

Adding non-traditional stable Sr isotope tracer ($\delta^{88}\text{Sr}$) to $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{234}\text{U}/^{238}\text{U}$ tracers of groundwater contamination in the oil-producing Williston Basin, USA.

Leonid Neymark, Wayne Premo, Poul Emsbo

U.S. Geological Survey, Denver, CO 80225, Denver Federal Center, Box25046, MS963.

The Williston Basin has produced oil and gas from conventional structural and stratigraphic traps for more than 60 years. Horizontal drilling and hydraulic fracturing of the Devonian-Mississippian Bakken Shale has increased the production of oil by a million barrels per day in North Dakota along with an estimated several billion barrels of recoverable reserves (Gaswirth and Marra, 2014). This oil producing basin partially overlaps the prairie pothole region of North America, which is named for a multitude of small lakes and wetlands that provide critical habitat for waterfowl and other wildlife. Oil production on such a massive scale increases the risk of accidental releases of coproduced formation water (brine) into the environment. Similarly, long-term use of fertilizers in local agriculture can impact natural wetland ecosystems. The increased risks raise the importance of developing robust tracers that can identify the source(s) and quantity of contamination of wetland ecosystems.

Radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{234}\text{U}/^{238}\text{U}$ isotope tracers are widely used in hydrological studies to detect potential sources of groundwater contamination. Traditionally, the stable Sr isotopic ratio ($^{88}\text{Sr}/^{86}\text{Sr}$) has been used only to correct for isotopic fractionation during laboratory analyses. New analytical advances, however, have detected natural mass-dependent Sr isotope fractionation. Here, we used a double spike (DS) TIMS method (Neymark et al., 2014) for analysis of paired $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88}\text{Sr}$ (permil deviation from $^{88}\text{Sr}/^{86}\text{Sr}$ in SRM-987 NIST standard) in wetland water, shallow groundwater, and brines from the Bakken Formation (tight black shale/siltstone) and Mississippian Charles Formation (dolomitic limestone and evaporite unit) to evaluate potential sources of contamination. Moreover, because U^{+6} is soluble in water under subaerial oxidizing conditions and U^{+4} content is orders of magnitude lower (ppt levels) in reducing brines, $^{234}\text{U}/^{238}\text{U}$ isotope tracer is not sensitive to the brine contamination, but elucidates potential variability of uncontaminated end-members and, therefore, helps to improve the accuracy of estimated degrees of brine contamination based on binary mixing relationships. In addition, U isotopes in groundwater have a potential of determining some U-rich anthropogenic contaminants (e.g., phosphate fertilizers).

For the first time, we combine conventional radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and non-traditional stable Sr ($\delta^{88}\text{Sr}$) isotope tracers to an oil-field brine contamination study at the Goose Lake and Fuller sites in Montana and North Dakota. The advantage of combining these two parameters is that the radiogenic and stable Sr isotope tracers belong to the same chemical element and, therefore, two-component mixing produces linear correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88}\text{Sr}$. Results of this combined approach confirm previous observations (Peterman et al., 2012) that the Sr isotopes are a very sensitive indicator of brine contamination in the Williston Basin prairie pothole environment because produced waters have different $^{87}\text{Sr}/^{86}\text{Sr}$ and orders of magnitude higher Sr contents than local groundwater.

Linear correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88}\text{Sr}$ cannot be modified by atmospheric precipitation and evaporation and thus allowed quantitative estimates of the brine contamination. Using these systematics we show that surface water and shallow groundwater in two studied sites are variably contaminated by produced water derived from the Charles formation. The degree of the contamination reaches ~11-18 % in one Goose Lake site sample collected close to a brine tank and is <0.5% in most other samples. Our Sr isotope data also provide no evidence for brine contamination from the deeper Bakken formation. The U isotope analyses in combination with the Sr isotope results helped outline variable groundwater pathways and uncontaminated end-members. Also, U isotopes showed no appreciable groundwater contamination from U-enriched P-fertilizers. Our study in the Williston Basin demonstrates the potential of using combined radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{234}\text{U}/^{238}\text{U}$) and non-traditional stable ($\delta^{88}\text{Sr}$) isotope systematics as tracers of anthropogenic contamination in surface and groundwater systems.

References

Gaswirth & Marra, 2014, *Oil & Gas J.*, Jan. 6, 48-53.

Neymark et al., 2014, *JAAS*, 29, 69-75.

Peterman et al., 2012, *Appl. Geoch.*, 27, 2403–2408.