Investigating Background Groundwater Quality at Contaminated Sites – A Hydrogeochemical Approach

Remediation Technologies Symposium 2011, Banff, Alberta (October 2011)

Presented by: Stephen Munzar

HEMMERA
Presentation Outline

- Introduction
- Determining Background - Approaches
- Case Study
  - Introduction
  - Data Collected
  - Results
  - Conclusions
Introduction

- **Common definition of background GW Quality:**
  - Natural ambient groundwater quality not influenced by anthropogenic sources
  - Commonly considered the groundwater quality “upgradient” of potential or known contaminant sources

- **Why and when do we determine background?**
  - Confirm natural presence of a substance
  - Prevent / limit unnecessary investigation / remediation of natural substances
  - To define a site specific local background concentration for a natural substance
  - To define the ambient or baseline groundwater conditions
Determining Background Conditions

- **Common Approach:**
  - Install upgradient monitoring wells outside of influence of site contamination
  - Groundwater chemistry represents ambient non-anthropogenic conditions
  - Statistically derive background concentration(s)

- **Potential Issues / Concerns:**
  - Upgradient wells completed in different geology and/or flow setting (not representative of background)
  - Concentrations of inorganic constituents tend to be “spotty” (variability)
  - Statistics may bias defined background concentrations
Regulatory Requirements in BC / Yukon:

- Install / sample min. 3 background wells
- Locate wells outside influence of anthropogenic sources within same geologic/hydrogeologic setting
- Sample wells min. two events
- Calculate 95$^{th}$ percentile concentration
Scientific Based Approach

1. Thorough desktop research:
   - Regional surficial & bedrock geology
   - Soil mapping studies
   - Hydrogeology & geochemistry
2. Site history (source & potential contaminants)
3. Develop preliminary conceptual model
4. Define local geology & hydrogeology
5. Soil/sediment mineralogy (if beneficial)
6. Collect additional groundwater geochemical data (major cations, anions, alkalinity)
7. Refine, confirm, or refute preliminary conceptual model
Case Study Background

- Located adjacent to Fort Nelson Airport, NE British Columbia
- Used as refuse dumping area from 1952-1960s from the housing barracks located at the airport
- 3 Historical dumping sites and a sewage system:
  - Site 9 – Former Lower Housing Dump
  - Site 10A – Former Concrete Debris Dump
  - Site 10B – Former Upper Housing Dump
  - Site 11 – Sewage Disposal System
- Material observed in dumps - concrete, garbage, sheet metal, electrical cable, glass, random metal debris, metal cans, dishes, tiles, lumber and coal (one site)
- Multiple site investigations completed to characterize soil and groundwater quality – **Dissolved [sulphate] > CSR AW Standards**
Study Objectives

1. Determine if sulphate is naturally occurring or anthropogenic

2. If naturally occurring, determine why it is elevated, and define a local background concentration
Study Location
Data Collected for Background

- Desktop information (geology, etc.)
- Local surficial geology (intrusive invest.)
- Collection and analysis of speciated sulphur in soil
- Mineralogical (petrographic) sample submission / analysis
- Site wide groundwater sampling for dissolved metals, anions
Results
Geology

**Surficial Geology**
- **Regional** - glaciolacustrine deposits (silts and clays) common to peace region
- **Local** - Silt and clay capped with thin (0.5-1.0 m) sand and gravel

**Bedrock Geology**
- **Local** – Not observed (anticipated >50 m deep)

**Published Regional Soil Maps/Reports**
- Soil chemistry reflects/mirrors the bedrock chemistry
- Marine shales commonly contain anhydrite (CaSO$_4$) and gypsum (CaSO$_4$·2H$_2$O) & other sulphate minerals
- Fort Nelson soils are relatively saline and contain accumulations of gypsum and carbonate minerals.
Local groundwater is mainly perched within the glaciolacustrine silt/clay deposits.

Groundwater flow directions and gradients mirror topography.

Groundwater flows either towards the north, east or south depending on location along the ridge.
Local Groundwater Flow Direction
Sulphate Distribution

<table>
<thead>
<tr>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.8</td>
<td>2590</td>
<td>1125</td>
</tr>
</tbody>
</table>

Sulfate Concentrations in Groundwater (mg/L)
Preliminary Assessment Results

- Housing dumps may have contained drywall?
- Thin layer of coal at one dump site (sulphide minerals in the coal?)
- Bedrock geology consists of marine shales
- Surficial geology consists of silt and clay
- Regional soil studies - chemistry mirrors marine bedrock chemistry (saline soils), gypsum (CaSO$_4$$\cdot$2H$_2$O) accumulation near surface
- Soil results - elevated barium (barite BaSO$_4$?)
- Groundwater chemistry - elevated SO$_4$ (widespread) not co-incident with potential sources
Preliminary Conceptual Model

- **SO₄** in groundwater associated with:
  - **Barite** (BaSO₄) that could be naturally occurring and sourced from marine shales
  - **Gypsum** (CaSO₄·2H₂O) sourced from drywall or naturally occurring gypsum in soil (regional soil survey)
  - **Coal** containing sulphide (FeS₂) minerals that have oxidized and released SO₄
Test Preliminary Conceptual Model

- To confirm or refute Barite, Gypsum or Sulphide source:
  - Need speciated sulphur analysis in soil
  - Soil mineralogy
  - Groundwater chemistry data (metals and anions)
  - Chemical cross-plots e.g. Ba vs. $\text{SO}_4$, Ca vs. $\text{SO}_4$, and Fe vs. SO4
## Soil Analytical Results: Speciated S

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample Location</th>
<th>Sample Depth (mbgs)</th>
<th>Soil Type</th>
<th>Sulfate Concentration (ppm)</th>
<th>Sulphide (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-10TP-50</td>
<td>Fort Nelson Airport - Site 9</td>
<td>1.8 - 2.0</td>
<td>Silt and Clay</td>
<td>11800</td>
<td>700</td>
</tr>
<tr>
<td>9-10TP-51</td>
<td>Fort Nelson Airport - Site 9</td>
<td>4.7 - 4.9</td>
<td>Clay</td>
<td>3200</td>
<td>300</td>
</tr>
<tr>
<td>9-10TP-74</td>
<td>Fort Nelson Airport - Site 9</td>
<td>3.6 - 3.9</td>
<td>Clay</td>
<td>5900</td>
<td>300</td>
</tr>
<tr>
<td>9-10TP-75</td>
<td>Fort Nelson Airport - Site 9</td>
<td>7.3 - 7.6</td>
<td>Clay</td>
<td>12200</td>
<td>1900</td>
</tr>
<tr>
<td>10A-10TP-63</td>
<td>Fort Nelson Airport - Site 10A</td>
<td>3.45 - 3.65</td>
<td>Clay</td>
<td>4000</td>
<td>100</td>
</tr>
<tr>
<td>10A-10TP-64</td>
<td>Fort Nelson Airport - Site 10A</td>
<td>4.1 - 4.3</td>
<td>Clay</td>
<td>1900</td>
<td>1700</td>
</tr>
<tr>
<td>10A-10TP-65</td>
<td>Fort Nelson Airport - Site 10A</td>
<td>3.9 - 4.0</td>
<td>Clay</td>
<td>4300</td>
<td>200</td>
</tr>
<tr>
<td>10A-10TP-66.1</td>
<td>Fort Nelson Airport - Site 10A</td>
<td>3.8 - 3.9</td>
<td>Clay</td>
<td>3200</td>
<td>200</td>
</tr>
<tr>
<td>10A-10TP-66.2</td>
<td>Fort Nelson Airport - Site 10A</td>
<td>3.8 - 3.9</td>
<td>Clay</td>
<td>2900</td>
<td>200</td>
</tr>
<tr>
<td>10A-10TP-67</td>
<td>Fort Nelson Airport - Site 10A</td>
<td>4.7 - 4.8</td>
<td>Clay</td>
<td>100</td>
<td>4300</td>
</tr>
<tr>
<td>10B-10TP-53</td>
<td>Fort Nelson Airport - Site 10B</td>
<td>4.1 - 4.2</td>
<td>Clay</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>10B-10TP-79</td>
<td>Fort Nelson Airport - Site 10B</td>
<td>3.3 - 3.4</td>
<td>Clay</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>10B-10TP-80</td>
<td>Fort Nelson Airport - Site 10B</td>
<td>3.3 - 3.4</td>
<td>Clay</td>
<td>200</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>11-10TP-1</td>
<td>Fort Nelson Airport - Site 11</td>
<td>3.05 - 3.15</td>
<td>Clay</td>
<td>800</td>
<td>300</td>
</tr>
<tr>
<td>10BMW-1.1</td>
<td>Fort Nelson Airport - Site 10B</td>
<td>1.2 - 1.4</td>
<td>Sand and Gravel</td>
<td>100</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>10BMW-1.4</td>
<td>Fort Nelson Airport - Site 10C</td>
<td>4.3 - 4.7</td>
<td>Clay</td>
<td>200</td>
<td>4000</td>
</tr>
</tbody>
</table>

- Sulphate is the dominant form of sulphur in the native soil.
Mineralogy Results

- Polished thin sections prepared for one sample where 12,200 ppm SO₄ was reported in soil
- Several grains of \textit{gypsum} >1\% (i.e. >10,000 ppm)
Chemical Cross-Plots & Piper Plots

Chemical Cross-Plots

- Conc. of 33 parameters (metals and anions) plotted vs SO$_4$ conc.
- Dissolved Ca, Mg, and Na correlated positively with SO$_4$ (Not Ba & Fe)

Piper Plots
Typical mineralogy containing Ca, Mg, Na and SO₄ include:

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Mineral Formula</th>
<th>Mass Ratio (Ca, Na, Mg:SO₄) in the mineral</th>
<th>Mass Ratio Based on Groundwater Analytical Results (Range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum / Anhydrite</td>
<td>CaSO₄ *2H₂O</td>
<td>0.42 (Ca:SO₄)</td>
<td>0.2 – 0.6 (Ca:SO₄)</td>
</tr>
<tr>
<td>Epsomite</td>
<td>MgSO₄ *7H₂O</td>
<td>0.25 (Mg:SO₄)</td>
<td>0.1-0.4 (Mg:SO₄)</td>
</tr>
<tr>
<td>Thenardite</td>
<td>Na₂SO₄</td>
<td>0.48 (Na:SO₄)</td>
<td>0.01 – 0.07 (Na:SO₄)</td>
</tr>
</tbody>
</table>

- Dissolved mass ratios agree well with mineral mass ratios
- These are minerals commonly occur in evaporitic sedimentary deposits such as marine shales
Refinement of Prelim. Conceptual Model

- Barite not a major source of dissolved $\text{SO}_4$
- Sulphide not a major source of diss. $\text{SO}_4$
- Gypsum is a more likely source
- Remaining questions:
  1. Could natural gypsum solubility account for concentrations measured?
  2. Is the source of gypsum from natural or anthropogenic?
1. Gypsum Solubility

- Max $\text{SO}_4$ concentration 2,590 mg/L
- Literature – 3,150 mg/L to 5,000 mg/L in more saline soil environments
  - Translates to $\text{SO}_4$ concentrations of 1,750 to 2,790 m/L
  - $[\text{SO}_4]$ in seawater ~2,700 mg/L

- Conclusion:
  - Gypsum alone could account for the concentrations reported in groundwater
2. Sources of SO$_4$

Potential Anthropogenic Sources:

**Drywall:** Potentially disposed during dumping?
- **BUT:**
  - Drywall *not* observed in fill materials
  - Only 3 of 4 sites were dump sites
  - Dissolved SO$_4$ concentrations at dump sites generally low

**Coal:** Can contain pyrite (FeS$_2$) when oxidized can release sulphate and iron.
- **BUT:**
  - Coal was only deposited at only one dump site
  - No correlation between SO$_4$ and Fe in groundwater

**Conclusion:** *Anthropogenic Derived Sulphate is Unlikely*
2. Sources of SO$_4$ (Cont’d)

Natural Sources:

**Natural Sulphate Minerals:** e.g. Gypsum

- Bedrock comprised of marine shales
- Soil mapping indicate presence/accumulation of gypsum in soils
- High SO$_4$ concentrations deep in native soil (>12,000 ppm)
- Mineralogy confirms natural gypsum (>10,000 ppm)
- Strong positive correlation between Ca & SO$_4$ and Mg & SO$_4$
- Ca:SO$_4$ and Mg:SO$_4$ ratios in groundwater suggest sulphate mineral source
- Gypsum is fairly soluble in water 3,150 mg/L pure
Study Conclusions

- Natural gypsum in soil was the source of $\text{SO}_4$ in groundwater
- Identifying 3 background well locations was challenging
- Ministry liked the approach due to the supplemental scientific based multiple lines of evidence provided

Lessons Learned:

- 3 background wells may often not be enough
- Always useful to develop a conceptual model to explain the occurrence of the constituent in question – and collect key data to support/refute the conceptual model
THANK YOU!

QUESTIONS?

Presenter Contact Information:

¹Stephen Munzar, M.Sc., P.Geo.
Hydrogeologist, Hemmera, Victoria, BC, Canada
smunzar@hemmera.com