Can Measurement of Nitrate, Oxygen, and Boron isotopes be useful for your nitrate problem?

A guideline

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Content

1 Introduction: ISONITRATE project ................................................................. 3
2 Guideline .............................................................................................................. 6
   2.1 Criteria for application of isotope measurements in the WFD ............ 6
   2.2 Stepwise approach to define possible use ............................................... 9
3 Additional information ....................................................................................... 11
1 Introduction: ISONITRATE project

The ISONITRATE project (Improved management of nitrate pollution in water using isotopic monitoring) is an EU-LIFE funded project that demonstrates the added value of coupling an isotope monitoring to a more “classical” chemical approach for a more effective river basin management regarding nitrate (NO$_3^-$) pollution. The multi-isotope approach used in ISONITRATE includes the isotope signature of the intrinsic nitrate ($\delta^{15}$N, $\delta^{18}$O) molecule as well as the boron molecule ($\delta^{11}$B), an ubiquitous co-migrant of nitrate. The demonstrated technology and methodology allows to:

1) Chemically characterize water bodies;
2) Trace and distinguish sources of dissolved nitrates in water;
3) Analyse pressure and impact of respective nitrate pollution sources.

Background, problem and objectives

Current approach for environmental management and control of water quality regarding nitrate is merely based on the sole monitoring of pollutant concentrations. However, chemical data alone do not permit to establish unambiguously the type, location and contribution of different nitrate sources in a river basin. In particular, differentiating urban and agricultural origin of nitrate is extremely difficult (even by increasing the number of monitoring stations or samples). Thus, the design and application of specifically targeted management plans for nitrate control is improbable. Recent research showed the great added value of using isotopes to precisely identify, apportion and quantify nitrate sources in water (both surface and groundwater). This innovative multi-isotope approach inherently provides more information, but had to be fully demonstrated through a suitable integrated pilot project. The objective of ISONITRATE was to demonstrate the technical/economical feasibility of integrating an isotope approach as part of characterising water bodies and analysing pressure and impact of nitrate pollution, for a more effective implementation of environmental management measures in river basins.

Relevance to the Water Framework Directive

Adequate monitoring programmes are required to assess the objectives of the Water Framework Directive (WFD) which aims to achieve a “good ecological and chemical status” in all water bodies (surface water and groundwater) across Europe by 2015 and to ensure long-term sustainable use of water. A good status requires low levels of chemical pollution as well as healthy ecosystems. Input of pollutants and deterioration of aquatic ecosystems must be prevented or limited by implementing targeted measures.

Considering nitrate pollution, multi-isotope measurements ($\delta^{15}$N, $\delta^{18}$O and $\delta^{11}$B) can be very advantageous to obtain adequate data from monitoring networks. According to the WFD, surveillance monitoring is needed to validate status, trend and risk assessments and
Can measurement of Nitrate, Oxygen and Boron isotopes be useful for your nitrate problem?  
A guideline

Can measurement of Nitrate, Oxygen and Boron isotopes be useful for your nitrate problem? Operational monitoring must be carried out in water bodies at risk to follow the water quality status and to evaluate the effect of measures taken to ameliorate the status, reduce the risks and reversing any upward trend in pollutant concentrations. The WFD does not exactly prescribe the methods to be used. The implementation of multi-isotope analysis into nitrate monitoring networks can increase the precision and the confidence of the results without increasing sampling frequency or number of sampling points. The knowledge obtained from multi-isotope analysis in nitrate monitoring can serve several requirements of the WFD: (i) status, risk and trend assessments, (ii) definition of measures, (iii) optimizing the design of future monitoring in efficiency and effectiveness, (iv) evaluation of measures.

Measuring nitrate ($\delta^{15}N$, $\delta^{18}O$) and boron ($\delta^{11}B$) isotope signatures in surveillance monitoring programmes will improve the level of information obtained from the samples taken in a water body. In case of high nitrate concentrations, the isotope composition of water samples can be compared with the isotope fingerprint of potential nitrate sources to look for the origin of the nitrate contamination. In this way, a better understanding of any nitrate pollution problem is already obtained in the assessment phases. Source identification derived from isotope analysis also supports the definition of targeted measures in water bodies at risk as required by the WFD. Measuring nitrate ($\delta^{15}N$, $\delta^{18}O$) and boron ($\delta^{11}B$) isotope signatures is very useful to operational monitoring programmes as well. The isotope composition of water samples provides information on the origin of any observed changes in the nitrate concentration levels and therefore allows improving the evaluation of specific measures.

Methodology

The demonstration phase of ISONITRATE included a survey over 15 months in a pilot area (Alsace, Rhine river basin, France-Germany) where the following 4 distinct study sites were selected, trying to cover the different natural contexts encountered when dealing with nitrate pollution:

1) natural, “pristine” water (not impacted by any anthropogenic input and not resulting from denitrification);
2) simple contamination (a sole source of nitrate pollution involved);
3) multiple-sources contamination (varying inputs from distinct nitrate sources);
4) denitrification (natural attenuation of nitrate by biotic/abiotic conversion into $N_2$).

Classical chemical and isotope analyses ($\delta^{15}N$, $\delta^{18}O$ and $\delta^{11}B$) of both water and nitrate source materials were carried out. Acquired data were processed, evaluated for quality and interpreted according to appropriate statistical procedures.
Results and environmental benefits

The outcomes of the project include a report demonstrating the practical feasibility (technologically and economically) of implementing an isotope approach for improved monitoring of water quality with regards to nitrate pollution in groundwater and surface water (i.e. nitrate source apportionment via distinct isotope fingerprints) and for a more efficient planning of induced environmental management measures. The ISONITRATE project demonstrated that a water quality monitoring network integrating isotope characterisation can deliver more information than nitrate concentrations alone, especially in terms of identifying pollution sources and their respective contributions to pollution pressure. Such an isotopic monitoring methodology will greatly enhance the understanding of nitrate pollution in water and lead to a more effective planning and design of measures related to nitrate pollution in river basins and water bodies as defined by the WFD. It is a feasible technology generating benefits both economically and in terms of environmental impact. The isotopic monitoring methodology can be readily reproduced and transferred to other sites and to the water bodies defined by the WFD, and it will ultimately provide a better management of nitrate pollution in water.
2 Guideline

The present document is a guideline dedicated to water managers, policy makers and administrations. The guideline includes:

1) A summary of criteria for application of isotope measurements;
2) A stepwise approach to define whether analyzing the nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) isotope compositions of nitrate and the boron ($\delta^{11}\text{B}$) isotope composition of boron can be useful for targeted cases.

2.1 Criteria for application of isotope measurements in the WFD

As shown in the ISONITRATE project, both non-isotopic and isotope measurements can be applied for implementing improved nitrate pollution monitoring programmes. The extent of a monitoring programme depends on the complexity of the nitrate contamination, the degree of information that needs to be obtained to solve the problem. Depending on the specific requirements, water quality monitoring can involve various classical parameters, a higher sampling intensity (temporal and/or spatial) or including isotope measurements. An overview of the information that can be obtained for different types of measurements is given below and is summarized in Table 1.

Nitrogen concentration levels

Sites under nitrogen pollution pressure can be identified by measuring nitrate (NO$_3^-$), ammonium (NH$_4^+$) and total nitrogen (N) concentrations in groundwater and/or surface water. Based on concentration levels and corresponding standards, a degree of pollution can be assigned as well as the status of the water body regarding nitrogen pollution, according to the WFD.

Water quality parameters

When other water quality parameters (in addition to NO$_3^-$, NH$_4^+$ and total N) are also measured, a more detailed characterisation of the pollution status is possible. It leads to better insight in both (i) the overall water quality and (ii) the extent of any potential contamination. Analysis of the correlation between water quality parameters related to anthropogenic inputs (e.g. chloride, boron, heavy metals, organic carbon ...) and nitrogen concentration levels can provide information on the potential occurrence of multiple pollution sources. Often, in simple cases (e.g. a single nitrate source and no or negligible impact of conversion processes), distinguishing relations between nitrogen levels and some other water quality parameters is possible. However, in complex cases (e.g. multiple source and/or substantial impact of conversion processes) it is more difficult to distinguish clear relations between parameters.
Can measurement of Nitrate, Oxygen and Boron isotopes be useful for your nitrate problem?
A guideline

**Table 1: Monitoring methods for nitrate pollution and information obtained from the data.**

<table>
<thead>
<tr>
<th>Obtained information</th>
<th>Measured parameters</th>
<th>Water Quality Pollution status</th>
<th>Conversion processes</th>
<th>Identification of pollution sources</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Non-isotope</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>NO₃⁻, NH₄⁺, Kjeldahl N, total N</td>
<td>(1) - Nitrogen pollution level</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH, conductivity, ion (balance)</td>
<td>(2) - Water type</td>
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<td></td>
<td>O₂, COD, BOD, TOC, TIC, DOC, DIC</td>
<td>(3) - Organic pollution level</td>
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<tr>
<td></td>
<td>O₂, NO₃⁻, NH₄⁺, Kjeldahl N, total N</td>
<td>(4) - Eutrophication status</td>
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<td></td>
<td>B⁻, Cl⁻ in addition to (1), (2), (3) and/or (4)</td>
<td>(5) - Anthropogenic pollution</td>
<td></td>
<td>- Single / multiple sources</td>
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<td></td>
<td></td>
<td></td>
<td>- Anthropogenic sources</td>
</tr>
<tr>
<td></td>
<td>Heavy metals in addition to (1), (2), (3) and/or (4)</td>
<td>(6) - Anthropogenic pollution</td>
<td></td>
<td>- Anthropogenic sources</td>
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<tr>
<td></td>
<td>δ¹⁵N and δ¹⁸O compositions of NO₃⁻ in addition to (1)</td>
<td>(7)</td>
<td></td>
<td>- Denitrification</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>- Nitrification</td>
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<td></td>
<td></td>
<td>- Mixing/Dilution</td>
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<td></td>
<td>Isotopic</td>
<td></td>
<td></td>
<td>- Precipitation</td>
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<tr>
<td></td>
<td>δ¹⁴B composition in addition to (7) and (5)</td>
<td>(8)</td>
<td></td>
<td>- Sewage</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>- Mineral fertilizers</td>
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<td>- Organic fertilizers</td>
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<td>- Soil nitrogen</td>
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</tbody>
</table>

**Nitrogen (δ¹⁵N) and oxygen (δ¹⁸O) isotopes of nitrate**

At sites where knowledge is required on both conversion processes (e.g. denitrification) and nitrate pollution sources (in case of multiple potential sources), the information derived from the study of non-isotope measurements data (i.e. “classical” chemistry) might be insufficient. Here, the application of a multi-isotope approach provides an added value (Figure 2): isotope fingerprinting of nitrate sources is used to estimate the origin of nitrate contamination. In order to reach conclusive identification of nitrate sources, coupling δ¹⁵N and δ¹⁸O in nitrate is required. Such a dual isotope approach allows distinguishing different nitrate source vectors: atmospheric nitrate (in precipitation), microbiologically produced...
Can measurement of Nitrate, Oxygen and Boron isotopes be useful for your nitrate problem?  
A guideline

nitrate (e.g. soil nitrification), mineral fertilizers and organic nitrogen (manure and sewage). As an example, typical $\delta^{15}N$ and $\delta^{18}O$ ranges in nitrate for various sources and sinks are shown in Figure 1.

**Boron isotopes ($\delta^{11}B$)**

In some cases, the interference of both isotope fractionation (linked to denitrification) and mixing processes (from the combination of multiple nitrate sources) might hamper the identification of nitrate sources, since the associated fractionation processes can alter the isotope composition of dissolved nitrate. Some of these limitations can be tackled by including the boron isotope composition ($\delta^{11}B$), as boron is an ubiquitous co-migrant of nitrate (present in nearly all water types). The $\delta^{11}B$ composition allows discriminating animal manure from sewage and mineral fertilizer inputs. Moreover, the boron isotope composition is not affected by biogeochemical transformation processes (e.g. natural denitrification) and therefore can be used as a conservative tracer. Nevertheless, the applicability of $\delta^{11}B$ signatures for identification of nitrate pollution sources is intimately linked to ratio of boron over total nitrogen content in the source material. In case boron levels in the source materials are very low, boron concentrations in groundwater and surface water will probably be under detection limit. For determining $\delta^{11}B$, detectable boron concentrations are a prerequisite.

![Figure 1: Box plots of $\delta^{15}N$ and $\delta^{18}O$ signatures of nitrate from various sources, sinks and processes. Data collected from literature. The box plots illustrate 25th, 50th and 75th percentiles; the whiskers indicate the 10th and 90th percentiles; and the circles represent outliers. (Figures adapted from Xue et al., 2009, Water Research 43: 1159-1170)](image)
2.2 Stepwise approach to define possible use

The flowchart in Figure 2 represents the guideline defining the application method of the multi-isotope approach in the monitoring of nitrate pollution. The different steps are described below.

**STEP 1:**

The nitrate data available from monitoring networks define the good (or bad) status of groundwater (and surface water) according to the Water Framework Directive (WFD). If the status is good, there is no need for specific measures (nor for the identification of specific nitrate sources). In that case, the chemical monitoring can be continued and may eventually be adjusted in terms of frequency and samples number. In case the status is not good, meaning that there are indications of nitrate concentrations close to or higher than the 50 mg L⁻¹ threshold, there is a need for measures. Therefore, it is necessary to identify the nitrate source(s).

**Flow chart: define possible use of isotope measurements**

- Monitoring status of groundwater:
  - Nitrate measurements (nitrate or water frame directive)

- Observations:
  - Status of groundwater = good
    - Continue measurements
    - Adapt planning to need of data
  - Status of groundwater = not good
    - Source known: defining actions to reduce nitrate input to ground and surface water

- Selection of samples:
  - Complex problem: several nitrate sources
    - Yes: Implement measures
    - No:
      - Selection of samples (water & source materials for isotope analyses)

- Identifying sources:
  - Defining for which source actions for nitrate reduction are needed (quantitative)

**Advantages of isotope analyses:**

- Source definition
- Identification of sources / contributions
- Effective definition of actions to reduce nitrate output for selected sources
- Not possible to distinguish sources using classic analyses
- Cost reducing effect:
  - Benefits of more efficient actions
  - Small amount of samples needed to define sources in comparison to “classic” analyses
  - Including isotope analyses introduces only a marginal cost compared to the gains

Figure 2: Stepwise approach for implementation of isotope analysis in nitrate monitoring.
**STEP 2:**
There are 3 distinct potential scenarios:

1) Nitrate pollution results from a single known source;
2) More than one source is involved, but their respective contributions are unknown.
3) Adding to already existing pollution mixing processes (i.e. mixing between a “non-polluted” pristine water and anthropogenic inputs, from either one or more sources); natural attenuation (i.e. natural denitrification) can also modify isotope compositions of dissolved nitrates (both $\delta^{15}$N and $\delta^{18}$O, but NOT $\delta^{11}$B).

In presence of a known single nitrate source (e.g. pig manure), specific remediation actions can be taken to reduce the nitrate input (e.g. reducing the amount of manure applied). Isotopic data will not be of an added value in that case as chemical data are sufficient to identify the problem. But, based on chemical data alone, absolute certainty on the presence of a single nitrate source of is usually unlikely.

In most cases several nitrate sources are involved (or potentially involved), arising the need for using the multi-isotope approach to identify these sources, as well as to assess their respective contributions to the nitrate pollution. However, mixing between “non-polluted” pristine water and water polluted due to anthropogenic inputs and/or mixing of water polluted by multiple source can modify the isotope composition of dissolved nitrates. Conversion processes such as natural attenuation (i.e. denitrification) can alter the isotope signature of nitrates as well. Conversion processes do affect the and the composition of nitrate but not the of boron, an ubiquitous co-migrant of nitrate. A multi-isotope approach including both the analysis of $\delta^{15}$N and $\delta^{18}$O in nitrate and $\delta^{11}$B in boron allows discriminating conversion processes and also some pollution sources (e.g. manure and sewage inputs) which show similar $\delta^{15}$N and $\delta^{18}$O signatures.

**STEP 3:**
After identification of a bad water quality status, a water sampling scheme (for isotope analyses) is defined. The location and number of sample points depend on different factors such as: hydrology, hydrogeology, land use and density of existing monitoring networks. Defining the number of sample points needed for an unbiased interpretation without knowing the field characteristics is nevertheless impossible. Therefore, before applying isotope analyses, a careful evaluation has to be carried out taking into account the extent of the problem, site characteristics and budget availability. In order to reduce costs, it is highly advised to take samples for isotope analyses in parallel to ongoing classical chemical monitoring.

**STEP 4:**
Can measurement of Nitrate, Oxygen and Boron isotopes be useful for your nitrate problem?

A guideline

An identification the potential nitrate sources (meteoric input, mineral fertilisers, animals’ manure and sewage effluents) involved is carried out, including, when possible, their relative importance (in terms of potential flux into the water body). These results have to be compared and confirmed by field information (e.g. information on volumes/types of fertilizers currently applied by farmers).

At this stage, the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope composition of nitrate as well the $\delta^{11}\text{B}$ signature of collected samples can be measured.

**STEP 5:**

When one or more important nitrate sources are identified by isotope analysis, it is then possible to define specific measures. Measures are implemented in order to improve the water quality, with the ultimate goal of reaching a good status (as defined by the WFD). After implementation of specific measures, water quality can then be re-evaluated, and isotope measurements can be applied again (i) to assess the real effect of the implemented measures and (ii) to monitor the respective contribution of the different identified nitrate sources (which should indeed decrease with time).

### 3 Additional information

More information about the ISONITRATE project and the implementation of multi-isotope analysis in nitrate monitoring is available on the project website [http://isonitrate.brgm.fr/](http://isonitrate.brgm.fr/)

In addition to the present guideline document, a user-friendly manual was developed in the framework of the ISONITRATE project. This user manual is dedicated to water managers, policy makers and administrations. The document includes method descriptions, step-by-step guidelines to implement the methodology and a discussing about the economical consequences and field applicability of the multi-isotope approach in nitrate monitoring.

The user manual and the guideline can be downloaded from the project website.