



# International Workshop

**Towards new methods to  
manage nitrate pollution within  
the Water Framework Directive**

**Programme v1.1**



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**10 & 11  
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Paris  
UNESCO**



**TOWARDS NEW METHODS TO MANAGE NITRATE POLLUTION WITHIN THE WATER FRAMEWORK DIRECTIVE**

**B**ased on results from ISONITRATE life project, an final international workshop “**Towards new methods to manage nitrate pollution within the Water Framework Directive**” will be organised at the UNESCO in Paris (France) by the BRGM, UGent, VITO, OIEau and UNESCO. This workshop aims at demonstrating the added value of multi-isotope technique to better design management of nitrate pollution in water and its future implementation.

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## TOWARDS NEW METHODS TO MANAGE NITRATE POLLUTION WITHIN THE WATER FRAMEWORK DIRECTIVE

### Context

At the European level, surface and groundwater nitrate pollution remains of major concern, despite considerable efforts made over the last decades via e.g. Nitrate Directive and Urban Waste Water Directive.

Currently, all parties from European to local level (governments, cities, water companies, farmers, general public...) dealing with nitrate pollution face the same challenge: significant improvement in managing and controlling human inputs of nitrate in the environment is urgently required. Appropriate and reliable tools are requested to improve nitrate pollution management and therefore to preserve water quality and environment quality.

The ISONITRATE is a demonstration project funded by the EU Life Environment Program aiming at demonstrating the added value of the isotope techniques to:

- characterise water bodies
- distinguish nitrates sources
- analyse pressure and impact of nitrate pollution

Indeed, recent research provided the proof that isotopic measurements in surface or groundwater can be successfully used to identify human sources of nitrate pollution. Isotope ratios of nitrate from different sources (atmospheric, mineral fertilizer, urban or industrial wastewater, animal manure, soil organic matter) are often significantly distinguishable.

In the overall context where nitrate pollution is expected to be one of the main reasons for water bodies not to reach the good status by 2015, the workshop aims at:

- addressing (on 10 December afternoon) a scientific state of the art dedicated to classical and most innovative approaches of nitrate monitoring;
- presenting and discussing (on 11 December morning) alternative methods to support water stakeholders in managing nitrate pollution.

### Targeted audience

The workshop is addressed to policy makers and implementers, environmental agencies, water stakeholders, scientists...

### Aims of the workshop

- To present and discuss innovative techniques to manage nitrate pollution in water;
- To demonstrate the added value of isotope techniques and their potential applications and limits;
- To facilitate experience sharing between scientists and water stakeholders in managing nitrate pollution within the context of WFD.



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**Expected outcomes**

- Knowledge sharing and dissemination
- Technical and decision making recommendations to implement innovative nitrate pollution management

**Call for posters**

Posters sessions will be organised. Contributions are therefore encouraged in both scientific and policy categories. To submit a poster, please send an abstract (in English only) to conf\_isonitrate@oieau by the 13 November 2009. Abstracts will be published in the proceedings.

Thursday 10 December 2009 Scientific state of the art dedicated to classical and most innovative approaches of nitrate monitoring	
12h30	Registration
13h30	Welcome and opening, Alice Aureli, UNESCO; David Widory, BRGM
13h45	Setting the scene: Nitrate pollution management: which issues within the WFD?, Jeroen Casaer, DG env.
14h00	Session 1 : Current nitrate pollution monitoring and management Chairperson : Kor Van Hoof, Flemish Environment Agency
15h30	Coffee break – Poster Session
16h00	Session 2 : Added value of Isotope techniques in the water management of nitrate pollution Chairperson : Pascal Boeckx, UGent
17h30	Social event

Friday 11 December 2009 Round table on alternative methods to support water stakeholders in managing nitrate pollution	
09h00	Introduction of day II, David Widory, BRGM Nitrate pollution management: the trans-boundary challenge Daniel Valensuela, INBO
09h15	Session 3: Added Value of isotope approach: demonstration of ISONITRATE case studies Chairperson: Jeroen Casaer, DG env
10h25	Coffee break – Poster session
10h55	Session 4: How to implement multi-isotope approach? Chairperson : Nicolas Domange, ONEMA
12h30	Closing remarks Take home messages, Jeroen Casaer, DG env. Conclusion and next steps, David Widory, BRGM
13h00	End of the workshop



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**Detailed agenda of Thursday 10 December 2009**

<b>Introduction</b>	
<b>12h30</b>	<b>Registration</b>
<b>13h30</b>	<b>Welcome and opening</b> Alice Aureli, UNESCO and David Widory, BRGM
<b>13h45</b>	<b>Setting the scene: Nitrate pollution management: which issues within the WFD?</b> Jeroen CASAER, DG environment
<b>Scientific state of the art dedicated to classical and most innovative approaches of nitrate monitoring</b>	
<b>14h00</b>	<b>Session 1: Current nitrate pollution monitoring and management</b> Chairperson: Kor Van Hoof, Flemish Environment Agency
<b>14h05</b>	▪ Classical surface and groundwater monitoring for N03: Flanders example. Kor Van Hoof and Ralf Eppinger, Flemish Environment Agency
<b>14h15</b>	▪ Statistical approaches to analysing trends in groundwater quality. Marianne Stuart, BGS
<b>14h28</b>	▪ Foreseeing nitrate concentration in water: A review of available modelling approaches. Philippe Orban, University de Liège
<b>14h36</b>	▪ Nitrate time transfer from surface to groundwater: A key parameter. Nicole Baran, BRGM
<b>14h55</b>	<b>Discussion</b>
<b>15h30</b>	<b>Coffee break – Posters session</b>
<b>16h00</b>	<b>Session 2: Added value of Isotope techniques in the water management of nitrate pollution</b> Chairperson: Pascal Boeckx, UGent
<b>16h05</b>	▪ Stable isotope techniques: a brief introduction. Pascal Boeckx, UGent
<b>16h20</b>	▪ The life ISONITRATE project. David Widory, BRGM
<b>16h35</b>	▪ Sources of riverine nitrate in a large Canadian watershed. Bernhard Mayer, University of Calgary
<b>16h50</b>	<b>Discussion</b>
<b>17h30</b>	<b>Social event</b>



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### Detailed agenda of Friday 11 December

Alternative methods to support water stakeholders in managing nitrate pollution	
09h00	<b>Introduction of day II</b> David Widory, BRGM <b>Nitrate Pollution Management: the transboundary challenge</b> Daniel Valensuela, INBO
09h15	<b>Session 3: Added Value of isotope approach: demonstration of ISONITRATE case studies</b> Chairperson: Jeroen Casaer, DG Environment
09h20	▪ Isonitrate project: four case studies for as many different implementations of isotope approaches. Emmanuelle Petelet and Agnes Brenot, BRGM
09h55	<b>Discussion</b>
10h25	<b>Coffee break – Posters session</b>
10h55	<b>Session 4: How to implement multi-isotope approach?</b> Chairperson: Nicolas Domange, ONEMA
10h55	▪ Introduction, Nicolas Domange, ONEMA
11h05	▪ ISONITRATE deliverables: Two guidelines documents to implement the multi-isotope approach. Jan Bronders, Kristof Tirez, VITO
11h25	▪ Cost of implementing an isotope approach. Madjid Bouzit, BRGM; Pascal Boeckx, UGent
11h45 12h25	<b>Discussion</b>
12h30	<b>Closing remarks</b> ▪ ‘Take home messages’, Jeroen Casaer – DG Environment ▪ Conclusion and next steps, David Widory, BRGM
13h00	<b>End of the workshop</b>



## TOWARDS NEW METHODS TO MANAGE NITRATE POLLUTION WITHIN THE WATER FRAMEWORK DIRECTIVE

### Summaries of presentations

#### Day I: Introduction

##### Setting the scene: Nitrate pollution management: which issues within the WFD?

Jeoren Casaer

DG Environment

The main policy instruments on EU level on nitrate pollution management are the Nitrates Directive<sup>1</sup> and the Urban Waste Water Directive<sup>2</sup>. Both directives form an integral part of the Water Framework Directive<sup>3</sup> and are essential to achieve good water quality status.

The objective of the Nitrates Directive is to protect waters against pollution caused or induced by nitrates from agricultural sources through a number of steps to be fulfilled by Member States: water monitoring (with regard to nitrate concentration and trophic status); designation of nitrate vulnerable zones (areas that drain into identified waters); the establishment of codes of good agricultural practices and action programmes (a set of measures to reduce nitrate pollution) and to review at least every 4 years designation of vulnerable zones and action programmes.

The Commission will publish at the start of 2010 its 4 yearly summary report on implementation, which is based on the reports submitted by the Member States for the period 2003-2007. Preliminary conclusions show that the overall water quality in the EU is improving; however, there are still several agricultural regions with worrying water quality, in particular in those areas characterized by intensive livestock activities or intensive use of fertilizers.

About 40% of the territory of the EU27 is currently designated as vulnerable zone, including the territory of ten Member States that apply an action programme on the whole territory.

<sup>1</sup> Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources; OJ L375 – 31/12/1991

<sup>2</sup> Council Directive 91/271/EEC of 21 May 1991 concerning urban waste water treatment, OJ L 135 of 30.5.1991, as amended by Commission Directive 98/15/EC of 27 February 1998

<sup>3</sup> Directive 2000/60/EC concerning the establishment of a framework for Community action in the field of water policy; OJ L327 - 22/12/2000

The quality of the action programmes further improved during the reporting period (2004-2007) for EU 15. For the EU12, the Commission noted relatively good action programmes, however, still some work need to be done in getting farmers familiar with new practices. It is worthwhile to mention that manure processing activities, that process manure into purified liquid fractions and/or valorized solid, gains increased interest, particularly in intensive livestock regions facing high nutrient surpluses.

The specific objective of the Urban Waste Water Directive is to protect the environment from the adverse effects of [urban waste water](#) discharges and discharges from certain industrial sectors. Specifically the Directive requires the collection and treatment of waste water in all [agglomerations](#) of >2000 [population equivalents](#) (p.e.); [the secondary treatment](#) of all discharges from almost all agglomerations of > 2000 p.e., and more advanced treatment for agglomerations >10 000 p.e. in designated [sensitive areas](#) and their relevant catchments; the requirement for pre-authorisation of all discharges of urban wastewater, of discharges from large food-processing industry and of industrial discharges into urban wastewater collection systems; monitoring of the performance of treatment plants and receiving waters and controls of sewage sludge disposal and re-use, and treated waste water re-use whenever it is appropriate. The latest summary report on implementation<sup>4</sup> shows that considerable progress has been achieved in implementing the Directive. Progress in addressing waste water related challenges has ensured notable improvements in water quality and has drastically improved the quality of EU beaches in line with the quality standards of the EU Bathing Water Directives. However, key challenges remain to align waste water treatment in the entire EU with the provisions of the Directive and the 'good status' environmental objective under the Water Framework Directive: (1) Secondary treatment needs to be improved in some EU-15 Member States. While some EU-12 Member States are progressing well towards full implementation, others are still at an early stage of implementation and greater efforts are needed. (2) Compliance rates for more stringent treatment are very low in some EU-15 countries and, overall greater efforts in implementation are needed. (3) While implementation in big cities is generally high,

<sup>4</sup> Commission Staff Working Document SEC(2009) 1114 final, 3.8.2009



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greater efforts are needed to ensure implementation of the Directive, especially in six big cities which had no waste water treatment at all, and four big cities which had only primary treatment in place by 2005.

Nutrient pollution from agriculture and waste water is a very diffuse source of pollution and it is not always easy to assess the exact source and flow paths of nutrient loads towards waters. The use of isotopes might be a good instrument to get better insights in this for specific catchments or river basins and could help in better fine tuning appropriate remedial measures. For this, the Commission decided to support this project through means of the life instrument<sup>5</sup>.

### Session 1: Current nitrate pollution monitoring and management

#### Classical surface and groundwater monitoring for NO<sub>3</sub>: Flanders example

**Kor Van Hoof and Ralf Eppinger**

Flemish Environment Agency

Nitrate monitoring by sampling surface and groundwater is used already for a long time as one of the key elements to determine the water quality. The results are used as a trigger in water policy in the field of 'functional' legislation since the 1970's (drinking water, fish and shellfish water and bathing water), in 'sectoral' policy since the 1990's for agriculture (Nitrates directive), industry and urban wastewater (Urban Wastewater directive). It remains an important parameter in the monitoring for the Water Framework directive (WFD) and its related daughter directives, e.g. Groundwater directive (GWD).

In a first part, the specific networks for nitrate monitoring in surface and groundwater in Flanders are described.

In Flanders, the surface water monitoring network has been enlarged in 1999 with specific sampling points to be able to assess the consequences of (evolving) agricultural practices. In a certain sense, this is a network for 'investigative monitoring' that was worked out before the adoption of the WFD.

A Manure Action Program (MAP) monitoring network for surface water has been worked out in Flanders during the last 10 years. The sampling strategy, the interpretation, communication and reporting of the results and the difference with the

monitoring of surface water for the WFD are clarified. In the monitoring programme for the WFD, much more attention is paid to the biological quality elements. Nitrate is there an important, but also only one of the supporting physical-chemical elements.

The groundwater monitoring network in Flanders has been completely renewed in 2003 to meet the obligations of the Nitrate directive in a better way. In addition, this new phreatic monitoring network with its 2100 multilevel-wells is set up to fulfil the requirements of the WFD, concerning aspects of diffuse pollution on qualitative status and qualitative evolution of groundwater bodies. In comparison to surface water, the phreatic groundwater monitoring network is a multifunctional instrument for the application of existing European Directives and associated Flemish Environmental Law.

A short description of the implementation procedure of the network is given, using the conceptual model of hydrogeologically homogeneous zones (HHZ) for the determination of nitrate vulnerable areas. The installed multilevel wells allow focusing on potential risk of horizontal and vertical spread of nitrate in the three-dimensional transport system of aquifers, counting on local physical and chemical boundary conditions (e.g. redox-related quality stratification). The phreatic groundwater network is fully operational since 2004, measuring besides nitrate all important anorganic parameters + pesticides.

Secondly, an overview of the results is given.

The MAP monitoring network for surface water has been used in the first place for communicating with the sector agriculture about the consequences of agricultural practices on surface water quality. In 2002, the MAP monitoring network has been a cornerstone in manure policy and the implementation of the Nitrates directive as it has been used for a detailed and partial designation of Nitrate vulnerable zones in Flanders.

Summarized, ten years of specific monitoring in surface water illustrate that the degree of pollution differs regionally inside Flanders in connection with the intensity of agricultural practice. Unattended was the conclusion that the impact of horticulture (in open air and from greenhouse discharges) is so clear. The evolution over time of some indicators unveil that the nitrate concentration in surface water closely follows important steps in manure policy.

Also the phreatic groundwater monitoring network is an important communication and policy instrument in relation to involved sectors (e.g. agriculture, drinking water supply). The nitrate vulnerability of certain zones and their associated aquifer systems is confirmed by the results of the first analyse

<sup>5</sup> More info about LIFE: <http://ec.europa.eu/environment/life/index.htm>



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campaigns. Regional differences are related to physico-chemical boundary conditions in combination with source-related pressures. A clear link between groundwater quality evolution and changes in manure policy cannot be seen yet, due to the short-term series of measurements over the last 5 years. It has to be considered that groundwater is a strongly buffered, slow transport system. Effects of taken measures occur with a certain delay, making long-term measurements essential.

Finally, some questions are difficult to be answered using classical nitrate monitoring in groundwater and surface water. It is difficult to make quantified source apportionments, to see clearly the relation between soil, surface water and groundwater and to assess the time scales with which they influence each other. Possibly, isotope techniques could be used to unveil answers to these questions. To better understand the source apportionment in surface water, isotope techniques have been developed in projects between VMM, IRMM and the University of Gent.

### Statistical approaches to analysing trends in groundwater quality

**Marianne Stuart**

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A trend is the underlying rate of change and is often used to distinguish a long-term tendency from erratic short-term fluctuations (noise). Groundwater quality varies with time over various timescales from daily, seasonal and annual. Trend estimation is complicated by cyclic behaviour, step changes and data censoring as well as short-term fluctuations. It is also dependent on the dataset characteristics, the sampling frequency, monitoring period and regularity of sampling. The better the quality of the dataset the more sophisticated tests that become possible. It is rarely possible to explain such variations in terms of the underlying physical processes because of the lack of the necessary supporting data.

Drivers for trend assessment include (i) the quantification of trend reversal under the Water Framework Directive, (ii) the prediction of peak concentrations to enable water utilities to meet drinking water regulations, and (iii) detecting the impacts of climate change and other environmental changes.

A semi-automated linear regression methodology has been developed to process irregular water quality timeseries using the 'R' statistical software.

This was used to analyse a large dataset of groundwater nitrate data from England to define past trends and to make estimates of future concentrations. Tests were included for lack of linearity, the detection of outliers, seasonality and breaks including reversals in trend. Our procedure provides annotated plots with estimates of trends. It also provides warnings of possible departures from the underlying assumptions. The method was not useful for series with step changes and other erratic behaviour.

21% of the series analysed showed a significant break in the trend and half of these indicated an increase in nitrate concentration with time. An assessment of seasonality in nitrate concentrations was also made by including a term for the month of sampling in the regression model. Significant seasonality was found in about one third of the series. In 2000, 34% of sites analysed exceeded the 50 mg/L standard. If present trends continue, 41% of groundwater sources could exceed the standard by 2015.

Nitrate concentrations can be regressed with covariates, such as water level, to improve the prediction of both trends and seasonal peak concentrations.

Long-term regular monitoring is the key to successful trend estimation. Purpose-built monitoring boreholes suffer less from operational disturbances than regularly pumped boreholes, and so are to be preferred.

### Reference

Stuart ME, Chilton PJ, Kinniburgh DG and Cooper DM. 2007. Screening for long-term trends in groundwater nitrate monitoring data, Quarterly Journal of Engineering Geology and Hydrogeology, 40, 361-376

### Foreseeing nitrate concentration in water: A review of available modelling approaches

**Philippe Orban and Serge Brouyère**

Hydrogeology and Environmental Geology, University of Liège, B52/3, 4000 Liège, Belgium

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In the scientific community, increasing concerns on groundwater quality and quantity have motivated the development of numerical models for groundwater management since the 1970's. Mathematical and numerical models are, for example, promising tools for prediction of concentration and they can be used to make the dynamic link between nitrogen manure and the resulting evolution of nitrate concentration in groundwater. However, from a practical and managerial perspective, there have been very few



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real attempts of developing efficient calibrated and validated transport models in particular at the scale of the groundwater body, which is the management unit of groundwater resource in the European Union. Actually two main challenges remains, (1) performing numerical tools are not really available and (2) parametrisation of such transport models at the regional scale is difficult due to the large amount of data required.

Generally speaking models can be grouped in different categories ranging from black box models to physically based distributed models. The black box models such as transfer function are simple but attractive because they require relatively less data but with the drawback that modelling result are not spatially distributed while the predictive capability of these models is questionable due to the semi-analytical nature of the process descriptions. On the contrary, physically based distributed model require more data but, due to a more advanced description of ongoing processes, such models are expected to have better predictive capabilities than the black box models. Black box model and physically based distributed model approaches have all proved their utilities and have all their justifications, advantages and disadvantages regarding the development of regional scale groundwater model.

A new flexible methodology (the Hybrid Finite Element Mixing Cell method) has been developed that allows combining in a single model, and in a fully integrated way, different mathematical approaches of various complexities for groundwater in complex environment. This method has been implemented in the SUFTD, a finite element groundwater flow and solute transport numerical model. Combining on the one hand the use of a spatially distributed groundwater flow and solute transport model taking advantages of this Hybrid Finite Element Mixing Cell Approach method and on the other hand spatial datasets of tritium and nitrate contents, an illustration on the problem of nitrate trend assessment and forecasting for an important groundwater resource located in the Geer groundwater body (480 km<sup>2</sup>) in the Walloon Region of Belgium will be proposed.

### Session 2: Added value of Isotope techniques in the water management of nitrate pollution

#### Stable isotope techniques: a brief introduction Pascal Boeckx & ISONITRATE consortium

Ghent University, Laboratory of Applied Biological Sciences, Coupure 653, 9000 Gent, Belgium, pascal.boeckx@ugent.be

Isotopes are nuclides of the same element that differ in the number of neutrons in their nucleus; they have similar chemical but different physical properties. Several isotopes, which can be stable or radioactive, for one element can exist. The isotopes considered within ISONITRATE are stable isotopes of nitrogen (N), oxygen (O) and boron (B), namely <sup>15</sup>N, <sup>18</sup>O and <sup>11</sup>B (the superscript is the mass number of the nuclide and is the sum of the number of protons and neutrons in its nucleus). These "heavy" isotopes are far less abundant than the "common" isotopes: <sup>14</sup>N, <sup>16</sup>O and <sup>10</sup>B. This natural abundance of stable isotopes is expressed as delta (δ) units relative to an international standard and is expressed in per mill deviations from that standard. An isotope ratio is the ratio of "heavy" over "light" isotope, e.g.  $^{15}R = ^{15}N/^{14}N$ .

Within ISONITRATE, the <sup>15</sup>N and <sup>18</sup>O natural abundance in nitrate (NO<sub>3</sub><sup>-</sup>) and the <sup>11</sup>B abundance in boron (B<sup>-</sup>) have been used and are denoted as: δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup>, δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> and δ<sup>11</sup>B, respectively. The isotopic composition of NO<sub>3</sub><sup>-</sup> and B can be measured using dedicated sample preparation techniques to remove interfering compounds and state of the art mass spectrometry. For δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> and δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> tree sample preparation techniques can be used: the so called "AgNO<sub>3</sub>", "bacterial denitrification" and "Cd-reduction" method. For analyses an Isotope Ratio Mass Spectrometer (IRMS) coupled to a high temperature elemental analyzer (AgNO<sub>3</sub> method) or a trace gas unit (bacterial denitrification and Cd-reduction) is needed. For δ<sup>11</sup>B analyses either Thermal Ionization Mass Spectrometry (TIMS) or High Resolution-Sector Field- Inductive Couple Plasma Spectroscopy (HR-SF-ICPS) can be used.

The isotopic composition of a specific element (or molecule) in the environment can vary due to (1) mixing of two or more sources with a different isotopic composition or (2) via phenomena known as isotope fractionation. Isotope fractionation involves a kinetic (or equilibrium) discrimination against the heavier isotope, i.e. <sup>15</sup>N, <sup>18</sup>O and <sup>11</sup>B. This implies that unidirectional reactions with



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molecules that contain the heavier isotope occur slower compared to the same reaction with the light isotope molecule. As a consequence instantaneously formed reaction products are depleted in the heavier isotope compared to the substrate, while the remaining (non-reacted) substrate will get gradually enriched in the heavier isotope.

During the workshop these basic principles will be explained for a non-specialist public in order to enable them to follow the isotope based presentations of the ISONITRATE project.

### The life ISONITRATE Project

David Widory & ISONITRATE Consortium

#### BRGM

Today, the environmental management of surface/groundwater quality with respect to nitrate contamination is almost exclusively based on monitoring nitrate ( $\text{NO}_3$ ) concentration levels in a selection of sites and samples through time. However, there is now ample evidence that this concentration approach does not allow to establish unambiguously the different sources and their respective contributions to nitrate pollution. It is also observed that increasing the density of data points by increasing the number of environmental monitoring stations and/or the number of samples (reducing periodicity between sampling) does not help much and generates extremely high additional costs. A direct consequence of this is that it is often difficult to design and verify the effect of environmental management measures and plans implemented to control nitrate contamination in a given area.

The results of recent research work showed that the limitations of the concentration monitoring approach can be overcome by using an isotopic approach. This approach is based on measuring natural isotopes of the nitrate molecule ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) and associated dissolved species ( $\delta^{11}\text{B}$ ) present in both pollution sources and water. Although the application of the isotopic tracing approach to nitrate pollution issues is recent, it has proven to be very effective at precisely discriminating the different vectors of nitrate in water (i.e. urban and agricultural sources), identifying these sources of pollution and quantifying their respective contributions to a contaminated water body.

The objective of the ISONITRATE project was to demonstrate to policy-makers and -implementers that a water quality monitoring network, operated over several years and integrating isotopic data (that inherently have a far greater information

content than chemical data alone) is feasible technologically and economically cost-gaining, and leads to more effective planning of environmental management measures specifically targeted against nitrate pollution in water bodies.

The demonstration project was carried out by characterising the isotopic composition of all identified potential nitrate sources, and by collecting and analysing (chemically and isotopically) water samples from boreholes and rivers over a period of 15 months, on four distinct locations representing the different hydrogeological contexts encountered by most authorities in charge of providing potable water:

- a) Natural nitrification of the soil: sampling sites representing the local background  $\text{NO}_3$  levels in water (i.e. samples with higher  $\text{NO}_3$  are considered polluted). The measured low  $\text{NO}_3$  concentrations need not to result from attenuation by natural denitrification, but clearly from natural nitrification.
- b) Natural denitrification: sampling sites along a gradient of natural denitrification, all groundwater.
- c) Simple case: sampling sites located in a zone where only one pollution source controls the  $\text{NO}_3$  budget in water.
- d) Complex case: sampling sites where  $\text{NO}_3$  in water results from the combination of distinct sources with various contributions along the hydrological cycle.

### Sources of riverine nitrate in a large Canadian watershed

Bernhard Mayer

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The South Saskatchewan River in western Canada is fed by three major tributaries: the Red Deer River, the Bow River and the Oldman River. These tributaries originate in pristine forested headwater catchments on the eastern slopes of the Rocky Mountains prior to flowing eastwards across the prairie provinces of Alberta and Saskatchewan, where the watersheds are progressively impacted by urban and agricultural land use practices. Hence, the South Saskatchewan River Basin provides an excellent opportunity to assess the cumulative



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impact of different land use along its tributaries on the quality of river water. The objective of this study was to combine hydrometric and chemical measurements to determine changes in nitrate fluxes along the river and assess their relation to land use, while stable isotope techniques were used to determine the sources that contribute nitrate to the rivers.

River water, sampled seasonally at 25 stations along the South Saskatchewan River and its key tributaries from the headwaters in Alberta to the mouth near Prince Albert (Saskatchewan), was analyzed for its chemical composition by standard techniques (liquid chromatography, AAS). The isotopic composition of nitrate was determined using the denitrifier technique and isotope ratio mass spectrometry (IRMS).

Nitrate fluxes in the headwater sections were low and N and O stable isotope data indicated that the nitrate was mainly derived from nitrification in forest soils. Downstream of major urban areas e.g. in the Bow River, both nitrate fluxes and the nitrogen isotope ratios increased, providing evidence of riverine nitrogen loading via wastewater treatment effluents. In the Oldman River watershed that is dominated by agricultural land use with no major urban centers, increasing nitrate fluxes and nitrogen isotope ratios provided evidence for influx of manure-derived nitrate with agricultural return-flows. After the confluence of the Bow and the Oldman Rivers to form the South Saskatchewan River it was however difficult to determine whether elevated nitrogen isotope ratios were caused by agricultural or urban nitrate sources. Therefore, additional tracer techniques are desirable to better quantify the respective source contributions from urban and agricultural sources in the lower part of this river basin.

This study demonstrates that stable isotope techniques are an effective tool for distinguishing natural and anthropogenic sources of nitrate in large riverine systems with different land use, particularly if used in concert with hydrometric and complementary geochemical data.

### Day II: Introduction

#### Nitrate Pollution Management : the transboundary challenge

**Daniel Valensuela**

International Office for Water / International Network of Basin Organisations

To be efficient, the management of surface and ground waters shared between several countries requires a high transboundary co-operation and integration. This requirement is particularly valid for the nitrate pollution management.

Indeed, it is on the consistent hydraulic scale of river, aquifer and lake basin that is set up an interdependence on water quality, which needs a coordination at transboundary basin level for fighting against accidental and diffuse pollutions and of establishing mechanisms of solidarity between upstream and downstream to prevent the risks of pollution.

The European Union is largely concerned by transboundary waters; most of countries share all or part of their surface and ground water resources with their neighbours. Bulgaria, Hungary, Luxembourg, the Nederland, Romania exceed the threshold of 2/3 of their resources coming from outside their borders.

It is thus indispensable in the shared basins to strengthen the cooperation and the integration of the actions to obtain tangible results in the implementation of the relevant directives, in particular for the "Nitrate Directive".

The challenge is multiple:

Above all, it is matter to develop in every transboundary basin an integrated system of water data and information, which has to be shared between the riparian countries. This system has to address, not only, the water quality but also the potential sources of pollution. Many European basins have got already a collaborative international body in shape of International Commission (eg. Escaut, Meuse, Danube, Rhine, Elbe...). This type of structure often allowed the development of joint data base on the basin scale. Where it exists, those data bases might be consolidated in particular with the information related to the potential and real pollution sources.

The challenge is also about a better knowledge in real time of the origin of nitrates presents in water. To get a tool allowing any time to certify the



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geographical origin (and therefore, the region or the country, the sub-basin, the area, etc and the sector like agriculture, domestic pollution, industry, environment...) would be a real progress for improving the performance of the actions programmes. It would be a way to avoid the usual questioning of the degree of importance and the source of pollution. This aspect is particularly relevant for the nitrate diffuse pollution for which the source is always difficult to identify.

Moreover, the transboundary cooperation might be the basis for a « more transboundary » application of the European directives. Indeed, the directives transposed into the member state legislation, is a general framework, and its implementation is defined at national or intra national level. It means that, in a cross-border basin given with the same degree of water degradation along the river, the approaches and the action plans are different. The approaches are different as we are on one side or of other one of the border.

### Session 3: Added Value of isotope approach: demonstration of ISONITRATE case studies

**ISONITRATE project: Four case studies for as many different implementations of isotope approaches**

**Emmanuelle Petelet-Giraud, Agnès Brenot and ISONITRATE consortium**

**BRGM**

ISONITRATE, a Life Demonstration Project, aims at demonstrating, to policy makers, the technical and economical feasibility of integrating the isotope approach as an integral 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.

The selected pilot site is located in the Alsace region (France & Germany border) and the groundwater bodies under investigation are the "2001: Alsace aquifer layer and Pliocene from Haguenau aquifer layer" and the "2002: Sundgau drainage area of the Rhin and alsacian Jura aquifer layer". The groundwater body 2001 is considered as one of the most important drinking water reservoirs in Europe.

Because of an intensive agricultural land use, the presence of industries and mining activities in the Upper Rhine Valley, natural water in this pilot site is strongly impacted by anthropogenic inputs. Nitrate can be considered as one of the most important

indicators of the anthropogenic pressure on natural water. The mean nitrate concentration of groundwater in the Upper Rhine Valley is closed to  $30 \text{ mg.L}^{-1}$ . Agricultural land use plays a key role in the nitrate contamination of natural water. In particular, areas with intensive maize growing present nitrate concentrations that exceed the EU-quality standard of  $50 \text{ mg.L}^{-1}$ .

The groundwater body 2001 was selected as a transboundary aquifer between France and Germany. Furthermore, this groundwater body offers a large knowledge of both geological and hydrological contexts, and also possesses a relevant historical dataset for groundwater quantity and quality. Nitrate concentrations have been monitored since the mid 90's in the Alsace region. In addition, isotopic analyses ( $\delta^{15}\text{N-NO}_3$ ,  $\delta^{11}\text{B}$ ) have been previously performed in both surface- and groundwaters, as well as anthropogenic inputs (animals' manure, sewage, chemical fertilisers) for selected subcatchments (Kloppmann, 2003; Kloppmann et al., 2005). These studies demonstrated that i) organic fertilizers used in the past or today are mainly responsible for high nitrate concentration levels in groundwater, and ii) some portions of the central plain are depleted in  $\text{NO}_3$ - due to natural denitrification (Göppel and Eichinger, 1997; Kloppmann et al., 2005). The selected pilot site thus presents the strong advantage of providing a solid knowledge of the characteristics of local nitrate sources (that reinforces the demonstration character of this project).

Four distinct scenarios were chosen within the pilot site, representing the typical hydrogeological and land use contexts encountered in the Alsace plain. Surface and groundwaters were sampled during 12 sampling campaigns over a 15 months period. The main (potential) contamination sources were also characterised in each considered catchments: various mineral fertilizers used for the different type of crops, organic fertilizers as well as sewage effluents.

- **Natural nitrification of the soil:** selected in a pristine area in the Vosges mountains in order to characterize the local background  $\text{NO}_3$  levels in water (i.e. samples with higher  $\text{NO}_3$  are considered polluted). This case constitutes the natural reference for the South part of the Alsace plain.
- **Natural denitrification:** located in the German part of the Upper Rhine Valley. Groundwater in this area has shown, through previous studies, to



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be affected by natural attenuation along a denitrification gradient.

- **Simple case:** located in the Vosgian vineyards (identified with the help of local authorities). In this area a single pollution source (mineral fertilizers from vineyards) is supposed to control the  $\text{NO}_3$  budget in water.
- **Complex case:** selected with the help of local authorities, and located in south of the Alsace region (Sundgau), where different sources of nitrate are expected to be involved (mineral fertilizer, organic fertilizer, sewage...).

### Session 4: How to implement multi-isotope approach?

#### Introduction to session 4: How to implement multi-isotope approach ?

##### Nicolas DOMANGE

PhD, Scientific officer in charge of non-point source pollution; Department of scientific and technical activities – ONEMA; Nicolas.domange@onema.fr

The French national agency for water and aquatic environment (ONEMA) is a young official agency created at the end of 2006 in order to implement the WFD in France.

The scientific department has a major role to pilot, orientate and fund some operational research actions in the border of the water environment and particularly non-point pollutions. It has to make sure that the research projects results are easily transferable to stakeholders, rightly support European directives' practical implementation and the associated French laws, and finally that they are the appropriate answers to the local problematic of the administrative agencies in charge of the regional implementations.

Most particularly, with respect to diffuse pollutions, the WFD sets a number of ambitious aims for the water resources quality for drinking water. The efficiency of the engaged actions will depend on the following conditions:

- a well delineated area of action
- a fine vulnerability study and a good knowledge of the processes
- and a relevant choice of measurements adapted to the local context

The quality of these three steps and the effectiveness of these measurements require the use of a pertinent and approved scientific common

methodology. Nonetheless, some technical gaps remain in the action plan. One reason is the difficulty to have interdisciplinary works on this subject and to compile all the scientific knowledge on the processes involved in diffuse pollutions. Even though the latter is often available in the research organisations independently, it is not frequently upgraded or even transferred to water stakeholders. This way, the French ministries of agriculture and environment have decided on the basis of ONEMA's scientific and technical support to create an interdisciplinary technical group ("protection of drinking water point vis-à-vis non-point pollutions"), to do an inventory of research results, to identify the existing gaps in operational methodology and in research in the domain and to facilitate knowledge transfer between scientists and water stakeholders.

Typically, ISONITRATE is the type of research project that ONEMA and the interdisciplinary technical group would like to support. The first sessions of the workshop have demonstrated the added value of such a technique and its potential applications and limits for nitrate pollution. The following step will provide the tools to ease knowledge transfer between scientists and water stakeholders. Face with nitrate pollution, a local water stakeholder has to be able to have technical and decision making recommendations at its disposal in order to implement this innovative nitrate pollution management technique.

#### ISONITRATE deliverables: Two guideline documents to implement the isotopic monitoring

##### Jan Bronders, Kristof Tirez & ISONITRATE consortium

VITO, Boeretang 200, 2400 Mol, Belgium

The outcomes of the ISONITRATE project include a report demonstrating the technological and economical feasibility of implementing an isotopic approach for improved monitoring of water quality with regards to nitrate pollution in ground and surface water (i.e. nitrate source apportionment via distinct isotopic fingerprints) and consequently a more efficient planning of induced environmental management measures. Additionally, in the framework of this EU-LIFE demonstration project two guidelines have been prepared to facilitate the implementation of this method:

- a guideline document dedicated to water managers, policy makers and administrations allowing to decide if isotopic monitoring can be useful for a particular nitrate problem



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- a user manual identifying all technical and analytical items to be taken into account when applying the isotopic monitoring

The guideline for identifying the added value of the isotopic monitoring contains a stepwise approach to define whether N, O and B isotopic information can be useful for certain cases. Therefore a selection of criteria for applying isotopic measurements are considered. This stepwise approach combined with a decision flow chart to define possible use is presented.

A second document is a user-friendly manual dedicated to water managers, monitoring administrations and laboratories. The manual includes sampling and analytical method descriptions and step-by-step guidelines to transfer the methodology to different catchments.

During the conference these two guidelines are presented.



## TOWARDS NEW METHODS TO MANAGE NITRATE POLLUTION WITHIN THE WATER FRAMEWORK DIRECTIVE

### Practical information

#### Contact

- For more information on the project

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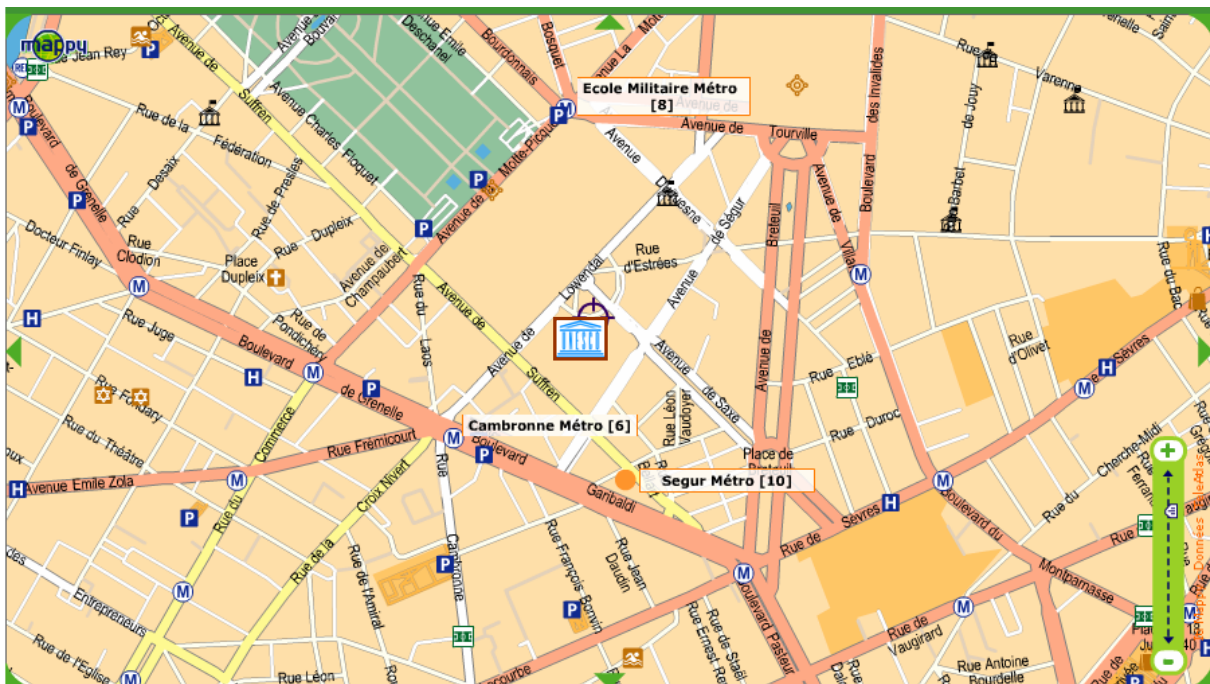
- For more information on the workshop

International Office for Water: [conf\\_isonitrate@oieau.fr](mailto:conf_isonitrate@oieau.fr), +33 (0)5 55 11 47 47

- On <http://isonitrate.brgm.fr>, you can download documents and have access to hotel recommendations

#### Venue

- UNESCO, 7 place de Fontenoy, 75007 Paris**
- Metro 6 (Cambronne), metro 8 (Ecole Militaire), metro 10 (Séгур)





**INTERNATIONAL WORKSHOP**  
**“Towards new methods to manage nitrate pollution within the Water Framework Directive”**  
**10 & 11 December 2009**  
**UNESCO, 7 place de Fontenoy, 75007 Paris**



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### I WILL PARTICIPATE TO

- The **10th December 2009 afternoon** dealing with the scientific state of the art dedicated to classical and most innovative approaches of nitrate monitoring
- The **11th December 2009 morning** round table on alternative methods to support water stakeholders in managing nitrate pollution

**PLEASE RETURN YOUR REGISTRATION FORM TO:**

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