

# Development of a geochemical tool for sourcing leaking well fluids in southwestern Ontario

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# **Summary**

A large suite of groundwater samples from the major bedrock aquifers in southwestern Ontario has been collected and analyzed for a number of geochemical parameters ( $\delta^{18}O_{H2O}$ ,  $\delta^{2}H_{H2O}$ ,  $\delta^{13}C_{DIC}$ ,  $\delta^{34}S_{SO4}$ ,  $\delta^{18}O_{SO4}$ ,  $\delta^{87}Sr/^{86}Sr$ , and ion chemistry). These data are integrated with similar data from previous studies (McNutt et al.,1987; Lowry et al., 1988; Dollar et al., 1991; Wilson and Long, 1993; Weaver et al., 1995; Husain et al.,1996; McIntosh and Walter, 2006; Freckelton, 2013) in the region, and also  $\delta^{37}Cl$  and  $\delta^{81}Br$  data from Kaufman et al. (1993) and Shouakar-Stash (2008). A Bayesian mixing model, SIAR (Parnell et al., 2010) has been applied to this dataset to create a tool for identifying probable source(s) of fluids leaking from abandoned oil and gas wells in southwestern Ontario, as part of a larger effort to plug such wells. Several hypothetical samples are presented herein to demonstrate the model's performance.

#### Introduction

The first commercial oil well in North America was drilled in southwestern Ontario in 1858 near Oil Springs in Lambton County. Well records are available for about 26,500 wells, but several thousand additional wells are believed to have since been drilled. Many of these wells were completed before the advent of well design and decommissioning regulations, which were first enacted in 1921. The problems of poor well construction and their age are compounded by the presence of a regional zone of sulphur water at shallow to intermediate depths, such that, today, the metal casings of many of these wells are highly corroded or absent altogether. Thousands of these older wells now lie abandoned, mostly in farmers' fields, in poor condition and not properly plugged.

These abandoned wells form potential pathways for movement of surface into groundwater. They also threaten the surface environment, as many bedrock formations contain oil, natural gas, brines, and/or sulphur water (with elevated levels of hydrogen sulphide), which in some places flow to the surface.

The Abandoned Works Program (AWP) was initiated by the Ontario Ministry of Natural Resources (MNR) in 2006 to locate and plug such abandoned wells. Because many of the wells are more than 50 years old, well records are often incomplete or non-existent. Accordingly, there is significant uncertainty regarding well depth and which units the leaking fluids originate. This makes the plugging process more challenging and more expensive.

The current project aims to more fully characterize the geochemistry of formation waters from various Paleozoic bedrock units in southwestern Ontario. Previous work (e.g. Dollar et al., 1991) showed that different formation waters have discrete isotopic signatures. This project builds on such work to better determine the unique geochemical 'fingerprints' for each unit. These fingerprints are then used in a mixing model to assess the probable sources of fluids emanating from leaky wells. This information, combined with existing knowledge of unit depths and other geological information for a given location, will give the AWP an improved target depth for their plugging efforts, and has already resulted in cost and time savings.

#### Method

To enhance the existing knowledge base regarding groundwater geochemistry in southwestern Ontario, 130 groundwater samples were collected, covering all major water-producing formations. Samples were collected from wellheads, production lines and brine tanks of active oil and gas wells, as well as quarries, artesian springs, abandoned works sites, and new wells being drilled by cable-tool rig.

Samples were analyzed for  $\delta^{18}O_{H2O}$ ,  $\delta^{2}H_{H2O}$ ,  $\delta^{13}C_{DIC}$ ,  $\delta^{34}S_{SO4}$ ,  $\delta^{18}O_{SO4}$ ,  $\delta^{7}Sr/^{86}Sr$ , and ion chemistry. Relatively unique fingerprints for the different formations were identified for several of these parameters, in particular  $\delta^{18}O_{H2O}$ ,  $\delta^{2}H_{H2O}$ , and  $\delta^{87}Sr/^{86}Sr$ .

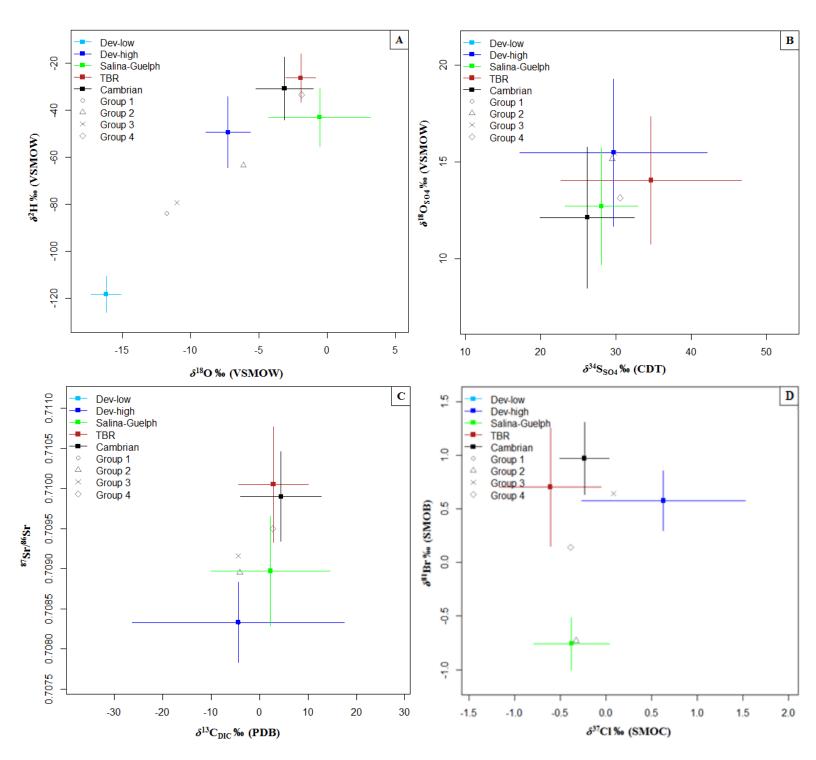
These data were combined with existing datasets from the literature with the same isotopes, plus  $\delta^{37}$ Cl and  $\delta^{81}$ Br. They were then applied to SIAR, a mixing model program utilizing a Bayesian statistical framework. This model allows determinations of probability distributions for the different source units that might be contributing to an unknown water sample. SIAR is a powerful tool in that it incorporates source variability, as well as concentration dependencies and variability in the case of solute-based tracers like  ${}^{87}$ Sr/ ${}^{86}$ Sr, and yields true probability data.

# **Examples**

Six different formational end-members were used in the SIAR model to represent different formation waters present in the region. The relatively shallow (< ~350m), mostly Devonian groundwaters, are fresh, brackish or saline waters mostly derived from modern or sub-modern meteoric recharge; they have more negative and more variable  $\delta^{18}O_{H2O}$  compositions (-17 to -6%) than the deeper groundwater systems. Because of their isotopic range and the fact that the model characterizes end-members by a mean and standard deviation, these shallow waters were split into high- and low-  $\delta^{18}O_{H2O}$  end-members ("Dev-high" and "Dev-low"). The deep aquifer system consists of highly concentrated brines with more <sup>18</sup>O-enriched compositions, plotting to the right of the Global Meteoric Water Line. Several different formations in this brine system have relatively distinct isotopic signatures. These are: the Salina Group and Guelph Formation ("Salina-Guelph" end-member), the Clinton and Cataract groups ("Clinton-Cataract" end-member), the Trenton and Black River groups ("TBR" end-member) and the undivided Cambrian strata ("Cambrian" end-member). All these end-members are included in the following example scenarios, except for Clinton-Cataract groups, for which some isotopes are less well-characterized, and whose geographic range does not overlap with some of the other units.

Four hypothetical samples were generated to assess the model's performance. The compositions of these samples are illustrated in Figures 1a-d (as Groups 1-4) alongside the end-

member compositions for the different isotope systems. The results of the model predictions are illustrated in Figure 2a-d as probability histograms, and described below.



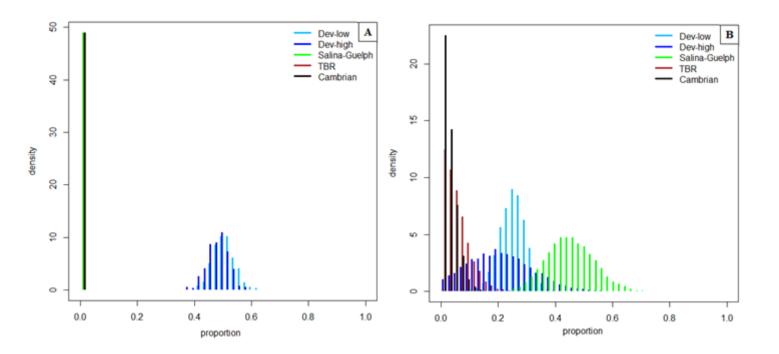
**Figure 1:** Isotope biplots of **(a)**  $\delta^2$ H vs.  $\delta^{18}$ O, **(b)**  $\delta^{18}$ O<sub>SO4</sub> vs.  $\delta^{34}$ S<sub>SO4</sub>, **(c)**  $\delta^{87}$ Sr/ $\delta^{86}$ Sr vs.  $\delta^{13}$ C<sub>DIC</sub>, and **(d)**  $\delta^{81}$ Br vs.  $\delta^{37}$ CI, illustrating the compositions of the end-members and test mixtures.

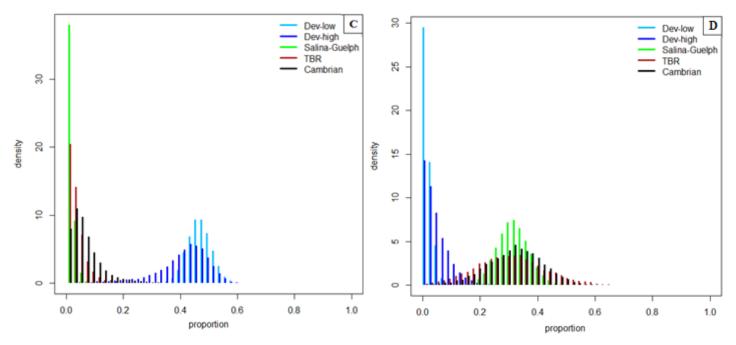
Mixture 1 (Figure 2a) is composed of 50% Dev-low and 50% Dev-high, representing an average shallow groundwater sample. The model predicts the correct proportions of all end-members extremely well. While it allows some variation in the Dev-low and Dev-high proportions due to variability in their source compositions, their ranges are relatively small and centered on the correct proportions; the deep end-members are correctly predicted at zero.

Mixture 2 (Figure 2b) is composed of 25% Dev-low, 25% Dev-high, and 50% Salina-Guelph. The proportions of these end-members are quite well estimated, although the Dev-high and Salina-Guelph distributions are slightly underestimated due to potential for substitution between each other, and between Salina-Guelph and TBR and Cambrian, which also explains the broader distributions of the latter two end-members, although their modes are still zero.

Mixture 3 (Figure 2c) is composed of 45% Dev-low, 50% Dev-high, and 5% TBR, designed to test the model's ability to identify a small amount of brine in an otherwise shallow water sample. While the Dev-low and Dev-high proportions are well-estimated, and the model seems to detect a brine component, there is some uncertainty as to which unit is contributing the brine. This uncertainty reflects the potential for substitution between these end-members, particularly TBR and Cambrian, given similarities in their compositions.

Mixture 4 (Figure 2d) is composed of 33% Salina-Guelph, 33% TBR, and 33% Cambrian. The mode proportions of all end-members are well-estimated, although the distributions of some are fairly broad due to the potential for substitution among many end-members, given the source/mixture geometry.





**Figure 2:** SIAR posterior probability distributions for the different end-members in Mixtures 1-4 (a-d, respectively).

#### **Conclusions**

Isotopic differences between groundwaters in the major bedrock units of southwestern Ontario have allowed the development of a tool that will help determine the probable unit(s) of origin for waters leaking from abandoned wells in the region. Use of this tool is expected to result in considerable cost and time savings for the AWP. While there is some unavoidable uncertainty in model predictions arising from variations in source compositions, the proportions are well-estimated in almost all mixtures tested.

## **Acknowledgements**

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