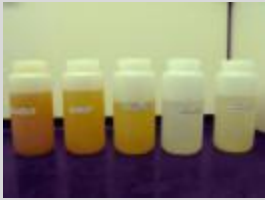


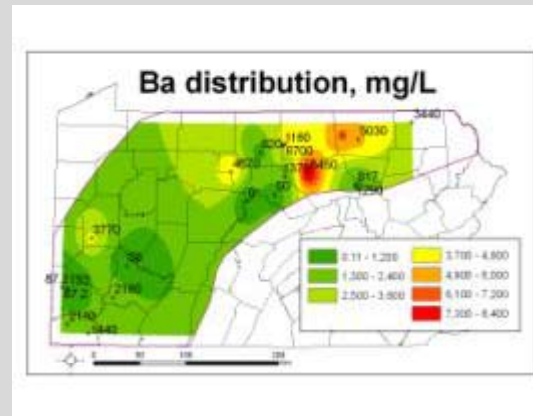
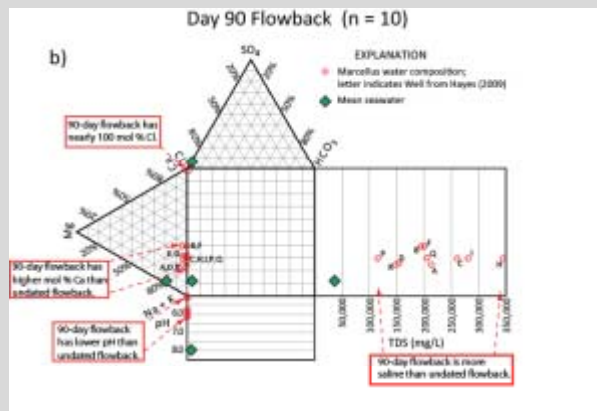
# Inorganic Geochemistry of Pennsylvania Marcellus Flowback Waters



Carl S. Kirby  
Department of Geology  
Director, BU Marcellus Shale Initiative



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



Photos from New York State SGEIS

## Acknowledgments:

Molly Pritz '10 for chemistry data  
Luke Swenson '11 for Conductivity research  
Scott Lunde '12 and Garyn Tate '12 for data mining

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Degenstein Foundation  
Forum for Pennsylvania Heartland

Presented at  
US EPA Hydraulic Fracturing Workshops  
Arlington VA  
February 24, 2011

# Bucknell MSI Database

The screenshot shows a Mozilla Firefox browser window displaying the Bucknell University Marcellus Shale Initiative Publications Database. The browser's address bar shows the URL: <http://www.bucknell.edu/script/environmentalcenter/marcellus/default.aspx>. The page features a navigation menu with links such as "About the Center", "Faculty and Departments", "Calendar", "Campus Greening Initiative", "Susquehanna River Initiative", "Nature and Human Communities Initiative", "Student Opportunities", "Associated Groups", and "Staff Contacts". The main heading is "Marcellus Shale Initiative Publications Database (beta)". Below this, a paragraph explains that the database lists primarily print-based publications and does not cover websites, blogs, news articles, newsletters, or other media. A search box is present with a "Go" button and a link to "Browse all publications (45)". There are also filter options for publication types: Report, Conference, Peer-reviewed article, Fact sheet, and Industry journal article. A notification states "2 publications have been added in the past 30 days." The "Ways to search:" section provides instructions on how to use the search function. On the right side, there are links for "What is the Bucknell University Marcellus Shale Initiative?", "How much can I trust information from various types of publications?", "Glossary (inactive)", and "How can I find publications?". A "Browse by Keyword" section lists popular keywords including: air quality, barium, benefit, brine, chemistry, development, disposal, economic, environmental, flowback, flowbackwater, fracture, gas, geology, government, health, history, hydraulic fracturing, impacts, industry, isotope, Marcellus, New York, oil, Pennsylvania, regulation, and saline.

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

## *Horizontal Well*

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

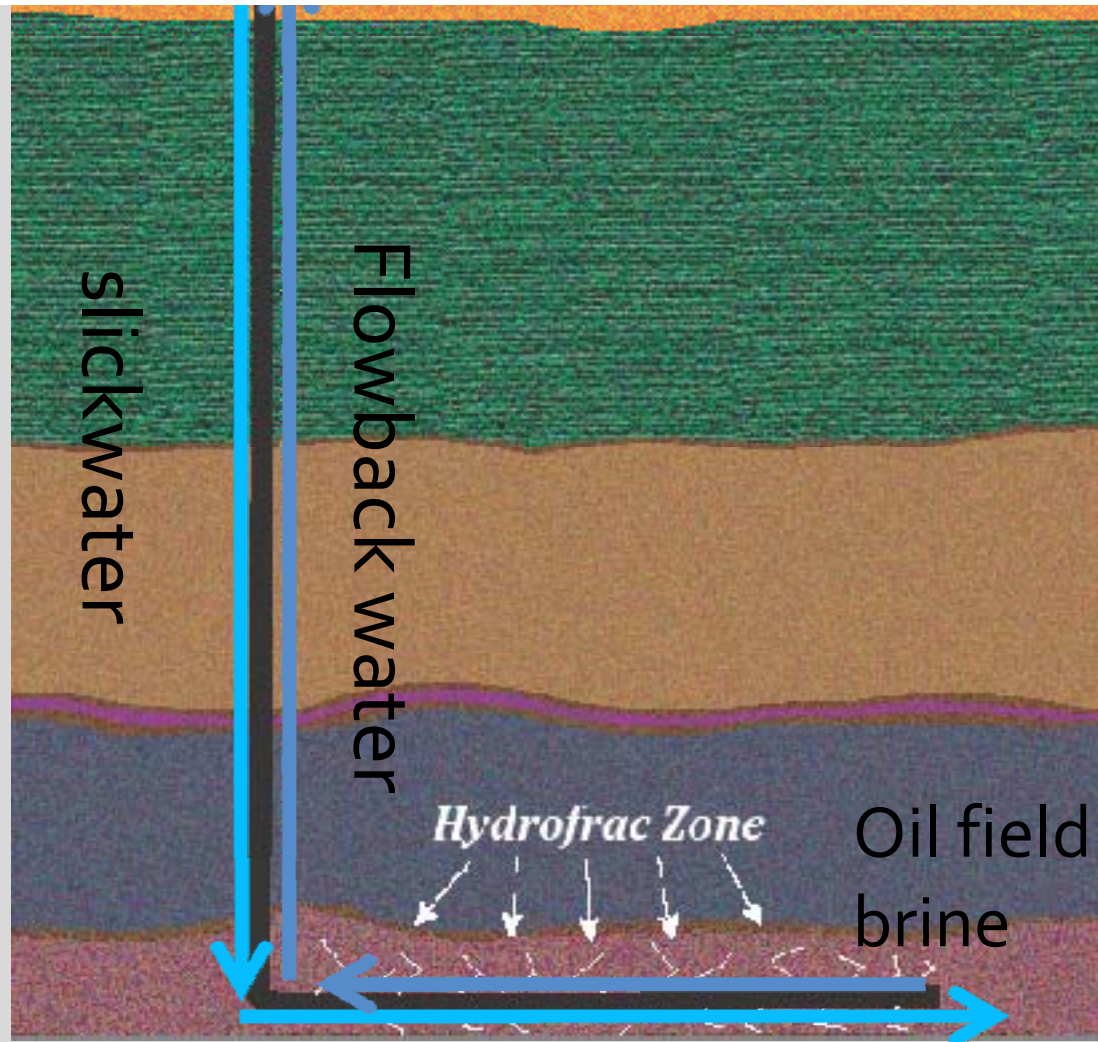


Diagram after  
Pritz, 2010



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



Photos from Molly Pritz '10

# Marcellus core section with salt blebs along bedding



TABLE 6—RELATIVE SOLUBLE CATION CONTENT

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

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

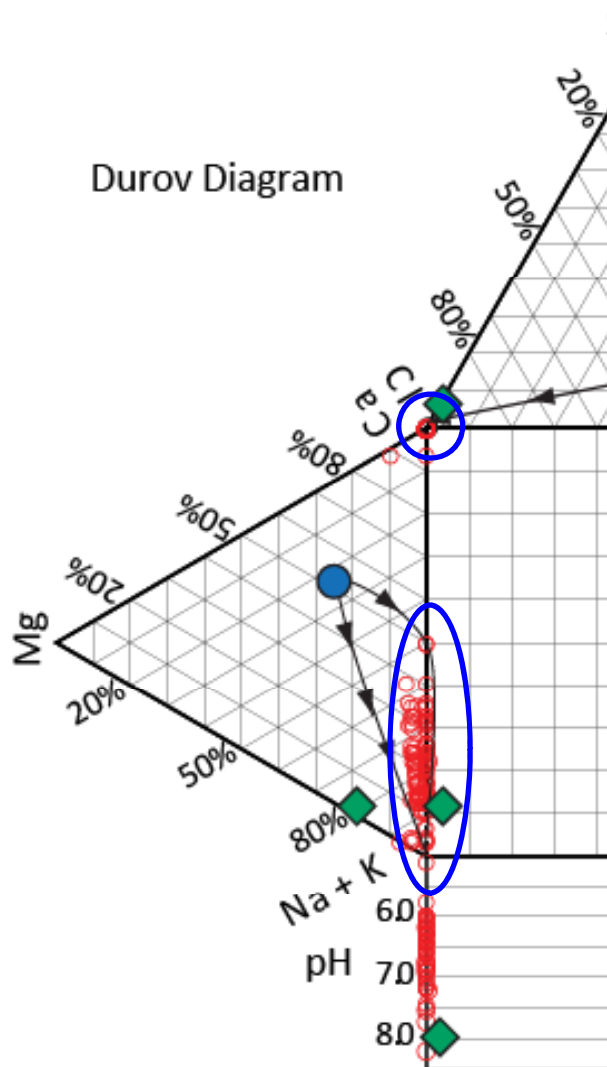
- Na/Ca/Cl dominated
- High TDS, Specific Conductance
- Often have very high Ba, Sr
- Most are radioactive
- Low Mg, SO<sub>4</sub>
- Near-neutral pH
  
- Endocrine disruptors?? Other organics

Marcellus fracwater has distinctive Na/Ca/Cl signature



EXPLANATION

○ Marcellus water composition



Some of the fracwaters are 1/3 solids!

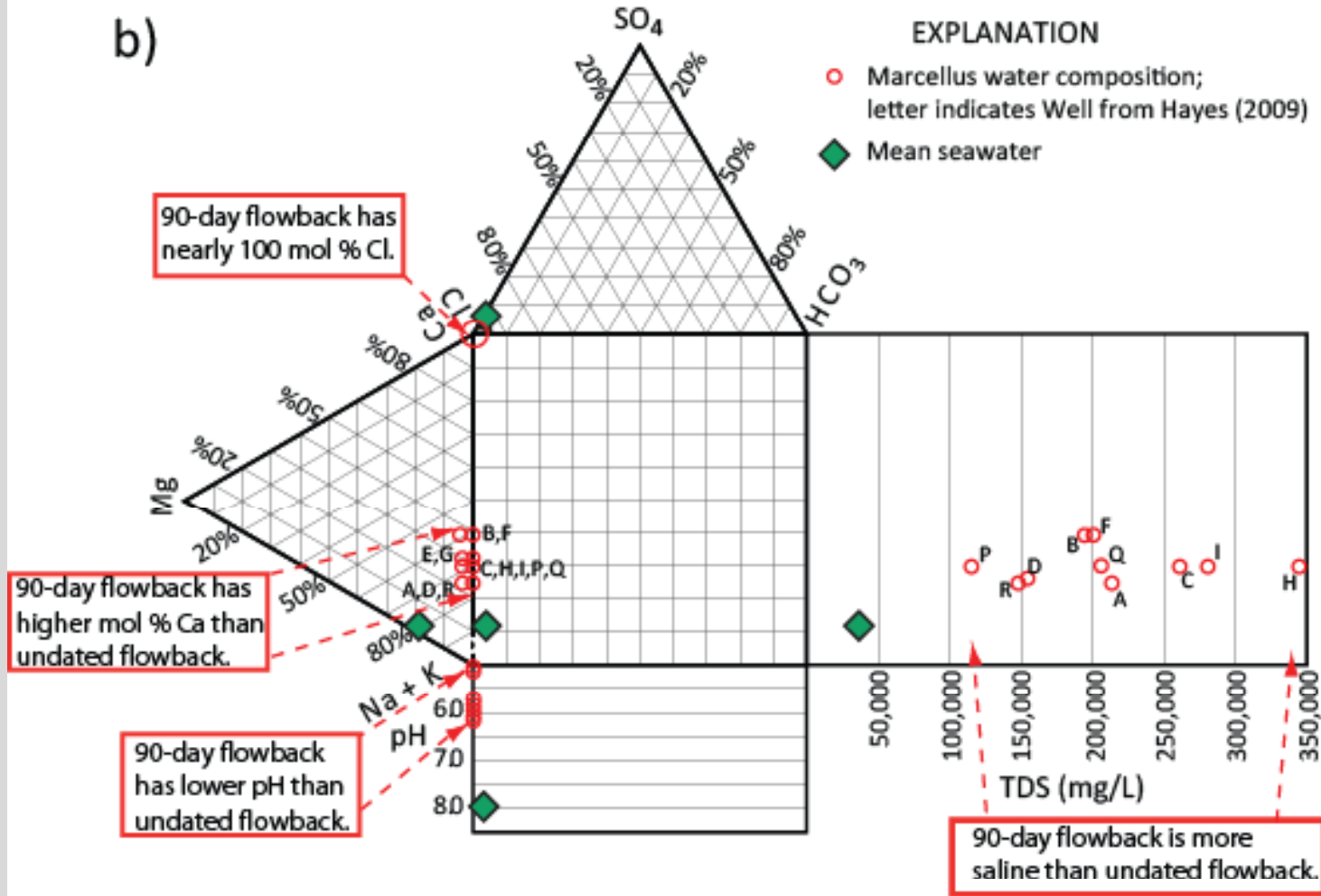
TDS (mg/L)

Data compiled by Molly Pritz

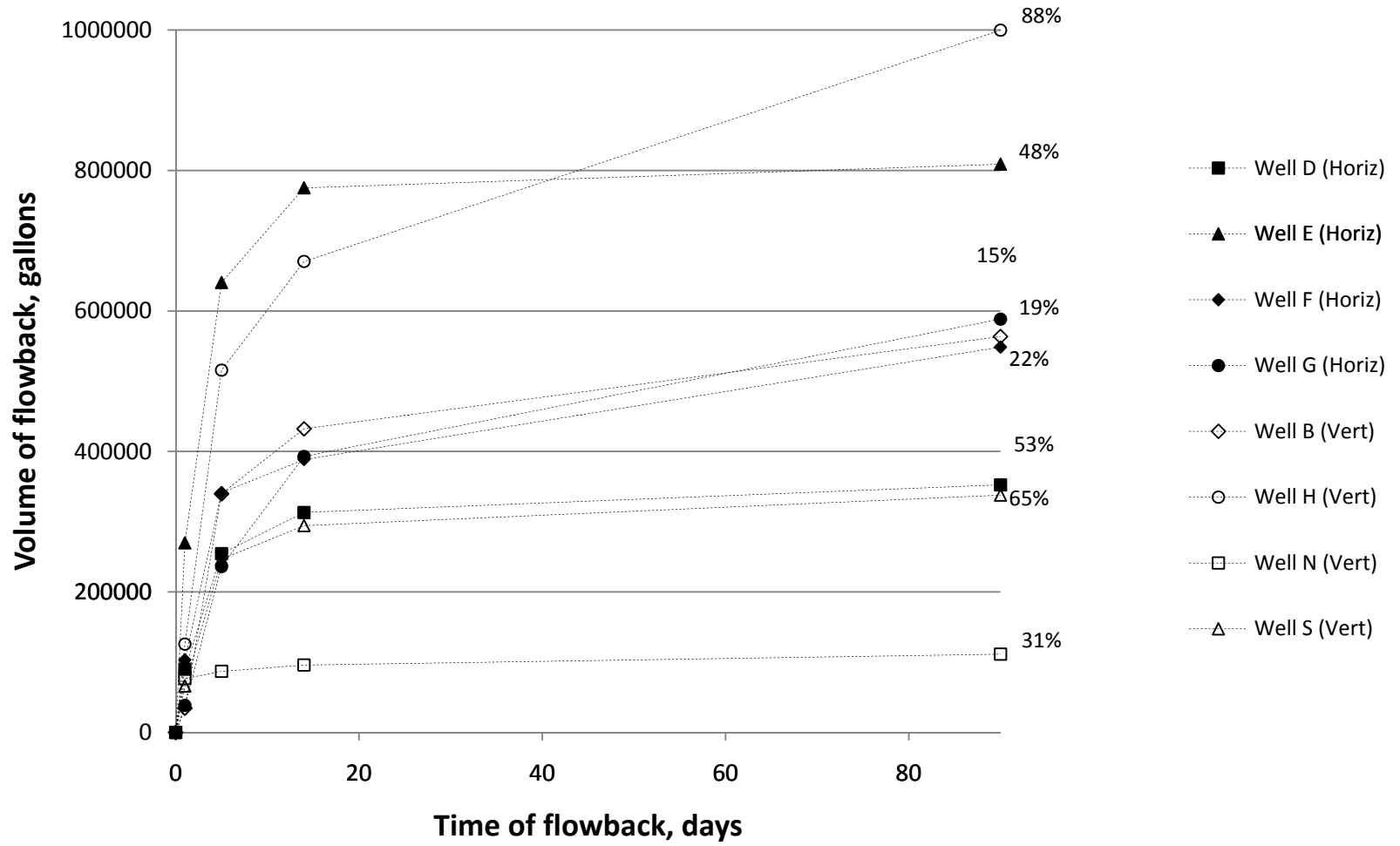


# Marcellus Flowback Water Geochemistry

Day 90 Flowback (n = 10)

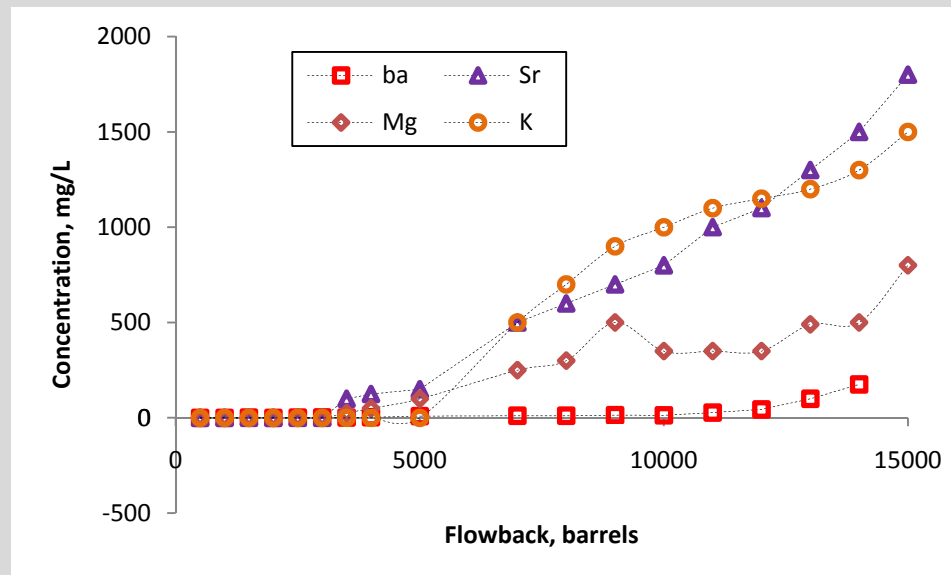
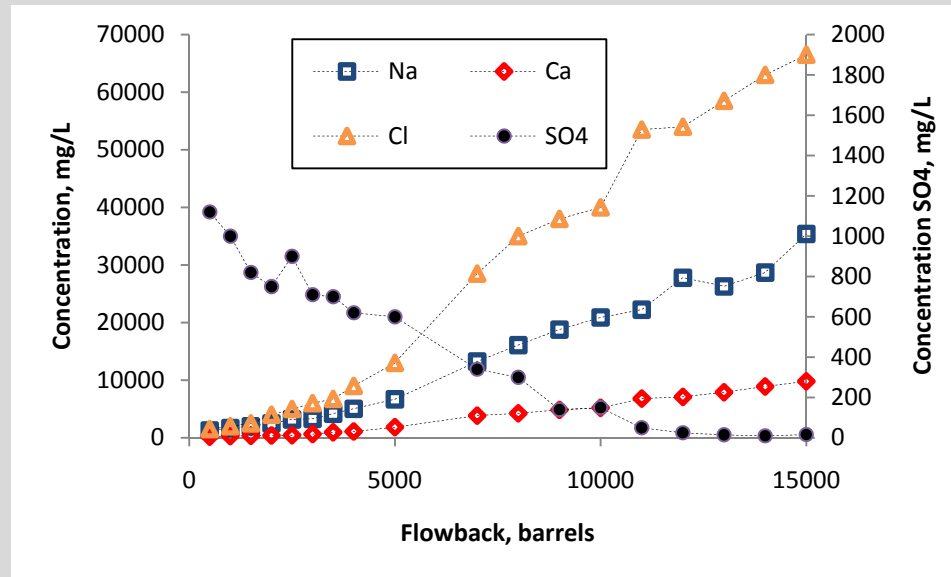


# Volume of flowback water *versus* time of flowback from Marcellus wells

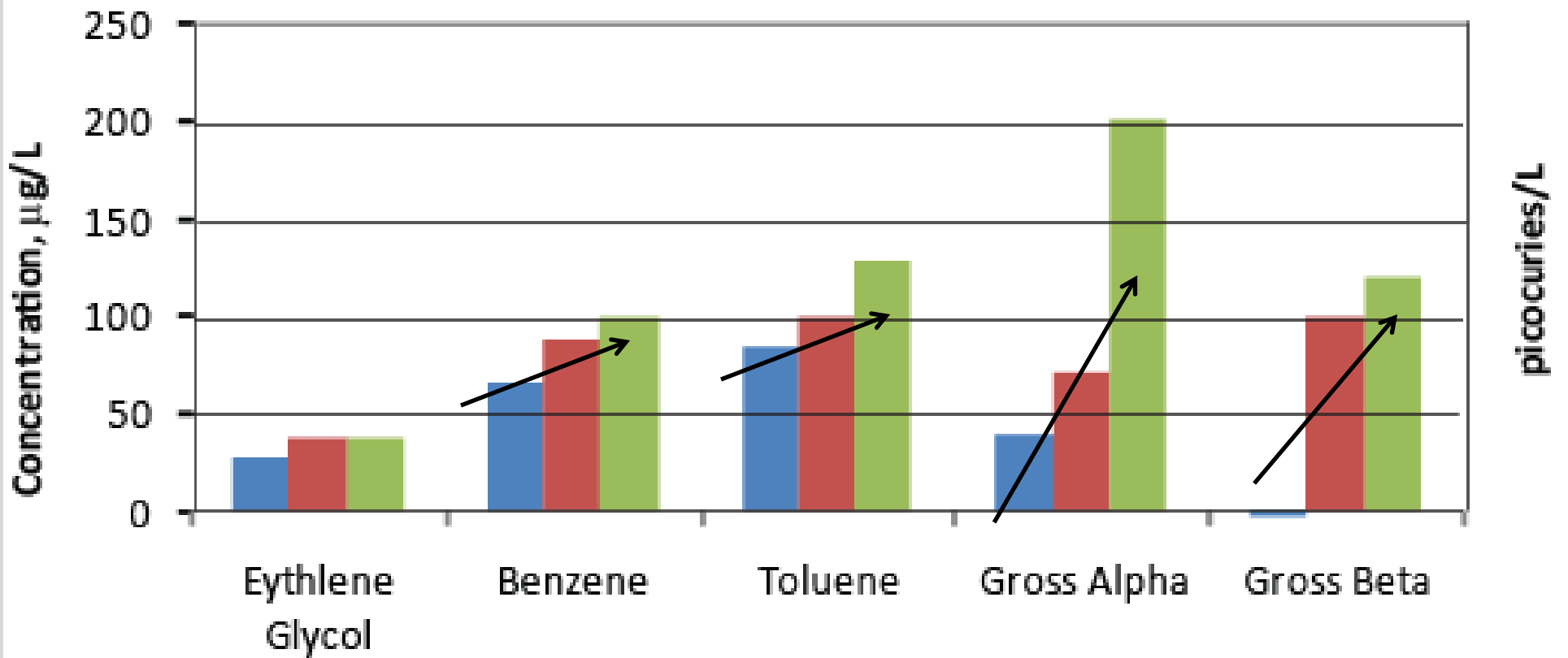


Data are from four horizontal and four vertical wells in Hayes (2009) that had data for 0 (injected water), 1, 5, 14, and 90-day flowback.

# Salinity increases with flowback time

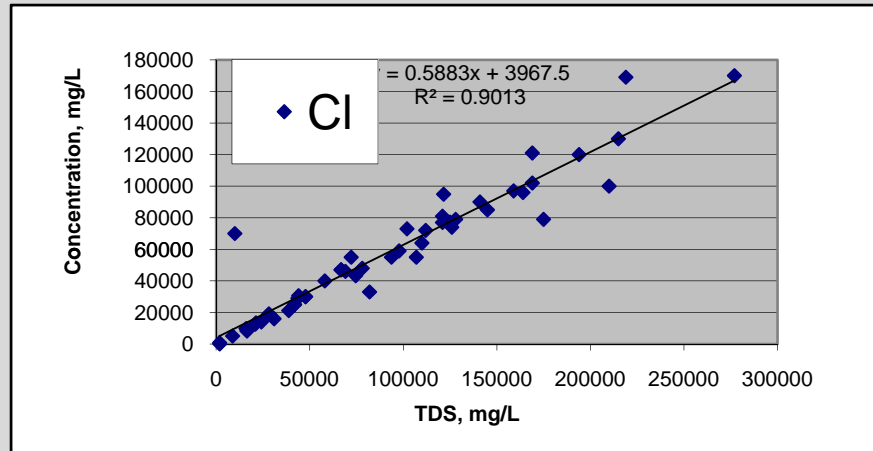


Data from Well A in  
Blauch *et al.* (2009).

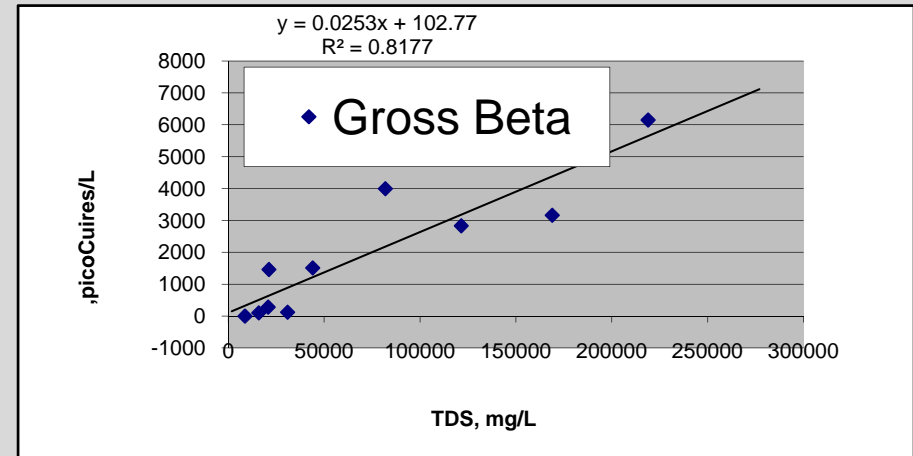


PA DEP

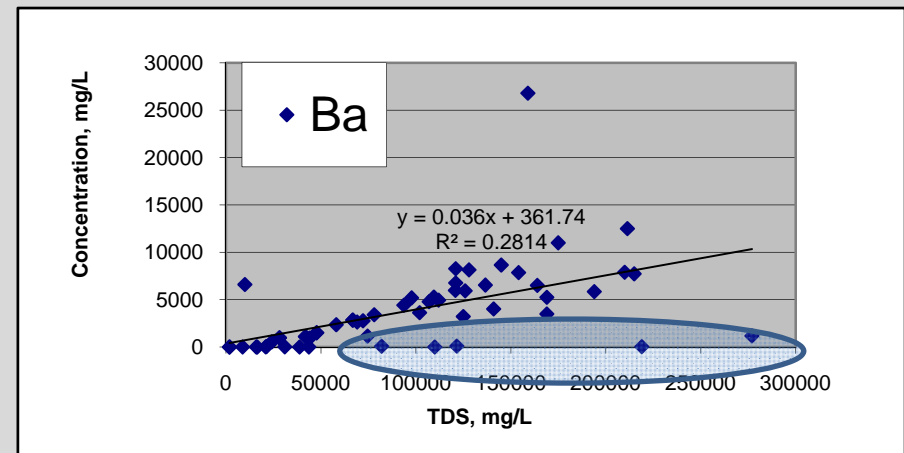
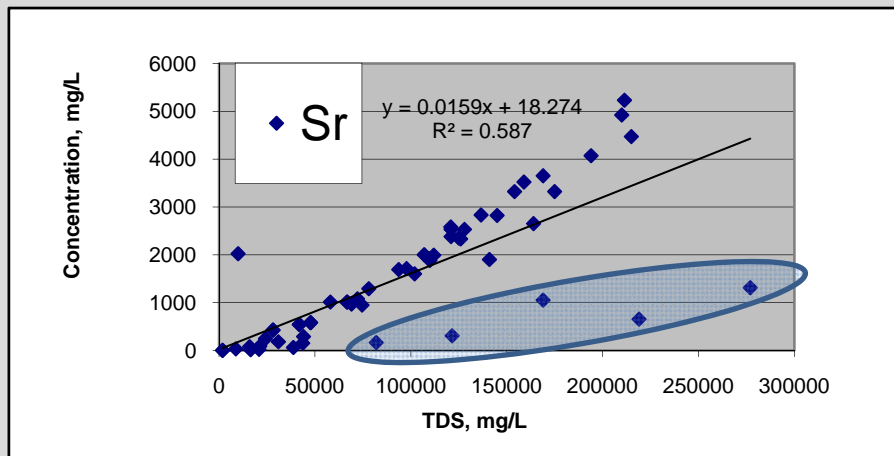
## Some clear correlations with TDS



## Some lack enough data for correlation

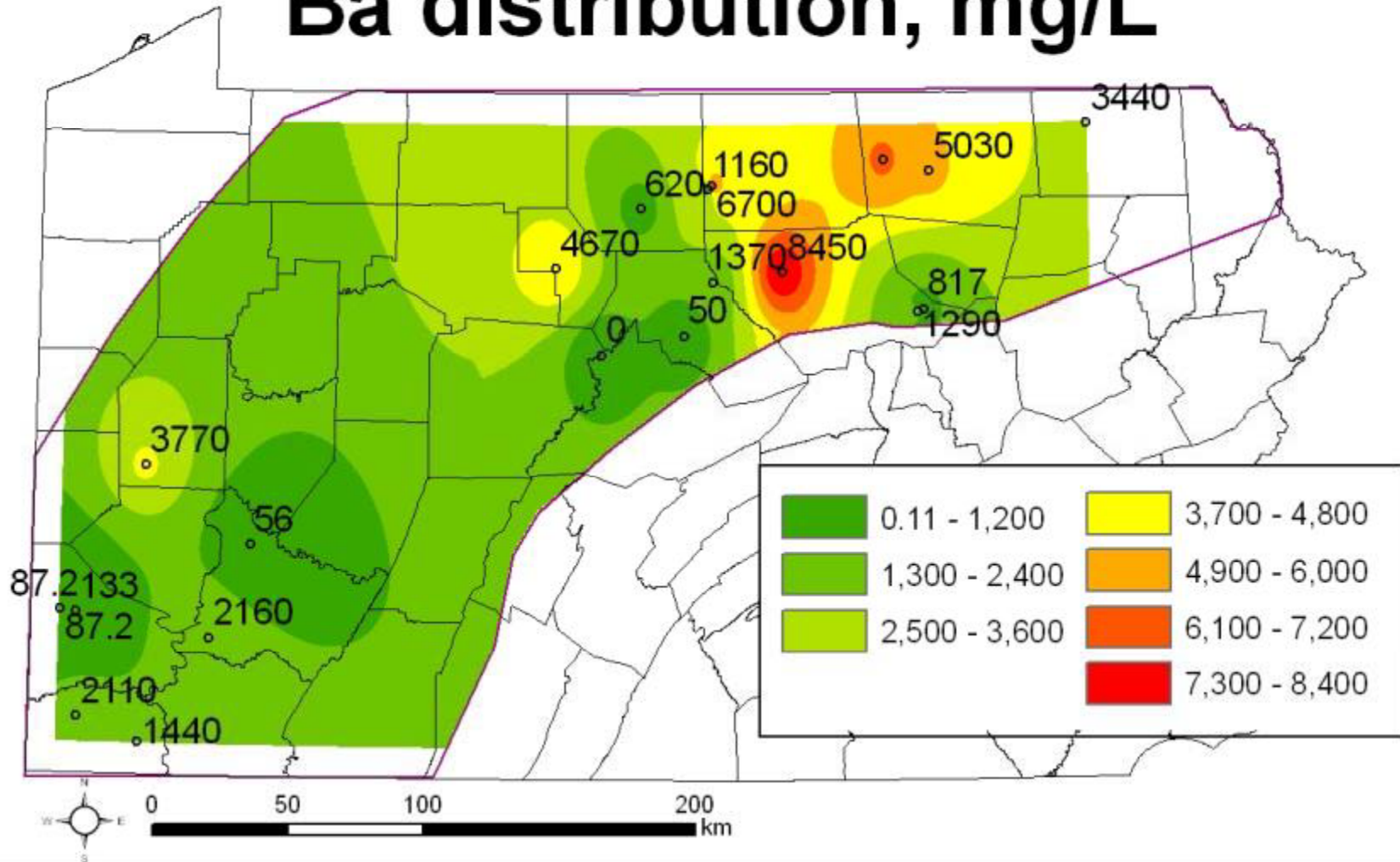


## Some mixed correlations with TDS

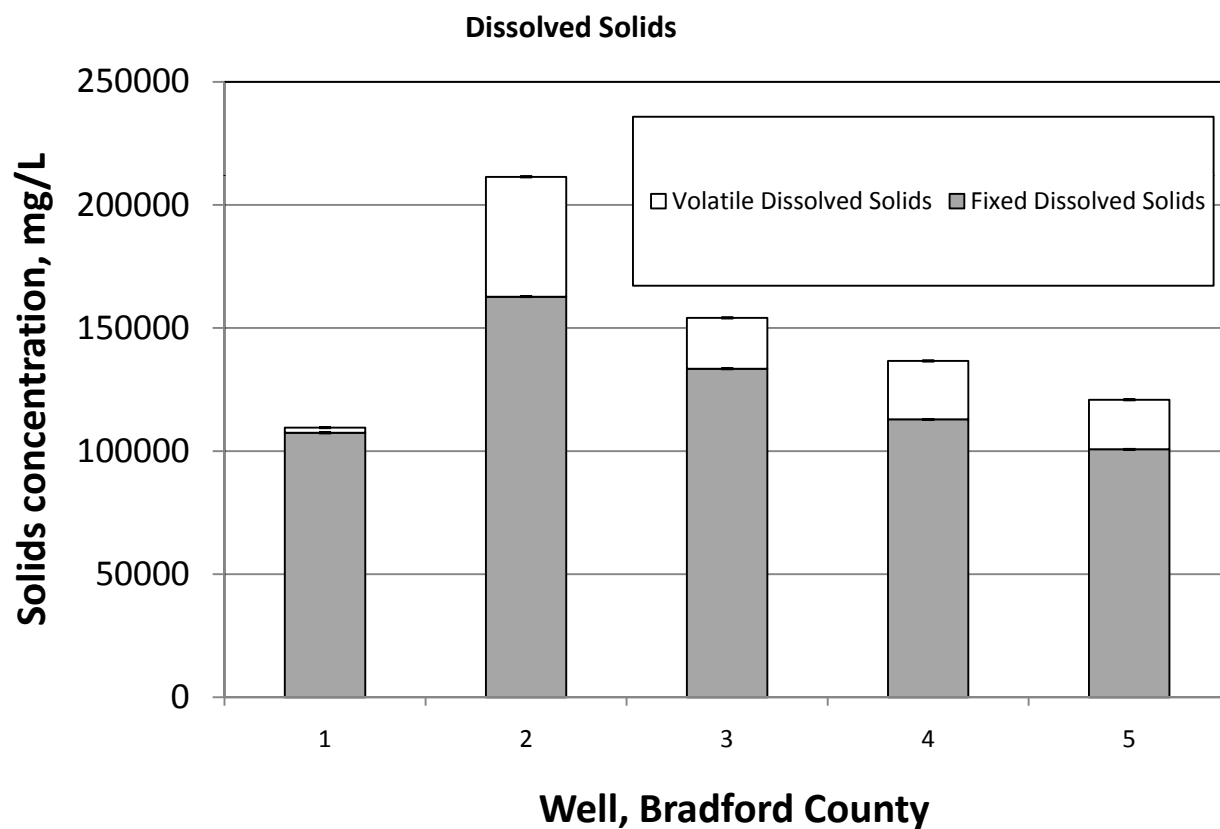




# Ba distribution, mg/L

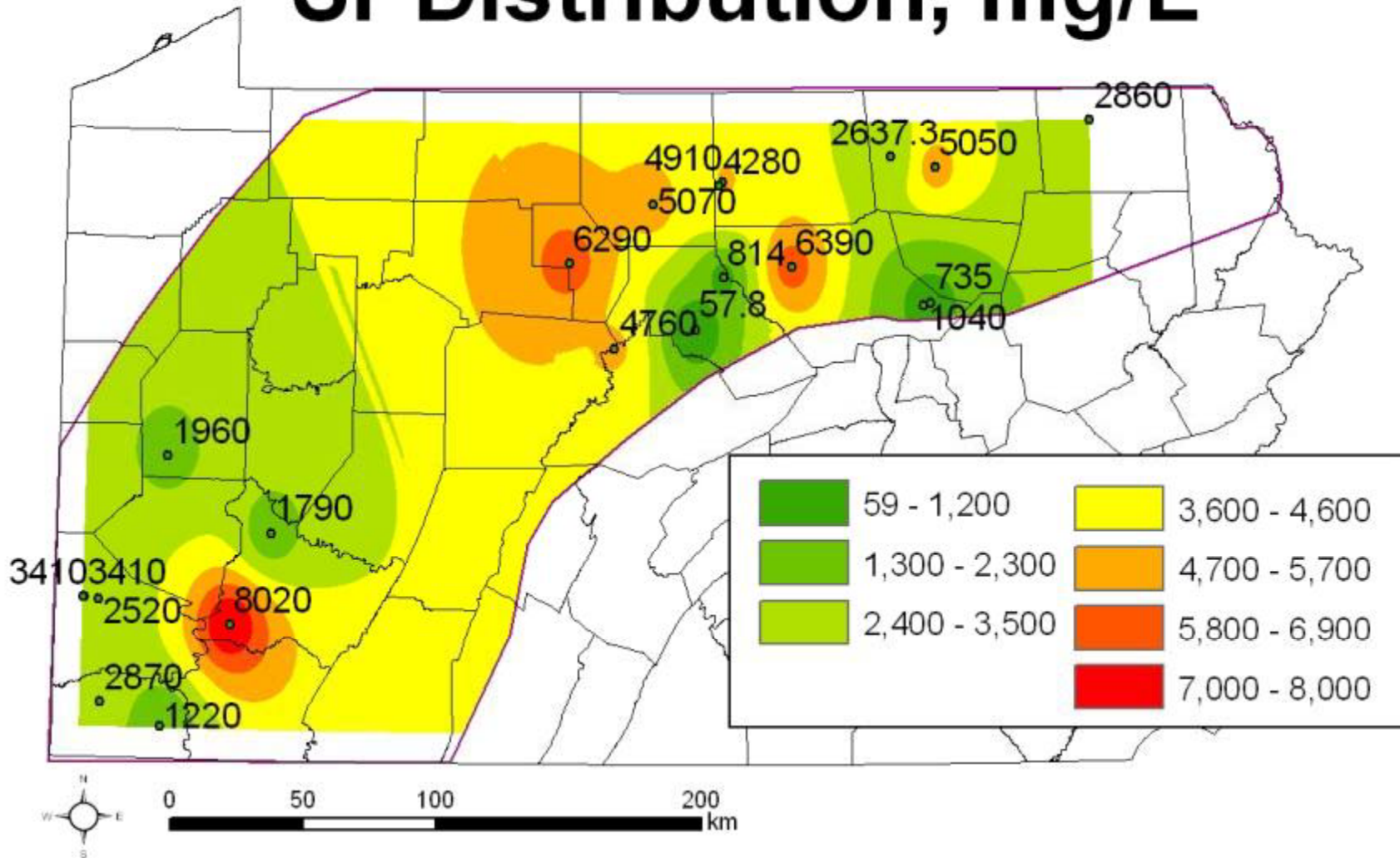


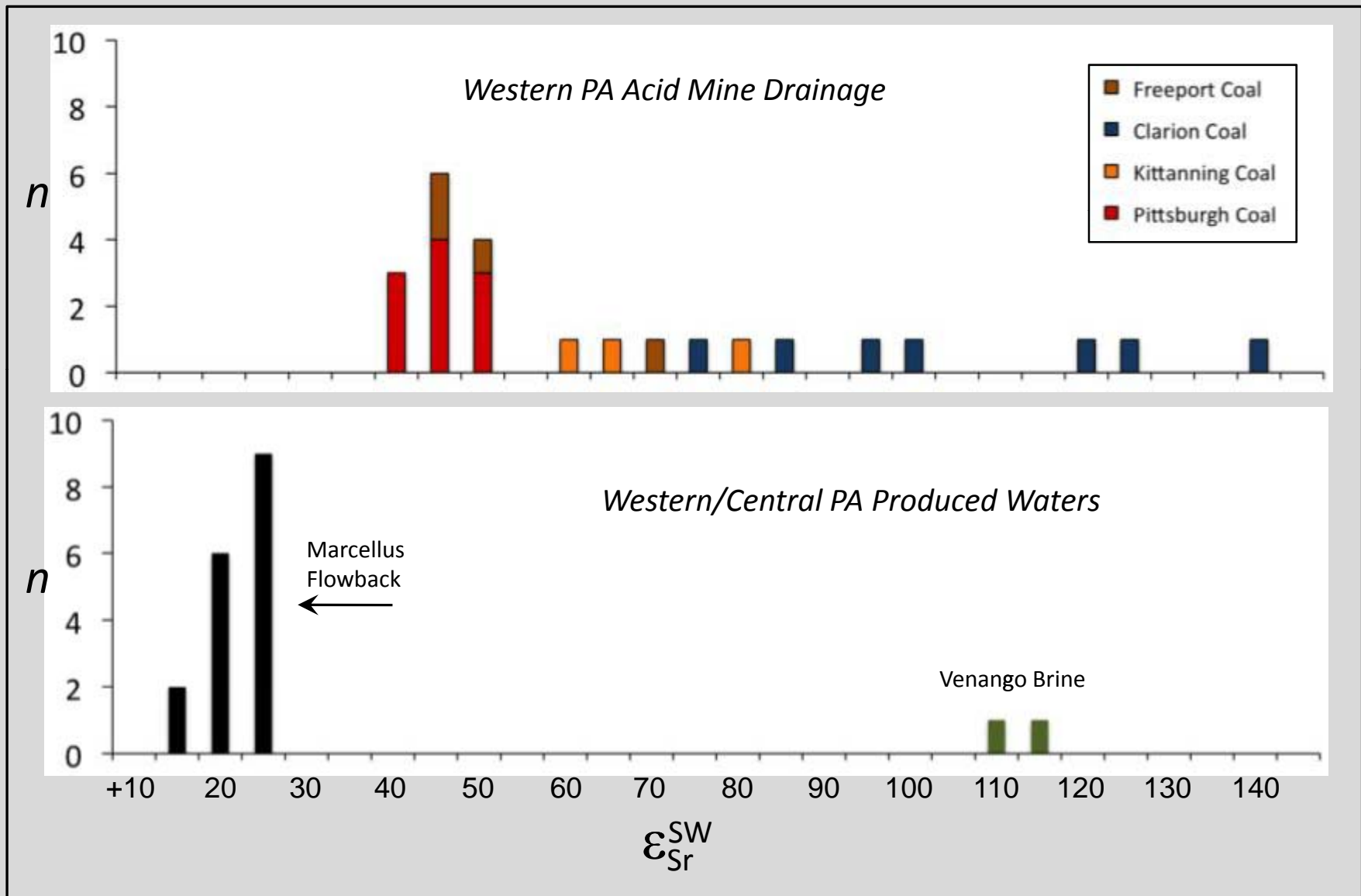
Volatile Dissolved Solids may suggest organic compounds that can complex metals such as Ba

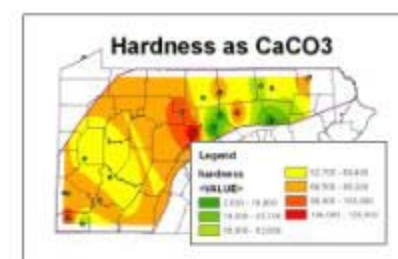
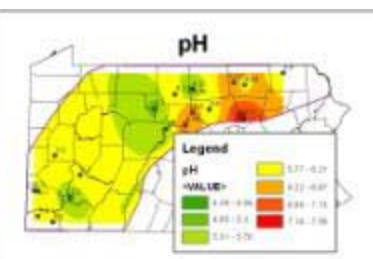
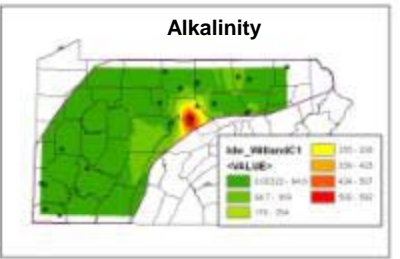
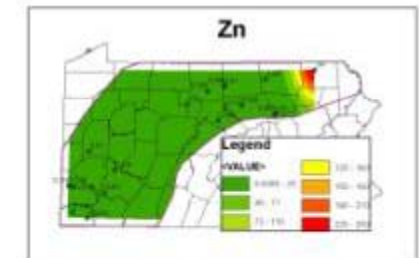
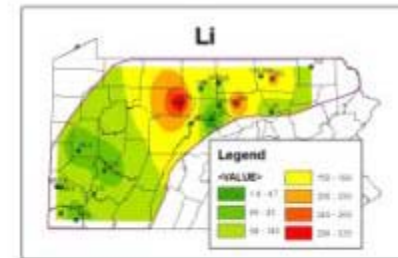
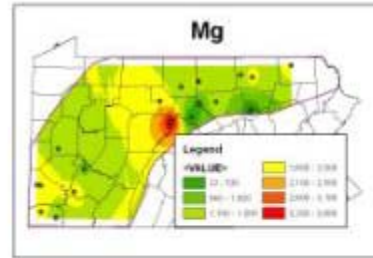
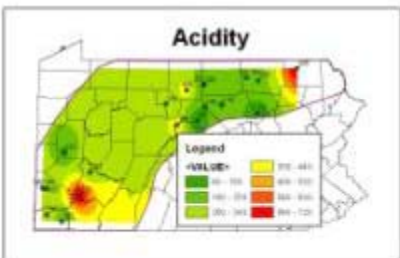
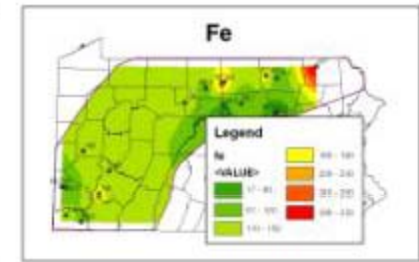
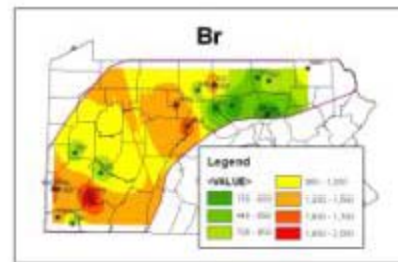
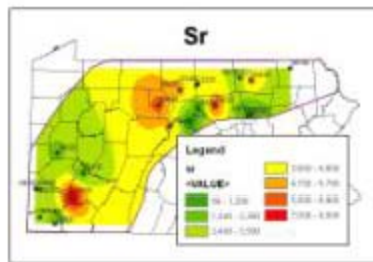
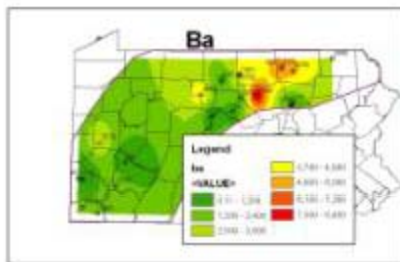
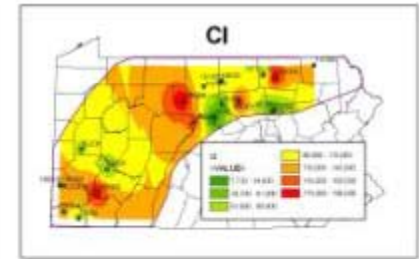
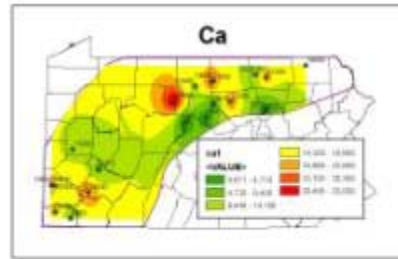
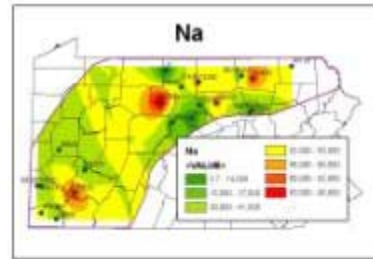
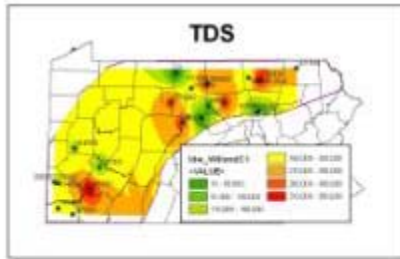


Data collected by Molly Pritz

# Sr Distribution, mg/L

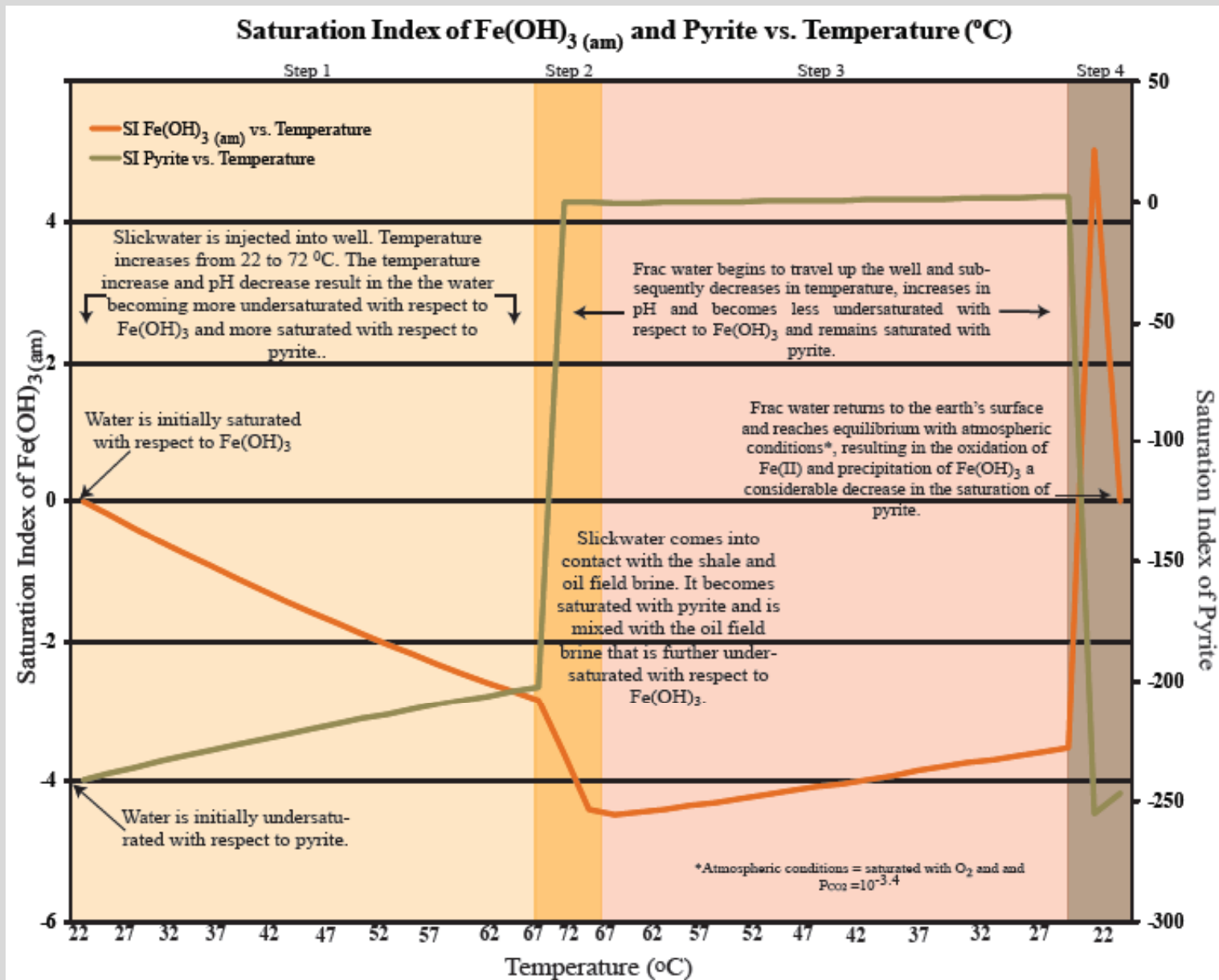






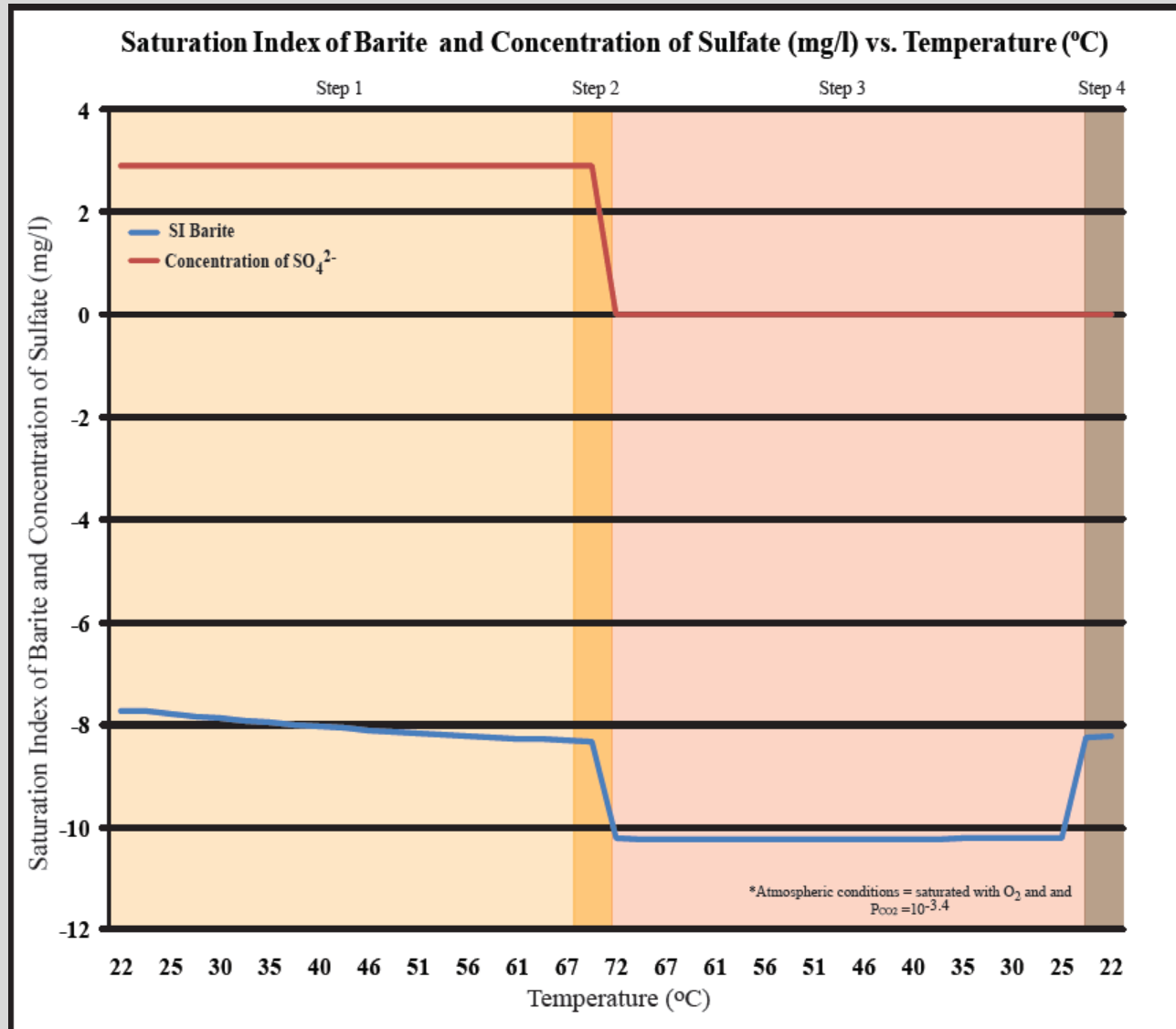


# Geochemical modeling (PHREEQCI)



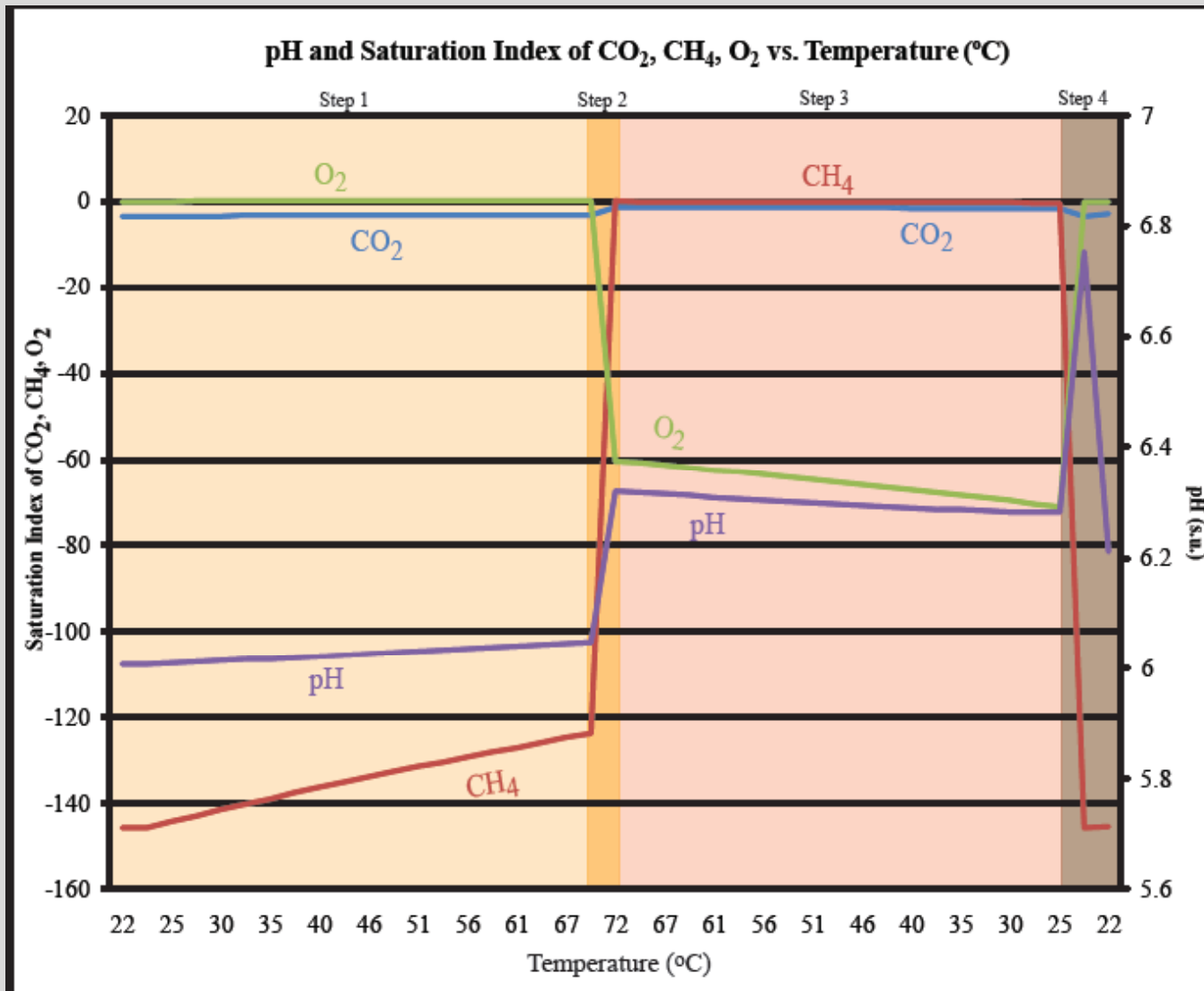
# Geochemical modeling (PHREEQCI)

## SI Barite, Conc. Of $\text{SO}_4^{2-}$ vs. Temperature

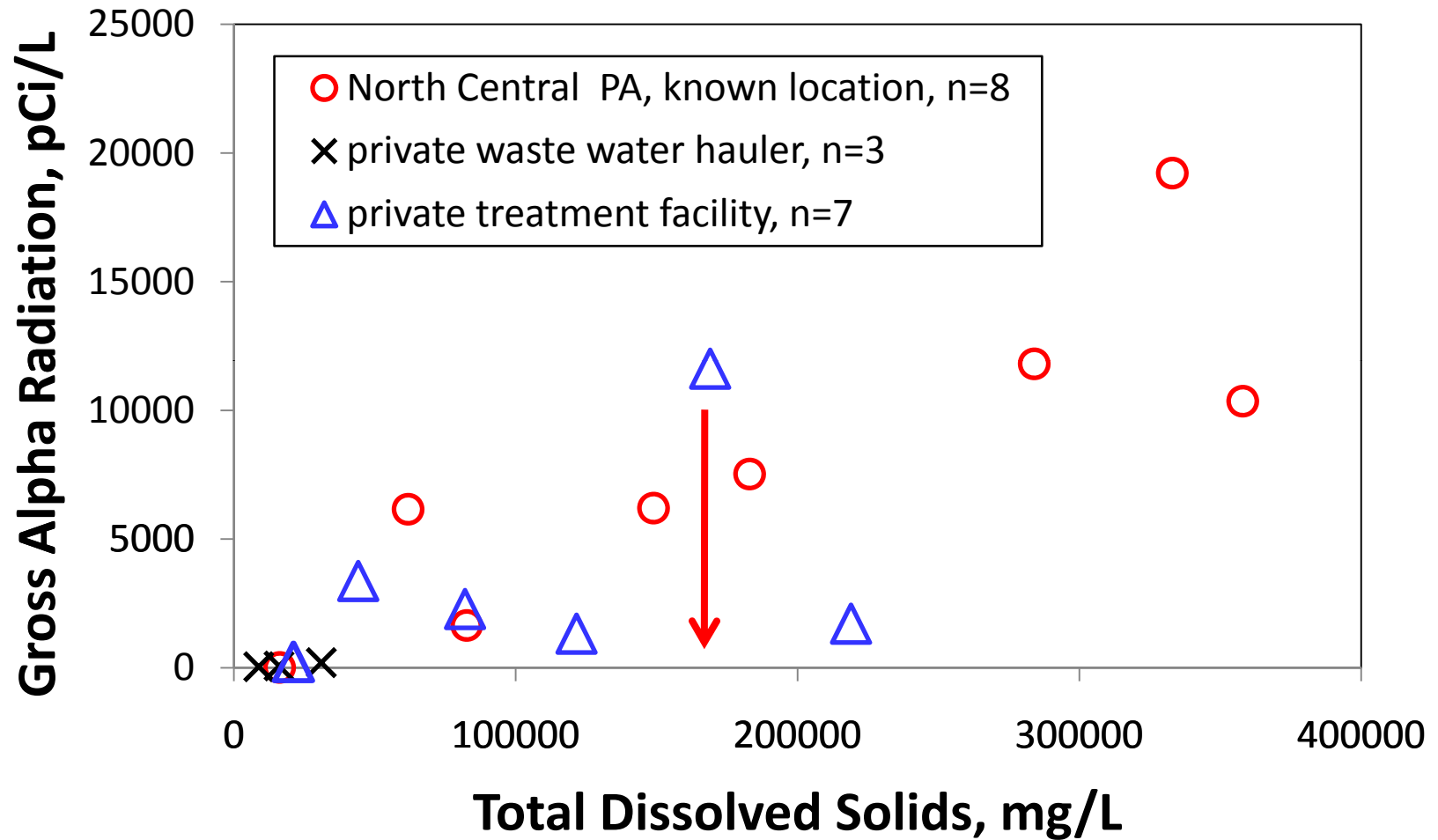


# Geochemical modeling (PHREEQCI)

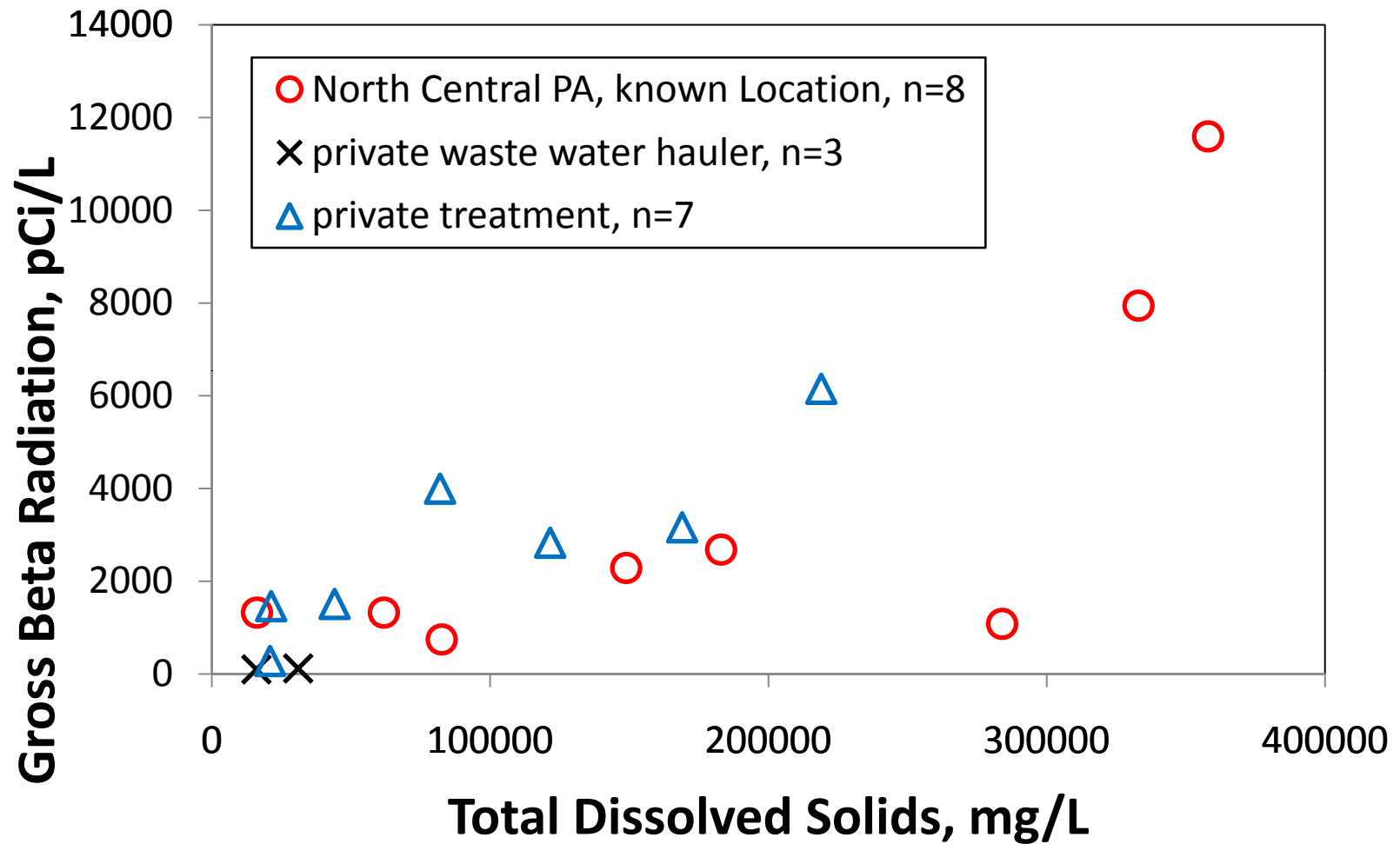
## pH, SI Gases vs. T



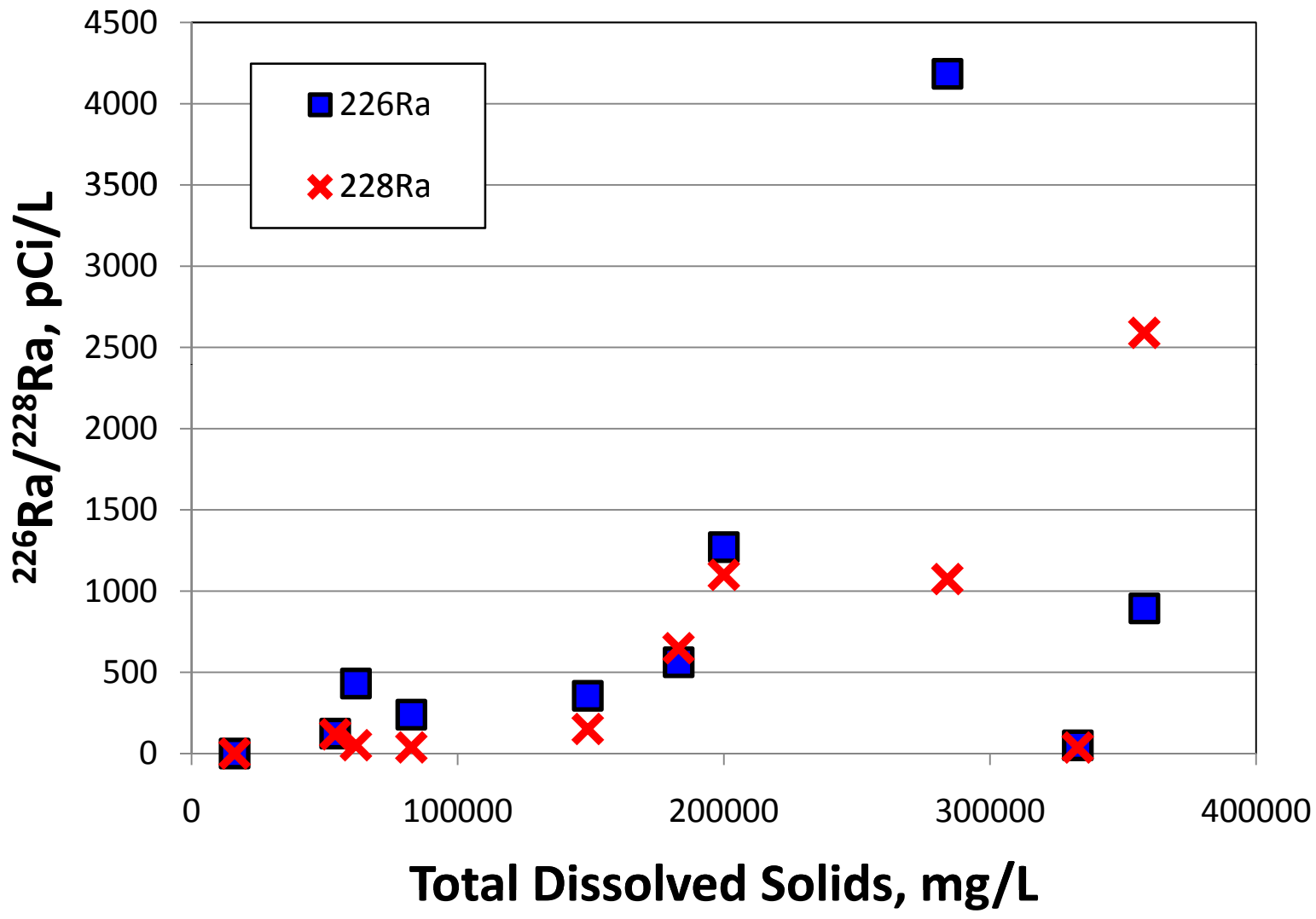
# Radiation in flowback waters



# Radiation in flowback waters

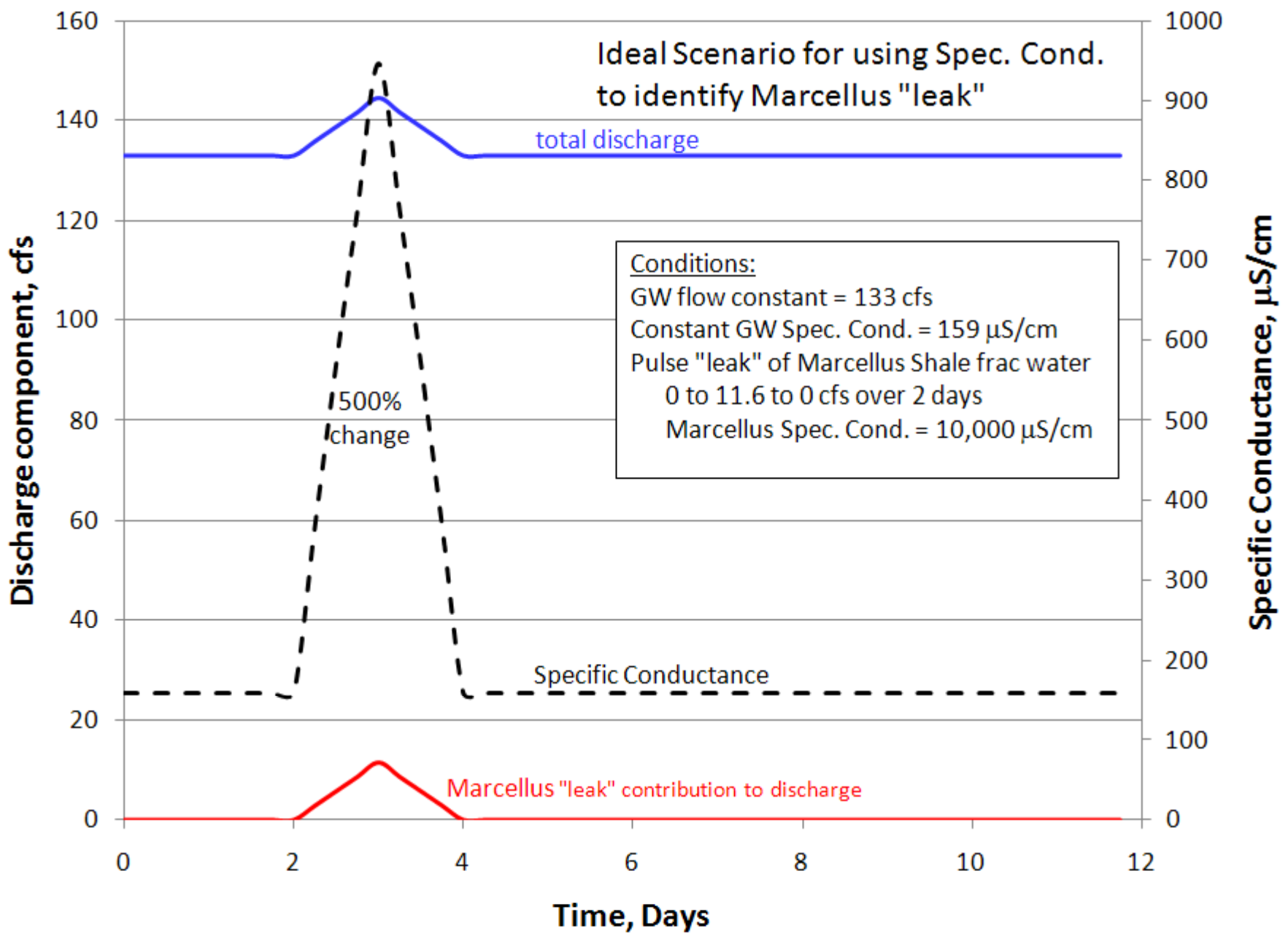


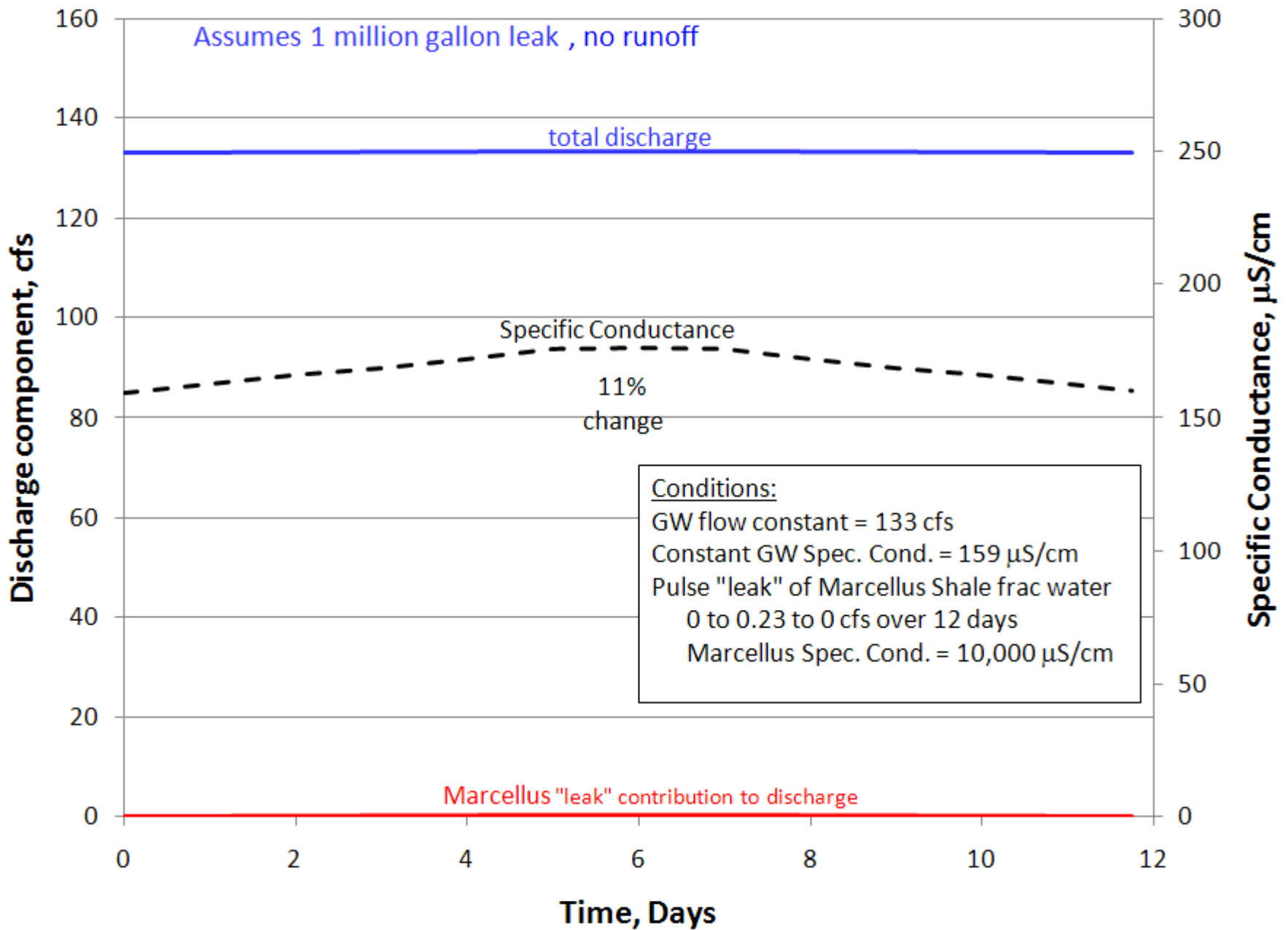




**Will increases in stream  
conductivity tell us we have a  
Marcellus “leak”?**

**Not consistently.**



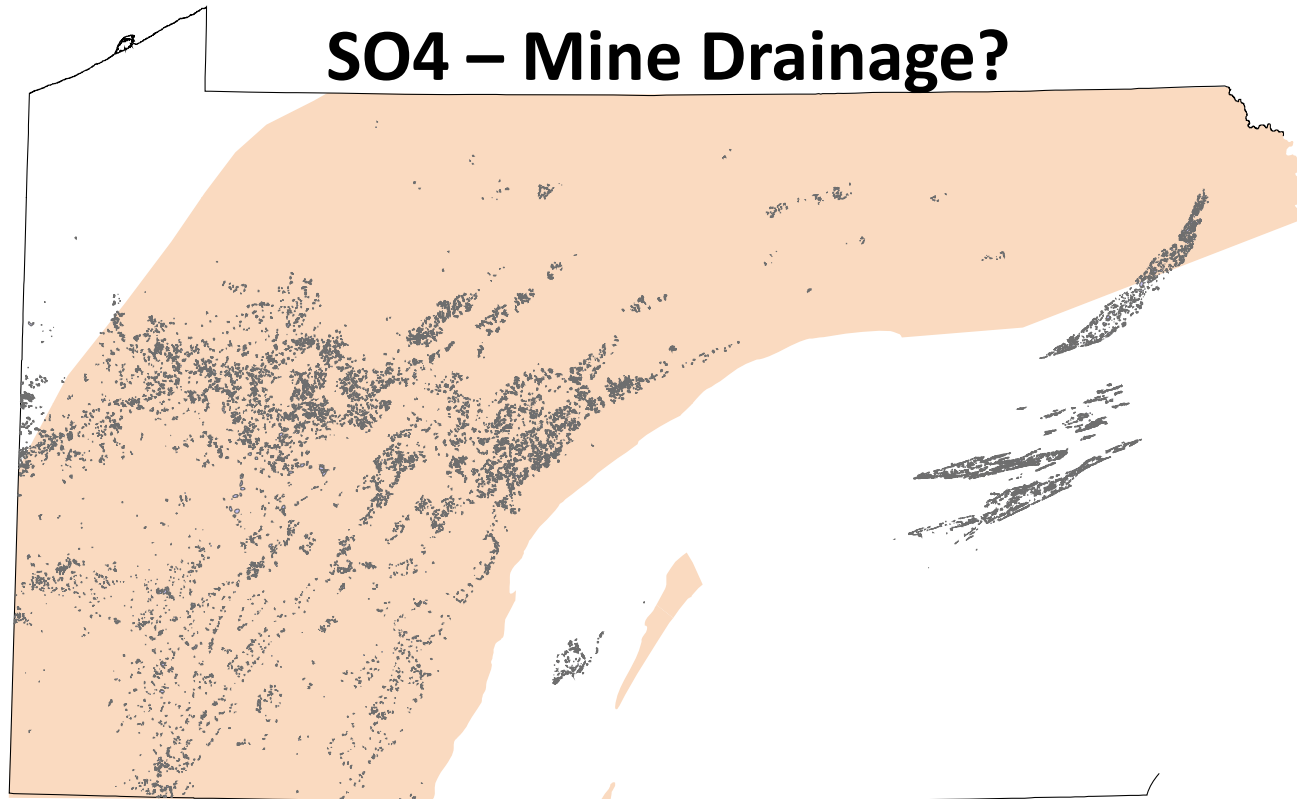


**AMD and road salt can cause high conductivity. Can we distinguish Marcellus “leaks” from them with conductivity?**

**Cl - Marcellus & road salt?**

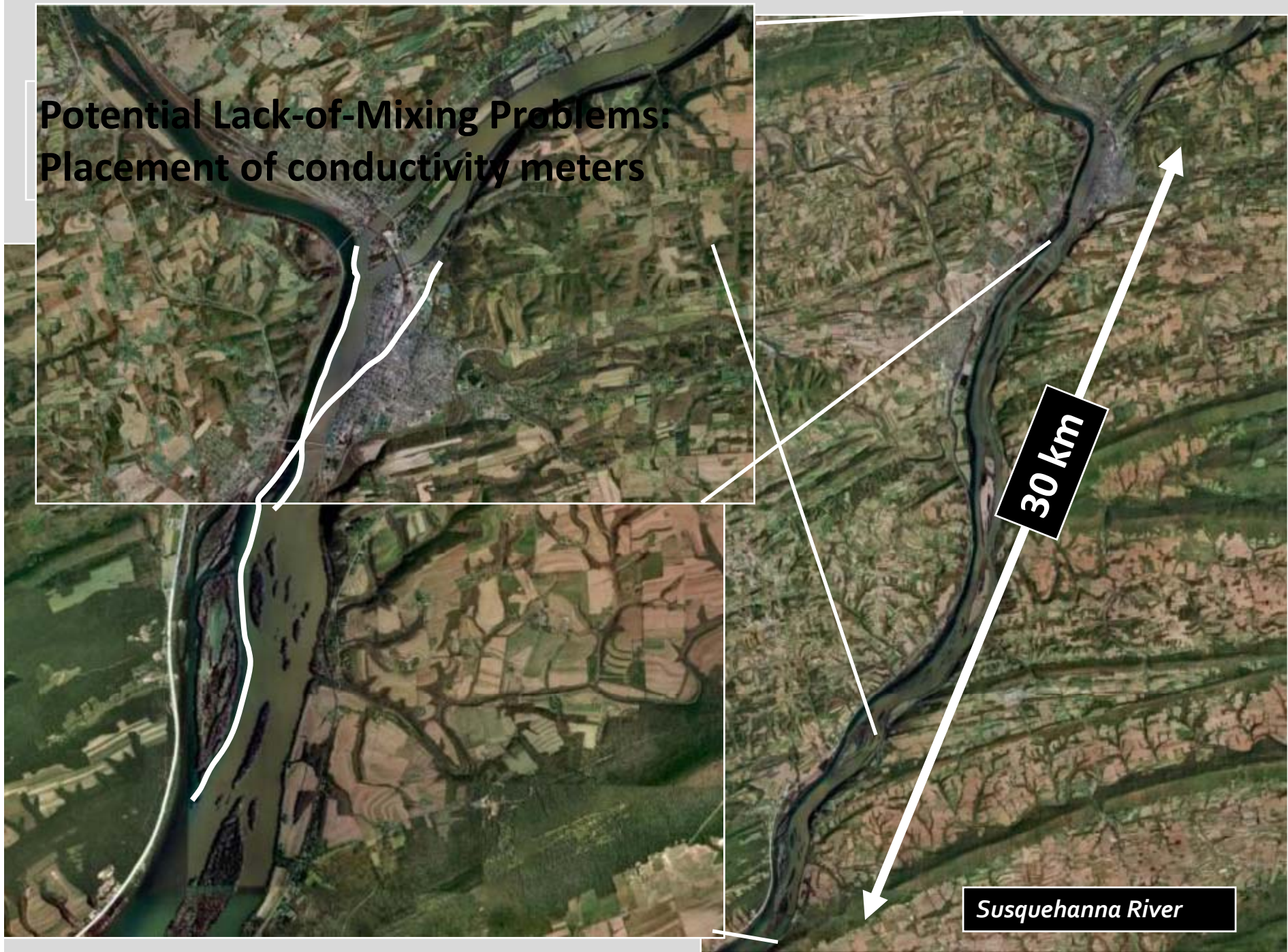
**Br - Marcellus?**

**SO<sub>4</sub> - Mine Drainage?**





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

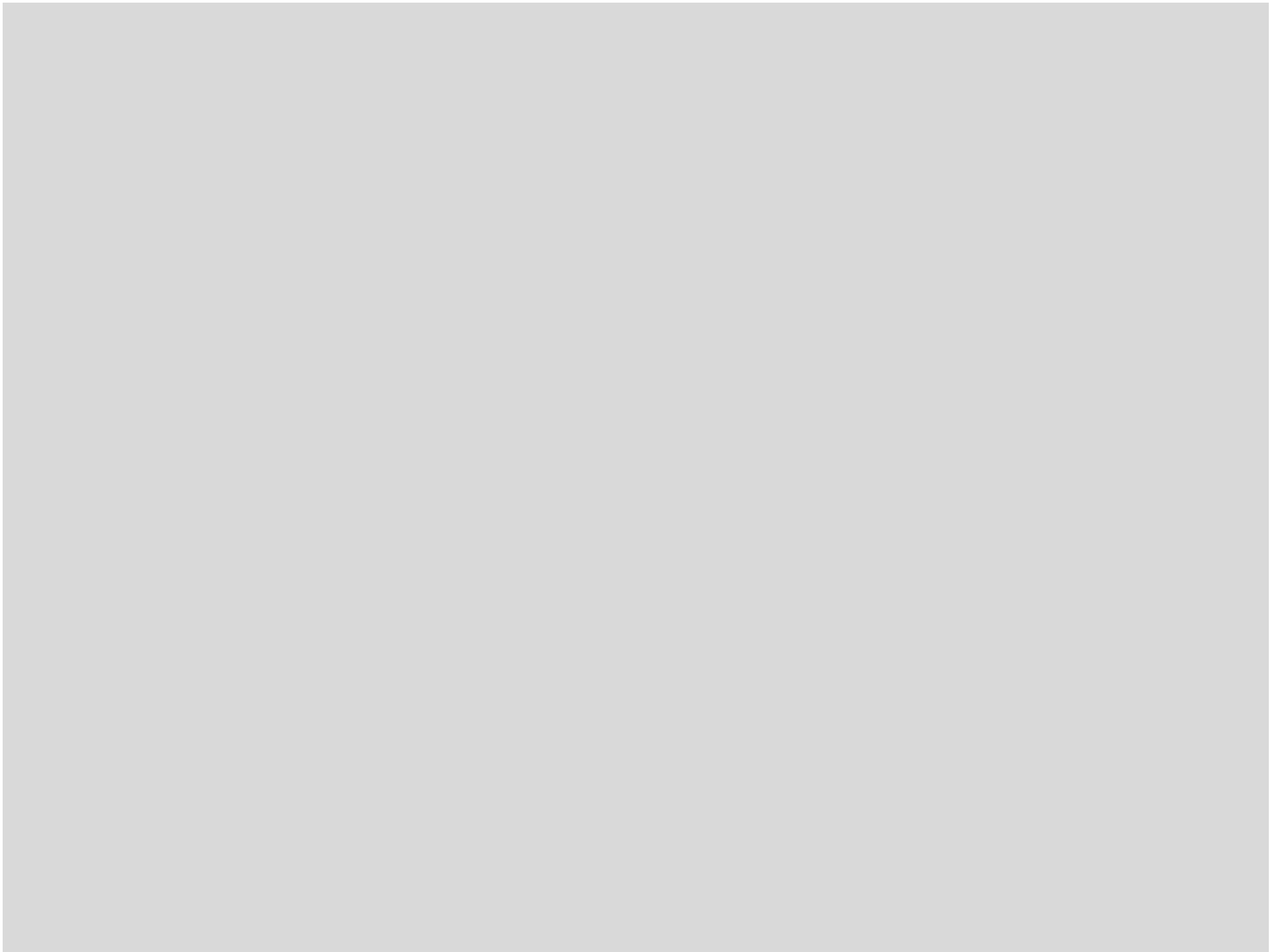


**30 km**

*Susquehanna River*

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

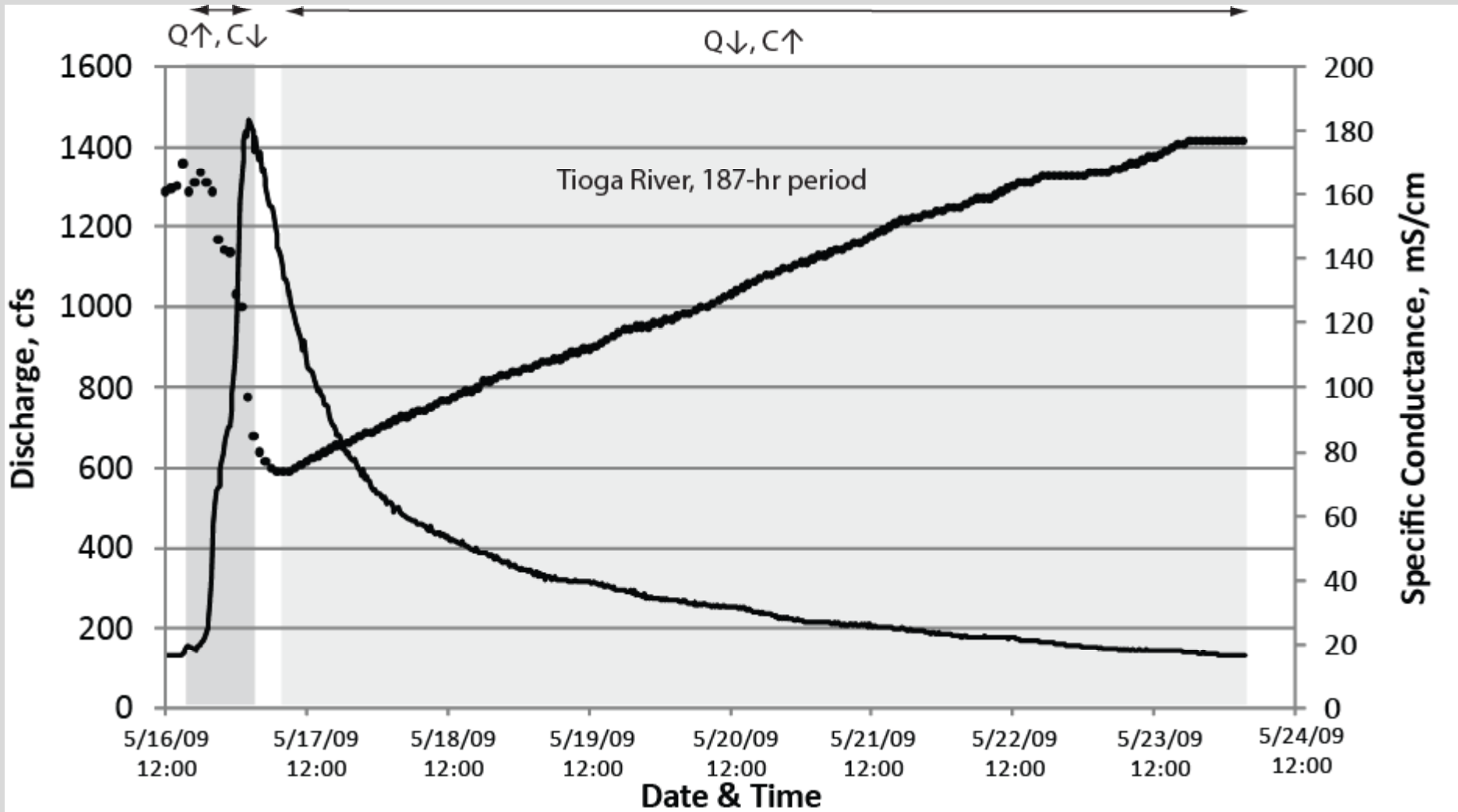
## **Monitoring?**

- 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:**

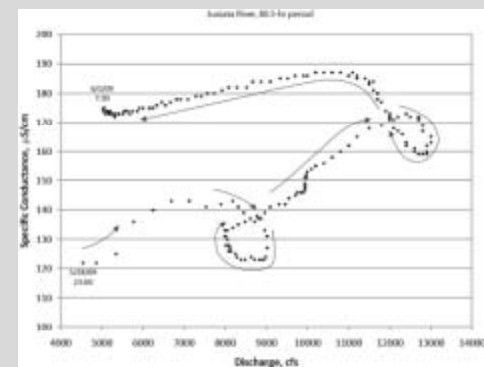
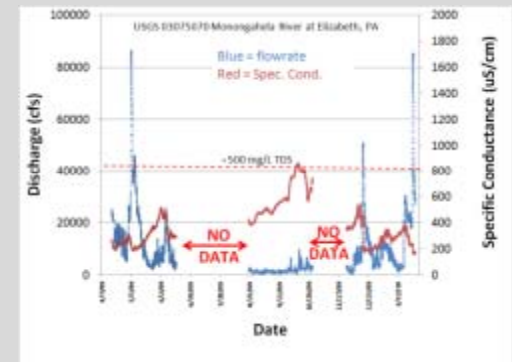
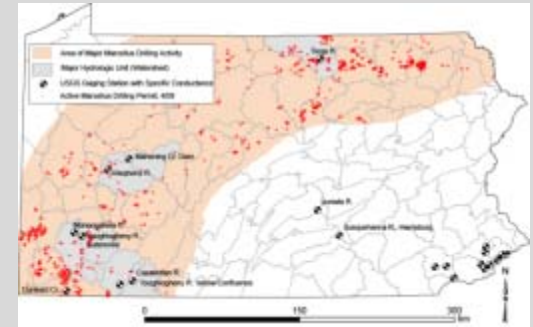
8 of 99 USGS gaging stations in PA measure SC. **These are on larger streams.**

- **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.

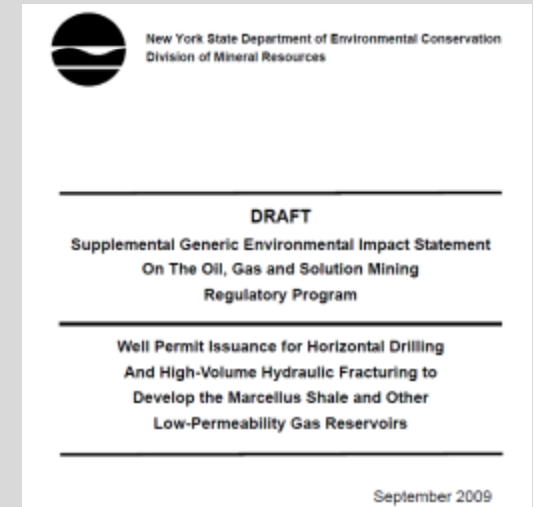




## New York State SGEIS considers the following potential environmental impacts

### 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 SGEIS considers the following potential environmental impacts

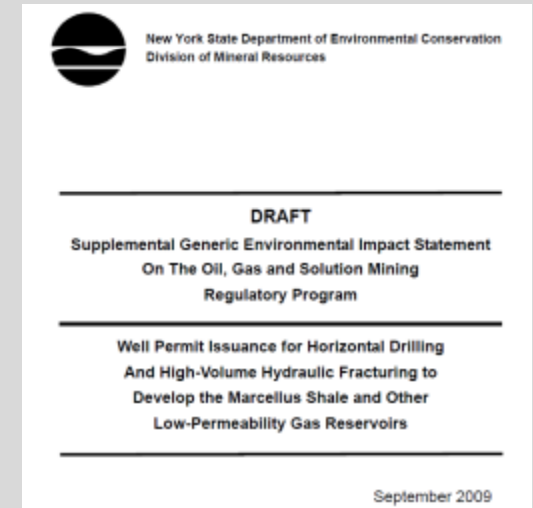
### 6.2 Floodplains

### 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*

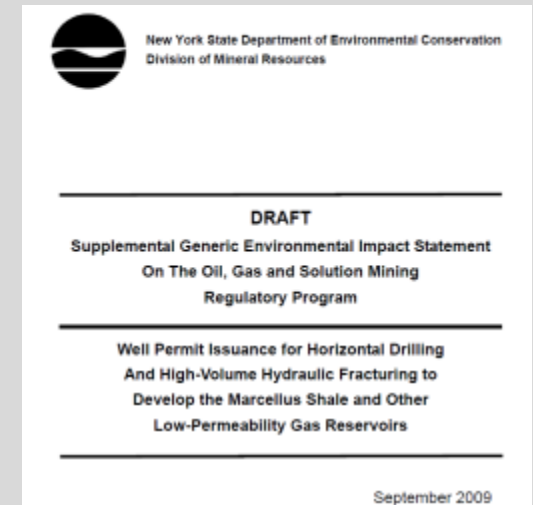
### **6.7 Centralized Flowback Water Surface Impoundments**

### **6.8 Naturally Occurring Radioactive Materials in the Marcellus Shale**

### **6.9 Visual Impacts**

### **6.10 Noise**

### **6.11 Road Use**



## 2<sup>nd</sup> 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<sup>3</sup> of natural gas equivalent (oil, gas, coal) does it take to produce 1 ft<sup>3</sup> 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-propanetricarboxylic 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

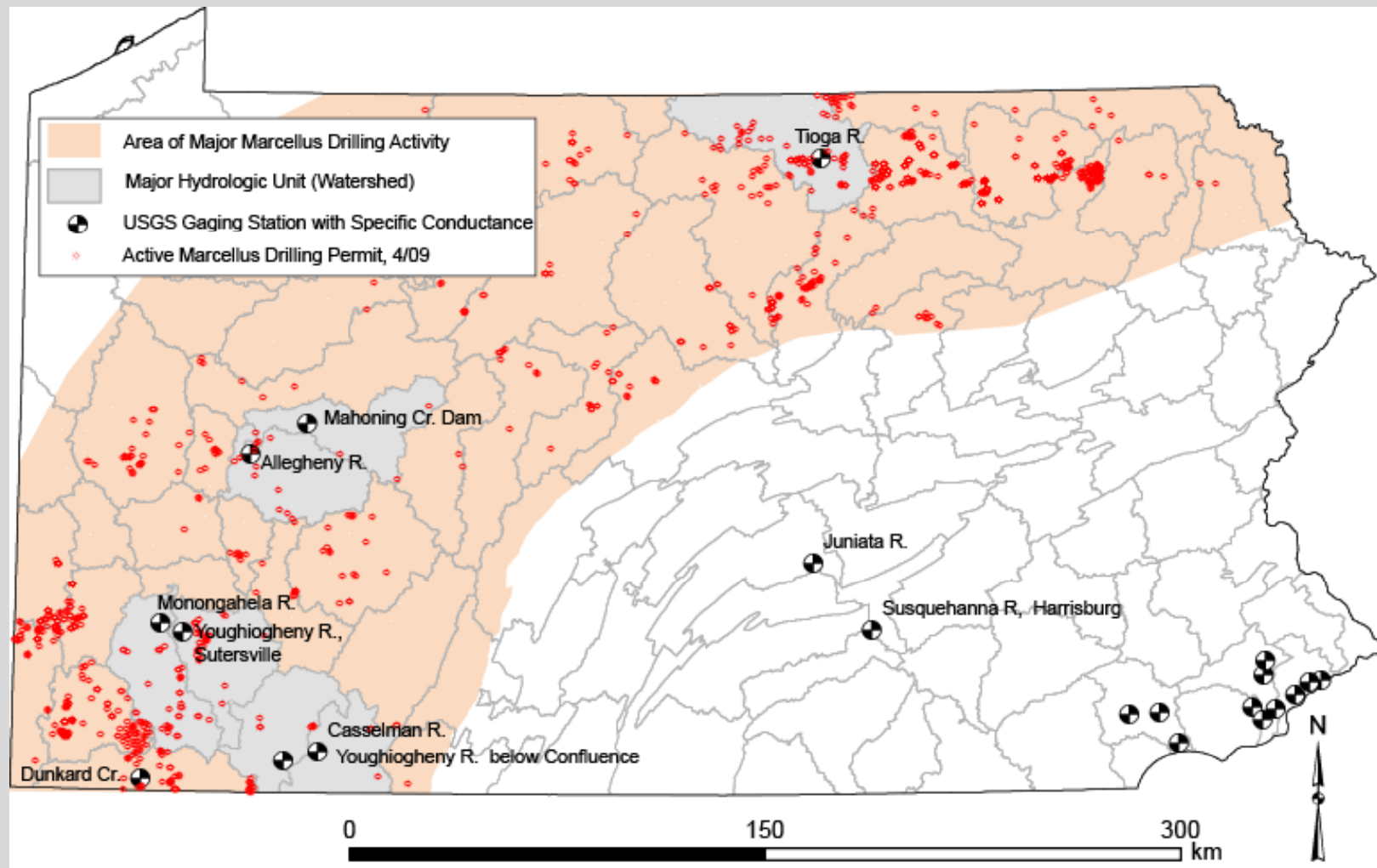
# Horizontal Drill Rig

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](http://www.donnan.com)



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



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



[tiogagawatch.blogspot.com/](http://tiogagawatch.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

## Real-time data on web



[www.srbc.net/](http://www.srbc.net/)

Not in Marcellus region

Juniata River, 6-day period

