Oilfield Mineral Scale Mitigation Technology Development

Presenter: Barbara Kutchko, PhD

R&IC-NETL

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U.S. Department of Energy

National Energy Technology Laboratory

Oil & Natural Gas

2020 Integrated Review Webinar

Oilfield Mineral Scale Mitigation Technology Development

Goal

- The objective of the effort is to investigate mineral scale deposition in wellbores (i.e. barite, calcite) including scale reaction rates and possible inhibitors, and mitigation efforts.

Challenge

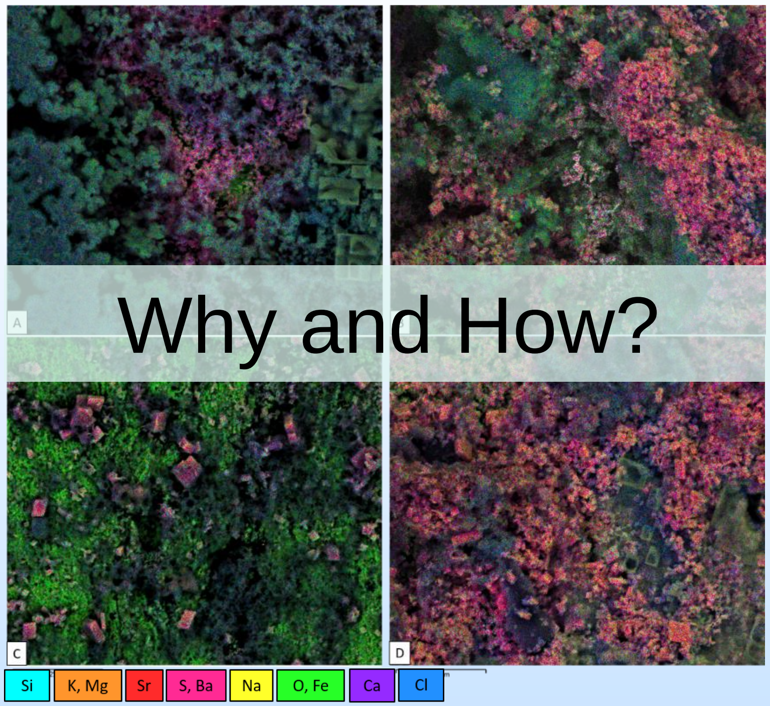
- **Mineral scale has serious deleterious effects on wells.**
  - Occludes pipes, chokes, safety valves, etc.
- **Threat to flow-assurance**
  - Pressure drop
  - Shut-ins
  - Expensive workover operations
- **Costs millions in lost sales and remediation expenses…**

Approach

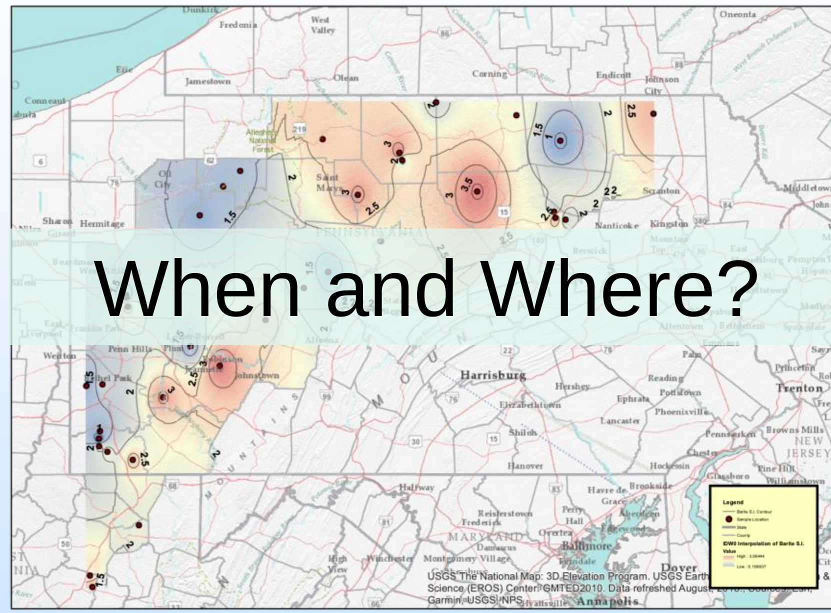
- Experimental and modeling approaches to prevent scale formation

Barite deposition in casing (pipe) during production. *From Stack, https://www.epa.gov/sites/production/files/documents/stack.pdf*

Experimental and Modeling Approaches to Preventing Scale Formation.



EDS Element maps of coupons exposed to HFF using de-ionized water as base fluid. A: aerated two-day exposure, B: aerated 14-day exposure , C: degassed two-day exposure, D: degassed 14-day exposure.



Inverse distance weighted map showing distributions of barite saturation indices. Saturation indices were calculated from Marcellus Shale production water as reported in the U.S. Geological Survey National Produced Waters Geochemical Database (Blondes et al, 2018).

(Mackey et al., 2020)

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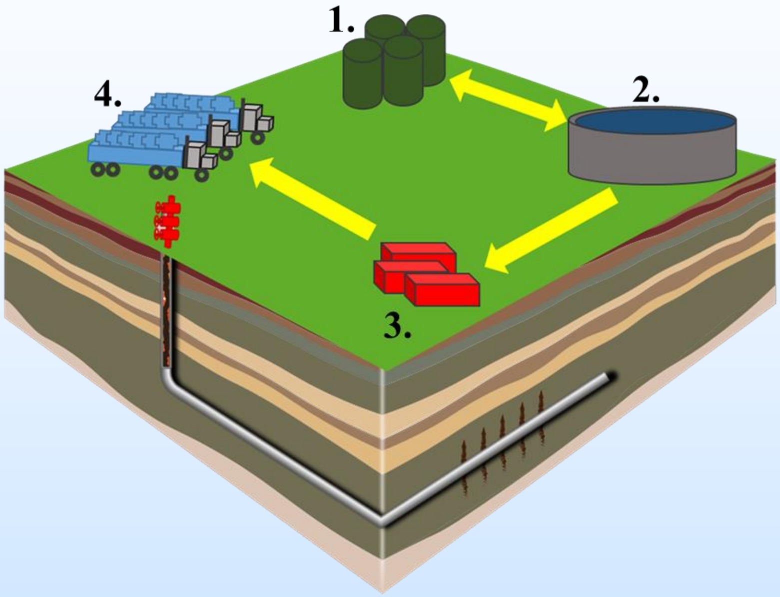
- What impacts do hydraulic fracturing fluids have on the steel production casing during the shut-in period of the well?
- Is there a relationship between corrosion and mineral scale formation?
- Aerated versus degassed hydraulic fracturing fluids?



Schematic of unconventional hydraulic fracturing operation. (1) Production water is transported from production tanks to (2) larger aboveground storage tanks, where it is combined with surface water and aerated. (3) Aerated base fluid is enhanced with chemical additives and combined with proppants then (4) pumped at high pressures through the production tubing into the reservoir.

"Characterizing mineralization on low carbon steel exposed to aerated and degassed synthetic hydraulic fracture fluids." (*Mackey et al., submitted*)

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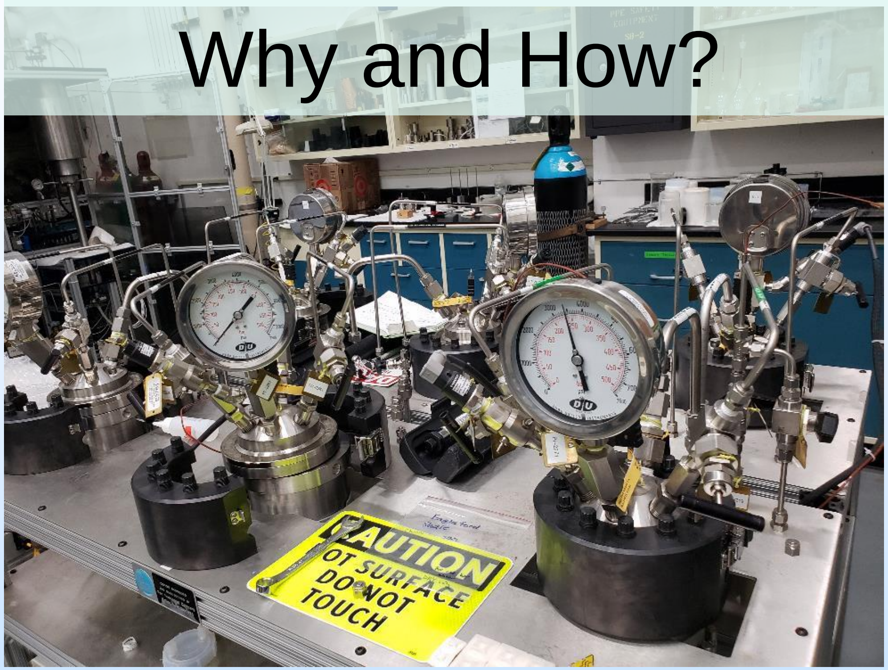
Experimental Matrix				
	Base fluid	**Sample ID**	**Exposure Time (days)**	**Experiment Conditions**
Aerated HFF	Spring water base fluid	ASP-0	0	Not Reacted
		ASP-2	2	2000 PSI, 50^{o}C, N_2 Headspace
		ASP-14	14	2000 PSI, 50^{o}C, N_2 Headspace
	Deionized water base fluid	ADI-0	0	Not Reacted
		ADI-2	2	2000 PSI, 50^{o}C, N_2 Headspace
		ADI-14	14	2000 PSI, 50^{o}C, N_2 Headspace
Degassed HFF (CO_2)	Spring water base fluid	DGSP-0	0	Not reacted
		DGSP-2	2	2000 PSI, 50^{o}C, CO_2 Headspace
		DGSP-14	14	2000 PSI, 50^{o}C, CO_2 Headspace
	Deionized water base fluid	DGDI-0	0	Not reacted
		DGDI-2	2	2000 PSI, 50^{o}C, CO_2 Headspace
		DGDI-14	14	2000 PSI, 50^{o}C, CO_2 Headspace

Why and How?



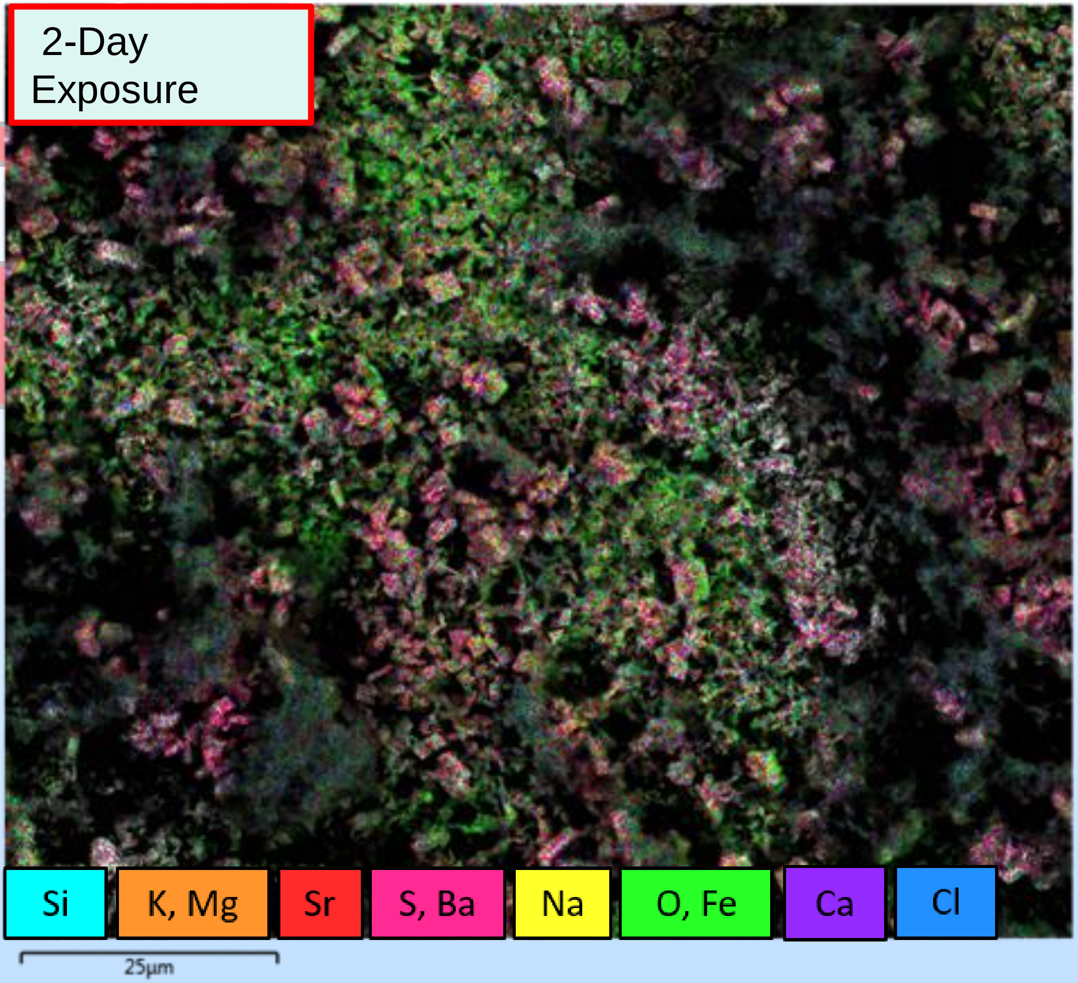
Surface morphology and mineralogy was characterized using SEM/EDS and XRD. Changes in fluid chemistry were analyzed via ICP-OES (Ba, Ca, Fe, K, Mg, and Sr) and IC (SO_4 and Cl).

“Characterizing mineralization on low carbon steel exposed to aerated and degassed synthetic hydraulic fracture fluids. (*Mackey et al., submitted*)

Oilfield Mineral Scale Mitigation Technology Development

Primary mineral precipitates

- Barite ($BaSO_4$)
- Halide group minerals ($NaCl$, $CaCl_2$, $SrCl_2$)
- Iron oxyhydroxides ($Fe^{+3}{}_2O_3 \cdot nH_2O$),
- Green rusts
  - ($[Fe^{2+}{}_4 Fe^{3+}{}_2(HO^-)_{12}]^{2+} \cdot [CO^{2-}{}_3 \cdot 2H_2O]^{2-}$)
  - ($[Fe^{2+}{}_3 Fe^{3+} (HO^-)_8]^{+} \cdot [Cl^- \cdot nH_2O]^-$)



(Mackey et al., *submitted*)

Oilfield Mineral Scale Mitigation Technology Development

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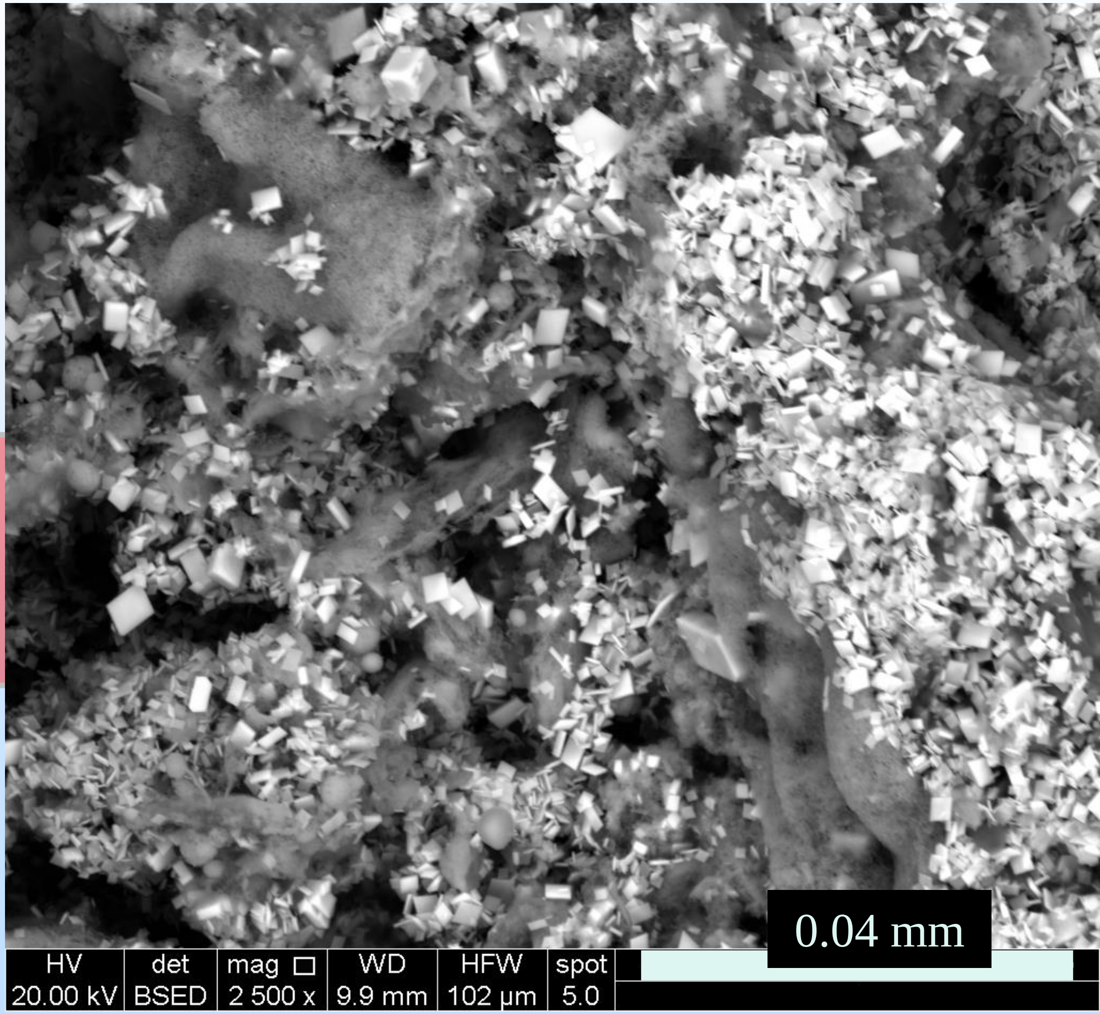
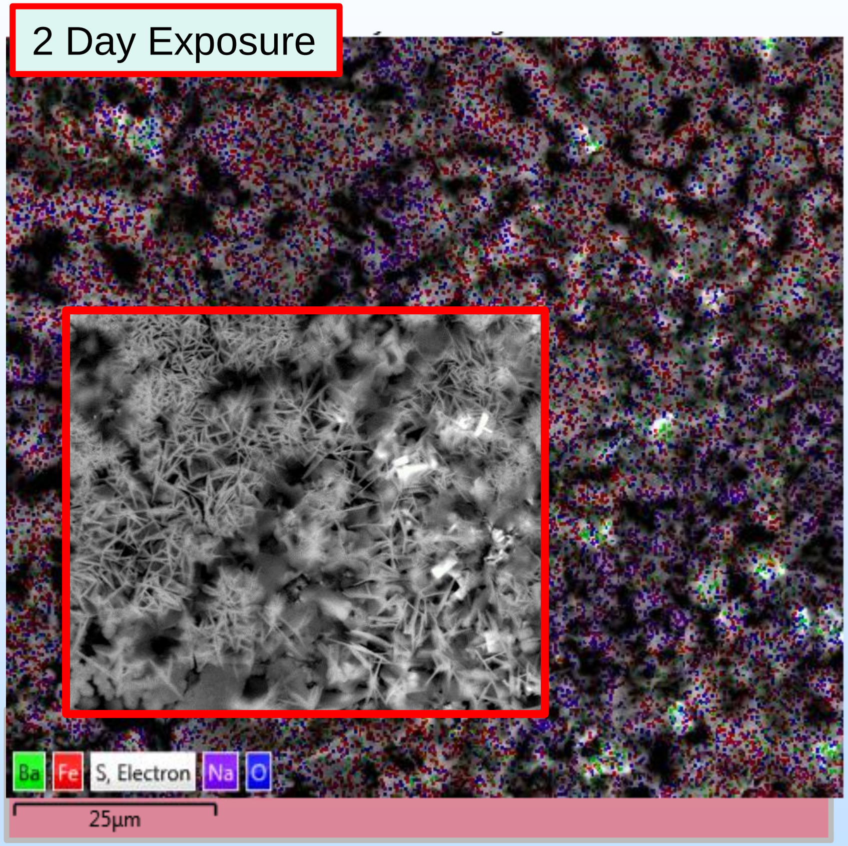
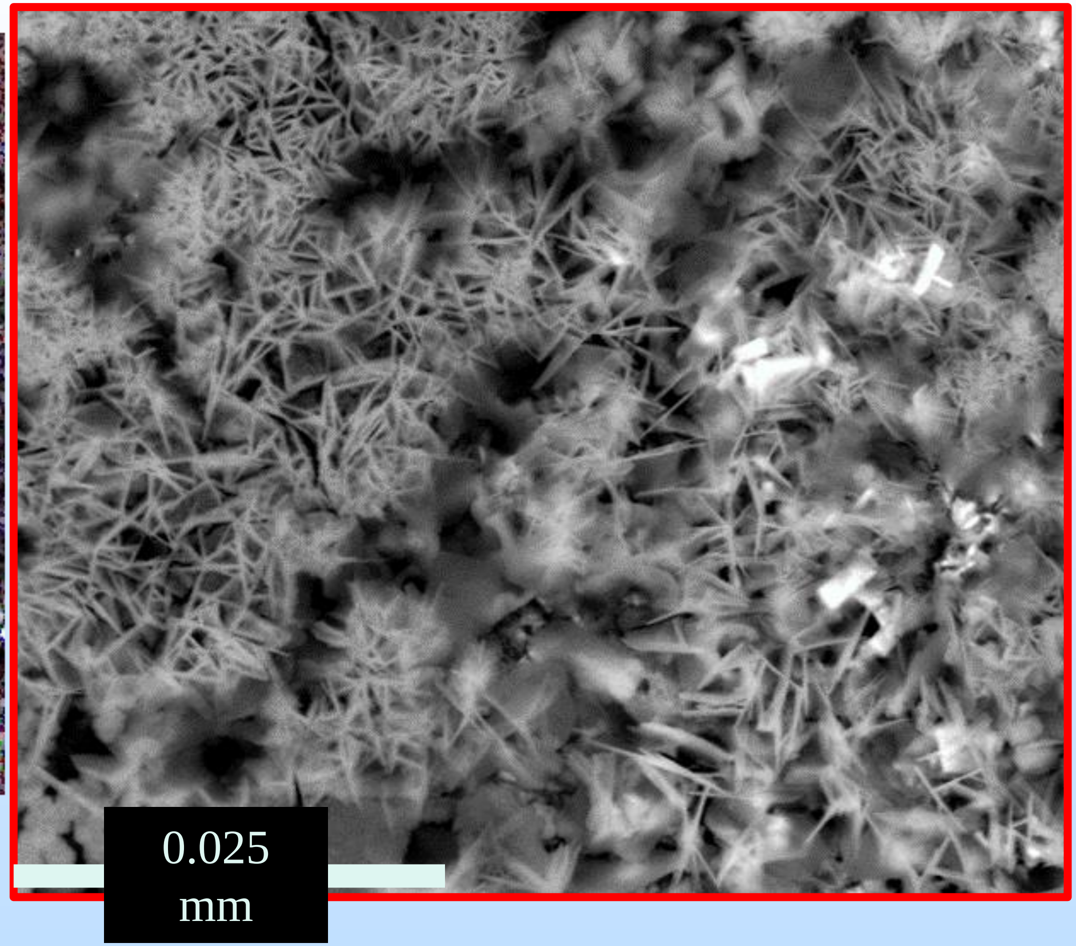
- Green rusts
  - ($[Fe^{2+}{}_4 Fe^{3+}{}_2(HO^-)_{12}]^{2+} \cdot [CO^{2-}{}_3 \cdot 2H_2O]^{2-}$)
  - ($[Fe^{2+}{}_3 Fe^{3+}(HO^-)_8]^+ \cdot [Cl^- \cdot nH_2O]^-$)
- **Iron Salts** occurred in mixed morphologies of amorphous, fibrous and flakey
- **$BaSO_4$ Crystals**
  - Euhedral with tabular crystal habit
  - Both single crystal and twinned aggregates
  - On surface and within interstitial corrosion fabrics



Oilfield Mineral Scale Mitigation Technology Development





- BSED images showing Z-contrast reveal adsorption of Ba onto Iron Salts

(Mackey et al., 2019)

Experimental Conclusions

- Major Findings:
  - Mineral scale precipitation occurs early on (first 48 hours) in solutions before interaction with reservoir mineralogy.
  - Barite scale can occur within the wellbore despite the addition of scale inhibitors to the injection fluid.
  - Scale formation is, in part, dually facilitated and worsened from sulfate release during oxidation of steel by persulfate breakers and the presence of iron oxyhydroxides.
  - Mineral scale and corrosion was ubiquitous despite varying base-fluid and dissolved gas compositions.

When and Where?

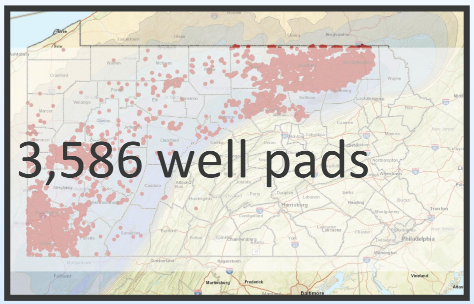


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Table 1. List of analytes measured in wastewater produced from the drilling, completion and production of a shale gas well.

Acidity	Lithium
Alkalinity (Total as CaCO3)	Magnesium
Aluminum	Manganese
Ammonia Nitrogen	MBAS (Surfactants)
Arsenic	Mercury
Barium	Molybdenum
Benzene	Nickel
Beryllium	Nitrite-Nitrate Nitrogen
Biochemical Oxygen Demand	Oil & Grease
Boron	pH
Bromide	Phenolics (Total)
Cadmium	Radium 226
Calcium	Radium 228
Chemical Oxygen Demand	Selenium
Chlorides	Silver
Chromium	Sodium
Cobalt	Specific Conductance
Copper	Strontium
Ethylene Glycol	Sulfates
Gross Alpha	Thorium
Gross Beta	Toluene
Hardness (Total as CaCO3)	Total Dissolved Solids
Iron – Dissolved	Total Kjeldahl Nitrogen
Iron – Total	Total Suspended Solids
Lead	Uranium
	Zinc

=

A LOT OF DATA

(182,886 data points)

georeferenced + time series + production data + geologic attribute data + operations data + etc.,

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Identify sources

Gather Data

Validate Data (Statistical QC)

Values represent single sampling event

Charge balance errors ≤±10 %

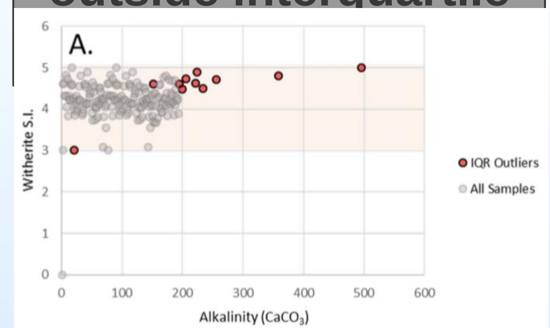
[Ca] > [Mg]

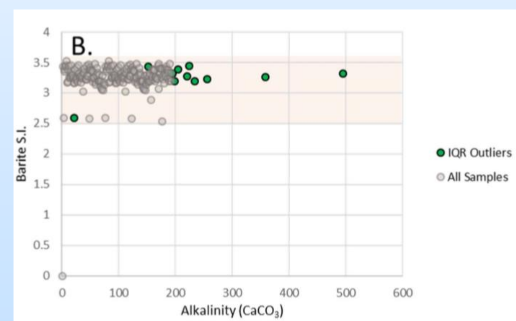
Major cations (Na, Ca, Mg) ≥ 0mg/L

[TDS] > 35,000 mg/ L

Major ions (Na, Ca, Mg, Cl) within interquartile range

Minor ions/alkalinity outside interquartile





Criteria based in part on Dahm et al., 2011; Jones et al., 2011; Sherwood et al., 2016

From Waste to Insight: Generating High Resolution Geochemical Models from Publicly Available Residual Waste Profiles. (Mackey et al., 2020)

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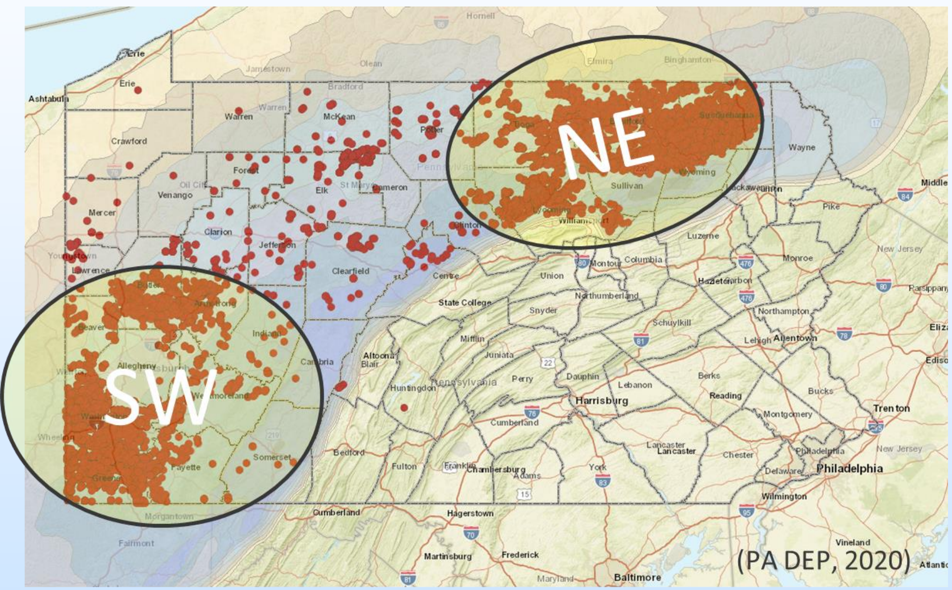

- **Two main producing regions**
  - Produced water heterogeneity?
- **Majority of PW is recycled in ongoing HF**
  - Mineral scale tendency?
- **Temporal Changes in reservoir chemistry?**

Calculated Mineral S.I. in Geochemist's Workbench

Geostatistics (IDW) and mapping in ArcMap 10

From Waste to Insight: Generating High Resolution Geochemical Models from Publicly Available Residual Waste Profiles. (Mackey et al., 2020)

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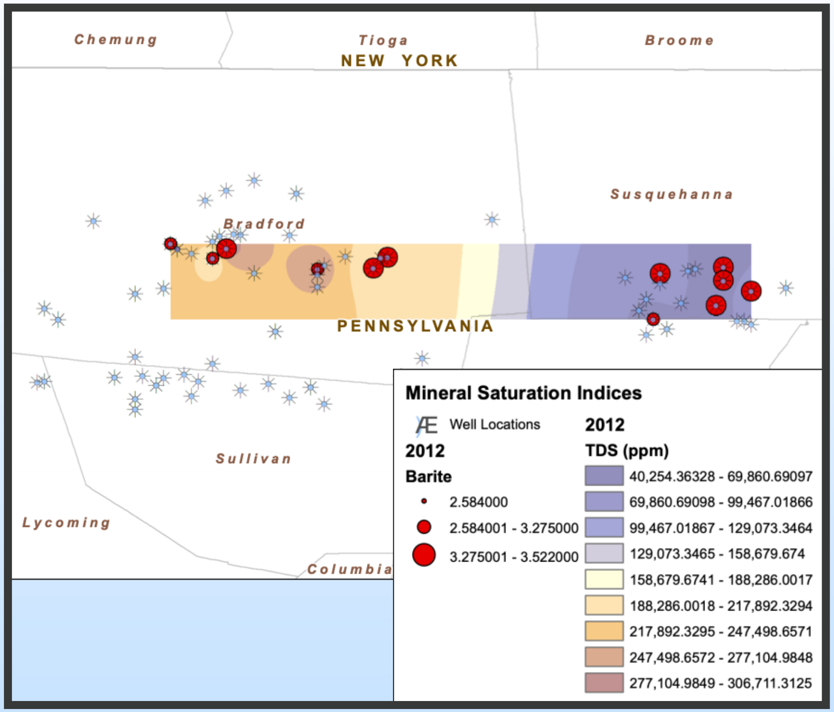
Table 3. Average TDS and mineral saturation indices listed per county.

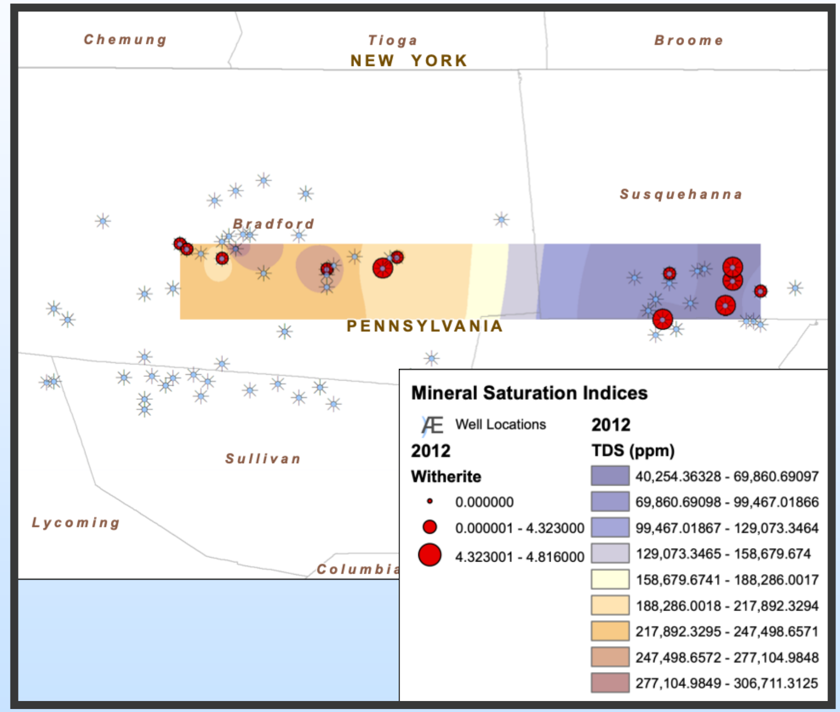
	n=	TDS (ppm)	Witherite	Barite	Strontianite	Calcite	Gypsum	Halite	Dolomite
Bradford	64	236646	4.15	3.26	2.36	-0.14	-1.89	-0.87	NA
Sullivan	19	223233	4.10	3.22	2.31	-0.15	-1.90	-1.00	NA
Susquehanna	21	86664	4.45	3.35	2.22	-0.17	-2.12	-1.91	NA
Wyoming	9	107342	4.51	3.28	2.37	-0.02	-2.10	-1.71	NA
Lycoming	3	210537	3.65	3.17	1.86	-0.55	-1.90	-1.10	NA
Washington	13	186615	2.59	1.73	2.07	-0.06	-1.81	-1.24	0.40

From Waste to Insight: Generating High Resolution Geochemical Models from Publicly Available Residual Waste Profiles. (Mackey et al., 2020)

Results



Chemung
Tioga
NEW YORK
Broome
Susquehanna
Bradford
PENNSYLVANIA
Sullivan
Lycoming
Columbia
Mineral Saturation Indices
Well Locations
2012
Barite
2.584000
2.584001 - 3.275000
3.275001 - 3.522000
2012
TDS (ppm)
40,254.36328 - 69,860.69097
69,860.69098 - 99,467.01866
99,467.01867 - 129,073.3464
129,073.3465 - 158,679.674
158,679.6741 - 188,286.0017
188,286.0018 - 217,892.3294
217,892.3295 - 247,498.6571
247,498.6572 - 277,104.9848
277,104.9849 - 306,711.3125



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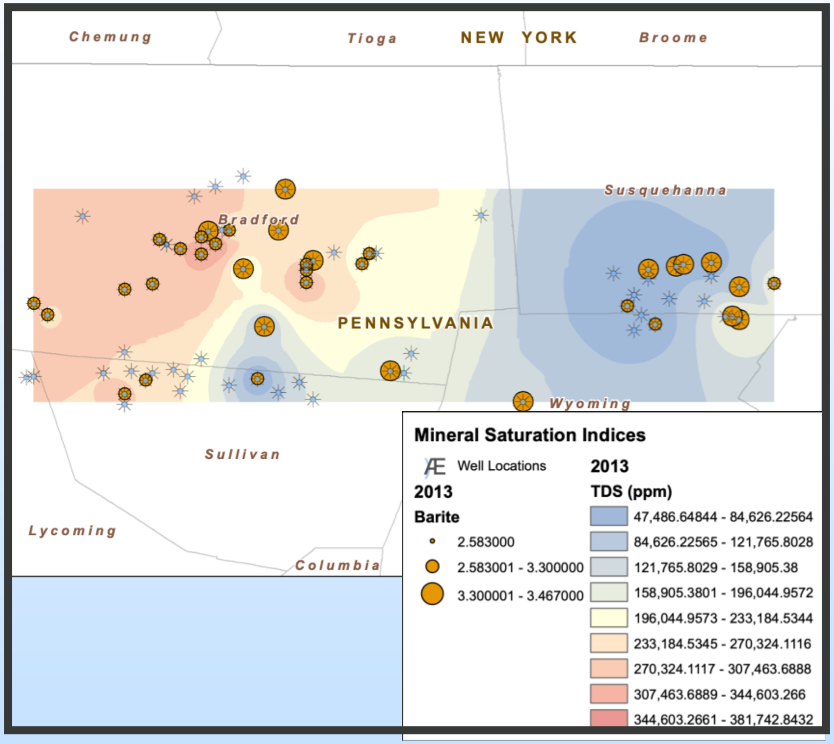
Lycoming
Columbia
Mineral Saturation Indices
Well Locations
2012
Witherite
0.000000
0.000001 - 4.323000
4.323001 - 4.816000
2012
TDS (ppm)
40,254.36328 - 69,860.69097
69,860.69098 - 99,467.01866
99,467.01867 - 129,073.3464
129,073.3465 - 158,679.674
158,679.6741 - 188,286.0017
188,286.0018 - 217,892.3294
217,892.3295 - 247,498.6571
247,498.6572 - 277,104.9848
277,104.9849 - 306,711.3125

Results



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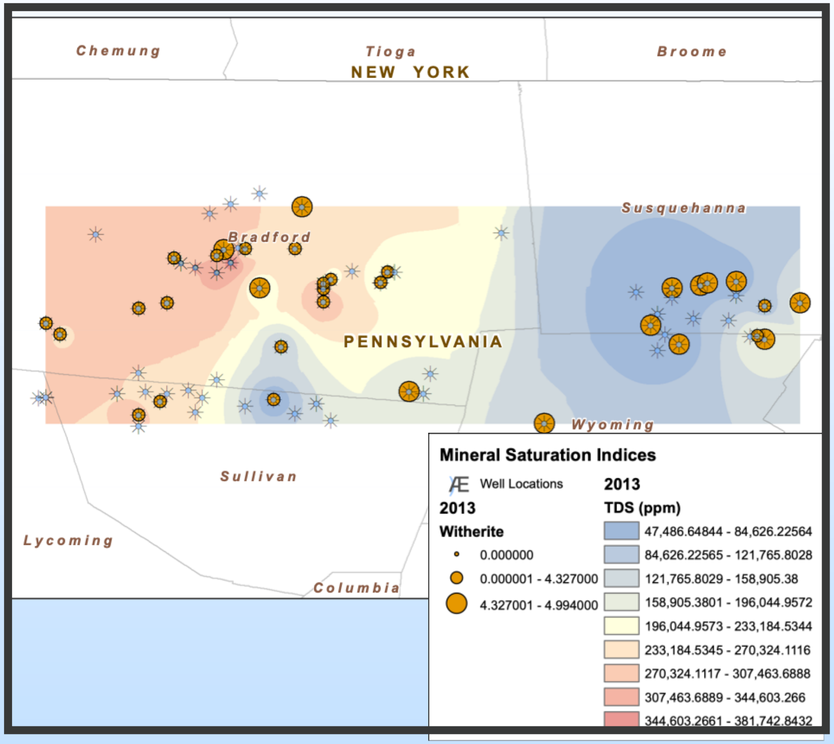
Mineral Saturation Indices
Well Locations
2013
Barite
2.583000
2.583001 - 3.300000
3.300001 - 3.467000
2013
TDS (ppm)
47,486.64844 - 84,626.22564
84,626.22565 - 121,765.8028
121,765.8029 - 158,905.38
158,905.3801 - 196,044.9572
196,044.9573 - 233,184.5344
233,184.5345 - 270,324.1116
270,324.1117 - 307,463.6888
307,463.6889 - 344,603.266
344,603.2661 - 381,742.8432



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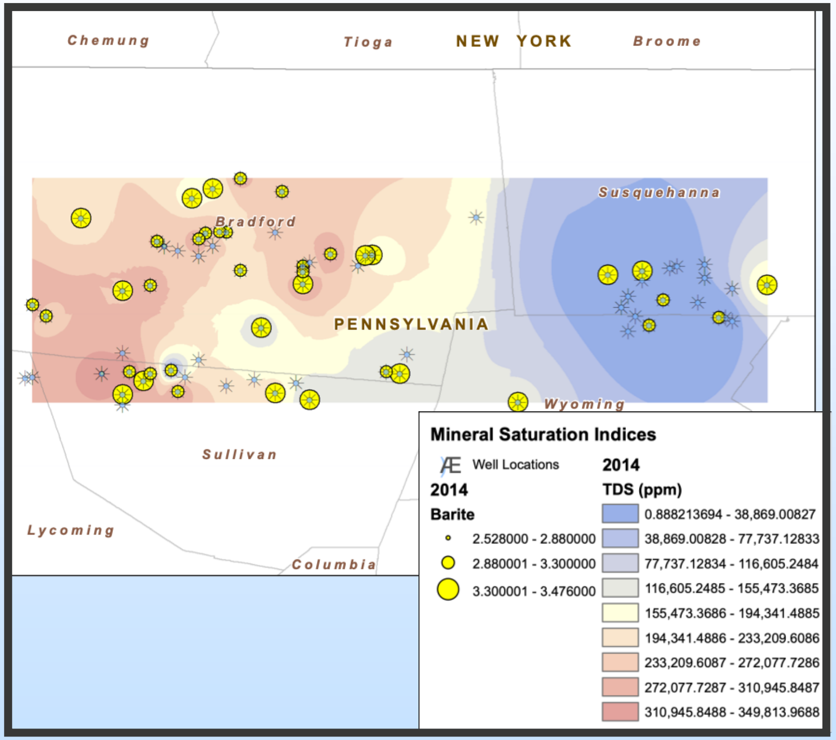
Mineral Saturation Indices
Well Locations
2013
Witherite
0.000000
0.000001 - 4.327000
4.327001 - 4.994000
2013
TDS (ppm)
47,486.64844 - 84,626.22564
84,626.22565 - 121,765.8028
121,765.8029 - 158,905.38
158,905.3801 - 196,044.9572
196,044.9573 - 233,184.5344
233,184.5345 - 270,324.1116
270,324.1117 - 307,463.6888
307,463.6889 - 344,603.266
344,603.2661 - 381,742.8432

Results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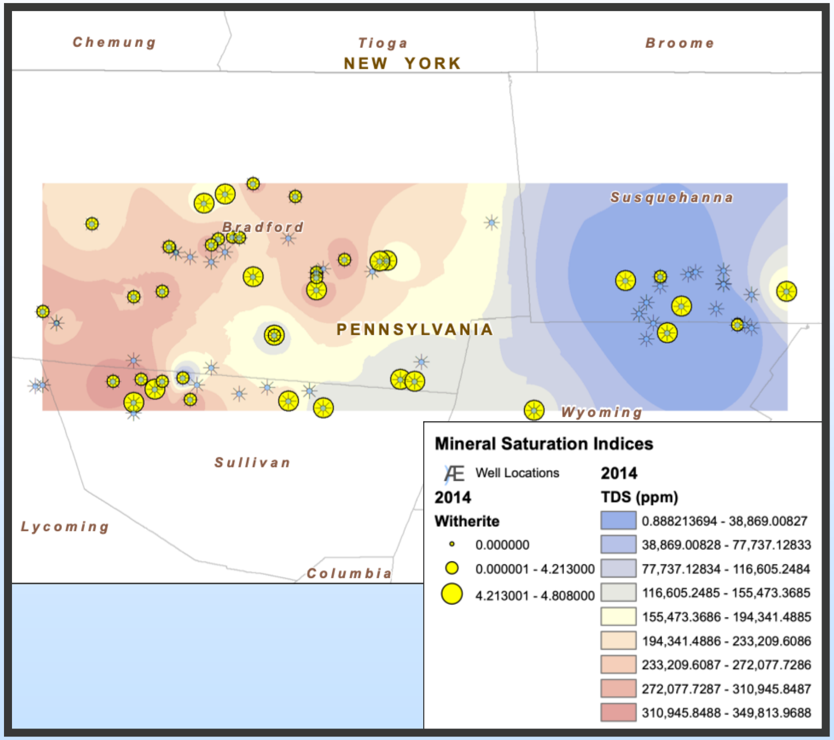
Mineral Saturation Indices
Well Locations
2014
Barite
2.528000 - 2.880000
2.880001 - 3.300000
3.300001 - 3.476000
2014
TDS (ppm)
0.888213694 - 38,869.00827
38,869.00828 - 77,737.12833
77,737.12834 - 116,605.2484
116,605.2485 - 155,473.3685
155,473.3686 - 194,341.4885
194,341.4886 - 233,209.6086
233,209.6087 - 272,077.7286
272,077.7287 - 310,945.8487
310,945.8488 - 349,813.9688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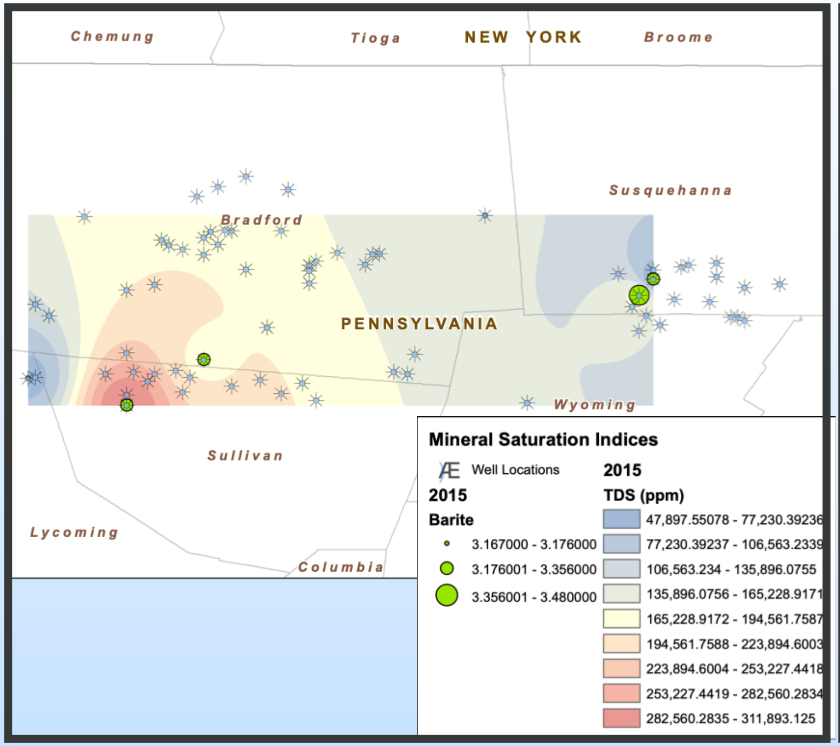
Columbia
Mineral Saturation Indices
Well Locations
2014
Witherite
0.000000
0.000001 - 4.213000
4.213001 - 4.808000
2014
TDS (ppm)
0.888213694 - 38,869.00827
38,869.00828 - 77,737.12833
77,737.12834 - 116,605.2484
116,605.2485 - 155,473.3685
155,473.3686 - 194,341.4885
194,341.4886 - 233,209.6086
233,209.6087 - 272,077.7286
272,077.7287 - 310,945.8487
310,945.8488 - 349,813.9688

Results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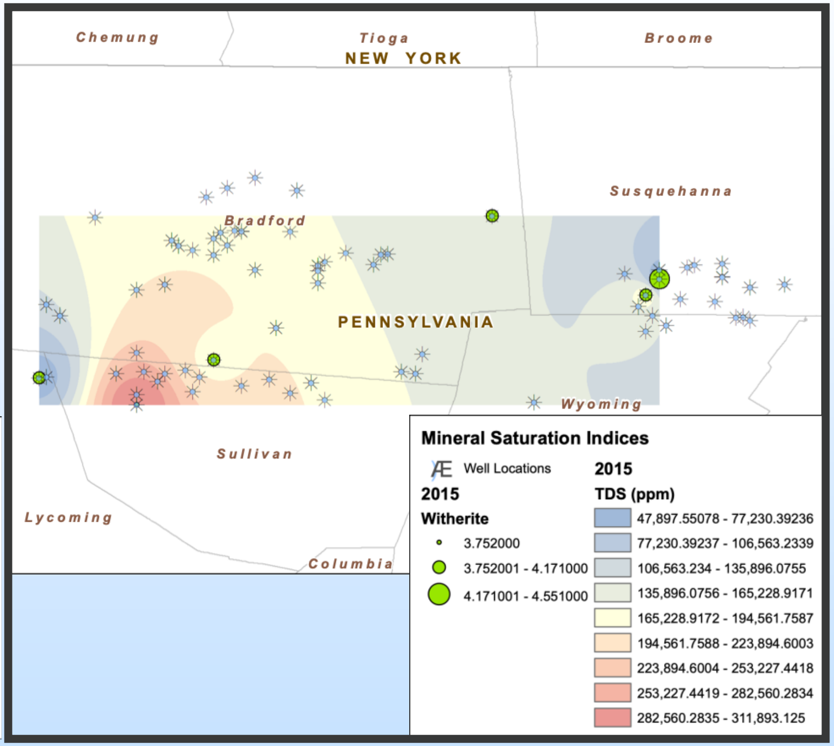
Columbia
Mineral Saturation Indices
Well Locations
2015
Barite
3.167000 - 3.176000
3.176001 - 3.356000
3.356001 - 3.480000
2015
TDS (ppm)
47,897.55078 - 77,230.39236
77,230.39237 - 106,563.2339
106,563.234 - 135,896.0755
135,896.0756 - 165,228.9171
165,228.9172 - 194,561.7587
194,561.7588 - 223,894.6003
223,894.6004 - 253,227.4418
253,227.4419 - 282,560.2834
282,560.2835 - 311,893.125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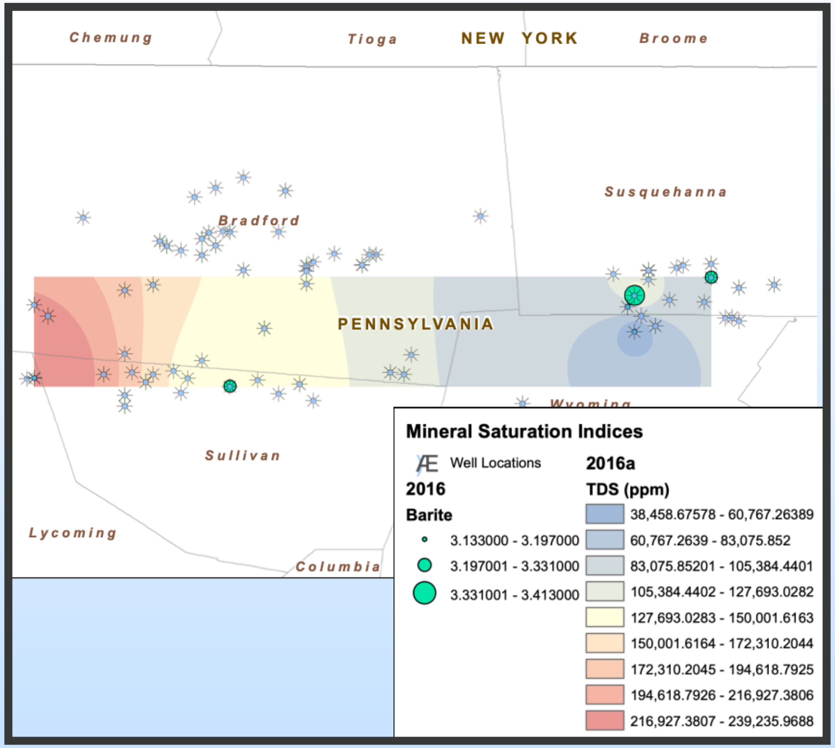
Lycoming
Columbia
Mineral Saturation Indices
Well Locations
2015
Witherite
3.752000
3.752001 - 4.171000
4.171001 - 4.551000
2015
TDS (ppm)
47,897.55078 - 77,230.39236
77,230.39237 - 106,563.2339
106,563.234 - 135,896.0755
135,896.0756 - 165,228.9171
165,228.9172 - 194,561.7587
194,561.7588 - 223,894.6003
223,894.6004 - 253,227.4418
253,227.4419 - 282,560.2834
282,560.2835 - 311,893.125

Results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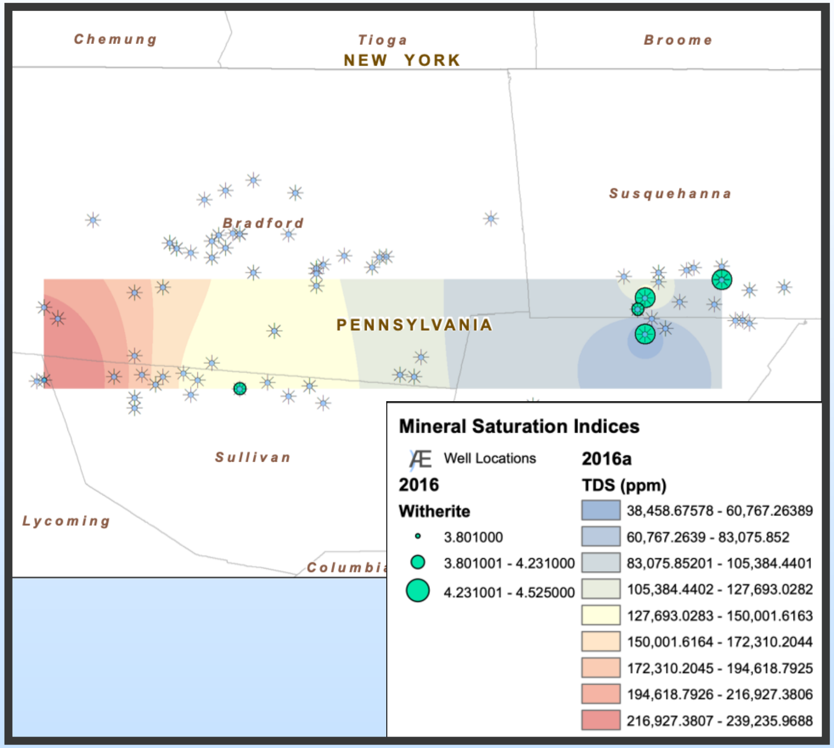
Mineral Saturation Indices
Well Locations
2016
Barite
3.133000 - 3.197000
3.197001 - 3.331000
3.331001 - 3.413000
2016a
TDS (ppm)
38,458.67578 - 60,767.26389
60,767.2639 - 83,075.852
83,075.85201 - 105,384.4401
105,384.4402 - 127,693.0282
127,693.0283 - 150,001.6163
150,001.6164 - 172,310.2044
172,310.2045 - 194,618.7925
194,618.7926 - 216,927.3806
216,927.3807 - 239,235.9688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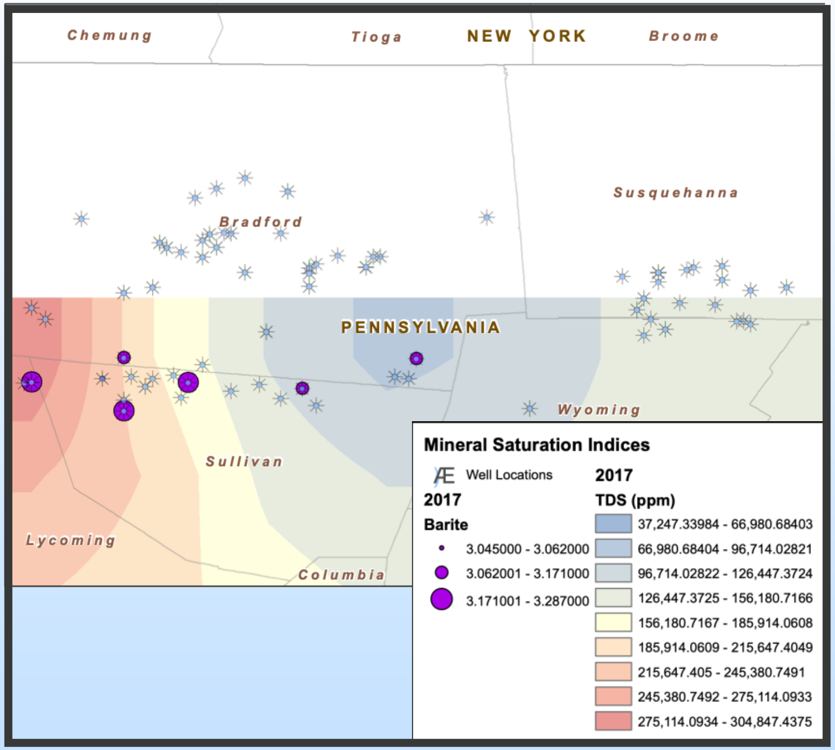
Mineral Saturation Indices
Well Locations
2016
Witherite
3.801000
3.801001 - 4.231000
4.231001 - 4.525000
2016a
TDS (ppm)
38,458.67578 - 60,767.26389
60,767.2639 - 83,075.852
83,075.85201 - 105,384.4401
105,384.4402 - 127,693.0282
127,693.0283 - 150,001.6163
150,001.6164 - 172,310.2044
172,310.2045 - 194,618.7925
194,618.7926 - 216,927.3806
216,927.3807 - 239,235.9688

Results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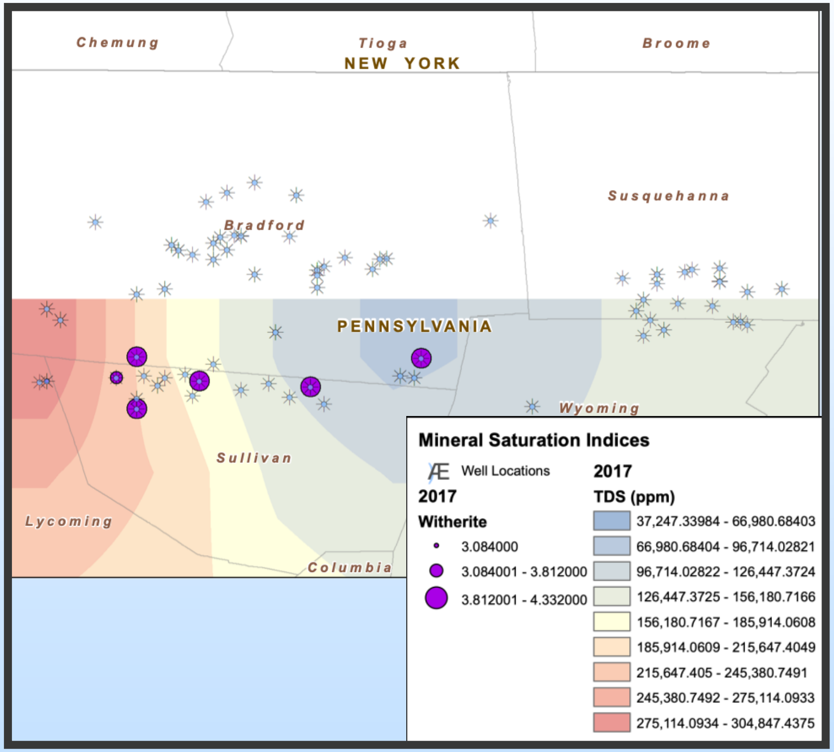
Mineral Saturation Indices
Well Locations
2017
Barite
3.045000 - 3.062000
3.062001 - 3.171000
3.171001 - 3.287000
2017
TDS (ppm)
37,247.33984 - 66,980.68403
66,980.68404 - 96,714.02821
96,714.02822 - 126,447.3724
126,447.3725 - 156,180.7166
156,180.7167 - 185,914.0608
185,914.0609 - 215,647.4049
215,647.405 - 245,380.7491
245,380.7492 - 275,114.0933
275,114.0934 - 304,847.4375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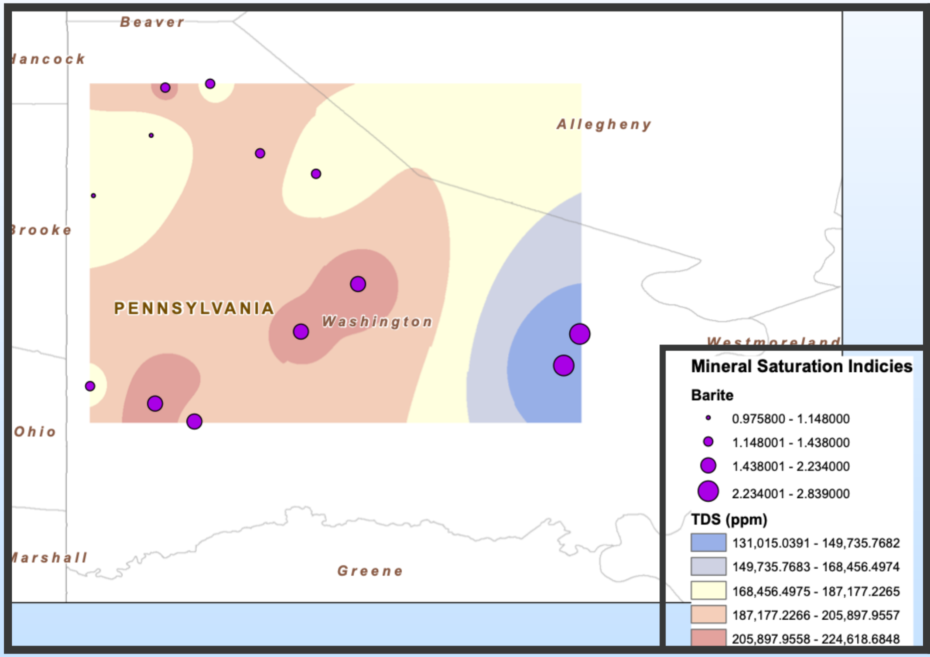
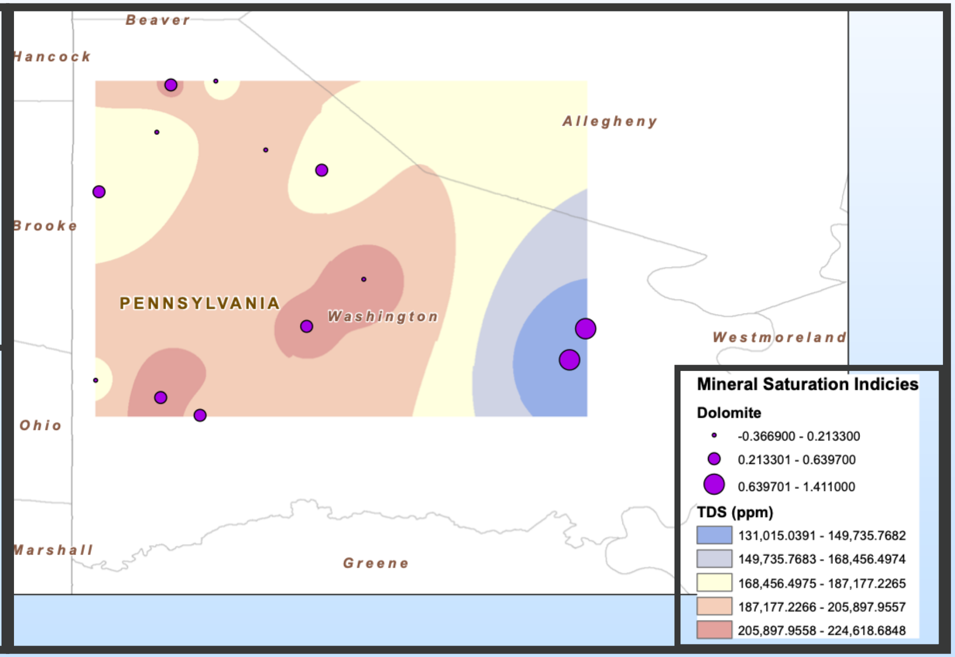
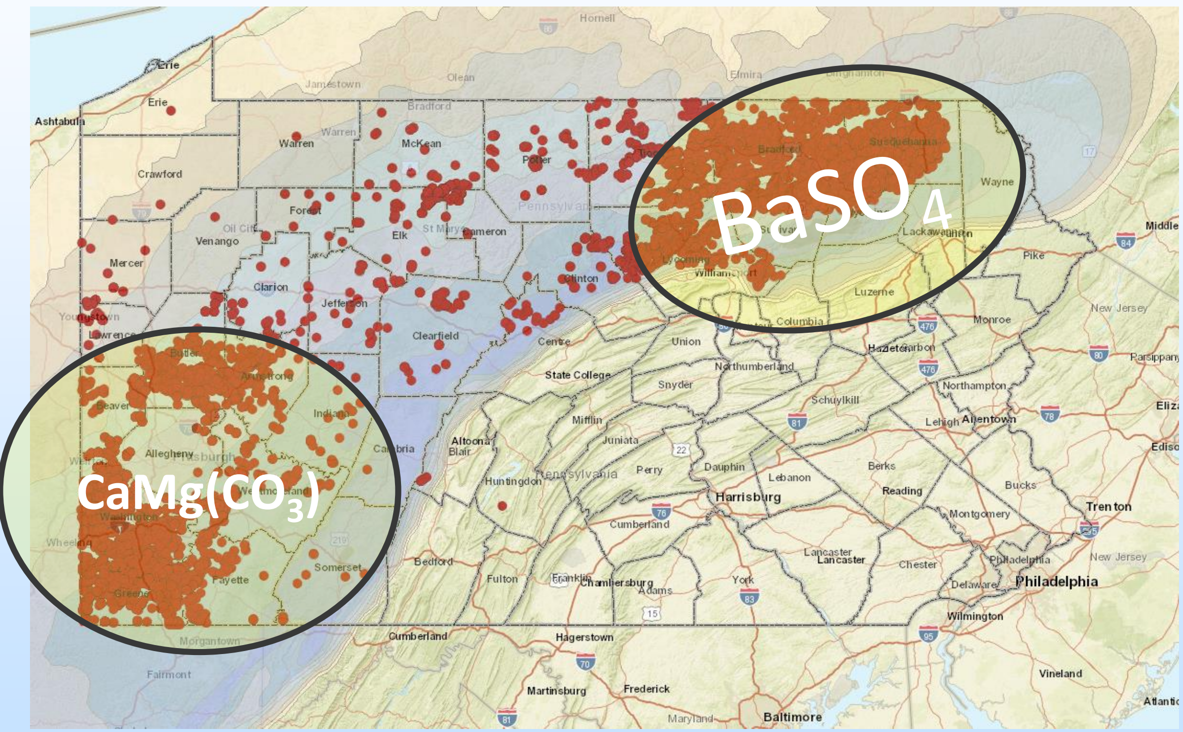
Columbia
Mineral Saturation Indices
Well Locations
2017
Witherite
3.084000
3.084001 - 3.812000
3.812001 - 4.332000
2017
TDS (ppm)
37,247.33984 - 66,980.68403
66,980.68404 - 96,714.02821
96,714.02822 - 126,447.3724
126,447.3725 - 156,180.7166
156,180.7167 - 185,914.0608
185,914.0609 - 215,647.4049
215,647.405 - 245,380.7491
245,380.7492 - 275,114.0933
275,114.0934 - 304,847.4375

Results


Beaver
Hancock
Allegheny
Brooke
PENNSYLVANIA
Washington
Westmoreland
Ohio
Marshall
Greene
Mineral Saturation Indicies
Barite
0.975800 - 1.148000
1.148001 - 1.438000
1.438001 - 2.234000
2.234001 - 2.839000
TDS (ppm)
131,015.0391 - 149,735.7682
149,735.7683 - 168,456.4974
168,456.4975 - 187,177.2265
187,177.2266 - 205,897.9557
205,897.9558 - 224,618.6848


Beaver
Hancock
Allegheny
Brooke
PENNSYLVANIA
Washington
Westmoreland
Ohio
Marshall
Greene
Mineral Saturation Indicies
Dolomite
-0.366900 - 0.213300
0.213301 - 0.639700
0.639701 - 1.411000
TDS (ppm)
131,015.0391 - 149,735.7682
149,735.7683 - 168,456.4974
168,456.4975 - 187,177.2265
187,177.2266 - 205,897.9557
205,897.9558 - 224,618.6848

Modeling Findings



- Regional and intra-regional heterogeneity in Marcellus sourced produced water.
- Mineral saturation in produced water varies between NE and SW
- Expressed interest from stakeholders in multiple O&G related industries.

Future Modeling and Analytics

Identify Data Sources

Gather Data

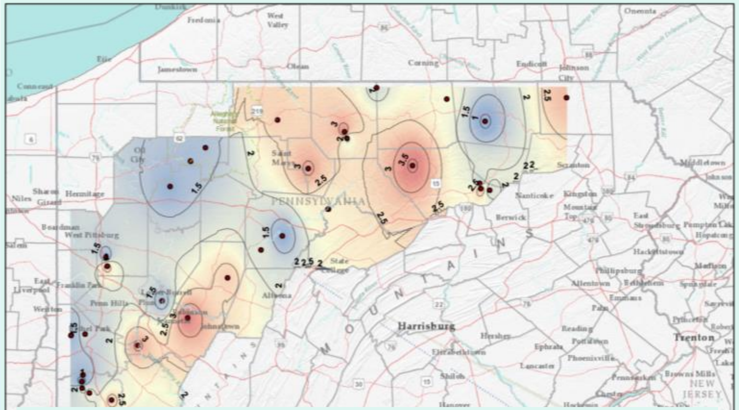
QC/QA

Data transformations
(ilr transformations, units, etc.)

Unsupervised Machine Learning Algorithm
(Emergent Self Organizing Map)

Test Scenarios

Geochemical Model
(OLI Systems, Inc.)



Inverse distance weighted map showing distributions of $BaSO_4$ saturation indices in Marcellus Shale produced water (*Mackey et al., submitted*)

Ground-truth to experimental and field samples

Objectives:

- Formation Heterogeneity
- Modeling scale risk and prevention.
- Can we identify frac hits?
- Parent/child relationship?

Synergy Opportunities

– Although we are focused specifically on the wellbore and related equipment, this project has cross-cutting ties to several other NETL projects - primarily those related to understanding and predicting reservoir behavior.

Benefit to the Program

- Mineral scale will coat perforations, casing, production tubulars, valves, pumps, and downhole completion equipment ***limiting production and eventually requiring abandonment of the well***
- It's expensive to deal with (often requiring the removal/replacement of the production lining) and makes for an unsafe environment around the well.

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