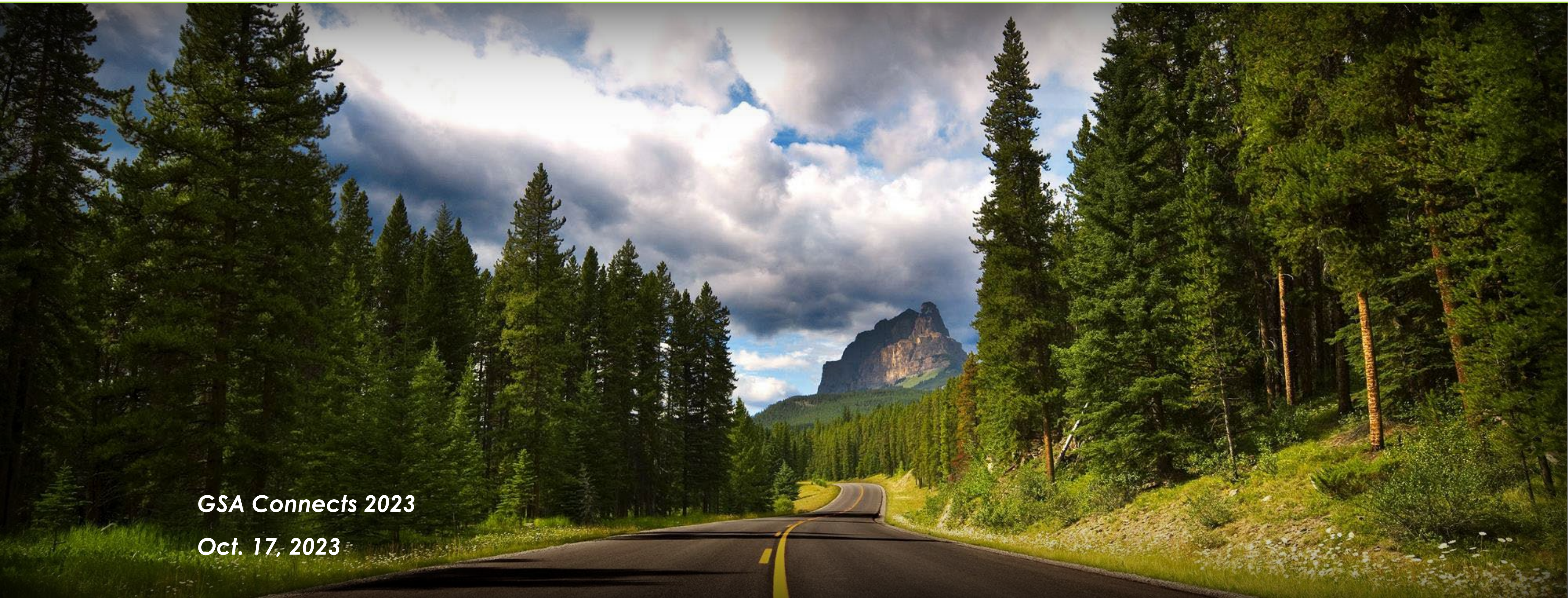
Predicting Lithium Fluxes from a Heterogenous Brine Source

Marcellus Shale

Justin Mackey
Research Scientist, LRST



GSA Connects 2023

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Authors and Contact Information

Justin Mackey[1,2,3], Dan Bain[3], James Gardiner[1], Greg Lackey[1], Djuna Gulliver[1], Barbara Kutchko[1]

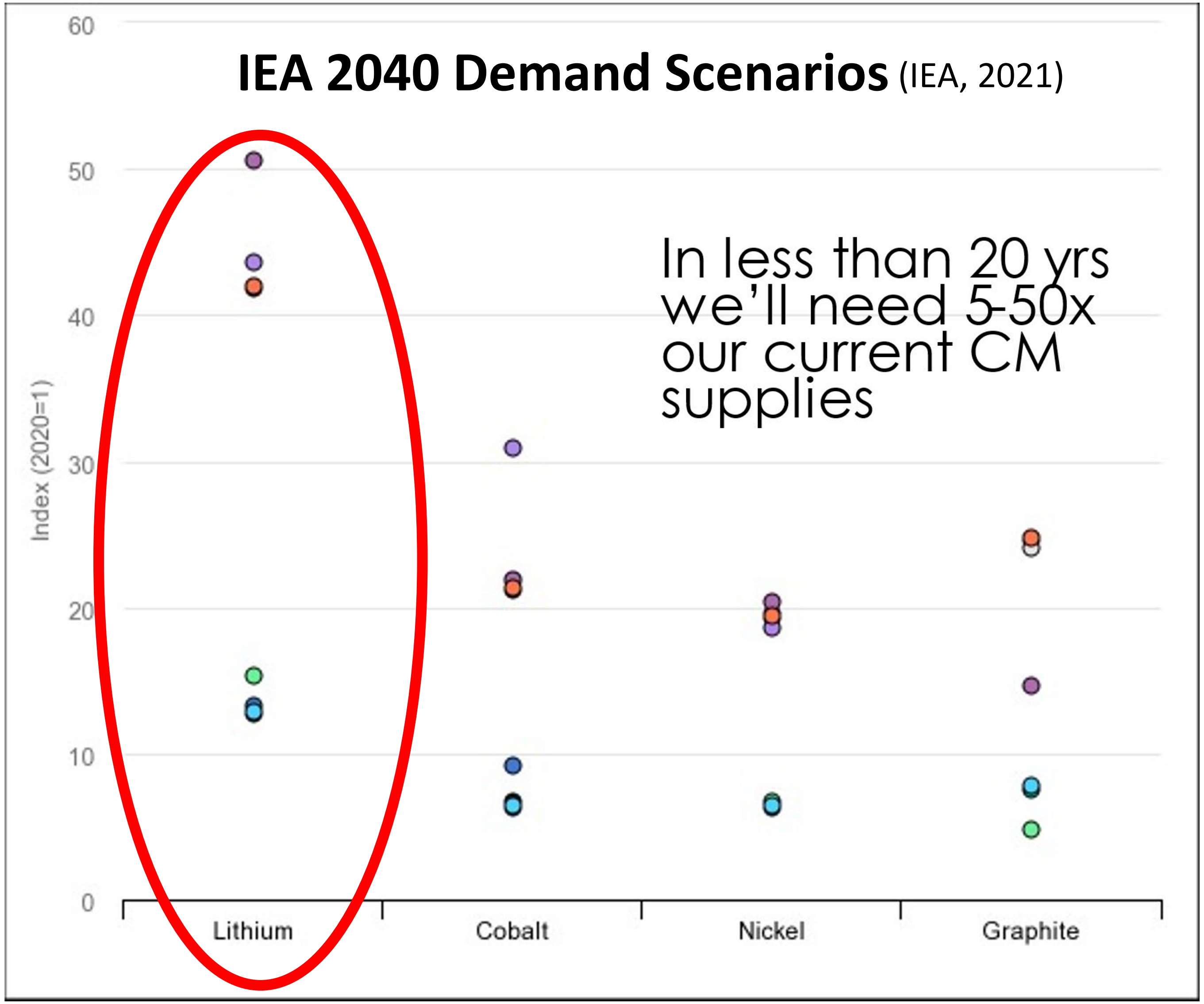
[1]National Energy Technology Laboratory, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA

[2]NETL Support Contractor, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA

[3]University of Pittsburgh, 4200 Fifth Ave, Pittsburgh, PA 15260, USA

Critical Minerals & Produced Water

50 x 2020 demand!!!

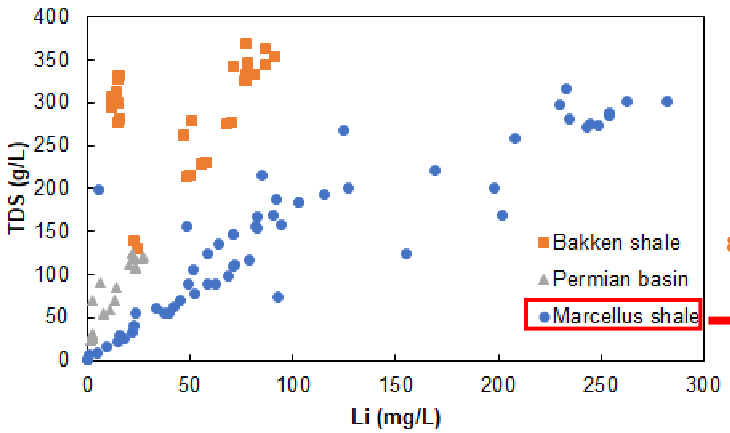


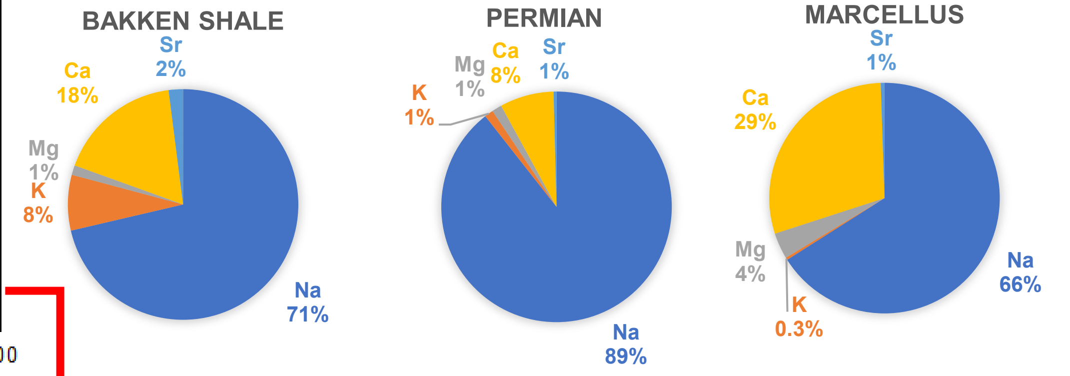
IEA (2021), The Role of Critical Minerals in Clean Energy Transitions, IEA, Paris https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions, License: CC BY 4.0

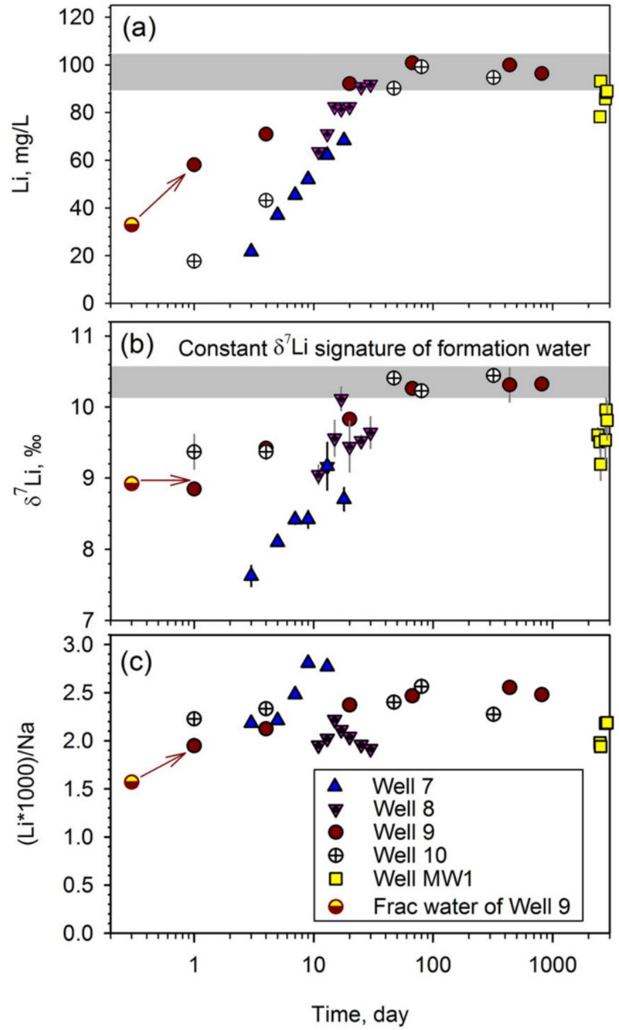
2.8 Billion Liters of PW a Day in US! (Veil, 2020)

Bakken shale[1]: ~30/yr; Permian Basin EOR Oil field[2]: ~30/Yr; Marcellus Shale: ~200[3]

- Up to 300mg/L Li was found in Marcellus shale produced waters, comparable to the dominant source of Li mining, the brine ponds in Chile (1000mg/L)
- At the same TDS level, Marcellus Shale waters contain more Li compared to Bakken Shale and Permian Basin waters
- Marcellus shale brine contain high percentages of Ca and Mg, whereas Permian basin brine contain up to 89% Na.

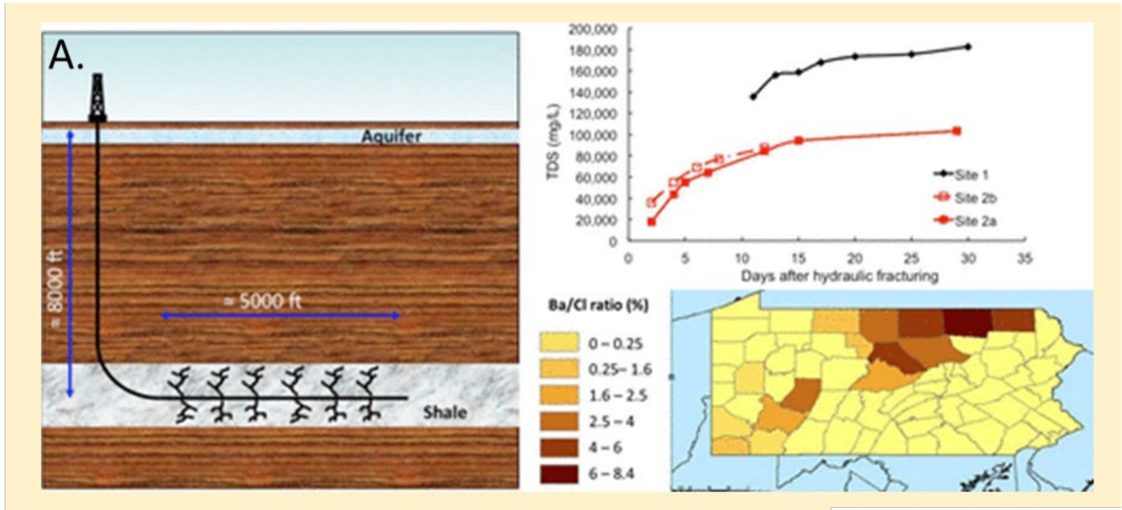


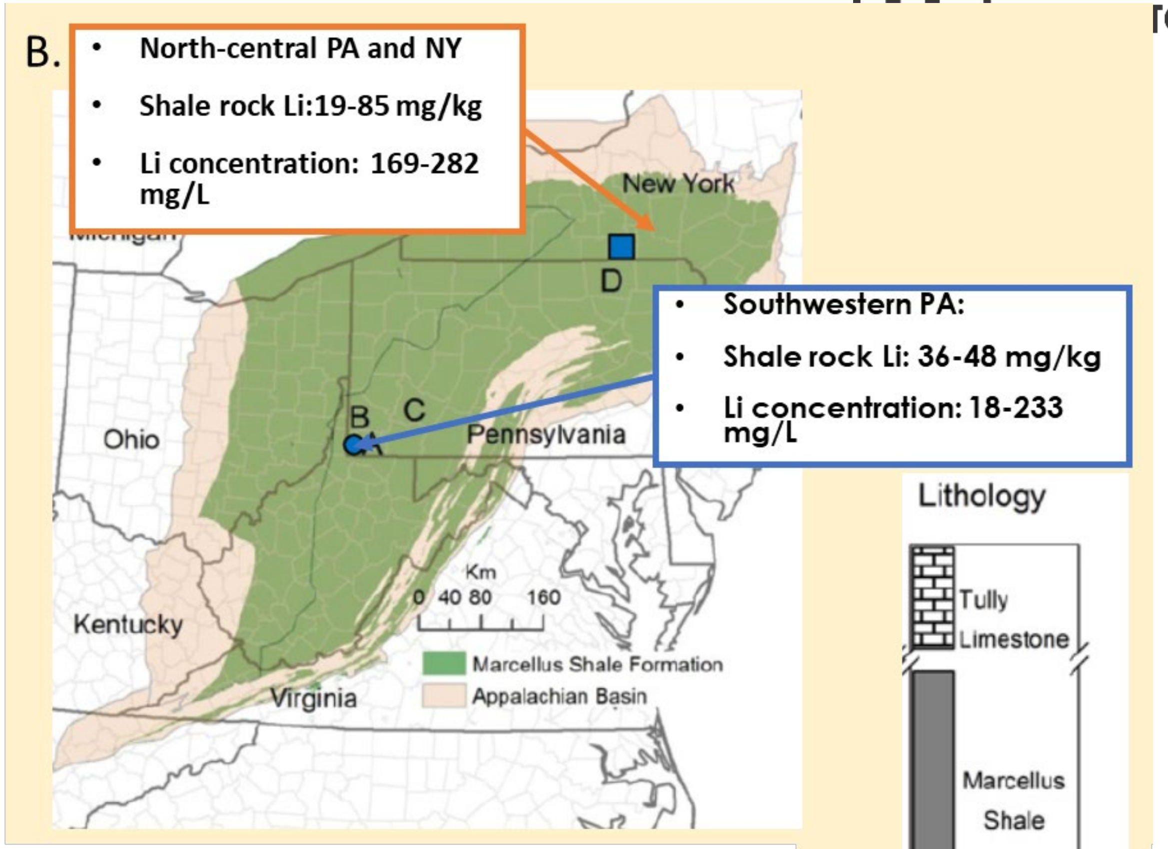


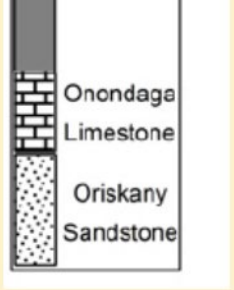


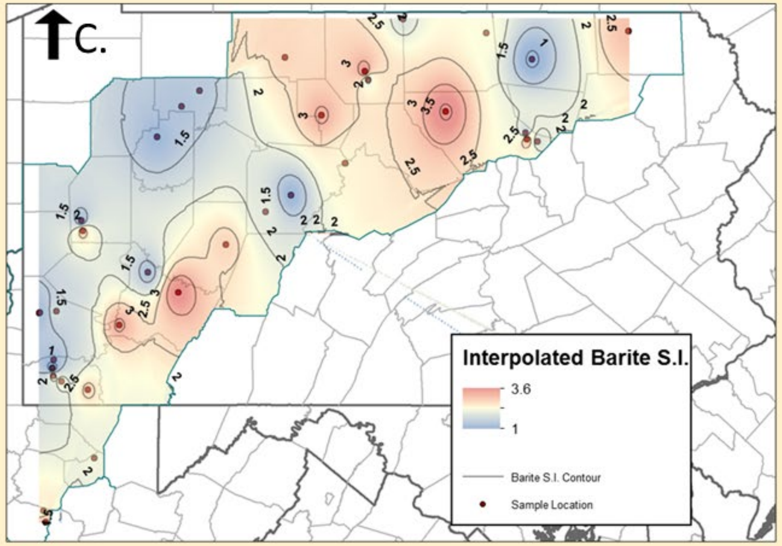
1: Tinker, K., J. et al., (2020). Frontiers in microbiology 11(1781).
2: Gardiner, J., et al. (2020). Applied Geochemistry 121: 104688.
3: Phan, T. T., et al. (2016). Chemical Geology **420**: 162-179
4: Veil, John. (2020) "US produced water volumes and management practices in 2017." *Groundwater Protection Council.*

Formation Heterogeneity









Previous work demonstrating spatial heterogeneity in Marcellus produced waters from **A**) Barbot et al., (2013), **B**) Phan et al., (2016) and **C**) Mackey et al., (2021).

1. Phan, T. T., et al. (2016). Chemical Geology **420**: 162-179
2. Barbot et al., (2016). Environmental Science and Technology **47**(6), 2562-2569
3. Mackey et al., (2021). Journal of Petroleum Science and Engineering **202**, 108514

Overview:

Does formation heterogeneity impact the ultimate recovery of the resource?

- Lithium composition of the produced water.
- Volume of produced water generated by a well.

What is most the likely annual lithium mass yield from Marcellus produced water in Pennsylvania?

Methods:

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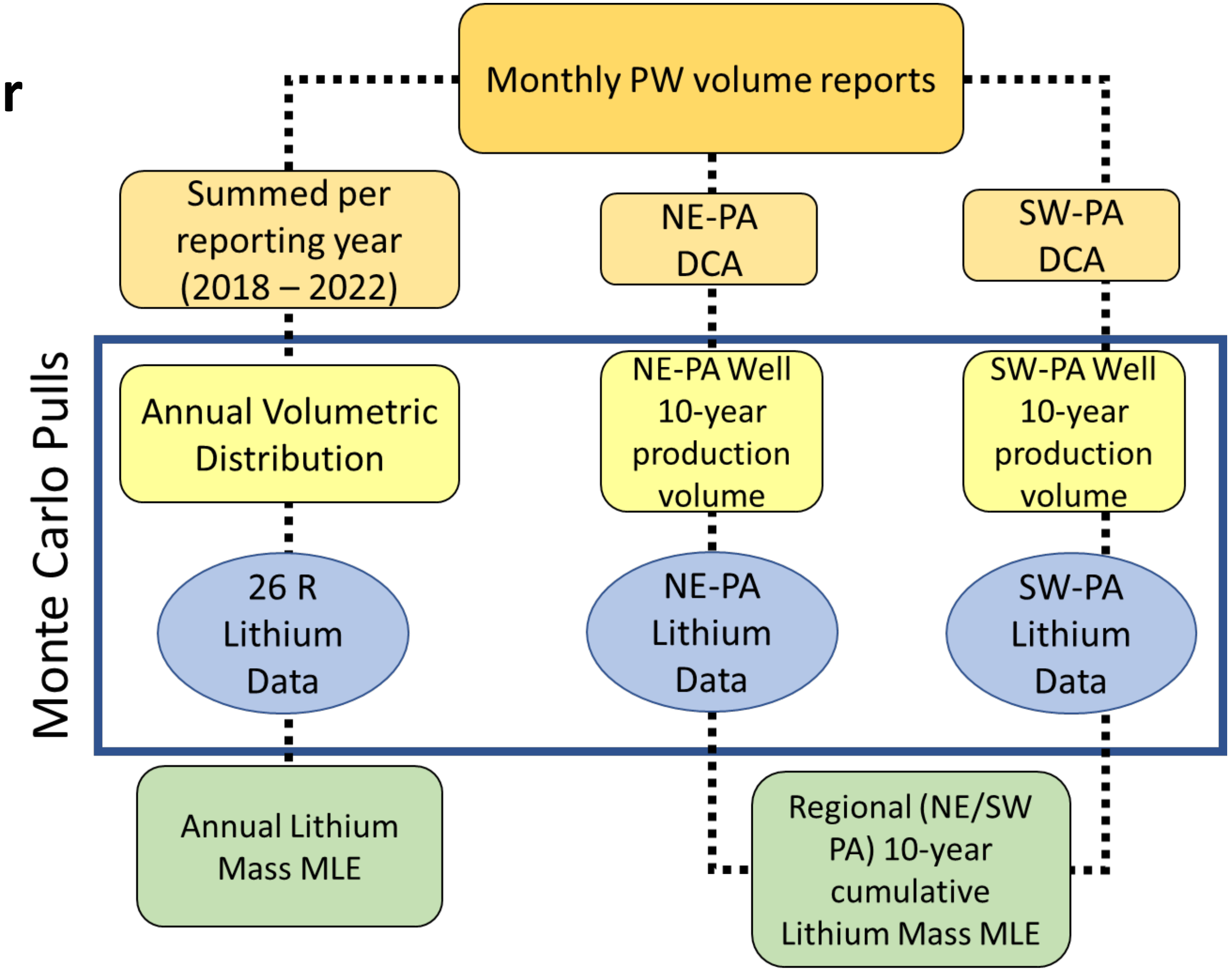
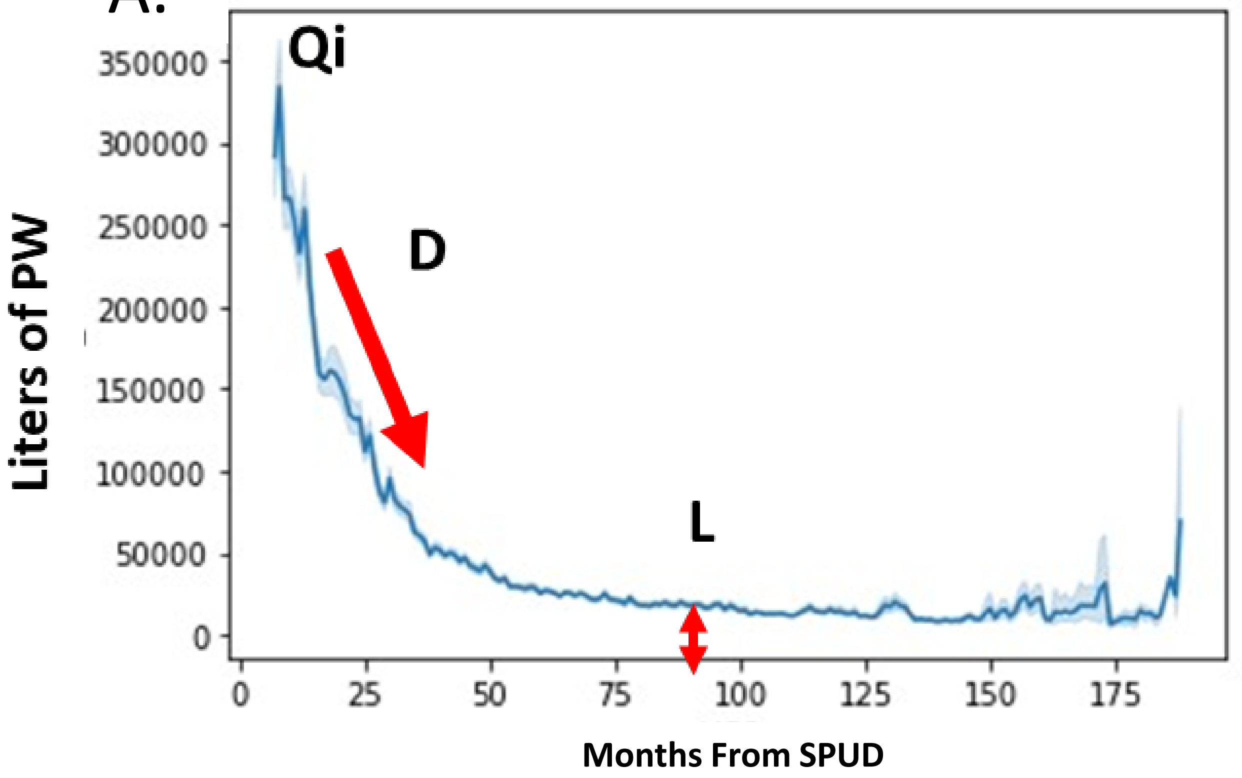
- **Decline curve analysis of production water volumes to determine the estimated ultimate recovery of produced water.**
- **Pair with large geochemistry data set of lithium concentrations.**
- **Used Monte Carlo simulations to reduce uncertainty in the estimations.**



Data Data Data

A.



A) Mean PW production rate with parameter explanations, B) Decline curve equation and variables

Oil and gas waste generator reports for Marcellus Wells.

- Provides PW Volumes

Normalized the volume measurement date with the SPUD of each well

- Well by well temporal analysis of water production.

B.

$$\int_0^{10} (Qi * e^{-Dt} + L)\, dt \quad (1)$$

Q_i is the initial production rate

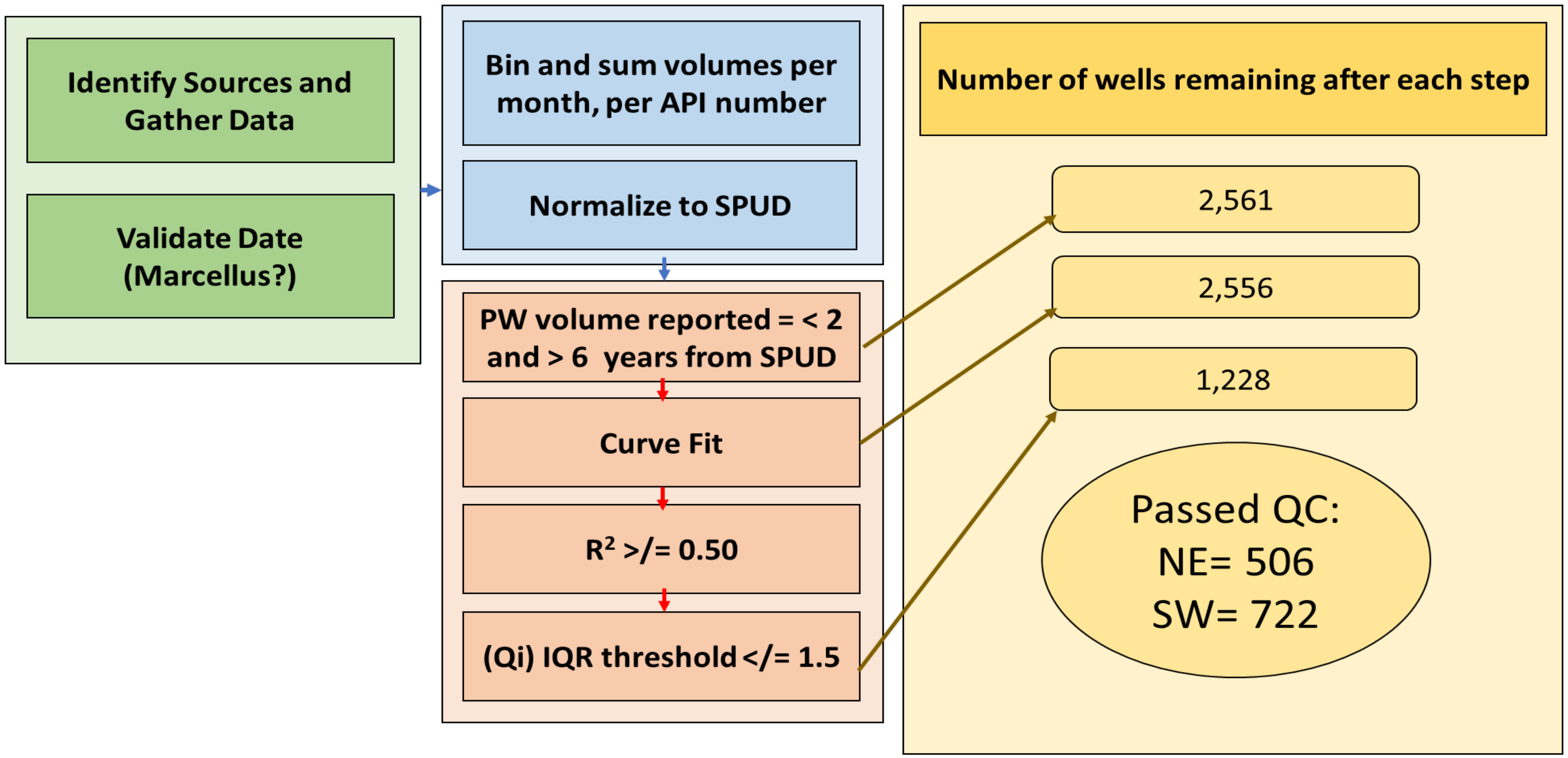
D is the rate of decline

t is the time after the well SPUD date

L is the lift factor.

Data Data Data

A.



B.

API	Qi	D	L
125-24199	13726884	0.587866	105107.3
131-20442	11043769	0.578672	0.008022
115-22285	22127614	0.560001	17575.12
117-21324	12362259	0.554136	44891.26
115-21271	1756191	0.545992	0.000866
125-24198	6930750	0.541851	105107.2
125-24307	6972186	0.537191	105107.3

A. Schematic of produced water (PW) volume data processing and QC methodology for decline curve analysis (DCA) on well production data from six of the top 10 gas producers (by volume) in Pennsylvania. 2,561 Marcellus initially considered for DCA. 2,556 of these wells had successful curve fits with an R^2 </= 0.5. Final fit totals after upper IQR threshold analysis were 506 for NE and 722 for SW Pennsylvania. B. Tabulated Results

Lithium Concentration Data

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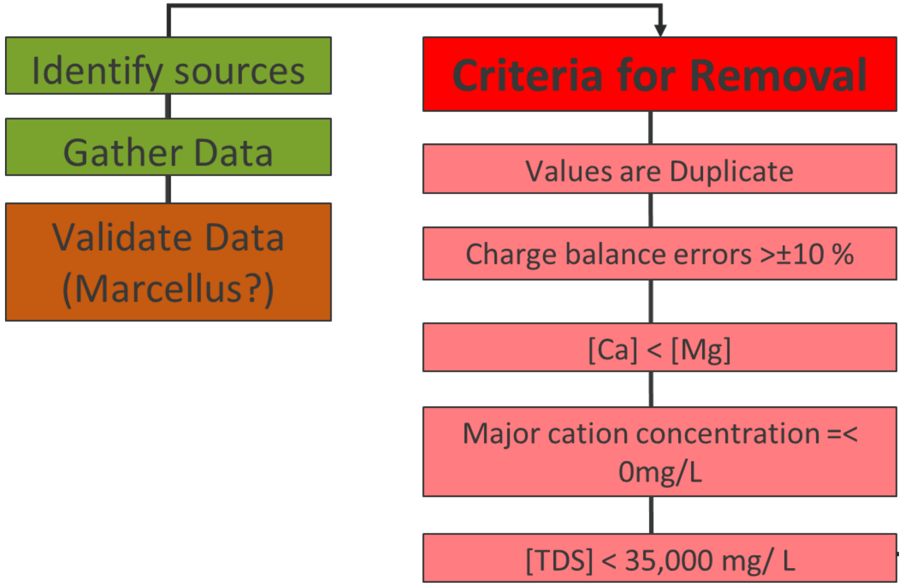
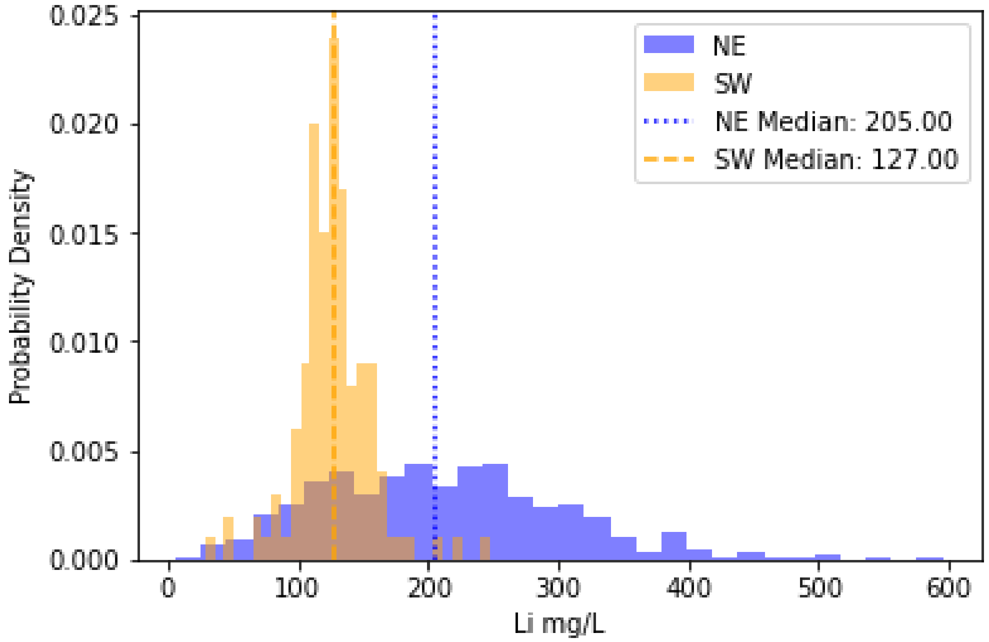
Form 26R Chemical Analysis of Residual Waste (802)

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



654 chemical reports from 553 well locations.



Pennsylvania Department of Environmental Protection, https://www.dep.pa.gov/Business/Land/Waste/SolidWaste/Re

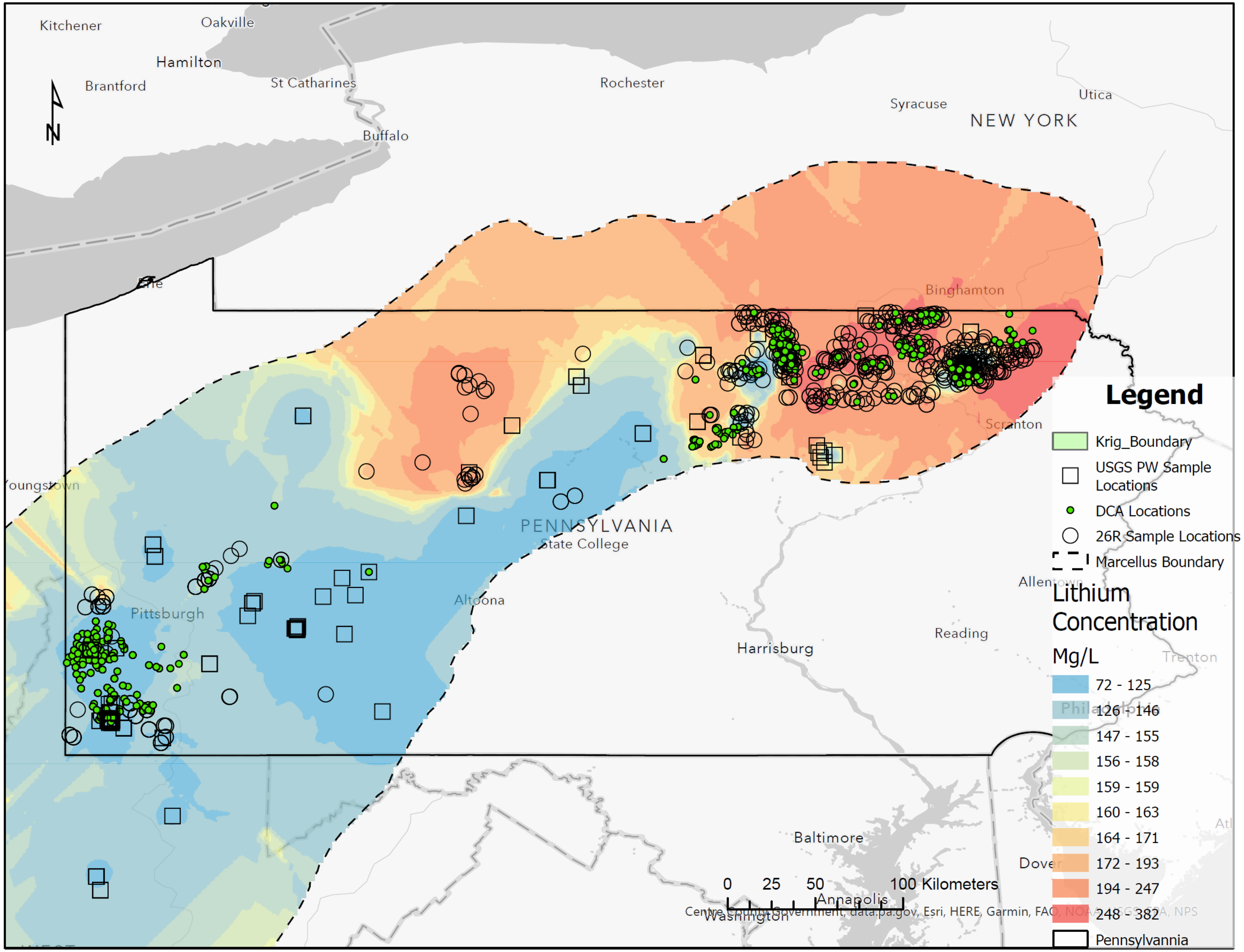


Figure 1. Map of study area showing the Marcellus shale extent, well locations using in decline curve analysis (DCA), PW samples used in this study, and previous USGS sample locations. Kriged lithium concentration layer includes USGS data as well as data reported in this manuscript (USGS, 2018)

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U.S. DEPARTMENT OF ENERGY

Regional Analysis

A.

$$PW = \int_0^{10} (Qi * e^{-Dt} + L)\, dt$$

Q_i is the initial production rate

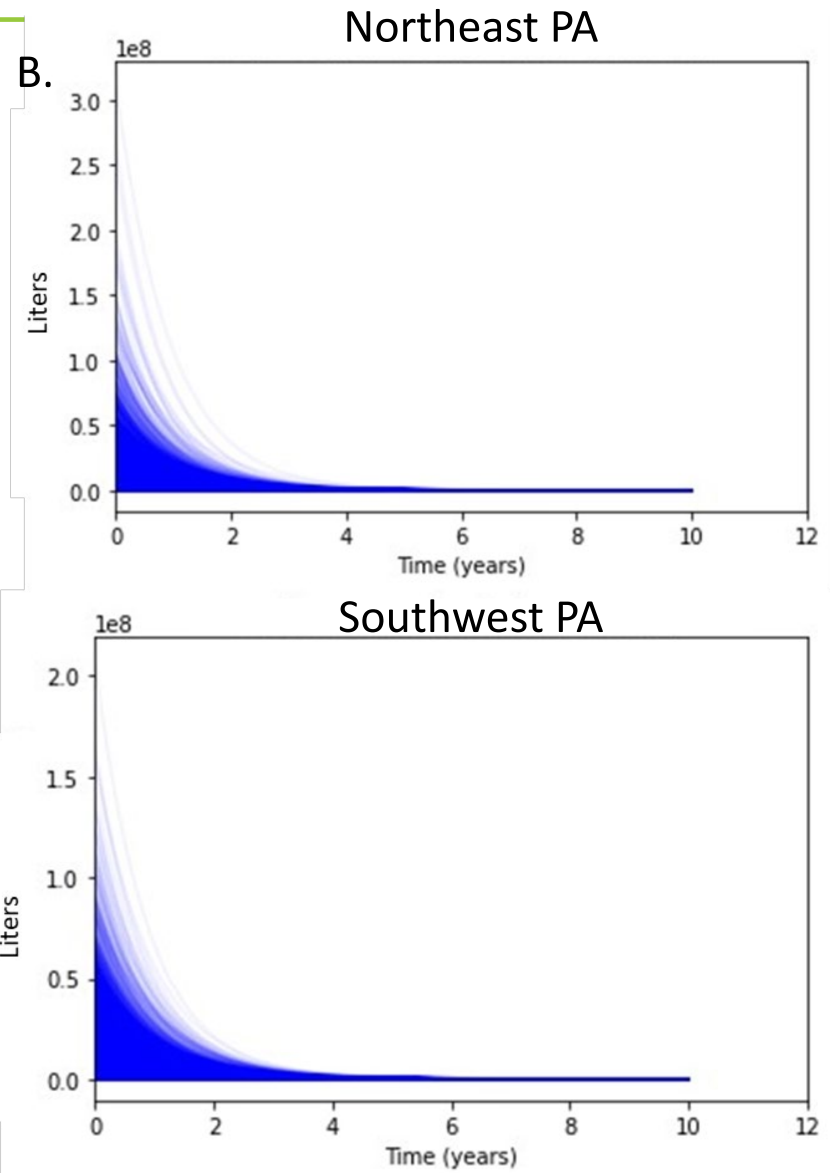
D is the rate of decline

t is the time after the well SPUD date

L is the lift factor.

Lithium Mass = PW*[Li]

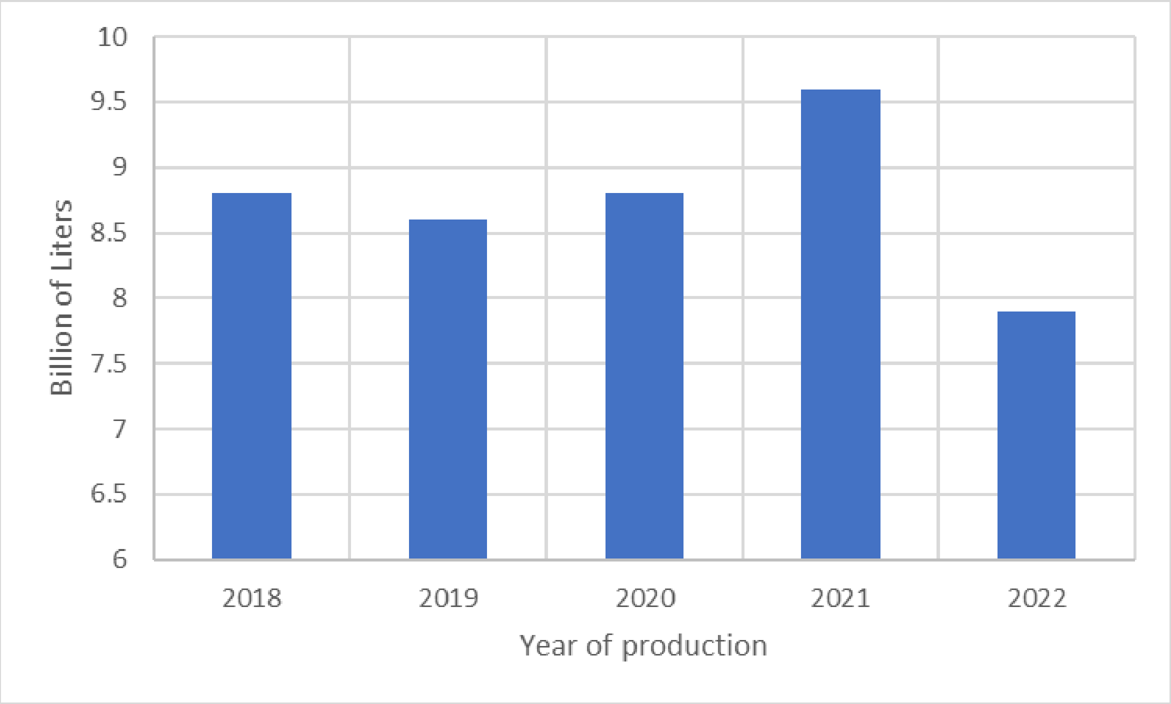
B.



A) Exponential decline curve equation used in this study with parameter definitions.
B) Plots of decline curves (n= 25,000) to calculate total produced water volumes from individual Marcellus wells in NE and SW PA

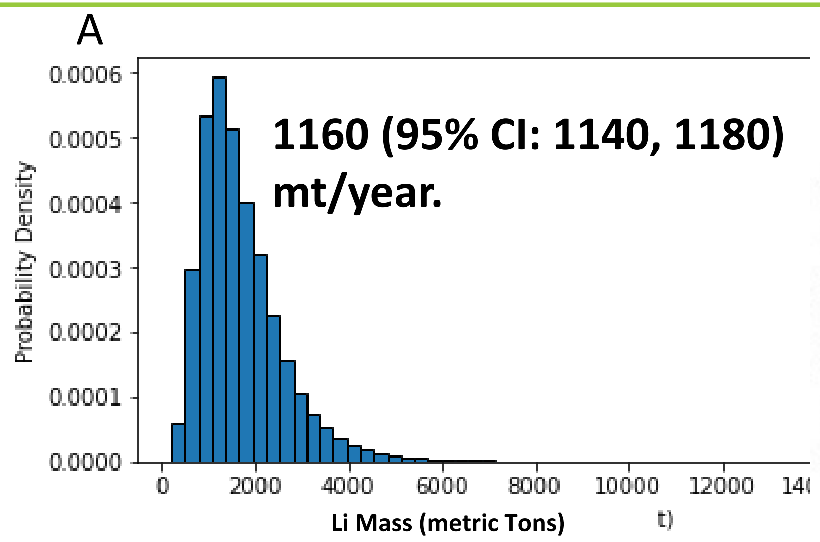
State Wide Lithium Mass Estimates

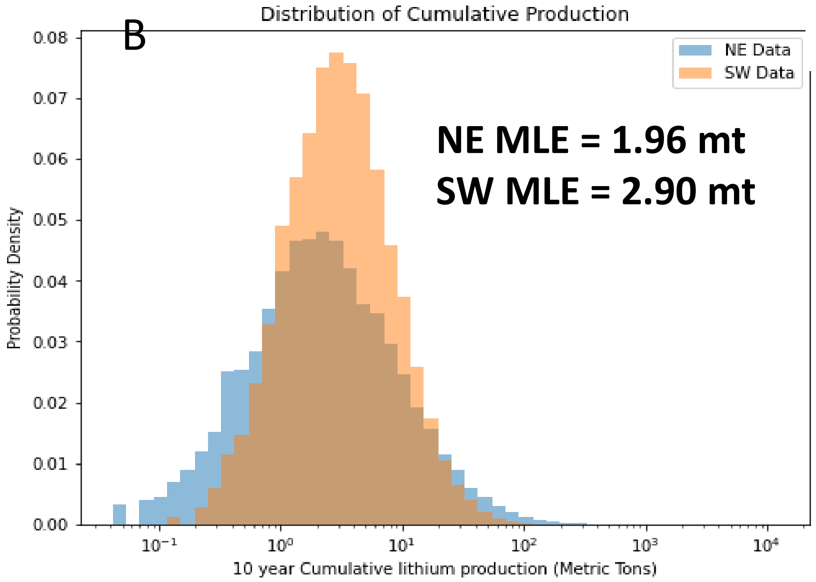
- Calculated the annual production water volumes reported to PA DEP for each year (2018-2022)
- Generated lithium distribution using statewide data

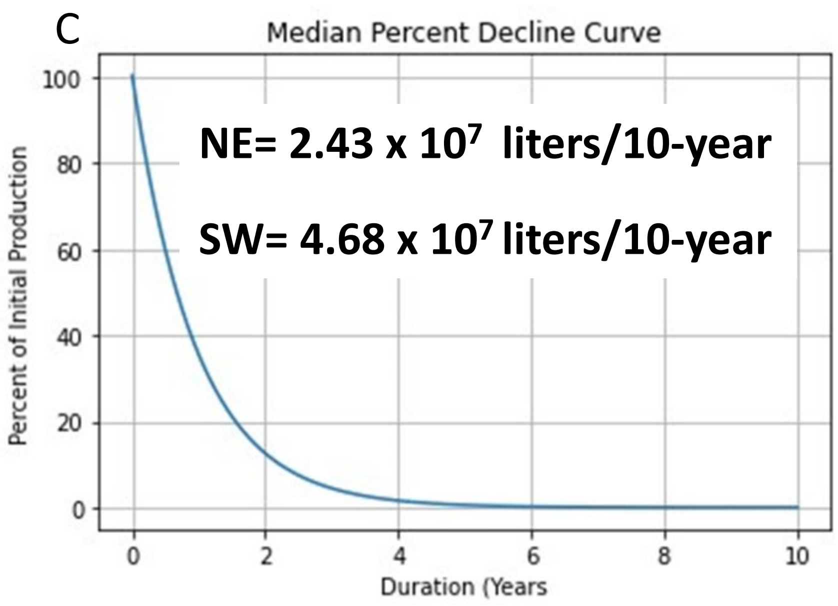


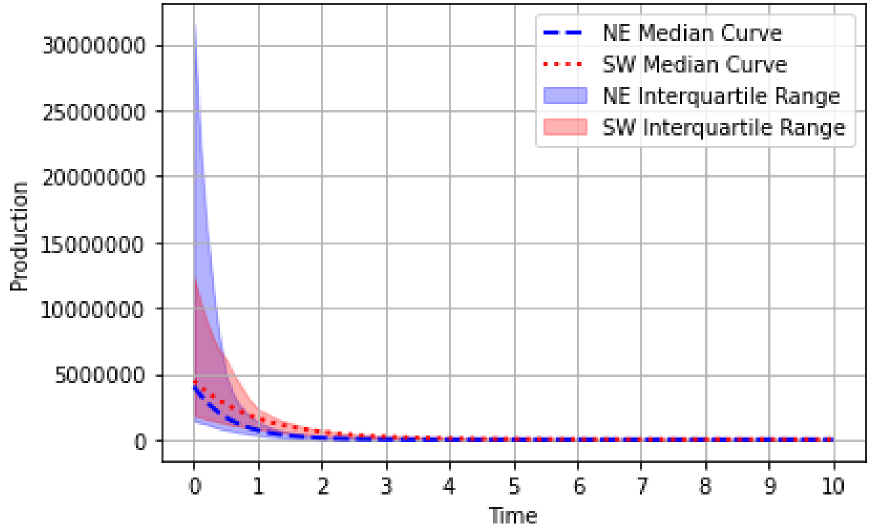
Annual Marcellus water production volumes reported to the PA DEP from 2018 to 2022. Volumes were calculated from monthly waste generator compliance reports.

Results:









A) Histogram showing statewide lithium simulation results. MLE of 1,160 mt supplies ~30% of current consumption estimates (USGS, 2023). **B**) Distributions of NE PA and SW PA results from Monte Carlo Simulations. **C**) Plot showing the percent decline in water production of the median Marcellus well over 10 years. **D)** Regional PW decline curve range. Annotation shows regional difference between NE and SW PA 10-year cumulative production water volumes.

Results

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Distributions of Lithium (Li), Magnesium (Mg), Mg/Li ratios with simulation results for statewide, northeast (NE PA) and southwest (SW PA) Pennsylvania with 95% confidence intervals (CI).

	n	Median	P25	P75	Lithium Mass Yield	95% CI
Chemical Paramters						
NE Mg (mg/L)	421	1000	460	1690	-	
SW Mg (mg/L)	137	2300	1790	2570	-	
NE Mg/Li	422	5.39	2.66	7.26	-	
SW Mg/Li	137	17.8	14.3	20.7	-	
NE Li (mg/Li)	422	205	139	267	-	
SW Li (mg/Li)	137	127	112	140	-	
	-	-	-	-	-	
PW Volume and Li Mass Yield Results	-	-	-	-	-	
NE 10-year Cumulative PW Vol (L)	506	2.43 x 10^7	-	-	-	
SW 10-year Cumulative PW Vol (L)	722	4.68 x 10^7	-	-	-	
NE PA Li mt/10-yr	-	-	-	-	1.96	1.86 – 2.07
SW PA Li mt/10-yr	-	-	-	-	2.90	2.80 – 2.99
Annual Statewide Li Mass Yield (mt)					1160	1140 – 1180

Summary

- Statewide estimates of lithium mass = 1,160 metric tons meets ~30% of US consumption (USGS, 2023)
- Northeastern PA has higher lithium concentrations and more favorable Mg/Li ratio than the Southwestern produced waters.
- Southwest PA lithium mass estimates are marginally (16%) higher than the northeastern PA due to higher water production.
- Median Marcellus water production rate declines rapidly, with an 80% decline in production water volumes in the first two years

Justin Mackey, Daniel J. Bain, Greg Lackey, Djuna Gulliver, Barbara Kutchko. Estimates of lithium mass yields from produced water sourced from the Devonian-aged Marcellus Shale, 15 January 2024, PREPRINT (Version 1) available at Research Square [https://doi.org/10.21203/rs.3.rs-3840288/v1]

Acknowledgments

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