

## **Origins of Brackish Spring Waters Discharging into the Clearwater River, NE Alberta**

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### **Summary**

The objective of this project is to determine the origin and the biogeochemical history of water obtained from seven brackish springs discharging from Devonian carbonates into the Clearwater River in northeastern Alberta, a major tributary of the Athabasca River. Chemical and isotopic analyses were conducted to determine water type and to assess sources of dissolved constituents and processes they may have undergone in the sub-surface. Major ion content and the isotopic analyses of water, sulphate and strontium indicate a dominant Na-Cl water type, that the water is of meteoric origin, and that it has gained dissolved solids through evaporite dissolution. This data may be used to understand the natural contributions to the Athabasca system from brackish springs and may provide a valuable baseline against which potential anthropogenic impacts can be evaluated.

### **Introduction**

The Clearwater River is a major tributary to the Athabasca River in northeastern Alberta. At their confluence near Ft. McMurray, both rivers have incised into Upper Devonian carbonates, mainly of the Waterways formation, which is part of the Beaverhill-Cooking Lake aquifer system (Bachu et al., 1993). Underlying units are Upper and Middle Devonian evaporite deposits of gypsum and anhydrite, which in turn overlie thick Lower Devonian deposits of relatively pure halite in some locations (Allan, 1943). Numerous springs discharge from this Paleozoic formation into the Athabasca and Clearwater Rivers, some of which have been found to be naturally saline (Hitchon, 1969; Grasby, 2006).

The overall groundwater flow regime in the Beaverhill – Cooking Lake aquifer system is of intermediate scale with some local topographic effects; flow is generally up-dip to the northeast (Bachu et al., 1993). Salinity generally increases with depth (Bachu et al., 1993) and it has been suggested that the salinity of the springs emerging at the Clearwater River is due to dissolution of the underlying Lower Devonian evaporites (Hitchon, 1969), although for the most part aquitards prevent contact between these formations (Bachu et al., 1993). The objective of this study is to use chemical and isotopic analyses to determine the origin of the

salt content and identify subsurface processes and potential mixing occurring in the Devonian carbonate units.

## Methods

Seven springs and seeps discharging into the Clearwater were sampled in October 2010. River water was also sampled above and below the springs. Field measurements were made for physical properties of temperature, conductivity, and pH. Samples were preserved for laboratory analysis of major ions and the following stable isotopic ratios:  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  of water,  $^{34}\text{S}/^{32}\text{S}$  and  $^{18}\text{O}/^{16}\text{O}$  of sulphate, and  $^{87}\text{Sr}/^{86}\text{Sr}$ . Chemical analyses in the laboratory were conducted using a Dionex ion chromatograph for anions and a Perkin Elmer flame absorption spectrometer for cations. Isotope ratio measurements were conducted by isotope ratio mass spectrometry.

## Preliminary Results and Discussion

Major ion concentrations and ratios allow for the designation of water-type and provide insight as to the source of salinity and water-rock interactions. Total dissolved solids concentrations were within the brackish range, varying from 7210.8 to 24151.1 mg/L. The springs have a Na-Cl water type, with Cl concentrations ranging from 3692.7 to 12648.9 mg/L and Na concentrations ranging from 2320.0 to 8338.0 mg/L. Major ion ratios as well as isotopic results discussed below suggest that the Na and Cl present are likely the result of dissolution of underlying evaporites as opposed to evaporated sea water.

Ratios of hydrogen and oxygen in spring water are often used to investigate its origin and to differentiate between meteoric water and formation water.  $\delta^{18}\text{O}$  values ranged from -23.5 to -18.8‰ and  $\delta^2\text{H}$  values ranged from -178.1 to -149.0‰. Values of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in spring water plot along the local meteoric water line, indicating that the springs discharge water of meteoric origin.

The isotopic ratios of sulphur and oxygen in sulphate often indicate water-rock reactions and allow the identification of the source of sulphate (Krouse & Mayer, 2000).  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  ranged from 22.4 to 27.6‰ and 6.7 to 11.7‰ respectively and hence indicate the dissolution of Devonian sulphates.

Strontium isotope ratios also often indicate water-rock interactions as well as the mixing of different types of water. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios varied from 0.708647 to 0.70944. The strontium ratio shows a distinct inverse trend with strontium concentrations, which suggests the mixing of waters of different Sr concentrations and isotope ratios, such as the mixing of a brine with dilute meteoric waters which often have elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (McNutt, 2000).

## Conclusions

The brackish springs discharging from Devonian carbonates into the Clearwater River are characterized by high total dissolved solids and have a Na-Cl water type. The isotopic composition of sulphate suggests the dissolution of Devonian evaporites as the major source of this water constituent. The hydrogen and oxygen isotope ratios of water are indicative of a meteoric origin. Strontium isotope ratios and concentrations suggest a mixing of water types, such as perhaps evaporite dissolution brines and more local meteoric water flow.

## **Acknowledgements**

University of Calgary ISEEE Grant and NSERC

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