

Identifying Groundwater Nitrate Sources and Sinks

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Effective management of nitrate-impacted aquifers requires identifying the sources of nitrate to the aquifer, and understanding the transport and fate of nitrate within the aquifer. Source identification is crucial to effective source mitigation; conversion of residential septic systems to sewer in a rural community will be ineffective if the primary source of nitrate contamination is agricultural operations.

Determining the source of nitrate in an aquifer, however, can be difficult. Nitrate occurs naturally and has a number of anthropogenic sources, including synthetic fertilizers, animal manure, septic systems, and municipal wastewater. More than one source may be present in a recharge area, and the sources may be diffuse, distributed, or localized. As a result, groundwater nitrate contamination is often widely distributed with limited concentration range, making traditional plume-tracking methods of placing wells upgradient and downgradient of a suspected source ineffective.

Characterizing nitrate transport is also essential to effective management. Since nitrate travels without significant

attenuation in oxygen-rich groundwaters, natural tracers of groundwater flow can help distinguish between ongoing and historic sources of nitrate, and can be used to identify appropriate wells for assessing the impact of land use or management changes on groundwater quality. The most significant process for degradation of nitrate in groundwater is *denitrification*, the microbial conversion of nitrate to nitrogen gas. Demonstrating that denitrification is occurring can lead to acceptance of monitored natural attenuation as a viable remediation plan, and can reconcile measured and modeled nitrate concentrations.

Source ID

Nitrate sources in groundwater can be determined from:

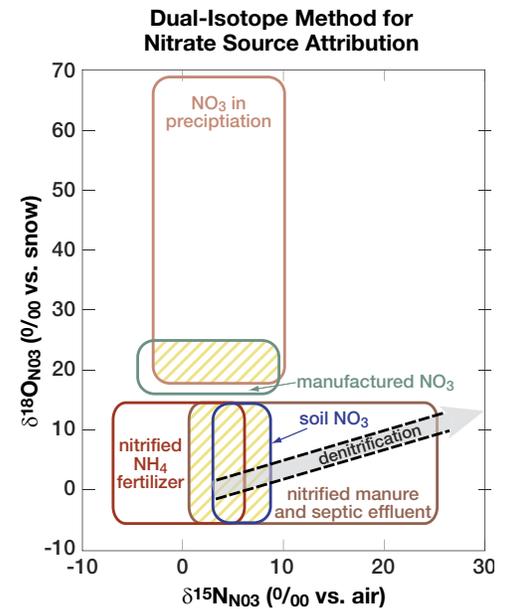
- nitrate isotopic composition;
- the presence of nitrate co-contaminants characteristic of specific sources;
- groundwater major and trace element chemical and isotopic composition;
- mean age of the groundwater;
- isotopic composition of water.

Isotopic Composition: The nitrate molecule contains nitrogen, with stable isotopes ^{14}N and ^{15}N , and oxygen, with stable isotopes ^{16}O , ^{17}O , and ^{18}O . Measuring the isotopic composition of both elements, known as the dual-isotope method, can be diagnostic for distinguishing atmospheric and synthetic fertilizer sources from organic fertilizer and septic sources, and for identifying denitrification (see figure, right). Septic discharge cannot usually be distinguished from manure application using this method, however, and there are large areas of overlap between various anthropogenic sources and natural soil nitrate. Since *nitrification*, the oxidation of ammonium to nitrate, typically incorporates oxygen from both the atmosphere and water, measurements of local water $\delta^{18}\text{O}$ can also be useful in assessing the importance of ammonium nitrogen from septic and municipal wastewater discharge, animal manure, soil organic matter, or ammonium fertilizers as a source of groundwater nitrate.

Co-contaminants: A difficult but important problem is distinguishing between residential (septic) wastewater

and fertilizer sources of nitrate in groundwater underlying residential areas either surrounded by farmlands or recently converted from agricultural use. A Lawrence Livermore National Laboratory study found that groundwater underlying Chico, California, contained trace concentrations of co-contaminants indicating a septic source: DEET, caffeine, surfactants, and widely prescribed anti-epileptics such as carbamazepine. In contrast, groundwater in surrounding farmlands contained herbicides and herbicide degradation products. The highest nitrate concentrations were in the youngest groundwater, indicating ongoing nitrate loading. Nitrate isotope composition was not definitive in this setting, as results fell in the area of overlap between animal waste, septic effluent, and soil nitrate. Boron and boron isotopic composition may also indicate the presence of wastewater.

Water tracers: Quantifying groundwater age and source can be useful in nitrate source identification (including distinguishing between ongoing and historic sources), identifying wells for nitrate monitoring (including background



The dual-isotope approach is a powerful method for tracing nitrate sources and cycling in groundwater. The highlighted fields on the dual-isotope plot (after Kendall, 1998) show areas of overlap in source isotopic composition. Definitive attribution of nitrate source for groundwater nitrate isotopic compositions in these fields requires other methods summarized in the text. Denitrification produces a characteristic trend on a dual-isotope plot with a slope that is relatively consistent across environmental settings.

wells), and predicting when impacts from surface source-mitigation efforts will be seen in a given well. Groundwater age tracers for young water are the most useful, and include tritium and chlorofluorocarbons. Tritium is a short-lived radioactive isotope of hydrogen, is produced in the atmosphere naturally and by above-ground nuclear weapons testing, and is incorporated into the water molecule, making it a suitable tracer for groundwater flow. The most accurate method for dating groundwaters less than 50 years old uses tritium in combination with its daughter product ^3He , a stable isotope of helium. In basins where water is imported, the isotopic composition of water can trace its source.

The dual-isotope approach can distinguish atmospheric and synthetic fertilizer sources from organic fertilizer and septic sources.

Specialized methods: Other methods for attributing nitrate source are useful in specific settings. Dissolved gas compositions unique to dairy manure lagoons make lagoon seepage distinguishable from both ambient groundwaters and from lagoon water applied to fields. Enrichment in nitrate ^{17}O indicates an atmospheric origin and is used in surface water and vadose zone leaching studies, and to identify groundwater nitrate derived from Chilean nitrate-phosphate deposits used as fertilizer.

Denitrification ID

Denitrification in groundwater can be demonstrated by:

- the presence of “excess” nitrogen gas;
- a characteristic trend in residual nitrate isotopic composition on a dual-isotope plot;
- changes in the abundance and isotopic composition of electron-donor oxidation products;
- downgradient decreases in the quantity of nitrate not resulting from dispersion.

Quantifying denitrification is important in assessing natural attenuation of nitrate in groundwater and in using nitrate isotopic composition for source attribution. Denitrification requires denitrifying bacteria (which are common), low-oxygen conditions, and an electron donor. At the watershed or basin scale, denitrification may be suspected when

low nitrate concentrations are observed along with reducing conditions (such as low dissolved oxygen or high Fe^{2+} and Mn^{2+}) and an electron donor (such as dissolved organic carbon). Evidence that denitrification has occurred along a flowpath is more convincing if dilution by mixing or dispersion can be quantified and if geochemical and isotopic changes indicating organic carbon oxidation are also observed.

A more robust and informative approach is demonstrating that nitrate loss is accompanied by accumulation of nitrogen gas (the end product of denitrification) in excess of the atmospheric nitrogen

incorporated into groundwater during recharge. This approach also allows the original nitrate concentration as well as the degree of denitrification in a groundwater sample to be estimated. This “excess” nitrogen can be easily measured in groundwater.

Denitrification also results in the enrichment of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in residual nitrate. As denitrification progresses, residual nitrate becomes increasingly isotopically enriched so that downgradient samples low in nitrate often provide the strongest isotopic evidence for denitrification. The dual-isotope method is especially powerful when used with the “denitrifier” technique for nitrate isotopic analysis, a method that allows rapid analysis of small-volume samples with low nitrate concentrations. Using the dual-isotope and excess-nitrogen methods together allows denitrification to be quantified in complex hydrogeologic settings where mixing or dispersion cannot be adequately quantified.

Stable isotopes of nitrate and water, excess nitrogen, nitrate co-contaminants, and groundwater age-dating are powerful supplements to traditional methods for attributing nitrate source identity and history, for validating and calibrating nitrate transport models, and for guiding and assessing nitrate management plans. This integrated approach has been used to win regulatory approval of monitored

natural attenuation for mitigation of nitrate-contaminated groundwater at a RCRA site in the Coast Range of California (Beller and others, 2004), and to distinguish historic from ongoing sources and septic from agricultural sources in a small basin in Northern California (Moore and others, 2006).

Stable isotopes of water are widely used, and stable isotopes of nitrate are becoming more widely used; both are commercially available. The excess nitrogen, groundwater age, and nitrate co-contaminants methods show great promise and are deserving of wider use. ■

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