

# ***NITRATE FORENSICS***

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by

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## **Introduction**

Contamination of groundwater by nitrate ( $\text{NO}_3^-$ ) from various sources continues to be a problem through much of the U.S., particularly in the midwest and California, where it is much more of a problem than perchlorate, with nitrate contaminating groundwater in many Central Valley alluvial aquifers. Most nitrate contamination sources are easily defined, particularly if there is a single known source such as a cattle feed lot, but in some areas – particularly rural locations that have been urbanized, distinguishing between human (anthropogenic) and natural (geogenic) sources is somewhat more complicated. This brief article describes one excellent method for fingerprinting nitrate sources. The U.S. Geological Survey's Isotope Group in Menlo Park and the Lawrence Livermore National Laboratory Nitrate Working Group at Lawrence Livermore National Laboratory have pioneered most of the recent research in isotope forensics.

## **Sources**

Sources of anthropogenic nitrate contamination to groundwater are septic systems, sanitary sewage effluent releases, domestic animal wastes, and home and farm usage of nitrogen fertilizer. Other nitrate sources include explosives and pyrotechnics such as fireworks, flares and torches, and munitions. Nitrate contamination also occurs from the degradation of cyanide ( $\text{CN}^-$ ) an industrial pollutant, particularly common to historic gasworks sites.

Nitrate in groundwater from geogenic sources include those that are desert-derived such as the Chilean Atacama Desert deposits (which also contain natural perchlorate), caliche and playa lake evaporate deposits, and desert vadose zone soils. Recent research at the New Mexico Institute of Mining and Technology at the University of Nevada and U.S. Geological Survey has shown that nitrate in desert soils occurred at much greater quantities than previously reported, with subsoil nitrate ranging from 2,000 to

10,000 kilograms per hectare (kg/ha). Farmers typically only apply nitrogen fertilizers in amounts ranging from 25 to 250 kg/ha per year. The researchers concluded that this naturally-occurring vadose zone nitrogen reservoir had the potential to become mobilized thereby leaching large amounts of nitrate to groundwater.

### **Fingerprinting Nitrate Sources Using Stable Isotopes**

How can one distinguish between anthropogenic and geogenic nitrate? Conventional nitrate analysis only gives quantitative data and does not discriminate between sources. However, if one examines the stable isotopes of nitrate, unique fingerprints for different sources can be obtained.

Most stable isotopes in substances are determined by using isotope ratio mass spectrometry (IRMS), in which a beam of charged ions is generated from the thermal ionization of a solid sample (known as a “solid source”) or by ionizing a gaseous sample (“gas source”). Solid source IRMS is used for elements with high atomic masses such as strontium, lead, and uranium. For most light elements (i.e., hydrogen, nitrogen, and oxygen) the analyzed material is converted to a gas prior to analysis. The isotopic concentrations are then measured as a ratio of the isotope to a common nuclide. In the case of gas source IRMS, it is measured against an international standard.

Stable nitrogen and oxygen isotopes are useful in indicating sources when nitrate is present in surface or groundwater. Delta nitrate-nitrogen ( $\delta^{15}\text{N}_{\text{nitrate}}$ ) and nitrate-oxygen ( $\delta^{18}\text{O}_{\text{nitrate}}$ ) isotope ratios in water can be used to identify nitrate sources and its fate in vadose zone soil and in groundwater. Nitrogen has two stable isotopes:  $^{14}\text{N}$ , with a natural abundance of 99.63% and  $^{15}\text{N}$ , with a natural abundance of 0.37%. The wide difference in the isotopic abundance allows for the determination of distinctive isotopic signatures to define specific natural and anthropogenic sources. In analyzed samples, the ratio of  $^{15}\text{N}/^{14}\text{N}$  is compared with a standard (atmospheric nitrogen) to provide  $\delta^{15}\text{N}^*$ . The abundance of  $^{15}\text{N}$  in the atmosphere remains relatively constant because of the inert character of atmospheric nitrogen resulting in a  $\delta^{15}\text{N}$  of zero. Nitrogen isotopes also fractionate, largely by biochemical processes. These include:

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\* By established convention, isotopic ratios are defined as delta ( $\delta$ ) values, which is obtained by the equation:

$$\delta (\text{isotope}) = \left\{ \frac{\text{R}_{(\text{sample})} - \text{R}_{(\text{standard})}}{\text{R}_{(\text{standard})}} \right\} - 1 (1,000).$$

Where:  $\delta$  (isotope) = values in per thousand (‰) or per mil and  $\text{R}_{(\text{sample})}$  = the ratio of the first and second isotope such as  $^{18}\text{O}/^{16}\text{O}$ , and  $\text{R}_{(\text{standard})}$  = the ratio of  $^{18}\text{O}/^{16}\text{O}$  used in international or other standards. For example, the standard for  $^{18}\text{O}/^{16}\text{O}$  is Standard Mean Ocean Water (SMOW). A positive (+)  $\delta$  value indicates that the heavier isotope (i.e.,  $^{18}\text{O}$ ) in the sample is enriched when compared to the standard. A negative (–) value indicates that the sample has more of the lighter ( $^{16}\text{O}$ ) isotope. The International Atomic Energy Agency (IAEA) and the National Institute of Standards and Technology (NIST) have established and published these standards.

- Nitrification: where nitrogen compounds are oxidized.
- Denitrification: in which nitrate is reduced to molecular nitrogen; and,
- Nitrogen fixation: where dissolved molecular nitrogen is converted to nitro-organic compounds.

The above processes occur mostly from bacterial action in which the lighter nitrogen isotope ( $^{14}\text{N}$ ) is more easily reacted resulting in more positive  $\delta^{15}\text{N}_{\text{nitrate}}$  values. Known ranges of  $\delta^{15}\text{N}_{\text{nitrate}}$  and  $\delta^{18}\text{O}_{\text{nitrate}}$  have been published (Table 1). Although  $\delta^{18}\text{O}_{\text{nitrate}}$  values are more difficult to determine, obtaining  $\delta^{18}\text{O}_{\text{nitrate}}$  can lead to defining nitrate source fields. Figure 1, graphically shows the relationship between  $\delta^{18}\text{O}_{\text{nitrate}}$  and  $\delta^{15}\text{N}_{\text{nitrate}}$ , which can be used to fingerprint nitrate sources

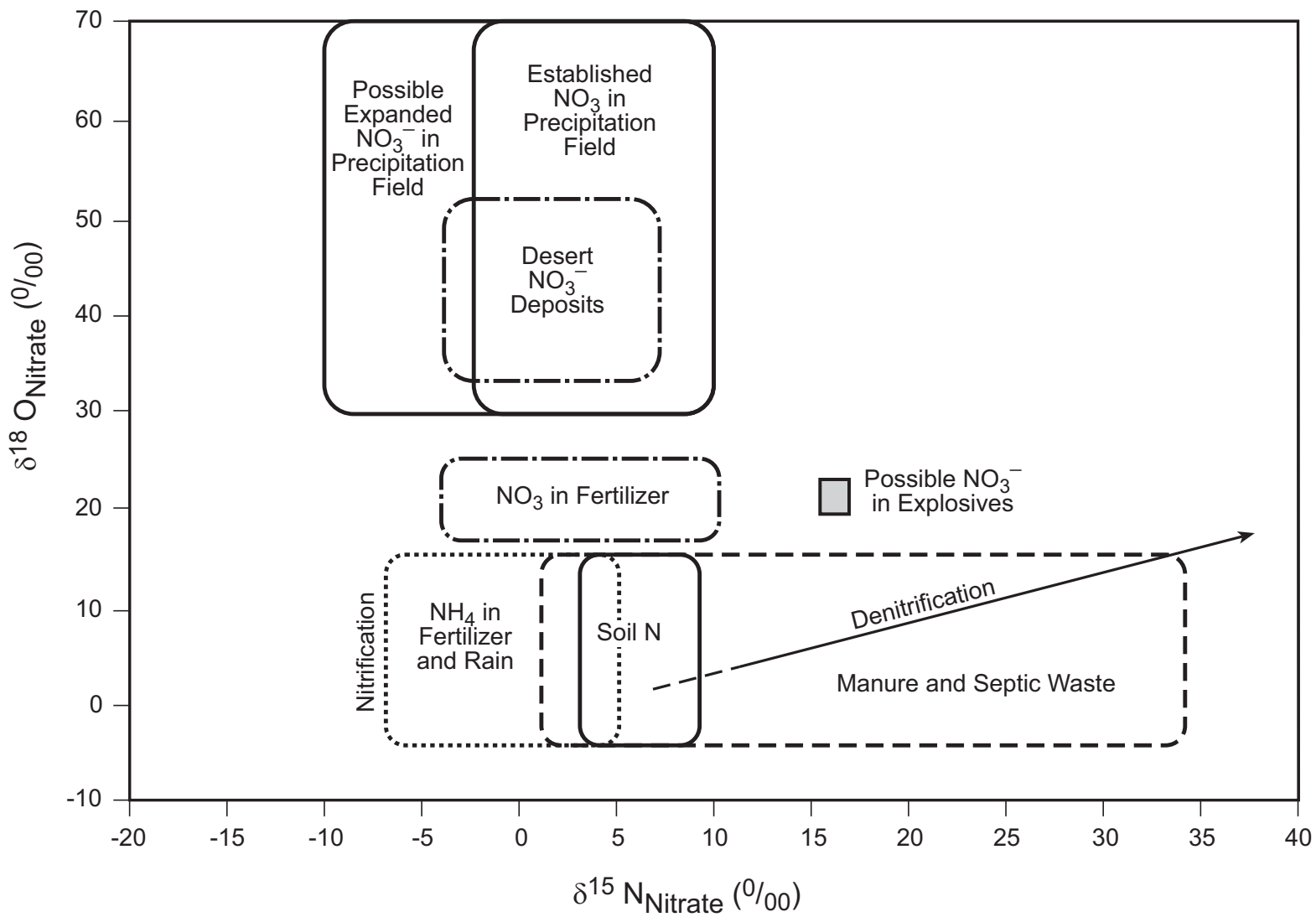
### **Conclusions**

Analysis of nitrogen-oxygen isotopes of dissolved nitrate provides an excellent technique for fingerprinting nitrate sources. However, as in any forensic investigation it is important to have more than one line of evidence and the technique should be combined with a complete understanding of the local environment or land use history and hydrogeology including groundwater geochemistry. The technique should be combined with other isotopic methods such as  $\delta^{18}\text{O}$  and delta deuterium ( $\delta\text{D}$ ) of water for determining water sources and “age” dating groundwater using tritium/helium-3 ratios ( $\text{T}/^3\text{He}$ ).

**TABLE 1**  
**Typical  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  Values in Dissolved Nitrate ( $\text{NO}_3^-$ )**  
**From Different Nitrate Sources**

Potential Contaminant Source	$\delta^{15}\text{N}$ (‰)	$\delta^{18}\text{O}$ (‰)
Commercial fertilizer	-4 to +4	+18 to +26
Animal or human waste	> +10	-4 to +12
Precipitation	-3	+18 to +60
Organic nitrogen in soil	+4 to +9	+1 to -4

FIGURE 1



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**Figure 1 Caption (if required):**

Delta ( $\delta$ )  $^{15}\text{N}$  and  $\delta^{18}\text{O}$  in per mil (‰) for environmental nitrate sources. Modified largely from Kendall (1998), Silva (2002).