



# Produced Water Characterization, Treatment, and Reuse

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Radioactive and Hazardous Materials Committee

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**New Mexico State University**

# NM Produced Water Research Consortium

<https://nmpwrc.nmsu.edu/>

- Created under the New Mexico 2019 Produced Water Act
- The objectives of the Consortium are to:
  - Fill the scientific and technical gaps associated with treatment and reuse of produced water
  - Inform future development of science-based policies and regulations
  - Coordinate a robust education, outreach, research, and development program
  - Encourage water stewardship through produced water treatment and reuse:
    - Reduce/eliminate fresh water use in the oil and gas sector
    - Provide new water for economic development
    - Assure public and environmental health and safety using cost-effective treatment

Consortium – a public-private partnership with state and federal agencies, organizations of industry, NGOs, companies, national labs, and academia



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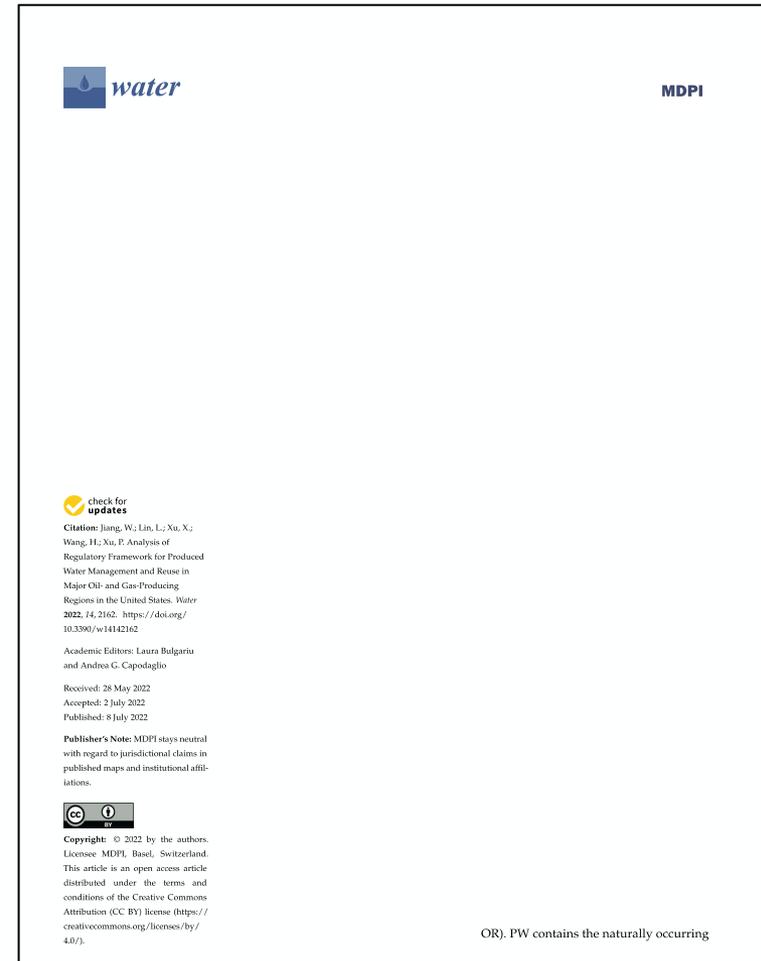
# Produced Water Characterization is Challenging

- Constituents of concern in produced water (formation water and flowback water):
  - Suspended solids, oils, and grease
  - Salts (referred to as dissolved solids) and metals
  - Dissolved organics (e.g., petroleum hydrocarbons, volatile and semi-volatile compounds)
  - Dissolved gases (e.g.,  $H_2S$ ,  $NH_3$ )
  - Naturally occurring radioactive material (NORM)
  - Microorganisms
  - Chemical additives (well completion and on-going well maintenance)
  - Transformation/degradation products, and unknowns
- Produced water quality and quantity are highly variable, spatial and temporal
- High salinity and complex water chemistry cause challenges in analytical methods and treatment
- Costly and time-consuming for “comprehensive” analysis

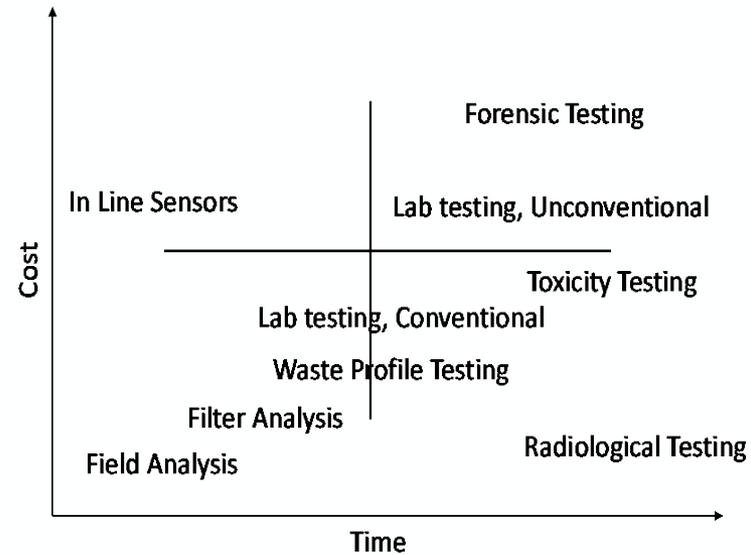
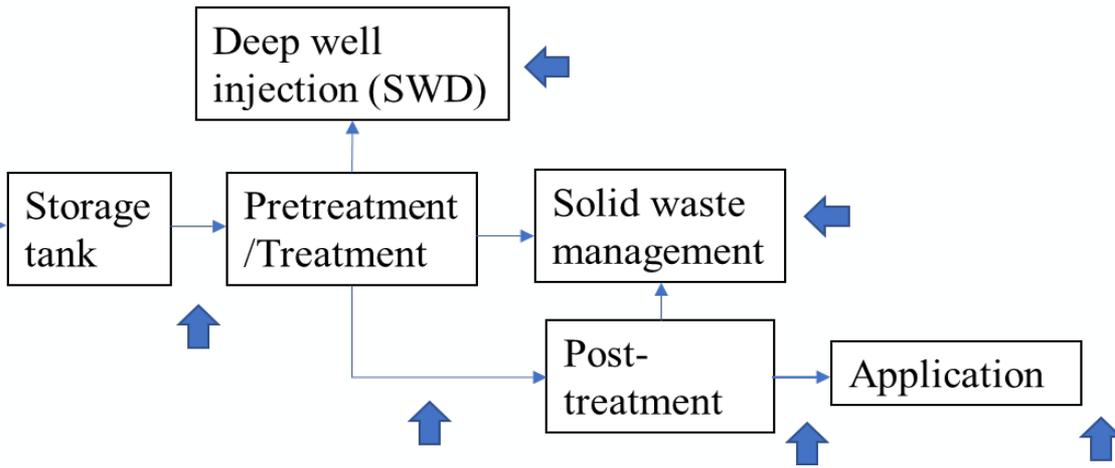
# What Constituents Should We Analyze?

## NPDES+ List

- Published in Water 2022, 14(14), 2162; <https://doi.org/10.3390/w14142162>
- Water quality standards for surface water discharge, land application, irrigation, wildlife and livestock watering, road application, dust control, and groundwater standards
- Developed a multi-tiered analytical approach with a comprehensive analytical list for characterization of physical, chemical, and biological properties of raw produced water and treated produced water using target and non-target analyses as well risks and toxicity assessment



# Multi-tiered Approach for Produced Water Characterization – NPDES+



The cost and turnaround time of produced water analysis

# Multi-tiered Approach for Produced Water Characterization – NPDES+

Level	Use	Parameters	Frequency	Sample
Tier 1	Continuous monitoring, bulk testing, rapid analysis, process control	Flow TSS/Turbidity TDS/EC TOC/DOC/COD pH ORP Iron (total, dissolved, Fe <sup>2+</sup> ) H <sub>2</sub> S NH <sub>3</sub> Alkalinity Hardness (total, dissolved) Specific gravity Percent Moisture Optional: UV-Vis, Fluorescence excitation-emission matrix (F-EEM)	Baseline, real-time, continuous, and routine	Feed/produced water Product water Brine

# Multi-tiered Approach for Produced Water Characterization – NPDES+

Level	Use	Parameters	Frequency	Sample
<b>Tier 2</b>	Detailed characterization, routine monitoring, and Tier 1 data verification	<b>Inorganics</b> <ul style="list-style-type: none"> <li>• Metal elements (33), SW-864 6020A, dissolved, total Hg, SW-846 7470</li> <li>• Anions (7), EPA 300</li> <li>• Radionuclides               <ul style="list-style-type: none"> <li>• Radium 226, 228</li> <li>• Gross Alpha/Beta</li> <li>• U 235, 236, 238</li> <li>• Strontium 90</li> </ul> </li> </ul>	Baseline (at least once) Demonstrating treatment efficacy and reliability, beneficial reuse investigation	Feed/produced water  Product water  Brine



# Multi-tiered Approach for Produced Water Characterization – NPDES+

Level	Use	Parameters	Frequency	Sample
<b>Tier 2</b>	Detailed characterization, routine monitoring, and Tier 1 data verification	<b>Organics</b> <ul style="list-style-type: none"> <li>• Oil and Grease</li> <li>• GRO [C6-C10] by 8015D</li> <li>• DRO [C10-C28] by 8015D</li> <li>• MRO (C28-40) by 8015D</li> <li>• VOCs SW-846 8260 (91)</li> <li>• SVOC - General by 8270E (139)</li> <li>• SVOC - TPH by 8015 (8)</li> <li>• <b>1-2 samples for screening:</b> <ul style="list-style-type: none"> <li>• VOC - TPH by 8015</li> <li>• SVOC - Explosives by 8330B</li> <li>• SVOC - Agent Breakdown Products</li> <li>• SVOC - Pesticides/Herbicides by 8081B</li> <li>• SVOC - Polychlorinated biphenyls (PCBs) (8280A)</li> <li>• SVOC - PAHs</li> <li>• SVOC - Organic Acids by 8015D</li> <li>• SVOC – Dioxins</li> <li>• TOX by SW 846 9020</li> <li>• PFOA, PFOS &amp; PFHxS by EPA 537.1 Modified</li> </ul> </li> </ul>	Baseline (at least once), Demonstrating treatment efficacy and reliability, beneficial reuse investigation	Feed/ produced water  Product water  Brine



# Multi-tiered Approach for Produced Water Characterization – NPDES+

Level	Use	Parameters	Frequency
Tier 3	Risks and toxicology assessment	WET Testing acute and chronic toxicity	Product water (at least once)
		HiRes LC-MS non-target screening	
	Fate/transport modeling.	Analysis of treated effluent on soil, plant, tissue samples	
Tier 4	Waste and residual characterization	Mass balance	As needed



# Characterization of Produced Water in the Permian Basin

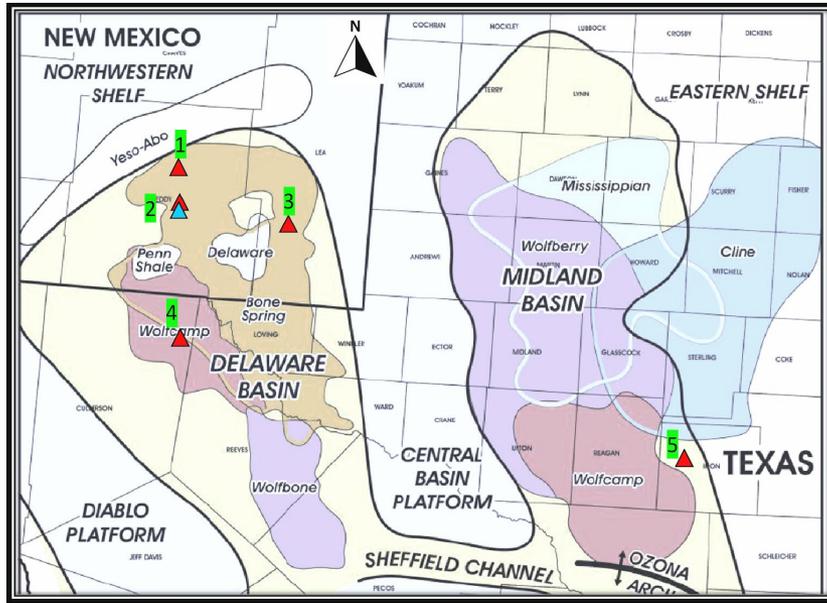
- Produced water quality is highly variable: by region, within an oil or gas play, with time
- Limited produced water quality data in existing database: primarily inorganic ions

	Permian Basin	Wolfcamp Formation	Delaware Formation	Artesia Formation	Yeso Formation	Bone Spring Formation	San Andres Formation
TDS (mg/L)	10,048-384,963/ 118,253	12,136-249,459/ 95,096	12,708-360,545/ 185,433	10,050-384,963/ 94,584	10,818-381,108/ 123,784	10,048-255,451/ 105,569	10,026-391,007/ 118,879
pH	0.5-11.7/6.8	4.5-8.6/7.0	4.8-8.9/6.9	4.6-9.7/7.1	0.5-8.8/6.7	6.3-7.1/6.8	0.6-11.7/6.9
Mg (mg/L)	3-27,910/ 1,901	84-5,965/ 1,103	3-10,800/ 2,509	12-18,400/ 1,593	12-18,980/ 2,281	54.4-3396.6/ 760	2.7-27,910/ 2,087
Ca (mg/L)	24-60,073/ 6,051	211-40,800/ 6,358	24-46,346/ 12,992	87-25,315/ 3,205	235-40,420/ 6,996	174.5-21,720/ 3347	107-60,073/ 6,952
Cl (mg/L)	40-245,700/ 71,224	3,951-151,900/ 56,362	2,460-225,612/ 113,116	3,794-222,596/ 56,580	2,350-237,245/ 74,606	4,076-156,699/ 60,184	40-245,700/ 70,738
Na (mg/L)	209-143,086/ 71,224	2,625-54,068/ 29,045	5,253-109,024/ 51,113	209-128,175/ 37,470	1,529-107,396/ 35,948	1,982-80,469/ 30,723	1,123-143,086/ 35,479
K (mg/L)	14-33,962/ 861	97-742/ 362	79-1,454/ 548	65-4,620/ 505	14-1,570/ 472	109.8-1,232/ 365	8-33,962/ 1,622
Sulfate (mg/L)	18-12,320/ 2,131	84-12,080/ 1,753	84-6,280/ 1,523	18-11,900/ 2,294	35-11,800/ 2,211	111-5,250/ 1,420	22.4-12,320/ 2,362
Br (mg/L)	10-1,064/ 430	10 - 756/ 390	NA	NA	240-963/ 481	152-1,065/ 382	17-517/ 153
HCO3 (mg/L)	5-7,440/ 731	5-4,204/ 619	5-5,558/ 376	9-7,440/ 878	5-3,851/ 645	5-891/ 390	7-3,960/ 663
TOC (mg/L)	53-184/123	86-184/138	NA	NA	NA	119	NA



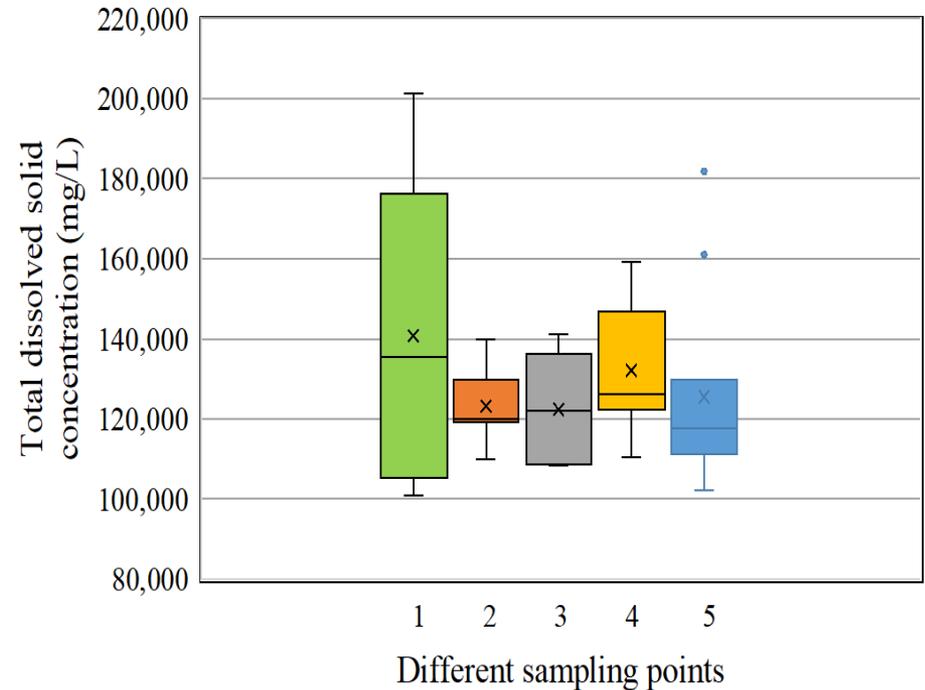
# Characterization of Produced Water in the Permian Basin

Sampling points of 46 PW and 10 Pecos River water



- ▲ Produced water sampling point
- ▲ Pecos River water sampling point

TDS distribution of PW at different sampling points



Source: Jiang et al., JHM 2022, 430, 128409

# Characterization of Produced Water in the Permian Basin

## Targeted Chemical Analysis

More than 300 targeted analytes were quantitatively analyzed, including wet chemistry, inorganics, radionuclides, organics such as VOCs, SVOCs, total petroleum hydrocarbons, organic acids, oil and grease, pesticides/herbicides, dioxins, and tentatively identified compounds, and per- and polyfluoroalkyl substances (PFAS).

**For 10 produced water samples collected in 2020, 91 analytes were quantified and 218 analytes were not detected (309 in total)**

**For 10 Pecos River samples collected in 2020, 67 analytes were quantified and 242 analytes were not detected (309 in total)**

Source: Jiang et al., JHM 2022, 430, 128409



# Water Quality Characterization

Statistical results of general quality parameters of the 46 PW samples collected from the Delaware and Midland Basins

		Mean	Max	Min	25th percentile	50th percentile	75th percentile
<b>Alkalinity</b>	mg/L as CaCO <sub>3</sub>	272	870	100	128	207	336
<b>Ammonia</b>	mg/L	432	750	320	330	400	495
<b>COD</b>	mg/L	1,626	3,100	930	1,250	1,400	1,950
<b>pH</b>	SU	6.6	8.1	3.9	6.3	6.7	7.0
<b>TDS</b>	mg/L	128,641	201,474	100,830	113,441	122,280	134,525
<b>TOC</b>	mg/L	103.5	248.1	2.4	28	90.6	173.3
<b>TSS</b>	mg/L	342.9	790	85	142.5	375	422.5
<b>Turbidity</b>	NTU	116.4	200	23	36	110	200
<b>MBAS</b>	mg/L	1.10	2.1	0.047	0.92	0.97	1.33

Source: Jiang et al., JHM 2022, 430, 128409



# Water Quality Characterization

Produced Water		Average	Max	Min
<b>Radionuclide</b>				
Gross Alpha	pCi/L	1105.6	1630	660
Gross Beta	pCi/L	874.6	1230	456
Radium-226	pCi/L	43.92	111	0.736
Radium-228	pCi/L	151.27	291	2.56

Water quality of Pecos River water samples		Average	Max	Min	Drinking water standards
<b>Radionuclide</b>					
<b>Gross Alpha</b>	<b>pCi/L</b>	<b>24.6</b>	<b>39.8</b>	<b>7.7</b>	<b>15</b>
Gross Beta	pCi/L	14.1	24.2	1.4	4 millirems per year
Radium-226	pCi/L	3.56	29.9	0.1	5 pCi/L for
Radium-228	pCi/L	0.42	0.8	0.2	Combined Ra226/228



# Water Quality Characterization

Produced Water		Average	Max	Min
<b>VOCs</b>				
Benzene	mg/L	2.61	4.90	1.90
Ethylbenzene	mg/L	0.11	0.16	0.07
Toluene	mg/L	2.53	3.70	1.70
Xylenes, Total	mg/L	1.19	1.60	0.71

## No VOCs detected in Pecos River (9 samples)

Produced Water		Average	Max	Min
<b>Oil and Others</b>				
Diesel Range Organics (C10-C20)	ug/L	45,750	130,000	22,000
Gasoline Range Organics [C6 - C10]	ug/L	21,625	46,000	13,000
Motor oil/lube range organics (MRO) (C20-C34)	ug/L	32,444	97,000	12,000
Tributyl phosphate	ug/L	34.6	74	3.3
Tentatively Identified Compound	ug/L	531	1000	280
<b>Pecos River water samples</b>		<b>Average</b>	<b>Max</b>	<b>Min</b>
<b>Oil and Others</b>				
Gasoline Range Organics [C6 - C10]	ug/L		54	ND
Motor oil/lube range organics (MRO) (C20-C34)	ug/L	230	310	180
Tributyl phosphate	ug/L	3.6	5.7	1.7
Tentatively Identified Compound	ug/L	-	55	-

# Water Quality Characterization

Produced water		Average	Max	Min
<b>Organic - SVOC - General</b>		Average	Max	min
1,1'-Biphenyl	ug/L	5.9	8.5	3.8
1,4-Dioxane	ug/L		21	ND
1-Methylnaphthalene	ug/L	23	36	15
2-Methylnaphthalene	ug/L	38	65	26
2-Methylphenol	ug/L	82	98	68
2,4-Dimethylphenol	ug/L	34	42	29
Ethylene glycol	mg/L		27	ND
Methylphenol, 3 & 4	ug/L	90	110	72
Phenol	ug/L	203	250	170
Pyridine	ug/L	238	300	120

**Not detected in Pecos River (9 samples)**

# Water Quality Characterization

Produced Water		Average	Max	Min
<b>Organic - SVOC - Pesticides/Herbicides</b>				
alpha-BHC	ug/L	0.018	0.027	0.0088
Endosulfan I	ug/L	0.855	0.98	0.73
Endrin	ug/L		0.0038	ND

Pecos River water		Average	Max	Min
<b>Organic - SVOC - Pesticides/Herbicides</b>				
Endosulfan I	ug/L	0.00405	0.0042	0.0039
4,4'-DDD	ug/L		0.01	ND
4,4'-DDT	ug/L		0.0057	ND

Produced Water		Average	Max	Min
<b>Organic - SVOC - PAH</b>				
Anthracene	ug/L		1.1	ND
Naphthalene	ug/L	15.44	24	11
Phenanthrene	ug/L	3.76	6.6	2.7
Fluorene	ug/L	4.35	5.6	3.1

Pecos River water		Average	Max	Min
<b>Organic - SVOC - PAH</b>				
Naphthalene	ug/L		6	ND
Fluorene	ug/L		1.2	ND



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# Water Quality Characterization

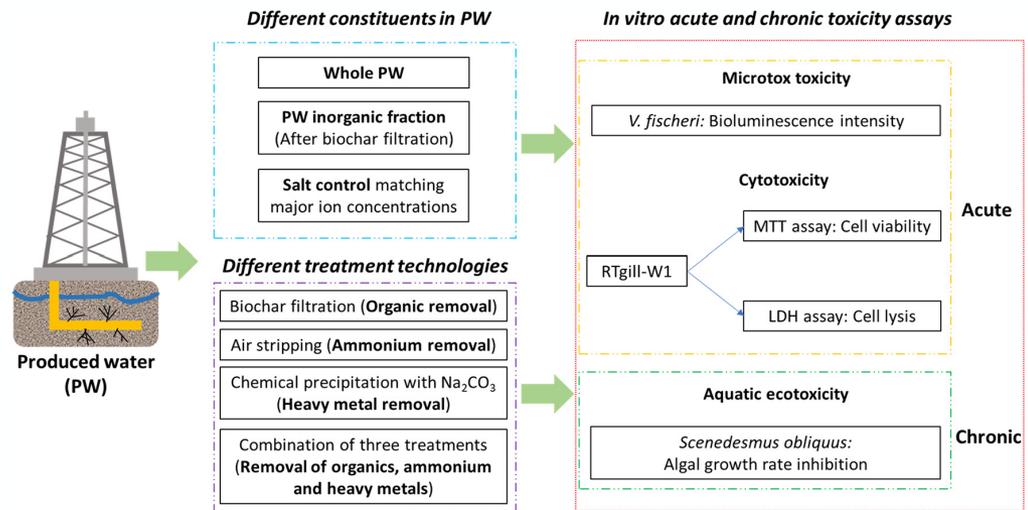
**Preliminary PFAS  
Results of 1  
Produced Water  
Sample (5/34  
detected) and 1  
Pecos River Sample  
(10/34 compounds  
detected)**

	PW/ Pecos	PW MDL/RL	Pecos MDL/RL		PW/ Pecos	PW MDL/RL	Pecos MDL/RL
PFBS	0.17 J/2.0	0.15/1.5	0.16/1.6	PFNS	ND/ND	0.12/1.5	0.13/1.6
PFBA	0.31 J B/ 1.3 J B	0.25/1.5	0.28/1.6	PFNA	ND/ND	0.2/1.5	0.21/1.6
PFDS	ND/ND	0.23/1.5	0.25/1.6	FOSA	ND/ 0.54 J B	0.25/1.5	0.28/1.6
PFDA	ND/ND	0.23/1.5	0.24/1.6	PFOS	ND/1.2 J	0.39/1.5	0.42/1.6
PFDoS	ND/ND	0.33/1.6	0.35/1.6	PFOA	ND/1.0 J	0.62/1.5	0.67/1.6
PFDoA	ND/ND	0.4/1.6	0.43/1.6	PFPeS	ND/0.24 J	0.22/1.5	0.24/1.6
PFHpS	ND/ND	0.14/1.6	0.15/1.6	PFPeA	ND/1.8	0.36/1.5	0.39/1.6
PFHpA	ND/0.35 J	0.18/1.5	0.2/1.6	PFTeA	0.24 J/ND	0.21/1.5	0.23/1.6
PFHxS	0.25 J B/ 1.0 J B	0.12/1.5	0.13/1.6	PFTriA	ND/ND	0.94/1.5	1/1.6
PFHxA	ND /1.2 J	0.42/1.5	0.46/1.6	PFUnA	ND/ND	0.8/1.5	0.87/1.6
NEtFOSA	ND/ND	0.63/1.5	0.68/1.6	NMeFOSA	ND/ND	0.31/1.5	0.34/1.6
NEtFOSE	0.98 J/ND	0.62/1.5	0.67/1.6	NMeFOSAA	ND/ND	2.3/15	2.4/16
NEtFOSAA	ND/ND	1.4/15	1.5/16	NMeFOSE	ND/ND	1/2.9	1.1/3.1
4:2 FTS	ND/ND	3.8/15		6:2 FTS	ND/ND	1.5/15	
8:2 FTS	ND/ND	1.5/15		10:2 FTS	ND/ND	0.14/1.5	
DONA	ND/ND	0.13/1.5		HFPO-DA (GenX)	ND/ND	1.1/2.9	
F-53B Major	ND/ND	0.17/1.5		F-53B Minor	ND/ND	0.23/1.5	



# Toxicological Characterization of Produced Water from the Permian Basin

- PW toxicity was studied using in vitro toxicity assays using various aquatic organisms (luminescent bacterium, fish gill cell line RTgill-W1, and microalgae).
- High salinity was the foremost toxicological driver in PW, followed by organic contaminants.
- Treatment required to reduce toxicity:
  - Salts - Desalination
  - Organic removal
  - Ammonia removal
  - Heavy metals removal



Source: Hu et al., Sci. Total Environ 2022, 815, 152943



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# Journal of Hazardous Materials

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Research Paper

## Characterization of produced water and surrounding surface water in the Permian Basin, the United States

Wenbin Jiang<sup>a</sup>, Xuesong Xu<sup>a</sup>, Ryan Hall<sup>b</sup>, Yanyan Zhang<sup>a</sup>, Kenneth C. Carroll<sup>c</sup>, Frank Ramos<sup>d</sup>, Mark A. Engle<sup>e</sup>, Lu Lin<sup>a</sup>, Huiyao Wang<sup>a</sup>, Matthias Sayer<sup>b</sup>, Pei Xu<sup>a,\*</sup>



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### Data in Brief

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Data Article

## Datasets associated with the characterization of produced water and Pecos River water in the Permian Basin, the United States



Wenbin Jiang<sup>a</sup>, Xuesong Xu<sup>a</sup>, Ryan Hall<sup>b</sup>, Yanyan Zhang<sup>a</sup>, Kenneth C. Carroll<sup>c</sup>, Frank Ramos<sup>d</sup>, Mark A. Engle<sup>e</sup>, Lu Lin<sup>a</sup>, Huiyao Wang<sup>a</sup>, Matthias Sayer<sup>b</sup>, Pei Xu<sup>a,\*</sup>

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<sup>e</sup> Department of Earth, Environmental and Resource Sciences, The University of Texas at El Paso, El Paso, TX 79968, United States



# Major Focus: State-of-the-Art Risk and Toxicology Testing

## Standardized:

- Standardized Sampling Protocol w/USEPA by NMSU
- NPDES+ Analysis (300 Constituents)
  - Certified Lab, NMSU, and USEPA
- TIC/Unknown Analysis – HR-LCMS @ NMSU
- Whole Effluent Toxicity Testing
  - Certified lab and NMSU
- Human cell-line analysis
  - USEPA and NMSU
- State of the Art - Risk and Tox Analysis
  - Predicted Env. Conc. (PEC)
  - Predicted No-effect Conc (PNEC) – supported and coordinated by ExMo and UofDE

## Challenges:

- TIC/Unknown analysis of raw PW difficult for HR-LCMS
- Need to develop advanced analytical tools and risk assessment methods to evaluate the impact on environmental and public health
- High analytical costs



# Summary

- Provide data, information, and knowledge to assist in developing science-based regulations for fit-for-purpose reuse of treated produced water
- Improve characterization of physical, chemical, microbiological, and environmental toxicity analysis of produced water and treated produced water
- Evaluate integrated treatment systems including pretreatment, treatment/desalination, and post-treatment for fit-for-purpose applications
- Evaluate economic, social, and environmental risks/benefits of produced water reuse
- Developed foundational documents such as produced water research roadmaps and gaps Analysis, research plan, testing guidance and protocols
- Published >20 journal papers on produced water characterization, treatment, and regulations
- Collaborate extensively with federal, state, industry, NGOs, TX and CO Consortiums, and other stakeholders



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