Inorganic Geochemistry of Pennsylvania Marcellus Flowback Waters

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

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

Photos from New York State SGEIS

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Arlington VA
February 24, 2011
Bucknell MSI Database

Marcellus Shale Initiative Publications Database (beta)

This database lists primarily print-based publications and how to obtain them. It does NOT provide coverage of websites, blogs, news articles, newsletters, or other media. The Initiative is dedicated to updating the database as rapidly as resources allow.

Search

Filter by type:

- Report
- Conference
- Peer-reviewed article
- Fact sheet
- Industry journal article

2 publications have been added in the past 30 days.

Ways to search:

- Click "Browse all publications" above.
- Choose a filter and click "Go" to see all of that type of publication.
- Type into the Search box above; this will search titles, year, authors, and other database fields.

http://www.bucknell.edu/script/environmentalcenter/marcellus/default.aspx
Slickwater + Oil Field Brine (+/dissolution) = flowback water
Flowback water must be stored, transported, and then treated or reinjected.
Marcellus core section with salt blebs along bedding

From Blauch et al., 2009

<table>
<thead>
<tr>
<th>Cation</th>
<th>Bulk Core</th>
<th>Salt Scraping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td>Ca</td>
<td>40%</td>
<td>42%</td>
</tr>
<tr>
<td>Fe</td>
<td>46%</td>
<td>5%</td>
</tr>
<tr>
<td>K</td>
<td>4%</td>
<td>7%</td>
</tr>
<tr>
<td>Mg</td>
<td>6%</td>
<td>3%</td>
</tr>
<tr>
<td>Na</td>
<td>2%</td>
<td>40%</td>
</tr>
<tr>
<td>Sr</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
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

Some of the fracwaters are 1/3 solids!
Marcellus Flowback Water Geochemistry

Day 90 Flowback (n = 10)

EXPLANATION
- Marcellus water composition; letter indicates Well from Hayes (2009)
- Mean seawater

90-day flowback has nearly 100 mol % Cl.

90-day flowback has higher mol % Ca than undated flowback.

90-day flowback has lower pH than undated flowback.

90-day flowback is more saline than undated flowback.
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).
Some clear correlations with TDS

\[ y = 0.0253x + 102.77 \]
\[ R^2 = 0.8177 \]

Some lack enough data for correlation

\[ y = 0.5883x + 3967.5 \]
\[ R^2 = 0.9013 \]

Some mixed correlations with TDS

\[ y = 0.0159x + 18.274 \]
\[ R^2 = 0.587 \]

\[ y = 0.036x + 361.74 \]
\[ R^2 = 0.2814 \]
Volatile Dissolved Solids may suggest organic compounds that can complex metals such as Ba

Data collected by Molly Pritz
Western PA Acid Mine Drainage

Western/Central PA Produced Waters

Chapman, Capo, Stewart, Kirby, 2011
Geochemical modeling (PHREEQCI)

Saturation Index of Fe(OH)$_3$ (am) and Pyrite vs. Temperature (°C)

1. Slickwater is injected into well. Temperature increases from 22 to 72 °C. The temperature increase and pH decrease result in the water becoming more undersaturated with respect to Fe(OH)$_3$ and more saturated with respect to pyrite.

2. Frac water begins to travel up the well and subsequently decreases in temperature, increases in pH and becomes less undersaturated with respect to Fe(OH)$_3$ and remains saturated with pyrite.

3. Frac water returns to the earth’s surface and reaches equilibrium with atmospheric conditions*, resulting in the oxidation of Fe(II) and precipitation of Fe(OH)$_3$ a considerable decrease in the saturation of pyrite.

4. Slickwater comes into contact with the shale and oil field brine. It becomes saturated with pyrite and is mixed with the oil field brine that is further undersaturated with respect to Fe(OH)$_3$.

* Atmospheric conditions = saturated with O$_2$ and and P$_{CO2}$=10$^{-3.4}$
Geochemical modeling (PHREEQCI)

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

![Graph showing saturation index of barite and concentration of sulfate (mg/l) vs. temperature (°C).](image)
Geochemical modeling (PHREEQCI)

pH, SI Gases vs. T

pH and Saturation Index of CO₂, CH₄, O₂ vs. Temperature (°C)
Radiation in flowback waters

- North Central PA, known location, n=8
- Private waste water hauler, n=3
- Private treatment facility, n=7
Radiation in flowback waters

- North Central PA, known Location, n=8
- Private waste water hauler, n=3
- Private treatment, n=7

Graph showing correlation between Gross Beta Radiation (pCi/L) and Total Dissolved Solids (mg/L).
The graph shows the relationship between total dissolved solids (TDS) and the radium isotopes $^{226}\text{Ra}$ and $^{228}\text{Ra}$. The y-axis represents the ratio of $^{226}\text{Ra}$ to $^{228}\text{Ra}$ in pCi/L, while the x-axis represents the total dissolved solids in mg/L. The data points are indicated by blue squares and red crosses, with blue squares representing $^{226}\text{Ra}$ and red crosses representing $^{228}\text{Ra}$. The graph suggests a trend where the $^{226}\text{Ra}$ ratio increases as the TDS increases.
Will increases in stream conductivity tell us we have a Marcellus “leak”? Not consistently.
Ideal Scenario for using Spec. Cond. to identify Marcellus "leak"

**Conditions:**
- GW flow constant = 133 cfs
- Constant GW Spec. Cond. = 159 μS/cm
- Pulse "leak" of Marcellus Shale frac water from 0 to 11.6 to 0 cfs over 2 days
- Marcellus Spec. Cond. = 10,000 μS/cm
Assumes 1 million gallon leak, no runoff

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

Cl - Marcellus & road salt?
Br – Marcellus?
SO4 – Mine Drainage?
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

Tioga River, 187-hr period
• **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
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
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?
Table 2: Fracturing Fluid Additives, Main Compounds and Common Uses.

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

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?

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

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

www.donnan.com
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

Real-time data on web

www.srbc.net/
Not in Marcellus region

Juniata River, 6-day period

Discharge, cfs

Specific Conductance, uS/cm