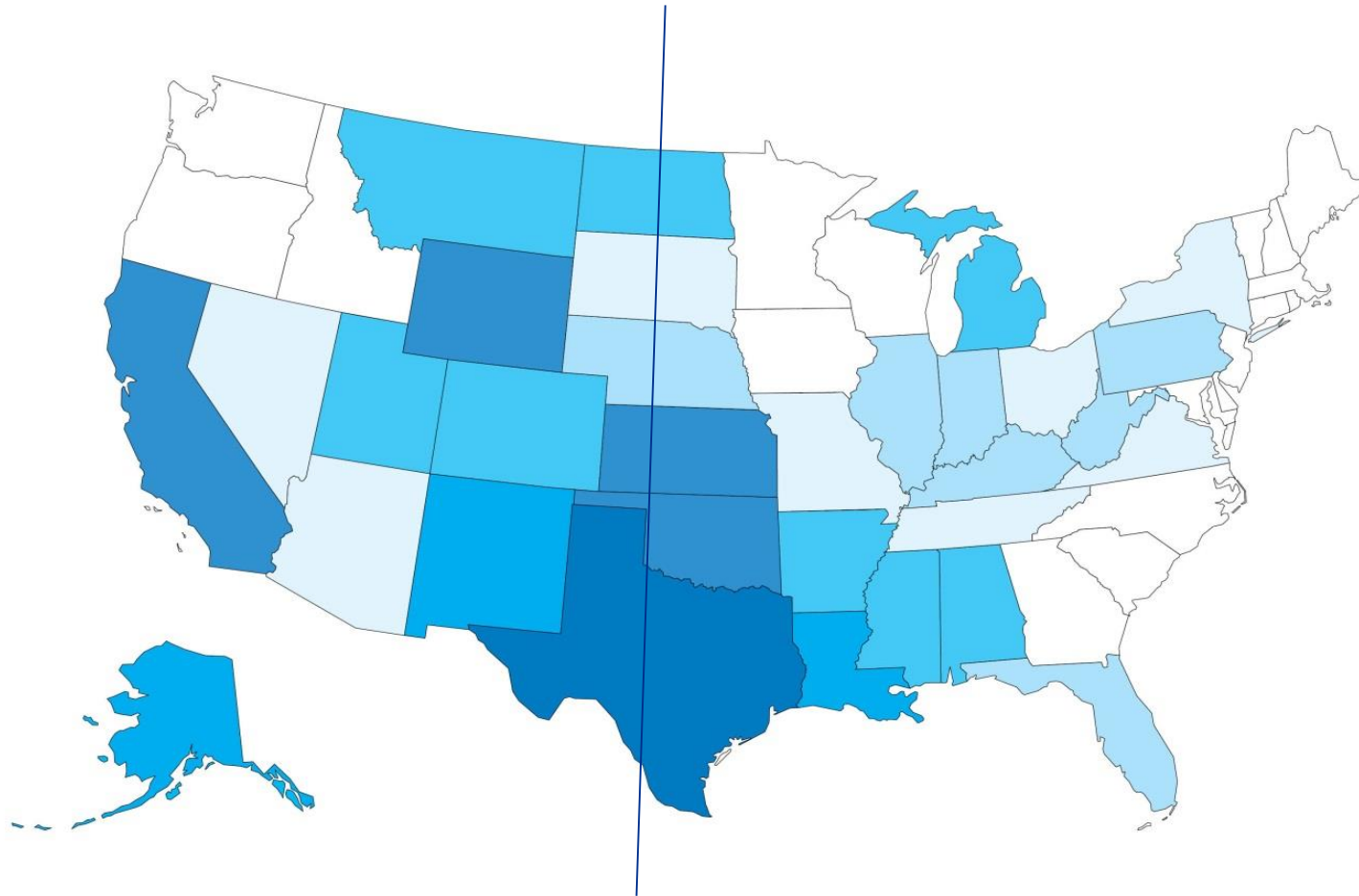


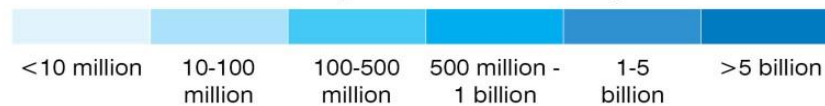
Research Strategies to Identify and Address Risks from Produced Water Reuse Outside the Oilfield

Cloelle Danforth, PhD

Wastewater production intensity



Billion barrels* of produced oil and gas wastewater



2018

- EPA HQ launches a study looking at state and industry interest in an expansion or modification of federal effluent limitation guidelines for PW
- Permian Basin – bottlenecks, seismicity, capacity
- New Mexico and EPA enter joint-MOU on produced water
- DOE launch of Water Security Grand Challenge (2030):
 - #2. Transform the energy sector's produced water from a waste to a resource

What are the gaps?

DETECTION

We struggle with finding chemicals that may be present in oil & gas wastewater...

AWARENESS

...which means we don't know exactly which chemicals or what amounts may be present because we can't find what we aren't looking for...

EXPOSURE

...which means we aren't researching who/what may come in contact with those chemicals...

HAZARDS

...so we can't determine whether chemicals are present at dangerous levels...

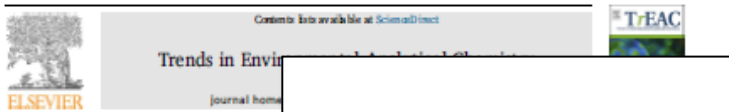
PROTECTION

...which means we don't have the information needed to treat or regulate unsafe chemicals and advance detection efforts....



EDF Science Partners

- Karl Linden, Mike Thurman, University of Colorado/Boulder
 - Biological treatment, chemical characterization
- Thomas Borch, Jens Blotevogal, J. Lucas Argueso, Colorado State University
 - Toxicity bioassay, soil health study
- Motoko Mukai, Cornell University
 - Toxicity bioassay (Zebrafish)
- Kartik Chandran, Columbia University
 - Microbial characterization for biological treatment
- Damian Helbling, Cornell University
 - Chemical Characterization
- April Gu, Cornell University
 - Toxicity bioassay
- Chris Higgins, Colorado School of Mines
 - Chemical characterization
- Nancy Denslow, University of Florida
 - Toxicity bioassay
- Bryan Brooks, Baylor University
 - Chemical characterization, toxicity identification evaluation
- Robert Tanguay, Oregon State University
 - Toxicity bioassay
- Mark Engle, Aaron Jubb, USGS
 - Chemical characterization (inorganic)
- Joe Ryan, Colorado State University
 - Database development/expansion
- Ivan Rusyn, Weihsueh Chiu, Texas A&M
 - QSAR, toxicity profiling of database



Emerging analytical methods for the organic contaminants in flowback and produced water

Karl Oetjen^a, Cloelle G.S. Giddings^b, Molly M. Damian E. Helbling^c, Dan Mueller^d, Christopher

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^b Environmental Engineer, New York, NY, USA
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^d School of Civil and Environmental Engineering, Cornell University, Ithaca, NY, USA

ARTICLE INFO

Keywords: Hydraulic fracturing; Oil and gas operations; Produced water; Liquid chromatography; Mass spectrometry; High-resolution mass spectrometry; Produced water

ABSTRACT: Flowback and produced water (FPW) contains a complex matrix of organic and inorganic compounds, including carbonates, organics, and heavy metals. These compounds can be toxic to the environment and to the health of humans. However, due to the large volume of FPW produced, it is often difficult to monitor and manage. This paper describes a new method for the detection and identification of organic compounds in FPW using liquid chromatography/mass spectrometry (LC/MS). The method involves the use of a high-resolution mass spectrometer to detect and identify organic compounds in FPW. The results show that the method is capable of detecting and identifying a wide range of organic compounds in FPW, including those that are not detectable by other methods.

1. Introduction

Hydraulic fracturing (HF) is a process used in the oil and gas industry to increase oil, natural gas, and water production from low-permeability rock formations. Horizontal fracturing, often at high-volume HF, is the preferred method for removing oil and gas from low-permeability rock formations, including shale gas. After HF, a portion of the fracturing fluid returns to the surface as flowback produced water, referred to here as oil and gas (O&G) water. As O&G exploration and development continues in the US, large quantities of wastewater are produced along with oil and gas. The United States produces 870 billion gallons of water annually from O&G activities [1]. It has been argued that produced water from O&G operations could potentially be a new water source in areas of water scarcity [2,3]. Although there are many uses for these waters, they contain numerous synthetic and geogenic constituents and

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<https://doi.org/10.1016/j.tenac.2017.07.002>
 Received 20 March 2017; Received in revised form 9 June 2017; Accepted 22 June 2017
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Environmental Science Processes & Impacts

PAPER

Check for updates

Cite this: DOI: 10.1039/c8em00155a

Exploitation of unconventional gas

Marika N. ...
 Hydraulic fracturing (HF) is a process used in the oil and gas industry to increase oil, natural gas, and water production from low-permeability rock formations. Horizontal fracturing, often at high-volume HF, is the preferred method for removing oil and gas from low-permeability rock formations, including shale gas. After HF, a portion of the fracturing fluid returns to the surface as flowback produced water, referred to here as oil and gas (O&G) water. As O&G exploration and development continues in the US, large quantities of wastewater are produced along with oil and gas. The United States produces 870 billion gallons of water annually from O&G activities [1]. It has been argued that produced water from O&G operations could potentially be a new water source in areas of water scarcity [2,3]. Although there are many uses for these waters, they contain numerous synthetic and geogenic constituents and

Received 24th March 2018
 Accepted 15th May 2018
 DOI: 10.1039/c8em00155a
 rsc.li/epi

Environmental significance

The complex matrix of hydraulic fracturing (HF) fluids is a major environmental concern. The essential prerequisite to evaluate wastewater disposal matrix recovery factors for seventeen priority HF fluids. Our approach allows us to overcome the one-dimensional view of HF fluids and shale formations.

Introduction

The use of hydraulic fracturing (HF), commonly known as fracking, has led to a boom in unconventional oil and gas production over the course of the past decade. The United States (US) sought to become a

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[†] Electronic supplementary information (ESI) available: See DOI: 10.1039/c8em00155a

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Identification of Produced Wastewater Flight Mass Spectro

Kurban A. Sitterley^a, Karl G.

Department of Environmental Engine

Supporting Information

ABSTRACT: This work describes poly(ethylene glycol)s, amino-poly(ethylene glycol)s, and amino-poly(ethylene glycol)s produced water samples from hydraulic fracturing operations in the western United States. These compounds, with m/z 120–986, were identified using high-resolution flight mass spectrometry. The poly(ethylene glycol)s gave good recovery for all three extraction and liquid chromatography methods. The poly(ethylene glycol)s were identified as the mass spectral signal of the mass spectral signal of the fragmentation pathways, and pure confirmation. Finally, because these proprietary surfactant blends, their toxicity of hydraulic fracturing wastewater.

Exploitation of unconventional gas, such as coalbed methane, has surged in recent years. Commonly used to access these formations involves drilling a well, either vertical or horizontal, and injecting a fracturing fluid at sufficient pressure to fracture the formation and allow oil and gas to flow. The escape of methane gas has led to concerns about the dangers of contamination near the well and explosions possible.¹ A second concern is that the fluid that can mix with the native geologic formation and subsequently produce gas.

The laws regarding disclosure of chemicals used in fracturing fluid vary from state to state.² Even in states that require disclosure, operators use vague terms and claim some additives as proprietary, listing only a general description or purpose. To date, the identity of these proprietary chemicals is largely unknown. Therefore, having appropriate analytical methods available that are capable of detecting and identifying proprietary compounds from hydraulic fracturing fluid is a critical tool in environmental monitoring, and is one of the challenges for the analytical chemistry of hydraulic fracturing fluids.

Liquid chromatography/mass spectrometry (LC/MS) has been the most effective instrumentation for analysis of wastewater associated with hydraulic fracturing, while gas chromatography/mass spectrometry (GC/MS) is the most



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



Succession of toxicity and microbiota in hydraulic fracturing flowback and produced water in the Denver–Julesburg Basin

Natalie M. Hull^a, James S. Rosenblum^a, Charles E. Robertson^b, J. Kirk Harris^c, Karl G. Linden^{a,*}

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^b University of Colorado School of Medicine, Anschutz Campus, Division of Infectious Disease, Aurora, CO 80045, USA
^c University of Colorado School of Medicine, Anschutz Campus

HIGHLIGHTS

- Horizontal drilling and hydraulic fracturing generate flowback and produced water (FPW).
- FPW toxicity and microbiota were characterized for 220 days in the Denver–Julesburg Basin.
- Temporal trends were similar between FPW toxicity and microbial communities.
- Fracking conditions are toxic and selective with long term ecological & industrial impacts.

ARTICLE INFO

Article history:
 Received 13 April 2018
 Received in revised form 5 June 2018
 Accepted 6 June 2018
 Available online xxxxx

Editor: Frederic Coulon

Keywords:
 Fracking
 In vitro bioassay
 Flowback
 Produced water
 16S rRNA gene amplicon sequencing

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<https://doi.org/10.1016/j.scitotenv.2018.06.067>
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Environmental Science: Processes & Impacts

View Article Online
 DOI: 10.1039/c8em00291f

Degradation of polyethylene glycols and polypropylene glycols in microcosms simulating a spill of produced water in shallow groundwater

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ENVIRONMENTAL SIGNIFICANCE STATEMENT

Given the frequency of surface spills of produced fluids from unconventional oil and gas operations, there is a need to better characterize resulting groundwater contamination. Produced fluids are known to have complex and variable chemical and microbial composition that could influence contaminant fate and transport in groundwater; however, studies on the behavior of compounds measured in produced water under environmentally-relevant conditions are limited. This study investigates degradation pathways and kinetics of the frequently-used ethoxylated surfactants polyethylene glycol and polypropylene glycol under conditions simulating a release to shallow groundwater of produced water from two hydraulically-fractured oil and gas wells at varying production times. These results may be utilized to better characterize shallow groundwater contamination following a release of produced water.

been carried out for application to wastewater. Thus, the work of sample preparation, several goals. contain salt levels so is necessary to design analysis in order to detect and identify surfactants. Some of

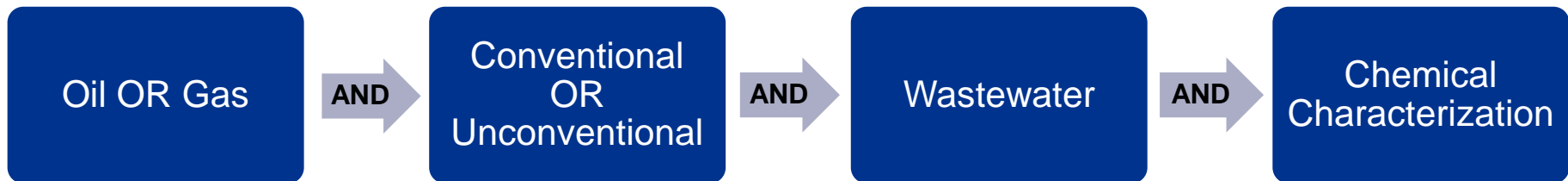
Received: May 31, 2018
 Accepted: August 24, 2018
 Published: August 24, 2018

On-going work

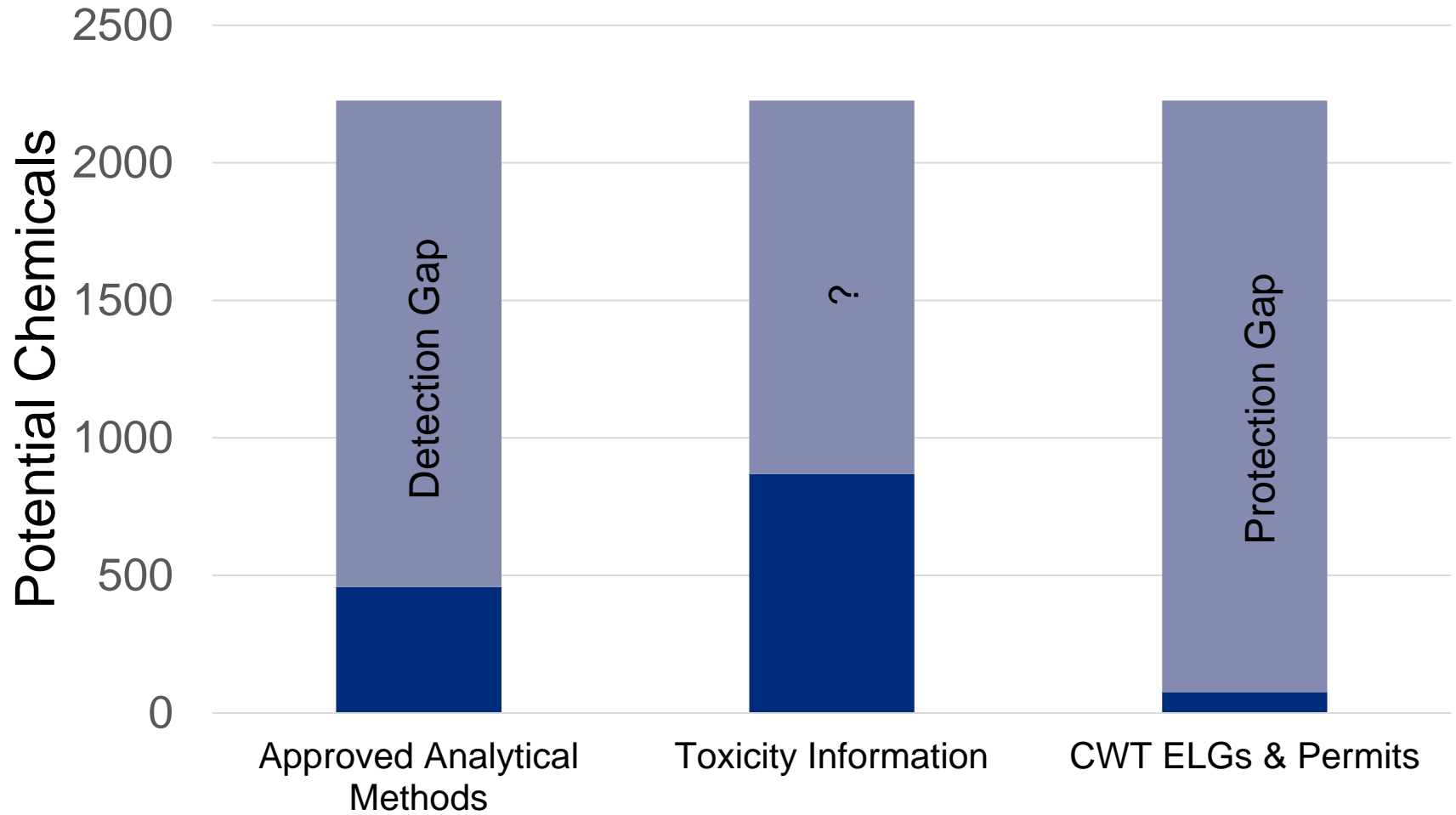
- Characterization
 - Comparing trace element quantification methods
 - Identification of recalcitrant biological compounds
 - Metabolic structure/function of MOs in various produced waters
- Treatment
 - Using enrichments to treat organics in hyper-saline wastewater; identifying MO community
 - Understanding metabolic function of halophilic microorganisms in degrading COCs in PW
- Toxicity
 - Toxicity identification evaluation of produced waters of different production ages
 - Early Life Effects of Produced Water on *Menidia beryllina*
 - Toxicity of produced water before/after various benchtop treatment schemes
 - Toxicological characterization of surface water impacted by discharge of minimally treated produced water
 - High-throughput Mechanistic Toxicity Assessment of Produced Water

Literature Review Objectives

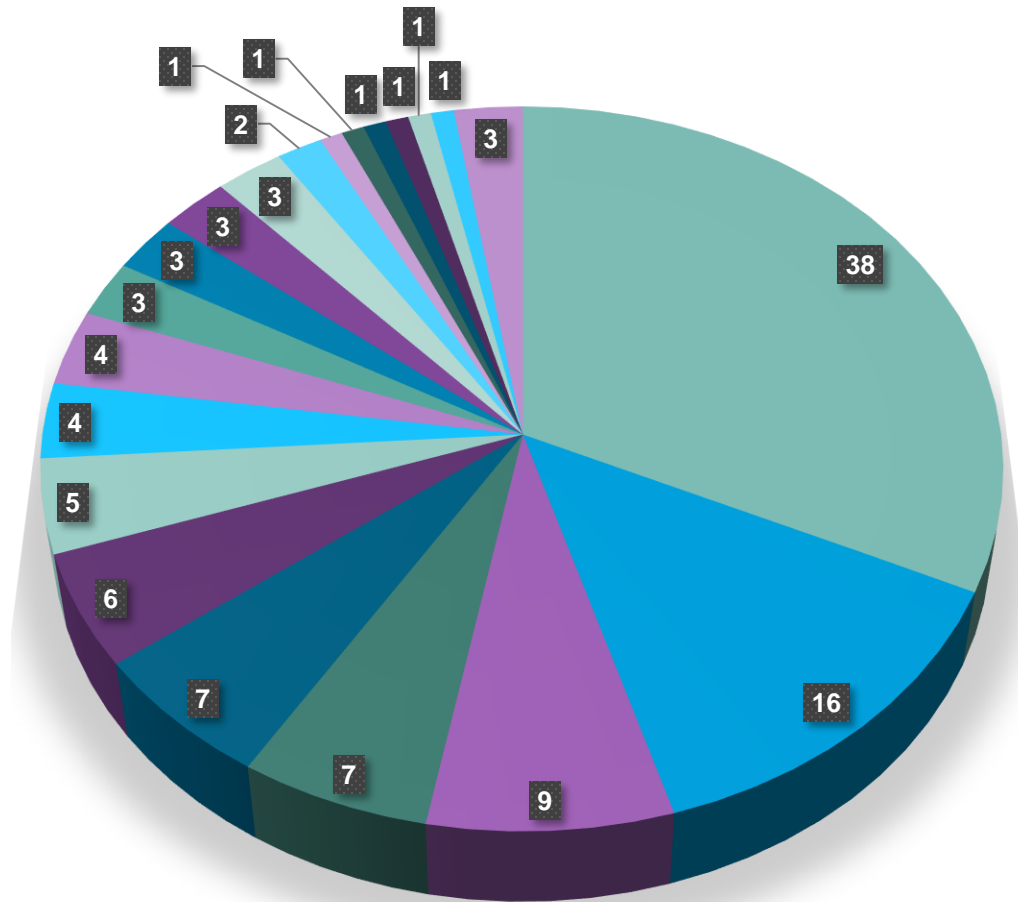
- Identify chemicals detected in wastewater from on on-shore oil and gas operations
- Prioritize based on known/unknown toxicity hazards
- Search logic:



Data Gaps & Produced Water

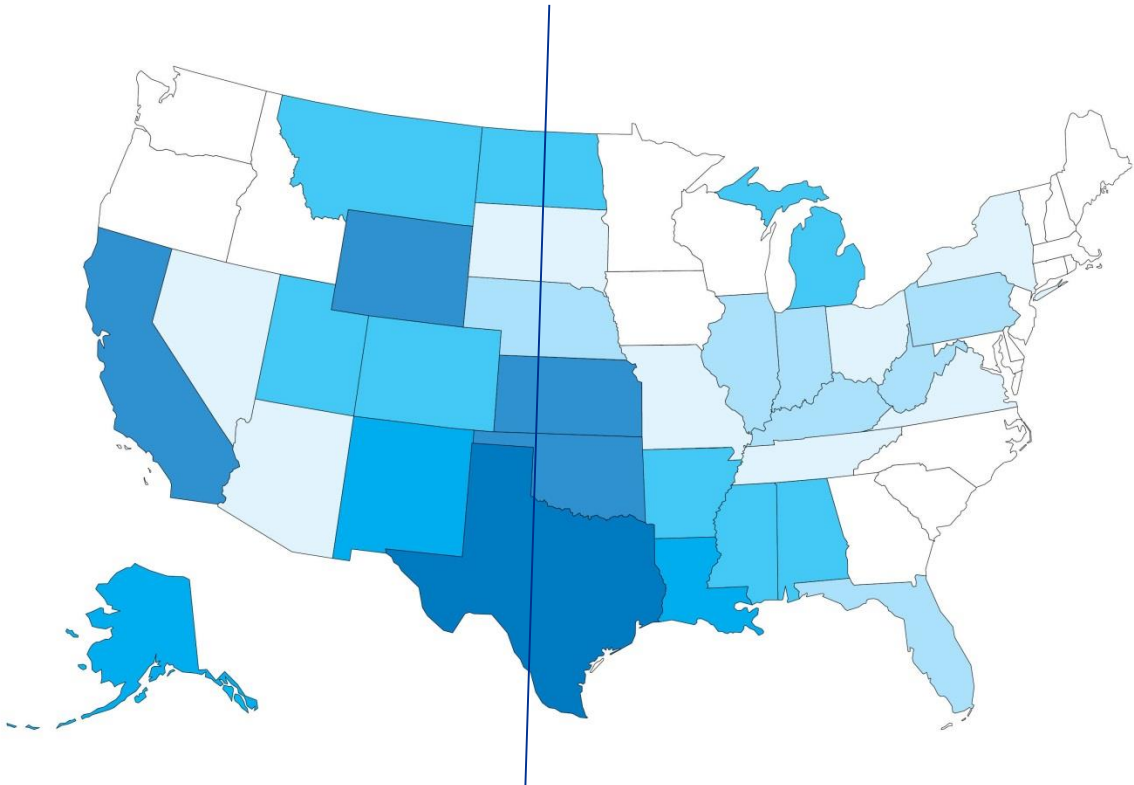


Distribution of Basins



- Appalachian Basin
- Denver-Julesburg Basin
- Powder River Basin
- Western Canadian Sedimentary Basin
- Bend Arch-Fort Worth Basin
- Permian Basin
- Arkoma Basin
- East Texas Basin
- Piceance Basin
- Williston Basin
- Green River Basin
- Raton Basin
- San Juan Basin
- Black Warrior Basin
- Gulf Coast Basin
- Illinois Basin
- Uintah Basin
- Central Basin
- Cherokee Basin
- Tongue River Basin
- N.S.

Wastewater production intensity



Billion barrels* of produced oil and gas wastewater



Chemicals Database

National_List_Update_07-09-18_cleaned.xlsx - Excel

File Home Insert Page Layout Formulas Data Review View Power Pivot Design Tell me what you want to do...

Clipboard Font Alignment Number Styles Cells

Normal 5 RowHeader Normal Bad Good Neutral

C1789 =ABS(NOT(ISNA(MATCH(\$A1789,FF_Natl!\$C\$7:\$C\$1154,0))))

A	B	C	D	E	F	G	H	I	J	K	L	M
1	Chemical Constituents associated with HF and produced water											
2	Updated March 1, Natl List											
3	2227_FF_National	1137	1079		Subtotals	473	1180				76	175
4	2227_Old FF	1137	1079		Counts	473	1180				76	175
5												
6	Chemical Name	Source	Regulated	Methods								
13	Perfluoro(3-ethylpentane)*		✓									
14	2690-05-3		✓		2016	4						
15	2765-11-9		✓		2016							
16	2863-02-5		✓		2014							
17	2863-05-8		✓		2014							
18	2935-07-1		✓		2014							
19	3452-07-1		✓		2014	28						
20	4719-04-4		✓		2017	226						
21	4810-09-7		✓									
22	5161-04-6		✓									
23	5470-11-1		✓		2017	886						
24	5744-03-6		✓									
25	5911-04-6		✓									
26	5968-11-6		✓		2017	2						
27	7440-09-7		✓		2011	22						
28	7446-09-5		✓		2017	2084						
29	7446-11-9		✓		2015	1						
30	7542-12-3		✓		2013	1						
31	7632-04-4		✓		2015	1						
32	7632-05-5		✓		2017	19						
33	7775-09-9		✓		2017	168						
34	7783-06-4		✓									
35	8002-05-9		✓		2017	140						
36	8002-09-3		✓		2017	979						
37	8009-03-8		✓		2014	1						
38	8013-01-2		✓		2016	606						
39	9000-11-7		✓		2013	1						
40	9003-01-4		✓		2015	3						
41	9003-04-7		✓		2017	1982						
42	9003-05-8		✓		2017	426						
43	9003-06-9		✓		2018	1391						
44	9003-11-6		✓		2017	3867						
45	9004-01-4		✓		2016	1000						

Chemical

Source

Regulated

Methods

40 CFR 136
SW846

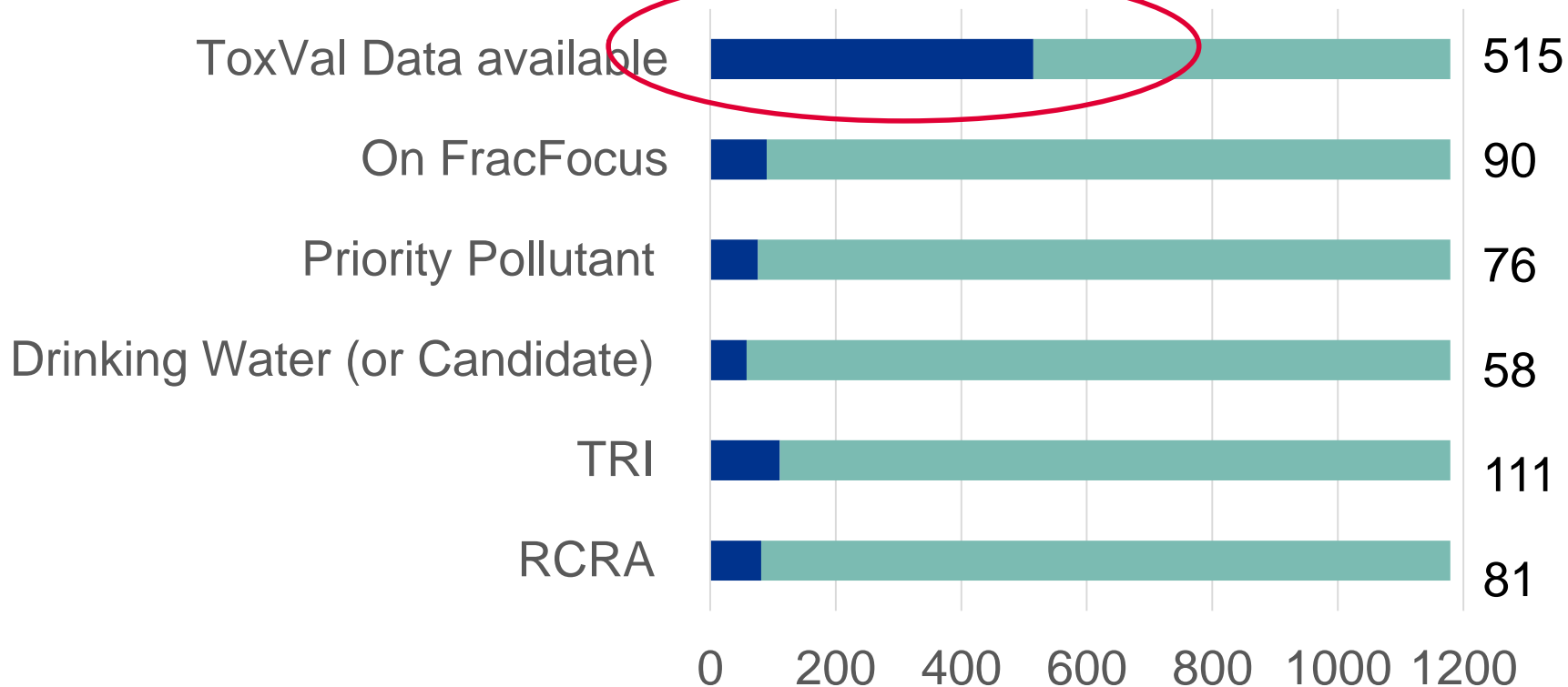
CWT permit
Priority Pollutant
TRI, RCRA
NPDWR or CC4

CAS
Chemical Name

FracFocus (count, date)
Literature (concentration, number of times sampled)

Produced water chemicals (are data-poor)

1179 PW chemicals

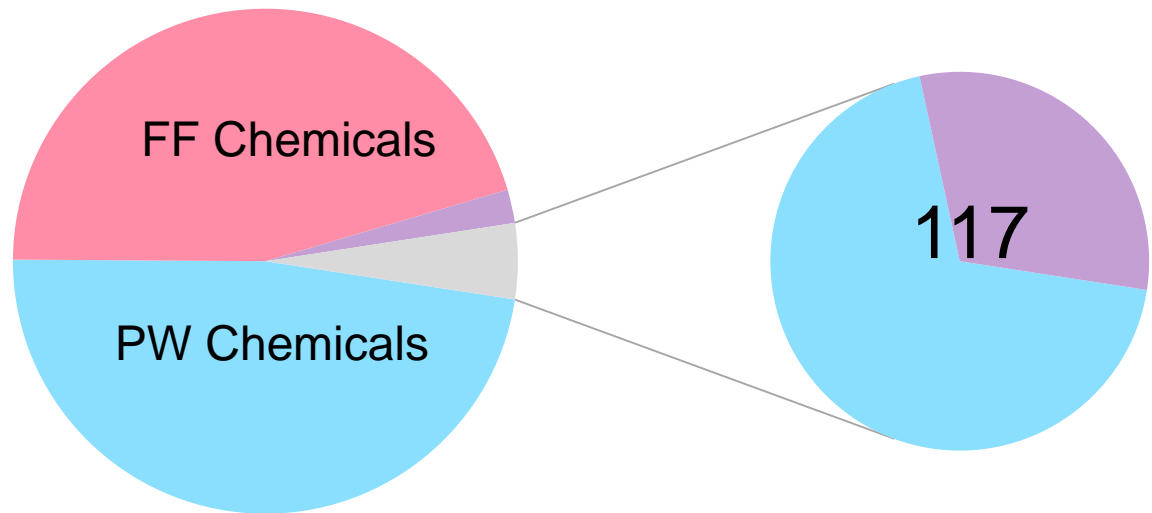


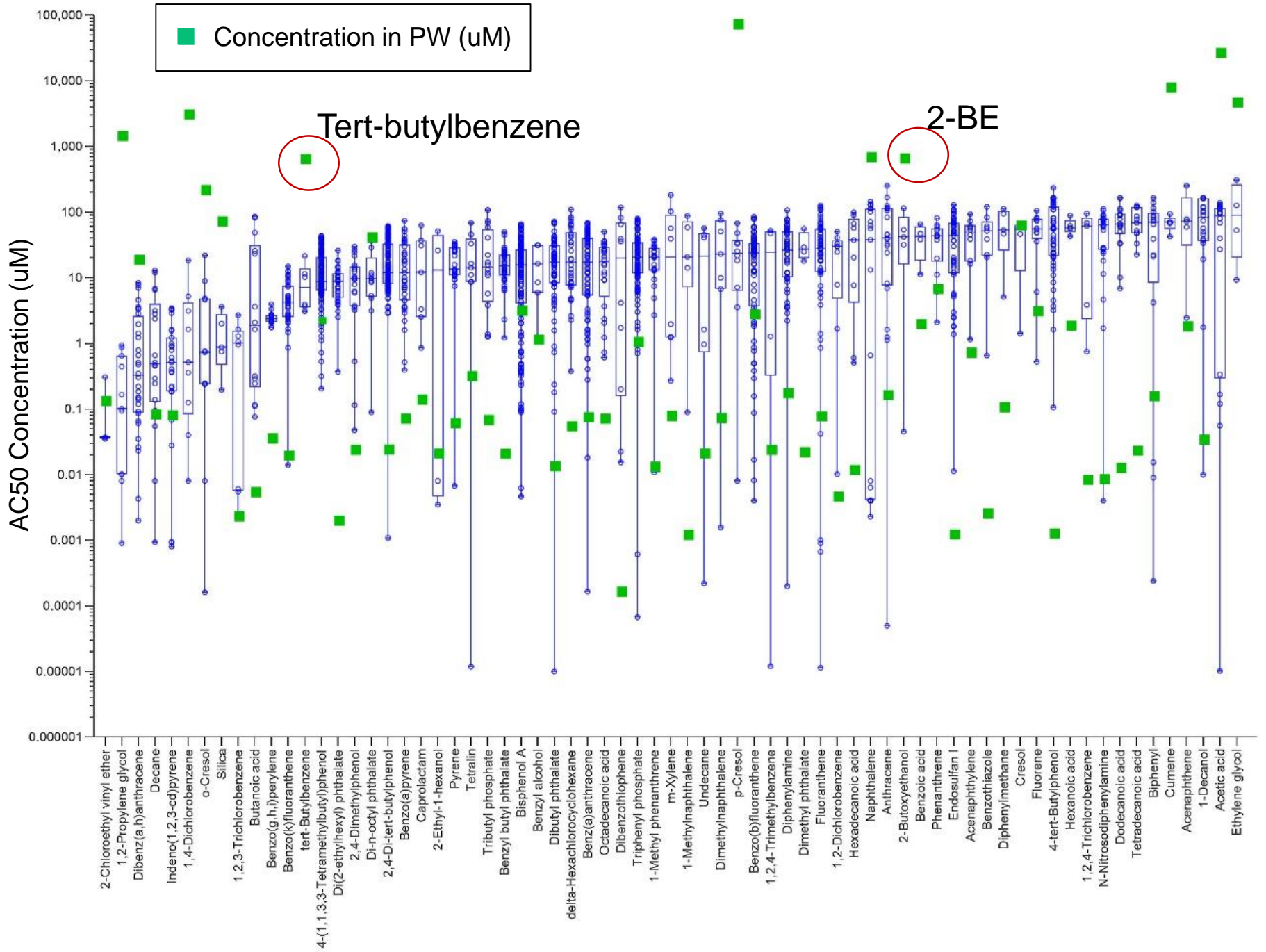
Deeper dive on subset

- Detected in PW more than once
- Concentration data
- Toxicity data (x2)
 - Bioassay (in vitro) – AC50
 - Ecotoxicity (in vivo) – EC50



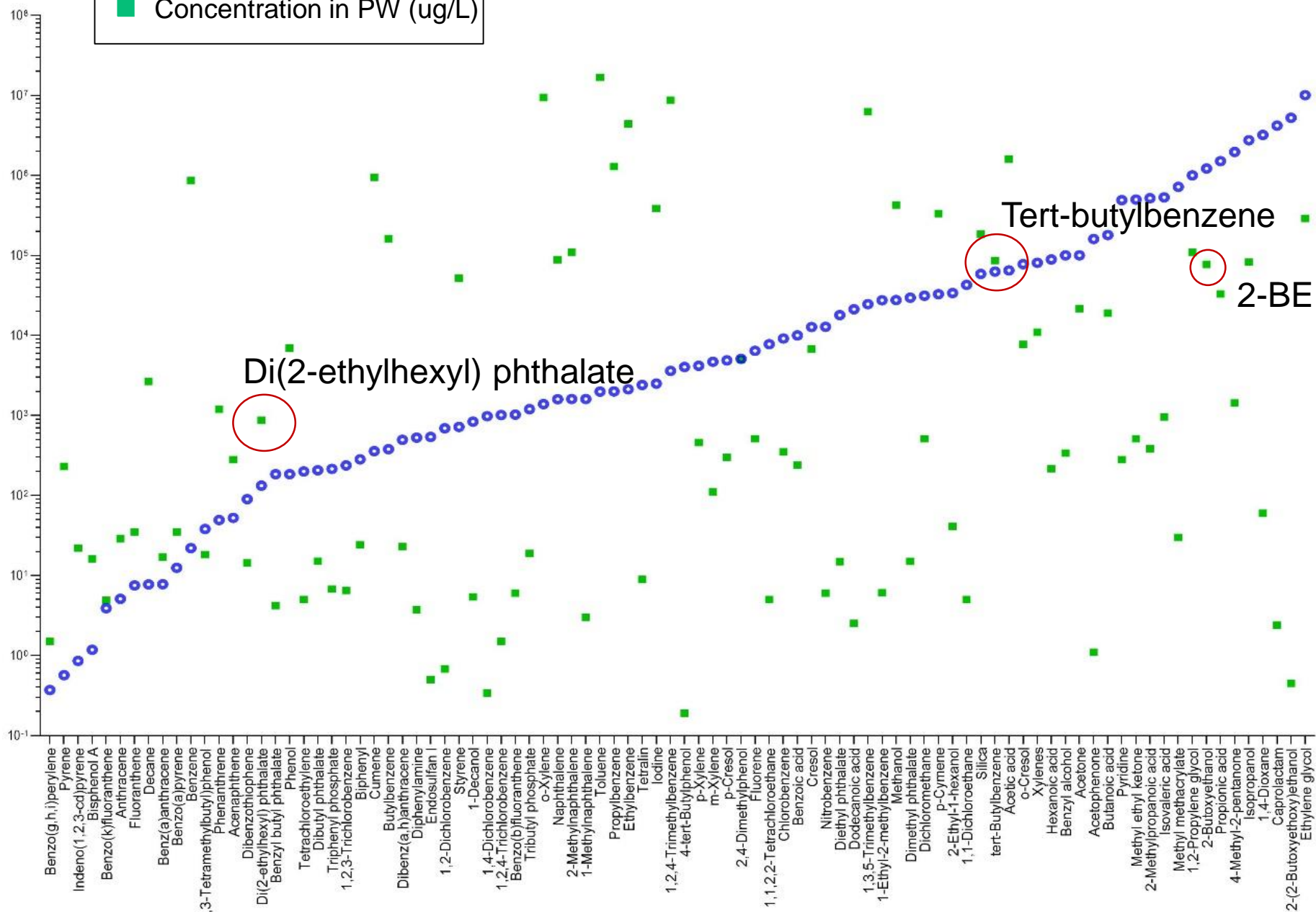
TEXAS A&M
UNIVERSITY®



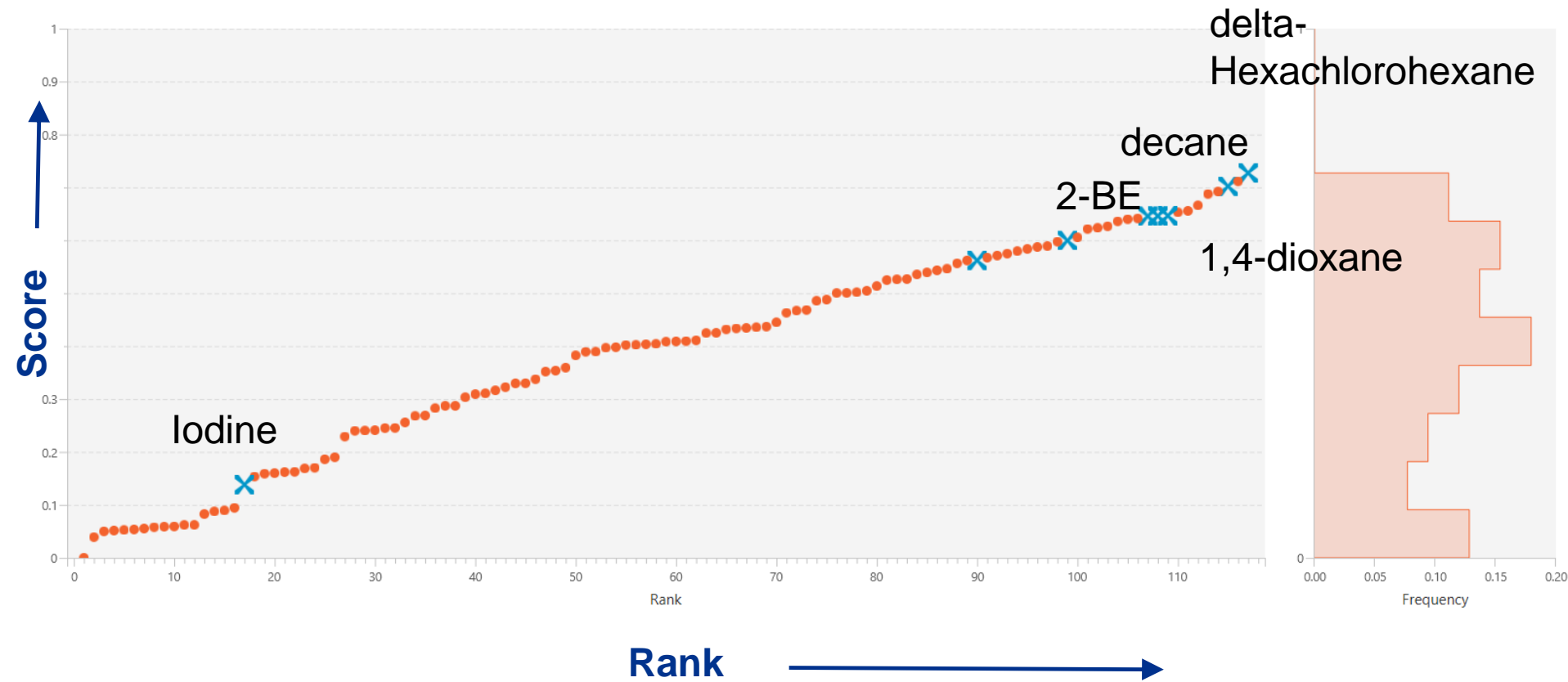


EC50 Concentration (ug/L)

■ Concentration in PW (ug/L)

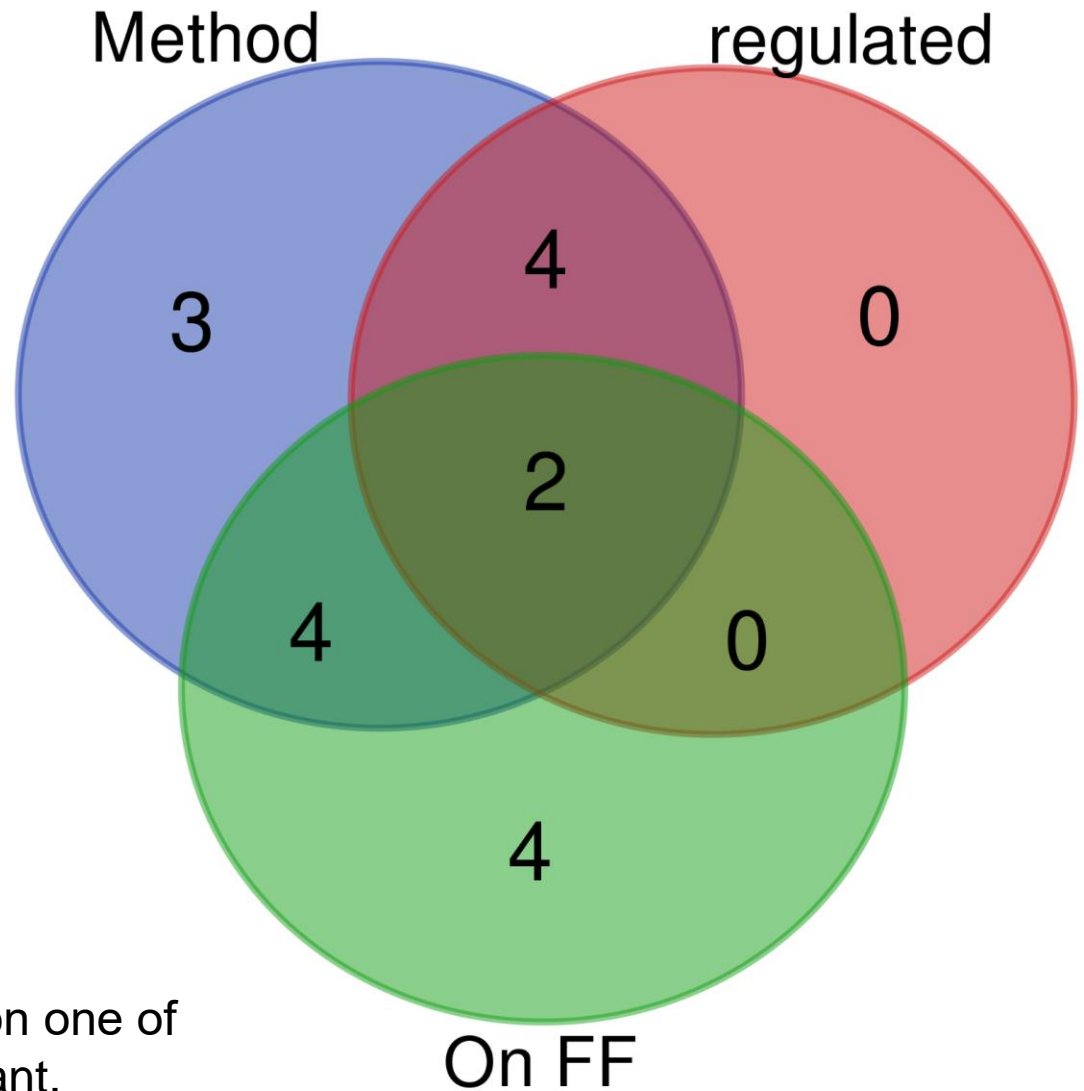


ToxPi

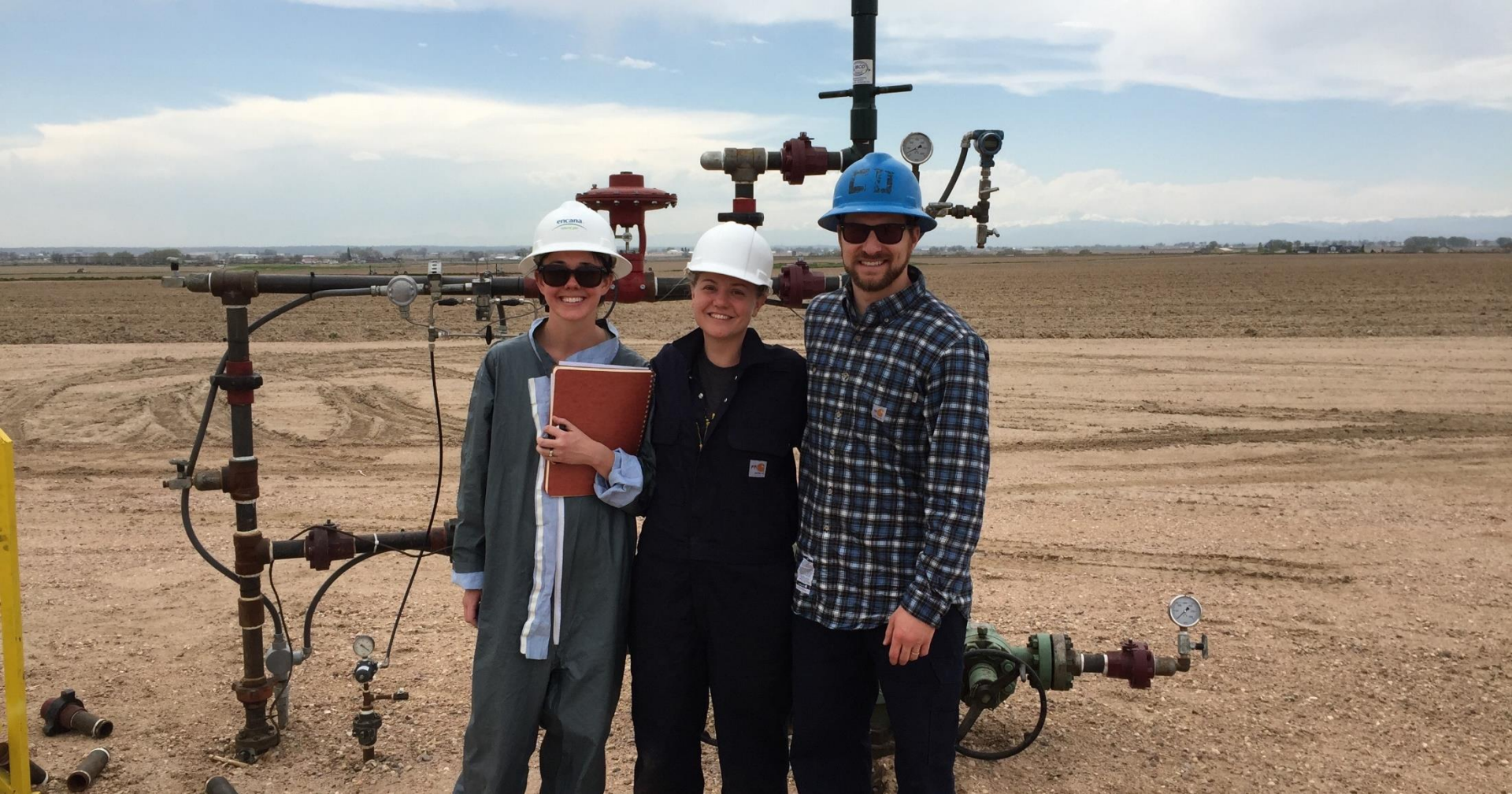


Top 20

- 10 are on FF
- 6 are “regulated”**
- 13 have standard method



**“Regulated” defined as being on one of the following lists: Priority Pollutant, RCRA, TRI, EPA DW/HA, CCL4



Cloelle Danforth

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