Title: Isotopes to study nitrogen pollution and eutrophication of rivers and lakes

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Summary

Water quality in thousands of lakes and rivers around the globe is deteriorating due to rising nutrient levels and other chemical pollutants mainly of anthropogenic origin (e.g., agriculture, sewage, industrial discharges, urban areas) causing changes in their ecological structure and function. The excessive nitrogen pollution (nitrate, ammonium) of surface waters has resulted in change of oligotrophic water bodies to eutrophic and sometimes to hypertrophic states. Environmental isotopes are used not only to assess hydrological processes in terms of surface water quantity, but also to address water quality issues, such as nitrogen pollution. This CRP aims to improve the suite of isotopic markers combined with other chemical / biological substances to better define the possible sources and re-cycling of nitrogen pollution in surface water bodies. The CRP aims to deepening the knowledge on the temporal (diel, seasonal) and in-depth variation of nitrogen isotope data, combined with additional substances, as deeper water bodies may sometimes prevent a complete understanding of nitrogen isotope dynamics from surface water collections. Moreover, improving conventional and promoting new methodologies on nitrogen species isotopic characteristics is expected to facilitate access to a more routine and low-cost use of nitrogen and oxygen isotope data of nitrogen species. Overall, the CRP will aim at improving the capability and expertise among participating Member States in the use of environmental isotopes to better assess the impact of nitrogen pollution and eutrophication on surface water resources availability and sustainability.

Background situation analysis

The exponential growth of the human population and the rapid co-development of agricultural and industrial sectors in recent decades have caused a sharp increase of nitrogen loading to surface water bodies worldwide (Appelo and Postma, 2005; Galloway et al., 2004; Mclsaak et al., 2001; Smil, 1999; van der Perk, 2007). Nitrogen species (e.g., nitrate, ammonia) are widely distributed compounds in lakes and rivers primarily as a result of diverse agricultural activities utilizing N-containing fertilizers. Other significant anthropogenic non-point sources of water contamination with nitrogen compounds are the disposal of sewage by centralized and individual systems, animal feeding operations, and elevated atmospheric N deposition.

Excess nitrogen loading has altered the global N cycle, often resulting in the cultural eutrophication of lakes and rivers, and reducing the biodiversity and ability of aquatic ecosystems to provide valuable services for the world’s population. Two of the most commonly recognized symptoms of eutrophication are harmful algal blooms and hypoxia. Moreover, eutrophication has become a serious threat to drinking water quality. Given that consumption of water with high concentrations of nitrate can pose risks to human health, e.g. infant methemoglobinemia, human gastric cancer (e.g., Cuello, 1976), organizations such as the World Health Organization (WHO) and governmental agencies, such as the US Environmental Protection Agency (EPA), have established quality standards for water resources and developed regulations and action guidelines for the use of water in the consumption sector (EPA, 2009; EU, 1998; WHO, 2004). Consequently, nitrogen pollution has been a matter of great concern throughout the world.
The pilot GNIR program (IAEA, 2012) showed that water isotopes can provide a deeper insight into hydrological processes in space and time, e.g., sources of river recharge and pathways, and the impact of anthropogenic activities such as nitrogen pollution. However, the development of effective management practices to preserve water quality and remediation plans for rivers and lakes that are already N-polluted, requires identification of the actual sources and thorough understanding of the biogeochemical processes affecting local nitrogen concentrations (Mayer and Wassenaar, 2012; Yue et al., 2014). Eutrophication processes are related to the temporal and spatial variation of the temperature and oxygen concentration of the water body and thus nitrogen concentrations can differ not only seasonally but also among hydrographic layers because of the vertical stratification of the water-column (Sutka et al., 2004; Yu et al., 2015). For example, during the summer oxygen concentration of the bottom waters of a river or lake may reduce significantly enough to become isolated hypoxic or anoxic while the upper waters may remain oxygenated (e.g., Kasai et al., 2004). Hence, spatially- and temporally- varying controlling factors of nitrogen concentrations in eutrophic surface water environments are not adequately covered so far.

Isotope techniques constitute a promising tool for determining the sources of nitrogen in surface water bodies and aid in assessing the biogeochemical processes nitrogen undergoes in the aquatic environment and in soils. Determination of the relation between nitrogen concentrations in surface water and the quantity of nitrogen introduced from a particular source is complicated by 1) the occurrence of multiple possible sources of nitrogen in the same area, 2) the presence of overlapping point and non-point sources, and 3) the co-existence of numerous biogeochemical processes (e.g., ammonium volatilization, nitrification, denitrification) that alter nitrogen and other chemical concentrations, 4) the occurrence of considerable inter-annual variations of nitrogen concentration (Chen et al., 2010; Curt et al., 2004; Kendall, 1998). A suite of complementary environmental isotopes (e.g., $^{15}$N, $^{18}$O, $^{34}$S) in conjunction with other indicators (e.g., chemical ions, pharmaceuticals) offer a powerful means of nitrogen source identification (Fenech et al., 2012). In addition, the seasonal biogeochemical changes of nitrogen, accompanied by changes in isotopic ratios (isotope fractionation) in horizontal and vertical directions of the water column, can be reconstructed from the isotopic composition in conjunction with other markers such as chlorophyll-a and Dissolved Oxygen (DO) (Sugimoto et al., 2009).

A common limitation to the widespread adoption of N and O isotopes tracers of nutrient sourcing is lack of analytical capacity. Preparative analytical techniques, such as bacteria denitrification (Sigman et al., 2001) and the graphite reduction method (Silva et al., 2000), have relatively laborious preparation procedures (e.g., microbial cultures, ion exchange resins) and further require advanced GC-isotope-ratio mass spectrometry assays. For this reason the IAEA Isotope Hydrology Section has acquired lower cost laser spectrography to simultaneously analyze nitrate converted N$_2$O directly. This laser-based nitrate capacity will function as an analytical resource for the CRP which is expected to help facilitate access to nitrate isotope data for Member States that currently do not have the nutrient isotope capability.

The overall aim of the CRP is to explore the use of nitrogen isotopes in N-nutrient dynamics in selected freshwater systems (lakes and rivers) facing eutrophication and nitrogen pollution. The isotopic ratios of nitrogen coupled with conventional aquatic assessment approaches should result in better informed efficacious remediation efforts (e.g., better nutrient management vs in stream remediation) of lakes and rivers undergoing eutrophication issues. Moreover, the routine use of new analysis technologies on N isotopes will be promoted leading to a greater confidence in assessments of pollution issues of surface waters and the adoption of sound remediation approaches.

**Nuclear Component**

Measurement of $^{18}$O and $^{15}$N of nitrogen compounds in water samples combined with additional environmental isotopes (e.g., $^{18}$O, $^2$H, $^{13}$C of DIC and/ or DOC, $^{13}$C, $^{15}$N, and $^{34}$S of POM) and selected radioactive isotopes of suspended matter (e.g., Sr, Nd, Pb, and Ca).
CRP overall objectives

To improve capability and expertise among Member States in the use environmental isotopes to better assess impacts of nitrogen pollution on water resources variability, availability and sustainability.

Specific research objectives

1. Assess and improve the suite of isotopes and other chemical and/or biological indicators to evaluate the environmental and anthropogenic impact on surface waters in terms of identifying more accurately the multiple sources of nitrogen pollution and eutrophication.

2. Assess and improve the understanding and interpretation of N-nutrient dynamics, eutrophication and sediment transport in lakes and rivers.

3. Explore improved analytical methods of N-related isotope parameters in order to facilitate access to isotope data of nitrogen species and build greater confidence in assessments of nitrogen pollution issues of surface waters.

4. Assess and improve the interpretation of hydrological processes, sources, interactions and pathways in rivers and lakes.

Expected research outputs

1. Isotope, hydro-geochemical, biological and other data will be generated from sampling at selected monitoring stations and depth profiles on a temporal basis.

2. Improved best-practise guidelines on integrating environmental isotopes and other chemical and/or biological indicators for assessment of N-dynamics in both horizontal and vertical water profiles and for evaluation of N-source identification in rivers and lakes.

3. Improved best-practise guidelines for already existing analytical techniques of nitrogen isotopes and development and use of new analysis technologies.

Expected research outcomes

1. More experienced participating Member States in the implementation of environmental isotopes for the assessment of N-pollution and eutrophication in surface waters.

2. Better understanding of possible environmental and anthropogenic impacts of Nitrogen substances on water resources for optimal water resources management and remediation strategies.

Activities
## PROPOSED WORK PLAN

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<th>ACTIVITY</th>
<th>2016</th>
<th>2017</th>
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<th>2019</th>
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<td>Announcement of CRP &amp; selection of participants</td>
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<td>Preparation of a preliminary work plan of activities (e.g., study areas, sampling sites, measurements)</td>
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<td>1&lt;sup&gt;st&lt;/sup&gt; Research Coordination Meeting in Vienna</td>
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<td>(Development of work plan)</td>
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<td>Preparation of detailed guidelines and final work plan of activities</td>
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<td>Implementation of field campaigns (i.e. <em>in situ</em> measurements and sampling)</td>
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<td>Preparation and submission of final progress reports</td>
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<td>Preparation of publications</td>
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Project funding and administrative information

The major objective of this CRP is to bring researchers together and to enhance exchange. For developed countries IAEA provides research agreements only, which means travel costs to RCM meetings in Vienna will be covered. For less developed countries, IAEA provides a project funding of about 3-8k EUR per year, plus the travel costs to Vienna (research contracts). Additional funding from the home institute should be available (about 50 %). Participation Constraints – Due to UN/IAEA rules there may be only one Principal Investigator (PI) per Member State (country), per CRP.

Participation of Agency’s laboratories

The Isotope Hydrology Laboratory will assist by providing assistance in analytical aspects and required inter-comparison exercises to participating laboratories.

Other resources required

Assumptions

- Interested participants from Member States are already engaged in the assessment of nitrogen pollution and eutrophication of rivers and lakes.

- Appropriate staffing is available for field and analytical work; laboratory premises and computing facilities are available at participating institutes to conduct isotopic, chemical and biological analysis.

- National authorities/institutes will provide all necessary permissions and field collection support in a timely manner.

- There is an on-going research or interested and competent professionals in the areas of hydrology, isotope analysis, water pollution, biogeochemistry.
List of cited references


