INVESTIGATING THE SOURCE AND AGE OF NITRATE IN DRINKING WATER WELLS

By **Mike Sklash** and **Fatemeh Vakili**

In the April 2019 issue of *Environmental Science & Engineering Magazine,* we published an article titled "Environmental Isotopes Help Solve Groundwater Issues" (Vakili and Sklash, 2019).

In it, we explained that environmental isotopes are naturally-occurring isotopes (versions of atoms) that we can use to help solve groundwater problems. The controlling factors for environmental isotopes in the hydrosphere are different from the typical groundwater investigation methods, which employ concepts like Darcy's Law and groundwater flow directions and/or the interpreting distributions of chemicals in groundwater. Therefore, the addition of environmental isotope data helps to build a more defendable conclusion than using traditional methods by themselves. In some cases, environmental isotopes can provide insight into hydrogeological problems without resorting to the expense of installing monitoring wells (e.g., Sklash and Mwangi, 1991).

In Vakili and Sklash (2019), we discussed the application of four environmental isotopes: oxygen-18 (^{18}O), deuterium (^{2}H), tritium (^{3}H), and nitrogen-15 (^{15}N) to help understand groundwater recharge, nitrate distributions in groundwater, and nitrate sources at a commercial dairy. In this article, we have summarized a recent preliminary isotopic investigation we conducted on the source(s) and age of nitrate in groundwater in drinking water wells in a small community.

ENVIRONMENTAL ISOTOPES IN WATER

The ratios of heavy to light stable isotopes of hydrogen ($^{2}H/^{1}H$) and oxygen ($^{18}O/^{16}O$) in water molecules are largely controlled by temperature. Concentrations of ^{18}O (oxygen-18) and ^{2}H (deuterium) are measured in specialized laboratories using mass spectrometers. Concentrations of ^{18}O and ^{2}H are expressed in standard delta notation (δ) of the ratio of the heavy isotope to light isotope in a water sample compared to a standard water. For example, the concentration of oxygen-18 in a water sample is expressed as:

$$\delta 18O = [\ \{(18Osample/16Osample) - (18Ostandard/16Ostandard)\}/\ (18Ostandard/16Ostandard)] \times 1000\ ‰$$

where: "δ" is read as "delta" or "del," the standard is "SMOW" (standard mean ocean water) and "‰" means parts per mille (or mil). $\delta^{2}H$ is determined similarly comparing ratios of $^{2}H/^{1}H$. $\delta^{18}O$ and $\delta^{2}H$ analyses cost about $50.00 for the pair, which can be used for the following:

- Identify the age of groundwater (recent or glacial age).
- Identify recharge mechanisms (direct infiltration versus infiltration of evaporated water from ponds, infiltration of ponded water into groundwater, etc.).
- Identify whether mixing of groundwater occurs in, or between, aquifers.
- Determine travel time through thick aquitards.
- Determine the percentage of current rainfall in storm runoff in a stream.

Tritium (^{3}H) is a radiogenic isotope of hydrogen, whose concentration in groundwater depends on when the groundwater was recharged. Concentrations of tritium are measured in spe-

cialized laboratories using scintillation counters. Concentrations of tritium are expressed in tritium units (TU) where 1 TU means one tritium atom in 10^{18} protium (^{1}H) atoms. ^{3}H analyses cost about $200. The basis for tritium aging of groundwater is:

- Groundwater takes on the tritium concentration of the precipitation that recharges groundwater.
- Before and during the early 1950s, natural tritium concentrations in precipitation were thought to be 10-25 TU (there were few measurements at that time).
- During the 1950s and early 1960s, tritium concentrations in precipitation increased greatly (to 1000s of TU) due to atmospheric testing of nuclear bombs; the explosions created "bomb tritium."
- In 1963, the USSR and the USA signed an atmospheric test ban treaty. Subsequently "bomb tritium" in precipitation was greatly reduced.
- Tritium is a radiogenic isotope with a half-life of about 12.3 years. This means that the concentration of tritium spontaneously is reduced by half about every 12.3 years.
- After 1963, the tritium concentrations in precipitation gradually diminished.
- Recent precipitation in the temperate areas of North America contains about 10 TU of tritium.

As a result of these factors and assuming no mixing in the groundwater flow system following recharge (that would mix the tritium concentration of the groundwater), groundwater recharged in, or before, the early 1950s now contains less than 1 TU. Groundwater recharged in about 1963 would now contain about 90-100 TU, and so on.

ENVIRONMENTAL ISOTOPES IN NITRATE

During the past several decades, isotope hydrogeologists have used the ratios of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ in nitrate dissolved in groundwater to differentiate between sources of nitrate, such as chemical fertilizer, soil nitrogen, and animal waste (manure or septage waste). Concentrations of ^{15}N and ^{18}O in nitrate are also measured in specialized laboratories using mass spectrometers. The ratios of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ in nitrate are

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expressed in δ-notation in ‰; however, different standards are used for $^{15}N/^{14}N$.

Fogg et al. (1998) clearly demonstrated how groundwater below test areas used exclusively for/with cattle, chemical fertilizer applications, no treatment, and septic systems, had characteristic $\delta^{15}N$ values. Spalding et al. (2019) show nitrate source fields using dual isotope plots of $\delta\ ^{15}N$ versus $\delta^{18}O$ in nitrate to identify source types.

CASE STUDY

We recently conducted a preliminary investigation of the source(s) of nitrate in groundwater in the drinking water wells in part of a rural village in the Great Lakes area. Data from the two previous years indicated that some of the drinking water wells had groundwater nitrate concentrations in excess of 20 mg/L. The drinking water criterion is 10 mg/L.

We used existing water well records for drinking water wells in, and around, the village to estimate groundwater flow directions and hydrostratigraphy (geologic strata and their associated hydraulic properties). These data indicated the groundwater flow direction was generally from northwest to southeast, which is consistent with published regional mapping.

According to the regional hydrogeologic information for the area, the overburden consists primarily of glacial till. Local water well records indicate the bedrock surface in the study area is between about 28 to 47 feet below ground level (fbgl). Records also indicate the drinking water wells are cased through the overburden and into bedrock and are completed as open boreholes in carbonate rock, generally between about 100 and 160 fbgl.

Ten target wells were selected for isotopic testing. We intended to establish one well transect aligned in the groundwater flow direction (to determine where the nitrate source might be) and one transect transverse to the groundwater flow direction (to evaluate the width of the groundwater body containing elevated nitrate).

In February 2022, we collected groundwater samples from the 10 target wells and evaluated these water samples for nitrate, water isotopes, nitrate isotopes, and other water quality parameters.

The highest nitrate concentrations we observed in the groundwater were in the area previously identified by the client as a high nitrate area. Our preliminary groundwater flow and nitrate data indicate the high nitrate groundwater occurs in a narrow band aligned in the groundwater flow direction.

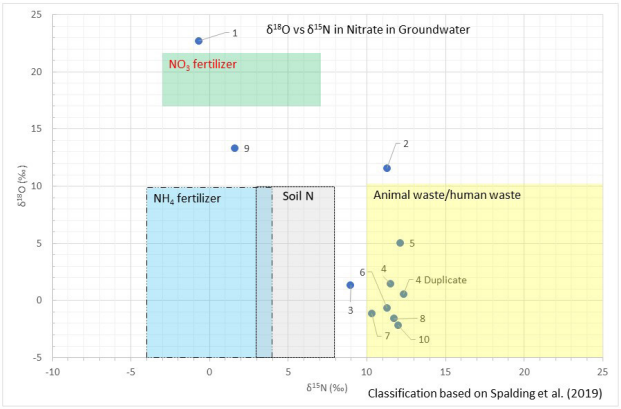

Figure 1. Plot of $\delta^{18}O$ versus $\delta^{15}N$ in nitrate in groundwater.

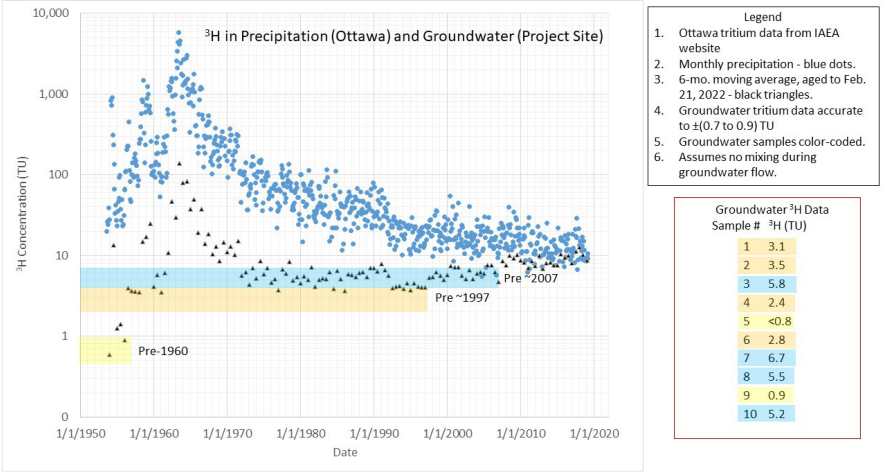

Figure 2. Plot of tritium concentrations in precipitation (Ottawa) and in groundwater (project site).

Figure 1 is a plot of the $\delta^{18}O$ versus $\delta^{15}N$ in the nitrate in groundwater and includes the "nitrate source" fields provided in Spalding et al. (2019). It clearly shows that seven of the 10 wells had groundwater nitrate that originated from animal/human waste. Two wells had groundwater that may have had some animal/human waste. Figure 1 also indicates that chemical fertilizer was not a significant source of the nitrate in the groundwater in the study area.

Figure 2 is a plot of tritium in monthly precipitation at Ottawa, Ontario, since about 1950. These data are from the International Atomic Energy Agency (IAEA) and Ottawa has the longest tritium record available for North America.

We reduced the number of data points for easier graph-reading by calculating a six-month moving average of the tritium concentrations in precipitation, and then "aged" these precipitation data to February 2022, based on when the precipitation fell and the half-life of tritium.

Assuming there is no mixing in the groundwater once the precipitation recharges into the groundwater, we colour-coded the data into "age" groups. The colour-coding in Figure 2 indicates the following:

- None of the groundwater samples contained about 10 TU of tritium; therefore, none of the groundwater was exclusively post-2007 groundwater.

- Two groundwater samples (#5 and #9) contained less than 1 TU of tritium. This groundwater must have recharged before 1960.
- Four groundwater samples (#1, #2, #4, and #6) contained between 2 and 4 TU of tritium. This groundwater likely recharged before about 1997.
- Four groundwater samples (#3, #7, #8, and #10) contained between 5 and 7 TU of tritium. This groundwater likely recharged before about 2007.

The oldest (#5 and #9) and newest (#7) groundwater samples (based on tritium) had $\delta^{18}O$ and $\delta^{2}H$ values that were significantly different (Figure 3). The difference in $\delta^{18}O$ and $\delta^{2}H$ values between the older and newer groundwater may be related to a local, progressive temperature increase between the mid-1950s and 2020 from about 6°C to 8°C (43°F to 47°F). These data suggest that $\delta^{18}O$ and $\delta^{2}H$ may be used as a less expensive method of age-dating groundwater in this area.

The highest nitrate concentrations align along a narrow band in the groundwater flow direction that coincides with the youngest groundwater. Nitrate isotope data indicate that the majority of the groundwater samples contained nitrate that originated from animal/human waste.

Finally, all of the groundwater samples evaluated during this investigation contain "legacy nitrate" that entered the groundwater before about 2007.

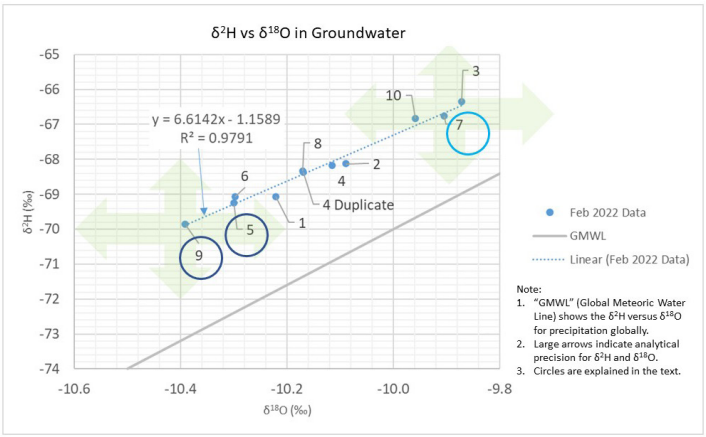

Figure 3. Plot of $\delta^{2}H$ versus $\delta^{18}O$ in groundwater.

CONCLUSIONS

In order to remedy a groundwater quality problem effectively and efficiently, one must delineate the spatial extent of the problem and understand how the problem began. This case study involved a preliminary environmental isotope investigation of groundwater in a small community where the groundwater was known to be impacted by nitrate in certain areas.

Without drilling new wells for the investigation, we now have a sense of where the elevated nitrate in groundwater originated geographically (somewhere northwest), when it originated (pre-2007), and that it originated from animal/human waste.

The next step in "fixing" the problem includes investigating up the groundwater hydraulic gradient (that is, to the northwest) from the observed "high nitrate from animal/human waste" groundwater to the source. ■

References available upon request.

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