NETL/RIC Produced Water Research Partnership FWP

NATIONAL ENERGY TECHNOLOGY LABORATORY

2024 Resource Sustainability Project Review Meeting

Technical Portfolio Lead: Nicholas Siefert

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Acknowledgment:

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DOE/FECM HQ Program Manager: Hichem Hadjeres

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NETL/TDC Technology Manager: John Rogers

Produced Water Research Partnership FWP

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Program Goal

The Produced Water Research Partnership FWP is a partnership between DOE, NETL, universities, and industry to characterize, manage, clean, and treat produced waters across the United States to reduce the environmental impact of O&G developing.

Task 2: Lowering the Cost of Zero Liquid Discharge+Resource Recovery (ZLD+RR)

- Demonstrate novel water treatment processes at the pilot-scale on real produced water

Task 3: Integtrating Artificial Intelligence into NEWTS for Produced Water Characterization

- Build off existing produced water datasets to provide validated, high-quality data for modeling
- Identify data gaps and work to fill them through data collection, AI/ML, and chemical analysis

Task 4: Leveraging PARETO for REE/CM Recovery from Produced Water

- Extend PARETO to design and operate multi-enterprise networks for REE/CM recovery from PW

Produced Water Research Partnership
Field Work Proposal (FWP)

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U.S. DEPARTMENT OF ENERGY | Fossil Energy and Carbon Management

University of Pittsburgh

Carnegie Mellon University

leidos

The University of Texas at Austin

UTEP

NEWTS DATABASE

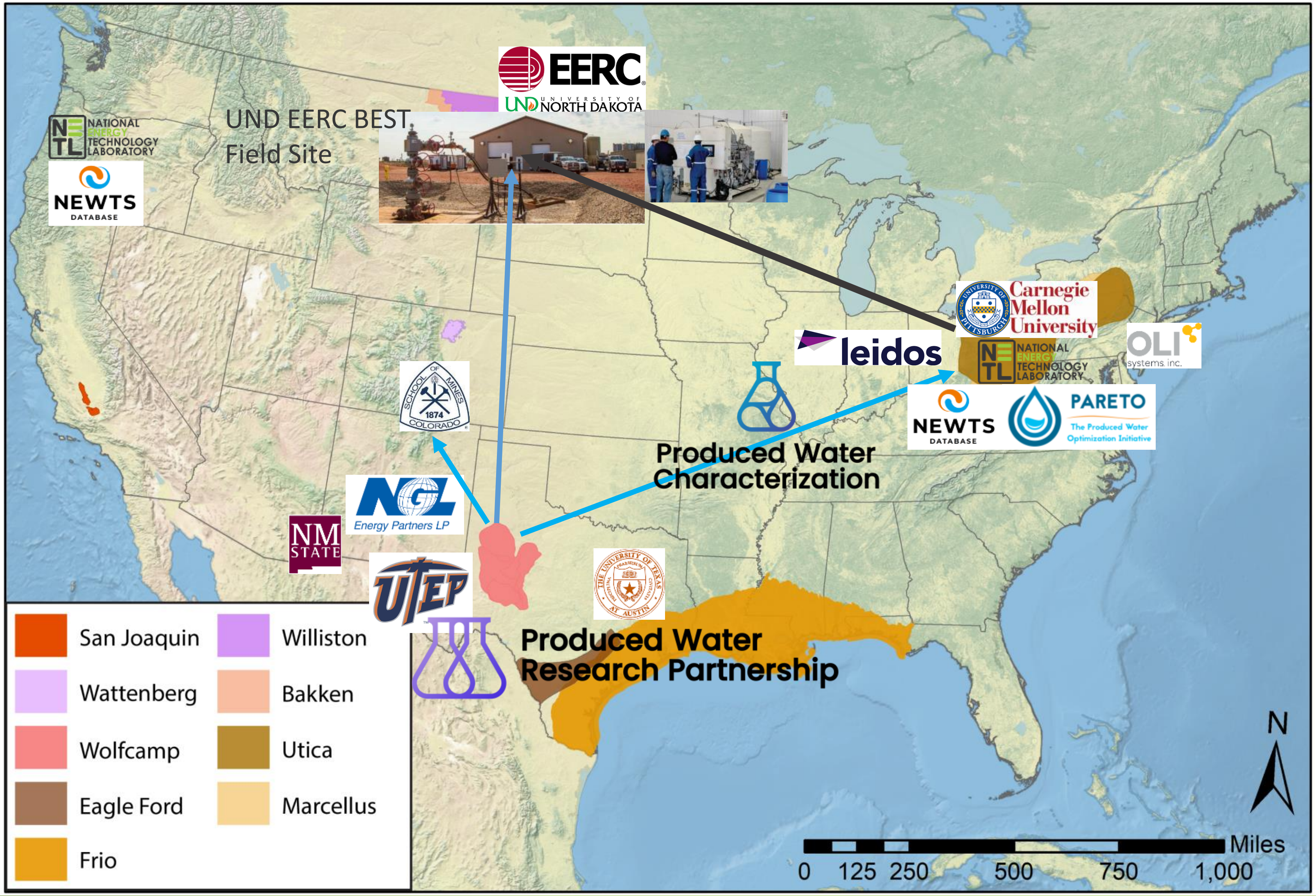
NM STATE

Colorado School of Mines 1874

EERC
University of North Dakota

PARETO
The Produced Water Optimization Initiative

Produced Water Research Partnership FWP & Associated NETL FWPs



Task 2: Lowering the Cost of Zero Liquid Discharge and Resource Recovery

- The Colorado School of Mines (w/ NGL)
- The University of Pittsburgh
- The University of North Dakota Energy and Environmental Research Center (BEST Field Site)

Task 3: Integrating Artificial Intelligence into NEWTS database for Produced Water Characterization

- The University of Texas at El Paso
- The University of Texas at Austin

Task 4: Leveraging DOE's PARETO Software for REE and other CM Recovery from Produced Water

- Carnegie Mellon University
- New Mexico State University

Produced Water Partnership Task 3 Goals

Utilize the NEWTS **national level dataset** in the following directions:

- Identify regions with high water use impact and low data availability.
- Determine constituents of greatest interest for treatment
- Generate samples which can be analyzed to expand ability to predict missing constituents of interest.
- Artificial intelligence (AI)/ML modeling will be performed to fill in the gaps in water chemistry

- Partnerships leads:

Texas BEG: Bridget Scanlon and J.P. Nicot
Univ. Texas at El Paso: Mark Engle and Joe Feuille

UT Austin Archived Historical Produced Water Samples

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- ~850 Historical Produced Water samples from across the U.S.
- Cation compositions analyzed in 1960s are available at the NETL NEWTS group site on EDX
  - Rittenhouse *et al.* Historical Archived Data
- UT Austin and UTEP have analyzed ~80 samples for training AI/ML networks

Samples stored at UT Austin, originally sampled around 1960

Examples of intact samples with minimal or no water loss

Task#2: Machine Learning Approaches for Energy Wastewater Characterization

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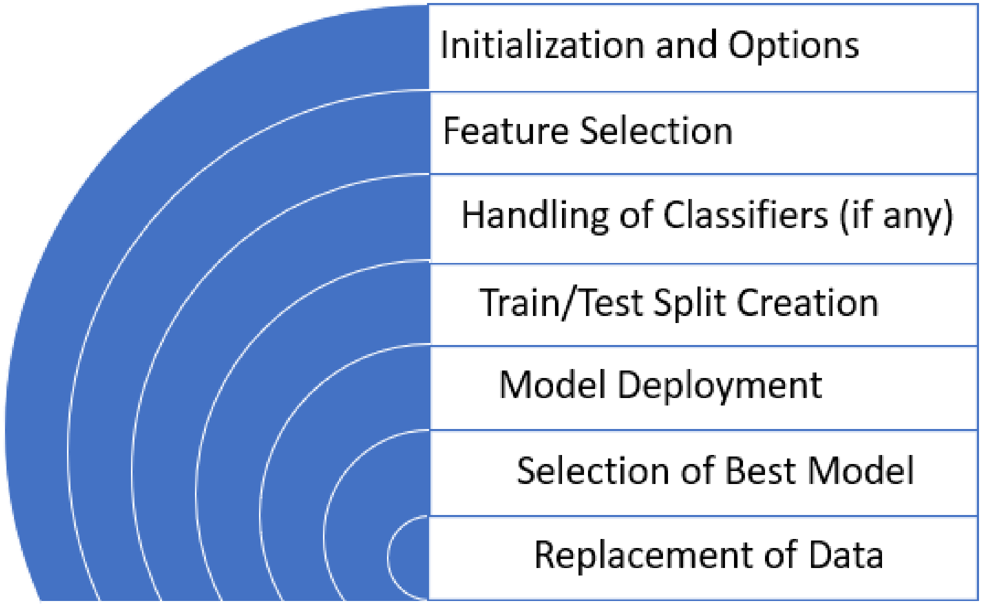
CO-DART
CONSTITUENT DATA REPLACEMENT TOOL

- To accurately model treatment and byproduct recovery costs for energy wastewaters, we need complete composition data.
- **CoDaRT (Constituent Data Replacement Tool)** was developed in python to predict missing constituents in a user's water data set using machine learning techniques.



- The tool applies machine learning algorithms to replace missing data
- The tool can use the user's data alone or combine user data with publicly-available NEWTS datasets.
- Will be made available in FY24 for public download via EDX

Task 2: Machine Learning Approaches for Energy Wastewater Characterization

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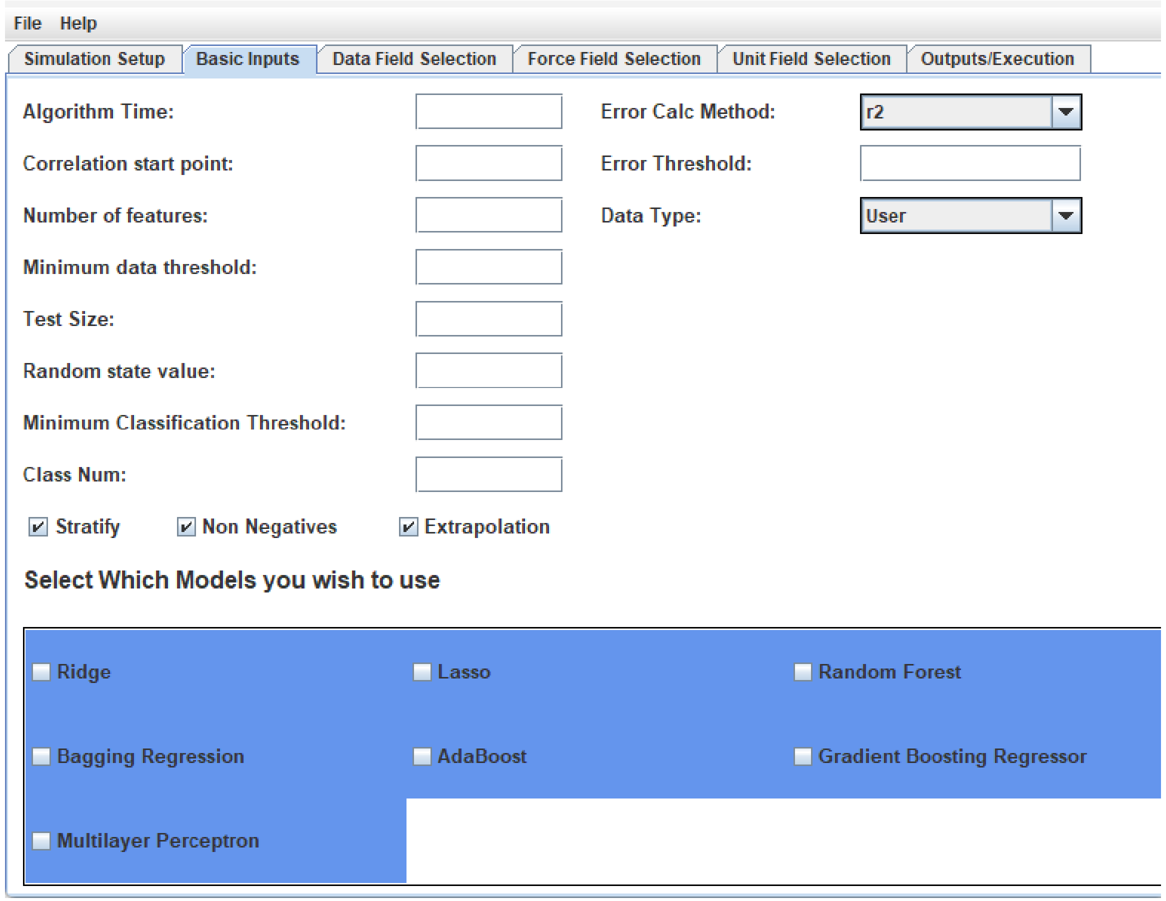
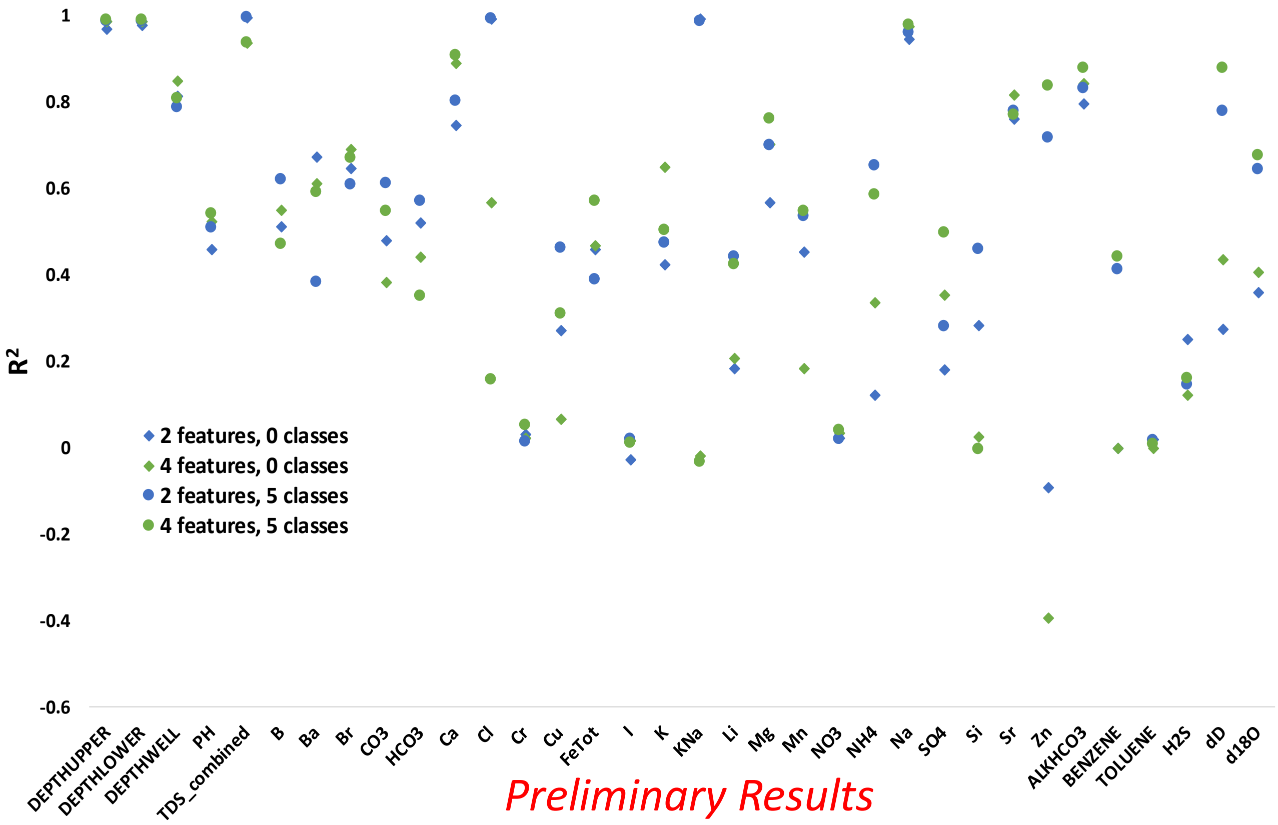
CO-DART GUI





Example data replacement performance for the NEWTS USGS Produced Water Database.

$$R^2 = 1 - \frac{\sum(y_i - \hat{y}_i)^2}{\sum(y_i - \bar{y})^2}$$

y_i = true value
$\hat{y}_i$ = predicted value
$\bar{y}$ = average value

Task 2: Machine Learning Approaches for Energy Wastewater Characterization

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Before data replacement

Si	Sn	Sr	V	W	Cl	SO4	Br	CO3	HCO3
9	0.003	50							
8	0.012	30							
15	0	60							
8	0.003	50	0						
4	0.003	60	0						
5	0.003	50	0	0.01					
0	0	100							
3	0.003	150	0						
5	0.003	50	0	0.01					
2	0.003	300							
7	0.003	60	0	0.01					
5	0.002	80	0						
100			0.02						
500									
200			0.01						
150			0.01						
150									
150		15	0.015						
100	0.013	10	0.04						
1	0.025	900							
1	0.07	300							
1	0.01	300	0.008						
0		1000	0.01						
0		1000	0.025						
0		300							
0		300							
0		150	0.01						

After data replacement

Si	Sn	Sr	V	W	Cl	SO4	Br	CO3	HCO3
9	0.003	50			72555.7	699.317	241.584		505.966
8	0.012	30			33319.8	657.754	107.375		534.926
15	0	60			36474.6	652.916	173.316		536.389
8	0.003	50	0		57912.9	681.402	209.881		567.832
4	0.003	60	0		88250	715.62	295.268		446.584
5	0.003	50	0	0.01	26524.2	645.571	102.513		507.962
0	0	100			131692	753.957	517.399		240.983
3	0.003	150	0		68915	674.23	302.664		452.968
5	0.003	50	0	0.01	36474.6	654.528	173.316		527.919
2	0.003	300			114946	703.783	441.735		330.563
7	0.003	60	0	0.01	45373.4	661.873	222.138		492.484
5	0.002	80	0		34371.4	649.69	129.355		483.481
100			0.02		669.15				
500									
200			0.01		3139.65		22.5239		
150			0.01						
150					669.15				
150		15	0.015		17107.6	640.467	70.3026		583.089
100	0.013	10	0.04		6372.5	631.419			454.124
1	0.025	900			232002	651.796	2202.49		140.296
1	0.07	300			189937	748.572	1323.28		121.017
1	0.01	300	0.008		197784	757.53	1350.12		360.498
0		1000	0.01		208301	644.625	1569.92		
0		1000	0.025		197784	644.625	1350.12		
0		300			176752	757.53	910.512		51.1679
0		300			176752	757.53	910.512		81.1031
0		150	0.01		176752	781.724	910.512		93.7455

Example using: Rittenhouse et al. 1960s Historical Archived Produced Water Dataset - Submissions - EDX (doe.gov)

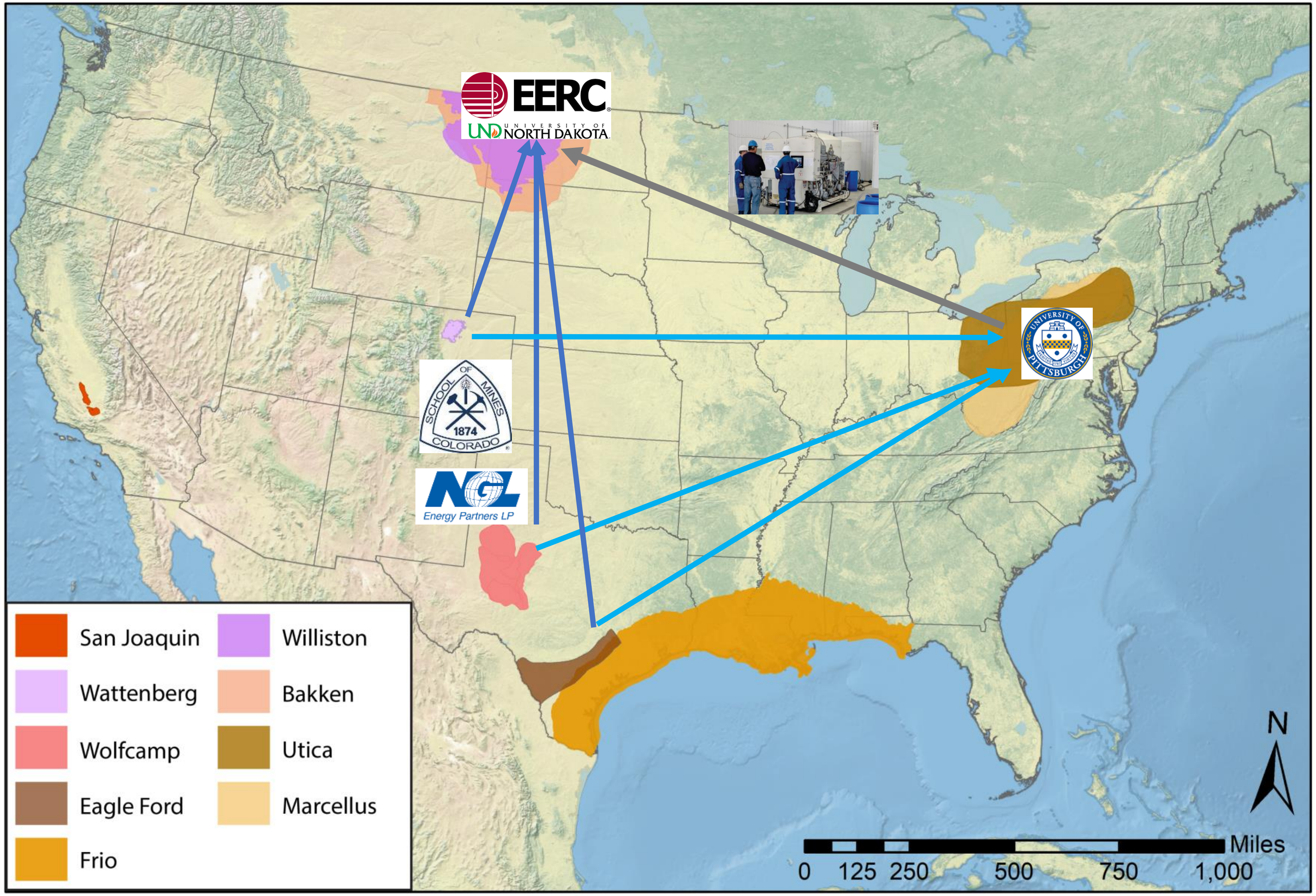
Task 2: Pilot Demonstration & Characterization of Zero Liquid Discharge with Resource Recovery

Challenge: Accurately measure the electrical efficiency of Zero Liquid Discharge Processes and determine which dissolved species end up in the permeate/distillate and the concentrated streams for resource recovery

Value: Provide the public with data on the compositions before/after pretreatment and brine concentration as well as electricity/energy consumption of water treatment equipment

Objective:
Determine the electrical efficiency under real-world conditions for advanced brine concentrating technologies and fully characterize the effluent before and after each major step in treatment process

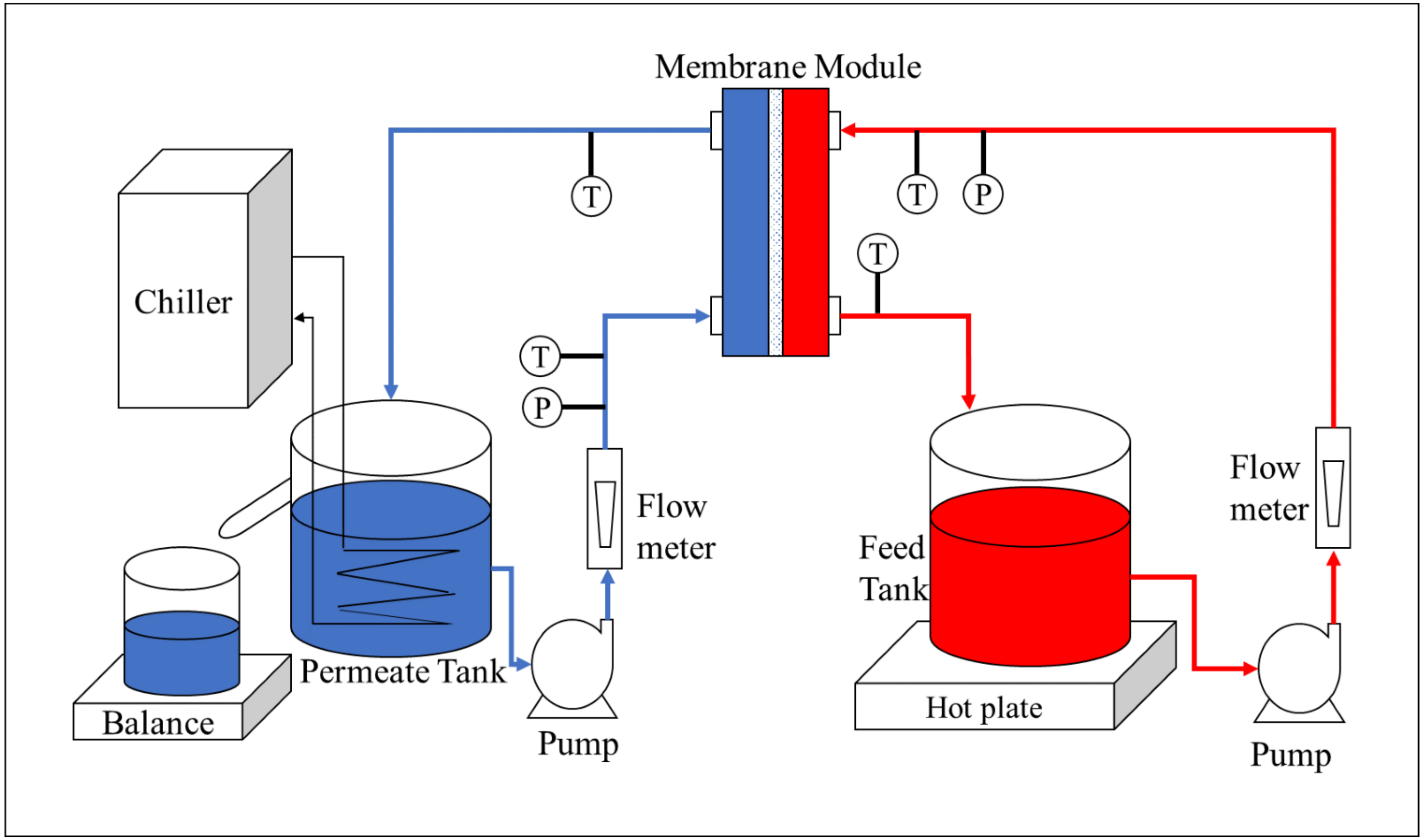
Task 2: High-Level Overview

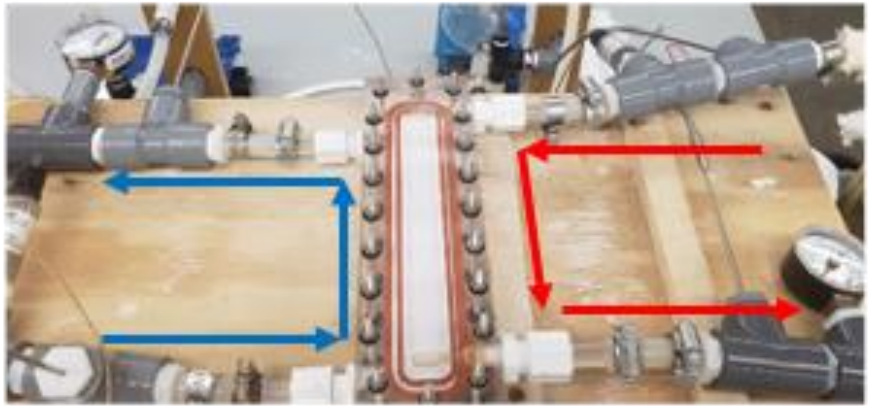


- Produced waters tested at pilot scale at Colorado School of Mines (MB/RO) and University of Pittsburgh (MD)
  - DJ Basin (CO)
  - Permian Basin (TX)
  - Eagle Ford (TX)
- Successfully tested of all three produced waters at the laboratory and small-pilot scale
- Totes of DJ Basin RO Concentrate, Permian Basin, and Eagle Ford were shipped to UND EERC BEST for MD pilot-scale testing

Step#1: MD Laboratory Analysis

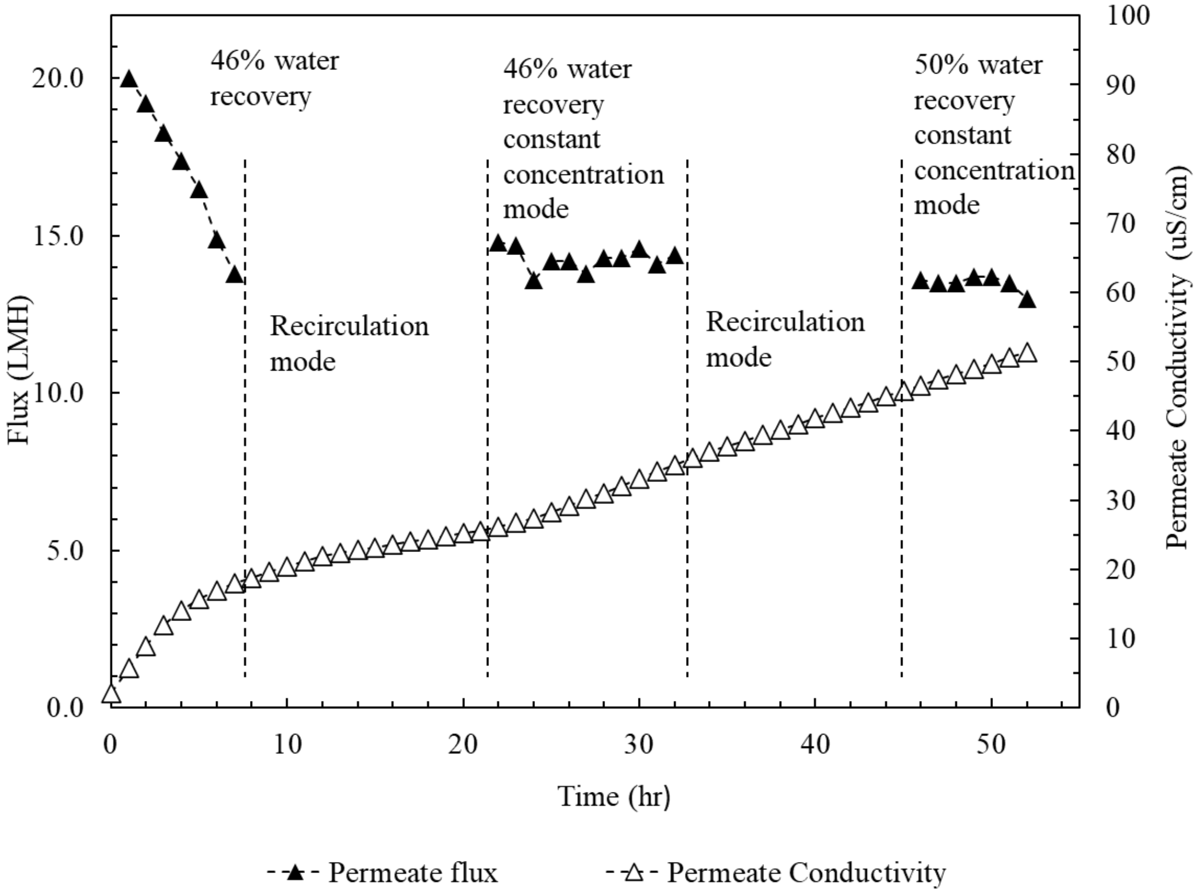
All produced waters were operated at the laboratory scale using Membrane Distillation (MD) at the University of Pittsburgh



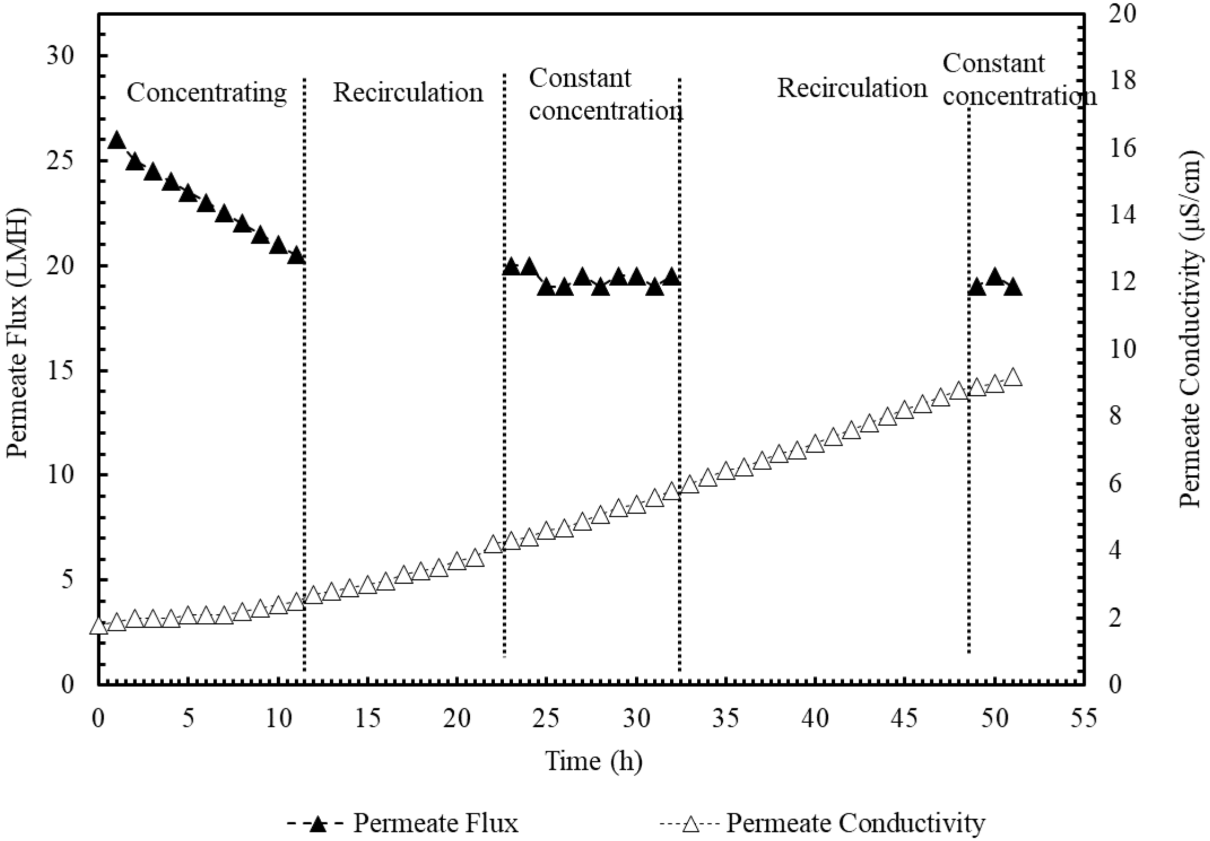


U.Pitt PI: Radisav Vidic, U.Pitt Researcher: Ritesh Pawar

Results: Laboratory Studies

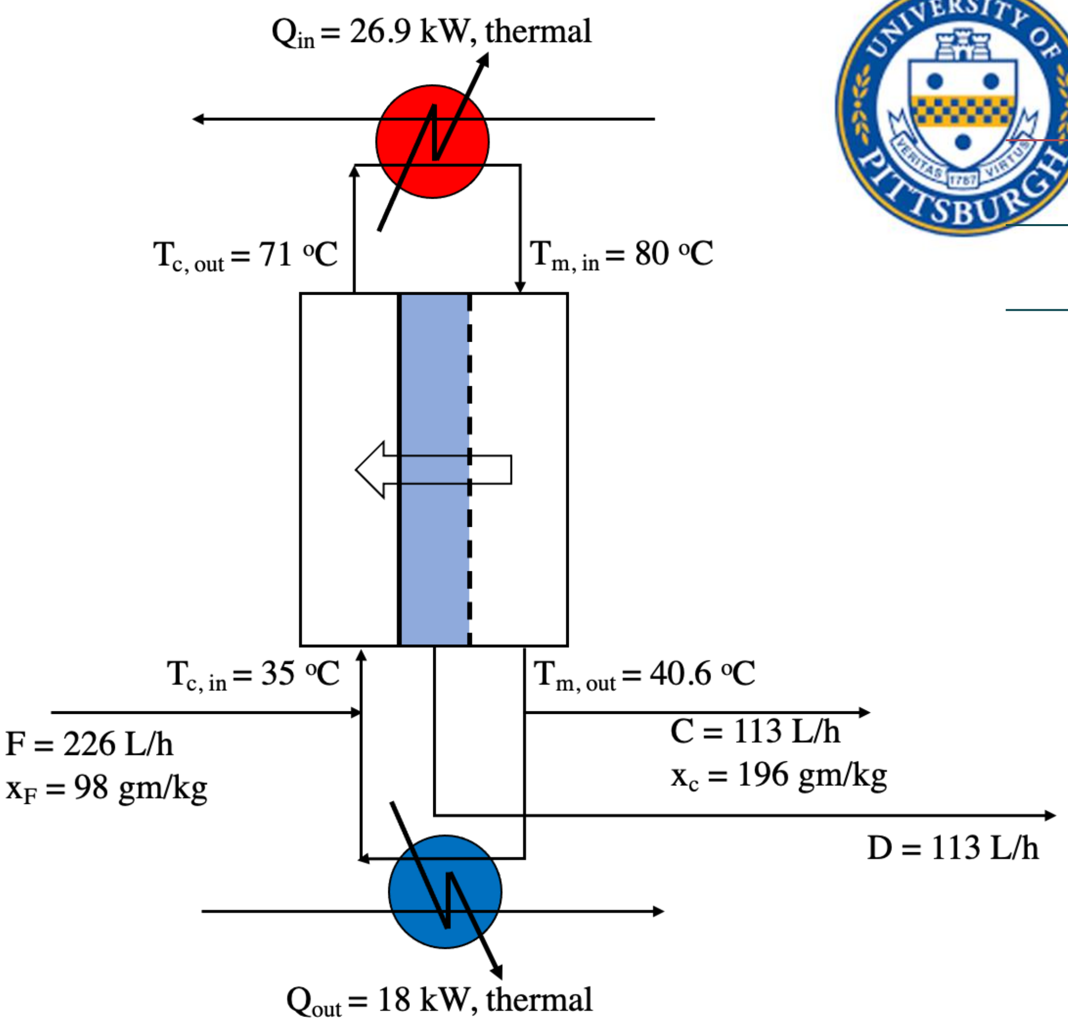


Permeate flux and conductivity in a long-term laboratory-scale test with pretreated Permian basin produced water



Permeate flux and conductivity in a long-term laboratory-scale test DJ basin RO concentrate

Design: Pilot Scale Steady-state heat and mass balance design conditions



Parameters	Value	Units
Process Conditions		
Circulation/module	1.6	m^3/h
T membrane, in	80	°C
T condenser, out	71	°C
T condenser, in	35	°C
T membrane, out	40.6	°C
Salinity at start	98	gr/kg
Recovery req.	50	%
Airgap pressure	550	mbar
T feed	30	°C

U.Pitt PI: Radisav Vidic, U.Pitt Researcher: Ritesh Pawar

MD Pilot Testing at UND EERC BEST

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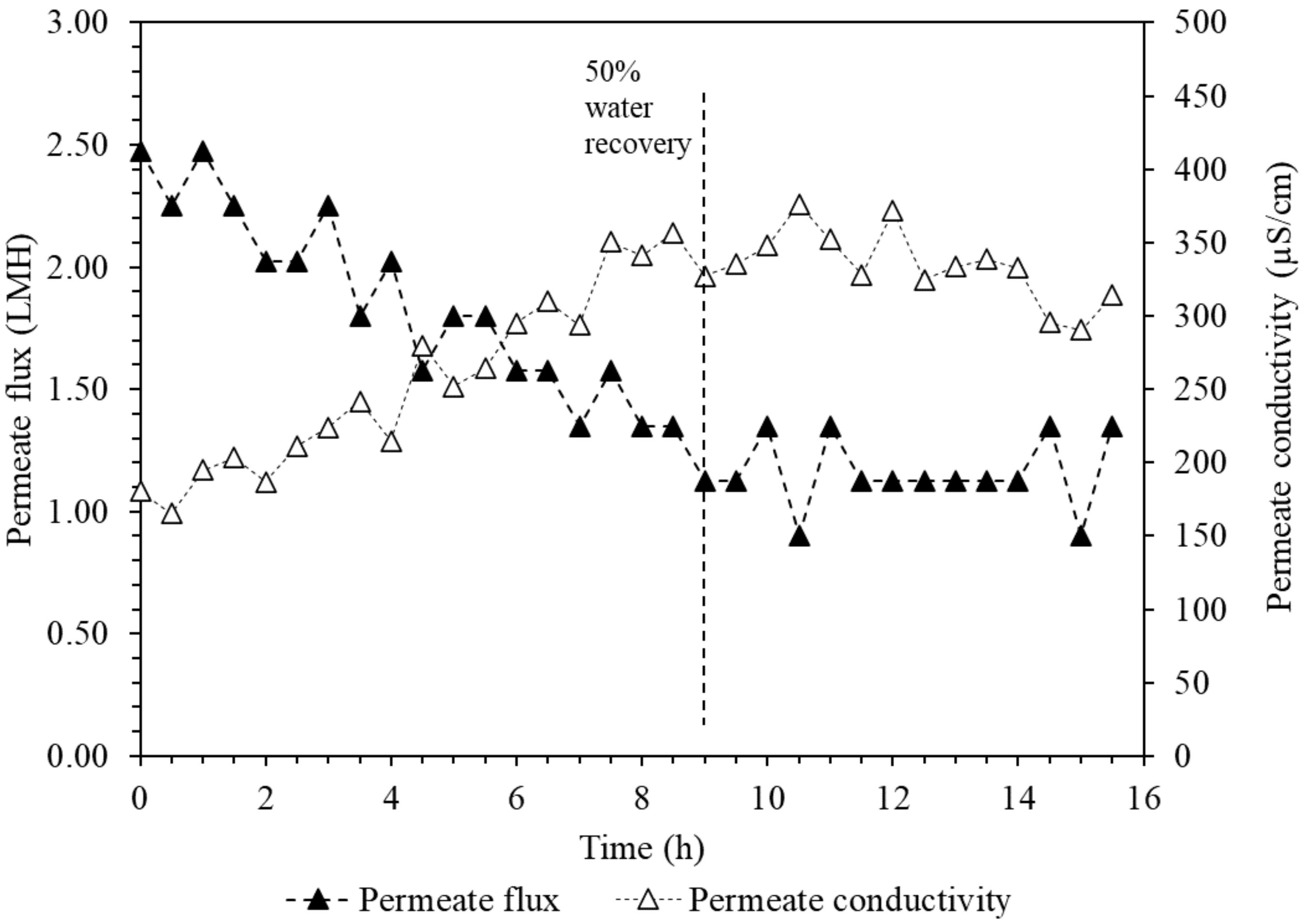
EERC®

UND UNIVERSITY OF NORTH DAKOTA

Pilot Testing Results: MD operation on Permian Water

Salt rejection of 99.86% and no membrane wetting

1.2 LMH during the steady-state operation



Permeate flux and conductivity using pretreated Permian basin produced water

Parameter	Value
Water recovery (%)	50
Feed flow rate (L/h)	81.7
Permeate flow rate (L/h)	63.5
Feed Conductivity (mS/cm)	121.5
Concentrate Conductivity (mS/cm)	214.9
Permeate Conductivity (mS/cm)	0.31
Salt Rejection (%)	99.86
Permeate flux (LMH)	1.17
T membrane, in (°C)	73.6
T condenser, out (°C)	63.9
T condenser, in (°C)	21
T membrane, out (°C)	31.8
Air gap vacuum (mbar)	-31.7
Steady state time (hr)	6.5
Total electrical consumption (kWh)	328.6
Specific electrical consumption (kWh/m^3 of feed)	618.7

Pilot Testing: Chemical Analysis

- **Water Quality**
  - *pH, alkalinity, nutrients, TDS, TSS, COD*
  - *TOC*, TN, *oil and grease*
  - *Anions (e.g., chloride, sulfate, etc.) & Metals (e.g., iron, lead, etc.)*
  - *Semi- and Volatile Organics*
- **Non-targeted**
  - GC-MS (MSD)
  - LC-qTOF-HRMS
- **Targeted Methods (commercial lab)**
  - PIANO Volatile Organics (USEPA 8260M)
  - PCBs (USEPA 8082A)
  - Pesticides (USEPA 8081B)
  - Metals (USEPA 6020B)
  - Mercury (USEPA 7474)
  - Alkylated PAHs & Biomarkers (USEPA 8270M)
  - *Volatile Organics (USEPA 8260C)*
  - *Semi Volatile Organics (USEPA 8270)*
  - Saturated Hydrocarbons (USEPA 8015D)
  - Herbicides (USEPA 8151A)
  - *Perfluoroalkyl Chemicals (PFAAs LC-QQQ)*
  - Glycols (USEPA 8015D)
  - Alcohols (USEPA 8015D)
  - Herbicides (USEPA 8151A)
  - Organic Acids
  - *NORM (USEPA 901.1)*
  - Dioxins and Furans (USEPA 8290A)
  - Cyanide, Surfactants, Perchlorate

> 700 Chemicals

Pilot Testing: Chemical Analysis


Analysis at Mines and NETL

Additional samples are being stored for other researchers that want to study the treated water

Analysis at Commercial Labs

Pilot Testing: DJ Basin Treatment Train

Coagulation → Iron and Softening → Pre-Filtration → Membrane Filtration → Media Adsorption → Reverse Osmosis

SCHOOL OF MINES
1874
COLORADO

Pilot Testing: Water Samples

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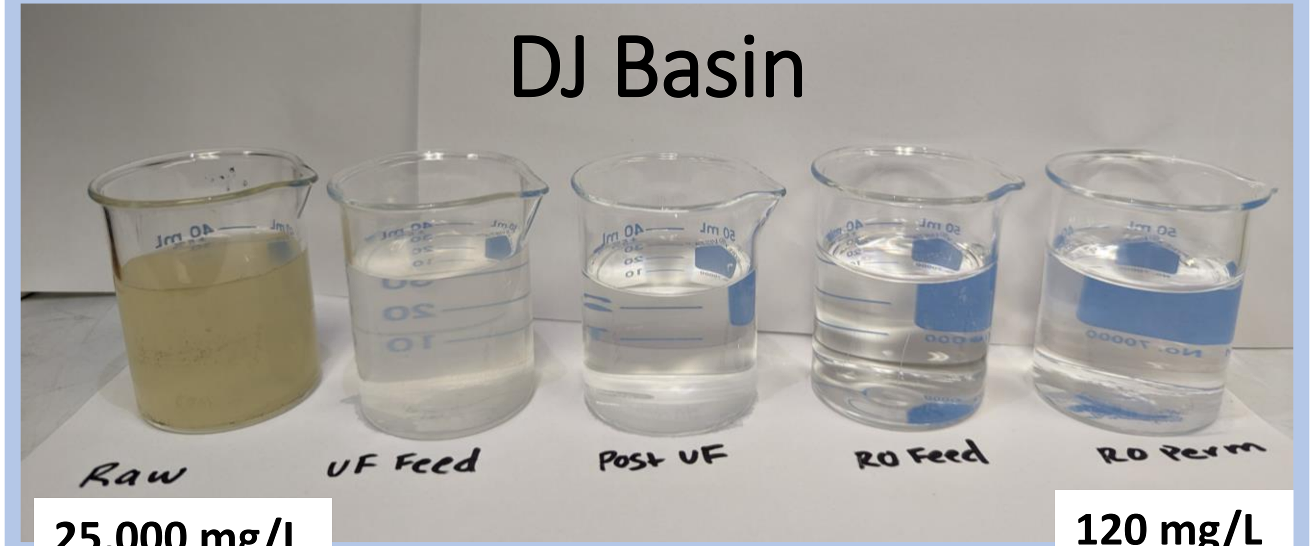
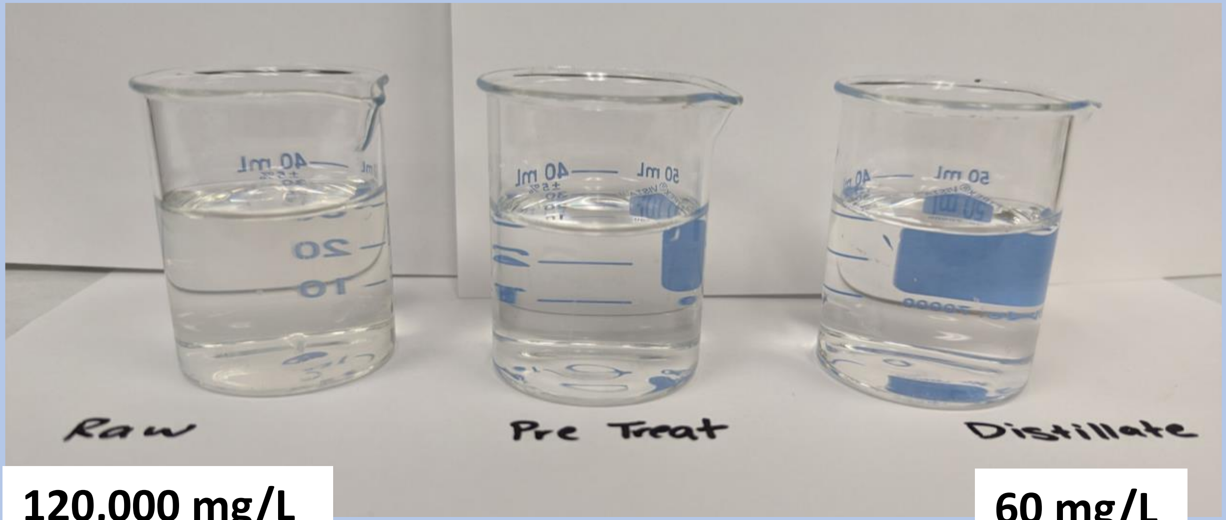
DJ Basin



25,000 mg/L

120 mg/L

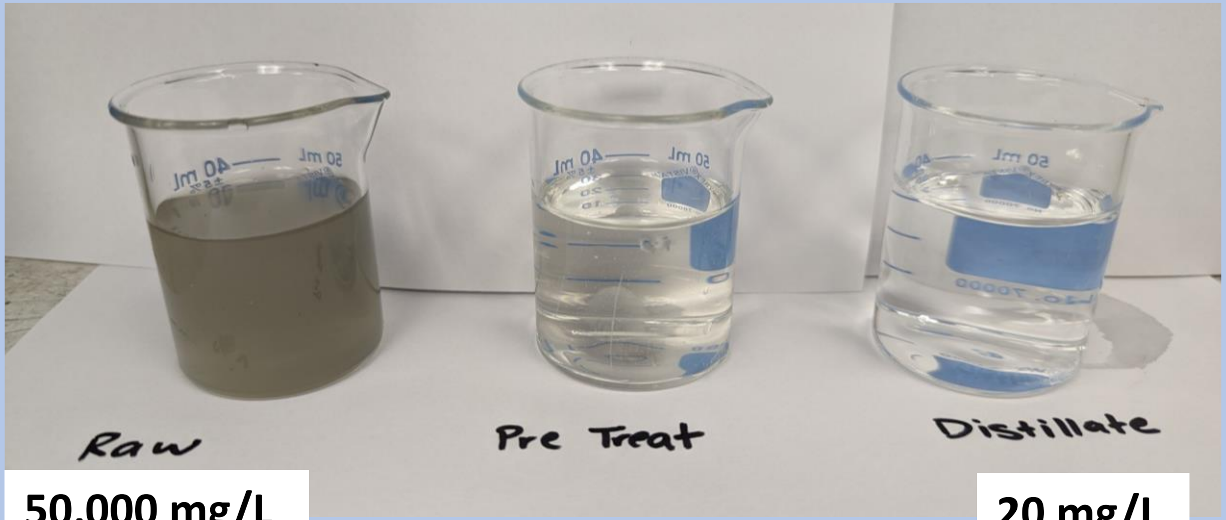
Permian Basin



120,000 mg/L

60 mg/L

Eagle Ford



50,000 mg/L

20 mg/L

Pilot Testing: Total Dissolved Solids

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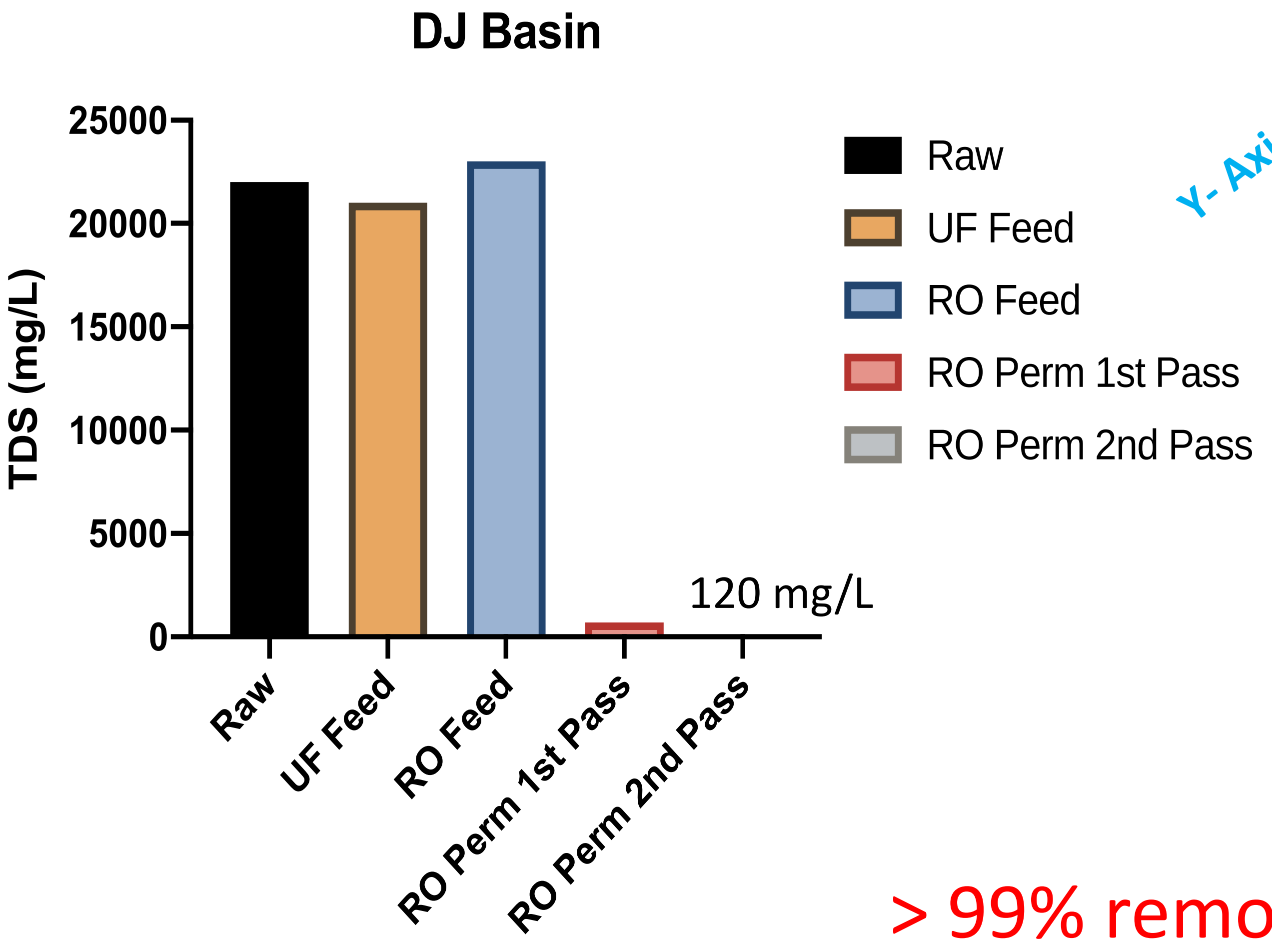
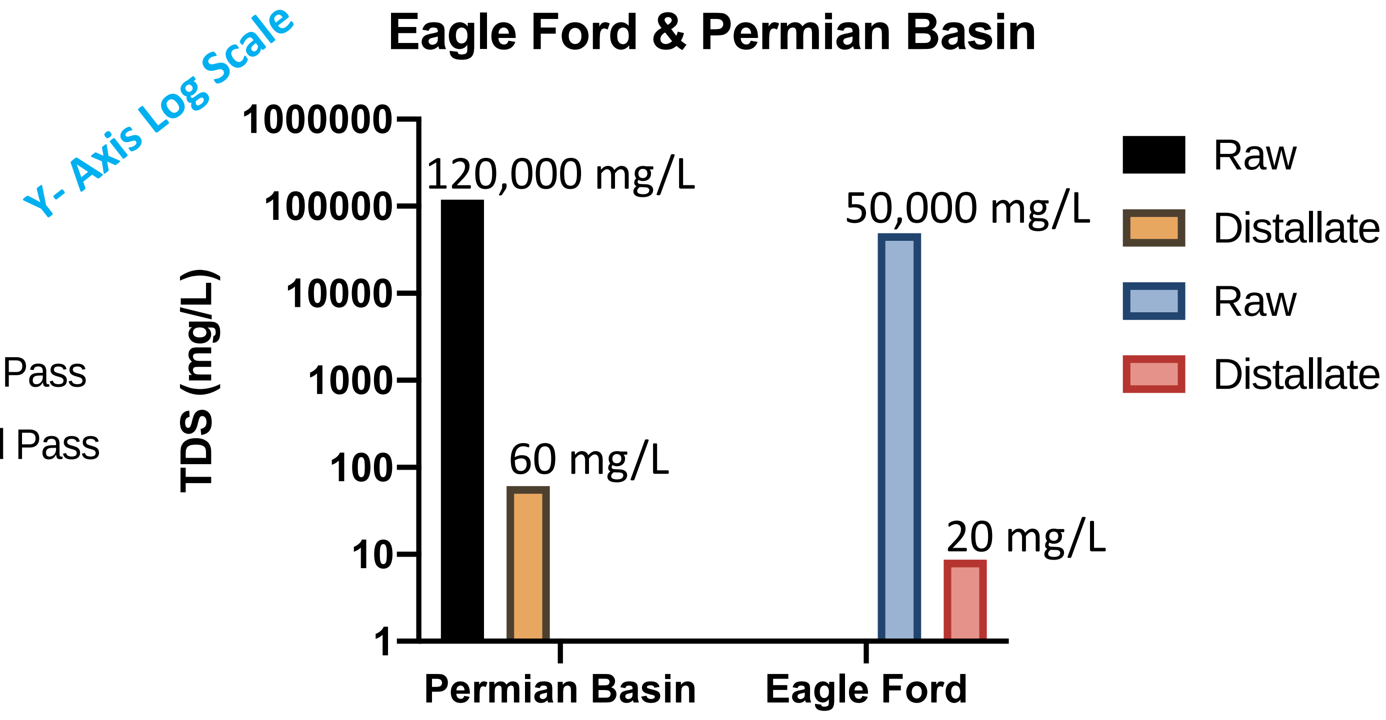
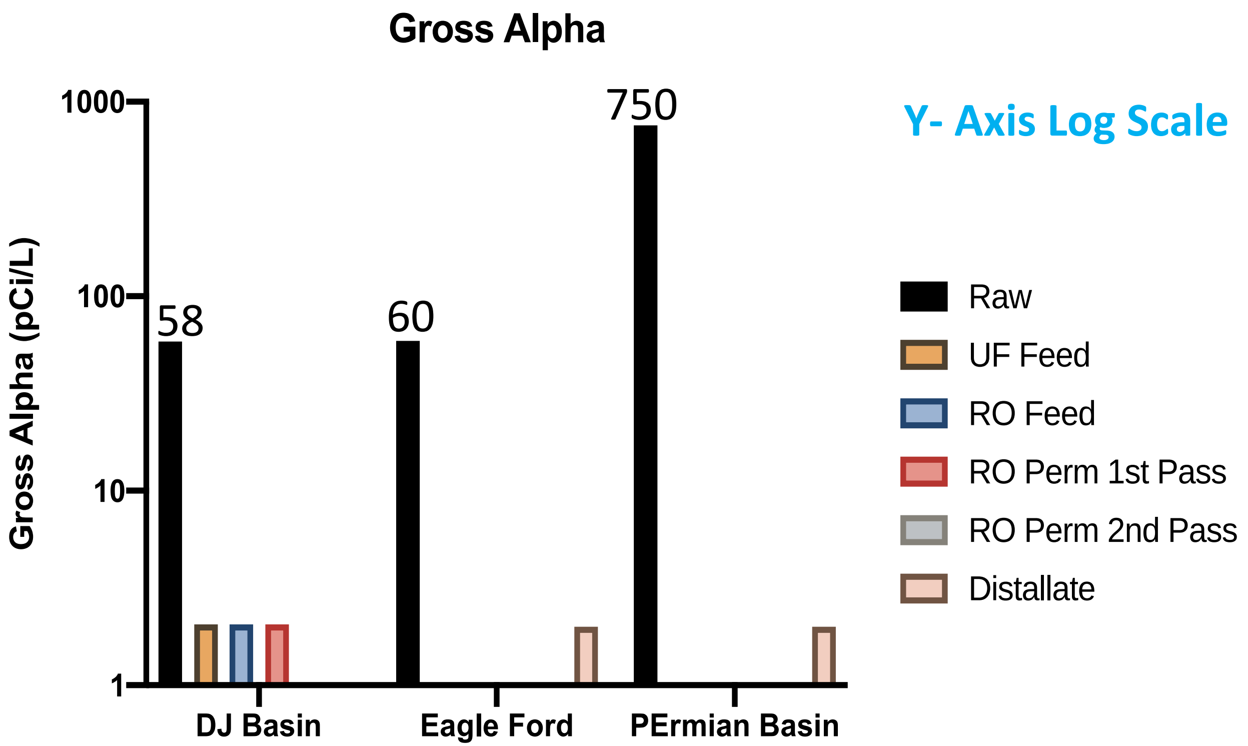
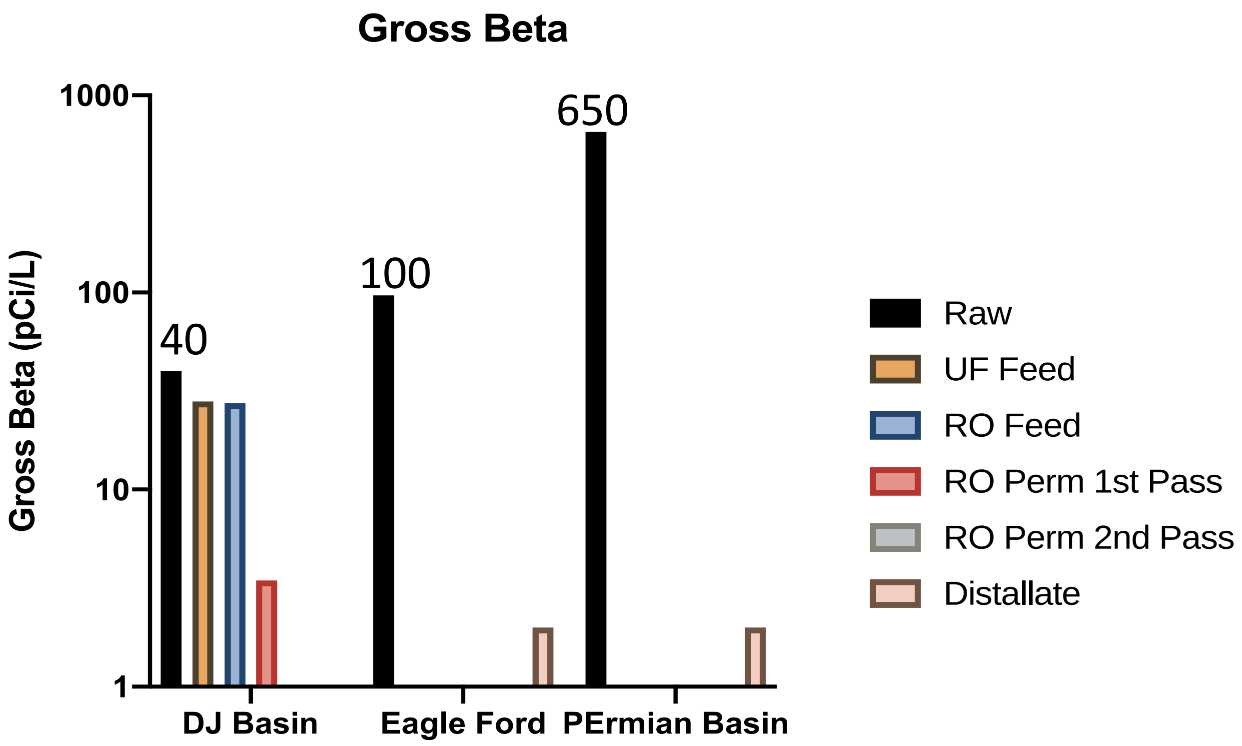




> 99% removal of TDS

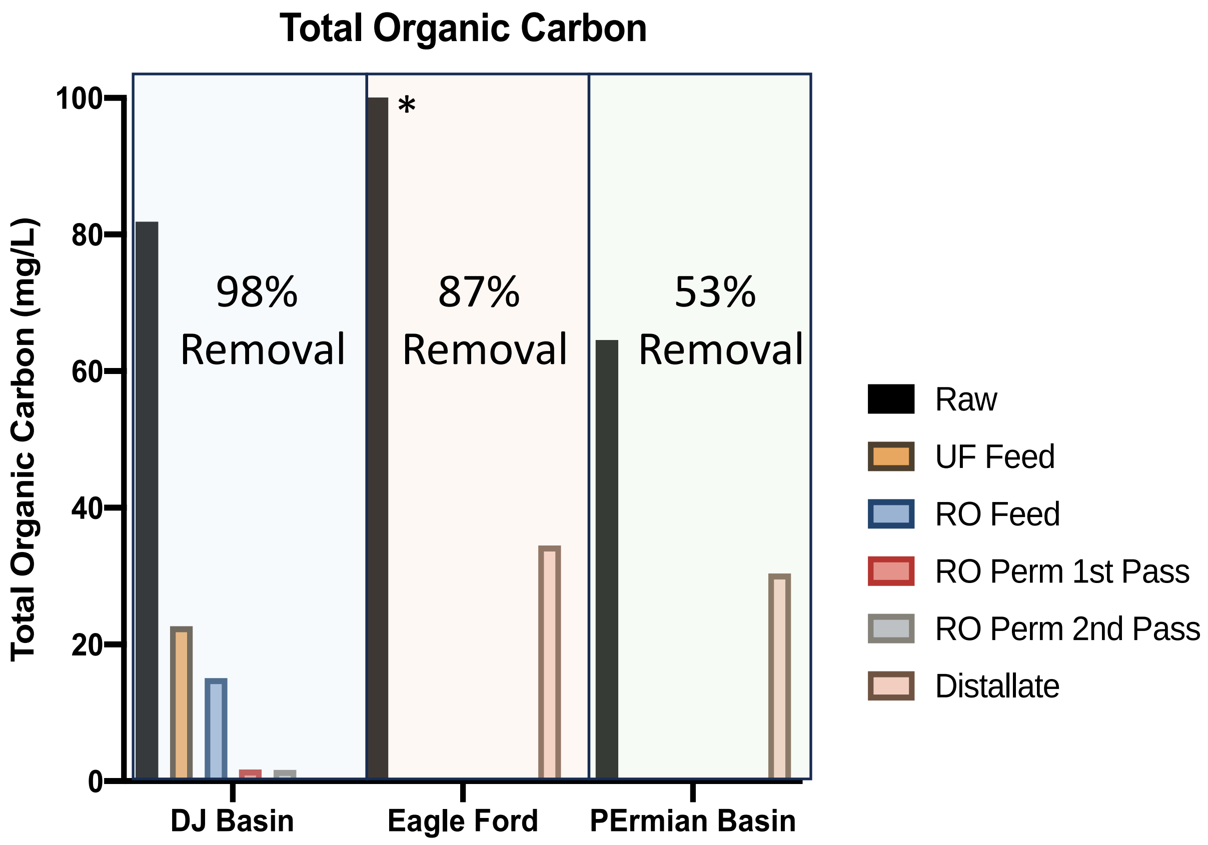
Pilot Testing: Naturally Occurring Radioactive Material

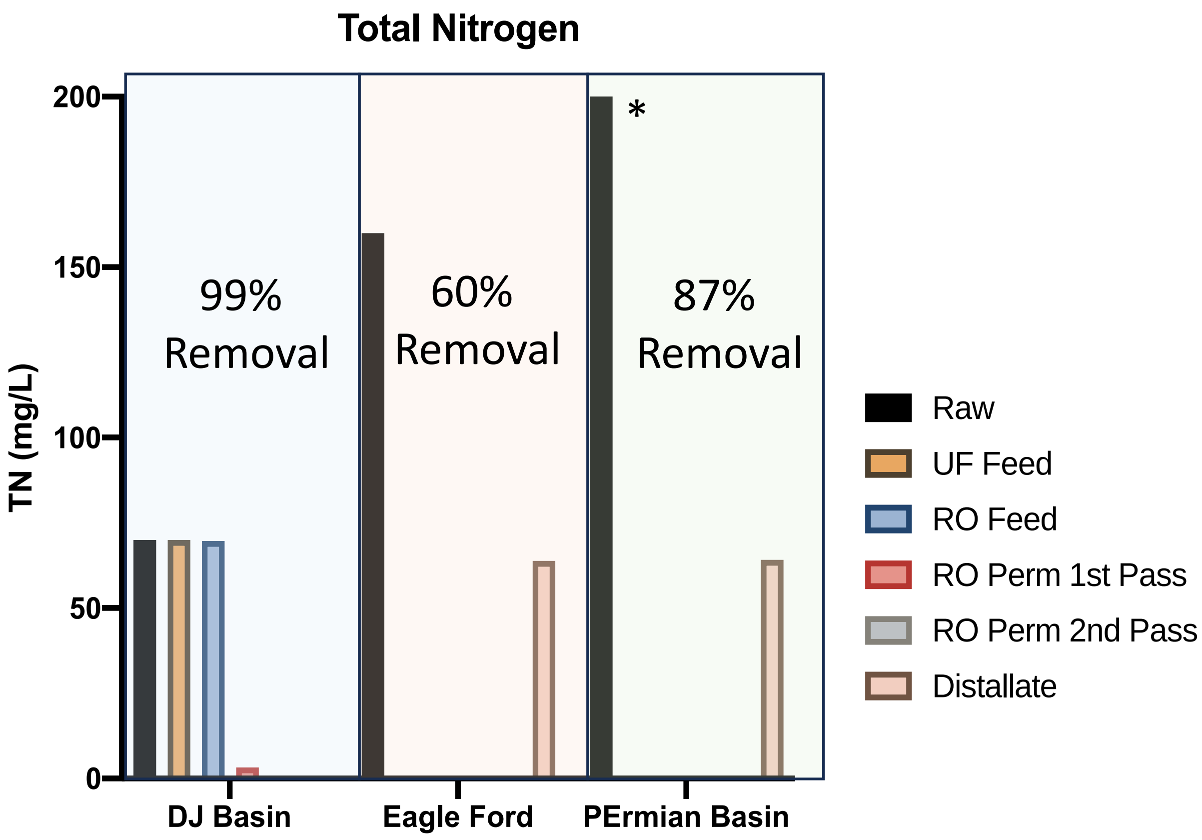




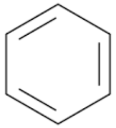
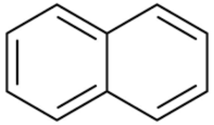
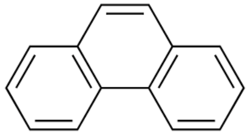
> 99% removal of Gross Alpha and Beta

Pilot Testing: Total Organic Carbon and Total Nitrogen





Pilot Testing: Hydrocarbon Indicators

		DJ Basin						Eagle Ford		Permian Basin		
	Unit	*Raw*	*UF Feed*	*RO Feed*	*RO 1st Pass*	*RO 2nd Pass*	*RO Conc*	*Raw*	*Distillate*	*Raw*	*Distillate*	
Gasoline Range Organics	*mg/L*	8	0.08	0.02	0.03	0.02	0.02	16	0.72	3.3	0.15	C2 – C10
Benzene	*ug/L*	3.4	0	0	0	0	0	2.2	0.2	1	0.02	
Naphthalene	*ug/L*	19.6	4.44	0	0	0	0	15.4	0	0	0	
Phenanthrene	*mg/L*	6.76	0	0	0	0	0	7.4	0	0	0	

> 95% removals across treatment trains

Pilot Testing: Semi Volatile Organic Compounds

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		DJ Basin					Eagle Ford		Permian Basin	
Analytes	*Units*	*Raw*	*UF Feed*	*RO Feed*	*RO 1st Pass*	*RO 2nd Pass*	*Raw*	*Distillate*	*Raw*	*Distillate*
Surfactant (MBAS)	*mg/L*	0.23	0.48	0.39	0	0	0.73	0	0.8	0
Methyl Alcohol	*mg/L*	10.1	4.63	4.48	2.56	3.57	63.8	64.1	52.2	57.7
2-butoxy-ethanol	*mg/L*	2.53	0.66	0	0	0	0	0	0	0.303
Acetone	*ug/L*	890	120	100	35	38	17,000	14,000	1,800	3,000
Phenol	*ug/L*	124	1.35	0	0	0.21	169	95	132	213

Pilot Testing: PFAs

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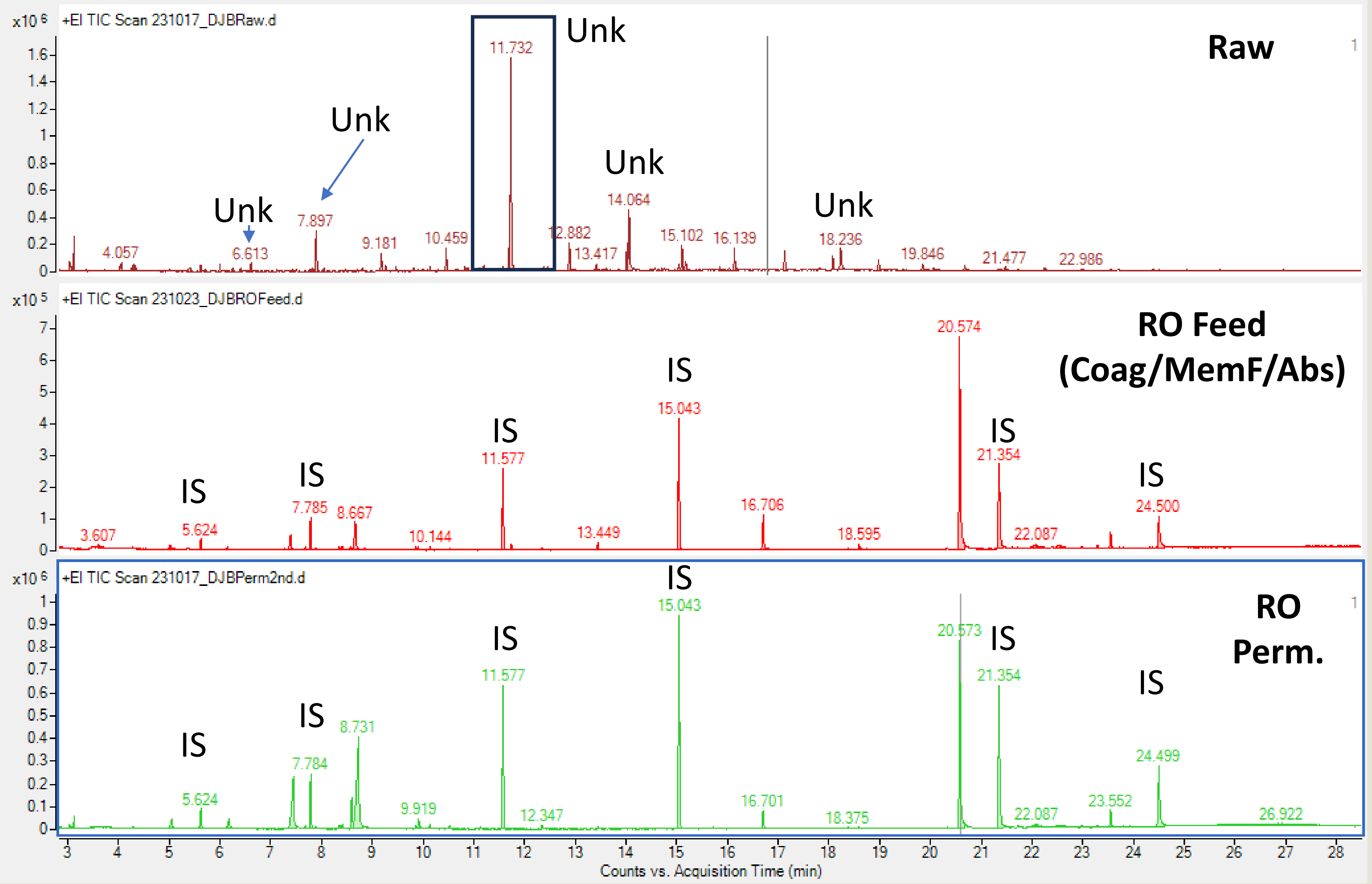
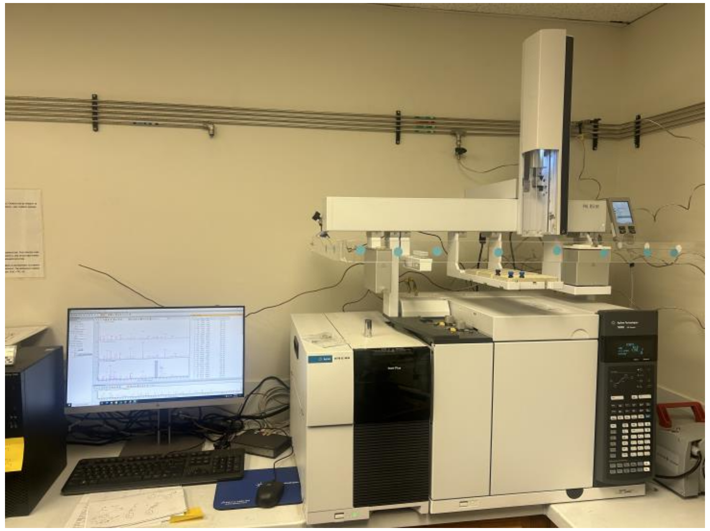
		DJ Basin						Eagle Ford		Permian Basin	
Analyte	Unit	Raw	UF Feed	RO Feed	RO 1st Pass	RO 2nd Pass	***RO Conc***	Raw	Distillate	Raw	Distillate
PERFLUOROBUTANOIC ACID (PFBA)	**ng/L**	**6.56**	**4.78**	**0**	**0**	**0**	**0**	**33.9**	**0**	**1.44**	**0**
PERFLUOROPENTANOIC ACID (PFPEA)	**ng/L**	**0**	**4.69**	**0**	**0**	**0**	**0**	**9.9**	**0**	**0**	**0**
PERFLUOROBUTANESULFONIC ACID (PFBS)	**ng/L**	**0**	**1.18**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
1H,1H,2H,2H-PERFLUOROHEXANESULFONIC ACID (4:2FTS)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUOROHEXANOIC ACID (PFHXA)	**ng/L**	**0**	**0.824**	**0**	**0**	**0**	**0.279**	**0**	**0**	**0**	**0**
PERFLUOROPENTANESULFONIC ACID (PFPES)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUOROHEPTANOIC ACID (PFHPA)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUOROHEXANESULFONIC ACID (PFHXS)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUOROOCTANOIC ACID (PFOA)	**ng/L**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0.21**	**0**
1H,1H,2H,2H-PERFLUOROOCTANESULFONIC ACID (6:2FTS)	**ng/L**	**0**	**0**	**0**	**0**	**0**	**2.9**	**0**	**0**	**0**	**0**
PERFLUOROHEPTANESULFONIC ACID (PFHPS)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUORONONANOIC ACID (PFNA)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUOROOCTANESULFONIC ACID (PFOS)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUORODECANOIC ACID (PFDA)	ng/L	0	0	0	0	0	0	0	0	0	0
1H,1H,2H,2H-PERFLUORODECANESULFONIC ACID (8:2FTS)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUORONONANESULFONIC ACID (PFNS)	ng/L	0	0	0	0	0	0	0	0	0	0
N-METHYL PERFLUOROOCTANESULFONAMIDOACETIC ACID (NMEFOSAA)	ng/L	0	0	0	0	0	0	0	0	0	0
PERFLUOROUNDECANOIC ACID (PFUNA)	ng/L	0	0	0	0	0	0	0	0	0	0

Pilot Testing: Non-Targeted GCMS (MSD)

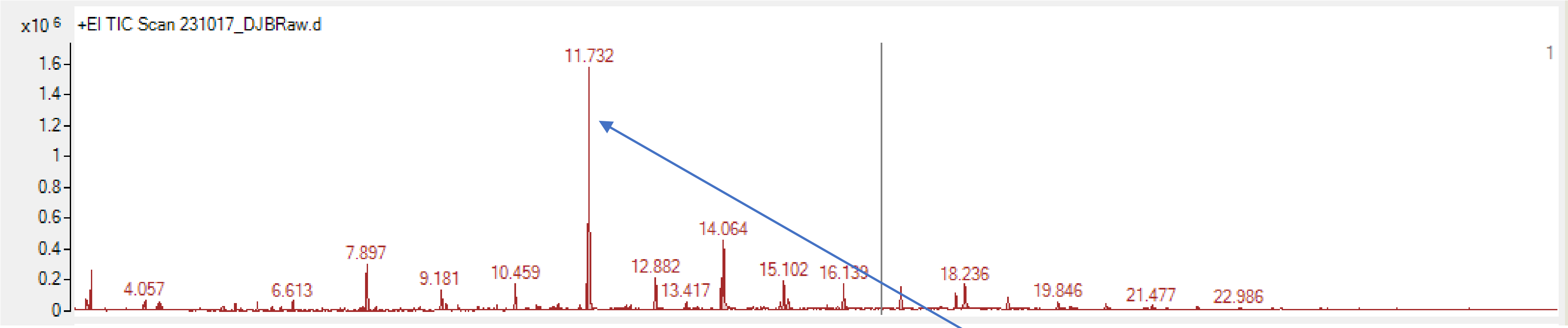


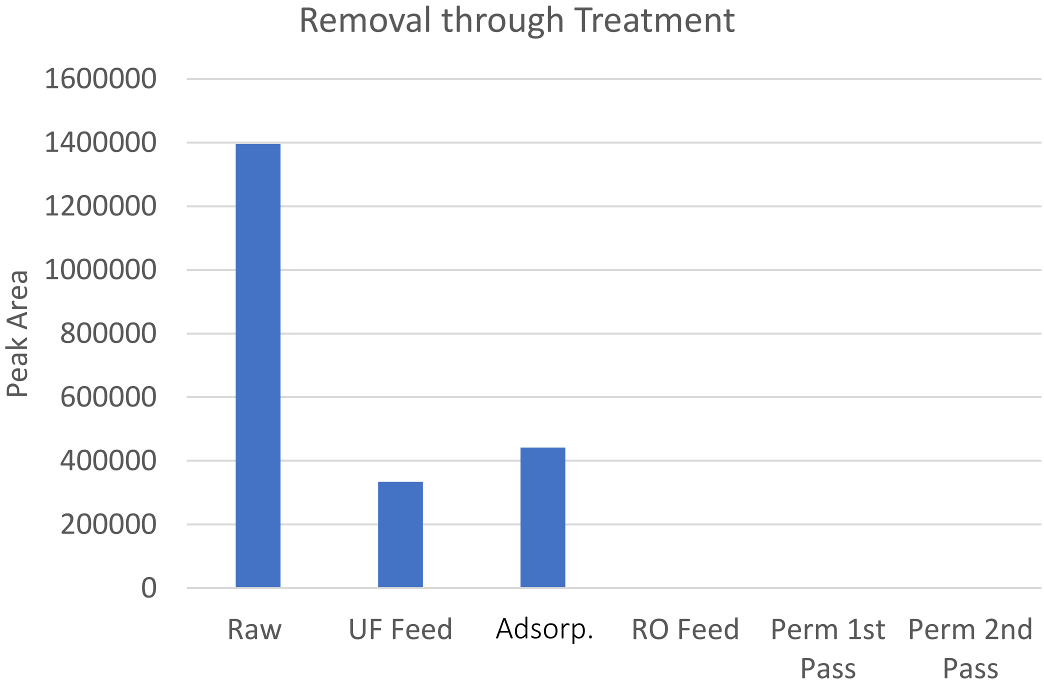


Internal Standards

- 1,4-dichlorobenzene-D4
- Napthelene-D8
- Acenaphthene-D10
- Phenanthrene-D10
- Chrysene-D12
- Perylene-D12

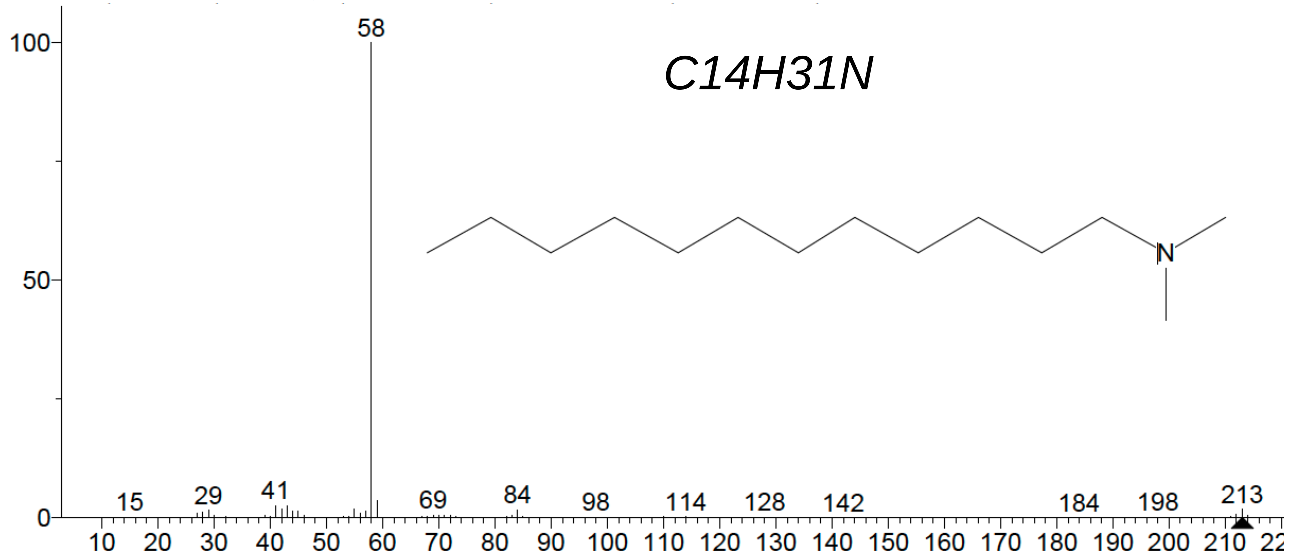
Pilot Testing: Unknown GCMS Identification (DJ-Basin)





1-Dodecanamine, N,N-dimethyl-

$C_{14}H_{31}N$



Pilot Testing: Unknown LCMS Identification (DJ-Basin)

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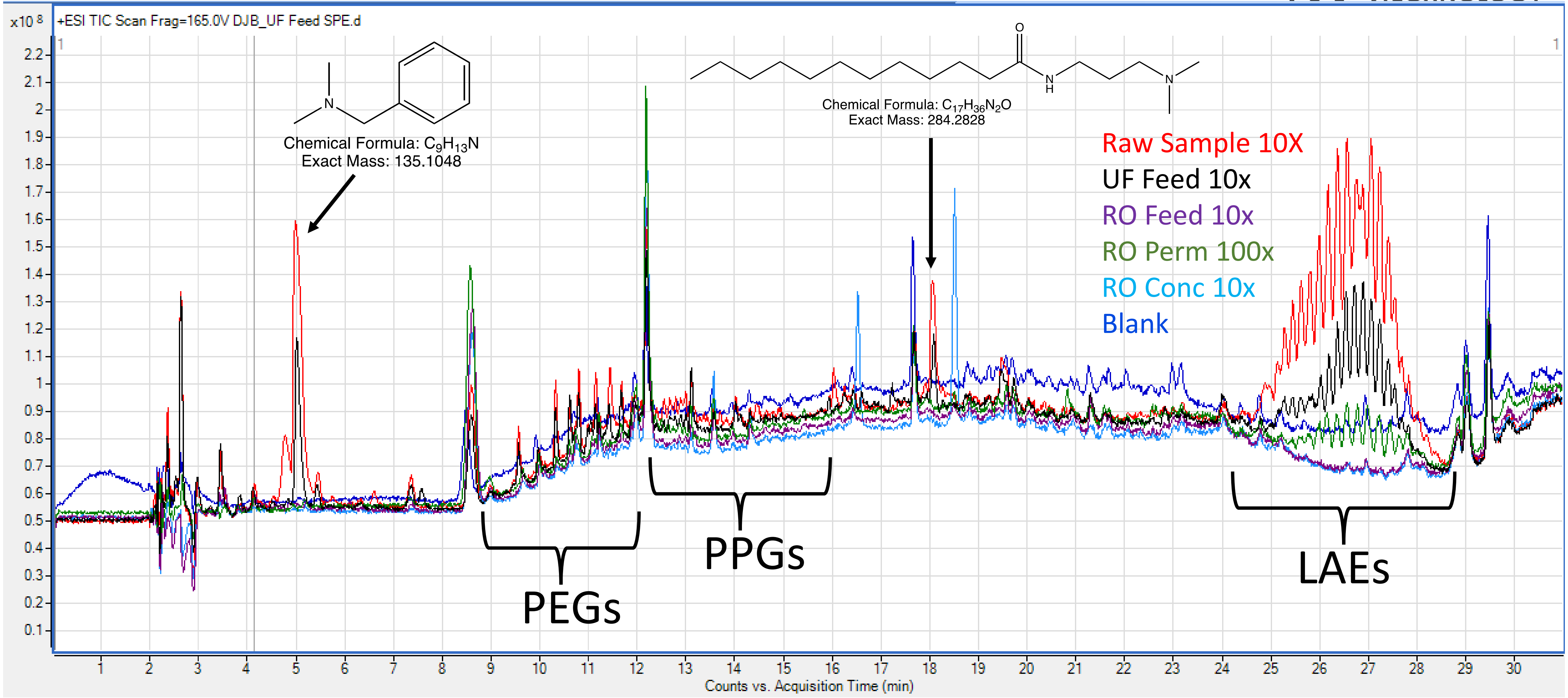
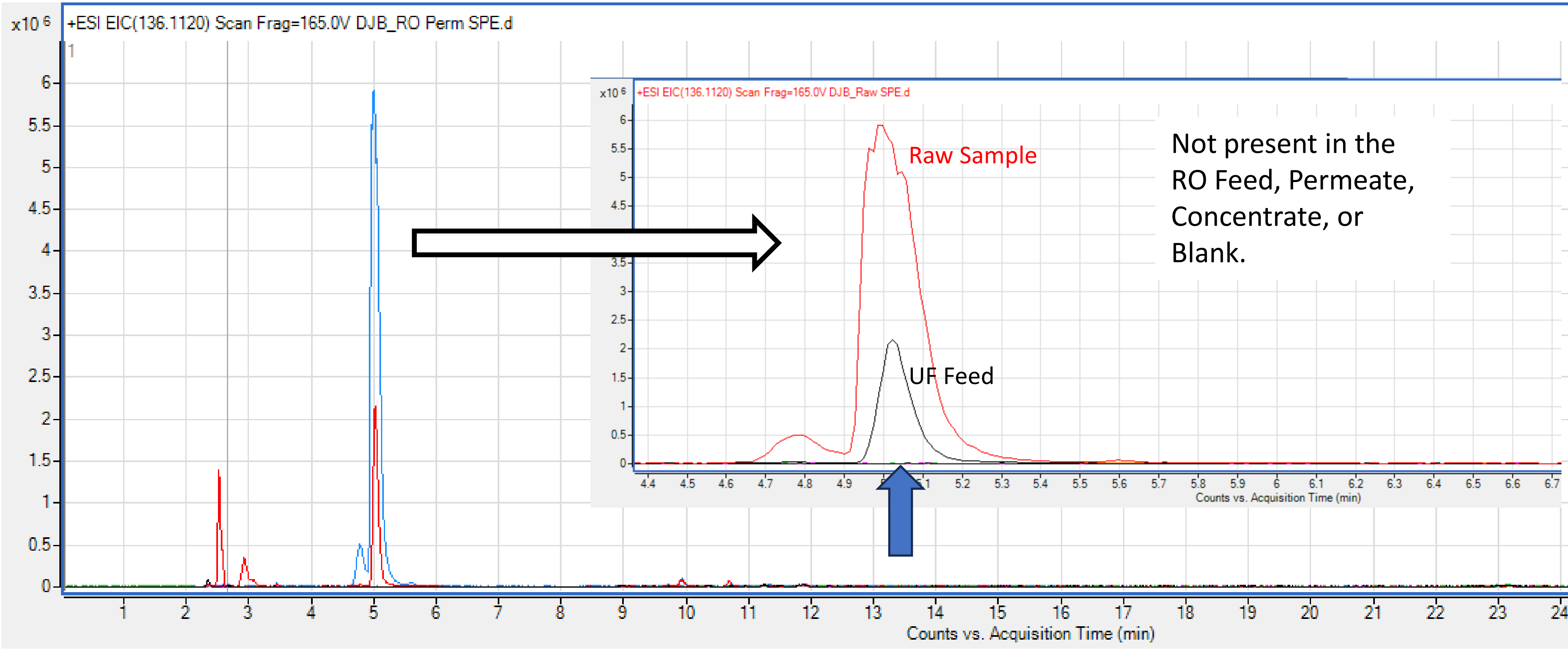
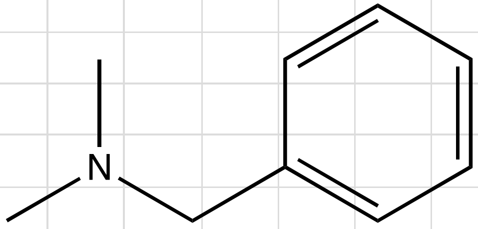


Pilot Testing: Unknown LCMS Identification (DJ-Basin)

Dimethylbenzylamine





Chemical Formula: $C_9H_{13}N$
Exact Mass: 135.1048

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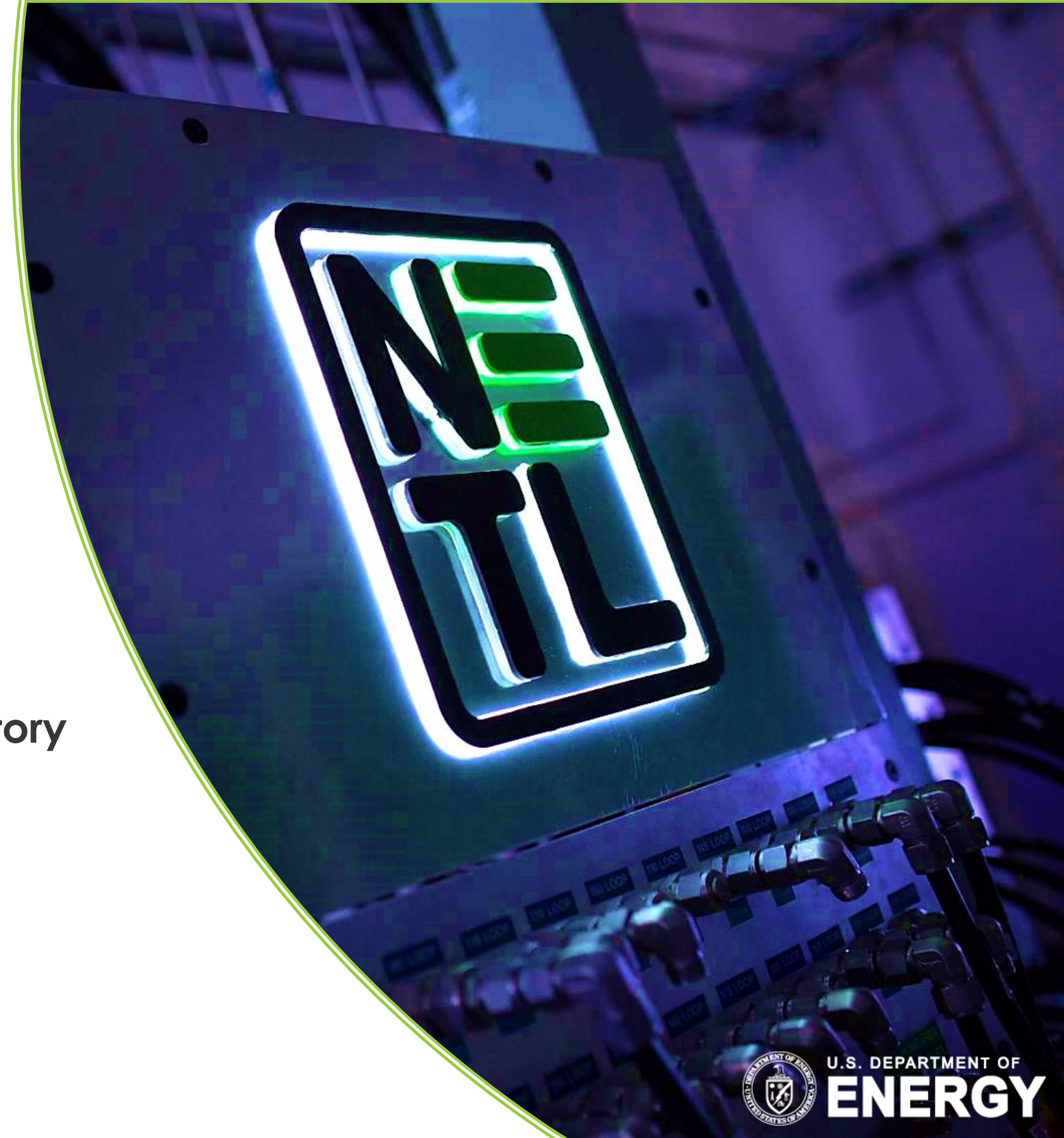

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