Advancing Research on Oil and Gas Produced Water

Data Aggregation and Democratization

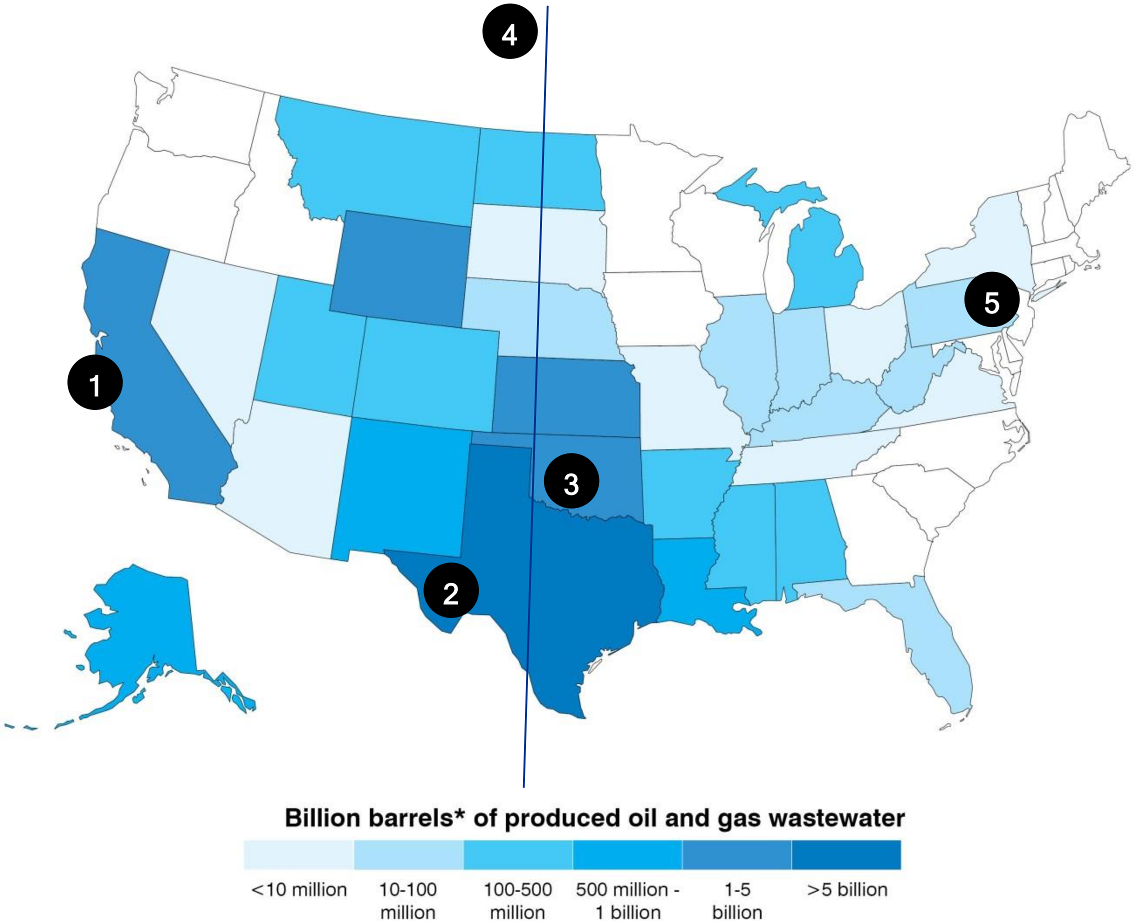
Cloelle Danforth, PhD

Environmental Defense Fund

Finding the ways that work

Managing oil and gas wastewater

Alternative methods to underground disposal



Total produced: 900 billion gallons <u>annually</u>

*1 barrel = 42 gallons

1. **Central Valley, California:**
30 year program – currently over 90K acres approved to use oilfield wastewater for food crop irrigation

2. **Pecos, Texas:**
2015 pilot to irrigate cotton with produced water

3. **Oklahoma:**
Governor task force examines alternatives to oil and gas wastewater disposal wells in 2016

4. **West of 98th Meridian:**
EPA rules allow discharges if "good enough quality" for ag and livestock

5. **Pennsylvania:**
Discharges to surface waters via centralized treatment facilities (PA rules, in effect, require thermal distillation)

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

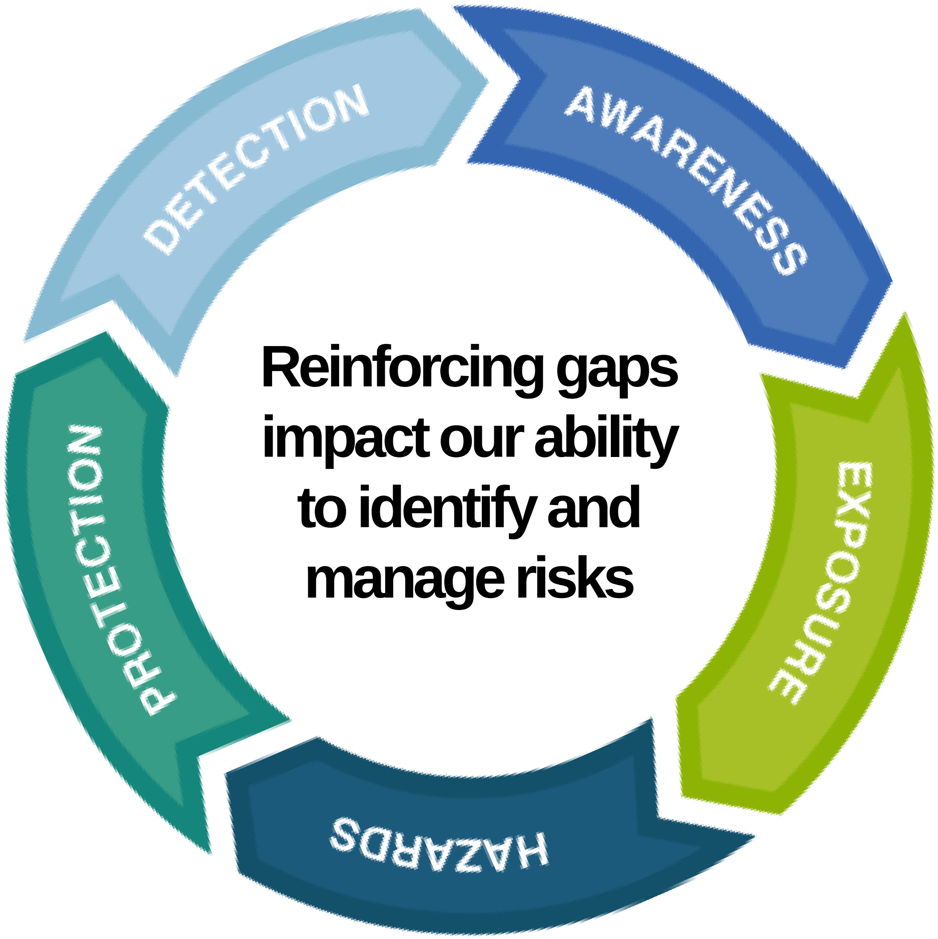
…which means we aren't researching who/what may come in contact with those chemicals…

HAZARDS

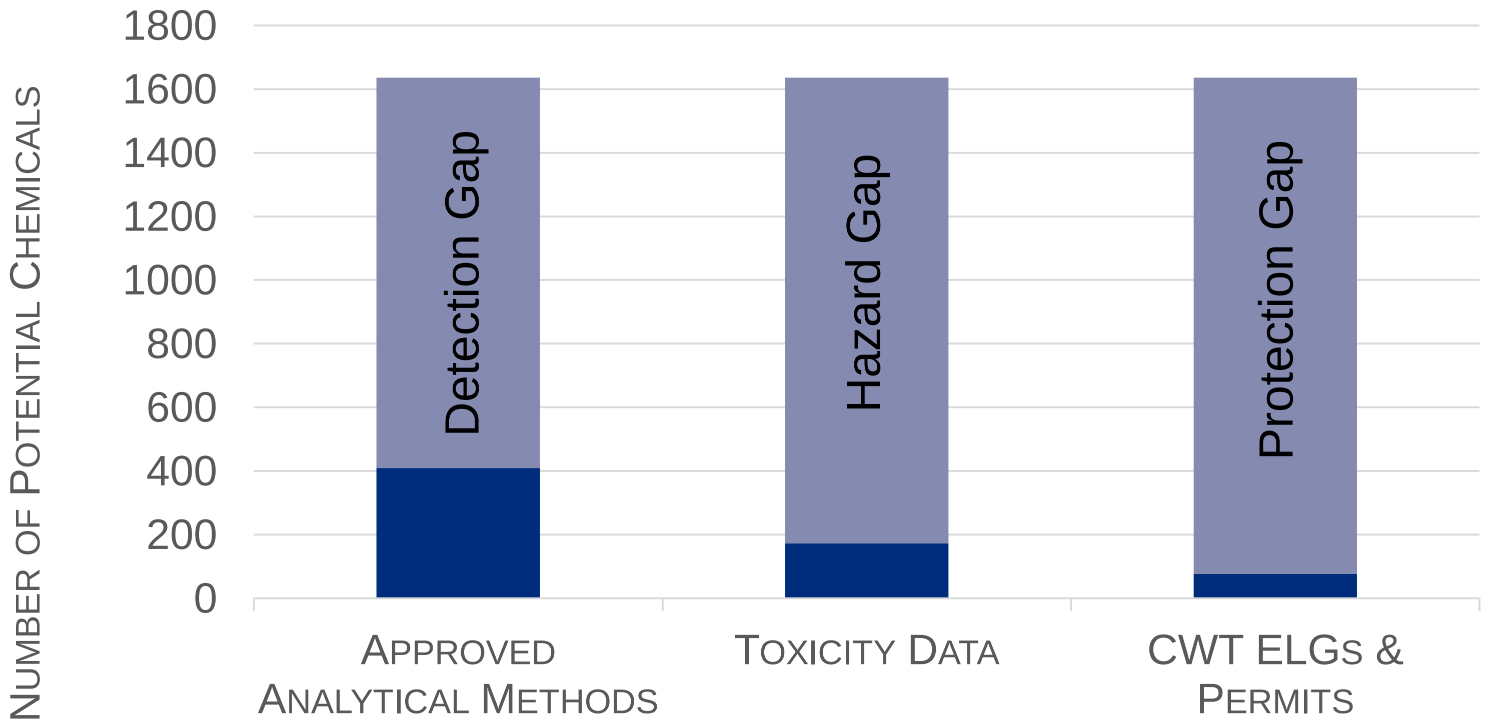
…so we can't determine whether chemicals are present at dangerous levels…

PROTECTION

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



Data Gaps & Produced Water



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

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ELSEVIER

TrEAC

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

Karl Oetjen[a], Cloelle G.S. Giddings[b], Molly McLaughlin[c], Marika Nell[d], Jens Blotev
Damian E. Helbling[d], Dan Mueller[b], Christopher P. Higgins[a,*]

[a] Civil and Environmental Engineering, Colorado School of Mines, Golden, CO 80401, USA
[b] Environmental Defense Fund, New York, NY 10010, USA
[c] Department of Civil and Environmental Engineering, Colorado State University, 1320 Campus Delivery, Fort Collins, CO 80523, USA
[d] School of Civil and Environmental Engineering, Cornell University, Ithaca, NY 14853, USA

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Hydraulic fracturing
Oil and gas wastewaters
Produced water
Liquid chromatography
Gas chromatography
High-Resolution mass spectrometry
Flowback water

ABSTRACT

Flowback and produced waters are extremely complex matrices con
additives. The geogenic fraction may contain large amounts of total d
carbons, organic acids, alcohols, radionuclides, and metals. The addi
inhibitors, biocides, and friction reducers. Recently, it has been sugg
potentially represent a new water source in areas of water scarcity
considered for applications outside the oil field, the chemical con
However, due to the complex nature of these matrices, many meth
groundwater matrices may not be suitable. In addition, many organi
geted approaches for organic chemical analysis alone will be insuffi
acterization. We assessed current trends and emerging technologies i
their applicability to flowback and produced waters. In addition, we pr
serve as potential solutions to address the issues created by the com
produced waters.

1. Introduction

Hydraulic fracturing (HF) is a process used in the extraction of underground resources to increase oil, natural gas, and water production rates when these resources are located in rock formations with a naturally low permeability [1]. Horizontal fracturing, often referred to as high-volume HF is the preferred method for removing oil and natural gas from tight formations, including shale facies. After HF is complete, a portion of injection waters returns to the surface as flowback water and produced water, referred to here as oil and gas (O&G) wastewater [2]. As O&G exploration and development continues in the United States, large quantities of wastewater are produced along with the targeted resources. The United States produces 870 billion gallons of produced water annually from O&G activities [3]. It has been suggested that produced waters from O&G operations could potentially represent a new water source in areas of water scarcity [4,5]. Although alternative uses for these waters could greatly benefit communities, these waters contain numerous synthetic and geogenic constituents and therefore,

careful consideration of the chemi
nature.

Numerous studies have aimed
back waters. However, there are
characterizing the chemical compo
concern in these wastewaters. F
originally designed for surface an
duced waters can have salinities
water [7]. Over the last few years
suitability of these existing metho
with complex matrices [13,14]. S
been developed for many of the
matrix. In fact, less than one quart
identified as being associated
method [15]. The implication is
they may not be appropriate for th
to completely characterize these
pounds, is likely insufficient. Th

* Corresponding author.
E-mail address: chiggins@mines.edu (C.P. Higgins).

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Environmental Science Processes & Impacts

ROYAL SOCIETY OF CHEMISTRY

PAPER

Check for updates

Cite this: DOI: 10.1039/c8em00135a

Exploring matrix effects and qu
additives in hydraulic fracturing
using liquid chromatography el
ionization mass spectrometry†

Marika Nell and Damian E. Helbling *

Hydraulic fracturing (HF) operations utilize millions of gallons of
including biocides, corrosion inhibitors, and surfactants. Fluids ir
surface as wastewaters, which contain a complex mixture of
geogenic chemical constituents. Quantitative analytical metho
disposal alternatives or to conduct adequate exposure assessme
of how matrix effects change the ionization efficiency of target a
polar to semi-polar HF additives by means of liquid chrom
spectrometry (LC-ESI-MS). To address this limitation, we explo
influences the ionization of seventeen priority HF additives with
We then used the data to quantify HF additives in HF-associated
additives generally exhibit suppressed ionization in HF-assoc
predominantly form sodiated adducts exhibit significantly en
samples, which is largely the result of adduct shifting. In
glutaraldehyde and 2-butoxyethanol along with homologue
polyethylene glycol (PEG), and polypropylene glycol (PPG) in HF
recovery factors to provide the first quantitative measurements o
and PPG in HF-associated fluids ranging from mg L^{-1} levels in
levels in PW samples. Our approach is generalizable across samp
important data to evaluate wastewater disposal alternatives or im

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rsc.li/espi

Environmental significance

The complex matrix of hydraulic fracturing (HF) associated fluids has limited the applicability of electrospray
quantitative analysis of polar to semi-polar chemical additives. Improved understanding of the concentrations of
essential prerequisite to evaluate wastewater disposal strategies or assess the environmental risk of contamination
matrix recovery factors for seventeen priority HF additives and applied them to provide the first known quantificat
fluids. Our approach allows us to overcome the uncertainties associated with complex matrices and can be generaliz
and shale formations.

Introduction

The use of hydraulic fracturing (HF), coupled with horizontal drilling, has led to a boom in unconventional shale gas production over the course of the past decade. For example, as the United States (US) sought to become a natural gas exporter,

hydraulic fracturing play
hydraulically fractured wel
gas production.[1,2] Howeve
and human health impact
hydraulic fracturing fluid (
(MW – *i.e.*, surface water, g
a proppant, and up to
injected into a well at high
the permeability of the
released from the well, a m
to the surface as flowbac
water will continue to flow

School of Civil and Environmental Engineering, Cornell University, 220 Hollister Hall, Ithaca, NY, 14853, USA. E-mail: damian.helbling@cornell.edu; Fax: +1 607 255 9004; Tel: +1 607 255 3146

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8em00135a

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

ELSEVIER

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

Check for updates

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

[a] University of Colorado Boulder, Department of Civil, Environmental, and Architectural Engineering, Boulder, CO 80303, USA
[b] University of Colorado School of Medicine, Anschutz Campus, Division of Infectious Disease, Aurora, CO 80405, USA
[c] University of Colorado School of Medicine, Anschutz Campus, Department of Pediatrics, Aurora, CO 80405, USA

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.

GRAPHICAL ABSTRACT

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Flowback
Produced water
16S rRNA gene amplicon sequencing

ABSTRACT

Hydraulic fracturing flowback and produced water (FPW) samples were analyzed for toxicity and microbiome characterization over 220 days for a horizontally drilled well in the Denver-Julesburg (DJ) Basin in Colorado. Cytotoxicity, mutagenicity, and estrogenicity of FPW were measured via the BioLuminescence Inhibition Assay (BLIA), Ames II mutagenicity assay (AMES), and Yeast Estrogen Screen (YES). Raw FPW stimulated bacteria in BLIA, but were cytotoxic to yeast in YES. Filtered FPW stimulated cell growth in both BLIA and YES. Concentrating 25× by solid phase extraction (SPE) revealed significant toxicity throughout well production by BLIA, toxicity during the first 55 days of flowback by YES, and mutagenicity by AMES. The selective pressures of fracturing conditions (including toxicity) affected bacterial and archaeal communities, which were characterized by 16S rRNA gene V4V5 region sequencing. Conditions selected for thermophilic, anaerobic, halophilic bacteria and methanogenic archaea from the groundwater used for fracturing fluid, and from the native shale community. Trends in toxicity echoed the microbial community, which indicated distinct stages of early flowback water, a transition stage, and produced water. Biota in another sampled DJ Basin horizontal well resembled similarly aged samples from this well. However, microbial signatures were unique compared to samples from DJ Basin vertical wells, and wells from other basins. These data can inform treatability, reuse, and management decisions specific to the DJ Basin to minimize adverse environmental health and well production outcomes.

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* Corresponding author.
E-mail addresses: natalie.hull@colorado.edu (N.M. Hull), james.rosenblum@colorado.edu (J.S. Rosenblum), charles.robertson@ucdenver.edu (C.E. Robertson), jonathan.harris@ucdenver.edu (J.K. Harris), karl.linden@colorado.edu (K.G. Linden).

1. Introduction

Technologies for horizontal drilling and hydraulic fracturing have enabled access to previously cost-prohibitive shale deposits, leading to

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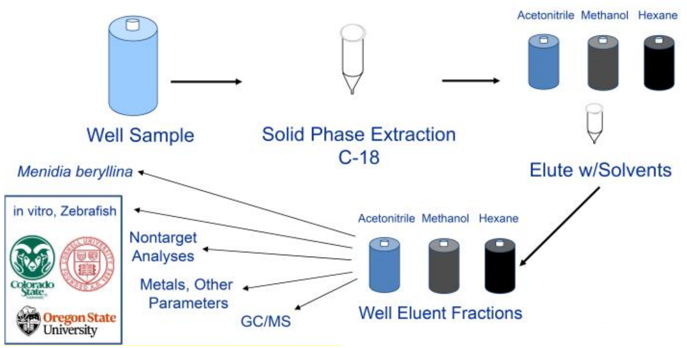
Ongoing work - toxicity

- Toxicity identification evaluation of produced waters of different production ages



- Toxicity of produced water before/after various benchtop treatment schemes

- Toxicological characterization of surface water impacted by discharge of minimally treated 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:

Oil OR Gas → AND → Conventional OR Unconventional → AND → Wastewater → AND → Chemical Characterization

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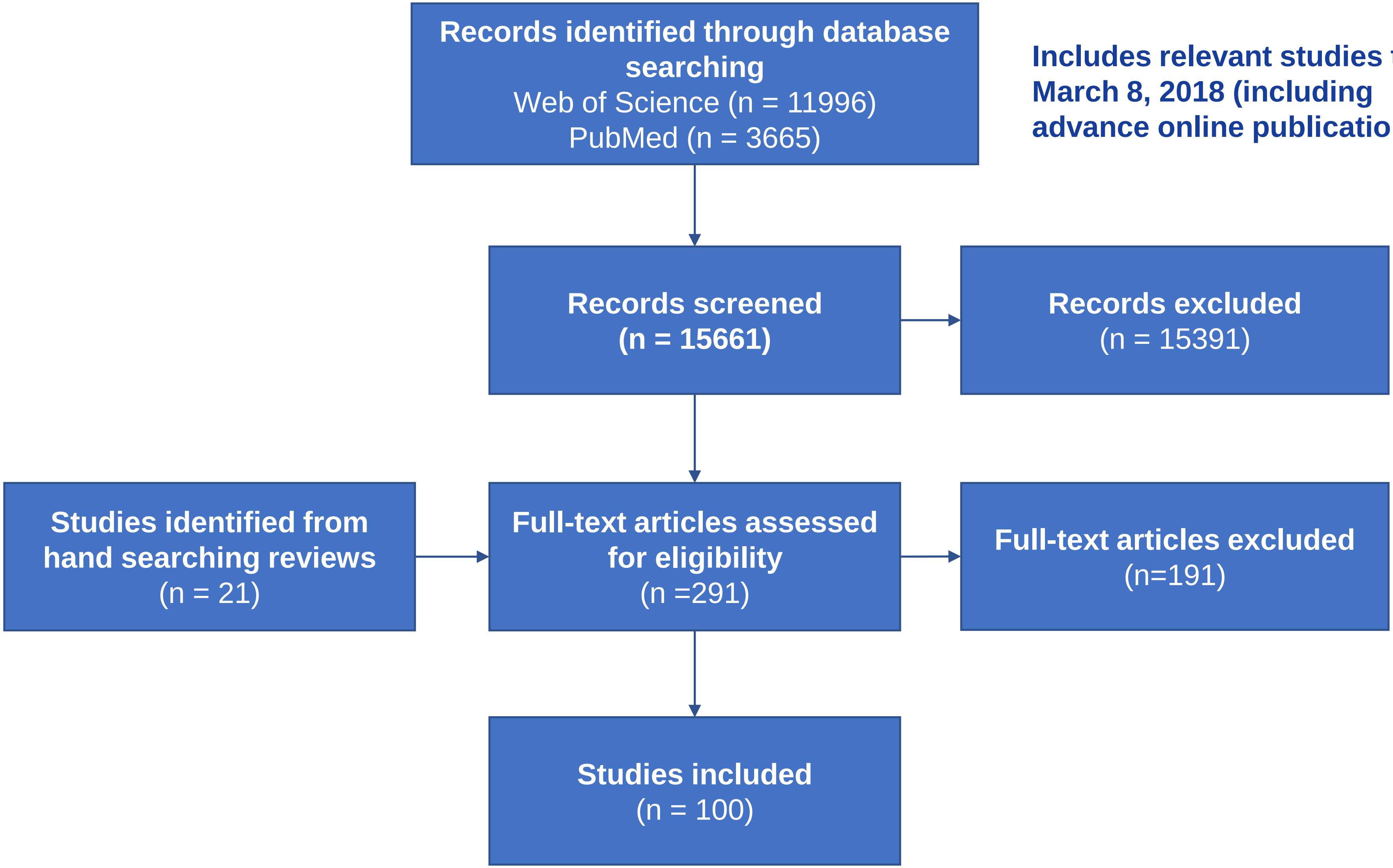

Includes relevant studies to March 8, 2018 (including advance online publications)

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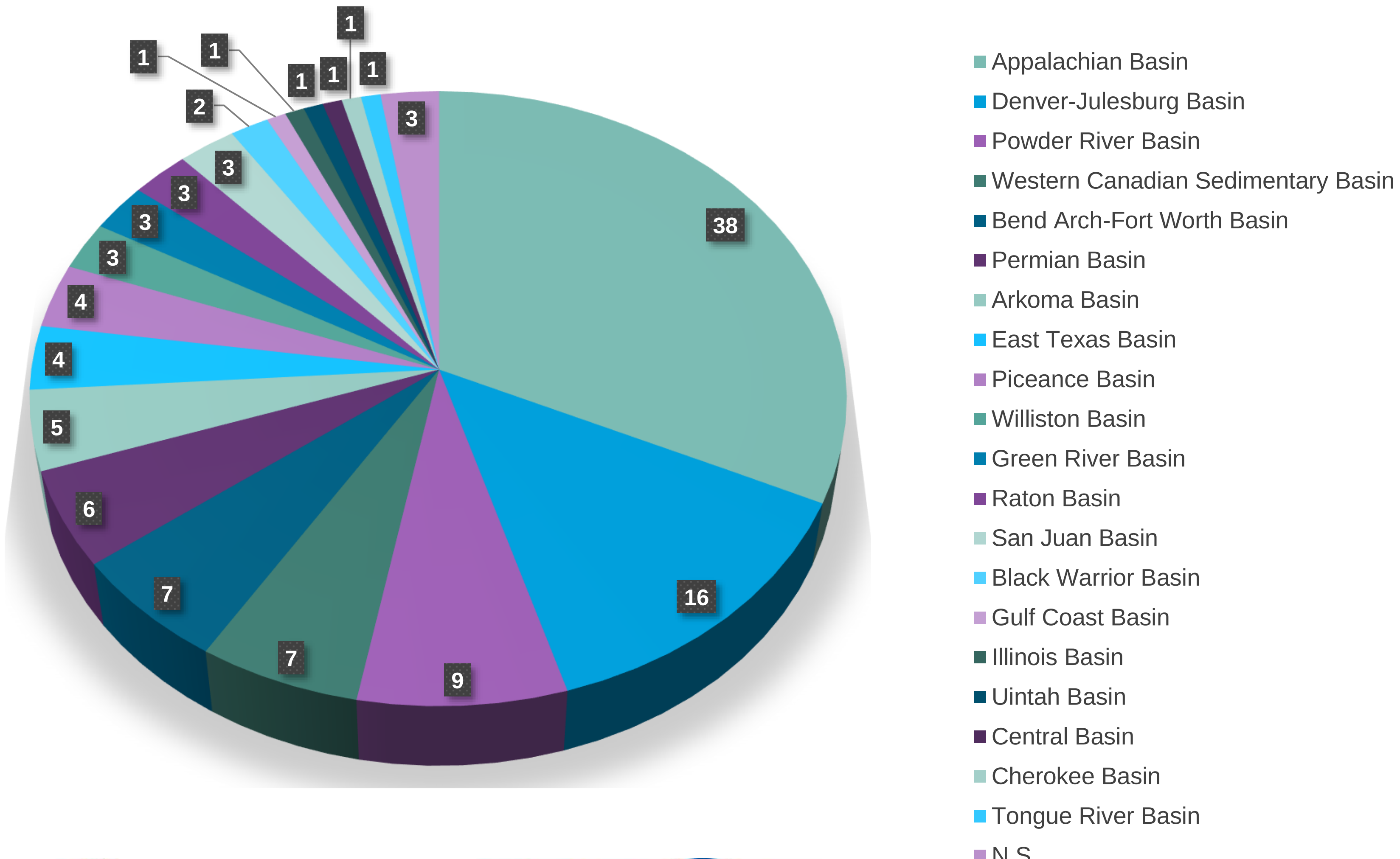
Distribution of Basins



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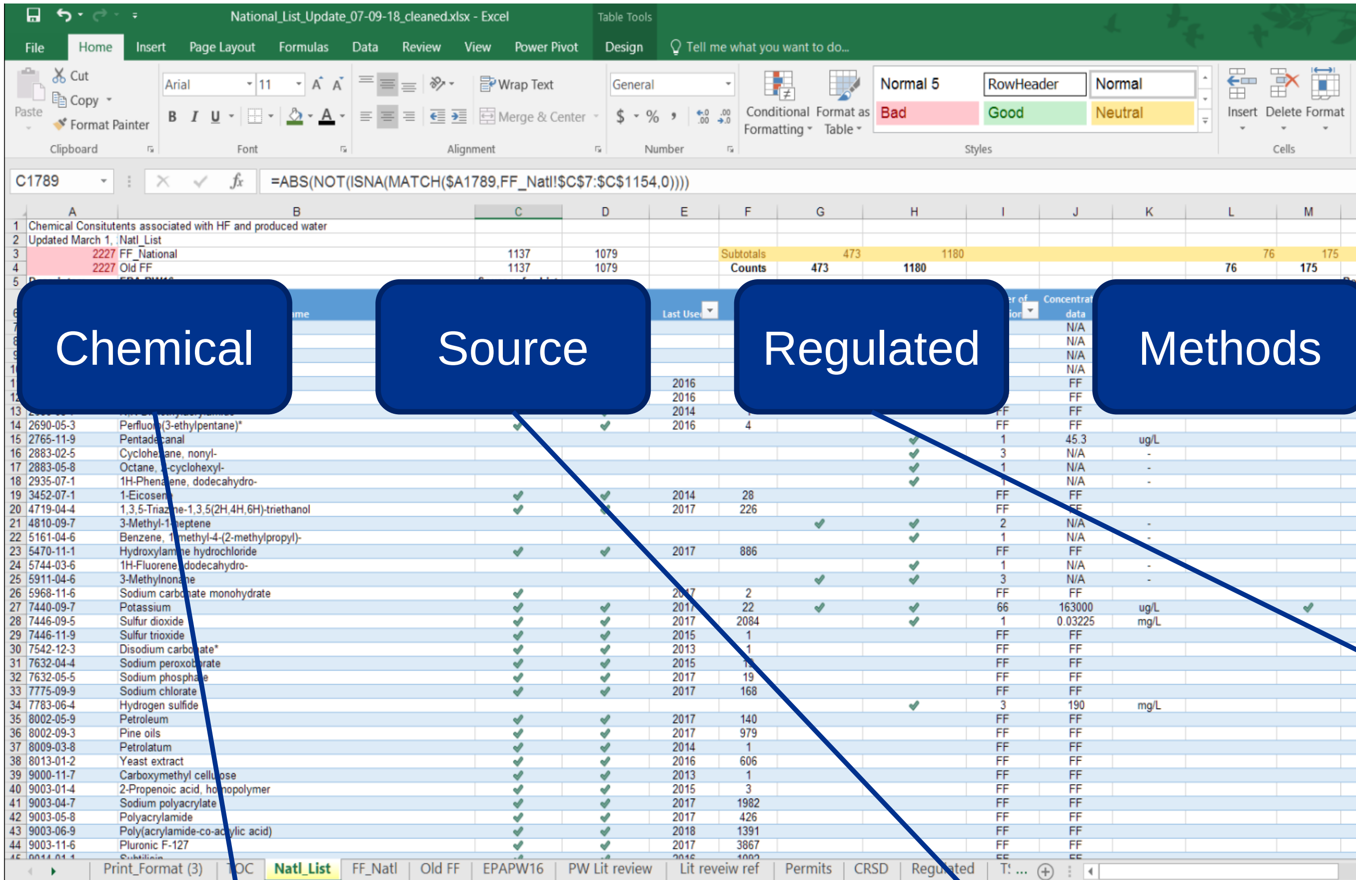
Chemicals x-walk list



40 CFR 136

SW846

CWT permit

Priority Pollutant

TRI, RCRA

NPDWR or CC4

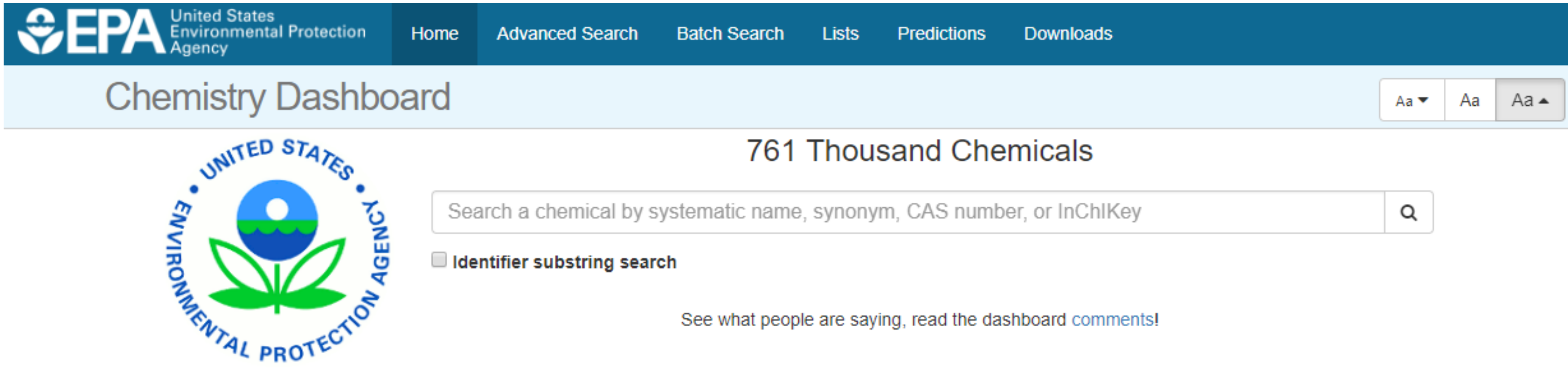
CAS

Chemical Name

FracFocus (count, date)

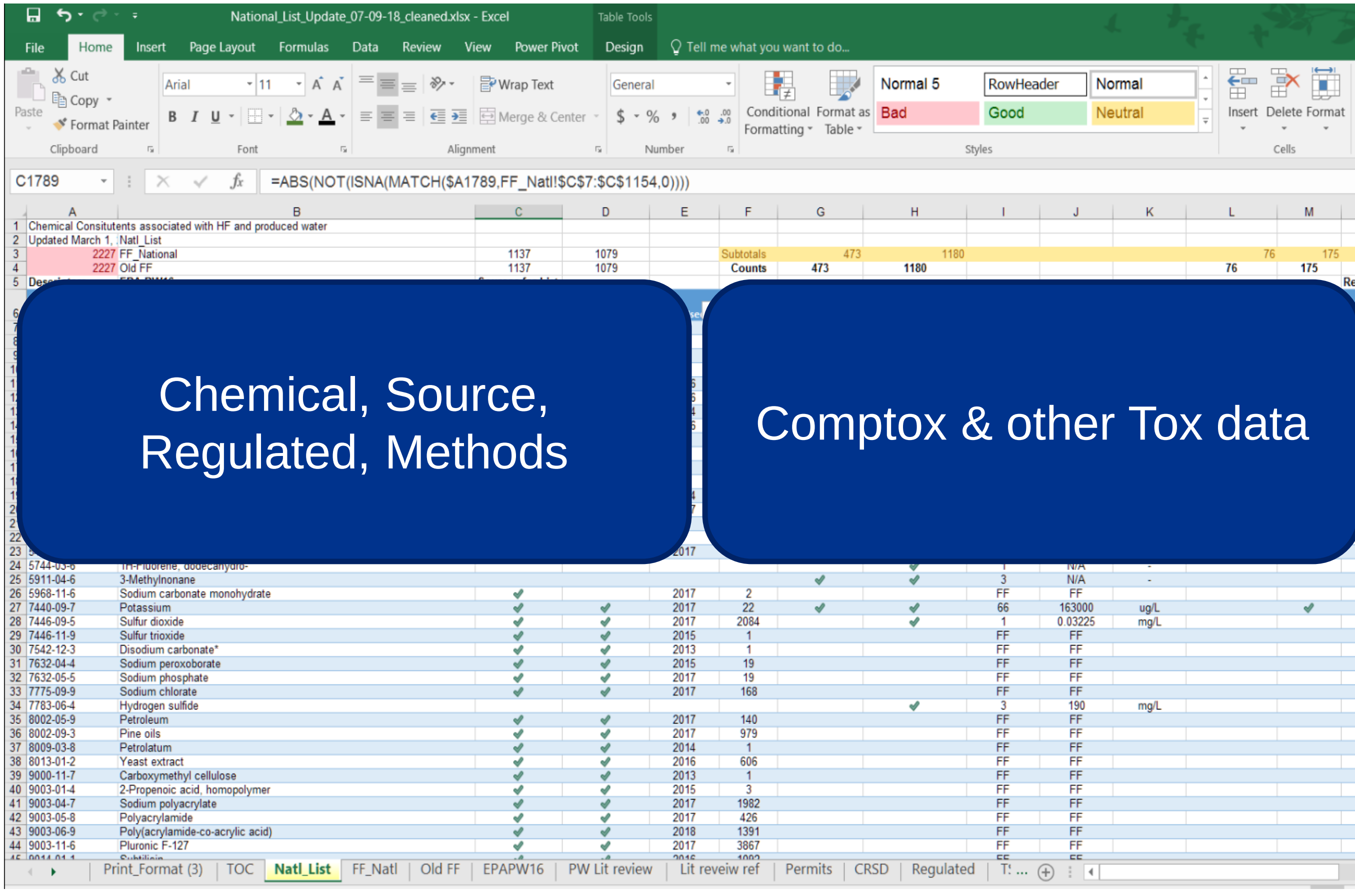
Literature (concentration, number of times sampled)

Comptox Dashboard x-walk



- Search 761 K chemicals by CAS/Name
- Returns data or modeling on
  - Chemical properties
  - Environmental Fate/Transport
  - Hazard
  - Exposure
  - Bioassays
- Links to literature
- Presence on Lists :
  - ToxVal Data availablity: 18 different databases, including ToxCast, Aggregated Computational Toxicology Online Resource (ACToR), TRI
  - National Environment Methods Index (NEMI)
  - Provisional Peer-Reviewed Toxicity Values (PPRTVs)

Chemicals x-walk list + Comptox



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Chemical Consitutents 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
25	5911-04-6	3-Methylnonane					✓	✓	3	N/A	-		
26	5968-11-6	Sodium carbonate monohydrate	✓		2017	2			FF	FF			
27	7440-09-7	Potassium	✓	✓	2017	22	✓	✓	66	163000	ug/L		✓
28	7446-09-5	Sulfur dioxide	✓	✓	2017	2084		✓	1	0.03225	mg/L		
29	7446-11-9	Sulfur trioxide	✓	✓	2015	1			FF	FF			
30	7542-12-3	Disodium carbonate*	✓	✓	2013	1			FF	FF			
31	7632-04-4	Sodium peroxoborate	✓	✓	2015	19			FF	FF			
32	7632-05-5	Sodium phosphate	✓	✓	2017	19			FF	FF			
33	7775-09-9	Sodium chlorate	✓	✓	2017	168			FF	FF			
34	7783-06-4	Hydrogen sulfide						✓	3	190	mg/L		
35	8002-05-9	Petroleum	✓	✓	2017	140			FF	FF			
36	8002-09-3	Pine oils	✓	✓	2017	979			FF	FF			
37	8009-03-8	Petrolatum	✓	✓	2014	1			FF	FF			
38	8013-01-2	Yeast extract	✓	✓	2016	606			FF	FF			
39	9000-11-7	Carboxymethyl cellulose	✓	✓	2013	1			FF	FF			
40	9003-01-4	2-Propenoic acid, homopolymer	✓	✓	2015	3			FF	FF			
41	9003-04-7	Sodium polyacrylate	✓	✓	2017	1982			FF	FF			
42	9003-05-8	Polyacrylamide	✓	✓	2017	426			FF	FF			
43	9003-06-9	Poly(acrylamide-co-acrylic acid)	✓	✓	2018	1391			FF	FF			
44	9003-11-6	Pluronic F-127	✓	✓	2017	3867			FF	FF			

Chemical, Source, Regulated, Methods

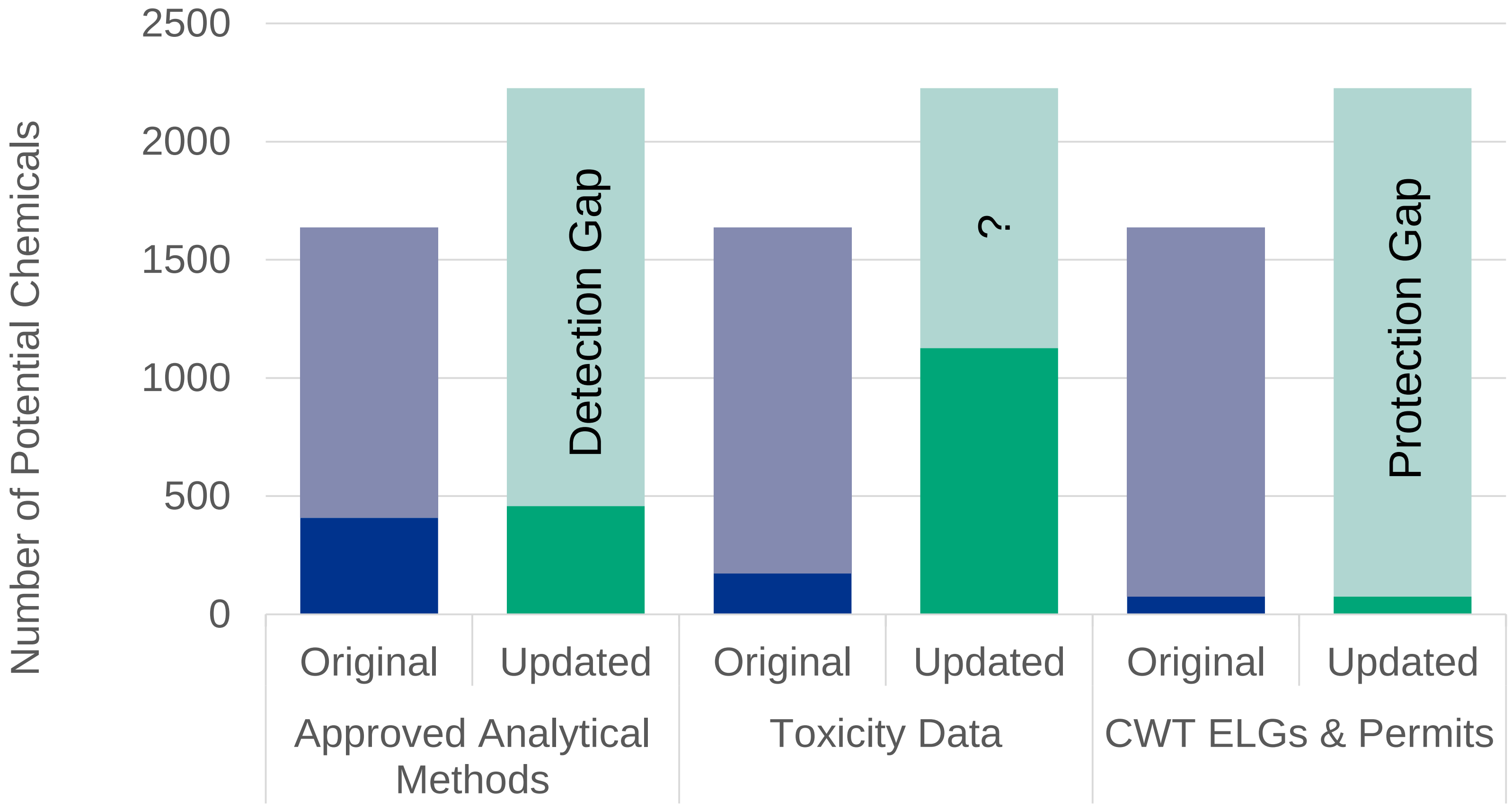
Comptox & other Tox data

ToxVal Availability

TEDX List

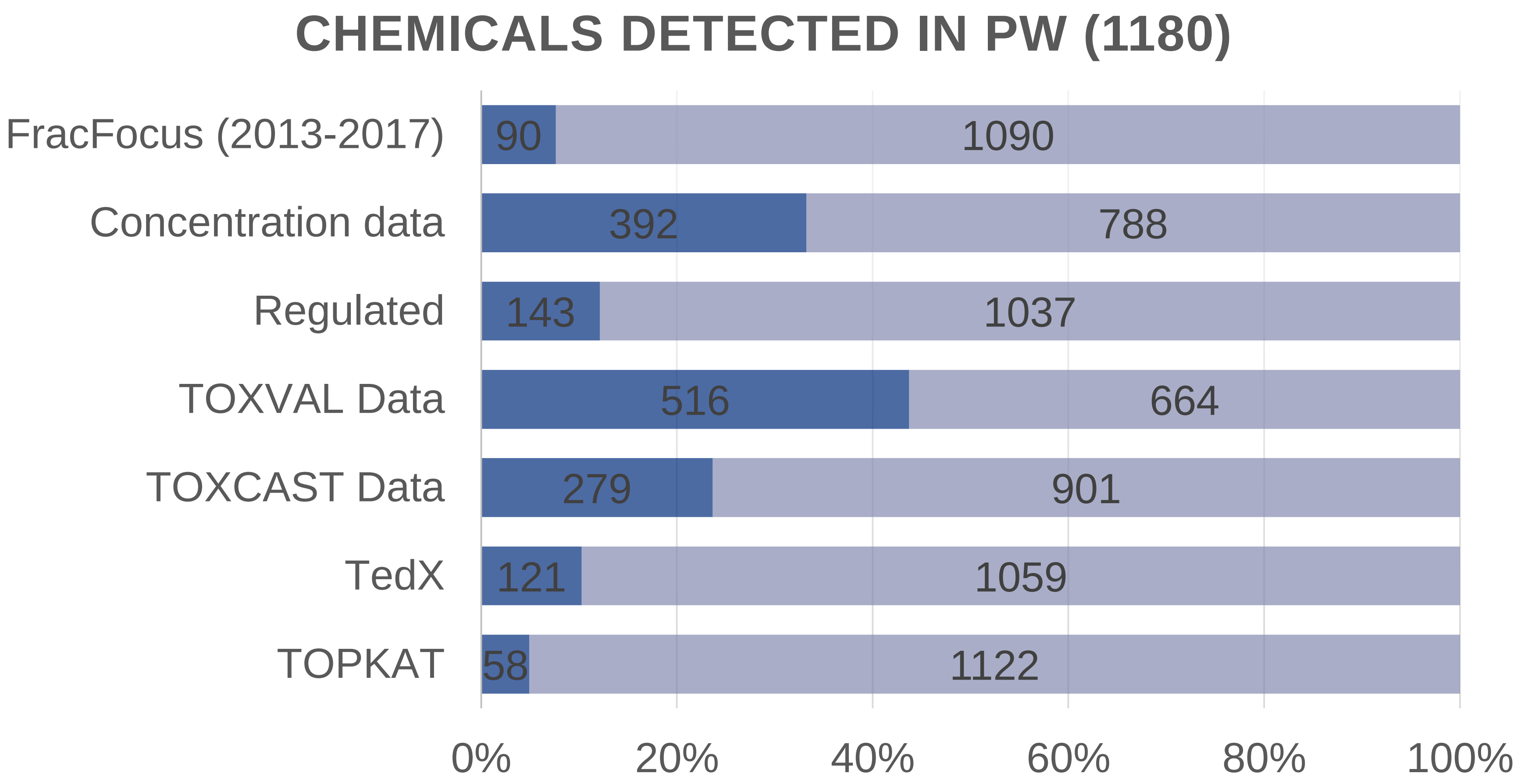
TOPKAT (Yost et. al.)

Data Gaps & Produced Water

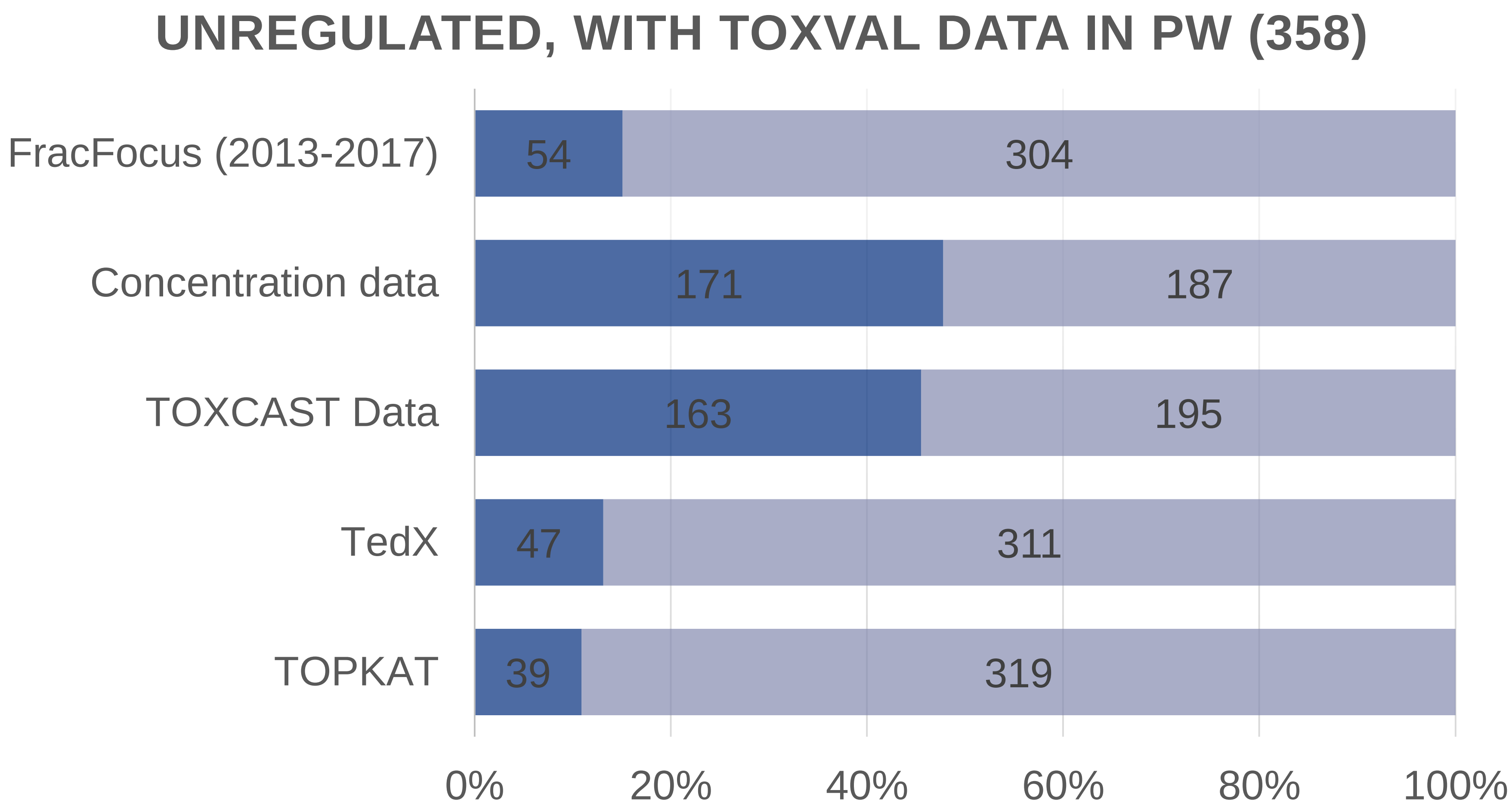


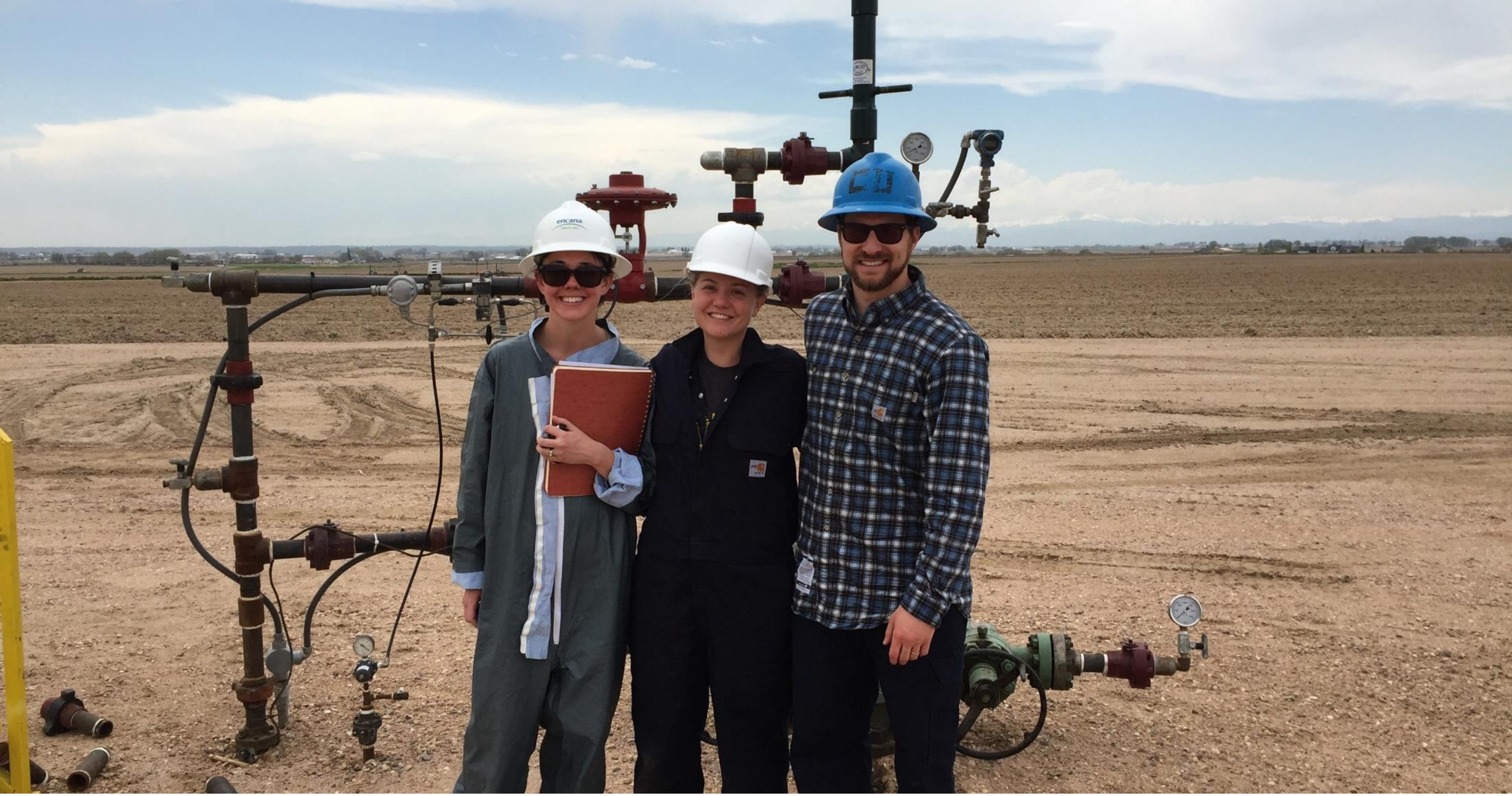
Updated: FF review, PW from literature review, ToxVal Data

Cross-walks


CHEMICALS DETECTED IN PW (1180)
FracFocus (2013-2017)
90
1090
Concentration data
392
788
Regulated
143
1037
TOXVAL Data
516
664
TOXCAST Data
279
901
TedX
121
1059
TOPKAT
58
1122
0%
20%
40%
60%
80%
100%

Cross-walks


UNREGULATED, WITH TOXVAL DATA IN PW (358)
FracFocus (2013-2017)
54
304
Concentration data
171
187
TOXCAST Data
163
195
TedX
47
311
TOPKAT
39
319
0%
20%
40%
60%
80%
100%



Cloelle Danforth
cdanforth@edf.org

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