thermo scientific

APPLICATION BRIEF 30768

IRMS: supporting the Nitrate Directive by using isotope fingerprints for detecting the sources of nitrate pollution

Authors: Oliver Kracht[1], Andrew Smith[2], Christopher Brodie[1], Mario Tuthorn[1];
[1]Thermo Fisher Scientific, Germany,
[2]National Environmental Isotope Facility, British Geological Survey, UK

Keywords: Pollution, isotope fingerprints, nitrates, nitrogen, oxygen, wastewater

Goal

Demonstrate how by analyzing nitrogen and oxygen isotopes of nitrates we can identify sources of pollution.

Introduction

Nitrates are a key nutrient for plants and are largely applied in agriculture to enhance crop productivity. They can be supplied as a solid, in the form of a mineral fertilizer, or as liquid manure. Increasing population size and the growing demand for food has resulted in the excessive use of nitrates in food production. This over application pollutes our environment on local levels, but also spreads globally through oceanic and atmospheric systems.

Consequentially, contamination of the hydrosphere affects human health through drinking water quality and environmental health due to increased algae growth linked to eutrophication. Alongside agriculture, the other major sources of nitrate pollution are human sewage and industrial process waste. Wastewater treatment plants can remove nitrates from wastewater by bacterial denitrification processes with varying degrees of success depending on the region. If the treatments are done poorly, high concentrations of ammonia, ammonium and nitrate can enter the environment, degrading ecosystem health.

ThermoFisher SCIENTIFIC

In order to protect our health from these pollutants it is critical to find ways of determining the sources of pollution, allowing for appropriate mitigation strategies. In 1991, the European Commission introduced the Nitrates Directive (91/676/EEC) for protection of waters against pollution caused by nitrates from agricultural sources. By promoting good farming practices in the use and storage of fertilizer and manure, Member States can conserve water quality across Europe and protect natural ecosystems. In this application brief we report how isotope fingerprints support the Nitrate Directive by offering a tool for nitrate source identification and tracking changes in our environment, as performed in different nitrates studies.

Nitrogen and oxygen isotopes in nitrates

Researchers use isotopes of nitrates to determine the source of nitrate compounds in surface and groundwater. Nitrates are composed of nitrogen and oxygen, with both, ^{15}N and ^{18}O isotope fingerprints, offering valuable indications about different formation processes and therefore different sources of nitrates. This helps us to understand the N-cycle in soils and to identify potential contributors of high-level nitrate inputs to the environment. While $\delta^{15}N$ is mainly used to distinguish natural from synthetic N-input, $\delta^{18}O$ can be used to understand bacterial activity and processes in the formation of nitrates.

Analytical setup

Nitrate compounds can be converted to silver nitrate. Using Thermo Scientific™ EA IsoLink™ IRMS System, silver nitrate is reduced in a combustion reactor to N_2 and subsequently analyzed for $^{15}N/^{14}N$ ratio using isotope ratio mass spectrometry. Furthermore, with EA IsoLink IRMS System it is possible to determine oxygen isotope composition of silver nitrate by using a high-temperature conversion reactor. Oxygen in compounds is quantitatively converted to CO to determine $^{18}O/^{16}O$ ratios.

For low concentrations of nitrate and small sample amounts, Thermo Scientific™ GasBench II Universal On-line Gas Preparation and Introduction System is used. The GasBench II System allows measuring gaseous N_2O evolved from bacterial degradation of nitrates in aqueous solutions (in-situ). N_2O can be used to determine $\delta^{15}N$ and $\delta^{18}O$ of nitrate in the water. This technique is about 10× more sensitive compared to EA-IRMS.

Identification of nitrate sources

Nitrogen isotope fingerprints display a range of values across different sources such as fertilizers, precipitation, urea, ground water and surface water[1] (see Figure 1 of Xue *et al.*, 2009 for a comprehensive overview of $\delta^{15}N$ values of NO^{3-} from various sources and sinks). $\delta^{15}N$ of sewage differs between the raw sewage and treated sewage. This is caused by fractionation due to microbially mediated nitrification and denitrification reactions occurring in the process.[2,3,4,5]

Oxygen isotope fingerprints allows for differentiation of nitrates derived from nitrate precipitation, fertilizer or nitrification[1] (see Figure 2 of Xue *et al.*, 2009 for a comprehensive overview of $\delta^{18}O$ values of NO^{3-} from these sources). High $\delta^{18}O$ value reflect inorganic derivation of oxygen entirely from atmospheric O_2 and thus contribution of nitrates from fertilizers. Autotrophic nitrification is typically thought to derive two oxygen atoms from water, and one from atmospheric O_2. Therefore, the oxygen isotopic fingerprint in nitrate resembles that of the water it is dissolved in.[6]

Whilst in some ideal scenarios a single isotope approach could definitively characterize nitrate source, it is often not so simple, especially as many nitrate sources have overlapping $\delta^{15}N$ isotope signatures. Most projects will apply a multi-isotope ($\delta^{15}N$ and $\delta^{18}O$) approach, allowing for better differentiation of sources of pollution in the environment. Figure 1 presents the isotope signature of major sources of nitrate and demonstrates how these can differentiate nitrate from precipitation, manure, soils and fertilizers.[2]

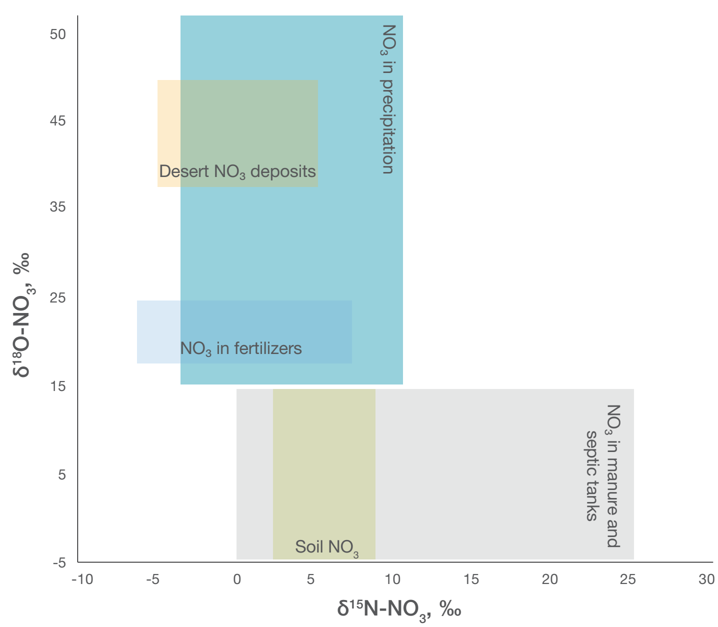

Figure 1. 2-D plot of potential sources of nitrates identified by oxygen and nitrogen isotope fingerprints (A. Smith adapted from Kendall *et al.*, 2007)

However, processes occurring within the nitrogen cycle, including the mixing of nitrate sources, nitrification, denitrification, assimilation and ammonification can alter the isotope value of nitrate.[7] It is therefore critical that researchers have as much site-specific understanding of the nitrate cycle as possible and that other geochemical parameters are measured alongside nitrate isotopes to help with interpretation of the isotope signature. When this geochemistry “toolkit” is applied with our knowledge of the nitrogen cycle, nitrate isotopes are an extremally powerful tool both to identify sources of nitrate but also to understand how this nitrate is cycled and utilized within the environment.

Summary

Protecting our environment from contamination is a global challenge, one that requires a range of analytical tools that can quantify pollution and identify the source. Using nitrate isotope fingerprints, it is possible to monitor water quality and trace the sources of pollution related to human activity, including the use of fertilizers and wastewater discharges. This information allows scientists to inform policy makers on the best strategies for improving water quality and preserving our environment, as guided by the EU Water Framework Directive.

Reference

1. Xue D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., Boeckx, P. 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. Water Research, 43, p. 1159-1170.
2. Kendall, C., Elliott, E.M., and Wankel, S.D. 2007. Tracing Anthropogenic Inputs of Nitrogen to Ecosystems. Stable Isotopes in Ecology and Environmental Science. Blackwell Publishing Ltd., p. 375-449.
3. McClelland, J.W., Valiela, I., 1998. Linking nitrogen in estuarine producers to land-derived sources. Am. Soc. Limnol. Oceanogr. 43 (4), p. 577–585.
4. Mariotti, A., Lancelot, C., Billen, G., 1984. Natural isotopic composition of nitrogen as a tracer of origin or suspended organic matter in the Scheldt estuary. Geochim. Cosmochim. Acta 48, p. 529–555.
5. Risk, M.J., Lapointe, B.E., Sherwood, O.A., Bedford, B.J., 2009. The use of $\delta^{15}N$ in assessing sewage stress on coral reefs. Mar. Pollut. Bull. 58 (6), p. 793–802.
6. Heaton, T.H.E., Stuart, M., Sapiano, M., Micallef Sultana, M. 2012. An isotope study of the sources of nitrate in groundwater in Malta. Journal of Hydrology, v. 414–415, p. 244-254.
7. Gooddy, D.C., Lapworth, D.J., Bennett, S.A., Heaton, T.H.E., Williams, P.J., Surridge, B.W.J. 2016. A multi-stable isotope framework to understand eutrophication in aquatic ecosystems. Water research, 88, p. 623-633.

Find out more at **thermofisher.com/IsotopeFingerprints**

For Research Use Only. Not for use in diagnostic procedures. © 2020 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details. **AB30768-EN 0920C**

ThermoFisher SCIENTIFIC