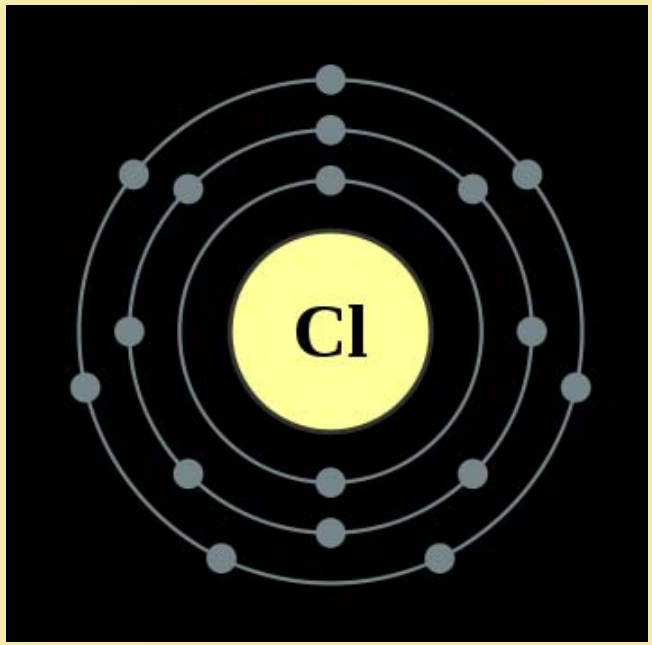
Differentiation of chloride source using stable chlorine isotopes



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Background:

DOW Chemical Canada ULC operates a chemical facility in Fort Saskatchewan, Alberta. Sodium chloride was solution mined from the Devonian Lotsberg Formation (~1900 m) and stored in surface ponds to be used in chemical processes.

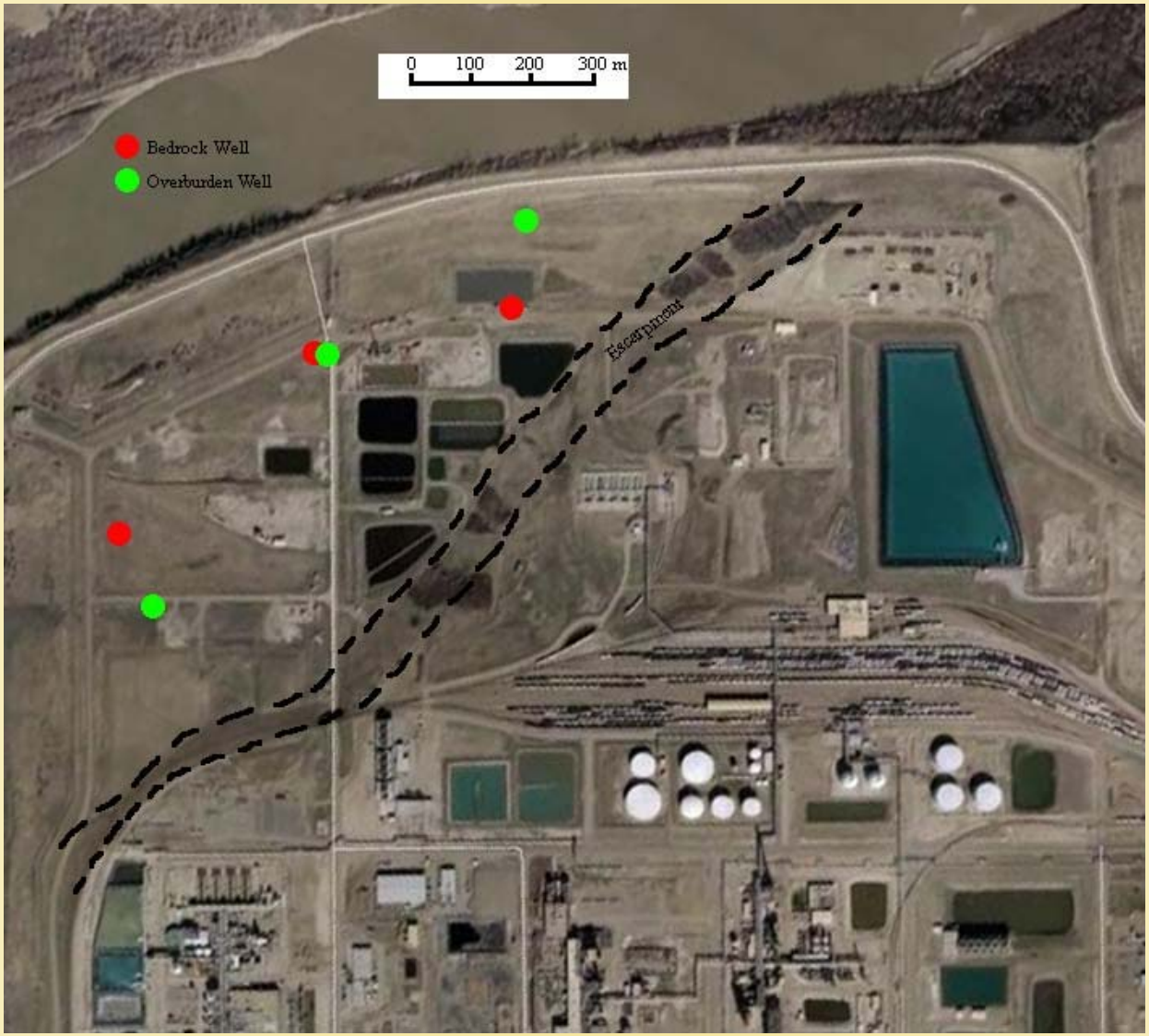
The Issue:

- Brine stored in surface ponds and used in production has been released into the soils and migrated to the regional overburden aquifer which overlies the bedrock formation.
- As part of a hydrogeological investigation to characterize the site, wells have been installed to monitor the bedrock formation.
- Analysis of groundwater samples from bedrock monitoring wells found elevated chloride.
- While historical ARC research (Stein, 1976) indicated that this could be a natural phenomena, it was important to determine if surface activities could be the cause.

The Implications:

- Characterization usually requires a significan number of wells to adequately understand the geology, hydrogeology and geochemistry of a site.
- There are large costs associated with characterization and remediation of bedrock aquifers.
- It was necessary to find other ways to understand the situation and determine the source of chloride in the bedrock.

Site: DOW Chemical Canada ULC – Fort Saskatchewan Facility



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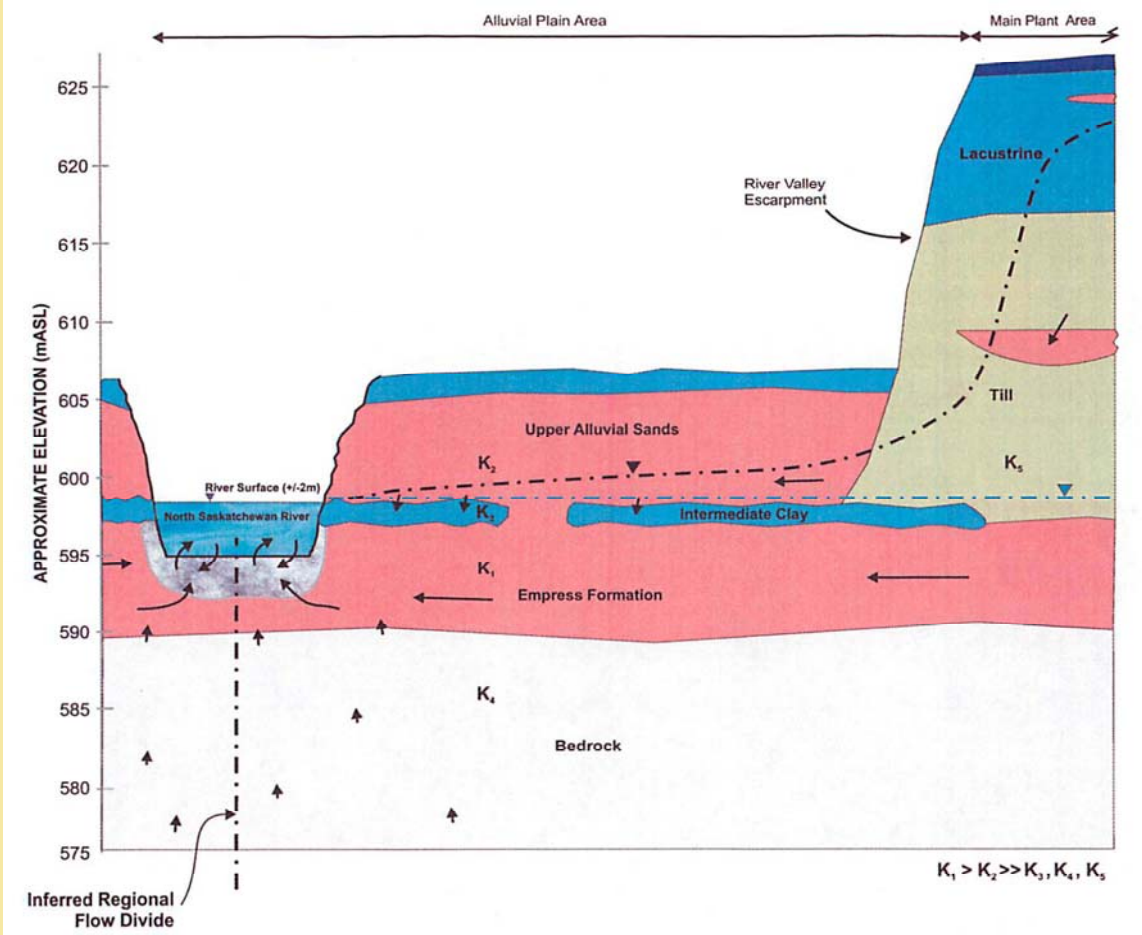
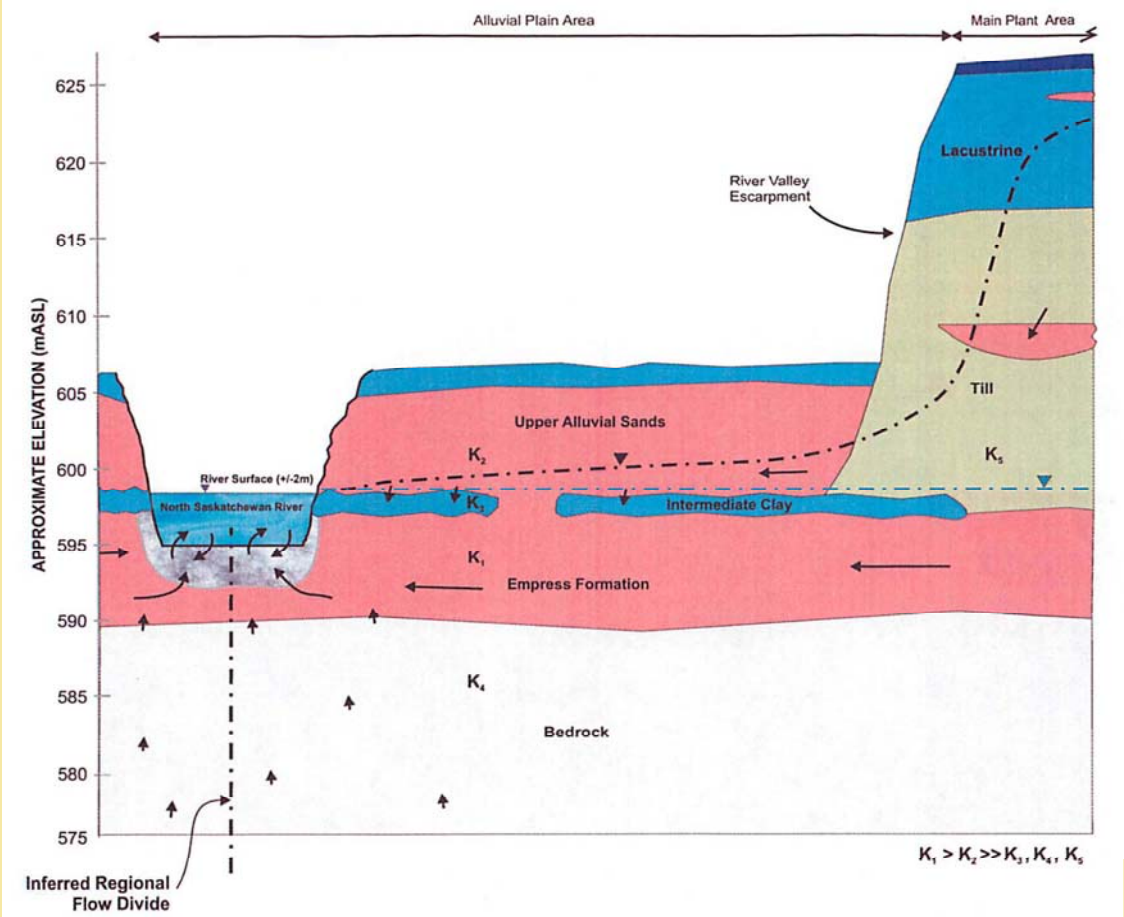
Geology:

- The main plant is located on Quaternary lacustrine deposits overlying till.
- The northwestern part of the plant is located on the buried Beverly Aquifer and consists of Upper Alluvial sands, discontinuous clay and the sands and gravel of the Empress Formation .
- The whole site is underlain by Late Cretaceous interbedded sandstone and shale of the Belly River Formation.



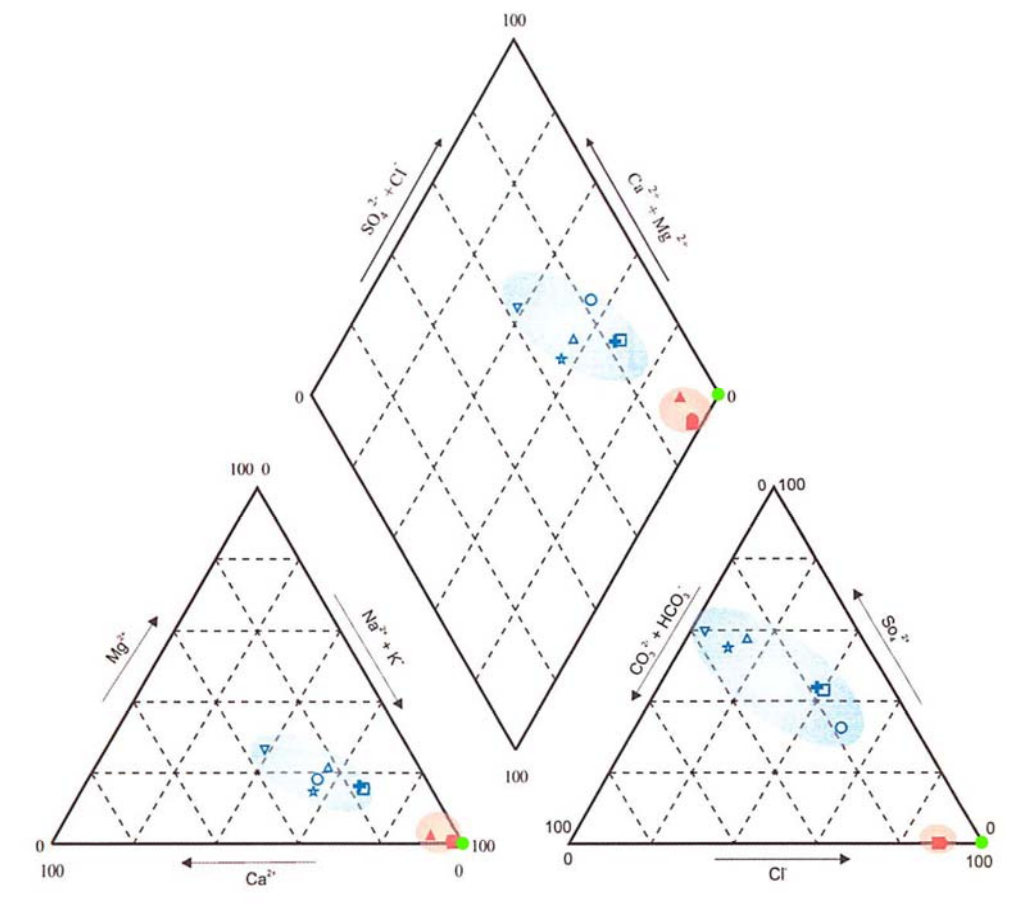
Hydrogeology:

- The North Saskatchewan River is a regional groundwater divide (Stein 1976). Lateral gradients are to the NSR (north – northwest).
- The piezometric data indicate upward vertical gradients. In the region of the alluvial plain area, groundwater discharges from the Belly River Formation bedrock into the overlying sand and gravels of the Empress Formation.



Hydrochemistry:

- The brine (Devonian Lotsberg evaporite) is a Na-Cl type water.
- The Cretaceous Belly River Bedrock is a Na-Cl dominated type water. Cl steady with time. Cl concentrations consistent with literature values.
- The Empress aquifer is Na-Ca-Cl-SO_4-HCO_3 type water. Cl varies with time.
- Empress and Belly River waters are distinct and it does not appear that Empress water (along with the brine) is in the bedrock wells.



Lines of Evidence:

- Hydrogeology indicates upward gradients at the site which should protect against chloride contamination of the bedrock. Brine releases into the alluvial aquifer water should not be dense enough, after mixing, to penetrate bedrock.
- Chemistry of end members is distinct. It does not appear from water types that Empress and Lotsberg brine are entering the bedrock.

But …

- More lines of evidence are required, as the sparse data available from the wells is not completely convincing.

Possible solution ?

Stable Chlorine Isotope ratios.

There are two stable isotopes of chlorine: ^{37}Cl and ^{35}Cl

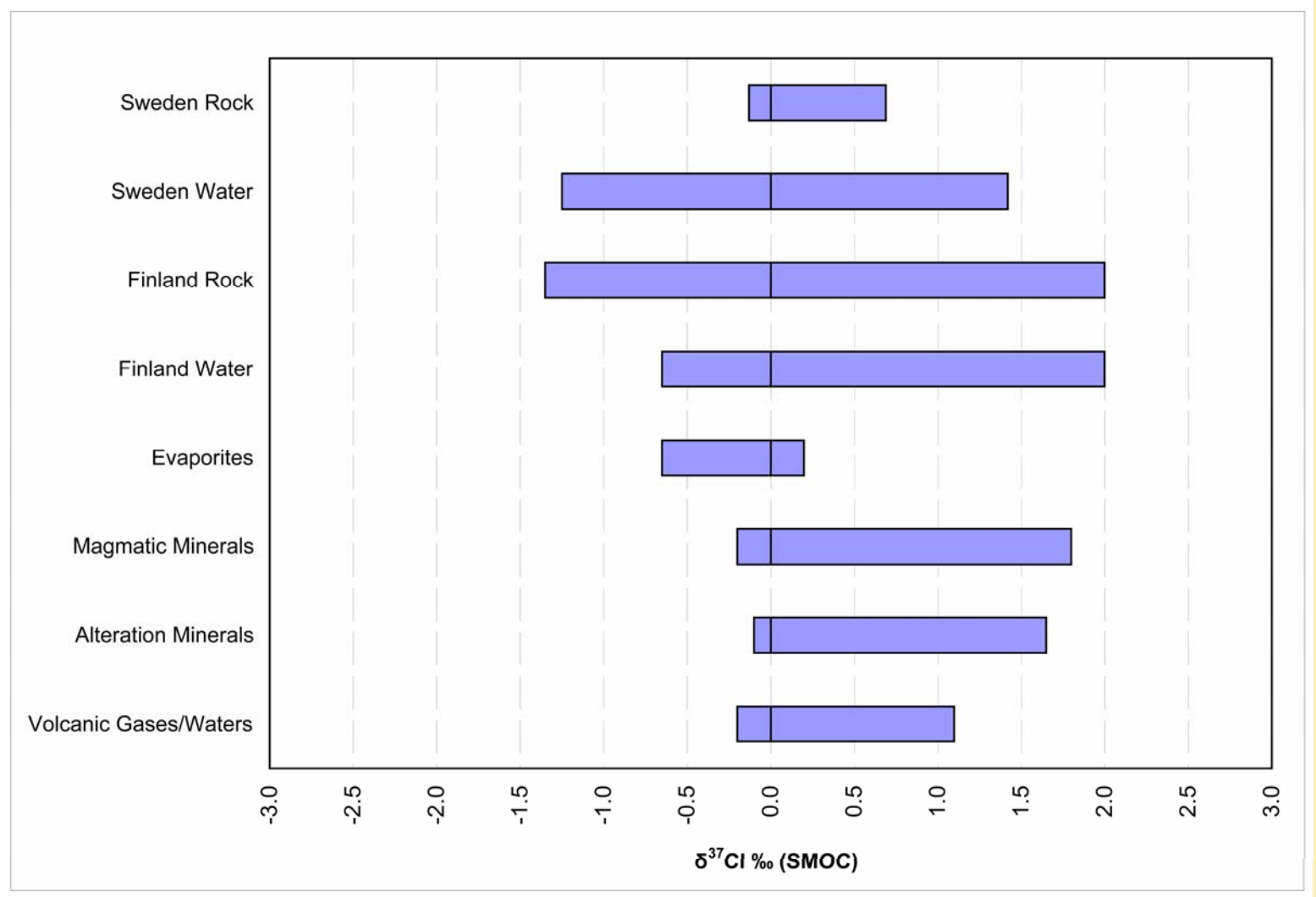
Abundance:

^{37}Cl = 25.47%

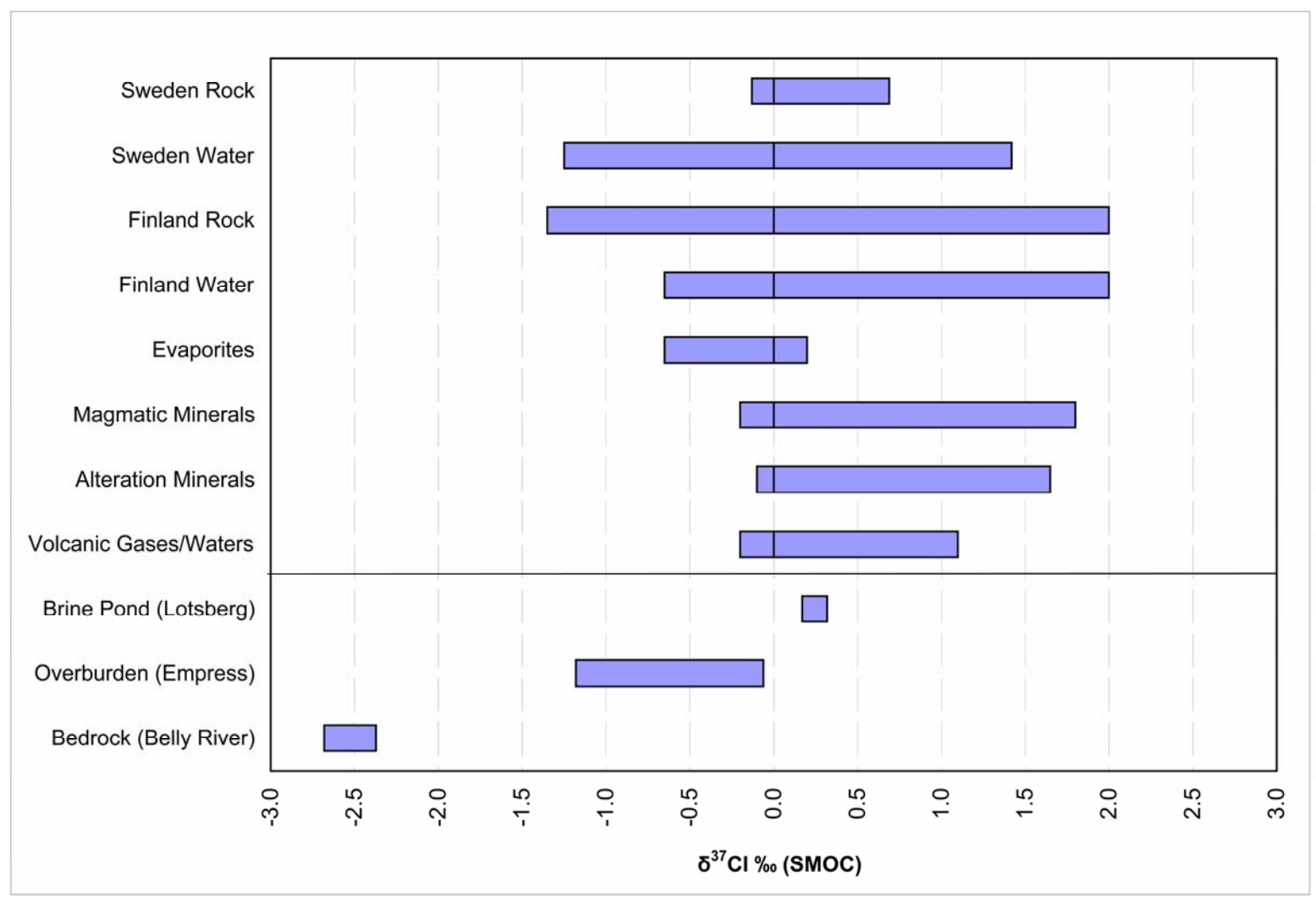
^{35}Cl = 75.53 %

$$\delta^{37}Cl = \frac{\left[\left(\frac{^{37}Cl}{^{35}Cl}\right)sample - \left(\frac{^{37}Cl}{^{35}Cl}\right)SMOC\right] \times 1000}{\left(\frac{^{37}Cl}{^{35}Cl}\right)SMOC}$$

$\delta^{37}Cl$ range of crystalline rock, minerals and water (brines)



$\delta^{37}Cl$ range of waters from DOW site



Interpretation of $\delta^{37}Cl$ signatures at DOW site

The source of chloride in sedimentary basins is evaporite deposits or remnant ancient seawater

Brine Pond (Lotsberg Formation)

- $\delta^{37}Cl$ = 0.17 to 0.32 ‰ SMOC
- Chlorine signature is consistent with an evaporite

Bedrock (Belly River Formation)

- $\delta^{37}Cl$ = -2.68 to -2.37 ‰ SMOC
- No Alberta Basin data to compare to. Signature consistent with values from sandstones in the Gulf (Frape personal comm.)
- Fractionation most likely due to membrane filtration or diffusion processes.

Overburden (Empress Formation)

- $\delta^{37}Cl$ = -1.18 to -0.06 ‰ SMOC
- Chlorine isotope signature a mixture of bedrock and brine

How much brine chloride is in the overburden?

By using concentration and isotope mass balance equations (Jenden et al., 1993), it is possible to estimate the component of brine in the overburden.

$$C_i^{mix} = f \times C_i^A + (1 - f) \times C_i^B$$

$$I_i^{mix} = \frac{\left[f \times C_i^A \times I_i^A + (1 - f) \times C_i^B \times I_i^B \right]}{C_i^{mix}}$$

An initial overburden aquifer water with low chloride (50 mg/L) and a Cl isotope signature of 0.25‰ SMOC was mixed with bedrock water. The resulting chloride concentration and isotope signature were used as a starting point to mix with the brine.

The brine fraction was mixed with the overburden water until the correct chloride concentration was achieved. The resulting modeled chlorine isotope signature was compared to the measured value. By iterating several times, a match to measured values was achieved.

The Result:

The chloride concentration and chlorine isotope ratio of the overburden aquifer is consistent with a meteoric water (low chloride) with a 26% bedrock water and 0.44% brine water component.

Conclusions

- Upward gradients in the bedrock measured at the site would tend to protect the bedrock from being contaminated from shallow groundwater impacts.
- The groundwater from bedrock wells has a distinctive chemical signature that is different than the water from the Empress Formation.
- The Belly River bedrock wells at the site have chloride concentrations that have been fairly consistent for the past 28 years. These concentrations are consistent with published values for the Belly River Formation elsewhere. In contrast, the Empress Formation groundwater wells have been variable for the last 15 years indicating a variable source, such as a surface release.

Conclusions

- The chloride measured in the bedrock groundwater samples likely represents regional discharge water that has evolved over a long period of time so that the dominant anion is chloride, as would be expected from the classic Chebotarev sequence of regional groundwater compositional change.
- The difference in $\delta^{37}Cl$ signature between the Belly River Formation and the brine ponds is very large (2.5 ‰ or greater). This large fractionation is likely caused by membrane filtration or diffusion in the low permeability bedrock.
- It is this evidence that is the most compelling and supportive of the idea that the bedrock groundwater has not been contaminated by industrial activities at the tested locations.