Trace-metal concentrations in seeps and springs discharging from acid-producing rocks at road cuts in Tennessee

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U.S. Geological Survey
in cooperation with
Tennessee Department of Transportation

Geohazards Impacting Transportation in Appalachia
2016
Partners

- Tennessee Dept. of Transportation
- UT- Knoxville, Civil and Env. Engineering
- Georgia College
- Tennessee State University
- USGS Mineral and Env. Resource Science Center
Objectives

• Evaluate occurrence and transport of acid-rock drainage

• Evaluate microbial activity that affect pyrite oxidation
Sites Sampled
Basic models of ARD formation

1 - seeps and springs from pyrite-bearing formations

2 – rainfall / runoff over the face of a road cut in a pyrite-bearing formation.
Bacteria

Recharge
DO

Groundwater

Oxidation of pyrite

High Volume Runoff

Acidic water

Dry Season Evaporation

Gypsum precipitation

Fe, Al, and Metal Sulfate co-precipitation

Sulfate mineral dissolution
Release of acid, runoff of dissolved metal and sulfate

Rainfall

Low Volume

Transport of acidic water and dissolved metals

Acidithiobacillus sp.
Thiobacillus sp.
Pyrite Weathering

- Presence of water (runoff or formation)
- Exposure to oxygen
- Initial weathering reaction
  \[
  \text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+
  \]
- Microbial activity -- iron reduction
  \[
  14 \text{Fe}^{3+} + \text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+
  \]
Seeps and Springs

- Typically low flow rate (< 2 to 10 gal/min)
- Seeps identified from all formations
  - Chattanooga Sh
  - Fentress Fm
  - Anakeesta Fm
Sites Sampled – Precambrian / Anakeesta
Polk Co. – Anakeesta Fm

Samples collected from:

- 3 seeps
- 2 surface water sites
- Spring in right of way

<table>
<thead>
<tr>
<th>Seeps</th>
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</thead>
<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>TDS</td>
</tr>
<tr>
<td>Zn</td>
</tr>
<tr>
<td>Al</td>
</tr>
</tbody>
</table>
Polk Co. – Anakeesta Fm

Road cut has alternating sequences of Anakeesta type shale/slate and coarse grain sandstone / graywacke.

Seeps from both units had low pH. Water samples from Anakeesta type unit had high dissolved solids and high trace metals.
Polk Co. – Anakeesta Fm

Spring in right of way

pH 3.9-4.0 units
TDS 128 mg/L
Zn 77 ug/L
Al 760 ug/L
Polk Co. – Anakeesta Fm

SW sites
pH  3.2 – 4.0 units
TDS  170 – 190 mg/L
Zn  80 – 120 ug/L
Al  1700-2400 ug/L
Sites Sampled – Fentress Formation
Fentress County
Fentress Formation

Large spoil pile / disposal area

Seeps occur along coal sequences in cut
Low pH seep near coal seam with high trace metals

- **Fentress Formation**
  - pH 3.1, S.C. 2000
  - Al 16,200 – 33,500
  - pH 2.9, SC 1,900
  - pH 3.8, S.C. 1,830

300 ft
pH increase and SC varies with flow along road ditch and rip-rap.

- pH 5.4, SC 1,880, Al 12,100
- pH 2.9, SC 1,900
- pH 3.8, S.C. 1,830
- pH 7 – 7.8, SC 1,740, Al <20

300 ft
Sites Sampled – Chattanooga Shale
Williamson Co – Chattanooga Shale

Long lateral exposure of shale on bench cut
Shale breakdown at base of cut
Spoil pile with shale covering west slope
Natural wetland formed on bench
Multiple seeps from different units
Seep at Chattanooga contact

pH 3.5, SC 1,900
Al 2,900
Seepage through breakdown

Mfp

Mmy

Dc

pH 6.4 – 7.0
SC 450 – 585
AL <20
Hickman County -- Chattanooga Shale
SSM at Hickman

Mineralization covers nearly full face of road cut.

Multi-colored – different metal accumulation (??)

Potential source of low pH and high metal
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
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<td>TDS</td>
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<tr>
<td>SO4</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Al</td>
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<tr>
<td>Zn</td>
<td>1,690</td>
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<tr>
<td>Cu</td>
<td>387</td>
</tr>
<tr>
<td>Ni</td>
<td>796</td>
</tr>
</tbody>
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Pyrite Weathering

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Lab experiments to control bacteria

Supplements that will reduce O2 and stimulate iron- & sulfur-reducing conditions in the aquifer
- Lactate & B-Vitamins

• 500 gr Chattanooga Shale – particle size 1/8 – 3/4 inch
• di H₂O flush out residue -- 5 volumes
Rationale & treatments

\[ \text{FeS}_2(\text{ppt}) + 8 \text{H}_2\text{O} + \text{O}_2 \leftrightharpoons \text{Fe}^{3+}(\text{O})_x + 2 \text{SO}_4^{2-} + 16\text{H}^+ \]

Geochemical reactions are reversible under reducing (anaerobic) conditions

- **3 Experiments, basic treatments:**
  1. +NaOH & bleach (temporary sterile shock)
  2. Control - no additions
  3. + Sodium Lactate – favorite food of SRB
  4. +Lactate & soy formula – favorite food, vitamin B, proteins & stick to shale
Experiment 3 – pre-injection
NaOH & extended time
1. NaOH + bleach
2. Control
3. NaOH + Lactate
4. NaOH + Lactate + Soy
Summary

- Cooperative investigation with TDOT to evaluate ARD from road cuts.
- Primary pyrite-bearing formations are Chattanooga Shale, Fentress Formation, and Anakeesta units.
- Low pH and high trace metals, very high Al concentrations
Summary

- Attenuation observed in pH and metals at Polk County and Fentress County.
- Lithologic control on sulfate and trace metals at Anakeesta (Polk Co).
- SSM can result in rapid change in pH and metals. Potential source to SW (??)
- Lab microcosms -- injection with NaOH, followed by Lactate had low iron, low conductivity, & elevated pH for 200+ days
Questions ??