Oil and Gas Wastewater Reuse/Recycle – Overview & Analytical Challenges

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August 7, 2019

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Agenda

- Produced Water Cycle, Governance, Options
- Produced Water Characteristics
- Analytical Challenges

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Hydraulic Fracturing Water Cycle: Follow the Water

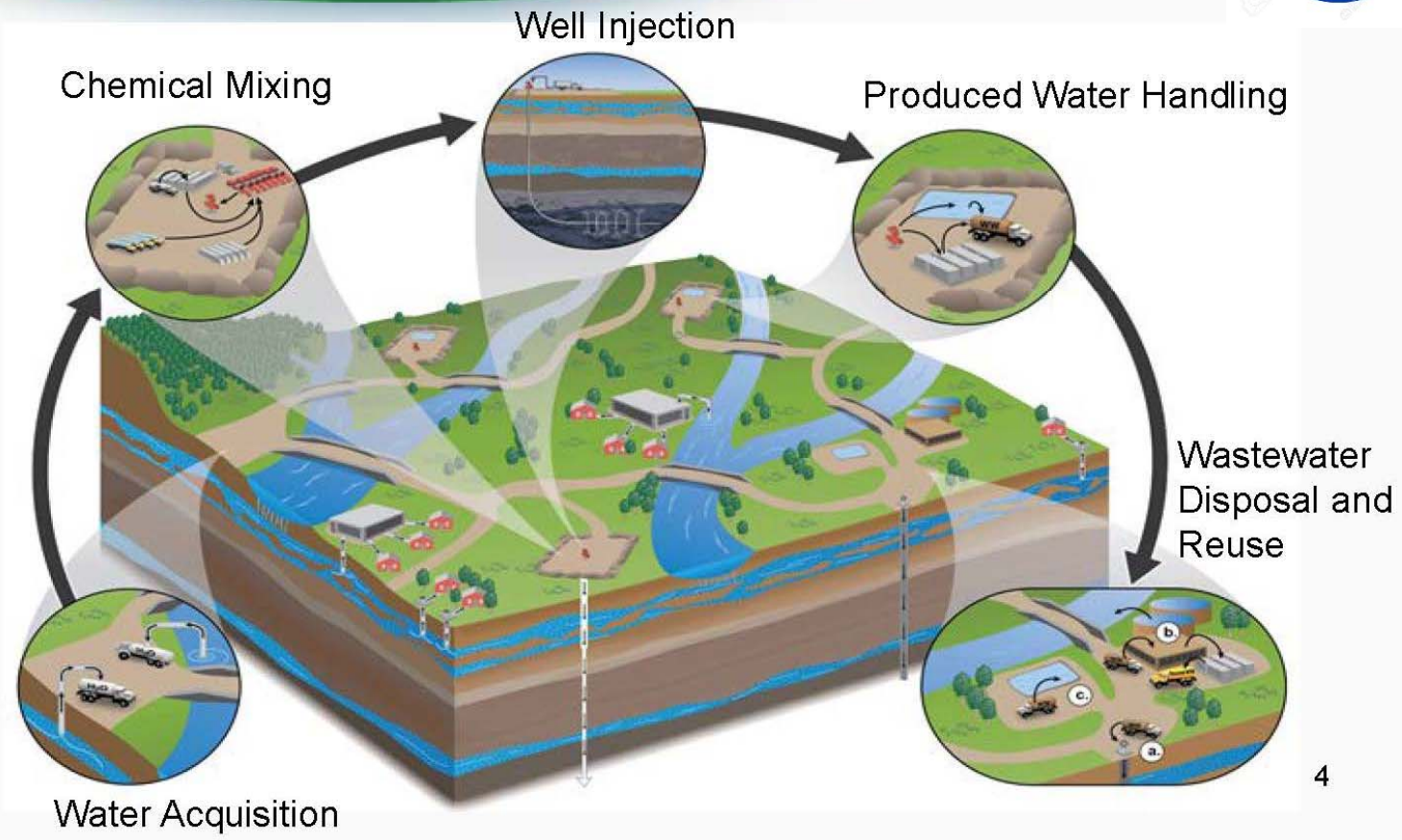

Figure Source: https://www.epa.gov/hfstudy/hydraulic-fracturing-oil-and-gas-impacts-hydraulic-fracturing-water-cycle-drinking-water and Water Drop World, Earth Globe in a Water Droplet - Elements of this image furnished by NASA

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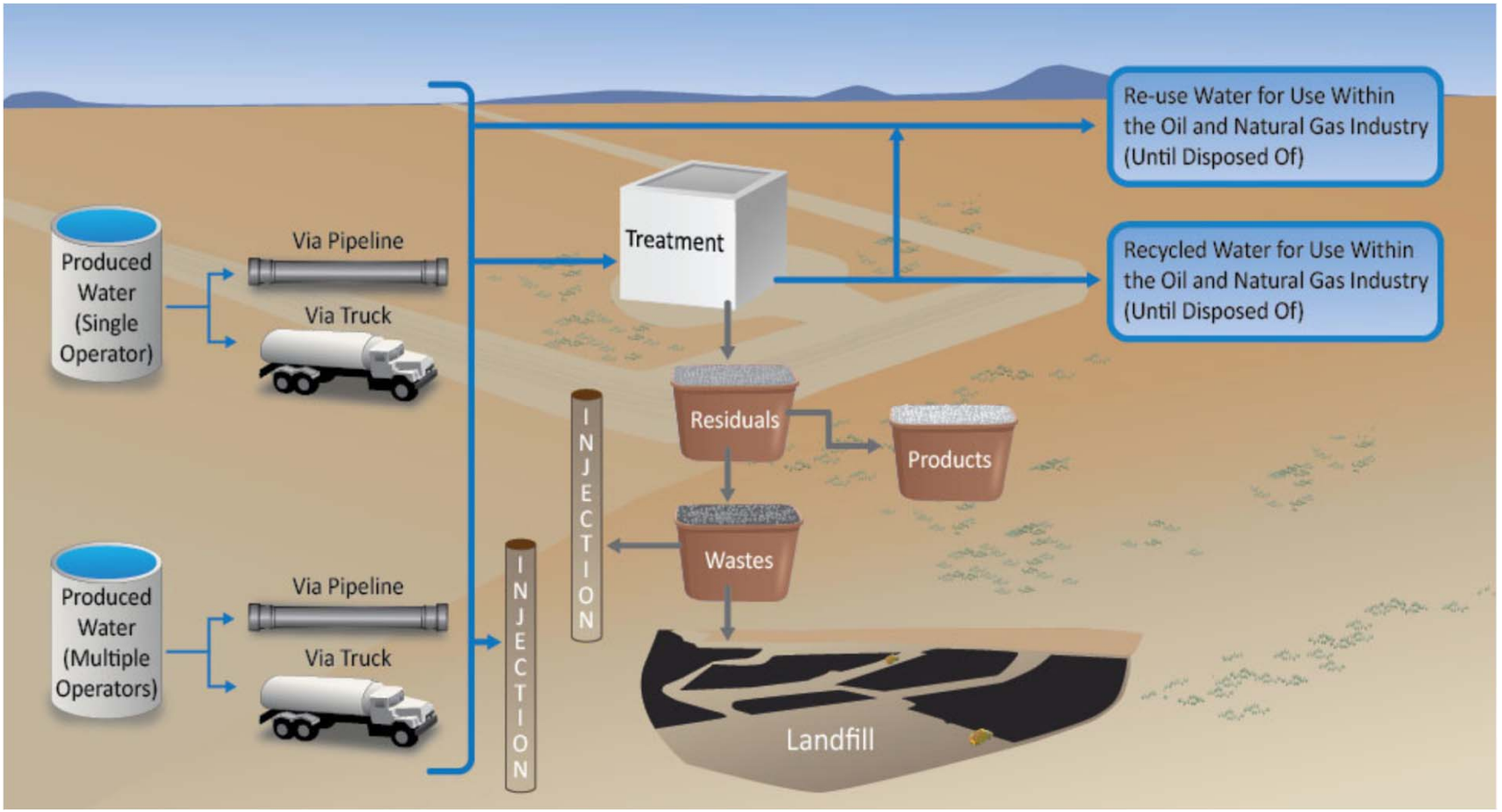
Reuse/Recycle



Oil and Natural Gas Produced Water Governance
in the State of New Mexico, White Paper, Nov, 2018 US EPA, State of New Mexico

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Uses

- Reuse – minimal treatment, used within the O&G cycle, then disposal (UIC Class II well injection for on-shore)
- Recycle - significant treatment, used within the O&G cycle, then final disposal

  - drilling, drilling muds, mixing of hydraulic fracturing fluids, cementing, workovers, secondary recovery, pressure maintenance, EOR via waterfloods, and plugging operations

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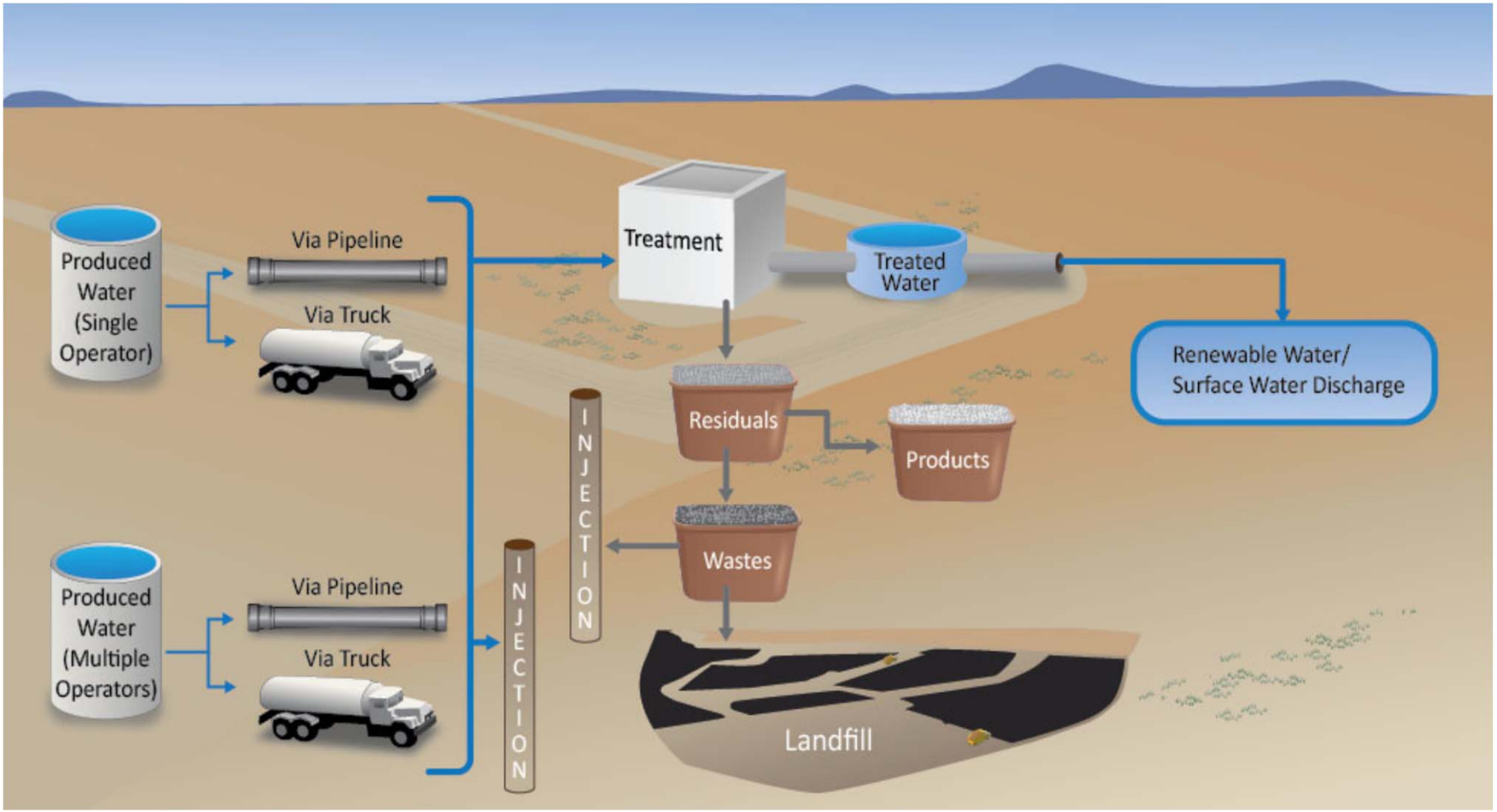
Renewable



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Uses

- Renewable – significant treatment, used outside the O&G cycle, added to hydrologic cycle
  - Surface Discharge - WOTUS
    - Agriculture
    - Wildlife
    - NPDES permit with technology-based effluent limitations (TBELs, aka ELGs) and water quality-based effluent limitations (WQBELs)
  - Sold for industrial Use, no discharge
    - NPDES does not apply
    - Industrial specifications, possibly government agencies
  - Municipal use (e.g., golf courses, drinking water??)

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Renewable

- TBEL for O&G under Effluent Limitations Guidelines (ELG) of 40 CFR parts 435 or 437
  - Five ELGs for Produced Water
- Where the EPA has not established ELGs for a particular industry, technology-based requirements established according to their BPJ
- Surface discharge permits also include WQBELS defined by applicable state WQS

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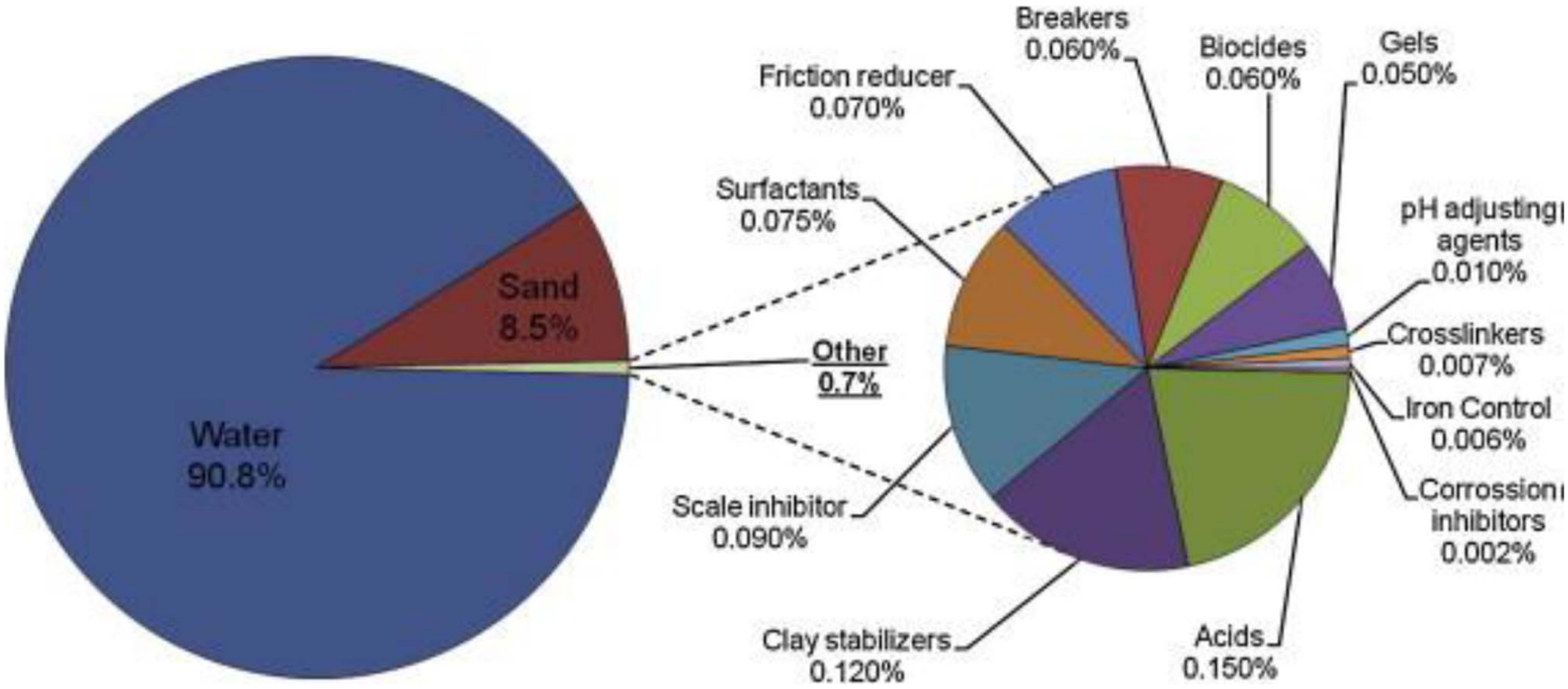
Hydraulic Fluid Components



Ferrer and Thurman (2015). Chemical constituents and analytical approaches for hydraulic fracturing waters. *Trends in Environmental Analytical Chemistry*. 5: 18-25.

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Produce Water Characteristics

- High to Very High TDS, median 30k-100k mg/L
  - In addition to Na & Cl, can have high levels of barium, bromide, calcium, iron, magnesium, strontium, bicarbonate. Vary widely with formation
- TOC and other natural (formation) organics
- Oil and Grease
- NORM
- Inorganic and organic additives
  - Function of the fracking fluid type

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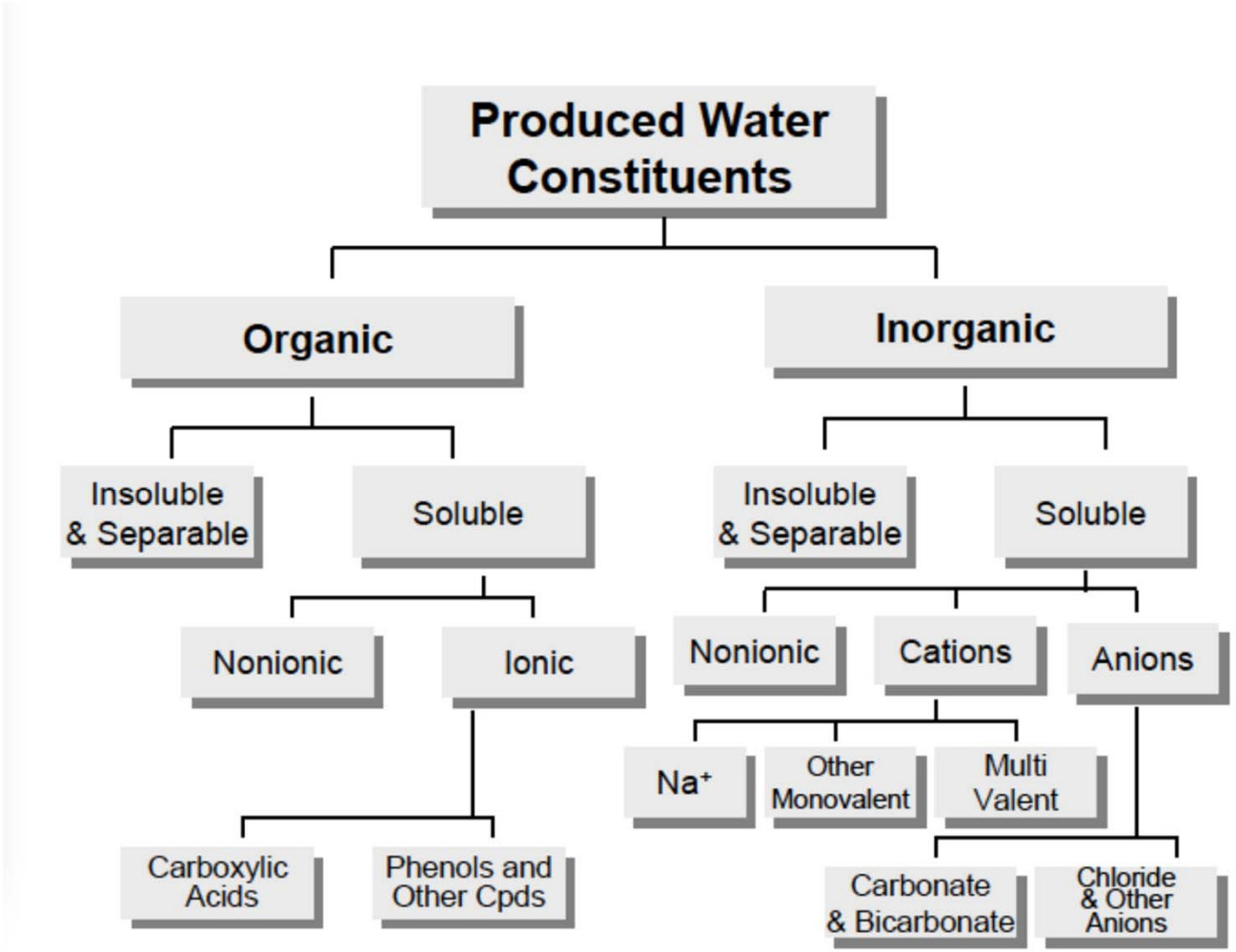
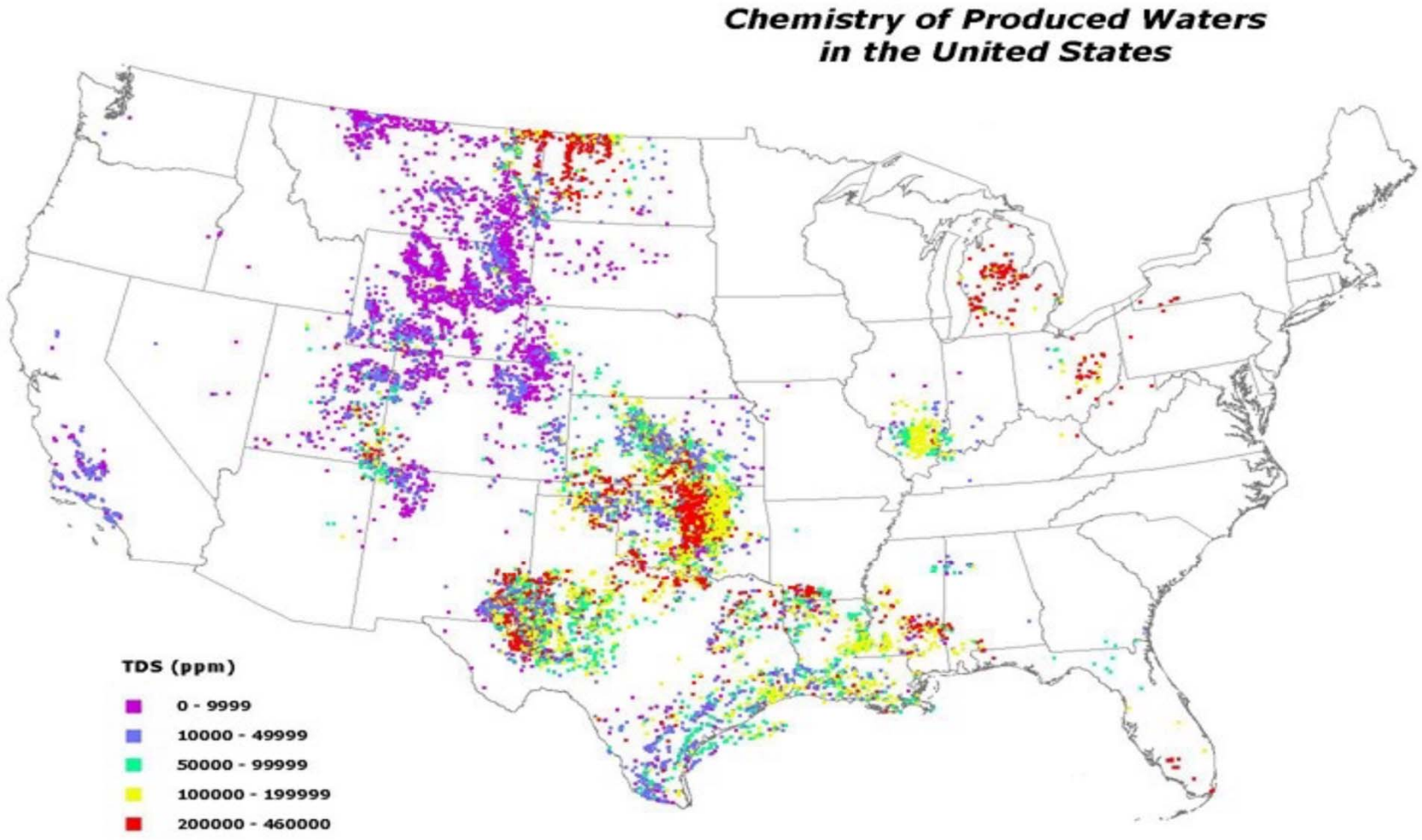
Produce Water Characteristics





The information in the USGS National Produced Waters Geochemical Database v2.3 should be used with careful consideration of its limitations

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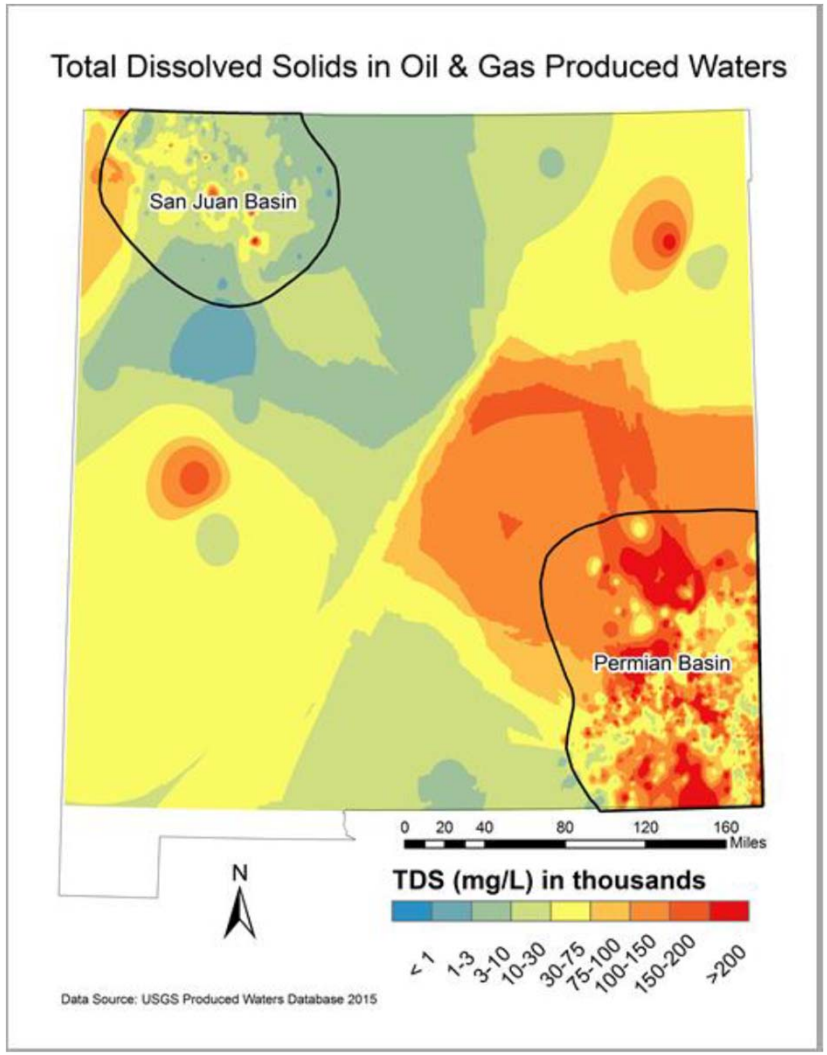
Produce Water Characteristics



Expect treatment prior to any renewable use

USGS Produced Water Database 2015, Harto and Veil (2011)

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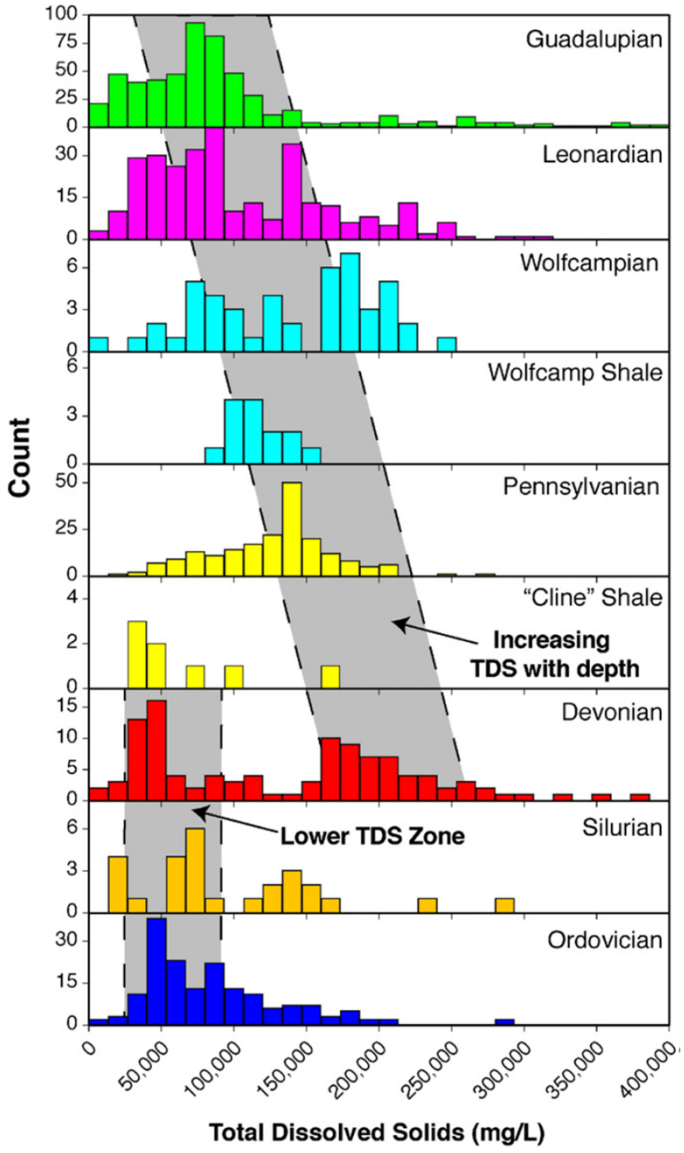
Produce Water Characteristics



Engle, et al., Chemical Geology 425 (2016) 76–92

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Current Typical/Required Analyses

- Off-shore (e.g., GoM) NPDES General Permit & On-shore
  - Whole Effluent Toxicity
  - Oil & Grease

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Other Analyses?

- Will permits for surface discharge, or industrial use (after treatment) require additional analyses beyond those currently employed?
- NMED

  "It would be advisable to evaluate treated produced water for both National Primary Drinking Water Regulations as well as the possible requirements for discharge to surface water or groundwater to guard against downstream WQS exceedances."
  "Voluntary sampling for unregulated contaminants of concern…"
- **Impossible to measure all potential additives and formation constituents**!

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Challenges & Methods for High TDS Matrices

- Interferences
- Precipitation
- Digestion and extraction efficiency

*https://www.epa.gov/hfstudy

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Methods for High TDS Matrices

- Bulk/quality – RCRA/SM methods likely applicable, though must still account for high TDS (even w/ conductivity, pH)
- Minor and Trace Elements/Ions & Organics
  - No published EPA, USGS, ASTM methods
- NORM
  - No published EPA, USGS, ASTM methods
  - EPA Report July 2014
    "Development of Rapid Radiochemical Method for Gross Alpha and Gross Beta Activity Concentration in Flowback and Produced Waters from Hydraulic Fracturing Operations. Schumacher et al."

Published = Validated, for these high TDS matrices

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Methods Options/Research

- US EPA conducted workshops associated with their 2011 – 2015 study* on the potential for hydraulic fracturing operations to impact drinking water
- Selective element/ion separation
  - Cloud point extraction (1)
- Additional or new toxicity testing methods(2)?
- Research (3) on selective preparation steps and detection (MS/MS, high resolution MS, GC-GC)

*https://www.epa.gov/hfstudy

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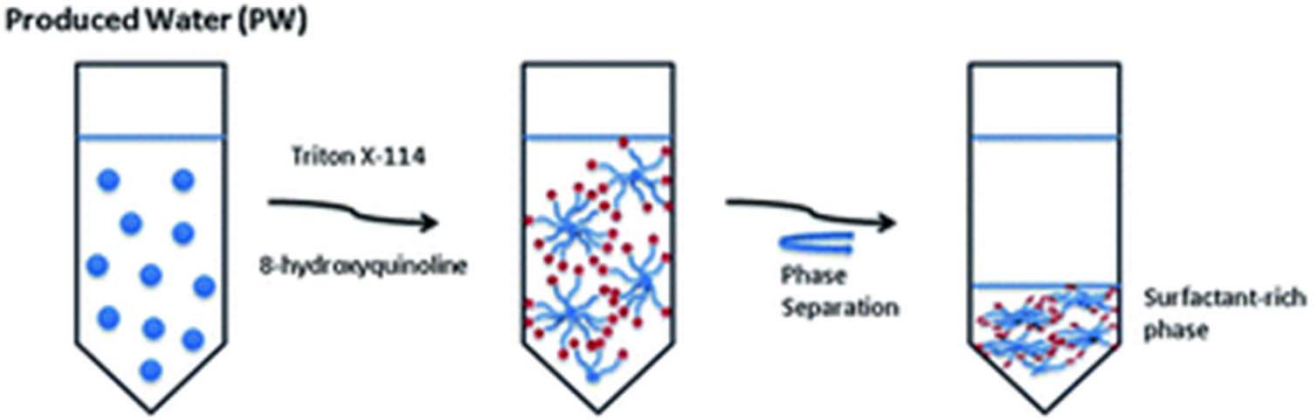
Methods Options/Research

- Additional or new toxicity testing methods(1, 2)?
- Selective element/ion separation
  - Cloud point extraction (3)

    Transfer of a non-ionic surfactant from one liquid phase to another by heating. Heating forms micelles, above the cloud point (CPT) the micelles become dehydrated and aggregate. This leads to macroscopic phase separation of the solution into a surfactant-rich phase and a solvent phase. Chelating agent + surfactant



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Methods Options/Research

Research (4) on selective preparation steps and detection (MS/MS, high resolution MS, GC-GC)

- Centrifugation for glycols
- Support-assisted LL extraction
- SPME/LC for alkylphenol ethoxylates
- TOF MS for glycols and ethoxylates
- FT-ICR-MS for halogens
- Suspected- screening and non-target screening using HR-MS/MS

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References and Other Sources

- (1) Application of toxicity identification evaluation procedures for characterizing produced water using the tropical mysid, Metamysidopsis insularis, Najila Elias-Samlalsingh and John B. R. Agard, Environmental Toxicology and Chemistry, 23, 5, (1194-1203), (2009)

- (2) Comparison of Whole Effluent Toxicity with Substance Based Hazard of produced water discharged by Norwegian platforms. Wageningen Marine Research, Den Helder, November 2018

- (3) Determination of cadmium, cobalt, copper, lead, nickel and zinc contents in saline produced water from the petroleum industry by ICP OES after cloud point extraction. Analytical Methods 07 December 2015, Issue 23

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References and Other Sources

- (4) Emerging analytical methods for the characterization and quantification of organic contaminants in flowback and produced water. Oetjen, et al, 2017. Trends in Environmental Analytical Chemistry 15 (2017) 12–23

- GWPC
  - http://www.gwpc.org/producedwater

- USGS PW Database
  - https://www.usgs.gov/centers/eersc/science/oil-and-gas-waters-project?qt-science_center_objects=0#qt-science_center_objects

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Thank You

QUESTIONS?

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