Coupling Pre-Treatment with Suspended Biological Reactors in the Treatment of Produced Water

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Collaborators

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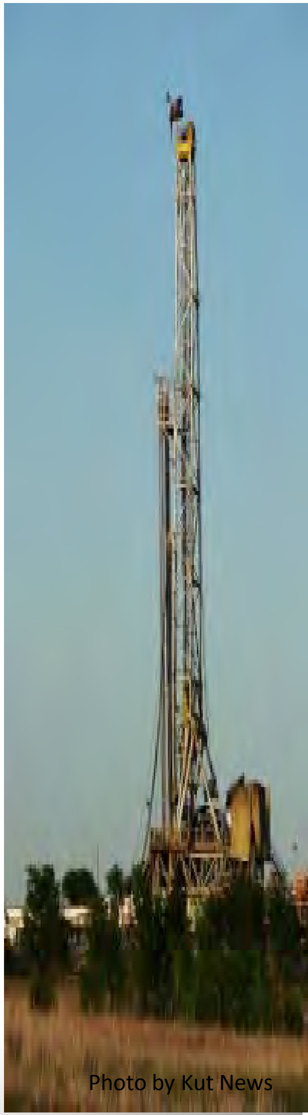
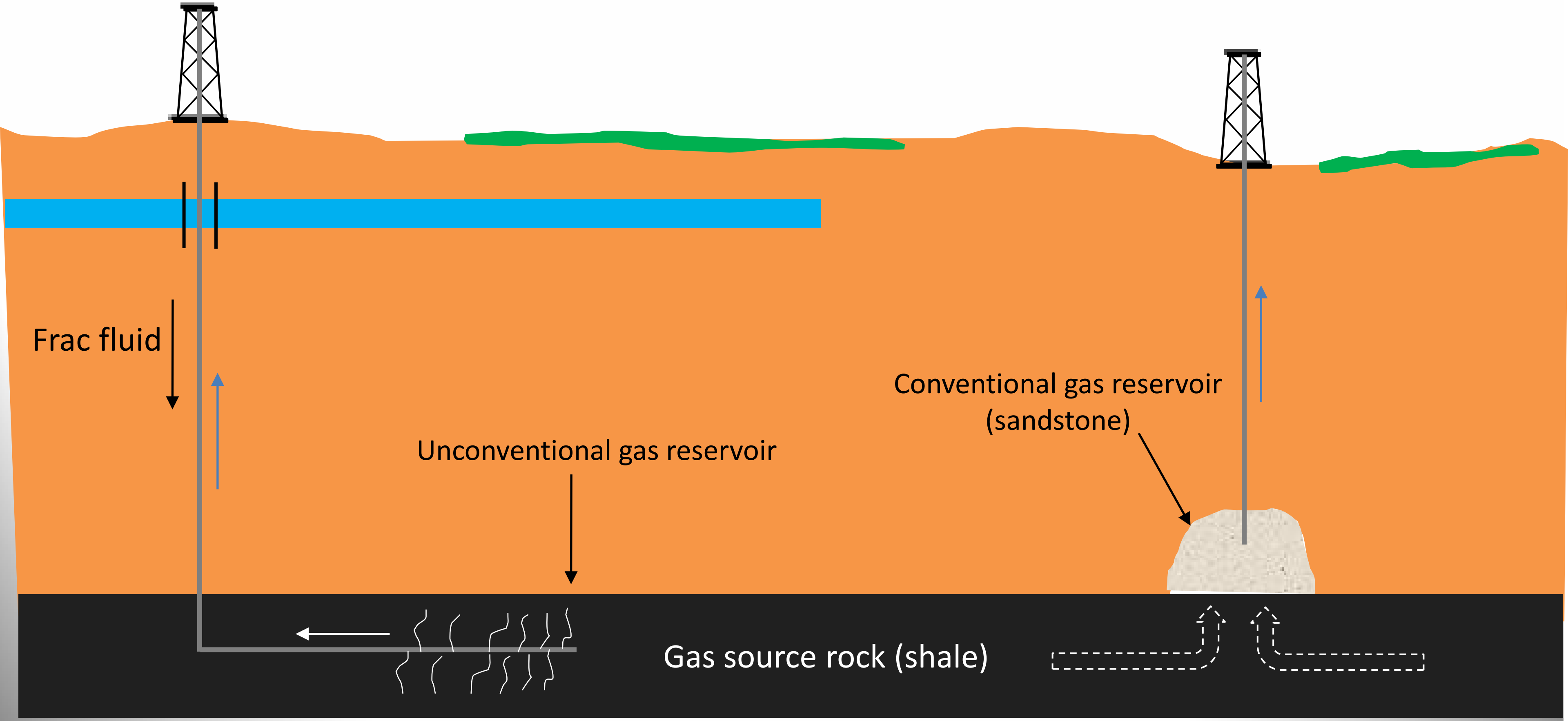
  - Amanda Connell, Masters Student
  - Robyn Hawkinson, Masters Student
- Acknowledge
  - South Adams County Water and Sanitation District
    - Blair Corning
    - MBBR Carriers (media)
  - Boulder Wastewater Treatment
    - Aerobic and Anaerobic sludge

Outline

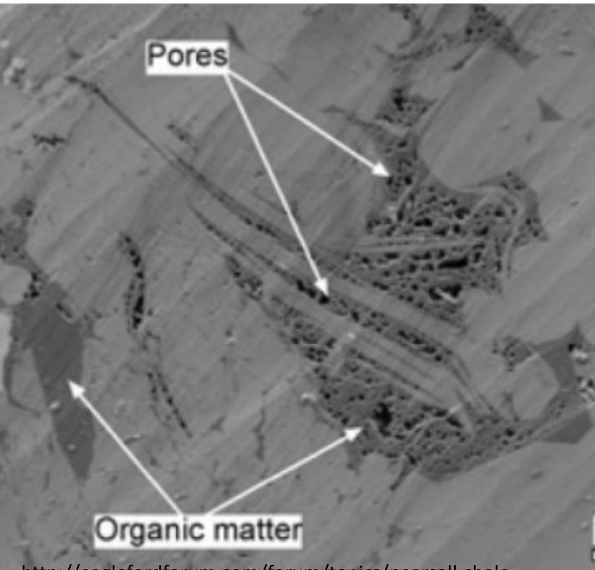
- Hydraulic Fracturing
  - Basics
  - The role water plays in the fracturing process
- Reusing Hydraulic Fracturing Wastewaters
  - Challenges associate with these waters
- Treatment
  - Pre-Treatment
    - Coagulation and Flocculation
  - Biological Treatment
    - Moving Bed Biofilm Reactor
- Conclusions
- Future Research



What is hydraulic fracturing of “unconventional gas sources” ?



Hydraulic Fracturing



http://eaglefordforum.com/forum/topics/pearsall-shale-what-area-does-it-cover?commentId=6447762%3AComment%3A36973

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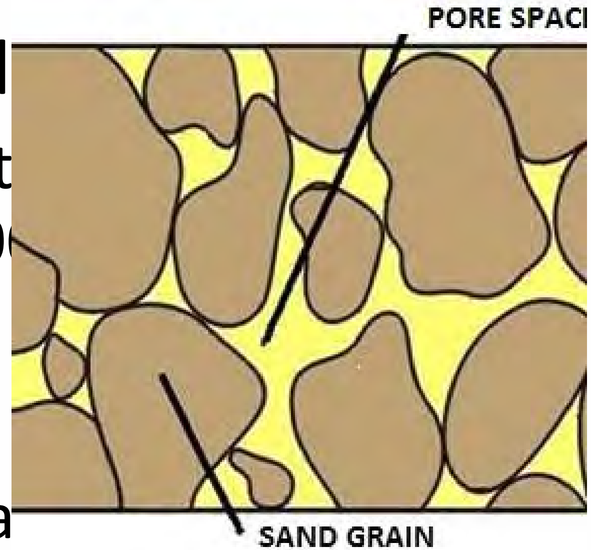


- Sand (porous)
  - Pore Size
- Source Rock
  - Tight formations
    - ~1000 times smaller pore size
    - Flow rates reduced by $1x10^6$

Factors in Drilling
1. Permeability
2. Viscosity
3. Reservoir Contact
   - Conventional Vertical Well
     - $20\ m^2$
   - Fracking
     - $500{,}000m^2$

- Hydraulic Fracturing has allowed us to access these tight formations

Fracturing Fluids

- **~85-90%** Water
- **~10%** Proppants
  - Sand
- **~1-2%** Chemical Additives
  - Friction Reducers
  - Crosslinkers
  - Gelling Agent
  - Breakers
  - Biocides
  - Surfactants
  - Corrosion Inhibitors

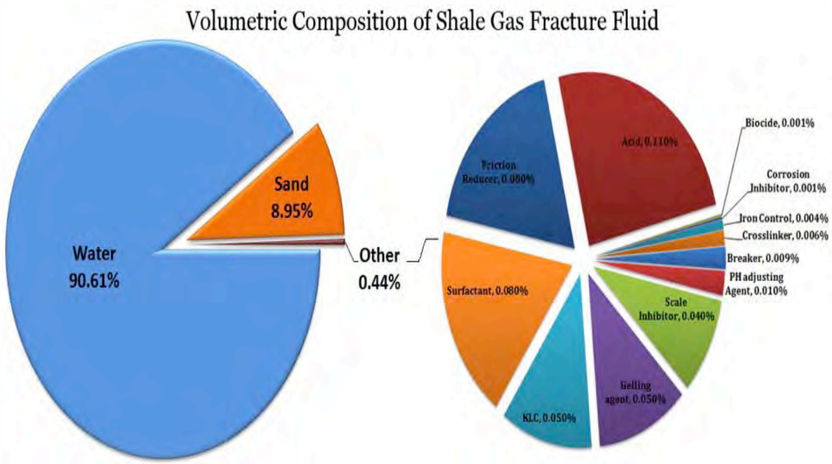
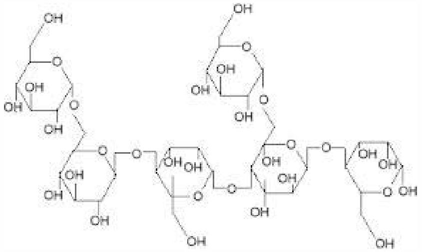


Photo courtesy of shalegaswiki.com. Data obtained from Environmental Considerations of Modern Shale Gas Development, SPE 122391

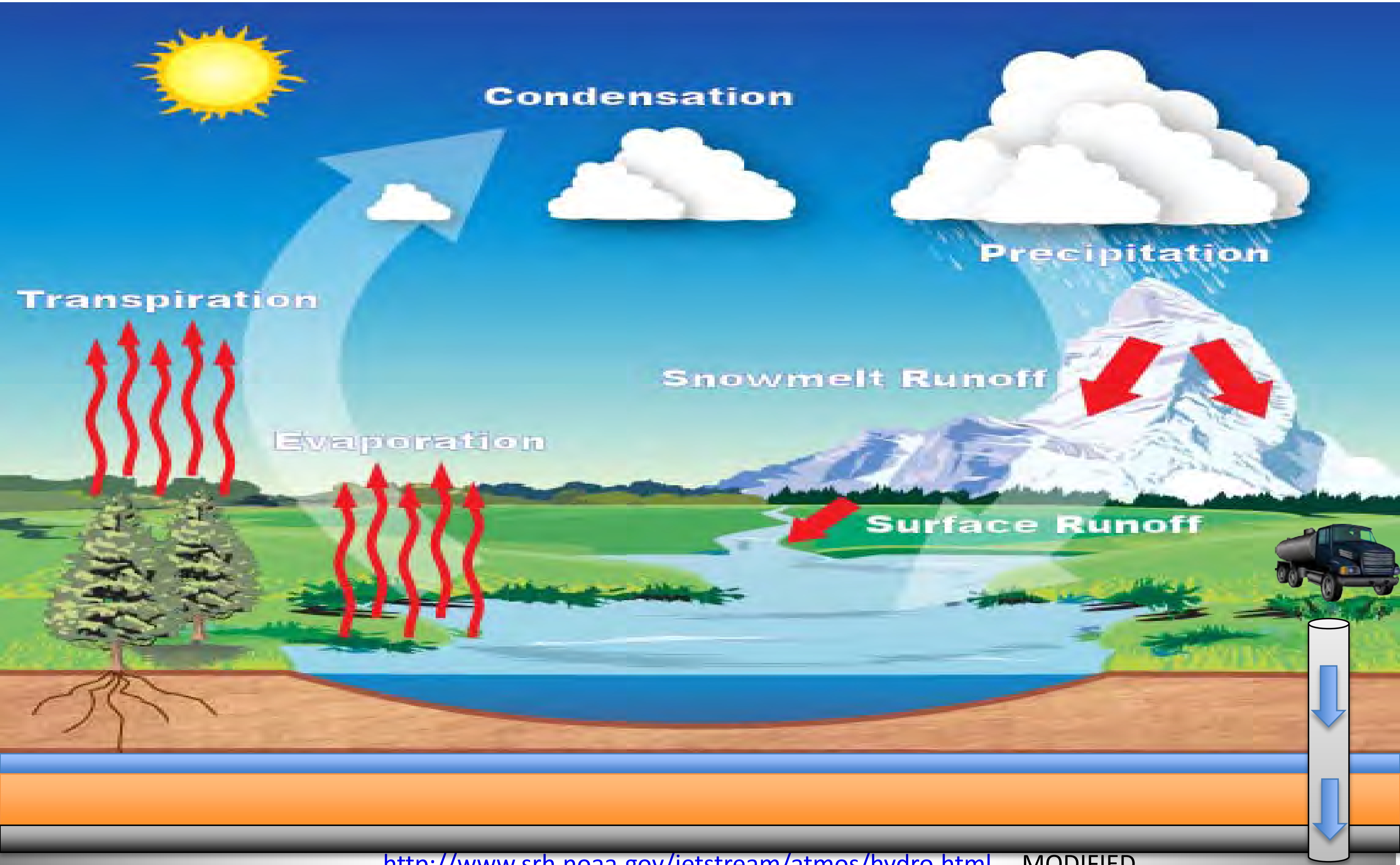


Role of Fracturing Fluid Agents

- Water
  - Media
- Sand (proppant)
  - Fissure remain porous (permeability)
- Friction Reducer
  - Guar
    - Helps with head loss
    - Transport of the proppant
      - Due to viscosity and turbulence within the water, the sand remains suspended,
- Cross Linkers
  - Boric Acid
    - Binds guar molecules, forming polymers of guar, further improving head loss
- Biocides
  - Guar is a carbohydrate (Food for Microbes), so biocides prevents microbes from degrading guar within the Frac Fluid
- Breakers
  - Hydrogen Peroxide
    - Break apart the gels allowing for the release of gas

Water

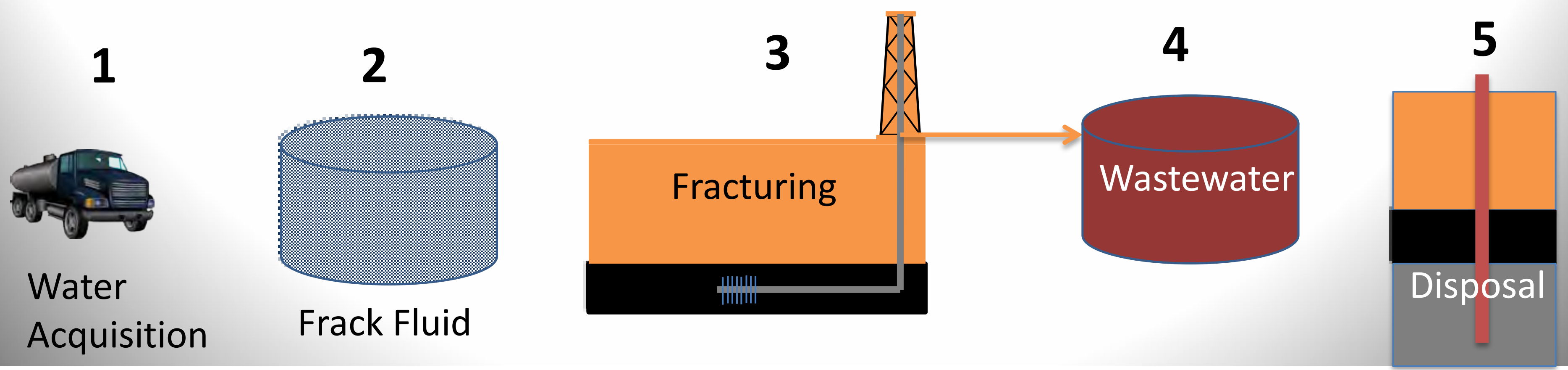
The Hydrologic Cycle



http://www.srh.noaa.gov/jetstream/atmos/hydro.html MODIFIED

Oil and Gas Hydrologic Cycle

1. Water Acquisition
2. Mixing (making) Fracturing Fluid
3. Act of Fracturing
4. Wastewater Flowback/Produced
5. Wastewater treatment or Disposal



Wastewater

What are the different wastewater streams ?

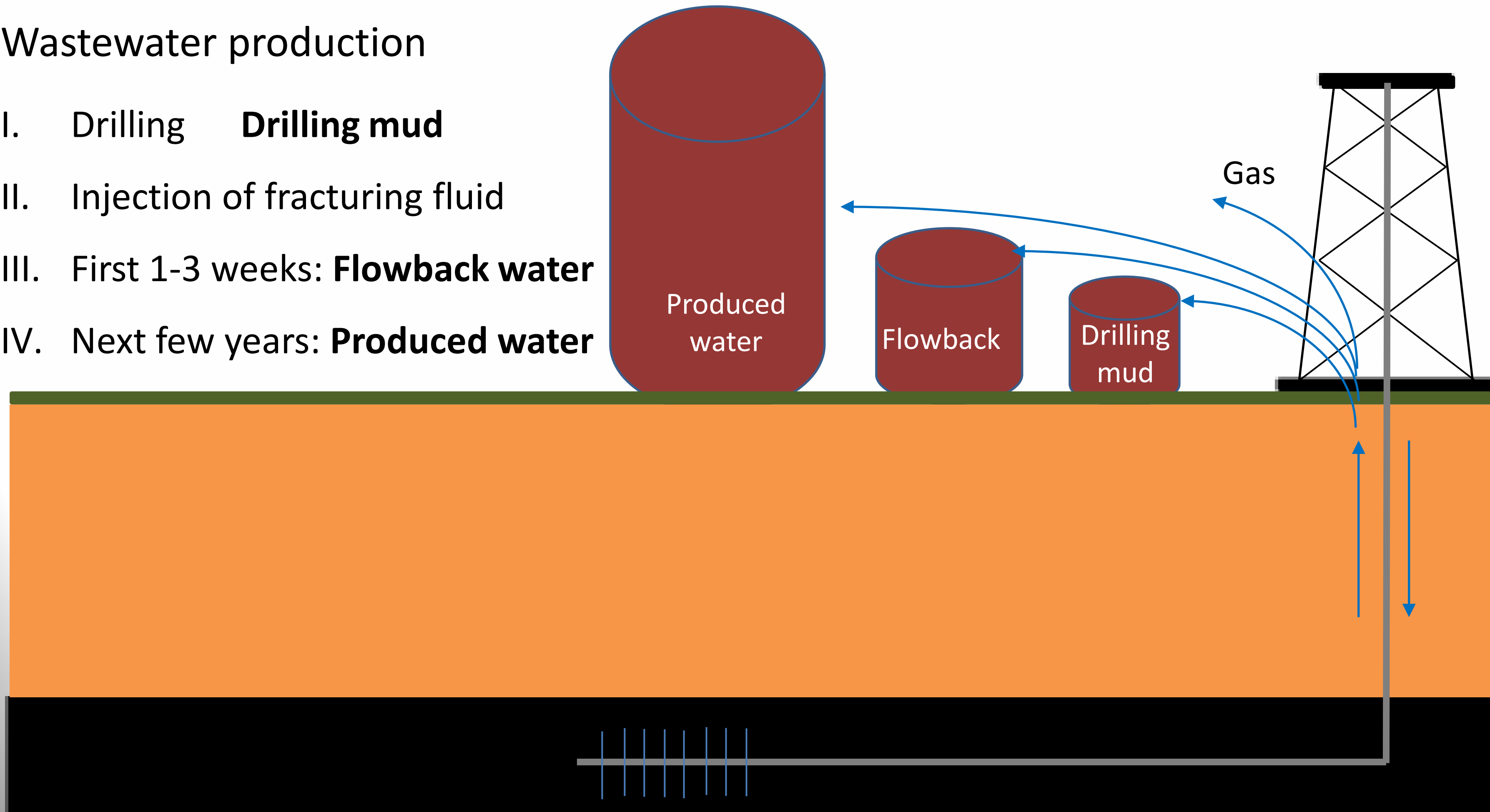
Wastewater production

I. Drilling **Drilling mud**

II. Injection of fracturing fluid

III. First 1-3 weeks: **Flowback water**

IV. Next few years: **Produced water**

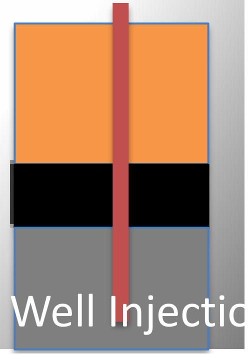


Water Management Options

- Deep well injection disposal
- Evaporation pits
- Treatment and surface water discharge

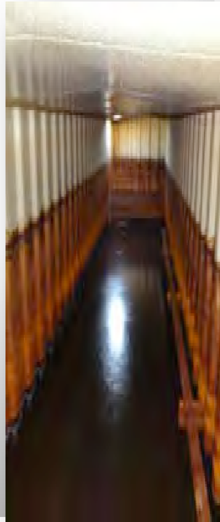
http://www.ecowren.net/2013/is-illinois-ready-for-fracking/

- On-site recycling/reuse
  - Relatively uncommon with no national estimates



Wastewater Composition

- Flowback and produced water are characterized by
  - High dissolved organic matter, including volatile compounds and hydrocarbons
  - High salt content (TDS)
    - DJ Basin ~20 g/L
    - Marcellus Shale > 200 g/L
  - Metals (e.g., iron, manganese, calcium, magnesium, barium, etc.)
  - Dissolved gases (e.g., H_2S)
  - Naturally occurring radioactive material (NORM)
  - High concentrations of suspended solids, oil, and grease
- Flowback and Produced Wastewater Quantity
  - High flowrates in the first days/weeks after fracturing
- Produced water
  - High flowrates at early life of well, decreasing with time (e.g., coalbed methane)
  - Very low flowrates throughout the life of the well (e.g., shale gas and others)



Re-Using Fracturing Wastewaters

Level 1

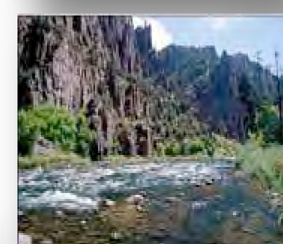
- Direct Reuse
  - Well-To-Well
  - Minimal Treatment

Level 2

- Usage Based Treatment
  - Removal of Specific Contaminants
  - Strict Usage (Industry)
    - Cooling towers
    - De-icing roads
    - Livestock Watering
    - Irrigation

Level 3

- Environmental Discharge
  - Contaminant, Organic, and TDS removal



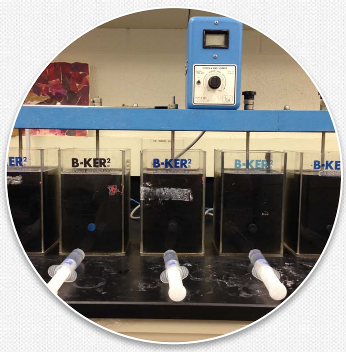
Treatment

What makes treating Hydraulic Fracturing Wastewaters a challenge?

A. High levels of total dissolved solids (TDS)
B. Dissolved organic content (DOC) over > 400ppm
C. Known and unknown chemical agents
D. Lack of a centralized collection system
E. None of the above
F. All of the above

Treatment Plan

Pre-Treatment



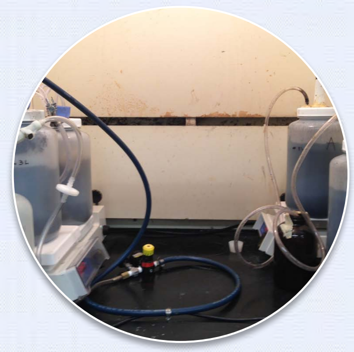
Coagulation-Flocculation

>$AlCl_3$ or $FeCl_3$

>Powder Activated Carbon

- Total Organic Carbon
- Total Petroleum Hydrocarbons
- Turbidity
- Total Suspended Solids
- Ionic contaminants

Organic Carbon Removal



-Biological Treatment

-Bio-Treat coupled with AOP

-MBBR

Aerobic / Anaerobic

- Total Organic Carbon
- Biochemical Oxygen Demand

Total Dissolved Solids Removal

-Membranes

- Salts and other dissolved solids not removed by the previous two methods

Assessing Treatment

- Wastewater Treatment Indicators
  - Total Organic Carbon, Turbidity, Total Suspended Solids, Total Dissolved Solids
- Advanced Chemical Markers
  - Ionizable Compounds
    - HPLC-TOF
  - Burnable Compounds (hydrocarbons)
    - GC-FID
- Advanced Biological Markers
  - Bacterial Toxicity Assays

Pre-Treatment

Coagulation and Flocculation

- Remove suspended and settleable solids
- Utilized Two Coagulants
  - $AlCl_3$ and $FeCl_3$
    - Compared varying doses on their ability to remove TOC
      - 40, 60, 80, 120mg/L
    - Compared them based on their ability to also remove
      - TSS and Turbidity
    - Advanced indicators
      - Hydrocarbons, Ionizable Compounds, Bacterial Tox Assays
- Utilized Powder Activated Carbon (PAC)
  - Compared varying doses on their ability to remove TOC, TPH, and Ionic contaminants
    - Coupled with either $AlCl_3$ or $FeCl_3$ at PAC doses of
      - 0.05, 0.25, 0.50, 1, and 10 g/L (PAC dose)
      - 120 mg/L (Coagulant dose)
    - PAC alone
      - 0.25, 0.50, 1, and 10 g/L

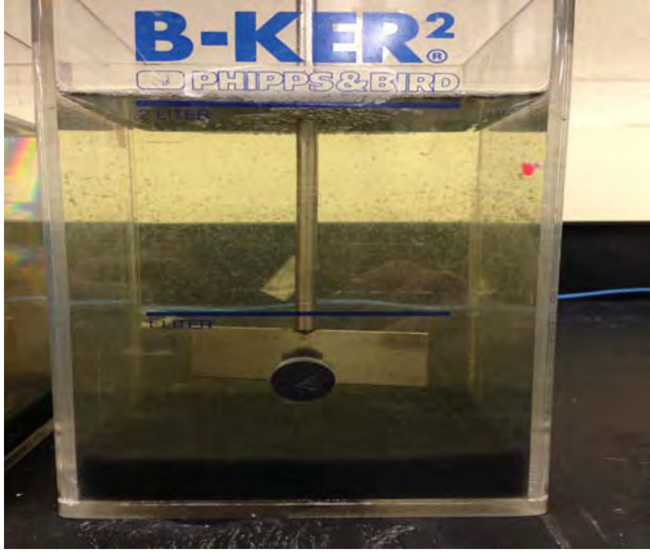
Pre-Treatment

Coagulation-Flocculation

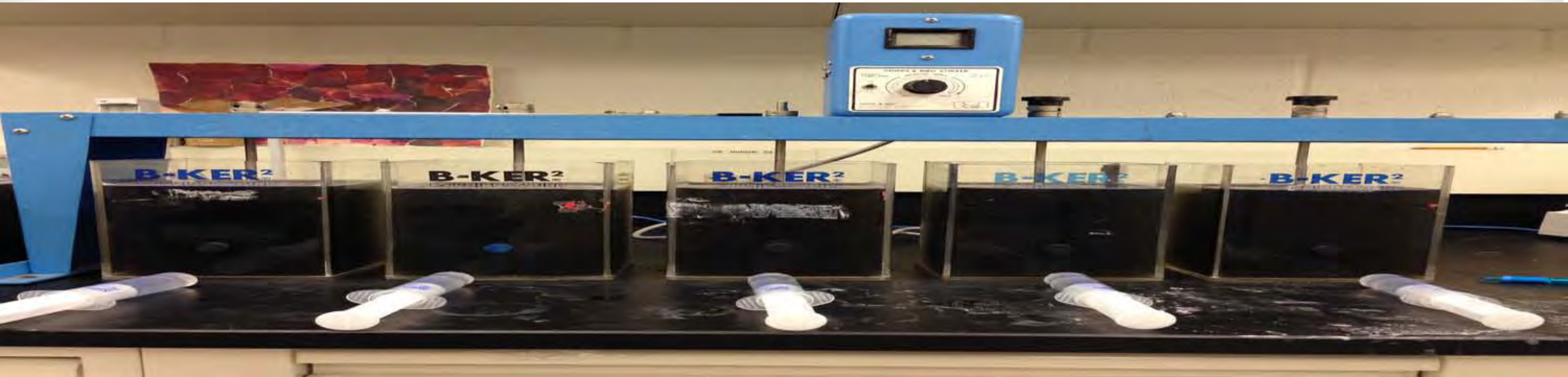
>AlCl3 or FeCl3

>Powder Activated Carbon

- Total Organic Carbon
- Total Petroleum Hydrocarbons
- Turbidity
- Total Suspended Solids
- Ionic Contaminants



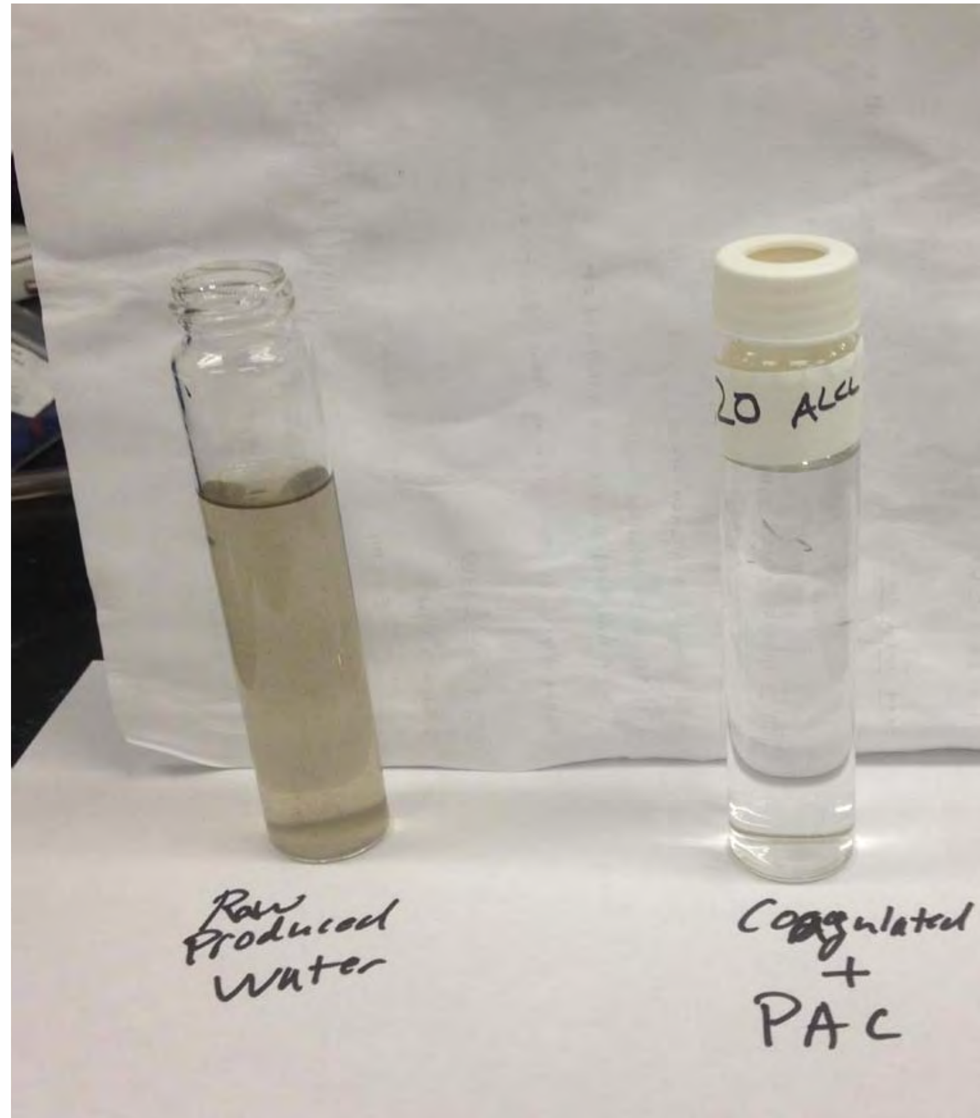
120 mg/L of $AlCL_3$



Pre-Treatment

- TOC Removal
  - $AlCl_3$ 120 mg/L
    - 5% TOC reduction
  - $AlCl_3$ 120 mg/L + 10g PAC
    - 16.8% TOC reduction
  - 10g PAC
    - 13.7% TOC reduction

- Turbidity
  - Raw Water
    - 60 NTU
  - $AlCl_3$ 120 mg/L
    - 14 NTU (76% reduction)
  - $AlCl_3$ 120 mg/L + 10g PAC
    - 1.5 NTU (99% reduction)
  - 10g PAC
    - 2.0 NTU (99% reduction)

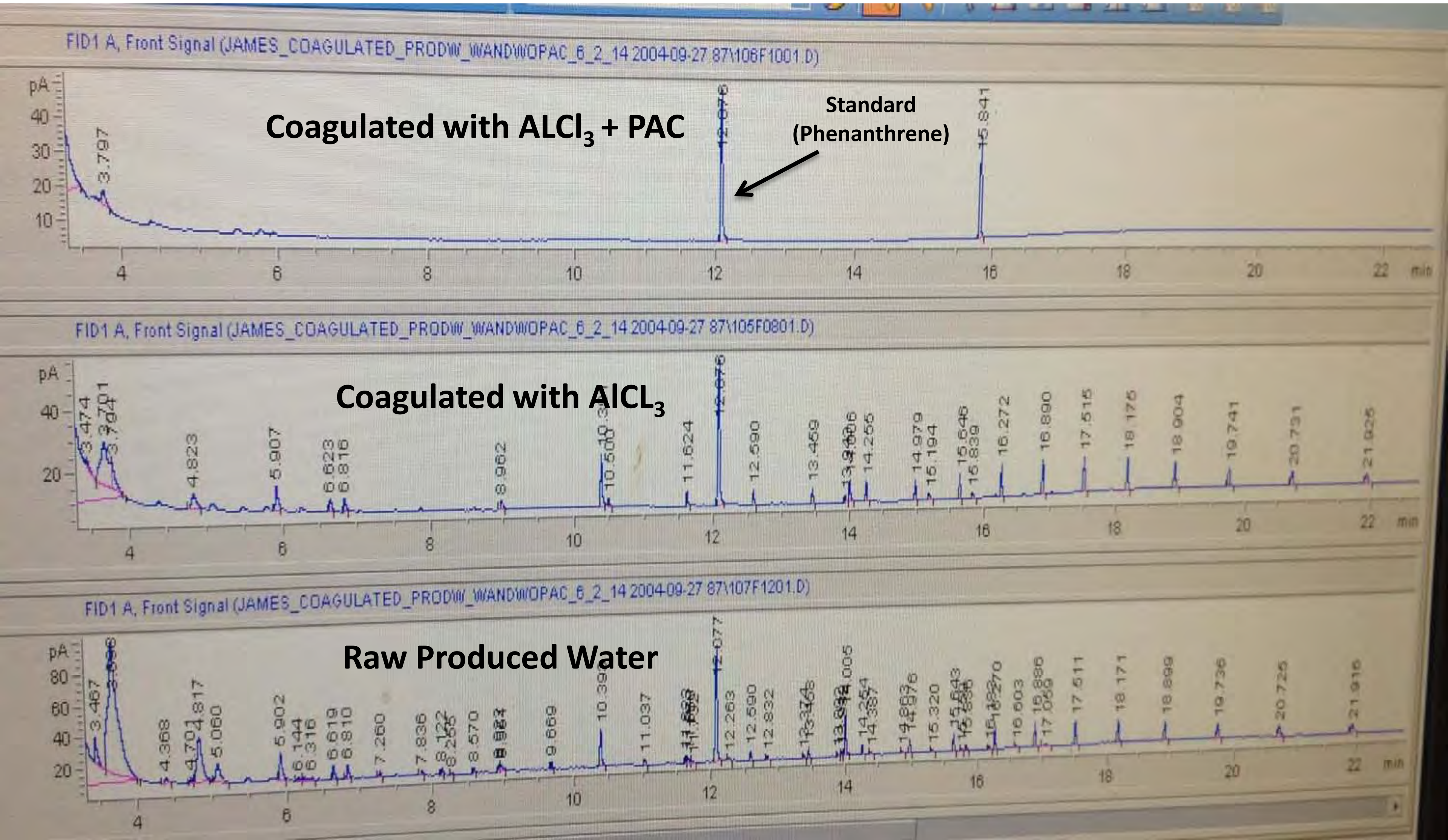


Total Petroleum Hydrocarbon

- Coagulation with FeCl3 and AlCL3
- Powder Activated Carbon (PAC)

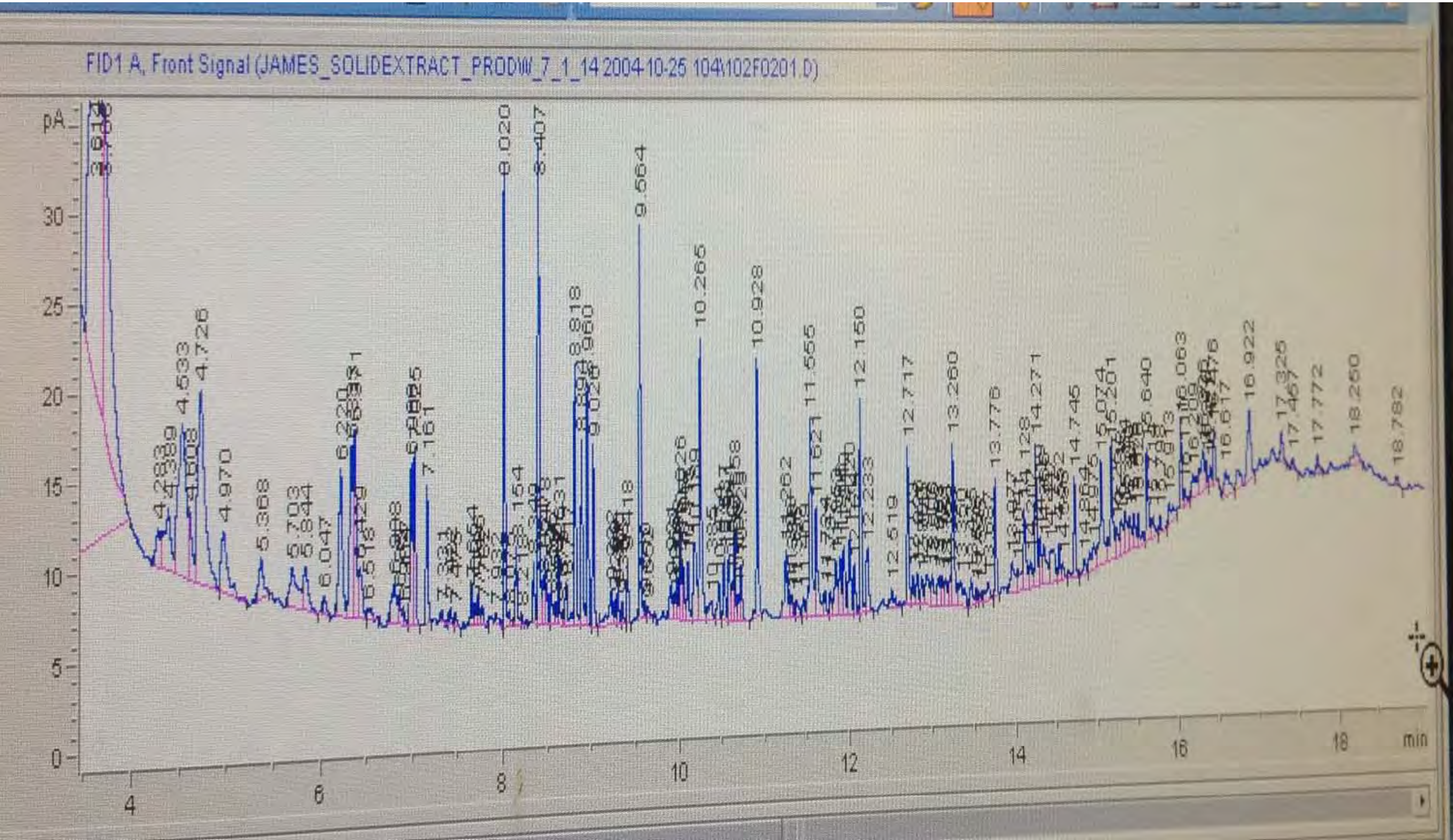
Pre-Treatment	mg/L	% Reduction
Produced Water (Raw)	14.9484	
120 (mg/L) FeCL3	5.258	64.83%
120 (mg/L) FeCL3 + 0.250g PAC	3.99	73.31%
120 (mg/L) FeCL3 + 0.50g PAC	2.4965	83.30%
120 (mg/L) FeCL3 + 1.0g PAC	0	100.00%
120 (mg/L) FeCL3 + 10.0g PAC	0	100.00%
120 (mg/L) ALCL3	5.54314	62.92%
120 (mg/L) ALCL3 + 0.250g PAC		
120 (mg/L) ALCL3 + 0.50g PAC	2.274	84.79%
120 (mg/L) ALCL3 + 1.0g PAC	1.76	88.23%
120 (mg/L) ALCL3 + 10.0g PAC	0	100.00%
0.25g/L PAC only		
0.5g/L PAC only		>80% (Filtered, did not settle)
1g/L PAC only		>90% (Filtered, did not settle)
10g/L PAC only	3.5008	76.58%

Hydrocarbon Chromatograms for Polyaluminum Chloride ($AlCl_3$) Coagulated with simultaneous addition of Powder Act. Carbon.



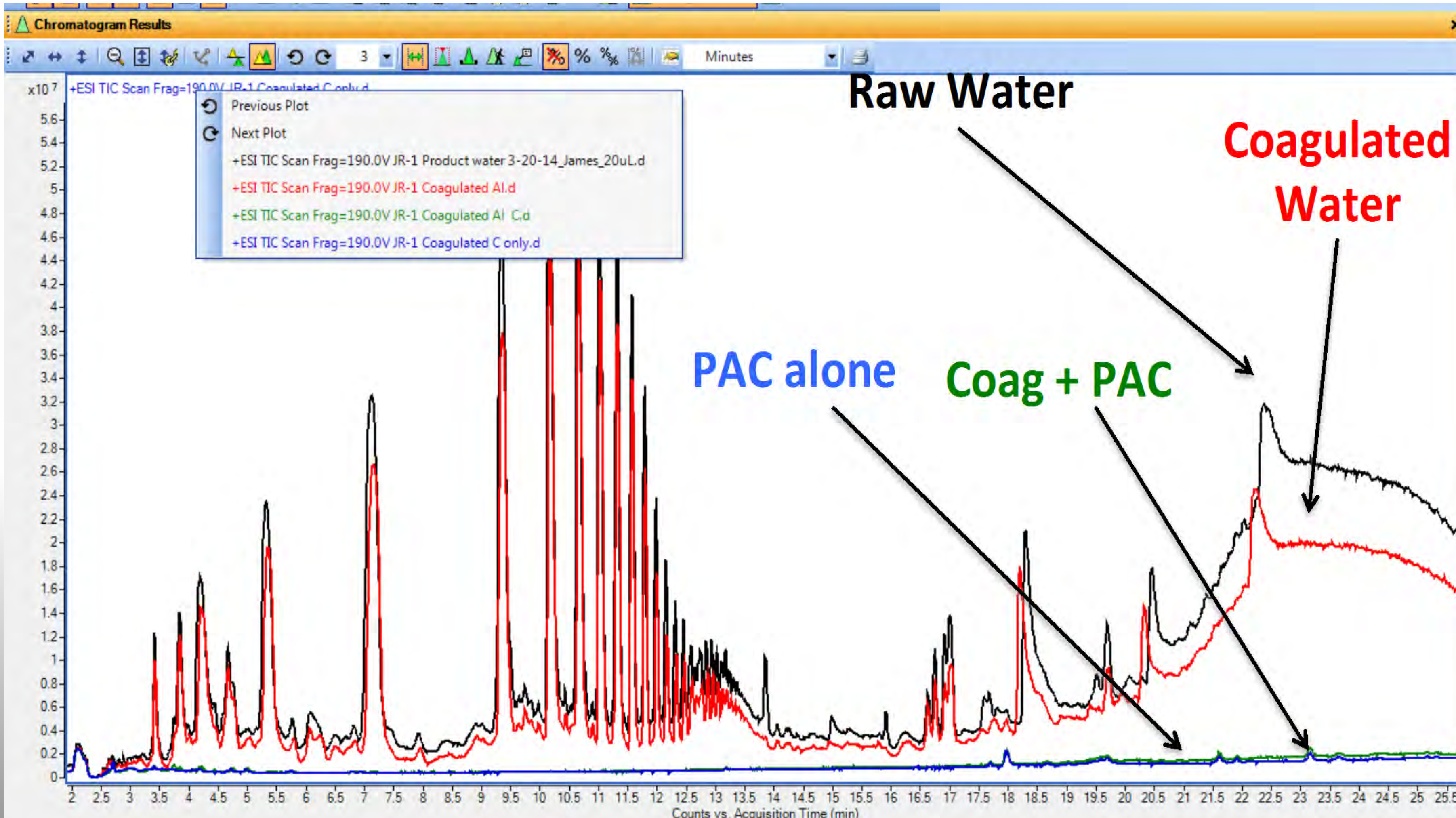
Solid-Phase Extraction

- Dried settled floc and performed a liquid-solid extraction

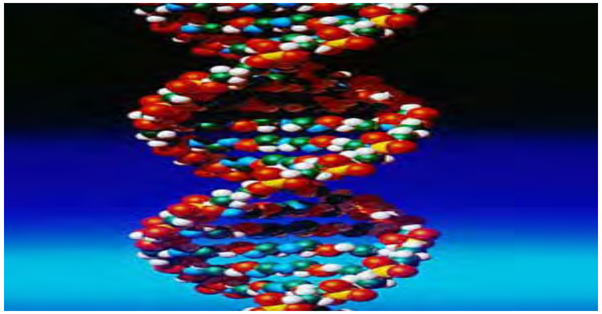


Treatment Studies

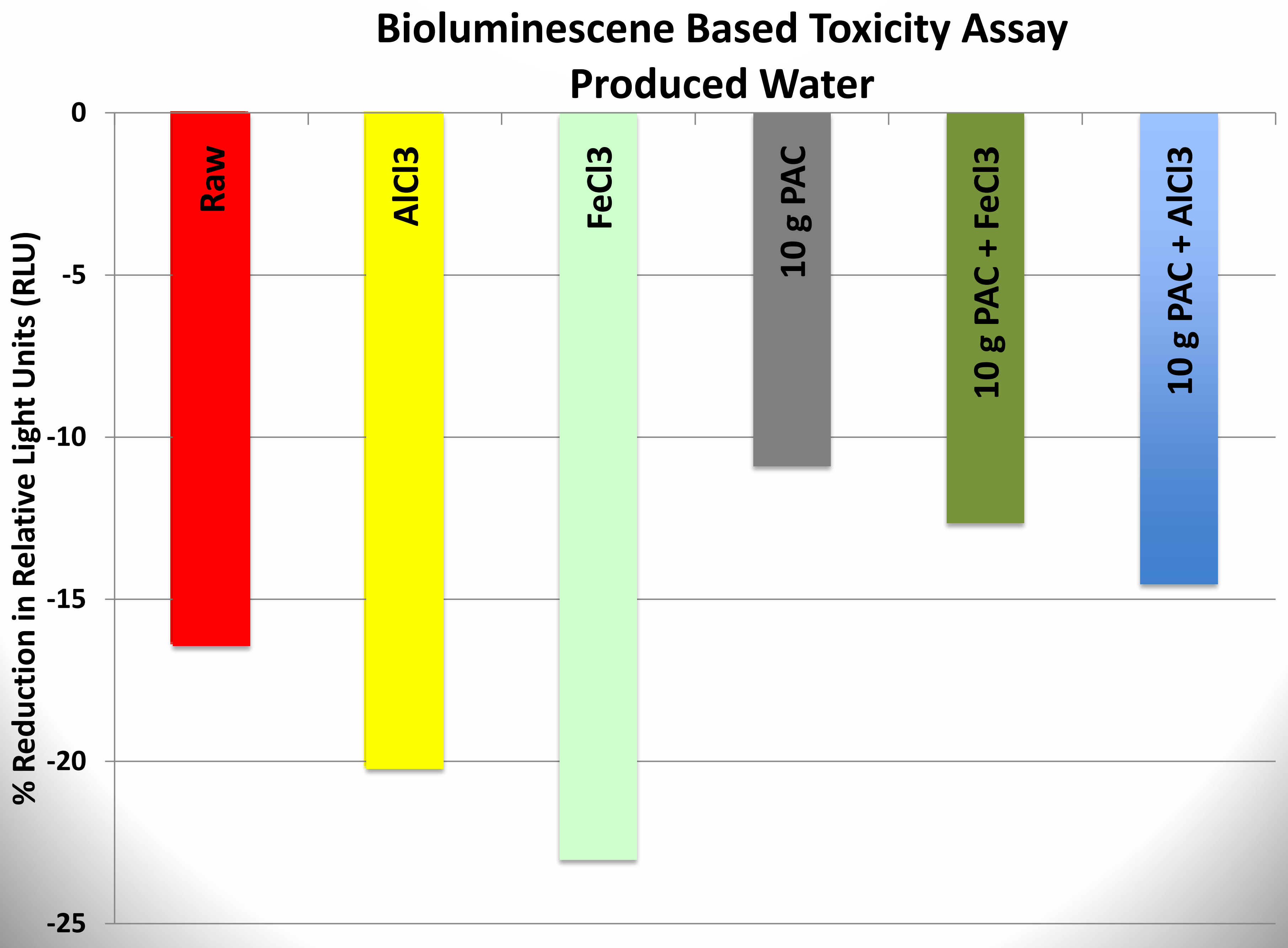
- LC Chromatograms:
- Coagulation and Powdered Activated Carbon treatments

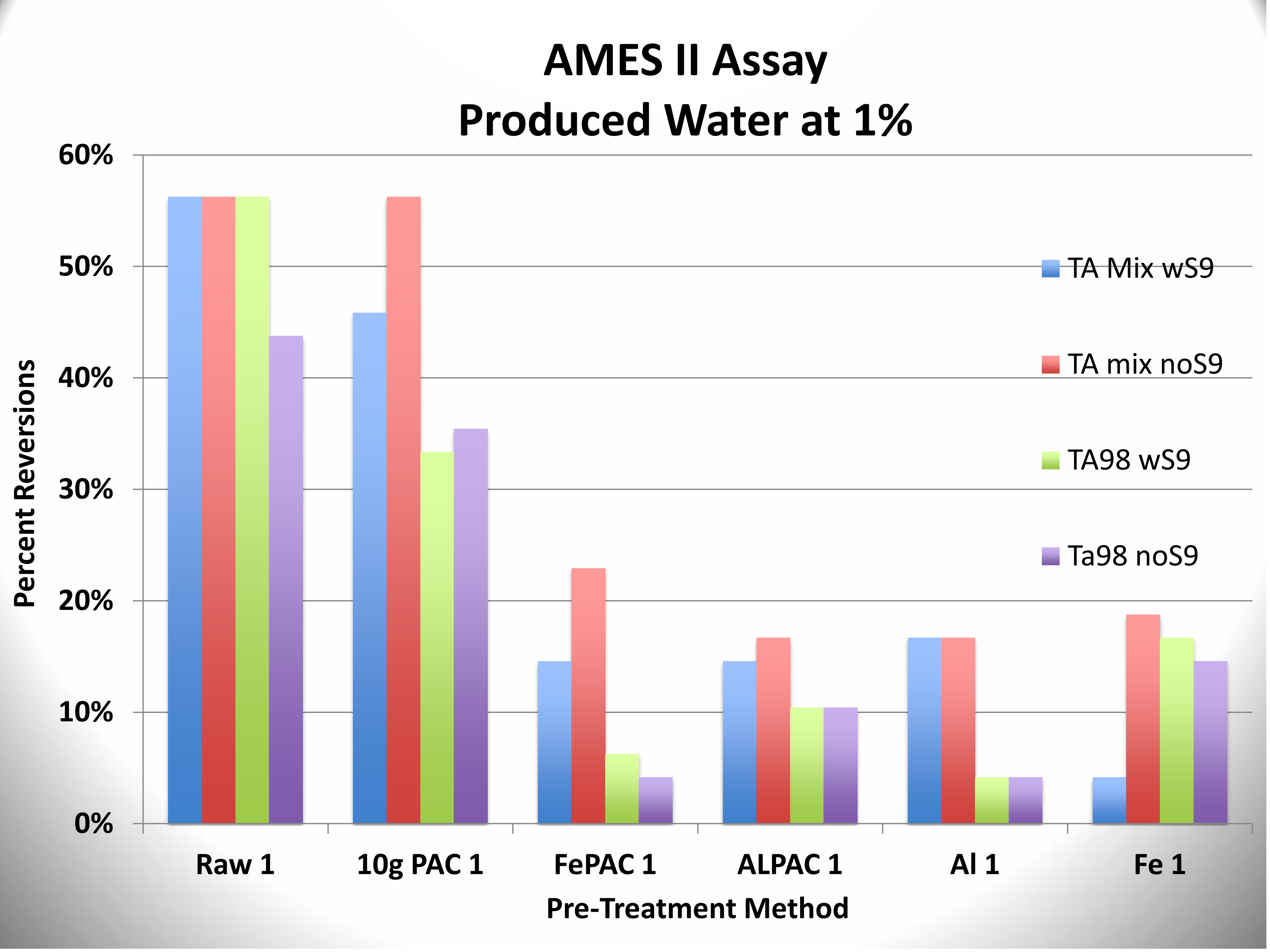


Bacterial Toxicity Assays



- AMES II
  - Measures gene mutations (reversions)
    - Genotoxicity
      - Frameshift Mutation
      - Base-Pair Substitution
  - Color change from purple to yellow
    - *Salmonella typhimurium*
- Bioluminescence Based Toxicity Assay
  - Photobacterium "*Vibrio fischeri*"
    - Salt Water Bacteria
  - If metabolic processes are changed upon cell damage by a toxic substance, a reduction in "bioluminescence" can be detected


Bioluminescene Based Toxicity Assay
Produced Water
% Reduction in Relative Light Units (RLU)
0
-5
-10
-15
-20
-25
Raw
AlCl3
FeCl3
10 g PAC
10 g PAC + FeCl3
10 g PAC + AlCl3


AMES II Assay
Produced Water at 1%
60%
50%
40%
30%
20%
10%
0%
Percent Reversions
TA Mix wS9
TA mix noS9
TA98 wS9
Ta98 noS9
Raw 1
10g PAC 1
FePAC 1
ALPAC 1
Al 1
Fe 1
Pre-Treatment Method

Biological Results

Biological

- Moving Bed Biofilm Reactor (MBBR)
  - Sequencing Batch Reactors
  - 2 L liquid, 50% carrier fill (1L)
    - 3 Liters total
- Aerobic and Anaerobic MBBRs
  - Duplicate
- Variables of interest
  - MLSS/TS, TDS, and pH
  - Dissolved Organic Carbon
- Slowly acclimated with pretreated produced water
  - 120 mg/L $AlCl_3$ with 10 g/L PAC
  - 100, 200, 300, 400,…..1000ml
    - Feed two times at each volume

Organic Carbon Removal

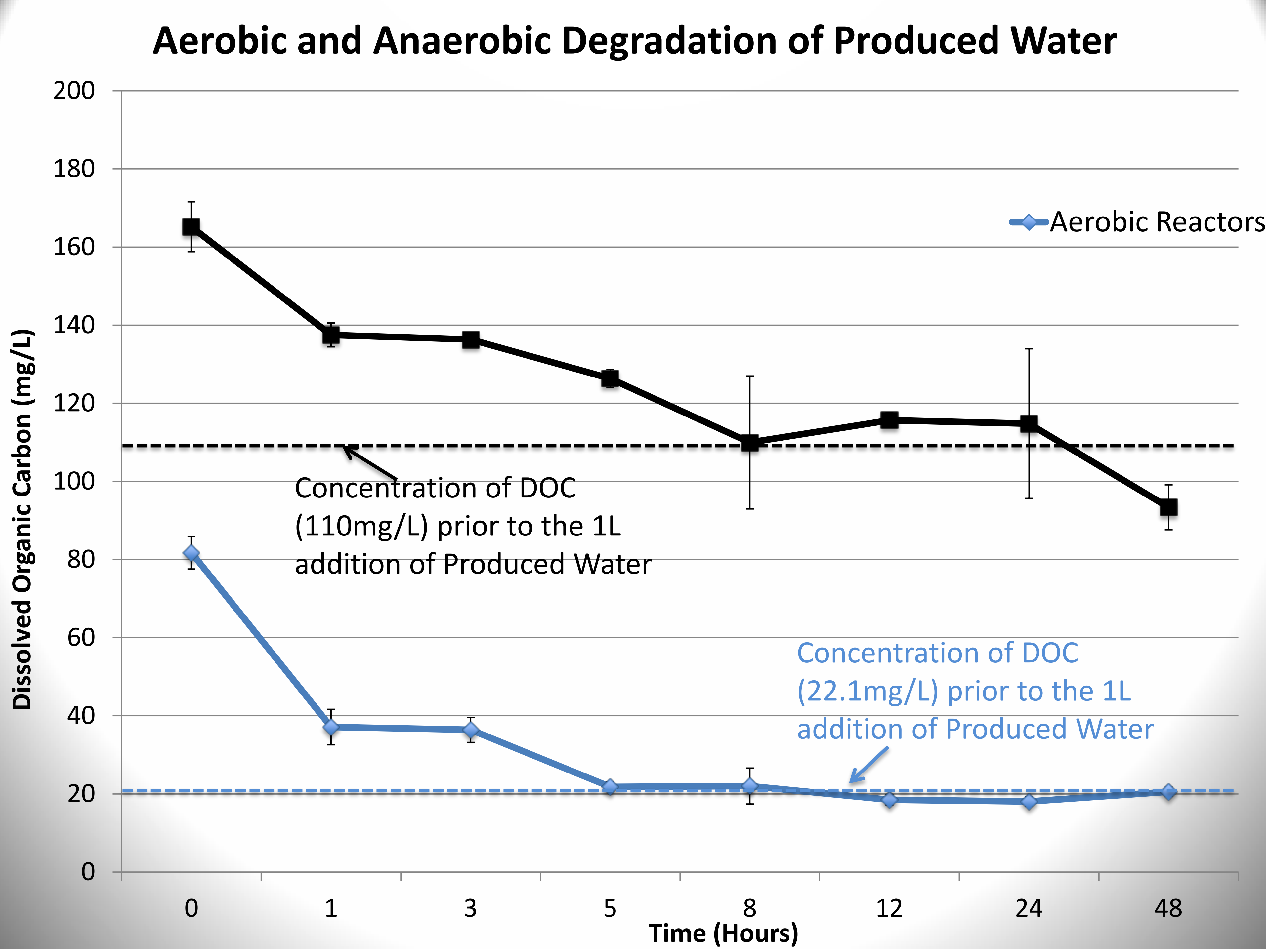
- Biological Treatment

-Bio-Treat coupled with AOP

-MBBR

Aerobic / Anaerobic

- Total Organic Carbon
- Biological Oxygen Demand


Aerobic and Anaerobic Degradation of Produced Water
Aerobic Reactors
Dissolved Organic Carbon (mg/L)
200
180
160
140
120
100
80
60
40
20
0
Concentration of DOC
(110mg/L) prior to the 1L
addition of Produced Water
Concentration of DOC
(22.1mg/L) prior to the 1L
addition of Produced Water
0
1
3
5
8
12
24
48
Time (Hours)

Conclusion

- We can treat this water!!...more research needed
  - Economics
  - Mobility
  - Generation of concentrated wastes
- Key to understanding what level of treatment is required
- Utilizing advanced indicators to study unknown compounds and assess their presence following treatment
  - Toxicity
  - HPLC
  - GC

Future Research and Challenges

- Other variables to assess treatment
  - Naturally Occurring Radioactive Material (NORM)
- Advanced Oxidation Processes
  - Degrading contaminants
    - Parent vs. Daughter compounds
  - Biologically available recalcitrant OM
- Bringing these different pieces together to develop a treatment train

Questions

National Science Foundation

- AirWaterGas Sustainability Research Network
- Grant No. CBET-1240584

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