An Executive
Summary

Fingerprinting Sources of Environmental Pollution Using Stable Isotopes

Evaluating isotopic signatures of nitrogen (N) promotes an understanding of the N cycle and enables the identification of the sources of human-derived N pollution, both modern and historic.

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Growing population sizes and continued development are stressing the sensitive balance of the environment. The ability to effectively tackle global pollution challenges, such as those contributing to modern climate change, will inevitably be a key task of the current generation and those that follow. Scientists interested in addressing these issues have a wide range of geochemical techniques at their disposal and they must combine them with experience and judgement to best evaluate the causes of pollution. This is accomplished by looking for geochemical clues for the origin of pollutants. One of the most effective fingerprinting techniques involves the acquisition of isotope signatures of a pollutant for source identification.

In stable isotope analysis, the two abundant isotopes of an element are measured using an isotope mass spectrometer, which can separate different isotopes based on their mass. The relative proportion of the heavier to lighter isotope is then calculated. Reported in permil (‰), or parts per thousand, this ratio is typically stable unless it is affected by natural processes or other outside forces. Measurements of small changes in isotope ratio (i.e., fractionations) provide clues for how the element has been cycled within the natural environment.

A simplified agricultural system that has inputs, biogeochemical cycling, and outputs fosters an understanding of changes in isotope values that may occur in nature. For example, suppose the isotope value of a fertilizer entering a soil system is +20‰. Uptake of this fertilizer by crops leads to a change of -5‰, so that the soil isotope value, which is a function of both the input and the change derived from biological cycling, is now +15‰. Further physical and chemical processes may cause some of this fertilizer to be lost from the system, perhaps into a local stream or river. This loss is also associated with an isotope change, in this case -7‰. Thus, the river water would have an isotope value of +8‰.

After biogeochemical cycling, the isotope value of river water is now very different from the fertilizer, which makes it challenging to identify the fertilizer as a source of pollution. However, the solution comes down to scale; in this example, most of the fertilizer is being used for crop growth. If over-fertilization occurs, only a small portion of the fertilizer will be used by the plants. While the same isotope changes will happen to the small fraction of the fertilizer on the plants, a much greater proportion will undergo no isotopic change at all, as it flows through the system unaltered. As such, the river water would contain high concentrations of the fertilizer and an isotope value close to that of the source.

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This value is the fingerprint that can be used to identify the source.

Pollutants and the Nitrogen Cycle

Some pollutants are of great interest for environmental monitoring. Carbon, nitrogen, and phosphorous are pollutants, though naturally occurring and required by all living organisms. They are critical for the formation of DNA and functioning of energy systems at the cellular level. In natural systems, limiting carbon, nitrogen, and phosphorous, among elements, controls vegetation growth and productivity, keeping the natural world in balance.

Increasing human population has led to greater demands upon food resources, thus requiring a far greater level of food production than could be accomplished under natural conditions. With this agricultural boom has come a rise in fertilization, which aims to provide increased levels of namely carbon, nitrogen and phosphorous to improve crop yields. If done carefully, fertilization can have the desired effect with minimal negative effects. Excess carbon, nitrogen, and phosphorous leave the agricultural system, however, and enter waterbodies and downstream environments. In these unmanaged sites, this can cause rapid and unchecked biological growth, thereby unbalancing the natural system and damaging fragile ecosystems.

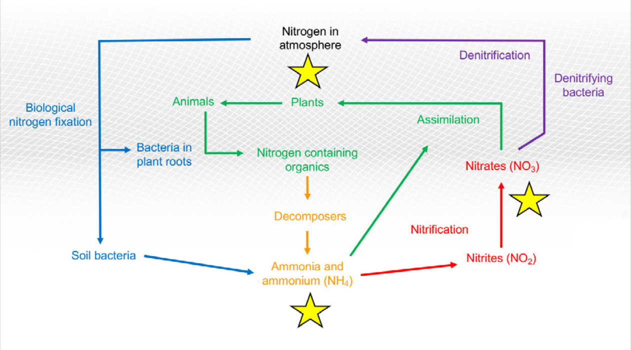
Nitrogen, a major ingredient in fertilizer, is found in several forms within the natural environment, including:

- N_2 which comprises approximately 78% of air
- organic N locked up in plants, animals, and soils
- inorganic N in the form of nitrate and ammonium.

A range of biological and inorganic processes can convert N from one form to the next; these chemical transformations are all part of the nitrogen cycle. This cycling of N through the atmosphere, soil, water, and plants is fundamental to good ecosystem health.

Figure 1 illustrates the nitrogen cycle. The major pool of all nitrogen is that found in the atmosphere, but for this to be available to living organisms, it must be converted into a form that can be taken up by plants. This process, called *nitrogen fixation*, is undertaken by specialist microbes, converting atmospheric nitrogen into ammonia and ammonium. This ammonia can then be directly taken up by plants or can be converted into nitrite and nitrate (i.e., nitrification), which are also bioavailable. The organic N cycle includes plant uptake and the introduction of N into animals as they consume plants. This process concludes with death and decay, where decomposition converts the organic N back to ammonia (i.e., ammonification). The final stage of the cycle is the loss of nitrate back to the atmosphere (i.e., denitrification). It is important to consider how human activities affect the N cycle with additional inputs from man-made sources. Human processes introduce N into the ecosystem from traffic and industrial pollution, as well as fertilizers and waste in both ammonium and nitrate forms. These additions stress the natural N cycle and can tip it out of balance, leading to common pollution problems.

Figure 1: The nitogren cycle and isotopes.



In terms of isotope tracing, nitrogen has two stable isotopes: ^{14}N comprising around 99.6% and ^{15}N making up the remaining 0.4%. Chemical and biological processes cause small changes in the ratio of these isotopes to one another. A study of these changes shows how N has been converted from one chemical form to another and to what extent any one form of N may be acting as a source of environmental pollution.

Environmental Pollution: A Nitrogen Case Study

Insight regarding the effect of excess nitrogen can be gained from a pollution case study in which geochemical analysis, including isotope fingerprinting, has helped to identify the main source of pollution within a stressed lake system. In natural systems, identifying pollution sources is complex, as there are many different inputs. The major potential N pollution sources in this study include agriculture, fishing, aquaculture, industry, human activities, and human waste. These sources may combine to cause a pollution event or there may be one key pollutant. The use of geochemical tracers allows scientists to deduce if this environment is affected by a wide range of diffuse pollutants or a singular major point source pollutant. Depending on the findings, appropriate mitigation strategies can be employed to reverse worsening pollution trends.

Temporal analysis of lake sediment. In any natural system, it is best practice to consider the process of understanding pollution issues and their scales. The spatial scale of an issue can be easily defined by simply looking at a water body with eutrophication issues, or by taking samples for geochemistry down the length of the river. The temporal scale, which indicates how long pollution has been an issue, is equally important when evaluating pollution and attributing a cause. In the lake system case study, core samples can be taken from the

Figure 2: Core sample data: nitrogen levels, 1850-2020.

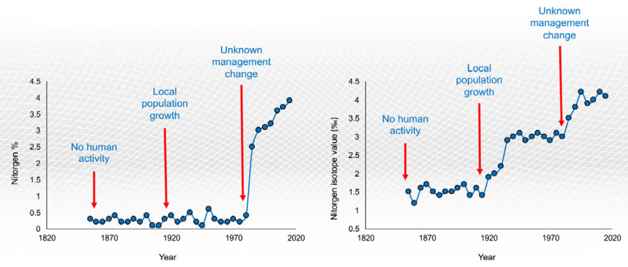
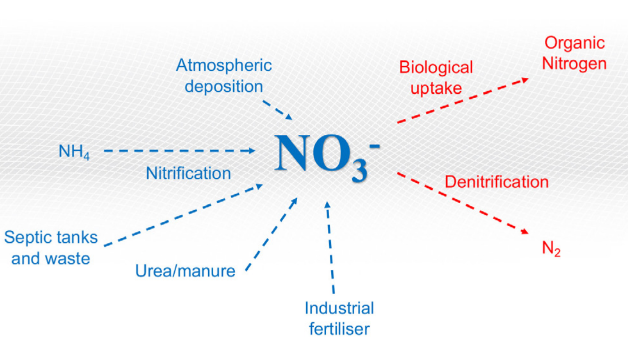


Figure 3: Nitrate sources.



last few hundred years to determine whether the pollution was an issue in the pre-industrial past or if it is related to modern human activities.

From these cores, a wide range of pollution indicators can be analyzed. The case study focused specifically on N pollution, measuring the N concentration in the core material as well as the N isotope signature. This is accomplished by sectioning the core sample from youngest to oldest, cleaning up the material, preparing it for analysis, and taking the measurements. The results generate a profile of N changes over time, which indicates if the pollution seen today is a modern problem or if the system has always had high N concentrations. Once the timing of the changes is known, potential causes are considered and the search for the major driver of this pollution begins, using isotope fingerprinting techniques.

The core sample data in **Figure 2** shows that the concentration of nitrogen in the lake was very low beginning with the earliest sample from 1850, but the lake experienced a huge N spike in the 1980s. Thus, even from this simple geochemical analysis, a distinct period of interest is observed in terms of nitrogen loading changes to the lake system.

The nitrogen isotope profile for the same core material is also shown in the figure. The 1850s section of the core has low isotope values around 1.5‰. These values remain stable until the early 1900s, when they increase to around 3‰, but again stabilize between 1930 and 1980. In the 1980s, a final transition sees a sharp rise in isotope values that remain high in modern times.

The high concentrations of N and the rapid increase in N isotope value both point to one potential cause for modern eutrophication problems with the lake, and explicitly indicate that this is a change from more natural conditions happening in the recent past. Although it is not conclusive evidence for a human-derived source of pollution, it is a strong indicator that N dynamics have been influenced by increased human usage of the lake and surrounding land.

The search for N pollutants can be targeted by combining the core sample information with other evidence from the site. It is known that the lake was relatively untouched by human activity until the early 1900s, when population numbers in the area increased and the land around it was used, as today, for localized, low-intensity farming. With this increase in population, the lake water resource became more intensively used for a whole range of human activities, including as a drinking source, for cleaning, as a raw material in building, and as an outlet for human waste. During this period, very little change in the N concentration is observed, but there was a difference in the isotope signature of N in the lake, potentially indicating a new source of N being deposited in sediments. The final, distinct transition in both records comes in the 1980s, which appears to reflect excess N loading in the lake as identified by a high percentage of N in the sediments. Using isotope tracing to fingerprint the cause of this specific change should enable well-defined strategies for mitigation.

Using nitrate to pinpoint sources of pollution. Studying only the bulk N isotope signature makes it difficult to pinpoint the cause of pollution, as it includes organic N forms from plant and soil material as well as inorganic forms of N. Alternatively, one inorganic form, nitrate, can be used as a very powerful tool for fingerprinting the source of nitrogen pollution. Nitrate is a key component of N uptake into plants. Most nitrate salts are readily soluble so that nitrate is easily bioavailable and can accumulate in high concentrations in environmental waters, becoming a major cause of eutrophication. Importantly, nitrate can be extracted from water without changing the isotope value and, because nitrate is formed from a composition of both nitrogen and oxygen, it contains two stable isotope systems to interrogate in the same molecule. This is significant, as different processes affect the isotope signature of the N and O atoms, such that different sources of nitrate have unique stable isotope fingerprints.

Figure 3 illustrates the most common transition of nitrate through the environment, with the oxidation of ammonia to nitrate and then loss through biological uptake or denitrification. There are other sources of nitrate that have quite distinct isotope values; these can include

Figure 4: Determing major sources of nitrate by plotting N and O.

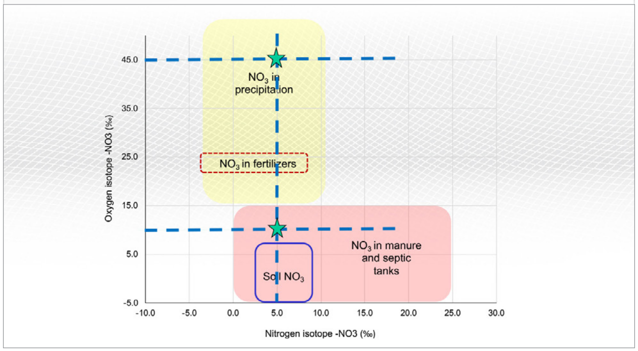
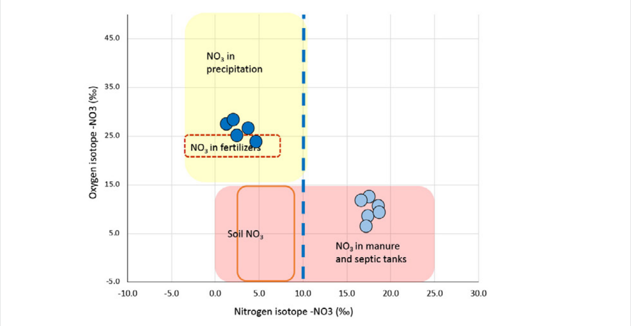


Figure 5: Potential sources in a stressed lake system.



atmospheric deposition, industrially produced fertilizer, manure and urea, or sewage from septic tanks. If these sources are in excess in the environment, their isotope fingerprints in surface or ground water will be discerned with nitrate N and O isotope analysis.

The major sources of environmental nitrate can be readily characterized by plotting nitrogen isotope values versus oxygen isotope values, as depicted in **Figure 4**. The expected ranges of major sources are distinguished in the graph: those of atmospheric deposition in rainfall, nitrate fertilizers, soil nitrate, and manure and septic tank nitrate. This demonstrates that using nitrate N and O isotopes is a powerful isotope fingerprinting tool. Note that if only the nitrogen isotopes were measured, and yielded a value, for instance, of +5‰, the sources could not be differentiated. However, addition of the oxygen isotope signature allows the measurements to be far more conclusive regarding the source. For example, a value of +45‰ for O would indicate atmospheric nitrate, while a value of +10‰ is more in the range of manure and septic tank nitrate. This approach helps shed light on pollution sources in the modern lake waters of the case study.

Lake water analysis. Antecedent to the lake water assessment, nitrate N and O isotopes were evaluated in samples of water from a stream feeding the lake system. These samples, represented by dark blue circles in **Figure 5**, fall into either the atmospheric nitrate or fertilizer nitrate category. As the region has only subsistence agriculture without intensive fertilization, synthetic fertilizer can be ruled out. It is more likely that these values signify atmospheric deposition. Regardless of source, the stream's low nitrogen concentration suggests that this is not a major source of pollution and not the cause for the rise in the lake's N pollution.

The set of lake samples were taken from its most polluted sections with the highest nitrate concentrations, namely, the edges of the lake closest to human populations and aquatic activities. These samples, designated in the figure by light blue circles, clearly display a very high N isotope signature, which is linked to waste and leaking septic tanks. These values strongly support the idea that the combination of human waste with poor sanitation is a major source of pollution in the lake. These high nitrate N isotope values may explain the transition from lower bulk isotope values in the core from 1850 toward higher values by the modern day.

One final complication in this system is the introduction of aquaculture, in which fish cages are implanted in the lake for high-intensity fish farming. These fish stocks are fed organic-rich feeds with high N concentrations and nitrogen isotope values near 10‰. Therefore, it appears there are two major causes of modern pollution in this system: 1) unprocessed human waste and sewage and 2) aquaculture.

Key learnings. Isotope fingerprinting has helped establish that the lake nitrogen balance has deteriorated over the last few hundred years, related to increases in human activity, poor sanitary conditions and the introduction of aquaculture. Significant inputs of nitrogen from soil, the atmosphere, or synthetic fertilizers have been ruled out as potential causes using measurements of O and N isotopes in nitrate. To improve water quality in this ecosystem, the best options would be improved human waste management and tighter regulation of aquatic farming practices for more sustainable aquaculture. These mitigation strategies are well aligned with a number of the UN's sustainable development goals of improving sanitation, health and hunger, while simultaneously protecting and preserving our natural environment and its delicate ecosystems.

Conclusion

Environmental pollution issues are a major cause for concern in many regions and on many scales. Nonetheless, by employing a range of fingerprinting tools, including isotope analysis, scientists and policy makers can work to help identify the causes of environmental degradation and put in place reasonable and effective mitigation. It is only through close study that the balance of key environmental systems and the impact of human development can be understood. Scientists are diligently using isotope techniques to discover the complexities of the natural world and strive to protect it for future generations.