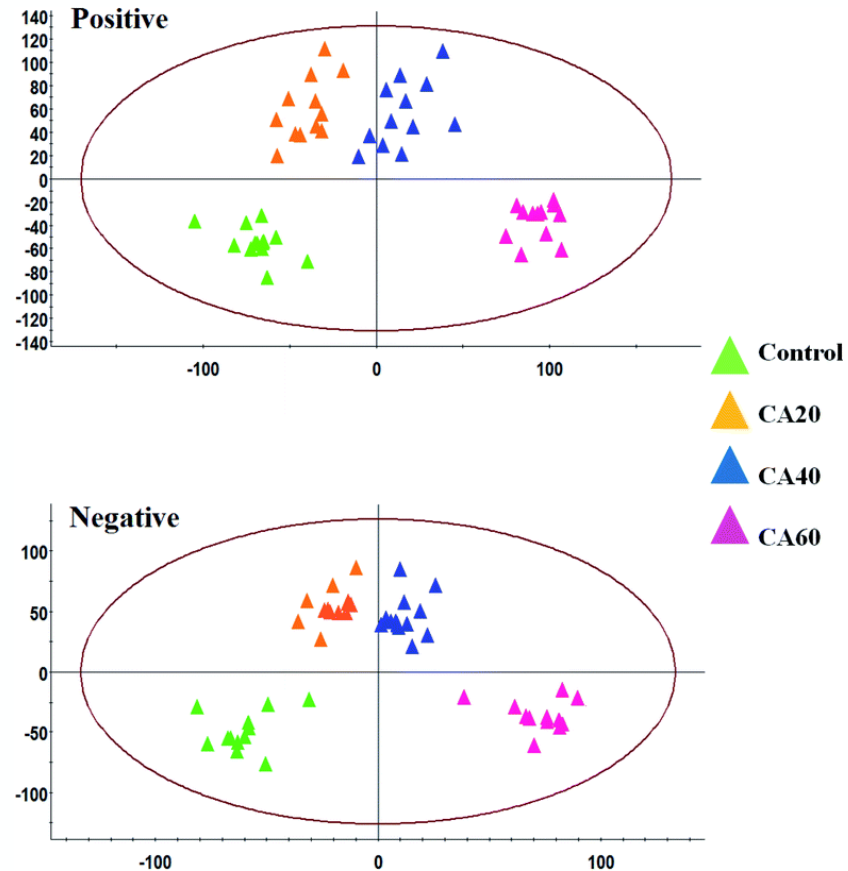
Study Planning Tool (under development)

Sample preparation, instrumental & data analysis
all vary with objectives and chemical space

Examples:

- Screen for suspects
- “Identify-everything-you-can”
- Compare treatments

Compare Treatments



- Identify components driving differences in samples
- Prioritize identifications

Our Analytical Methods

Sample
Preparation

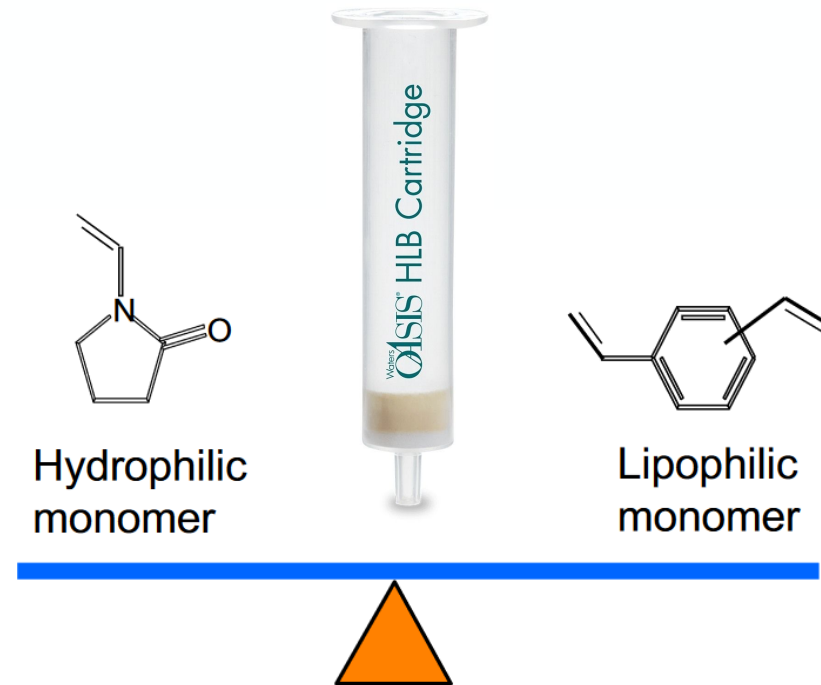
Instrumental
Analysis

Data
Analysis

Oasis HLB

Solid phase extraction

- Hydrophilic-lipophilic balanced
 - Extracts acidic, basic & neutral compounds
 - Removes salts
- Rinsed with water
- Elute with Methanol
- No pH adjustments



Sample
Preparation

Instrumental
Analysis

Data
Analysis

LC-Orbitrap MS

- C18 reversed phase chromatography
- Positive & negative nanoelectrospray ionization
- Data-dependent MS/MS collection
 - Noise threshold
 - Exclusion list
 - Apex detection

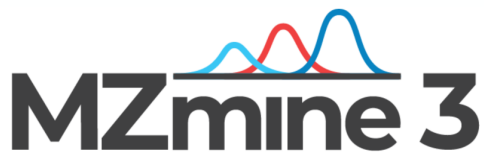


Sample Preparation

Instrumental Analysis

Data Analysis

- Open source tools
- No coding required!



- Detects precursor peaks
- Associates peaks with MS/MS spectra
- Aligns peaks across samples
- Searches MS/MS spectral databases



- Group similar MS/MS spectra into molecular networks



- Predicts molecular formulas using accurate mass, isotope patterns, and MS/MS spectra
- Predicts molecular "fingerprints" from MS/MS spectra
- Matches molecular "fingerprints" to public databases
- Predicts compound classes

Suspect List Screening

- NORMAN suspect list (109,631 entries)
- Danforth list (1198 entries)
- EPA produced water chemical list (1639 entries)

~~NCIS~~ Investigative Approach

- Focus on water-soluble contaminants amenable to LC-ESI-MS analysis (particularly in treated wastewaters)
 - Like limiting the search area
- Screen against suspect lists and databases
 - Like using criminal histories, fingerprints and DNA databases
- Sirius & GNPS to relate unknown chemicals to known ones
 - Like genetic genealogy
- Compare toxic to non-toxic samples (when available)
 - Like eliminating everyone who wasn't in the area



Application of proposed NTA methodology

- Study 1: Permian Basin produced water treated via vacuum and photocatalytic membrane distillation processes
- Study 2: San Juan Basin produced water treated via SWRO process
- Study 3: Permian Basin produced water treated via thermal distillation and GAC/Zeolite media filtration

Study 1

Sample source

- Produced water from Permian Basin

Sample pretreatment



- Electrocoagulation
- Two-stage cartridge filtration (5 μm and 0.15 μm)
- Salinity after pretreatment = 17.5% NaCl

Sample type

- Pre-treated produced water (Feed)
- Effluent after vacuum membrane distillation (VMD)
- Effluent after photocatalytic membrane distillation w/o UV treatment (PMD_UV_OFF)
- Effluent after photocatalytic membrane distillation with UV treatment (PMD_UV_ON)



Multifunctional photocatalytic membrane distillation for treatment of hypersaline produced water using hydrophobically modified tubular ceramic membranes

[Lin Chen](#)^a, [Pei Xu](#)^a, [Deepak A. Musale](#)^b, [Yanyan Zhang](#)^a, [Raed Asfan](#)^a,
[Carlos Galdeano](#)^b, [Ganesh L. Ghurye](#)^b, [Huiyao Wang](#)^a  

Study 2

Sample source

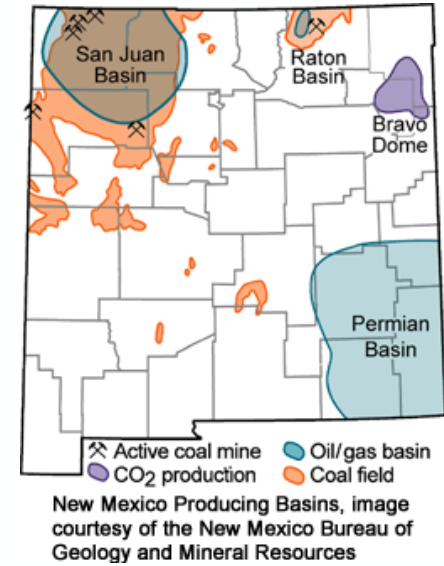
- Produced water from Eagle Springs Field in San Juan Basin – Kanalis Resources

Sample pretreatment

- Filtration (5 μ m)
- Activated charcoal filtration

Sample type

- Pre-treated produced water (Feed water)
- Product water resulting from the SWRO system (Product water)



SWRO system at the brackish groundwater national desalination research facility (BGNDRF)

Study 3

Sample source

- Produced water from Permian Basin - Crystal Clearwater Resources (CCR)

Sample pretreatment

- Hydrogen Peroxide (H₂O₂) injection
- Filtration with basket strainer with a 1/16" mesh screen

Sample type

- CCR feed water
- CCR distillate from Low Temperature Distillation (LTD[®])
- Effluent after Zeolite media filtration
- Effluent after GAC and Zeolite media filtration



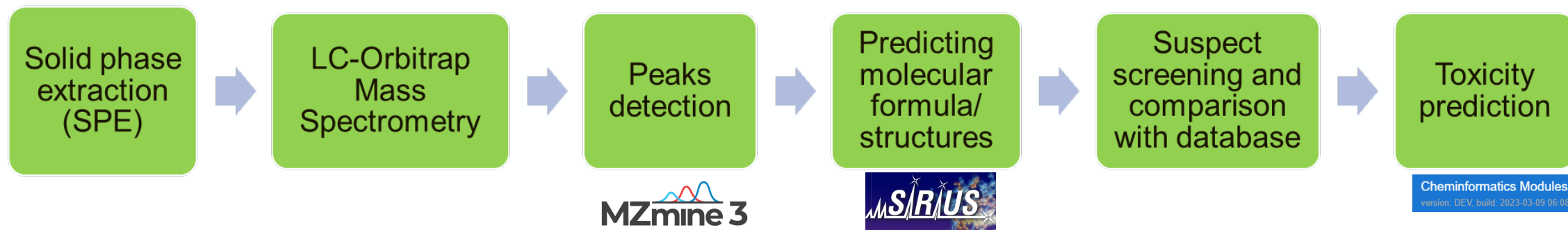
<https://permianpartnership.org/>



Low temperature distillation (LTD[®]) system (captured from Crystal Clearwater Resources Final Technical Completion Report)

Nontargeted Analysis Summary

- Proposed NTA pathway preliminary contaminant identification:



- Proposed methodology helps identify potential targets for follow up targeted analyses
- Ability to identify human health, ecological and environmental fate-based concerns associated with compounds helps to prioritize chemicals
- Makes water quality assessment cost efficient

Nontargeted Analysis Summary

- We are using the best available technology
- We can accurately identify chemicals that aren't currently being targeted
- Every nontargeted analysis has limitations
- Level of confidence in identifications varies
- Nontargeted analysis helps to identify relevant targets
- Nontargeted analysis helps to make risk assessment defensible

Acknowledgements

- New Mexico Produced Water Research Consortium (NMPWRC) for research leadership and funding
- Bureau of Reclamation DWPR program (R22AC00428) for funding
- Brackish Groundwater National Desalination Research Facility (BGNDRF) for supporting and allowing us use their facility and SWRO pilot system.
- Kanalis Resources for providing pre-treated PW from San Juan basin.
- Crystal Clearwater Resources (CCR) for providing PW from Permian basin and distillate samples

Thank you

Robert B. Young

Director, Chemical Analysis & Instrumentation
Laboratory

Research Cores Program, Office of the Vice
President for Research

(917) 620-8154

rbyoung@nmsu.edu

Himali M. K. Delanka-Pedige

Postdoc, Department of Civil Engineering

New Mexico State University

(575) 650-1873

himalimk@nmsu.edu



BE BOLD. Shape the Future.

