

# Characterization of Produced Water and Surrounding Surface Water in the Permian Basin

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# Acknowledgement

- Technical support and review
  - New Mexico Produced Water Research Consortium (NMPWRC)
  - New Mexico Environment Department
  - New Mexico Oil and Gas Association
- Co-authors
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  - NGL Partners LP: Ryan Hall, Matthias Sayer
  - UTEP: Mark A. Engle

# Challenge in Produced Water Characterization

- Complex water chemistry - constituents of concern in produced water (formation water and flowback water) including:
  - Suspended solids, oils, and grease
  - Salts (referred to as dissolved solids)
  - Dissolved organics (e.g., petroleum hydrocarbons, volatile and semi-volatile compounds)
  - Metals
  - 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
  - Unknowns
- High salinity and complex water chemistry causes challenges in analytical methods.

# Challenge in Produced Water Characterization

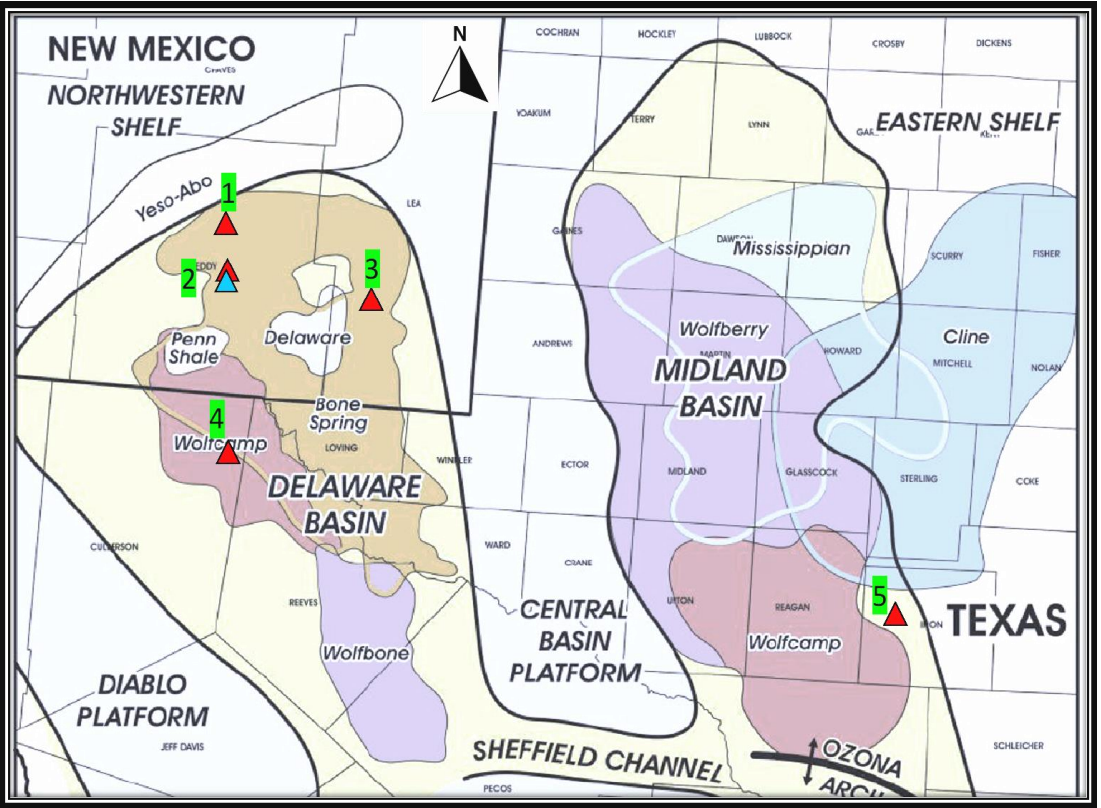
- Produced water quality is highly variable: by region, within an oil or gas play, with time
- Limited produced water quality data in existing database: primarily inorganic ions

	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

# Objectives

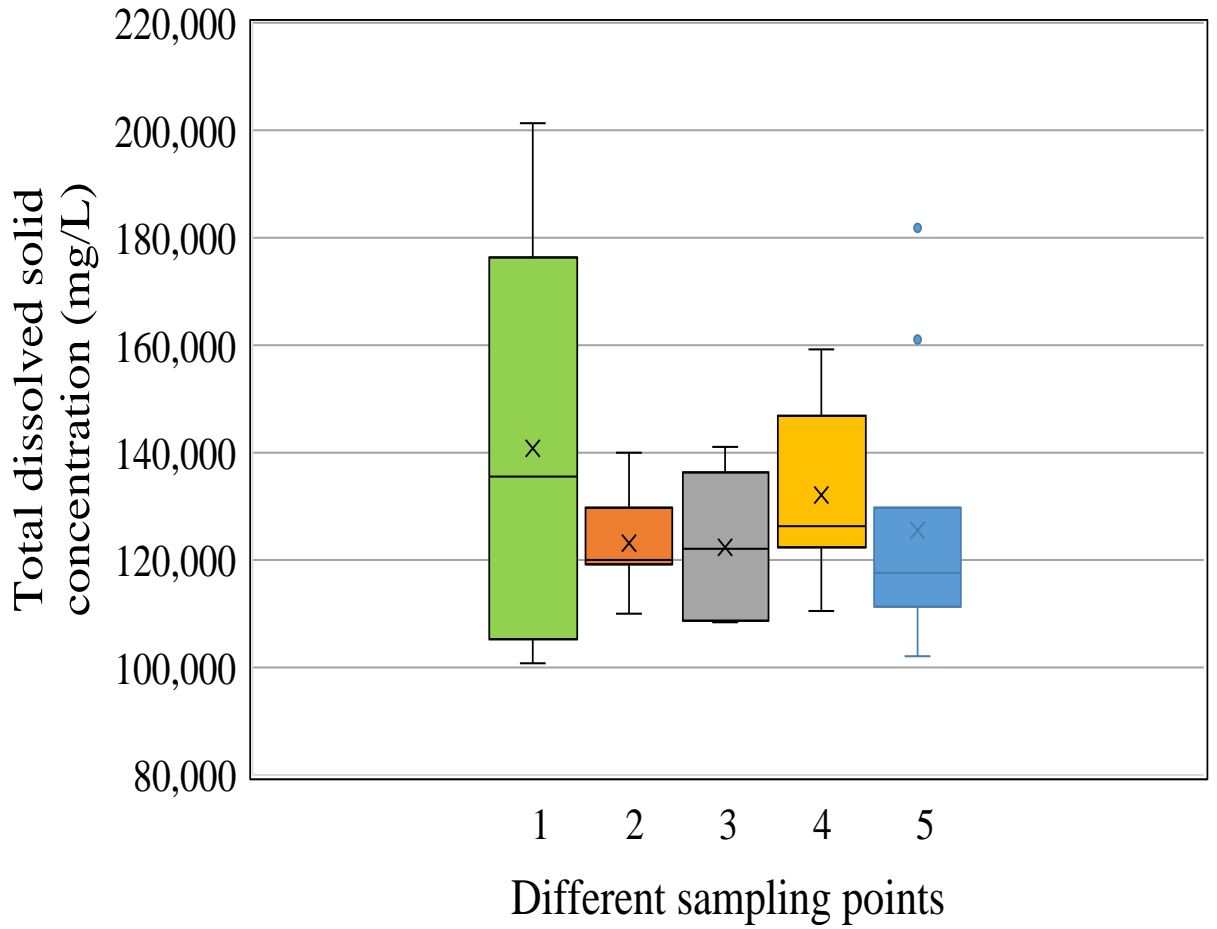
- A thorough understanding of produced water quality is critical to advance the knowledge and tools for effective produced water management, treatment, risk assessment, and feasibility for beneficial reuse outside the oil and gas industry.
- Characterization of water quality of nearby water bodies provides background analytical information and baseline data for potential discharge and reuse of treated produced water.

# 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



# 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 detected and 218 analytes were not detected (309 in total)**

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

# 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



# 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

Pecos River water		Average	Max	Min
<b>Radionuclide</b>				
<b>Gross Alpha</b>	<b>pCi/L</b>	<b>24.6</b>	<b>39.8</b>	<b>7.7</b>
Gross Beta	pCi/L	14.1	24.2	1.4
Radium-226	pCi/L	3.56	29.9	0.1
Radium-228	pCi/L	0.42	0.8	0.2

# Water Quality Characterization

Produced Water VOCs		Average	Max	Min
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)**

# Water Quality Characterization

Produced Water Samples		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

Pecos River water samples		Average	Max	Min
<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

# Water Quality Characterization

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

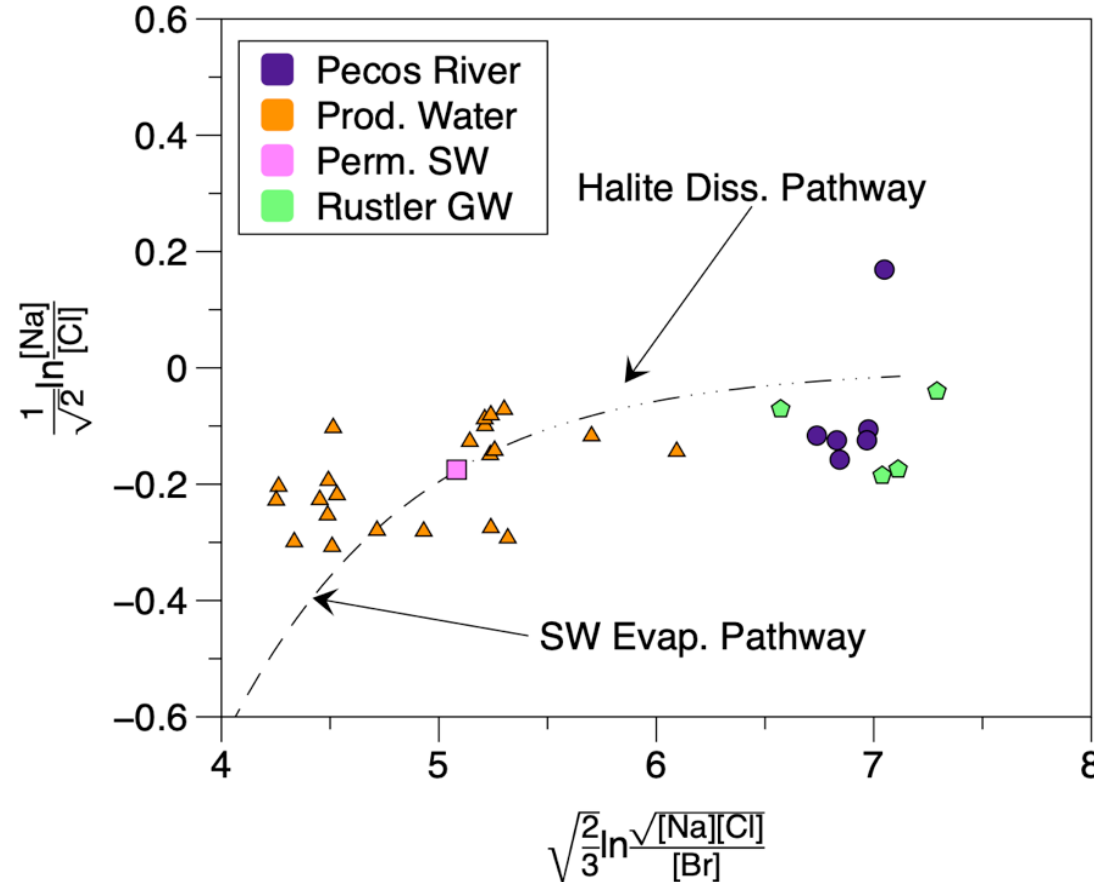
<b>Perfluoroalkyl substances (PFAS)</b>		Produced Water	Pecos River
Perfluorobutanesulfonic acid (PFBS)	ng/L	0.17	2
Perfluorobutanoic acid (PFBA)	ng/L	0.31	1.3
Perfluorodecanesulfonic acid (PFDS)	ng/L	ND	ND
Perfluorodecanoic acid (PFDA)	ng/L	ND	ND
Perfluorododecanesulfonic acid (PFDoS)	ng/L	ND	ND
Perfluorododecanoic acid (PFDoA)	ng/L	ND	ND
Perfluoroheptanesulfonic Acid (PFHpS)	ng/L	ND	ND
Perfluoroheptanoic acid (PFHpA)	ng/L	ND	0.35
Perfluorohexanesulfonic acid (PFHxS)	ng/L	0.25	1
Perfluorohexanoic acid (PFHxA)	ng/L	ND	1.2
Perfluorononanesulfonic acid (PFNS)	ng/L	ND	ND
Perfluorononanoic acid (PFNA)	ng/L	ND	ND
Perfluorooctanesulfonamide (FOSA)	ng/L	ND	0.54
Perfluorooctanesulfonic acid (PFOS)	ng/L	ND	1.2
Perfluorooctanoic acid (PFOA)	ng/L	ND	1
Perfluoropentanesulfonic acid (PFPeS)	ng/L	ND	0.24
Perfluoropentanoic acid (PFPeA)	ng/L	ND	1.8
Perfluorotetradecanoic acid (PFTeA)	ng/L	0.24	ND
Perfluorotridecanoic acid (PFTriA)	ng/L	ND	ND
Perfluoroundecanoic acid (PFUnA)	ng/L	ND	ND

Preliminary PFAS Results of 1 Produced Water Sample and 1 Pecos River Sample

Based on FracFocus database, no PFAS were used in HF chemical additives in the Permian Basin.

EPA health advisory 70 ng/L

# Water Quality Characterization



**Strongly overlapping data of these conservative relationships suggest that shallow brines from evaporite mineral dissolution is the dominant source of salinity to the Pecos River samples.**

Isometric log-ratio Na-Cl-Br plot showing data from Permian Basin PW, Pecos River, and Rustler aquifer groundwater samples against modeled pathways for ancient (late Permian) seawater evaporation and halite mineral dissolution.



# Concluding Remarks and Future Research

- Analytical results and data are published in Journal of Hazardous Materials.
- Provide the first step to better understand produced water quality and surrounding surface water as baseline to develop beneficial reuse programs that are protective of human health and the environment.
- Assist in determining management strategies, treatment methods, potential beneficial reuse applications, and potential environmental impacts specific to intended beneficial use of treated produced water
- Need more data to better understand produced water quality and the spatial and temporal variability
- Characterize the quality of produced water and treated water, including non-target analysis of “unknown” constituents in produced water and treated water.
- Conduct risks and toxicology assessment of produced water treatment and reuse for fit-for-purpose applications.

# Thank You!

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