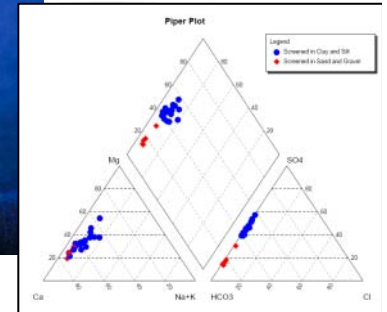




 **HEMMERA**



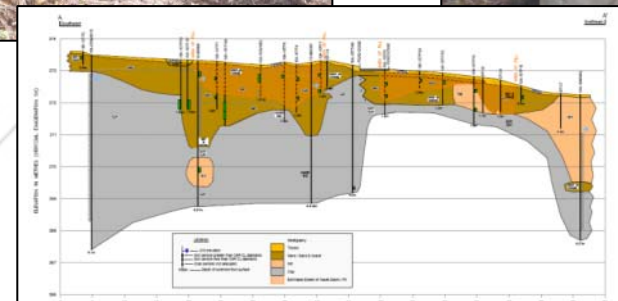
Investigating Background Groundwater Quality at Contaminated Sites – A Hydrogeochemical Approach

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

Presented by: Stephen Munzar¹

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:**

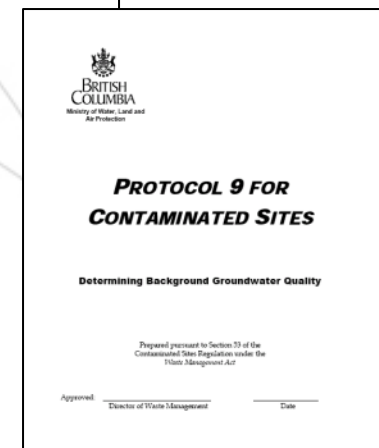
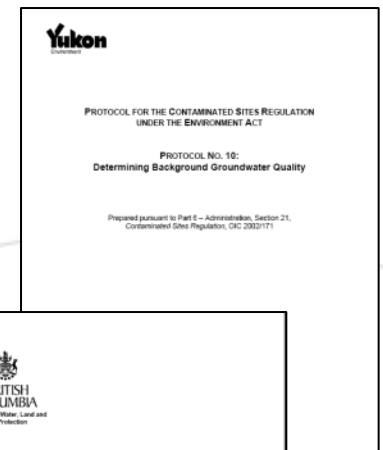
- Install upgradient monitoring wells outside of influence of site contamination
- Groundwater chemistry represents ambient non-anthropogenic conditions
- Statistically derive background concentration(s)

■ **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

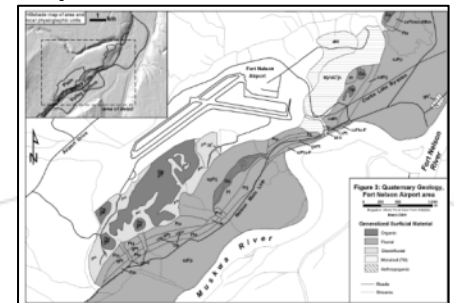
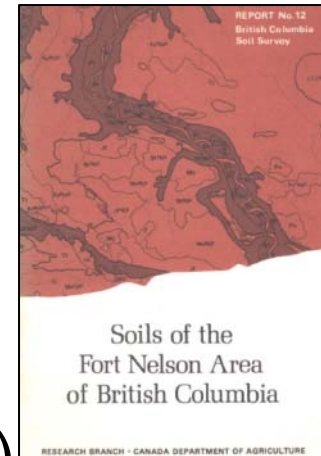
Regulatory

- **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 95th 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

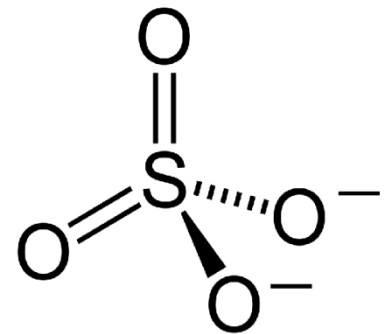
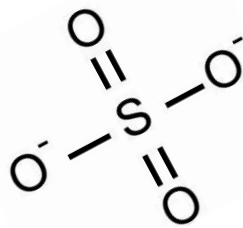


Case Study Background

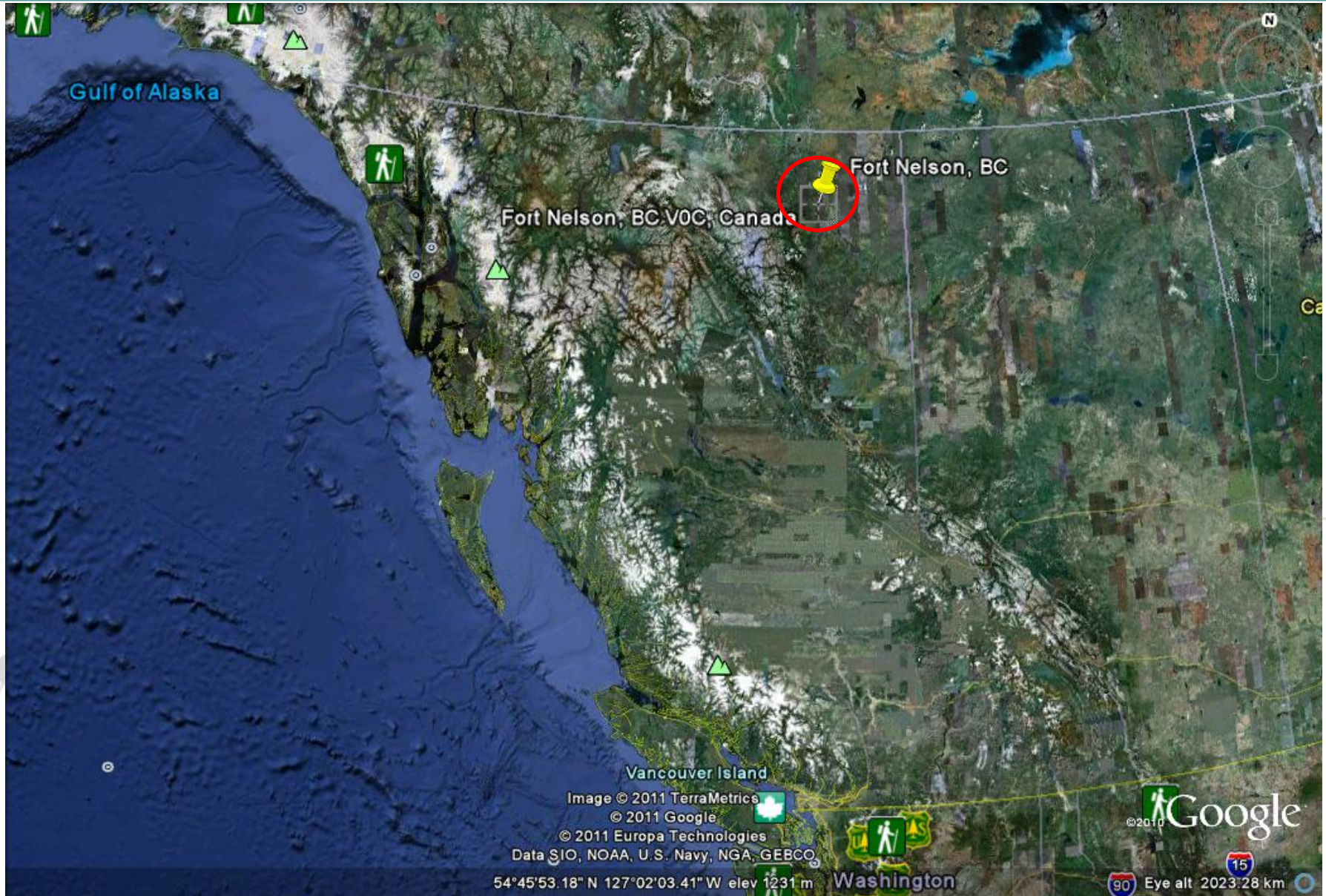
- Located adjacent to Fort Nelson Airport, NE British Columbia
- Used as refuse dumping area from 1952-1960s from the housing barracks located at the airport
- 3 Historical dumping sites and a sewage system:
 - Site 9 – Former Lower Housing Dump
 - Site 10A – Former Concrete Debris Dump
 - Site 10B – 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

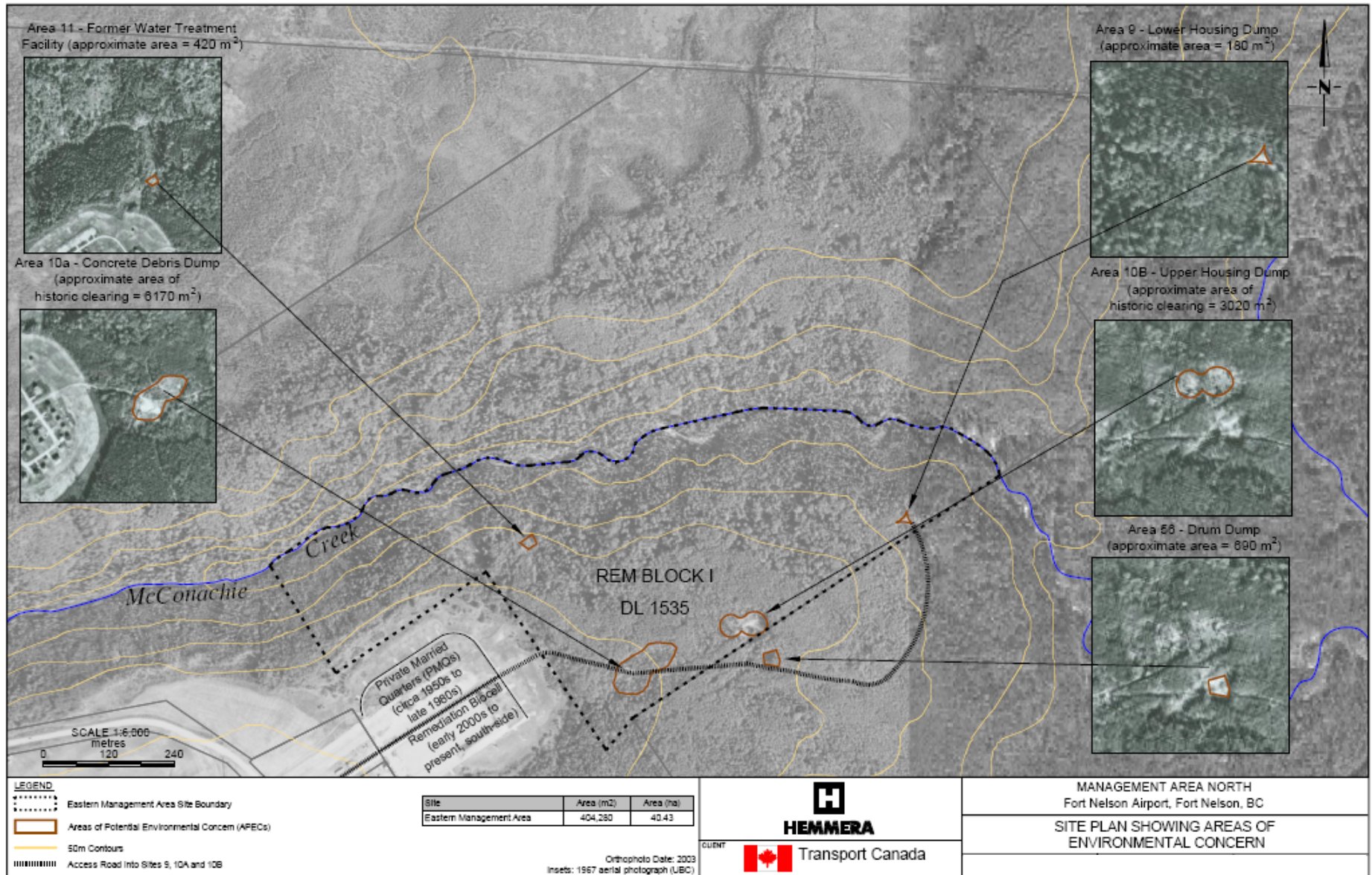
1. Determine if sulphate is naturally occurring or anthropogenic
2. If naturally occurring, determine why it is elevated, and define a local background concentration



Study Location



Site Layout



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

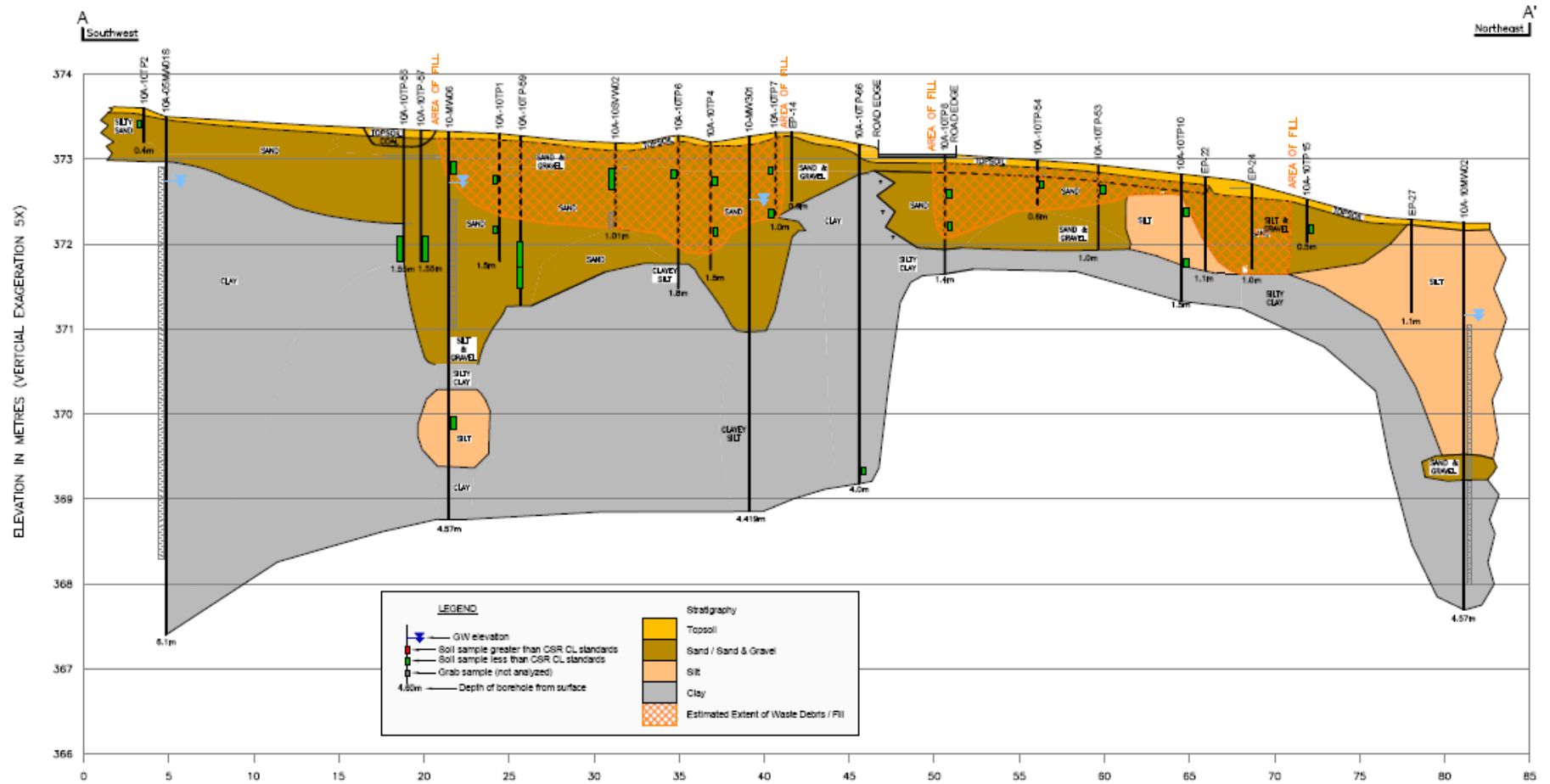
Bedrock Geology

- *Regional* - Marine shales and siltstones of the Lower Cretaceous Buckingham Formation, Fort St. John Group.
- *Local* – Not observed (anticipated >50 m deep)

Published Regional Soil Maps/Reports

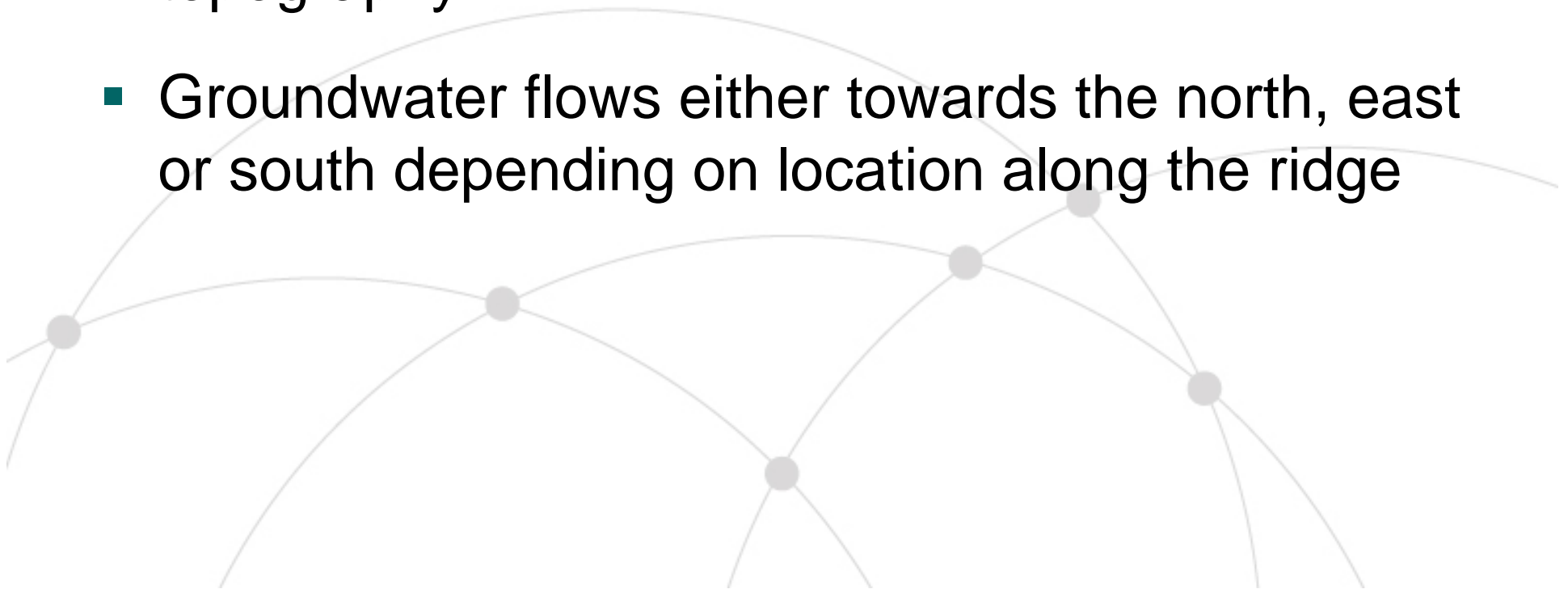
- Soil chemistry reflects/mirrors the bedrock chemistry
- Marine shales commonly contain anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) & other sulphate minerals
- Fort Nelson soils are relatively saline and contain accumulations of gypsum and carbonate minerals.

Geologic Cross-Section

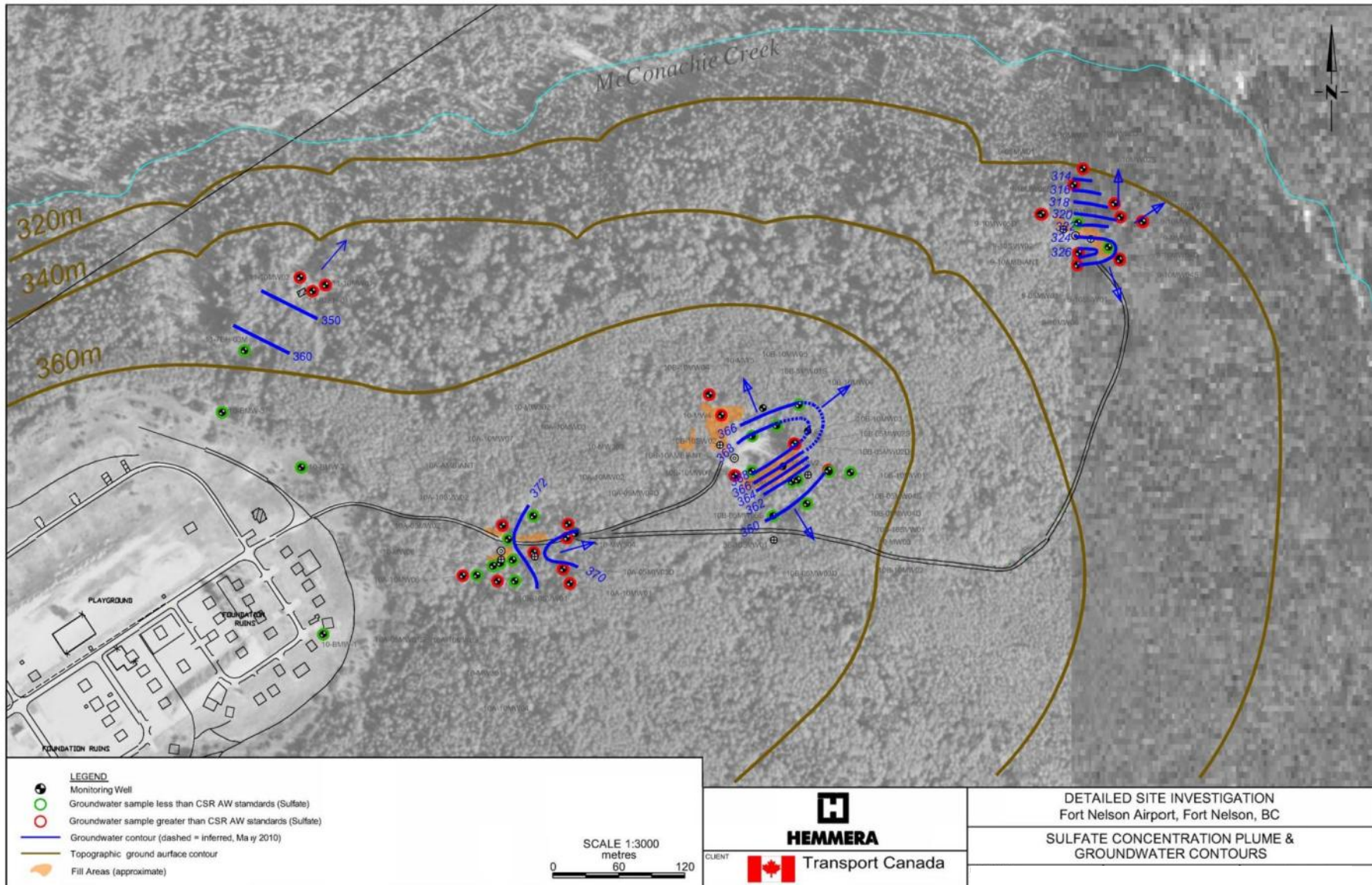


Hydrogeology

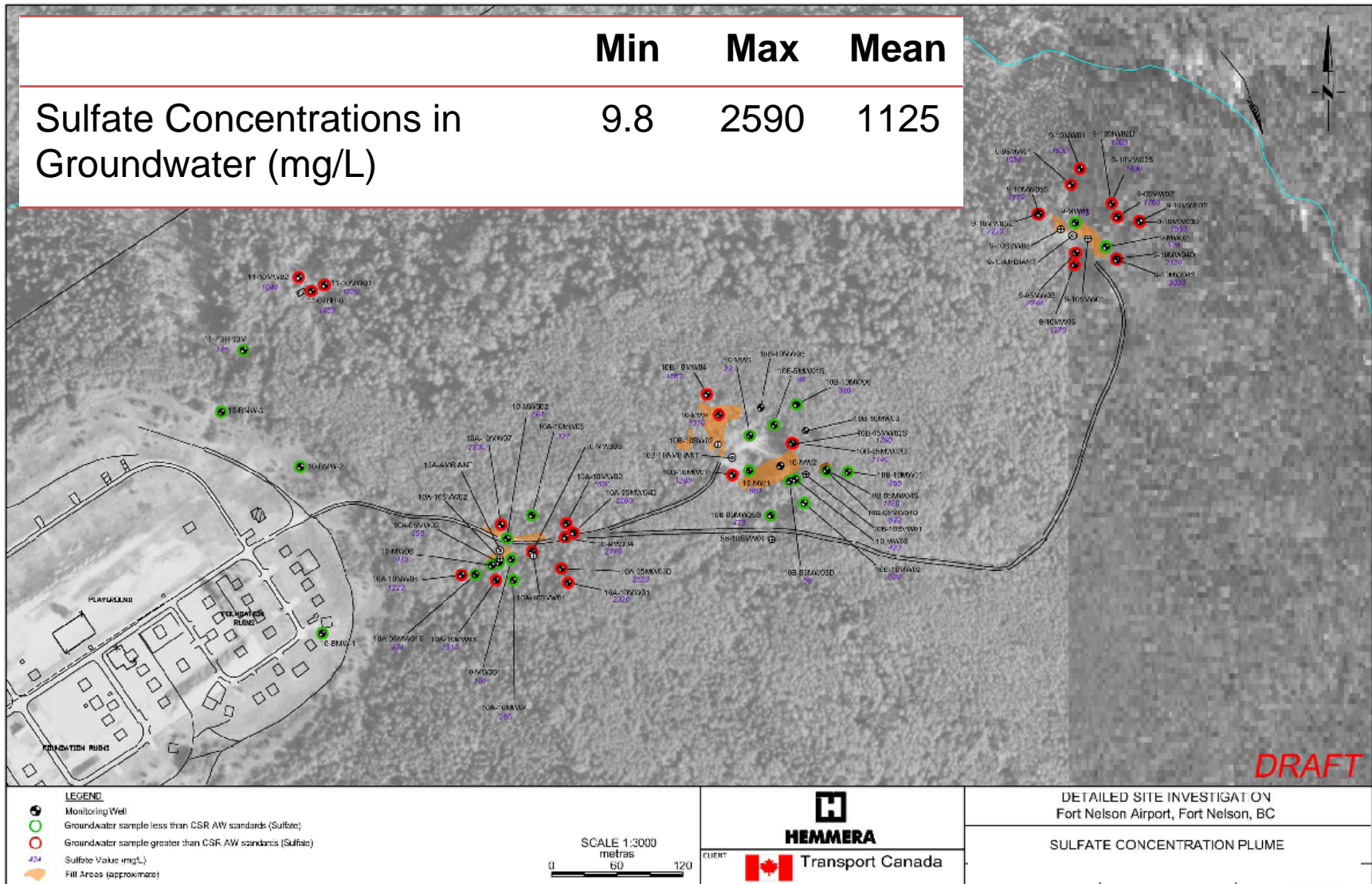
- Local groundwater is mainly perched within the glaciolacustrine silt/clay deposits
- Groundwater flow directions and gradients mirror topography
- Groundwater flows either towards the north, east or south depending on location along the ridge



Local Groundwater Flow Direction



Sulphate Distribution



Preliminary Assessment Results

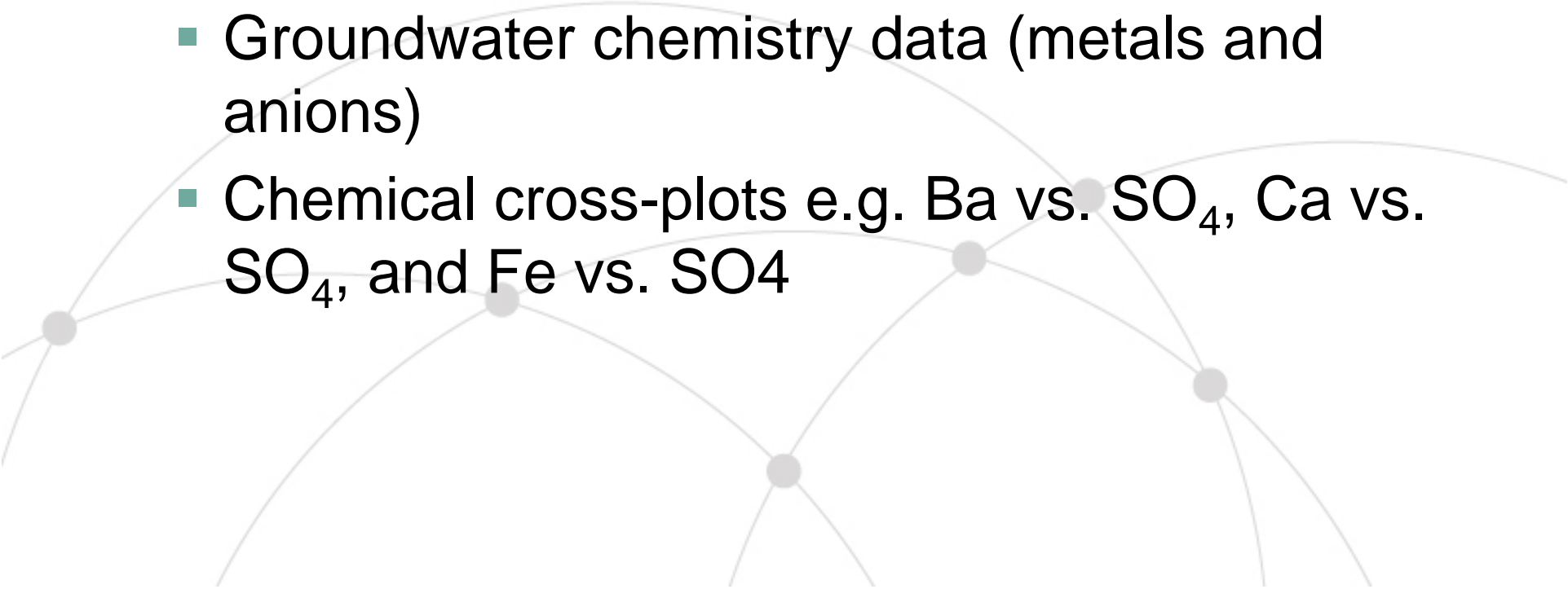
- Housing dumps may have contained drywall?
- Thin layer of coal at one dump site (sulphide minerals in the coal?)
- Bedrock geology consists of *marine* shales
- Surficial geology consists of silt and clay
- Regional soil studies - chemistry mirrors marine bedrock chemistry (saline soils), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) 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

- SO_4 in groundwater associated with:
 - **Barite** (BaSO_4) that could be naturally occurring and sourced from marine shales
 - **Gypsum** ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) sourced from drywall or naturally occurring gypsum in soil (regional soil survey)
 - **Coal** containing sulphide (FeS_2) minerals that have oxidized and released SO_4



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. SO_4 , Ca vs. SO_4 , and Fe vs. SO_4
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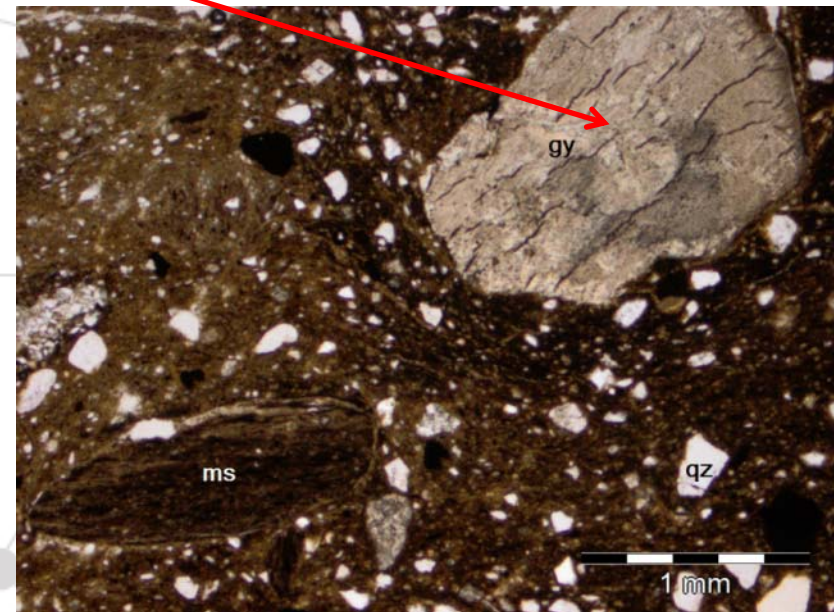
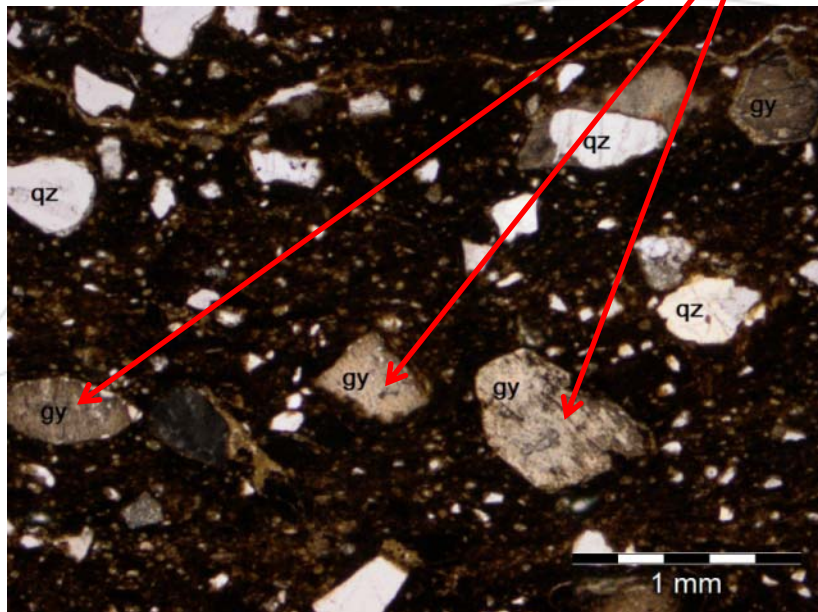
Soil Analytical Results: Speciated S

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

Mineralogy Results

Mineralogy Results

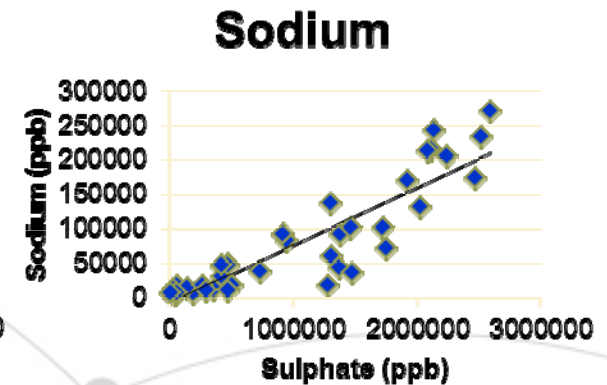
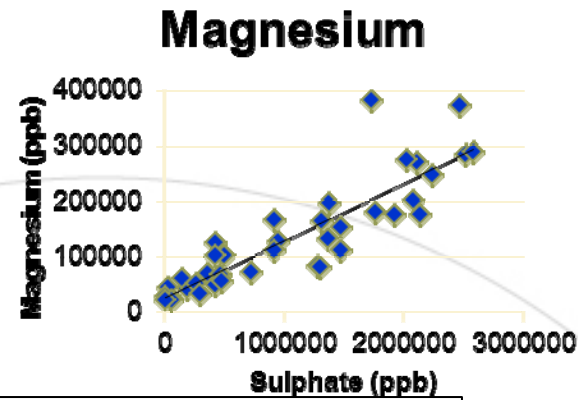
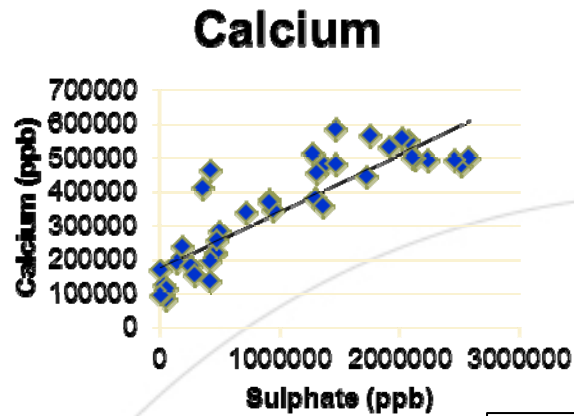
- Polished thin sections prepared for one sample where 12,200 ppm SO_4 was reported in soil
- Several grains of gypsum >1% (i.e. >10,000 ppm)



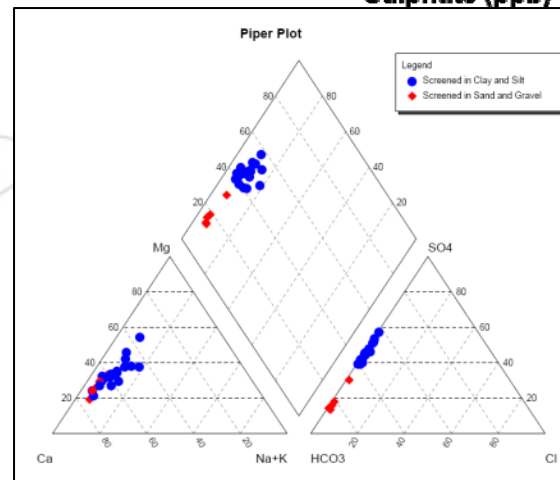
Chemical Cross-Plots & Piper Plots

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



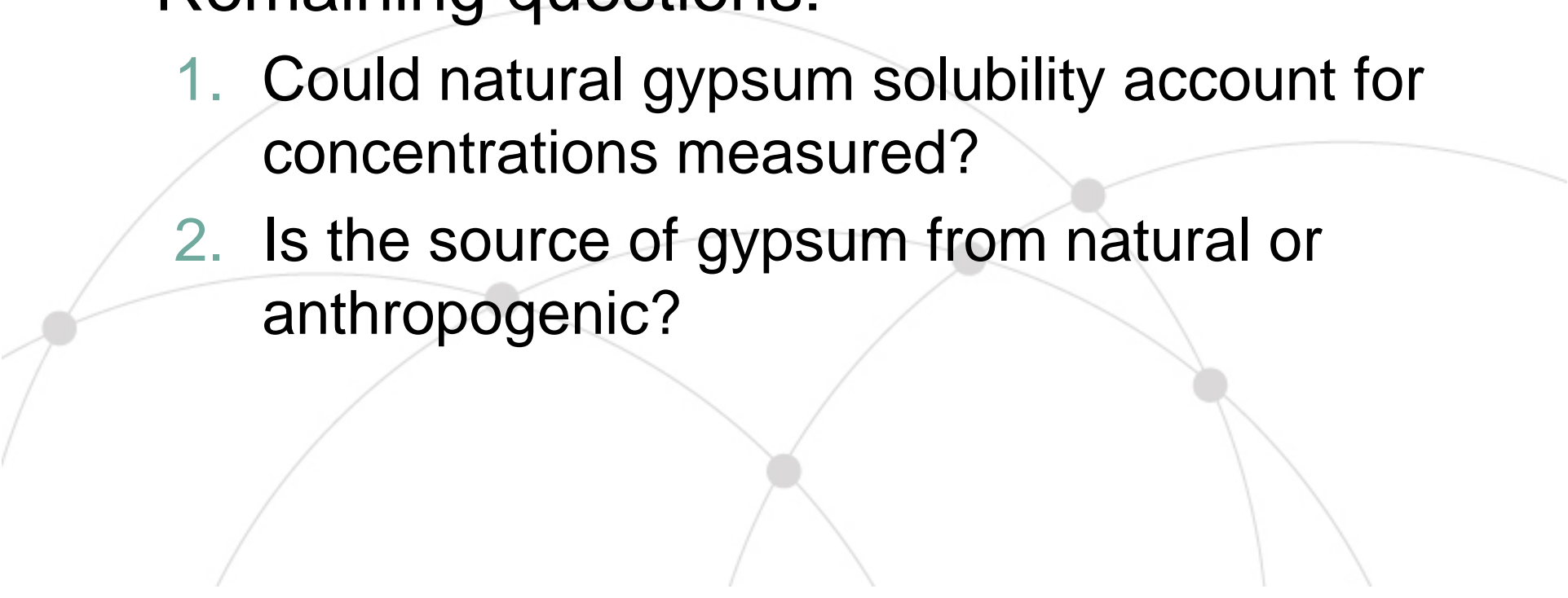
Dissolved SO₄ Chemical Signature

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

Mineral Name	Mineral Formula	Mass Ratio (Ca, Na, Mg:SO ₄) in the mineral	Mass Ratio Based on Groundwater Analytical Results (Range)
Gypsum / Anhydrite	CaSO ₄ *2H ₂ O	0.42 (Ca:SO ₄)	0.2 – 0.6 (Ca:SO ₄)
Epsomite	MgSO ₄ *7H ₂ O	0.25 (Mg:SO ₄)	0.1-0.4 (Mg:SO ₄)
Thenardite	Na ₂ SO ₄	0.48 (Na:SO ₄)	0.01 – 0.07 (Na:SO ₄)

- 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 SO_4
 - Sulphide not a major source of diss. 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 SO_4 concentration 2,590 mg/L
- Literature – 3,150 mg/L to 5,000 mg/L in more saline soil environments
 - Translates to SO_4 concentrations of 1,750 to 2,790 mg/L
 - $[\text{SO}_4]$ in seawater ~2,700 mg/L
- **Conclusion:**
 - Gypsum alone could account for the concentrations reported in groundwater

2. Sources of SO₄

Potential Anthropogenic Sources:

Drywall: Potentially disposed during dumping?

BUT:

- Drywall *not* observed in fill materials
- Only 3 of 4 sites were dump sites
- Dissolved SO₄ concentrations at dump sites generally low



Coal: Can contain pyrite (FeS₂) when oxidized can release sulphate and iron.

BUT:

- Coal was only deposited at only one dump site
- No correlation between SO₄ 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 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?

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