

Use of Strontium Isotopes to Detect Produced-Water Contamination in Surface Water and Groundwater in the Williston Basin, Northeastern Montana

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The Williston Basin (fig. 1) is undergoing a resurgence of petroleum activity because of advances in drilling and production technologies that allow new development of oil and gas in the Late Devonian–Early Mississippian Bakken Formation and associated units. In this region, prairie potholes (small lakes and sloughs) and shallow groundwater have been at risk from possible contamination by produced water during a half century of previous petroleum production. Produced water is composed of formation water, hydrocarbons, and fluids introduced during drilling. The natural salinity of many of these lakes increases seasonally due to evaporation while others are perennially saline due to a balance between recharge and evaporation. Water in the naturally saline lakes is a sodium and sulfate type, whereas produced water is a sodium and chloride type. Distinguishing between natural salinity and salinity from oil field brines can be challenging using only major-ion chemistry because of widely ranging and similar dissolved ion compositions. However, used as a tracer, strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) can be a powerful tool for distinguishing among different sources of water.

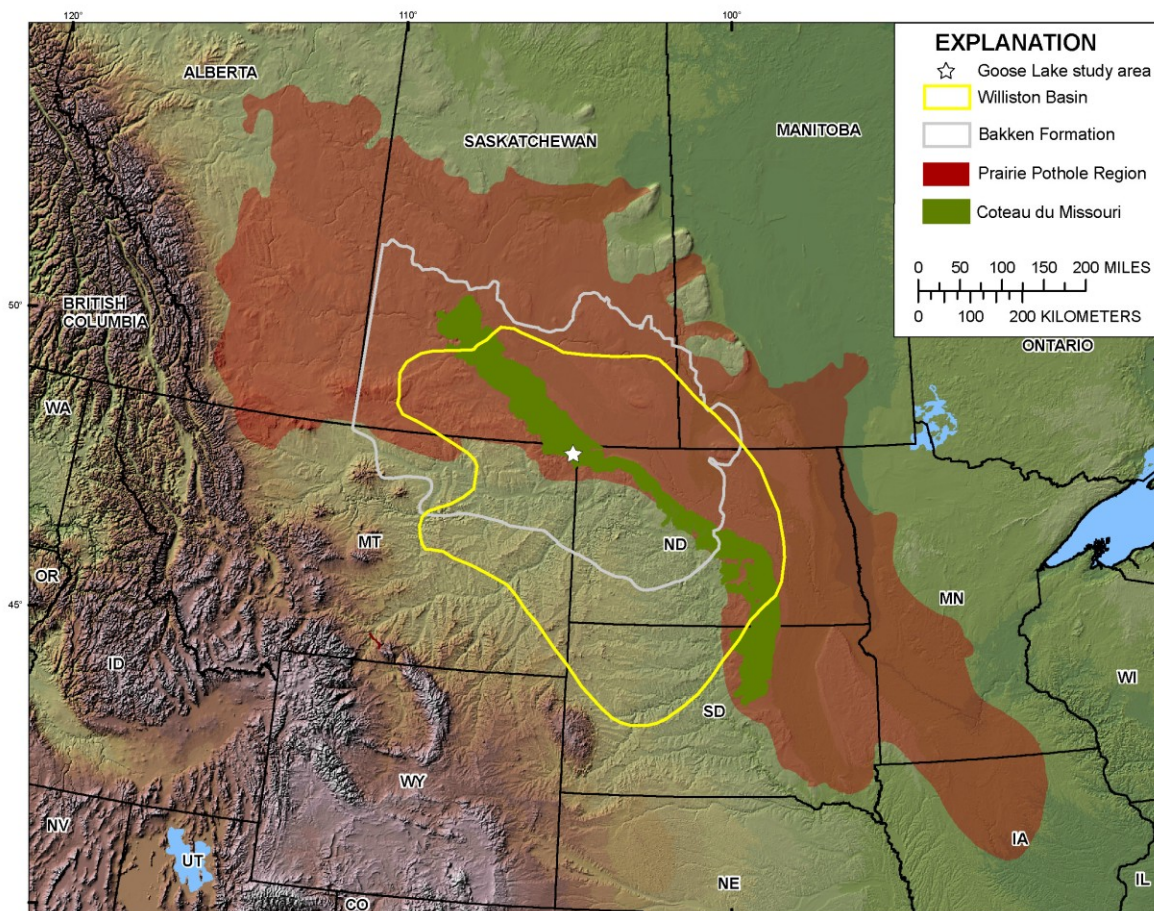


Figure 1. Location of study area.

Surface water (lakes and wetlands), shallow groundwater, and produced water in an approximately one square mile area in northeastern Montana near Goose Lake were sampled as part of a U.S. Geological Survey (USGS) multidisciplinary study of the effects of petroleum production on the prairie pothole region [Science Team for Energy in Prairie Pothole Environments (STEPPE), <http://steppe.cr.usgs.gov/>]. This paper describes a method that can provide reliable assessments of produced-water contamination even when the amounts are very small in surface water and groundwater.

The Goose Lake site is part of the Prairie Pothole Region, which was formed by glaciers during the Pleistocene Epoch (fig. 1). A series of advancing and retreating continental ice sheets deposited silt, sand, gravel, and rock ranging in thickness from several feet to several hundred feet (Donovan, 1988). The lithology and structure of the glacial deposits throughout this region influence the movement of the shallow groundwater and affect the hydrology of the potholes. The glacial drift includes till, outwash, and lacustrine deposits. The most conspicuous glacial feature of the Prairie Pothole Region is the Coteau du Missouri— a narrow plateau beginning in the southwest part of Saskatchewan and extending southeast into central South Dakota (fig. 1). The glacial deposits at the Goose Lake site (fig. 2) primarily contain sands and gravels typical of the Coteau du Missouri outwash. These sands and gravels rapidly transmit groundwater and thus the shallow wetlands (potholes and sloughs) exhibit marked seasonal changes in response to fluctuations of the water table.

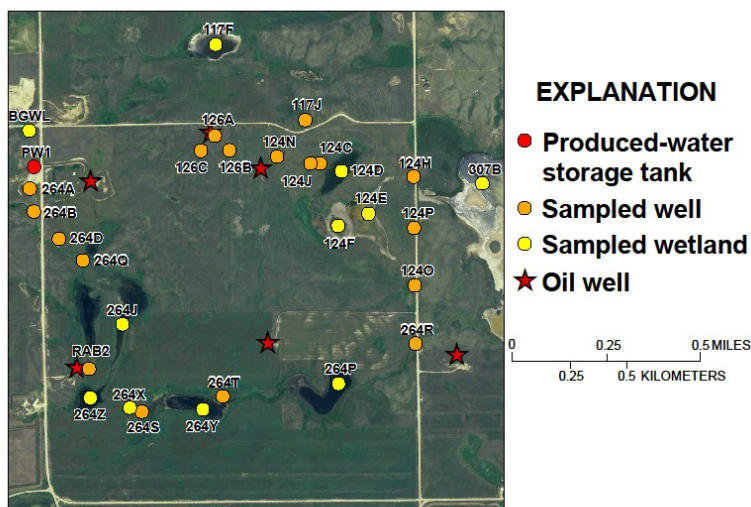


Figure 2. Sample sites and oil-related features in Goose Lake study area.

Previous hydrochemical and geophysical studies identified various degrees of surface water and groundwater contamination. Analyses of strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) were added to the analytical methods during 2009 to evaluate whether or not the use of this environmental tracer might detect small amounts contamination from produced water. Produced waters typically have large ionic strengths including large Sr concentrations compared to surface water and shallow groundwater. If the Sr isotopic compositions of

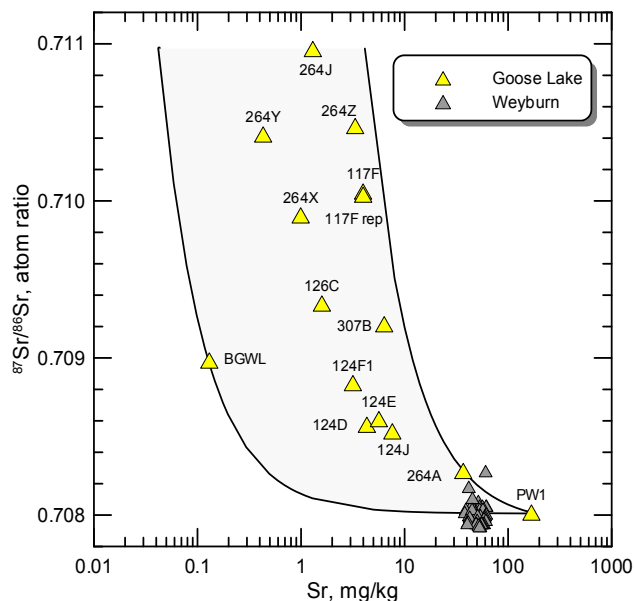
produced waters differ substantially from surface water and groundwater, then the Sr ratios could be a valuable and sensitive indicator of small amounts of contamination from produced water.

In the Prairie Pothole Region, the surface and shallow groundwater systems are recharged by precipitation and snowmelt. These low ionic strength waters react quickly with minerals in the soil and soil substrate. As the soil-water reactions approach chemical equilibrium, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios will become stabilized and any subsequent changes in $^{87}\text{Sr}/^{86}\text{Sr}$ are likely due to mixing with other waters including those produced during petroleum extraction. In small areas such as the Goose Lake site, this shallow groundwater will likely have a limited range in $^{87}\text{Sr}/^{86}\text{Sr}$ values. When the produced water also has a limited variability of $^{87}\text{Sr}/^{86}\text{Sr}$ values, a binary mixing systems model can be used to assess relative contribution of the end members in any water

sample. An important consideration is that evaporation of both fresh and contaminated waters will increase the Sr concentration but will not change the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

At the Goose Lake site, 13 water samples from wetlands, shallow groundwater, and produced water from a holding tank were analyzed for Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (fig. 3). The produced-water sample (PW1) has the largest Sr concentration (168 mg/kg) and smallest $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.70802) of all the samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ value for PW1 is in the range of values (0.7079 to 0.7083) for 43 produced-water samples from the Weyburn oil field in Saskatchewan (Quattrocchi and others, 2006), about 60 miles north of Goose Lake (fig. 1). Strontium concentrations in the Weyburn oil field produced-water samples (39 to 62 mg/kg) are slightly smaller than the value for PW1, which probably is the result of long-term injection of water with lower Sr concentrations (Quattrocchi and others, 2006).

One wetland sample, 264J, has the largest $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.71097 and a Sr concentration of 1.30 mg/kg. Uncontaminated surface and groundwater is expected to have the largest $^{87}\text{Sr}/^{86}\text{Sr}$ because of reaction with the glacial deposits, which contain a component of Precambrian material transported from the Canadian Shield to the northeast. $^{87}\text{Sr}/^{86}\text{Sr}$ values for other wetland and groundwater samples range between those of the produced water and sample 264J with Sr concentrations varying by more than two orders of magnitude. A mixing model for data from the Goose Lake site (fig. 3) was constructed on the basis of the following assumptions: (1) sample PW1 represents the $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration of produced water, (2) sample 264J represents the $^{87}\text{Sr}/^{86}\text{Sr}$ value of uncontaminated or the least contaminated water, and (3) the other samples are assumed to be mixtures of PW1 and water with variable Sr concentrations but a constant $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.71097.



According to Faure and Mensing (2005), mixing of two components produces a hyperbolic curve described by the following equation:

$$(^{87}\text{Sr}/^{86}\text{Sr})_m = (a/\text{Sr}_m) + b, \text{ where the subscript } m \text{ refers to any mixture of the two components}$$

The coefficients of the equation are the slope (a) and intercept (b) of lines passed through the point for PW1 and points for each sample on a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ against $1/\text{Sr}$. The intersections of these lines with the line with the equation $^{87}\text{Sr}/^{86}\text{Sr} = 0.71097$ give the Sr concentrations for the “uncontaminated” end members, which for the two bounding curves (fig. 3) are 0.043 and 4.138 mg/kg. The percentage of produced water (PW) in any

particular sample can be calculated from the Sr concentrations of PW1, and those of the

Figure 3. Relation of strontium concentrations to strontium isotopes in water from the Goose Lake study area, northwestern Montana.

“uncontaminated” end members. For example, sample 264A contains about 20 percent of water with the Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of PW1; sample

124F1 contains about 1.4 percent; sample 264Z contains 0.3 percent; and BGWL and 264Y both contain about 0.05 percent. The mixing process is probably more complex and may involve

several stages including contamination, subsequent mixing of contaminated waters, and periodic episodes of dilution by recharge. However, the net effect will be the same as simple binary mixing and the water compositions will ultimately move along mixing lines towards the produced-water end member.

The results of this study of surface water and groundwater at the Goose Lake site demonstrate that Sr isotopes can be sensitive quantitative indicators of small amounts of produced water contamination when the fresh water and the produced water differ significantly in Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ values. Baseline strontium isotope characterization of surface and shallow groundwater would be useful in areas where petroleum extraction is just beginning or in areas where renewed activities could benefit from baseline assessments of previous levels of contamination.

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