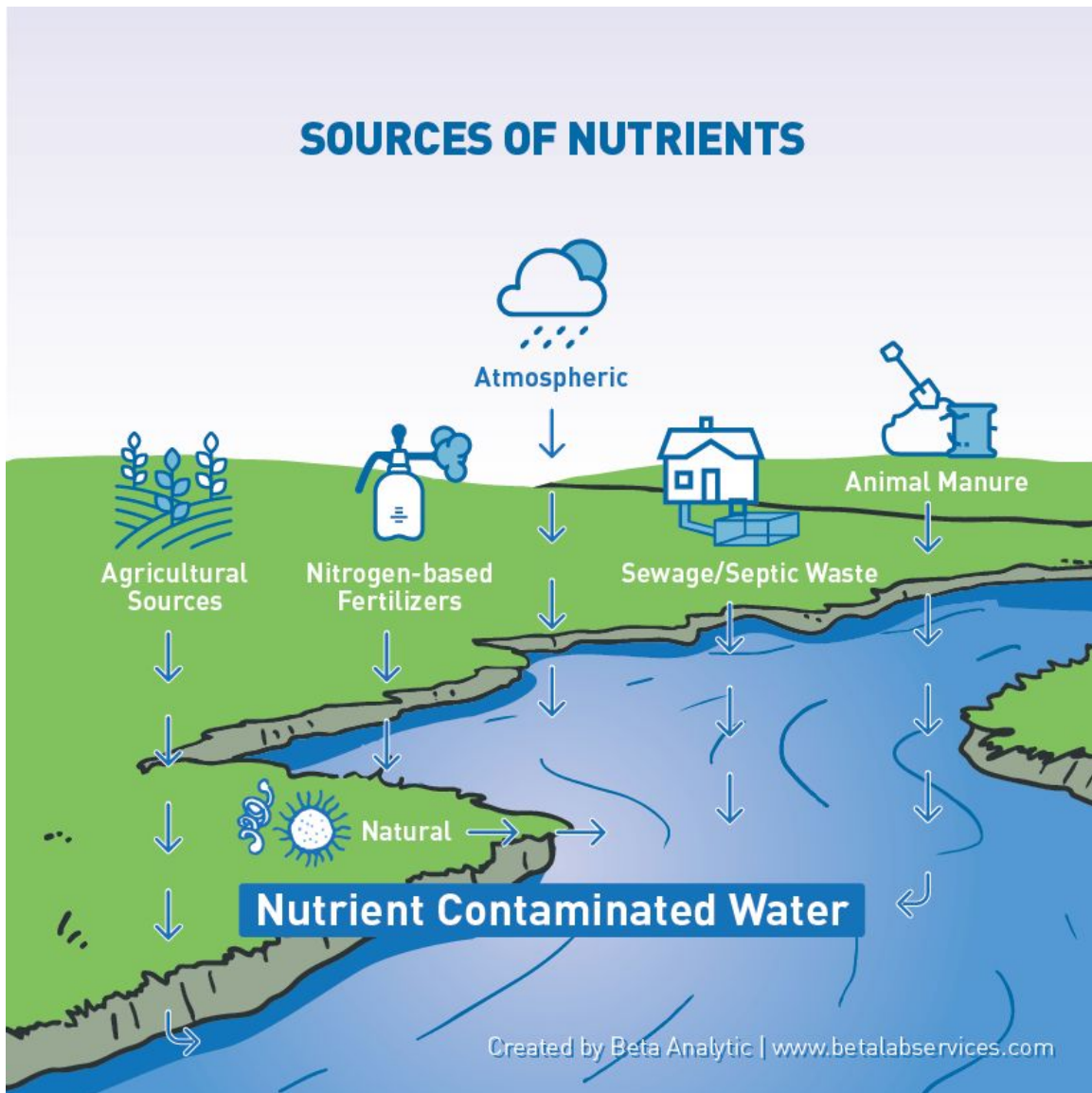


Nutrient Source Tracking of Dissolved Nitrate by Isotopes Ratio Mass Spectroscopy (IRMS)



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Purpose

One of the major obstacles with contamination of water by nitrate (NO_3^-) is the identification of the source(s) of pollution. Various studies have proven the added value of analyzing the isotopic composition of nitrate ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$) to identify the human (anthropogenic) and natural (biogenic/geogenic) sources of nitrate contamination in water. The purpose of this document is to summarize the key points of Nutrient Source Tracking (NST) of dissolved nitrate via Isotope Ratio Mass Spectroscopy (IRMS).

The Nitrogen Cycle

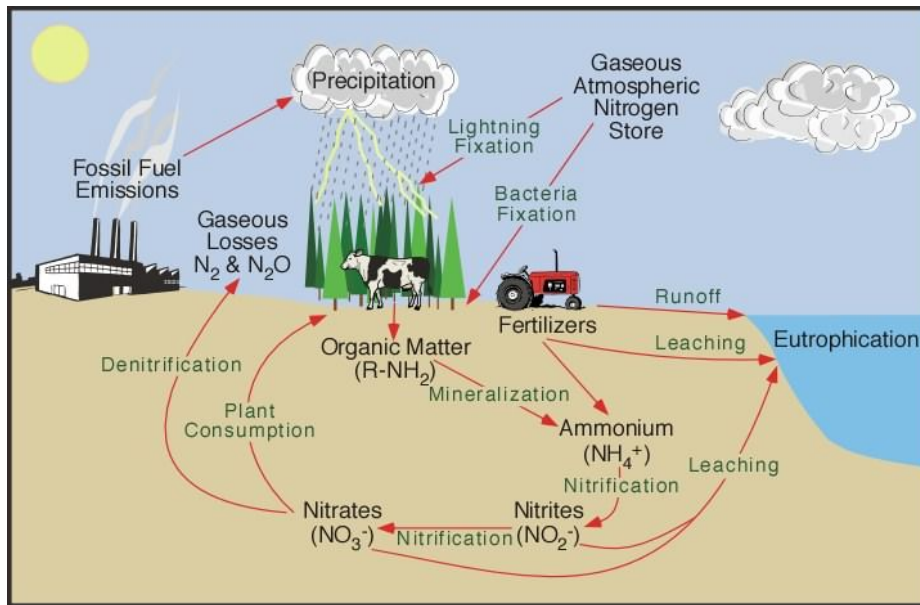


Figure 1. A schematic diagram of the nitrogen cycle from Pidwirny, 2006.

Nitrogen exists in nature in several forms, some of which are seen in Figure 1. Nitrogen gas (N_2), nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) are examples of the wide variety of sources of nitrogen in an ecosystem. Furthermore, nitrogen can be converted from one form into another through several means such as bacterial fixation, mineralization, denitrification, nitrification. Because oxygen is usually available in unsaturated soils, most of the nitrogen that reaches surface and groundwater has undergone nitrification and is therefore found in the oxidized form nitrate (NO_3^-).

Fingerprinting Nitrate Sources Using Stable Isotopes

Concentration measurements of nitrogen are useful when determining whether there is a nutrient imbalance since some measurements target nitrogen species while others total differing nitrogen species to measure Total Nitrogen(TN). Distinguishing differing sources, however, requires an extended dataset of spatially and temporally staggered concentration measurements as well as detailed information about potential nitrogen sources in the surrounding area, hydrology, and soil characteristics. Research has shown that the addition of $\delta^{15}\text{N}$ values can aid in confirming sources of nitrogen into a system. Dissolved nitrate can be measured for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, which can be used to distinguish sources of nitrate and to evaluate whether nitrate concentrations are changing due to mixing of different sources or due to conversion processes (Kendal et al 2007).

A stable isotopic value or delta value ($\delta^n\text{X}$) expressed in parts per thousand (‰), is a measure of the ratio of stable isotopes of an atom present in an unknown sample compared to a known standard (Hoefs, 2009). For example, $\delta^{15}\text{N}$, nitrogen has two stable isotopes: ^{14}N , with a natural abundance of 99.63% and ^{15}N with a natural abundance of 0.37%. The ratio of $^{15}\text{N}/^{14}\text{N}$ is compared with standard atmospheric nitrogen to provide $\delta^{15}\text{N}$ values. The abundance of ^{15}N in the atmosphere remains relatively constant because of the inert character of atmospheric nitrogen resulting in a $\delta^{15}\text{N}$ of zero. The wide difference in the isotopic abundance allows for the determination of distinctive isotopic signatures to better define specific natural and anthropogenic sources.

Isotopic Fractionation Within the Nitrogen Cycle

Isotopic fractionation refers to the processes that change delta values. Several fractionation processes take place during the nitrogen cycle. The nitrification process, which occurs during nitrogen migration in the soil, leads to specific isotopic signatures for different nitrate sources. Therefore, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in nitrate can be used to identify the origin and fate of nitrate in water.

Isotopic fractionation during conversion reactions results from the preference to convert the isotope with the smaller mass before converting the isotope with the larger mass (e.g. preference for ^{14}N over ^{15}N and preference for ^{16}O over ^{18}O). As a result, the products of a conversion reaction are selectively enriched in lighter isotopes (depleted δ -values) while the substrates become enriched in heavier isotopes (enriched δ -values) (Lamb-Wozniak, 2007). Fractionation mechanisms for nitrogen isotopes include volatilization of $\text{NH}_3(\text{g})$ after ammonification, conversion of ammonium to nitrate during nitrification, the conversion of nitrite to $\text{N}_2(\text{g})$ during denitrification and nitrate assimilation towards organic nitrogen (Figure 2). Denitrification affects the signature of both the nitrogen and oxygen isotopes of nitrate. As denitrification occurs, the nitrogen and oxygen isotopes in nitrate are typically enriched in heavy isotopes.

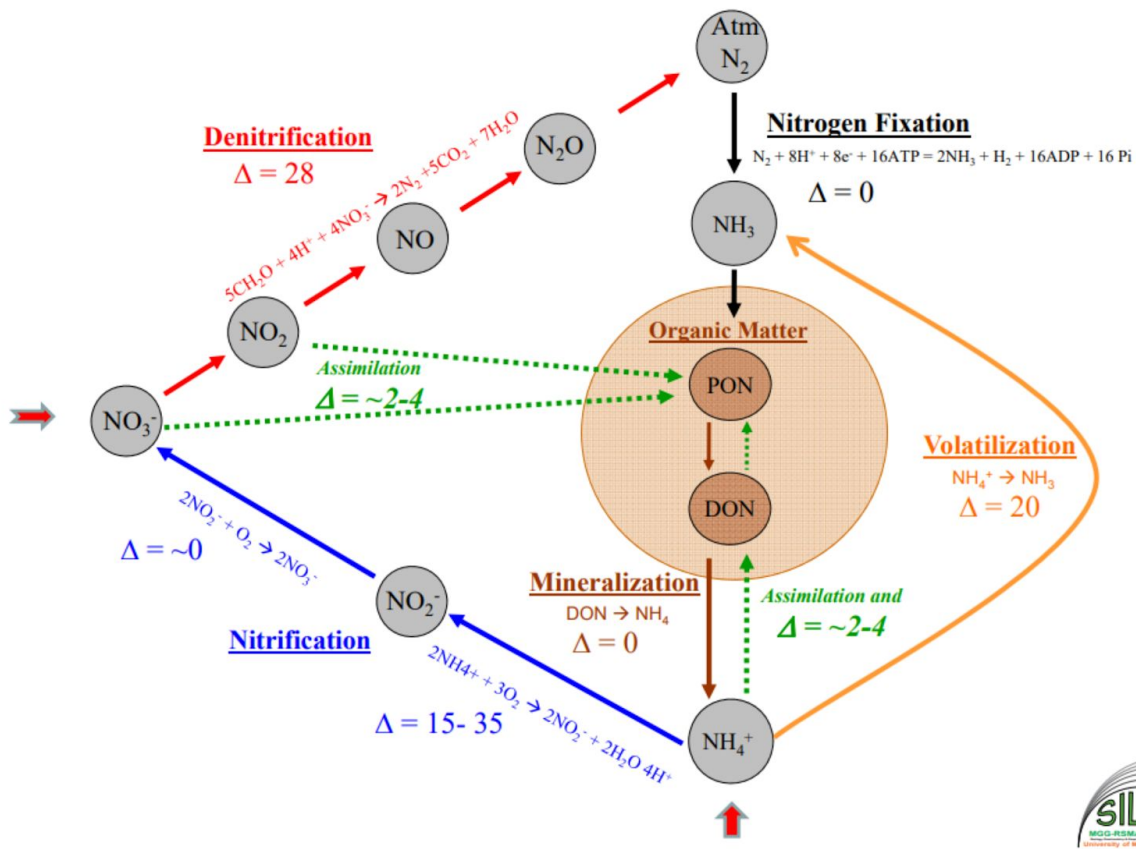


Figure 2. From Lamb-Wozniak shows various fractionation reactions that take place in the nitrogen cycle. The capital delta suggests fractionation factors or the rate by which fractionation is taking place during a reaction.

Source Identification

Due to the complexity of the biogeochemical nitrogen cycle, the $\delta^{15}\text{N}$ isotope composition is usually combined with the $\delta^{18}\text{O}$ isotope composition of the NO_3^- molecule to trace nitrate sources and to identify the effect of potential conversion processes such as natural attenuation on the nitrogen budget (Figure 3).

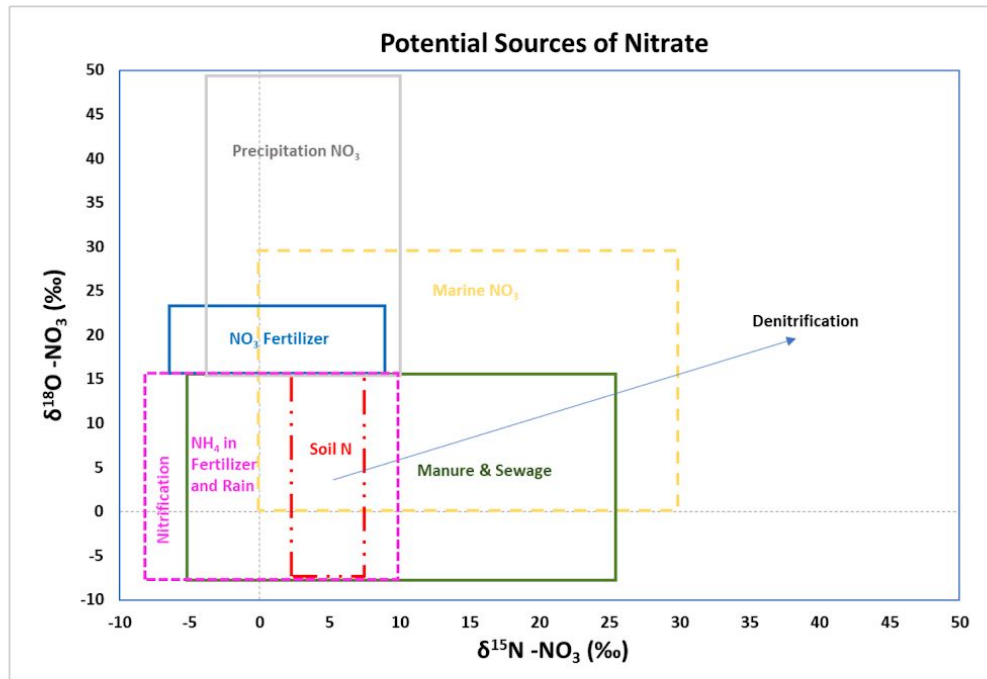


Figure 3. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of typical nitrogen sources, modified from Kendall, 1998.

Mixing processes and conversion reactions lead to a modification of the isotope composition of dissolved nitrate. Therefore, discriminating multiple NO_3^- sources based on the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope composition of nitrate alone may be difficult with a single result. The application of continuous monitoring for isotopic values leads to improved characterization and more effective management of nitrate contamination problems.

Analysis of nitrogen-oxygen isotopes of dissolved nitrate provides an additional technique for fingerprinting nitrate sources. However, incorporation of hydrochemistry may help to confirm nitrate source identification. Linking isotope compositions with concentrations of anions and cations in water also provide valuable information for identifying nitrate sources, as chemical constituents from anthropogenic sources are inclined to dominate those of natural sources (Spruill *et al.*, 2002).

As in any forensic investigation, it is important to have several lines of evidence and the techniques should be combined with a complete understanding of the local environment or land

use history and hydrogeology including groundwater geochemistry. This technique should also be combined with other isotopic methods such as $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water for determining water sources and “age” dating groundwater using tritium/helium-3 ratios (T/3He).

Conclusion

In order to effectively control nitrate contamination, detailed knowledge on the contribution of different nitrate sources is necessary. The application of isotopic measurements leads to a more efficient characterization of nitrate pollution problems since stable isotopic composition of N and O reflect their origins and the conversion processes that are taking place. Once the sources are identified, targeted measures can be proposed to reduce pollution. This allows for elaborating improved and more effective water quality management strategies.

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