Chemical Composition of Produced and Flowback Water Collected from Different Hydraulic Fracturing Sites and Wells

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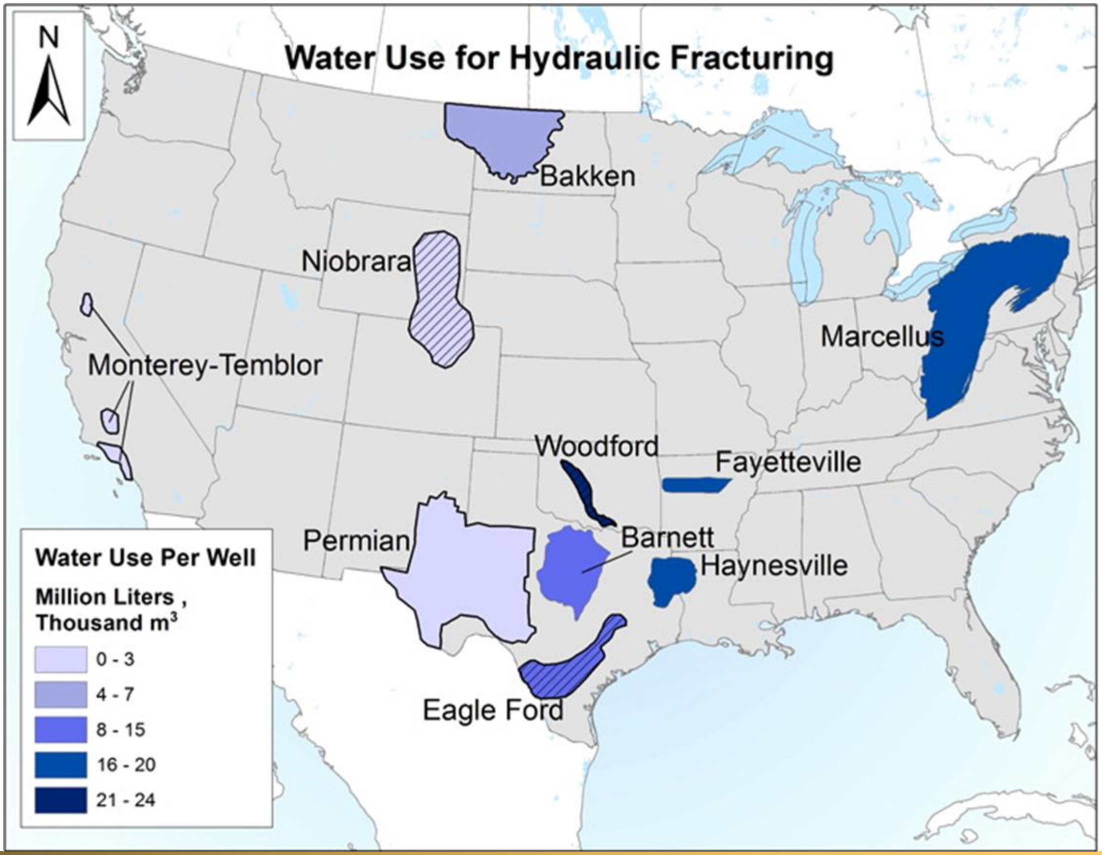
WATER RESOURCES

- **1.4 billion km^3 water available on earth**
- **Nearly 97% is salt water in the oceans**
- **World freshwater reserves are estimated at around 35 million km^3 (mostly locked up in glaciers and permanent snow cover, or in deep groundwater, inaccessible to humans)**
- **By the year 2025, 2/3 of the world population will face drinking water scarcity**

Hydraulic Fracturing

- **Fresh water used for fracking: 1000 - 30,000 m^3/well-year**
- **The United States produces 870 billion gallons of produced water annually**
- **OK is one of the highest gas/oil producing states (top 5 states) in the US**



Environ. Sci. Technol. Lett. 2015, 2, 276–280

Types of Water Generated during Hydraulic Fracturing

- **Flowback water: Following the fracturing process, a portion of the fracking fluid returns to the surface for about two weeks.**
- **Produced Water: More water may be produced along with oil and gas after the flowback period is over and well is in production.**

Flowback and Produced Water Chemical Composition

Chemical composition of flowback and produced water is affected by;

- **Geographic location of the well**
- **Duration of well operation/production**
- **Composition of fracturing fluid**

Chemical Components of Fracturing Fluid

Additives	Chemical composition	Purpose	%
Water	H_2O	Main carrier (base carrier fluid)	90.800
Sand	Water and crystalline silica (quartz)	Propping agent use to hold open fractures	8.500
Acids	Hydrochloric acid, acetic acid,	Clean and help dissolve minerals and initiate cracks in the rock	0.150
Clay stabilizers	Choline chloride, tetramethylammonium chloride	Prevent swelling of clays found in shale	0.120
Scale inhibitors	Carboxylic acids and acrylic acid polymers	Prevent formation of scale (mineral) deposits in the pipe	0.090
Surfactants	Amido-amines, quaternary amines, phosphate esters, alcohol polyethoxylates, ethylenene glycols, isopropanol	Increase the viscosity of the fluid	0.075
Friction reducers	Polyacrylamide	Minimize friction between the fluid and the pipe, thus allowing to pump at a higher rate	0.070
Breakers	NaCl and KCl	Reverse crosslinking allowing the production gas to flow through	0.060
Biocides	Gluteraldehyde, DBNPA, quaternary ammonium compounds	Prevent bacteria growth in water	0.060
Gels	Guar gum	Thicken the water to suspend the sand and also increases viscosity of the fluid to deliver proppant more efficiently	0.050
pH adjusting agents	Sodium or potassium carbonate	Maintain effectiveness of crosslinkers	0.010
Crosslinkers	Borate salts	Maintain fluid viscosity as temperature increases	0.007
Iron control	Citric acid	Prevent precipitation of iron oxides	0.006
Corrosion inhibitors	Amines, amides and amido-amines	Prevent corrossion of the pipe	0.002

I. Ferrer, E.M. Thurman / Trends in Environmental Analytical Chemistry 5 (2015) 18–25

Wastewater Handling Methods

Historically four approaches have been considered for produced water handling:

- **surface disposal or spreading,**
- **reuse and recycling,**
- **deep-well injection at approved wastewater injection sites**
- **wastewater treatment on-site in and industrial facilities,**

Produced Water Treatment Methods

- Reverse Osmosis (RO)
- Membrane Distillation (MD)
- Multi-Effect Distillation (MED)
- Multi-Stage Flash (MSF)
- Mechanical Vapor Compression (MVC)
- Biological treatment

Motivation for the Study

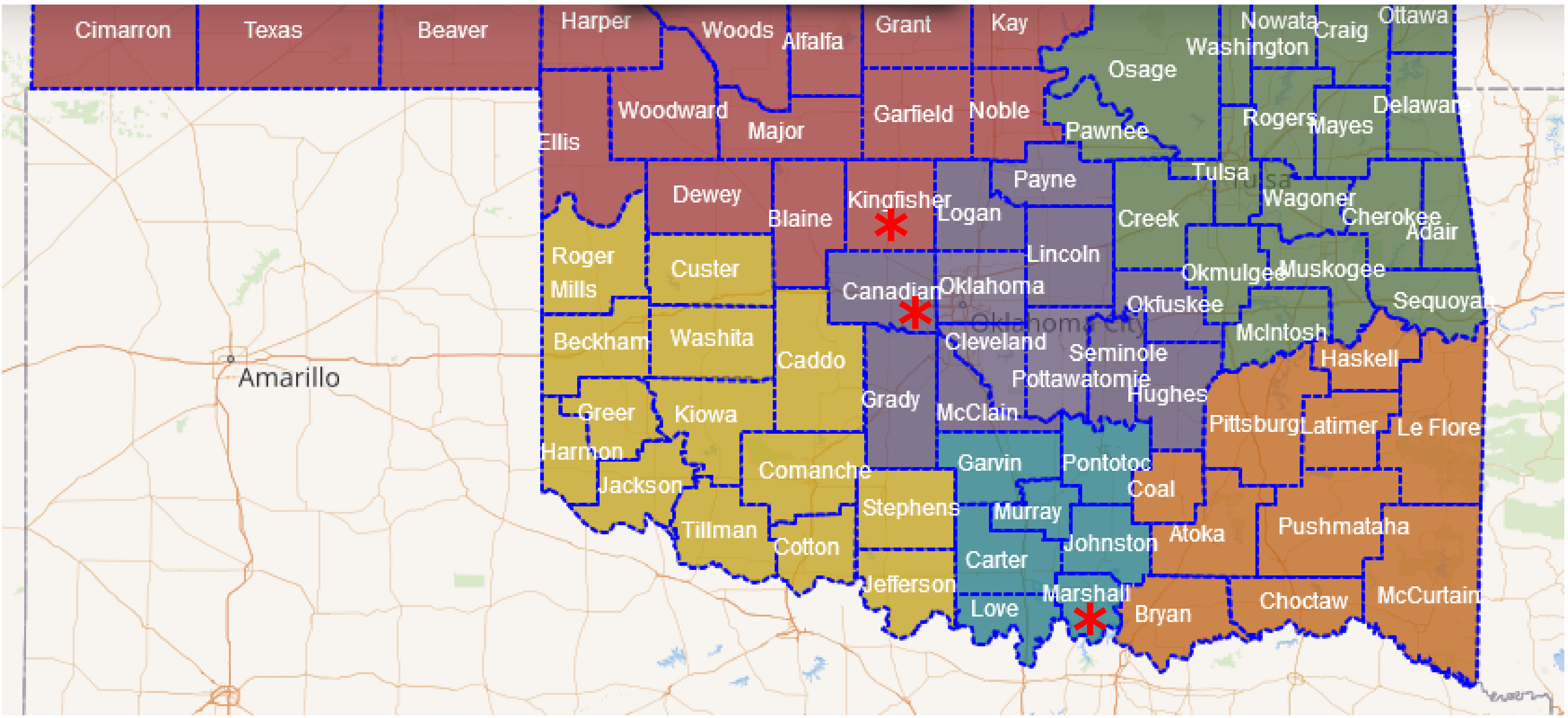
- **Sustainable use of limited fresh water resources**
- **Development of an integrated system that will clean up wastewater while producing biomass that can be converted to bio-products including biofuels.**

Giovanni Antonio Lutzu & Nurhan Turgut Dunford. 2019. Algal treatment of wastewater generated during oil and gas production using hydraulic fracturing technology. ENVIRONMENTAL TECHNOLOGY, 2019, VOL. 40, NO. 8, 1027–1034

Sample Collection Sites and Water Type

Site	County	Extraction	Water type
El Reno (1)	Canadian, OK	gas	flowback
Cumberland (2)	Marshall, OK	gas	produced
Okarche (3)	Kingfisher, OK	oil	produced
Okarche (4)	Kingfisher, OK	oil	produced
Okarche (5)	Kingfisher, OK	oil	produced
Okarche (6)	Kingfisher, OK	oil	flowback
Okarche (7)	Kingfisher, OK	oil	flowback
Okarche (8)	Kingfisher, OK	oil	produced

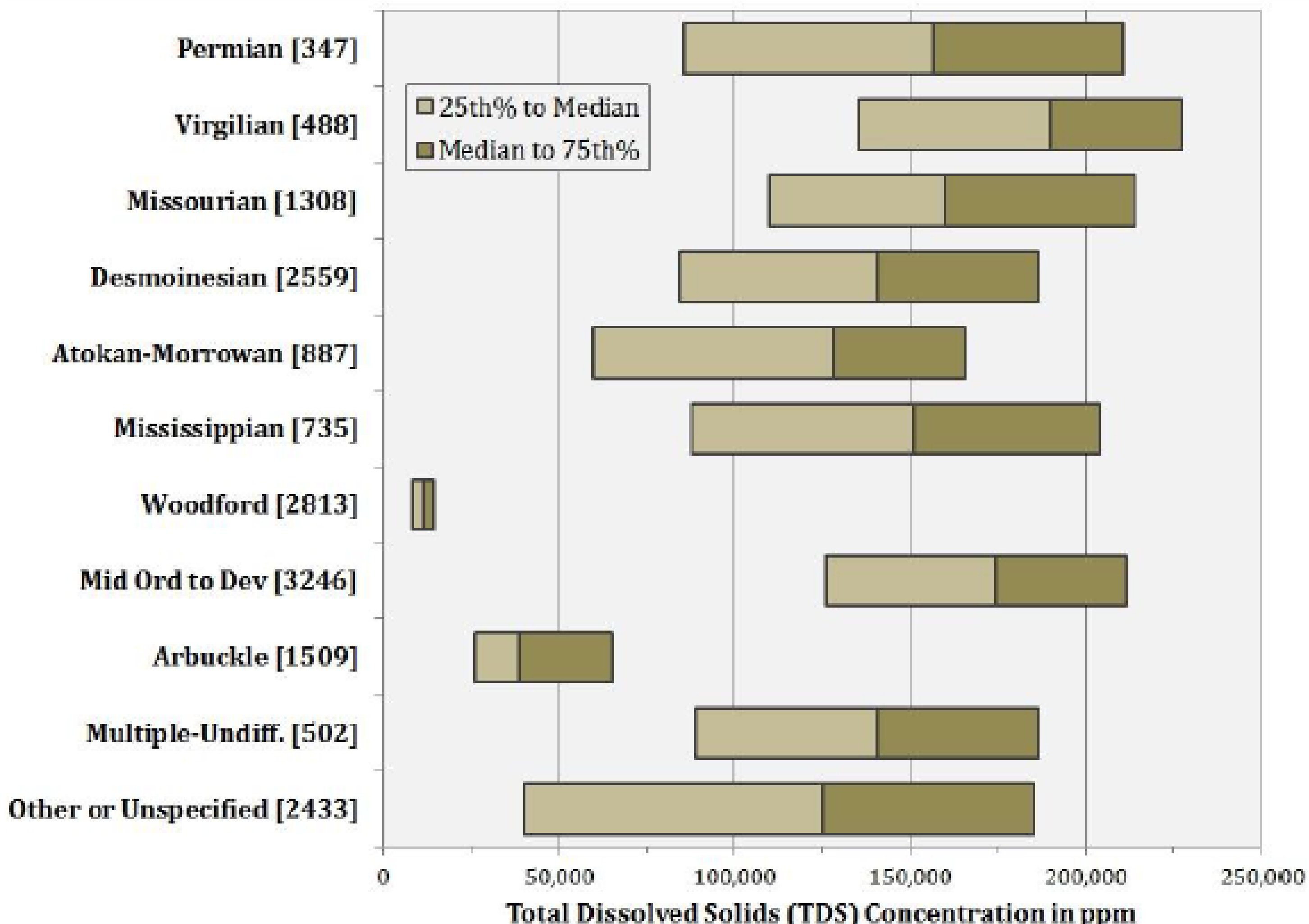
Location of the Wells



Chemical Composition of Wastewater

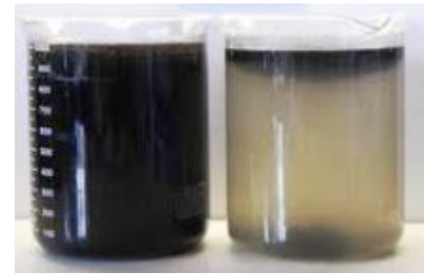
	FB-1	FB-6	FB-7	PW-2	PW-3	PW-4	PW-5	PW-8
Cations (mg L^{-1})								
Sodium	5,111	3,309	2,242	8,596	10,452	3,332	17,447	5,025
Calcium	8	92	49	101	979	68	2,237	109
Magnesium	50	13	5	36	135	12	319	19
Potassium	48	42	53	179	160	63	411	125
Anions (mg L^{-1})								
Nitrate-N	39	0.1	0.2	0.2	0.1	0.1	0.1	231
Chloride	7,065	3,824	1,406	13,492	17,348	3,473	29,565	6,836
Sulfate	21	283	1,012	18	651	816	548	1,064
Boron	30	48	64	114	51	49	55	78
Bicarbonate	1,396	1,130	1,577	868	570	1,258	415	530
Carbonate	340	ND	ND	77	ND	ND	ND	ND
pH	9	7.6	7.4	8.5	7.1	7.7	5.5	8.2
EC (µmhos cm^{-1})	24,400	15,130	9,340	37,900	47,300	14,010	72,900	23,700
Trace elements (mg L^{-1})								
Zinc	0.06	0.08	0.08	-	0.04	0.03	-	0.03
Copper	0.03	0.06	0.06	-	0.08	-	0.03	0.08
Manganese	-	-	-	-	-	-	1	-
Iron	0.17	1.04	4.54	-	7.6	1.6	13	0.03
Ammonium	-	0.3	0.3	86	24	6	59	17.3
ICAP_P	-	0.15	0.28	0.01	0.29	0.20	0.18	1.2
Derived values								
TDS (mg L^{-1})	16,104	9,986	6,345	25,014	31,218	9,246	50,942	15,642
SAR (%)	148	85	81	186	83	98	91	116
PAR (%)	1	0.6	1.1	2	0.7	1.1	1.3	1.7
Residual carbonates (meq L^{-1})	30	13	23	9	ND	16	ND	1.6
Sodium percentage (%)	98	96	97	98	88	97	84	97
Hardness (mg L^{-1})	224	283	145	403	2,997	218	6,890	352
Alkalinity (mg L^{-1} as $CaCO_3$)	1,712	926	1,292	839	467	1,031	340	434
COD (mg O_2 L^{-1})	1,874	2,770	1,964	1,764	2,645	1,083	2,024	NA
BOD5 (mg O_2 L^{-1})	NA	14.5	12.8	NA	21.3	14.3	13.1	NA

Total Dissolve Solid Content of Produced Water from Wells Operating in Oklahoma



K. Murray, 2016

Produced Water Pre-treatment Prior to Microalgae Growth Tests

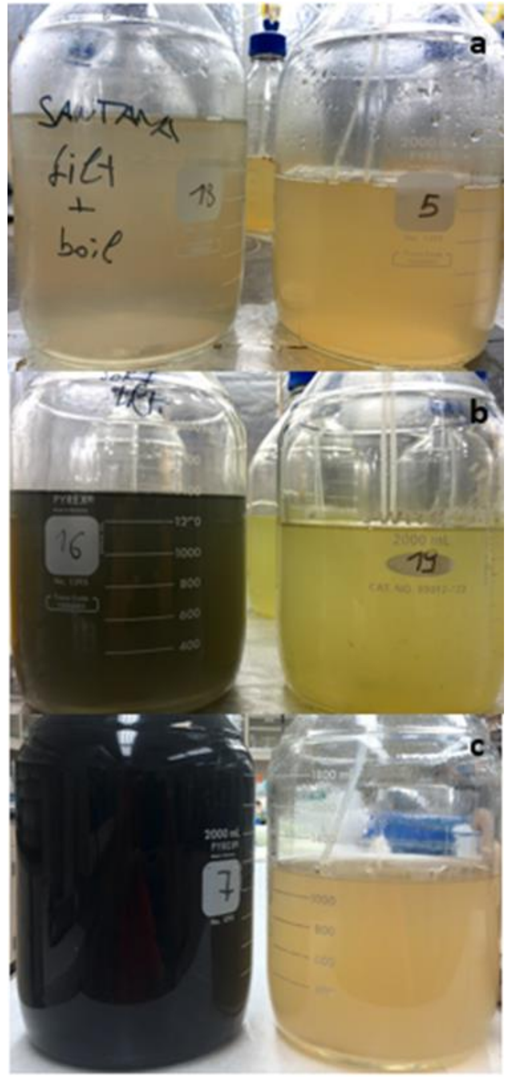


- Oil separation
- Microfiltration
- Heat treatment

Produced Water from Oil Wells

Oil Removal

Effect of Heat Treatment



Effect of Pre-treatment on Wastewater Chemical Composition

	Step 1	Step 2	Step 3	Step 4	Step 5
***Cations* (mg L^{-1})**					
Sodium	**4,488**	**4,471**	**4,483**	**4,500**	**4,766**
Calcium	**98**	**98**	**100**	**99.1**	**98.4**
Magnesium	**10**	**10.5**	**10.3**	**10.3**	**10.7**
Potassium	**90**	**89**	**89**	**89**	**95**
***Anions* (mg L^{-1})**					
Nitrate-N	**-**	**-**	**-**	**0.2**	**0.1**
Chloride	**5,985**	**5,595**	**5,461**	**5,633**	**5,796**
Sulfate	**1,294**	**1,296**	**1,305**	**1,306**	**1,386**
Boron	**61**	**61**	**61.5**	**61.6**	**65.3**
Bicarbonate	**865**	**793**	**881**	**858**	**762**
Carbonate	**ND**	**28**	**ND**	**ND**	**41**
pH	**8**	**8.4**	**8.1**	**7.6**	**8.5**
EC (μmhos cm^{-1})	**19,770**	**19,690**	**19,800**	**19,680**	**20,600**
***Trace elements* (mg L^{-1})**					
Zinc	**0.01**	**0.03**	**0.01**	**0.01**	**0.02**
Copper	**0.08**	**0.08**	**0.08**	**0.08**	**0.08**
Manganese	**0.58**	**1**	**1**	**1**	**0**
Iron	**6.88**	**0.22**	**0.01**	**0.09**	**0.28**
Ammonium	**12.6**	**12.2**	**11.1**	**12.2**	**8.9**
ICAP_P	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**
Derived values					
TDS (mg L^{-1})	**13,048**	**12,995**	**13,068**	**12,989**	**13,596**
SAR (%)	**115**	**114.6**	**114.1**	**115**	**122**
PAR (%)	**1.4**	**1.3**	**1.3**	**1.3**	**1.4**
Residual carbonates (meq L^{-1})	**8.4**	**8.2**	**8.6**	**8.3**	**8.1**
Sodium percentage (%)	**97**	**97**	**97**	**97**	**97**
Hardness (mg L^{-1})	**287**	**288**	**292**	**290**	**289**
Alkalinity (mg L^{-1} as $CaCO_3$)	**709**	**697**	**722**	**703**	**693**

Step 1: **wastewater as received**
Step 2: **Oil removal**
Step 3: **Micro filtration**
Step 4: **Heat treatment**
Step 5: **High temperature heat treatment**

Effect of Effect of Microalgae Growth on Produced Water Chemical Composition

	Before	% reduction after SP31 growth	% reduction after 2525 growth
Cations (ppm)			
Sodium	5111	68	73
Calcium	8	NR	NR
Magnesium	50	NR	46
Potassium	48	69	83
Anions (ppm)			
Nitrate–N	39	100	100
Chloride	7065	65	69
Sulfate	21	NR	NR
Boron	30	97	98
Bicarbonate	1396	88	88
Carbonate	341	NA	NA
pH	9	16	12
EC (μmhos cm^{-1})	24,400	65	68
Trace elements (ppm)			
Zinc	0.06	NR	NR
Copper	0.03	33	100
Iron	0.2	100	100
ICAP_P	ND	ND	ND
Derived values			
TDS (ppm)	16,104	65	71
SAR (%)	149	72	69
PAR (%)	0.8	75	75
Residual carbonates (meq L^{-1})	30	NA	NA
Sodium percentage (%)	98	6	2
Hardness (ppm)	224	NR	21
Alkalinity (ppm as $CaCO_3$)	1712	92	92
COD (mg O_2 L^{-1})	1874	26	NR

Challenges in Designing Produced Water Treatment Systems

- Availability of water quality data
- Reliability of the available data (sampling protocols, complexity of chemical composition and lack of standard analytical methods, etc..)
- Large volume of wastewater generated
- Lack of guidance on reuse water quality targets for the industry
- High cost of conventional wastewater remediation techniques
- Variability of the water quality data with time and location

ACKNOWLEDGEMENTS

- **Dr. Giovanni Lutzu**
- **Oklahoma Water Resources Center**
- **Oklahoma Center for the Advancement of Science and Technology**

Produced Water Quality in Colorado

Time (Days)	COD (mg/L)	pH	Alkalinity (mg/L)	TDS (mg/L)
GW	46.8	7.37	119	2120
Frac Fluid	115,000	4.65	600	3330
1	8215	7.42	1070	14,220
4	3900	7.10	700	14,613
130	2650	7.01	479	17,482
220	2543	6.80	475	18,756

TDS: Barnett, 60,000 mg/L; Woodford, 110,000 mg/L; Permian, 140,000 mg/L; Marcellus Shale, 180,000 mg/L (*Osborn et al., 2012; Warner et al., 2013*)