What the Shale?!?

Impacts on shallow soil and groundwater quality from near surface marine shale bedrock in Alberta

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MONTROSE
ENVIRONMENTAL

Outline

- **Introduction:** Why is shallow marine shale bedrock a concern for site assessment?

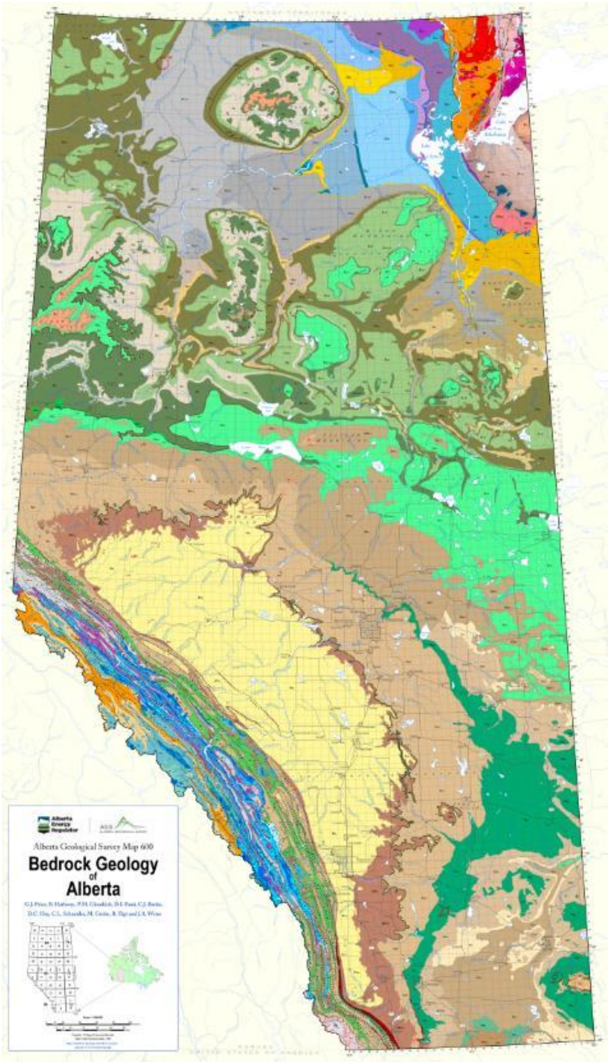
- **Case Studies:** Demonstrate how shallow marine shale bedrock can influence background soil and groundwater quality at sites and what parameters and what data analysis techniques can we use to diagnose

- **Next steps:** The technical and financial implications and why an area-based background approach may make sense

Acknowledgements: The (geo) chemists: Hugh Abercrombie, Maurice Shevalier, Phil Richards, Dan Pollard

Alberta is a Sedimentary Province

- Most of Alberta is underlain by the Western Canadian Sedimentary Basin (WCSB)
- The Mesozoic rocks in the WCSB are dominantly siliciclastic (made up of sand, silt and clay) that were deposited in a marginal marine to marine setting
- These rocks were exposed in various places during glaciation and covered with relatively thin drift in many places
- Rocks reworked into the overlying glacial drift, and comprise the parent material for overlying mineral soils
- Affect groundwater chemistry through water-rock interactions



Prior et al 2013

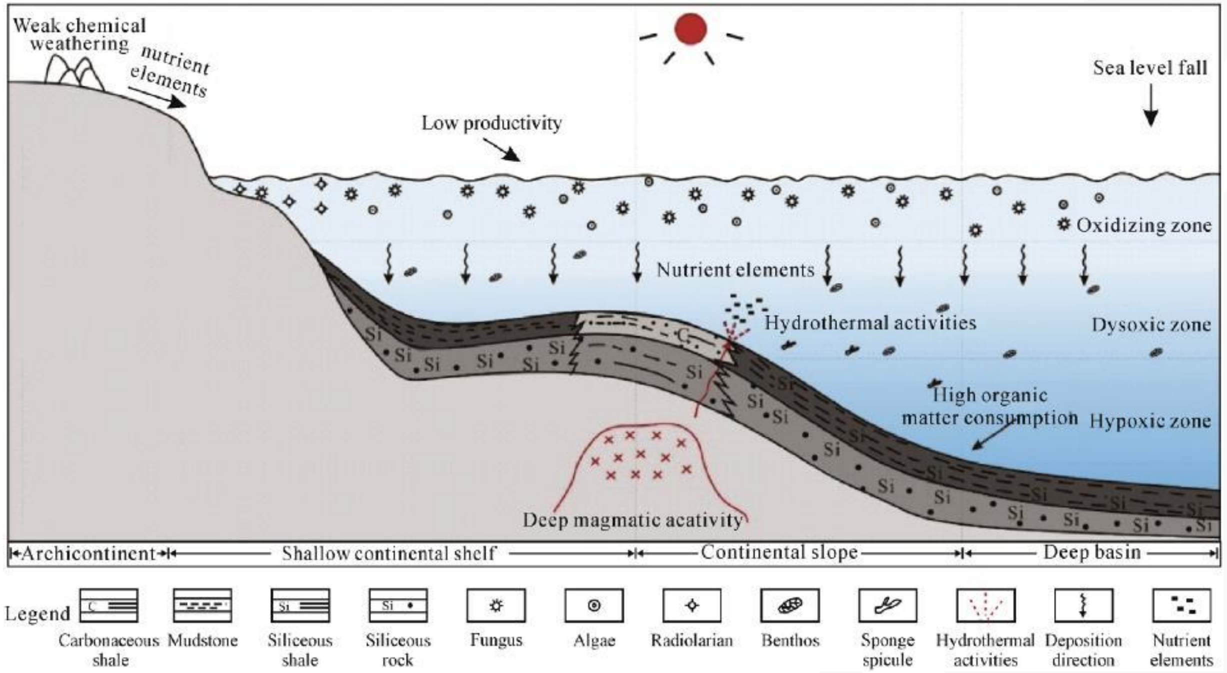
Yellows and browns = sandstone dominated

Green = shale dominated

Blues and purples = carbonates

Oranges and reds = evaporites and volcanics

What is Unique About Marine Shales?

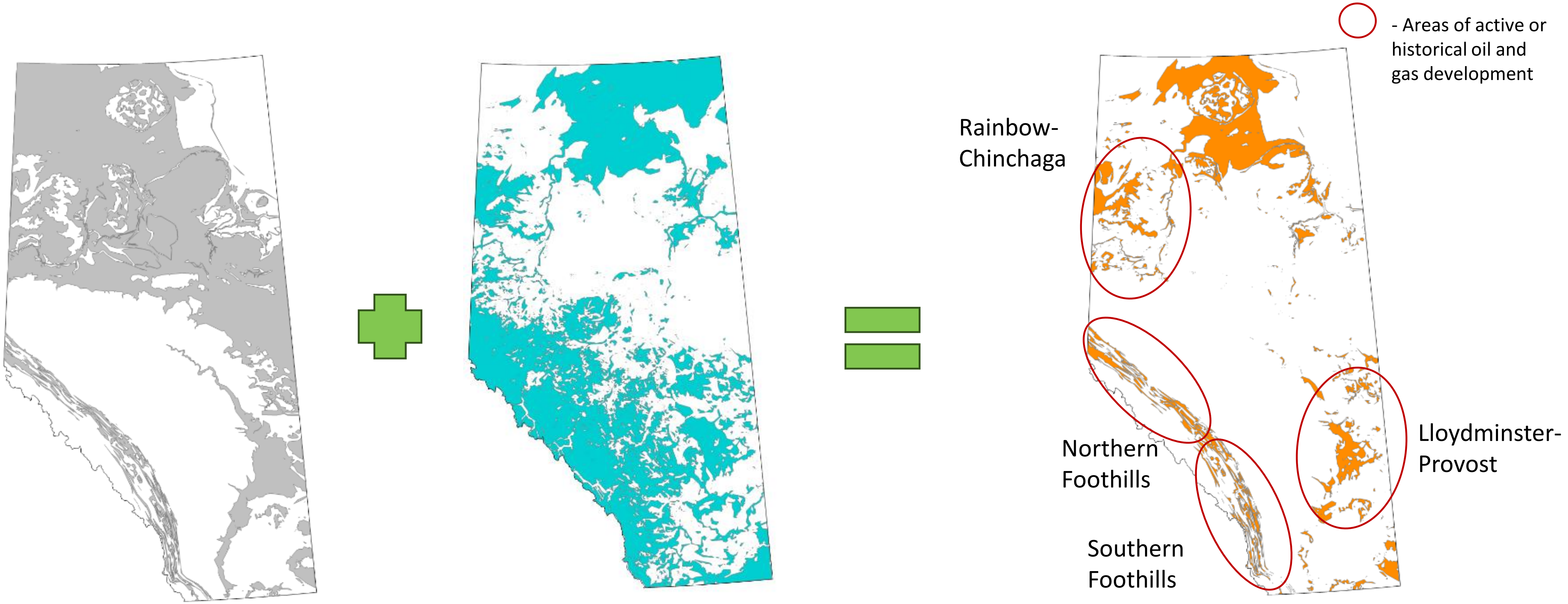


Yang et al 2021

- Shales are deposited in a marine environment by suspension settling through the water column
- Coarser grains drop out closer to continental margins. Fine particles in suspended load get transported further out in water or via wind blown dust. Can undergo little chemical or physical weathering before deposition, preserving otherwise unstable particles (i.e. **clays**)
- **Organic material** generated in shallower water drops down and gets preserved in anoxic zone
- Reducing conditions on seafloor generate sulfide that reacts to form metal sulfides like **pyrite**
- Because of fine grained texture **saline water** gets entrapped in pore space

Where do Marine Shales Occur Near Surface?

- Simple GIS exercise using polygon intersections: select all formations from bedrock map representing marine shale and intersect with drift thickness map

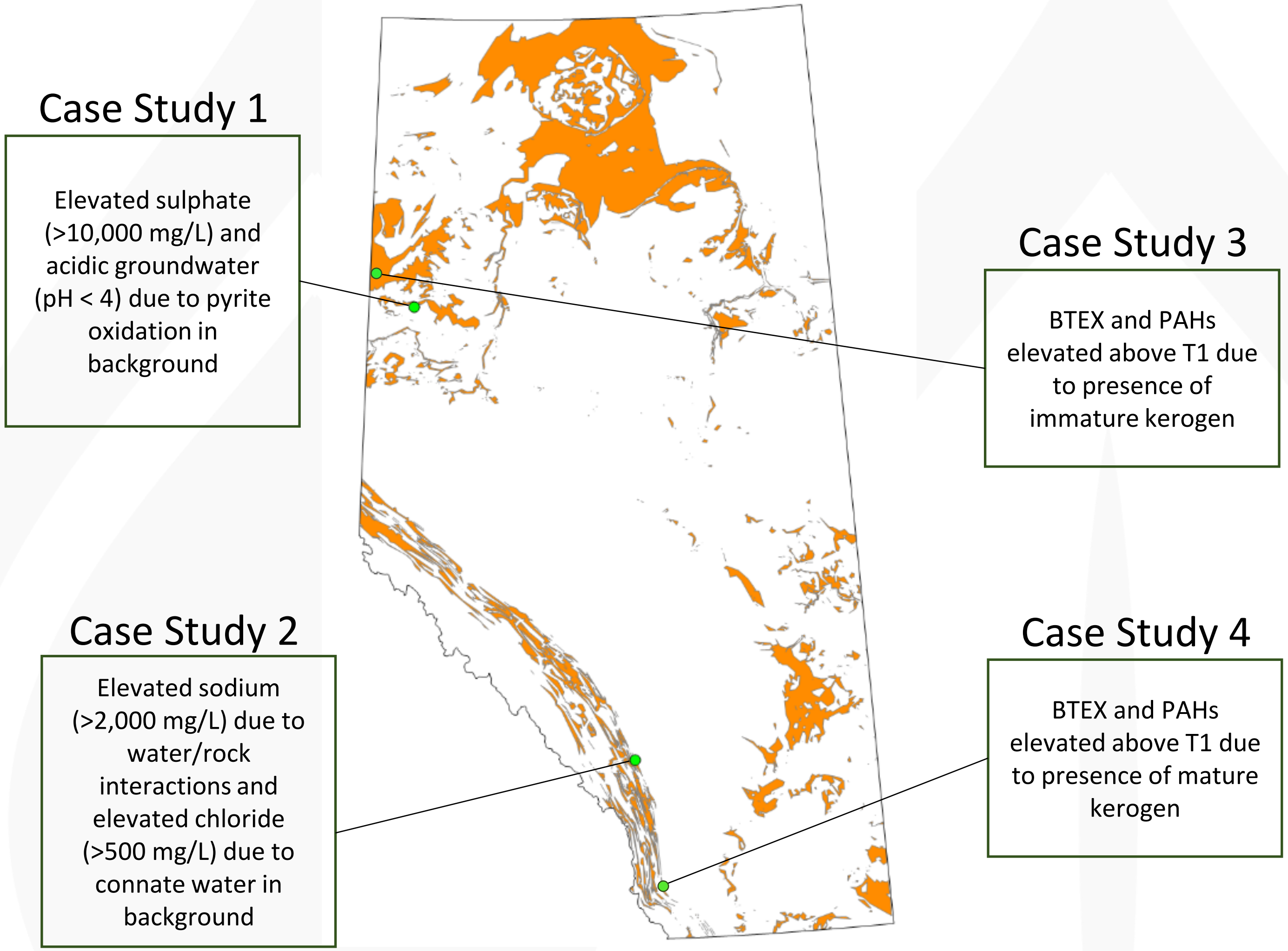


Marine Shale Bedrock Units

Drift Thickness < 15 m

Case Studies – How Can Marine Shale affect Baseline GW Chemistry?

- Case studies show how presence of marine shale can affect routine parameters and hydrocarbons in soil and groundwater resulting in exceedances of AB Tier 1 Guidelines that are naturally occurring in background
- Metals (particularly heavy metals molybdenum, uranium, vanadium, arsenic and zinc but also aluminum, iron, selenium, barium) can also be elevated naturally in shale matrix but not subject of these case studies



Case Study 1 – Sulphate and Acidic Groundwater

- Decommissioned sweet gas plant in Clear Hills
- Only anthropogenic source of sulphate was minor amount of gypsum amendment during decommissioning
- Lower Smoky Group marine shale bedrock near surface (< 8 m)

- regional groundwater flow direction

- locations with elevated sulphate interpreted to not be site related, concentrations in 1000's of mg/L range

Case Study 1 – Sulphate and Acidic Groundwater

- Pyrite oxidation generates sulphate and acidic conditions:

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \leftrightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

- Confirm presence of pyrite using analytical techniques (XRD, XRF and SEM)
    - XRF analysis give the elemental composition of the soils in terms of metal oxides
    - XRD gives mineralogical composition of the soils
    - SEM-EDS allows direct observation of mineralogy and structure

- Collect sulfur isotope data from minerals and groundwater to confirm isotopic signature consistent with pyrite source

Case Study 1 – Sulphate and Acidic Groundwater

- Linear programming to determine the best fit to the set of linear equations governing the distribution of the oxides from XRF analysis into minerals (LPNORM)
- LPNORM also uses XRD data to estimate mineral assemblage

Sample	Quartz (wt%)	Kaolinite (wt%)	K-feldspar (wt%)	Dolomite (wt%)	Siderite (wt%)	Pyrite (wt%)	Gypsum (wt%)
1	34.69	27.51	16.72	2.14	7.35	1.03	0
2	37.5	29.65	16.13	1.35	6.83	0.32	0
3	34.67	25.39	15.66	4.44	0	4.43	3.81
4	34.98	21.05	13.3	5.08	2.97	3.93	5.64
5	30.21	29.72	15.31	5.9	7.42	3.2	0.14
6	67.61	11.51	6.58	0.33	9.03	0	0
7	35.5	30.94	16.01	3.26	7.81	0.21	0
8	83.86	4.45	2.66	0.49	3.8	0	0
9	34.88	30.62	15.72	2.47	5.42	0.95	0

- SEM-EDS validated the estimated mineral assemblage

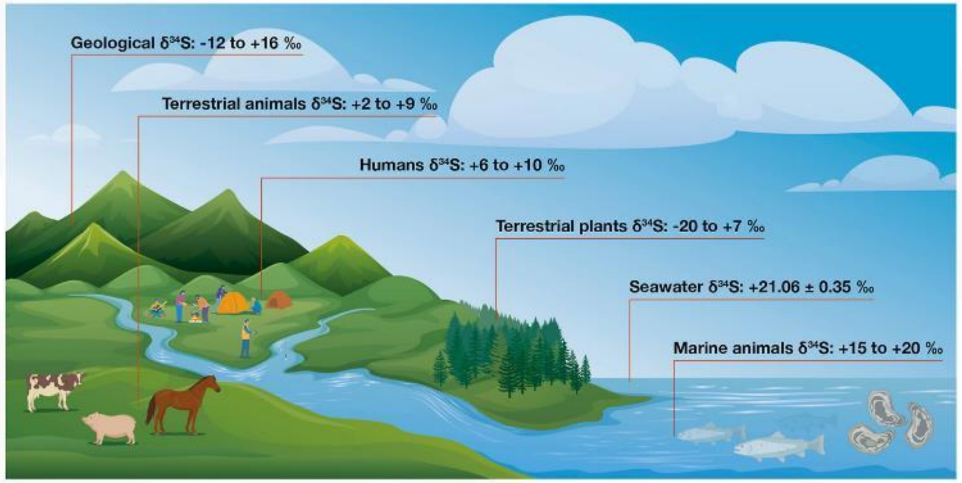
Case Study 1 – Sulphate and Acidic Groundwater

- Isotopic results from soil/rock:

Sample	d34S-pyrite (‰ CDT)	d34S-gypsum (‰ CDT)
1	-27.7	-26.6
2	-24.6	-23.6
3	-24.2	-24.4
4	-25.9	-25.9
5	-26.6	-25.3
6	---	---
7	ns	-15.3
8	---	---
9	-28.4	-26.7

- Isotopic results from sulphate in groundwater:

Sample Point	δ34S (‰ CDT)
1	-26.60
2	-25.10
3	-18.90
4	-24.30

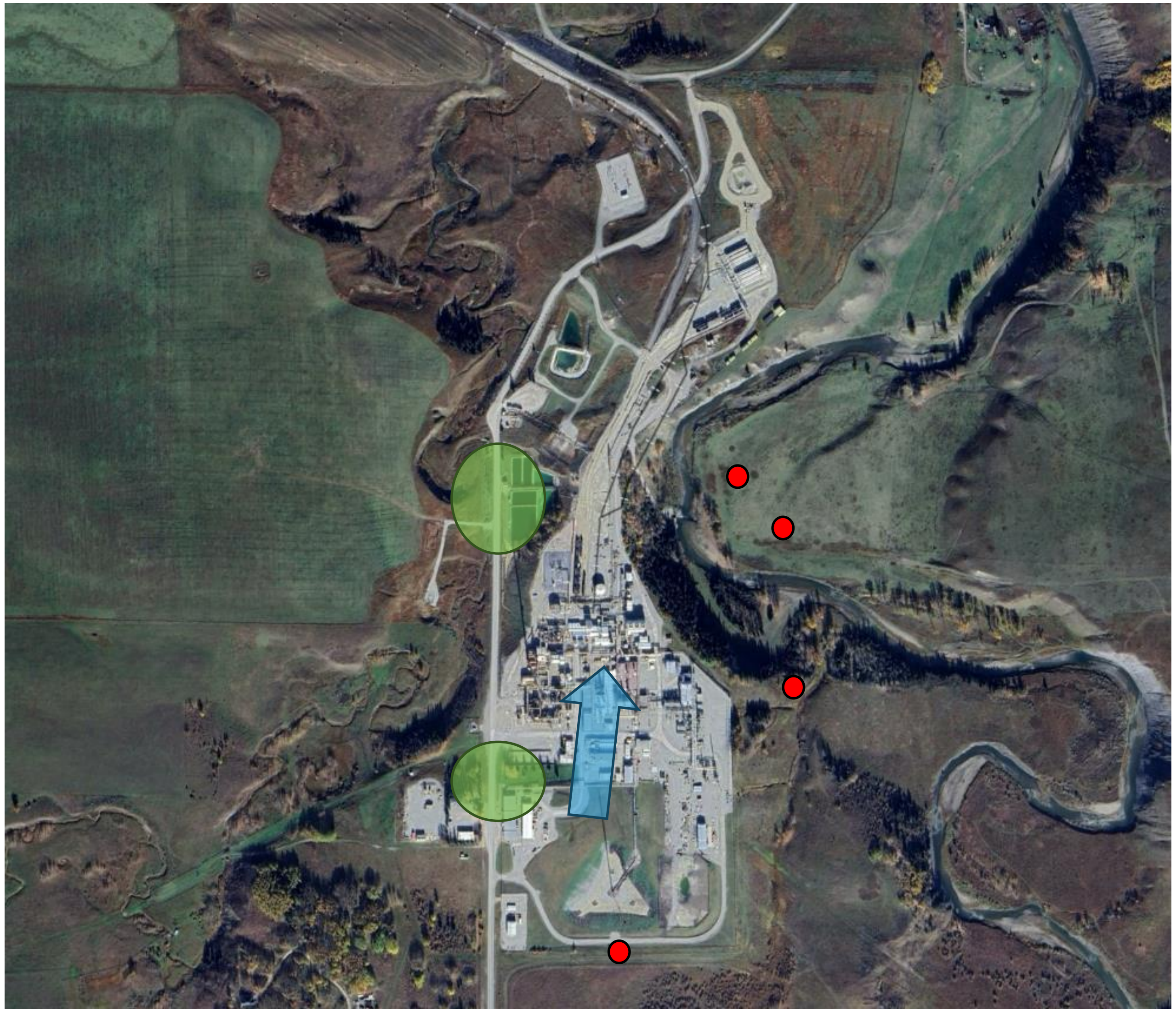


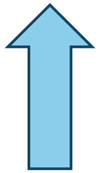
Rodiouchkina et al 2023

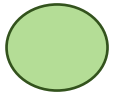
- Isotopic signature from pyrite is depleted, typical for pyrite generated by bacterial sulphate reduction
- Some gypsum also shows same depleted signature, likely same sulfur source
- Soil sample 7 shows different signature; may represent isotopic signature of gypsum amendment (shallow overburden)
- **Groundwater samples from sulphate are predominantly aligned with depleted signature (inferred pyrite source)**

Case Study 2 – Sodium and Chloride

- Operating sour gas plant in the foothills
- Alberta Group marine shale bedrock near surface (< 5 m) and exposed in valley cuts



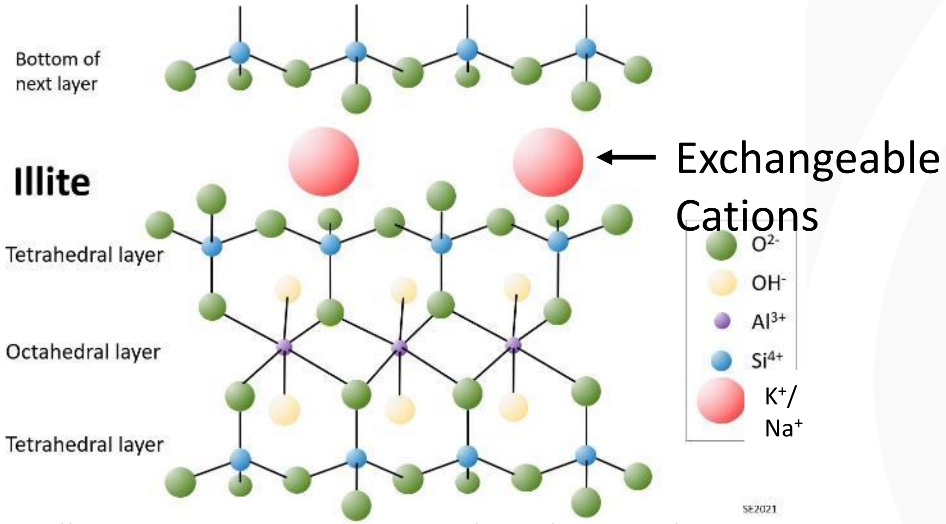

- regional groundwater flow direction


- major APEC's associated with produced water/road salt

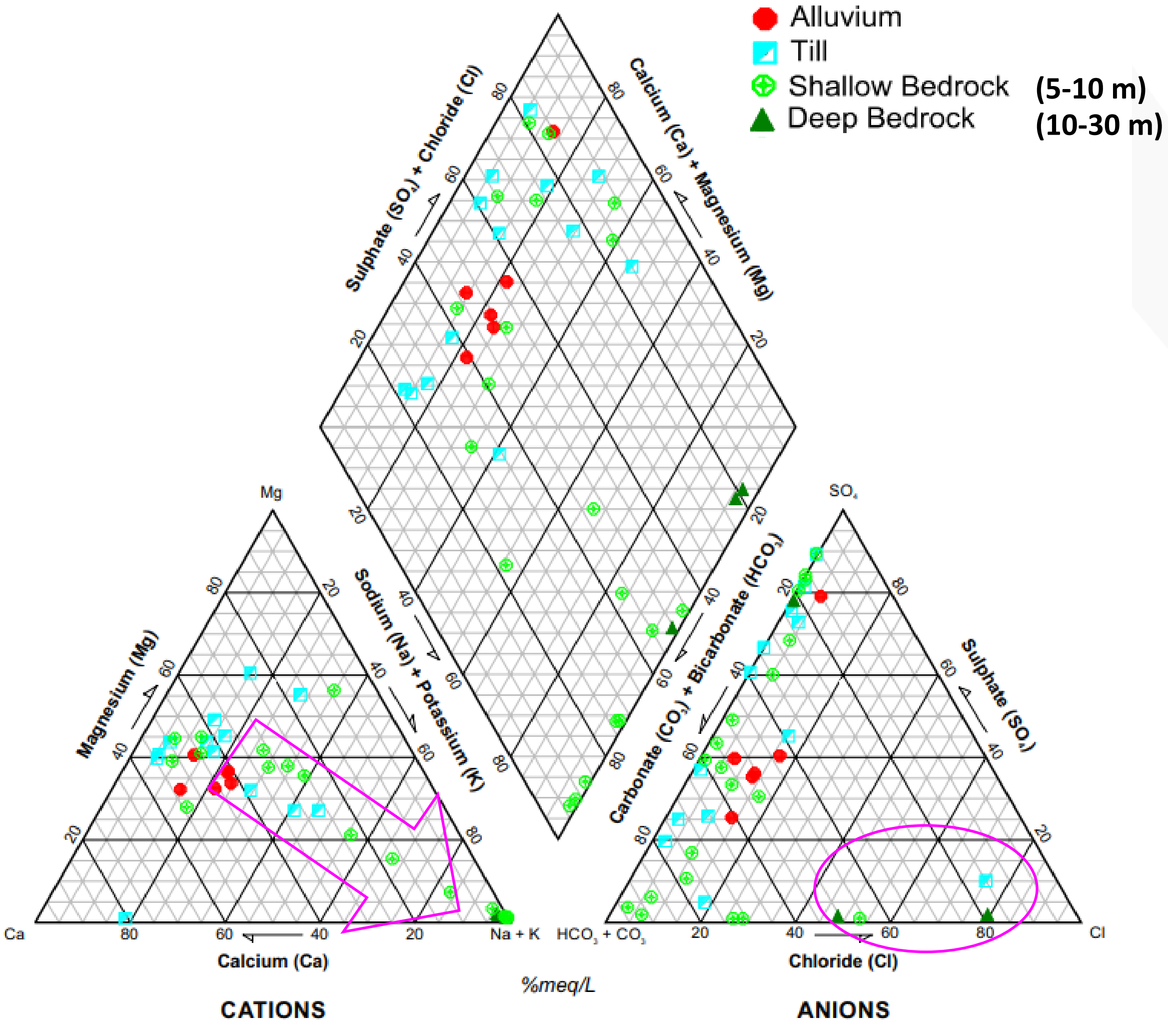

- locations with elevated sodium and chloride interpreted to not be site related; concentrations in the 100's to 1000's of mg/L range

Case Study 2 – Sodium and Chloride

- Natural transition from Ca+Mg dominated shallow groundwater to Na dominated cation chemistry
- Some samples show Cl dominated anion chemistry
- Divalent cations replace monovalent cations for greater stability in the clay structure

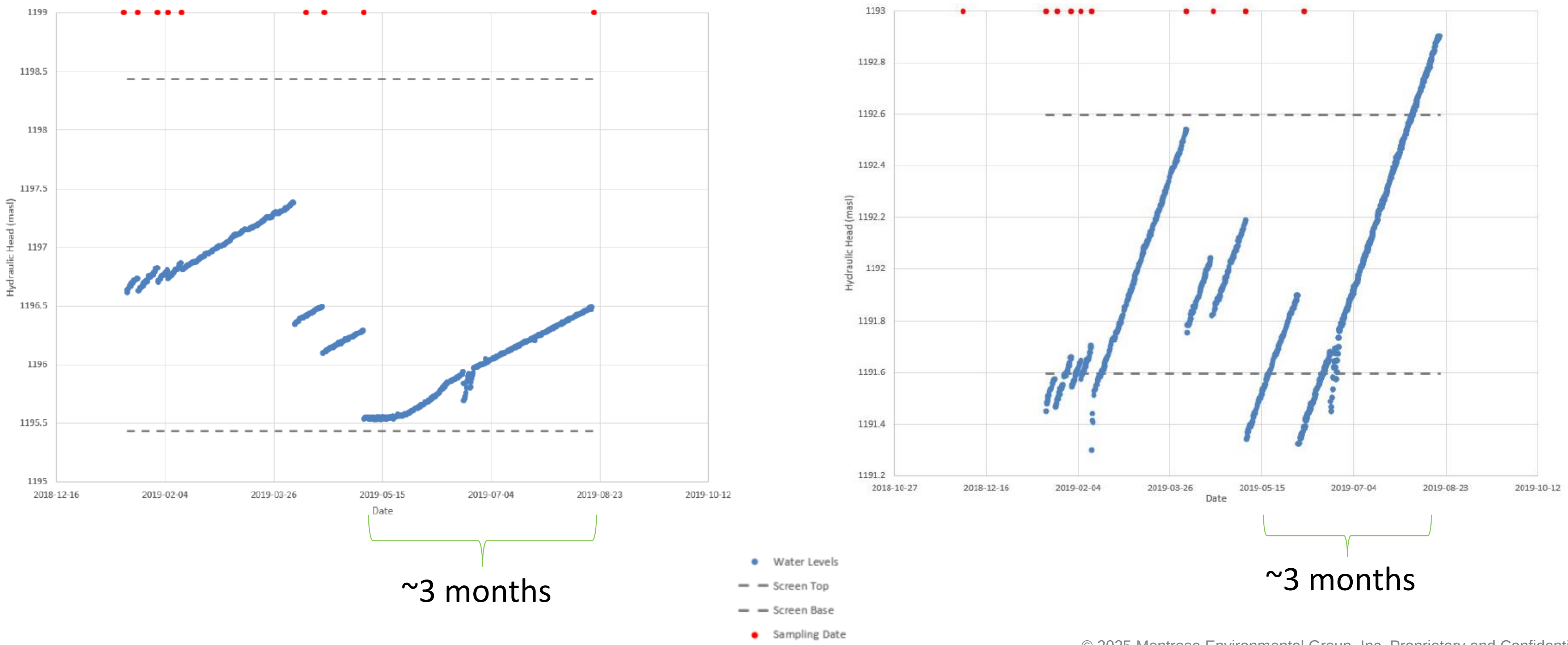


https://environmental-geology-dev.pressbooks.tru.ca/chapter/clay-minerals/



Case Study 2 – Sodium and Chloride

- Wells completed in the deeper shale bedrock show extremely slow recovery rates indicative of hydraulic conductivity values <10^{-8} m/s
- Provides additional line of evidence that elevated chloride could be related to connate water



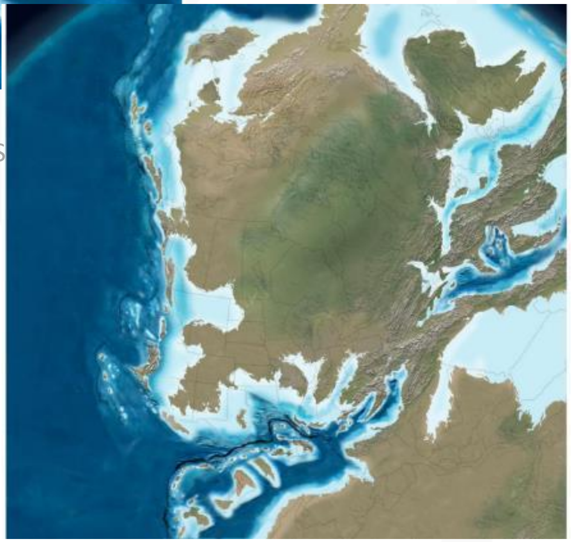
Case Study 2 – Sodium and Chloride

- Challenges with "proving" chloride is naturally occurring:
  - If original source of chloride was Cretaceous seawater, it would be chemically similar to produced water from oil and gas producing formations

- Should consider a lines of evidence approach and Occam's Razor

North America, Late Cretaceous (85 mya)

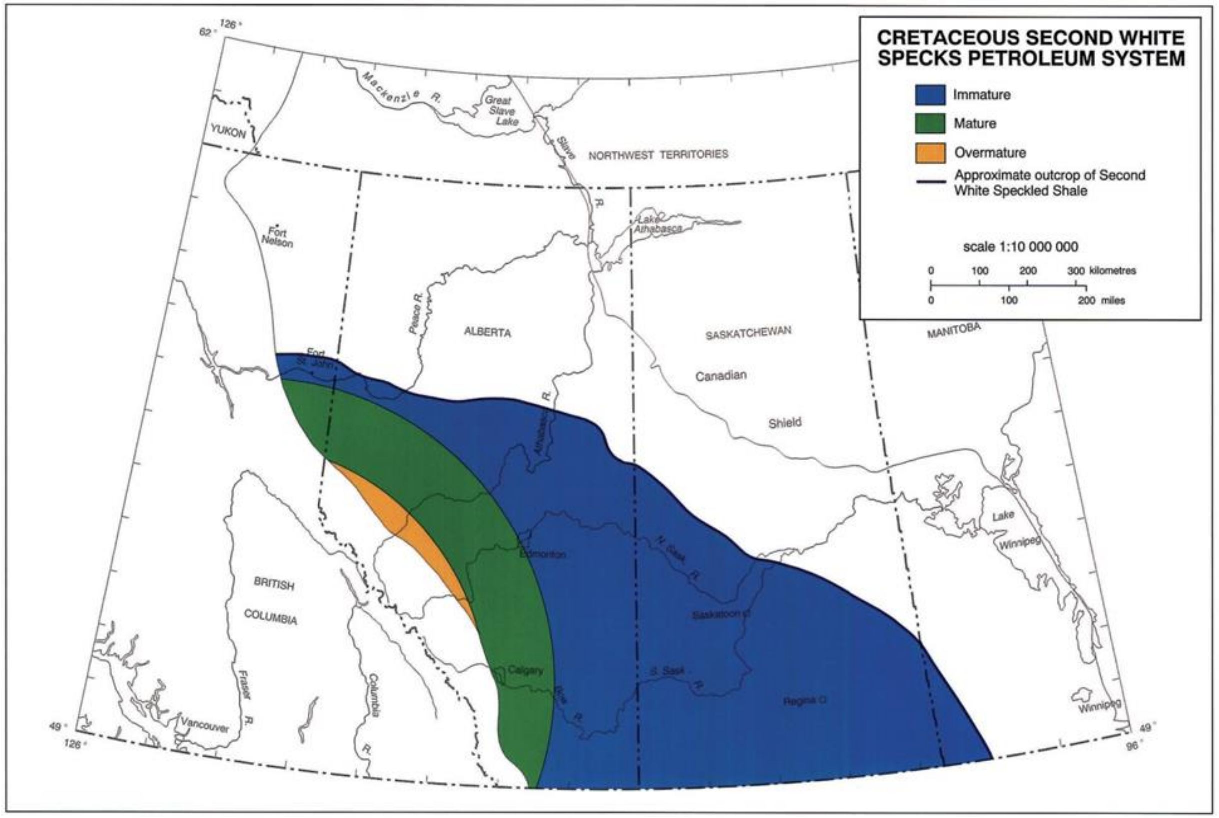
North America, Late Mississippian (325 mya)



http://neotectonics.seismo.unr.edu/0_COURSES/Geo730-2024/aapowerpoints-2020/80-Neal%20-%20North%20America%20Paleogeographic%20Maps.pdf

Case Studies 3 and 4 – Hydrocarbons

- Marine shales represent important oil and gas generation horizons in WCSB
- Based on burial depth, generally immature in the north and east
- Increase in maturity towards the Disturbed Belt
    - Maturity is something we can investigate using forensic chemistry processes as part of demonstration of natural sources.

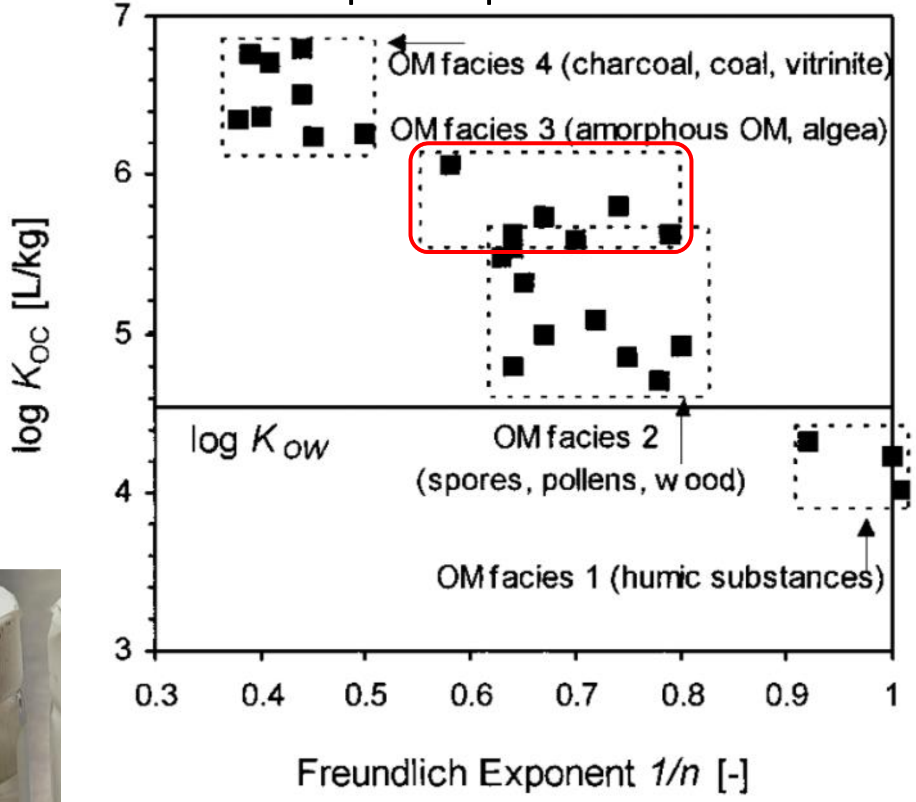


From Atlas of the WCSB: https://ags.aer.ca/publications/atlas-western-canada-sedimentary-basin

Case Studies 3 and 4 – Hydrocarbons

- Strongly bound within shale matrix
- Low free solubility in pore water; can see extraction with aggressive laboratory methods
- GW can be naturally turbid or sampling methods can create turbidity and will include sediment that contains natural hydrocarbons.
- Can lead to highly variable concentrations

Example for phenanthrene:



Kleineidam et al 1999

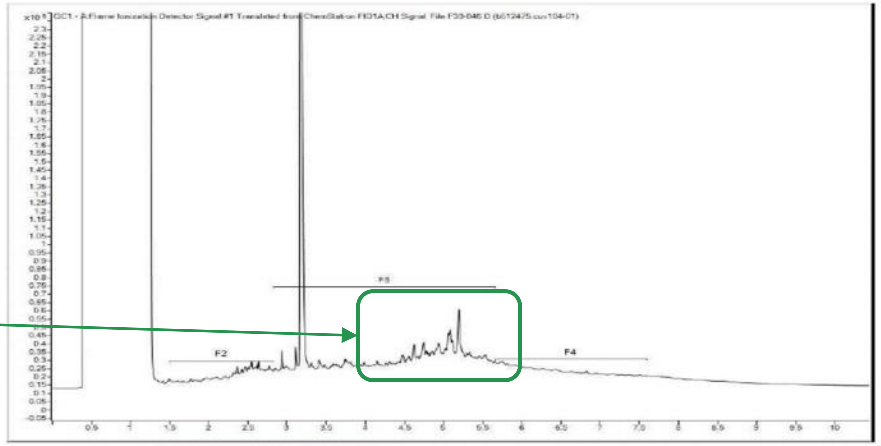
Case Study 3 – Immature oil shale in Clear Hills

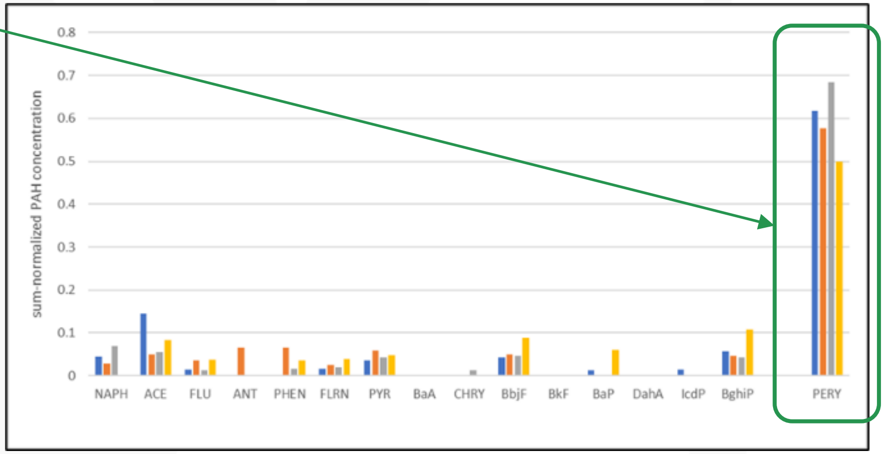
- Guidelines applied AB Tier 1 Natural Areas
- Overburden presents no detection of PHCs/PAHs
- Bedrock presents consistent detection of PHCs/PAHs
- GW may present detection of PHCs/PAHs

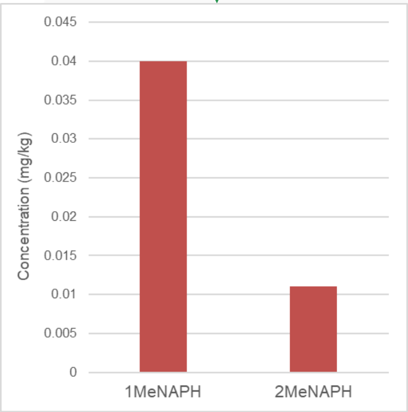
Sample Point	Start Depth m	End Depth m	Sample Date	Sample Location	Acenaphthene mg/kg	Acenaphthylene mg/kg	Anthracene mg/kg	Acridine mg/kg	Fluoranthene mg/kg	Fluorene mg/kg	Naphthalene mg/kg	Phenanthrene mg/kg	Pyrene mg/kg	Benz[a]anthracene++ mg/kg	Benzo[b&j]fluoranthene++ mg/kg	Benzo[k]fluoranthene++ mg/kg	Benzo[g,h,i]perylene++ mg/kg	Benzo[a]pyrene++ mg/kg	Chrysene ++ mg/kg	Dibenz[a,h]anthracene++ mg/kg	Indeno[1,2,3-cd]pyrene++ mg/kg	1-Methylnaphthalene mg/kg	2-Methylnaphthalene mg/kg	Quinoline mg/kg	Perylene mg/kg
BH24-22	4.00	4.50	03-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	0.014	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	0.021
BH24-22	7.00	7.50	03-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	0.0066	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	NC	<0.0050
BH24-22	8.00	8.50	03-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	0.0083	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	NC	<0.0050
BH24-22	9.00	9.50	03-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	0.011	0.0081	0.008	<0.0050	0.015	<0.0050	0.01	<0.0050	<0.0050	<0.0050	<0.0050	0.021	0.0099	NC	0.047
BH24-22	10.00	10.50	03-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	0.024	0.0088	0.0091	<0.0050	0.014	<0.0050	0.013	<0.0050	<0.0050	<0.0050	<0.0050	0.057	0.023	NC	0.14
BH24-22	11.00	11.50	03-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	0.0058	0.0071	0.0069	<0.0050	0.015	<0.0050	0.01	<0.0050	<0.0050	<0.0050	<0.0050	0.017	0.0081	NC	0.046
BH24-22	12.00	12.50	03-Sep-24	APEC 1	0.076	<0.0050	<0.0040	<0.010	0.0077	0.0086	0.032	<0.0050	0.018	<0.0050	0.02	<0.0050	0.024	<0.0050	<0.0050	<0.0050	0.0059	0.058	0.021	NC	0.28
BH24-22	13.00	13.50	03-Sep-24	APEC 1	0.075	<0.0050	<0.0040	0.018	0.0079	0.011	0.042	0.0075	0.017	<0.0050	0.015	<0.0050	0.014	0.006	<0.0050	<0.0050	<0.0050	0.069	0.036	<0.010	0.32
BH24-23	0.30	0.60	08-Sep-24	APEC 5	<0.0050	<0.0050	<0.010	<0.0040	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	<0.0050
BH24-23	4.00	4.50	08-Sep-24	APEC 5	<0.0050	<0.0050	<0.010	<0.0040	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	<0.0050
BH24-23	6.00	6.50	08-Sep-24	APEC 5	<0.0050	<0.0050	<0.010	<0.0040	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	<0.0050
BH24-23	8.00	8.50	08-Sep-24	APEC 5	<0.0050	<0.0050	<0.010	<0.0040	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	<0.0050
BH24-23	10.00	10.50	08-Sep-24	APEC 5	<0.0050	<0.0050	<0.010	<0.0040	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	<0.0050
BH24-23	11.00	11.50	08-Sep-24	APEC 5	<0.0050	<0.0050	0.025	<0.0040	0.0064	<0.0050	0.024	0.017	0.011	<0.0050	0.015	<0.0050	0.015	<0.0050	<0.0050	<0.0050	<0.0050	0.037	0.023	<0.010	0.1
BH24-23	12.00	12.50	08-Sep-24	APEC 5	<0.0050	<0.0050	0.034	<0.0040	0.0098	<0.0050	0.038	0.026	0.017	<0.0050	0.018	<0.0050	0.013	<0.0050	0.0055	<0.0050	<0.0050	0.052	0.034	<0.010	0.11
BH24-23	13.00	13.50	08-Sep-24	APEC 5	0.049	<0.0050	0.012	<0.0040	<0.0050	0.017	0.0087	<0.0050	0.011	<0.0050	0.013	<0.0050	0.018	<0.0050	<0.0050	<0.0050	<0.0050	0.011	<0.0050	<0.010	0.098
BH24-23	14.50	15.00	08-Sep-24	APEC 5	<0.0050	<0.0050	0.012	<0.0040	0.038	<0.0050	<0.0050	0.02	0.026	<0.0050	0.0086	<0.0050	0.0075	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	0.015
BH24-25	1.00	1.50	02-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	0.0071	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	0.037
BH24-25	3.00	3.50	02-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	0.027
BH24-25	4.00	4.50	02-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	<0.0050
BH24-25	6.00	6.50	02-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	0.0054
BH24-25	7.50	8.00	02-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.010	<0.0050
BH24-25	8.50	9.00	02-Sep-24	APEC 1	<0.0050	<0.0050	<0.0040	<0.010	<0.0050	0.0085	<0.0050	0.014	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	0.044	0.081	<0.010	<0.0050
BH24-25	9.50	10.00	02-Sep-24	APEC 1	0.12	0.041	0.016	<0.010	<0.0050	0.22	0.16	0.16	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	0.44	0.24	0.079	<0.0050
BH24-25	10.00	10.50	02-Sep-24	APEC 1	0.046	0.013	<0.0040	<0.010	<0.0050	0.063	0.59	0.093	<0.0050	<0.0050	0.0059	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	0.54	1.3	NC	<0.0050
BH24-25	11.00	11.50	02-Sep-24	APEC 1	0.10	0.022	0.0095	<0.010	0.0073	0.17	0.97	0.16	0.011	<0.0050	0.014	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	1.1	2.6	NC	0.012

Case Study 3 – Immature Oil Shale in Clear Hills

- Forensic chemistry framework built on key drivers connecting geology expectations to chemistry data.
- Evidence of immature sources is key driver:
  - Biological hydrocarbons within F3b range
  - High perylene concentration
  - Low Methylnaphthalene Ratio (MNR)

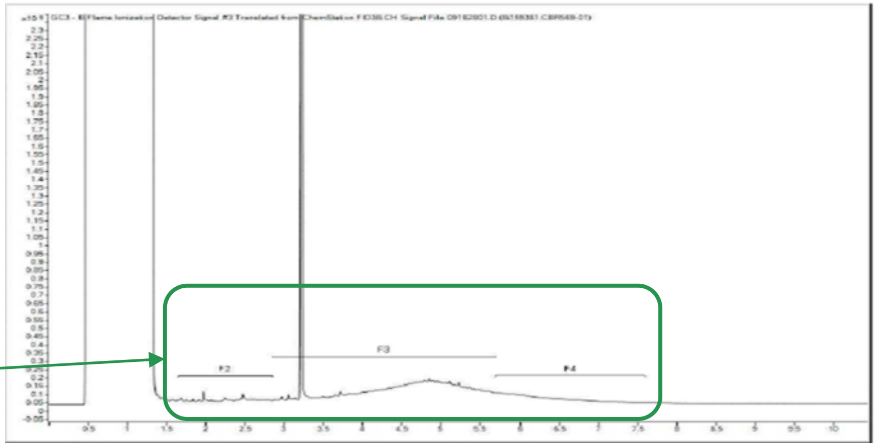


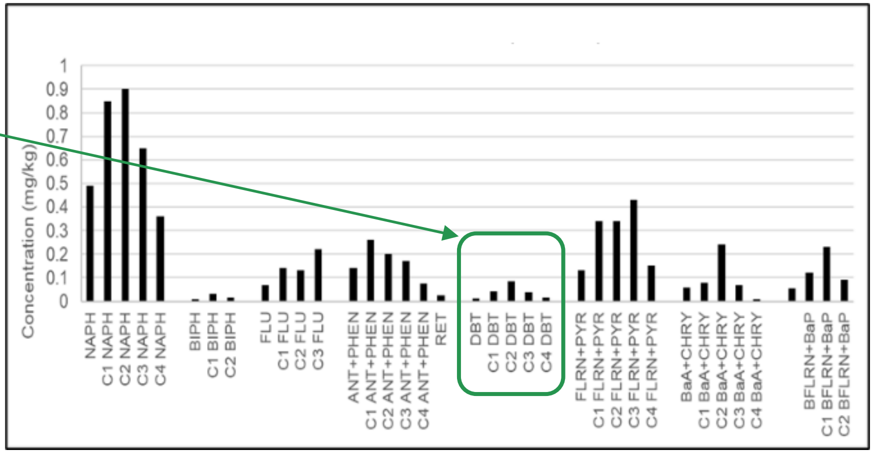




Case Study 4 – Mature Oil Shale in Southern Foothills

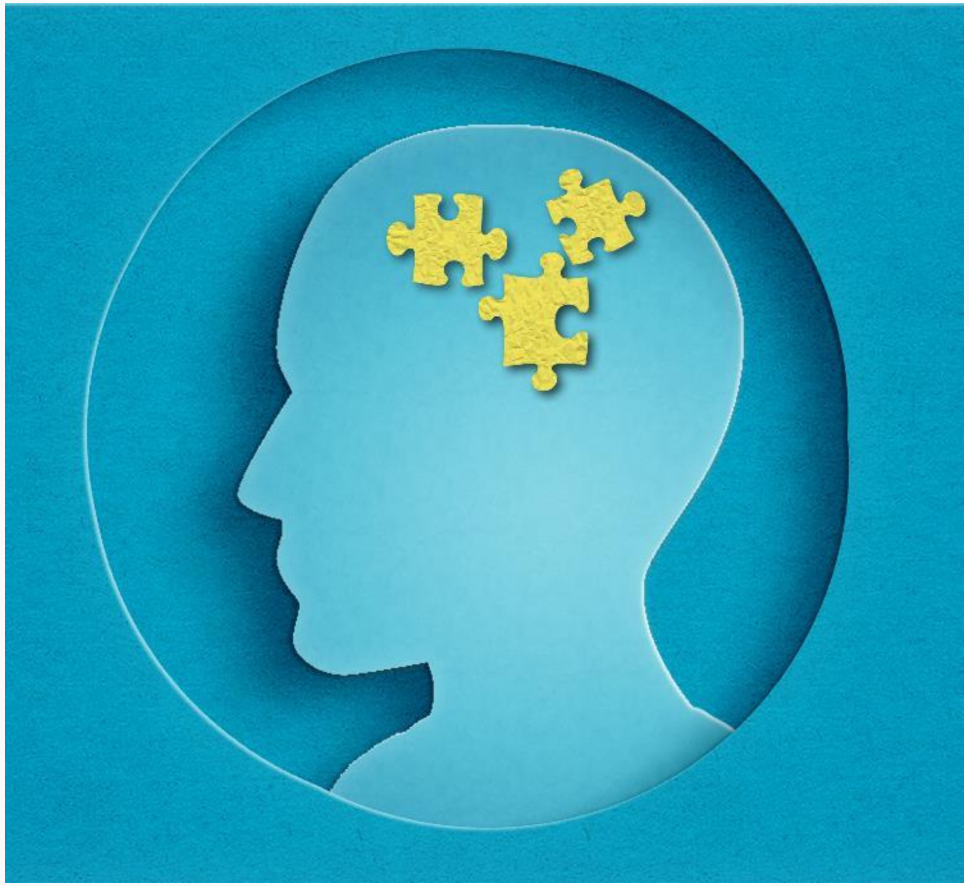
- Same guideline exceedances as immature (BTEX, PAHs), but different composition
- Maturity means less easy to distinguish from typical anthropogenic sources (drilling additives, releases of extracted fluids)
    - PHCs composition – low concentration, wide-ranging / heavy
    - PAH composition – low sulphur content, wide-ranging





Summary and Next Steps

- Marine shales can significantly influence background soil and groundwater quality
- Methods to evaluate and validate exist; on a single project basis costs may be manageable but:
    - We know this is a regional issue that could affect 100's or 1000's of sites
    - On a large scale could significantly affect the total remediation/reclamation costs for the province
- What do other jurisdictions do?



Regional Background Guideline Development

Ministry of Environment and Climate Change Strategy

BRITISH COLUMBIA

PROTOCOL 9

FOR CONTAMINATED SITES

Regional backgound concentrations in groundwater in Table 1 may be used without approval from the director as they are considered representative of local background groundwater at any site located within a particular region. Regional boundaries can be viewed at any scale at the iMapBC website (iMapBC webpage).

Regional Background Guideline Development

ANNEXE 1 : CRITÈRES GÉNÉRIQUES A (TENEURS DE FOND) DES SOLS POUR LES MÉTAUX ET MÉTALLOÏDES, PAR PROVINCE GÉOLOGIQUE

Métaux et métalloïdes	Critères A (teneurs de fond)[1] par province géologique[2] (mg/kg)				
	Basses-terres du Saint-Laurent	Appalaches	Grenville	Supérieur	Fosse du Labrador (sous-province)
Argent (Ag)	2	0,8	2	0,5	0,8
Arsenic (As)	6	19	10	5	14
Baryum (Ba)	340	350	200	240	355
Cadmium (Cd)	1,5 (2,2[3])	1,3	0,9	0,9	1,5 (1,6[3])
Cobalt (Co)	25	25	25	30	35
Chrome total (Cr)	100 (110[3])	100	45	100	100 (140[3])
Cuivre (Cu)	50	65	50	65	65 (140[3])
Étain (Sn)	5	5	5	5	5
Manganèse (Mn)	1 000 (1 210[3])	1 000 (2 025[3])	1 000 (1 445[3])	1 000	1 000 (5 280[3])
Mercure (Hg)	0,2	0,3	0,6	0,3	0,3
Molybdène (Mo)	2	2	6	8	7
Nickel (Ni)	50 (65[3])	50 (90[3])	30	50 (65[3])	50 (170[3])
Plomb (Pb)	50	40	50	40	30
Sélénium (Se)	1	3	3	3	1
Zinc (Zn)	140	155	120	150	200 (335[3])

Regional Background Guideline Development

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Controls on regional sulphate distribution in shallow groundwater in the western Canadian Interior Plains

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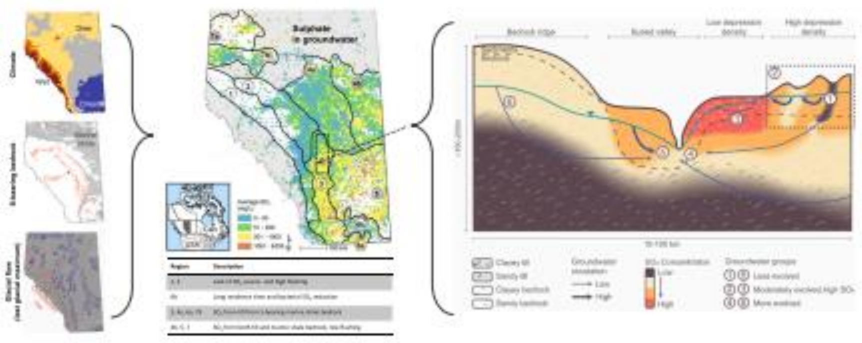
HIGHLIGHTS

- Natural SO_4 in till increases groundwater salinity impacting water quality and use.
- Glacial flow patterns, bedrock geology and climate drive provincial SO_4 occurrence.
- Regionally, post-glacial circulation of SO_4 driven by hydrogeological setting
- Thick sediments and oxidation zone contribute to high SO_4 production.
- Slow travel times (low recharge, permeability, gradient) contribute to high SO_4.

GRAPHICAL ABSTRACT



Conclusions

- Marine shales have natural characteristics that result in soil and groundwater quality that often exceed AB Tier 1 guidelines
- A strong conceptual site model with properly placed background wells is key starting point
- Different chemistry data analysis/forensic techniques can add lines of evidence
- Given the issue is regionalized, could be a good opportunity for a regulatory or other unbiased party initiative to provide a framework to reduce overall liability and future rem/rec costs associated with these facilities

Thank You!

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