Groundwater Quality

Agency Meeting
January 31 – February 3, 2012

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Piteau Associates

Acknowledgements

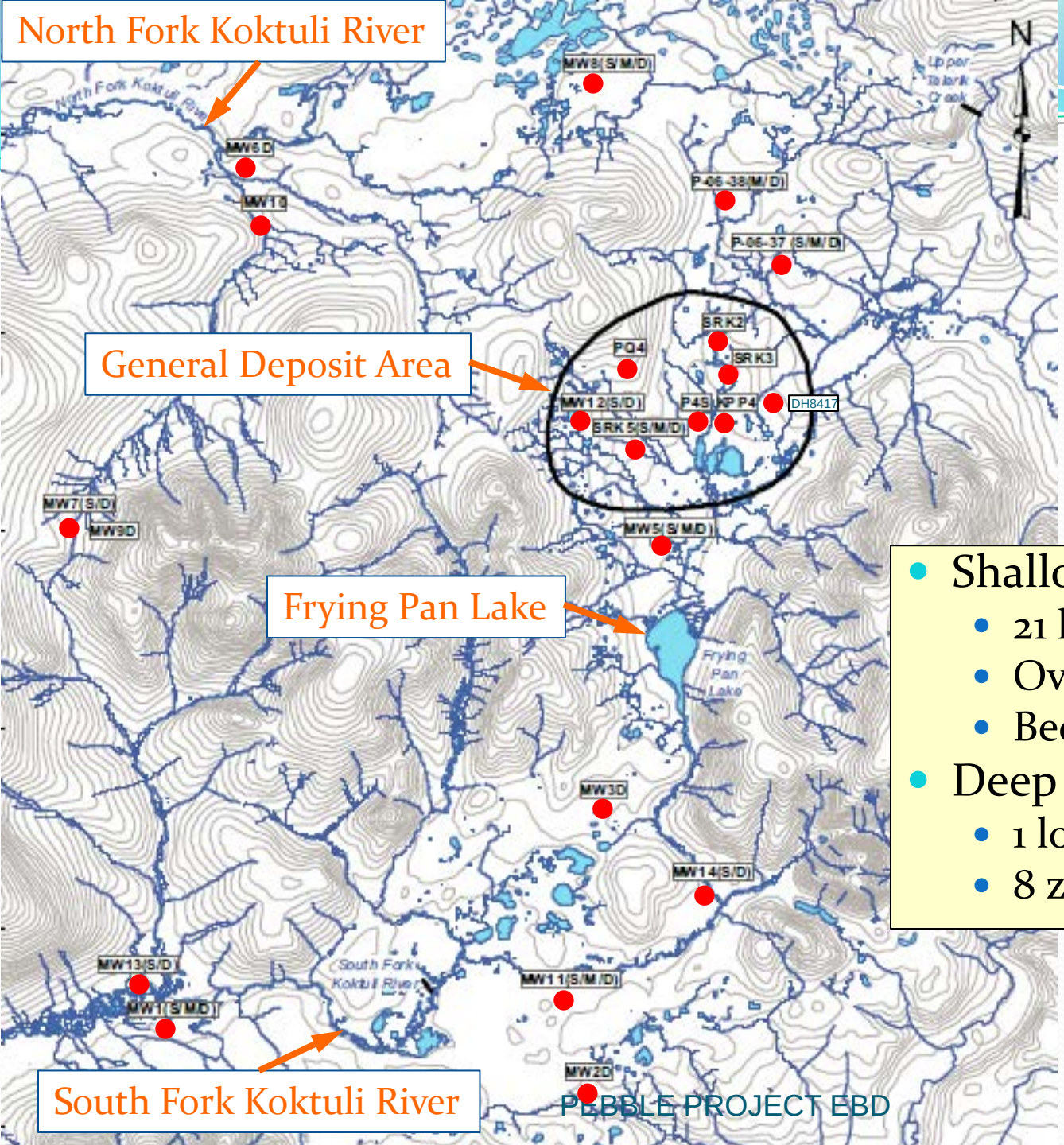
- SLR International Corp
- Schlumberger Water Services

Outline

1. Objective and Sampling Program
2. Index Parameters
3. Major Ions
4. Trace Elements
5. Nutrients
6. Summary

Groundwater Sampling Objective

- Characterize the baseline groundwater quality



Groundwater Sampling Locations (Well Nests)

- Shallow (up to 200 ft)
  - 21 locations (well nests)
  - Overburden: 25 wells
  - Bedrock: 14 wells
- Deep (up to 4000 ft)
  - 1 location
  - 8 zones

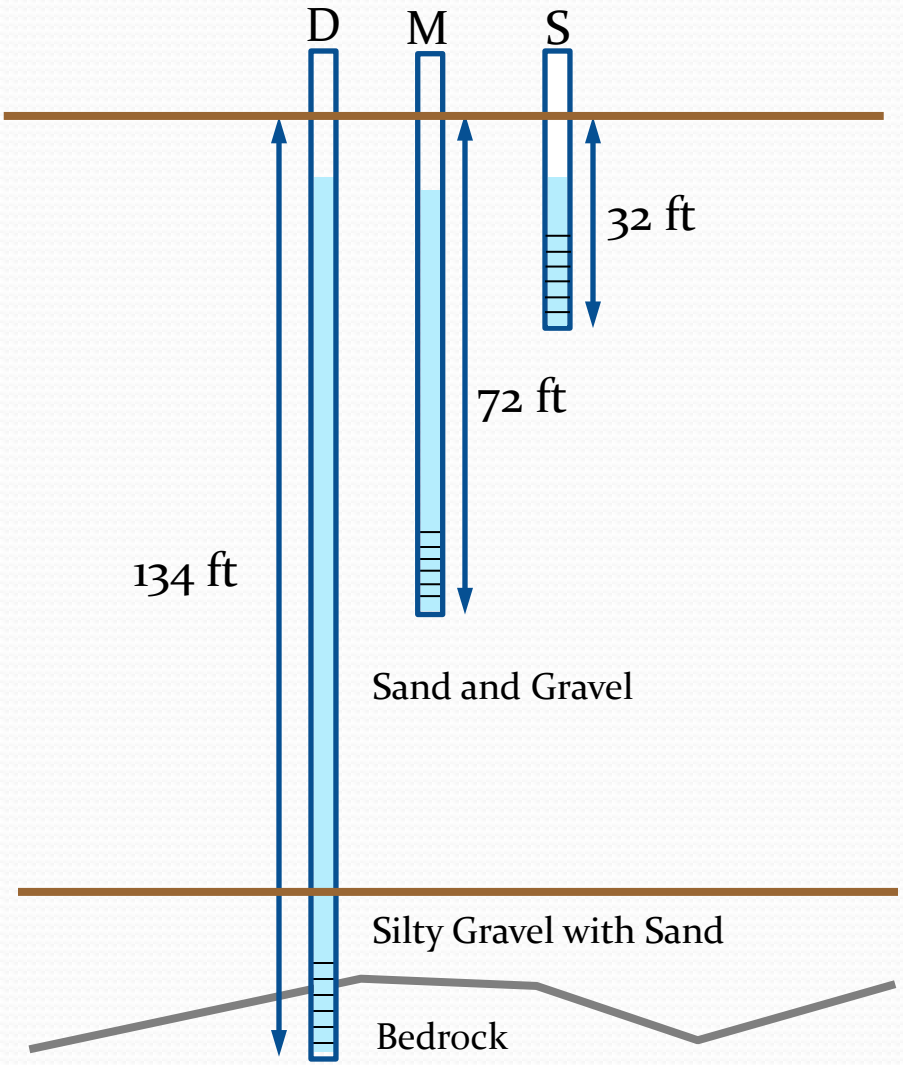
Schlumberger WATER SERVICES

Example of monitoring well nest

MW-1

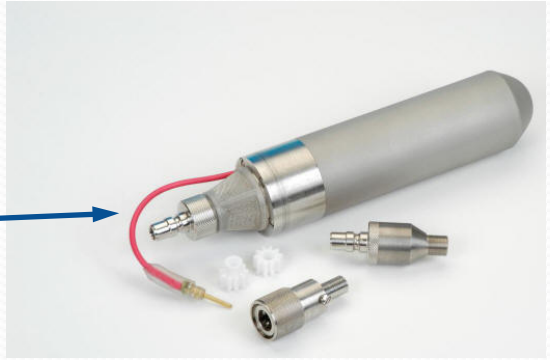
Relative Depth

"D" – deep
"M" – medium
"S" - shallow



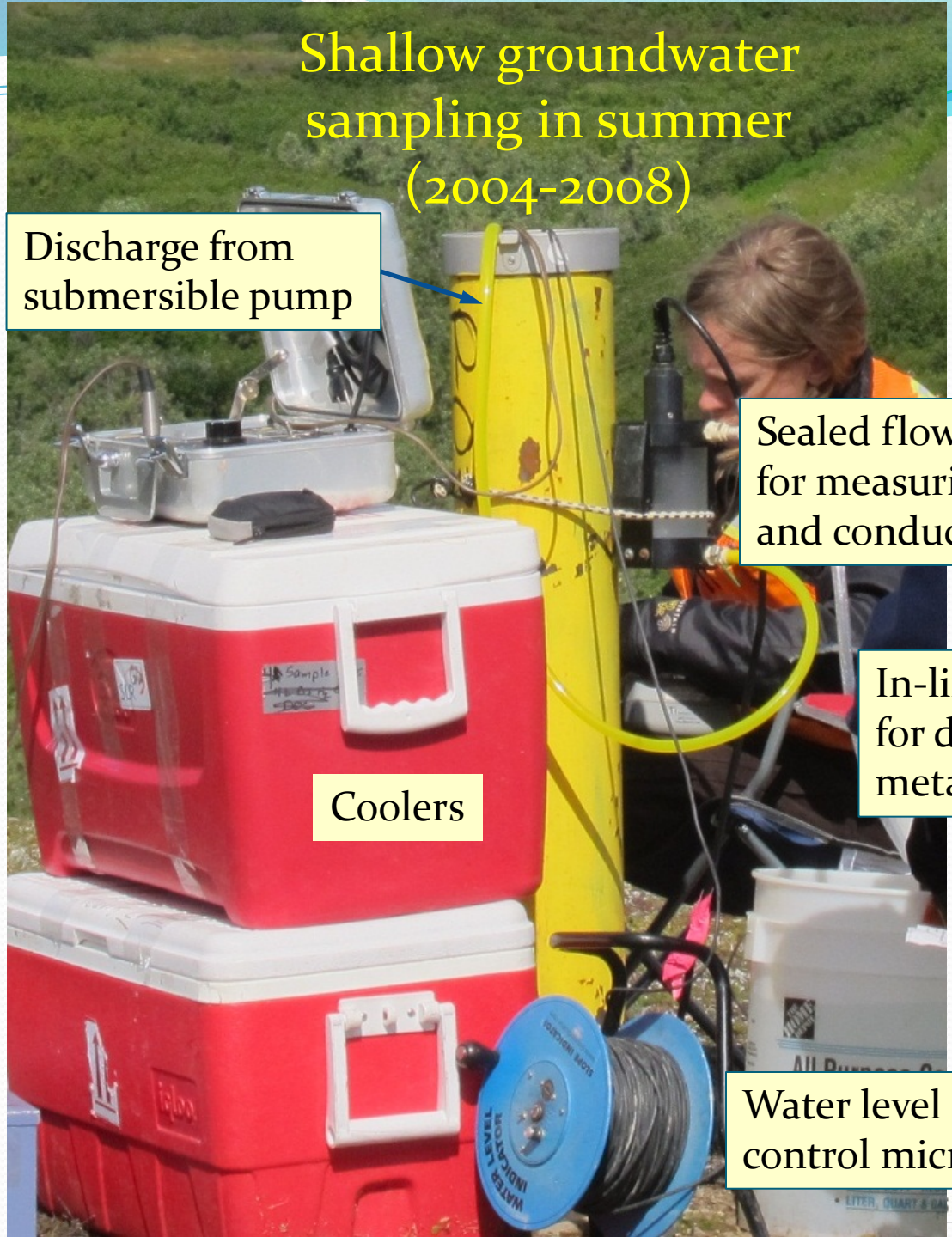
Sampling Methodology: Key Points

- Dedicated submersible pumps
- Low-flow micro-purging
- Field parameters measured in flow-through cell
- Dissolved metals samples filtered in-line in the field with disposable filters
- 10% of samples collected in triplicate
- Detailed QA/QC

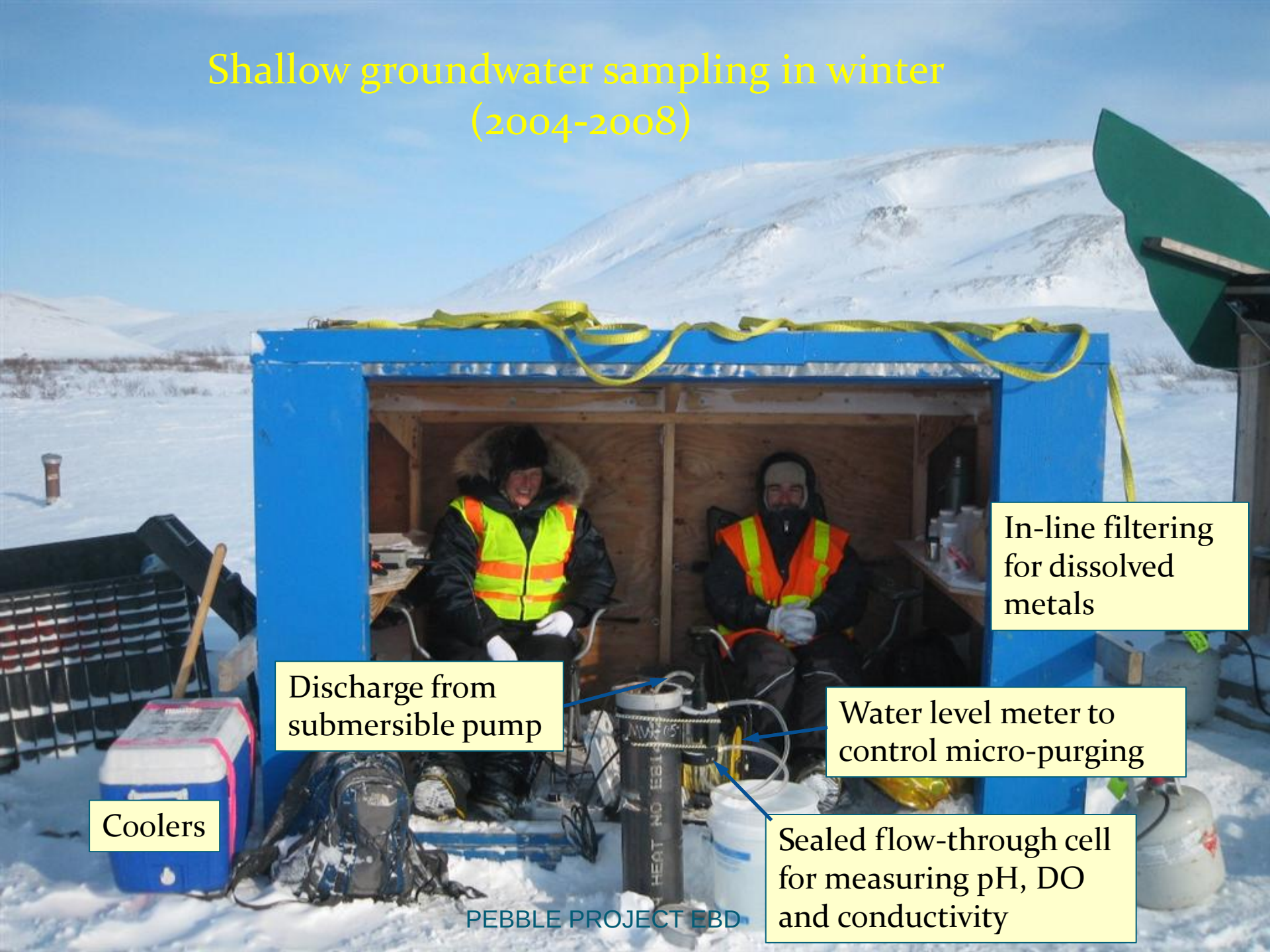


THE pebble PARTNERSHIP

Shallow groundwater sampling in summer (2004-2008)

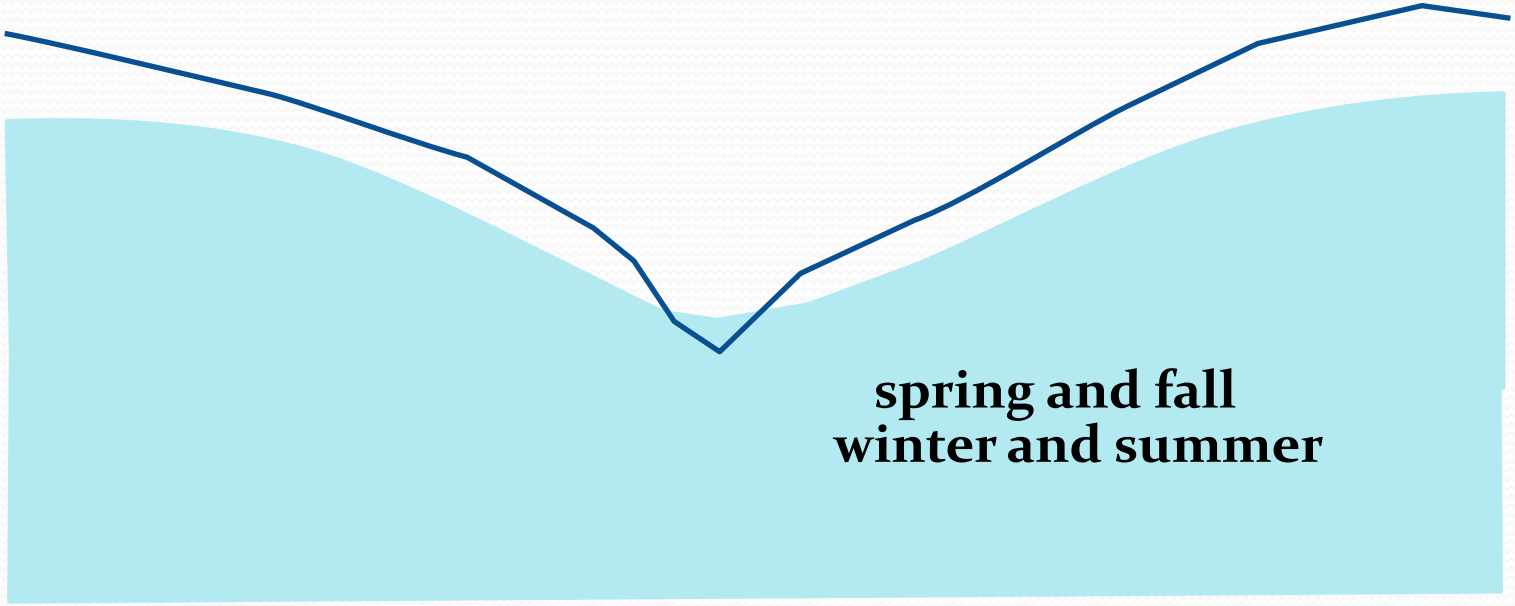


Shallow groundwater sampling in winter (2004-2008)

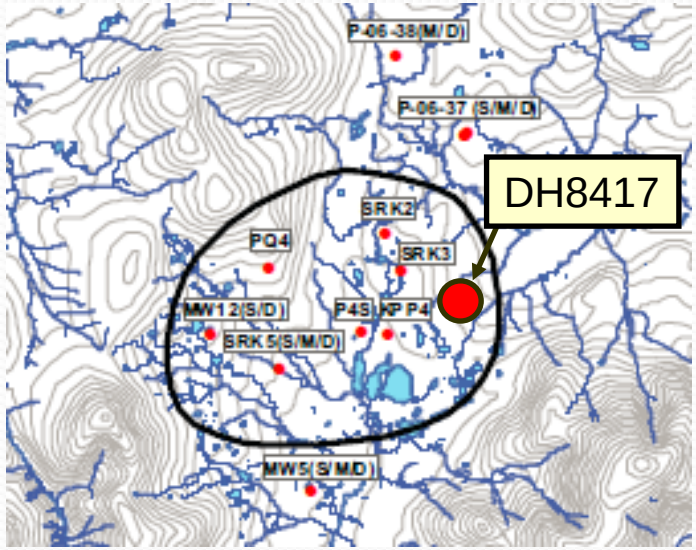


Timing of Shallow Groundwater Samples

… designed to capture seasonality of groundwater elevations



Deep groundwater sampling at DH8417 (2008)



Timing of Groundwater Samples

- Shallow Sampling (up to 200 ft depth)
  - 2004-present
  - March (late winter, low water)
  - May (spring runoff, high water)
  - August (summer, low water)
  - November (fall rains, high water)
- Deep Sampling (up to 4000 ft depth)
  - 2008 (one sampling event)
  - one hole
  - eight depth intervals

Analyses

- Index parameters
  - Total Dissolved Solids
  - Dissolved Oxygen
  - pH
  - Temperature
- Major ions
  - Ca, Mg, Na, K
  - Alkalinity (CO_3 and HCO_3), SO_4, Cl
- Total and dissolved trace elements
- Nutrients
  - NH_3, NO_3, PO_4, total P

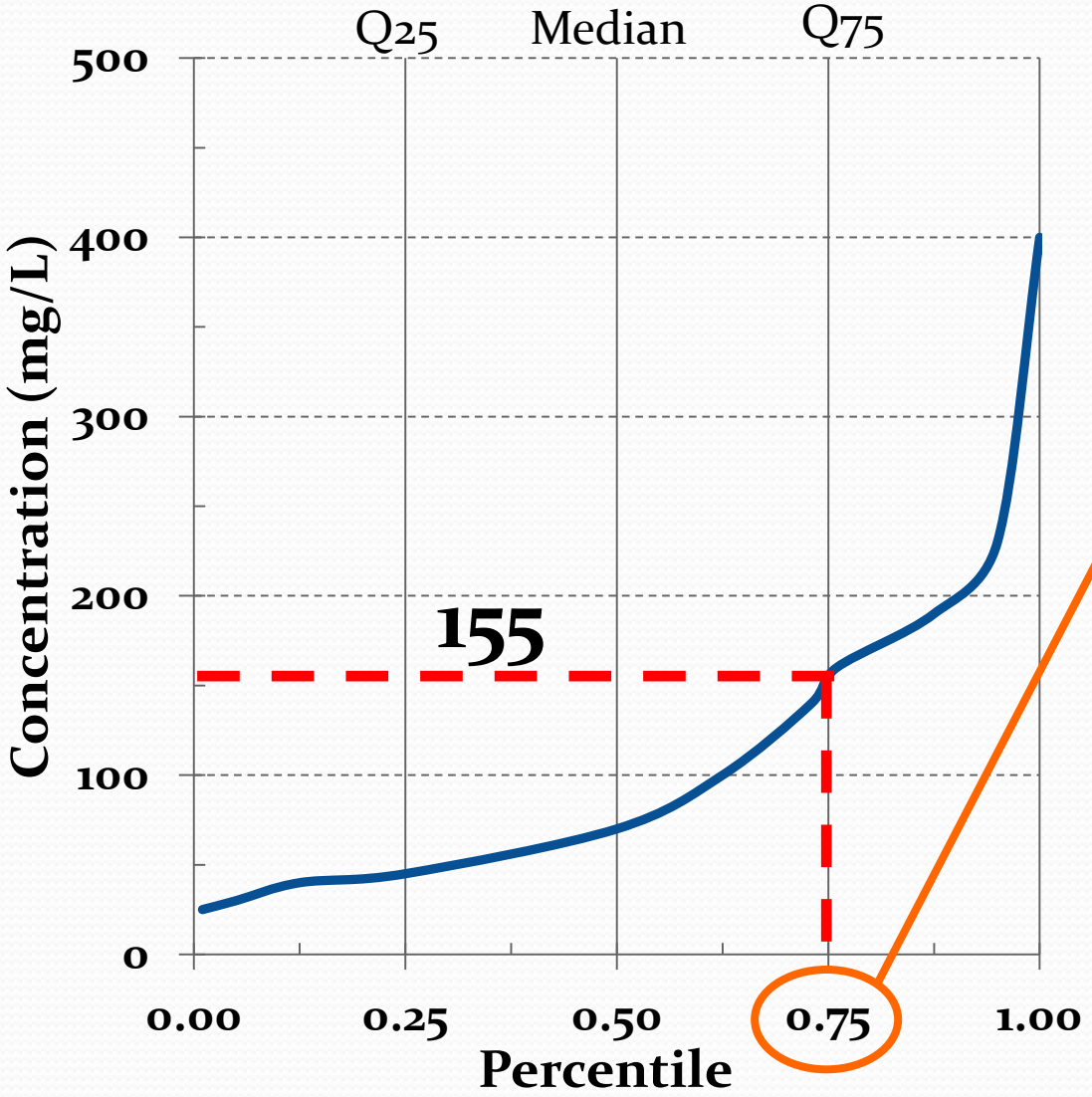
Outline

1. Objectives
2. **“Index Parameters”**
3. Major Ions
4. Trace Elements
5. Nutrients
6. Summary

Examining TDS …

- spatial variation
- **comparisons of data sets**
  - **bedrock vs. overburden**
  - **one watershed vs. another**
- depth variation
- temporal changes
- parameter correlation
- ionic composition

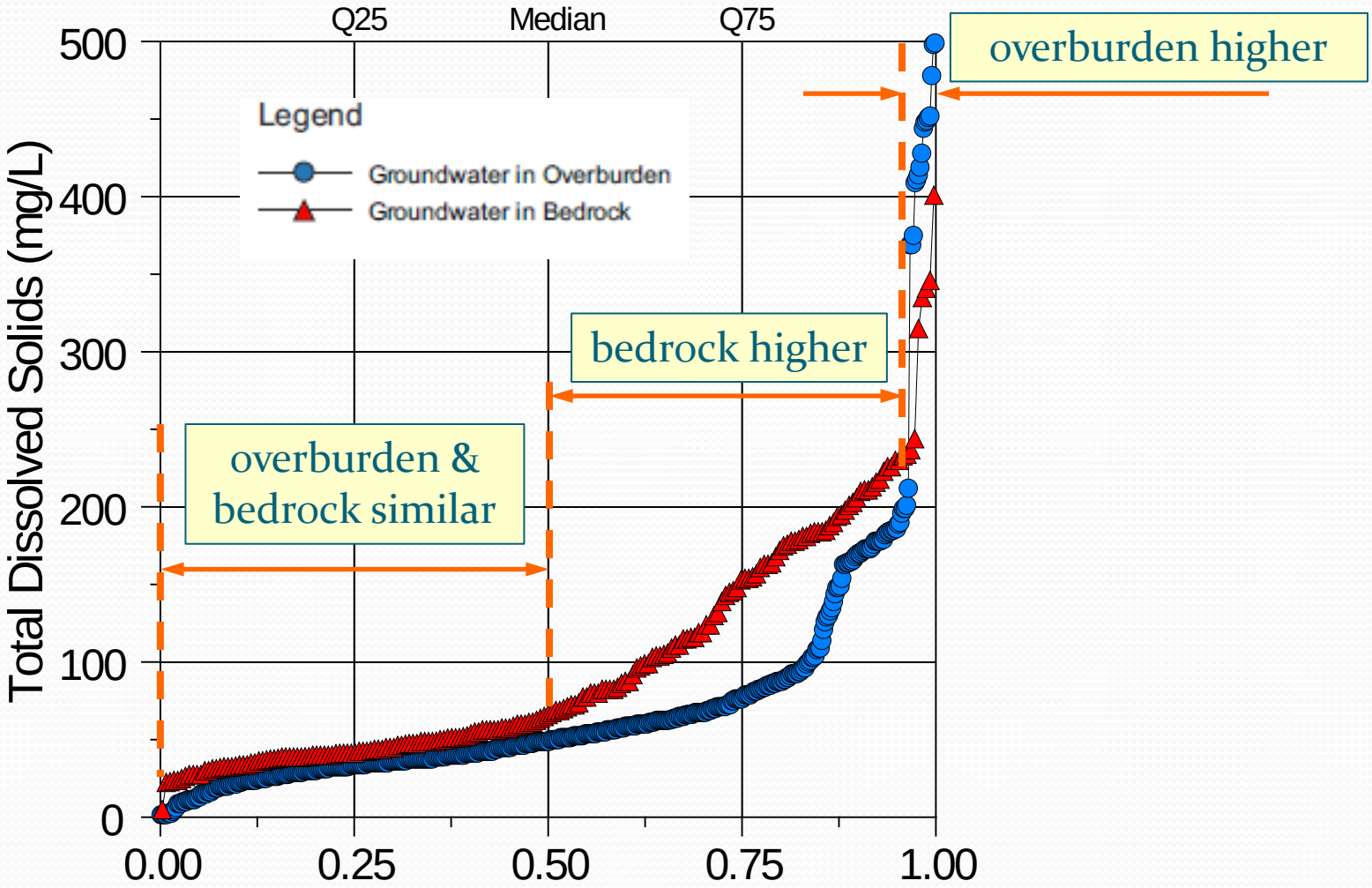
Interpretation with Cumulative Frequency



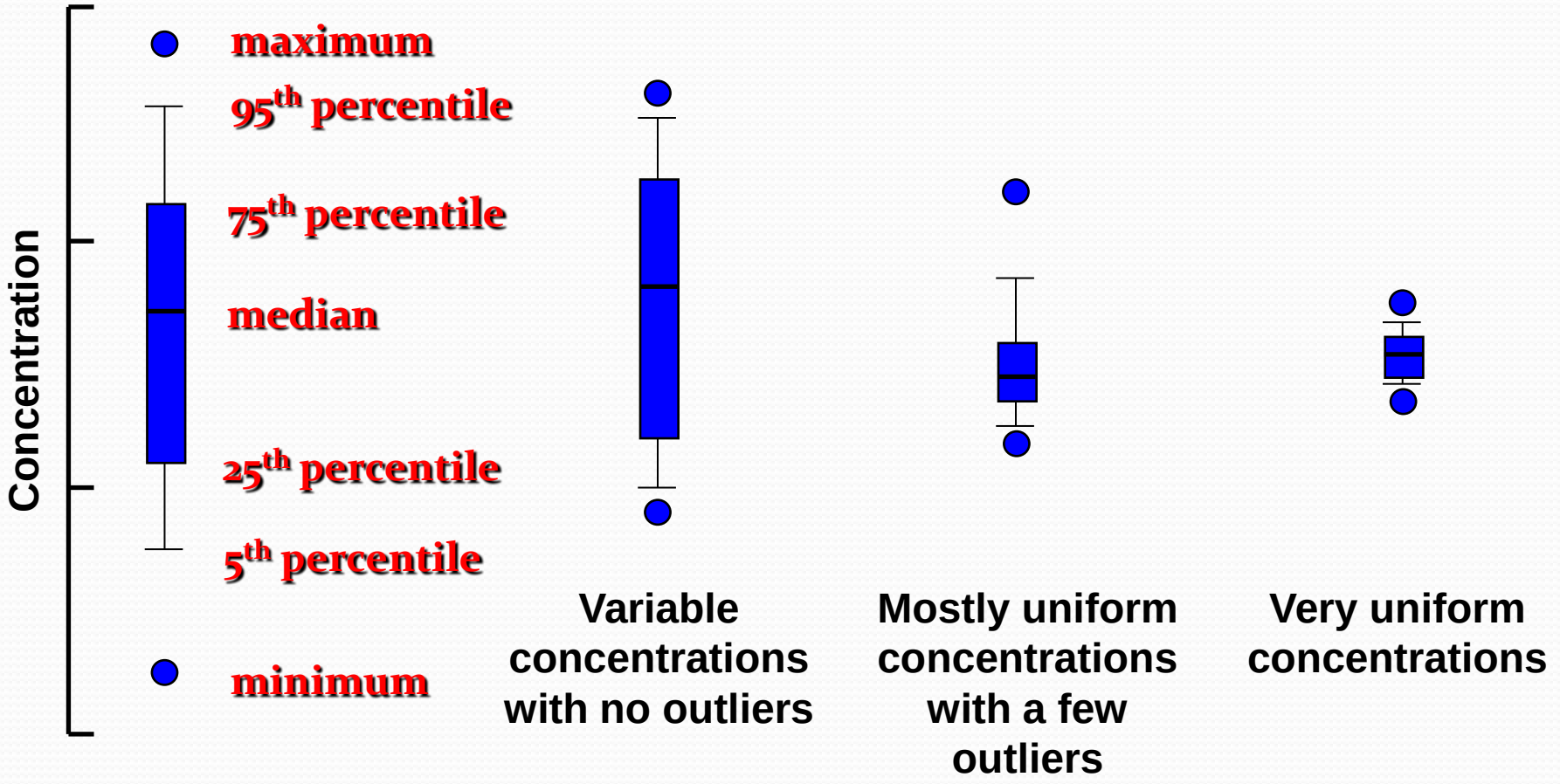
75% of the concentrations are less than 155 mg/L

TDS of overburden and bedrock

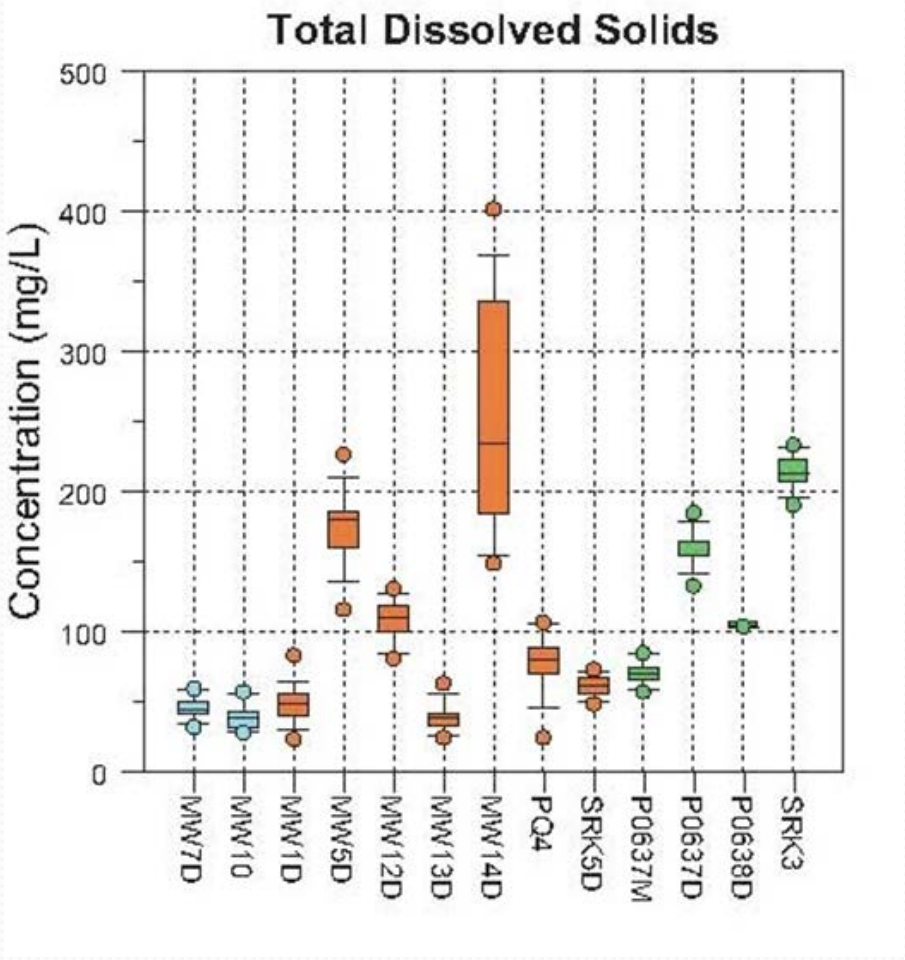
Cumulative Frequency



Another comparison method: Box and Whisker Plot



Box and Whisker Plot

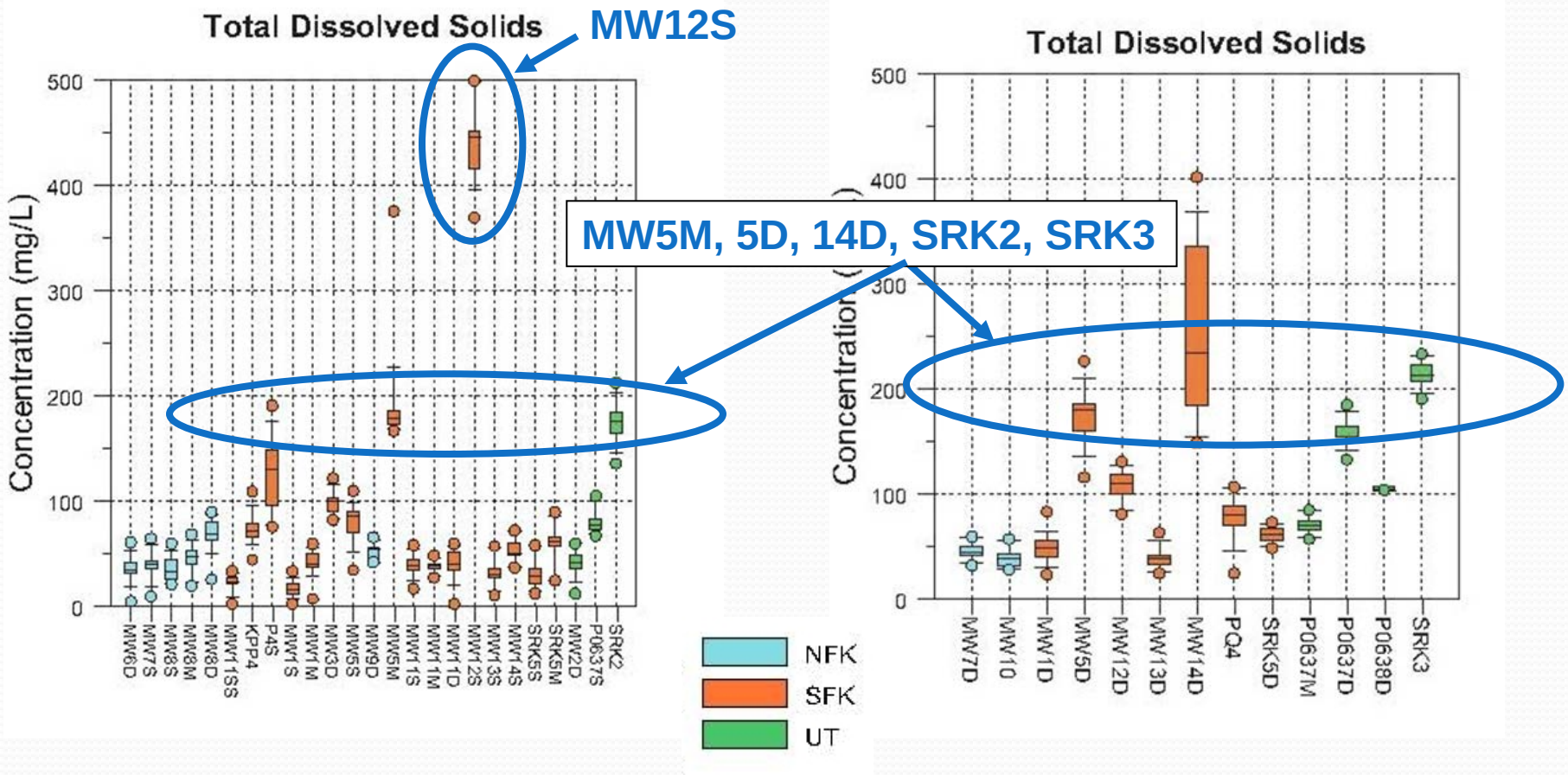


- **overview**
- **detail**

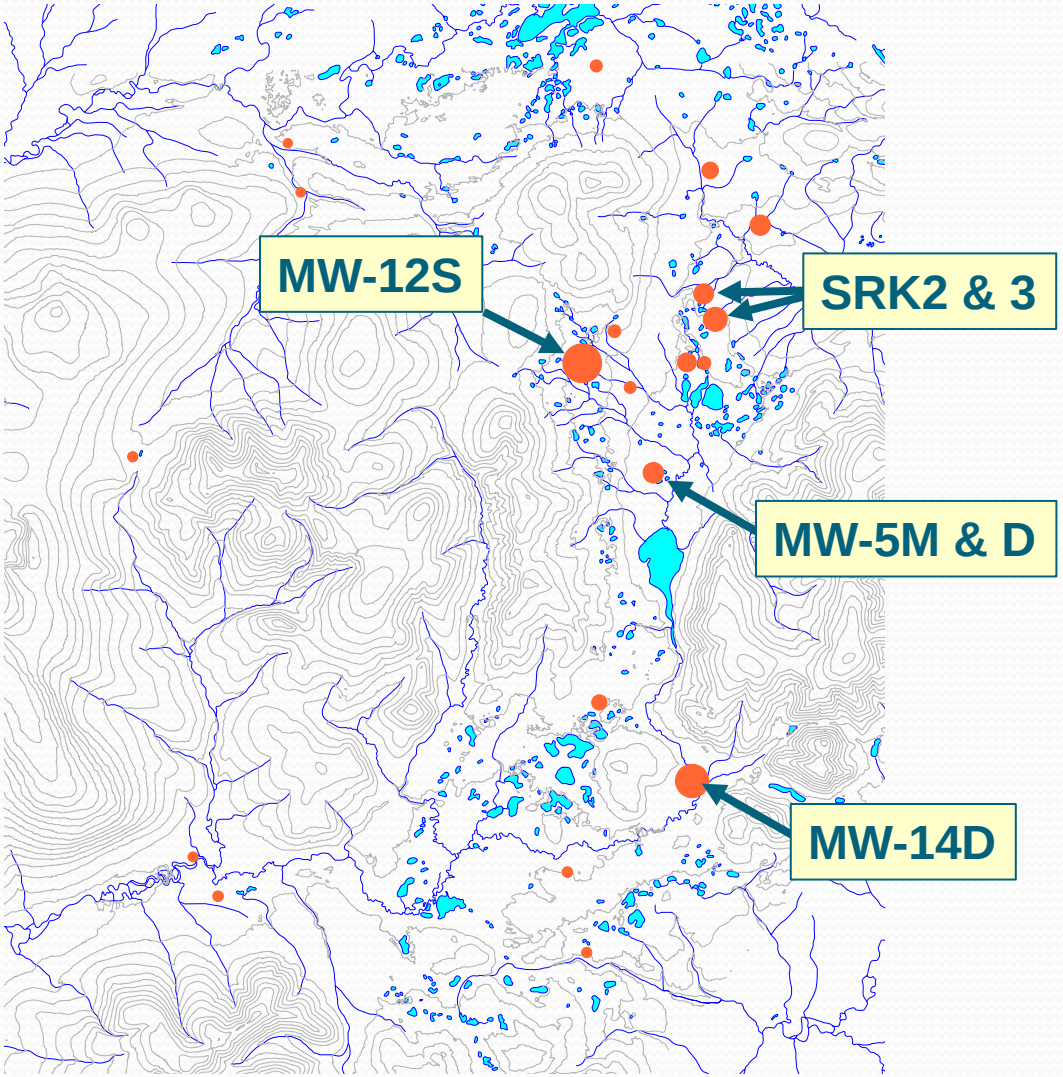
Total Dissolved Solids

Overburden

Bedrock

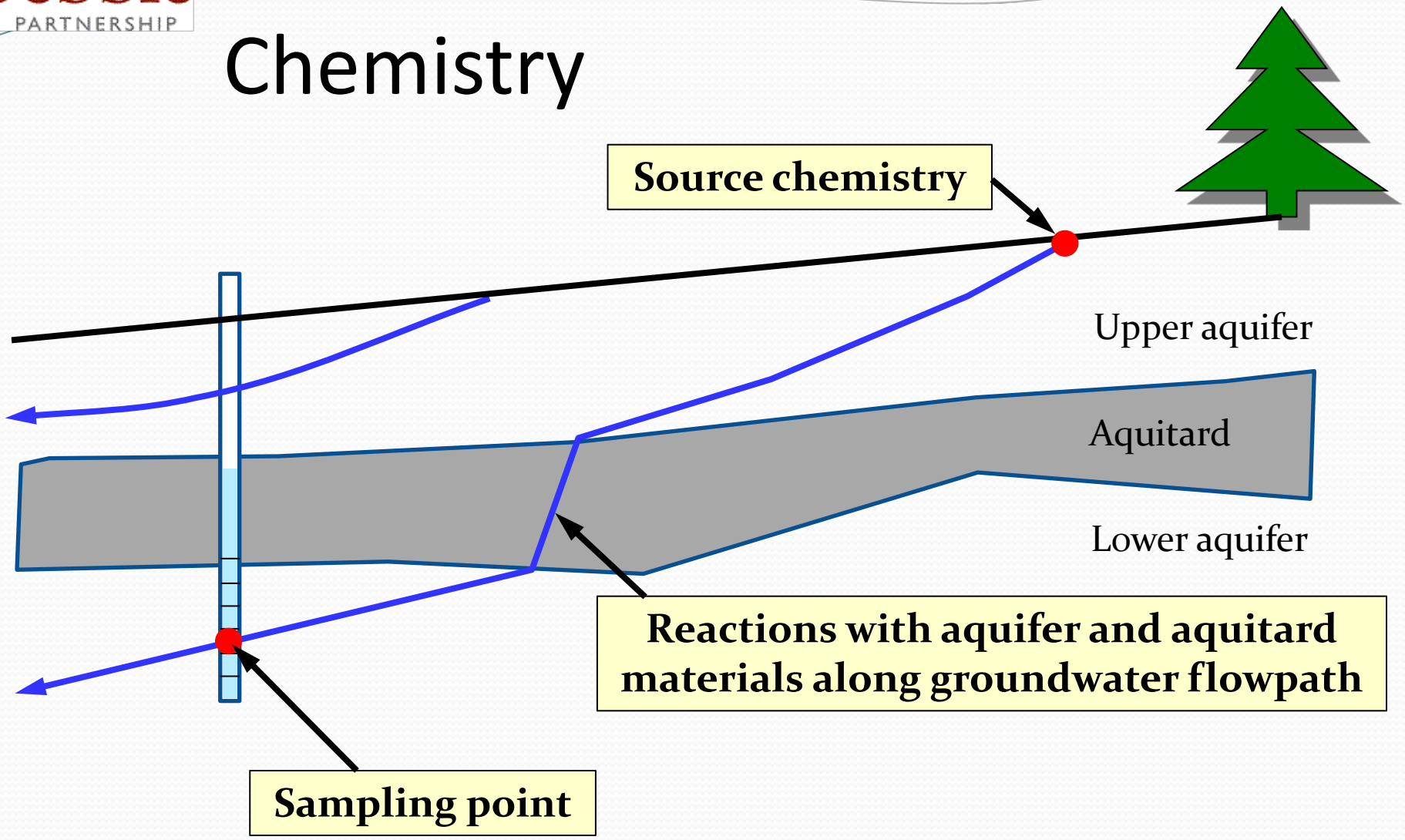


Total Dissolved Solids (TDS)



minimum = 9 mg/L
maximum = 414 mg/L

Influences on Groundwater Chemistry

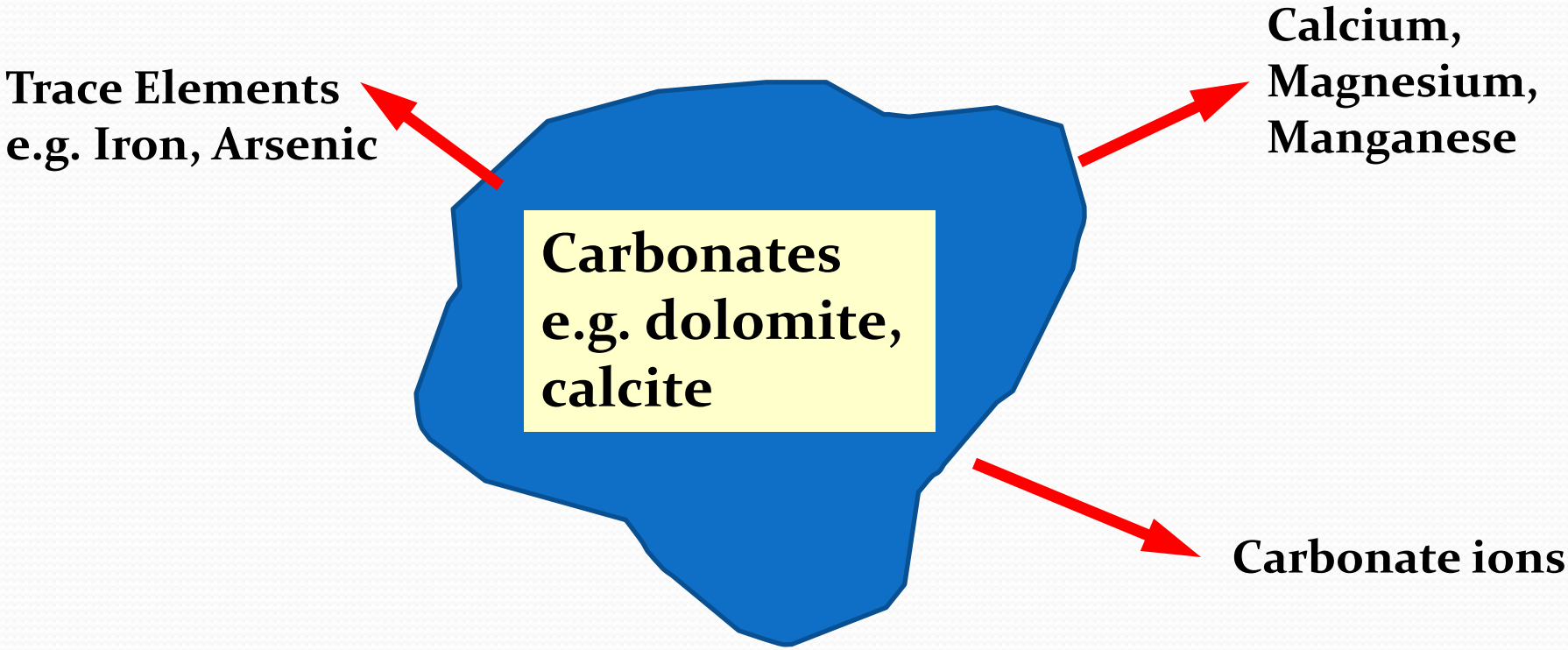


Influences on Groundwater Chemistry

- source chemistry
  - oxygen
  - pH
  - geochemical processes e.g. sulfide oxidation
- aquifer composition
  - carbonates (sources of calcium, magnesium, manganese, iron, trace elements, carbonates)
  - silicates (sources of sodium, potassium, silica)
  - sulfides (oxygen consumption)
  - organic carbon (oxygen consumption)
  - clays (ion exchange and adsorption)
  - iron hydroxides (adsorption)

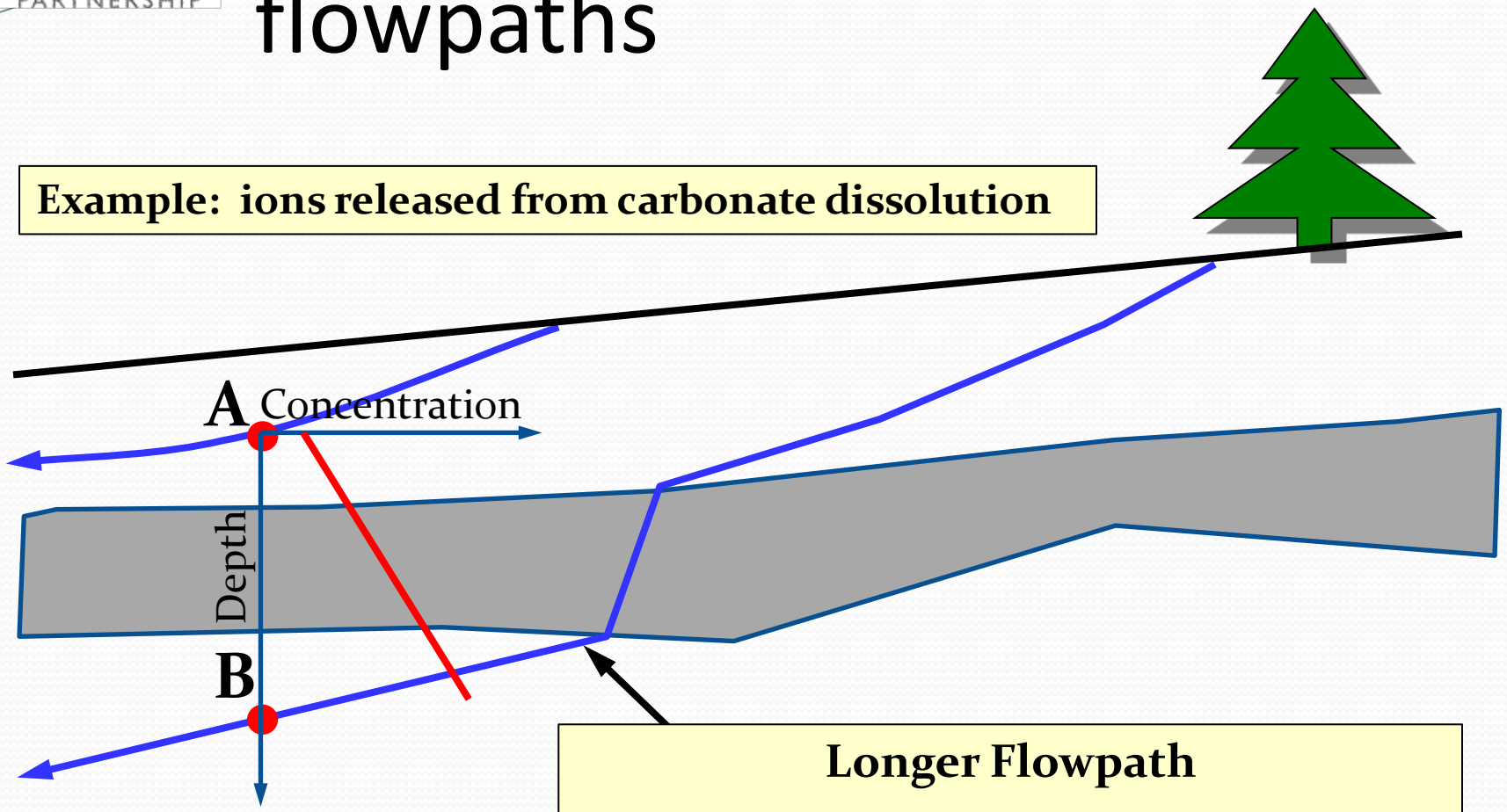
Example:

Acid from sulfide oxidation dissolving carbonates



Dissolution reactions along flowpaths

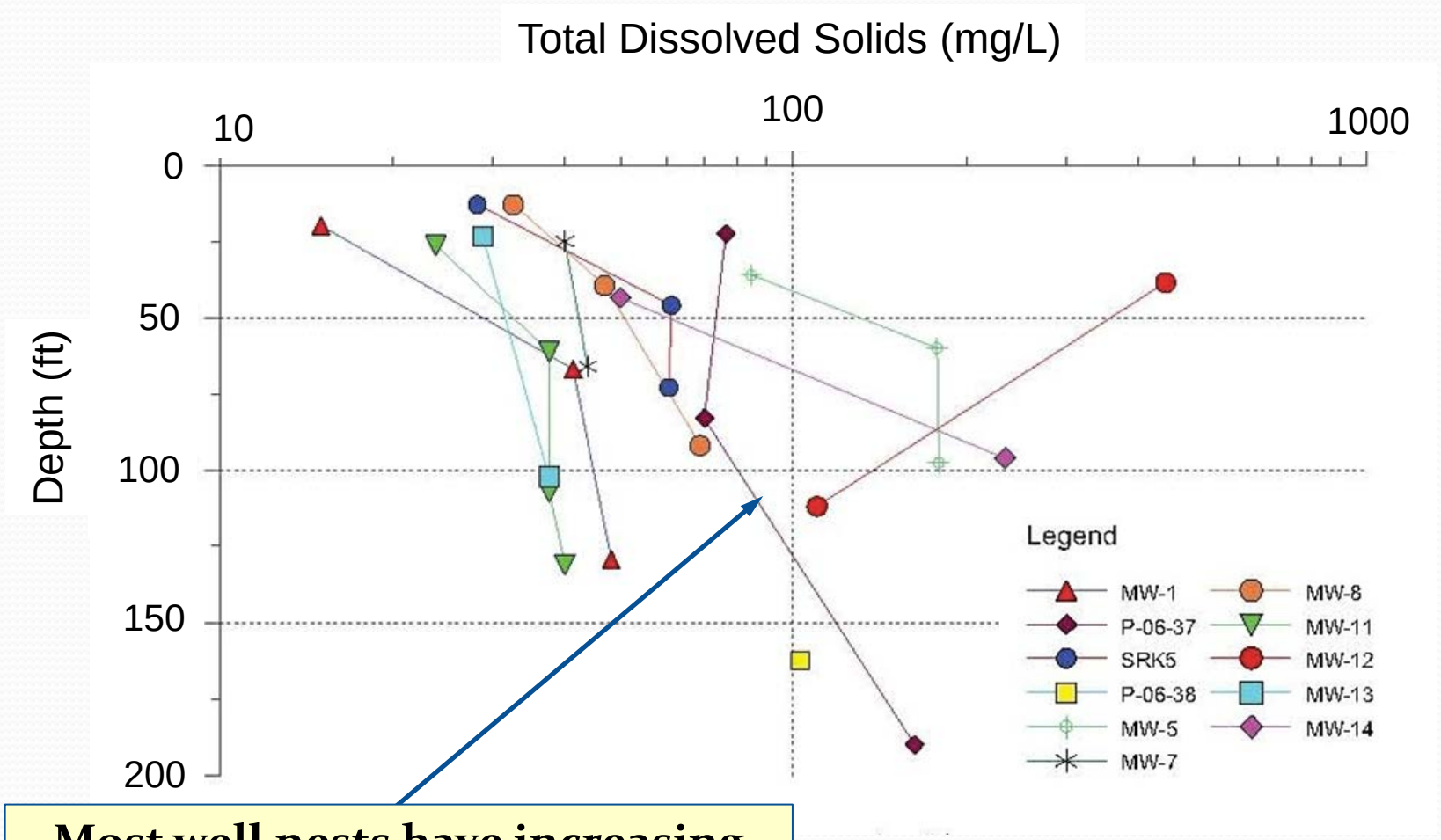
Example: ions released from carbonate dissolution



Longer Flowpath

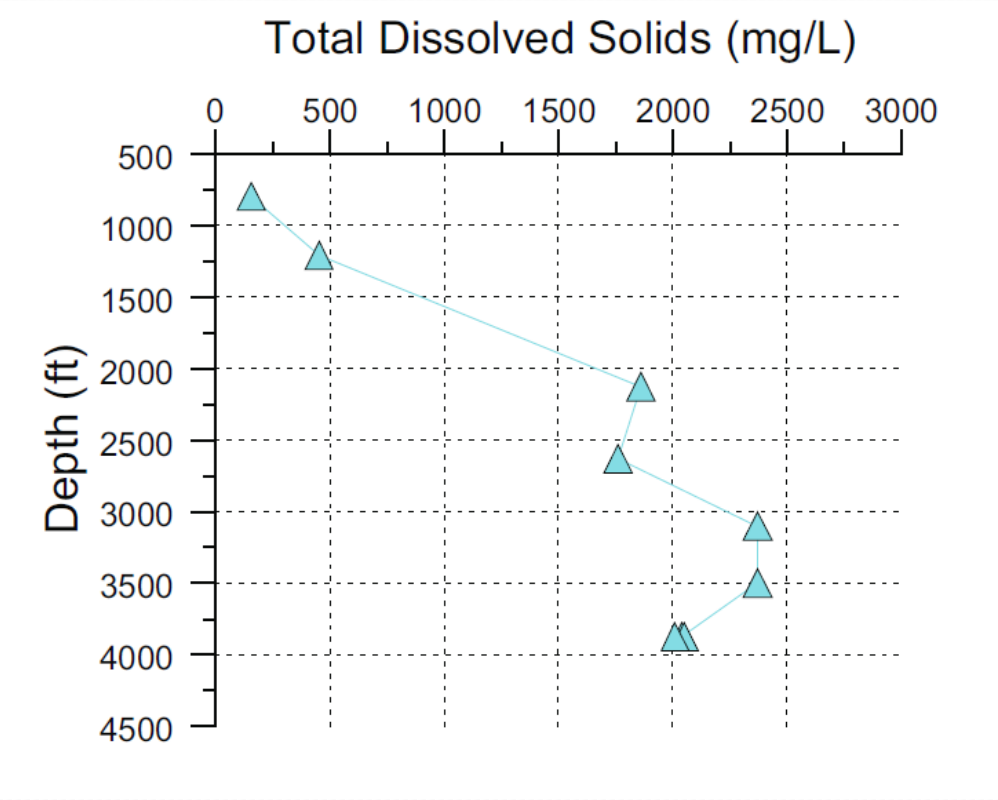
Therefore, potential for concentration to be higher at "B" than "A"

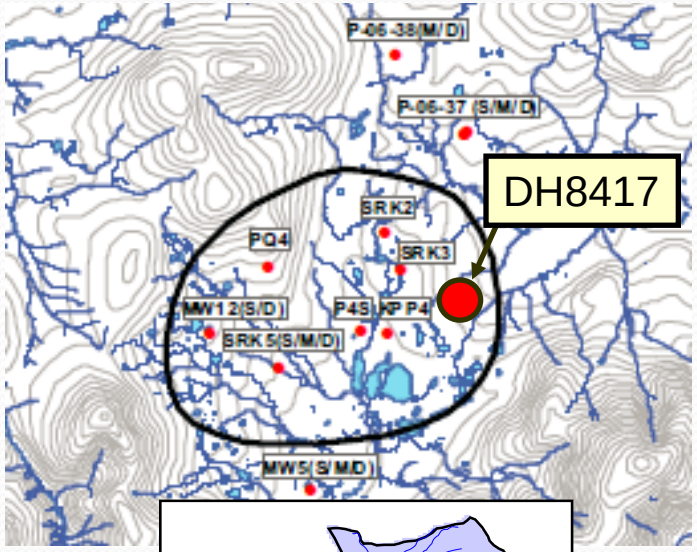
Total Dissolved Solids vs. Depth

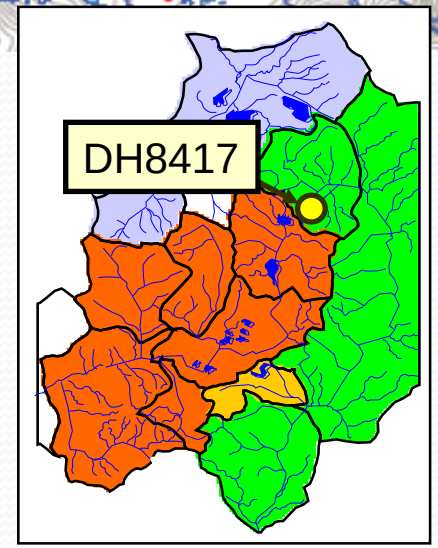


Most well nests have increasing TDS with depth

TDS vs. Depth
Deep Groundwater (DH8417)



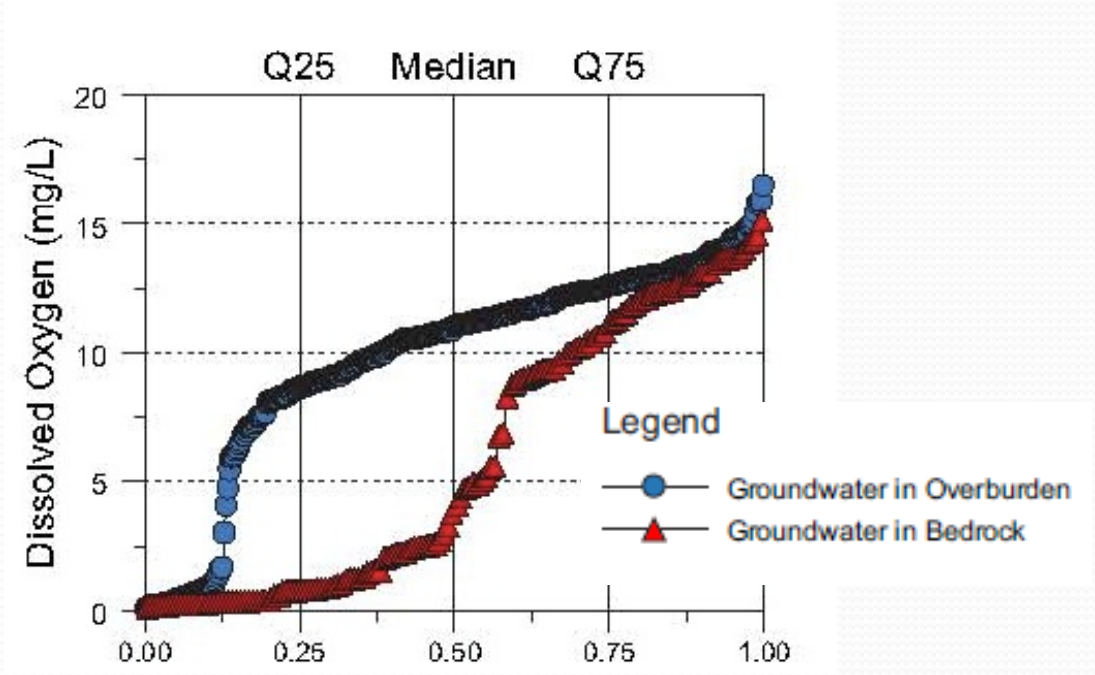




Index Parameters

- Total Dissolved Solids
- **Dissolved Oxygen**
- pH
- Temperature

Dissolved Oxygen Overburden vs. Bedrock



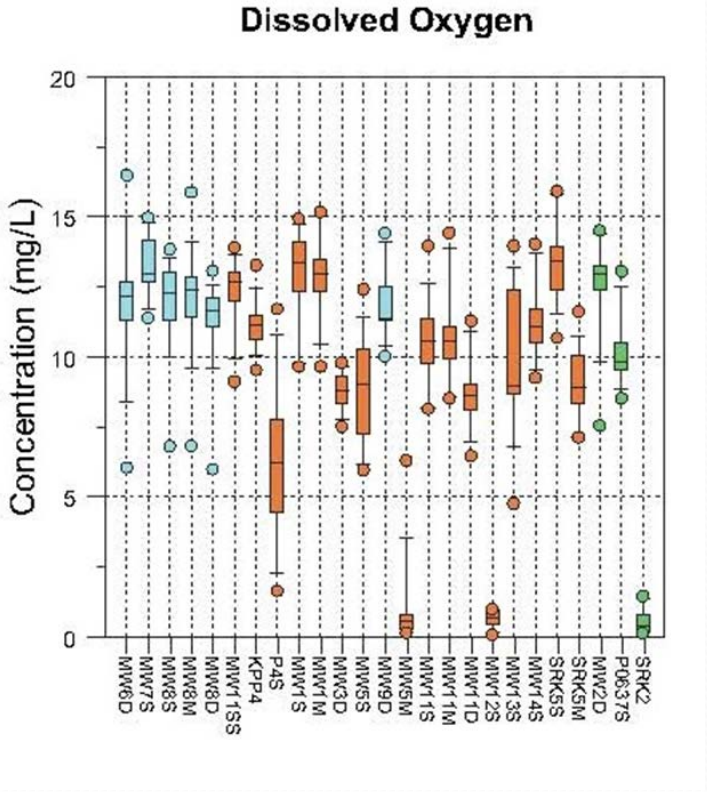
Dissolved Oxygen

- **2-12 mg/L: overburden higher**
- **<2 & >12 mg/L: similar**

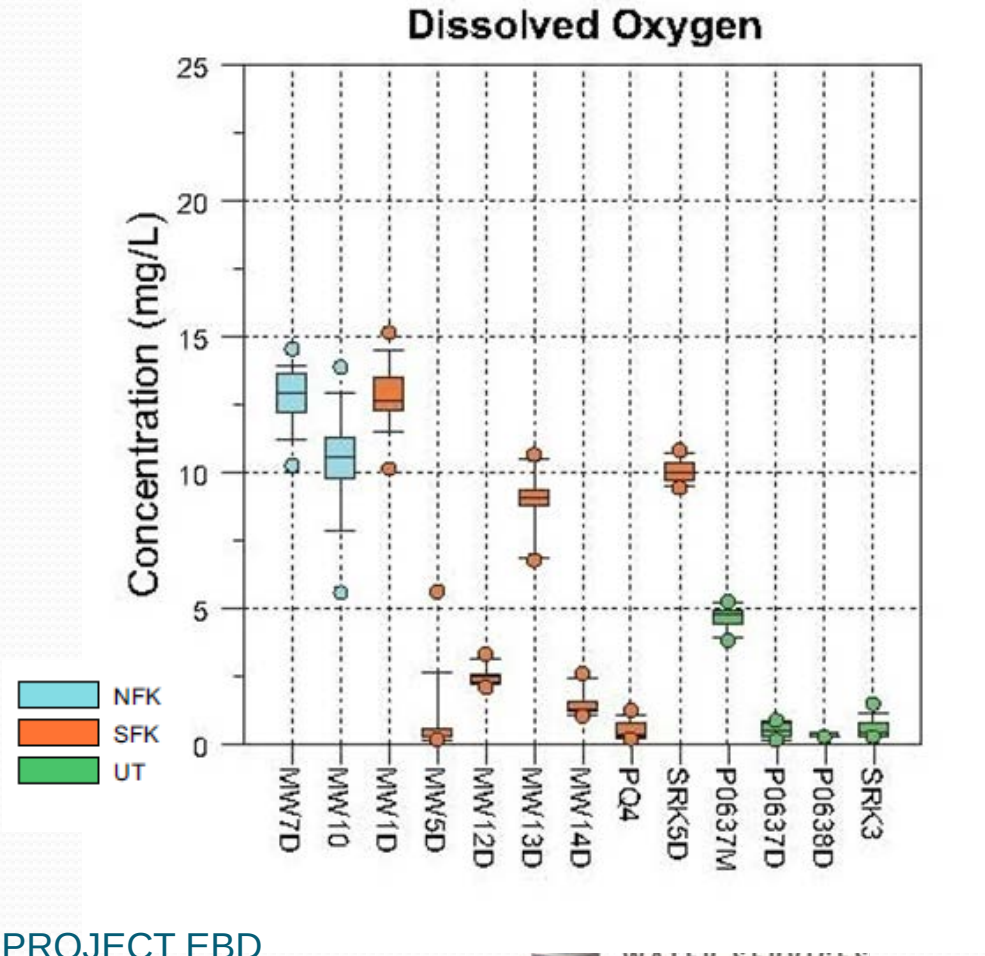
Dissolved Oxygen by Well

Comparing Overburden vs. Bedrock and Watersheds

Overburden

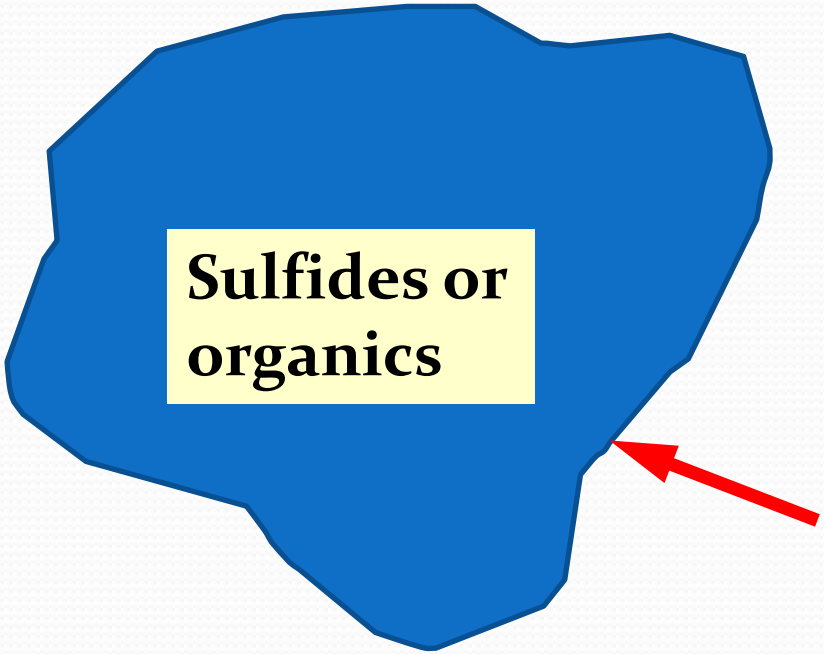


Bedrock



Example:

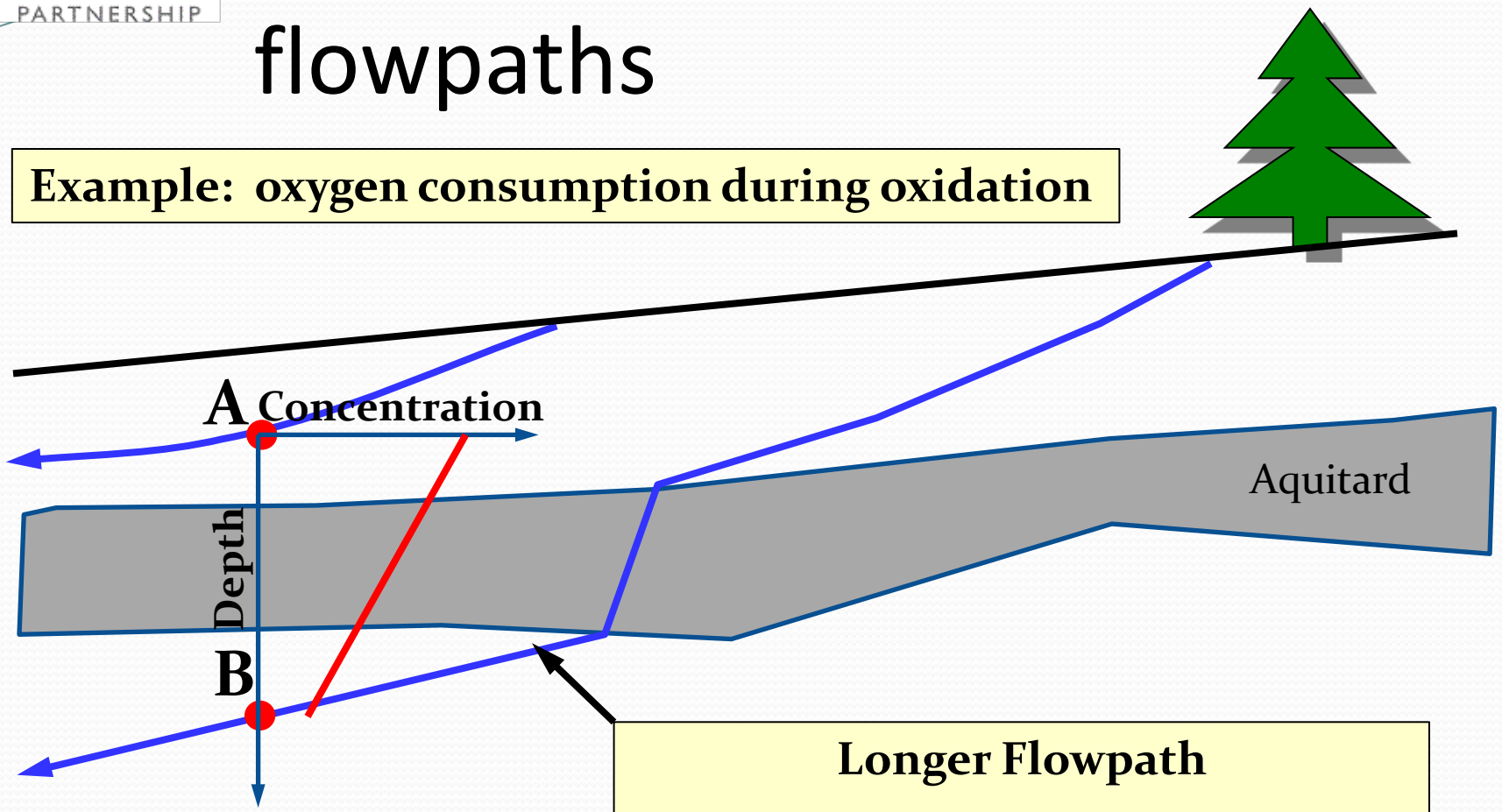
Oxygen reacting with sulfide minerals or organic matter



O_2 consumed

Consumption reactions along flowpaths

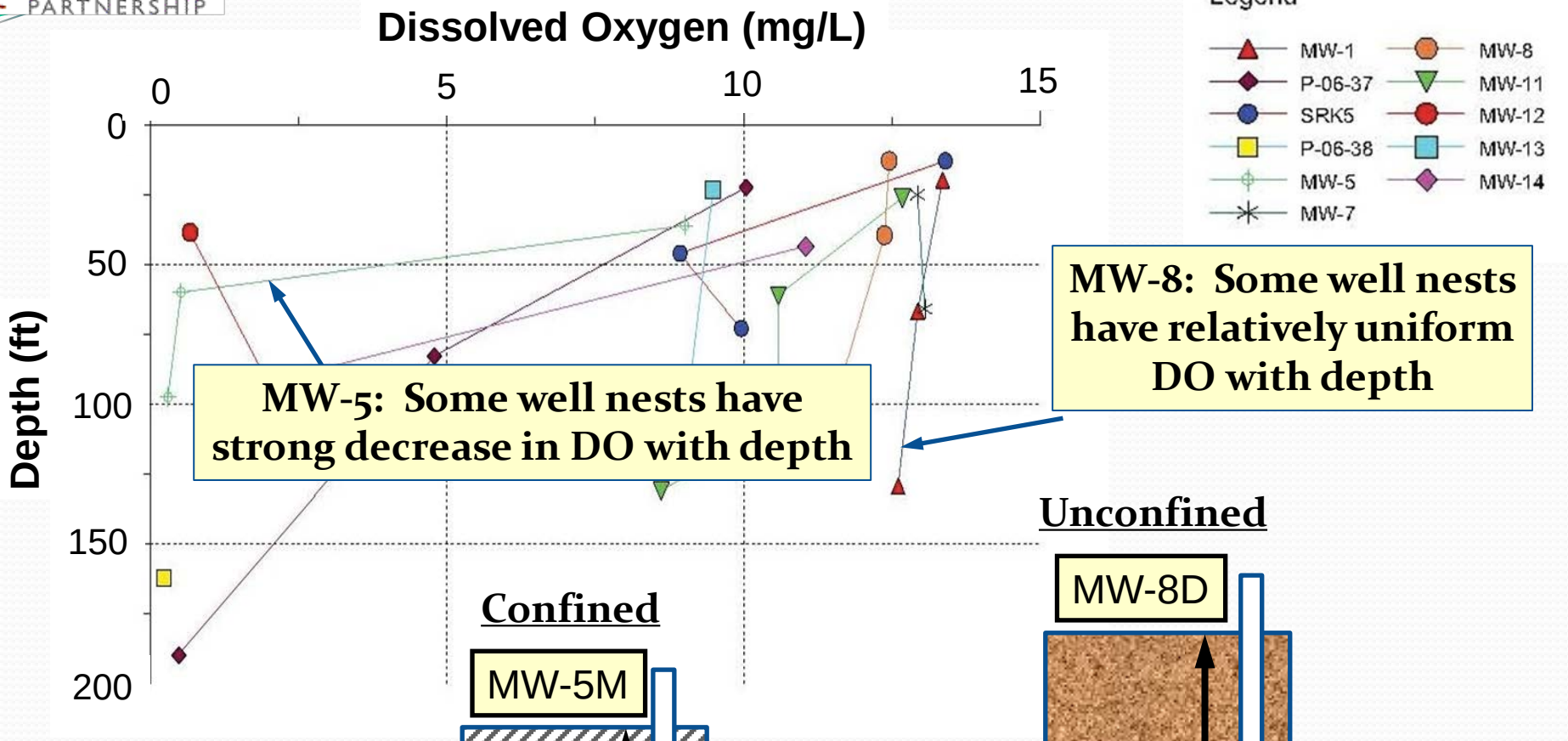
Example: oxygen consumption during oxidation

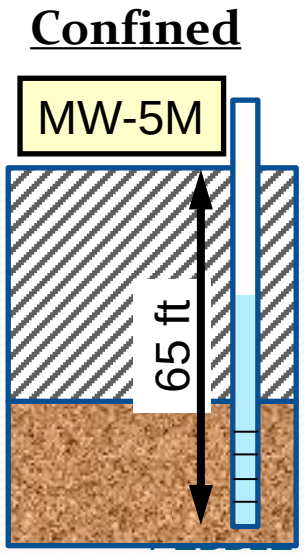


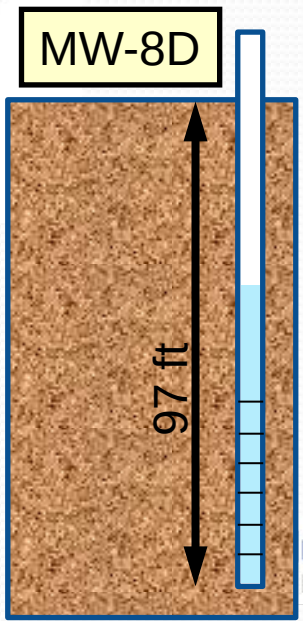
Longer Flowpath

Therefore, potential for concentration to be lower at "B" than "A"

Dissolved Oxygen vs. Depth



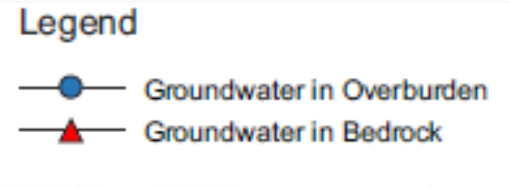


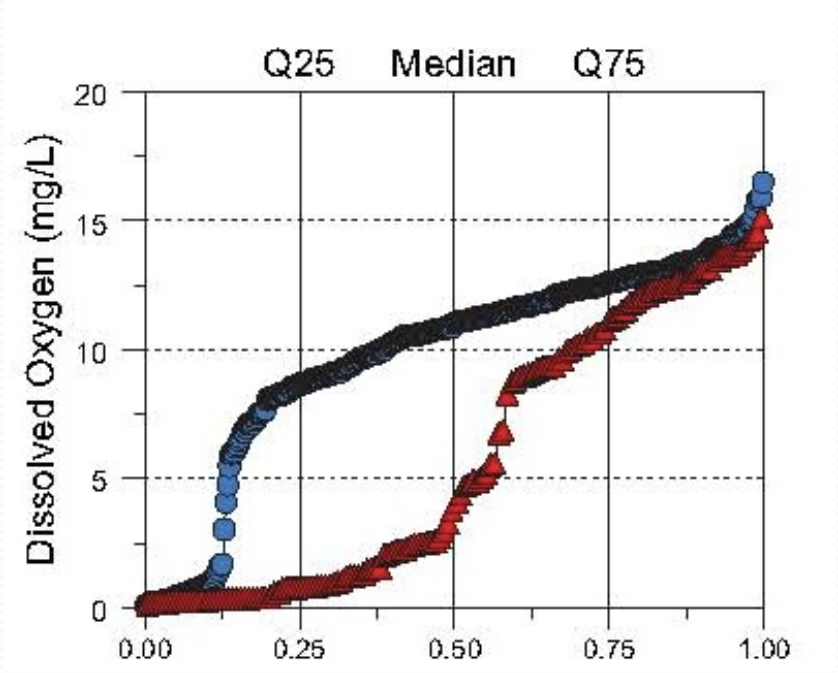


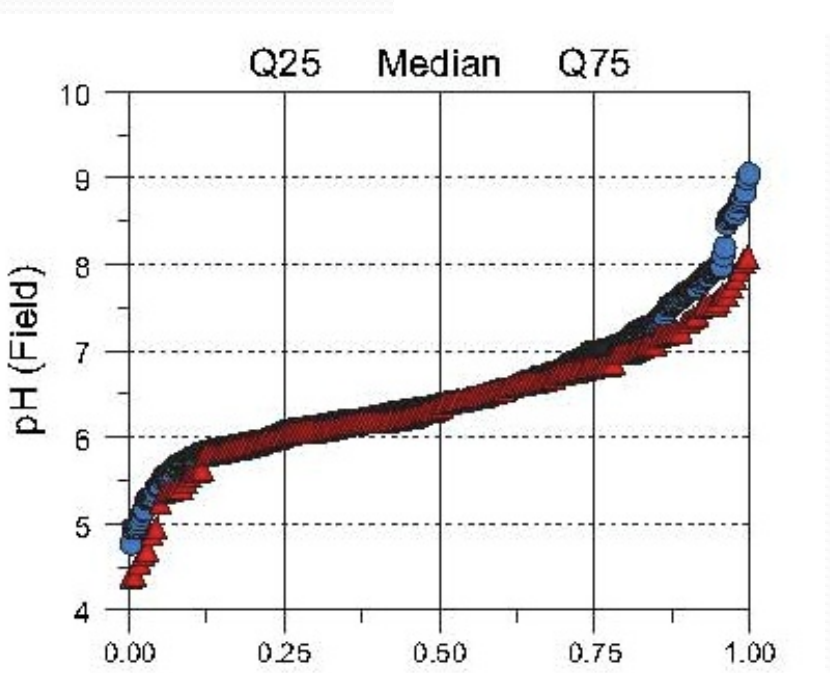
Index Parameters

- Total Dissolved Solids
- Dissolved Oxygen
- **pH**
- Temperature

Dissolved Oxygen and pH Bedrock vs. Overburden







Dissolved Oxygen

- 2-12 mg/L: overburden higher
- <2 & >12 mg/L: similar

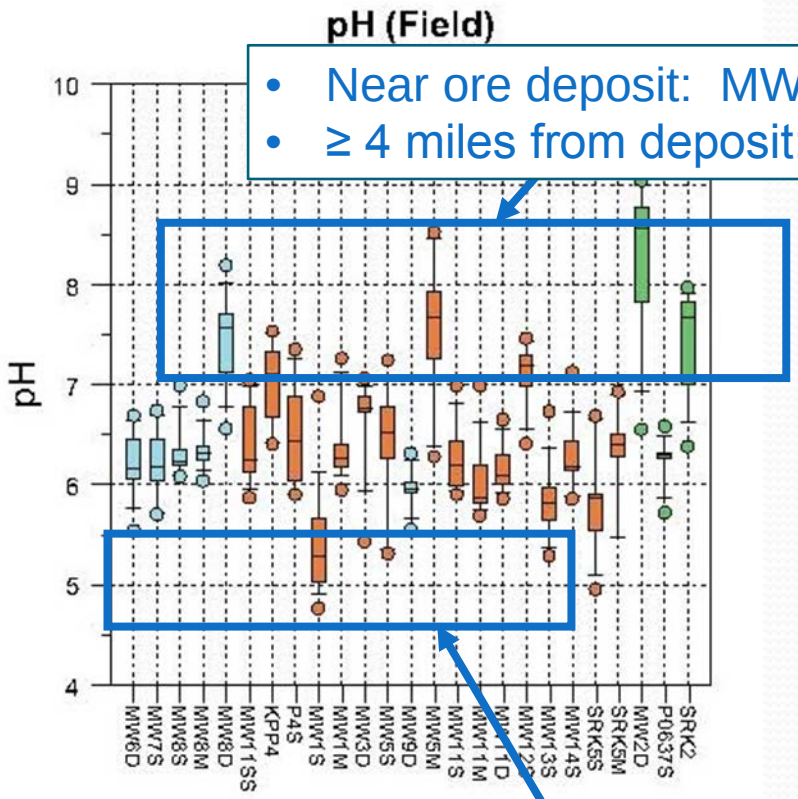
pH

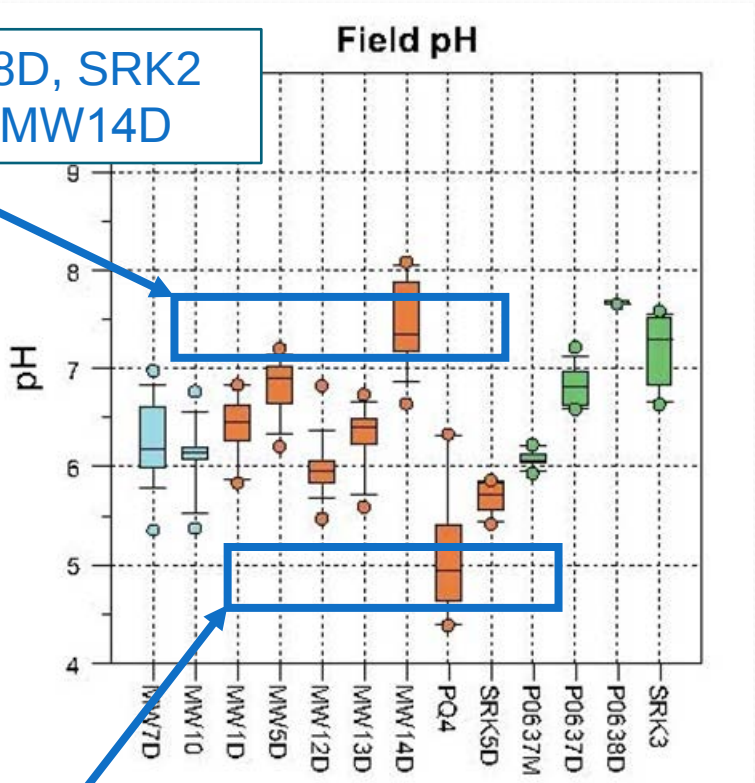
- 5.8 - 6.5: similar
- <5.8 & >6.5: overburden higher

pH

Overburden

Bedrock



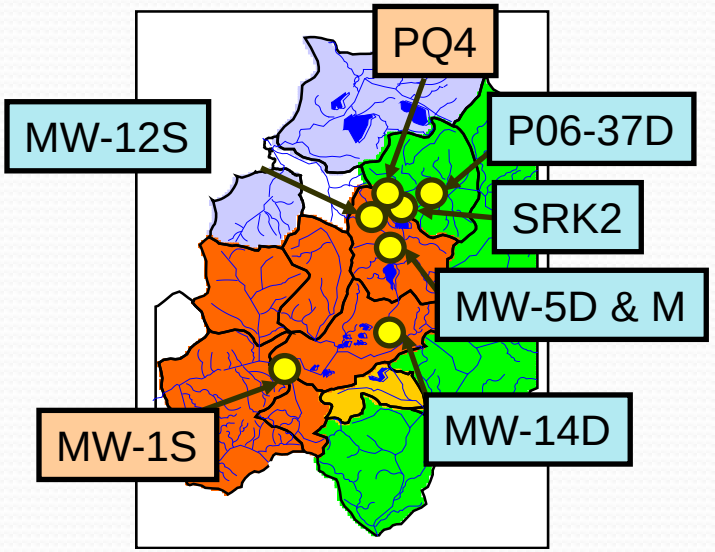


- Near ore deposit: MW5M, MW8D, SRK2
- ≥ 4 miles from deposit: MW2D, MW14D

- Near ore deposit: PQ4
- 8 miles from deposit: MW1S

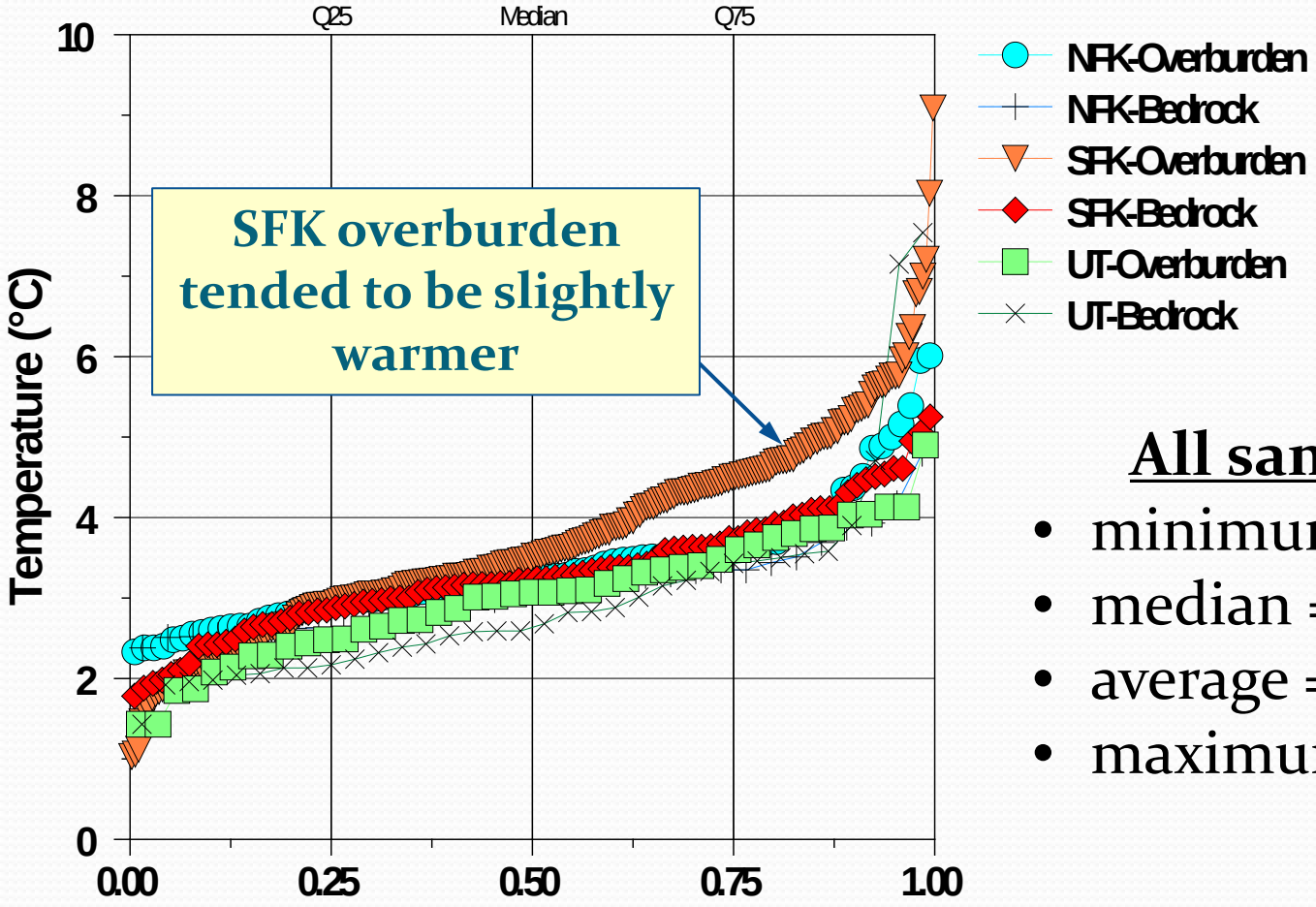
NFK
SFK
UT

Index Parameters: some specifics



- High TDS, low DO, high pH
  - MW-5D, -5M, -12S, -14D, SRK-2, P06-37D
- Lowest pH:
  - MW-1S, PQ4

Temperature comparison by watershed
All samples

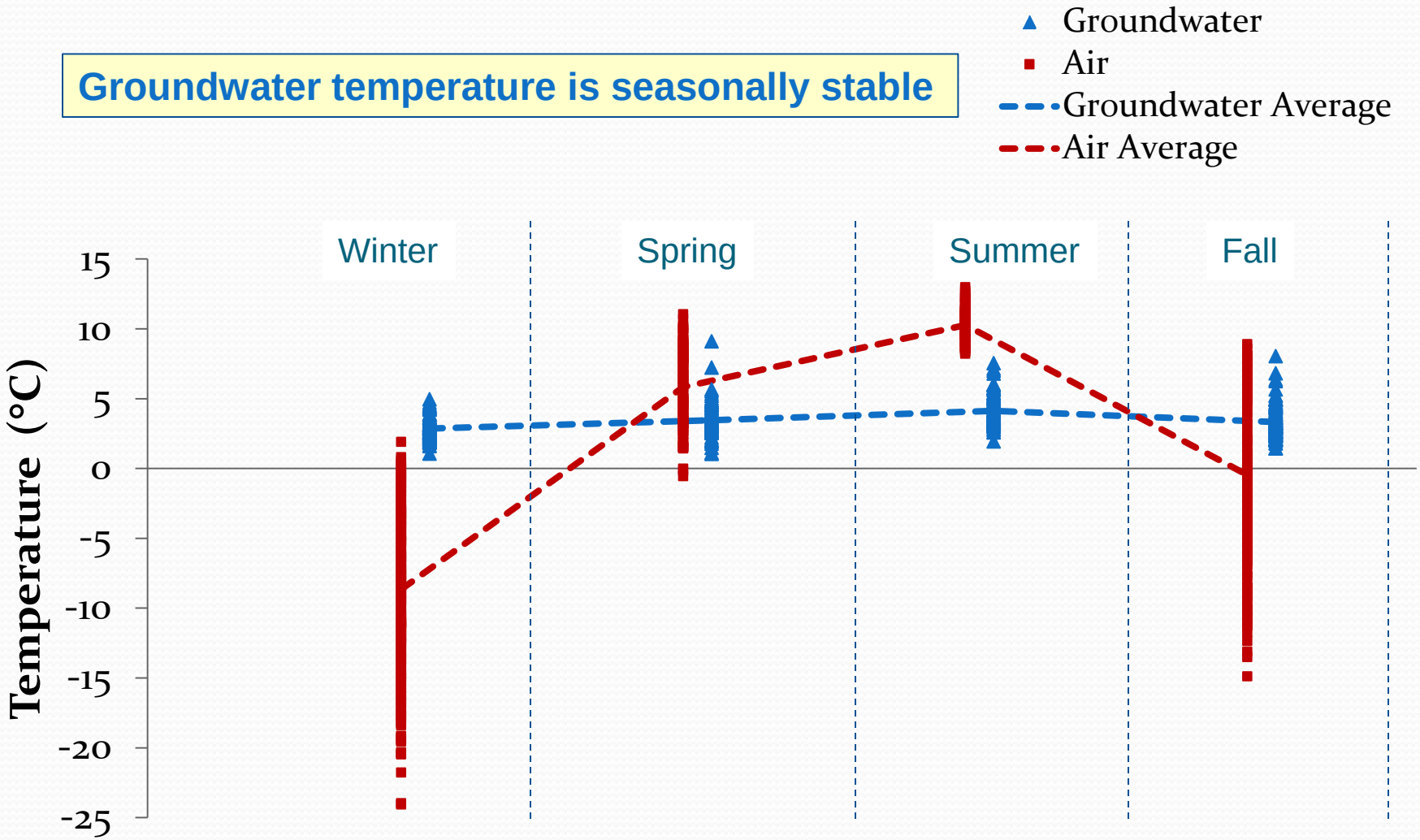


All samples

- minimum = 1 °C
- median = 3.2 °C
- average = 4 °C
- maximum = 9 °C

Seasonal Temperature All locations

Groundwater temperature is seasonally stable



Summary of Index Parameters

- Total Dissolved Solids:
  - shallow groundwater:
    - typically less than 100 mg/L
    - sometimes up to 450 mg/L
    - well MW-14D, 4 miles from the deposit, has among highest TDS
  - deep groundwater: up to 2400 mg/L
- pH:
  - typically between 6 and 7
  - highest values (up to 9) tend to occur in overburden
  - lowest values (down to 4.5) tend to occur in bedrock
  - lower values are typically in proximity to the ore deposit
  - well MW-1S, 8 miles from the deposit, has second lowest values
- Dissolved Oxygen:
  - Often at or near solubility even in some deep wells
  - Decreasing concentration with depth observed at some well nests
- Temperature:
  - Average 4^{o}C
  - Somewhat variable across the study area but no consistent pattern
  - Seasonally stable

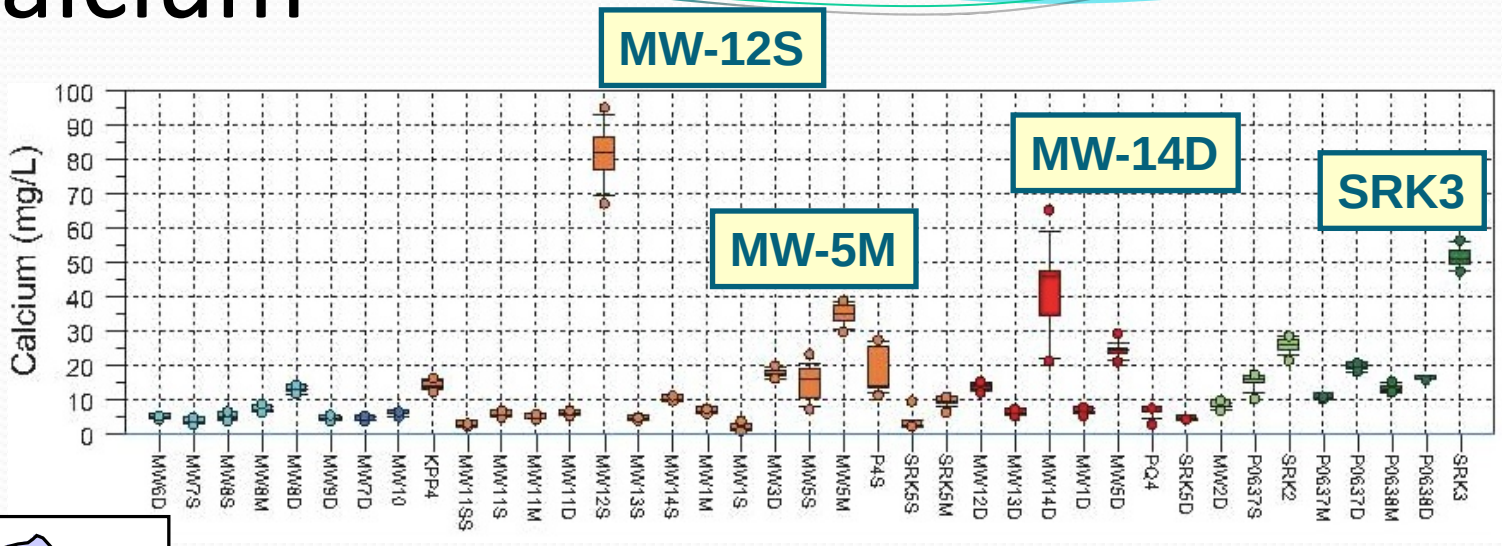
Outline

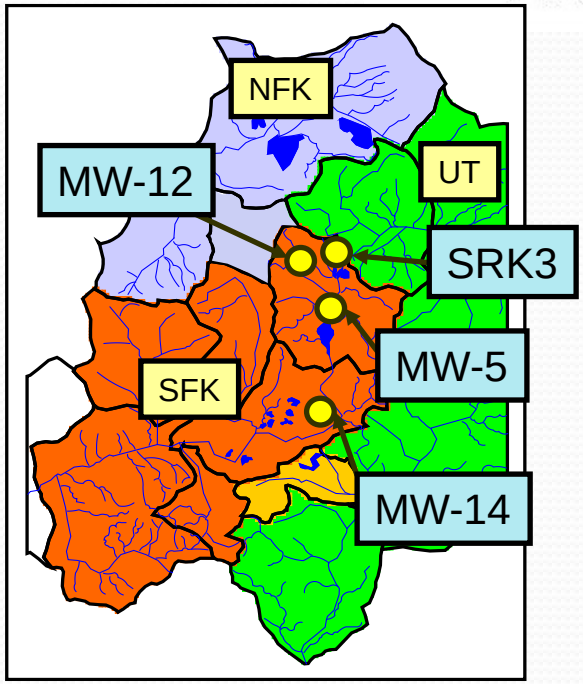
1. Objectives
2. Index Parameters
3. **Major Ions**
4. Trace Elements
5. Nutrients
6. Summary

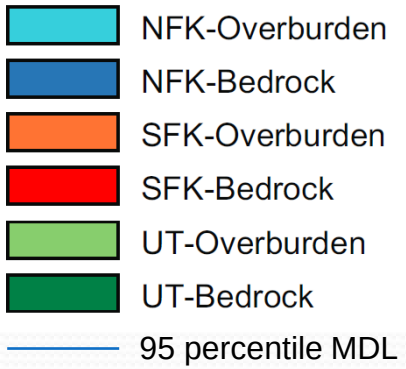
Major Ions

- Cations
  - Ca, Mg, Na, K
- Anions
  - HCO_3, SO_4, Cl
- comprise most of the dissolved solids

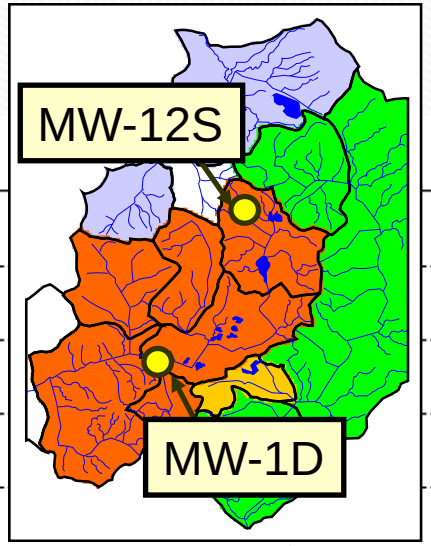
Calcium


MW-12S
MW-14D
SRK3
MW-5M
Calcium (mg/L)
100
90
80
70
60
50
40
30
20
10
0
MW6D
MW7S
MW8S
MW8M
MW8D
MW9D
MW7D
MW10
KPP4
MW11SS
MW11S
MW11M
MW11D
MW12S
MW13S
MW14S
MW1M
MW1S
MW3D
MW5S
MW5M
P4S
SRK5S
SRK5M
MW12D
MW13D
MW14D
MW1D
MW6D
PQ4
SRK5D
MW2D
P0637S
SRK2
P0637M
P0637D
P0638M
P0638D
SRK3

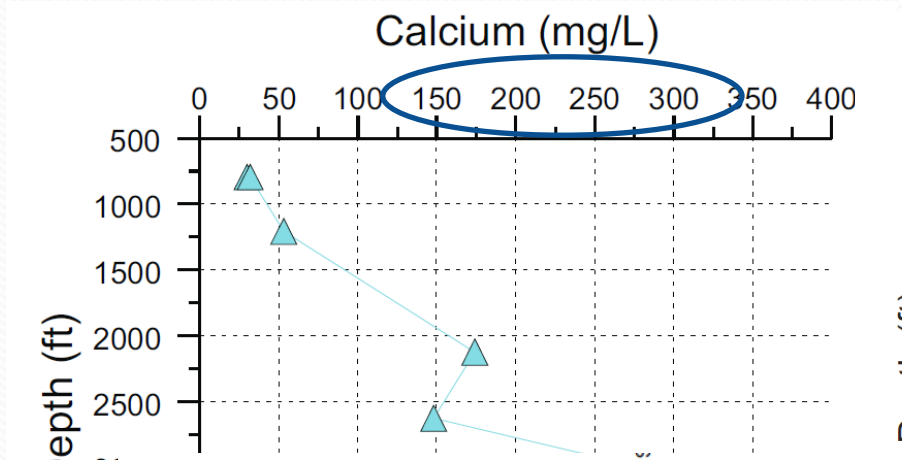

NFK
MW-12
UT
SRK3
MW-5
SFK
MW-14

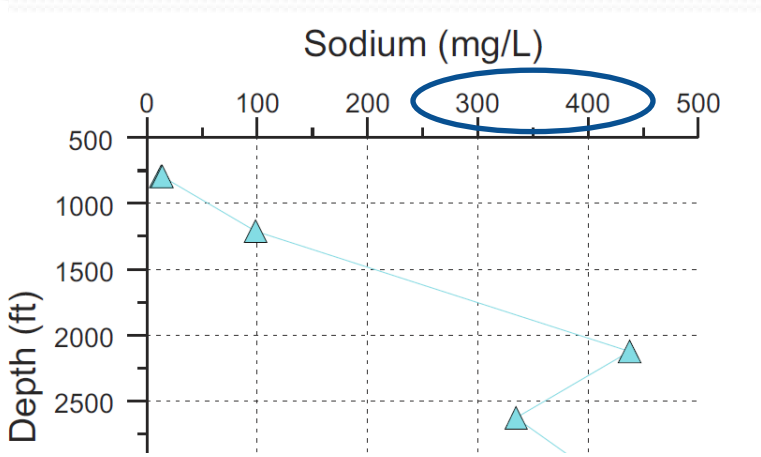

NFK-Overburden
NFK-Bedrock
SFK-Overburden
SFK-Bedrock
UT-Overburden
UT-Bedrock
95 percentile MDL

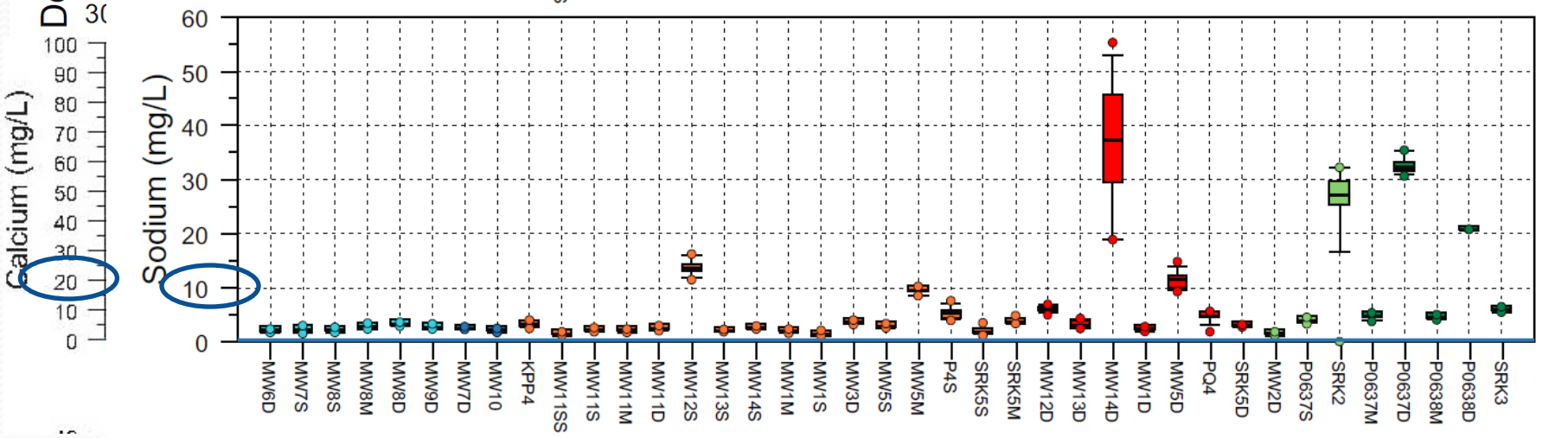
Cation Time Series



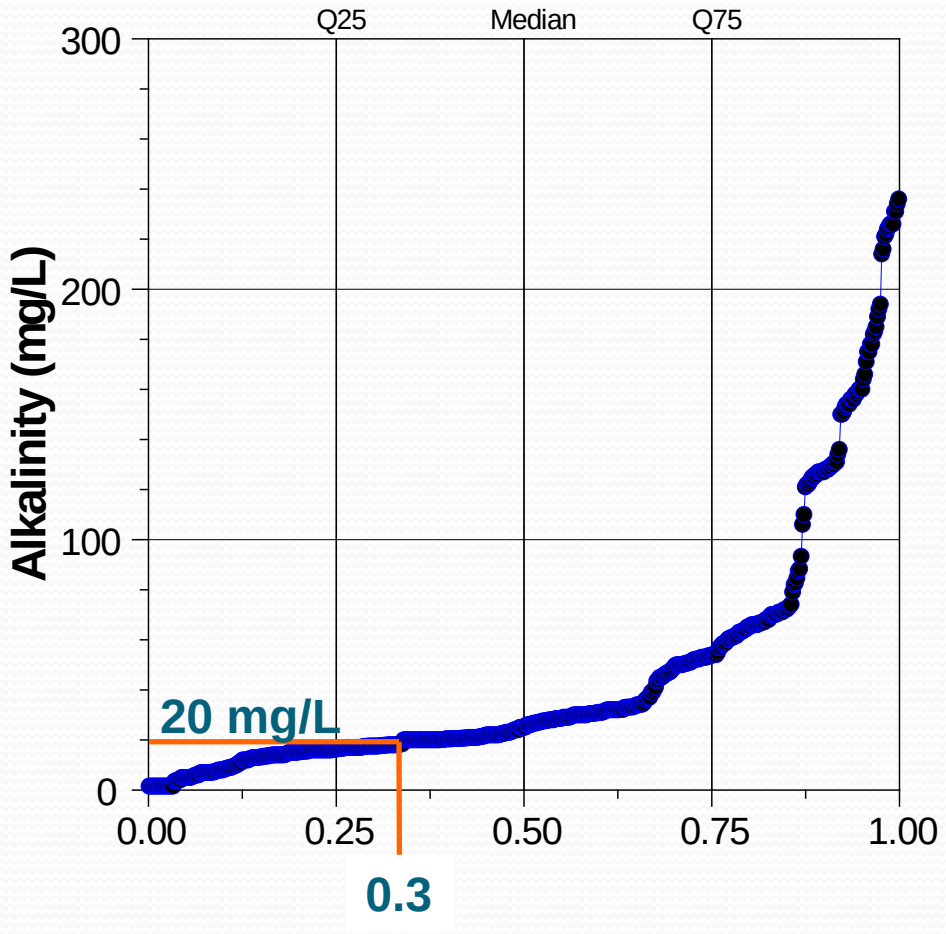
Cation Concentration vs. Depth Deep Groundwater (DH8417)





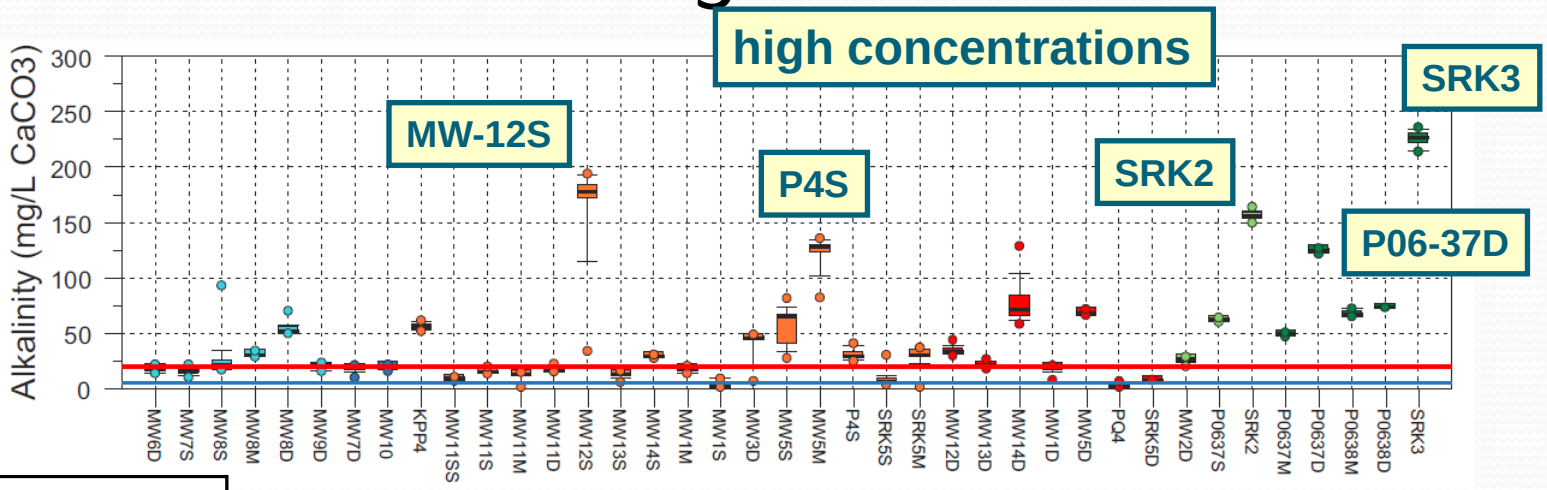


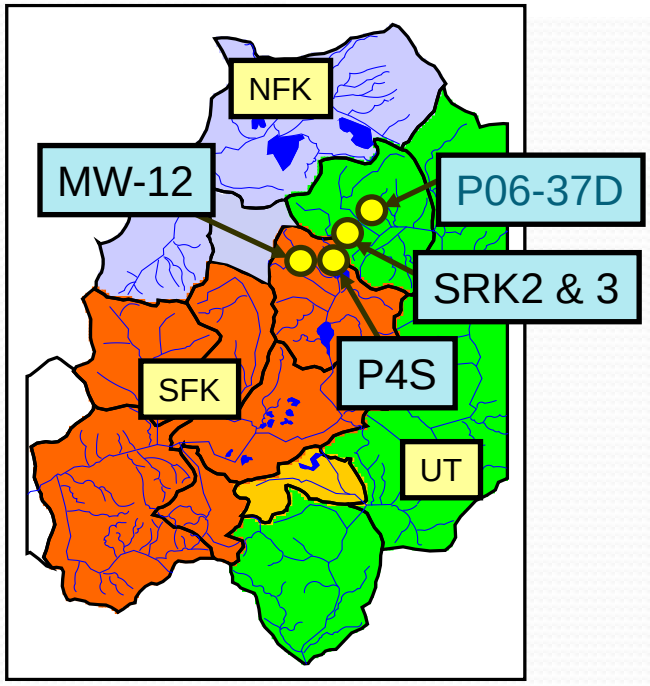
Alkalinity cumulative frequency



30% of the samples do not meet the ADEC criterion of 20 mg/L for minimum alkalinity

Alkalinity (CO_3 species)

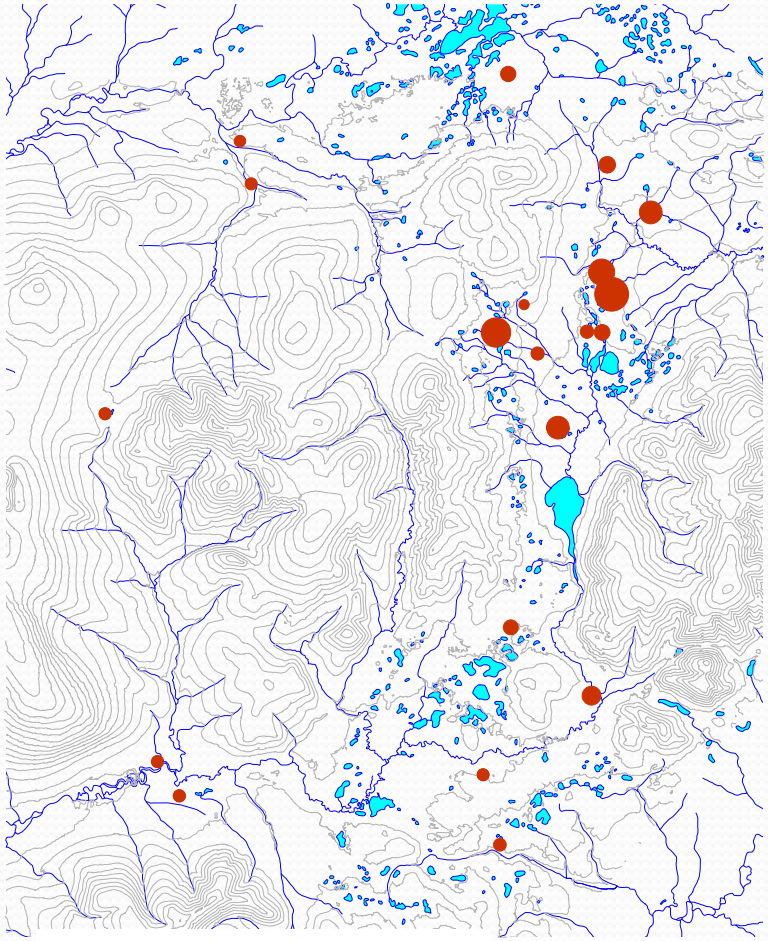




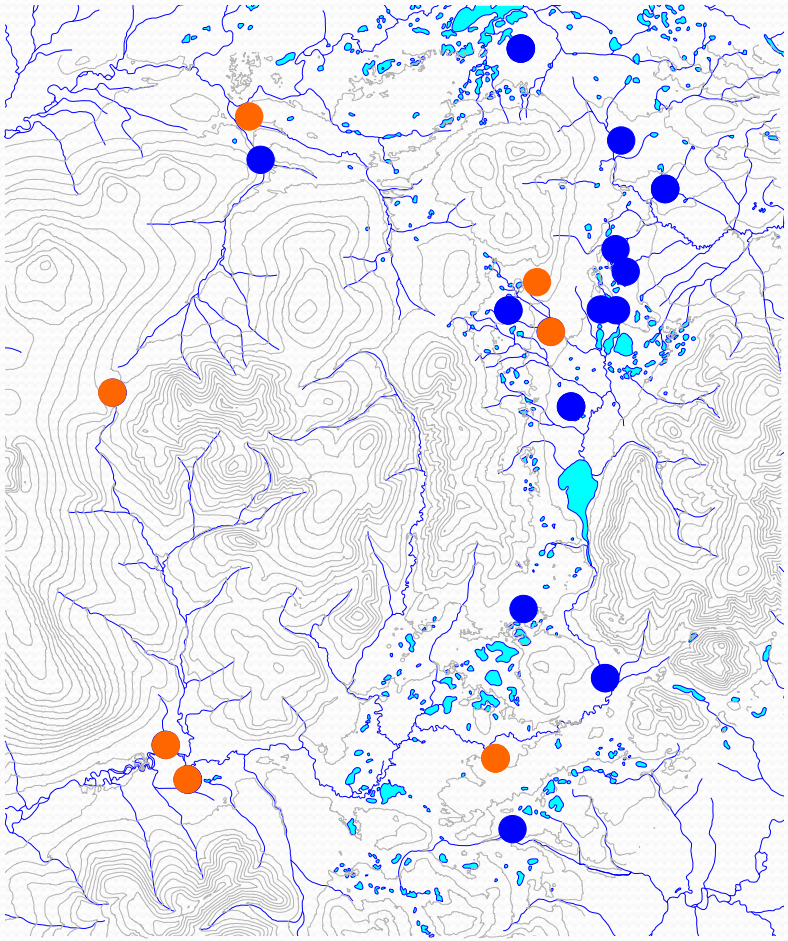
NFK-Overburden
NFK-Bedrock
SFK-Overburden
SFK-Bedrock
UT-Overburden
UT-Bedrock
ADEC criterion
95 percentile MDL

Note: for alkalinity, the criterion is a minimum

Alkalinity map October, 2008

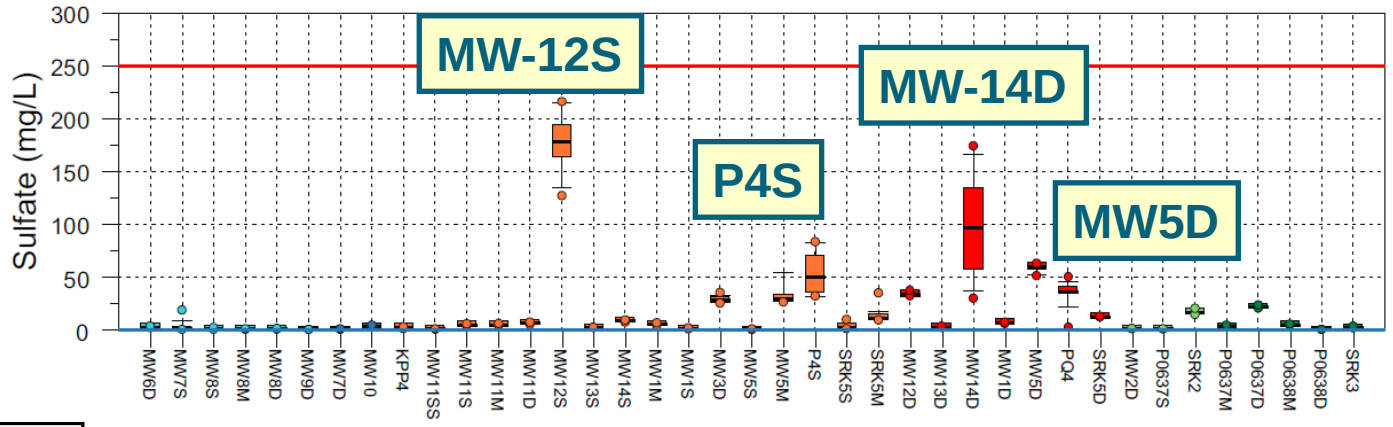


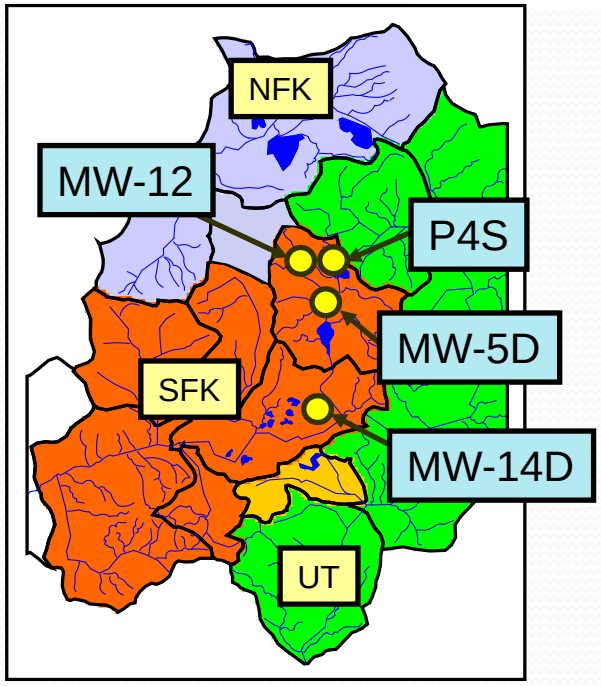
minimum = 1.5 mg/L
maximum = 269 mg/L

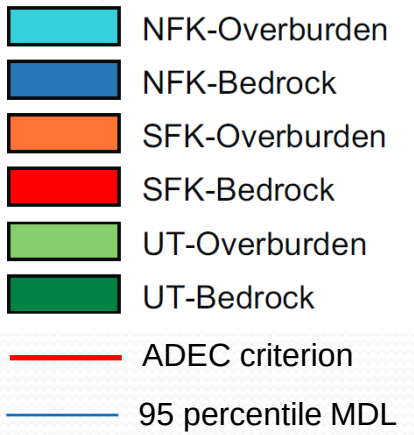


<20 mg/L (does not meet criterion)
>20 mg/L

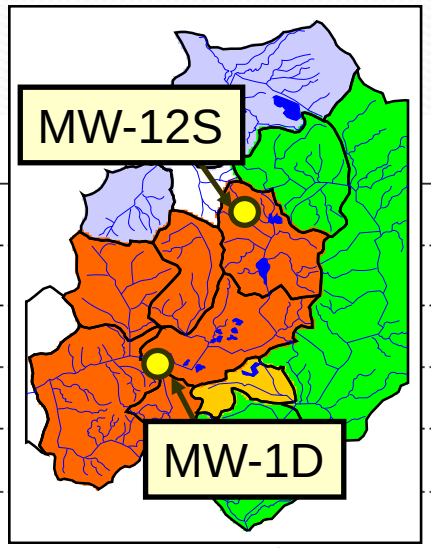
Sulfate

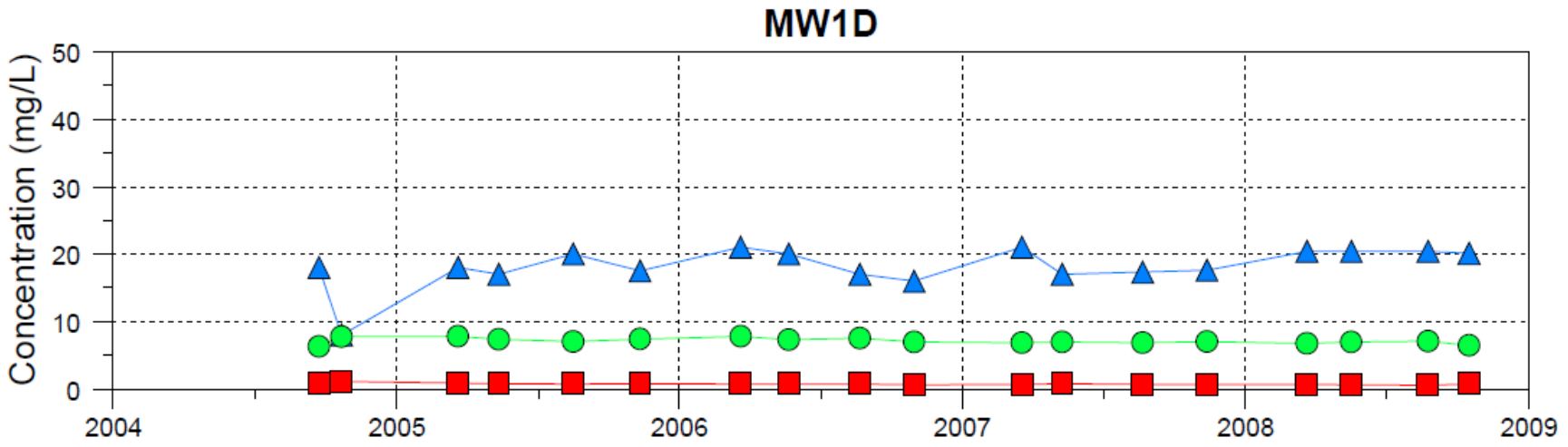

MW-12S
MW-14D
P4S
MW5D
Sulfate (mg/L)
300
250
200
150
100
50
0
MW6D
MW7S
MW8S
MW8M
MW8D
MW9D
MW7D
MW10
KPP4
MW11SS
MW11S
MW11M
MW11D
MW12S
MW13S
MW14S
MW1M
MW1S
MW3D
MW5S
MW5M
P4S
SRK5S
SRK5M
MW12D
MW13D
MW14D
MW1D
MW5D
PQ4
SRK5D
MW2D
P0637S
SRK2
P0637M
P0637D
P0638M
P0638D
SRK3


NFK
MW-12
P4S
MW-5D
SFK
MW-14D
UT

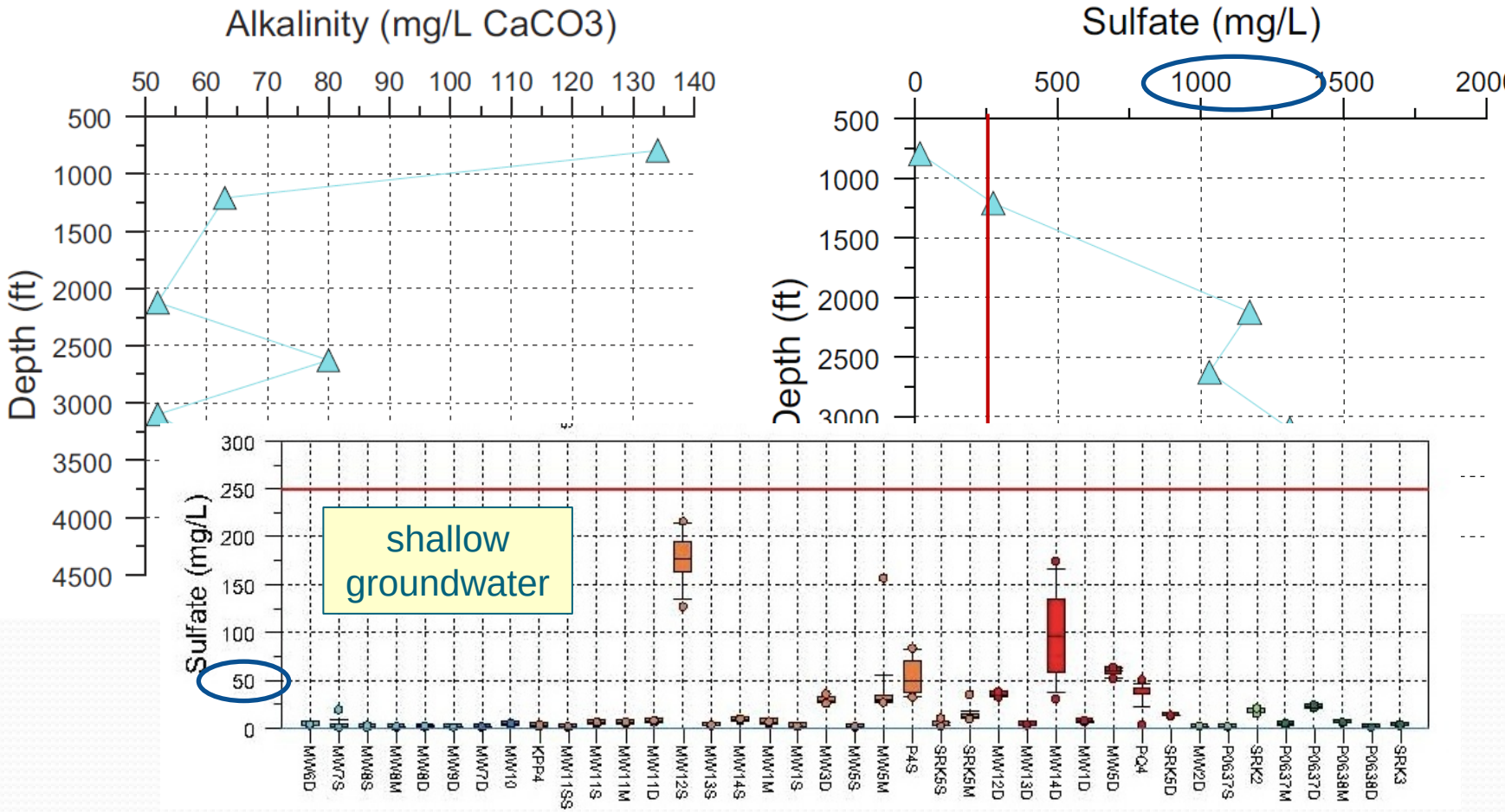

NFK-Overburden
NFK-Bedrock
SFK-Overburden
SFK-Bedrock
UT-Overburden
UT-Bedrock
ADEC criterion
95 percentile MDL

Anion Time Series





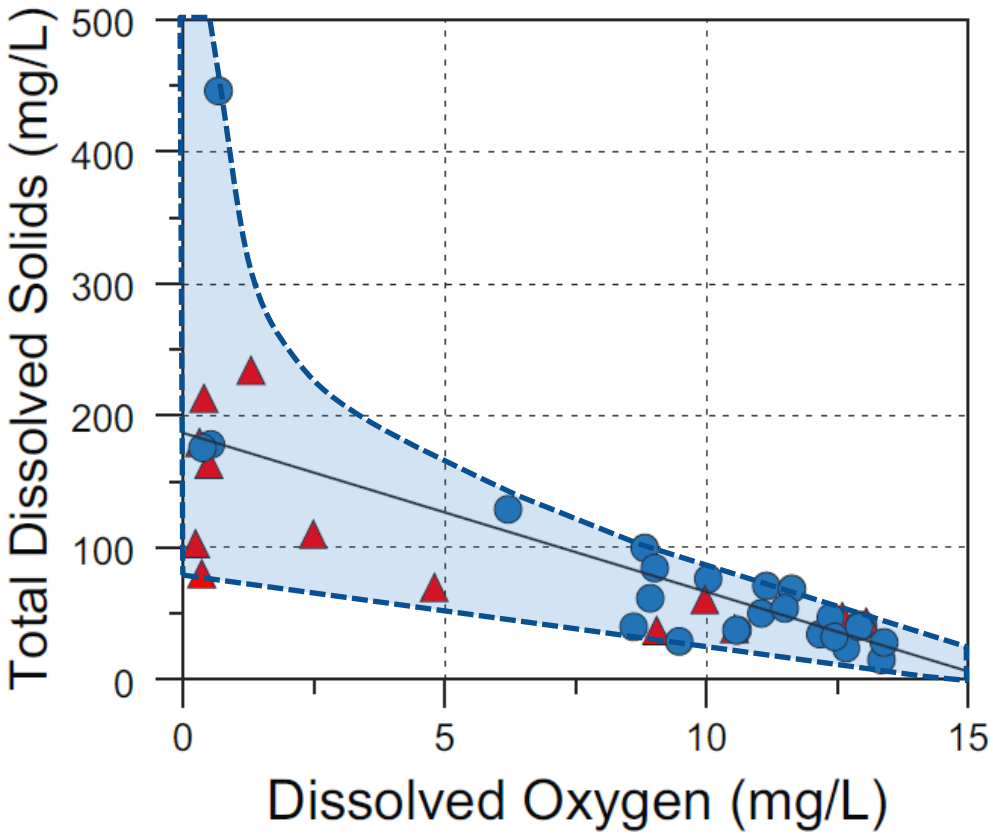
Anion Concentration vs. Depth Deep Groundwater (DH8417)



Distinguishing processes…

- spatial variation
- depth variation
- comparisons of data sets
  - bedrock vs. overburden
  - one watershed vs. another etc.
- temporal changes
- **parameter correlation**
- ionic composition

Relating Concentrations to Processes – Simple Level



Legend

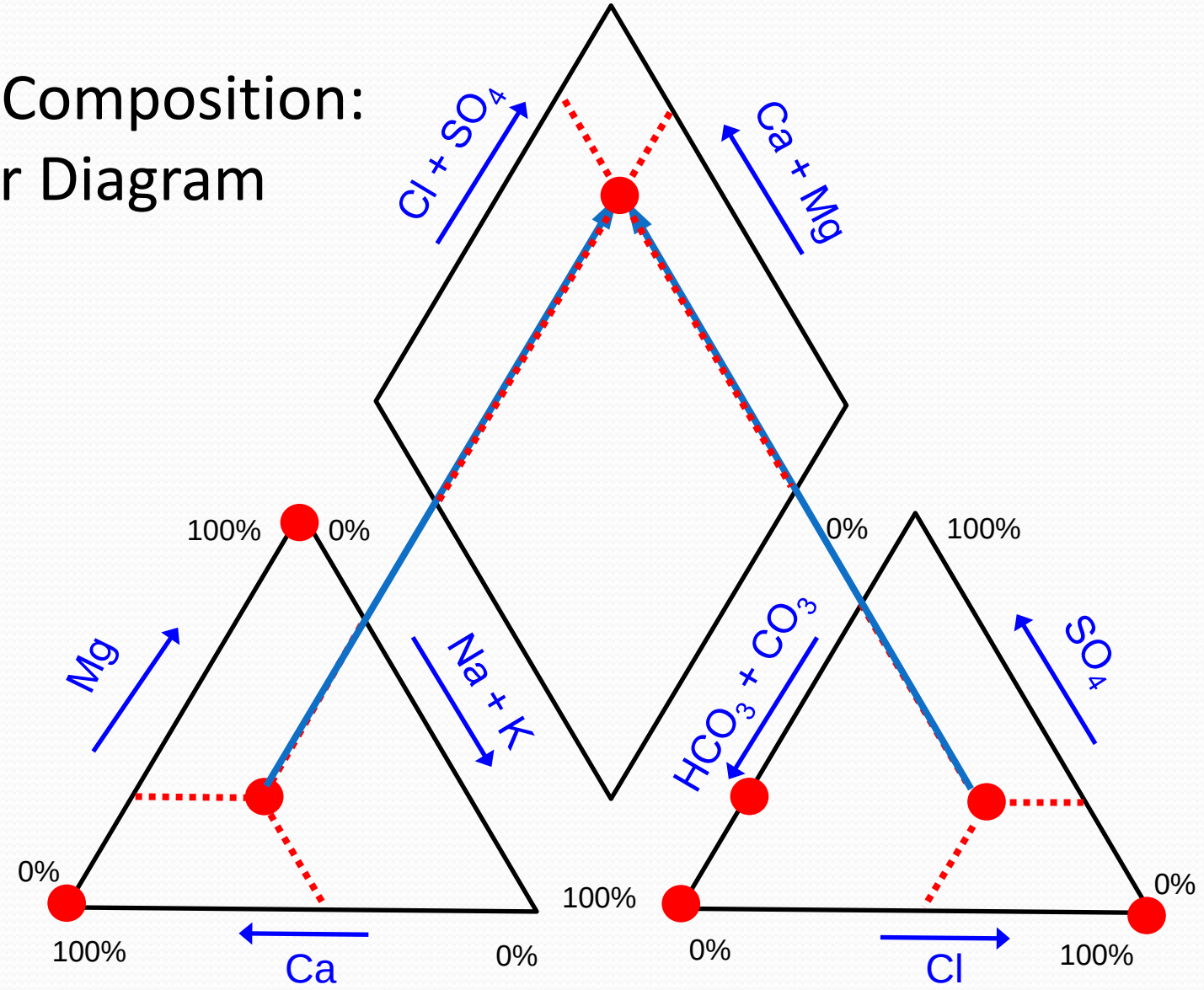
Groundwater in Overburden

Groundwater in Bedrock

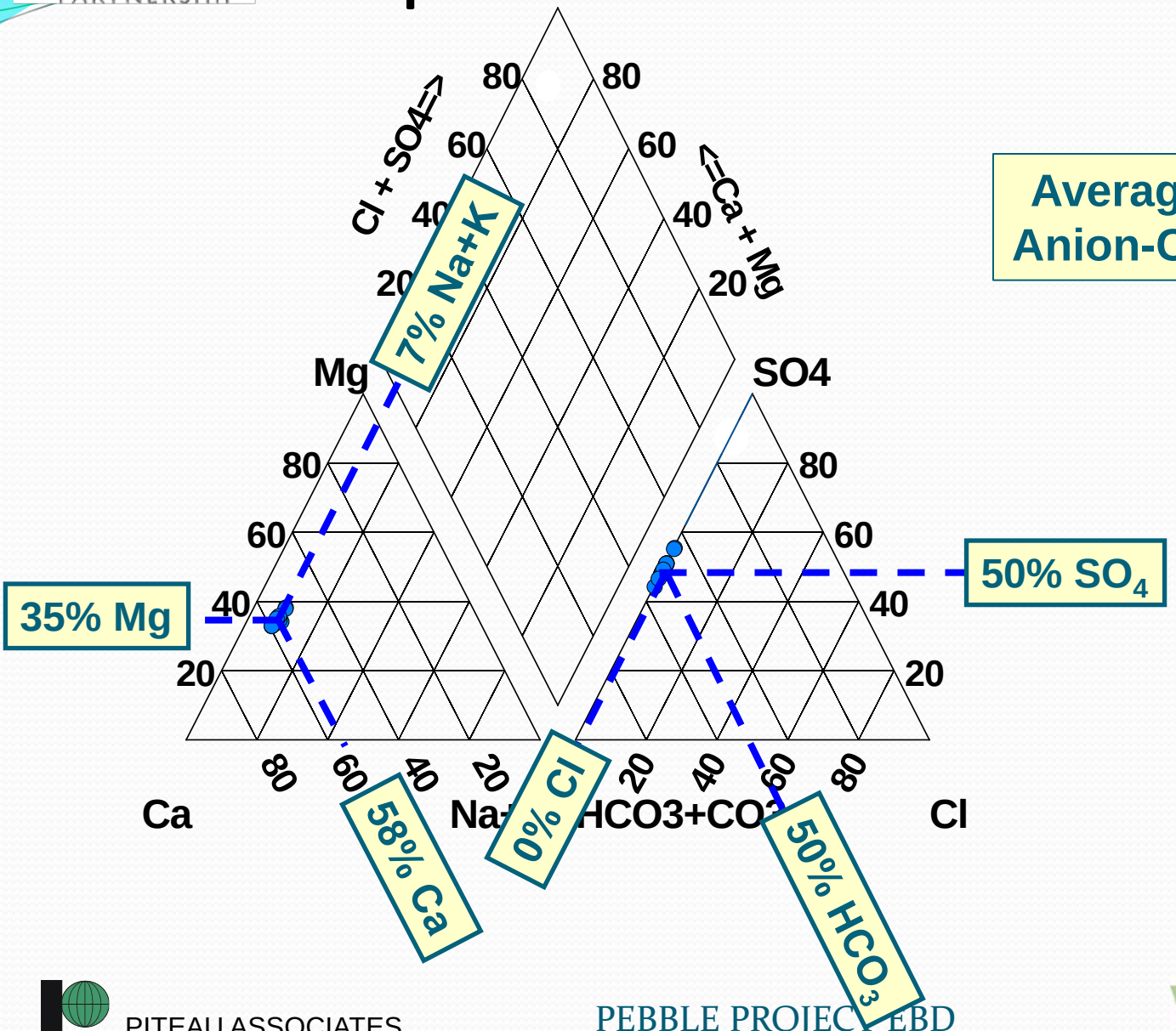
Examining major ion composition …

- spatial variation
- depth variation
- comparisons of data sets
  - bedrock vs. overburden
  - one watershed vs. another etc.
- temporal changes
- parameter correlation
- **ionic composition**

Groundwater Composition: Tri-linear Piper Diagram (meq as %)

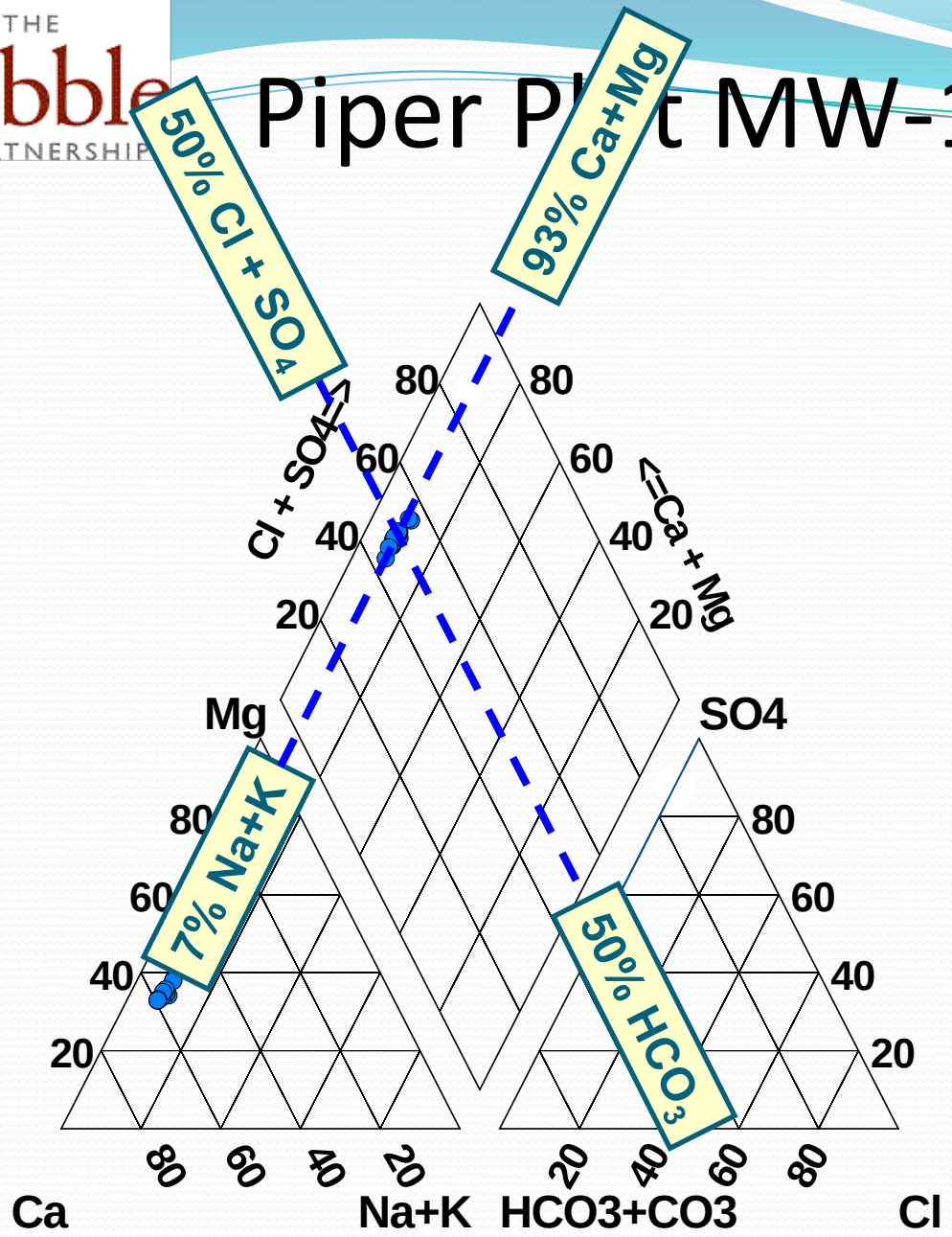


Piper Plot MW-12S all samples



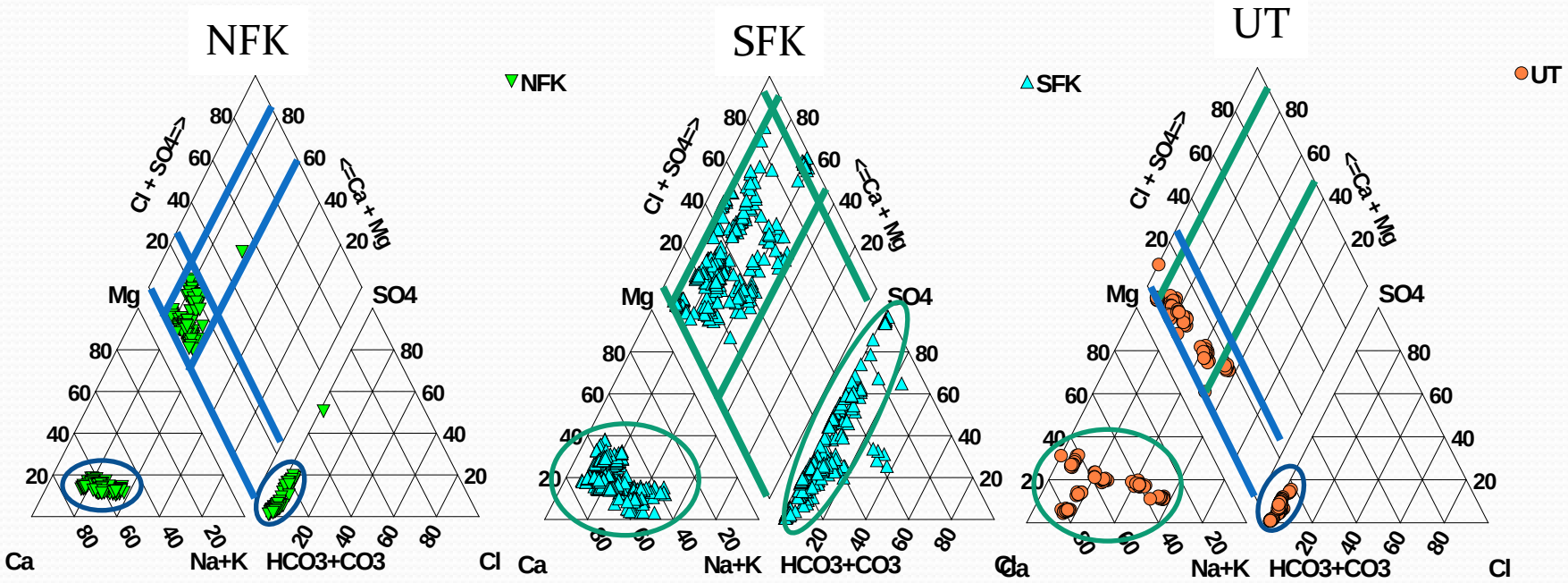
Average Composition Anion-Cation Diagrams

Piper Plot MW-12S all samples



Average Composition Combined Diagram

Groundwater Composition by Watershed



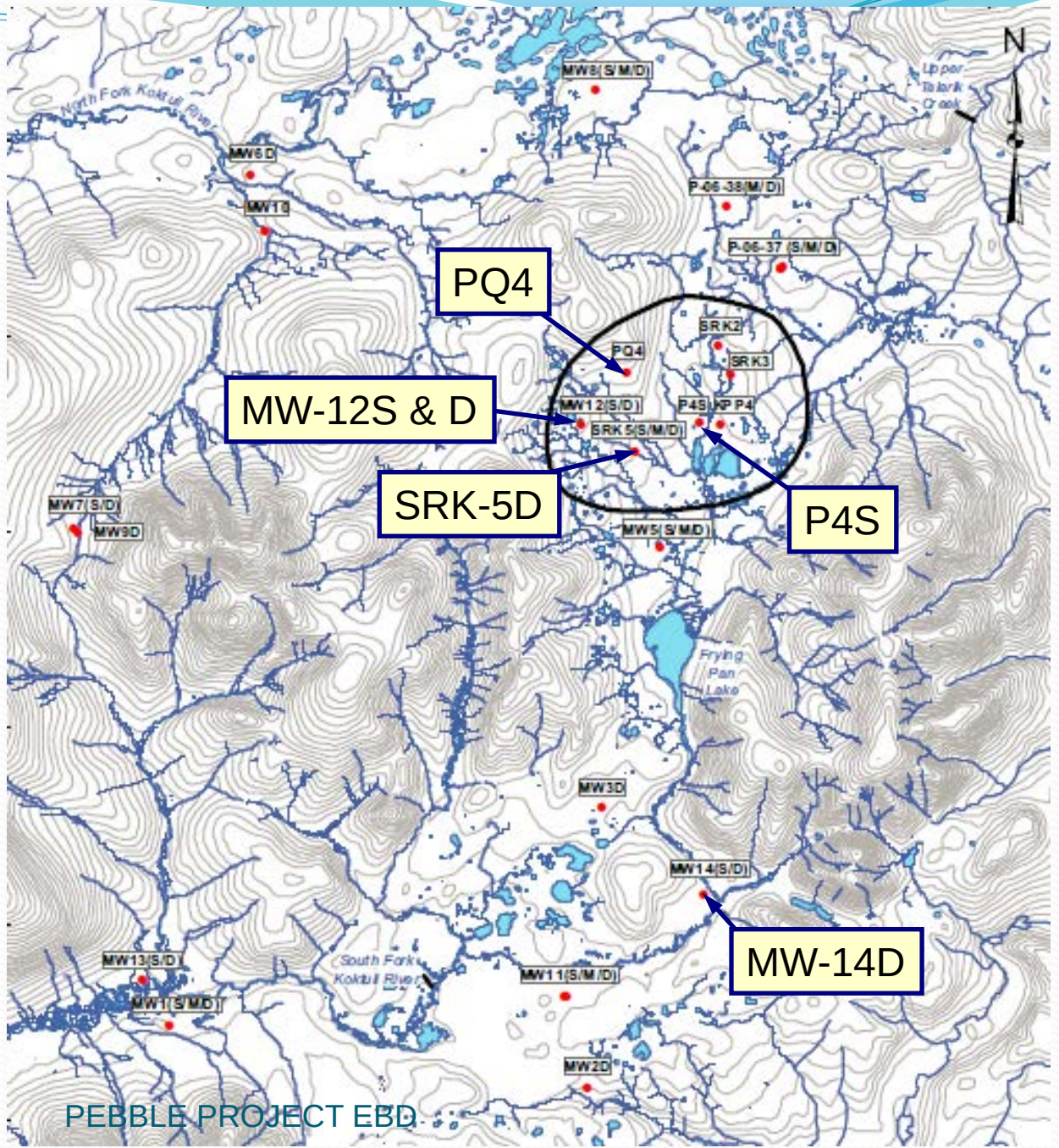
Cations

- NFK: tightest range, lowest Na
- SFK and UT: similar range, highest Ca (80%), highest Mg (40%), highest Na+K (50%)

Anions

- NFK and UT: similar range
- SFK: highest SO_4 (98%), highest Cl (40%)

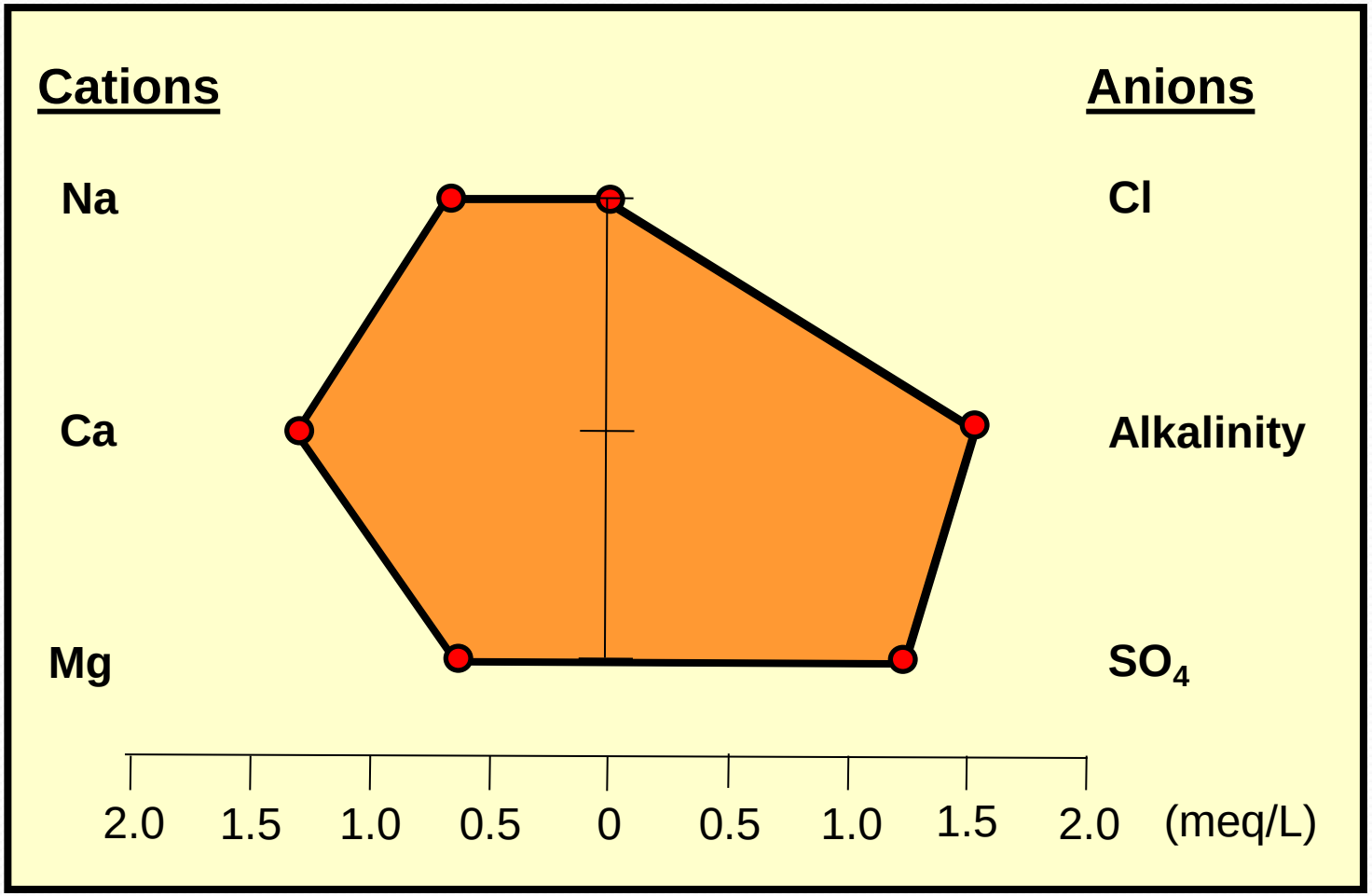
Wells with anions dominated by sulfate



Major Anion Composition

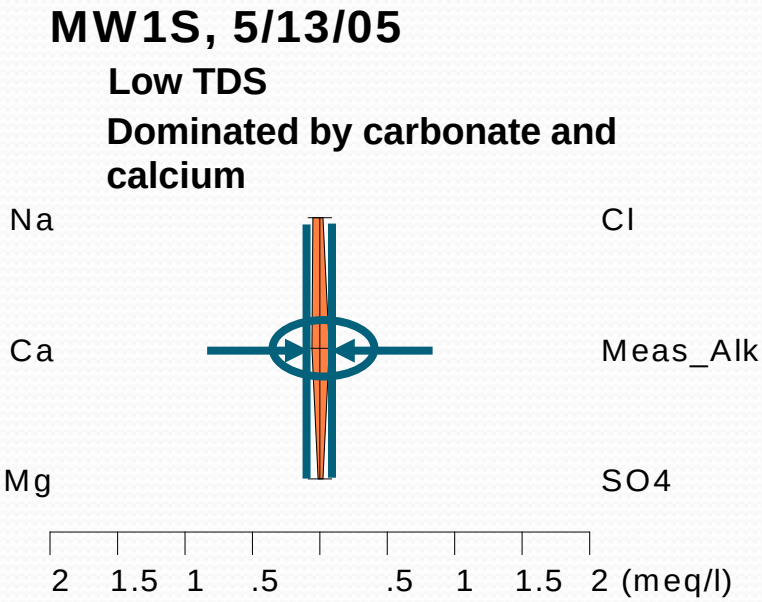
- Most wells dominated by bicarbonate
- Some wells dominated by sulphate:
  - PQ4
  - MW-12S & D
  - SRK-5D
  - P4S
  - MW-14D
- Well MW-14D is more than 4 miles from deposit area

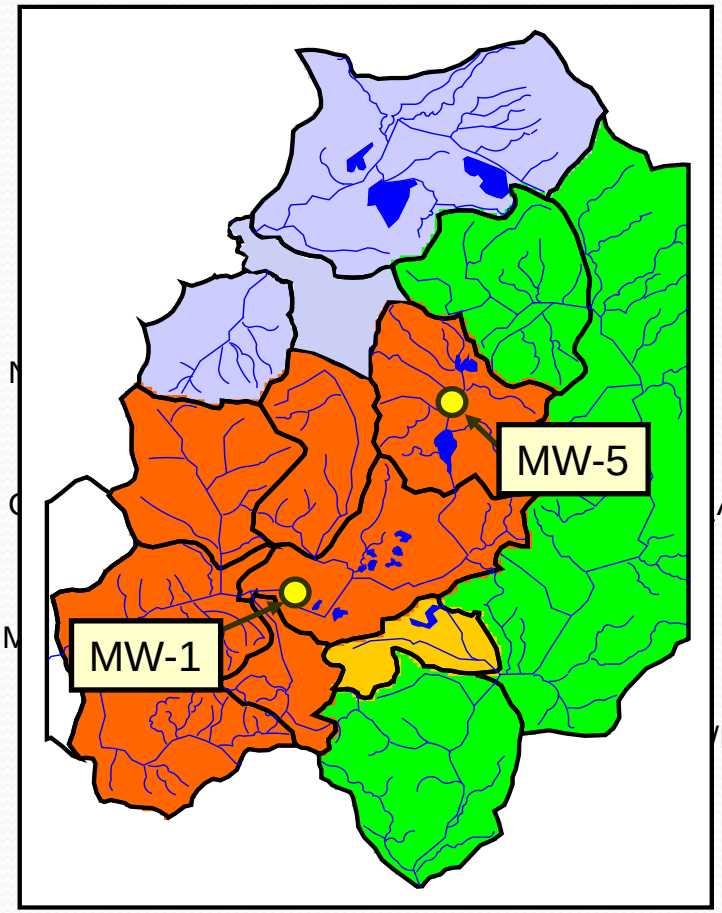
Simultaneously assessing composition and concentration – Stiff Diagram



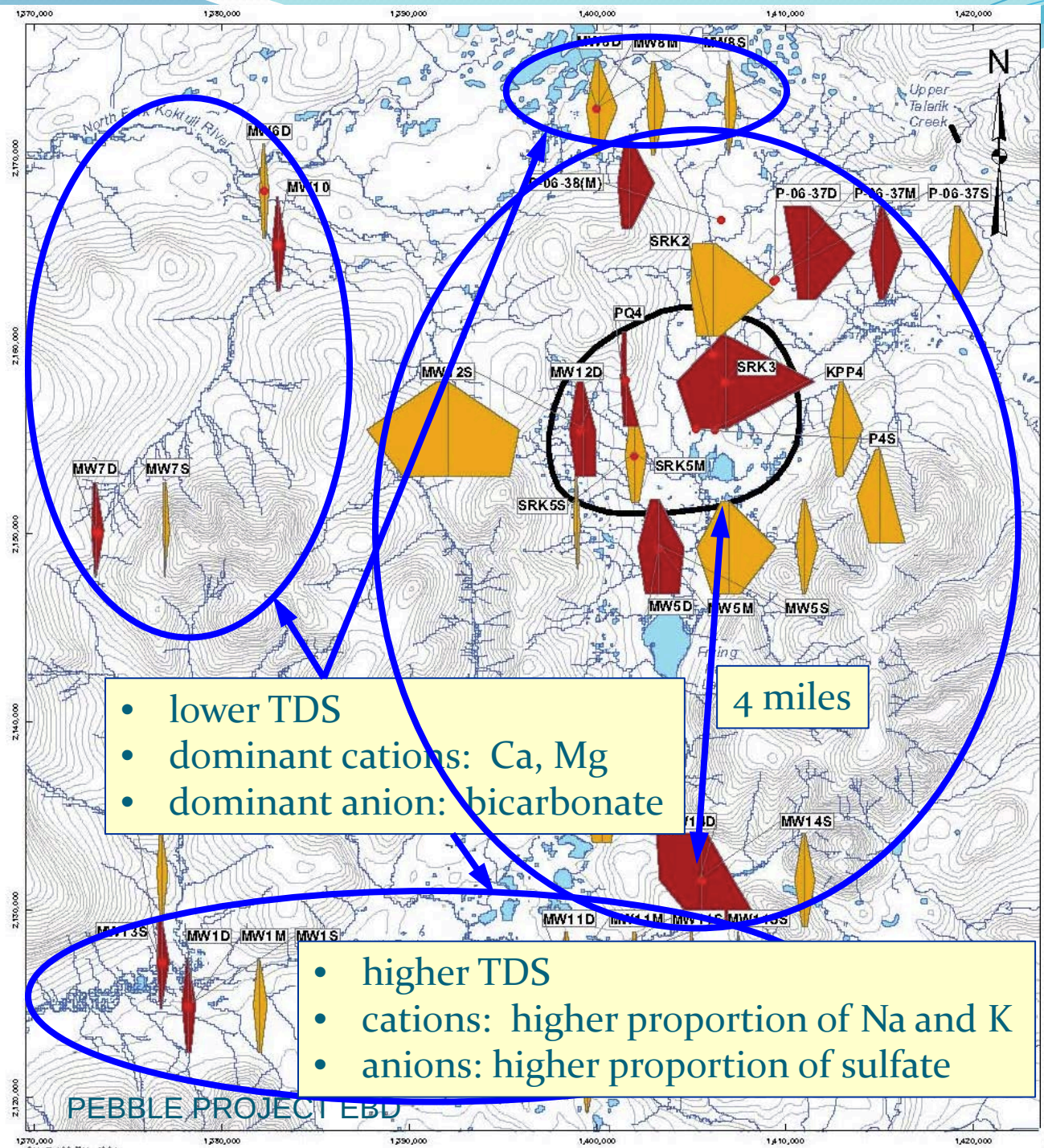
Assessing composition and concentration - spatial

- Stiff Diagram: MW-1S vs. MW-5D





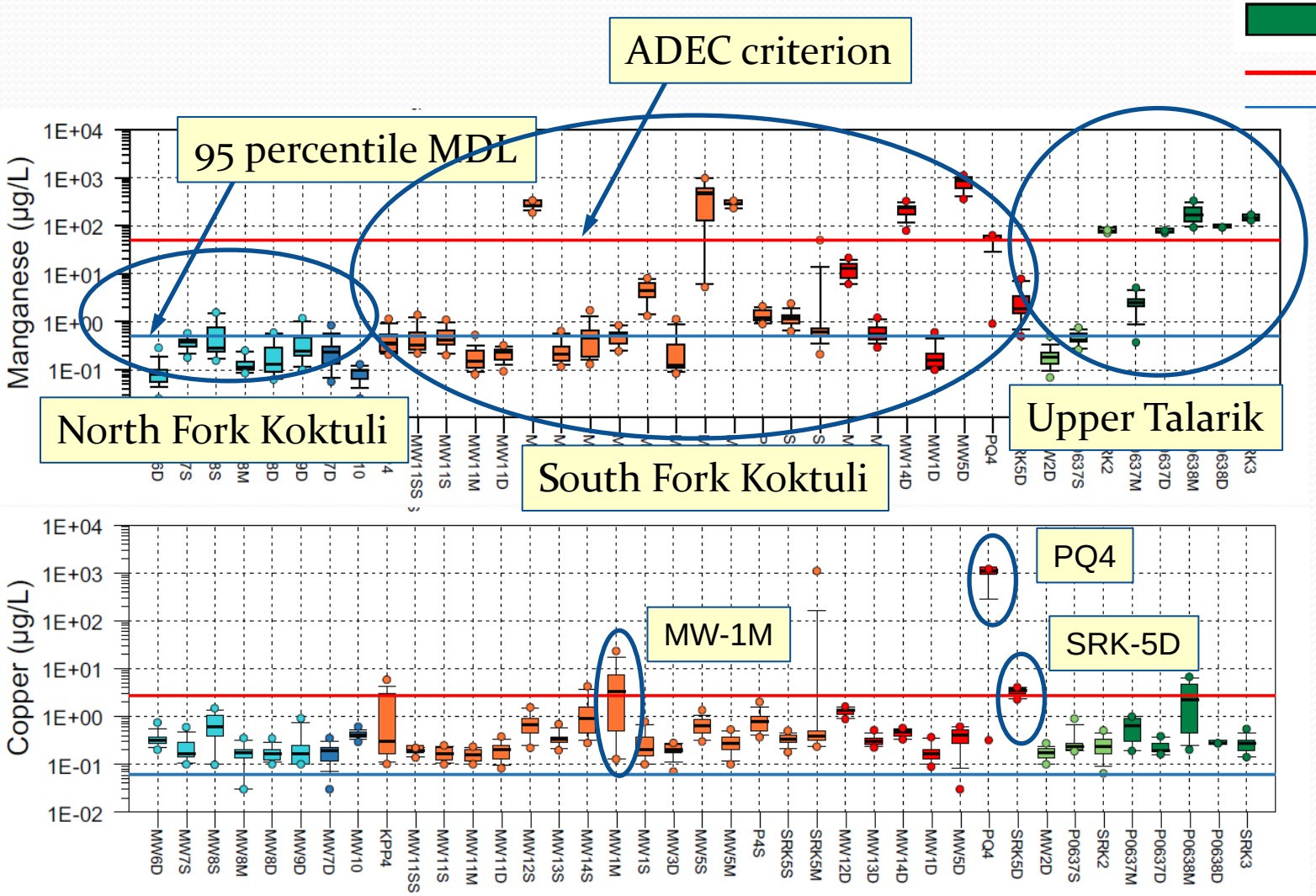
Spatial Distribution: Stiff Diagrams October 08



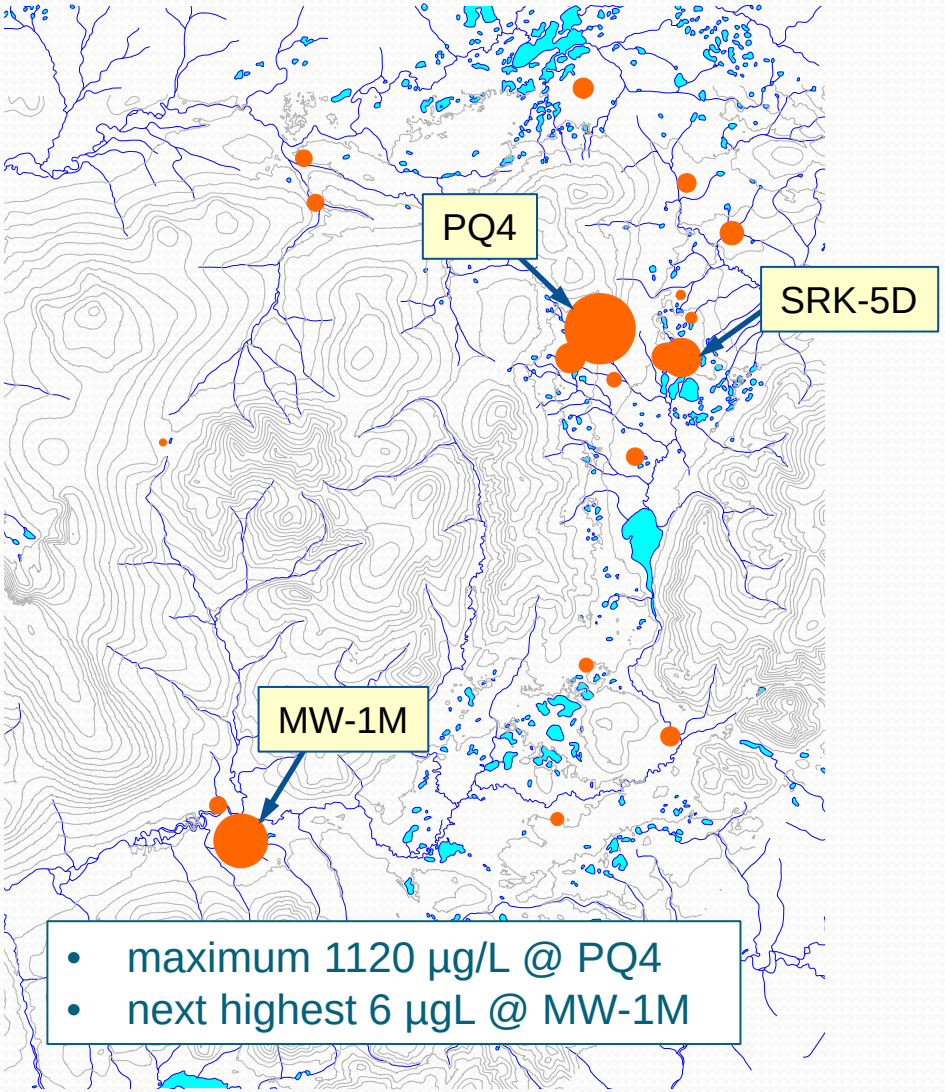
Outline

1. Objectives
2. Index Parameters
3. Major Ions
4. **Trace Elements**
5. Nutrients
6. Summary

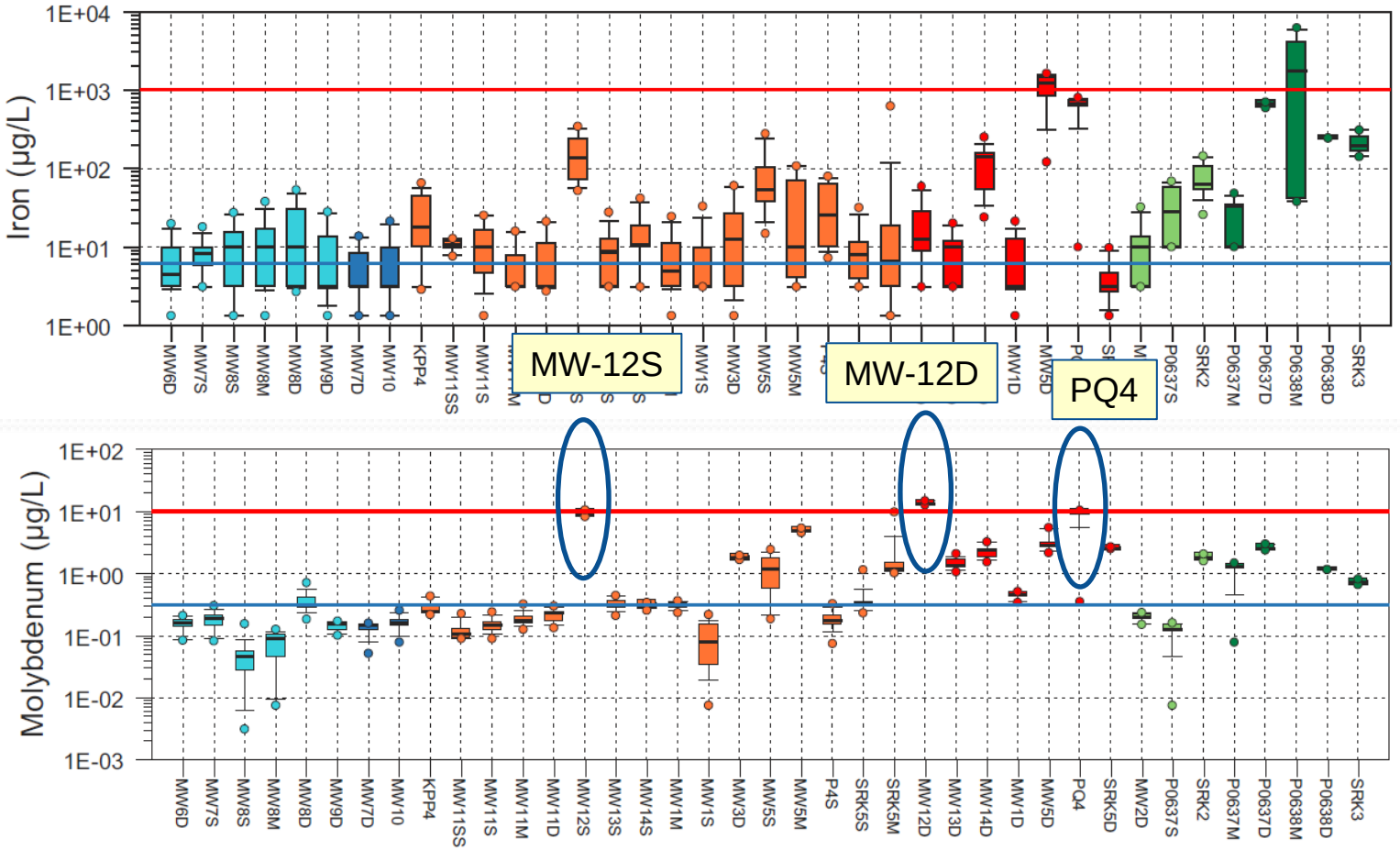
Mn, Cu (2005-2008)



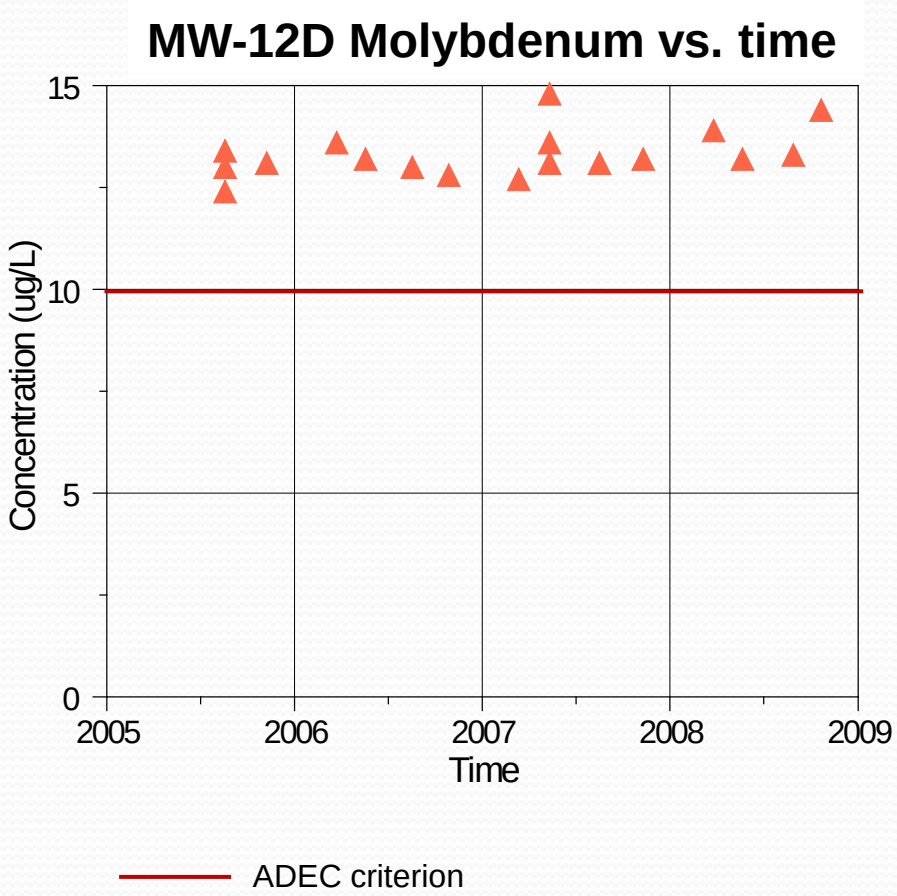
Copper map October, 2008

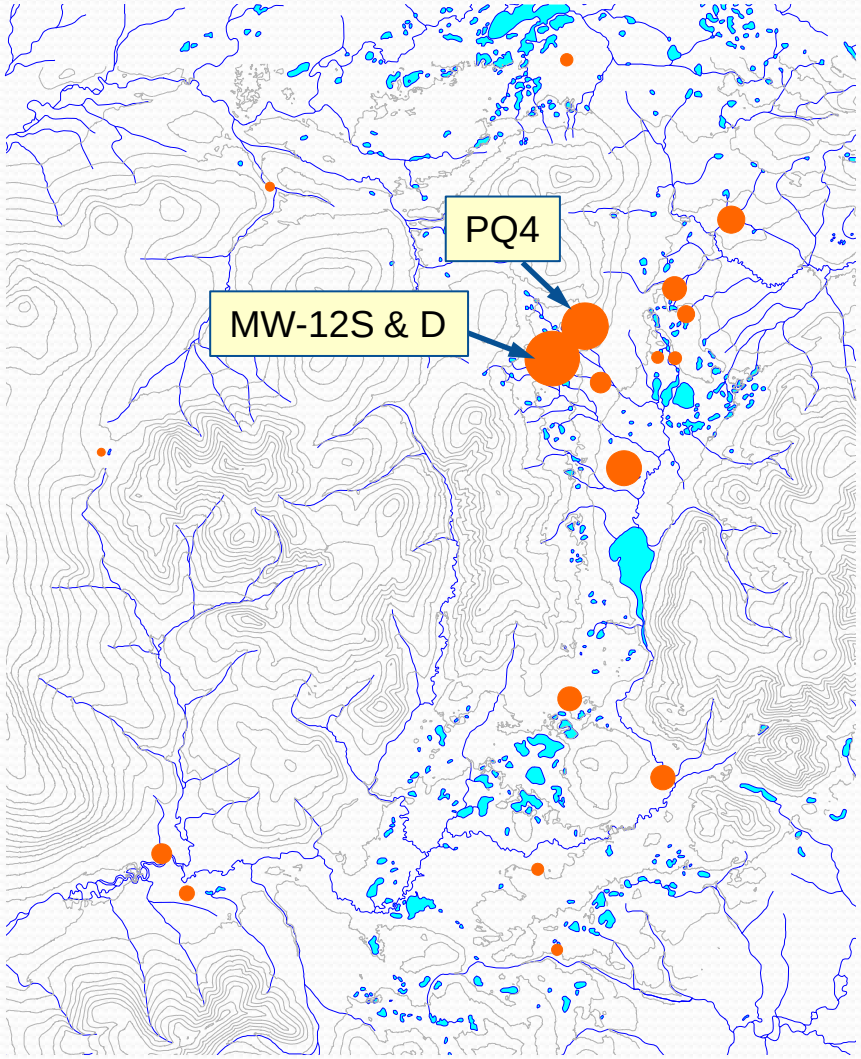


Fe, Mo (2005-2008)



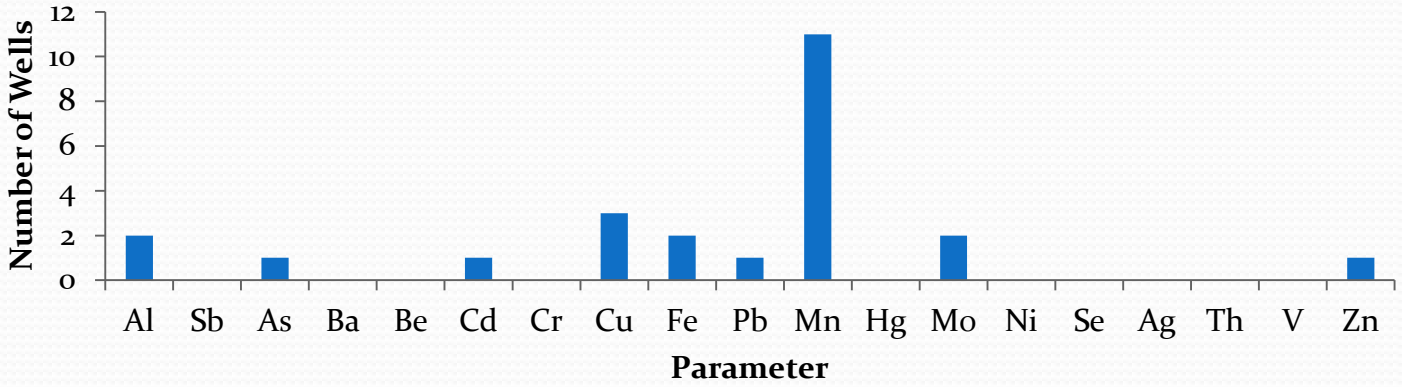
Molybdenum map Oct, 2008





Dissolved Trace Elements Summary

- Concentrations are generally low
- Some naturally occurring concentrations exceed the most stringent ADEC criterion



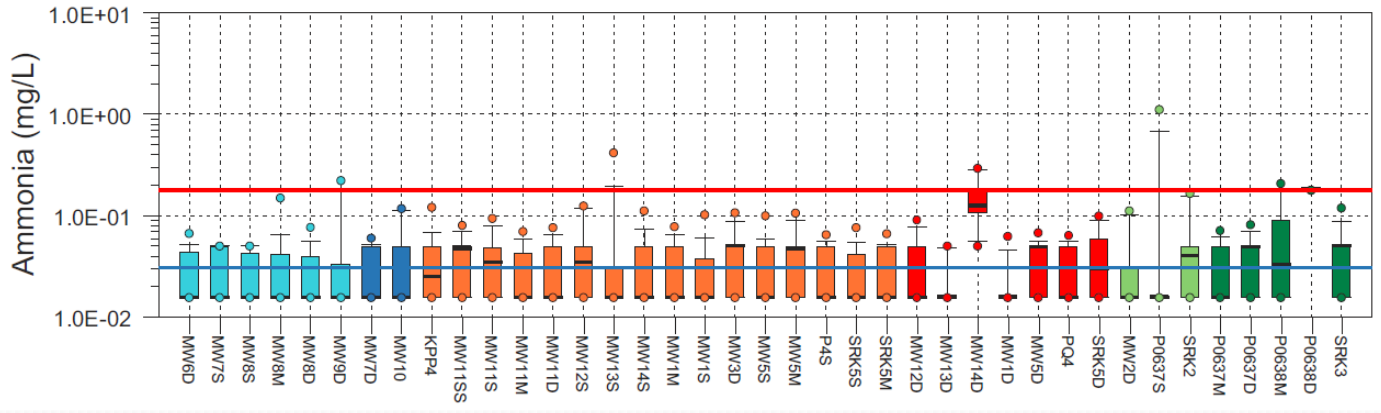
- Some of the exceedances are located several miles from the general deposit area
- Data are consistent with constituent release by sulfide oxidation

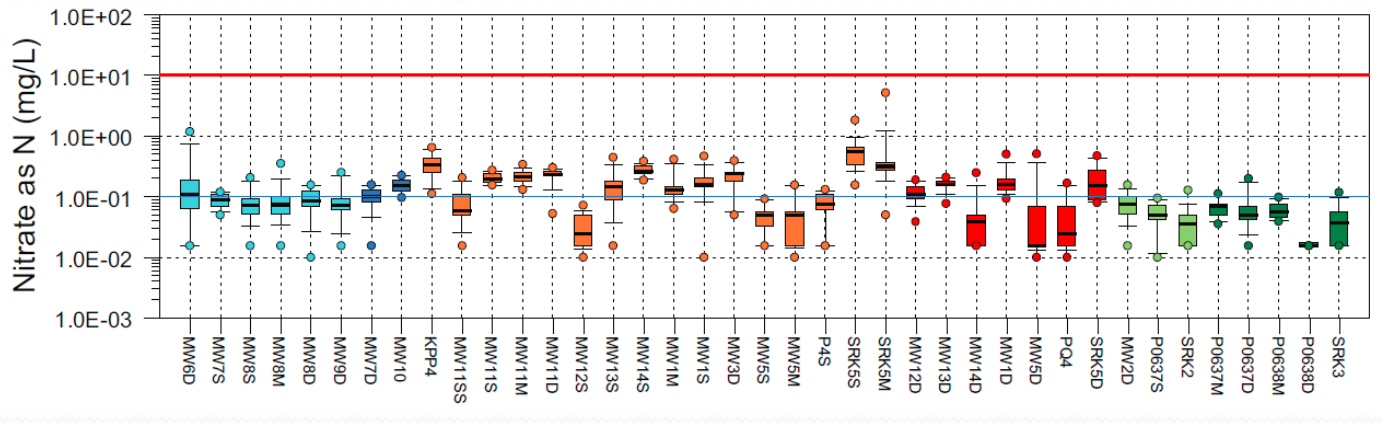
Outline

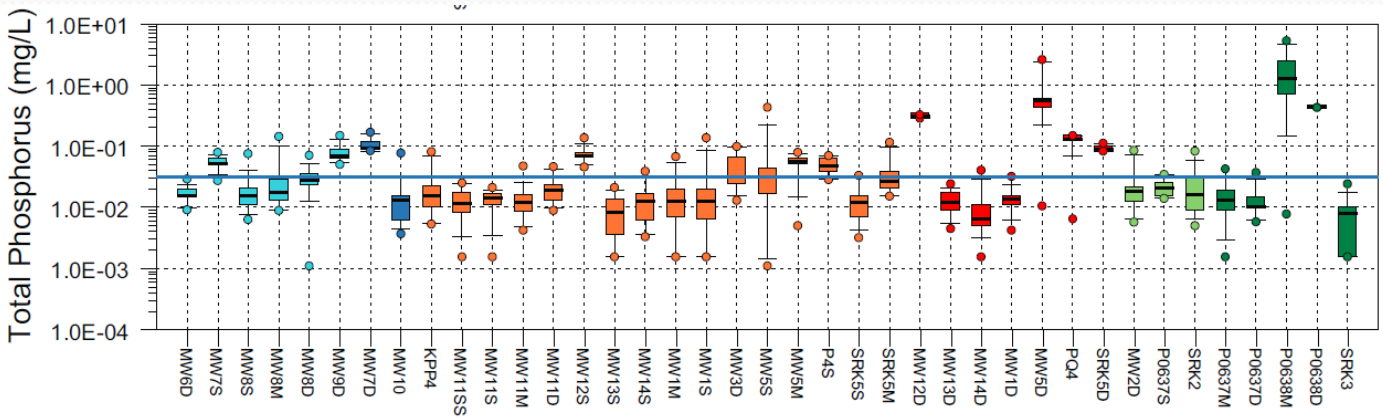
1. Objectives
2. Index Parameters
3. Major Ions
4. Trace Elements
5. **Nutrients**
6. Summary

N & P

- NFK-Overburden
- NFK-Bedrock
- SFK-Overburden
- SFK-Bedrock
- UT-Overburden
- UT-Bedrock
- ADEC criterion
- 95 percentile MDL







Nitrogen and Phosphorous

- Many non-detects
- Nitrogen (ammonia, nitrite and nitrate) occur sporadically at a few locations
- Concentrations mostly below the lowest criterion

Outline

1. Objectives
2. Index Parameters
3. Major Ions
4. Trace Elements
5. Nutrients
6. Summary

Summary

- **Total dissolved solids**
  - mostly low concentrations
  - some wells noticeably higher
    - usually in proximity to the deposit area
    - well MW-14D, 4 miles from the deposit area
  - deep groundwater has much higher TDS
- **pH**
  - most wells near neutral
  - well with second lowest pH values is 8 miles from the deposit
- **Dissolved oxygen**
  - often near saturation and sometimes consistent with depth
  - sometimes decreases with depth
- **Temperature**
  - average 4 °C and stable

Summary

- **Major Ions**
  - cations generally dominated by calcium
  - anions generally dominated by carbonate
  - some wells dominated by sulfate, including one well 4 miles from deposit
  - deep groundwater strongly dominated by sulfate
  - major ion concentrations typically increase with depth
- **Nutrients generally undetectable**

Summary

- **Trace Elements**
  - Al, As, Cd, Cu, Fe, Pb, Mn, Mo, Zn and alkalinity often failed the ADEC criteria at selected wells
  - Mn and alkalinity were the parameters that failed the criterion most frequently
  - wells that failed the criteria generally had distinctive index parameters
- **General patterns**
  - concentrations and composition relatively constant over time in all watersheds
  - lowest and most stable concentrations generally observed in NFK watershed
  - evidence of sulfide oxidation and geochemical reactions with aquifer materials

Questions …