Inorganic Geochemistry of Pennsylvania Marcellus Flowback Waters

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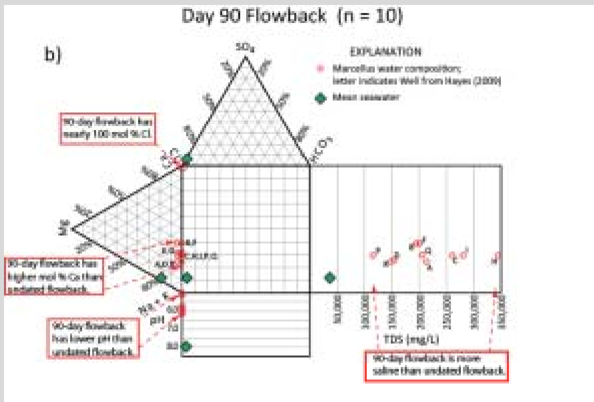

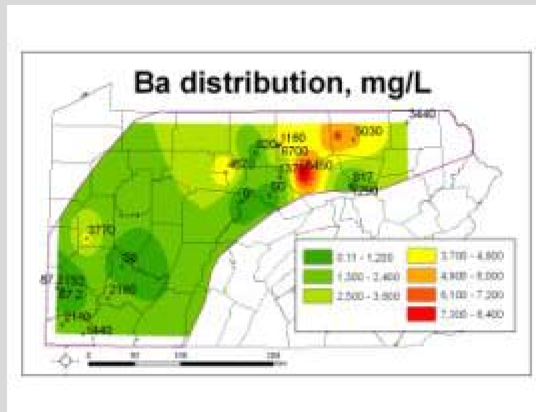

http://www.geosc.psu.edu/~engelder/marcellus/marcellus.html

Photos from New York State SGEIS

Acknowledgments:
Molly Pritz ’10 for chemistry data
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Degenstein Foundation
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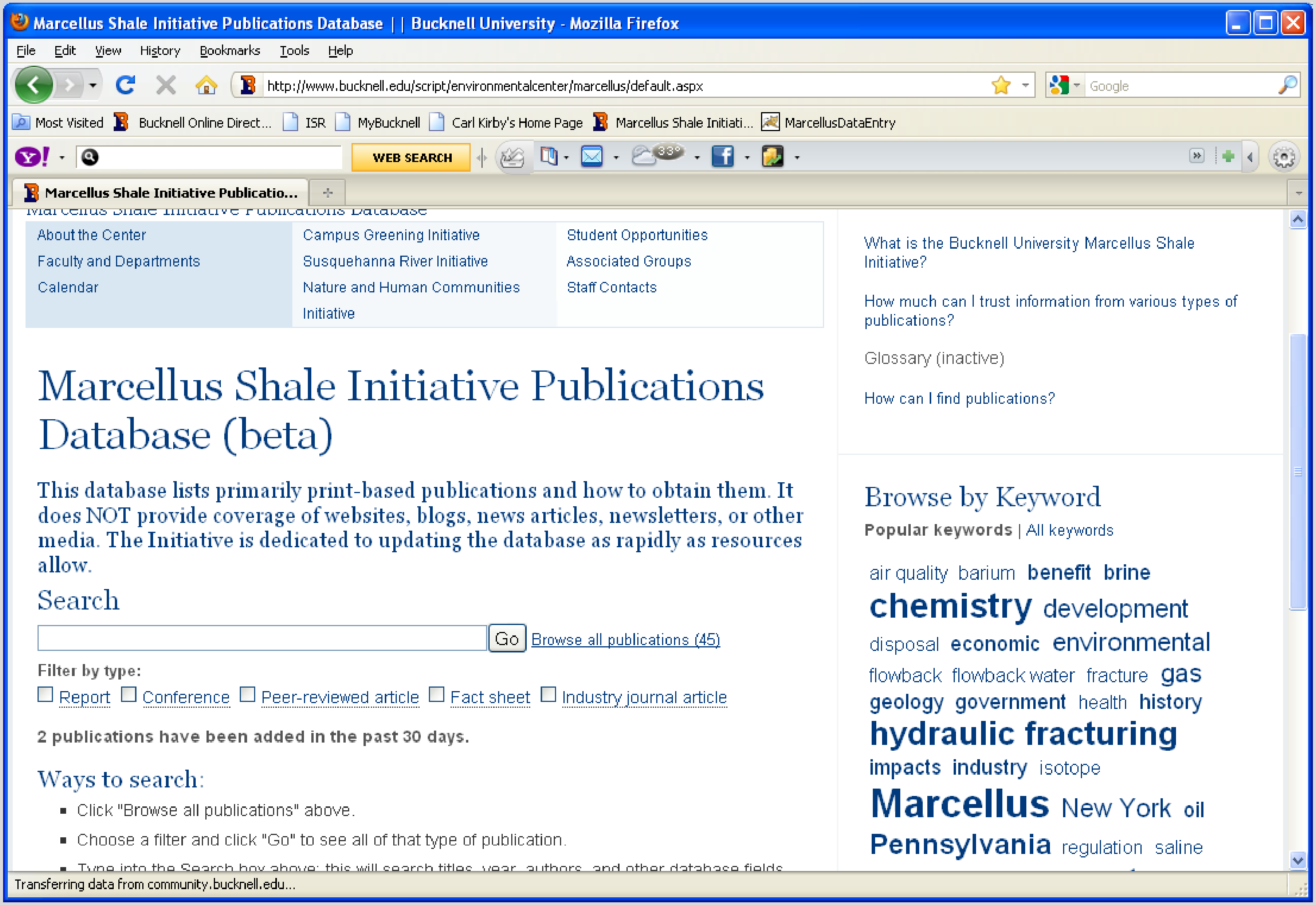
Arlington VA
February 24, 2011

Bucknell MSI Database



http://www.bucknell.edu/script/environmentalcenter/marcellus/default.aspx

Slickwater + Oil Field Brine (+/dissolution) = flowback water

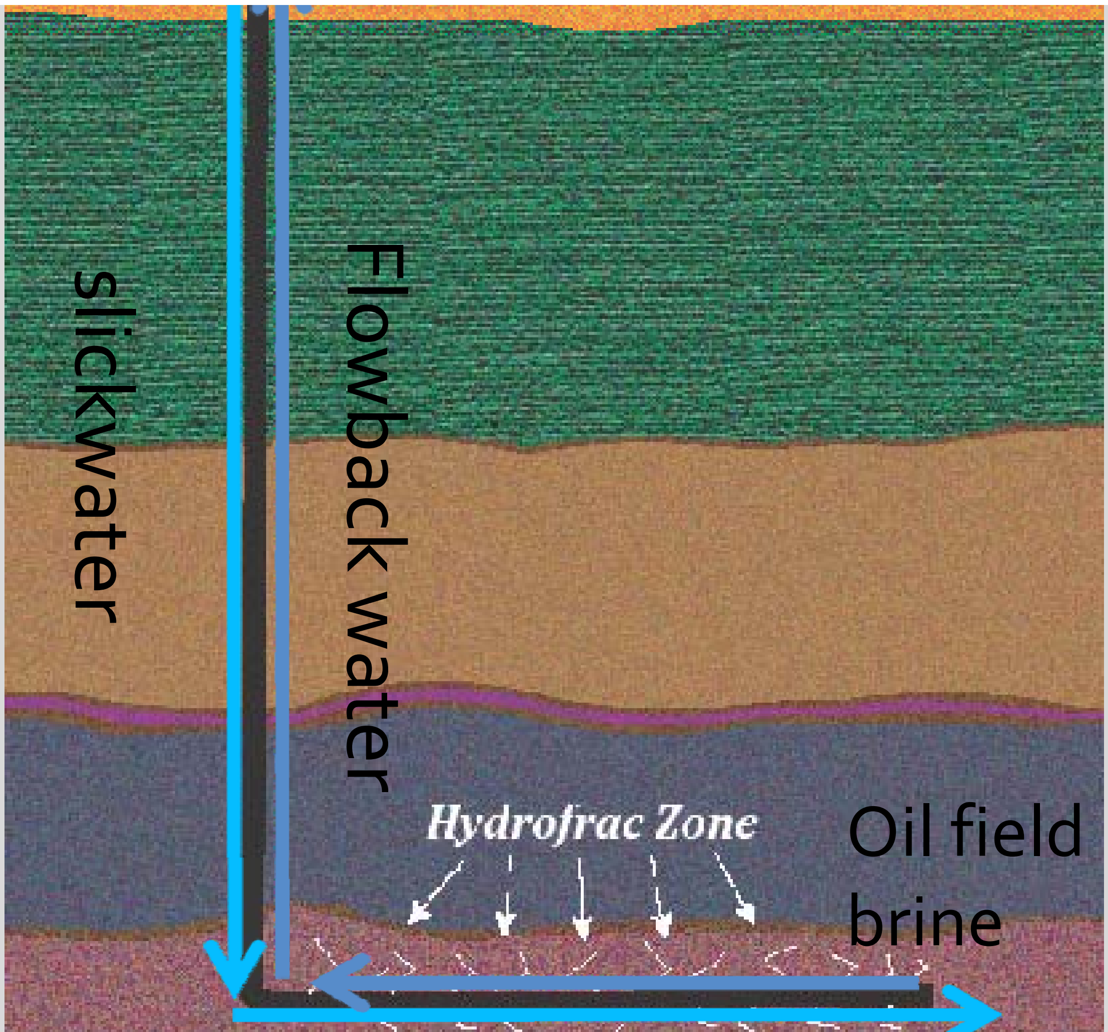


Diagram after Pritz, 2010

Flowback water must be stored, tranported, and then treated or reinjected

Photos from Molly Pritz '10

Marcellus core section with salt blebs along bedding

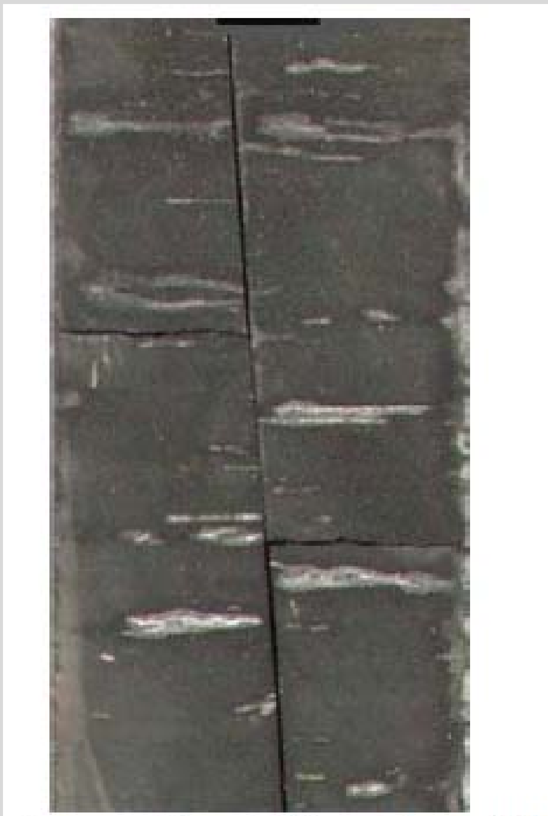


TABLE 6—RELATIVE SOLUBLE CATION CONTENT

Cation	Bulk Core	Salt Scraping
Ba	1%	2%
Ca	40%	42%
Fe	**46%**	5%
K	4%	7%
Mg	6%	3%
Na	2%	**40%**
Sr	1%	1%
Total	**100%**	**100%**

From Blauch et al., 2009

Marcellus Flowback Water Geochemistry

Data Sources:

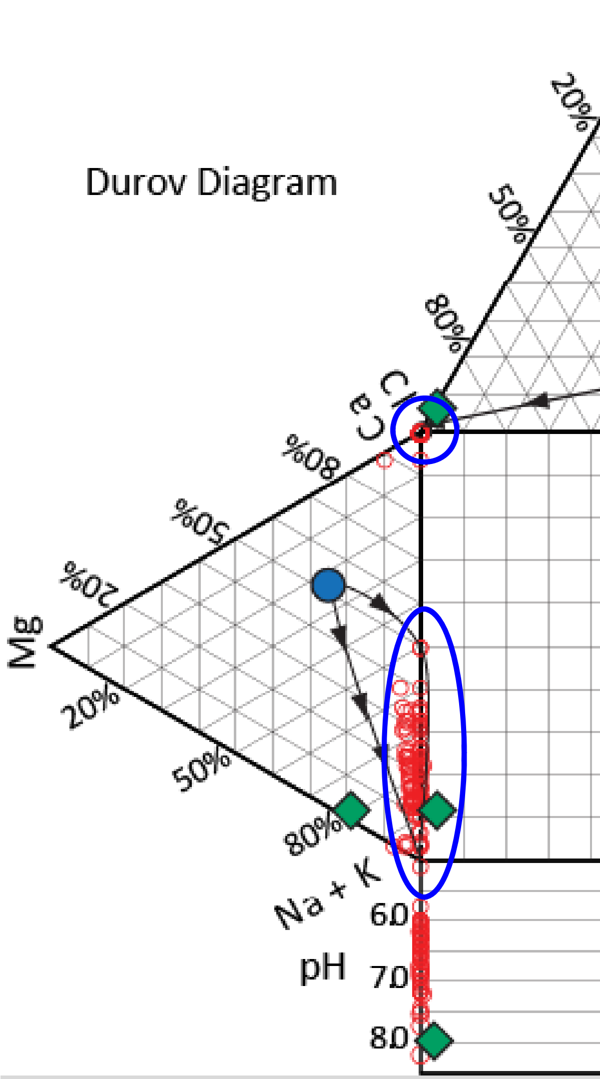
- 5 Bradford County, PA, wells
- Data from energy companies provided to a private wastewater treatment facility
- Data from energy companies provided to a private waste water hauler
- Data provided by energy companies to the PA Dept of Env Protection as required yearly by Form 26R (PA DEP, 2010)
- Data from a report prepared for the Marcellus Shale Coalition (Hayes, 2009)
- Data from Blauch *et al*., (2009).

Marcellus Flowback Water Geochemistry

- Na/Ca/Cl dominated
- High TDS, Specific Conductance
- Often have very high Ba, Sr
- Most are radioactive
- Low Mg, SO4
- Near-neutral pH

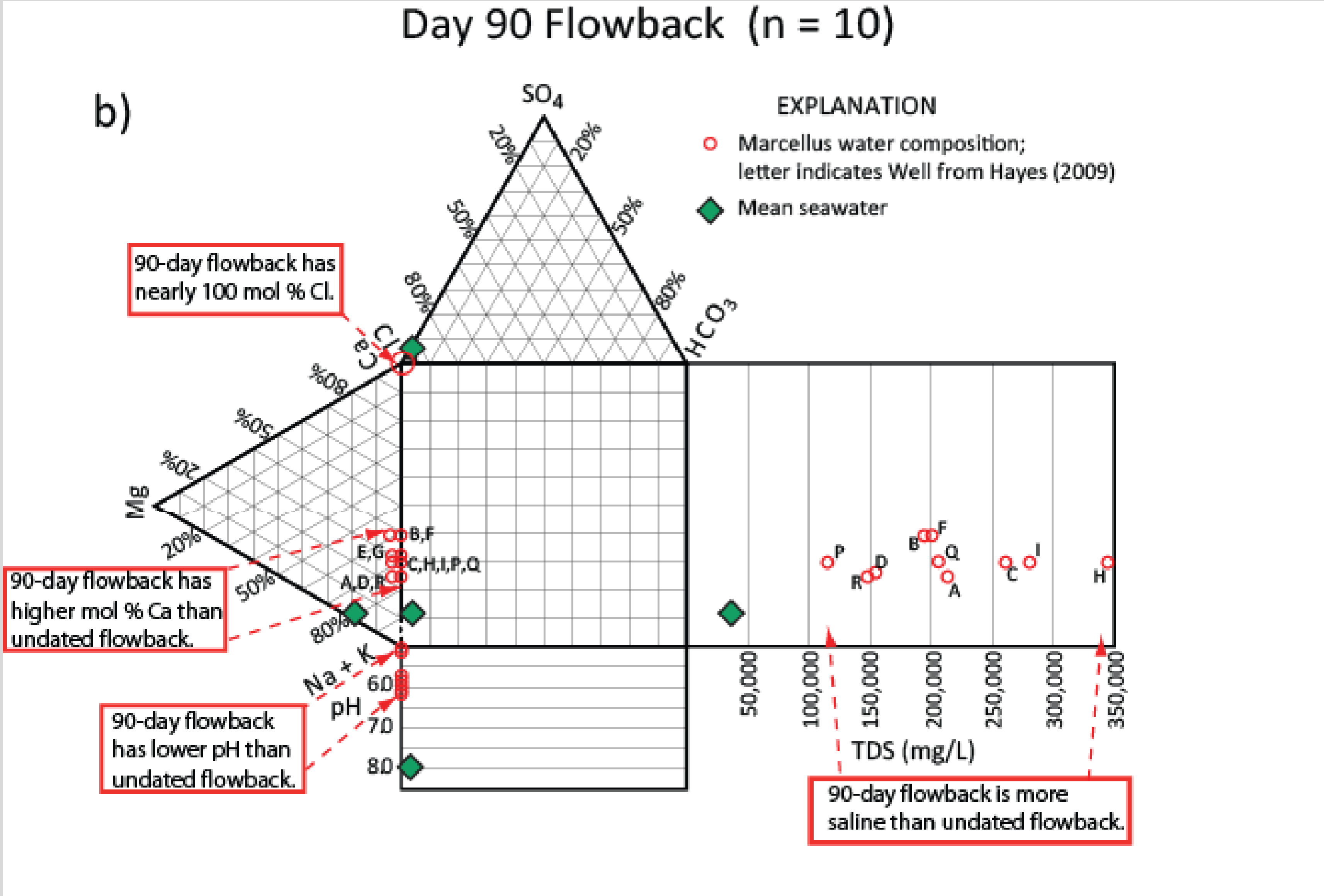
- Endocrine disruptors?? Other organics

Marcellus fracwater has distinctive Na/Ca/Cl signature

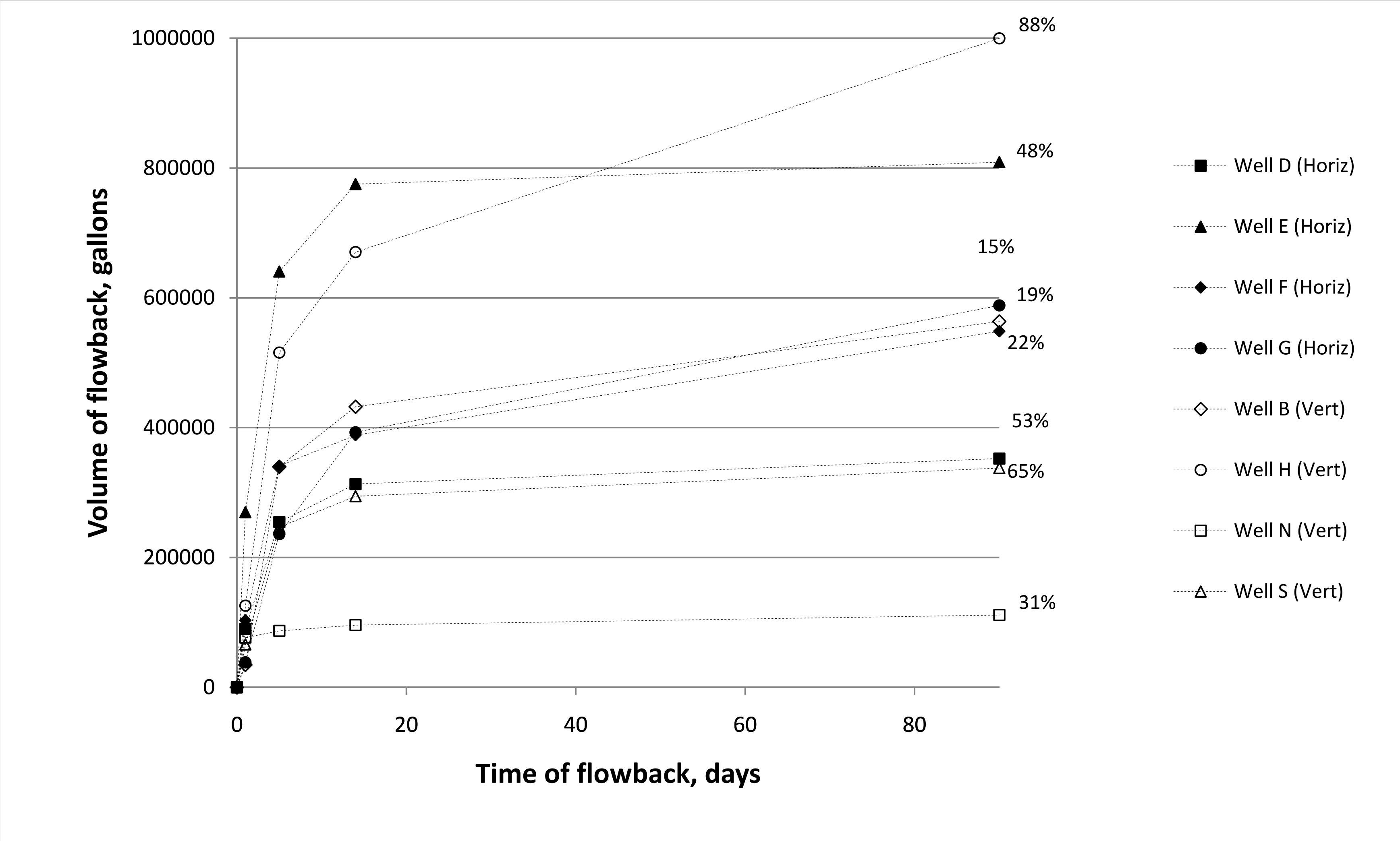


Data compiled by Molly Pritz

Marcellus Flowback Water Geochemistry

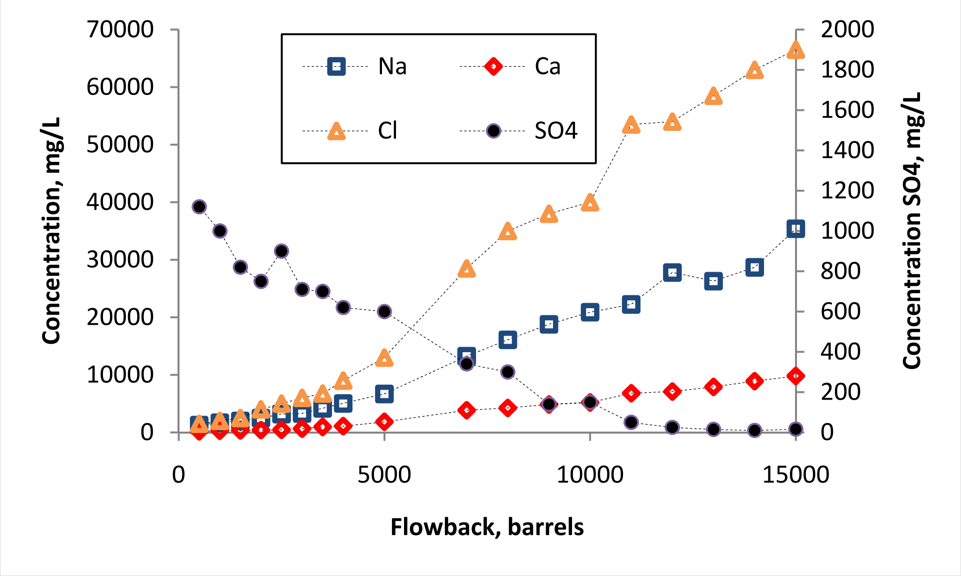


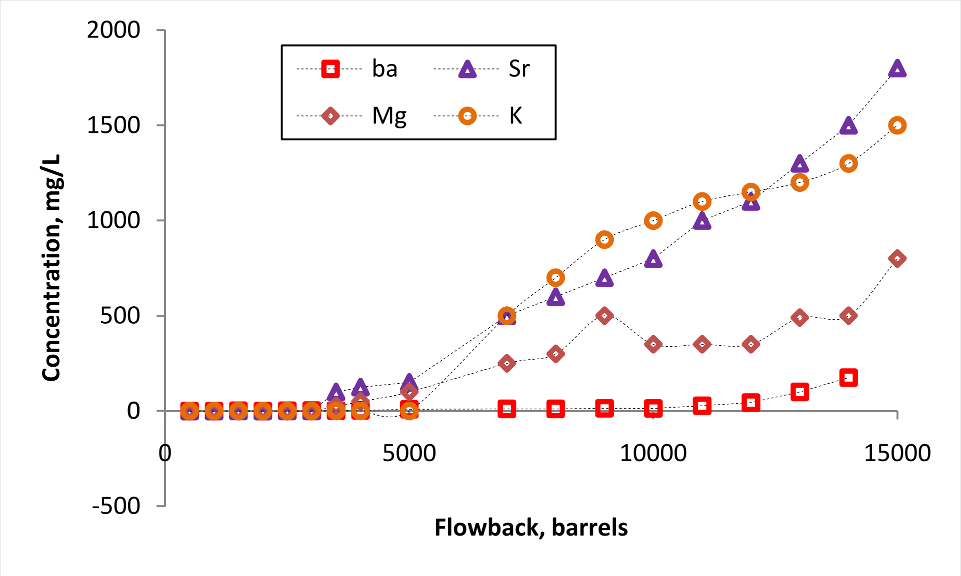
Volume of flowback water *versus* time of flowback from Marcellus wells



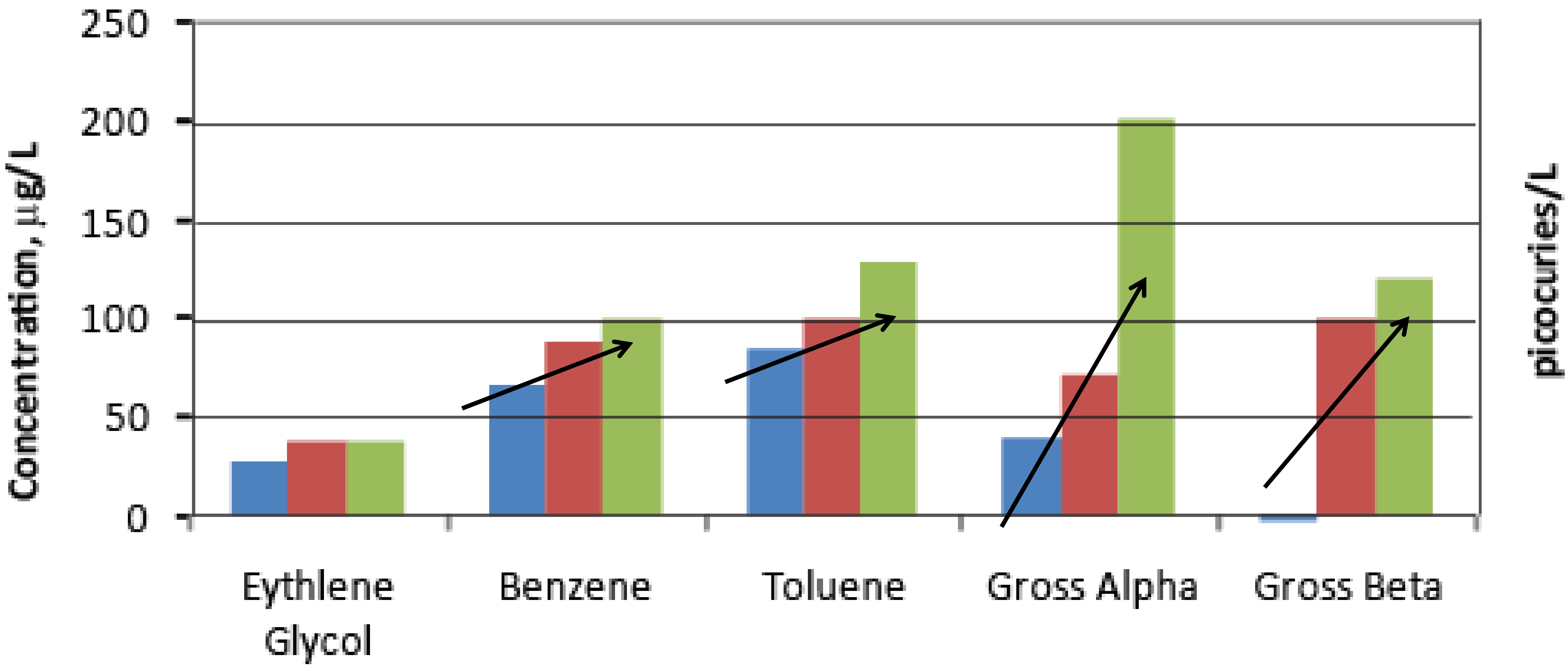
Data are from four horizontal and four vertical wells in Hayes (2009) that had data for 0 (injected water), 1, 5, 14, and 90-day flowback.

Salinity increases with flowback time



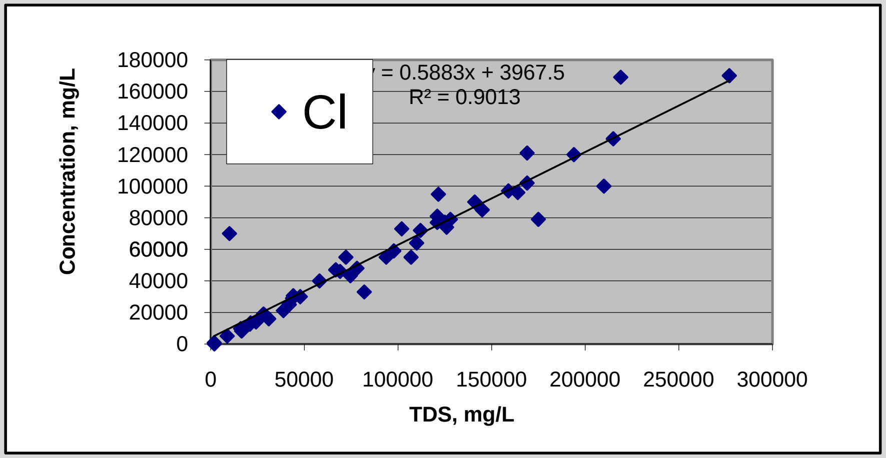


Data from Well A in Blauch *et al*. (2009).

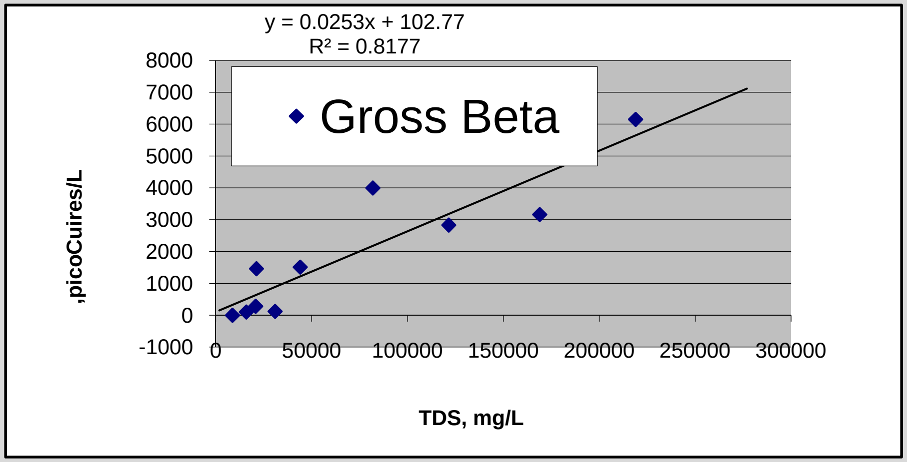

250
200
150
100
50
0
Concentration, µg/L
picocuries/L
Eythlene Glycol
Benzene
Toluene
Gross Alpha
Gross Beta

PA DEP

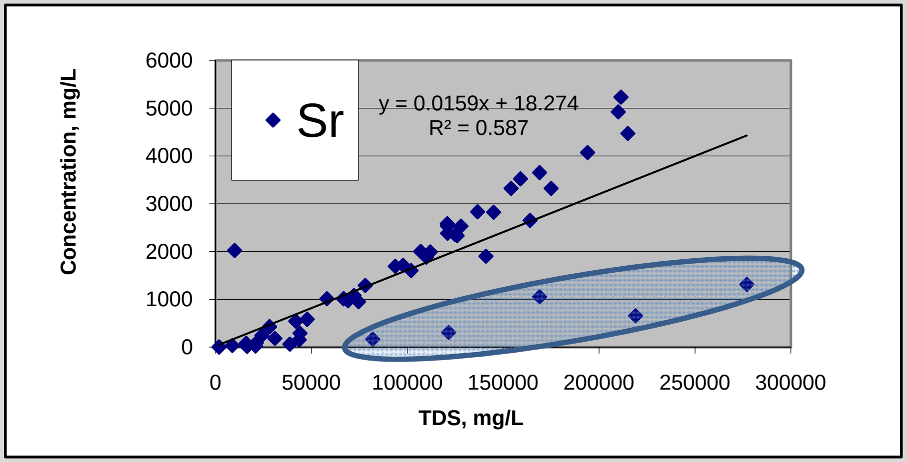
Some clear correlations with TDS

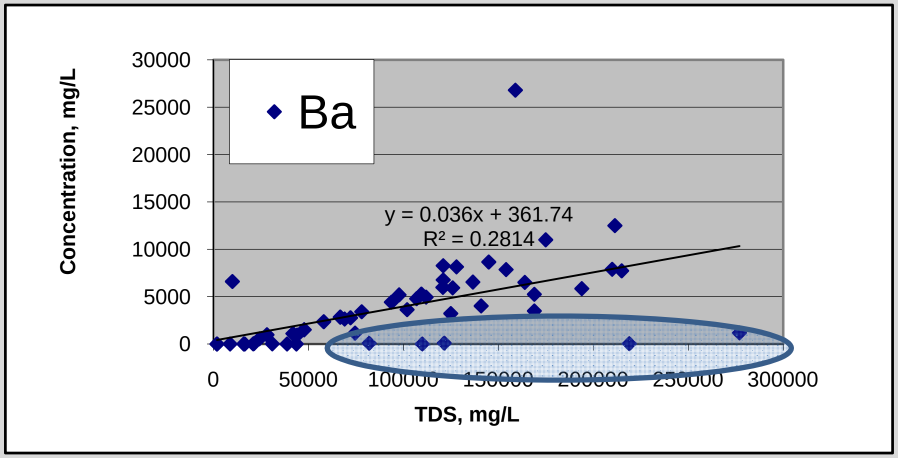


Some lack enough data for correlation

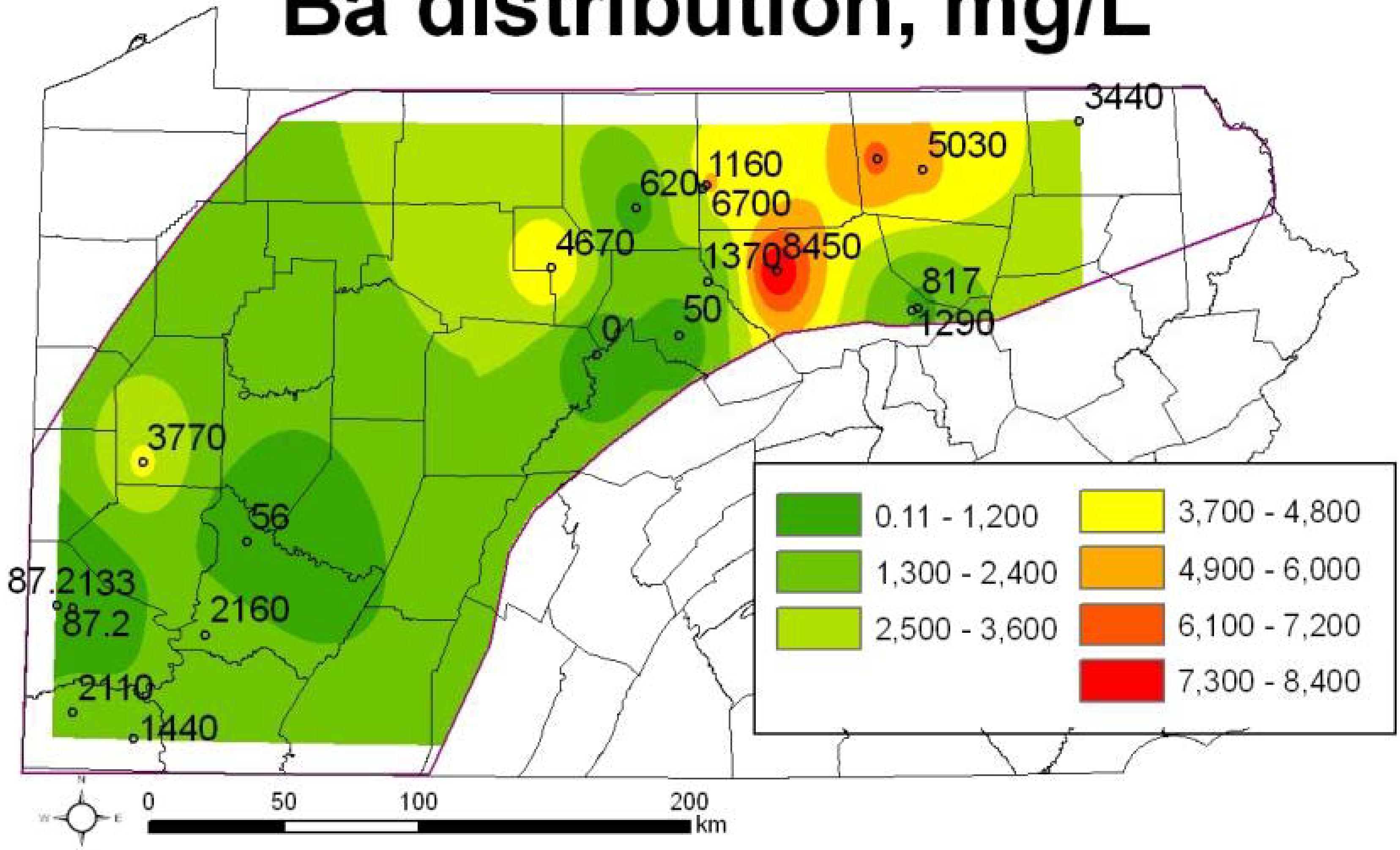


Some mixed correlations with TDS

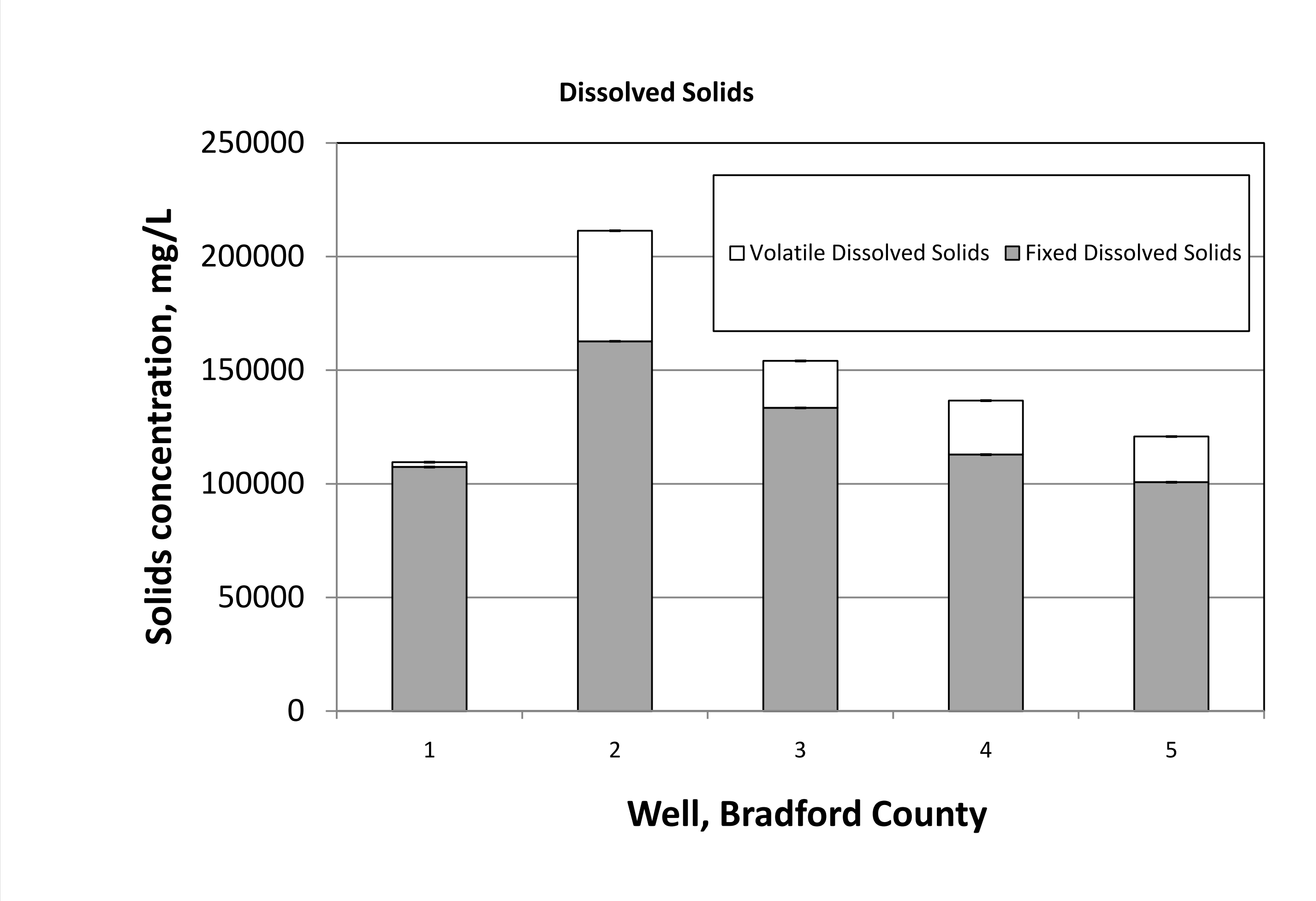




Ba distribution, mg/L

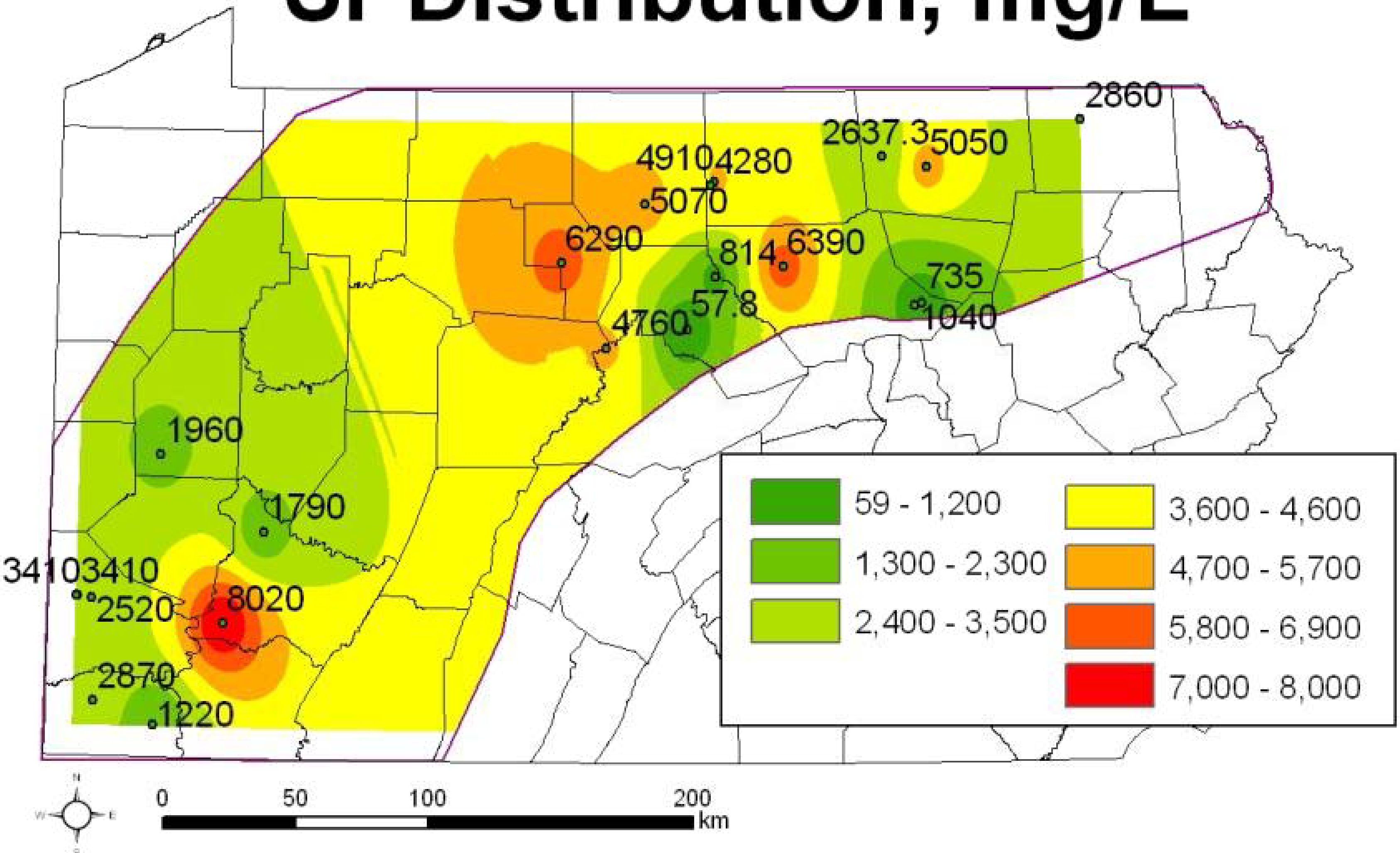


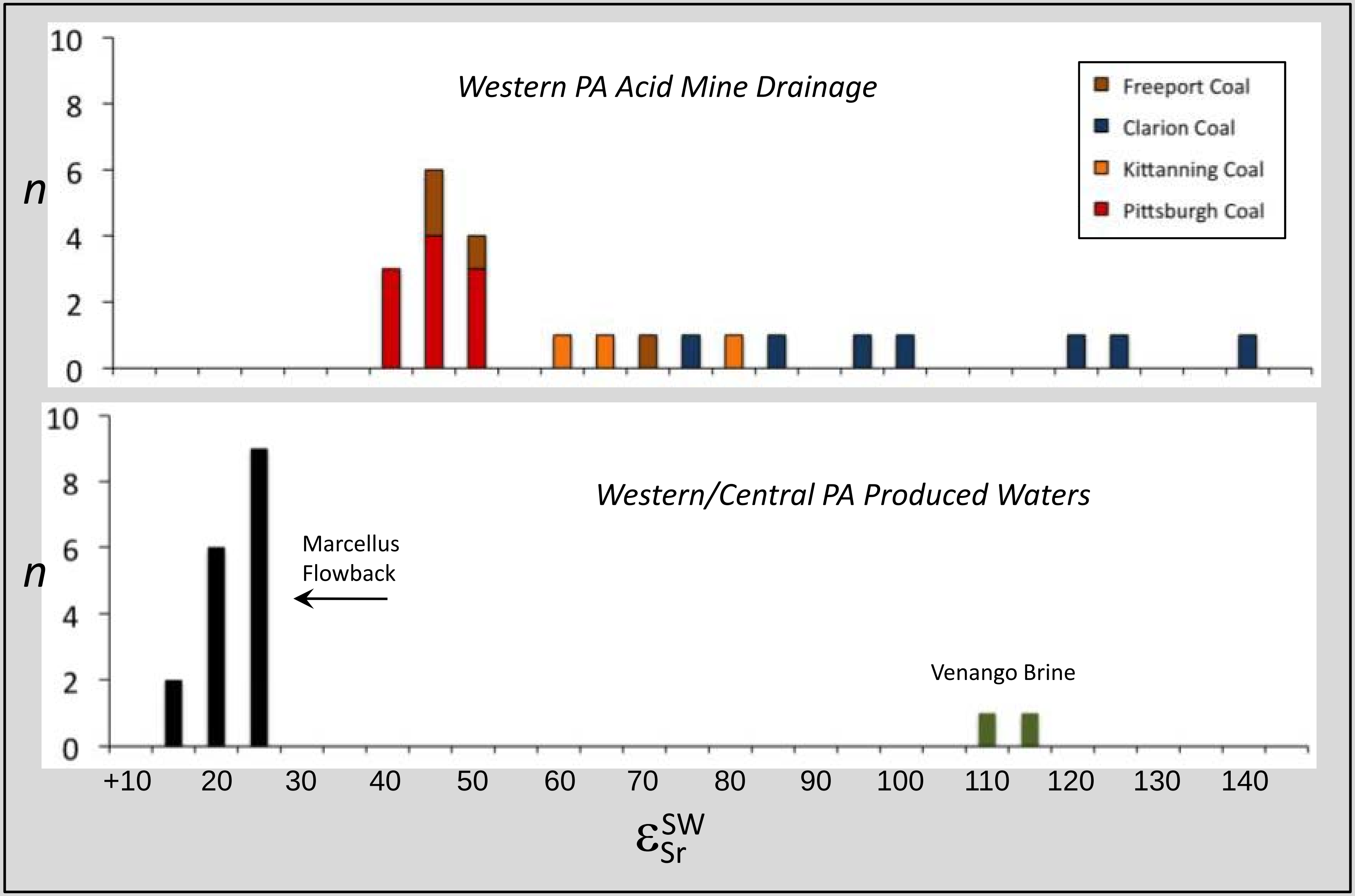
Volatile Dissolved Solids may suggest organic compounds that can complex metals such as Ba



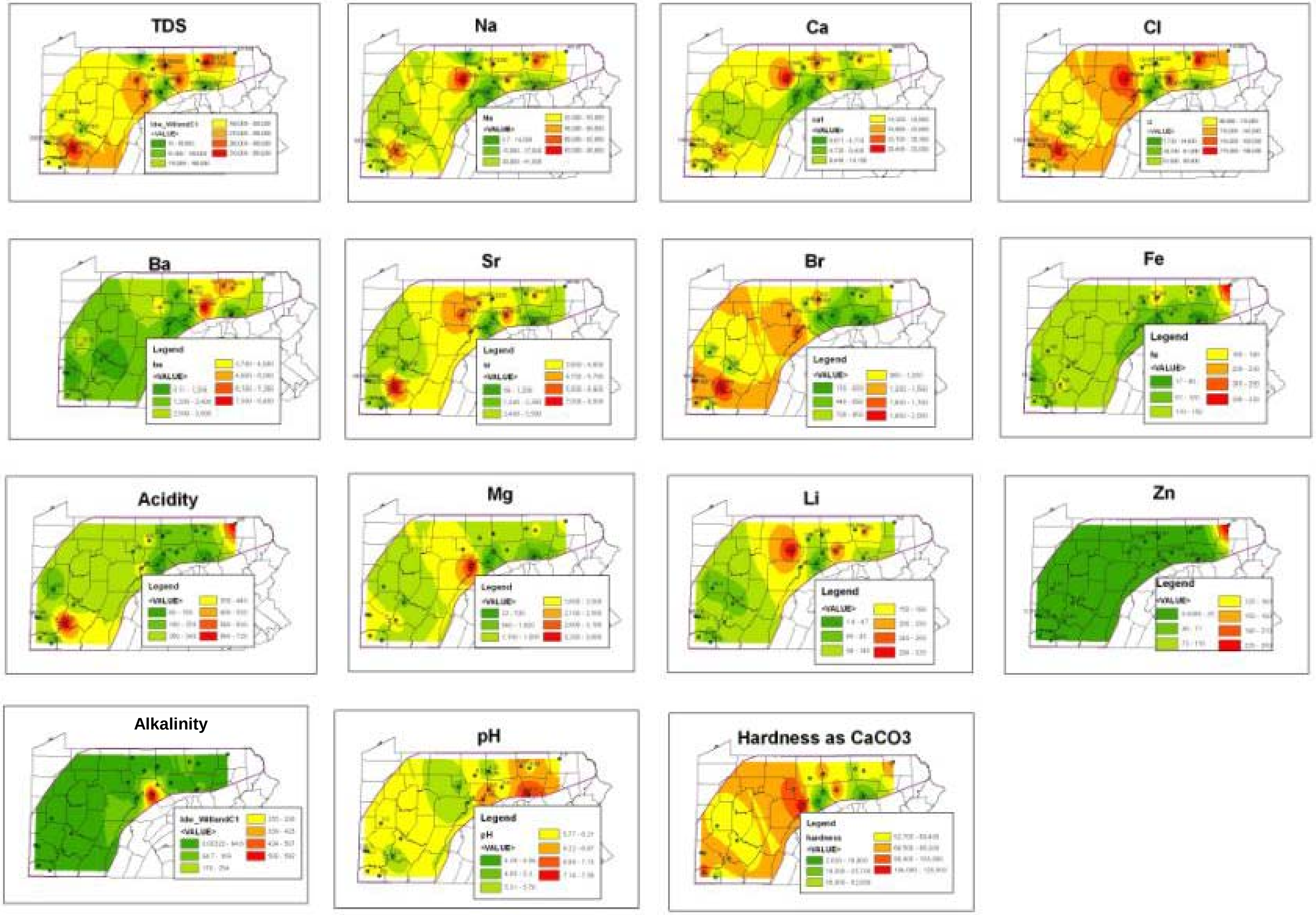
Data collected by Molly Pritz

Sr Distribution, mg/L

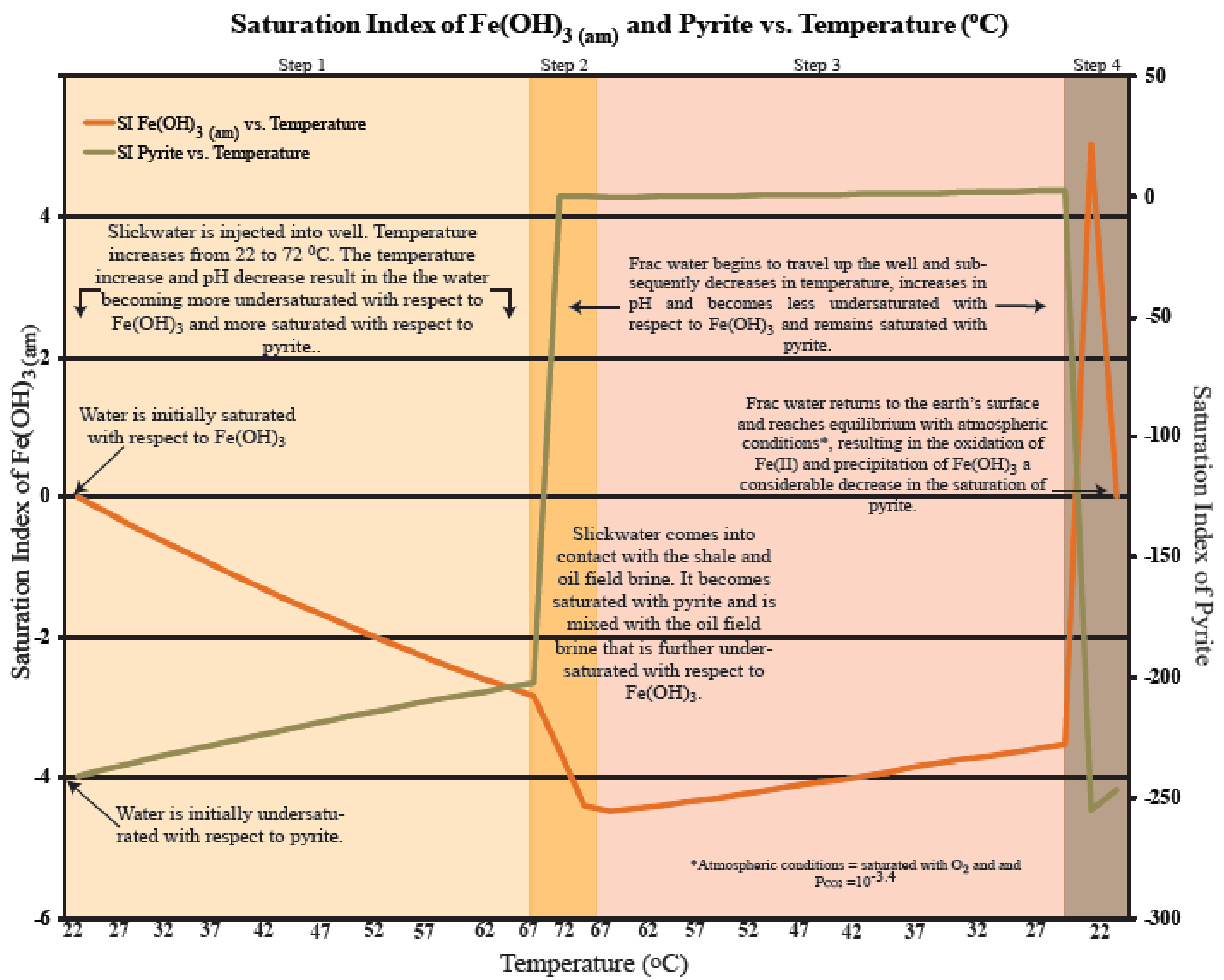




Chapman, Capo, Stewart, Kirby, 2011

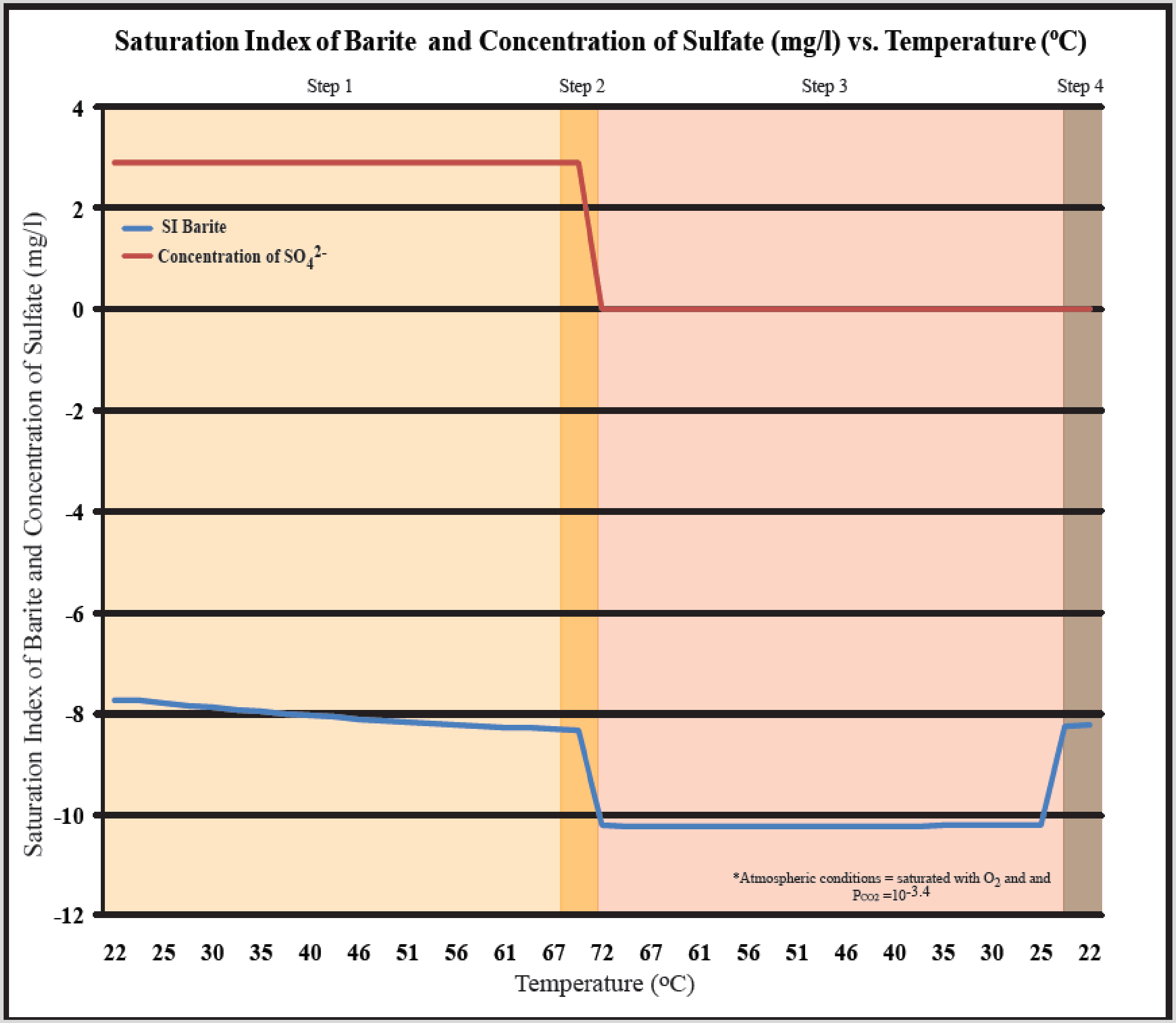

TDS
Na
Ca
Cl
Ba
Sr
Br
Fe
Acidity
Mg
Li
Zn
Alkalinity
pH
Hardness as CaCO3

Geochemical modeling (PHREEQCI)



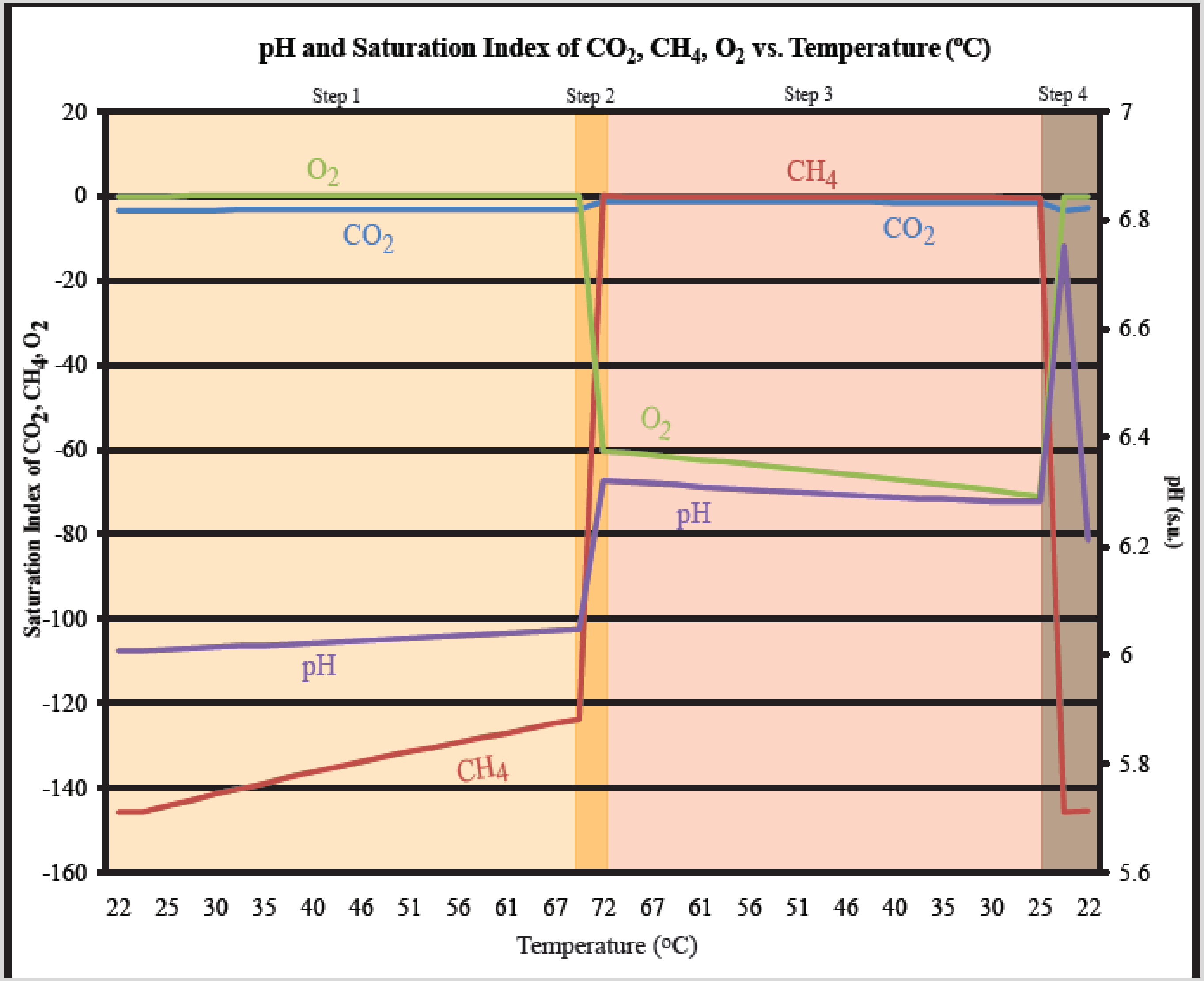
Geochemical modeling (PHREEQCI)

SI Barite, Conc. Of SO_4^{2-} vs. Temperature

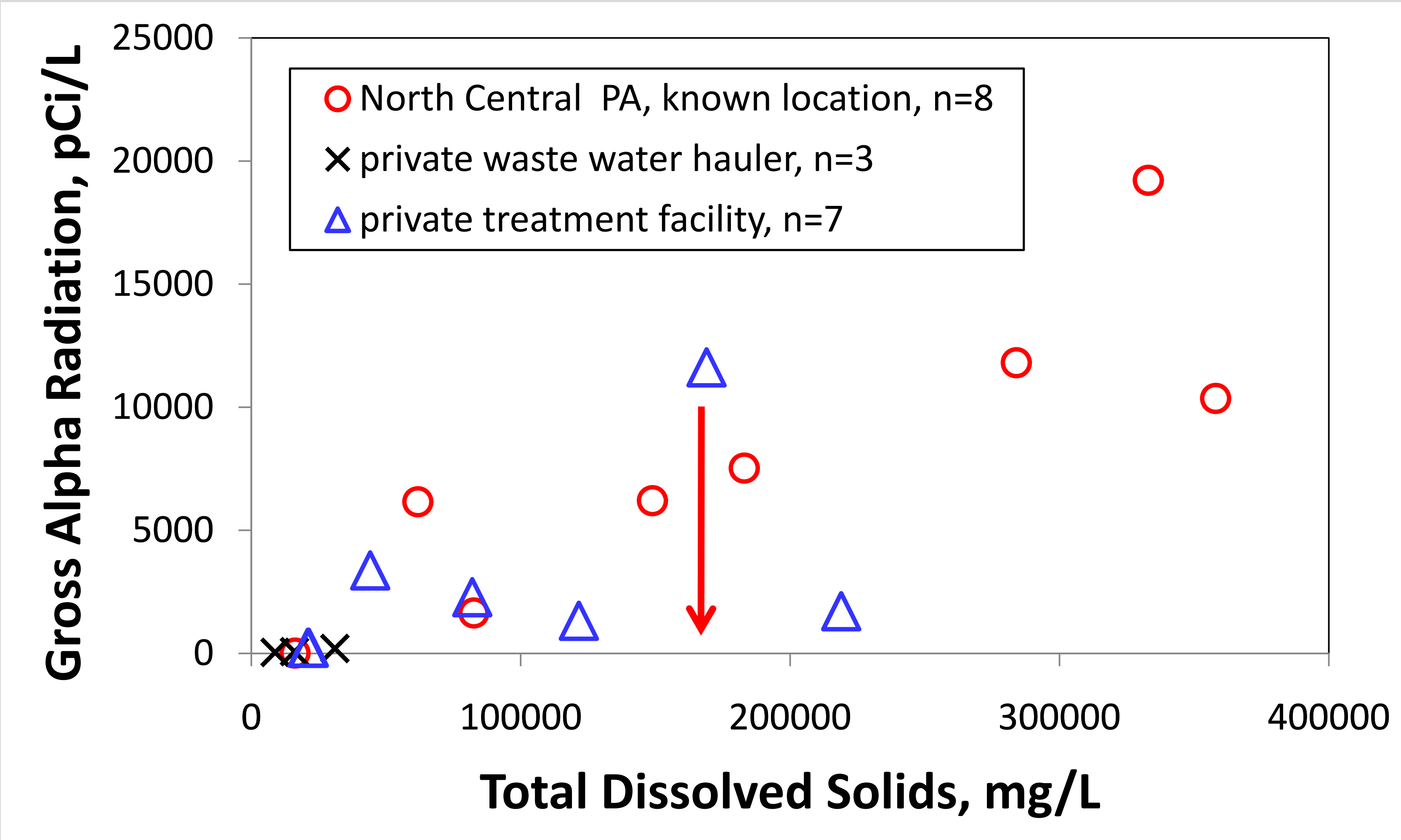


Geochemical modeling (PHREEQCI)

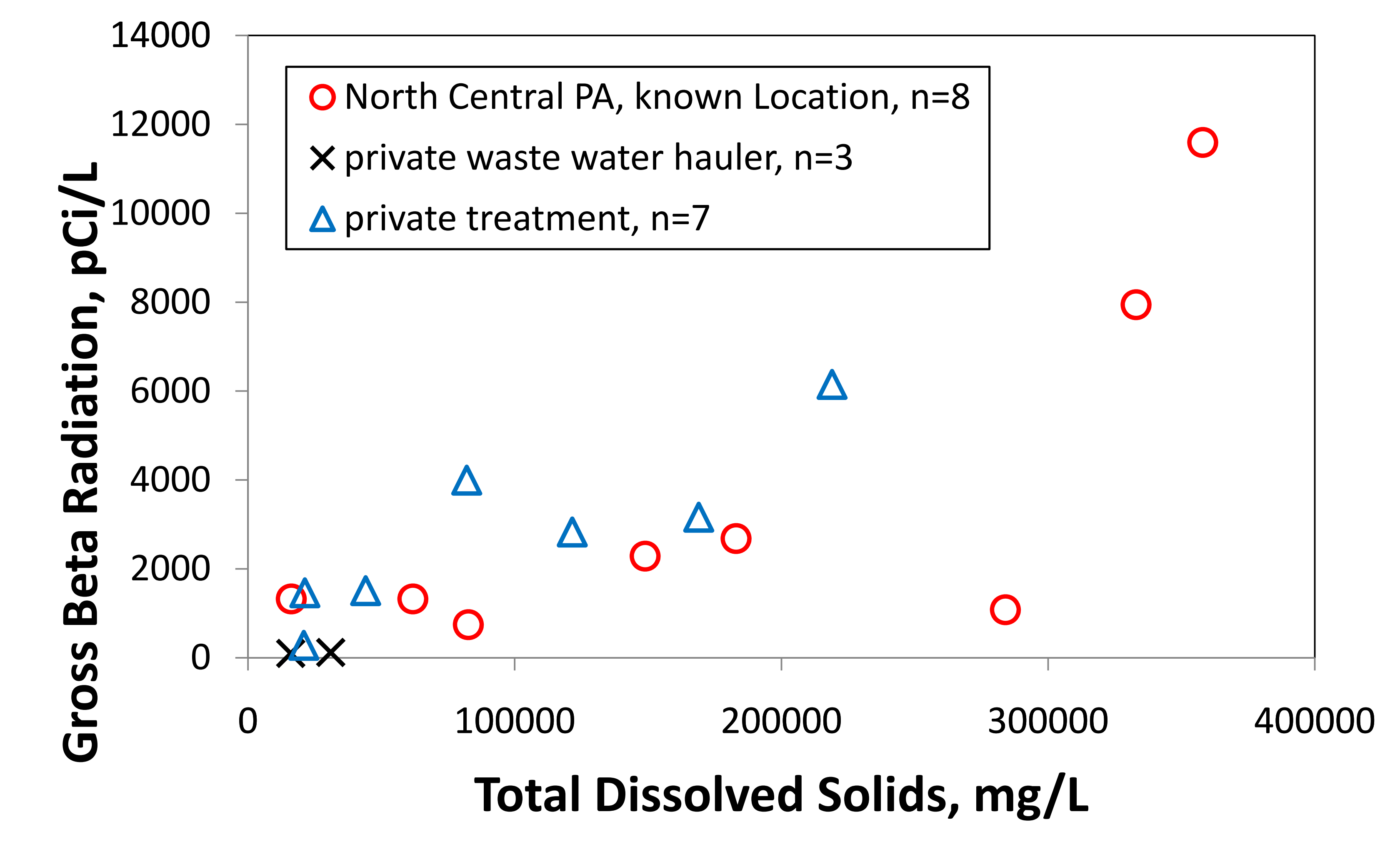
pH, SI Gases *vs*. T

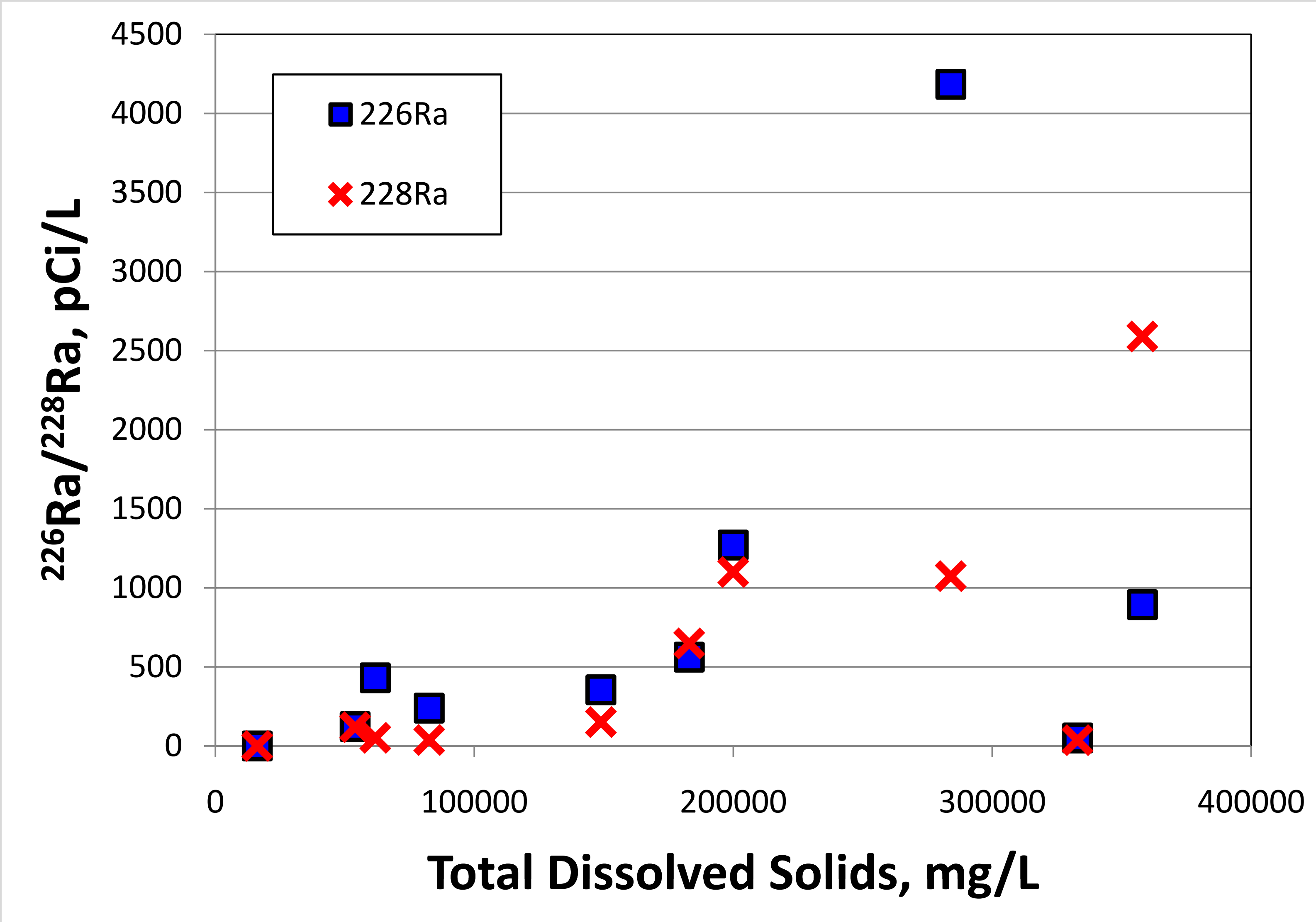


Radiation in flowback waters



Radiation in flowback waters

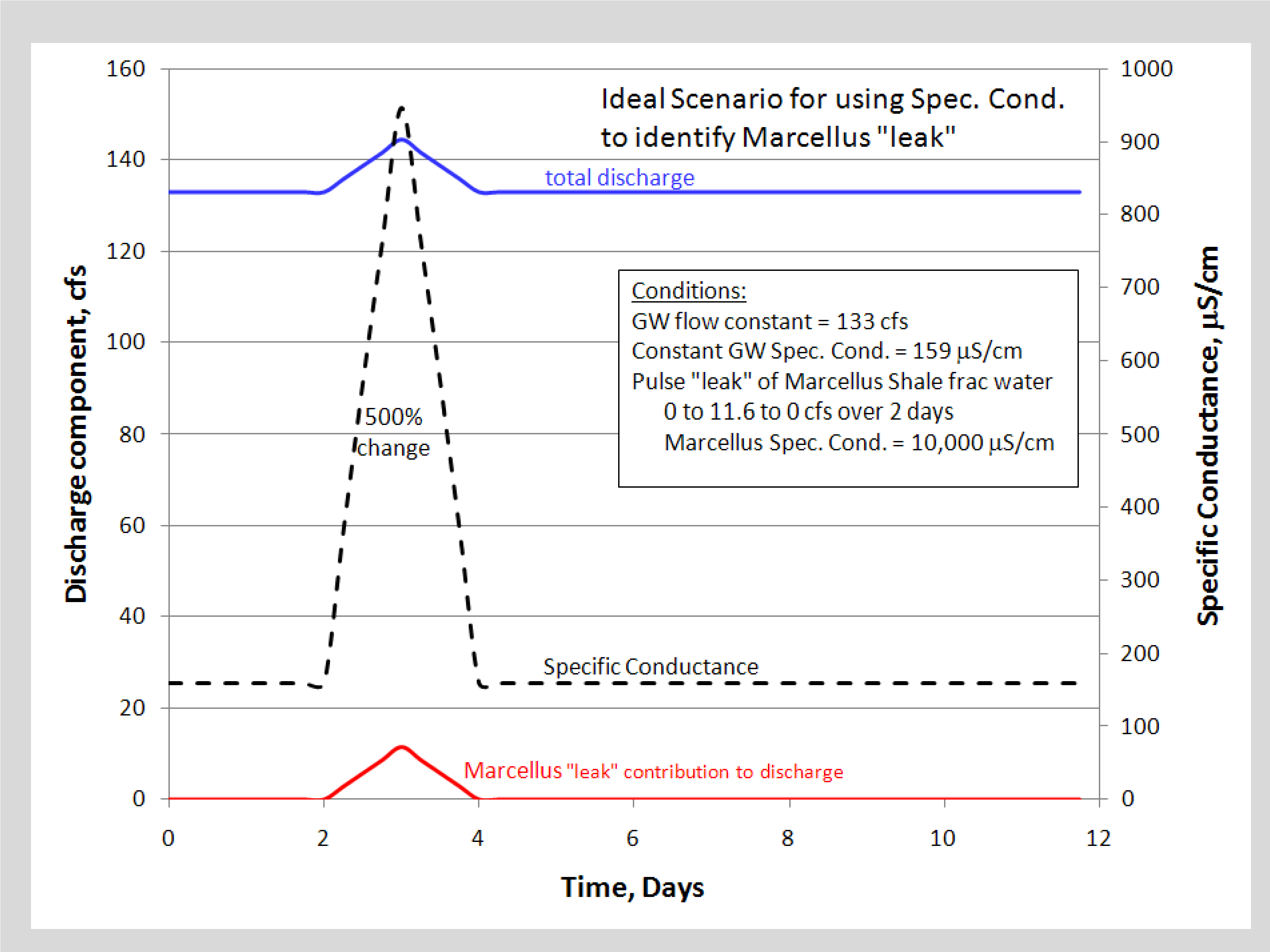




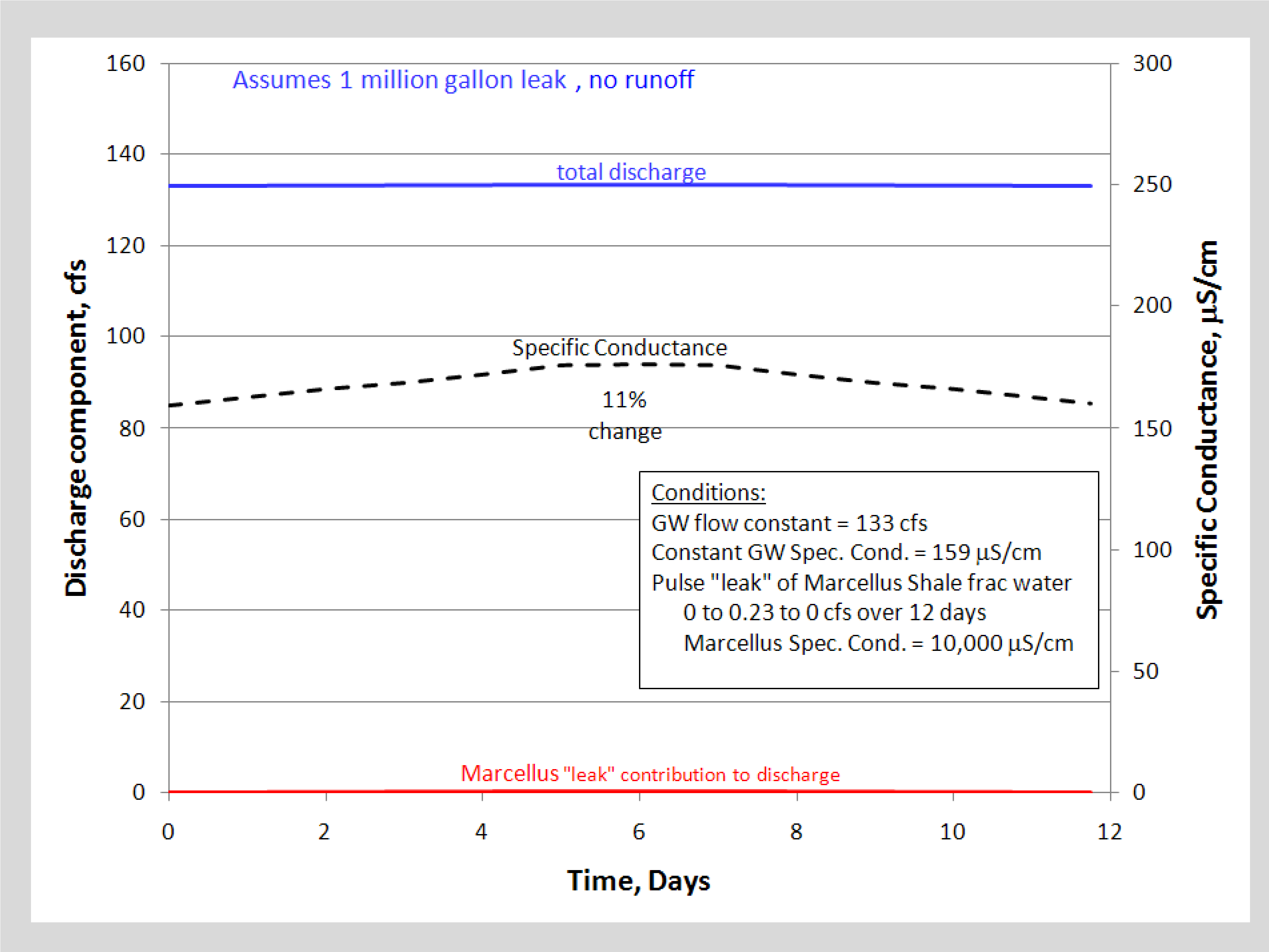
4500
4000
3500
3000
2500
2000
1500
1000
500
0
226Ra
228Ra
0
100000
200000
300000
400000
^{226}Ra/^{228}Ra, pCi/L
Total Dissolved Solids, mg/L

Will increases in stream conductivity tell us we have a Marcellus "leak"?

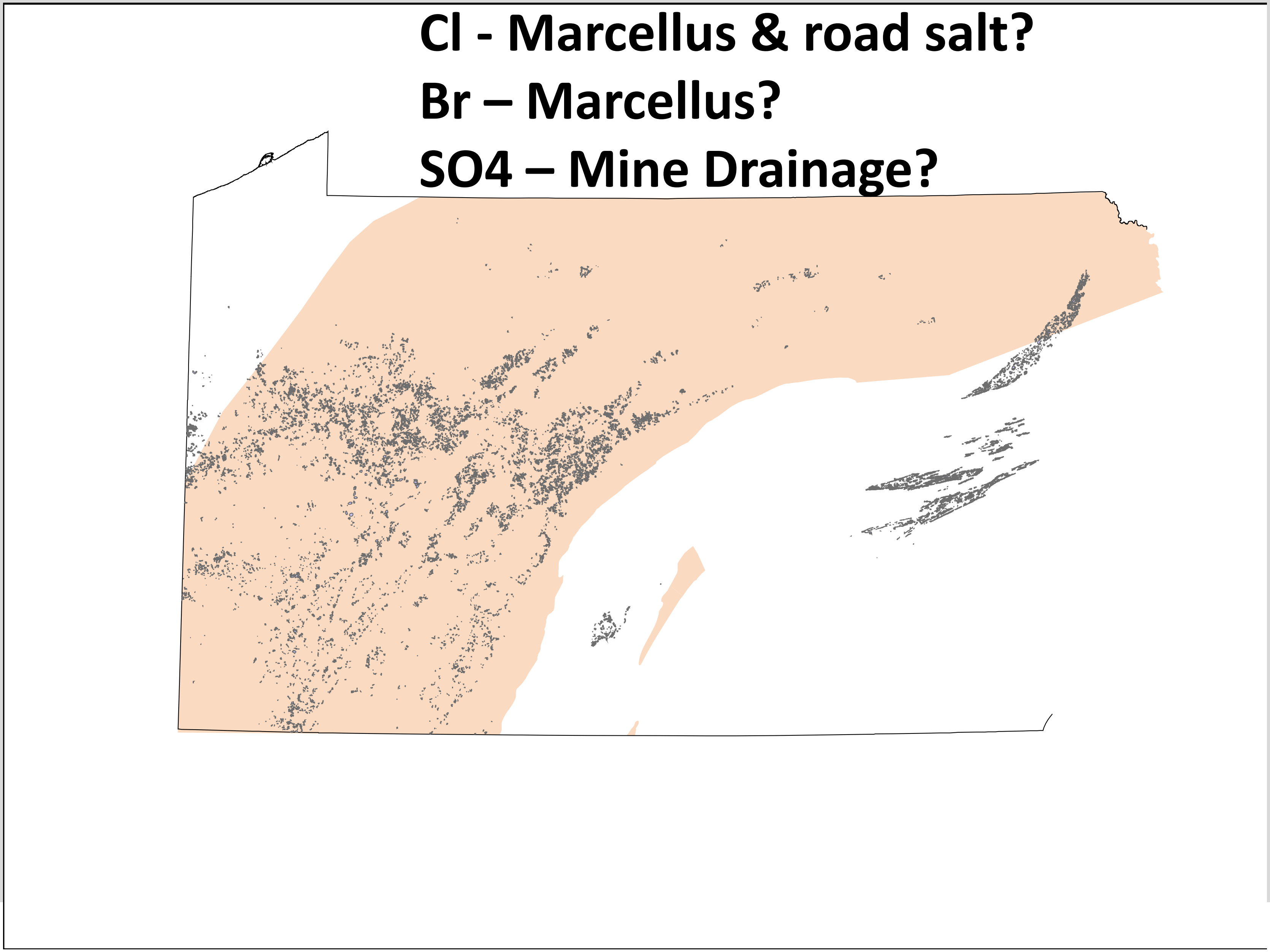
Not consistently.



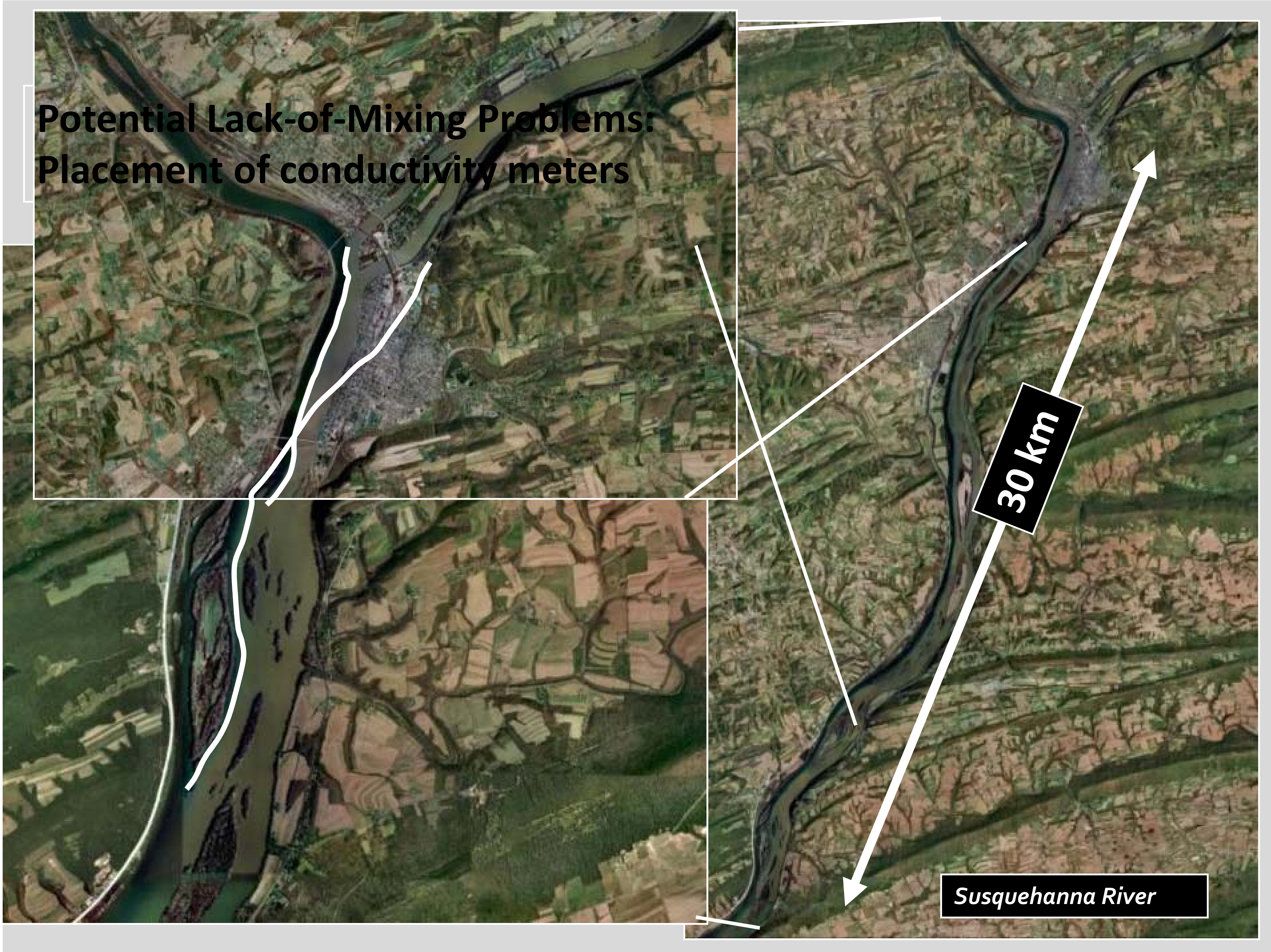
Ideal Scenario for using Spec. Cond.
to identify Marcellus "leak"
total discharge
Conditions:
GW flow constant = 133 cfs
Constant GW Spec. Cond. = 159 µS/cm
Pulse "leak" of Marcellus Shale frac water
0 to 11.6 to 0 cfs over 2 days
Marcellus Spec. Cond. = 10,000 µS/cm
500%
change
Specific Conductance
Marcellus "leak" contribution to discharge
Discharge component, cfs
Specific Conductance, µS/cm
Time, Days
0
20
40
60
80
100
120
140
160
0
100
200
300
400
500
600
700
800
900
1000
0
2
4
6
8
10
12


Assumes 1 million gallon leak , no runoff
total discharge
Specific Conductance
11%
change
Conditions:
GW flow constant = 133 cfs
Constant GW Spec. Cond. = 159 µS/cm
Pulse "leak" of Marcellus Shale frac water
0 to 0.23 to 0 cfs over 12 days
Marcellus Spec. Cond. = 10,000 µS/cm
Marcellus "leak" contribution to discharge
Discharge component, cfs
Specific Conductance, µS/cm
Time, Days
0
20
40
60
80
100
120
140
160
0
50
100
150
200
250
300
0
2
4
6
8
10
12

AMD and road salt can cause high conductivity. Can we distinguish Marcellus “leaks” from them with conductivity?



Potential Lack-of-Mixing Problems: Placement of conductivity meters



Questions?

Actual and
Potential Impacts

Bucknell University Marcellus Shale Initiative Goals

- Fund research in physical & social sciences, engineering, and humanities that will benefit all stakeholders.

- Comprehensive, objective web-based clearinghouse for:
  - accurate and verifiable (*i.e.*, peer-reviewed) scientific information
  - annotated non-scientific information from industry, regulatory agencies, print and web media, environmental groups, citizens' groups
    - hyperlinked
    - organized
    - searchable
    - critically evaluated

- Facilitate teaching and additional outreach efforts

Marcellus Shale in Outcrop

http://www.geosc.psu.edu/~engelder/marcellus/marcellus.html

Outline

- What & Where is the Marcellus Formation?
- Formation of the Marcellus & Natural Gas
- Horizontal Natural Gas Drilling
- Location of Drilling Activity in PA

Characterization of waters

- Chemical signature of fracwater

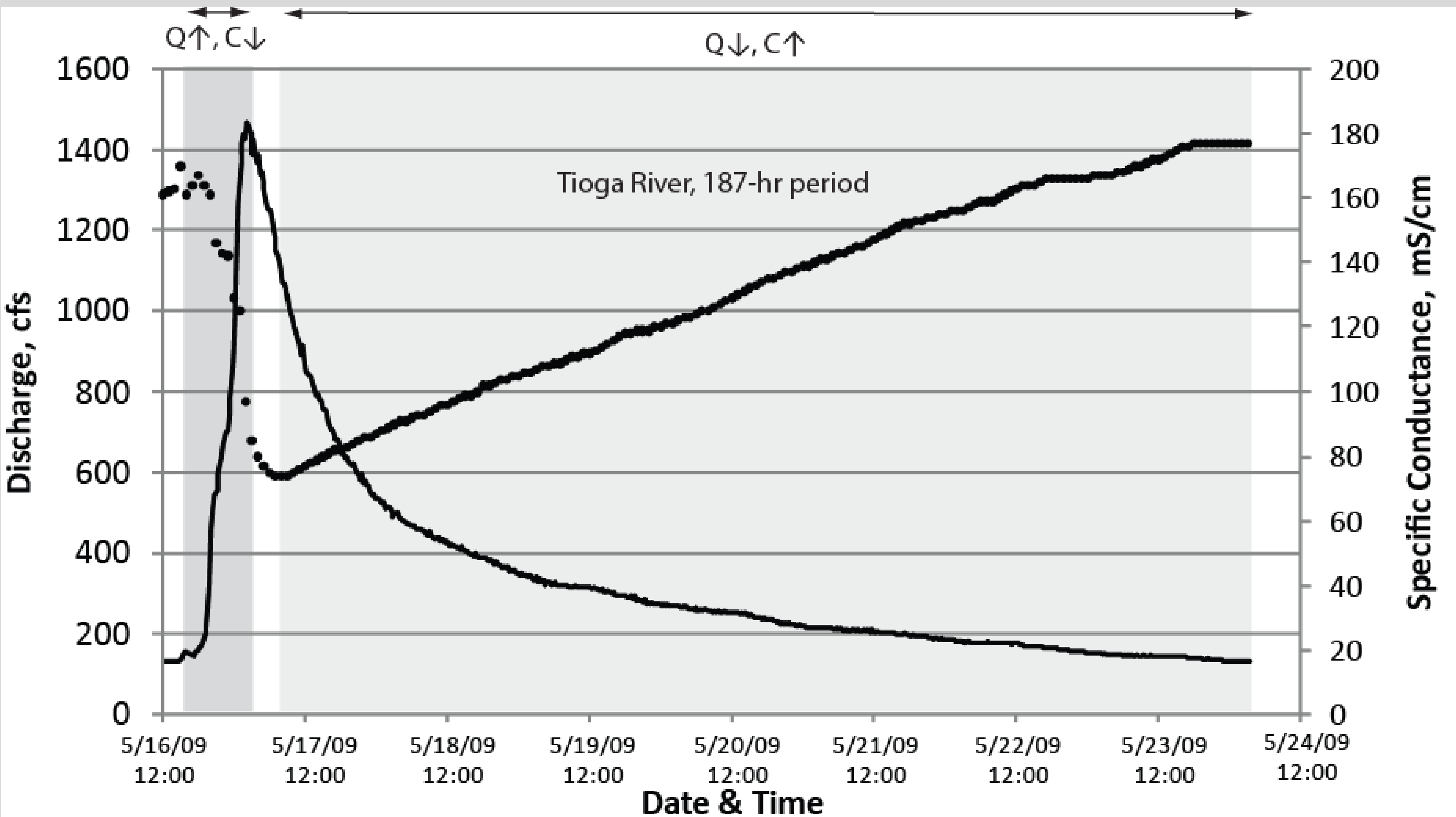
Monitoring?

- Discharge and conductivity with time
- Discharge vs. conductivity curves – hysteresis
- Mass balance modeling
- Problems associated with poor mixing

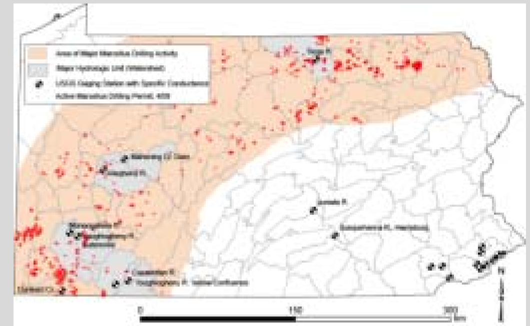
Actual and Potential Environmental Impacts

Perspective

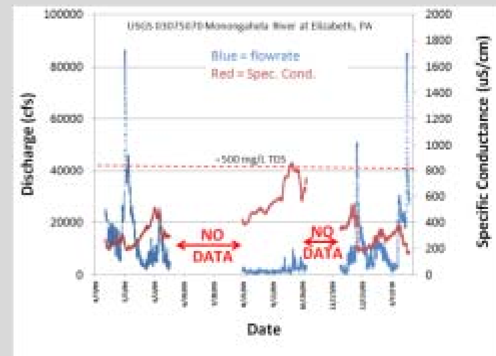
Could be Marcellus-influenced



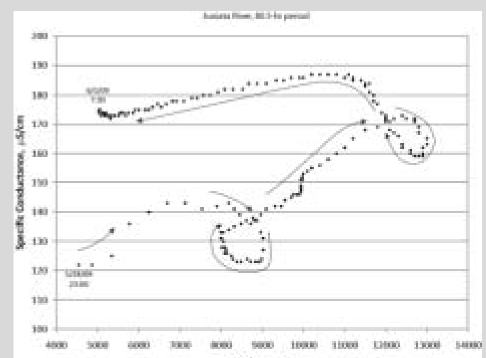
- **Inadequate coverage:**
  8 of 99 USGS gaging stations in PA measure SC. **These are on larger streams**.



- **Data Gaps:**
  Two years of hydrographs from 9 (7 in the Marcellus region) gaging stations that collect SC data showed **gaps in SC data between 4 and 71% of the time** for individual stations.



- **Hysteresis:**
  Plots of SC *vs.* Q for several time periods show considerable & variable hysteresis effects dependent upon the stream chosen and antecedent hydrologic conditions.



New York State SGEIS considers the following potential environmental impacts

6.1 Water Resources

•*6.1.1 Water Withdrawals*

  •*6.1.1.1 Reduced Stream Flow*

  •*6.1.1.2 Degradation of a Stream's Best Use*

  •*6.1.1.3 Impacts to Aquatic Habitat*

  •*6.1.1.4 Impacts to Aquatic Ecosystems*

  •*6.1.1.5 Impacts to Downstream Wetlands*

  •*6.1.1.6 Aquifer Depletion*

  •*6.1.1.7 Cumulative Water Withdrawal Impacts*

•6.1.2 Stormwater Runoff

•*6.1.3 Surface Spills and Releases at the Well Pad*

  •*6.1.3.1 Drilling*

  •*6.1.3.2 Hydraulic Fracturing Additives*

  •*6.1.3.3 Flowback Water*

•*6.1.4 Groundwater Impacts Associated With Well Drilling and Construction*

  •*6.1.4.1 Turbidity*

  •*6.1.4.2 Fluids Pumped Into the Well*

  •*6.1.4.3 Natural Gas Migration*

•*6.1.5 Hydraulic Fracturing Procedure*

  •*6.1.5.1 Wellbore Failure*

  •*6.1.5.2 Subsurface Pathways*

•*6.1.6 Waste Transport*

•*6.1.7 Centralized Flowback Water Surface Impoundments*

•*6.1.8 Fluid Discharges*

  •*6.1.8.1 Treatment Facilities*

  •*6.1.8.1 Disposal Wells*

•*6.1.9 Solids Disposal*

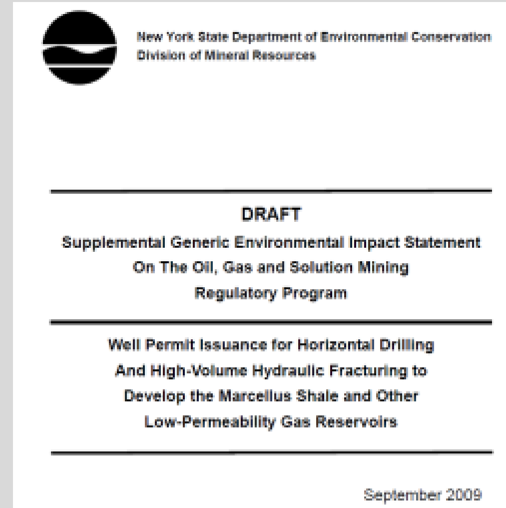
  •*6.1.9.1 Naturally Occurring Radioactive Material (NORM) Considerations - Cuttings*

  •*6.1.9.2 Cuttings Volume*

  •*6.1.9.3 Cuttings and Liner Associated With Mud-Drilling*

•*6.1.10 Potential Impacts to Subsurface NYC Water Supply Infrastructure*

•*6.1.11 Degradation of New York City's Drinking Water Supply*



New York State Department of Environmental Conservation
Division of Mineral Resources

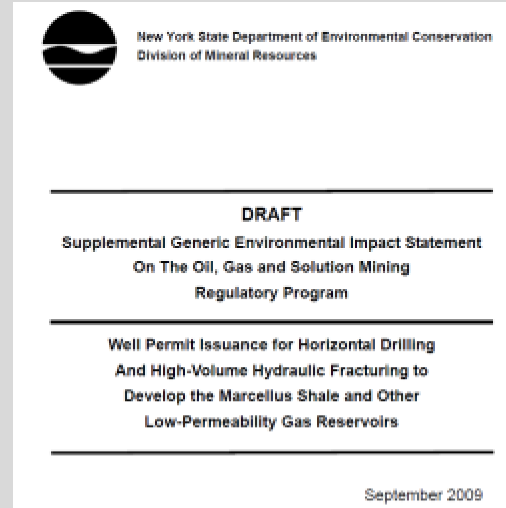
DRAFT

Supplemental Generic Environmental Impact Statement
On The Oil, Gas and Solution Mining
Regulatory Program

Well Permit Issuance for Horizontal Drilling
And High-Volume Hydraulic Fracturing to
Develop the Marcellus Shale and Other
Low-Permeability Gas Reservoirs

September 2009

New York State SGEIS considers
the following potential environmental impacts



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September 2009

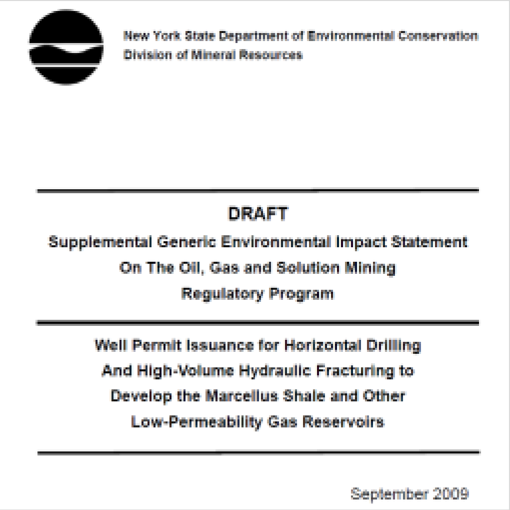
6.2 Floodplains
6.X Primary and Principal Aquifers
6.3 Freshwater Wetlands
6.4 Ecosystems and Wildlife

- *6.4.1 Invasive Species*
    - *6.4.1.1 Terrestrial*
    - *6.4.1.2 Aquatic*
    - *6.4.2 Centralized Flowback Water Surface Impoundments*

New York State SGEIS considers The following potential environmental impacts

6.5 Air Quality

- *6.5.1 Regulatory Analysis*
  - *6.5.1.1 NOx - Internal Combustion Engine Emissions*
  - *6.5.1.2 Natural Gas Production Facilities NESHAP 40 CFR Part 63, Subpart HH (Glycol*
  - *Dehydrators)*
  - *6.5.1.3 Flaring Versus Venting of Wellsite Air Emissions*
  - *6.5.1.4 Number of Wells Per Pad Site*
  - *6.5.1.5 Emissions Tables*
  - *6.5.1.6 Offsite Gas Gathering Station Engine*
  - *6.5.1.7 Natural Gas Condensate Tanks*
  - *6.5.1.8 Potential Emission of Fracturing Water Additives from Surface Impoundments*
- *6.5.2 Air Quality Impact Assessment*
- *6.6.1 Greenhouse Gases*
- *6.6.2 Emissions from Oil and Gas Operations*
  - *6.6.2.1 Vented Emissions*
  - *6.6.2.2 Combustion Emissions*
  - *6.6.2.3 Fugitive Emissions*
- *6.6.3 Emissions Source Characterization*
- *6.6.4 Emission Rates*
- *6.6.5 Drilling Rig Mobilization, Site Preparation and Demobilization*
- *6.6.6 Completion Rig Mobilization and Demobilization*
- *6.6.7 Well Drilling*
- *6.6.8 Well Completion*
- *6.6.9 Well Production*



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September 2009

6.7 Centralized Flowback Water Surface Impoundments
6.8 Naturally Occurring Radioactive Materials in the Marcellus Shale
6.9 Visual Impacts
6.10 Noise
6.11 Road Use

2nd Law of Thermodynamics

"Useful energy is lost in any physical or chemical transformation"

It takes (fossil fuel) energy to produce energy, so each added step makes a fuel less efficient than if it is used more directly.

Greenhouse gasses – how many ft^3 of natural gas equivalent (oil, gas, coal) does it take to produce 1 ft^3 of natural gas?

Slickwater additives

Table 2: Fracturing Fluid Additives, Main Compounds and Common Uses.		
Additive Type	**Main Compound**	**Common Use of Main Compound**
Acid	Hydrochloric acid or muriatic acid	Swimming pool chemical and cleaner
Biocide	Glutaraldehyde	Cold sterilant in health care industry
Breaker	Sodium Chloride	Food preservative
Corrosion inhibitor	N,n-dimethyl formamide	Used as a crystallization medium in Pharmaceutical Industry
Friction Reducer	Petroleum distillate	Cosmetics including hair, make-up, nail and skin products
Gel	Guar gum or hydroxyethyl cellulose	Thickener used in cosmetics, sauces and salad dressings.
Iron Control	2-hydroxy-1,2,3-propanetricaboxylic acid	Citric Acid it is used to remove lime deposits Lemon Juice ~7% Citric Acid
Oxygen scavenger	Ammonium bisulfite	Used in cosmetics
Proppant	Silica, quartz sand	Play Sand
Scale inhibitor	Ethylene glycol	Automotive antifreeze and de-icing agent

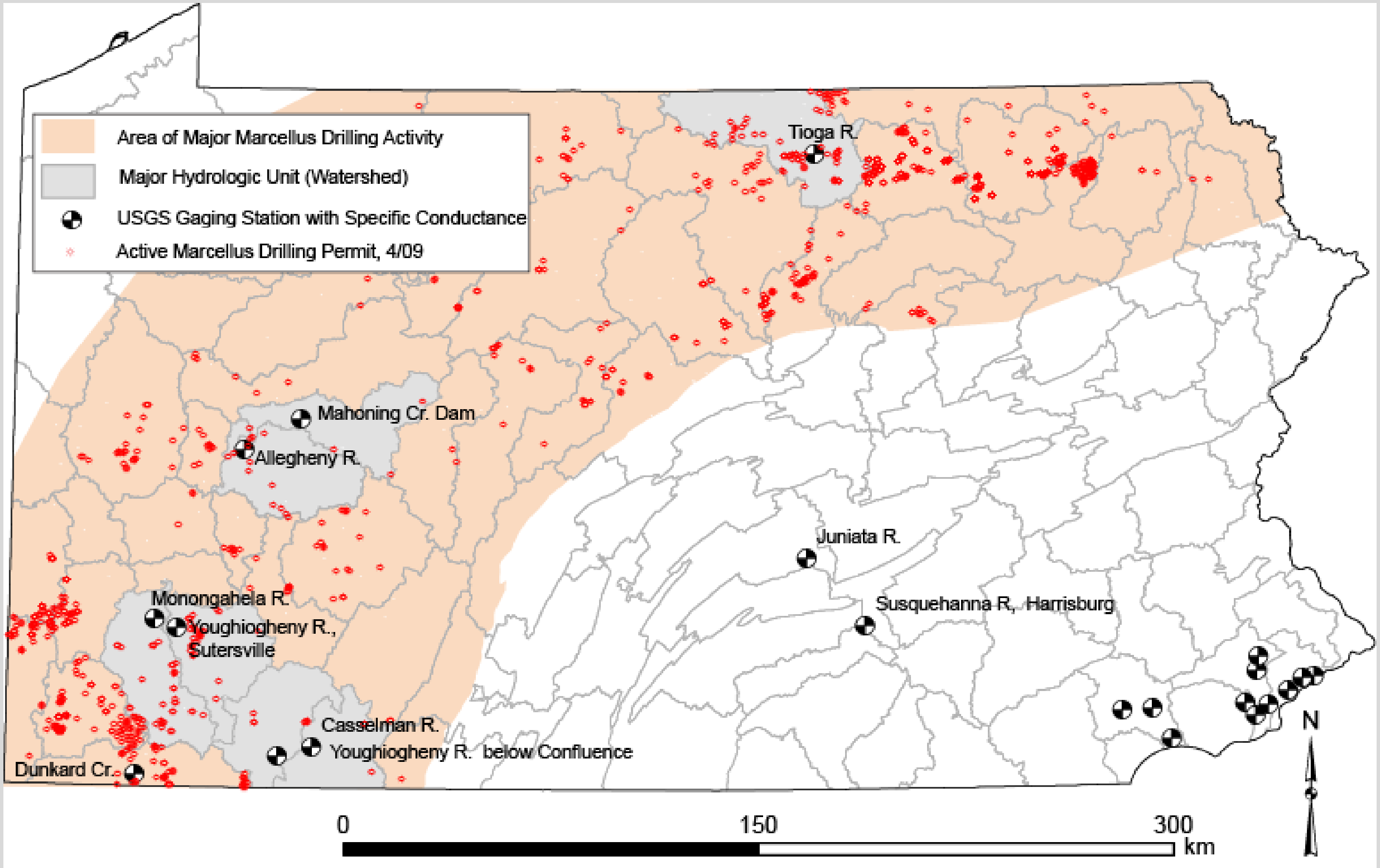
http://www.dec.ny.gov/about/47291.html

Horizontal Drill Rig

Frac jobs take 1-8 million gallons of water from streams, reservoirs, GW, or reused water

Photos from Molly Pritz '10

Drilling Activity in Pennsylvania



Map by Carl Kirby from Pennsylvania Spatial Data Access information

How can “leaks” occur?

www.donnan.com

Hydraulic fracturing operation, horizontal Marcellus well, Bradford County, PA

Transport trucks for water (above) and hydraulic fracturing acid (HCl) (below)

tiogagaswatch.blogspot.com/

Brine Pit

Courtesy of J. Henry Fair through Michel Boufadel

Susquehanna River Basin Commission
Remote Water Quality Monitoring Network

- **Plan 30 monitoring stations in PA & NY**
- **T, pH, conductance, DO, turbidity, stage**

www.srbc.net/

Real-time data on web

Not in Marcellus region