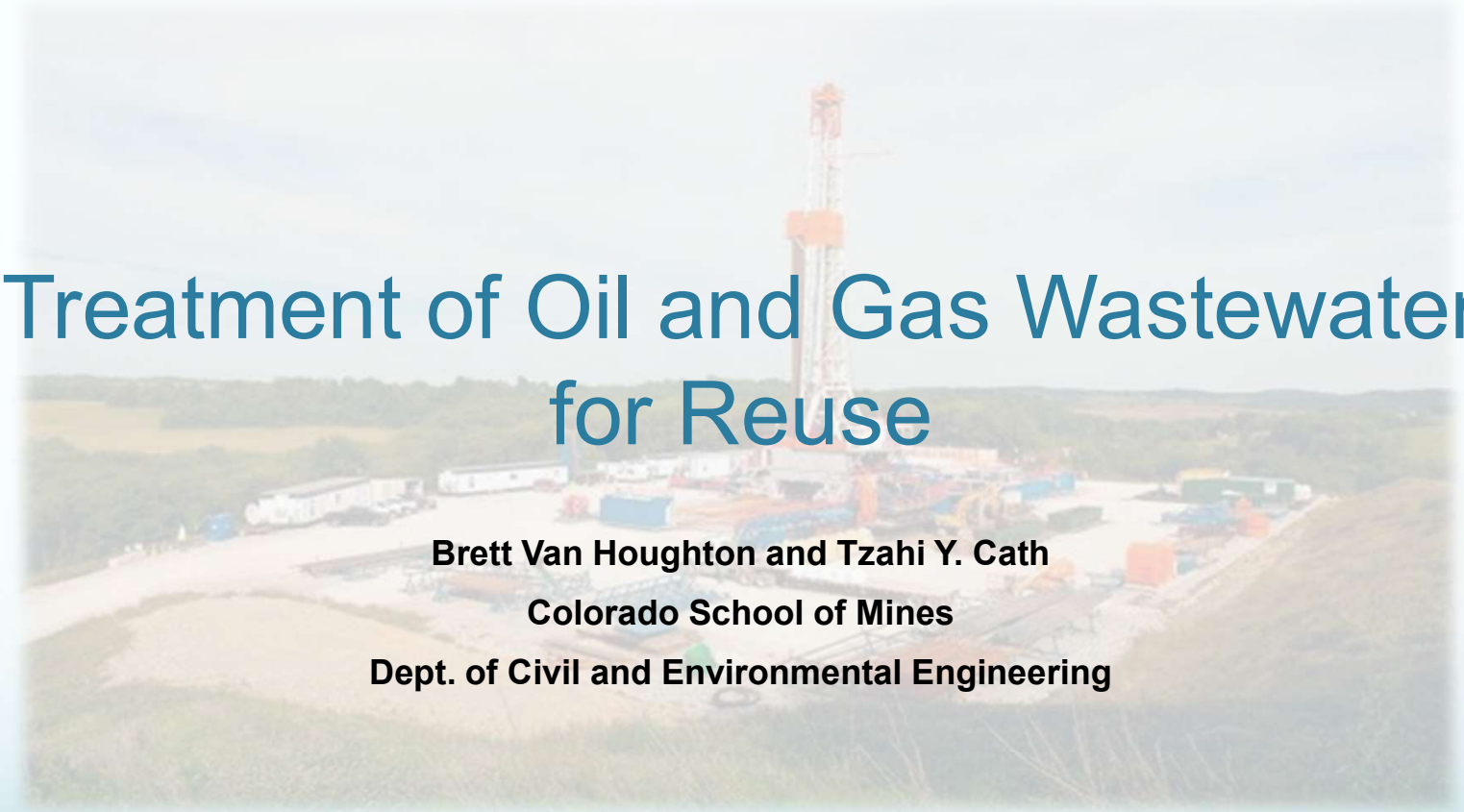

Treatment of Oil and Gas Wastewater for Reuse

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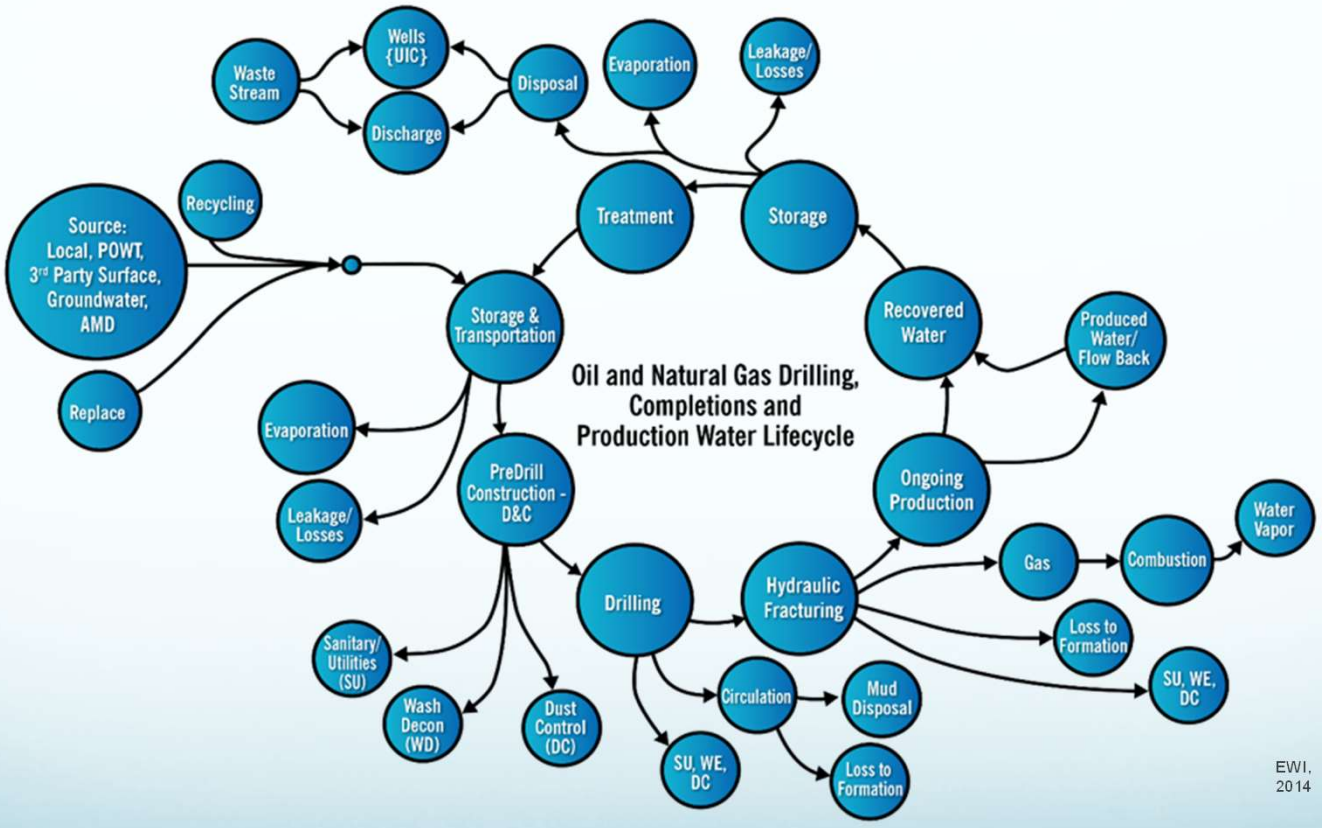
Dept. of Civil and Environmental Engineering

Life Cycle of Water in the Upstream O&G Operations



Wastewater Composition

- Flowback and produced water are characterized by
  - High concentrations of suspended solids, oil, and grease
  - High concentrations of dissolved organic matter, including volatile compounds and hydrocarbons
  - High salt concentrations (often > 35 g/L)
  - Metals (e.g., Fe, Mn, Ca, Mg, Ba, etc.)
  - Dissolved gases (e.g., H_2S, CH_4)
  - Naturally occurring radioactive material (NORM)
- Major challenges:
  - Highly variable wastewater quality (spatial and temporal)
  - High salinity

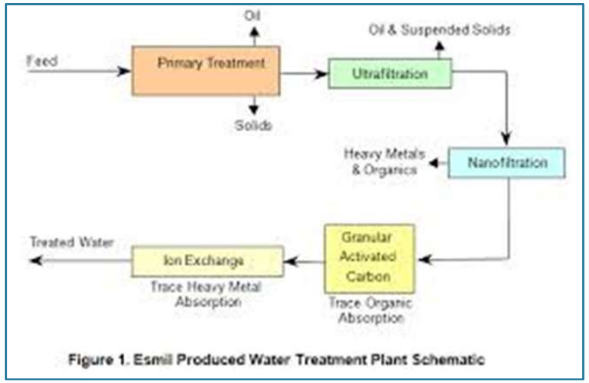
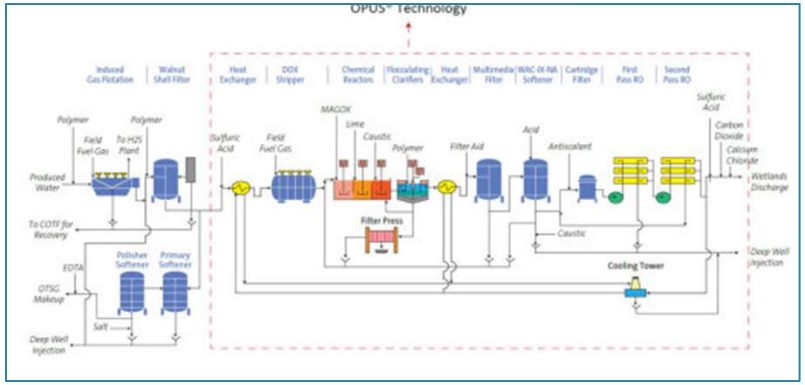
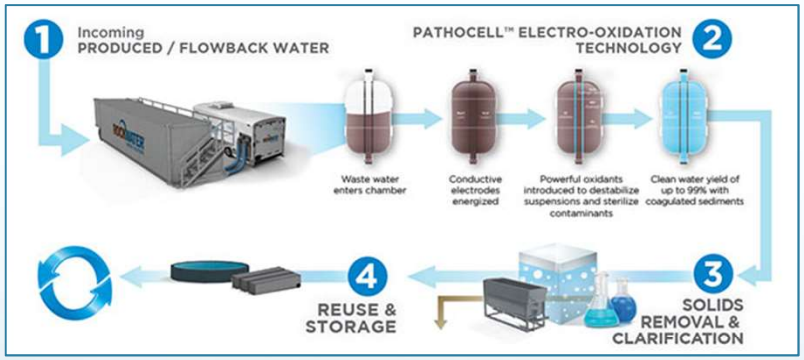
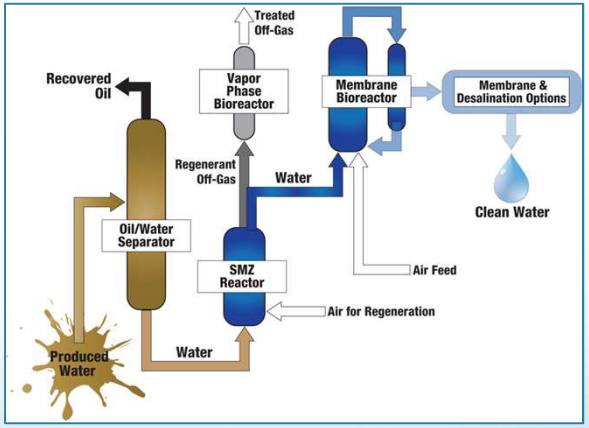


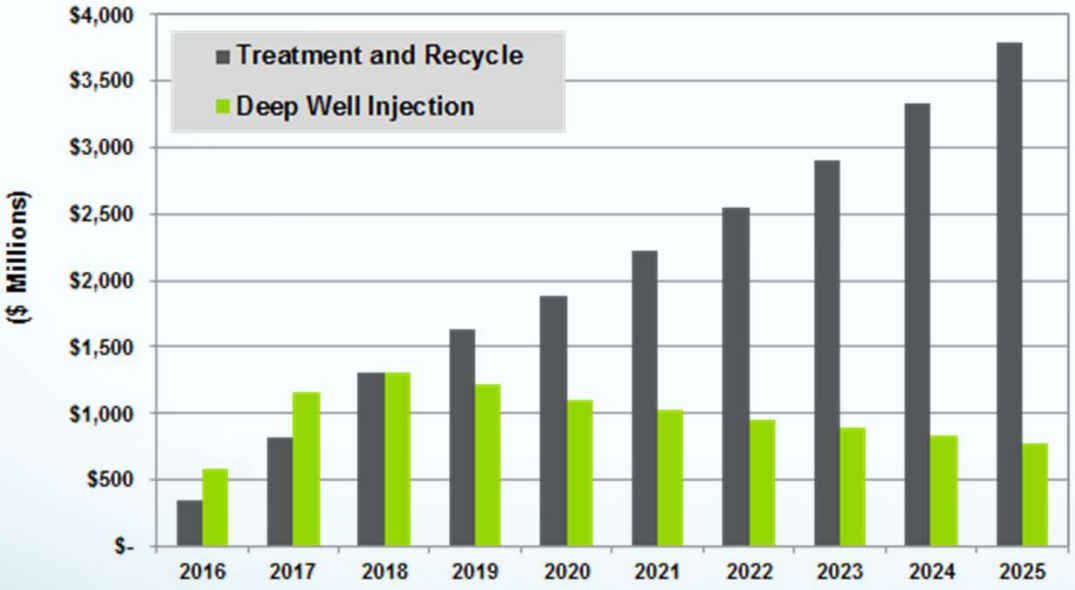
Figure 1. Esmil Produced Water Treatment Plant Schematic







Emerging Markets



- Treatment and recycling of produced water is estimated to be a $3.8 billion dollar industry by 2025.
- Oil and gas operations are not going anywhere

Source: Navigant Research, 2016

Oil & Gas Water Research @ Mines

Fields & Scale of Water Treatment Research @ Mines

Research Across Scale: Bench ➢ Lab ➢ Pilot ➢ Demo

NSF/ERC ReNUWIt
- Urban Systems
- Water Reuse in Urban Development
- Resource Recovery
- Energy–Water (waste to energy)

WE²ST
- Treatment of O&G Wastewater
- Energy–Water (waste to energy)
- Water Resources in the Western USA

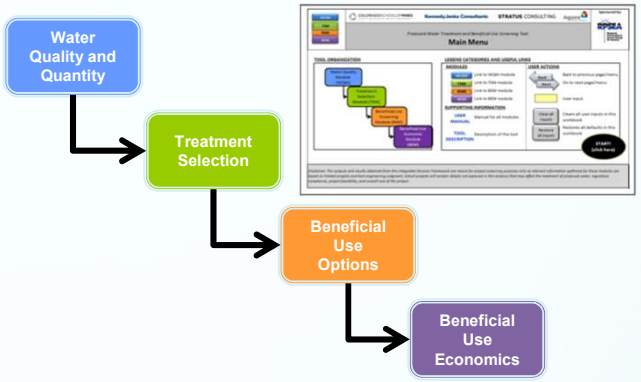
CESEP
- Subsurface environmental processes
- Geological storage of carbon dioxide

AQWATEC
- Water Reuse (WRF, NSF)
- Energy–Water (NREL, NSF, ARPA–e)
- Desalination/Concentrate Management (NSF, industry)
- Natural Treatment Systems
- Treatment of O&G Wastewater (RPSEA, NSF, Private)

NSF/SRN AWG
- Treatment of O&G Wastewater
- Energy–Water (waste to energy)

Decision Support Tools for Unconventional Oil & Gas Development

- Objectives
  - Development of a computer-based integrated decision support tool (iDST) for management of water in the upstream oil and gas sector, focusing on produced and flowback water treatment & beneficial use
  - Establish new databases for shale gas produced and flowback water



- Timeline/Outcomes/Outputs
  - Phase I: 2009-2011 (CBM)
  - Phase II: 2012-2016 (all unconventionals)
  - Spinoffs: Urban Water iDST and Renewable Energy iDST
  - Multiple publications and industry interest

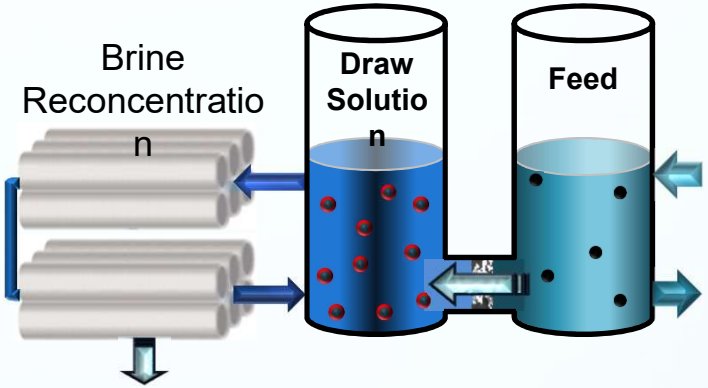
- A large number of permutations
  - 32 treatment processes
  - 46 water quality parameters
  - Intelligent process selection
    - On-the-fly data trimming

8 corners, 12 edges
> 3 billion combinations

RPSEA U.S. DEPARTMENT OF ENERGY

Engineered Osmosis Treatment of Produced and Flowback Water

- Objectives
  - Develop and optimize engineered osmosis membranes for treatment of oil and gas wastewater
  - Field test the process on drilling and produced waters in the DJ Basin
  - Develop process design tools and life cycle assessment
- Timeline/Outcomes/Outputs
  - 2011-2016
  - 11 Peer reviewed publications
  - >15 conference presentations
  - Pilot testing in DJ Basin (Jun.-Aug., 15)
  - Industrial collaborations
    - Resulted in a major new research facility for Mines

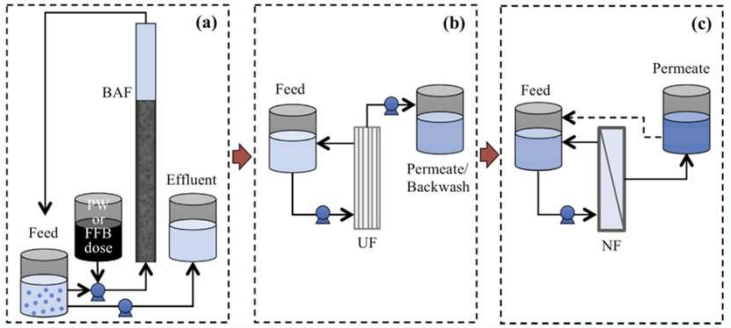


	Phase 1		Phases 2 – 5	
	FO system % removal (n = 6)	FO-RO system % removal (n = 6)	FO system % removal (n = 6)	FO-RO system % removal (n = 21)
Saturated hydrocarbons				
n-Alkanes C_{11}-C_{30}	96.8±1.2	98.2±0.8	95.8±0.9	95.2±0.8
Volatile fatty acids	97.8±1.5	98.0±3.0	97.1±2.9	99.3±0.8
Fatty aldehydes	94.9±4.9	98.4±0.8	94.6±3.4	99.0±2.0
PAHs				
Naphthalene	92.1±8.0	95.2±2.8	94.8±1.4	93.6±1.7
Fluorene	58.8±17.4	<MDL (4 ng/L)	84.7±4.8	<MDL
Phenanthrene	82.9±5.1	<MDL (9 ng/L)	85.5±5.0	<MDL
Anthracene	<MDL (8 ng/L)	<MDL	-	-
Fluoranthene	<MDL (10 ng/L)	<MDL	<MDL	<MDL
Pyrene	<MDL (7 ng/L)	<MDL	<MDL	<MDL
Benz(a)anthracene	<MDL (10 ng/L)	<MDL	-	-
Chrysene	<MDL (10 ng/L)	<MDL	-	-
Benzo(b)fluoranthene	<MDL (12 ng/L)	<MDL	-	-
Benzo(k)fluoranthene	<MDL (11 ng/L)	<MDL	-	-
Benzo(a)pyrene	91.2±4.8	<MDL (7 ng/L)	-	-
Indeno(1,2,3-c,d)pyrene	<MDL (9 ng/L)	<MDL	-	-
Dibenz(a,h)anthracene	<MDL (13 ng/L)	<MDL	-	-
Benzo(ghi)perylene	<MDL (8 ng/L)	<MDL	-	-

RPSEA U.S. DEPARTMENT OF ENERGY

Integrated Bio-Physical Systems for Treatment of O&G Wastewater

- Objectives
  - Optimize biologically-active filtration (BAF) pretreatment for sustainable membrane desalination of O&G wastewaters
  - Evaluate the long-term performance of ultrafiltration and nanofiltration following BAF pretreatment
- Timeline/Outcomes/Outputs
  - 2012-2018
  - 7 Peer reviewed publications
  - >10 conference presentations
  - Substantial removal of dissolved organic carbon (96%) and chemical oxygen demand (89%) in produced water from the DJ and Piceance



Analyte	Raw Feed	Pretreatment: BAF effluent (UF feed)**	Pretreatment: UF perm (NF feed)**	NF Permeate: 1035 kPa	NF Permeate: 1380 kPa	NF Permeate: 1725 kPa	NF Permeate: 2070 kPa
Turbidity (NTU)	19.6	1.07	0.160	0.096	0.086	0.078	0.062
COD	1157	132	125	BDL*	BDL*	BDL*	BDL*
DOC	385	40.3	31.6	1.61	1.21	1.61	1.35
TN	26.6	13.3	8.72	2.27	1.98	1.29	1.02
B	9.85	9.85	7.28	6.33	5.18	4.17	3.71
Ba	2.52	2.52	4.80	0.072	0.056	0.026	0.015
Ca	43.3	43.3	41.9	0.841	0.515	0.27	0.220
K	526	526	520	119	61.3	46.1	37.3
Li	3.95	3.95	4.10	0.586	0.299	0.248	0.196
Mg	11.5	11.5	9.55	0.155	0.104	0.045	0.024
Na	4968	4968	4432	776	400	344	271
P	0.724	0.724	0.736	0.017	0.026	0.025	0.006
S	10.6	10.6	5.20	0.085	0.063	0.204	0.028
Si	5.63	5.63	3.31	0.292	0.188	0.454	0.182
Sr	4.98	4.98	7.59	0.113	0.080	0.022	0.016
Cl	8919	8919	8858	1595	785	717	568
Br	62.3	62.3	55.1	13.1	6.76	6.06	4.89
Sum Cations	5588	5588	5036	903	468	397	312
Sum Anions	8982	8982	8913	1608	792	723	573
TDS	14569	14569	13950	2512	1260	1120	885
% TDS Removal	N/A	0.0%	4.3%	82.0%	91.0%	92.0%	93.7%

AirWaterGas

Other O&G Water Research @ Mines

- Irrigation with diluted and treated produced water
- Wetland treatment of produced water
- Selective removal of salts from produced water (electrodialysis)
- Other biological processes (sequencing-batch reactors coupled to membrane bioreactors) and co-treatment with domestic wastewater
- Energy recovery from O&G wastewater solids
- High recovery desalination of hypersaline streams

Continuing O&G Water Research @ Mines

Focus

- Shortening the treatment train
  - Reduced O&M costs
  - Reduced footprint
  - Increased mobility

Combining Several Processes into One

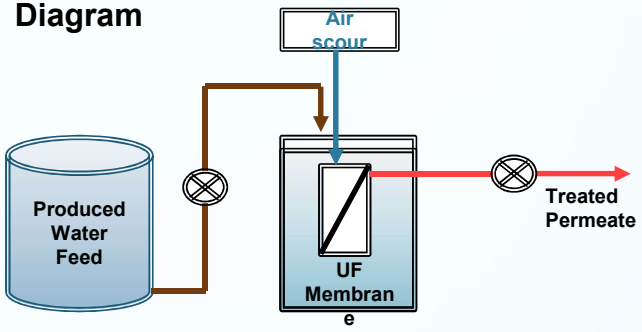
- The Goal
  - Remove multiple contaminants in one process

- The Systems
  - Membrane bioreactor (MBR)
    - Suspended growth / Continuous flow
  - Biologically-active filtration (BAF)
    - Attached growth / Recirculated batch flow

Membrane Bioreactor

- **Advantages**
  - Simple combination of biological and physical processes
  - Commercial process
  - Small footprint
  - Easy to automate and maintain
  - Flexible hydraulic retention time
  - Removal of DOC for reduced fouling of RO/NF membrane

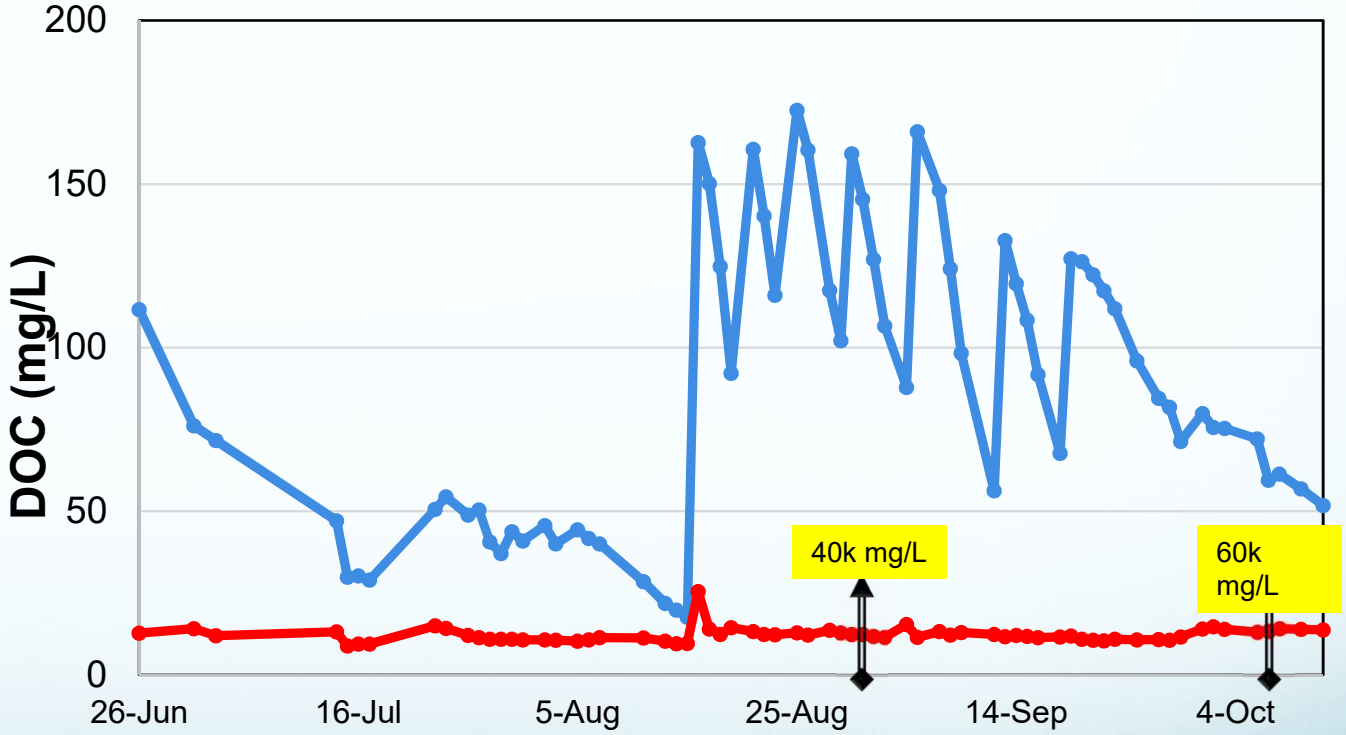
Membrane Bioreactor System Diagram



- Submerged UF membrane
- Aeration/air Scour
- Constant mixing
- Fully automated system (permeation rate, backwashing,…)

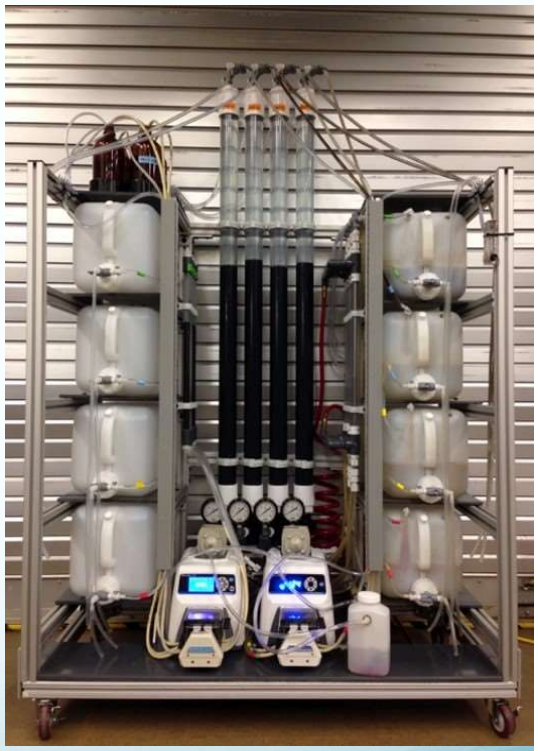
MBR Results

DOC = 13 mg/L



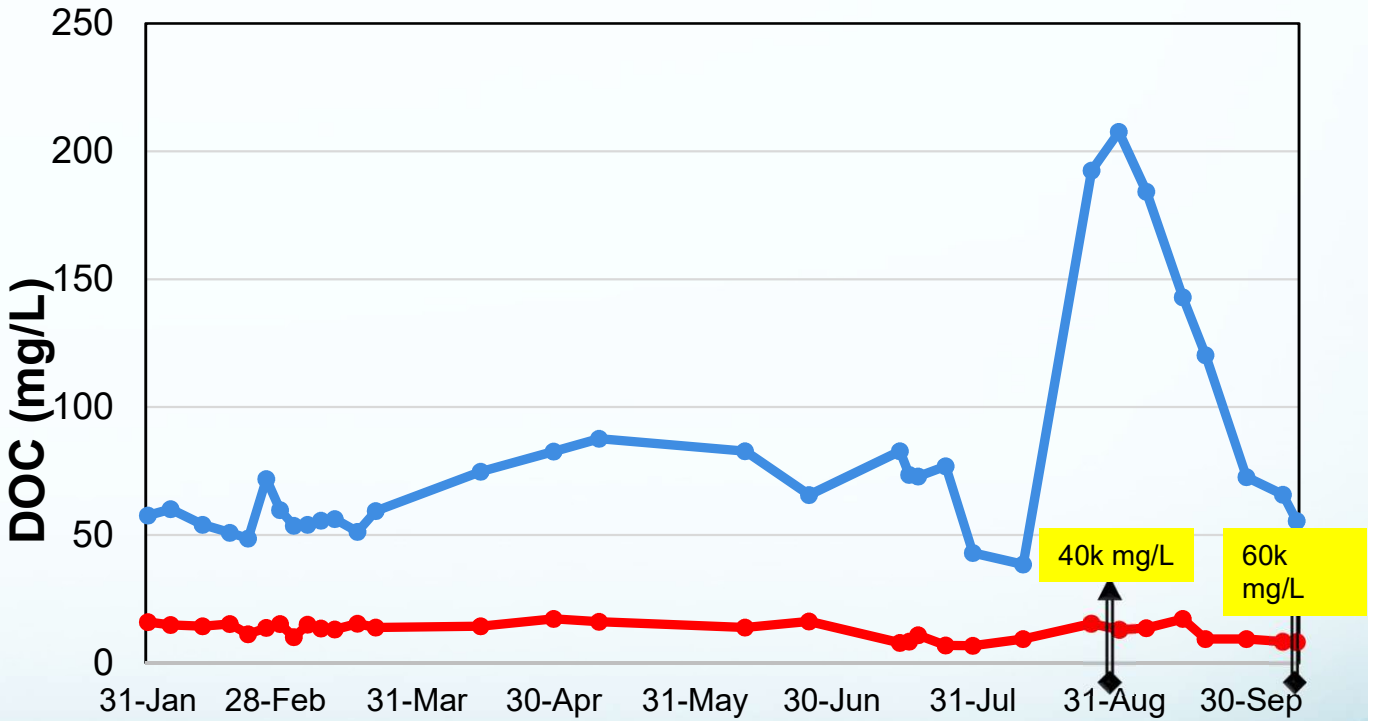
Biologically Active Filtration

- Advantages
  - Highly effective combination of biological and physical processes
  - Can remove organics, metals, radionuclides
  - Commercial process
  - Removal of DOC for reduced fouling of RO/NF membrane



BAF Results

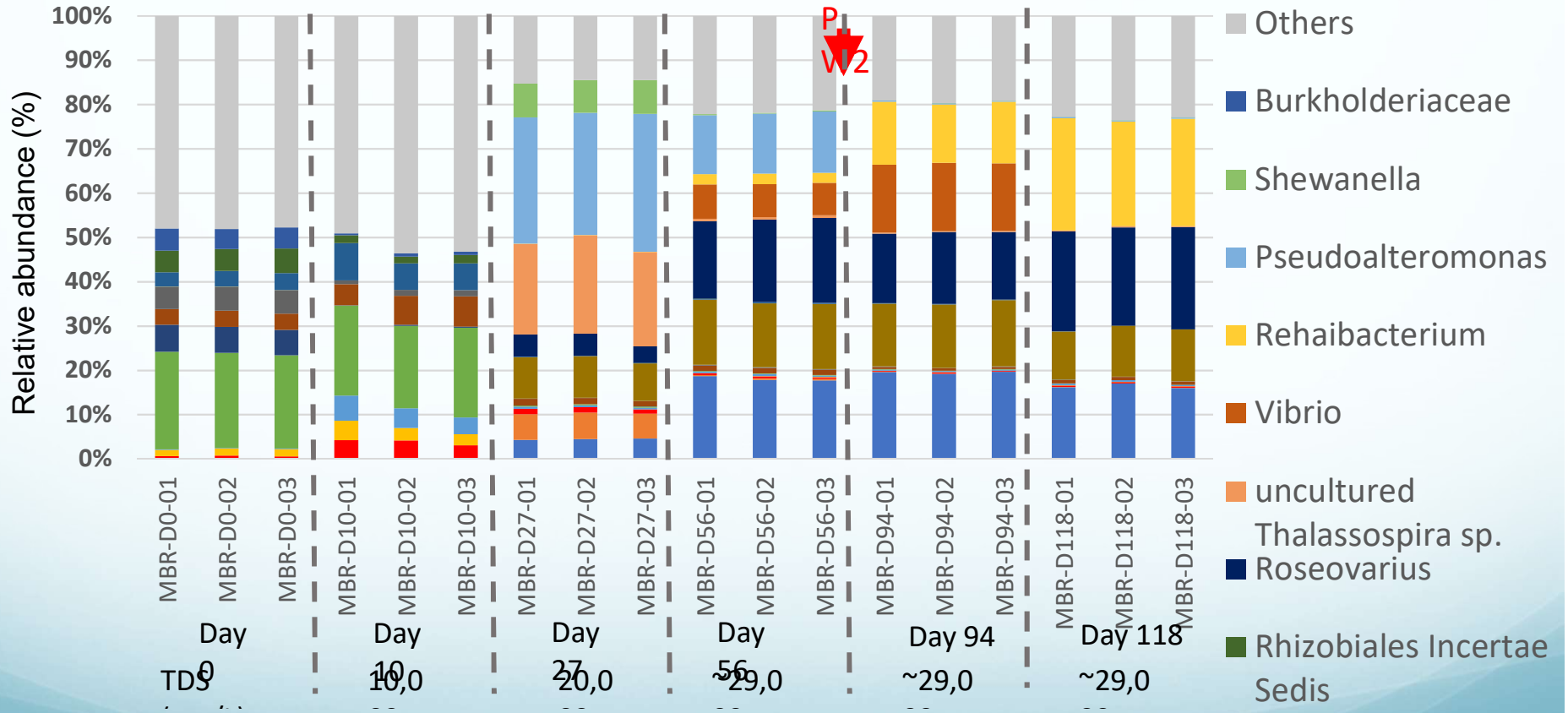
DOC = 13 mg/L



Tailor Made Microbial Communities

- Microbial community analysis
- Isolate genes responsible for halophilicity
- Determine gene transfer mechanisms
- Understand metabolic pathways of biodegradation

MBR Sludge -16S rRNA Community Analysis



Analytics

LC-MS-qTOF

- Surfactants (PEGs, PPGs, etc.)
  - Non-volatile

GC-MS

- Polycyclic aromatic hydrocarbons
  - Semi-volatile

Toxicity

- MicroTox (general toxicity)
- Aryl Hydrocarbon Receptor (AhR)

Future Goals of Research

- Analyitics-LC-MS, GC-MS, Toxicity
- Economic cost/benefit analysis to determine the most appropriate biological process
- Identifying recalcitrant DOC and its toxicity
- Formation and removal of oxidation byproducts
- Testing effluents with desal processes: RO / MD
- Tailored treatment trains for specific basins

Acknowledgments

- Zoma Foundation
- NGL – Energy Partners
- Lawrence Berkeley National Labs – JGI